***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***

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Prepared by:

Continental Shelf Associates, Inc.
759 Parkway Street
Jupiter, Florida 33477
Telephone: (561) 746-7946

Prepared for:

U.S. Department of Energy
Mrs. Rhonda P. Lindsey
Contracting Officer's Representative
220 North Virginia Avenue
Bartlesville, Oklahoma 74003
Telephone: (918) 337-4407

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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) accidentally 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 ($\geq 10,000$ 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 $\mu\text{g/g}$ 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ 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 ($<0.1 \mu\text{g/L}$) 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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$. 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 $\mu\text{g/g}$ dry weight. Most concentrations are below 1.0 $\mu\text{g/g}$. 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

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1.5 ACKNOWLEDGEMENTS

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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 $\times$ 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 fluorometrically 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 (Sonmier Bank)	28° 19' 51" 97° 27' 42"	25	NA	

Lease Areas:

EI - Eugene Island
GA - Galveston
HI - High Island
MI - Matagorda Island

SMI - South Marsh Island
VR - Vermilion
WC - West Cameron

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 THC).

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 $\text{pH} \leq 2$. 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 $\geq 2,000$ 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).

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 HNO₃ to interstitial water samples until the samples were at a pH $\leq$ 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 an 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 CH ₃ Cl-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												
<i>Arca zebra</i>	turkey wing				x	x	x	x		x		
<i>Barbatia</i> spp.	ark	x	x		x	x	x	x		x		
<i>Chama macerophylla</i>	jewelbox	RMP	RMP		RMP	RM	RM	RM	RM	RM		
<i>Crassostrea virginica</i>	eastern oyster			RMP							RM	
<i>Isognomon</i> spp.	purse-oyster	x	x		x	x	x	x		x		
<i>Pinctada imbricata</i>	Atlantic pearl-oyster				x							
<i>Spondylus americanus</i>	thorny oyster	x	x					x				
<i>Calappa</i> sp.	box crab		x									
<i>Callinectes</i> spp.	blue crab			RMP	RMP					R	R	R
<i>Hepatus</i> sp.	calico box crab		x									
<i>Libinia</i> sp.	spider crab				x							
<i>Menippe adina</i>	stone crab			x							x	
Penaeidae	shrimp	x				x		x				x
<i>Penaeus</i> spp.	shrimp		R	RMP	x	R	R	R		R	R	R
<i>Portunus</i> spp.	swimming crab	x	RMP			R	R	R		R		R
<i>Sicyonia brevirostris</i>	rock shrimp		RP		RMP	R	x			x		R
<i>Trachypenaeus</i> sp.	roughneck shrimp				P					x		
FISH												
<i>Arius felis</i>	hardhead catfish			RMP							R	
<i>Balistes capriscus</i>	gray triggerfish	R	RMP		RMP	R	R	R		R		RM
<i>Caranx crysos</i>	blue runner						x					
<i>Caulolatilus cyanops</i>	blackline tilefish		x									
<i>Centropristis</i> spp.	sea bass	R	RP		R	R	R	R		R		R
<i>Chaetodipterus faber</i>	spadefish			x							x	
<i>Cynoscion arenarius</i>	sand seatrout					x						x
<i>Cynoscion nebulosus</i>	spotted seatrout			x							x	
<i>Cynoscion nothus</i>	silver seatrout			RMP							R	
<i>Diplectrum bivittatum</i>	dwarf sand perch				x							
<i>Equetus umbrosus</i>	cubbyu	x	x		x	x	x	x				x
<i>Etrumeus teres</i>	round herring				x							
<i>Gymnachirus texae</i>	fringed sole					x						
<i>Hemanthias leptus</i>	longtail bass	RP										
<i>Lagodon rhomboides</i>	pinfish	R	RP		R	R	R	R		R		
<i>Leiostomus xanthurus</i>	spot											x
<i>Lutjanus campechanus</i>	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
<i>Lutjanus synagris</i>	lane snapper				R							
<i>Micropogonias undulatus</i>	Atlantic croaker		x	RMP							R	R
<i>Mycteroperca phenax</i>	scamp				x							
<i>Orthopristis chrysoptera</i>	pigfish			x							x	
<i>Paralichthys</i> spp.	flounder	x								R		
<i>Peprilus burti</i>	gulf butterfish		x	x	x	x						x
<i>Pogonias cromis</i>	black drum			R								
<i>Priacanthus cruentatus</i>	glasseye snapper					x						
<i>Pristipomoides aquilonaris</i>	wenchman	RP	x					R				R
<i>Rhomboplites aurorubens</i>	vermillion snapper	RMP	RM				R					
<i>Sciaenops ocellatus</i>	red drum			R								
<i>Seriola dumerili</i>	greater amberjack		R		R		R	R				
<i>Sphyræna barracuda</i>	great barracuda							R				
<i>Stenotomus caprinus</i>	longspine porgy	RMP	RMP		RP	R	R	R		x		R
<i>Syacium</i> spp.	dusky flounder				P							
<i>Symphurus</i> spp.	tonguefish			x							x	
<i>Trachurus lathami</i>	rough scad				x							
<i>Trichiurus lepturus</i>	Atlantic cutlassfish			RMP							R	
<i>Trinectes maculatus</i>	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 brevirostris*), 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
<i>Archosargus probatocephalus</i>	sheepshead			x	
<i>Balistes capriscus</i>	gray triggerfish	x	x		x
<i>Caranx crysos</i>	blue runner				
<i>Caranx latus</i>	horse-eye jack	x	x		
<i>Caulolatilus cyanops</i>	blackline tilefish		x		
<i>Centropristis</i> spp.	sea bass	x	x		x
<i>Cynoscion</i> spp.	seatrout			x	
<i>Elagatis bipinnulata</i>	rainbow runner	x			
<i>Epinephelus nigritus</i>	warsaw grouper	x	x		
<i>Epinephelus niveatus</i>	snowy grouper	x	x		
<i>Haemulon</i> spp.	grunts				x
<i>Lagodon rhomboides</i>	pinfish	x	x		x
<i>Leiostomus xanthurus</i>	spot				
<i>Lutjanus campechanus</i>	red snapper		x		x
<i>Lutjanus griseus</i>	gray snapper				x
<i>Lutjanus jocu</i>	dog snapper		x		
<i>Lutjanus synagris</i>	lane snapper				x
<i>Micropogonias undulatus</i>	Atlantic croaker		x	x	
<i>Mycteroperca phenax</i>	scamp				x
<i>Paralichthys</i> spp.	flounder	x			
<i>Peprilus burti</i>	gulf butterfish		x	x	x
<i>Pogonias cromis</i>	black drum			x	
<i>Rhomboplites aurorubens</i>	vermillion snapper	x	x		
<i>Sciaenops ocellatus</i>	red drum			x	
<i>Scomberomorus cavalla</i>	king mackerel				x
<i>Seriola dumerili</i>	greater amberjack		x		x
<i>Seriola rivoliana</i>	almaco jack		x		
<i>Sphyrnaena barracuda</i>	great barracuda				
<i>Thunnus atlanticus</i>	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 brevirostris*), 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 (Sonmier Bank)

Sonmier 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 Sonmier 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.).

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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. Boycouse 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 ($\pm 2^\circ\text{C}$) 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 CO₂ 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 CO₂ 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 $\geq 50\%$ 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 $\geq 50\%$ 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 $\geq 40\%$ 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 $\geq 50\%$ 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 $\geq 97\%$ 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 $\pm$ 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 $\pm$ 1.74	79.48 $\pm$ 5.69
Silt	7.84 $\pm$ 1.36	20.52 $\pm$ 5.69 ^a
Clay	10.96 $\pm$ 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 $\text{HNO}_3\text{-H}_2\text{O}_2$, and finally $\text{HNO}_3\text{-HClO}_4\text{-HF}$ 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 $\text{Pb}(\text{NO}_3)_2$ 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 reprecipitated 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 were reviewed and audited prior to submission to CSA. Along with a case narrative and a complete QC summary, each data package was submitted in hardcopy and spreadsheet format. According to laboratory SOP, data reports, working documents, and project files will be archived for at least 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 ($\pm$ 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 ($\pm$ 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 $\pm$ 13	239 $\pm$ 67	12.3 $\pm$ 4.3	81.7 $\pm$ 10.1	1.3 $\pm$ 0.7
Vermilion 214A	300 $\pm$ 157	228 $\pm$ 29	7.7 $\pm$ 4.7	77.6 $\pm$ 12.3	1.3 $\pm$ 0.7
South Marsh Island 130B	362 $\pm$ 43	164 $\pm$ 146	5.6 $\pm$ 5.5	43.1 $\pm$ 17.3	2 $\pm$ 1.1
High Island A-595CF	1,494 $\pm$ 1,989	356 $\pm$ 19	12.5 $\pm$ 2.6	79 $\pm$ 6.7	1 $\pm$ 0.6
Component 3 Sites					
Matagorda Island 703A	56 $\pm$ 3	69 $\pm$ 7	2.6 $\pm$ 0.5	11.4 $\pm$ 4.9	0.7 $\pm$ 0.5
High Island A-323A	112 $\pm$ 6	162 $\pm$ 12	5.2 $\pm$ 2.5	29 $\pm$ 4.4	0.6 $\pm$ 0.2
Eugene Island 313A	270 $\pm$ 16	388 $\pm$ 15	13.8 $\pm$ 1.9	62.6 $\pm$ 9	2.3 $\pm$ 1.4
High Island A-382F	255 $\pm$ 43	600 $\pm$ 107	16.7 $\pm$ 4.1	120.7 $\pm$ 7.4	1.9 $\pm$ 0.6
Component 2 Sites					
West Cameron 448	0.3 $\pm$ 0.17	<0.30	0.37 $\pm$ 0.15	-----	-----
Galveston A-90	0.07 $\pm$ 0.06	0.7 $\pm$ 0.66	0.23 $\pm$ 0.21	-----	-----
South Marsh Island 186/195	0.13 $\pm$ 0.06	0.6 $\pm$ 0.53	0.03 $\pm$ 0.06	-----	-----
Galveston A-205	0.13 $\pm$ 0.06	0.93 $\pm$ 1.21	0.3 $\pm$ 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 $\pm$ 13	300 $\pm$ 157	362 $\pm$ 43	1,494 $\pm$ 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 $\pm$ 1	60 $\pm$ 8	196 $\pm$ 97	
	2 mo after initial sampling	65 $\pm$ 2	77 $\pm$ 11	315 $\pm$ 7	101 $\pm$ 11
	3 mo after initial sampling	38 $\pm$ 6	90 $\pm$ 25	265 $\pm$ 26	165 $\pm$ 259
	4 mo after initial sampling	292 $\pm$ 11	238 $\pm$ 71	287 $\pm$ 18	434 $\pm$ 13
	5 mo after initial sampling	321 $\pm$ 33		286 $\pm$ 12	
^{228}Ra	Initial sampling	239 $\pm$ 67	228 $\pm$ 29	164 $\pm$ 147	356 $\pm$ 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 $\pm$	279	257
	1 mo after initial sampling	119 $\pm$ 14	242 $\pm$ 6	193 $\pm$ 17	
	2 mo after initial sampling	277 $\pm$ 52	318 $\pm$ 11	188 $\pm$ 5	276 $\pm$ 30
	3 mo after initial sampling	126 $\pm$ 3	278 $\pm$ 26	156 $\pm$ 57	190 $\pm$ 297
	4 mo after initial sampling	274 $\pm$ 17	228 $\pm$ 63	196 $\pm$ 27	470 $\pm$ 55
	5 mo after initial sampling	306 $\pm$ 16		196 $\pm$ 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) ($\pm$ 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 $\pm$ 12.61	300.33 $\pm$ 156.87	362.33 $\pm$ 43.02	1494.00 $\pm$ 1988.78
Discharge Plume/ Receiving Water	5 m	0.40 $\pm$ 0.17	0.18 $\pm$ 0.13	0.53 $\pm$ 0.21	0.93 $\pm$ 0.31
	10 m	0.30 $\pm$ 0.10	0.70 $\pm$ 0.35	0.97 $\pm$ 0.32	0.87 $\pm$ 0.32
	30 m	0.53 $\pm$ 0.12	0.45 $\pm$ 0.24	0.57 $\pm$ 0.31	0.47 $\pm$ 0.12
	50 m	0.50 $\pm$ 0.20	0.33 $\pm$ 0.60	0.90 $\pm$ 0.26	0.45 $\pm$ 0.23
	100 m	0.57 $\pm$ 0.15	0.33 $\pm$ 0.06	0.07 $\pm$ 0.06	0.23 $\pm$ 0.06
Ambient Seawater >2,000 m		0.20 $\pm$ 0.00	0.07 $\pm$ 0.06	0.10 $\pm$ 0.00	0.03 $\pm$ 0.06
		0.23 $\pm$ 0.12	0.07 $\pm$ 0.06	0.07 $\pm$ 0.06	0.03 $\pm$ 0.06
		0.07 $\pm$ 0.16	0.10 $\pm$ 0.00	0.10 $\pm$ 0.00	0.03 $\pm$ 0.06
Component 2 Lease Block					
Water Sample Type		WC 448	SMI 186/195	GA A-205	GA A-90
Ambient Seawater		0.30 $\pm$ 0.17	0.13 $\pm$ 0.06	0.13 $\pm$ 0.06	0.07 $\pm$ 0.06

Table 6.6. Mean ^{228}Ra activities (pCi/L) ($\pm$ 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 $\pm$ 67.47	227.67 $\pm$ 28.54	164.00 $\pm$ 146.50	356.00 $\pm$ 19.31
Discharge Plume/ Receiving Water	5 m	0.83 $\pm$ 0.49	0.30 $\pm$ 0.35	0.63 $\pm$ 0.60	2.20 $\pm$ 0.52
	10 m	0.60 $\pm$ 0.56	1.87 $\pm$ 0.21	0.90 $\pm$ 0.66	1.93 $\pm$ 0.75
	30 m	1.07 $\pm$ 1.22	0.93 $\pm$ 0.85	0.33 $\pm$ 0.29	2.03 $\pm$ 1.10
	50 m	3.60 $\pm$ 4.94	0.50 $\pm$ 0.10	1.30 $\pm$ 0.20	1.93 $\pm$ 0.21
	100 m	3.87 $\pm$ 2.25	1.60 $\pm$ 0.20	1.23 $\pm$ 0.40	1.07 $\pm$ 0.72
Ambient Seawater >2,000 m		3.20 $\pm$ 2.31	0.30 $\pm$ 0.52	1.67 $\pm$ 0.65	0.63 $\pm$ 0.45
		0.10 $\pm$ 0.17	0.60 $\pm$ 0.52	1.27 $\pm$ 1.22	0.53 $\pm$ 0.35
		1.60 $\pm$ 0.70	1.03 $\pm$ 0.95	0.13 $\pm$ 0.23	1.20 $\pm$ 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 $\pm$ 0.53	0.93 $\pm$ 1.21	0.70 $\pm$ 0.66

< = Below lower limit of detection.

Table 6.7. Mean ^{210}Pb activities (pCi/L) ($\pm$ 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 $\pm$ 4.31	7.70 $\pm$ 4.70	5.60 $\pm$ 5.50	12.50 $\pm$ 2.60
Discharge Plume/ Receiving Water	5 m	0.17 $\pm$ 0.15	0.10 $\pm$ 0.14	0.07 $\pm$ 0.12	0.53 $\pm$ 0.12
	10 m	0.17 $\pm$ 0.15	0.23 $\pm$ 0.06	0.13 $\pm$ 0.12	0.80 $\pm$ 0.10
	30 m	0.03 $\pm$ 0.06	0.10 $\pm$ 0.14	0.07 $\pm$ 0.06	0.70 $\pm$ 0.20
	50 m	0.13 $\pm$ 0.12	0.33 $\pm$ 0.35	0.03 $\pm$ 0.06	0.53 $\pm$ 0.35
	100 m	<0.10	0.80 $\pm$ 0.20	0.13 $\pm$ 0.12	0.17 $\pm$ 0.29
Ambient Seawater >2,000 m		0.33 $\pm$ 0.29	0.50 $\pm$ 0.10	0.13 $\pm$ 0.06	<0.20
		0.13 $\pm$ 0.15	0.13 $\pm$ 0.15	0.03 $\pm$ 0.06	<0.20
		0.30 $\pm$ 0.10	0.53 $\pm$ 0.21	0.07 $\pm$ 0.06	<0.20
Component 2 Lease Block					
Water Sample Type		WC 448	SMI 186/195	GA A-205	GA A-90
Ambient Seawater		0.37 $\pm$ 0.15	0.03 $\pm$ 0.06	0.30 $\pm$ 0.26	0.23 $\pm$ 0.21

< = Below lower limit of detection.

Table 6.8. Means and standard deviations ($\pm$) 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) ($\pm$ 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 $\pm$ 2.79	NS	NS	NS
20 ^a	<1.50	<1.70	0.90 $\pm$ 1.56	0.44 $\pm$ 0.76
50 ^a	<1.60	<1.30	1.03 $\pm$ 1.79	0.31 $\pm$ 0.54
100	<1.50	1.90 $\pm$ 3.29	0.16 $\pm$ 0.28	<2.50
150	<1.80	<1.80	0.93 $\pm$ 1.62	2.97 $\pm$ 2.71
300	0.50 $\pm$ 0.87	1.86 $\pm$ 3.23	<1.60	<2.00
2,000	<2.00	<2.60	1.32 $\pm$ 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) ($\pm$ 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 $\pm$ 2.01	NS	NS	NS
20 ^a	1.17 $\pm$ 1.01	2.10 $\pm$ 0.44	0.83 $\pm$ 0.76	0.14 $\pm$ 0.25
50 ^a	0.63 $\pm$ 1.10	0.43 $\pm$ 0.75	0.67 $\pm$ 0.58	0.10 $\pm$ 0.18
100	0.43 $\pm$ 0.75	0.60 $\pm$ 1.04	<0.11	<0.30
150	<0.60	0.83 $\pm$ 1.44	0.37 $\pm$ 0.64	1.03 $\pm$ 0.91
300	<0.60	0.30 $\pm$ 0.53	1.37 $\pm$ 0.25	<0.60
2,000	<0.70	0.37 $\pm$ 0.98	1.40 $\pm$ 1.21	1.43 $\pm$ 0.55
Component 2 Lease Block				
	WC 448	SMI 186/195	GA A-205	GA A-90
	0.77 $\pm$ 0.68	1.00 $\pm$ 1.41	0.93 $\pm$ 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) ($\pm$ 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	1.77 $\pm$ 0.81	NS	NS	NS
20 ^a	1.30 $\pm$ 0.87	2.27 $\pm$ 0.65	1.23 $\pm$ 0.85	1.49 $\pm$ 0.18
50 ^a	0.73 $\pm$ 0.42	1.57 $\pm$ 0.06	1.40 $\pm$ 0.10	1.81 $\pm$ 0.43
100	0.50 $\pm$ 0.10	2.17 $\pm$ 0.47	1.61 $\pm$ 0.29	1.87 $\pm$ 0.29
150	0.70 $\pm$ 0.10	2.57 $\pm$ 0.72	1.37 $\pm$ 0.12	2.17 $\pm$ 0.32
300	0.93 $\pm$ 0.25	2.70 $\pm$ 0.26	3.67 $\pm$ 0.06	3.27 $\pm$ 0.59
2,000	1.53 $\pm$ 0.21	3.23 $\pm$ 0.21	3.78 $\pm$ 0.20	3.97 $\pm$ 0.80
Component 2 Lease Block				
	WC 448	SMI 186/195	GA A-205	GA A-90
	2.27 $\pm$ 0.55	3.15 $\pm$ 0.21	2.40 $\pm$ 0.26	4.53 $\pm$ 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. ²²⁶Ra 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. ²²⁸Ra 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 caprisкус*) 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	<0.017 - 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 - 0.058 (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.

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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 $\times$ discharge rate) and ^{226}Ra , ^{228}Ra , and ^{210}Pb activities in edible tissues of the jewelbox (*Chama macerophylla*) and oyster (*Crassostrea virginica*).

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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 EC₅₀ 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 caprisus*), 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 $\text{HF-HNO}_3\text{-HClO}_4$. 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 $\leq 25\%$
Continuing Calibration	Every 5-10 samples	Percent relative standard deviation $\leq 30\%$ for 90% of analytes
Matrix SRM	One per batch or 5% of field samples	Values must be within $\pm 20\%$ 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 $\leq 20\%$

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 $\mu\text{g/g}$
Arsenic	Produced Water Ambient Seawater Tissue Sediment and Produced Sands	0.3 $\mu\text{g/L}$ 0.3 $\mu\text{g/L}$ 0.011 $\mu\text{g/g}$ 0.1 $\mu\text{g/g}$
Barium	Produced Water Ambient Seawater Tissue Sediment and Produced Sands	4.6 $\mu\text{g/L}$ 0.5 $\mu\text{g/L}$ 0.013 $\mu\text{g/g}$ 0.1 $\mu\text{g/g}$
Cadmium	Produced Water Ambient Seawater Tissue Sediment and Produced Sands	0.1 $\mu\text{g/L}$ 0.001 $\mu\text{g/L}$ 0.002 $\mu\text{g/g}$ 0.002 $\mu\text{g/g}$
Chromium	Produced Water Tissue Sediment and Produced Sands	0.2 $\mu\text{g/L}$ 0.001 $\mu\text{g/g}$ 0.1 $\mu\text{g/g}$
Copper	Produced Water Ambient Seawater Tissue Sediment and Produced Sands	0.2 $\mu\text{g/L}$ 0.001 $\mu\text{g/L}$ 0.005 $\mu\text{g/g}$ 2.0 $\mu\text{g/g}$
Iron	Produced Water Ambient Seawater Tissue Sediment and Produced Sands	0.9 mg/L 0.004 $\mu\text{g/L}$ 1.0 $\mu\text{g/g}$ 5 $\mu\text{g/g}$
Lead	Produced Water Ambient Seawater Tissue Sediment and Produced Sands	0.2 $\mu\text{g/L}$ 0.001 $\mu\text{g/L}$ 0.004 $\mu\text{g/g}$ 0.1 $\mu\text{g/g}$
Mercury	Produced Water Ambient Seawater Tissue Sediment and Produced Sands	0.01 $\mu\text{g/L}$ 0.01 $\mu\text{g/L}$ 0.001 $\mu\text{g/g}$ 0.001 $\mu\text{g/g}$
Manganese	Produced Water Ambient Seawater Tissue Sediment and Produced Sands	0.1 $\mu\text{g/L}$ 0.001 $\mu\text{g/L}$ 0.40 $\mu\text{g/g}$ 2.0 $\mu\text{g/g}$

Table 7.2. (Continued).

Metal	Sample Matrix	Method Detection Limit
Molybdenum	Produced Water Ambient Seawater Tissue Sediment and Produced Sands	0.1 µg/L 0.1 µg/L 0.007 µg/g 0.1 µg/g
Nickel	Produced Water Ambient Seawater Tissue Sediment and Produced Sands	1.0 mg/L 0.003 µg/L 0.006 µg/g 0.2 µg/g
Vanadium	Produced Water Ambient Seawater Tissue Sediment and Produced Sands	1.2 µg/L 0.005 µg/L 0.009 µg/g 10 µg/g
Zinc	Produced Water Ambient Seawater Tissue Sediment and Produced Sands	0.1 µg/L 0.2 µg/L 0.2 µg/g 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 ($[\text{standard deviation}]/[\text{mean}] \times 100\%$) 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 $\pm$ 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 $\mu\text{g/L}$. 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 $\pm$ 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 $\mu\text{g/g}$ 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 ($\pm$ 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 ($\mu\text{g/L}$)	Ba (mg/L)	Cd ($\mu\text{g/L}$)	Cr ($\mu\text{g/L}$)	Cu ($\mu\text{g/L}$)	Fe (mg/L)	Hg ($\mu\text{g/L}$)	Mn (mg/L)	Mo ($\mu\text{g/L}$)	Ni ($\mu\text{g/L}$)	Pb ($\mu\text{g/L}$)	V ($\mu\text{g/L}$)	Zn (mg/L)
SMI 236A PW (n=12)	90 $\pm$ 1	700 $\pm$ 40	0.78 $\pm$ 0.18	162 $\pm$ 3	<0.1	0.4 $\pm$ 0.2	<0.2	12 $\pm$ 1	0.08 $\pm$ 0.07	1.2 $\pm$ 0.03	1.4 $\pm$ 0.3	<2	0.3 $\pm$ 0.2	<1.2	0.02 $\pm$ 0.01
VR 214A PW (n=8)	97 $\pm$ 1	440 $\pm$ 20	5.9 $\pm$ 0.5	215 $\pm$ 2	0.3 $\pm$ 0.3	<0.2	<0.2	12 $\pm$ 1	0.04 $\pm$ 0.02	4.5 $\pm$ 0.1	1.7 $\pm$ 0.2	<1	<0.2	<1.2	0.09 $\pm$ 0.01
SMI 130B PW (n=9)	129 $\pm$ 1	140 $\pm$ 10	0.74 $\pm$ 0.10	87 $\pm$ 4	<0.3	0.3 $\pm$ 0.2	<0.2	29 $\pm$ 4	<0.02	1.4 $\pm$ 0.1	0.8 $\pm$ 0.4	3 $\pm$ 2	0.7 $\pm$ 0.3	<1.2	0.02 $\pm$ 0.01
HI A-595CF PW (n=8)	175 $\pm$ 3	760 $\pm$ 50	25 $\pm$ 4	320 $\pm$ 14	0.6 $\pm$ 0.3	<0.1	<0.2	35 $\pm$ 2	0.04 $\pm$ 0.02	7.1 $\pm$ 0.3	1.4 $\pm$ 0.3	<1	20 $\pm$ 6	<1.2	3.0 $\pm$ 0.4
SMI 236A AS (n=4)	7 $\pm$ 1	(2) ^a	1.1 $\pm$ 0.1	0.088 $\pm$ 0.002	0.04 $\pm$ 0.03	ND	1.5 $\pm$ 0.2	<0.002	<0.01	<0.0002	3	1.3 $\pm$ 0.2	0.04	1.5 $\pm$ 0.2	0.005
VR 214A AS (n=3)	26 $\pm$ 2	(1) ^a	0.6 $\pm$ 0.1	0.023 $\pm$ 0.002	0.01	ND	0.5	<0.0001	<0.01	<0.0003	8	0.5	0.06	1.2 $\pm$ 0.1	0.005
SMI 130B AS (n=3)	33 $\pm$ 1	(1) ^a	1.1 $\pm$ 0.1	0.015	0.01	ND	0.2	<0.001	--	0.001	10	0.3	--	1.2 $\pm$ 0.1	0.005
HI A-595CF AS (n=3)	34 $\pm$ 1	(1) ^a	1.6 $\pm$ 0.1	0.015	0.01	ND	0.2	<0.0001	--	<0.0003	10	0.3	0.03	1.2 $\pm$ 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 $\geq 10,000$ (**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 m³ (5,269 bbl/day) at HI A-595CF and 2,353 m³ (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 $\pm$ 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 ($\mu\text{g/L}$)	Ba (mg/L)	Cd ($\mu\text{g/L}$)	Cu ($\mu\text{g/L}$)	Fe ($\mu\text{g/L}$)	Hg ($\mu\text{g/L}$)	Mn ($\mu\text{g/L}$)	Mo ($\mu\text{g/L}$)	Ni ($\mu\text{g/L}$)	Pb ($\mu\text{g/L}$)	V ($\mu\text{g/L}$)	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 $\pm$ 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 $\pm$ 0.001
GA A-90	1.0 ± 0.1	.014 ± 0.001	0.01	0.3 $\pm$ 0.1	<0.001	<0.01	<0.003	10	0.3	0.12 ± 0.08	<1.2	0.003 $\pm$ 0.001

EF (Produced Water/Ambient Seawater)

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 $43 \pm 9 \mu\text{g}$ arsenic/g (dry weight) relative to values of $26 \pm 6 \mu\text{g}$ 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 $1.6 \pm 0.1 \mu\text{g/L}$ relative to $1.1 \pm 0.1 \mu\text{g/L}$ 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:

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

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 $83.0 \pm 2.7\%$ 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 $\pm$ 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 $\mu\text{g/g}$. 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 $\pm$ 11	22 $\pm$ 13	7 $\pm$ 2	0.8 $\pm$ 0.2	4.8 $\pm$ 0.4	60 $\pm$ 10	0.051 ^a	7 $\pm$ 2	5 $\pm$ 1	9 $\pm$ 1	0.2 $\pm$ 0.1	1.6 $\pm$ 0.3	170 $\pm$ 50
HI A-323A	58 ^a	79 $\pm$ 74	11 $\pm$ 1	2.4 $\pm$ 0.3	6.6 $\pm$ 1.7	290 $\pm$ 330	0.125 ^a	12 $\pm$ 2	47 $\pm$ 13	12 $\pm$ 1	0.3 $\pm$ 0.2	3.5 $\pm$ 1.3	151 $\pm$ 42
EI 313A	47 $\pm$ 8	13 $\pm$ 1	14 $\pm$ 6	2.5 $\pm$ 0.6	5.2 $\pm$ 1.1	80 $\pm$ 30	0.065 ^a	11 $\pm$ 3	32 $\pm$ 24	8 $\pm$ 1	0.3 $\pm$ 0.1	2.8 $\pm$ 0.6	200 $\pm$ 95
HI A-595CF	41 $\pm$ 9	43 $\pm$ 24	7 $\pm$ 3	1.4 $\pm$ 0.8	6.0 $\pm$ 0.6	210 $\pm$ 100	0.046 ^a	9 $\pm$ 3	6 $\pm$ 3	6 $\pm$ 2	0.7 $\pm$ 0.5	2.2 $\pm$ 0.6	145 $\pm$ 70
MI 703A	29 $\pm$ 3	14 $\pm$ 15	4 $\pm$ 1	4 $\pm$ 3	6.8 $\pm$ 1.3	110 $\pm$ 60	0.110 ^a	9 $\pm$ 3	34 $\pm$ 11	11 $\pm$ 5	0.2 $\pm$ 0.1	2.3 $\pm$ 0.2	100 $\pm$ 30
SMI 130B	26 $\pm$ 8	14 $\pm$ 2	5 $\pm$ 1	1.3 $\pm$ 0.5	11 $\pm$ 3	180 $\pm$ 40	0.054 ^a	19 $\pm$ 10	6 $\pm$ 4	4 $\pm$ 2	0.2 $\pm$ 0.04	3.0 $\pm$ 2.5	90 $\pm$ 10
VN 214A	24 $\pm$ 6	20 $\pm$ 20	5 $\pm$ 1	2.0 $\pm$ 0.3	6.2 $\pm$ 0.4	70 $\pm$ 20	0.051 ^a	15 $\pm$ 2	47 $\pm$ 13	5 $\pm$ 1	0.2 $\pm$ 0.1	4.1 $\pm$ 1.1	180 $\pm$ 90
Eastern oyster													
SMI 229C	10 $\pm$ 1	12 $\pm$ 6	5 $\pm$ 1	0.7 $\pm$ 0.1	98 $\pm$ 90	320 $\pm$ 170	0.13 ^a	28 $\pm$ 13	0.24 ^a	1.0 $\pm$ 0.3	0.4 $\pm$ 0.2	1.4 $\pm$ 0.1	1760 $\pm$ 90
SMI 236A	11 $\pm$ 1	11 $\pm$ 4	7 $\pm$ 2	1.3 $\pm$ 0.2	140 $\pm$ 30	480 $\pm$ 210	0.06 ^a	18 $\pm$ 5	0.22 ^a	1.0 $\pm$ 0.1	0.6 $\pm$ 0.02	1.6 $\pm$ 0.3	1810 $\pm$ 300
GOM ^b	8 $\pm$ 3	--	6 $\pm$ 2	0.6 $\pm$ 0.3	250 $\pm$ 120	370 $\pm$ 140	0.05 ^a	18 $\pm$ 8	--	2.2 $\pm$ 0.6	0.6 $\pm$ 0.5	--	1880 $\pm$ 730
GOM ^c	10 $\pm$ 7	--	4 $\pm$ 2	0.6 $\pm$ 0.4	150 $\pm$ 100	290 $\pm$ 160	0.13 ^a	14 $\pm$ 7	--	1.8 $\pm$ 1.6	0.6 $\pm$ 0.9	--	2150 $\pm$ 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 $\mu\text{g/g}$ 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 ($\geq 10,000$) 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 $\mu\text{g/g}$ 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 $1.1 \mu\text{g/g}$ relative to $0.5 \mu\text{g/g}$ 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 $\pm$ 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 $\mu\text{g/g}$. Reference sites are indicated in **bold**. Any number from this study shown as less than (<) a given value (e.g., <0.01 $\mu\text{g Cd/g}$ 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 $\pm$ 1.8	0.06 $\pm$ 0.03	<0.01	0.03 $\pm$ 0.02	0.8 $\pm$ 0.1	9 $\pm$ 2	0.72 $\pm$ 0.19	--	<0.04	1.4 $\pm$ 0.1	0.1 $\pm$ 0.05	0.86 $\pm$ 0.23	13.3 $\pm$ 0.7
VR 214A	1.1 $\pm$ 0.6	0.1 $\pm$ 0.1	0.03 $\pm$ 0.01	0.10 $\pm$ 0.14	0.8 $\pm$ 0.1	12 $\pm$ 5	0.37 $\pm$ 0.20	0.4 $\pm$ 0.1	2.4 $\pm$ 3.5	1.2 $\pm$ 0.1	<0.1	0.52 $\pm$ 0.03	14.6 $\pm$ 0.4
SMI 130B	0.8 $\pm$ 0.4	0.05 $\pm$ 0.05	--	0.04 $\pm$ 0.02	0.8 $\pm$ 0.1	7 $\pm$ 1	0.28 $\pm$ 0.03	0.2	0.08 $\pm$ 0.07	1.4 $\pm$ 0.1	<0.1	0.70 $\pm$ 0.07	13.2 $\pm$ 0.7
Gray Triggerfish													
VR 298/305	83 $\pm$ 26	0.07 $\pm$ 0.02	<0.01	0.10 $\pm$ 0.08	1.2 $\pm$ 0.3	8 $\pm$ 2	0.47 $\pm$ 0.31	--	<0.06	1.6 $\pm$ 0.1	0.13 $\pm$ 0.07	1.0 $\pm$ 0.3	24 $\pm$ 8
VR 214A	24 $\pm$ 9	0.06 $\pm$ 0.04	<0.03	0.05 $\pm$ 0.05	1.0 $\pm$ 0.1	8 $\pm$ 1	1.1 $\pm$ 0.3	1.1 $\pm$ 0.4	0.25 $\pm$ 0.50	1.5 $\pm$ 0.1	0.07 $\pm$ 0.05	0.7 $\pm$ 0.1	19 $\pm$ 1
SMI 130B	33 $\pm$ 13	0.6 $\pm$ 0.5	<0.10	0.11 $\pm$ 0.16	1.2 $\pm$ 0.2	9 $\pm$ 3	0.44 $\pm$ 0.52	1.1 $\pm$ 0.7	<0.03	1.6 $\pm$ 0.1	0.09 $\pm$ 0.06	0.8 $\pm$ 0.1	23 $\pm$ 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 = Vermillion 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 $\mu\text{g/g}$ (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 $\pm$ 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 $\mu\text{g/g}$.

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

Lease Areas:

VR - Vermilion

SMI- South Marsh Island

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

Biota/Metal	As ($\mu\text{g/g}$)	Ba ($\mu\text{g/g}$)	Cd ($\mu\text{g/g}$)	Cr ($\mu\text{g/g}$)	Cu ($\mu\text{g/g}$)	Fe ($\mu\text{g/g}$)	Hg ($\mu\text{g/g}$)	Mn ($\mu\text{g/g}$)	Mo ($\mu\text{g/g}$)	Ni ($\mu\text{g/g}$)	Pb ($\mu\text{g/g}$)	V ($\mu\text{g/g}$)	Zn ($\mu\text{g/g}$)
<u>Invertebrates</u>													
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
<u>Fish</u>													
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 ($>4,000 \mu\text{g/g}$) 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 $30 \mu\text{g/g}$ 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 $\pm$ 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/g)	Ba (μ g/g)	Ca (%)	Cd (μ g/g)	Cr (μ g/g)	Cu (μ g/g)	Fe (%)	Hg (μ g/g)	Mn (μ g/g)	Mo (μ g/g)	Ni (μ g/g)	Pb (μ g/g)	V (μ g/g)	Zn (μ g/g)
SMI 130B	3.9 $\pm$ 0.1	3.7 $\pm$ 0.3	1,181 $\pm$ 832	0.79 $\pm$ 0.10	0.43 $\pm$ 0.06	28 $\pm$ 3	18.7 $\pm$ 2.7	1.6 $\pm$ 0.3	0.003 $\pm$ 0.001	99.5 $\pm$ 2.6	3.4 $\pm$ 0.3	12.9 $\pm$ 0.5	14.5 $\pm$ 1.6	16.3 $\pm$ 0.2	140 $\pm$ 27
SMI 236A	2.0 $\pm$ 0.1	2.1 $\pm$ 0.2	816 $\pm$ 57	0.24 $\pm$ 0.03	0.1 $\pm$ 0.00	8 $\pm$ 1	7.4 $\pm$ 6.2	0.5 $\pm$ 0.1	0.005 $\pm$ 0.001	32.6 $\pm$ 2.9	0.8 $\pm$ 0.2	< 5.0	8.5 $\pm$ 0.0	10.7 $\pm$ 0.9	25 $\pm$ 2

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

Site (m) ^a	Al (%)	As ($\mu\text{g/g}$)	Ba ($\mu\text{g/g}$)	Ca (%)	Cd ($\mu\text{g/g}$)	Cr ($\mu\text{g/g}$)	Cu ($\mu\text{g/g}$)	Fe (%)	Hg ($\mu\text{g/g}$)	Mn ($\mu\text{g/g}$)	Mo ($\mu\text{g/g}$)	Ni ($\mu\text{g/g}$)	Pb ($\mu\text{g/g}$)	V ($\mu\text{g/g}$)	Zn ($\mu\text{g/g}$)
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 $\pm 1,560$	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 $\pm 1,750$	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 ± 10 8
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 $\pm 4,550$	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 discharge 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 $\geq 10,000$. 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 $\leq 4,000 \text{ m}^3/\text{day}$ (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 capricus*). 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.

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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 C₁₀ to usually C₄₀ 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 C₄₀ 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.

<u>VAHs^a</u>
*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)
<u>Polycyclic Aromatic and Heterocyclic Compounds (PAHs)^a</u>
*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.

^aC₁, C₂, C₃, C₄ refer to number of alkyl (CH₂) substitutions on the parent compound.

the n-alkane distribution. Natural (i.e., biogenic) hydrocarbons of marine origin have SHC compounds in the C₁₅ to C₂₂ n-alkane range, whereas hydrocarbons of terrestrial origin are represented by higher molecular weight SHCs in the C₂₇ to C₃₅ 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 C₁₀ to C₄₀ plus the concentration of the unresolved complex mixture (UCM) between n-alkanes C₁₀ and C₄₀. 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 (C₁, C₂, C₃, C₄ 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 (C₀ > C₁ > C₂ > C₃ > C₄). 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 C₂ or C₃ 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: $C_1 > C_2 > \dots$). 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-d₆, ethylbenzene-d₁₀, and naphthalene-d₈) and recovery internal standards (chlorobenzene-d₅) 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.

Water and Interstitial Water

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

Sediment Extraction

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

Tissue Extraction

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 ($\mu\text{g/kg}$) 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

Extract Cleanup

Figure 8.4. Extract cleanup column procedure.

HPLC Fractionation

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, C₁-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 $\mu\text{g/kg}$	1-7 $\mu\text{g/kg}$	5-20 ng/L
THC	1-2 $\mu\text{g/g}$	--	10-20 $\mu\text{g/L}$
SHC	0.05-0.1 $\mu\text{g/g}$	--	0.5-1.0 $\mu\text{g/L}$
VAH	--	--	0.2-0.5 $\mu\text{g/L}$

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 C₁-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, C₃-benzenes, and C₄-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 $\pm 25\%$ from the mean. SMI 236A produced water had the highest individual and total VAH concentrations at 5,200 $\mu\text{g/L}$ mean total VAHs; and HI A-595CF produced water had the lowest at 1,800 $\mu\text{g/L}$ 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 $\mu\text{g/L}$. BTEX concentrations in produced water discharged into the central Gulf of Mexico ranged from 68 to 38,000 $\mu\text{g/L}$ (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 C₁₀ to C₃₂ (**Figures 8.9 through 8.12**). The SHC distribution reflects the solubilities and produced oil composition of the analytes. Due to the volatility of C₁₀ through C₁₄, 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; $\mu\text{g/L}$) 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 ($\mu\text{g/L}$)	Total PAH ($\mu\text{g/L}$)
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 C₂-phenanthrenes and C₂-dibenzothiophenes (C2P/C2D) and C₃-phenanthrenes and C₃-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 8.15. 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 C₃-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 C₂-phenanthrenes and C₂-dibenzothiophenes (C2P/C2D) is 1.25 and the ratio of C₃-phenanthrenes and C₃-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 8.20. 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 C₁₆ and C₁₇. 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 (C₁) 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 C₁₆ and C₁₇ 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 (C₂₉ and C₃₁). 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 (μ g/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 Replicates A, B, and C at SMI 236A, discharge.

Sample: SMI236-SED-I 20-0-2cm-A

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 $\mu\text{g/kg}$. 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 C₂-phenanthrenes relative to the C₂-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 (C₂₁) and terrestrial (C₂₉ and C₃₁) 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 $\mu\text{g/kg}$), 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 C₁₈ 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 $\mu\text{g/kg}$, 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 naphthalenes 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.

Sample: SMI236-SED-I 2000-0-2cm-B

Figure 8.27. SHC and PAH distributions in Sediment Replicate B at SMI 236A, 2,000 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 $\mu\text{g/kg}$) were lower than those from SMI 236A, 2,000-m station; however, in some samples, fluoranthene, pyrene, benzo(b)fluoranthene, 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 $\mu\text{g/kg}$). 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 8.32. SHC distribution in Sediment Replicates A, B, and C at SMI 130B, 2,000 m.

Sample: SMI130-SED-I 2000-0-2cm-B

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 $\mu\text{g/kg}$. Except for perylene which was approximately 30 $\mu\text{g/kg}$, individual and alkyl group PAH concentrations were low, generally less than 6 $\mu\text{g/kg}$, 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 $\mu\text{g/kg}$ (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 $\mu\text{g/kg}$ with individual concentrations usually less than 3 $\mu\text{g/kg}$, 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 $\mu\text{g/kg}$, 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.

Sample: HI595-SED-I 60-0-2cm-A

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

Sample: HI595-SED-I 2000-0-2cm-B

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

Sample: SMI186/195-SED-0-2cm-C

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 $\mu\text{g/kg}$. The SHC and PAH concentrations were at trace levels generally below the detection limits of the methods (<0.01 mg/kg SHCs and <2 $\mu\text{g/kg}$ 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 $\mu\text{g/kg}$ 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 $\mu\text{g/kg}$ (total PAH concentrations ranged from 180 to 220 $\mu\text{g/kg}$). 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.

Sample: G205-SED-0-2cm-A

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 $\mu\text{g/kg}$. Brooks *et al.* (1990) determined total PAHs in nearshore sediments at a mean concentration of $96 \pm 112 \mu\text{g/kg}$ and offshore sediments (Texas shelf) at a mean concentration of $29 \pm 28 \mu\text{g/kg}$, comparable to the results in this study. SHC concentrations were very low (<0.03 $\mu\text{g/g}$) with little to no UCM and THC concentrations no higher than 10 $\mu\text{g/g}$. 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 ($\mu\text{g/kg}$ dry weight)	Range ($\mu\text{g/kg}$ dry weight)
<u>SMI 236A</u>			
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*
<u>VR 214A</u>			
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*
<u>SMI 130B</u>			
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*
<u>HI A-595CF</u>			
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 crustaceans 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 $\mu\text{g/kg}$ dry weight). Traces of C₀, C₁-naphthalenes, biphenyl, and phenanthrene (<2 $\mu\text{g/kg}$) 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 $\mu\text{g/kg}$ 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 bioaccumulation 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 $\mu\text{g/kg}$ for Atlantic croaker to 40 $\mu\text{g/kg}$ 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 $\mu\text{g/kg}$. Without this replicate, the croaker mean total PAH concentration would be approximately 120 $\mu\text{g/kg}$, similar to the catfish. The blue crab mean total PAH concentration was also relatively high at 450 $\mu\text{g/kg}$, 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 C₀- through C₂-phenanthrenes and dibenzothiophenes (<5 $\mu\text{g/kg}$) were detected in most replicates and were accompanied with larger amounts of all the alkyl naphthalenes (10-50 $\mu\text{g/kg}$). 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 ($<10 \mu\text{g/kg}$ 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 $245 \mu\text{g/kg}$ 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 $\sim 20 \mu\text{g/kg}$) with one high total PAH replicate at $180 \mu\text{g/kg}$ (**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 $\mu\text{g/kg}$ 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 $\mu\text{g/kg}$ total PAHs. Four out of five replicates of each of the fish species and rock shrimp contained no more than 10 $\mu\text{g/kg}$ total PAHs. A representative PAH distribution is presented in **Figure 8.49**. The occasional replicate with elevated PAH concentrations still contained less than 40 $\mu\text{g/kg}$ 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 $\mu\text{g/kg}$, and the range for the replicates was consistent from 24 to 87 $\mu\text{g/kg}$. 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 8.50. 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 $\mu\text{g/kg}$ 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 ($<10 \mu\text{g/kg}$). Except for one replicate of the wenchman, total PAH concentrations of fillets and whole tissue ranged from 2 to 23 $\mu\text{g/kg}$ 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 $\mu\text{g/kg}$ 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 $\mu\text{g/kg}$. 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 8.54. 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 THC_s, SHC_s, VAH_s, and PAH_s 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 VAH_s, SHC_s, and PAH_s. Total VAH concentrations ranged from 1,800 $\mu\text{g/L}$ at HI A-595CF to 5,200 $\mu\text{g/L}$ at SMI 236A with compositions typical of other Gulf discharges (Neff, 1996). The SHC distribution of n-alkanes from C₁₀ to C₃₂ 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 $\mu\text{g/L}$ THC_s (60 $\mu\text{g/L}$ total PAH_s) than the other produced waters. For the three produced water sites except SMI 130B, over 95% of the PAH_s 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, C₂-phenanthrenes and C₂-dibenzothiophenes (C₂P/C₂D) and C₃-phenanthrenes and C₃-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 PAH_s - 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 $\mu\text{g/kg}$) and trace levels of alkyl phenanthrenes and dibenzothiophenes (<5 $\mu\text{g/kg}$) 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 $\mu\text{g/kg}$. At SMI 130B, the full suite of petrogenic PAHs was accompanied by equal amounts of pyrogenic PAHs at 1,700 $\mu\text{g/kg}$ 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 $\mu\text{g/kg}$ 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 depuration influencing the PAH distribution in the organism. The effect of these processes in this organism presently is not well known.

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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 ($\approx$ 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 $\mu\text{g/L}$ (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 $\mu\text{g/L}$ (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 $\mu\text{g/L}$ (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 $\mu\text{g/L}$) 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 $\mu\text{g/L}$ (parts per billion) (**Table 9.2**). The range of arsenic concentrations in individual samples is 0.53 to 31 $\mu\text{g/L}$. Arsenic concentrations in produced waters from the Gulf of Mexico have been reported in the range of less than 0.11 to 320 $\mu\text{g/L}$ (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 $\mu\text{g/L}$.

Platform	Sample	Arsenic	Barium	Cadmium	Mercury
Discharge Sites					
SMI 236A	Produced Water	0.78	160,000	<0.10	0.08
	Ambient Seawater	1.0	88	0.03	<0.01
SMI 130B	Produced Water	0.74	87,000	<0.3	<0.02
	Ambient Seawater	1.1	15	0.01	0.02
VR 214A	Produced Water	5.9	220,000	0.31	0.04
	Ambient Seawater	0.64	23	0.01	<0.01
HI A-595CF	Produced Water	25	320,000	0.62	0.04
	Ambient Seawater	1.6	15	0.01	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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$, with an average of about 1.7 $\mu\text{g/L}$ (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 $\mu\text{g/L}$ total arsenic (overall mean, 1.1 $\mu\text{g/L}$) (**Table 9.2**). Seawater from reference stations contains mean concentrations of 0.81 to 1.2 $\mu\text{g/L}$ arsenic (overall mean, 1.0 $\mu\text{g/L}$) (**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 $\mu\text{g/L}$ to 320,000 $\mu\text{g/L}$ (**Table 9.2**). Produced waters from throughout the Gulf of Mexico contain 1.0 to as high as 650,000 $\mu\text{g/L}$ barium (Neff and Sauer, 1995). Barium concentrations as high as 2,000,000 $\mu\text{g/L}$ 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 $\mu\text{g/L}$) 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 $\mu\text{g/L}$ (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 $\mu\text{g/L}$ (overall mean, 16 $\mu\text{g/L}$) (**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 $\mu\text{g/L}$ (overall mean, 35 $\mu\text{g/L}$). 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 0.62 $\mu\text{g/L}$ (**Table 9.2**). Produced waters from elsewhere in the Gulf of Mexico contain 0.06 to 98 $\mu\text{g/L}$ cadmium (Neff, 1996a). Concentrations of cadmium in produced water from the North Sea range from less than 0.0005 $\mu\text{g/L}$ to 490 $\mu\text{g/L}$ (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 $\mu\text{g/L}$) (**Chapter 7** and Trefry *et al.*, 1995). Cadmium concentrations may be as high as 0.2 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ (Yeats *et al.*, 1995). Surface water samples from the four reference locations contain 0.01 to 0.02 $\mu\text{g/L}$ cadmium (overall mean, 0.02 $\mu\text{g/L}$) (**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 $\mu\text{g/L}$ (overall mean, 0.02 $\mu\text{g/L}$). 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ (Neff, 1996a). Mercury concentrations as high as 33 $\mu\text{g/L}$ 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 $\mu\text{g/L}$). Concentrations of total mercury in uncontaminated coastal and estuarine waters may be as high as 0.02 $\mu\text{g/L}$ (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 11,800 $\mu\text{g/kg}$ total adsorbed mercury (Lindberg *et al.*, 1975).

Surface water from the four reference locations contains <0.01 to 0.02 $\mu\text{g/L}$ total mercury (overall mean, 0.01 $\mu\text{g/L}$) (**Table 9.2**). Mercury in surface water 2,000 m from the four produced water discharges contain averages of <0.01 to 0.04 $\mu\text{g/L}$ (overall mean, 0.02 $\mu\text{g/L}$). 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 $\mu\text{g/L}$, range 0.03 to 0.04 $\mu\text{g/L}$) is near produced water discharge HI A-595CF; the produced water from this platform contains a mean of 0.04 $\mu\text{g/L}$ (range 0.02 $\mu\text{g/L}$ to 0.06 $\mu\text{g/L}$) 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, Natchez, 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$. All other produced water samples from this platform contain less than 0.20 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$, have been reported in produced waters from other sources (Neff, 1996a). Most produced waters contain less than 500 $\mu\text{g/L}$ dissolved copper.

Mean copper concentrations in surface water samples from the four reference locations are in the range of 0.20 to 0.40 $\mu\text{g/L}$ (overall mean, 0.30 $\mu\text{g/L}$). Mean copper concentrations in surface waters 2,000 m from the four produced water discharges range from 0.22 to 1.4 $\mu\text{g/L}$ (overall mean, 0.58 $\mu\text{g/L}$) (**Table 9.4**). These concentrations are in reasonable agreement with reported concentrations of copper in clean oceanic water of 0.03 to 0.35 $\mu\text{g/L}$ (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 $\mu\text{g/L}$ copper (DeLeon *et al.*, 1986). Coastal waters and bays in Louisiana and Texas contain 0.13 to 1.70 $\mu\text{g/L}$ 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 $\mu\text{g/L}$) 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 $\mu\text{g/L}$ (**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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$. Produced water from two coastal platforms analyzed by Neff *et al.* (1992) contains 0.40 and 1.27 $\mu\text{g/L}$ nickel. Produced water from oil and gas platforms discharging to the North Sea contain 10 to 170 $\mu\text{g/L}$ nickel (Stephenson *et al.*, 1994).

Mean concentrations of nickel in surface seawater from the four reference sites are 0.24 to 0.35 $\mu\text{g/L}$ (overall mean, 0.29 $\mu\text{g/L}$) (**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 $\mu\text{g/L}$.

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 $\mu\text{g/L}$.

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 $\mu\text{g/L}$ copper; ten analyses resulted in <0.20 $\mu\text{g/L}$ copper.

(overall mean, 0.55 $\mu\text{g/L}$). 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 $\mu\text{g/L}$) 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 $\mu\text{g/L}$ to 20 $\mu\text{g/L}$ (**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 $\mu\text{g/L}$. All but one replicate sample of produced water from the other three platforms contain less than 1 $\mu\text{g/L}$ lead. Produced water from discharges to Louisiana coastal waters analyzed by Rabalais *et al.* (1991) contain ND to 29 $\mu\text{g/L}$ lead. Lead concentrations as high as 18,000 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ (overall mean, 0.26 $\mu\text{g/L}$) (**Table 9.4**). Similar concentrations (0.03 to 0.34 $\mu\text{g/L}$; overall mean, 0.12 $\mu\text{g/L}$) 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 $\mu\text{g/L}$ (Neff, 1996a). In coastal waters and estuaries, concentrations of dissolved lead may increase to more than 1.0 $\mu\text{g/L}$. 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 $\mu\text{g/L}$ dissolved lead and 0.026 to 0.53 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ zinc. Individual samples contain 0.3 to 3,600 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ to 150,000 $\mu\text{g/L}$ (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 $\mu\text{g/L}$ (overall mean, 5.1 $\mu\text{g/L}$) (**Table 9.4**). Mean zinc concentrations in surface seawater 2,000 m from the four produced water discharges are 4.6 to 5.8 $\mu\text{g/L}$ (overall mean, 5.4 $\mu\text{g/L}$). 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 $\mu\text{g/L}$ (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 $\mu\text{g/L}$ having been reported (Morse *et al.*, 1993; Law *et al.*, 1994). The waters of Galveston Bay contain 0.3 to 4.5 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ zinc (DeLeon *et al.*, 1986). **Chapter 7** and Trefry *et al.* (1996) reported a mean zinc concentration of 5 $\mu\text{g/L}$ in seawater in the vicinity of oil platforms in the northwestern Gulf of Mexico. Concentrations of dissolved zinc in seawater below about 0.8 $\mu\text{g/L}$ may cause deficiency for this essential trace element in marine organisms (vanTilborg and van Assche, 1995); concentrations above about 100 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$) are only slightly higher than concentrations in surface water near the other three produced water discharges (3.0 to 9.8 $\mu\text{g/L}$, overall mean 5.3 $\mu\text{g/L}$), and roughly comparable to zinc concentrations in surface water from most of the reference stations (2.1 to 9.5 $\mu\text{g/L}$, overall mean 5.1 $\mu\text{g/L}$). 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 $\mu\text{g/L}$ (**Table 9.5**). Concentrations of iron in produced waters discharged to the North Sea are in the range of less than 10 $\mu\text{g/L}$ to 32,000 $\mu\text{g/L}$ (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 $\mu\text{g/L}$ (overall mean, 0.29 $\mu\text{g/L}$) (**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 $\mu\text{g/L}$ (overall mean, 0.55 $\mu\text{g/L}$). 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 $\mu\text{g/L}$ in the channel to about 0.06 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ at the surface to 0.02 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ manganese. North Sea produced water contains 100 to 22,000 $\mu\text{g/L}$ 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 $\mu\text{g/L}$.

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 $\mu\text{g/L}$ (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 $\mu\text{g/L}$ (overall mean, 0.51 $\mu\text{g/L}$). 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 $\mu\text{g/L}$ in the English Channel to 0.03 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ (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 $\mu\text{g/L}$ (Burton and Statham, 1982); the average concentration in surface waters of the eastern North Pacific Ocean is 10.3 $\mu\text{g/L}$ (Collier, 1985). Typically, molybdenum concentrations increase from 0.5 $\mu\text{g/L}$ or less in the freshwater portion of river estuaries to about 10 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ (overall mean, 9.9 $\mu\text{g/L}$) (**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 $\mu\text{g/L}$ (overall mean, 8.0 $\mu\text{g/L}$). 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 $\mu\text{g/L}$ (**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 $\mu\text{g/L}$ (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 $\mu\text{g/L}$) (**Table 9.5**). Means *et al.* (1990) reported concentrations of 1.2 to 60 $\mu\text{g/L}$ 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 $\mu\text{g/L}$). 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$. However, surface waters of the North Atlantic Ocean contain 1.62 to 1.72 $\mu\text{g/L}$ vanadium (Middleburg *et al.*, 1988); in the North Pacific Ocean, average vanadium concentration increases from 1.67 $\mu\text{g/L}$ at the surface to 1.85 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ (overall mean, 1.2 $\mu\text{g/L}$) (**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 $\mu\text{g/L}$ (overall mean, 1.3 $\mu\text{g/L}$). 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 $\mu\text{g/L}$.

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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ (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 $\mu\text{g/L}$) 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 $\mu\text{g/L}$ (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 $\mu\text{g/L}$.

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 $\mu\text{g/L}$) and zinc (mean 3,000 $\mu\text{g/L}$) in this produced water by 100-fold would yield ambient concentrations of 0.2 and 30 $\mu\text{g/L}$, 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 $\mu\text{g/L}$) 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 $\mu\text{g/L}$ (**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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$. 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 $\mu\text{g/L}$ (Neff, 1996a). BTEX concentrations as high as 578,000 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$.

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 ($9.9 \mu\text{g/L}$) 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 $\mu\text{g/L}$.

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
<i>m,p</i> -Xylenes	180	360	460	350
<i>o</i> -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 $\mu\text{g/L}$.

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
<i>m,p</i> -Xylenes	0.86	0.16	0.11	210
<i>o</i> -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 $\mu\text{g/L}$.

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
<i>m</i> -, <i>p</i> -Xylenes	9.4	0.20	ND	38
<i>o</i> -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 $\mu\text{g/L}$.

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
<i>m</i> -, <i>p</i> -Xylenes	3.3	0.67	0.32	140
<i>o</i> -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 $\mu\text{g/L}$.

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
<i>m,p</i> -Xylenes	0.30	3.3	0.83	1,200
<i>o</i> -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 $\mu\text{g/L}$ in the produced water effluent from the Buccaneer Platform off Galveston, TX, to 65 $\mu\text{g/L}$ at the air/water interface below the outfall, to less than 2 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ in the effluent to 0.43 $\mu\text{g/L}$ (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 $\mu\text{g/L}$. One sample contains 2.9 $\mu\text{g/L}$ and may have been contaminated from an exogenous source. The presence of 0.35 $\mu\text{g/L}$ 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 $\mu\text{g/L}$, though concentrations up to about 0.5 $\mu\text{g/L}$ 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 $\mu\text{g/L}$; in coastal waters of the Gulf, background concentrations of toluene are in the range of 0.01 to 0.06 $\mu\text{g/L}$ (Sauer, 1981). Surface water from the mouth of the Brazos River, TX contains up to 0.11 $\mu\text{g/L}$ toluene and 0.23 $\mu\text{g/L}$ benzene (McDonald *et al.*, 1988). The surface water sample from SMI 186/195 contains 0.88 $\mu\text{g/L}$ toluene.

Table 9.14. Range of concentrations of total monocyclic aromatic hydrocarbons in surface waters from the four reference sites. Concentrations are $\mu\text{g/l}$.

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, ethylbenzene, 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 $\mu\text{g/L}$.

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
<i>m</i> -, <i>p</i> -Xylenes	730	1.8	0.002
<i>o</i> -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 $\mu\text{g/L}$.

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
<i>m</i> -, <i>p</i> -Xylenes	730	3.6	0.005
<i>o</i> -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 $\mu\text{g/L}$.

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
<i>m,p</i> -Xylenes	730	4.6	0.006
<i>o</i> -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 $\mu\text{g/L}$.

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
<i>m,p</i> -Xylenes	730	3.5	0.005
<i>o</i> -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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ (**Table 9.19**). These concentrations are in the low to middle part of the range of PAH concentrations (80 to 1,860 $\mu\text{g/L}$) 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 ($\approx 0.001 \mu\text{g/L}$). Produced water from SMI 130B contains the highest concentrations of total PAHs and most individual PAHs. Mean concentrations above about 1 $\mu\text{g/L}$ 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 $\mu\text{g/L}$.

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 ₃ -Dibenzothiophenes	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 C₂-naphthalenes, biphenyl, fluorene, and C₁-phenanthrenes. Dibenzothionene and alkyl dibenzothionenes 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$. One of the three replicate samples from this site contains 1.1 $\mu\text{g/L}$ total PAHs, 97% of which are low molecular weight compounds. The other two samples contain 0.06 and 0.02 $\mu\text{g/L}$ (mean 0.04 $\mu\text{g/L}$) 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 $\mu\text{g/L}$), compared to the other two replicates (0.05 and 0.11 $\mu\text{g/L}$, average 0.08 $\mu\text{g/L}$). 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 $\mu\text{g/L}$.

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 $\mu\text{g/L}$.

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 $\mu\text{g/L}$.

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 ₃ -Dibenzothiophenes	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 $\mu\text{g/L}$.

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 $\mu\text{g/L}$ (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 $\mu\text{g/L}$. 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 $\mu\text{g/L}$ (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 $\mu\text{g/L}$ for phenanthrene to 710 $\mu\text{g/L}$ 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 $\mu\text{g/L}$.

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 ₃ -Dibenzothiophenes	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 $\mu\text{g/L}$.

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 C₂-naphthalenes, C₃-chrysenes, and C₄-chrysenes. C₄-naphthalenes, C₃-phenanthrenes, and C₄-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 C₂-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 $\mu\text{g/L}$.

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 $\mu\text{g/L}$.

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 $\mu\text{g/L}$.

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 $\mu\text{g/L}$.

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 $\mu\text{g/L}$. 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 ($\sum \text{SEM}$) 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 $[\Sigma \text{SEM}] < [\text{AVS}]$. 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 metalloids in surficial sediments (0-2 cm) from the four Component 2 reference sites in the northwest Gulf of Mexico. Concentrations, except where noted, are $\mu\text{g/g}$ 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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ 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 -MnO₂) 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 (FeS₂), and possibly greigite (Fe₃S₄) (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 $\mu\text{g/g}$ dry weight (discharge station at SMI 236A) to 15 $\mu\text{g/g}$ (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 $\mu\text{g/g}$ to 21 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ (Moore and Ramamoorthy, 1984). However, the average concentration of arsenic in deep sea sediments is about 40 $\mu\text{g/g}$ (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 $\mu\text{g/g}$ (**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 $\mu\text{g/L}$ (station at the produced water discharge at SMI 236A) to 6,500 $\mu\text{g/g}$ (60-m station at HI A-595CF) (**Tables 9.29** through **9.32**). Mean barium concentrations in sediments are above 1,000 $\mu\text{g/L}$ at five of the nine sampling stations near produced water discharges. At a sixth station, the mean concentration is 960 $\mu\text{g/L}$. 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 $\mu\text{g/g}$ (**Table 9.28**).

Table 9.33. Proposed sediment quality guidelines ($\mu\text{g/g}$ dry weight) and "high" concentrations (geometric mean plus one standard deviation) from the National Status and Trends database for metals in marine sediments. The effects range-low (ERL) is the lower 10th percentile effects concentration and the effects range-median (ERM) is the 50th percentile effects concentration. From Long *et al.* (1995) 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 $\mu\text{g/g}$ and a range in marine sediments from less than 1 $\mu\text{g/g}$ to at least 2,000 $\mu\text{g/g}$ (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 $\mu\text{g/g}$ barium, whereas, fine grained sediments, rich in clay minerals, may contain more than 1,000 $\mu\text{g/g}$ barium (Neff, 1996a). Boothe and James (1985) reported barium concentrations ranging from 245 to 1,000 $\mu\text{g/g}$ 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 $\mu\text{g/L}$) 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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$, sediments near the four produced water discharges contain excess barium ranging from 200 to 6,000 $\mu\text{g/g}$ at stations 20, 50, and 60 m from the discharges and 240 to 5,800 $\mu\text{g/g}$ 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 $\mu\text{g/g}$. However, it is probable that it is substantially less than 6,000 $\mu\text{g/L}$. 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 $\mu\text{g/g}$ (**Tables 9.29** through **9.32**). The “high” concentration of cadmium in marine sediments is 0.54 $\mu\text{g/g}$ (**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 $\mu\text{g/g}$. 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 $\mu\text{g/g}$, 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 $\mu\text{g/g}$. Cadmium concentrations in uncontaminated marine sediments usually fall in the range of 0.1 to 0.6 $\mu\text{g/g}$ (Warren, 1981). Sediments from uncontaminated estuaries along the Atlantic and Gulf coasts of Florida contain 0.01 $\mu\text{g/g}$ to about 0.3 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ (Salomons and Förstner, 1984; Mayer, 1988). The “high” concentration of chromium in U.S. coastal marine sediments is 125 $\mu\text{g/g}$ (**Table 9.33**). Sediments from the coastal zone of Louisiana contain 17 to 66 $\mu\text{g/g}$ chromium. Galveston Bay, Texas, sediments contain 4 to 102 $\mu\text{g/g}$ chromium (Morse *et al.*, 1993). Sediments from the Calcasieu River estuary, Louisiana, contain 10 to 150 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ at the produced water discharge station at SMI 236A to 96 $\mu\text{g/g}$ 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 $\mu\text{g/g}$.

The chromium concentrations for the four produced waters examined in this study ranged from <0.1 to 0.4 $\mu\text{g/L}$, 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 $\mu\text{g/L}$ to approximately 390 $\mu\text{g/L}$ chromium. By comparison, concentrations of chromium in clean oceanic water usually fall in the range of 0.10 to 0.55 $\mu\text{g/L}$ (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 $\mu\text{g/g}$ (Salomons and Förrester, 1984; Ridgway and Price, 1987). Sediments from Galveston Bay, Texas, and coastal Louisiana contain 2 to 30.3 $\mu\text{g/g}$ copper. The “high” concentration of copper in National Status and Trends coastal marine sediments is 42 $\mu\text{g/g}$ (**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 of natural sediment copper concentrations (**Tables 9.28 through 9.32**). Sediments from the reference sites contain 4.3 to 12 $\mu\text{g/g}$ copper; sediments collected at different distances from the four produced water discharges contain means of 6.2 to 25 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ (**Table 9.33**). Surficial sediments from the four reference sites in this study

contain 0.01 to 0.04 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ 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 $\mu\text{g/L}$ total mercury (**Table 9.30**). Sediments 2,000 m from this discharge contain 0.05 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ (Turekian and Wedepohl, 1961). Molybdenum in sediments from a eutrophic area of the continental shelf off west Africa contained 0.74 to 2.62 $\mu\text{g/g}$; 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 $\mu\text{g/g}$ molybdenum (Bowen, 1979). Mean molybdenum concentrations in sediments near the four reference sites are in the range of 0.74 to 4.4 $\mu\text{g/g}$ (**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 $\mu\text{g/g}$. 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 $\mu\text{g/g}$ nickel. The “high” concentration of nickel in sediments from National Status and Trends monitoring sites is 42 $\mu\text{g/g}$ (**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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ (**Table 9.28**). Surficial sediments near the four produced water discharges contain means of 5.8 to 31 $\mu\text{g/g}$ (**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 $\mu\text{g/g}$ (the highest mean concentration measured) at the 20-m station and 21 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ (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 $\mu\text{g/g}$ (**Table 9.33**). Sediments from Galveston Bay, Texas, contain 12 to 46 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ (**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 $\mu\text{g/g}$ at the 50-m station at SMI 130A to 78 $\mu\text{g/g}$ at the 60-m station at HI A-595CF and 110 $\mu\text{g/g}$ 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ 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 $\mu\text{g/g}$ (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 $\mu\text{g/g}$ (Kennicutt, 1995).

Mean concentrations in surficial sediments near the four reference sites are in the range of 29 to 96 $\mu\text{g/g}$ (**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 $\mu\text{g/g}$ at the discharge station at SMI 236A to 130 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ zinc (Morse *et al.*, 1993). Sediments from the coastal zone of Louisiana contain 52 to 133 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ zinc (**Chapter 7** and Trefry *et al.*, 1996). The “high” concentration of zinc in sediments from the National Status and Trends Program is 135 $\mu\text{g/g}$ (**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 $\mu\text{g/g}$ zinc (**Table 9.28**). Zinc concentrations in sediments near the four produced water discharges are higher; mean concentrations range from 96 $\mu\text{g/g}$ at the 2,000-m station at HI A-595CF to 800 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ lead. The ERM for lead in marine sediments is 218 $\mu\text{g/g}$. 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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ nickel, equivalent to 0.50 toxic units. However, as discussed above, nickel concentrations in apparently uncontaminated sediments frequently are much higher than 26 $\mu\text{g/g}$. 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 $\mu\text{g/g}$ 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 $\mu\text{g/L}$ produced water and $\mu\text{g/g}$ 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 $\mu\text{g/g}$ (**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 $\mu\text{g/g}$. 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 $\mu\text{g/g}$. 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 $\mu\text{g/g}$) are comparable to or only slightly higher than PAH concentrations (means, 0.023 to 0.210 $\mu\text{g/g}$) 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 $0.029 \pm 0.028 \mu\text{g/g}$; nearshore sediments contained a mean of $0.096 \pm 0.112 \mu\text{g/g}$ total PAHs. Mean total PAH concentrations generally were less than 0.05 $\mu\text{g/g}$ 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 $\mu\text{g/g}$, 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 $\mu\text{g/g}$ 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 ₃ -Dibenzothiophenes	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 $\mu\text{g/g}$ 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 ₃ -Dibenzothiophenes	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 $\mu\text{g/g}$ 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 ₃ -Dibenzothiophenes	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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ total PAHs, including 0.57 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ (Michibata, 1996); and accumulation of zinc to concentrations approaching 150,000 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ (**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 $\mu\text{g/g}$) and the “high” concentration (17 $\mu\text{g/g}$). 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 $\mu\text{g/L}$ at VR 214A (nearshore) to 1.6 $\mu\text{g/L}$ at HI A-595CF (offshore). Open ocean waters may contain up to 3 $\mu\text{g/L}$ 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 $\mu\text{g/g}$ dry weight.

Species	Arsenic	Barium	Cadmium	Mercury
Atlantic croaker (<i>Micropogonias undulatus</i>)	1.5	8.4	0.06	0.029
Hardhead catfish (<i>Arius felis</i>)	0.48	1.4	0.04	0.36
Silver seatrout (<i>Cynoscion nothus</i>)	0.12	5.9	0.18	0.037
Atlantic cutlassfish (<i>Trichiurus lepturus</i>)	0.20	1.8	0.19	0.054
Penaeid shrimp (<i>Penaeus</i> spp.)				
muscle	4.1	4.6	0.14	0.040
other	2.9	99	0.38	0.029
Blue crab (<i>Callinectes</i> spp.)	10	6.8	0.39	0.29
Eastern oyster (<i>Crassostrea virginica</i>)	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 $\mu\text{g/g}$ dry weight.

Species	Arsenic	Barium	Cadmium	Mercury
Red snapper (<i>Lutjanus campechanus</i>)				
fillet	1.1	0.15	0.04	0.37
carcass	0.77	1.5	0.05	0.16
Gray triggerfish (<i>Balistes capriscus</i>)				
fillet	22	0.06	<0.04	1.0
carcass	13	8.3	0.63	0.62
Jewelbox (<i>Chama macerophylla</i>)	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 $\mu\text{g/g}$ dry weight.

Species	Arsenic	Barium	Cadmium	Mercury
Red snapper (<i>Lutjanus campechanus</i>)				
fillet	0.72	0.07	<0.05	0.28
carcass	0.60	2.0	0.18	0.16
Gray triggerfish (<i>Balistes capriscus</i>)				
fillet	33	0.61	<0.10	0.44
carcass	20	15	0.58	0.41
Longspine porgy (<i>Stenotomus caprinus</i>)	0.24	32	0.13	0.42
Vermilion snapper (<i>Rhomboplites aurorubens</i>)	3.2	0.05	0.02	0.13
Swimming crab (<i>Portunus</i> spp.)	35	120	0.87	0.094
Jewelbox (<i>Chama macerophylla</i>)	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 $\mu\text{g/g}$ dry weight.

Species	Arsenic	Barium	Cadmium	Mercury
Vermilion snapper (<i>Rhomboplites aurorubens</i>)	3.2	0.15	0.02	0.37
Longspine porgy (<i>Stenotomus caprinus</i>)	0.40	26	0.25	0.65
Jewelbox (<i>Chama macerophylla</i>)	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 $\mu\text{g/g}$ dry weight.

Species	Location	Arsenic	Barium	Cadmium	Mercury
Red snapper (<i>Lutjanus campechanus</i>)	Bank	4.2	0.06	<0.02	0.72
Gray triggerfish (<i>Balistes caprisus</i>)	Bank	86	0.08	0.01	0.47
Jewelbox (<i>Chama macerophylla</i>)	EI 313A (D)	43	13	14	0.065
Jewelbox (<i>C. macerophylla</i>)	HI A-323A (D)	59	79	11	0.12
Jewelbox (<i>C. macerophylla</i>)	HI A-389 (R)	32	74	7.1	0.051
Jewelbox (<i>C. macerophylla</i>)	MI 703A (D)	29	14	4.2	0.11
Eastern oyster (<i>Crassostrea virginica</i>)	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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ barium, respectively, in muscle tissue. Jewelbox from discharge sites contain means of 26 to 59 $\mu\text{g/g}$ barium in soft tissues, compared to a mean of 32 $\mu\text{g/g}$ 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 $\mu\text{g/g}$) than from a natural hard bank (mean, 0.08 $\mu\text{g/g}$). The carcass (including organ tissues and bone) of gray triggerfish from the discharge site contains a mean of 15 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ wet weight (equivalent to approximately 475 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$, 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 $\mu\text{g/g}$. Fish muscle tissue contains 0.001 to 5.8 $\mu\text{g/g}$ (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 of marine animals are 2.97 $\mu\text{g/g}$ and 5.7 $\mu\text{g/g}$, 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 $\mu\text{g/g}$ (**Tables 9.41** through **9.45**). Crustaceans contain 0.029 to 0.29 $\mu\text{g/g}$ total mercury. The two species of bivalves contain mean concentrations of 0.05 to 0.12 $\mu\text{g/g}$. These concentrations are consistent with concentrations reported in the published scientific literature for these taxa. Fish may contain up to more than 100 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$. 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 of marine animals from throughout the world. Concentrations are $\mu\text{g/g}$ 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 $\mu\text{g/g}$ (**Tables 9.49** through **9.53**). Tissues of portunid crabs and penaeid shrimp contain higher mean concentrations, ranging from 26 to 61 $\mu\text{g/g}$. However, oysters contain the highest mean concentrations of copper in their tissues, with means of 140 $\mu\text{g/g}$ at discharge site SMI 236A and 160 $\mu\text{g/g}$ at nearby reference site SMI 229C. Mean concentrations of copper in soft tissues of jewelboxes range from 4.7 to 11 $\mu\text{g/g}$.

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 $\mu\text{g/g}$, 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 $\mu\text{g/g}$ nickel. Carcass of gray triggerfish also contains elevated levels of nickel. Swimming crabs from discharging site SMI 130B contain a mean of 7.1 $\mu\text{g/g}$ nickel. Other crustaceans contain low concentrations of nickel. Mean nickel concentrations in soft tissues of jewelboxes are high, ranging from 3.7 to 12 $\mu\text{g/g}$, 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 $\mu\text{g/g}$ dry weight.

Species	Copper	Nickel	Lead	Zinc
Atlantic croaker (<i>Micropogonias undulatus</i>)	2.6	2.4	0.23	54
Hardhead catfish (<i>Arius felis</i>)	2.4	0.11	0.60	54
Silver seatrout (<i>Cynoscion nothus</i>)	5.2	1.4	0.21	72
Atlantic cutlassfish (<i>Trichiurus lepturus</i>)	2.2	1.5	0.12	41
Penaeid shrimp (<i>Penaeus</i> spp.)				
muscle	32	1.0	0.10	54
other	60	3.9	0.52	62
Blue crab (<i>Callinectes</i> spp.)	61	1.3	0.16	194
Eastern oyster (<i>Crassostrea virginica</i>)	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 $\mu\text{g/g}$ dry weight.

Species	Copper	Nickel	Lead	Zinc
Red snapper (<i>Lutjanus campechanus</i>)				
fillet	0.75	1.2	0.28	15
carcass	1.9	1.5	0.20	48
Gray triggerfish (<i>Balistes capriscus</i>)				
fillet	1.1	1.5	0.10	20
carcass	3.6	1.6	7.5	280
Jewelbox (<i>Chama macerophylla</i>)	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 $\mu\text{g/g}$ dry weight.

Species	Copper	Nickel	Lead	Zinc
Red snapper (<i>Lutjanus campechanus</i>)				
fillet	0.75	1.4	0.08	13
carcass	1.5	1.4	0.84	34
Gray triggerfish (<i>Balistes caprisus</i>)				
fillet	1.2	1.6	0.11	23
carcass	20	7.0	1.5	320
Longspine porgy (<i>Stenotomus caprinus</i>)	1.5	1.8	0.90	45
Vermilion snapper (<i>Rhomboplites aurorubens</i>)	1.4	1.5	0.08	13
Swimming crab (<i>Portunus</i> spp.)	26	7.1	0.93	78
Jewelbox (<i>Chama macerophylla</i>)	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 $\mu\text{g/g}$ dry weight.

Species	Copper	Nickel	Lead	Zinc
Vermilion snapper (<i>Rhomboplites aurorubens</i>)	1.6	1.4	0.22	13
Longspine porgy (<i>Stenotomus caprinus</i>)	1.8	5.3	0.56	56
Jewelbox (<i>Chama macerophylla</i>)	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 $\mu\text{g/g}$ dry weight.

Species	Location	Copper	Nickel	Lead	Zinc
Red snapper (<i>Lutjanus campechanus</i>)	Bank	0.83	1.4	0.09	13
Gray triggerfish (<i>Balistes caprisus</i>)	Bank	1.2	1.6	0.12	24
Jewelbox (<i>Chama macerophylla</i>)	EI 313A (D)	5.1	7.8	0.41	200
Jewelbox (<i>C. macerophylla</i>)	HI A-323A (D)	6.6	12	0.43	150
Jewelbox (<i>C. macerophylla</i>)	HI A-389 (R)	4.7	9.1	0.24	170
Jewelbox (<i>C. macerophylla</i>)	MI 703A (D)	6.8	11	4.3	100
Eastern oyster (<i>Crassostrea virginica</i>)	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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ nickel in soft tissues (Presley *et al.*, 1990). Clams and shrimp from lower Chesapeake Bay, VA, contain 6.5 to 11.5 $\mu\text{g/g}$ and 23.5 to 59.5 $\mu\text{g/g}$, 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 $\mu\text{g/g}$ (**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 $\mu\text{g/g}$ lead in soft tissues. Carcass of gray triggerfish from two discharge sites contain means of 7.5 and 1.5 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ lead (NOAA, 1995). Benthic crustaceans from the New York Bight contain 0.05 to 17.5 $\mu\text{g/g}$ lead (Steimle *et al.*, 1994). Twenty-six species of teleost fish from the western Mediterranean Sea contain 0.05 to 55.9 $\mu\text{g/g}$ lead (Pastor *et al.*, 1994).

The TSC concentration for lead in tissues of aquatic animals is 2.08 $\mu\text{g/g}$. The “high” concentration is 4.3 $\mu\text{g/g}$ in mussels and 0.96 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ (**Tables 9.49** through **9.53**). Carcass of gray triggerfish from two discharge sites contains means of 280 and 320 $\mu\text{g/g}$ zinc. Crustaceans contain mean zinc concentrations of 54 to 190 $\mu\text{g/g}$. Oysters contain the highest concentrations of zinc (means of 1,800 $\mu\text{g/g}$ in animals from a discharge site and 1,800 $\mu\text{g/g}$ in animals from a nearby reference site). Jewelboxes contain lower concentrations of zinc than oysters. Mean concentrations range from 91 to 200 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ zinc in whole tissues (Ridout *et al.*, 1989). Twelve species of fish from the eastern Mediterranean Sea contain 4.1 to 59 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ in muscle of red snapper from Sonnier Bank to 13 $\mu\text{g/g}$ 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 $\mu\text{g/g}$) and discharging site HI A-595CF (13 $\mu\text{g/g}$). 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 $\mu\text{g/g}$) 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 $\mu\text{g/g}$, 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 $\mu\text{g/g}$ in whole blue crabs to 7.2 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ dry weight.

Species	Chromium	Iron	Manganese	Molybdenum	Vanadium
Atlantic croaker (<i>Micropogonias undulatus</i>)	1.9	240	29	0.58	2.0
Hardhead catfish (<i>Arius felis</i>)	0.54	38	1.5	0.02	0.11
Silver seatrout (<i>Cynoscion nothus</i>)	2.6	280	15	0.18	0.54
Atlantic cutlassfish (<i>Trichiurus lepturus</i>)	2.2	150	8.6	0.13	0.27
Penaeid shrimp (<i>Penaeus</i> spp.) muscle	0.36	44	5.1	0.11	0.44
other	7.2	860	51	0.28	1.9
Blue crab (<i>Callinectes</i> spp.)	0.17	300	5.4	0.24	1.0
Eastern oyster (<i>Crassostrea virginica</i>)	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 $\mu\text{g/g}$ dry weight.

Species	Chromium	Iron	Manganese	Molybdenum	Vanadium
Red snapper (<i>Lutjanus campechanus</i>) fillet	0.12	12	0.36	4.0	0.52
carcass	0.50	48	4.2	0.56	1.9
Gray triggerfish (<i>Balistes capriscus</i>) fillet	0.06	8.6	0.98	0.51	0.72
carcass	0.64	68	54	0.75	2.1
Jewelbox (<i>Chama macerophylla</i>)	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 $\mu\text{g/g}$ dry weight.

Species	Chromium	Iron	Manganese	Molybdenum	Vanadium
Red snapper (<i>Lutjanus campechanus</i>)					
fillet	0.04	50	0.22	0.18	0.70
carcass	0.45	35	3.3	0.45	1.4
Gray triggerfish (<i>Balistes capriscus</i>)					
fillet	0.11	9.1	0.70	<0.03	0.79
carcass	0.74	67	24	0.47	1.7
Longspine porgy (<i>Stenotomus caprinus</i>)	5.4	250	23	0.22	2.4
Vermilion snapper (<i>Rhomboplites aurorubens</i>)	0.13	11	0.22	2.2	0.75
Swimming crab (<i>Portunus</i> spp.)	2.7	460	90	0.31	8.0
Jewelbox (<i>Chama macerophylla</i>)	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 $\mu\text{g/g}$ dry weight.

Species	Chromium	Iron	Manganese	Molybdenum	Vanadium
Vermilion snapper (<i>Rhomboplites aurorubens</i>)	0.19	8.9	0.23	0.10	0.75
Longspine porgy (<i>Stenotomus caprinus</i>)	13	310	25	0.21	2.8
Jewelbox (<i>Chama macerophylla</i>)	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 $\mu\text{g/g}$ dry weight.

Species	Location	Cr	Fe	Mn	Mo	V
Red snapper (<i>Lutjanus campechanus</i>)	Bank	0.03	8.2	---	<0.04	0.88
Gray triggerfish (<i>Balistes caprisus</i>)	Bank	0.10	8.2	---	0.06	0.96
Jewelbox (<i>Chama macerophylla</i>)	EI 313A (D)	2.5	83	11	32	2.8
Jewelbox (<i>C. macerophylla</i>)	HI A-323A (D)	2.4	290	12	47	3.5
Jewelbox (<i>C. macerophylla</i>)	HI A-389 (R)	0.84	62	7.0	4.7	1.6
Jewelbox (<i>C. macerophylla</i>)	MI 703A (D)	4.0	111	8.9	34	2.3
Eastern oyster (<i>Crassostrea virginica</i>)	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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ (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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ in different species (**Table 9.55**). Concentration ranges in shrimp and fish muscle are 4.5 to 78 $\mu\text{g/g}$ and 7.7 to 36 $\mu\text{g/g}$, 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 $\mu\text{g/g}$ iron, respectively (Morse *et al.*, 1993). Concentrations as high as 1,300 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ (**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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ (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 $\mu\text{g/g}$ dry weight. Thompson (1990) reports typical concentrations of iron in fish muscle of <5 to 70 $\mu\text{g/g}$ 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 $\mu\text{g/g}$. The highest mean concentration is in oysters from a shallow reference site, SMI 229. Oysters from the nearby discharging site contain 18 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ and 14.8 ± 8.8 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ in muscle tissues, and the shrimp contain 51 $\mu\text{g/g}$ manganese in non-muscle tissues. Portunid crabs from discharging site SMI 130B contain a mean of 90 $\mu\text{g/g}$ manganese. Shrimp from the south Texas outer continental shelf contain 0.8 to 13 $\mu\text{g/g}$ manganese in muscle and up to 17 $\mu\text{g/g}$ in viscera (Table 9.55). Frenet and Alliot (1985) reported an average of 30 $\mu\text{g/g}$ manganese in shrimp (*Palaemonetes varians*) from coastal waters of France. Prawns (*Pandalus platyceros*) from coastal waters of British Columbia contain 5 to 14 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ manganese, but occasionally as

much as 75 $\mu\text{g/g}$ (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 $\mu\text{g/g}$ at a discharge and reference site, respectively. Jewelboxes contain means of 4.7 to 47 $\mu\text{g/g}$ molybdenum. Crustaceans contain low concentrations, ranging from 0.11 to 0.31 $\mu\text{g/g}$. Mean molybdenum concentrations in fish muscle range from less than 0.03 to 4.0 $\mu\text{g/g}$.

Li (1991) reports an average molybdenum concentration of 0.39 $\mu\text{g/g}$ in tissues of marine animals. Oysters from different locations in Mississippi Sound contain a mean of 13 $\mu\text{g/g}$ molybdenum (Lytle and Lytle, 1990). Spot prawns from British Columbia contain 0.24 to 1.6 $\mu\text{g/g}$ molybdenum in different tissues (Whyte and Boutillier, 1991). Liver of cod from Newfoundland, Canada, contains 0.08 to 0.34 $\mu\text{g/g}$ molybdenum (Hellou *et al.*, 1992). Muscle tissue contains 0.01 to 0.06 $\mu\text{g/g}$. 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 $\mu\text{g/g}$ (**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 $\mu\text{g/g}$.

These tissue concentrations of vanadium probably are normal. The average concentration of vanadium in tissues of marine animals is 3.5 $\mu\text{g/g}$ (Li, 1991). Several species of mesopelagic crustaceans from the open northeastern Atlantic Ocean contain 0.17 to 1.84 $\mu\text{g/g}$ (Ridout *et al.*, 1989). Prawns from British Columbia, Canada, contain 0.33 to 1.34 $\mu\text{g/g}$ vanadium in different tissues (Whyte and Boutillier, 1991). Deposit-feeding clams (*Scrobidularia plana*) from the Bou Regreg estuary, Morocco, contain 18 to 25 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ (Phillips *et al.*, 1987). Vanadium concentrations in a pelagic food chain in the open Mediterranean sea range from 1.45 $\mu\text{g/g}$ in microplankton to 0.07 $\mu\text{g/g}$ in shrimp and 0.08 $\mu\text{g/g}$ in myctophid fish (Fowler, 1986). Myctophids from elsewhere in the Mediterranean contain up to 1.12 $\mu\text{g/g}$ 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 $\mu\text{g/L}$ for naphthalene (MW 128 daltons) to about 4 $\mu\text{g/L}$ 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:

$$\log \text{BCF} = a \log K_{ow} + b$$

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 $\log \text{BCF}$. 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:

$$\log \text{BCF} = 0.79 \log K_{ow} - 0.40$$

and was derived from a regression of $\log \text{BCF}$ 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 Pruett *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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ total PAHs. A composite sample of oysters from the fourth platform, SMI 236A, contains 0.026 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ and a range of 0.02 to 1.92 $\mu\text{g/g}$. Whole specimens of the other three species of fish from SMI 236A generally contain less than 0.1 $\mu\text{g/g}$ 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 $\mu\text{g/g}$.

Blue crabs from SMI 236A also contain somewhat elevated concentrations of total PAHs, ranging from 0.031 to 0.97 $\mu\text{g/g}$ in muscle tissue and 0.61 $\mu\text{g/g}$ (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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$).

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 $\mu\text{g/L}$ total PAHs (**Table 9.19**), and ambient seawater 2,000 m from the platform contains only about 0.07 $\mu\text{g/L}$ 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 $\mu\text{g/g}$ dry weight.

Species	Tissue	Total PAHs	Concentration Range
Red snapper (<i>Lutjanus campechanus</i>)	muscle	0.015	0.007 - 0.026
	carcass	0.076	0.035 - 0.117
Gray triggerfish (<i>Balistes caprisus</i>)	muscle	0.011	0.002 - 0.021
	carcass	0.092	0.010 - 0.272
Seabass (<i>Centropristis philadelphica</i>)	muscle	0.009	0.002 - 0.037
Pinfish (<i>Lagodon rhomboides</i>)	muscle	0.010	0.003 - 0.012
Longspine porgy (<i>Stenotomus caprinus</i>)	whole	0.009	0.004 - 0.013
Rock shrimp (<i>Squilla brevirostris</i>)	muscle	0.0007	ND - 0.001
	other	0.019	0.019*
Swimming crab (<i>Portunus</i> sp.)	whole	0.054	0.024 - 0.087
Jewelbox (<i>Chama macerophylla</i>)	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 $\mu\text{g/g}$ dry weight.

Species	Tissue	Total PAHs	Concentration Range
Red snapper (<i>Lutjanus campechanus</i>)	muscle	0.012	0.007 - 0.020
	carcass	0.109	0.034 - 0.110
Gray triggerfish (<i>Balistes caprisus</i>)	muscle	0.025	0.002 - 0.078
	carcass	0.033	0.014 - 0.070
Longspine porgy (<i>Stenotomus caprinus</i>)	whole	0.006	ND - 0.009
Dusky flounder (<i>Syacium</i> sp.)	whole	0.0002	ND - 0.001
Rock shrimp (<i>Squilla brevirostris</i>)	muscle	0.051	0.001 - 0.245
	other	0.028	0.028*
Roughneck shrimp (<i>Trachypenaeus</i> sp.)	muscle	0.003	ND - 0.011
	other	0.016	0.016*
Blue crab (<i>Callinectes</i> spp.)	whole	0.052	0.014 - 0.182
Jewelbox (<i>Chama macerophylla</i>)	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 $\mu\text{g/g}$ dry weight.

Species	Tissue	Total PAHs	Concentration Range
Vermilion snapper (<i>Rhomboplites aurorubens</i>)	muscle	0.025	0.002 - 0.058
	carcass	0.098	0.060 - 0.208
Longspine porgy (<i>Stenotomus caprinus</i>)	whole	0.002	0.001 - 0.008
Lefteye Flounder (Bothidae)	whole	0.014	0.005 - 0.023
Wenchman (<i>Pristipomoides aquilonaris</i>)	muscle	0.051	0.004 - 0.194
Longtail bass (<i>Hemanthias leptus</i>)	muscle	0.015	0.003 - 0.023
Jewelbox (<i>Chama macerophylla</i>)	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 $\mu\text{g/g}$ dry weight.

Species	Tissue	Total PAHs	Concentration Range
Atlantic croaker (<i>Micropogonias undulatus</i>)	whole	0.476	0.022 - 1.924
Hardhead catfish (<i>Arius felis</i>)	whole	0.110	0.051 - 0.130
Silver seatrout (<i>Cynoscion nothus</i>)	whole	0.040	0.023 - 0.053
Atlantic cutlassfish (<i>Trichiurus lepturus</i>)	whole	0.062	0.049 - 0.072
Penaeid shrimp (<i>Penaeus</i> spp.)	muscle	0.009	0.003 - 0.011
	other	0.041	0.041*
Blue crab (<i>Callinectes</i> spp.)	muscle	0.446	0.031 - 0.972
	other	0.608	0.608*
Eastern oyster (<i>Crassostrea virginica</i>)	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 ($0.15 \mu\text{g/g}$), 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 $0.24 \mu\text{g/g}$ 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 $1.92 \mu\text{g/g}$ 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 $0.28 \mu\text{g/g}$ 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 $0.97 \mu\text{g/g}$ total PAHs. Four replicate blue crab muscle samples from the same platform contain 0.031 to $0.85 \mu\text{g/g}$ 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, alkylfluorenes, and phenanthrene. The other blue crab from the platform with an elevated PAH content ($0.85 \mu\text{g/g}$) 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 9.2. 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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$. 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 (11.68 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ 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.

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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 C₁₉ to 90.4% for anthracene.

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Table 10.2. Selected saturated hydrocarbon results ($\mu\text{g/g}$ 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 ($\mu\text{g/g}$ 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

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

June 1997

Prepared by:

Continental Shelf Associates, Inc.
759 Parkway Street
Jupiter, Florida 33477
Telephone: (561) 746-7946

Prepared for:

U.S. Department of Energy
Mrs. Rhonda P. Lindsey
Contracting Officer's Representative
220 North Virginia Avenue
Bartlesville, Oklahoma 74003
Telephone: (918) 337-4407

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LIST OF ACRONYMS

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

ABSTRACT

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

EXECUTIVE SUMMARY

Introduction

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

Study Sites

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

Quality Assurance Program

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

Sampling Program

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

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

invertebrates were also collected in the vicinity of the two facilities where multiple surveys were conducted.

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

Radionuclide Activities

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

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

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

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

Environmental Risk Assessment for Metals and Aromatic Hydrocarbons

Produced Water and Ambient Water

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

Sediment and Sediment Interstitial Water

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

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

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

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

Infauna

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

CHAPTER 1 - INTRODUCTION

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

1.1 BACKGROUND

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

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

1.2 OBJECTIVES OF THE PROJECT

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

1.3 OBJECTIVES OF THE STUDY

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

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

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CHAPTER 2 - STUDY DESIGN AND OVERVIEW

*Alan Hart
Continental Shelf Associates, Inc.
Jupiter, Florida*

2.1 SELECTION OF SITES

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

Three facilities were selected as study sites:

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

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

2.2 SURVEYS AND SAMPLING ELEMENTS

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

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

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

Table 2.1. Survey schedule.

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

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

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

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

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

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

2.3 SAMPLE AND DATA COLLECTION

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

Table 2.2. Summary of sampling to be conducted.

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

Table 2.2. (Continued).

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

Table 2.2. (Continued).

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

* Four Isle Dome only.

2.3.1 Water Quality and Currents

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

2.3.2 Produced Water

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

2.3.3 Sediments

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

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

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

VAH Target Compounds	Alkane and Isoprenoid (SHC) Target Compounds	PAH and alkyl PAH Target Compounds
Benzene Toluene Xylene C ₃ -benzene C ₄ -benzene Naphthalene	n-C ₁₀ Decane n-C ₁₁ Undecane n-C ₁₂ Dodecane n-C ₁₃ Tridecane n-C ₁₄ Tetradecane n-C ₁₅ Pentadecane n-C ₁₆ Hexadecane n-C ₁₇ Heptadecane n-C ₁₈ Octadecane n-C ₁₉ Nonadecane n-C ₂₀ Eicosane n-C ₂₁ Heneicosane n-C ₂₂ Docosane n-C ₂₃ Tricosane n-C ₂₄ Tetracosane n-C ₂₅ Pentacosane n-C ₂₆ Hexacosane n-C ₂₇ Heptacosane n-C ₂₈ Octacosane n-C ₂₉ Nonacosane n-C ₃₀ Triacontane n-C ₃₁ Hentriacontane n-C ₃₂ Dotriacontane Pristane Phytane	Naphthalene 1-Methylnaphthalene 2-Methylnaphthalene 2,6-Dimethylnaphthalene 1,3,5-Trimethylnaphthalene C ₁ -Naphthalenes C ₂ -Naphthalenes C ₃ -Naphthalenes C ₄ -Naphthalenes Biphenyl Acenaphthylene Acenaphthene Fluorene C ₁ -Fluorenes C ₂ -Fluorenes C ₃ -Fluorenes Dibenzothiophene C ₁ -Dibenzothiophenes C ₂ -Dibenzothiophenes C ₃ -Dibenzothiophenes Phenanthrene Anthracene 1-Methylphenanthrene C ₁ -Phenanthrenes/Anthracenes C ₂ -Phenanthrenes/Anthracenes C ₃ -Phenanthrenes/Anthracenes C ₄ -Phenanthrenes/Anthracenes Fluoranthene Pyrene C ₁ -Fluoranthenes/Pyrenes Benzo[a]anthracene Chrysene C ₁ -Chrysenes C ₂ -Chrysenes C ₃ -Chrysenes C ₄ -Chrysenes Benzo[b]fluoranthene Benzo[k]fluoranthene (BKF) Benzo[e]pyrene (BEP) Benzo[a]pyrene (BAP) Perylene (PERY) Indeno[1,2,3-c,d]pyrene Dibenzo[a,h]anthracene Benzo[g,h,i]perylene

2.3.4 Sediment Interstitial Water

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

2.3.5 Infauna

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

2.3.6 Biological Tissue

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

2.3.7 Marsh Sediments

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

2.4 QUALITY ASSURANCE AND QUALITY CONTROL

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

It should be noted that due to budgetary constraints, the field and analytical program was reduced with the agreement of DOE and the SRC. These modifications to the original SAP and rationale are documented in CSA's project files. The data quality objectives (DQOs) were

substantially achieved with the exception of meeting target detection limits for radionuclides in sediment samples. The QA Program ensured that the data quality was adequate to meet the study objectives.

2.4.1 Purpose

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

2.4.2 Components and Characteristics

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

- Accuracy - the degree of agreement between a measurement and an accepted reference or known (certified true) value. Accuracy is quantified and usually expressed as percent recovery, the difference between the mean and true value expressed as a percentage of the true value. Analytical instruments and methods are calibrated with known samples (standards) or reference materials for each sample run to ensure accuracy. Accuracy may be documented using procedural blanks, matrix spikes/matrix spike duplicates, surrogate compounds, internal standards, and Standard Reference Materials (SRMs). Consistent differences between a set of measurements and a reference standard due to instrumental or analytical problems or limitations is known as bias.
- Precision - a quantitative measure of the variability of two measurements taken under similar conditions and usually expressed in terms of either the relative standard deviation (RSD), the relative percent difference (RPD), or as a range. Analytical laboratory precision may be evaluated through the use of analytical duplicates. Comparison of matrix spike/matrix spike duplicates, and reference analyses/laboratory control values can also be calculated to provide an estimate of laboratory precision.
- Comparability - a qualitative characteristic expressing the confidence with which one set of data can be compared with another. Assurance of the comparability of two or more sets of data can be achieved through the use of standard techniques to collect and analyze representative samples, and by reporting analytical results in appropriate units. Comparability may be assessed through the use of matrix spike/matrix spike duplicates, surrogate compounds, duplicates, SRMs, equipment rinsate blanks, and field blanks. Interlaboratory calibration of methods also assure comparability of data and results.
- Representativeness - a qualitative expression of how well a sample or group of samples reflect the characteristics of the media at the sampling point.

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

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

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

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

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

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

2.5 ACKNOWLEDGEMENTS

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

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

*Maureen Mulino and Michael Rayle
Steimle & Associates, Inc.
Metairie, Louisiana*

*Bruce Graham and Luis Lagera
(Interstitial Water Sampling and Quality Assurance/Quality Control)
Continental Shelf Associates, Inc.
Jupiter, Florida*

3.1 FIELD METHODS AND LABORATORY SAMPLE PROCESSING

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

Table 3.1. Produced water termination and surveys schedule.

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

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

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

3.1.1 Water Quality and Current Data Collection

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

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

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

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

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

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

3.1.2 Produced Water Sampling

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

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

3.1.2.1 Radionuclides

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

3.1.2.2 Metals

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

3.1.2.3 Hydrocarbons

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

Samples for SHCs/PAHs were collected from the discharge pipe in pre-cleaned 1 L glass containers, preserved with 100 mL methylene chloride, and stored at 4°C. Samples were

collected hourly for 8 hours and shipped to ADL for compositing into two, 4-hour composite samples.

3.1.2.4 Total Organic Carbon

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

3.1.3 Sediment and Interstitial Water Sampling

3.1.3.1 Discharge and Reference Stations

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

3.1.3.1.1 Sediment Sampling

Long Sediment Cores

Collection

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

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

Laboratory Processing

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

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

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

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

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

Short Sediment Cores

Collection

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

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

Laboratory Processing

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

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

3.1.3.1.2 Interstitial Water Sampling

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

Collection

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

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

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

Laboratory Processing

Radionuclides

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

A diagram of the cylinder/piston unit used to hold sediment during interstitial water extraction is presented in **Figure 3.4**. The cylinder/piston unit was comprised of thick-walled cylinder and a piston equipped with dual o-rings to provide an air-tight seal between the walls of the cylinder and the piston. Cylinder/piston units were constructed of both teflon and polyvinyl chloride (PVC). The base of the cylinder had a small centered opening for funneling extracted interstitial water into a sample container. The cylinder/piston unit was cleaned with Liquinox and

distilled water and thoroughly rinsed with distilled water prior to the initial "squeezing" for each day of operations; the cylinder/piston unit was only thoroughly rinsed with distilled water following the initial "squeezing." The cylinder/piston unit was completely dried prior to use. The process for loading sediment into the cylinder/piston unit was performed as follows:

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

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

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

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

Figure 3.5. Diagram of "squeezer" device.

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

Metals

Three replicate samples of interstitial water for metal analyses were extracted from the 0 to 5 cm sediment increment. Interstitial water samples for metal analyses were extracted using the same method previously described for radionuclide samples. However, the cylinder/piston unit used for extracting metal interstitial water samples was additionally cleaned in 10% to 20% solution of HNO₃ prior to the initial "squeezing" for each day of operations.

A 25-mL interstitial water sample was required for metal analyses and the sample was collected directly in a pre-cleaned 30-mL Nalgene bottle. Samples were preserved with HNO₃ a pH of ≤ 2 and HNO₃ was added to the sample using a 1-mL calibrated pipette with disposable plastic volume tip. Before HNO₃ was added to the samples the plastic volume tip was filled with acid and the acid discarded to clean the volume tip and prevent possible contamination to the interstitial water samples. The volume tips were discarded following the preservation of the replicate samples. After the samples were preserved, the sample bottle was capped, a sample custody seal attached, and the samples stored at room temperature. Interstitial water samples for metal analyses had a recommended holding time of 6 months.

Hydrocarbons (PAHs)

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

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

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

Total Organic Carbon

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

Chlorinity/Sulfate

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

3.1.3.2 Transect Stations - Sediment Sampling

3.1.3.2.1 Collection

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

3.1.3.2.2 Laboratory Processing

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

3.1.3.3 Marsh Stations

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

3.1.4 Biological Sampling

3.1.4.1 Infauna Sampling

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

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

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

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

3.1.4.2 Tissue Sampling

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

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

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

3.2 QUALITY ASSURANCE/QUALITY CONTROL

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

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

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

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

3.2.1 Mobilization and Sample Collection

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

3.2.2 Sample Logging and Tracking

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

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

3.2.3 Sample Custody

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

3.2.4 Quality Control Samples

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

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

3.2.5 Sample Summary and Shipping

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

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

Matrix and Sample Type	Minimum Sample Volume	Preservative	Container	Holding Time
Produced Water, Ambient Seawater, Discharge Plume and Interstitial Water				
Radionuclides	2 L except 150 mL (interstitial water)	HNO ₃ at a pH ≤2; stored at 4°C	polyethylene	6 months (recommended) ^a
Volatile Aromatic Hydrocarbons	40 mL	HCl at a pH ≤2; stored at 4°C	amber open top glass vial with teflon/silicone septa	14 days from collection to extraction ^b
Saturated Hydrocarbons and Polycyclic Aromatic Hydrocarbons	2.5 L (includes preservative)	200 ml of methylene chloride; stored at 4°C	amber glass with teflon-lined lid with insert of purified aluminum foil	40 days after extraction; addition of methylene chloride considered beginning of extraction process ^b
Metals	1 L (produced water); 2 L (ambient seawater)	HNO ₃ at a pH ≤2; stored at 4°C	polyethylene	7 days from collection (laboratory specified) ^c
Total Organic Carbon	20 mL	frozen	glass vial with teflon-lined lid	28 days ^b
Sediment				
Radionuclides	100 g	frozen	pre-cleaned 500 mL plastic jar	6 months (recommended) ^a
Volatile Aromatic Hydrocarbons	150 g	4°C	120 mL glass	14 days (EPA)
Saturated Hydrocarbons and Polycyclic Aromatic Hydrocarbons	100 g	frozen	pre-cleaned 250 mL glass jar	Unspecified
Metals	30 g	frozen	pre-cleaned 100 mL plastic jars	Unspecified

Table 3.2. (Continued).

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

^a Dr. David Demorest (Core Laboratories, Inc.).

^b EPA, 1991.

^c Dr. John Trefry (Florida Institute of Technology).

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

3.3 ACKNOWLEDGMENTS

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

CHAPTER 4 - DESCRIPTION OF THE STUDY SITES

Maureen Mulino and Michael Rayle
Steimle & Associates, Inc.
Metairie, Louisiana

4.1 ENVIRONMENTAL DESCRIPTION

4.1.1 Delacroix Island

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

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

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

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

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

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

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

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

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

4.1.2 Bay de Chene

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

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

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

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

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

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

4.1.3 Four Isle Dome

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

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

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

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

4.2 HISTORICAL RADIONUCLIDES AND DISCHARGE DATA

4.2.1 Delacroix Island Tank Battery #1

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

during 19 to 25 March 1993 varied from 357,056 L/day (2,246 bbl/day) to 358,636 L/day (2,256 bbl/day).

4.2.2 Bay de Chene Tank Battery #5

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

4.2.3 Four Isle Dome Central Production Facility

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

CHAPTER 5 -

SEDIMENT GRAIN SIZE AND TOTAL ORGANIC CARBON CONTENT

Bruce Graham

Continental Shelf Associates, Inc.

Jupiter, Florida

5.1 INTRODUCTION

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

5.2 LABORATORY METHODS

5.2.1 Grain Size

Grain size samples were washed in demineralized water, dried, and weighed. The coarse and fine fractions (sand/silt) were separated by sieving through a U.S. Standard Sieve Mesh No. 230 (62.5 μm). Sediment texture of the coarse fraction was determined at half-phi intervals by passing the sediment through nested sieves on a Ro-Tap apparatus. The weight of the material collected in each size was recorded. Boyocouse hydrometer analyses was used to determine the fine fraction (<62.5 μm). A computer algorithm was used to determine the complete size distribution and provide interpolated size information for the fine fraction at 0.25-phi intervals. A Sedigraph 5,000 ET Particle Size Analyzer was used to check the hydrometer 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 ($\pm 2^\circ\text{C}$) to avoid loss of semivolatile and volatile compounds. Each sample was then cooled to room temperature in a desiccator. The sample was then ground to a fine powder using an agate mortar and pestle. A 0.2 to 0.5 g aliquot of sample was transferred to a clean pre-weighed combustion crucible. Several drops of 10% HCl were added to the sample to remove any carbonates present. Acid was added until effervescing ceased (the acid was added slowly to prevent loss of sample by "overflow" during effervescence). The sample was then re-dried at 70°C to a constant weight and cooled to room temperature in a desiccator. A pre-measured scoop of copper was then added to the sample as a combustion aid. The sample was combusted in the induction furnace in the presence of oxygen and the evolved CO₂ 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 CO₂ obtained by weighing the ascarite collection bulb before and after combustion of the sample;

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

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

5.2.3 Quality Assurance and Quality Control

5.2.3.1 Procedures

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

5.2.3.1.1 Grain Size Analysis

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

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

5.2.3.1.2 Total Organic Carbon

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

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

5.2.3.2 Results

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

5.3 RESULTS AND DISCUSSION

5.3.1 Delacroix Island

Pre-termination Survey

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

First Post-termination Survey

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

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

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

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

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

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

Second Post-termination Survey

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

5.3.2 Bay de Chene

Pre-termination Survey

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

First Post-Termination Survey

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

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

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

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

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

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

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

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

Second Post-termination Survey

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

5.3.3 Four Isle Dome

Pre-termination Survey

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

5.4 REFERENCES

- Folk, R. L. 1954. The distinction between grain size and mineral composition in sedimentary-rock nomenclature. *Jour. Geol.* 62(4):344-359.
- Shepard, F. P. 1954. Nomenclature based on sand-silt-clay ratios. *Jour. Sedimen. Petrol.* 24(3):151-158.

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

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

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

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

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

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

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

*Michael Rayle and Maureen Mulino
Steimle & Associates, Inc.
Metairie, Louisiana*

*John Francis
University of New Orleans
New Orleans, Louisiana*

*Bruce Graham (Interstitial Water and Biological Tissues)
and Luis Lagera, Jr. (Quality Assurance)
Continental Shelf Associates, Inc.
Jupiter, Florida*

6.1 INTRODUCTION

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

6.2 LABORATORY METHODS

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

6.2.1 Water Samples

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

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

Preparation of the samples for ^{226}Ra and ^{228}Ra analysis followed the sequential method of Percival and Martin (1974) with modification. Radium was initially co-precipitated on lead sulfate out of a hot solution of saturated potassium sulfate by multiple additions of lead nitrate with heating between each addition. In cases where there were elevated total dissolved solids levels (200,000 mg/L of chloride or 10,000 mg/L of calcium), the aliquot size was adjusted down and the materials were diluted 20 to 40 fold (100 mL sample diluted to 2 L with deionized

water). This dilution, the principal modification of the Percival and Martin method, eliminates interferences from high chloride and calcium content. The sample was then precipitated with lead sulfate. This precipitate was dissolved in diethylenetriaminepentaacetic acid (DTPA) and the radium was re-precipitated with barium sulfate leaving thorium, lead, and actinide daughters in the solution.

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

6.2.2 Sediment Samples

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

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

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

6.2.3 Tissue Samples

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

6.2.4 Quality Assurance and Quality Control

6.2.4.1 Procedures

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

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

According to CORE's SOP, each sample was assessed for adequate sample volume and the sample information was entered into the CORE Laboratory Information Management System (LIMS) including client, laboratory sample identification number, processing instructions,

and count times. Upon completion of the log-in procedure, summary reports were generated with the LIMS for sample receipt verification and reviewed by the Radiochemistry Section Supervisor. Following review, copies of the log-in verification, chain-of-custody, and sample verification forms were sent to S&A or CSA.

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

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

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

6.2.4.2 Results

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

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

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

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

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

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

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

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

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

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

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

of detection for ^{226}Ra and ^{228}Ra activity in interstitial water samples from all sites and surveys were generally within the target limits for produced water.

6.3 RESULTS

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

6.3.1 Produced Water

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

6.3.1.1 Delacroix Island

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

6.3.1.2 Bay de Chene

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

6.3.1.3 Four Isle Dome

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

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

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

+/- = Two standard deviations.

LLD = Lower limit of detection.

ND = Not detected, below LLD.

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

6.3.1.4 All Sites

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

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

6.3.2 Sediments

6.3.2.1 Delacroix Island

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

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

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

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

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

Table 6.3. (Continued).

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

* = Shallowest depth of 5 cm sediment stratum.

+/- = Two standard deviations.

LLD = Lower limit of detection.

ND = Not detected, below LLD.

@ = Discharge station.

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

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

* = Shallowest depth of 5 cm sediment stratum.

+/- = Two standard deviations.

LLD = Lower limit of detection.

ND = Not detected, below LLD.

@ = Discharge station.

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

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

Table 6.5. (Continued).

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

* = Shallowest depth of 5 cm sediment stratum.

+/- = Two standard deviations.

LLD = Lower limit of detection.

ND = Not detected, below LLD.

@ = Discharge station.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

6.3.2.2 Bay de Chene

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

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

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

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

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

Table 6.6. (Continued).

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

* = Shallowest depth of 5 cm sediment stratum.

+/- = Two standard deviations.

LLD = Lower limit of detection.

ND = Not detected, below LLD.

@ = Discharge station.

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

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

* = Shallowest depth of 5 cm sediment stratum.

+|- = Two standard deviations.

LLD = Lower limit of detection.

ND = Not detected, below LLD.

@ = Discharge station.

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

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

* = Shallowest depth of 5 cm sediment stratum.

+/- = Two standard deviations.

LLD = Lower limit of detection.

ND = Not detected, below LLD.

@ = Discharge station.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

6.3.2.3 Four Isle Dome

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

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

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

6.3.3 Interstitial Water

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

6.3.3.1 Delacroix Island

Pre-termination Survey

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

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

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

* = Shallowest depth of 5 cm sediment stratum.

+/- = Two standard deviations.

@ = Discharge station.

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

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

Second Post-termination Survey

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

6.3.3.2 Bay de Chene

Pre-termination Survey

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

6.3.3.3 Four Isle Dome

Pre-termination Survey

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

6.3.4 Biological Tissue

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

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

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

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

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

6.3.4.1 Delacroix Island

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

Pre-termination Survey

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

Second Post-termination Survey

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

6.3.4.2 Bay de Chene

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

6.4 DISCUSSION

6.4.1 Produced Water

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

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

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

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

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

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

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

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

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

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

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

6.4.2 Sediment

While the surface sediment radionuclide activities were generally low at all of the stations, statistical analysis of the Delacroix Island data showed that ^{226}Ra activities were

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

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

The Bay de Chene surface sediment post hoc analysis showed that the discharge ^{226}Ra activities were significantly ($p \leq 0.001$) higher than in all the other zones. The ^{226}Ra activities from the 100-m zone was significantly ($p \leq 0.05$) higher than the 300, 500, 1,000 m, and reference zones. This produces a grouping of stations by decreasing ^{226}Ra activity with the discharge having the highest activity, the 100-m zone the next lower activity, and the 300, 500, 1,000 m, and reference stations having the lowest activities. The separation of the 100-m zone from the 300, 500, 1,000 m, and reference zones appears to be due to higher activities in the unadjusted second post-termination sediment data at two of the three 100-m zone stations. The analysis also showed a statistically significant ($p < 0.005$) decrease in sediment ^{226}Ra activity between the Pre-termination and First Post-termination Surveys and between the Pre-termination and Second Post-termination Surveys ($p < 0.05$).

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

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

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

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

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

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

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

6.4.3 Interstitial Water

Radionuclide activities in interstitial waters were generally very low (<0.31 to 12.5 pCi ^{226}Ra /L and <0.08 to 19.4 pCi ^{228}Ra /L) at survey locations with two exceptions. The sediment strata sampled at the Delacroix Island discharge during the Pre-termination Survey had radionuclide activities which were relatively high and had ranges of 108 to 143 pCi ^{226}Ra /L and 118 to 162 pCi ^{228}Ra /L in the 0 to 5 cm increment and 2.4 to 18.3 pCi ^{226}Ra /L and 2.8 to 29.4 pCi ^{228}Ra /L in the 20 to 25 cm increment. The deep sediment (20 to 25 and 35 to 40 cm) ^{226}Ra and ^{228}Ra activities from the discharge (range was 14.8 to 37.8 pCi ^{226}Ra /L and 10.0 to 39.2 pCi ^{228}Ra /L) and ^{228}Ra activity from the reference stations (range was 2.9 to 56.8 pCi/L) at Bay de Chene was also relatively high. There was a noticeable decline in radionuclide activities at the Delacroix Island discharge between the Pre-termination Survey and the Second Post-termination (see **Table 6.9**). Comparison of interstitial water radionuclide activities determined during this study with other studies is difficult because of lack of available data. Radionuclide activities in

the interstitial waters excluding the aforementioned exceptions are similar to radionuclide activities reported for interstitial waters from stations located near offshore platforms discharging produced water (Lagera et al., 1997). ^{226}Ra and ^{228}Ra levels at these stations ranged from <0.6 to 3.3 and from <5.3 to 13.5 pCi/L, respectively. Cochran and Krishnaswami (1980) reported activities of 0.22 to 6.39 pCi ^{226}Ra /L for deep-sea sediments from the eastern tropical Pacific Ocean.

6.4.4 Biological Tissue

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

6.5 SUMMARY

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

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

The surface sediment ^{226}Ra and ^{228}Ra activities at Bay de Chene were generally higher than at Delacroix Island. The sediment ^{226}Ra activities at the discharge station were significantly higher than the those from the transect and reference stations. The sediment ^{228}Ra activities at the discharge station were not significantly different from the transect or reference stations. Both ^{226}Ra and ^{228}Ra activities significantly decreased after the termination of the

produced water discharge. For both radionuclides, the decrease occurred between the Pre-termination and First Post-termination Surveys (9 months post-termination).

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

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

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

*John H. Trefry, Simone Metz, and Robert P. Trocine
Division of Marine & Environmental Systems
Florida Institute of Technology, Melbourne, Florida*

7.1 INTRODUCTION

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

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

7.2 LABORATORY METHODS

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

Produced and interstitial water samples were analyzed directly following appropriate dilution with distilled-deionized water. Sediment was completely digested using a mixture of HF-HNO₃-HClO₄ (Trefry and Metz, 1984). Instrumental analyses were carried out by one or more of the following techniques, depending on sample type and metal levels: (1) atomic absorption spectrometry (AAS), using either flame atomization with a Perkin-Elmer (PE) model 4000 instrument (aluminum, calcium, chromium, copper, iron, manganese, nickel, vanadium, zinc) or heated graphite atomization using a PE model 5100 or 4000 system (arsenic, cadmium, copper, manganese, nickel, lead, vanadium); (2) hydride generation in tandem with the PE model 4000 AAS using flame atomization (arsenic); (3) cold-vapor AAS using a Laboratory Data Control system (mercury); (4) inductively coupled plasma-mass spectrometry using a PE ELAN 5000 (barium, cadmium, molybdenum, and lead); and (5) instrumental neutron activation analysis (barium) using the research and training reactor at the University of Florida. Concentrations of TOC in interstitial water were determined with good agreement by both the wet digestion method of Fredericks and Sackett (1970) using an OI Corporation model 524C T.O.C. analyzer and by high-temperature combustion using a Shimadzu model TOC-500 instrument. Chlorinity levels in the interstitial water were determined by Mohr titration using silver nitrate that was standardized with IAPSO standard seawater. Sulfate levels in interstitial water (0 to 5 cm) were determined using EPA Method 9038-1 (turbidimetric).

7.2.1 Quality Assurance and Quality Control

7.2.1.1 Procedures

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

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

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

river water; and (2) BCSS-1 marine sediment from the National Research Council (NRC) of Canada.

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

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

7.2.1.2 Results

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

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

7.3 RESULTS AND DISCUSSION

7.3.1 Metals in Produced and Ambient Water

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

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

Element or Sample Type	Minimum Frequency	Data Quality Objective/ Acceptance Criteria
Initial Calibration	Prior to every analytical batch	3 to 5 point calibration curve over two orders of magnitude. Percent relative standard deviation $\leq 25\%$
Continuing Calibration	Every 5-10 samples	Percent relative standard deviation $\leq 30\%$ for 90% of analytes
Matrix SRM	One per batch or 5% of field samples	Values must be within $\pm 20\%$ 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 $\leq 20\%$

MDL = Method detection limit.

SRM = Standard reference material.

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

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

Table 7.3. Results (mean $\pm$ 1 standard deviation) from analyses of standard reference coastal seawater CASS-2 and riverine water SLRS-1 from the National Research Council (NRC) of Canada. All concentrations in $\mu\text{g/L}$.

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

Results (mean $\pm$ 1 standard deviation) from analyses of standard reference sediment BCSS-1 from the National Research Council (NRC) of Canada. All concentrations in $\mu\text{g/g}$ unless specified.

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

^a Non-certified value.

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

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

^a From Neff and Sauer (1995).

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

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

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

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

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

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

EF (Prod. Water/Amb. Water)

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

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

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

$$F = -D_s \frac{dCl^-}{dx} \quad (1)$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Where:

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

Table 7.3. Results (mean $\pm$ 1 standard deviation) from analyses of standard reference coastal seawater CASS-2 and riverine water SLRS-1 from the National Research Council (NRC) of Canada. All concentrations in $\mu\text{g/L}$.

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

Results (mean $\pm$ 1 standard deviation) from analyses of standard reference sediment BCSS-1 from the National Research Council (NRC) of Canada. All concentrations in $\mu\text{g/g}$ unless specified.

	Al (%)	As	Ba	Cd	Cr	Cu	Fe (%)	Mn	Mo	Ni	Pb	V	Zn
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BCSS-1 Certified Value (NRC)	6.26 ± 0.22	11.1 ± 1.4	(330) ^a	0.25 ± 0.04	123 ± 14	18.5 ± 2.7	3.29 ± 0.10	229 ± 15	(1.9) ^a	55.3 ± 3.6	22.7 ± 3.4	93.4 ± 4.9	119 ± 12

^a Non-certified value.

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

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

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

7.3.3 Interstitial Water from Bay de Chene and Four Isle Dome

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

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

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

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

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

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

7.3.4 Metals in Sediments

7.3.4.1 Identifying Sediment Metal Contamination

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

7.3.4.2 Delacroix Island

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

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

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

Table 7.6. (Continued).

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

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

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

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

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

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

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

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

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

7.3.4.3 Bay de Chene

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

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

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

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

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

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

Table 7.7. (Continued).

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

Table 7.7. (Continued).

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

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

7.3.4.4 Four Isle Dome

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

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

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

7.4 SUMMARY

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

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

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

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

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

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

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

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

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

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

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

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

^a Trefry *et al.* (1997).

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

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

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

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

8.1.2 Saturated Hydrocarbon and Polycyclic Aromatic Hydrocarbon Background Characteristics

SHCs are a group of semivolatile hydrocarbons that consist of n-alkanes with carbon numbers from C₁₀ to usually C₄₀ and selected isoprenoids (branched chain alkanes) such as pristane and phytane. They make up approximately 5% to 20% of the hydrocarbons in crude oils and are major hydrocarbon constituents in unpolluted aquatic environments. Although they are not of general biological or toxicological concern, these hydrocarbons are useful in assessing the sources of hydrocarbons in the environment. SHCs are used as tracers of spilled oil and used to monitor the extent of weathering in the environment. They are also used in distinguishing biogenic and petrogenic hydrocarbons in the environment (Blumer et al., 1971, 1973; Atlas, 1981; NRC, 1985).

The distribution of n-alkanes serves as an initial fingerprint of sources of hydrocarbons. The presence of petroleum hydrocarbons is usually indicated by a wide range of n-alkanes up to C₄₀ with no predominance of odd or even carbon numbers. The branched alkanes, pristane and phytane, provide information of the effect of biodegradation on the loss of hydrocarbons in an oil impacted environment. Hydrocarbons that have a biogenic origin have a predominance of odd carbon number compounds over the even carbon number compounds in

the n-alkane distribution. Natural (i.e., biogenic) hydrocarbons of marine origin have SHC compounds in the C_{15} to C_{22} n-alkane range, whereas hydrocarbons of terrestrial origin are represented by higher molecular weight SHCs in the C_{27} to C_{35} n-alkane range. There are some marine blue-green algae that have high-molecular-weight n-alkanes in the terrestrial n-alkane range. Terrestrial plant signatures may be evident as part of wetland environments and from land runoff or wind carrying plant debris or pollen.

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

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

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

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

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

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

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

8.1.3 Site Descriptions and Sampling Design

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

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

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

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

8.1.3.1 Delacroix Island

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

8.1.3.2 Bay de Chene

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

8.1.3.3 Four Isle Dome

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

8.2 ANALYTICAL METHODS

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

8.2.1 Volatile Aromatic Hydrocarbons

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

Prior to use for individual component analysis, a five-point calibration was established to demonstrate the linear range of the analysis. Check standards were analyzed with every analytical batch to validate the integrity of the initial calibration. Quantitation of the compounds was performed by the method of internal standards using the response factors established in the initial calibration. Surrogate internal standards (benzene-d₆, ethylbenzene-d₁₀, and naphthalene-d₈) and recovery internal standards (chlorobenzene-d₅) were spiked into the samples just before analysis.

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

<u>VAH^a</u>
*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)
<u>Polycyclic Aromatic and Heterocyclic Compounds (PAHs)^a</u>
*Naphthalene (C0N)
C ₁ -Naphthalenes (C1N), plus individual PAH--1-methylnaphthalene and 2-methylnaphthalene
C ₂ -Naphthalenes (C2N), plus individual PAH--2,6-dimethylnaphthalene
C ₃ -Naphthalenes (C3N), plus individual PAH--1,3,5-trimethylnaphthalene
C ₄ -Naphthalenes (C4N)
*Acenaphthene (ACE)
*Acenaphthylene (ACEY)
Biphenyl (BIP)
*Fluorene (C0F)
C ₁ -Fluorenes (C1F)
C ₂ -Fluorenes (C2F)
C ₃ -Fluorenes (C3F)
*Anthracene (C0A)
*Phenanthrene (C0P)
C ₁ -Phenanthrenes/anthracenes (C1P/A), plus individual PAH--1-methylphenanthrene
C ₂ -Phenanthrenes/anthracenes (C2P/A)
C ₃ -Phenanthrenes/anthracenes (C3P/A)
C ₄ -Phenanthrenes/anthracenes (C4P/A)
Dibenzothiophene (C0D)
C ₁ -Dibenzothiophenes (C1D)
C ₂ -Dibenzothiophenes (C2D)
C ₃ -Dibenzothiophenes (C3D)
*Chrysene (C0C)
C ₁ -Chrysenes (C1C)
C ₂ -Chrysenes (C2C)
C ₃ -Chrysenes (C3C)
C ₄ -Chrysenes (C4C)
*Fluoranthene (FLU)
*Pyrene (PYR)
C ₁ -Fluoranthenes/pyrene (C1F/P)
C ₂ -Fluoranthenes/pyrene (C2F/P)
C ₃ -Fluoranthenes/pyrene (C3F/P)
*Benzo(a)anthracene (BAA)
*Benzo(b)fluoranthene (BBF)
*Benzo(k)fluoranthene (BKF)
*Benzo(a)pyrene (BAP)
Benzo(e)pyrene (BEP)
Perylene (PER)
*Indeno(1,2,3-cd)pyrene (INDP)
*Dibenzo(a,h)anthracene (DAHA)
*Benzo(g,h,i)perylene (BGP)

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

^a C₁, C₂, C₃, C₄ refer to number of alkyl (CH₂) substitutions on the parent compound.

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

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

GC/MS conditions for this analysis were as follows:

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

8.2.2 Saturated Hydrocarbons and Polycyclic Aromatic Hydrocarbons

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

8.2.2.1 Sample Extraction

8.2.2.1.1 Water

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

8.2.2.1.2 Sediment

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

8.2.2.2 Extract Cleanup

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

8.2.2.3 Extract Fractionation

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

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

Sediment Extraction

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

Extract Cleanup

Figure 8.4. Extract cleanup column procedure.

HPLC Fractionation

Figure 8.5. HPLC fractionation procedure.

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

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

8.2.2.4 Instrumental Analysis

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

8.2.3 Quality Assurance and Quality Control

8.2.3.1 Procedures

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

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

Prior to each analysis all instruments were initially calibrated according to manufacturer's specifications and SOPs. Similarly, SOPs for continuing calibration and other QC requirements were observed. With each batch of samples of similar matrix (20 samples to a batch), QC samples were processed that included a procedural blank, blank spikes, matrix spikes, sample duplicate, and SRM (NIST SRM-1941 for sediment analysis). Field blank samples were also processed. Data quality objectives for the PAH target analytes and SHCs are

summarized in **Table 8.2**, and MDLs for all target analyte groups are provided in **Table 8.3**. Any values that were below the analyte and matrix specific MDL are reported as ND.

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

8.2.3.2 Results

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

In some water samples, the qualifier “B” was applied to PAH target analytes, naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, C₁-naphthalenes, biphenyl, and phenanthrene. The “B” qualifier signifies that these particular PAH analytes were found at significantly high levels in the procedural blank of the analytical batch in which the qualified environmental samples were part. Any analyte labeled with a “B” qualifier was in the range of the procedural blank concentration and therefore the analyte was not used in the interpretation.

8.3 RESULTS AND DISCUSSION

8.3.1 Produced Waters

The VAH, SHC, and PAH distributions in produced water should reflect the respective solubilities of the individual hydrocarbon compounds and the composition of the produced crude oil in contact with the produced water. For PAHs, naphthalene or C₁-naphthalenes (depending on the hydrocarbon composition of the produced oil) will have the highest concentration in the produced water with decreasing alkyl concentrations as alkyl carbon number increases. Concentrations of the three-ring PAHs (fluorenes, phenanthrenes, and dibenzothiophenes) will be considerably lower in concentration compared to the naphthalenes, and the relative concentration differences between the alkyl groups in each of the families will be considerably smaller because the relative solubility differences of alkyl group compounds are lower. Of course, the composition of the produced crude oil with its characteristic ‘bell shaped’ distribution of the alkyl groups will also complicate the composition of the produced water. The concentrations of the four- through six-ring PAHs will be negligible or non-detectable because of the low-level presence of these compounds in produced oil and the low solubilities in water.

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

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

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

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

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

Table 8.3. Method detection limits of target compound groups.

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

Table 8.4. Volatile aromatic hydrocarbon concentrations ($\mu\text{g/L}$) in produced water.

Study Site	Delacroix Island	Delacroix Island	Bay de Chene	Bay de Chene	Bay de Chene	Four Isle Dome	Four Isle Dome
Station	Discharge	Discharge	Discharge	Discharge	Discharge	Discharge	Discharge
Replicate	A	D	A	D	FB (BLANK)	B	D
Field ID	I-DI-EOP-A	I-DI-EOP-D	I-BDC-EOP-PW-A	I-BDC-EOP-PW-D	I-BDC-EOP-PW-FB	I-FID-EOP-PW-B	I-FID-EOP-PW-D
Analyte							
Benzene	230	470	630	590	ND	2700	2500
Toluene	610	780	560	550	ND	1600	1500
Ethylbenzene	41	48	52	54	ND	100	100
Total Xylenes	410	430	360	360	ND	750	780
<i>m,p</i> -Xylenes	NA	NA	NA	NA	NA	490	520
<i>o</i> -Xylene	NA	NA	NA	NA	NA	260	260
C ₃ -Benzenes	NA	NA	NA	NA	NA	200	220
C ₄ -Benzenes	NA	NA	NA	NA	NA	36	42

NA = Not analyzed.

ND = Not detected.

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

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

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

Concentrations of the individual VAHs--benzene, toluene, ethylbenzene, the xylenes, C₃-benzenes, and C₄-benzenes--are summarized for the replicate produced water analyses in **Table 8.4**. PAH and SHC distributions are presented in **Figures 8.8** through **8.13**. THC and total PAH and THC concentrations are provided in the figures.

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

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

The PAH distribution of the Delacroix Island samples (**Figure 8.8**) showed a relatively large amount of naphthalenes (greater than 95% of the total PAHs) with decreasing alkyl concentrations as alkyl carbon number increased, and very small amounts of the three-ring PAHs (non-detectable amounts of four- through six-ring PAHs) with generally constant alkyl concentrations. The PAH compositions of this produced water reflect the solubility properties for PAHs, as discussed previously. Relatively higher concentrations of the phenanthrene, fluorene, and dibenzothiophene alkyl groups were, however, evident in the Bay de Chene and Four Isle Dome produced waters (**Figures 8.10** and **8.12**). The relatively large amounts of the three- and four-ring PAHs and the characteristic 'bellshaped' distribution of the alkyl homologues reflects the composition of the produced crude oil. SHC concentrations decreased with increasing carbon number from C₁₄ to C₃₂ in all produced waters (**Figures 8.9, 8.11, and 8.13**), which reflected the solubilities and produced oil composition of the analytes. Due to the volatility of the C₁₀ through C₁₄, the trend of lower concentrations in produced water samples from Bay de Chene and Four Isle Dome may be due to volatile compound loss during processing/analysis of the samples, not indicative of the actual distribution. The prominent presence and 'bellshaped' distribution of the alkyl PAHs and the higher hydrocarbon concentrations indicated that there were probably oil droplets in the Bay de Chene and Four Isle Dome samples.

As a tool in determining potential sources of hydrocarbons in environmental (sediment) samples, the PAH diagnostic ratios of C₂-phenanthrenes and C₂-dibenzothiophenes (C2P/C2D) and C₃-phenanthrenes and C₃-dibenzothiophenes (C3P/C3D) were calculated for the produced waters at each site (**Table 8.5**).

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

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

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

8.3.2 Sediments

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

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

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

Survey Number	I	I	I	I	I	I
Study Site	Delacroix Island	Delacroix Island	Delacroix Island	Bay de Chene	Bay de Chene	Bay de Chene
Station	Discharge	R1	R2	Discharge	Discharge	R1
Replicate	A	A	A	A	B	A
Field ID	I-DI-@-S-O-A	I-DI-R1-S-A	I-DI-R2-S-A	I-BDC-@-S-O-A	I-BDC-@-S-O-B	I-BDC-R1-S-O-A
Analyte						
Benzene	91	ND	ND	ND	ND	ND
Toluene	ND	ND	ND	ND	ND	ND
Ethylbenzene	69	ND	ND	ND	ND	ND
Total Xylenes	420	ND	ND	ND	ND	ND
<i>m,p</i> -Xylenes	NA	NA	NA	NA	NA	NA
<i>o</i> -Xylene	NA	NA	NA	NA	NA	NA
C ₃ -Benzenes	NA	NA	NA	NA	NA	NA
C ₄ -Benzenes	NA	NA	NA	NA	NA	NA

Table 8.6. (Continued).

Survey Number	I	I	I	I
Study Site	Bay de Chene	Four Isle Dome	Four Isle Dome	Four Island Dome
Station	R2	Discharge	R1	R2
Replicate	A	A	A	A
Field ID	I-BDC-R2-S-O-A	1-FID-@-S-O-A	1-FID-R1-S-O-A	1-FID-R2-S-O-A
Analyte				
Benzene	ND	13	ND	ND
Toluene	ND	45	0.56	0.25
Ethylbenzene	ND	19	0.1	ND
Total Xylenes	ND	163	0.45	ND
<i>m,p</i> -Xylenes	NA	120	0.31	ND
<i>o</i> -Xylene	NA	43	0.14	ND
C ₃ -Benzenes	NA	190	ND	ND
C ₄ -Benzenes	NA	152	ND	ND

Table 8.6. (Continued).

Survey Number	III	III	III	III	III
Study Site	Delacroix Island	Delacroix Island	Delacroix Island	Delacroix Island	Delacroix Island
Station	Discharge	Discharge	R1	R2	R2
Replicate	A	B	A	A	A (DUP)
Field ID	111-DI-@-S-A	111-DI-@-S-B	111-DI-R1-S-O-A	111-DI-R2-S-O-A	111-DI-R2-S-O-A
Analyte					
Benzene	ND	ND	ND	ND	ND
Toluene	ND	ND	ND	ND	ND
Ethylbenzene	ND	0.24	ND	ND	ND
Total Xylenes	ND	0.81	ND	ND	ND
<i>m,p</i> -Xylenes	ND	0.58	ND	ND	ND
<i>o</i> -Xylene	ND	0.23	ND	ND	ND
C ₃ -Benzenes	ND	ND	ND	ND	ND
C ₄ -Benzenes	ND	ND	ND	ND	ND

NA = Not analyzed.

ND = Not detected.

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

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

Table 8.7. (Continued).

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

Table 8.7. (Continued).

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

ND = Not detected.

8.3.2.1 Delacroix Island

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

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

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

The hydrocarbon compositions were dominated by the higher molecular weight SHC_s from C₂₃ to C₃₂. Example SHC distributions for Bay de Chene are presented in (**Figure 8.15**). The contribution of lower molecular weight SHC_s, C₁₆ to C₂₂ n-alkanes, was significantly lower (<20% of total SHC_s) except in those sediments at the discharge station sampled during the Pre-termination Survey. For this SHC group, the C₁₇ n-alkane was the dominate compound, not the isoprenoids--pristane or phytane. The relatively higher concentrations of the C₁₇ n-alkane compared to the other lower molecular weight SHC_s, low concentrations of the isoprenoids, and the large odd/even n-alkane preference (4 to 1) indicated a biogenic source for the SHC_s, probably of terrestrial and wetland origin.

Lower molecular weight SHC_s (C₁₀ to C₂₀), which were highly representative of a petrogenic input, dominated the SHC composition only at the discharge station (**Figure 8.16**). In later surveys, the content of these SHC_s decreased considerably to levels similar to the other sediments (**Figure 8.17**) where the higher molecular weight SHC_s greatly dominated. Since

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

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

Table 8.8. (Continued).

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Very few PAHs, mostly naphthalenes and C₁-naphthalenes, were detected in sediment interstitial waters of discharge and reference stations (**Table 8.7**). No samples were collected for interstitial water analysis at the other site locations. Concentrations were highest in the pre-termination interstitial waters at approximately 1,000 ng/L. Most replicates had non-detectable amounts of PAHs. Only one reference replicate contained PAHs and had concentrations of naphthalenes similar to the discharge sediments. A year after discharge termination (Survey III), PAH (naphthalenes and phenanthrene) concentrations decreased to approximately 20 to 100 ng/L. These PAHs were present in most replicates of both discharge and reference interstitial waters.

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

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

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

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

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

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

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

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

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

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

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

8.3.2.2 Bay de Chene

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

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

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

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

Table 8.9. (Continued).

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

8.3.2.3 Four Isle Dome

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

8.4 SUMMARY AND CONCLUSIONS

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

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

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

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

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

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

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

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

Delacroix Island sediments had consistent low concentrations of hydrocarbons in sediments from the outer (500 and 1,000 m) stations (25 to 50 $\mu\text{g/g}$ THC_s, 220 to 280 ng/g PAH_s), slight increases in the inner (100 and 300 m) stations (140 to 230 $\mu\text{g/g}$ THC_s, 330 to 2,500 ng/g PAH_s), and highest concentrations at the discharge station.

Unlike Delacroix Island, the sediments at Bay de Chene had both spatial and temporal hydrocarbon concentration trends. Northeast transect hydrocarbon concentrations at the inner stations (1,000 $\mu\text{g/g}$ THC_s and 50,000 ng/g PAH_s at 100 m) were generally 5 to 10 times higher than northwest or southwest transect sediment concentrations. Concentrations decreased in northeast and northwest transect sediments from Pre- to Post-termination Surveys.

Sediments at Four Isle Dome had different hydrocarbon trends in each transect. North transect THC and PAH sediment concentrations increased from outer stations to the discharge facility. On the south transect hydrocarbon concentrations were consistently high at all stations (500, 300, and 100 m) at 300 to 460 $\mu\text{g/g}$ for THC_s and 3,200 to 3,600 ng/g total PAH_s. At 100 m, hydrocarbon concentrations were the same on both transects.

Only naphthalene and C_1 -naphthalenes were detected in interstitial water samples from discharge and reference stations of Delacroix Island at concentrations less than 100 ng/L. Delacroix Island and Four Isle Dome (not Bay de Chene) sediments contained VAH_s (15 to 160 mg/g VAH) at the discharge stations sampled during the Pre-termination Survey only.

At all sites except at the stations nearest the facility (discharge) the resolvable hydrocarbon composition in sediments was dominated by pyrogenic PAH_s and high molecular weight biogenic SHC_s (C_{23} to C_{32}). Sediments at stations nearest the facility and the discharge

station had a petrogenic signature superimposed on the pyrogenic PAHs and biogenic SHCs. Petrogenic PAHs although present at the nearest stations (100 m) in most cases, dominated the PAH composition only in sediments at the discharge stations from the Pre-termination Survey (example: **Figure 8.64**).

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

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

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

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

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

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

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

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

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

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8.6 ACKNOWLEDGEMENTS

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

*Maureen Mulino and Michael Rayle
Steimle & Associates, Inc.
Metairie, Louisiana*

*Michael Poirrier and John Francis
University of New Orleans
New Orleans, Louisiana*

9.1 INTRODUCTION

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

9.2 LABORATORY METHODS

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

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

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

Multiple regression analyses were used to relate the number of species and number of individuals at Delacroix Island and Bay de Chene to sediment parameters (TOC, grain size,

naphthalenes, acenaphthylenes, fluorenes, dibenzothiophenes, anthracenes, fluoranthenes, benzo[a] anthracene, and chrysenes). The 100 m station on the northeast transect at Bay de Chene was excluded from the analysis because it was located at an abandoned fuel dock.

9.3 RESULTS

9.3.1 Water Quality Data

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

9.3.2 Benthos

9.3.2.1 Delacroix Island

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

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

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

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

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

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

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

Table 9.1 (Continued).

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

Table 9.1. (Continued).

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

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

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

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

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

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

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

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

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

9.3.2.2 Bay de Chene

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

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

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

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

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

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

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

Table 9.2. (Continued).

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

Table 9.2. (Continued).

	Order Amphipoda
	Family Ampeliscidae
	<i>Ampelisca</i> sp.
	Family Aoridae
	<i>Grandidierella bonnieroides</i>
	Family Corophiidae
	<i>Corophium louisianum</i>
	<i>Cerapus benthophilis</i>
	Family Gammaridae
	<i>Mucrogammarus mucronatus</i>
	<i>Melita</i> sp.
	Family Oedicerotidae
	<i>Monoculodes</i> sp.
	Order Mysidacea
	Family Mysidae
	Order Decapoda
	Family Palaemonidae
	<i>Palaemonetes</i> spp.
	Family Ogyrididae
	<i>Ogyrides</i> sp.
	Family Callianasidae
	Family Paguroidea
	Family Portunidae
	<i>Callinectes sapidus</i>
	Family Xanthidae
	<i>Rhithropanopeus harrisii</i>
Subphylum Uniramia	
Class Insecta	
	Order Diptera
	Family Chironomidae
	Subfamily Tanypodinae
	Chironomid B
	Subfamily Chironomidae
	Chironomid A and C
Phylum Chordata	
Subphylum Vertebrata	
Class Osteichthyes	
	Order Perciformes
	Family Gobiidae
	<i>Gobiosoma bosci</i>
	Order Anguilliformes
	Family Ophichthidae
	<i>Myrophus punctatus</i>

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

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

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

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

9.3.2.3 Four Isle Dome

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

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

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

9.3.3 Chloride Concentration of Interstitial Water

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

9.3.4 Sediment Contamination

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

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

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

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

Table 9.3. (Continued).

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

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

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

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

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

Figure 9.13. Sediment PAH concentrations at the discharge station at Delacroix Island during all sampling periods. CON=Naphthalene; C1N=C₁-Naphthalenes; C2N=C₂-Naphthalenes; C3N=C₃-Naphthalenes; C4N=C₄-Naphthalenes; BP=Biphenyl; C0F=Fluorene; C1F=C₁-Fluorenes; C2F=C₂-Fluorenes; C3F=C₃-Fluorenes; C0D=Dibenzothiophenes; C1D=C₁-Dibenzothiophenes; C2D=C₂-Dibenzothiophenes; C3D=C₃-Dibenzothiophenes; C0P=Phenanthrene; C0A=Anthracene; FLANT=Fluoranthene; PYR=Pyrenes; C1FP=C₁Fluoranthenes/Pyrenes; C2FP=C₂Fluoranthenes/Pyrenes; C3FP=C₃Fluoranthenes/Pyrenes; C0C=Chrysene; C1C=C₁-Chrysenes; C2C=C₂-Chrysenes; C3C=C₃-Chrysenes; C4C=C₄-Chrysenes; PER=Perylene.

Figure 9.14. Sediment PAH concentrations at the discharge station at Bay de Chene during all sampling periods. CON=Naphthalene; C1N=C₁-Naphthalenes; C2N=C₂-Naphthalenes; C3N=C₃-Naphthalenes; C4N=C₄-Naphthalenes; BP=Biphenyl; C0F=Fluorene; C1F=C₁-Fluorenes; C2F=C₂-Fluorenes; C3F=C₃-Fluorenes; C0D=Dibenzothiophene; C1D=C₁-Dibenzothiophenes; C2D=C₂-Dibenzothiophenes; C3D=C₃-Dibenzothiophenes; C0P=Phenanthrene; C0A=Anthracene; FLANT=Fluoranthene; PYR= Pyrenes; C1FP=C₁Fluoranthenes/Pyrenes; C2FP=C₂Fluoranthenes/Pyrenes; C3FP=C₃Fluoranthenes/Pyrenes; C0C=Chrysene; C1C=C₁-Chrysenes; C2C=C₂-Chrysenes; C3C=C₃-Chrysenes; C4C=C₄-Chrysenes; PER=Perylene.

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

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

9.4 DISCUSSION

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

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

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

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

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

Figure 9.15. Sediment PAH concentrations at the discharge station at Bay de Chene 100NE during all sampling periods. CON=Naphthalene; C1N=C₁-Naphthalenes; C2N=C₂-Naphthalenes; C3N=C₃-Naphthalenes; C4N=C₄-Naphthalenes; BP=Biphenyl; C0F=Fluorene; C1F=C₁-Fluorenes; C2F=C₂-Fluorenes; C3F=C₃-Fluorenes; C0D=Dibenzothiophenes; C1D=C₁-Dibenzothiophenes; C2D=C₂-Dibenzothiophenes; C3D=C₃-Dibenzothiophenes; C0P=Phenanthrene; C0A=Anthracene; FLANT=Fluoranthene; PYR=Pyrenes; C1FP=C₁Fluoranthenes/Pyrenes; C2FP=C₂Fluoranthenes/Pyrenes; C3FP=C₃Fluoranthenes/Pyrenes; C0C=Chrysenes; C1C=C₁-Chrysenes; C2C=C₂-Chrysenes; C3C=C₃-Chrysenes; C4C=C₄-Chrysenes; PER=Perylene.

Figure 9.16. Sediment PAH concentrations at Four Isle Dome during Pre-Termination sampling. CON=Naphthalene; C1N=C₁-Naphthalenes; C2N=C₂-Naphthalenes; C3N=C₃-Naphthalenes; C4N=C₄-Naphthalenes; BP=Biphenyl; C0F=Fluorene; C1F=C₁-Fluorenes; C2F=C₂-Fluorenes; C3F=C₃-Fluorenes; C0D=Dibenzothiophene; C1D=C₁-Dibenzothiophenes; C2D=C₂-Dibenzothiophenes; C3D=C₃-Dibenzothiophenes; C0P=Phenanthrene; C0A=Anthracene; FLANT=Fluoranthene; PYR=Pyrenes; C1FP=C₁Fluoranthenes/Pyrenes; C2FP=C₂Fluoranthenes/Pyrenes; C3FP=C₃Fluoranthenes/Pyrenes; C0C=Chrysene; C1C=C₁-Chrysenes; C2C=C₂-Chrysenes; C3C=C₃-Chrysenes; C4C=C₄-Chrysenes; PER=Perylene.

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

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

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

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

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

Hydrocarbons present in produced water also have the potential to impact benthos. Hydrocarbons adsorb preferentially onto fine grained clays (Boehm, 1987) which predominate in

the bottom sediments of Louisiana estuaries. At the Delacroix Island discharge station, sediment PAH concentrations decreased (**Figure 9.13**) over time and between the discharge station and all 100 m stations. The number of benthic species and individuals increased dramatically at the discharge station after termination. Recovery was rapid with a large number of species and individuals inhabiting the former discharge station six months post-termination.

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

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

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

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

The taxa which predominated in the Delacroix Island study area also varied seasonally. The October 1993 sampling (6 months post-termination) was characterized by a

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

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

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

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

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

9.5 SUMMARY

Depressed numbers of species and individuals were evident at the discharge site at Delacroix Island Tank Battery #1 during the Pre-termination Survey. Statistically, over all three sampling periods, the number of species at the discharge was significantly lower than in all other zones. The infauna data from Delacroix Island appear to exhibit spatial recovery to a stable

number of species on all transects by the 100 m station. Recovery to a stable number of individuals appears to have been realized by the 100 m station for all discharge times on the northeast and northwest transects. Recovery on the south transect appears to have been realized by the 300 m station for all sampling times.

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

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

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

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APPENDIX 1

Water Quality Data

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

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

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

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

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

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

APPENDIX 2.

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

TAXONOMIC COMPOSITION-DELAWARE ISLAND NORTHWEST TRANSECT - APRIL 1993

TAXONOMIC COMPOSITION-DELAWARE ISLAND NORTHEAST TRANSECT - APRIL 1993

APPENDIX 3.

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

TAXONOMIC COMPOSITION-BAY DE CHENE NORTHEAST TRANSECT - MAY 1993

TAXONOMIC COMPOSITION-BAY DE CHENE SOUTHEAST TRANSECT - MAY 1993

TAXONOMIC COMPOSITION-BAY DE CHENE NORTHWEST TRANSECT - MAY 1993

TAXONOMIC COMPOSITION-BAY DE CHENE SOUTHWEST TRANSECT - MAY 1993

TAXONOMIC COMPOSITION-BAY DE CHENE NORTHEAST TRANSECT - MAY 1994

TAXONOMIC COMPOSITION-BAY DE CHENE SOUTHEAST TRANSECT - MAY 1994

TAXONOMIC COMPOSITION-BAY DE CHENE NORTHWEST TRANSECT - MAY 1994

TAXONOMIC COMPOSITION-BAY DE CHENE SOUTHWEST TRANSECT - MAY 1994

TAXONOMIC COMPOSITION-BAY DE CHENE NORTHEAST TRANSECT - OCTOBER 1994

TAXONOMIC COMPOSITION-BAY DE CHENE SOUTHEAST TRANSECT - OCTOBER 1994

TAXONOMIC COMPOSITION-BAY DE CHENE NORTHWEST TRANSECT - OCTOBER 1994

TAXONOMIC COMPOSITION-BAY DE CHENE SOUTHWEST TRANSECT - OCTOBER 1994

TAXONOMIC COMPOSITION-DELAWARE ISLAND SOUTH TRANSECT - APRIL 1993

TAXONOMIC COMPOSITION-DELAWARE ISLAND NORTHWEST TRANSECT - OCTOBER 1993

TAXONOMIC COMPOSITION-DELAWARE ISLAND NORTHEAST TRANSECT - OCTOBER 1993

TAXONOMIC COMPOSITION-DELAWARE ISLAND SOUTH TRANSECT - OCTOBER 1993

TAXONOMIC COMPOSITION-DELAWARE ISLAND NORTHWEST TRANSECT - APRIL 1994

TAXONOMIC COMPOSITION-DELAWARE ISLAND NORTHEAST TRANSECT - APRIL 1994

TAXONOMIC COMPOSITION-DELAWARE ISLAND SOUTH TRANSECT - APRIL 1994

APPENDIX 4.

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

TAXONOMIC COMPOSITION-FOUR ISLE DOME NORTH TRANSECT - NOVEMBER 1993

TAXONOMIC COMPOSITION-FOUR ISLE DOME SOUTH TRANSECT - NOVEMBER 1993

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

*Jerry M. Neff
Battelle Ocean Sciences
Duxbury, Massachusetts*

10.1 INTRODUCTION

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

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

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

10.2 METHODS

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

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

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

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

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

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

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

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

10.3 RESULTS AND DISCUSSION

10.3.1 Characteristics of Study Sites

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

Delacroix Island

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

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

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

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

Bay de Chene

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

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

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

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

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

Four Island Dome

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

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

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

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

10.3.2 Environmental Risk of Metals in Produced Water

Metals in Produced Water

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

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

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

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

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

Dilution of Metals in Receiving Waters

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

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

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

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

Environmental Risk of Metals in Produced Water

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

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

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

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

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

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

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

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

10.3.3 Environmental Risk of Aromatic Hydrocarbons in Produced Water

Aromatic Hydrocarbons in Produced Water

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

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

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

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

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

Hydrocarbon	Delacroix Island	Bay de Chene	Four Isle Dome
Benzene	230 - 470	590 - 630	2,500 - 2,700
Toluene	610 - 789	550 - 560	1,500 - 1,600
Ethylbenzene	41 - 48	<0.5 - 41	100
Total Xylenes	410 - 430	360	750 - 780
C ₃ -Benzenes	NA	NA	200 - 220
C ₄ -Benzenes	NA	NA	36 - 42
Total Monocyclic Aromatic Hydrocarbons	1,291 - 1,728	1,554 - 1,602	5,142 - 5,386
Total PAHs	24 - 28	350 - 520	410 - 420
Total Petroleum Hydrocarbons	210 - 370	13,000 - 19,000	18,000 - 21,000

NA = Not analyzed.

Dilution of Aromatic Hydrocarbons in Ambient Water

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

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

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

Environmental Risk of Aromatic Hydrocarbons in Produced Water

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

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

Aromatic Hydrocarbon	Estimated Concentration Range	Water Quality Criterion	Toxic Units
Benzene	2.3 - 27	700	<0.01 - 0.04
Toluene	5.5 - 16	5,000	<0.01
Ethylbenzene	<0.005 - 1.0	43	<0.01 - 0.02
Xylenes	3.6 - 7.8	600	<0.01 - 0.01
C ₃ -Benzenes	2.0 - 2.2	393	<0.01
C ₄ -Benzenes	0.36 - 0.42	173	<0.01
Total PAHs	0.24 - 5.2	300	<0.01 - 0.02
Total Toxic Units			<0.06 - 0.09

Even a 10-fold dilution of these three produced waters would not be toxic to aquatic organisms in the vicinity of the produced water discharges. Therefore, the aromatic hydrocarbons in produced water from the three production facilities did not pose a risk to local water column organisms and ecosystems before the produced water discharges were terminated.

Following termination of the discharges, the concentrations of petroleum hydrocarbons in the water column near the former discharges probably dropped rapidly to essentially background levels. However, there are other sources of aromatic hydrocarbons in the local coastal environment (runoff from land and the Mississippi River, aerial fallout, creosote from platform structures, and other releases from the platforms and vessels in the vicinity). Thus, hydrocarbons will not disappear completely from the local waterways following termination of produced water discharges.

10.3.4 Environmental Risk of Metals in Sediments

Concentrations of Metals in Sediments

A large fraction of the metals entering the ocean from natural and anthropogenic sources precipitates or becomes bound to suspended particles and colloidal and dissolved organic matter (Salomons and Förstner, 1984). These precipitated, adsorbed, or complexed metals tend to be deposited in more or less labile forms in surficial sediments. The sediment particles themselves may contain high concentrations of some metals. The metals that are part of the structure of the sediment particles are not readily mobilized and usually are termed residual metals.

Adsorbed, precipitated, and complexed metals may be mobilized under some conditions. In anoxic marine sediments, most of which contain high concentrations of sulfur, sulfides and to a lesser extent organic matter control metal speciation and the forms of metals present. Sulfur concentrations in some freshwater and estuarine sediments are low enough that speciation of metals in anoxic layers is controlled by other chemicals, particularly organic matter. In oxidized, fine-grained marine sediments, hydrous oxides of iron, aluminum, and manganese, clay minerals, carbonates, and organic matter all compete for binding of metals (Luoma and Bryan, 1981; Louma and Davis, 1983). Metals adsorbed to iron and manganese oxide phases, sediment organic matter, or present as solid sulfide salts may be released from the solid phase and be mixed into the overlying water column, particularly during periods of redox potential changes (up or down) in the sediments. Thus, marine sediments are not only a sink for metals, but also a source of dissolved, bioavailable metals in the overlying water column (Salomons et al., 1987).

The chemical species, complexes, adsorbed, and solid forms in which different metals occur in marine and estuarine sediments have a profound effect on their bioavailability and toxicity to marine organisms (Nelson and Donkin, 1985). Only bioavailable metals (dissolved or sometimes organically bound) in sediments are toxic to marine organisms if concentrations are high enough.

Concentrations of different metals in surficial sediments vary widely depending on the geochemistry of the sediments and proximity to natural and anthropogenic sources. All marine sediments contain measureable concentrations of most metals. Therefore, it often is difficult to determine with any certainty whether a sediment is contaminated with metals or reflects the natural concentrations. Normalization to aluminum (a major natural component of clay minerals)

is used sometimes to identify the presence of some metals from anthropogenic sources (Windom et al., 1989; Trefry et al., 1996. See also **Chapter 7**). Aluminum normalization corrects for differences among sediments in grain size and mineralogy.

Trefry et al. (**Chapter 7**) concluded, based on aluminum normalization, that concentrations of arsenic, cadmium, chromium, copper, iron, manganese, nickel, lead, vanadium, and zinc in sediments near the three production facilities are at or near natural levels. On the other hand, concentrations of barium are in excess of expected values at most locations near the production facilities, probably as a result of discharges of drilling fluids and produced water from the platforms. Arsenic and mercury concentrations were elevated above expected concentrations in some sediments near the facilities. Concentrations of cadmium, chromium, mercury, lead, and zinc in sediments near a former fuel dock and pipe storage facility at the Bay de Chene facility were elevated. The metals probably were derived from the pipe storage facility and not from produced water.

Much of the metals in sediments is tightly bound to particles and are not readily bioavailable. Elevated concentrations of one or more metals in surficial sediments is not necessarily an indication that the local benthic plants and animals are being adversely affected.

Concentrations of metals in surface sediments at different distances from the three production facilities varied widely over spatial and temporal scales. There were not large differences in sediment metal concentrations among the three field surveys (**Table 10.8** through **10.10**). Metal concentrations in sediments near the two discharges for which post-termination data are available did not decrease substantially after termination of the discharges. As discussed by Trefry et al. (**Chapter 7**), most of the metals were present in sediments near the platforms at expected concentrations. The only metal that was consistently present at substantially elevated concentrations in sediments at all distances from the three discharges was barium. Barium undoubtedly was derived from produced water and water-base drilling mud discharges (both rich in barium). Somewhat elevated concentrations of a few other metals (arsenic and mercury) were observed at a few locations on one or more surveys. There is not evidence of significant accumulation of any metals other than barium in sediments from produced water.

Environmental Risk of Metals in Sediments

The sediment metals data summarized in **Tables 10.8** through **10.10** can be used to estimate the risk of sediment metals to benthic organisms living near the three production facilities. The measured concentrations can be compared to sediment threshold concentrations developed by Long et al. (1995) as indices of potentially toxic concentrations of chemical contaminants in sediments (**Table 10.11**).

A concerted effort has been made in the United States in recent years to develop sediment quality criteria to protect freshwater and marine life from contaminants associated with sediments (e.g., Di Toro et al., 1991; Ankley et al., 1996). Much of the data on the association between concentrations of different chemical contaminants in marine and estuarine sediments and biological responses in bottom-living marine and estuarine organisms has been evaluated to produce sediment quality guidelines that provide some indication of the concentrations of contaminants in sediments that may be associated with adverse biological effects (Long and

Table 10.8. Concentration ranges of potentially toxic metals in sediments near the Delacroix Island production facility before and after cessation of produced water discharges. Concentrations are $\mu\text{g/g}$ dry weight.

Metal	Pre-termination Survey	First Post-termination Survey	Second Post-termination Survey
Arsenic	3.1 - 11.2	3.6 - 6.7	2.0 - 5.6
Barium	278 - 2,850	53.6 - 2,490	473 - 4,290
Cadmium	0.04 - 0.92	0.17 - 0.41	0.16 - 0.42
Chromium	28.9 - 56.1	27.2 - 59.6	34.7 - 61.9
Copper	8.7 - 23.4	8.3 - 19.6	8.4 - 22.4
Lead	4.1 - 27.4	6.2 - 22.9	11.9 - 24.1
Mercury	0.023 - 0.075	0.022 - 0.054	0.022 - 0.054
Molybdenum	0.5 - 2.2	0.6 - 4.9	0.5 - 1.6
Nickel	14.1 - 35.6	16.9 - 30.7	14.5 - 34.9
Vanadium	35.6 - 101	47.6 - 115	40.4 - 101
Zinc	30.0 - 101	27.0 - 82.5	41.7 - 95.6

Table 10.9. Concentration ranges of potentially toxic metals in sediments near the Bay de Chene production facility before and after cessation of produced water discharges. Concentrations are $\mu\text{g/g}$ dry weight.

Metal	Pre-termination Survey	First Post-termination Survey	Second Post-termination Survey
Arsenic	4.6 - 13.9	4.5 - 11.4	7.6 - 13.1
Barium	466 - 1,670	143 - 3,740	41 - 2,170
Cadmium	0.20 - 0.55	0.22 - 1.0	0.27 - 0.81
Chromium	32.2 - 66.7	41.5 - 73.8	40.8 - 60.8
Copper	10.8 - 30.1	11.0 - 50.7	13.4 - 36.1
Lead	12.1 - 35.7	14.5 - 68.0	4.8 - 40.5
Mercury	0.029 - 0.423	0.027 - 0.462	0.036 - 0.314
Molybdenum	0.9 - 4.0	0.8 - 2.8	0.7 - 2.3
Nickel	14.0 - 32.1	14.1 - 33.6	16.8 - 29.5
Vanadium	53.4 - 115	58.0 - 111	77.0 - 132
Zinc	51.8 - 159	56.3 - 362	67.1 - 304

Table 10.10. Concentration ranges of potentially toxic metals in sediments near the Four Isle Dome production facility before termination of produced water discharge. Concentrations are $\mu\text{g/g}$ dry weight.

Metal	Pre-termination Survey
Arsenic	4.5 - 7.2
Barium	78.6 - 3,880
Cadmium	0.28 - 0.54
Chromium	53.6 - 69.9
Copper	17.9 - 27.3
Lead	10.8 - 25.7
Mercury	0.045 - 0.139
Molybdenum	1.0 - 2.8
Nickel	24.7 - 35.8
Vanadium	84.1 - 161
Zinc	75.2 - 192

Table 10.11. Proposed sediment quality guidelines ($\mu\text{g/g}$ dry weight) and "high" concentrations (geometric mean plus one standard deviation) from the National Status and Trends database for metals in marine sediments. The effects range-low (ERL) is the lower 10th percentile effects concentration and the effects range-median (ERM) is the 50th percentile effects concentration. (From: Long et al., 1995; Daskalakis and O'Connor, 1995).

Chemical	ERL	ERM	High Concentration
Arsenic	8.2	70	13
Cadmium	1.2	9.6	0.54
Chromium	81	370	125
Copper	34	270	42
Lead	46.7	218	45
Mercury	0.15	0.71	0.22
Nickel	20.9	51.6	42
Zinc	150	410	135

Morgan, 1990; Long, 1992; Long et al., 1995). Two guideline values are generated from this analysis, an effects range-low (ERL) and an effects range-median (ERM). The ERL value represents the lower 10th percentile response concentration and the ERM value represents the median (50th percentile) response concentration (50% of recorded responses to the chemical are at lower concentrations and 50% are at higher concentrations). The two guideline values define concentrations of a particular chemical in sediments that are rarely (below the ERL), occasionally (between the ERL and ERM values), or frequently (above the ERM value) associated with adverse biological effects. Because most marine sediments that exhibit toxicity to benthic marine organisms contain several metals and potentially toxic organic chemicals at elevated concentrations, it often is difficult to identify the fraction of the total toxicity that can be attributed to a particular metal. Thus, the ERL and ERM values are conservative estimates of the toxicity of individual chemicals in sediments. Therefore, the ERM values (**Table 10.11**) were used in the present investigation as screening values for comparison with metal concentrations measured in sediments near the three sites.

Marine sediment screening concentrations are not available for aluminum, barium, calcium, iron, manganese, molybdenum, and vanadium. All but molybdenum and vanadium are abundant natural constituents of marine sediments and are unlikely to be present in solution in seawater or sediment interstitial water at toxic concentrations. Aluminum and calcium are matrix components of some of the sediment particles. Iron and manganese are present in oxidized sediment layers almost exclusively as various insoluble oxyhydroxides. In reduced sediment layers, the oxyhydroxides may dissolve, but much of the iron and manganese precipitates as sulfides. These reactions keep concentrations of dissolved, bioavailable iron and manganese low in sediment interstitial water (Schimmield and Pedersen, 1990; Thamdrup et al., 1994). Barium is present in sediments primarily as highly insoluble barite or as inclusions in clay particles (Neff and Sauer, 1995).

Daskalakis and O'Connor (1995) examined chemical residue data for large numbers of marine sediment samples collected as part of the National Status and Trends Program and several other monitoring programs in coastal marine environments of the U.S. They identified a "high" concentration of contaminants in sediments as the geometric mean plus one standard deviation of all National Status and Trend site means. "High" concentrations are included in **Table 10.11** for comparison.

Concentrations of several metals in sediments exceeded the National Status and Trends "high" concentrations at one or more stations or times. Most exceedences were in sediments near the Bay de Chene facility. One or more sediment samples at Bay de Chene contained elevated concentrations of arsenic, cadmium, copper, lead, mercury, or zinc. As discussed above, most of these elevated metal concentrations were in sediments near a former fuel and pipe storage facility in the Bay de Chene field and probably were not derived from produced water discharges.

Sediments collected at several platform and reference stations around the Delacroix Island production facility contained metal concentrations fairly typical of nearshore fine-grained sediments in the northwestern Gulf of Mexico. None of the metals was present in the bulk surficial sediments at concentrations in excess of their respective ERM values (**Table 10.12**). The highest values for toxic units (concentration in sediments/ERM value) were for nickel and zinc collected on both the Pre-termination and Post-termination Surveys.

Table 10.12. Estimated ranges of toxic units (concentration in sediment/effects range-median [ERM] value) of several metals in sediments from the vicinity of the Delacroix Island production facility before and after termination of produced water discharge. Concentrations are $\mu\text{g/g}$ dry weight.

Metal	Pre-termination Concentration	Toxic Units	Post-termination Concentration	Toxic Units
Arsenic	3.1 - 11.2	0.04 - 0.16	2.0 - 6.7	0.03 - 0.10
Cadmium	0.04 - 0.92	<0.01 - 0.10	0.16 - 0.42	0.02 - 0.04
Chromium	28.9 - 56.1	0.08 - 0.15	27.2 - 61.9	0.07 - 0.17
Copper	8.7 - 23.4	0.03 - 0.09	8.3 - 22.4	0.03 - 0.08
Lead	4.1 - 27.4	0.02 - 0.13	6.2 - 24.1	0.03 - 0.11
Mercury	0.023 - 0.075	0.03 - 0.11	0.022 - 0.054	0.03 - 0.08
Molybdenum	0.5 - 2.2	NV	0.5 - 4.9	NV
Nickel	14.1 - 35.6	0.27 - 0.69	14.5 - 34.9	0.28 - 0.68
Vanadium	35.6 - 101	NV	47.6 - 115	NV
Zinc	30.0 - 101	0.07 - 0.25	27.0 - 95.6	0.07 - 0.23

NV = No ERM value available.

Highest concentrations of nickel and zinc at the time of the Pre-termination Survey were in sediments from the discharge site. After termination of the produced water discharge, the highest concentrations of nickel and zinc were in sediments from reference and transect stations. Nickel concentrations in produced water from Delacroix Island were not significantly higher than expected concentrations in ambient waters. Therefore, the source of nickel in the sediments near the discharge are unclear. Zinc was abundant in the produced water from the facility, so some of the zinc in the sediments may have come from produced water. Zinc in produced water may come from microcrystalline particles of zinc sulfide (spaeralite) or from metal chips from galvanized pipes, as well as from dissolved zinc.

Concentrations of all the metals evaluated in sediments from the vicinity of the Delacroix Island facility were below levels considered potentially toxic to benthic organisms. There was little or no change in toxic units for the different metals between the Pre-termination Survey and the two Post-termination Surveys. Most of the metals probably were natural and were not derived from the produced water discharge. Therefore, it is likely that the metals present in the sediments were not posing a significant risk to the local benthic communities.

Concentrations of most metals in sediments from the vicinity of the Bay de Chene facility were slightly higher than those in sediments from the vicinity of the Delacroix Island facility. However, none of the metals evaluated were present in sediments near the produced water discharge at a concentration greater than the ERM values (**Table 10.13**). Metal concentrations and the corresponding toxic units were not notably different for sediments collected before and after termination of the produced water discharge. Highest values for toxic units were for nickel, mercury, and zinc. Before termination of the produced water discharge, the highest mercury concentration was in sediments from the discharge site. Zinc and nickel concentrations in sediments collected during this survey were highest along the northeast transect. After termination of produced water discharge, most high concentrations of the three metals were in sediments from the northeast transect near the former fuel dock and pipe storage facility.

Toxic units for metals are not necessarily additive. However, it is possible that the presence of several metals in a sediment at concentrations below, but approaching their respective ERM values, could be toxic to local benthic organisms. These sediments contained toxic units of about 0.6 for nickel and mercury, and toxic units of 0.4 to 0.9 for zinc. Thus, sediments in the vicinity of the former fuel dock and pipe storage facility pose a moderate risk to the local benthic infauna. Metal concentrations, particularly of mercury, in sediments from the discharge site before termination of the produced water discharge also may have posed a risk to sensitive species and life stages of benthic organisms. Sediments from all other stations in the vicinity of the Bay de Chene facility before and after termination of the produced water discharge did not contain concentrations of metals high enough to represent a risk to the local benthic communities.

Concentrations of metals in sediments near the Four Isle Dome facility before termination of its produced water discharge were roughly similar to those in sediments from the vicinity of the other two production facilities. As with the other facilities no metals were present in sediments at concentrations higher than their ERM values (**Table 10.14**). The highest metal concentrations and toxic unit values were for nickel and zinc.

Table 10.13. Estimated ranges of toxic units (concentration in sediment/effects range-median [ERM] value) of several metals in sediments from the vicinity of the Bay de Chene production facility before and after termination of produced water discharge. Concentrations are $\mu\text{g/g}$ dry weight.

Metal	Pre-termination Concentration	Toxic Units	Post-termination Concentration	Toxic Units
Arsenic	4.6 - 13.9	0.07 - 0.20	4.5 - 13.1	0.06 - 0.19
Cadmium	0.20 - 0.55	0.02 - 0.06	0.22 - 1.0	0.02 - 0.10
Chromium	32.2 - 66.7	0.09 - 0.18	40.8 - 73.8	0.11 - 0.20
Copper	10.8 - 30.1	0.04 - 0.11	11.0 - 50.7	0.04 - 0.19
Lead	12.1 - 35.7	0.06 - 0.16	4.8 - 68.0	0.02 - 0.31
Mercury	0.029 - 0.423	0.04 - 0.60	0.027 - 0.462	0.04 - 0.65
Molybdenum	0.9 - 4.0	NV	0.7 - 2.8	NV
Nickel	14.0 - 32.1	0.27 - 0.62	14.1 - 33.6	0.27 - 0.65
Vanadium	53.4 - 115	NV	58.0 - 132	NV
Zinc	51.8 - 159	0.13 - 0.39	56.3 - 362	0.14 - 0.88

NV = No ERM value available.

Table 10.14. Estimated ranges of toxic units (concentration in sediment/effects range-median [ERM] value) of several metals in sediments from the vicinity of the Four Isle Dome production facility before termination of produced water discharge. Concentrations are $\mu\text{g/g}$ dry weight.

Metal	Pre-termination Concentration	Toxic Units
Arsenic	4.5 - 7.2	0.06 - 0.10
Cadmium	0.28 - 0.54	0.03 - 0.06
Chromium	53.6 - 69.9	0.14 - 0.19
Copper	17.9 - 27.3	0.07 - 0.10
Lead	10.8 - 25.7	0.05 - 0.12
Mercury	0.045 - 0.139	0.06 - 0.20
Molybdenum	1.0 - 2.8	NV
Nickel	24.7 - 35.8	0.48 - 0.69
Vanadium	84.1 - 161	NV
Zinc	75.2 - 192	0.18 - 0.47

NV = No ERM available.

Nickel concentrations in sediments actually were quite uniform throughout the area (range of concentrations from 24.7 to 35.8 $\mu\text{g/g}$) and were not higher in sediments near the discharge. Some sediment samples from the other two facilities contained lower nickel concentrations, in the range of 14 to 20 $\mu\text{g/g}$. It is possible that nickel concentrations up to about 35 $\mu\text{g/g}$ are normal for sediments from the area. Apparently clean marine sediments often contain nickel concentrations up to 50 $\mu\text{g/g}$ and even as high as 350 $\mu\text{g/g}$ (Bowen, 1979; Loring and Asmund, 1996). Nickel concentrations usually are positively correlated with clay content of sediments; much of the nickel may be associated with the aluminosilicate lattice of the clay particles (Loring, 1982). Thus, the nickel concentrations in sediments near production facilities in coastal Louisiana probably are natural and not derived from produced water discharges.

10.3.5 Environmental Risk of Metals in Sediment Interstitial Water

Concentrations of Metals in Interstitial Water

Concentrations of dissolved or colloidal metals in sediment interstitial water collected from the vicinity of the three production facilities before termination of the produced water discharges generally were higher than expected concentrations in the overlying water column (**Tables 10.15** and **10.16**). This is typical for most freshwater and marine sediments, particularly where redox cycling is taking place (Gaillard et al., 1986). In most cases, interstitial water from reference stations contained lower concentrations of metals than interstitial water from the two discharge stations. Concentrations of copper, molybdenum, nickel, vanadium, and zinc were higher in interstitial water from some reference stations than in interstitial water from the corresponding discharge site. Sulfate concentrations usually were higher in reference site interstitial water than in discharge site interstitial water, reflecting the higher concentrations of this anion in seawater than in most produced waters. The elevated concentrations of iron and manganese in interstitial water from most sediment sampling sites, particularly the discharge sites, indicates that the sediments probably were hypoxic. These metals are insoluble in interstitial waters of oxidized sediments and tend to precipitate as sulfides in anoxic sediments. The high concentrations of barium and chloride and low concentrations of sulfate in interstitial water from the discharge sites indicate that produced water was penetrating into the sediments and mixing with the sediment interstitial water. Despite this contamination of interstitial water with produced water before termination of the produced water discharges, there was little difference in concentrations of toxic metals in interstitial water from discharge and reference sites. Concentrations of most metals were lower in sediment interstitial water from Four Isle Dome than in interstitial water from the other two facilities.

Post-termination samples of interstitial water were collected and analyzed for metals only at the discharge and reference sites at the Delacroix Island facility. Concentrations of most metals in the interstitial waters decreased between the Pre-termination and the Second Post-termination Surveys (**Table 10.15**). In particular there was a several-fold decrease in concentrations of barium, iron, and manganese in interstitial water samples from the discharge site. Concentrations of a few metals, arsenic and vanadium, actually increased in sediment interstitial water between the Pre-termination and Second Post-termination Surveys. This could be due to changes in sediment redox potential and a redistribution of metals adsorbed to dissolved organic matter in the sediments.

Table 10.15. Concentration ranges of metals in interstitial water from sediments collected from the discharge and reference sites at the Delecroix Island production facility during the Pre-termination and Second Post-termination Surveys. Concentrations are $\mu\text{g/L}$ unless noted otherwise.

Metal	Pre-termination		Second Post-termination	
	Discharge	Reference	Discharge	Reference
Chloride (g/L)	37.6 - 53.0	1.8 - 2.8	---	---
Sulfate (g/L)	0.11 - 0.14	0.19 - 0.28	---	---
Arsenic	4.7 - 8.5	0.9 - 5.8	6.4 - 10.5	5.6 - 10.0
Barium	42,000 - 74,000	270 - 600	300 - 340	230 - 290
Cadmium	<0.25 - 1.25	<0.1 - 0.1	<0.1	<0.1
Chromium	0.42 - 0.56	0.56 - 0.72	0.75 - 1.1	0.61 - 0.93
Copper	1.6 - 2.7	2.9 - 5.9	0.75 - 1.0	0.40 - 0.80
Iron	7,360 - 13,550	140 - 3,440	480 - 550	80 - 260
Lead	0.8 - 1.6	0.3 - 0.5	0.49 - 0.80	0.40 - 0.71
Mercury	0.028 - 0034	<0.01 - 0.023	<0.01 - 0.43	<0.01 - 0.01
Manganese	21,900 - 25,250	5,870 - 14,990	210 - 330	60 - 130
Molybdenum	2.0 - 2.3	1.4 - 6.8	2.4 - 3.3	1.2 - 5.3
Nickel	1.1 - 3.8	3.3 - 4.9	1.3 - 2.1	0.90 - 1.9
Vanadium	<0.25	1.7 - 2.4	2.4 - 4.4	5.6 - 11.6
Zinc	2.5 - 4.5	3.4 - 16.1	5.6 - 11.6	2.6 - 7.6

Table 10.16. Concentration ranges of metals in interstitial water from sediments collected from the discharge and reference sites at the Four Isle Dome and Bay de Chene production facilities before termination of produced water discharge. Concentrations are $\mu\text{g/L}$ unless noted otherwise.

Metal	Four Isle Dome Discharge	Four Isle Dome Reference	Bay de Chene Discharge	Bay de Chene Reference
Chloride (g/L)	3.6	2.4 - 3.1	6.8 - 7.6	3.8 - 4.3
Sulfate (g/L)	---	---	0.21 - 0.33	0.39 - 0.56
Arsenic	<0.20 - 8.6	<0.2 - 6.9	25.7 - 44.6	3.3 - 5.6
Barium	<1.0 - 370	<1.0 - 160	1,400 - 1,940	160 - 1,550
Cadmium	<0.10	<0.10	<0.1 - 0.27	<0.1 - 0.23
Chromium	<0.10 - 1.81	<0.10 - 1.3	0.87 - 0.95	0.38 - 0.46
Copper	0.20 - 3.7	0.48 - 3.0	0.4 - 1.9	0.4 - 2.1
Iron	<1.0 - 21,800	9.0 - 160	9,130 - 23,460	90 - 1,330
Lead	<0.1 - 0.27	<0.10	0.2 - 3.9	0.2 - 1.1
Mercury	<0.01	<0.01	0.031 - 1.57	<0.01
Manganese	<1.0 - 7,200	1.0 - 1,700	7,660 - 11,100	1,400 - 4,750
Molybdenum	<0.10 - 2.8	<0.10 - 4.4	5.0 - 6.9	2.3 - 8.5
Nickel	<0.10 - 8.7	0.11 - 1.9	3.1 - 4.9	0.2 - 1.7
Vanadium	<0.10 - 16.3	<0.10 - 2.8	4.0 - 5.1	1.7 - 4.9
Zinc	0.17 - 4.2	0.89 - 4.8	5.5 - 7.9	4.6 - 9.4

Environmental Risk of Metals in Interstitial Water

If it is assumed that all or most of the metals in interstitial water are present in a dissolved, bioavailable form (probably not true), the measured concentrations can be compared to water quality criterion values to derive values for toxic units (**Table 10.16**). The resulting toxic units range from less than 0.01 to more than 200 (**Tables 10.17** and **10.18**). Toxic units for chromium, nickel, and zinc are below 1.0 for all interstitial water samples. A few sediment interstitial water samples contain arsenic, cadmium, copper, lead, or mercury at a concentration equivalent to about 1.0 toxic units. These metals probably do not represent a significant risk to benthic marine animals in the vicinity of the production facilities.

Concentrations of barium in interstitial water from the discharge site at the Delacroix Island facility, iron and manganese in interstitial water from all three discharge sites, and manganese in interstitial water from the reference sites before termination of produced water discharges are considerably higher than 1 toxic unit. One year after termination of produced water discharges at the Delacroix Island facility, concentrations and toxic units of most metals had decreased substantially (**Table 10.17**). Only manganese was present at a concentration equivalent to more than 1 toxic unit.

One year after termination of the produced water discharge from the Delacroix Island facility, toxic units for metals in interstitial water generally were similar to or lower than toxic units in interstitial water samples collected during the Pre-termination Survey (**Table 10.17**). Largest decreases were for barium, iron, and manganese. Only manganese was still present at concentrations equivalent to more than 1 toxic unit.

Iron and manganese are abundant natural components of marine and estuarine sediments and it is doubtful that they are toxic to benthic organisms in the forms in which they occur in the sediment interstitial water. They probably are present in the interstitial water as amorphous particles of iron and manganese oxide or complexed with dissolved or colloidal organic matter in the sediment interstitial water. However, the barium, if it is present in the interstitial water at the discharge sites in a soluble, bioavailable form could be toxic to benthic organisms, particularly larval stages (Spangenberg and Cherr, 1996). Highest interstitial water barium concentrations were in sediments from Delacroix Island where sulfate concentrations were lower (0.11 to 0.14 g/kg) than in interstitial water of sediments from the other discharge site (0.21 to 0.33 g/kg). Water containing 0.11 g/L of sulfate and 0.074 g/L (74,000 $\mu\text{g/L}$) of barium would be substantially supersaturated with respect to barium sulfate (solubility product, 1.05×10^{-10} M). Therefore, most of the barium in the interstitial water at the discharge sites probably is complexed with organic matter or present as microcrystals, and may not be toxic.

10.3.6 Environmental Risk of Aromatic Hydrocarbons in Sediments

Concentrations of Aromatic Hydrocarbons in Sediments

As expected, concentrations of VAHs, BTEX, were low in sediments near the three produced water discharges before termination of the discharges (**Chapter 8**). Most sediment samples near the discharges did not contain quantifiable concentrations of any BTEX compounds. None of the sediment samples from the discharge and reference sites at Bay de Chene contained BTEX. A sediment sample from the discharge at Four Isle Dome contained

Table 10.17. Water quality criteria and toxic units (concentration in water/water quality criterion value) for metals in interstitial water of sediments collected from discharge and reference sites at the Delacroix Island facility on the Pre-termination and Second Post-termination Surveys. Concentrations are $\mu\text{g/L}$.

Metal	Water Quality Criteria	Toxic Units			
		Pre-termination		Second Post-termination	
		Delacroix Island Discharge	Delacroix Island Reference	Delacroix Island Discharge	Delacroix Island Reference
Arsenic	36	0.13 - 0.24	0.02 - 0.16	0.18 - 0.29	0.16 - 0.28
Barium	1,000	42 - 74	0.27 - 0.60	0.30 - 0.34	0.23 - 0.29
Cadmium	1.1	<0.23 - 1.14	<0.09 - 0.09	<0.09	<0.09
Chromium	11	0.04 - 0.05	0.05 - 0.07	0.07 - 0.10	0.06 - 0.08
Copper	2.9	0.55 - 0.93	1.0 - 2.03	0.26 - 0.34	0.14 - 0.28
Iron	1,000	7.36 - 13.55	0.14 - 3.44	0.48 - 0.55	0.08 - 0.26
Lead	3.2	0.25 - 0.50	0.09 - 0.16	0.15 - 0.25	0.12 - 0.22
Mercury	1.11*	0.03	<0.01 - 0.02	<0.01 - 0.38	<0.01 - 0.01
Manganese	100	219 - 252	58.7 - 150	2.1 - 3.3	0.60 - 1.3
Molybdenum	NV	---	---	---	---
Nickel	8.3	0.13 - 0.46	0.40 - 0.59	0.16 - 0.25	0.11 - 0.23
Vanadium	NV	---	---	---	---
Zinc	86	0.03 - 0.05	0.04 - 0.19	0.07 - 0.13	0.03 - 0.09

* Water quality criterion for inorganic mercury; criterion for methylmercury is $0.025 \mu\text{g/L}$.

NV = No water quality criterion value available.

Table 10.18. Water quality criteria and toxic units (concentration in water/water quality criterion value) for metals in interstitial water of sediments collected from discharge and reference sites at the Four Isle Dome and Bay de Chene facilities during the Pre-termination Survey. Concentrations are $\mu\text{g/L}$.

Metal	Water Quality Criteria	Toxic Units			
		Four Isle Dome Discharge	Four Isle Dome Reference	Bay de Chene Discharge	Bay de Chene Reference
Arsenic	36	<0.01 - 0.24	<0.01 - 0.19	0.71 - 1.24	0.09 - 0.16
Barium	1,000	<0.01 - 0.37	<0.01 - 0.16	1.40 - 1.94	0.16 - 1.55
Cadmium	1.1	<0.09	<0.09	<0.09 - 0.25	<0.09 - 0.21
Chromium	11	<0.01 - 0.16	<0.01 - 0.12	0.08 - 0.09	0.03 - 0.04
Copper	2.9	0.07 - 1.3	0.16 - 1.0	0.14 - 0.66	0.14 - 0.72
Iron	1,000	<0.01 - 21.8	0.01 - 0.16	9.13 - 23.46	0.09 - 1.33
Lead	3.2	<0.03 - 0.08	<0.03	0.06 - 1.22	0.06 - 0.34
Mercury	1.11*	<0.01	<0.01	0.03 - 1.41	<0.01
Manganese	100	<0.01 - 72	<0.01 - 17	76.6 - 111	14.0 - 47.5
Molybdenum	NV	---	---	---	---
Nickel	8.3	<0.01 - 1.0	0.01 - 0.22	0.37 - 0.59	0.02 - 0.20
Vanadium	NV	---	---	---	---
Zinc	86	<0.01 - 0.05	0.01 - 0.06	0.06 - 0.09	0.05 - 0.11

* Water quality criterion for inorganic mercury; criterion for methylmercury is $0.025 \mu\text{g/L}$.

NV = No water quality criterion value available.

0.745 $\mu\text{g/g}$ total monoaromatic hydrocarbons, compared to 0.0016 to 0.0002 $\mu\text{g/g}$ in sediments from the reference sites. A sediment sample collected from the discharge site at Delacroix Island before termination of the discharge contained 0.58 $\mu\text{g/g}$ total BTEX, mostly xylenes. A year later at the time of the Second Post-termination Survey, sediment from the same location contained 0.002 $\mu\text{g/g}$ total monoaromatic hydrocarbons. The only monocyclic aromatic hydrocarbons remaining were the less volatile C_2 - through C_4 -benzenes. None of the sediments from reference stations at Delacroix Island contained detectable concentrations of monocyclic aromatic hydrocarbons.

Concentrations of PAHs in sediments near the three production facilities were highly variable in both space and time. Total PAH concentrations in sediments from different locations ranged from 0.22 to 80 $\mu\text{g/g}$ dry weight (**Table 10.19**). Highest concentrations of total PAHs at the time of the Pre-termination Surveys were in sediments from the discharge from the Bay de Chene production facility (72 $\mu\text{g/g}$). However, highest PAH concentrations were observed in the two Post-termination Surveys at transect stations near the Bay de Chene facility. Most of the highest concentrations were in sediments near the former fuel dock and pipe storage facility. Sediments from the discharge site at the Four Isle Dome facility also contained an elevated concentration of total PAHs.

Sediments from reference stations near the three production facilities contained relatively uniform low concentrations ranging from 0.22 to 0.75 $\mu\text{g/g}$. Concentrations were highest in reference sediments in the vicinity of the Four Isle Dome facility. These concentrations of total PAHs in reference sediments can be considered background concentrations for coastal areas of Louisiana.

Advanced hydrocarbon fingerprinting methods were used (**Chapter 8**) to determine the sources of PAHs in sediments from the vicinity of the three production facilities. Most of the PAHs in sediments near the production facilities contained predominantly PAHs from a pyrogenic source, probably creosote. Most of the older shallow-water production facilities in coastal waters of Louisiana were built on wood pilings that had been treated with creosote to slow decay. Extensive use was made at many facilities of wooden walkways between wellheads and the different platform facilities. These wooden structures probably are the source of the creosote in the sediments near the three facilities. Some of the PAHs were derived from produced water and from refined petroleum products, primarily fuel oils. However, it is not possible to quantify the relative contributions of different sources to the total PAHs in sediments at different locations near the facilities. It is reasonable to assume that most of the PAHs in sediments under the discharges before termination of the produced water discharges were derived from the produced water discharges. However, after the termination of these discharges, concentrations of PAHs in sediments at the former discharge sites decreased rapidly (**Table 10.19**), indicating that the low molecular weight PAHs from produced water were not persistent in the sediments. The higher molecular weight PAHs characteristic of creosote and other pyrogenic sources were much more persistent in the site sediments. Their concentrations in sediments did not decrease rapidly following termination of the discharges.

Environmental Risk of Aromatic Hydrocarbons in Sediments

There are no screening values for VAHs in sediments. Because of their volatility and low sediment organic carbon/water partition coefficients (K_{oc}), they do not bind strongly

Table 10.19. Concentration ranges of total polycyclic aromatic hydrocarbons in surface sediments from the vicinity of three production facilities in coastal Louisiana. Concentrations are $\mu\text{g/g}$ dry weight.

Site	Stations	Pre-termination Survey	First Post-termination Survey	Second Post-termination Survey
Delacroix Island	Discharge	12	2.8	7.7
	Transects	0.33 - 2.5	0.27 - 2.1	0.29 - 1.5
	Reference	0.26 - 0.27	0.22 - 0.28	0.24 - 0.28
Bay de Chene	Discharge	72	9.6	8.3
	Transects	0.26 - 35	0.15 - 80	0.27 - 66
	Reference	0.30 - 0.49	0.23 - 0.42	0.30 - 0.35
Four Isle Dome	Discharge	49	No Sampling	No Sampling
	Transects	0.45 - 3.6	---	---
	Reference	0.73 - 0.75	---	---

to sediments and rarely are found at greater than trace concentrations, even near point sources, such as waste-water effluents (Neff, 1997). The highest concentration in sediment was about 0.75 $\mu\text{g/g}$ dry weight at the discharge from the Four Isle Dome facility. The VAHs in this sample undoubtedly were derived from the produced water discharge. Sediments from this location also contained 700 $\mu\text{g/g}$ total petroleum hydrocarbons and 49 $\mu\text{g/g}$ total PAHs. It is possible that the sediments contained small amounts of fresh oil droplets. Produced water from the Four Isle Dome facility contained the highest concentrations of monocyclic aromatic hydrocarbons, PAHs, and total petroleum hydrocarbons of the three discharges (**Table 10.6**), indicating that some dispersed oil droplets may have been present in the discharge.

The concentrations of monocyclic aromatic hydrocarbons in the sediments from the discharge sites probably were not sufficiently high to cause harm to local benthic organisms. Based on aquatic toxicity information for BTEX compounds, it is probable that toxic concentrations of BTEX in sediments are in the range of several parts per million, many times higher than measured concentrations.

Concentrations of total PAHs in some sediments were high enough that they posed a risk of harm to benthic organisms. Sediments collected during the Pre-termination Surveys from the discharge at the Bay de Chene and Four Isle Dome facilities contained total PAHs equivalent to slightly more than 1 toxic unit (**Table 10.20**). Sediments collected during the two Post-termination Surveys from a few transect stations near the Bay de Chene facility also contained PAHs equivalent to slightly more than 1 toxic unit. These stations were near the former fuel dock and pipe storage facility. The PAHs there probably did not come from the produced water discharges at Tank Battery #5.

Concentrations of total PAHs in sediments were high enough at a few locations before and after termination of the produced water discharge that they may pose a risk to benthic organisms living in sediments near the production facilities. The PAHs in the sediments under the discharge from the Bay de Chene and Four Isle Dome facilities probably were derived in large part from the produced water discharges. At the time of the First Post-termination Survey about six months after termination of the produced water discharge, concentrations of total PAHs in sediments under the Bay de Chene discharge had dropped from 72 $\mu\text{g/g}$ to 9.6 $\mu\text{g/L}$, lending support to the hypothesis that the PAHs present in the sediments under the discharges when produced water was being discharged were from the produced water. Concentrations of total PAHs in discharge site sediments at the Delacroix Island facility also decreased between the Pre-termination Survey and the First Post-termination Survey from 12 to 2.8 $\mu\text{g/g}$. These results indicate that PAHs derived from produced water readily desorb from the sediments when concentrations in the overlying water decrease. They are not persistent.

However, PAHs in transect sediments near the Bay de Chene facility appear to be much more persistent. Alternatively, the sediments are being re-contaminated with PAHs from some source. The sediments from these transect locations contain PAHs from combined pyrogenic and petrogenic sources, possibly creosote and fuel oils (**Chapter 8**). PAHs associated with creosote are quite persistent in estuarine and marine sediments, particularly if the redox potential is low (Mueller et al., 1989).

Table 10.20. Estimated toxic units (concentration in sediment/effects range-median [ERM] value) for total polycyclic aromatic hydrocarbons (PAHs) in surface sediments from the vicinity of three production facilities in coastal Louisiana. The ERM value for total PAHs in sediments is 44.79 $\mu\text{g/g}$ dry weight (Long et al., 1995).

Site	Stations	Pre-termination Survey	First Post-termination Survey	Second Post-termination Survey
Delacroix Island	Discharge	0.27	0.06	0.17
	Transects	0.01 - 0.06	0.01 - 0.05	0.01 - 0.03
	Reference	0.01	0.01	0.01
Bay de Chene	Discharge	1.61	0.21	0.19
	Transects	0.01 - 0.78	<0.01 - 1.79	0.01 - 1.47
	Reference	0.01	0.01	0.01
Four Isle Dome	Discharge	1.09	No Sampling	No Sampling
	Transects	0.01 - 0.08	---	---
	Reference	0.02	---	---

10.3.7 Environmental Risk of PAHs in Sediment Interstitial Water

Low concentrations of a few PAHs were detected in sediment interstitial water from discharge and reference sites at the Delacroix Island production facility before and after termination of the produced water discharge. The only other interstitial water sample containing a quantifiable concentration of PAHs was collected on the Pre-termination Survey from a reference site for the Bay de Chene facility. This sample contained 0.3 $\mu\text{g/L}$ of naphthalene (see **Chapter 8**).

Two interstitial water samples collected during the Pre-termination Survey from the discharge site at the Delacroix Island facility contained 3.9 and 5.2 $\mu\text{g/L}$ total PAHs, including naphthalene and alkyl-naphthalenes. One interstitial water sample collected at the same time from a reference station contained 4.2 $\mu\text{g/L}$ total PAHs. Interstitial water samples collected during the Second Post-termination Survey from sediments at discharge and reference stations near the Delacroix Island production facility contained 0.10 to 0.31 $\mu\text{g/L}$ total PAHs. There was no difference in concentrations between discharge and reference stations. The dominant PAHs in all samples were naphthalene and alkyl-naphthalenes. These PAHs probably were derived primarily from produced water.

The chronic water quality criteria for naphthalene and alkyl-naphthalenes estimated by the regression of McCarty et al. (1992) range from 8 to 214 $\mu\text{g/L}$. Thus, concentrations of total PAHs (consisting primarily of naphthalenes) in sediment interstitial water are well below potentially toxic concentrations. Therefore, PAHs in the interstitial waters of sediments near the produced water discharge from the three production facilities do not pose a significant risk to benthic marine organisms.

10.3.8 Impacts on Benthic Infauna

The composition and distribution of the benthic infauna in the vicinity of the three production facilities was investigated in **Chapter 9**. Benthic infaunal communities were significantly different from those at reference stations at locations within 100 m of the Delacroix Island and Bay de Chene production facilities. There was not a statistically significant difference in benthic community parameters at stations near the Four Isle Dome facility. There was apparent partial recovery of the benthic infauna near the discharges from the Delacroix Island and Bay de Chene facilities after termination of produced water discharges.

The risk assessment described earlier in this chapter provides evidence that the altered benthic infauna at stations near the platforms was caused by a combination of elevated concentrations of a few metals (barium, iron, and manganese) in sediment interstitial water, and total PAHs in bulk sediments. Elevated chloride concentrations, particularly in interstitial water at the Delacroix Island discharge site before termination of the produced water discharge, may have contributed substantially to alterations in benthic community structure near the platforms. Depressed redox potentials in surficial sediments near the platforms, as often occurs because of accumulation of biodegradable hydrocarbons in the sediments (Kingston, 1992), may also have contributed to benthic community alteration near the platforms.

10.4 CONCLUSIONS

Before produced water discharges were terminated in 1993 and 1995, shallow water production facilities at Delacroix Island, Bay de Chene, and Four Isle Dome discharged 852 to 3,825 bbl/day of produced water containing elevated concentrations (compared to the estimated concentrations in local receiving waters) of several metals and hydrocarbons to shallow coastal waterways of Louisiana. Concentrations of all metals, except barium, in a 100-fold dilution of the produced waters (the maximum likely exposure concentration to local aquatic biota) were below concentrations equivalent to 1 toxic unit. Concentrations below 1 toxic unit are not expected to be toxic to estuarine and marine organisms. Barium probably precipitated as barite following discharge and so may have been present in a dissolved, bioavailable form in the receiving water at a concentration much lower than 1/100 the concentration in the produced water. VAHs and PAHs were present in 100-fold dilutions of the produced water at concentrations well below 1 toxic unit. Therefore, after initial dilution in the receiving waters, treated produced water from the three facilities was not expected to be toxic to local estuarine and marine organisms.

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

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

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

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

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

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SYNTHESIS OF SEAFOOD CATCH, DISTRIBUTION, AND CONSUMPTION PATTERNS IN THE GULF OF MEXICO REGION

Final Report

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Prepared by:

Steimle & Associates, Inc.
3826 Airline Highway
Metairie, Louisiana 70001
Telephone: (504) 831-2574

Under subcontract to:

Continental Shelf Associates, Inc.
759 Parkway Street
Jupiter, Florida 33477
Telephone: (561) 746-7946

Prepared for:

U.S. Department of Energy
Mrs. Rhonda P. Lindsey
Contracting Officer's Representative
220 North Virginia Avenue
Bartlesville, Oklahoma 74003
Telephone: (918) 337-4407

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ABSTRACT

The purpose of this task was to gather and assemble information that will provide a synthesis of seafood catch, distribution and consumption patterns for the Gulf of Mexico (GOM) region. This task was 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." Personal interviews were conducted with a total of 905 recreational fishermen and 218 commercial fishermen (inclusive of shrimpers, crabbers, oystermen and finfishermen) in Louisiana and Texas using survey questionnaires developed for the study. Results of these interviews detail the species and quantities caught, location of catch, mode of fishing, distribution of catch, family consumption patterns and demographics of the fishermen.

A total of 95 wholesaler/processors completed and returned surveys by mail which delineate the location of seafood sources, the quantities of seafood handled, the distribution of the product to consumers and the form of the product sold. Products available and the form in which the products were available was determined in 341 retail outlets near population centers in coastal Louisiana and Texas.

Restaurant surveys were conducted by mail to determine the popularity of seafood dishes sold, the source of the seafood and the cooking methods. One hundred fifty-four restaurants from Louisiana and Texas responded.

Data quality was analyzed by means of analysis of variance to confirm that survey information obtained concerning finfish species was consistent both within and among surveys.

The study concluded that over the two state area surveyed, a large percentage of seafood was harvested commercially and recreationally near inshore and offshore oilfield structures. This was particularly true in Louisiana. Seafood harvested by commercial fishermen was most often sold to wholesaler/processors who ship the seafood with little value added to retail outlets and restaurants.

Retail outlets provide mostly uncooked seafood to the general public. Restaurants which serve seafood do so as a large percentage of their meals. Most of the seafood is fried although seafood stock is in a large percentage of dishes.

Seafood harvested by recreational fishermen was usually kept for home consumption and prepared fried. Most of the seafood harvested locally, both commercially and recreationally, remains in the local population. Very little fresh seafood sold locally was imported from out of state or out of country.

EXECUTIVE SUMMARY

ES.1 INTRODUCTION

This task is part of a U.S. Department of Energy (DOE)-sponsored project entitled "Environmental and Economic Assessment of Discharges from Gulf of Mexico (GOM) Region Oil and Gas Operations." The objective of this project is to increase scientific knowledge about the fate and effects of contaminants found in produced water. This task was intended to detail the seafood catch, distribution and consumption patterns for the GOM region.

ES.2 METHODOLOGY

A thorough review of the literature revealed significant gaps in the existing information necessary to determine the catch, consumption and use patterns in the GOM region. Surveys were therefore developed to obtain the pertinent information from commercial fishermen, recreational fishermen, processors, wholesalers, retail outlets and restaurants in Louisiana and Texas.

Commercial fishermen (including oystermen) and recreational fishermen were surveyed by personal interview. Wholesalers and processors were surveyed by personal interview and by mail. Retail outlets were surveyed by site visits, and restaurants were surveyed by mail. All personal interviews and site visits were conducted by FISHIE (Fisheries Information and Seafood Harvest Inquiry Enterprise), a nonprofit organization who conducted the surveys.

Commercial fishermen (shrimpers, crabbers and finfishermen) and recreational fishermen were surveyed from May through November 1993 to determine categories of seafood fished over the previous three months, types of license(s) held, and information on the number, gender and ages of individuals in the household and their seafood consumption habits. Respondents were also interviewed about locations fished, the estimated distance from oilfield structures and species caught. An identification guide with fish illustrated in color was shown to respondents to enable them to correctly identify species. Recreational fishermen were additionally asked about fishing mode (i.e., private boat, party boat, charter boat).

To determine the distribution of the catch, all fishermen were asked to estimate by species the percentage sold, the percentage given away to others and the percentage kept for personal consumption. Fishermen were also asked to estimate frequency of seafood consumption and cooking methods employed.

Oystermen surveys were conducted during April and May 1994 in Louisiana and Texas. Oystermen were asked for the number of acres of oyster bottoms under lease in addition to the questions asked other commercial fishermen.

Processing plants and wholesalers were surveyed in Louisiana and Texas from June through December 1993. The survey questions referred to a 12 month period of 1 January through 31 December 1992. These entities were surveyed to determine their sources of seafood (i.e., in-state vs. out-of-state) and the origin of the seafood sold (i.e., fishing zones and ports of commercial fishermen). They were further asked to estimate the relative percentage of commercial fishermen suppliers fishing inshore and offshore. Respondents were also asked to estimate percentage of commercial fishermen suppliers fishing near oilfield structures both inshore and offshore.

Processors and wholesalers were requested to estimate the quantity of seafood handled through the year and the distribution of the seafood by species (i.e., in-state vs. out-of-state). Respondents were also asked to identify the most commonly sold form of seafood.

Site surveys of seafood retailers were conducted May through November 1993 to determine the types of shellfish and saltwater finfish sold, the parts of the seafood sold and the types of prepared seafood sold. Retailers were also asked if they shipped seafood to other areas of the state or out-of-state.

Restaurant surveys were conducted during the calendar year 1992. Respondents were asked to provide information concerning the source, quantities and method of preparation of seafood sold/served by the restaurant.

ES.3 DATA QUALITY ANALYSIS

A data quality analysis was performed on the finfish information from all surveys. Finfish information was used because it was common to all surveys. The objective of the analysis was to determine whether survey information concerning finfish species was consistent within and among surveys.

Analysis of variance (randomized block design) was used on the Louisiana recreational fishermen data (transformed) and the Texas recreational fishermen data (transformed) to determine if similar finfish species were caught in the geographic zones in the surveys. In both cases, the differences were not significant between zones.

Analysis of variance was also used on nine data sets from the ten surveys. The Louisiana and Texas commercial fishermen data were pooled because of a lack of data from Texas commercial finfishermen. The analysis was to determine whether there was consistent reporting concerning the finfish species among the surveys. There were not significant differences among the nine data sets in species reported.

Finfish catches reported by commercial and recreational fishermen are therefore representative of finfish availability in retail markets and restaurants.

ES.4 RESULTS

Louisiana Recreational Fishermen Survey

The survey organization, FISHIE, interviewed approximately 0.21% of all individuals in the state holding salt water fishing licenses.

Finfishing was the most popular form of recreational fishing (95%) with most fishermen possessing an in-state license (92%). The majority of respondents were white (92%), fished from a private boat inshore (62%), often near an oilfield structure, and most commonly caught speckled trout and red snapper.

Fishermen reported keeping 80% of finfish, 97% of blue crab catch and 83% of shrimp for personal consumption. They reported serving the seafood 1.8 times per week. Their preference was to consume the meat only from the fish over 90% of the time, and the most popular cooking method was frying (30%).

Texas Recreational Fishermen Survey

FISHIE interviewed approximately 0.06% of all individuals in the state holding salt water fishing licenses. Finfishing was the most popular form of recreational fishing (97%) with most fishermen possessing

an in-state license (93%). The majority of the respondents were white (93%), fished from a private boat inshore (45%) or offshore (42%), often near an oilfield structure (33%) and most commonly caught red snapper.

Fishermen reported keeping 70% of finfish, 100% of blue crabs and 62% of shrimp for personal consumption. They reported serving seafood 1.6 times per week. Their preference was to consume meat only (73% to 84% of the time) from the fish and the preferred method of cooking was frying (31%).

Louisiana and Texas Commercial Fishermen Survey

Approximately 0.6% of the total individuals holding commercial fishing licenses in Louisiana and Texas were interviewed by FISHIE. The Louisiana and Texas fishermen profiled fish shrimp (77%), finfish (12%), crabs (8%) and oysters (4%). The majority of respondents were white (65%) and fished largely inshore (39%). Thirty-three percent of all trips were made within 300 m (1,000 ft) of an oilfield structure. The majority of seafood caught was sold to either wholesaler/processors or retailers/restaurants.

Louisiana Oyster Fisherman Survey

FISHIE interviewed approximately 1.6% of all individuals holding a license for oyster fishing. The Louisiana oyster fisherman profiled in this survey leased an average of 1,164 acres of water bottoms from the state for oyster culture. Most respondents were white (91%), and 99% of all oysters fished were sold to wholesaler processors. Oysters were served in the household an average of three times per week, and the most popular method of preparation was frying (30%). For the oysterman himself, the most popular method of preparation was raw (49%).

Texas Oyster Fisherman Survey

Eleven licenses were issued to oystermen in Texas, and FISHIE interview 16 oystermen. The average number of acres of water bottom leased by the Texas oyster fisherman profiled could not be determined due to insufficient responses. Most respondents were of Hispanic origin (60%), and 100% of all oysters fished were sold to wholesaler/processors. Oysters were served in the fisherman's household 2.3 times per week on average and the most popular method of preparation was frying (36%). For the oysterman himself, the most popular method of preparation was raw (42%).

Louisiana Wholesalers and Processors Survey

The response rate was 24.7% for the wholesaler/processors surveyed in Louisiana. Of the survey respondents, 52% operate as a wholesaler/dealer only and 42% function as wholesalers and processors. The typical source of seafood was in-state commercial fishermen with generally more than 33% of the seafood received from this source. Respondents indicated that their sources of seafood fished inshore and offshore. Of those sources who fished inshore, 56% were reported to fish near and oilfield structures, and 72% of those who fished offshore were reported to fish near oilfield structures.

The average quantity of saltwater finfish received by respondents was 307,600 kg (678,141 lb) of whole fish, 605,624 kg (1,335,173 lb) whole shrimp (heads-on), 224,200 kg (494,717 lb) of hard shell blue crabs and 486,150 sacks of oysters. The Louisiana wholesalers/processors sent less than 33% of their shellfish out-of-state. Twenty-five percent of black drum, flounder, red snapper and speckled trout and 40% of vermilion snapper were sold to out-of-state sources.

The seafood was sold in a variety of forms. Oysters were most often sold shucked (55%). Blue crabs were sold whole (47%) and shrimp were sold heads-on (32%). Over 55% of finfish were sold whole.

Texas Wholesalers and Processors Survey

Response rate was 5.0% of all Texas wholesalers/processors. Of the survey respondents, 53% operate as a wholesaler/dealer only, and 41% function as wholesalers and processors. The typical source of seafood was in-state commercial fishermen with generally more than 25% of the seafood received from this source. Respondents indicated that their sources of seafood fished inshore and offshore. Of those sources who fished inshore, 30% were reported to fish near oilfield structures, and 54% of those who fished offshore were reported to fish near oilfield structures.

The average quantity of saltwater finfish received by respondents was 24,479 kg (53,967 lb) of whole fish and 105,746 kg (233,130 lb) whole shrimp (heads-on). Few responses were received regarding hard shell blue crabs and oysters. The Texas wholesalers/processors sent less than 30% of their shellfish out-of-state. Nine percent of flounder and red snapper and 25% of tuna were sold to out-of-state sources.

The seafood was sold in a variety of forms. Oysters were most often sold in the shell (54%). Blue crabs were sold whole (50%) and shrimp were sold heads-on (33%). Over 60% of finfish were sold whole.

Louisiana Retail Seafood Market Survey

FISHIE personnel surveyed products at 226 retail outlets in or near population centers in coastal Louisiana parishes. Shellfish (blue crabs, oysters and shrimp) were sold uncooked more than 50% of the time. Finfish were sold as whole fish (gutted) and fillets. None of the markets surveyed sold fish parts. Only flounder (1.2%), speckled trout (3%) and a few miscellaneous species were sold cooked.

Shipping of seafood products was generally to other parts of the state (33%). About 23% reported that they shipped seafood out-of-state.

Texas Retail Seafood Market Survey

FISHIE personnel surveyed products at 115 retail outlets in or near population centers in coastal Texas counties. Most shellfish were sold uncooked. Most fish were sold as whole fish. Both tuna (15%) and grouper (13%) were sold as fish parts. Most fish were sold uncooked although some speckled trout (24%), black drum (11%), flounder (5%), red snapper (4%), and sheepshead (4%) were sold cooked.

Shipping of seafood products was generally to other parts of the state (18%). About 8% of respondents reported that they shipped seafood out-of-state.

Louisiana Restaurant Survey

Seventy-nine questionnaires were received completed from the 1,500 mailed (5.3%). Results showed that an average of 1,096 seafood dishes were served each week in 1992 among responding restaurants. Of the seafood dishes served in 1992, 48% consisted of shellfish, 46% involved finfish and 29% contained both shellfish and finfish. Shrimp was the most popular shellfish (52%), and the most common finfish was tuna (29%). Many restaurants used stock in the preparation of their meals.

About 31% of seafood was imported from out-of-state sources. Wholesaler/processors provided about 86% of the seafood served. Over 60% of finfish were served meat only, and the most common method of preparation was fried (18%).

Texas Restaurant Survey

Seventy-five questionnaires were received completed from the 1,500 mailed (5.0%). Results showed that an average of 678 seafood dishes were served each week in 1992 among responding restaurants. Of the seafood dishes served in 1992, 55% consisted of shellfish, 45% involved finfish and 36% contained both shellfish and finfish. Shrimp was the most popular shellfish (74%), and the most common finfish was red snapper (31%). Many restaurants used stock in the preparation of their meals.

About 62% of seafood was imported from out-of-state sources. Wholesaler/processors provided about 91% of the seafood served. Over 58% of finfish were served meat only, and the most common method of preparation was fried (22%).

ES.5 DISCUSSION

Recreational fishermen in Louisiana and Texas reported they prefer to fish for finfish, keep their catch and infrequently serve it in their household. When their catch was served, it was usually filleted, skinned and fried. Louisiana recreational fishermen more commonly fish near oilfield structures than Texas recreational fishermen.

Commercial fishermen interviewed, primarily shrimpers, sell the vast majority of their catch. Texas and Louisiana commercial fishermen reported commonly fishing near oilfield structures. Louisiana oyster fishermen also report commonly developing oyster beds in closer proximity to oilfield structures than their counterparts in Texas.

In-state commercial fishermen were the prime suppliers of seafood to Louisiana and Texas wholesalers/processors, and wholesalers/processors in both states report that their commercial suppliers often fish in close proximity to oilfield structures. Louisiana wholesalers/processors handled significantly more seafood than those in Texas. Wholesalers/processors were the main source of seafood to restaurants and retailers in both states.

Both Louisiana and Texas restaurants reported similar consumption patterns. For each state shellfish dishes were more popular than finfish dishes or a combination of the two. The preferred method of seafood preparation was fried as reported by all fishermen and restaurants.

ES.6 CONCLUSIONS

Over the two state area surveyed, a large percentage of seafood was harvested commercially and recreationally near inshore and offshore oilfield structures. This was particularly true in Louisiana. Finfish species whose reported catch frequencies were at least 50% greater in close proximity to oilfield structures included amberjack, grouper, king mackerel, red snapper, shark and vermilion snapper. Seafood harvested by commercial fishermen was most often sold to wholesalers/processors who ship the seafood with little value added to retailers and restaurants.

Retail outlets provide mostly uncooked seafood to the public. Restaurants which serve seafood do so as a large percentage of their total meals served. Fresh seafood served to consumers was most often fried, and seafood stock was often used in the preparation of seafood dishes.

Seafood harvested by recreational fishermen was most often kept for home consumption and prepared fried. Most of the seafood harvested locally, both commercially and recreationally, remains in the local population.

1.0 INTRODUCTION

1.1 Purpose of the Task

This 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." The objective of the project is to increase scientific knowledge on the fate and effects of contaminants found in produced water and to increase knowledge on the economic impacts of proposed regulations on offshore oil and gas producers in the Gulf of Mexico (GOM) region. Additionally, the project was implemented to detail the catch, consumption and human use patterns of seafood collected from coastal and offshore waters of the GOM. These data are provided for input into a human health risk analysis to be conducted by Brookhaven National Laboratory.

The specific purpose of this task was to gather and assemble information that will provide a synthesis of seafood catch, distribution and consumption patterns for the GOM region. The task results provide a description of market availability of finfish and shellfish species caught in onshore and offshore Louisiana and Texas near oilfield operations. Results also provide an estimate of the amount of seafood harvested by recreational and commercial fishermen which becomes food locally and out-of-state through wholesalers/processors, retail outlets and restaurants. It also profiles the personal consumption patterns of seafood by fishermen and their families.

1.2 Objectives of the Task

The overall objective for this task was to identify the edible seafood catch, distribution and consumption patterns in the GOM region. In meeting this objective, a detailed review of pertinent literature and descriptive field surveys were conducted. Specifically, this task addressed the following questions:

- What seafood species are caught?
- Where are the seafood caught?
- What quantities of seafood are caught?
- How was the seafood distributed to the consumer?
- What seafood species are consumed/utilized?
- With what frequency was seafood served/eaten?
- What specific parts of the seafood are consumed/utilized?
- What cooking methods are used?
- What was the demographic profile of the fishermen's household?

1.3 Limitations of Study

The limitations of this study include the following:

- The primary target population for this study was fishermen who had the ability to fish near produced water discharge locations. The recreational fishermen respondents were, therefore, limited to those who fished from boats;
- The majority of the surveys of fishermen and wholesalers/processors were conducted during the period May through November 1993, representing the peak fishing activity in Louisiana and Texas. Surveys of retailers were conducted during the period March through August 1993. Restaurant surveys were collected from July to December 1993, and oystermen surveys were conducted during April and May 1994;
- Intercept surveys were conducted during daylight hours, excluding night fishermen;
- Only restaurants in Louisiana and Texas that served fresh seafood were included in this study. This excluded such establishments as fast food chains which utilize frozen, packaged seafood;
- For the purpose of identifying the distribution patterns of seafood, seafood processing plants and seafood wholesalers were combined into one survey. Some operations function both as processing plants and as wholesale outlets; and
- Produced water discharges are not always evident to the recreational or commercial fisherman, therefore, the survey questioned only the nearness of the fisherman to oilfield structures. This assumes that all oilfield structures have produced water discharges, a very conservative assumption.

1.4 Special Terms and Definitions

The following terms are the operational definitions specific to this study.

- Commercial Fishermen: Commercial fishermen are those individuals who make their living or supplement family income by fishing and selling those portions of their catch of commercial value. Commercial fishermen are shrimpers, crabbers, oystermen and finfishermen;
- Oilfield Structure: This term refers to any type of offshore and inshore platform, tank battery, wellhead or facility;
- Oystermen: Oystermen lease water bottoms along the coastal areas of Louisiana and Texas for the primary purpose of growing and harvesting oysters for wholesale or retail outlets;
- Processing Plant: These are sites where seafood is prepared for market. Preparations may include grading, filleting, shelling, shucking, picking, packaging and/or quick freezing;

- Recreational Fishermen: Recreational fishermen are individuals who fish primarily for enjoyment and personal consumption of catch. Recreational fishermen are those who fish from seawalls, shorelines, private boats in inshore waters, private boats in offshore waters, charter boats and/or party boats;
- Restaurant: A restaurant is a place where meals are cooked and served to the public;
- Retailer: A retail market is a store or outlet for fresh and/or cooked seafood. These markets sell to the final consumers in small quantities;
- Seafood: Seafood includes saltwater finfish, blue crabs, shrimp, and oysters; and
- Wholesaler/Processor: These are providers of seafood products to retailers, restaurants and consumers. Wholesalers generally sell in large quantities.

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2.0 HISTORICAL PERSPECTIVE

Rabalais *et al.* (1991) estimated the amount of produced water discharged into the Outer Continental Shelf (OCS) and inshore coastal waters of Texas and Louisiana at 563 million liters/day (3.45 million bbl/day). A map of discharge locations in inshore and offshore Louisiana and Texas is given in **Appendix A**. This map was plotted using industry data (i.e., gathered for the Offshore Operators Committee) for offshore discharge points. The inshore data was obtained from the Texas Railroad Commission and Louisiana Department of Environmental Quality (LDEQ) as of mid-1992.

Produced waters contain oil, heavy metals, radionuclides, treating chemicals, salt and dissolved oxygen (Stephenson, 1992). These constituents, which vary widely in concentration among produced waters from place to place, have the potential to affect the distribution and survival of aquatic organisms. Accumulation of these constituents by species commonly used for human consumption may also result in health risks.

Hydrocarbons from produced water discharges have been shown to accumulate in sediments. Boesch and Rabalais (1989a) found moderately elevated sediment hydrocarbon levels a maximum of 500 m (1,640 ft) from inshore Louisiana discharges. St. Pe' (1990) found elevated hydrocarbons and Ra^{226} in sediments within 300 m (1,000 ft) of the discharge. Steimle & Associates (1991) found during sampling at 36 produced water locations throughout coastal Louisiana, that 14 sites showed sediment contamination above background levels up to 300 m (1,000 ft) from the discharge.

The accumulation of constituents in the sediments is known to affect species diversity in benthic communities close to shallow water discharges (Middleditch, 1984; Neff, 1987). Neff *et al.* (1989) found elevated total petroleum hydrocarbon concentrations less than 300 m (1,000 ft) from a shallow water discharge and less than 100 m (328 ft) from a deep water discharge. Neff *et al.* (1989) concluded that benthic communities within 20 m (66 ft) of both discharges were influenced by sediment contamination.

The significance of naturally occurring radionuclide concentrations in produced waters discharged to coastal habitats is largely unknown. Kraemer and Reid (1984) studied the geochemistry of radium (Ra) in formation waters from the U.S. Gulf Coast region. Their findings show a direct relationship between the salinity of the produced water and the Ra content.

Hanan (1981) documented a doubling of the Ra^{226} concentration in bottom sediments near a 3.5 million liters/day (22,000 bbl/day) produced water discharge when compared to a nearby control site in a fresh marsh habitat off the mouth of the Mississippi River. In conjunction with Hanan's work, Landa and Reid (1983) demonstrated that the Ra^{226} associated with the sediments from the same study site was associated with the mineral fraction of the sediments, not the organic fraction. This demonstrated that the organic matter is unlikely to provide a pathway into the food chain.

Little data are available on tissue concentrations of hydrocarbons, metals and radionuclides in fish or other edible shellfish collected in the vicinity of shallow water produced water discharges. Neff (1988) reviewed the primarily offshore literature on the bioaccumulation potential of oilfield wastes including produced waters. He found that produced water related hydrocarbons were bioavailable and rapidly accumulated, but they were not persistent in animal tissue and did not generally magnify in marine food webs.

Boesch and Rabalais (1989a,b) collected American oysters *Crassostrea virginica* and the mussel *Geukensia demissa* from near several produced water discharges in coastal Louisiana. Limited tissue data showed clear potential for these bivalves to concentrate produced water associated hydrocarbons from the vicinity of the discharges. The metals data showed smaller differences between near discharge and control samples and no clear trend of accumulation in bivalve tissues.

St. Pe' (1990) studied the accumulation of hydrocarbons and radionuclides in caged oysters placed at three of the discharge locations and one control station. He found elevated hydrocarbon levels in all of the experimental oyster tissues with respect to controls. One of the three composited oyster samples near a produced water discharge showed a detectable Ra^{226} activity.

Although little is known about the accumulation of produced water constituents in edible seafood tissue, one of the stated project objectives was to provide a determination of radionuclide concentrations in fish and shellfish species which spend some of their life in the vicinity of produced water discharges in inshore and offshore Gulf Coast waters. A limited amount of data also exists regarding the availability and personal consumption of seafood along the Gulf Coast. The data reveal the large amounts of seafood available for human consumption after processing and retailing. Species of seafood which are more often found in proximity to oilfield structures and/or potential discharge sites become exposed to contaminants and therefore may present a greater risk if consumed by humans. It may also be reasonable to assume that human populations residing near readily available sources of fresh seafood are more likely to consume it than populations where fresh seafood is less available.

Fisheries data show that 4.7 billion kg (5.23 million tons) of fish and shellfish were landed in the U.S. in 1993. This total has increased slightly over the past few years due to increased landings reported for the state of Alaska. The total for 1993 represents record commercial landings for both Alaska and the U.S. Louisiana landings for that year were approximately 12% of the U.S. total, while Texas landings represented 0.9% of that total. Fisheries landing data for 1993 for Louisiana show that the most common commercial saltwater sport finfish species landed was mullet with sheepshead and black drum following in succession (Usie, pers. comm. 1994, National Marine Fisheries Service [NMFS]). In Texas, the yellowfin tuna was listed as the most common commercial saltwater finfish species landed in 1992 with nearly 635,600 kg (1.4 million lb) caught. Red snapper was the next most common with 408,600 kg (0.9 million lb) landed (Hightower, pers. comm. 1994, Texas Parks and Wildlife Department [TPWD]).

Several families of fish are typically associated with offshore oilfield structures. Two of these families (i.e., Serranidae, Lutjanidae) include the commercially important groupers and snappers. Commercial landings of grouper and snapper in Louisiana for 1993 totaled 128,366 kg (283,000 lb) and 896,752 kg (1,977,000 lb), respectively. This represents 1.12% and 7.81% of the total Louisiana fish landings (excluding menhaden) for 1993. In Texas, the grouper and snapper species totaled 60,781 kg (134,000 lb) and 481,443 kg (1,061,400 lb), respectively, representing 2.71% and 21.51% of the total fish catch for 1992.

One of the most effective methods of determining the species-specific amounts of shellfish and finfish caught by residents of coastal areas is by conducting surveys. The NMFS has been conducting a series of marine recreational surveys for the Atlantic and Gulf Coasts since 1979. Surveys of recreational fishermen were designed to identify catch and general location of catch, plus some expenditure and demographic information. The most recent published survey information, covering the 1991 fishing season (NMFS, 1992), shows that 1991 marine recreational anglers caught spotted seatrout 15% of the time they fished in the GOM. Other frequently caught fish included white grunt, gray snapper, yellowtail snapper, black seabass, Spanish mackerel and sheepshead. The 1991 survey also showed that anglers primarily fished in private/rental boats (64-67%) in inshore waters (43%) catching 9.1-11.3 fish/trip (NMFS, 1992).

Kelso *et al.* (1991) performed a survey of Louisiana fishermen to determine their fishing activities for 1989. Surveys were mailed to both freshwater and saltwater fishermen, although the results were kept separate for each group. The surveys included questions regarding fishing expenditures in addition to the fishing activity data. Survey results indicated that 82% of all saltwater fishermen fished in a private boat in inshore waters during 1989. Approximately 76% of the fishermen targeted a specific species when planning a fishing trip. Spotted seatrout and red drum were the most sought after fish, representing 50% and 42% of the targeted species, respectively.

Surveys have also been performed not only to determine fishing habits but also to determine seafood consumption patterns. Dellenbarger *et al.* (1993) performed a survey of residents in south Louisiana over the Lenten period of 1993. The results of their study show that 70% of the respondents consumed seafood during the five-day period. Crawfish and shrimp were the most commonly consumed shellfish, while catfish and bass were the most common freshwater fish eaten and redfish and speckled trout were the most popular saltwater fish consumed. The authors concluded that for the five-day period respondents consumed an average meal of 60 g (2.1 oz) of finfish and shellfish on a per capita basis (i.e., 16 g [0.6 oz] of freshwater finfish, 13 g [0.4 oz] of saltwater finfish and 31 g [1.1 oz] of shellfish). The study also indicated that income and family size positively influenced shellfish consumption as well as recreational fishing habits. Therefore, they concluded that higher income families and large families had higher health risks from consuming seafood if the seafood had been exposed to human health contaminants.

Anderson and Rice (1992) completed a survey of fish and shellfish consumption patterns for the greater New Orleans area. Their study consisted of telephone interviews of residents regarding their seafood consumption habits for the week prior to the interview. Their results showed that 61.2% of the respondents ate seafood the week prior to the interview. Shrimp was the most popular seafood with catfish, speckled trout, crab and other saltwater fish next in order. The study calculated that those respondents who ate one serving of seafood the week before the interview consumed between 10.4 and 30.8 g (0.4-1.1 oz) of fish and between 13.6 and 32.6 g (0.5-1.1 oz) of shellfish, while those respondents who reported consuming two meals per week ate 20.9 to 61.5 g (0.7-2.2 oz) of fish and 26 to 65.1 g (0.9-2.3 oz) of shellfish.

A study by Devonald and Maxted (1989) provided average fisheries consumption data varying from 6.5 g to 180 g (0.2-6.3 oz) when site-specific data were unavailable for risk assessment projects. West *et al.* (1989) found that Michigan sport fishermen consume an average of 19.2 g (0.7 oz) per day per person during a survey completed in 1989.

The U.S. annual per capita consumption of fresh and frozen commercial fish and shellfish has risen nearly 2.5 times since 1908 when data were first recorded. In 1993, the annual consumption rate

was 4.6 kg (10.2 lb), reflecting the second highest rate behind the 4.9 kg (10.7 lb) consumed per person in 1987. The average annual per capita consumption of fresh and frozen seafood for the past ten years was 4.5 kg (9.9 lb) (NMFS, 1994).

There is a dearth of information regarding the distribution of seafood from the source (i.e., fishermen) through the various outlets (e.g., wholesaler, retailer, etc.) to the consumer. The primary purpose of this task was to obtain these data.

3.0 METHODOLOGY

3.1 Introduction

The first subtask was to conduct a thorough review of existing information, extract and assemble appropriate available data and identify significant data gaps. The literature search consisted of a detailed review of pertinent literature and information available from federal, state and local agencies and research institutions. A comprehensive electronic search was conducted through BRS Information Technologies.

Data bases searched included Life Sciences; Zoological Record; National Environmental Referral Service; CAB - Economics, Development and Education; Agricultural Biology and Environmental Sciences; and Health Industry Research Reports.

Additionally, the manual literature search included the following:

- Data published in the open literature (i.e., journals, government agency reports, conference and meeting abstracts and dissertation abstracts);
- Data available from trade associations and commercial organizations; and
- Data available from quasi-public groups such as seafood promotion boards, tourist commissions, etc.

Because the data search phase of the study revealed significant gaps in the existing information needed to determine the seafood catch, consumption and use patterns in the GOM region, the need to design and conduct field surveys was evident. The second subtask, therefore, was to design and to conduct descriptive field surveys that would fill the recognized deficiencies in existing information.

3.2 Field Surveys

In order to conduct the necessary interviews, contact was made with Fisheries Information and Seafood Harvest Inquiry Enterprise (FISHIE). This group agreed to perform the surveys and provide personnel for training. FISHIE personnel were instructed how to present the surveys, shown the areas of concern and provided with other pertinent information regarding the project.

3.3 Population Surveyed

Intercept/personal interviews, mail questionnaires and telephone questionnaires were used to survey the following groups in the states of Louisiana and Texas: 1) commercial fishermen (i.e., shrimpers, crabbers, oystermen and finfishermen); 2) recreational fishermen; 3) processing plants and wholesalers; 4) restaurants; 5) retailers; and 6) oystermen. Commercial and recreational fishermen were surveyed primarily by intercept/personal interviews although some telephone surveys were made to recreational fishermen. Oystermen were interviewed by personal interview. Fish farms were excluded from the surveys because fish raised in these facilities have no potential exposure to produced water.

Processors and wholesalers were surveyed by personal interview and by mail. Lists of processors and wholesalers for Louisiana and Texas were provided by the Seafood Division of the Louisiana State Department of Natural Resources (LDNR) and the TPWD. Retailers were surveyed by site visits.

Restaurants were surveyed by mail. The Louisiana Restaurant Association and the Texas Restaurant Association provided assistance in accomplishing these surveys.

3.4 Survey Zones

The coastal areas of Louisiana and Texas were divided into nine zones. The most important criterion for the delineation of each zone was that there be at least one, possibly two, port cities within it. Parish and county lines were followed to delineate the zones. Fishermen responding to the intercept questionnaire were shown a zone chart (see **Appendix B**) to aid in their response. Telephone survey respondents were asked which port city they used during fishing excursions.

3.5 Types of Surveys Used

Table 3.1 lists the types of surveys used in this study for each of the six fishermen groups. Two of the six groups were surveyed by two modes. Secondary modes provided additional sample information in addition to providing a check on the sample information obtained with the primary mode. Secondary modes were not used for groups in which the sample size obtained met the statistical requirements for the study.

Table 3.1. Summary of survey types employed by fishermen type.

Group Surveyed	Primary Mode	Secondary Mode
Recreational Fishermen	Personal Interview	Telephone
Commercial Fishermen	Personal Interview	--
Oystermen	Personal Interview	--
Processing Plants/Wholesalers	Mail	Personal Interview
Retailers	Site Visit	--
Restaurants	Mail	--

Each primary survey mode was selected because it was the best and most efficient means of acquiring data from that particular group. For example, the intercept interview is the most labor intensive survey approach but it is accepted as the most effective for commercial and recreational fishermen (Dillman, 1978; Ary *et al.*, 1990; Guthrie *et al.*, 1990; U.S. Environmental Protection Agency (EPA), Office of Water, 1992; Pollock *et al.*, 1994). The intercept interviews were performed at docking areas used by either commercial or recreational fishermen, or both.

3.6 Development of Survey Forms

To meet the objectives of this study, seven questionnaires were developed. The same survey was used for both the personal interview and the telephone interview to survey recreational fishermen. The following sources were used to develop the survey forms: 1) input from Brookhaven National Laboratory; 2) input from scientists affiliated with Steimle & Associates, Louisiana State University and the University of New Orleans; and 3) a review of existing fish consumption surveys from the following studies:

- "Marine Recreational Fishery Statistics Survey, Atlantic and Gulf Coasts, 1990-1991," Current Fisheries Statistics Number 9204 compiled by NMFS (1992);
- "Survey of Louisiana Sport Fishermen--1990" by Kelso *et al.* (1991);
- "A Survey of Fish and Shellfish Consumption by Residents of the Greater New Orleans Area" by Anderson and Rice (1992); and
- "Michigan Sport Anglers Fish Consumption Survey. A Report to the Michigan Toxic Substance Control Commission" by West *et al.* (1989).

The questionnaires were constructed to minimize the time required to collect the information. The items on the surveys were written concisely so that they would be easily understood. Every effort was made to avoid bias that might predetermine a respondent's answer. The direct approach was employed to avoid questions that might elicit reactions of embarrassment, suspicion, and hostility in the respondents. Redundancy was built into the surveys to ensure internal consistency.

A panel of experts was used to check content validity and reliability of the surveys. Separate field testing for each of the different surveys was conducted. Modifications to each survey were made based on the results of the field testing. A team of FISHIE technicians was then trained as interviewers and a second field testing was conducted. The surveys were revised again based on the results of the second field testing. The surveys are presented in **Appendices C through I**.

3.7 Fishermen Survey (Recreational and Commercial)

3.7.1 Introduction

The primary mode for surveying both commercial and recreational fishermen was the intercept/personal interview. The telephone interview method was used as secondary mode for the recreational fishermen in Zone IX. Recreational fishermen were most often interviewed at docks and at sports club meetings.

The intercept and telephone surveys were designed to determine a profile of the fishermen, the mode of fishing, location of seafood catch, the species of seafood caught, the quantity of seafood catch, the distribution of seafood catch, the frequency of seafood served, personal consumption patterns, the cooking methods used to prepare the seafood and the zip code of the respondent's residence. Examples of the surveys are given in **Appendices C, D, and E**.

3.7.2 Fishermen Profile

Demographic information was obtained from respondents for use in the health risk assessment. The following questions/items were addressed:

- What category(s) of seafood was fished over the last three months?
- What type of fishing license(s) was held --in-state, out-of-state, both in-state and out-of-state, and/or federal?
- How many people in the household eat seafood?
- Demographic information about the people in the household, include gender and ages of adults, number of children under the age of 18, race and number of females between the ages of 14 and 50.

3.7.3 Mode of Fishing

In order to determine the frequency of fishing and the locations fished, the questionnaire included a section on the mode of fishing. Recreational fishermen were asked how many fishing trips were made in the last three months and the number of times these fishing trips were spent at the following situations/locations:

- Off pier, dock, jetty, breakwater, seawall, bridge and/or shorelines/beach/bank;
- Private boat in inshore waters;
- Private boat in offshore waters; and
- Charter boats/party boats.

Since commercial fishermen fish exclusively in boats, the fishing mode was not asked on that questionnaire.

3.7.4 Location of Seafood Catch

To determine the locations fished, respondents to the intercept survey were shown a map of the regions in Louisiana and Texas and asked to indicate which of the nine zones they fished in the last three months. For the telephone questionnaire used with recreational fishermen (secondary mode), respondents were asked to indicate the closest port to their fishing location. A list of Louisiana and Texas ports was provided.

For the data analysis the ports were coded to match the zones. To determine what section of the region(s) they fished, the respondents were asked to indicate the location in relation to the shoreline: inshore, 0 to 4.8 km (0 to 3 mi) offshore, 4.8 to 16 km (3 to 10 mi) offshore and greater than 16 km (10 mi) offshore. For these locations, approximate percentage of catch was requested.

To determine how close fishing was conducted near potential produced water discharges, fishermen were asked to estimate distance from oilfield structures i.e., within 300 m (1,000 ft), from 300 m to 0.8 km (1,000 ft to 0.5 mi), from 0.8 km to 1.6 km (0.5 to 1.0 mi) and greater than 1.6 km (1.0 mi).

3.7.5 Species Caught

The species selected for the surveys were the ones most commonly caught and of commercial value along the GOM coast according to NMFS landing data (Usie, pers. comm. 1994, NMFS). Shellfish species included shrimp, blue crab and oysters. Finfish species included amberjack, black drum, croaker, dolphin, flounder, grouper, kingfish, king mackerel, redfish (recreational only), red snapper, shark, sheepshead, Spanish mackerel, speckled trout, tuna and vermilion snapper.

An identification guide with fish illustrated in color was shown to the respondents to enable them to correctly identify species (**Appendix J**). The illustrations were either of the species in question or were representative of a larger group of related fish. For example, illustrations were shown of the amberjack, croaker, sheepshead, red snapper, speckled trout, Spanish mackerel, redfish and king mackerel. A common representative of the genus *Thunnus* was shown as tuna and a common representative of the family Carcharhinidae was shown to represent shark.

The special restriction on redfish in Louisiana and Texas was addressed by the project team. For commercial fishermen, the catch and resale of redfish is not allowed. Recreational fishermen have a restricted number of fish allowed and weight limitations (Louisiana Department of Wildlife and Fisheries [LDWF], Wildlife and Fisheries Commission, 1993; TPWD, 1993).

The recreational and commercial fishermen were asked to estimate the quantity of fish or shellfish caught in terms of either number of fish, pounds, dozens, sacks or other common units of measure.

3.7.6 Distribution Patterns

To determine the distribution of seafood catch through the population, both commercial and recreational fishermen were asked to estimate by species the percentage given away to others for consumption and the percentage kept for personal consumption. Commercial fishermen were asked to specify what percentage of the listed species were sold and to whom (i.e., wholesalers or processing plant, retailers or restaurants, consumers--friends/relatives and others). To ascertain whether there was agreement among the different groups surveyed, the questionnaires asked respondents a series of redundant questions (e.g., processors/wholesalers were asked about the sources of seafood; and commercial fishermen were asked about the destination of their catch).

3.7.7 Consumption Patterns

To identify the frequency of fish served and/or eaten by recreational and commercial fishermen, respondents were asked to estimate how many times on average per week that fish that they had caught during the last three months had been served/eaten in their household. Respondents were also asked to estimate how many days it had been since the last meal of fish was served in their household (i.e., for fish that they had caught during the past three months). The respondents were asked which species were eaten and which parts of the fish (i.e., meat and/or skin) were consumed.

To obtain further information on consumption patterns, the fishermen were asked to give all the cooking methods used to prepare the seafood they caught during the three months prior to the questionnaire interview. The cooking methods listed on the questionnaires included baked, barbecued, blackened, boiled/poached, broiled, fried, grilled, smoked, stew/soup and other.

3.7.8 Administration of the Fishermen Survey

Both recreational and commercial fishermen surveys were conducted during spring, summer and fall (May through November, 1993). A team of FISHIE technicians was trained to administer the intercept questionnaires designed by the project team. For the intercept surveys (i.e., the primary survey mode), recreational and commercial fishermen were interviewed at the docking areas. Recreational fishermen were also interviewed at sports clubs.

3.8 Commercial Oyster Fishermen Survey

3.8.1 Introduction

The intercept/personal interview was the primary mode used for both the Louisiana and Texas commercial oyster fishermen. A copy of this form is provided in **Appendix F**.

3.8.2 Fishermen Profile

The survey addressed the following demographics:

- How many acres of oyster grounds were under lease?
- What type of fishing license(s) was held: in-state, out-of-state, both in-state and out-of-state and federal?
- How many people in the household eat oysters?
- Demographic information about the people in the household, including gender and ages of adults, number of children under the age of 18, race and number of females between the ages of 14 and 50.

3.8.3 Location of Seafood Catch

To determine the location of the seafood catch, the same types of questions that were used on the recreational and commercial fishermen surveys were used on the oyster fishermen survey. The oystermen were asked to identify zones or regions across the Gulf Coast of Louisiana and Texas where they fished in the last three months. To determine whether the oystermen fished near areas of produced water discharges, the respondents were asked to indicate the fishing location in relation to offshore or inshore oilfield structures.

3.8.4 Distribution Patterns

To identify the distribution of oysters harvested, the fishermen were asked to estimate the percentage sold and to whom (i.e., wholesalers or processing plants, retailers or restaurants and other), the percentage given away to others and the percentage kept for personal consumption.

3.8.5 Consumption Patterns

The oystermen were asked to estimate the average number of times per week that oysters they harvested were served or eaten in their household. A second question sought information on how recently oysters had been consumed by the fishermen or by members of their household. The respondents were also asked what percentage of the oysters eaten by them and their family was eaten raw.

To determine the cooking methods used to prepare oysters that were harvested during the past three months, the fishermen were asked to check all methods that applied. The cooking methods listed were baked, barbecued, blackened, boiled/poached, broiled, fried, grilled, smoked, stew/soup and other.

3.8.6 Administration of the Oyster Fishermen Survey

The oystermen intercept survey was administered by the field technician during the period of April to May 1994 in Louisiana and Texas at docks or at the oysterman's residence.

3.9 Processing Plants and Wholesalers Survey

3.9.1 Introduction

The survey design for the processors and wholesalers concentrated on identifying the sources and quantities of seafood species, as well as the distribution patterns of the seafood handled. The primary mode used to survey processing plants and wholesalers in Louisiana and Texas was a mail survey. The secondary mode utilized was the personal interview method.

Only processing plants that process seafood for human consumption were included in the study database. The respondents were asked whether they operated as a processor only, as a wholesaler/dealer only or both as a processor and a wholesaler/dealer. The surveys were designed to gather information on the source, quantities and distribution of saltwater seafood sold during the time period of 1 January through 31 December 1992. This time period was selected because the respondents would have access to the monthly reports that they complete and submit to state agencies, therefore ensuring a higher rate of return. The questionnaires were administered from June through December 1993.

3.9.2 Sources of Seafood

To determine the sources of seafood to processing plants and wholesalers, the respondents were asked to estimate the percentage of saltwater finfish and shellfish (i.e., shrimp, oyster and blue crab) which were bought from the following sources:

- In-state commercial fishermen;
- In-state wholesalers/dealers;
- In-state processing plants;
- Out-of-state sources; and
- Out-of-country sources.

To further define the origin of seafood catch, the respondents were asked to identify the fishing zones and ports of their commercial fishermen suppliers. If commercial fishermen were suppliers of their seafood, the respondents were asked to estimate the relative percentages of the fishermen fishing inshore (i.e., inside the barrier islands) and offshore (i.e., outside the barrier islands). To determine whether the fishing sites were near oilfield structures, the respondents were also asked to estimate the percentage of suppliers who fished inshore and the percentage fishing near inshore oilfield structures. Similarly, they were asked the percentage of suppliers who fish offshore and the percentage fishing near offshore oilfield structures.

To determine the zone(s) where the seafood was obtained, the respondents were asked to check all Louisiana and Texas port(s) where their commercial fishermen suppliers were based. This catch

distribution information was also used to check for agreement among the different types of groups surveyed.

3.9.3 Quantity of Seafood Obtained

To obtain an estimate of the quantities of seafood handled by processing plants and wholesalers for the 1992 calendar year, the questionnaire was constructed to have the respondents specify the quantity in terms of product weight and units of measurements. This information was gathered for the following four categories:

- Saltwater fish (i.e., whole fish and fish parts);
- Shrimp (i.e., heads-on and heads-off);
- Oysters (i.e., oysters in shell and oyster meat); and
- Blue crabs (i.e., hard shell, soft shell and crab meat).

3.9.4 Distribution Patterns

To determine importation and exportation patterns of seafood handled, the survey addressed the distribution of the end product. The processing plants and wholesalers were asked to provide estimates of the percentages of the total shellfish and saltwater finfish that were sold to various outlets for all of the 1992 calendar year. The two major categories of outlets used on the survey were in-state and out-of-state. The in-state outlets were further subdivided into wholesalers/dealers, processing plants, restaurants/retailers and other outlets. The out-of-state category was not subdivided.

The distribution information was requested for the following shellfish: shrimp, oysters, hard shell blue crabs, soft shell blue crabs and blue crab meat. Individual estimates for distribution outlets for saltwater finfish were requested for the most popular species (i.e., black drum, flounder, red snapper, sheepshead, speckled trout, tuna and vermilion snapper). For the remaining and less popular species (i.e., amberjack, croaker, dolphin, grouper, king mackerel, shark, kingfish and Spanish mackerel), the respondents were asked whether they handled any of these species and what percentage of the total finfish handled these eight species combined represented.

3.9.5 Product Form of Seafood Sold

Information was sought on which parts and in what product form the seafood was processed and/or sold. The processing plants and wholesalers were asked to identify the most commonly sold form of seafood. For shellfish, the following forms were listed:

- Oysters--in shell, shucked, and prepared products (e.g., breaded/gumbo);
- Blue crabs--whole, meat, prepared products (e.g., stuffed); and
- Shrimp--heads-on, heads-off, shell on, peeled & undeveined, peeled & deveined, and prepared products (e.g., breaded/gumbo).

The product forms for the most popular finfish listed on the survey were as follows:

- Whole fish;
- Fillets with skin;
- Fillets without skin; and
- Other.

For other finfish sold, the respondents were asked to indicate the species and the form in which they were sold.

3.9.6 Administration of the Wholesalers/Processors Survey

Lists of processors and wholesalers were obtained from the LDWF, Seafood Division and from the TPWD. Questionnaires were mailed to all processors and wholesalers on the list who dealt primarily with saltwater species. The survey form is shown in **Appendix G**. An endorsement was obtained from the executive director of the Louisiana Seafood Marketing and Promotion Board. In memorandum form, it was addressed to Louisiana seafood processors and it requested their participation in the survey (see **Appendix K**).

3.10 Retailer Seafood Market Onsite Survey

3.10.1 Introduction

To ensure a higher rate of response, a team of FISHIE technicians was trained to conduct on-site surveys of retailer seafood markets in Louisiana and Texas. The survey team gathered data on the type of shellfish and saltwater finfish sold, the parts of the seafood sold and the types of prepared seafood sold.

3.10.2 Species Sold

The two main categories of seafood used for this survey were shellfish and finfish. The shellfish were listed as follows:

- Blue crabs--hard shell, soft shell, meat;
- Oysters--whole with shell, meat; and
- Shrimp--heads-on, heads-off, peeled.

For the list of commonly consumed saltwater finfish, the technicians were asked to indicate whether the fish was sold whole or as fillets and whether the whole fish or fillets were sold with or without skin. If the finfish was sold as parts, the surveyors were asked to specify the parts.

3.10.3 Distribution Patterns

To determine the distribution of the seafood, the surveyors were instructed to ask the retailers if they shipped seafood to other areas of the state and if they shipped out-of-state.

3.10.4 Cooking Methods

If either shellfish or saltwater finfish was sold cooked, the FISHIE technicians were instructed to indicate how the seafood was prepared. Space was provided on the survey form for inserting in the information.

3.10.5 Administration of the Retail Seafood Market Onsite Survey

Telephone directories were used to locate the retail seafood markets in the nine zones. Large supermarket chains were excluded because of their diversity of seafood sources which may or may not represent local sources. These onsite surveys were conducted at approximately the same time the fishermen intercept questionnaires were administered by the field technicians. The technicians recorded the name, address, and parish/county of the retailers. The date and time the market data was collected was also recorded. The survey is presented in **Appendix H**.

3.11 Restaurant Survey

3.11.1 Introduction

The restaurant surveys were designed not only to provide data on seafood consumption in restaurants, but to infer population consumption preferences in the areas of the restaurants. The respondents were asked to provide information concerning the source, quantities, and method of preparation of seafood served/sold by their restaurant for the time period of 1 January through 31 December 1992 (**Appendix I**).

3.11.2 Seafood Served

To determine the popularity of seafood dishes in the restaurants surveyed, respondents were asked approximately how many seafood dishes were served per week for the year 1992. Of the seafood dishes served, they were asked to estimate the percentage of shellfish, finfish and/or a combination of shellfish and finfish for the year 1992. The respondents were also asked to provide the average percentage of the different types of shellfish dishes and the different species of finfish served per week.

The survey was designed to determine whether restaurants served dishes that included seafood stock and what shellfish and/or finfish parts were used to prepare the stock. Data were gathered on the frequency of consumption of finfish parts by asking the respondents what parts of the fish (i.e., meat and/or skin) were consumed and what parts of the fish were used for stock.

3.11.3 Source of Seafood

The mail survey also focused on gathering data on the identification of the providers of seafood: commercial fishermen, wholesalers/processors, retailers and other. The respondents were asked to indicate what percentage of their seafood was imported from areas other than Louisiana or Texas for the year 1992.

3.11.4 Cooking Methods

To determine the most frequently used cooking methods for seafood served in the restaurants surveyed for the year 1992, the respondents were asked to check all of the following categories that were applicable to seafood available on their menu: baked, barbecued, blackened, boiled/poached, broiled, fried, grilled, smoked, stew/soup and other.

3.11.5 Administration of the Restaurant Survey

The Louisiana Restaurant Association allowed the project team to add the restaurant questionnaire to their newsletter that was mailed to approximately 1,500 association members. A short narrative describing the purpose of the project and a request to the membership to participate by completing the survey were included in the newsletter (**Appendix L**).

The Texas Restaurant Association provided mailing labels and a letter of endorsement (**Appendix K**) to be included with the survey. A bulk mailing procedure was used for the Texas Restaurant Survey. The Texas survey was sent to 1,500 restaurants that were located in the eastern portion of the state.

3.12 Sampling Plan

The sampling procedure was designed to provide a stratified random sample of the various subgroups of the population. The coastal area of Louisiana and Texas was divided into nine zones. Within each zone survey information was obtained from recreational fishermen, commercial fishermen, processors and wholesalers, retail seafood markets and restaurants concerning shellfish and finfish consumption and use.

The sample size objective was to have at least 30 responses for each subgroup within surveys. Sample sizes of 30 or more permit assumptions associated with the central limit theorem concerning the normality of sampling distributions employed in statistical analyses. The sample size objective of at least 30 was realized in all survey subgroups except the commercial finfishermen.

3.13 Statistical Procedures

The statistical procedures employed in the data quality analyses presented in Section 4, and in the interpretation of survey information presented in Section 5, are described in Sokal and Rohlf (1994).

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4.0 DATA QUALITY ANALYSIS

4.1 Introduction

The objective of the data quality analysis was to determine whether survey information concerning finfish species was consistent both within and among surveys. The data quality analysis focused only on finfish information from the ten surveys. This was a necessary choice because finfish species information was the only information common to all surveys. Nine data sets were constructed from the ten surveys; data from the two commercial fishermen surveys were pooled to increase sample size. The nine data sets are listed below with their respective sample sizes.

■ Louisiana Recreational Finfishermen	N = 513
■ Texas Recreational Finfishermen	N = 381
■ POOLED Commercial Fishermen	N = 28
- Louisiana Commercial Finfishermen	N = 23
- Texas Commercial Finfishermen	N = 5
■ Louisiana Wholesalers and Processors	N = 74
■ Texas Wholesalers and Processors	N = 22
■ Louisiana Retail Seafood Markets	N = 226
■ Texas Retail Seafood Markets	N = 115
■ Louisiana Restaurants	N = 79
■ Texas Restaurants	N = 75

The data quality analysis was performed in three parts, including;

- 1) An intrasurvey analysis of the Louisiana recreational finfishermen data set. The question addressed was whether fishermen reported similar species caught in the six different Louisiana geographic zones used in the survey. An analysis of variance was conducted on fishermen responses in the six zones to determine if they were significantly different;
- 2) An intrasurvey analysis of the Texas recreational finfishermen data set. The question addressed was whether fishermen reported similar species caught in the three different Texas geographic zones used in the survey. An analysis of variance was conducted on fishermen responses in the three zones to determine if they were significantly different; and
- 3) An intersurvey analysis that included all nine data sets indicated above. The question addressed was whether the information obtained in the nine surveys was consistent with respect to finfish species. An analysis of variance was conducted on the nine data sets to determine if they were significantly different with respect to the information on select finfish.

4.2 Conversion of Data to Proportions

In each survey, the data reported on finfish species were converted to proportions. This procedure was employed because it provided a common measure for comparisons among surveys where the reporting units were different. The procedure followed in calculating proportions for the several data sets is outlined below.

4.2.1 Louisiana and Texas Recreational Fishermen

Six geographic zones were used in the Louisiana survey. Three geographic zones were used in the Texas survey. Fishermen responses for finfish species were either 1) number of fish caught or 2) weight (e.g., lb) of fish caught. The two responses were mutually exclusive. For intrasurvey analyses, the responses were counted for each species within each zone and then divided by the total number of fishermen reporting catch within that zone. For the intersurvey analysis, the responses were counted for each species over all zones and then divided by the total number of fishermen reporting.

4.2.2 Louisiana and Texas Commercial Fishermen

Fishermen responses for finfish species were percent of catch sold to 1) wholesalers/processors or 2) restaurants/retailers. For the intersurvey analysis, the responses were counted for each species over all zones and then divided by the total number of fishermen reporting finfish information.

4.2.3 Louisiana and Texas Wholesalers and Processors

Wholesaler's and processor's responses for distribution of saltwater finfish species were as follows: 1) wholesalers/dealers; 2) processing plants; 3) restaurants/retailers; 4) other outlets; and 5) out-of-state. For the intersurvey analysis, the responses were counted for each species over all zones and then divided by the total number of survey responses.

4.2.4 Louisiana and Texas Retail Markets

Retailer's responses for distribution of finfish species were as follows: 1) whole fish with skin; 2) whole fish without skin; 3) fish fillets with skin; 4) fish fillets without skin; 5) parts; and 6) cooked. For the intersurvey analysis, the responses were counted for each species over all zones and then divided by the total number of surveys conducted.

4.2.5 Louisiana and Texas Restaurants

The restaurateurs' responses for distribution of finfish species were limited to the percentage of dishes served using particular species. For the intersurvey analysis, the responses for each species were counted and then divided by the total number of survey responses.

4.3 Analysis of Variance

4.3.1 Introduction

The randomized block design was used in both intrasurvey analyses and the intersurvey analysis. It was a two-way analysis of variance since an observation was categorized on the basis of two criteria -- the block (species) to which it belongs as well as the treatment group to which it belongs. There was, however, only a single factor of interest -- the treatment group, which was geographical zone in the intrasurvey analyses, and survey in the intersurvey analysis.

The objective in using the randomized block design was to isolate and remove from the error term the variation attributable to blocks, while assuring that treatment means were free of block effects.

The model equation:

$$x_{ij} = U + B_i + T_j + e_{ij}$$

$i = 1, 2, \dots, n; \quad j = 1, 2, \dots, k.$

In this model:

x_{ij} is a typical value from the overall population;
U is an unknown constant;
 B_i represents a block effect reflecting the fact that the experimental unit fell in the i th block;
 T_j represents a treatment effect, reflecting the fact that the experimental unit received the j th treatment; and
 e_{ij} is a residual ("error") component representing all sources of variation other than treatments and blocks.

Major assumptions of the model include:

- The e_{ij} are independently and normally distributed with mean 0 and common variance σ^2 ; and
- The block and treatment effects are additive.

4.3.2 Intrastudy Analysis -- Louisiana Recreational Fishermen

The objective of this analysis was to determine whether fishermen were reporting similar finfish species caught in the six geographic zones used in the survey.

Methodology

- Sample proportions were calculated for each species in each zone as indicated above;
- Sample proportions (p) were transformed with the transformation, $\Theta = \arcsin \sqrt{p}$; and
- Transformed proportions (zero) were approximately normally distributed with common variance.

Analysis of Variance

- Randomized block design. The block effect was species with interest focused on the zone effect;
- The hypothesis under test, H_0 : Proportions in the six zones are not significantly different; and
- Results: The nonsignificant zone effect ($p = 0.219$) indicates that one cannot reject the hypothesis under test. One can conclude that there are not significant differences among the six zones in species reported. Results of the analysis of variance for the Louisiana recreational fishermen survey are given in **Table 4.1**.

Table 4.1. Results of the analysis of variance for the Louisiana recreational fishermen survey.

Source	Sum-of-Square	DF	Mean-Square	F	P
Species	6.999	16	0.437	33.163	--
Zone	0.095	5	0.019	1.439	0.219
Error	1.055	80	0.013	--	--
Total	8.149	101	--	--	--

4.3.3 Intrsurvey Analysis -- Texas Recreational Fishermen

The objective of this analysis was to determine whether fishermen were reporting similar finfish species caught in the three geographic zones used in the survey.

Methodology

- Sample proportions were calculated for each species in each zone as indicated above;
- Sample proportions (p) were transformed with the transformation, $\Theta = \arcsin \sqrt{p}$; and
- Transformed proportions (zero) were approximately normally distributed with common variance.

Analysis of Variance

- Randomized block design. The block effect was species with interest focused on the zone effect;
- The hypothesis under test, H_0 : Proportions in the three zones are not significantly different; and
- Results: The nonsignificant zone effect ($p = 0.887$) indicates that one cannot reject the hypothesis under test. One can conclude that there are not significant differences among the three zones in species reported. Results of the analysis of variance for the Texas recreational fishermen survey are given in **Table 4.2**.

Table 4.2. Results of the analysis of variance for the Texas recreational fishermen survey.

Source	Sum-of-Square	DF	Mean-Square	F	P
Species	1.595	16	0.100	7.661	--
Zone	0.003	2	0.002	0.120	0.887
Error	0.416	32	0.013	--	--
Total	2.014	50	--	--	--

4.3.4 Intersurvey Analysis -- Nine Data Sets from Ten Surveys

The objective of this analysis was to determine whether there was consistent reporting concerning finfish species among the nine data sets derived from the ten surveys.

Methodology

- Sample proportions were calculated for each species in each survey as indicated above;
- Sample proportions for individual species were converted to a common base (i.e., normalized) by dividing the proportions for a given survey by the largest proportion in that survey. This procedure permitted direct comparison of species proportions from different surveys;
- Sample proportions (p) were transformed with the transformation, $\Theta = \arcsin \sqrt{p}$; and
- Transformed proportions (zero) were approximately normally distributed with common variance.

Analysis of Variance

- Randomized block design. The block effect was species. Some blocks were incomplete because some species (e.g., redfish) were not considered in all surveys. Interest is focused on the survey effect;
- The hypothesis under test, H_0 : Species proportions in the nine surveys are not significantly different; and
- Results: The nonsignificant survey effect ($p = 0.177$) indicates that one cannot reject the hypothesis under test. One can conclude that there are not significant differences among the nine data sets in species reported. Results of the analysis of variance for the intersurvey analysis are given in **Table 4.3**.

Table 4.3. Results of the analysis of variance for the intersurvey comparisons.

Source	Sum-of-Square	DF	Mean-Square	F	P
Species	13.353	16	0.835	9.807	--
Zone	0.997	8	0.125	1.465	0.177
Error	10.297	121	0.085	--	--
Total	24.647	145	--	--	--

Consistent reporting of finfish information among the several surveys suggests, for example, that finfish catches reported by commercial and recreational fishermen are representative of finfish availability in retail markets and restaurants.

5.0 RESULTS

5.1 Introduction

The responses to the various surveys were tabulated and graphed. Tabulated data are included in a separate data appendix (**Data Appendix 1**). The results of all survey responses are summarized below.

5.2 Louisiana Recreational Fishermen Survey

Of the 245,952 individuals holding saltwater sport fishing licenses issued by LDWF in 1993, 524 individuals (0.21%) were interviewed by FISHIE personnel.

5.2.1 Fishermen Profile

Recreational fishermen answered questions concerning their fishing and seafood consumption habits as well as personal information. Among the respondents, finfishing was the most popular form of recreational fishing (95%), followed by crabbing (2.5%), shrimping (2.4%) and oystering (0.4%) (**Figure 5.1**). Most recreational fishermen possessed an in-state fishing license (92%), while 2% held an out-of-state license and 6% retained both (**Figure 5.2**). The majority of respondents (92%) were white (**Figure 5.3**).

The respondents indicated the mean number of fish consumers per household was 3.3. The household consisted of a mean of 1.7 males and 1.7 females with the adults having a mean age of 37 years. The household also contained a mean of 1.8 children under the age of 18 and a mean of 1.4 females of child bearing years (i.e., 14-50 years).

Figure 5.1. Frequency distribution of category fished for Louisiana recreational fishermen.

Figure 5.2. Frequency distribution of types of fishing licenses for Louisiana recreational fishermen.

Figure 5.3. Frequency distribution of race for Louisiana recreational fishermen.

5.2.2 Mode of Fishing

The majority of the respondents fished from a private boat in inshore waters (62%) or a private boat in offshore waters (29%) (**Figure 5.4**). The mean number of fishing trips in the past three months was 10.5.

Figure 5.4. Frequency distribution of fishing mode for Louisiana recreational fishermen.

5.2.3 Location of Seafood Catch

In Louisiana, the most popular fishing area was Zone IV (21.4%), followed by Zone II (20.8%) and Zone III (18.4%) (**Figure 5.5**). The recreational fishermen primarily fished in the inshore areas (60%), although trips greater than 16 km (10 mi) from shore were also common (22%) (**Figure 5.6**). The frequency of trips within 300 m (1,000 ft) of an oilfield structure was 38%, although 36% of the trips were greater than 1.6 km (1.0 mi) from an oilfield structure (**Figure 5.7**).

Figure 5.5. Frequency distribution of fishing zones for Louisiana recreational fishermen.

Figure 5.6. Frequency distribution of fishing location for Louisiana recreational fishermen.

Figure 5.7. Frequency distribution of trips in proximity to oilfield structures for Louisiana recreational fishermen.

5.2.4 Species Caught and Distribution Patterns

The average number of shellfish and finfish by species caught among Louisiana recreational fishermen over the six-month period is given in **Figure 5.8**. Speckled trout and red snapper were the most common species caught. Estimates of the average weight of species caught are given in **Figure 5.9**.

Fishermen reported that they generally kept 80% or more of their catch for personal consumption. Only tuna and vermilion snapper, at 77% and 75%, respectively, were kept less often than the other species. The fish species most commonly saved included kingfish (94%), sheepshead (93%), black drum (93%), flounder (92%) and redfish (91%). Blue crabs and shrimp were kept for personal consumption 97% and 83% of the time, respectively (**Figure 5.10**).

Figure 5.8. Average number of shellfish and finfish species caught by Louisiana recreational fishermen over a six month period.

Figure 5.9. Estimates of average weight of shellfish and finfish species caught by Louisiana recreational fishermen over a six month period.

Figure 5.10. Average percentage of shellfish and finfish species kept for personal use by Louisiana recreational fishermen.

5.2.5 Consumption Patterns

Of the seafood caught and kept for personal consumption, fishermen reported that they served seafood a mean of 1.8 times per week in their household. The mean number of days since the last fish meal was 4.6 days.

The fishermen responded that they would rather consume the meat only from the fish species they caught and kept. With the exception of Spanish mackerel, redfish, flounder and croaker, fishermen ate the meat only in excess of 90% of the time (**Figure 5.11**).

The preferred method of cooking seafood among the respondents was fried (30%). Other popular methods included baked (17%), broiled (14%), grilled (14%) and barbecued (11%) (**Figure 5.12**).

Figure 5.11. Percentage of finfish parts consumed by Louisiana recreational fishermen.

Figure 5.12. Frequency distribution of cooking methods used by Louisiana recreational fishermen.

5.3 Texas Recreational Fishermen Survey

Of the approximately 600,000 individuals holding saltwater sport fishing licenses issued by TPWD in 1993, 381 individuals (0.06%) were interviewed by FISHIE personnel.

5.3.1 Fishermen Profile

Texas recreational fishermen were asked questions regarding their fishing and seafood consumption habits as well as personal information. The fishermen responded that they primarily recreationally pursued finfish (97%), compared to 1.8% for crabbing, 1.3% for shrimping and 0.3% for oystering (**Figure 5.13**). Respondents indicated they possess an in-state fishing license (93%) rather than an out-of-state license (6%) or both types of licenses (0.8%) (**Figure 5.14**). The majority of respondents (93%) were white (**Figure 5.15**).

The mean number of seafood consumers in each household was 2.9 with an average mean of 1.7 males, 1.5 females and one child under the age of 18 years. The mean age of the adults in the household was 34 years. The respondents reported an average of 1.5 females of child bearing years.

Figure 5.13. Frequency distribution of category fished for Texas recreational fishermen.

Figure 5.14. Frequency distribution of types of fishing licenses for Texas recreational fishermen.

Figure 5.15. Frequency distribution of race for Texas recreational fishermen.

5.3.2 Mode of Fishing

The majority of the respondents fished in a private boat in either inshore waters (45%) or offshore waters (42%) (**Figure 5.16**). The mean number of fishing trips in the past three months was 11.6.

Figure 5.16. Frequency distribution of fishing mode for Texas recreational fishermen.

5.3.3 Location of Seafood Catch

Zone VIII was the most popular area fished (37%) followed closely by Zone VII (36%) and Zone IX (21%). Zone VI, along the Louisiana coast, was fished 4.9% of the time, but the other Louisiana zones (i.e., Zones I-V) were fished less than 0.5% of the time (**Figure 5.17**). Fishermen reported they primarily fished inshore (48%), although fishing offshore greater than 16 km (10 mi) was also common (40%) (**Figure 5.18**). A large percentage of fishermen (33%) fished within 300 m (1,000 ft) of an oilfield structure, although slightly more (39%) fished more than 1.6 km (1.0 mi) such a structure (**Figure 5.19**).

Figure 5.17. Frequency distribution of fishing zones for Texas recreational fishermen.

Figure 5.18. Frequency distribution of fishing location for Texas recreational fishermen.

Figure 5.19. Frequency distribution of trips in proximity to oilfield structures for Texas recreational fishermen.

5.3.4 Species Caught and Distribution Patterns

The average number of shellfish and finfish caught by species among Texas recreational fishermen over the six-month period is given in **Figure 5.20**. The most common species caught was red snapper. Other species caught frequently included vermilion snapper, speckled trout and king mackerel. Estimates of the average weight of species caught are given in **Figure 5.21**.

Texas recreational fishermen were more likely to keep their catches of blue crabs (100%) and oysters (100%) than their catch of shrimp (62%). Finfish species caught were kept over 70% of the time. Flounder (92%) and redfish (90%) represented the most commonly retained fish, with speckled trout (88%), sheepshead (87%) and kingfish (87%) also representing coveted fish. Tuna (73%), king mackerel (76%), vermilion snapper (77%) and amberjack (77%) were less often kept by the respondents (**Figure 5.22**).

Figure 5.20. Average number of shellfish and finfish species caught by Texas recreational fishermen over a six month period.

Figure 5.21. Estimates of average weight of shellfish and finfish species caught by Texas recreational fishermen over a six month period.

Figure 5.22. Average percentage of shellfish and finfish species kept for personal use by Texas recreational fishermen.

5.3.5 Consumption Patterns

The fishermen reported that they preferred to consume the meat portions of the finfish rather than the meat and the skin. Vermilion snapper (95%) and kingfish (93%) were consumed primarily as meat only. Other finfish species were consumed as meat only 73% to 84% of the time (**Figure 5.23**). Species most commonly eaten as meat with skin were flounder (27%), sheepshead (26%) and croaker (25%).

The finfish caught during the previous three months were served an average of 1.6 times per week. The respondents indicated that the last fish meal served from the catch in the previous three months was, on average, 5.3 days. The preferred method of cooking the seafood was fried (31%) followed by grilled (19%), broiled (16%), baked (13%) and barbecued (9%). Remaining methods of preparation were all less than 5% (**Figure 5.24**).

Figure 5.23. Percentage of finfish parts consumed by Texas recreational fishermen.

Figure 5.24. Frequency distribution of cooking methods used by Texas recreational fishermen.

5.4 Louisiana and Texas Commercial Fishermen Survey

In 1993, commercial fishing licenses issued by LDWF were held by 33,036 individuals. This is inclusive only of shrimpers, crabbers, oystermen and finfishermen. Of these, 146 (0.44%) were interviewed for this survey.

Texas commercial finfishermen (i.e., shrimpers, crabbers, oystermen and finfishermen) numbered 4,336 in 1993, based on TPWD data. Of these, 72 (1.66%) were interviewed for this survey.

5.4.1 Fishermen Profile

The Louisiana and Texas commercial fishermen profiled in this survey fished shrimp (77%), finfish (12%), crabs (8%) and oysters (4%), as shown in **Figure 5.25**. Of the respondents, the majority were white (65%), while 13% were of oriental origin and 13% were of Hispanic origin (**Figure 5.26**).

Average makeup of the household by gender was 2.2 males and 2.1 females. Females of child bearing age averaged 1.9 individuals. Average number of children (i.e., under age 18) was 2.4. Average age of adults was 37 years.

Of those residing in the household, a mean number of four individuals were seafood consumers. Seafood was served in the household 2.6 times per week on average.

Figure 5.25. Frequency distribution of category fished for Louisiana and Texas commercial fishermen.

Figure 5.26. Frequency distribution of race for Louisiana and Texas commercial fishermen.

5.4.2 Location of Seafood Catch

The zones fished by Louisiana and Texas commercial fishermen is given in **Figure 5.27**. Zone III was the most fished area (20%) although the other zones were also frequently fished. The number of days fished in the last three months averaged 45.

Frequency of fishing location, which is shown in **Figure 5.28**, was largely inshore (39%) with frequent fishing also reported 4.8 to 16 km (3 to 10 mi) offshore (21%) and greater than 16 km (10 mi) offshore (28%). Of all fishing trips, frequency of trips in proximity to oilfield structures is shown in **Figure 5.29**. Of all trips, 33% were within 300 m (1,000 ft) of an oilfield structure. By comparison, 24% were between 300 m and 0.8 km (1,000 ft and 0.5 mi) of an oilfield structure, while 21% were between 0.8 and 1.6 km (0.5 and 1.0 mi) and 22% were more than 1.6 km (1.0 mi) from such a structure.

Figure 5.27. Frequency distribution of fishing zones for Louisiana and Texas commercial fishermen.

Figure 5.28. Frequency distribution of fishing location for Louisiana and Texas commercial fishermen.

Figure 5.29. Frequency distribution of trips in proximity to oilfield structures for Louisiana and Texas commercial fishermen.

5.4.3 Species Caught and Distribution Patterns

Distribution of seafood catch by commercial fishermen is given in **Figures 5.30** and **5.31** by average percentage. These data clearly show that the majority of seafood caught was sold to either wholesaler/processors or retailers/restaurants. The predominate species which were given away included blue crabs and speckled trout. The predominate species which were kept for personal consumption included blue crab, amberjack, croaker, flounder, king mackerel, shark and speckled trout.

Figure 5.30. Average percentage of shellfish distribution for Louisiana and Texas commercial fishermen.

Figure 5.31. Average percentage of finfish distribution for Louisiana and Texas commercial fishermen.

5.4.4 Consumption Patterns

The personal consumption patterns of Louisiana and Texas commercial fishermen are shown in **Figure 5.32**. Most of the species were consumed by the fishermen in the form of meat only, particularly croaker (100%), redfish (100%), red snapper (100%) and shark (100%). Only amberjack and king mackerel were eaten as meat and skin (100%).

The frequency distribution of the cooking methods used in the household for the seafood consumers is given in **Figure 5.33**. For the household consumption, fried was the most popular method of seafood preparation (29%), followed by boiled/poached (18%). The average number of days since the last seafood meal was prepared in the household was four.

Figure 5.32. Percentage of finfish parts consumed by Louisiana and Texas commercial fishermen.

Figure 5.33. Frequency distribution of cooking methods used by Louisiana and Texas commercial fishermen.

5.5 Louisiana Oyster Fishermen Survey

The total number of licenses issued to resident oystermen in 1993 by LDWF was 1,027. Seventeen interviews (1.66%) were conducted by FISHIE in spring 1994.

5.5.1 Fishermen Profile

The Louisiana oyster fisherman profiled in this survey leased an average of 1,164 acres of water bottom from the state for oyster culture. Ninety-one percent of respondents were white with the remaining 9% of Hispanic origin (**Figure 5.34**). There was insufficient response to determine the type of fishing license held (e.g, in-state, out-of-state, etc.).

Average makeup of the household by gender was 1.6 males and 1.9 females. Females of child bearing age averaged 2.4 individuals. Average number of children (under age 18) was three. Average age of adults was 47 years. Of those residing in the household, a mean number of 3.1 individuals were oyster consumers.

Figure 5.34. Frequency distribution of race for Louisiana oystermen.

5.5.2 Location of Seafood Catch

The Louisiana oystermen surveyed fished primarily in Zone I although there was some fishing conducted in Zones III and IV (**Figure 5.35**). The number of days fished in the last three months averaged 37. Frequency of fishing location, which is shown in **Figure 5.36**, was largely inshore (94%) with some fishing reported 4.8 to 16 km (3 to 10 mi) offshore. Frequency of trips in proximity to oilfield structures is shown in **Figure 5.37**. Approximately 60% of all trips were within 0.8 km (0.5 mi) of an oilfield structure.

Figure 5.35. Frequency distribution of fishing zones used by Louisiana oystermen.

Figure 5.36. Frequency distribution of fishing location for Louisiana oystermen.

Figure 5.37. Frequency distribution of trips in proximity to oilfield structures for Louisiana oystermen.

5.5.3 Distribution Patterns

Oystermen reported that 99% of all oysters fished during the previous 90 days were sold to wholesaler/processors and 1% were retained for household consumption.

5.5.4 Consumption Patterns

Oysters were served in the household three times per week on average. The frequency distribution of the cooking methods used in the household for the oyster consumers is given in **Figure 5.38**. For household consumption, fried was the most popular method of oyster preparation (30%), followed by raw (28%) and stewed or in soups (26%). For the oysterman himself, the most popular method of preparation of oysters was raw (49%). The average number of days since the last oyster meal was prepared in the household was 7.6 days.

Figure 5.38. Frequency distribution of methods of cooking oysters for consumption by Louisiana oystermen.

5.6 Texas Oyster Fishermen Survey

Eleven licenses were issued to oystermen by TPWD in 1993/1994. Sixteen oystermen interviews were conducted by FISHIE.

5.6.1 Fishermen Profile

The number of acres of water bottom leased from the state by the Texas oyster fishermen profiled in this study could not be determined due to insufficient responses. One hundred percent of the oyster fishermen interviewed held in-state fishing licenses. The racial mix of Texas oystermen surveyed is given in **Figure 5.39**. Sixty percent of respondents were of Hispanic origin with the remaining respondents being equally divided among black, white and Native American (13% each).

Average makeup of the household by gender was 1.6 males and 1.7 females. Females of child bearing age averaged 2.2 individuals. Average number of children (under age 18) was 1.6. Average age of adults was 32 years. Of those residing in the household, a mean number of 2.9 individuals are oyster consumers.

Figure 5.39. Frequency distribution of race for Texas oystermen.

5.6.2 Location of Seafood Catch

The Texas oystermen surveyed fished primarily in Zone VII, although there was some fishing conducted in Zones II and III (**Figure 5.40**). The number of days fished in the last three months averaged 14. The frequency of fishing location was exclusively inshore. For those trips during which oysters were fished, the frequency of trips in proximity to oilfield structures is shown in **Figure 5.41** for all respondents. For all trips evaluated, 58% were beyond 1.6 km (1.0 mi) from an oilfield structure while 37% were between 0.8 and 1.6 km (0.5 and 1.0 mi) from such a structure.

Figure 5.40. Frequency distribution of fishing zones used by Texas oystermen.

Figure 5.41. Frequency distribution of trips in proximity to oilfield structures for Texas oystermen.

5.6.3 Distribution Patterns

Oystermen reported that 100% of all oysters fished during the previous 90 days were sold to wholesaler/processors.

5.6.4 Consumption Patterns

Oysters were served in the household 2.3 times per week on average. For the household consumption, fried was the most popular method of oyster preparation (36%), followed by raw (31%). For the oysterman himself, the most popular method of preparation of oysters was raw (42%). The average number of days since the last oyster meal was prepared in the household was 4.4 days. The frequency distribution of cooking methods used in the household for the oyster consumers is given in **Figure 5.42**.

Figure 5.42. Frequency distribution of methods of cooking oysters for consumption by Texas oystermen.

5.7 Louisiana Wholesalers and Processors Survey

A total of 300 wholesalers/processors dealing in saltwater species were operational in Louisiana, according to numbers obtained from NMFS. Questionnaires were sent to all of these wholesalers/processors and 74 (24.7%) responses were returned.

5.7.1 Sources of Saltwater Seafood

Among respondents to the Louisiana Wholesalers and Processors Survey, 5.3% act as a processor only, 52% operate as a wholesaler/dealer only and 42% function as both wholesalers and processors. Their typical source of seafood was in-state commercial fisherman with generally greater than 33% of the finfish, crabs, oysters and shrimp received from this group. Approximately 25% of blue crabs and 10% of finfish were obtained from other in-state processors. Approximately 6% of shrimp and 19% of finfish were obtained from out-of-state sources. Imports from other countries provided less than 6% of the seafood (**Figure 5.43**).

The wholesalers/processors indicated that their sources of seafood fished in both inshore and offshore locations. Of those sources fishing inshore, 56% of them fished near an oilfield structure. Of those sources fishing offshore, 72% fished near an oilfield structure (**Figure 5.44**). Fishing Zone IV provided nearly 28% of the seafood received at the wholesaler/processor, with Zone III contributing 22% and Zone V supplying 16%. The remaining zones in Louisiana (i.e., Zones I and VI) and all zones off Texas (i.e., Zones VII-IX) each furnished less than 7% of the catch (**Figure 5.45**).

Figure 5.43. Frequency distribution of sources of seafood for Louisiana wholesalers/processors.

Figure 5.44. Average percent of suppliers' fishing location for Louisiana wholesalers/processors.

Figure 5.45. Frequency distribution of suppliers' fishing zones for Louisiana wholesalers/processors.

5.7.2 Quantity of Seafood Obtained

The average quantity of saltwater finfish received by the wholesalers/processors was 307,600 kg (678,141 lb) of whole fish and 31,720 kg (69,930 lb) of fish parts. Shrimp averaged 605,624 kg (1,335,173 lb) for heads-on and 173,173 kg (381,782 lb) for heads-off. Oysters in the shell accounted for 486,150 sacks, representing 11,470 kg (25,287 lb) of meat or 9,958 liters (2,631 gal). Average weights or quantities for blue crabs included 224,400 kg (494,717 lb) for hard shell, 4,412 doz for soft shell, and 30,054 kg (66,257 lb) for blue crab meat. Thirty percent of shrimp and 53% of soft shell blue crabs were sold to in-state retailers and restaurants.

5.7.3 Distribution Patterns

The Louisiana wholesalers/processors sent less than 33% of their shellfish out-of-state. Thirty-two percent of hard shell blue crabs and 30% of the blue crab meat were shipped out-of-state. Twenty-seven percent of shrimp were transported out-of-state. Eleven percent of hard shell blue crabs and 29% of oysters were sold to wholesalers/dealers. Any small percentages of shellfish were transported to processing plants (**Figure 5.46**).

Twenty-five percent of black drum, flounder, red snapper and speckled trout and 40% of vermilion snapper were sold to out-of-state sources. Fifty percent of red snapper, 40% of tuna and 40% of vermilion snapper were sold to other in-state wholesalers/dealers. Forty-four percent of flounder, 42% of speckled trout, 33% of black drum and 31% of sheepshead were sold to in-state retailers/restaurants. Few species of finfish were sold to in-state processing plants (**Figure 5.47**).

Figure 5.46. Frequency distribution of shellfish destinations from Louisiana wholesalers/processors.

Figure 5.47. Frequency distribution of saltwater finfish destinations from Louisiana wholesalers/processors.

5.7.4 Product Form of Seafood Sold

The seafood was sold in a variety of forms. Oysters were most often sold shucked (55%), in the shell (39%) or prepared (7%). Blue crabs were sold whole (47%), as meat (44%) and prepared (8%). Shrimp were sold in the form of heads-on (32%), heads-off (30%), peeled and undeveined (21%), peeled and deveined (12%) and prepared (such as breaded for frying) (5%) (**Figure 5.48**). Over 55% of finfish species were sold whole. Flounder and tuna, at 79% and 71%, respectively, were commonly sold whole. Speckled trout were marketed as whole fish 56% of the time, filleted with no skin 31% of the time, filleted but with skin 6% of the time, or marketed in some other form 6% of the time. Approximately 20% to 30% each of sheepshead, black drum and red snapper were also sold filleted with no skin (**Figure 5.49**).

Figure 5.48. Frequency distribution of shellfish product sold by Louisiana wholesalers/processors.

Figure 5.49. Frequency distribution of finfish product sold by Louisiana wholesalers/processors.

5.8 Texas Wholesalers and Processors Survey

The TPWD reported 420 wholesalers/processors dealing in saltwater species in Texas in 1993. Questionnaires were sent to all of these wholesalers/processors and 21 (5.0%) completed surveys were received.

5.8.1 Sources of Saltwater Seafood

Among respondents to the Texas wholesalers and processors survey, 6% act as a processor only, 53% operate as a wholesaler/dealer only and 41% function as both wholesalers and processors. Their typical source of seafood was in-state commercial fisherman and in-state wholesalers/dealers with generally greater than 25% of the finfish, crabs, oysters and shrimp received from these groups. Approximately 25% of blue crabs and 10% of finfish were obtained from other in-state processors. Approximately 6% of shrimp and 19% of finfish were obtained from out-of-state sources. Imports from other countries provided 13% of the shrimp and 19% of the finfish (**Figure 5.50**).

The wholesalers/processors indicated that their sources of seafood fished in both inshore and offshore locations. Of those sources fishing inshore, 30% of them fished near an oilfield structure. Of those sources fishing offshore, 54% fished near an oilfield structure (**Figure 5.51**). Fishing Zone VII provided 34% of the seafood received at the wholesaler/processor, with Zone VIII contributing 31% and Zone IX supplying 21%. The zones in Louisiana each furnished less than 7% of the catch (**Figure 5.52**).

Figure 5.50. Frequency distribution of sources of seafood for Texas wholesalers/processors.

Figure 5.51. Average percentage of suppliers' fishing location for Texas wholesalers/processors.

Figure 5.52. Frequency distribution of suppliers' fishing zones for Texas wholesalers/processors.

5.8.2 Quantity of Seafood Obtained

The average quantity of saltwater finfish received by the wholesalers/processors was 24,479 kg (53,967 lb) of whole fish and 14,742 kg (32,500 lb) of fish parts. Shrimp amounts averaged 105,746 kg (233,130 lb) for heads-on and 316,001 kg (696,663 lb) of heads-off. Oyster and blue crab responses were limited and were provided with inconsistent units of measure.

5.8.3 Distribution Patterns

The Texas wholesalers/processors sent less than 30% of their shellfish out-of-state. No hard shell blue crabs and blue crab meat were shipped out-of-state. About 21% percent of shrimp and 29% of oysters were transported out-of-state. Approximately 28% of shrimp were sold to wholesalers/dealers. Less than 18% of shellfish were transported to processing plants (**Figure 5.53**).

Nine percent of flounder and red snapper and 25% of tuna were sold to out-of-state sources. Thirty-eight percent of black drum, 27% of red snapper and 18% of flounder were sold to other in-state wholesalers/dealers. One hundred percent of speckled trout, 80% of sheepshead, 75% of tuna and 67% of vermilion snapper were sold to in-state retailers/restaurants. No species of finfish were sold to in-state processing plants (**Figure 5.54**).

Figure 5.53. Frequency distribution of shellfish destinations from Texas wholesalers/processors.

Figure 5.54. Frequency distribution of saltwater finfish destinations from Texas wholesalers/processors.

5.8.4 Product Form of Seafood Sold

The seafood was sold in a variety of forms. Oysters were most often sold in the shell (54%), shucked (39%) or prepared (8%). Blue crabs were sold whole (50%), as meat (33%) and prepared (17%). Shrimp were sold in the form of heads-on (33%), heads-off (38%), peeled and undeveined (10%), peeled and deveined (15%) and prepared (5%) (**Figure 5.55**). Over 60% of finfish species were typically sold whole. Sheepshead (80%), speckled trout (75%), flounder (75%) and vermilion snapper (74%) were commonly sold whole. Red snapper were marketed as whole fish (71%), filleted but with skin (14%) and filleted with no skin (14%). About 38% of black drum and 33% of tuna were sold filleted with no skin (**Figure 5.56**).

Figure 5.55. Frequency distribution of shellfish product sold by Texas wholesalers/processors.

Figure 5.56. Frequency distribution of finfish product sold by Texas wholesalers/processors.

5.9 Louisiana Retail Seafood Market Survey

FISHIE personnel surveyed products at 226 retail outlets in or near population centers in coastal Louisiana parishes.

5.9.1 Species Sold and Cooking Methods

Data for the Louisiana Retail Seafood Market Survey was collected for both shellfish and finfish species. The types of shellfish were categorized into cooked and uncooked. Finfish were categorized into whole or filleted including skinned or unskinned versions, along with fish parts (i.e., heads, fins, roe, etc.) and cooked fish.

Shellfish were typically sold uncooked. Blue crabs, oysters and shrimp were sold in the uncooked state more than 50% of the time. Hard shell blue crabs had the lowest percentage of meats sold uncooked at 52%. Shelled oysters were sold uncooked (100%) as were soft shell blue crabs (94%) and headed shrimp (94%), as reflected in **Figure 5.57**.

Finfish were sold as whole fish (gutted) and fillets, and may or may not have head and skin removed. Croaker, king mackerel, sheepshead, flounder and black drum were sold as whole fish with the skin left on more than 60% of the time. A majority of grouper (50%) and shark (56%) were usually sold as fillets with no skin. None of the markets surveyed sold fish parts. Only flounder (1.2%), speckled trout (3%) and some miscellaneous species of fish (19%) were sold in a cooked state (**Figure 5.58**).

Figure 5.57. Frequency distribution of shellfish product sold by Louisiana retailers.

Figure 5.58. Frequency distribution of finfish product sold by Louisiana retailers.

5.9.2 Distribution Patterns

Shipping of seafood products to other parts of the state occurred in 33% of the markets. About 23% reported that they shipped seafood out-of-state.

5.10 Texas Retail Seafood Market Survey

FISHIE personnel surveyed products at 115 seafood retail outlets in population centers in coastal Texas counties.

5.10.1 Species Sold and Cooking Methods

Results of the Texas retail seafood market survey for shellfish are given in **Figure 5.59**. This figure shows the relative abundance of prepared and unprepared shellfish available in retail markets. Most shellfish were available unprepared with peeled shrimp having the largest frequency of occurrence (68%). About 36% of crab meat and 35% of oyster meats were available prepared.

Figure 5.60 details the form in which the finfish were available in retail markets. All of the croaker and kingfish available in the market were whole with skin. Over 50% of the total available black drum, flounder, grouper, red snapper, sheepshead, and Spanish mackerel were sold whole with skin. Only sheepshead were available whole with no skin and only 2% were offered in this form.

Of those fish available filleted, most were available without skin. Of the amberjack available, 75% were filleted without skin. One hundred percent of dolphin, 55% of shark, 29% of Spanish mackerel, 29% of tuna and 25% of grouper were available in this form. Less than 15% each of black drum, flounder, red snapper, sheepshead and speckled trout were available filleted with no skin.

Approximately 21% of tuna, 18% of shark, 16% of red snapper, 15% of speckled trout and 14% of Spanish mackerel were available as fillets with skin. Less than 5% each of black drum, flounder and sheepshead were available in this form.

Both tuna (15%) and grouper (13%) were available in parts (e.g., steaks). Most finfish were available unprepared although some of the speckled trout (24%), black drum (11%), flounder (5%), red snapper (4%) and sheepshead (4%) were available prepared.

Figure 5.59. Frequency distribution of shellfish product sold by Texas retailers.

Figure 5.60. Frequency distribution of finfish product sold by Texas retailers.

5.10.2 Distribution Patterns

Shipping of seafood products to other parts of the state occurred in 18% of the markets. About 8% of the respondents reported that they shipped seafood out-of-state.

5.11 Louisiana Restaurant Survey

Fifteen hundred survey questionnaires were sent to members of the Louisiana Restaurant Association which served seafood. Seventy-nine (5.3%) were returned complete.

5.11.1 Seafood Served

The results from the Louisiana Restaurant Mail Survey showed that an average of 1,096 seafood dishes were served each week in 1992. Of the dishes served during this period, 48% consisted of shellfish, 46% involved finfish and 29% contained both shellfish and finfish (**Figure 5.61**).

Shrimp was the most popular shellfish dish comprising 52% of the average weekly shellfish dishes. Hard shell blue crab meat comprised 22% of shellfish dishes. Soft shell blue crabs (13%) and oysters on the half shell (15%) were the least common shellfish dishes served weekly (**Figure 5.62**).

The most common finfish species served were tuna (29%), speckled trout (25%) and red snapper (21%). Spanish mackerel and kingfish were not served by any of the responding restaurants (**Figure 5.63**).

Many restaurants used seafood stock in the preparation of their meals. Shellfish stock was used in an average of 335 meals per week in 1992, while finfish stock was used in an average of 272 meals per week during that same time period. Both shellfish and finfish stocks were combined in an average of 164 meals per week (**Figure 5.64**). Shrimp were the most common shellfish used to prepare stock (56%) followed by blue crab (28%) and oysters (16%) (**Figure 5.65**).

Figure 5.61. Average percentage of types of seafood dishes served in 1992 by Louisiana restaurants.

Figure 5.62. Average percentage of shellfish dishes served per week in 1992 by Louisiana restaurants.

Figure 5.63. Average percentage of finfish dishes served per week in 1992 by Louisiana restaurants.

Figure 5.64. Average number of meals served in 1992 by Louisiana restaurants which included seafood stock.

Figure 5.65. Frequency distribution of shellfish used in stock by Louisiana restaurants in 1992.

5.11.2 Sources of Seafood

About 31% of seafood was imported from out-of-state sources. Wholesalers/processors provided about 86% of the seafood served at restaurants. Commercial fishermen and retailers supplied about 36% of seafood products, while other sources contributed 12% (**Figure 5.66**).

Figure 5.66. Average percentage of source of seafood for Louisiana restaurants in 1992.

5.11.3 Cooking Methods

Over 60% of finfish species were served as meat only. King mackerel was usually served with skin on (**Figure 5.67**). In the preparation of fish stock, king mackerel and sheepshead were used 40% and 25% of the time, respectively (**Figure 5.68**).

The most common seafood cooking methods were fried (18%), grilled (15%), broiled (15%) and baked (13%). Smoking and barbecuing, with each representing about 4%, were the least popular methods for cooking seafood (**Figure 5.69**).

Figure 5.67. Percentage of finfish parts served in 1992 by Louisiana restaurants.

Figure 5.68. Percentage of finfish species used in stock by Louisiana restaurants in 1992.

Figure 5.69. Frequency distribution of cooking methods of seafood served in Louisiana restaurants in 1992.

5.12 Texas Restaurant Survey

Fifteen hundred survey questionnaires were sent to members of the Texas Restaurant Association who serve seafood. Seventy-five surveys (5.0%) were returned complete.

5.12.1 Seafood Served

The results from the Texas Restaurant Mail Survey showed that an average number of 678 seafood dishes were served per week in 1992. Of the dishes served during this period, 55% consisted of shellfish, 45% involved finfish and 36% contained both shellfish and finfish (**Figure 5.70**).

Shrimp was the most popular shellfish dish comprising 74% of the average weekly shellfish dishes. Oyster meats and oysters on the half shell comprised 22% and 19%, respectively, of shellfish dishes. Hard shell blue crab meats (14%) and soft shell blue crabs (6%) were the least common shellfish dishes served weekly (**Figure 5.71**).

The most common finfish species served were red snapper (31%), speckled trout (26%) and flounder (23%). Vermilion snapper was not served by any of the responding restaurants (**Figure 5.72**).

Many restaurants used seafood stock in the preparation of their meals. Shellfish stock was used in an average of 132 meals per week in 1992, while finfish stock was used in an average of 230 meals per week during that same time period. Both shellfish and finfish stocks were combined in an average of 197 meals per week (**Figure 5.73**). Shrimp were the most common shellfish used to prepare stock (69%) followed by blue crab (19%) and oysters (12%) (**Figure 5.74**).

Figure 5.70. Average percentage of types of seafood dishes served in 1992 by Texas restaurants.

Figure 5.71. Average percentage of shellfish dishes served per week in 1992 by Texas restaurants.

Figure 5.72. Average percentage of finfish dishes served per week in 1992 by Texas restaurants.

Figure 5.73. Average number of meals served in 1992 by Texas restaurants which included seafood stock.

Figure 5.74. Frequency distribution of shellfish used in stock by Texas restaurants in 1992.

5.12.2 Sources of Seafood

Texas restaurant survey respondents indicated that they import nearly twice as much seafood as the Louisiana restaurant survey respondents, 62% versus 31%, respectively. Wholesalers/processors provided about 91% of the seafood served at restaurants. Other seafood sources were retailers (50%), commercial fishermen (40%) and other sources (15%) (**Figure 5.75**).

Figure 5.75. Average percentage of source of seafood for Texas restaurants in 1992.

5.12.3 Cooking Methods

Over 58% of finfish species consumed were served as meat only. Flounder (31%), redfish (27%), speckled trout (26%) and red snapper (24%) were usually served with skin on (**Figure 5.76**). In the preparation of fish stock red snapper, amberjack and dolphin were each used about 15% of the time (**Figure 5.77**).

The most common seafood cooking methods were fried (22%), grilled (14%), broiled (12%), stew/soup (11%), boiled/poached (11%) and baked (11%) (**Figure 5.78**).

Figure 5.76. Percentage of finfish parts served in 1992 by Texas restaurants.

Figure 5.77. Percentage of finfish species used in stock by Texas restaurants in 1992.

Figure 5.78. Frequency distribution of cooking methods of seafood served in Texas restaurants in 1992.

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6.0 DISCUSSION

Data were presented previously which summarized survey results pertaining to various Louisiana and Texas fisheries (i.e., recreational, commercial, oyster) and the distribution and consumption patterns for fish and invertebrate species caught (i.e., fish wholesalers and processors, retail seafood markets, restaurants). The following section discusses the trends and findings evident in the survey data.

6.1 Intrasyrvey Comparisons

6.1.1 Recreational Fishermen

Recreational fishermen from Louisiana and Texas were interviewed at several sites including sporting club meetings, boat docks, fishing tournament weigh-in locations as well as over the telephone. Most respondents reported they finfish rather than shrimp, crab or harvest oysters. All of the fishermen surveyed fished from a boat in inshore waters rather than onshore fishermen who would not be able to fish in proximity to oilfield structures.

Recreational fishermen reported they preferred to keep their catch instead of giving it away. The respondents indicated that they infrequently served their catch in their household, but when they did, it was usually filleted, skinned and fried.

Louisiana recreational fishermen reported fishing in close proximity to oilfield structures more often than the Texas respondents. This may be due to the large number of well canals and oilfield structures in the marshes and bayous of south Louisiana where many of the fishing trips occurred.

6.1.2 Commercial Fishermen

Commercial fishermen depend primarily on their catch for their livelihood. Commercial shrimpers comprised 77% of the commercial fishermen interviewed. Shrimpers were more accessible for survey since their hours of operating were more predictable than the other types of commercial fishermen. Shrimp unloading locations were more numerous and easier to access.

Commercial fishermen, although more likely to fish inshore waters, were more likely to fish near oilfield structures which they believed attracted organisms. The fishermen reported that they consume seafood on a regular basis in their household, but sell the vast majority of their catch to wholesalers/processors or restaurants/retailers.

6.1.3 Oyster Fishermen

A number of similarities were observed between the Louisiana and Texas oyster fishermen. The average make up of the household by gender for both states was similar. The results also show that oystermen prefer to eat their oysters raw, although their household inhabitants preferred their oysters fried. Oysters are a favorite food of oystermen from both states being served two to three times per week.

Some differences between the oystermen from the two states are noteworthy. In Louisiana, 91% of the respondents were white reflecting the heritage of the oyster fishermen who settled in Louisiana. Texas respondents were primarily Hispanic. Due to Louisiana's myriad bayous and well canals, features not common in Texas, the Louisiana oyster fishermen are usually in closer proximity, less than 0.8 km (0.5 mi), to oilfield structures than their Texas counterparts.

6.1.4 Wholesalers and Processors

Good response was obtained from the wholesalers/processors for both Louisiana and Texas. Their primary source of seafood was from in-state commercial fishermen with very little seafood coming in from other countries. They indicated that their offshore suppliers fish in proximity to oilfield structures a large percentage of their time. Finfish species associated with oilfield structures and wellheads would be more frequently caught under these conditions.

Louisiana wholesalers/processors handle significantly more finfish and shellfish than their Texas counterparts. Louisiana respondents handled an average of 12 times more finfish and almost six times more shrimp. This is in agreement with the landings data which show Louisiana landings nearly twice as great as Texas landings.

6.1.5 Retail Seafood Markets

Retail seafood outlets in Louisiana and Texas primarily offer and serve their seafood in similar forms. Outlets typically have uncooked portions of shellfish and finfish. Among prepared seafood, Louisiana retailers were more likely to offer prepared hard shell blue crabs, while Texas retailers commonly prepared their peeled and headed shrimp. The finfish species were well represented by both states' retailers, although Texas outlets offered more finfish species in parts, typically "steaks" or cross-sectional pieces of fish meat. Louisiana retailers are more likely to ship fresh and prepared seafood to other parts of the state and out-of-state than the Texas retailers.

6.1.6 Restaurants

Respondents to the restaurant survey for both Louisiana and Texas reported similar trends and tendencies in seafood preparation and service. For each state shellfish dishes were more popular than finfish or a combination of the two. Shrimp was the most common ingredient in those dishes. Speckled trout and red snapper were the finfish species most often served.

Restaurants in Louisiana and Texas depend on wholesalers/processors to provide them with their seafood. More than 60% of the Texas restaurant respondents depend on out-of-state sources for their seafood. This is a very large number in view of the fact that Louisiana was not considered an out-of-state source for purposes of this survey. Since Louisiana has the largest fisheries landings for the continental U.S. and is adjacent to Texas, it is not surprising that Texas would import some of Louisiana's seafood.

6.1.7 Statistical Findings

Data quality analyses were conducted to determine whether survey responses concerning finfish species were consistent both within and among surveys. The analyses focused only on finfish information from the ten surveys. This was a necessary choice because finfish species information was the only

information common to all ten surveys. The results of analysis of variance presented in Section 4 indicate consistency of reporting both within and among surveys.

6.2 Intersurvey Comparisons

6.2.1 Location of Seafood Catch

The data indicate that the recreational and commercial fishermen (excluding commercial oystermen) for both Louisiana and Texas choose to fish near an oilfield structure on approximately 30% of their fishing trips. Louisiana and Texas commercial fishermen and Louisiana recreational fishermen more commonly fish near oilfield structures than Texas recreational fishermen. This may be attributable to location and accessibility of the Louisiana oilfield structures and to the life cycle and migratory habits of the finfish.

Louisiana oyster fishermen commonly developed their beds in proximity to the oilfield structures in contrast to their Texas counterparts. This may be attributable to the numerous well canals and oilfield structures along the major bayous and waterways of south Louisiana. In Texas, Galveston Bay is the most prolific oyster-producing location.

The Texas and Louisiana wholesalers/processors report that significant amounts of their seafood comes from waters near oilfield structures, particularly from suppliers who fish offshore. Louisiana wholesalers/processors report their suppliers fishing near oilfield structures because of a large number of oilfield structures along the Louisiana coast.

6.2.2 Sources of Seafood

Information obtained from the Louisiana and Texas wholesalers/processors indicates that a large amount of the seafood was supplied by in-state commercial fishermen and other in-state wholesalers/processors. For the purpose of this study, Louisiana and Texas were not considered out-of-state in either states' survey. Therefore, large amounts of seafood from the neighboring state could be received by a wholesaler/processor and significantly affect the reported source of seafood. The data show only a small percentage of the seafood comes from out-of-state and out-of-country sources.

Products from wholesalers/processors represent a major source of seafood to restaurants. The data indicates that restaurants attempt to provide fresh seafood to their customers and the acquisition of seafood from local or in-state sources helps ensure that fresh seafood will be served.

6.2.3 Distribution Patterns

As one would expect, the recreational fishermen from Louisiana and Texas reported that they typically kept their seafood catch. Surprisingly the respondents stated that they were more likely to give away popular eating finfish species such as grouper, snapper and tuna. Commercial fishermen most likely sell their seafood catch to wholesalers/processors. Many wholesalers/processors are located on the major waterways of Louisiana and Texas making them readily accessible to the commercial fishermen. Wholesalers/processors were more likely to purchase the entire catch of the commercial fishermen, eliminating the commercial fishermen's need to transport and sell his catch to various outlets.

Wholesalers/processors usually sell their products to restaurants and retailers. Since they do not necessarily change the form of the seafood prior to sale, they serve as an intermediate step in transferring seafood from fishermen to consumer. The large volume of seafood handled by the wholesaler/processor suggests that they are able to supply seafood to various parts of the region. The respondents indicated that a small percentage of the seafood was transported out-of-state.

6.2.4 Consumption Patterns

The data from the wholesalers/processors and retailers indicate that these groups prefer to sell their finfish products whole (gutted but not skinned). Few of the respondents reported filleting their finfish. This probably allows them to move large volumes of product with very little preparation and therefore very little cost.

Recreational and commercial fishermen on the other hand prefer their finfish filleted and skinned. The restaurants also report that they usually serve filleted and skinned finfish to their customers. This is probably done to make the fish more appetizing and appealing.

The preferred method of cooking seafood was fried. This was the method of choice reported by all types of fishermen and the restaurants. Fried seafood has long been a favorite method of preparation in the South. Except for oyster fishermen who still enjoy eating their oysters raw, broiled and grilled seafood were the next most popular methods of preparing seafood.

6.3 Proximity to Oilfield Structures

Some finfish species are more frequently observed in close proximity to oilfield structures than are other species. One might reasonably expect, therefore, that Louisiana and Texas recreational fishermen would report catching some species in close proximity to oilfield structures more frequently than other species. This expectation was indeed realized in an analysis of the Louisiana and Texas recreational fishermen data sets which are shown in **Figures 6.1** and **6.2**, respectively.

Two distances relative to oilfield structures were particularly significant: 1) closer than 300 m (1,000 ft); and 2) farther away than 0.8 km (0.5 mi). Finfish species whose reported catch frequencies were at least 50% greater in close proximity to oilfield structures included amberjack, grouper, king mackerel, red snapper, shark and vermilion snapper. Finfish species whose reported catch frequencies were at least 50% greater at distances of one mi or more from oilfield structures included flounder, redfish and speckled trout.

Figure 6.1. Frequency distribution of finfish species caught in proximity to oilfield structures in summer and fall of 1992 in Louisiana.

Figure 6.2. Frequency distribution of finfish species caught in proximity to oilfield structures in the summer and fall of 1992 in Texas.

6.4 Seasonality of Finfish Catch

Louisiana and Texas Recreational Fishermen were surveyed during the summer (June-August) and fall (September-November) seasons. Analysis of the Louisiana and Texas data sets revealed a marked difference in frequencies of finfish species caught during the two seasons as in **Figures 6.3** and **6.4**, respectively. Finfish species more frequently caught in the summer season included amberjack, dolphin, grouper, king mackerel, red snapper and vermilion snapper. Finfish species more frequently caught in the fall season included black drum, croaker, flounder, redfish and speckled trout.

Figure 6.3. Frequency distribution of finfish species caught in summer and fall of 1992 in Louisiana.

Figure 6.4. Frequency distribution of finfish species caught in summer and fall of 1992 in Texas.

7.0 CONCLUSIONS

Over the two state area surveyed, a large percentage of seafood was harvested commercially and recreationally near inshore and offshore oilfield structures. This was particularly true in the large expanses of Louisiana estuaries from which was harvested much of Louisiana's landings, the second largest landings in the U.S. Seafood harvested by commercial fishermen - primarily shrimp fishermen - was most often sold to wholesaler/processors. These middlemen ship the seafood with little value added to retail outlets and restaurants.

Retail outlets provide mostly uncooked fresh seafood to the public. Restaurants which serve seafood do so as a large percentage of their total meals served. Fresh seafood served to consumers was fried. Stock was often used in the preparation of seafood dishes.

Seafood harvested by recreational fishermen was usually kept for home consumption and prepared fried. Most of the seafood harvested locally, both commercially and recreationally, remains in the local population. Very little of the fresh seafood sold locally was imported from out-of-state or out-of-country.

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8.0 PROJECT TEAM

The project team consisted of the following individuals:

Mr. Fred E. Schultz, Team Leader, Biologist
Dr. Maureen M. Mulino, Biologist
Dr. Stephen E. Steimle, Environmental Engineer
Dr. Donna H. Redmann, Survey Specialist
Dr. John Francis, Biostatistician
Dr. Walter Keithly, Economist
Mr. Ray Albert, Technician
Mr. Floyd Belsome, Jr., Technician
Mr. John Ferrell, Technician
Mr. Randall Poincot, Technician

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APPENDICES

APPENDIX A
Discharge Locations

A-3

LEGEND

- - ONSHORE DISCHARGE LOCATIONS
- ▲ - OFFSHORE DISCHARGE LOCATIONS (ONLY THOSE PLATFORMS WITH DISCHARGE DATA)

NOTES

1. THE INSHORE AND TERRITORIAL SEA DATA WAS OBTAINED FROM
 - TEXAS - TEXAS RAILROAD COMMISSION
 - LOUISIANA - LOUISIANA DEPARTMENT OF NATURAL RESOURCES
2. THE OFFSHORE DATA WAS OBTAINED FROM THE U.S. MINERALS MANAGEMENT SERVICE FOR DATA AS OF 20 AUGUST 1992
3. FOR THE INSHORE AND TERRITORIAL SEA, PLATFORMS WITH ZERO DISCHARGE WERE NOT PLOTTED.
4. FOR THE OFFSHORE, NUMBER OF PLATFORMS DO NOT INCLUDE ABANDONED PLATFORMS.
5. PLOTTED DOTS FOR ONSHORE AND TERRITORIAL DISCHARGE LOCATIONS MAY REPRESENT MORE THAN ONE DISCHARGE OF THE CLOSENESS OF SOME DISCHARGES AND THE RESULTANT PLOTTING OVERLAPS.
6. ZONE BOUNDARIES ARE CONSIDERED AS EXTENDING INLAND FOR PURPOSES OF RECORDING THE ZONES OF INLAND DISCHARGES.

ZONES ESTABLISHED FOR STUDY

- I - LAKE PONTCHARTRAIN & BORGNE AREA
- II - POINTE-A-LA-HACHE, DELACROIX, HOPEDALE AREA
- III - EMPIRE, VENICE AREA
- IV - GOLDEN MEADOW, HOUMA, GRAND ISLE AREA
- V - MORGAN CITY, NEW IBERIA AREA
- VI - CAMERON, PORT ARTHUR AREA
- VII - GALVESTON AREA
- VIII - PORT LAVACA, PORT ARANSAS, CORPUS CHRISTI AREA
- IX - BROWNSVILLE AREA

ZONE	ONSHORE* NUMBER OF DISCHARGES	OFFSHORE NUMBER OF PLATFORMS
I	6	0
II	31	49
III	124	513
IV	90	881
V	121	929
VI	20	461
VII	105	264
VIII	96	157
IX	5	10
TOTAL	598	3264

* - INCLUDES INLAND WATER BODIES

DISCHARGE AND PLATFORMS IN THE
OCS AND COASTAL ZONES
TEXAS AND LOUISIANA
PREPARED FOR
USDOE, PITTSBURGH ENERGY TECHNOLOGY CENTER
BRUCESTON RESEARCH CENTER,
BRUCESTON, PA

PREPARED BY
STEMBLE & ASSOCIATES, INC.
3828 AIRLINE HIGHWAY (P.O. BOX 865)
METairie, LA 70004
TELEPHONE: (504) 831-2374

UNDER SUBCONTRACT TO:
CONTINENTAL SHELF ASSOCIATES, INC.
738 PARKWAY STREET
JUPITER, FL 33477-4367
TELEPHONE: (407) 746-7946

DATE: 10/12/91 JOB NO. 92-375-01
DRAWN BY: R.A.P. CHECKED BY: S.E.S. SCALE: 1"=100,000'

APPENDIX B

Survey Zones

APPENDIX C

Louisiana/Texas Recreational Fishermen Intercept Survey

FISHIE

P. O. BOX 1165 • METAIRIE, LA 70004
TELEPHONE (504) 831-2099 • FAX (504) 835-9410

LOUISIANA/TEXAS RECREATIONAL FISHERMEN INTERCEPT QUESTIONNAIRE

Date of interview: _____

Case I.D. Number: _____

Time: _____ a.m. _____ p.m.

Name of Interviewer: _____

Location of interview: _____
(dock, city, state)

Introduction:

Hello, I am _____ (name of interviewer), with FISHIE. We are conducting a profile study for the United States Department of Energy to determine what seafood is caught, distributed, and consumed. The purpose of this study is to gather information on the effects of oil/gas structures on the inshore and offshore waters and fisheries of coastal Louisiana and Texas. We have a letter of endorsement from _____ (assoc/organization) concerning this study. (Show fisherman letter of endorsement.) May we take a few minutes of your time today to ask you a few questions about your seafood catch from today's fishing trip. Your name will not be associated with your response.

QUESTIONS:

1. FISHERMAN PROFILE.

- a. What category(s) have you fished over the past 3 months?
____ fin fish ____ shrimp ____ crab ____ oyster
- b. What type of fishing license(s) do you hold?
____ in-state
____ out-of-state
____ both in-state and out-of-state
- c. How many people in your household eat seafood? _____
- d. Please provide the following demographic information about you and all the people in your household:
 - (1) Gender: ____ Number of all Males ____ Number of all Females
 - (2) Ages of Adults: _____, _____, _____, _____, _____, _____, _____
 - (3) Number of children (under the age of 18): _____
 - (4) Race: ____ Black ____ Hispanic ____ Native American
____ Oriental ____ White ____ Other: _____
 - (5) How many females within your household are between the ages of 14 and 50? _____

2. MODE OF FISHING.

- a. How many fishing trips during the last three months have you made? _____ trips
- b. How many of the fishing trips you indicated above were spent in each of the following situations/locations?
____ off pier, dock, jetty, breakwater, seawalls, bridge, causeway,
and/or shorelines/beach/bank
____ private boat in inshore waters
____ private boat in offshore waters
____ charter/party boats

3. LOCATION OF SEAFOOD CATCH.

- a. On the map we have here, please show us the zone or region(s) across the Gulf Coast (Louisiana & Texas) where you fished in the past 3 months. (Indicate all that apply.)
Zone/Regions: ____ 1 ____ 2 ____ 3 ____ 4 ____ 5 ____ 6 ____ 7 ____ 8 ____ 9.
- b. During the past 3 months approximately what percentage of your catch was caught
____ % inshore (inside the barrier islands)?
____ % less than 3 miles offshore (outside the barrier islands)?
____ % 3 to 10 miles offshore?
____ % greater than 10 miles offshore?
100 % Total
- c. Based on your answers to question 2.b., please estimate the number of trips that were made at the following distances from offshore/inshore oil/gas platforms?
____ within 1,000 feet ____ from ½ mile to a mile
____ from 1,000 feet to ½ mile ____ more than a mile

4. SPECIES, QUANTITY, & DISTRIBUTION OF SEAFOOD CAUGHT. What species and approximate quantity of finfish and shellfish were caught and kept from your catch during the past 3 months? Of your total catch for each species, what percentage will be for personal consumption and what percentage will be given to others for consumption? Indicate (circle) the unit of measurements for quantity caught.

(Key: # = number, lb = pounds, doz = dozen, sa = sack)

<u>Shellfish Caught</u>	<u>Quantity Caught</u>	<u>% Kept for Personal Use</u>	<u>% Given Away to Others</u>
Shrimp	_____ # lb	_____ %	_____ %
Blue Crab	_____ # doz	_____ %	_____ %
Oysters	_____ doz sa	_____ %	_____ %
 <u>Finfish Caught</u>			
Amberjack	_____ # lb	_____ %	_____ %
Black Drum	_____ # lb	_____ %	_____ %
Croaker	_____ # lb	_____ %	_____ %
Dolphin	_____ # lb	_____ %	_____ %
Flounder	_____ # lb	_____ %	_____ %
Grouper	_____ # lb	_____ %	_____ %
Kingfish	_____ # lb	_____ %	_____ %
King Mackerel	_____ # lb	_____ %	_____ %
Redfish	_____ # lb	_____ %	_____ %
Red Snapper	_____ # lb	_____ %	_____ %
Shark	_____ # lb	_____ %	_____ %
Sheepshead	_____ # lb	_____ %	_____ %
Spanish Mackerel	_____ # lb	_____ %	_____ %
Speckled Trout	_____ # lb	_____ %	_____ %
Tuna	_____ # lb	_____ %	_____ %
Vermilion Snapper	_____ # lb	_____ %	_____ %
 <u>Other (Specify)</u>			
_____	_____ # lb	_____ %	_____ %
_____	_____ # lb	_____ %	_____ %
_____	_____ # lb	_____ %	_____ %

5. FREQUENCY OF FISH SERVED.

- On the average, how many times per week has fish that you caught during the past 3 months been served/eaten in your household? _____
- How many days has it been since the last meal served in your household was of fish you caught during the past 3 months? _____ days _____ This fish meal was not served.

6. **PERSONAL CONSUMPTION AND USE PATTERNS.** Of the fish you kept for your personal use, which species were eaten by you and the members of your household? What parts of the fish (meat and/or skin) were eaten?

<u>Finfish</u>	<u>Finfish Parts Consumed</u>	
	<u>Meat Only</u>	<u>Skin & Meat</u>
Amberjack	_____	_____
Black Drum	_____	_____
Croaker	_____	_____
Dolphin	_____	_____
Flounder	_____	_____
Grouper	_____	_____
Kingfish	_____	_____
King Mackerel	_____	_____
Redfish	_____	_____
Red Snapper	_____	_____
Shark	_____	_____
Sheepshead	_____	_____
Spanish Mackerel	_____	_____
Speckled Trout	_____	_____
Tuna	_____	_____
Vermilion Snapper	_____	_____
Other	_____	_____

7. **COOKING METHODS.** What method(s) of cooking were used to prepare the seafood you caught during the past 3 months? Check all that apply?
 ____ baked, ____ barbecued, ____ blackened, ____ boiled/poached, ____ broiled, ____ fried,
 ____ grilled, ____ smoked, ____ stew/soup, ____ other (please specify _____)
8. What is the ZIP CODE where you currently live? _____
9. Have you been interviewed by us before? ____ Yes ____ No
10. Do you belong to a fishing sports club? ____ Yes ____ No
 If yes, please provide name of club: _____
 location of club: _____

Follow Up Information:

Would you provide us your name and telephone number for the purpose of a follow-up interview?

____ Yes ____ No

If Yes, what is your name? _____

What is your telephone: area code (____) _____

What is your current address?

_____ Zip Code _____

Thank you for your valuable time in providing this information!

APPENDIX D

Louisiana/Texas Recreational Fishermen Group Survey

FISHIE

P. O. BOX 1165 • METAIRIE, LA 70004
TELEPHONE (504) 831-2099 • FAX (504) 835-9410

LOUISIANA/TEXAS RECREATIONAL FISHERMEN GROUP SURVEY

Dear Respondent:

We are conducting a profile study for the United States Department of Energy to determine what saltwater seafood is caught, distributed, and consumed. Your help is needed in gathering this information, and your responses will be kept confidential. The overall purpose of the study is to gather information that will be helpful in maintaining the integrity of our Seafood industry in the northern Gulf of Mexico.

DIRECTIONS:

Please answer all the following questions, as accurately as possible, concerning the source, quantities, and distribution of SALTWATER seafood caught by you during the last three months.

Please return in the enclosed self-addressed stamped envelope to:

FISHIE
P. O. Box 1165
Metairie, LA 70004

If you have any questions, contact:

Fred Schultz
504-831-2099

Saltwater Species Only
Time Period: Last Three Months

THANK YOU

QUESTIONS:

PLEASE PRINT

1. FISHERMAN PROFILE.

- a. What category(s) have you fished over the past 3 months?
☐ fin fish ☐ shrimp ☐ crab ☐ oyster
- b. What type of fishing license(s) do you hold?
☐ in-state
☐ out-of-state
☐ both in-state and out-of-state
- c. How many people in your household eat seafood? _____
- d. Please provide the following demographic information about you and all the people in your household:
 - (1) Gender: ☐ Number of All Males ☐ Number of All Females
 - (2) Ages of Adults: _____, _____, _____, _____, _____, _____, _____
 - (3) Number of children (under the age of 18): _____
 - (4) Race: ☐ Black ☐ Hispanic ☐ Native American
☐ Oriental ☐ White ☐ Other: _____
 - (5) How many females within your household are between the ages of 14 and 50? _____

2. MODE OF FISHING.

- a. How many fishing trips during the last three months have you made? _____ trips
- b. How many of the fishing trips you indicated above were spent in each of the following situations/locations?
 _____ off pier, dock, jetty, breakwater, seawalls, bridge, causeway,
 and/or shorelines/beach/bank
 _____ private boat in inshore waters
 _____ private boat in offshore waters
 _____ charter/party boats

3. LOCATION OF SEAFOOD CATCH.

- a. Please check all the ports which you fish near. If you do not fish near any listed, please check the closest one to your fishing locations.

Louisiana Ports			Texas Ports
☐ Barataria	☐ Empire	☐ New Iberia	☐ Aransas Pass
☐ Bucktown	☐ Golden Meadow	☐ Venice	☐ Brownsville
☐ Cameron	☐ Grand Isle	☐ Yscloskey	☐ Freeport
☐ Chauvin	☐ Lafitte		☐ Galveston
☐ Delecroix	☐ Leesville		☐ Port Arthur
☐ Delcambre	☐ Mandeville		☐ Port Isabel
☐ Dulac	☐ Morgan City		☐ Rockport

- b. During the past 3 months, approximately what percentage of your catch was caught
 _____ % inshore (inside the barrier islands)?
 _____ % less than 3 miles offshore (outside the barrier islands)?
 _____ % 3 to 10 miles offshore?
 _____ % greater than 10 miles offshore?
 100 %

- c. Based on your answers to question 2.b., please estimate the number of trips that were made at the following distances from offshore/inshore oil/gas platforms?

_____ within 1,000 feet _____ from ½ mile to a mile
 _____ from 1,000 feet to ½ mile _____ more than a mile

4. SPECIES, QUANTITY, & DISTRIBUTION OF SEAFOOD CAUGHT. What species and approximate quantity of finfish and shellfish were caught and kept from your catch during the past 3 months? Of your total catch for each species, what percentage will be for personal consumption and what percentage will be given to others for consumption? Circle the unit of measurements for quantity caught.

(Key: #=number, lb=pounds, doz=dozen, sa=sack)

<u>Shellfish Caught</u>	<u>Quantity Caught</u>	<u>% Kept for Personal Use</u>	<u>% Given Away to Others</u>
Shrimp	_____ # lb	_____ %	_____ %
Blue Crab	_____ # doz	_____ %	_____ %
Oysters	_____ doz sa	_____ %	_____ %
 <u>Finfish Caught</u>			
Amberjack	_____ # lb	_____ %	_____ %
Black Drum	_____ # lb	_____ %	_____ %
Croaker	_____ # lb	_____ %	_____ %
Dolphin	_____ # lb	_____ %	_____ %
Flounder	_____ # lb	_____ %	_____ %
Grouper	_____ # lb	_____ %	_____ %
Kingfish	_____ # lb	_____ %	_____ %
King Mackerel	_____ # lb	_____ %	_____ %
Redfish	_____ # lb	_____ %	_____ %
Red Snapper	_____ # lb	_____ %	_____ %
Shark	_____ # lb	_____ %	_____ %
Sheepshead	_____ # lb	_____ %	_____ %
Spanish Mackerel	_____ # lb	_____ %	_____ %
Speckled Trout	_____ # lb	_____ %	_____ %
Tuna	_____ # lb	_____ %	_____ %
Vermilion Snapper	_____ # lb	_____ %	_____ %
 <u>Other (Specify)</u>			
_____	_____ # lb	_____ %	_____ %
_____	_____ # lb	_____ %	_____ %
_____	_____ # lb	_____ %	_____ %

5. FREQUENCY OF FISH SERVED.

- a. On the average, how many times per week was fish that you caught during the past three months served/eaten in your household? _____
- b. How many days has it been since the last meal served in your household was of fish you caught during the past 3 months? _____ days _____ This fish meal was not served.

6. **PERSONAL CONSUMPTION AND USE PATTERNS.** Of the fish listed below, please identify the species kept and eaten by you and members of your household by checking the appropriate column that describes which part(s) of the fish were eaten?

	<u>Finfish Parts Consumed</u>			<u>Finfish Parts Consumed</u>	
	<u>Meat Only</u>	<u>Skin & Meat</u>		<u>Meat Only</u>	<u>Skin & Meat</u>
<u>Finfish</u>			<u>Finfish</u>		
Amberjack	_____	_____	Shark	_____	_____
Black Drum	_____	_____	Sheephead	_____	_____
Croaker	_____	_____	Spanish Mackerel	_____	_____
Dolphin	_____	_____	Speckled Trout	_____	_____
Flounder	_____	_____	Tuna	_____	_____
Grouper	_____	_____	Vermilion Snapper	_____	_____
Kingfish	_____	_____	Other: (Please Specify)	_____	_____
King Mackerel	_____	_____	_____	_____	_____
Red Snapper	_____	_____	_____	_____	_____

7. **COOKING METHODS.** What method(s) of cooking were used to prepare the seafood you caught during the past 3 months? Check all that apply?
 ___baked, ___barbequed, ___blackened, ___boiled/poached, ___broiled, ___fried,
 ___grilled, ___smoked, ___stew/soup, ___other (please specify _____).
8. What is the ZIP CODE where you currently live? _____
9. Have you been interviewed by us before? ___Yes ___No

Follow Up Information:

Your name will not be associated with your response. Would you provide us your name and telephone number for the purpose of a follow-up interview? ___Yes ___No

If Yes, what is your name? _____
 What is your telephone: area code (____) _____

What is your current address?

 _____ Zip Code _____

Thank you for your valuable time in providing this information!

APPENDIX E

Louisiana/Texas Commercial Fishermen Intercept Survey

FISHIE

P. O. BOX 1165 • METAIRIE, LA 70004
TELEPHONE (504) 831-2099 • FAX (504) 835-9410

LOUISIANA/TEXAS COMMERCIAL FISHERMEN INTERCEPT QUESTIONNAIRE

Date of interview: _____ Case I.D. Number: _____
Time: _____ a.m. _____ p.m. Name of Interviewer: _____
Location of interview: _____
(dock, city, state)

Introduction:

Hello, I am _____ (name of interviewer), with FISHIE. We are conducting a profile study for the United States Department of Energy to determine what seafood is caught, distributed, and consumed. The purpose of this study is to gather information on the effects of oil/gas structures on the inshore and offshore waters and fisheries of coastal Louisiana and Texas. We have a letter of endorsement from _____ (assoc/organization) concerning this study. (Show fisherman letter of endorsement.) May we take a few minutes of your time today to ask you a few questions about your seafood catch from today's fishing trip. Your name will not be associated with your response.

QUESTIONS:

1. FISHERMAN PROFILE.

- a. What category(s) have you fished in the past 3 months?
_____ fin fish _____ shrimp _____ crab _____ oyster
- b. What type of fishing license(s) do you hold?
_____ in-state
_____ out-of-state
_____ both in-state and out-of-state
_____ Federal
- c. How many people in your household eat seafood? _____
- d. Please provide the following demographic information about you and all the people in your household:
 - (1) Gender: _____ Number of all Males _____ Number of all Females
 - (2) Ages of Adults: _____, _____, _____, _____, _____
 - (3) Number of children (under the age of 18): _____
 - (4) Race: _____ Black _____ Hispanic _____ Native American
_____ Oriental _____ White _____ Other: _____
 - (5) How many females within your household are between the ages of 14 and 50? _____

2. LOCATION OF SEAFOOD CATCH.

- How many days have you fished in the past 3 months? _____ days
- On the map we have here, please show us the zone or region(s) across the Gulf Coast (Louisiana & Texas) where you fished in the past 3 months. (Indicate all that apply.)
Zone/Regions: ___ 1 ___ 2 ___ 3 ___ 4 ___ 5 ___ 6 ___ 7 ___ 8 ___ 9.
- Approximately what percentage of your catch was caught:
 _____ % inshore (inside the barrier islands)?
 _____ % less than 3 miles offshore (outside the barrier islands)?
 _____ % 3 to 10 miles offshore?
 _____ % greater than 10 miles offshore?
 100 % Total
- During the last 3 months, please estimate the number of trips that were made at the following distances from offshore/inshore oil/gas structures?
 _____ within 1,000 feet _____ from ½ mile to a mile
 _____ from 1,000 feet to ½ mile _____ more than a mile

3. SPECIES CAUGHT AND DISTRIBUTION OF SEAFOOD CATCH. During the past 3 months,

- What percentage of species were sold and to whom (Wholesalers or Processing Plants, Retailers or Restaurants, Consumers--friends/relatives, and Other)?
- What percentage for each species were given to others for consumption and/or were for personal consumption? (Indicate all that apply.)

	(A) % To be Sold To				(B) % Given Away to Others	(C) % to be Kept for Personal	(A + B + C = 100%)
	Whls/Process	Retail/Restr	Consumer	Other			
<u>Shellfish</u>							
Shrimp	_____	_____	_____	_____	_____	_____	= 100%
Blue Crab	_____	_____	_____	_____	_____	_____	= 100%
Oysters	_____	_____	_____	_____	_____	_____	= 100%
<u>Finfish</u>							
Amberjack	_____	_____	_____	_____	_____	_____	= 100%
Black Drum	_____	_____	_____	_____	_____	_____	= 100%
Croaker	_____	_____	_____	_____	_____	_____	= 100%
Dolphin	_____	_____	_____	_____	_____	_____	= 100%
Flounder	_____	_____	_____	_____	_____	_____	= 100%
Grouper	_____	_____	_____	_____	_____	_____	= 100%
Kingfish	_____	_____	_____	_____	_____	_____	= 100%
King Mackerel	_____	_____	_____	_____	_____	_____	= 100%
Red Snapper	_____	_____	_____	_____	_____	_____	= 100%
Shark	_____	_____	_____	_____	_____	_____	= 100%
Sheepshead	_____	_____	_____	_____	_____	_____	= 100%
Spanish Mackerel	_____	_____	_____	_____	_____	_____	= 100%
Speckled Trout	_____	_____	_____	_____	_____	_____	= 100%
Tuna	_____	_____	_____	_____	_____	_____	= 100%
Vermilion Snapper	_____	_____	_____	_____	_____	_____	= 100%
<u>Other</u>							
_____	_____	_____	_____	_____	_____	_____	= 100%
_____	_____	_____	_____	_____	_____	_____	= 100%
_____	_____	_____	_____	_____	_____	_____	= 100%

5. FREQUENCY OF SEAFOOD SERVED.

- a. On the average, how many times per week was fish that you caught during the last 3 months served/eaten in your household? _____
- b. How many days has it been since the last meal served in your household was of seafood you caught and kept for personal consumption during the past 3 months? _____ days _____ This fish meal was not served.

6. PERSONAL CONSUMPTION AND USE PATTERNS. Of the fish you kept for your personal use, which species were eaten by you and the members of your household? What parts of the fish (meat and/or skin) were served/eaten?

	<u>Finfish Parts Consumed</u>			<u>Finfish Parts Consumed</u>	
	<u>Meat Only</u>	<u>Skin & Meat</u>		<u>Meat Only</u>	<u>Skin & Meat</u>
<u>Finfish</u>			<u>Finfish</u>		
Amberjack	_____	_____	Shark	_____	_____
Black Drum	_____	_____	Sheepshead	_____	_____
Croaker	_____	_____	Spanish Mackerel	_____	_____
Dolphin	_____	_____	Speckled Trout	_____	_____
Flounder	_____	_____	Tuna	_____	_____
Grouper	_____	_____	Vermilion Snapper	_____	_____
Kingfish	_____	_____	Other: (Please Specify)	_____	_____
King Mackerel	_____	_____	_____	_____	_____
Redfish	_____	_____	_____	_____	_____
Red Snapper	_____	_____	_____	_____	_____

7. COOKING METHODS. What method of cooking were used to prepare the seafood you caught during the past 3 months? Indicate all that apply (please specify).

___ baked, ___ barbecued, ___ blackened, ___ boiled/poached, ___ broiled, ___ fried,
___ grilled, ___ smoked, ___ stew/soup, ___ other (please specify _____)

8. What is the ZIP CODE where you currently live? _____

9. Have you been interviewed by us before? ___ Yes ___ No

Follow-Up Information:

For the purpose of a follow-up interview, would you provide us with your name and address?

___ Yes ___ No

If Yes, what is your name? _____

What is your telephone: area code (_____) _____

What is your current business name & address?

_____ Zip Code _____

Thank you for your valuable time in providing this information!

APPENDIX F

Louisiana/Texas Oyster Fishermen Intercept Survey

FISHIE

P. O. BOX 1165 • METAIRIE, LA 70004
TELEPHONE (504) 831-2099 • FAX (504) 835-9410

LOUISIANA/TEXAS COMMERCIAL OYSTER FISHERMEN INTERCEPT QUESTIONNAIRE

Date of interview: _____ Case I.D. Number: _____
Time: _____ a.m. _____ p.m. Name of Interviewer: _____
Location of interview: _____
(dock, city, state)

Introduction:

Hello, I am _____ (name of interviewer), with FISHIE. We are conducting a profile study for the United States Department of Energy to determine what seafood is caught, distributed, and consumed. The purpose of this study is to gather information on the effects of oil/gas structures on the inshore and offshore waters and fisheries of coastal Louisiana and Texas. May we take a few minutes of your time today to ask you a few questions about your seafood catch from today's fishing trip. Your name will not be associated with your response.

QUESTIONS:

1. FISHERMAN PROFILE.

- a. How many acres of oyster grounds under lease? _____ Include leases you and/or family members hold and others.
- b. What type of fishing license(s) do you hold?
_____ in-state
_____ out-of-state
_____ both in-state and out-of-state
_____ Federal
- c. How many people in your household eat oysters? _____
- d. Please provide the following demographic information about you and all the people in your household:
 - (1) Gender: _____ Number of all Males _____ Number of all Females
 - (2) Ages of Adults: _____, _____, _____, _____, _____, _____
 - (3) Number of children (under the age of 18): _____
 - (4) Race: _____ Black _____ Hispanic _____ Native American
_____ Oriental _____ White _____ Other: _____
 - (5) How many females within your household are between the ages of 14 and 50? _____

2. LOCATION OF SEAFOOD CATCH.

- a. How many days have you fished in the past 3 months? _____ days
- b. On the map we have here, please show us the zone or region(s) across the Gulf Coast (Louisiana & Texas) where you fished in the past 3 months. (Indicate all that apply.)
Zone/Regions: ____ 1 ____ 2 ____ 3 ____ 4 ____ 5 ____ 6 ____ 7 ____ 8 ____ 9.
- c. Approximately what percentage of your catch was caught:
____ % inshore (inside the barrier islands)?
____ % less than 3 miles offshore (outside the barrier islands)?
____ % 3 to 10 miles offshore?
- 100 % Total
- d. During the last 3 months, please estimate the number of trips that were made at the following distances from offshore/inshore oil/gas structures?
____ within 1,000 feet ____ from ½ mile to a mile
____ from 1,000 feet to ½ mile ____ more than a mile

3. DISTRIBUTION OF OYSTER CATCH. During the past 3 months,

- What percentage of species were sold and to whom (Wholesalers or Processing Plants, Retailers or Restaurants, Consumers—friends/relatives, and Other)?
- What percentage for each species were given to others for consumption and/or were for personal consumption? (Indicate all that apply.)

	(A)				(B)	(C)	
	% To be Sold To				% Given	% to be	
	Whls/Process	Retail/Restr	Consumer	Other	Away to Others	Kept for Personal	(A + B + C = 100%)
Shellfish							
Oysters	_____	_____	_____	_____	_____	_____	= 100%

4. FREQUENCY OF OYSTERS SERVED.

- a. On the average, how many times per week were oysters that you caught during the last 3 months served/eaten in your household? _____
- b. How many days has it been since the last meal served in your household was of oysters you caught and kept for personal consumption during the past 3 months? _____ days _____ This oyster meal was not served.

5. PERSONAL CONSUMPTION AND USE PATTERNS. What percentage of oysters eaten by you and your family are eaten raw? _____ %

6. COOKING METHODS. What method of cooking were used to prepare the seafood you caught during the past 3 months? Indicate all that apply (please specify).

____ raw, ____ baked, ____ barbecued, ____ blackened, ____ boiled/poached, ____ broiled, ____ fried,
____ grilled, ____ smoked, ____ stew/soup, ____ other (please specify _____)

7. What is the ZIP CODE where you currently live? _____

8. Have you been interviewed by us before? ____ Yes ____ No

Follow-Up Information:

For the purpose of a follow-up interview, would you provide us with your name and address?

____ Yes ____ No

If Yes, what is your name? _____

What is your telephone: area code (____) _____

What is your current business name & address?

_____ Zip Code _____

Thank you for your valuable time in providing this information!

APPENDIX G

Louisiana/Texas Processors & Wholesalers Mail Survey

FISHIE

P. O. BOX 1165 • METAIRIE, LA 70004
TELEPHONE (504) 831-2099 • FAX (504) 835-9410

LOUISIANA/TEXAS PROCESSOR'S & WHOLESALE'S SURVEY

Dear Respondent:

We are conducting a profile study for the United States Department of Energy to address the lack of information on the effects of oil and structures on the inshore and offshore coastal waters and fisheries of Louisiana and Texas. Specifically, this study is being conducted to determine what saltwater seafood is caught, distributed, and consumed. Your help is needed in gathering this data, and your responses will be kept confidential. The overall purpose of the study is to gather information that will be helpful in maintaining the integrity of our Seafood industry in the northern Gulf of Mexico.

DIRECTIONS:

Please answer all the following questions, as accurately as possible, concerning the source, quantities, and distribution of SALTWATER seafood sold by your company from January 1, 1992 through December 31, 1992.

Please indicate whether you operate: _____ *as a Processor only*
_____ *as a Wholesaler/Dealer only*
_____ *both as a Processor and a Wholesaler/Dealer*

PLEASE PRINT

Saltwater Species Only

Time Period: January 1, 1992 through December 31, 1992

Please return in the enclosed self-addressed stamped envelope to:

**FISHIE
P. O. Box 1165
Metairie, LA 70004**

If you have any questions, contact:

**Fred Schultz
(504)-831-2099**

THANK YOU

QUESTIONS:

1. SOURCES OF SALTWATER SEAFOOD: Please provide an estimate of the percentage of saltwater finfish and shellfish you bought from the following sources for the time period of January 1 through December 31, 1992.

Source	Percentage			
	Saltwater Finfish	Shrimp	Shellfish Oyster	Blue Crab
a. in-state commercial fishermen?	_____ %	_____ %	_____ %	_____ %
b. in-state wholesalers/dealers?	_____ %	_____ %	_____ %	_____ %
c. in-state processing plants?	_____ %	_____ %	_____ %	_____ %
d. out-of-state sources?	_____ %	_____ %	_____ %	_____ %
e. out-of-country sources?	_____ %	_____ %	_____ %	_____ %
	100 %	100 %	100 %	100 %

2. FISHING SITES: If commercial fishermen are the suppliers of your saltwater seafood, what percentage of them fish:
 - a. inshore (inside barrier islands)? _____ %
 - b. of those who fish inshore (a.), how many fish near inshore oil/gas platforms? _____ %
 - c. offshore (outside barrier islands)? _____ %
 - d. of those who fish offshore (c.), how many fish near offshore oil/gas platforms? _____ %
3. SUPPLIERS'S FISHING PORTS: If you use commercial fishermen/docks for suppliers of your seafood, please check all the port(s) where these suppliers are located.

Louisiana Ports			Texas Ports	
_____ Barataria	_____ Empire	_____ New Iberia	_____ Aransas Pass	
_____ Bucktown	_____ Golden Meadow	_____ Venice	_____ Brownsville	
_____ Cameron	_____ Grand Isle	_____ Yscloskey	_____ Freeport	
_____ Chauvin	_____ Lafitte		_____ Galveston	
_____ Delecroix	_____ Leesville		_____ Port Arthur	
_____ Delcambre	_____ Mandeville		_____ Port Isabel	
_____ Dulac	_____ Morgan City		_____ Rockport	

4. QUANTITY OBTAINED: Please provide an estimate of the quantities of saltwater seafood you handled for the time period of January 1 through December 31, 1992. Please specify quantity in product weight and units of measurement.

(PLEASE SPECIFY UNITS)					
Saltwater Fish:	Qty.	Unit	Shrimp:	Qty.	Unit
whole fish*	_____	_____	heads-on	_____	_____
fish parts	_____	_____	heads-off	_____	_____

*includes gutted and headless

(PLEASE SPECIFY UNITS)					
Oysters:	Qty.	Unit	Blue Crabs:	Qty.	Unit
Oysters in shell	_____	_____	Hard shell	_____	_____
Oyster meat	_____	_____	Soft shell	_____	_____
			Crab meat	_____	_____

5. DISTRIBUTION OF SHELLFISH: Please provide an estimate of the percentage of the total shellfish sold to the following outlets for all of 1992. Note: For the purpose of this study, Louisiana and Texas are not considered out-of-state.

	<u>S O L D T O I N - S T A T E O U T L E T S</u>				<u>O U T - O F - S T A T E</u>
	<u>Wholesalers</u> <u>/Dealers</u>	<u>Processing</u> <u>Plants</u>	<u>Restaurants</u> <u>/Retailers</u>	<u>Other*</u> <u>Outlets</u>	<u>All Outlets</u> <u>(except LA/TX)</u>
Shrimp	_____ %	_____ %	_____ %	_____ %	_____ % = 100 %
Oysters	_____ %	_____ %	_____ %	_____ %	_____ % = 100 %
Blue Crabs:					
Hard shell	_____ %	_____ %	_____ %	_____ %	_____ % = 100 %
Soft shell	_____ %	_____ %	_____ %	_____ %	_____ % = 100 %
Crab meat	_____ %	_____ %	_____ %	_____ %	_____ % = 100 %
*For Other Outlets please list. _____					

6. DISTRIBUTION OF SALTWATER FINFISH: Please provide an estimate of the percentage of the total saltwater finfish sold to the following outlets for all of 1992. Note: For the purpose of this study, Louisiana and Texas are not considered out-of-state.

	<u>S O L D T O I N - S T A T E O U T L E T S</u>				<u>O U T - O F - S T A T E</u>
	<u>Wholesalers</u> <u>/Dealers</u>	<u>Processing</u> <u>Plants</u>	<u>Restaurants</u> <u>/Retailers</u>	<u>Other*</u> <u>Outlets</u>	<u>All Outlets</u> <u>(except LA/TX)</u>
Black Drum	_____ %	_____ %	_____ %	_____ %	_____ % = 100 %
Flounder	_____ %	_____ %	_____ %	_____ %	_____ % = 100 %
Red Snapper	_____ %	_____ %	_____ %	_____ %	_____ % = 100 %
Sheepshead	_____ %	_____ %	_____ %	_____ %	_____ % = 100 %
Speckled Trout	_____ %	_____ %	_____ %	_____ %	_____ % = 100 %
Tuna	_____ %	_____ %	_____ %	_____ %	_____ % = 100 %
Vermilion					
Snapper	_____ %	_____ %	_____ %	_____ %	_____ % = 100 %
*For Other Outlets please list. _____					

7. OTHER SALTWATER FINFISH.

- a. Do you handle any of the following finfish? Please circle "YES" or "NO", as appropriate.

	<u>Handle?</u>	
1. Amberjack	YES	NO
2. Croaker	YES	NO
3. Dolphin	YES	NO
4. Grouper	YES	NO
5. King Mackerel	YES	NO
6. Shark	YES	NO
7. Kingfish	YES	NO
8. Spanish Mackerel	YES	NO
9. Other: _____	YES	NO

- b. What percentage of your total finfish is represented by the species listed in 7.a.(1-9) combined? _____ %

8. **PRODUCT FORM OF SEAFOOD SOLD.** Please circle the form(s) you commonly sell of the following seafood:

	<u>Form Commonly Sold</u>			
<u>Shellfish</u>				
Oysters	in shell	shucked	prepared products (e.g. breaded/gumbo)	
Blue Crabs	whole	meat	prepared products (e.g. stuffed)	
Shrimp	heads-on headless shell on	peeled & undeveined peeled & deveined	prepared products (e.g. breaded/gumbo)	
<u>FinFish</u>				
Black Drum	whole fish	fillets with skin	skinless fillets	other
Flounder	whole fish	fillets with skin	skinless fillets	other
Red Snapper	whole fish	fillets with skin	skinless fillets	other
Sheepshead	whole fish	fillets with skin	skinless fillets	other
Speckled Trout	whole fish	fillets with skin	skinless fillets	other
Tuna	whole fish	fillets with skin	skinless fillets	other
Vermilion Snapper	whole fish	fillets with skin	skinless fillets	other
<u>Other Finfish (Please indicate)</u>				
_____	whole fish	fillets with skin	skinless fillets	other
_____	whole fish	fillets with skin	skinless fillets	other
_____	whole fish	fillets with skin	skinless fillets	other

9. For other phases of this study, will you permit us to contact you for a list of your major seafood suppliers? ☐ Yes ☐ No

10. What is the ZIP CODE where your company is located? _____

Follow-up Information:

Your name and the name of your company will not be associated with your response. For the purpose of conducting a follow-up interview, would you provide us with your name and address?
☐ Yes ☐ No.

If Yes, please print your name, company name, company address, and telephone:

Telephone: Area Code () _____

THANK YOU

APPENDIX H

Louisiana/Texas Retail Seafood Market Onsite Survey

FISHIE

P. O. BOX 1165 • METAIRIE, LA 70004
TELEPHONE (504) 831-2099 • FAX (504) 835-9410

LOUISIANA/TEXAS RETAIL SEAFOOD MARKET ON-SITE SURVEY

RETAIL SEAFOOD MARKET PROFILE:

Name of Market: _____

Address: _____

State: _____

Parish/County: _____

DATE & TIME MARKET DATA WAS COLLECTED:

Date: _____ Day of Week: _____ Time of Day: _____

MARKET DATA GATHERED BY: _____

DIRECTIONS: Use a check mark to indicate whether type of shellfish or finfish was sold. Also indicate how seafood was prepared if sold cooked (e.g. boiled, gumbo, stuffed, etouffee, etc.).

SHELLFISH SOLD	SOLD UNCOOKED	SOLD COOKED (Specify how prepared)
Blue Crabs--Hard Shell		
Blue Crabs--Soft Shell		
Blue Crabs--Crab Meat		
Oysters--Whole (with shell)		
Oysters--Meat		
Shrimp--Heads-on		
Shrimp--Heads-off		
Shrimp--Peeled		

Continue to backside of page.....

FINFISH SOLD	WHOLE FISH		FISH FILLETS		PARTS	COOKED
	With Skin	Without Skin	With Skin	Without Skin	(Specify parts)	(Specify how prepared)
Amberjack						
Black Drum						
Croaker						
Dolphin						
Flounder						
Grouper						
Kingfish						
King Mackerel						
Red Snapper						
Shark						
Sheepshead						
Spanish Mackerel						
Speckled Trout						
Tuna						

Do you ship saltwater seafood to other areas of the state? ____ Yes ____ No

Do you ship saltwater seafood out of State? ____ Yes ____ No

APPENDIX I

Louisiana/Texas Restaurant Mail Survey

FISHIE

P. O. BOX 1165 • METAIRIE, LA 70004
TELEPHONE (504) 831-2099 • FAX (504) 835-9410

TEXAS RESTAURANT MAIL SURVEY

Dear Respondent:

We are conducting a profile study for the United States Department of Energy to address the lack of information on the effects of oil and gas structures on the inshore and offshore coastal waters and fisheries of Louisiana and Texas. Specifically, this study is being conducted to determine what saltwater seafood is caught, distributed, and consumed. Your help is needed in gathering this data, and your responses will be kept confidential. The overall purpose of the study is to gather information that will be helpful in maintaining the integrity of our Seafood industry in the northern Gulf of Mexico.

DIRECTIONS:

Please answer all the following questions, as accurately as possible, concerning the source, quantities, and method of preparation of SALTWATER seafood served/sold by your restaurant from January 1, 1992 through December 31, 1992.

P L E A S E P R I N T

Saltwater Species Only

Time Period: January 1, 1992 through December 31, 1992

Please return in the enclosed self-addressed stamped envelope to:

**FISHIE
P. O. Box 1165
Metairie, LA 70004**

If you have any questions, contact:

**Fred Schultz
(504)-831-2099**

THANK YOU

QUESTIONS:

1. Approximately how many seafood dishes were served per week for the year 1992? _____
2. Approximately what percentage of the seafood dishes served for the year 1992 were shellfish and/or were finfish?
 - a. _____ % Shellfish
 - b. _____ % Finfish
 - c. _____ % Shellfish & Finfish
 - 100 % TOTAL
3. On the average per week for the year 1992, what percentage of shellfish dishes were:
 - a. _____ % Blue Crabs--Soft Shell
 - b. _____ % Blue Crabs--Other
 - c. _____ % Oysters on the Half Shell
 - d. _____ % Oyster Meat
 - e. _____ % Shrimp
 - f. _____ % Other
 - 100 % TOTAL
4. For the year 1992, what type of shellfish was used to prepare stock?
 - a. _____ Blue Crab
 - b. _____ Shrimp
 - c. _____ Oysters
5. On the average per week for the year 1992, what percentage of finfish dishes were:
 - a. _____ % Amberjack
 - b. _____ % Black Drum
 - c. _____ % Croaker
 - d. _____ % Dolphin
 - e. _____ % Flounder
 - f. _____ % Grouper
 - g. _____ % Kingfish
 - h. _____ % King Mackerel
 - i. _____ % Redfish
 - j. _____ % Red Snapper
 - k. _____ % Shark
 - l. _____ % Sheepshead
 - m. _____ % Spanish Mackerel
 - n. _____ % Speckled Trout
 - o. _____ % Tuna
 - p. _____ % Vermilion Snapper
 - q. _____ % Other
 - 100 % TOTAL
6. Approximately how many seafood meals per week for the year 1992, included seafood stock in their preparation?
 - a. _____ Stock made from Shellfish
 - b. _____ Stock made from Finfish
 - c. _____ Stock made from both Shellfish and Finfish

7. What percentage of your saltwater seafood was imported from areas other than Louisiana or Texas for the year 1992? _____ %
8. What percentage of your seafood did you receive from the following sources for the year 1992?
- _____ % Commercial Fisherman
 _____ % Wholesalers/Processors
 _____ % Retailers
 _____ % Other
 100 % TOTAL
9. Of the fish served for consumption by your restaurant for the year 1992, what parts of the fish (meat and/or skin) were consumed? What fish were used for stock? Check all that apply.

<u>Finfish</u>	<u>Finfish Parts Consumed</u>		
	<u>Meat Only</u>	<u>Skin & Meat</u>	<u>Used In Stock</u>
Amberjack	_____	_____	_____
Black Drum	_____	_____	_____
Croaker	_____	_____	_____
Dolphin	_____	_____	_____
Flounder	_____	_____	_____
Grouper	_____	_____	_____
Kingfish	_____	_____	_____
King Mackerel	_____	_____	_____
Redfish	_____	_____	_____
Red Snapper	_____	_____	_____
Shark	_____	_____	_____
Sheepshead	_____	_____	_____
Spanish Mackerel	_____	_____	_____
Speckled Trout	_____	_____	_____
Tuna	_____	_____	_____
Vermilion Snapper	_____	_____	_____
Other:(specify) _____	_____	_____	_____

10. What method(s) of cooking were used for the year 1992 to prepare the seafood you served? Check all that apply.
- _____ baked, _____ barbequed, _____ blackened, _____ boiled/poached, _____ broiled,
 _____ fried, _____ grilled, _____ smoked, _____ stew/soup, _____ other.
11. What is the ZIP CODE where your restaurant is located? _____

Follow-Up Information:

Your name and the name of your restaurant will not be associated with your response. For the purpose of conducting a follow-up interview, would you provide us with your name and address?

____ Yes ____ No.

If Yes, please print your name, restaurant name, address, and telephone:

Telephone: Area Code (_____) _____

Thank you for your valuable time in providing this information!

APPENDIX J

Finfish Identification Guide

SHARK

GROUPER

SHEEPSHEAD

CROAKER

BLACK DRUM

KINGFISH

RED SNAPPER

RED FISH

SPECKLED TROUT

VERMILION SNAPPER

AMBERJACK

FLOUNDER

SPANISH MACKEREL

KING MACKEREL

DOLPHIN

TUNA

APPENDIX K

Letters of Support/Endorsements

Louisiana Seafood

M E M O R A N D U M

TO: Louisiana Seafood Processors

FROM: ^{KT}
Karl Turner, Executive Director

DATE: March 17, 1993

This letter is sent to request your participation in a survey that is being conducted by Fisheries Information & Seafood Harvest Inquiry Enterprise (FISHIE) in conjunction with the US Department of Energy. The purpose of the survey is to determine what saltwater seafood is caught, where it is distributed and who consumes it.

I have reviewed the research proposal as well as the survey questionnaire. I strongly encourage you to cooperate.

The information obtained through this project will be helpful in maintaining the integrity of the Louisiana Seafood Industry.

KT:wgh

Dear Restaurant Operator:

Fisheries Information & Seafood Harvest Inquiry Enterprise (FISHIE) is conducting a survey for the U. S. Department of Energy to study the effects of oil and gas structures on the inshore and offshore coastal waters along with the fisheries industry of Texas and Louisiana.

One phase of the study involves analyzing the collection, distribution and consumption patterns of saltwater seafood caught from the coastal regions of Texas and Louisiana. Surveys are being conducted of restaurants, commercial/recreational fishermen, wholesalers, processors and retailers to obtain some of this data.

Upon completion of the project, the findings of the study will be made available to the public. Prior to the completion of the study, preliminary results can be made available to respondents of the survey questionnaire. Restaurateurs may find the results useful for the offerings of the restaurant, e.g. seafood items which are most popular or the most common method of preparation.

We encourage you to participate in this valuable research. The results of the research will benefit restaurateurs by identifying the preferred eating habits of consumers, as well as the commonly served type of saltwater seafood. Your assistance and cooperation will be greatly appreciated towards the completion of this project. If you have any questions, please contact Mr. Fred E. Schultz, FISHIE, 504/831-2099

Sincerely

A handwritten signature in black ink that reads "W. Kent Hughes". The signature is written in a cursive, flowing style.

W. Kent Hughes, CAE
Senior Vice President

APPENDIX L

Louisiana Restaurant Association Newsletter

Louisiana Restaurant Association

HOSPITALITY NEWSLINE

2800 Veterans Blvd., Suite 160 • Metairie, LA 70002-6101 • (504) 831-7788 • FAX (504) 837-4967

VOLUME XIII, NUMBER 7

JULY 1993

Dear LRA Members:

I want to take the opportunity to extend to you a special invitation to attend the LRA's 40th annual Louisiana Foodservice & Hospitality Exposition to be held August 7, 8 and 9, 1993. The New Orleans Convention Center, Hall F will be the site of this year's Expo. Over 14,000 industry professionals are expected to visit the record 445 booths, which will display innovations in foodservice products, services and equipment.

There is an entire menu of activities planned in conjunction with this year's expo, including the New Orleans Chapter's annual golf tournament and the first-ever LRA Culinary Classic Sprint. One event you won't want to miss is the **President's Grand Reception & Awards Banquet**, which will be held at the Westin Canal Place on Sunday, August 8. It is on this night that the LRA bestows its most prestigious honors: *Restaurateur of the Year, Hall of Fame and Distinguished Service Awards, Active and Associate Members of the Year, Chapter and Chapter President of the Year*. Come join other members and friends from around the state for this elegant evening of exquisite cuisine, honoring outstanding members of Louisiana's foodservice industry.

I am pleased to announce that we will have our most extensive educational seminar schedule ever at this year's show. The diverse listing has something for everyone and will certainly draw many to the show. All seminars will be free of charge with expo registration. We will again be offering at this year's show the Foodservice Management Professional (FMP) Certification.

Expo '93 represents an outstanding opportunity. It's a unique showcase where you can see your peers, exchange ideas and benefit from an interchange of experiences. Expo is the symbol of our industry at its best and at the same time, it is our working platform for advancing the foodservice industry as a collective force.

Sincerely,

Jim

NEWSLETTER HIGHLIGHTS

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EDITOR'S NOTE: BECAUSE OF THE TIME REQUIRED TO PRINT *HOSPITALITY NEWSLINE*, THE STATUS OF VARIOUS ISSUES DISCUSSED MAY HAVE CHANGED BY THE TIME THE NEWSLETTER REACHES OUR MEMBERS. OUR GOAL IS TO PROVIDE ACCURATE AND AUTHORITATIVE INFORMATION, ALTHOUGH THE LRA IS NOT ENGAGED IN RENDERING LEGAL OR ACCOUNTING SERVICES. IF LEGAL OR OTHER EXPERT ASSISTANCE IS REQUIRED, THE SERVICES OF A COMPETENT PROFESSIONAL PERSON SHOULD BE SOUGHT.

PRESIDENT'S TAX PLAN SQUEAKS BY IN SENATE; NOW HEADED FOR CONFERENCE COMMITTEE

President Clinton's \$500 billion tax plan, which includes a reduction in the business meal deductibility from 80% to 50%, passed the Senate on Friday, June 25. The bill passed by the slimmest of margins 50 - 49, with Vice President Gore casting the tie-breaking vote.

Senator J. Bennett Johnston voted against the bill, while Senator John Breaux voted for the tax measure. Earlier in the month LRA members held meetings with Johnston's staffers in his three Louisiana district offices in Shreveport, Baton Rouge and New Orleans. Those meetings proved to be successful as restaurateurs convinced the Senator of the ramifications the tax plan would have on the industry. LRA members made a strong case against the reduction arguing that it would cost Louisiana nearly 3,000 jobs. In addition, if restaurant sales drop and employees lose their jobs, personal income tax and business taxes paid to city and state governments will decrease as well. In Louisiana alone, business meals account for \$522 million of all restaurant sales (\$3.2 billion in total). The reduction of the deductibility of business meals would result in a decrease of \$52 million in sales. Nationally, the reduction would mean a loss of \$3.76 billion.

NRA economists also foresee fiscal woes for state and local governments as a result of the President's proposal.

Currently, Louisiana has a four percent sales tax on restaurant meals. Individual cities within the state levy a second sales tax, ranging from 3 to 5 1/2 percent. A decrease in restaurant sales due to a reduction in business meals would mean a decrease in tax revenues. Faltering tax revenue would add to the state deficit and to the deficit many local governments are experiencing.

The tax bill, however, is far from being final, since the House and Senate will have to undergo lengthy negotiations to reconcile their differing versions of the legislation. According to reports from some Capitol Hill insiders, the business-meal provision has a chance of being modified during these negotiations.

BE SURE TO VISIT THE LRA BOOTH AT THIS YEAR'S EXPO

The LRA is busy gearing up for what promises to be our biggest and best Expo to date. While you're at the Expo, be sure to visit the LRA booth for complete information on all of the association's services and programs including a few exciting new programs that will be introduced at the Expo.

Education First Program - We will kick off the Education First Program at a press conference just before the opening ceremonies on Saturday, August 7. The Education First Program is a vehicle that will help create and build a partnership between the foodservice industry and youth education. If you are interested and want to know more about the program, just stop by the LRA booth. The

program materials will be available for a cost of only \$10.00

Association Distributor Program - The LRA will now have the opportunity to offer our members superior educational and training materials from the Education Foundation of the National Restaurant Association at - **discounted prices!** The Association Distributor Program will drastically discount products from the Foundation's retail prices on:

- *Videos and video programs*
- *Manager Training Kits*
- *Manager Handbooks, Employee Guides and other written materials*
- *Reference books*

In addition to the aforementioned new programs, the LRA booth will contain information on all LRA services

HOW TO GET THE MOST OUT OF YOUR VISIT TO THE EXPO

The Louisiana Foodservice & Hospitality Exposition running August 7, 8 and 9 at the New Orleans Convention Center offers you a great opportunity. At the expo you will see the latest in equipment, furnishings, services and products for the hospitality industry, but...you have to have a plan of action. With so much to see and absorb, veteran show-goers suggest a smart strategy for organizing your time at the event. If you don't, you will miss the opportunity to see and learn all that you can during the three day expo. So here it is.....

The "How To See The Expo Like A Veteran" Checklist

- 1 Have a specific goal in mind
- 2 Be sure to review those exhibitors who are offering "Show Specials" and "New Products"
- 3 Review the floorplan of the Expo (one is available in the Show Directory)
- 4 Bring supplies so that you can take notes
- 5 Don't rush - give the exhibits the time they require
- 6 Do not load up with too much product literature
- 7 Attend the educational seminars
- 8 Relax and enjoy yourself

The Louisiana Foodservice & Hospitality Exposition allows you the opportunity to see what's new in your industry and make your operations more cost-effective. You can add to that appeal with a little advanced planning and a sound Expo-visit strategy.

P.S. No children under 18 will be allowed into the show. And, wear comfortable shoes.

*It pays to
Advertise in
a la Carte*

FOOD & DRUG ADMINISTRATION REVOKES RESTAURANT EXEMPTION ON MENU LABELING

The Food and Drug Administration (FDA) has announced it will revoke a decision by the Bush Administration to exempt restaurant menus from new food labeling laws regarding nutrient content and health claims.

The restaurant industry is very disappointed with this last-minute reversal, especially since we had hoped FDA would work with us to develop a lexicon of nutritional terms that apply to menu items yet are still compatible with the terms used on packaged retail foods. Instead, FDA is simply imposing on us regulations expressly written for standardized supermarket products. FDA spent years researching the cost and effectiveness of labeling on packaged foods, and no time at all on menu-specific research. A restaurant meal can have significant variations from day to day, depending on available ingredients, and even from serving to serving. In effect, these regulations put a straightjacket on the chef.

To call a dish "reduced" or "less" under the current regulations, a restaurant would have to show that it contained 25 percent less of a nutrient or calories per 100 grams when compared to a "reference food." But there are no reference foods in restaurants. Unlike supermarkets, where a full-fat product sits on the shelf next to its reduced fat counterpart, there is no recognized

standard of comparison in the restaurant industry. Chefs don't formulate an entree to have a "reduced fat" version. They will create a completely new dish from scratch.

What about the single-unit "mom and pops" that make up more than three-quarters of our industry? How are they going to calculate 25 percent less of something per 100 grams? The end result is that they will drop health claims from their menus altogether making the American consumer less able to make informed choices when eating out than before.

STATE WARNS CRAWFISH PACKERS, FINES NEXT

Four crawfish packers have received warnings from state officials that their goods had better measure up the next time they're checked. Fines of \$500 per package will be levied next.

You may recall that Act 804 of 1991 gives the Commissioner of Agriculture the authority to assess civil penalties for violations of weights and standards for oysters, crawfish, shrimp and other commodities. The fine of up to \$500 is not per total violation; it is per each shorted package. So 100, one-pound packages of crawfish that don't measure up could net a packer a fine of up to \$50,000. Also, the department seizes the goods. This law now makes it easier to enforce the discrepancies restaurants are finding in their orders and the actual merchandise received, resulting in reduced losses to the restaurant. Act 804 was a legislative priority of the

association in 1991.

Three of the packers are located in Acadiana with the fourth being located in the New Orleans area. Three of the four violations were in Lafayette grocery stores.

The four of 18 processors' goods didn't measure up in late April when state Agriculture and Forestry department officials checked crawfish packages weighed on 47 retail locations' shelves in Southwest Louisiana. Altogether 5,215 pounds of crawfish was weighed a second time in late April, this time by the department's Weights and Measures police. Packages containing a total 3,802 pounds measured up. The remaining 1,413 pounds, or 27 percent, didn't, according to a state report. The goods were immediately removed from the shelves.

According to Larry Michaud, state department spokesman, "Shorting has been a common problem since packing depends on water and sometimes isn't by the pound but by the number of the product instead, such as shrimp." The warning letters are to notify processors of the new enforcement. "We're not going to tolerate that kind of activity," Michaud went on to say.

If you have a shortage to report call the state department at 504/925-3780. Michaud mentioned that those who have been frustrated in the past should give the state a second chance.

NO DEDUCTIONS FOR "LOBBYING", INCLUDING ASSOCIATION DUES

Also hidden in the President's tax plan is a provision which would not allow businesses to deduct expenditures for "lobbying activities". You could not deduct expenses for travelling to Washington D.C. to discuss the plan with your Congressman. And the portion of your LRA membership dues that is expended by the association for "lobbying" -- including analyzing legislation, mailing this newsletter, as well as lobbying in Washington or Baton Rouge or your local city hall -- would be non-deductible to you. LRA would be required to inform you of the portion of dues for "lobbying" activities, and you would need to reduce your deductible expenses accordingly.

This is a power-grab, pure and simple. It's an elitist proposal which will disenfranchise business owners and consolidate power within the legislature, their staffs and bureaucrats. If you need to fight a government proposal against your business, you'll be taxed on your efforts.

SEAFOOD SURVEY TO BE CONDUCTED

Fisheries Information & Seafood Harvest Inquiry Enterprises (FISHIE) is conducting a survey for the U.S. Department of Energy to study the effects of oil and gas structures on the inshore and offshore coastal waters and fisheries in Louisiana and Texas. One phase of the study involves analyzing the

collection, distribution, and consumption patterns of saltwater seafood caught from the coastal regions of Louisiana and Texas. Surveys are being conducted of commercial/recreational fishermen, wholesalers, processors, retailers, as well as restaurants.

Upon completion of the project, the findings of the study will be made available to all those participating. Prior to the completion of the study, preliminary results will also be made available to respondents of the survey questionnaire. Restaurateurs may find the results useful, e.g. types of seafood which are most popular or the most common method of preparation. To obtain an accurate description of the seafood consumption pattern, assistance is needed from LRA members. Please take time to fill out the enclosed questionnaire.

If you have any questions on the study, please contact Mr. Fred Schultz of FISHIE at 504/831-2099

GET YOUR TICKETS EARLY

Get your tickets early for this year's **President's Grand Reception & Awards Banquet**, to be held at the Westin Canal Place on Sunday evening, August 8. It is at this banquet that the Louisiana Restaurant Association will bestow its most prestigious honors including *Restaurateur of the Year*, *Hall of Fame and Distinguished Service Awards*, *Active and Associate Members of the Year*, *Chapter and Chapter President of the Year*.

Put on your dancing shoes and come prepared for Na Na Sha, a 12 - piece 50s and 60s show and dance band. To make your reservations, call 504/831-7788 or 800/256-4572. Tickets are \$40.00 per person or \$400.00 for a table of ten, with cocktails at 6:00 p.m. and dinner starting promptly at 7:00. Black tie will be optional.

UNEMPLOYMENT COMPENSATION TAX SET TO EXPIRE....MAYBE

For the past six years, you have been paying a special unemployment compensation (UC) tax at an annual rate of 1.4 percent on the first \$15,000 of wages paid to each of your employees. As you are aware, this tax is to pay off the \$1 billion UC bond issue of 1987, and it will end after the second quarter of this year.

The state UC law permits the Department of Labor to adjust the taxable wage base on which the 1.4 percent rate is assessed to collect no less than an amount necessary to pay the bonds which remain outstanding. However, the Governor and Department of Labor have elected not to reduce the taxable wage base, which will result in an overcollection of the second quarter's tax by approximately \$50 million.

They even introduced a bill this session to place this \$50 million overcollection in a special account in order to use the interest accruing from it to fund unspecified "training and re-employment programs." With your help, we were able to stop the bill, thereby removing any

incentive the Governor and Department had for overcollecting the tax.

Unfortunately, the Department of Labor responded by expediting its mailing of the assessment notices, and you probably already received yours. However, payment of the assessment is not due until July 31, 1993, and it is still possible for the Department of Labor to mail a corrected assessment notice with an adjusted taxable wage base figure.

Letters to the Governor from you and other employers around the state stating your indignation at this unnecessary confiscation of your money could yet persuade him to change his position on overcollecting the tax. Please write the Governor and demand that he direct the Department of Labor to correct the assessment notice to collect only an amount necessary to pay off the bonds. It is only through a strong grassroots effort of this magnitude that you have any hope of retaining your hard-earned dollars.

SIN TAX WILL RESULT IN FEWER JOBS

Louisiana will have 2,300 fewer jobs and nationally 180,000 jobs will be lost if the proposed "Sin tax" wins approval, according to David Wyss, research director for DRI/McGraw-Hill of Lexington, Mass. DRI/McGraw-Hill recently completed a study of the sin tax for the beer industry.

President Clinton has discussed the tax increase on several occasions as a possible way of financing a federal

healthcare program.

The current federal tax on a six-pack of beer is 33 cents, which was doubled in 1991 from 16 cents. The latest tax boost could impose another 48 cents on a six-pack, bringing the federal tax to 81 cents. The higher tax would create annual revenue of \$4.4 billion.

Beer taxes are among the most regressive of all taxes, hitting the lower- and middle-income taxpayers - those least able to pay - the hardest. The 1991 tax increase on beer cost the country an estimated 30,000 beer-industry jobs.

FIRST LRA SANITATION CERTIFICATION SUCCESSFUL; ROOM STILL AVAILABLE FOR NEXT SESSION

The LRA recently held the first class of the initial three-day sanitation course in Metairie and there's every indication that it was a resounding success. The ServSafe sanitation course that has been developed by the Educational Foundation of the National Restaurant Association was presented to 25 LRA members who learned valuable information on sanitation practices from purchasing, storing and food preparation, to service. The course is based on the *Applied Foodservice Sanitation, Fourth Edition* text.

There is still plenty of room available in the Baton Rouge classes to be held at the Ralph & Kacoo's on Bluebonnet July 14, 21 & 28 from 1 p.m. until 5 p.m. Also, the association will be holding classes in

Monroe. The classes will be held Sunday, July 18 from 1:00 p.m. until 5:00 p.m. and Monday July 19 and Tuesday July 20 either from 9:00 a.m. until 1:00 p.m. or 2: p.m. until 6:00 p.m. To register or if you have any questions, please call Director of Education Mary Weber at 504/831-7788 or 800/256-4572.

Education and training contributes to growth of the foodservice industry as well as the personal and professional growth of the employees.

LRA CREDIT CARD ACCEPTANCE PROGRAM ANNOUNCES NEW RATES

CNET Card Acceptance Services, the official company of the LRA Credit Card Program, recently announced a new rate schedule for Louisiana. The new rates are designed with the low to mid range restaurant in mind. Effectively immediately, there is a new tier to the MasterCard/Visa rate grid. The new tier is:

- Average ticket of \$0.00 to \$19.99
= 2.99%

Currently the grid starts at "\$15.99 to \$19.99". That has been replaced by the new tier. Additionally, CNET has lowered the rate from 3.09% to 2.99%

For additional information concerning the LRA Credit Card Program, contact Eric Minshew at 504/831-7896 or stop by the CNET booth at the Louisiana Foodservice & Hospitality Expo at the New Orleans Convention Center, August 7, 8 and 9.

1993 Louisiana Foodservice & Hospitality Exposition August 7, 8 and 9 New Orleans Convention Center

CALENDAR OF SPECIAL EVENTS

AUGUST 5

9TH ANNUAL NORA
GOLF TOURNAMENT,
EASTOVER COUNTRY CLUB

AUGUST 7-9

40TH ANNUAL LOUISIANA
FOODSERVICE &
HOSPITALITY EXPOSITION,
NEW ORLEANS

AUGUST 8

CULINARY CLASSIC SPRINT,
MORIAL CONVENTION CENTER,
NEW ORLEANS

SEPTEMBER 13-15

NRA PUBLIC AFFAIRS CONFERENCE,
WASHINGTON, D.C.

ALONG THE BAYOU

***Slidell has been chosen as the site of the 1993 Dizzy Dean World Series. The series will bring over 2,000 people to the area between July 23 and July 29. The estimated economic impact on area restaurants will be approximately \$225,000.

***While the President likes to point to Canada when talking about a model for the U.S. healthcare system, he might want to look there for a federal budget. The Canadian government left the business meal deductibility at 80% in its recently passed budget. In addition to the deductibility remaining at 80%, the budget contained no new taxes, no increased taxes and a reduction of costs for government programs. (Is Reagan living in the Great White North?)

***The Rotary Club of New Orleans will be presenting its 5th Annual Waiter of the Year Award this August. If you have someone you'd like to nominate, call Meg or Lloyd at the LRA office at 504/831-7788. Nominations must be received by July 23.

***Pursuant to By-Law 6, Section 1 of the By-Laws of the Louisiana Restaurant Association, please be advised of the annual meeting of the Members of the Corporation scheduled for Sunday, August 8, 1993 at 3:00 p.m. at the New Orleans Convention Center. Keynote speaker for the meeting will be Ron Magruder, president of Olive Garden Restaurants. Please show support for your association by making every effort to attend.

YOUR NEWS IS GOOD NEWS

The **ACADIANA CHAPTER** held its June meeting at Bertrand's Riverfront Restaurant in Abbeville. Legislative Committee Chairman Charlie Goodson gave a complete recap of the 1993 legislative session.

The **GREATER BATON ROUGE CHAPTER** held its June meeting at Hunan Chinese Restaurant. Davis Rhorer, Director of the Baton Rouge Downtown Development District was the guest speaker.

The **NEW ORLEANS/NORTHSHORE CHAPTERS** held a "Family Day Picnic" at Ahmeek (The Blitch family home) in Abita Springs on Sunday June 6. Over 100 members and their families enjoyed outdoor activities such as swimming, boating, tennis, volleyball and a few mean games of bacci ball. Barbecued hamburgers, hotdogs and sausage were cooked by LRA architect Ron Blitch.

The **NORTHEAST CHAPTER** held its June meeting at Red Lobster Restaurant in Monroe. Nolan Sharon of Laboratory Specialists, Inc. explained the variety of assistance available through the association and LSI to start and implement the Drugfree Workplace Program. Russ Bergeron of the Department of Immigration and Naturalization addressed the group on the federal requirements and the regulations concerning I-9 form documentation.

The **NORTHSHORE CHAPTER** held its June meeting at Zazou Cafe in Mandeville. Bill Oiler, Consultant for the Rails and Trails Conversion discussed the economic impact on St. Tammany restaurants and businesses.

The **NORTHWEST CHAPTER** held its June meeting at Kon Tiki in Shreveport. LRA EVP Jim Funk gave a recap of the 1993 Legislative Session and discussed current federal issues.

*Au
Revoir*

UTTIN'
ON
THE
RITZ

AUG. 7

AUG. 8

AUG. 9

1993

New Orleans
Convention Center

DATA APPENDIX 1

Tabulated Survey Responses

Reference Figure 5.1. Frequency distribution of category fished for Louisiana recreational fishermen.

CATEGORY FISHED	NUMBER
Finfish	513
Shrimp	13
Crab	14
Oyster	2

Reference Figure 5.2. Frequency distribution of types of fishing licenses for Louisiana recreational fishermen.

TYPE OF FISHING LICENSE	NUMBER
In-State	465
Out-of-State	9
Both	30

Reference Figure 5.3. Frequency distribution of race for Louisiana recreational fishermen.

RACE	NUMBER	RACE	NUMBER
Black	32	Oriental	1
Hispanic	0	White	438
Native American	1	Other	2

Reference Figure 5.4. Frequency distribution of fishing mode for Louisiana recreational fishermen.

FISHING MODE	NUMBER
Other than Boat	42
Private Boat Inshore	408
Private Boat Offshore	193
Charter Boat	18

Reference Figure 5.5. Frequency distribution of fishing zones for Louisiana recreational fishermen.

ZONE	NUMBER	ZONE	NUMBER
I	97	VI	98
II	150	VII	3
III	133	VIII	0
IV	154	IX	0
V	86		

Reference Figure 5.6. Frequency distribution of fishing location for Louisiana recreational fishermen.

FREQUENCY OF FISHING LOCATION	NUMBER
Inshore	403
< 4.8 km (3 mi) Offshore	44
4.8 to 16 km (3 to 10 mi) Offshore	77
> 16 km (10 mi) Offshore	152

Reference Figure 5.7. Frequency distribution of trips in proximity to oilfield structures for Louisiana recreational fishermen.

PROXIMITY	NUMBER
< 300 m (1000 ft)	262
300 m to 0.8 km (1000 ft to 0.5 mi)	82
0.8 to 1.6 km (0.5 to 1 mi)	93
> 1.6 km (1 mi)	249

Reference Figure 5.8. Average number of shellfish and finfish species caught by Louisiana recreational fishermen over a six month period.

NUMBER CAUGHT	RESPONSES	NUMBER CAUGHT	RESPONSES
<u>Shrimp</u>		<u>Black Drum</u>	
600	1	1	31
<u>Crab</u>		2	16
10	1	3	13
<u>Oyster</u>		4	9
0	0	5	13
<u>Amberjack</u>		6	10
1	5	8	1
2	8	10	10
3	7	12	1
4	1	15	4
5	1	20	1
6	4	30	5
8	1	40	1
9	1	45	1
10	6	50	1
12	2	1000	1
15	1	<u>Croaker</u>	
17	1	1	7
20	3	2	7
21	1	3	6
25	1	4	3
28	1	5	5
40	1	6	8
50	1	8	1
200	1	10	12

Reference Figure 5.8. Average number of shellfish and finfish species caught by Louisiana recreational fishermen over a six month period.

NUMBER CAUGHT	RESPONSES	NUMBER CAUGHT	RESPONSES
<u>Croaker</u>		<u>Flounder (continued)</u>	
12	5	18	1
15	3	20	10
20	1	25	4
24	1	30	6
25	2	35	1
30	4	40	1
30	2	50	3
40	2	60	1
45	1	70	1
50	3	75	1
75	1	100	1
100	1	150	1
260	1	240	1
<u>Dolphin</u>		<u>Grouper</u>	
1	5	1	8
3	4	2	4
4	2	3	3
5	4	4	4
6	1	6	1
7	1	8	1
8	1	10	2
10	8	12	3
15	2	22	1
20	3	30	3
30	3	<u>Kingfish</u>	
48	1	1	1
50	3	2	1
60	2	3	1
100	1	4	1
200	1	10	1
<u>Flounder</u>		16	1
1	21	20	1
2	34	25	1
3	27	<u>King Mackerel</u>	
4	23	1	5
5	23	2	11
6	21	3	3
7	3	4	1
8	6	5	3
10	21	6	1
11	2	7	1
12	9	8	1
15	8	9	1

Reference Figure 5.8. Average number of shellfish and finfish species caught by Louisiana recreational fishermen over a six month period.

NUMBER CAUGHT	RESPONSES	NUMBER CAUGHT	RESPONSES
<u>King Mackerel</u>		<u>Redfish</u> (continued)	
10	4	70	3
12	1	75	2
14	1	80	1
15	5	100	9
20	1	108	1
30	5	150	5
40	1	200	4
50	2	250	1
85	1	300	2
100	3	400	2
120	1	<u>Red Snapper</u>	
150	1	1	2
<u>Redfish</u>		2	5
1	16	3	1
2	12	4	2
3	19	5	2
4	11	6	4
5	35	7	6
6	14	8	3
7	7	10	9
8	13	12	3
10	38	14	3
11	1	15	7
12	16	16	2
14	1	18	1
15	32	20	6
16	1	21	1
17	2	24	1
18	2	25	3
20	40	28	2
25	11	29	1
26	1	30	2
28	2	35	6
30	28	40	4
33	1	42	1
35	10	50	5
36	1	60	3
40	6	65	1
45	3	70	1
50	16	80	3
55	1	84	2
56	1	90	1
60	14	100	7

Reference Figure 5.8. Average number of shellfish and finfish species caught by Louisiana recreational fishermen over a six month period.

NUMBER CAUGHT	RESPONSES	NUMBER CAUGHT	RESPONSES
<u>Red Snapper</u>		<u>Sheepshead (continued)</u>	
105	2	200	1
120	1	<u>Spanish Mackerel</u>	
130	1	1	8
200	1	2	7
250	1	3	1
280	1	4	4
400	1	5	8
500	1	6	4
1000	1	8	1
<u>Shark</u>		10	11
1	11	12	4
2	10	13	1
3	5	15	7
4	2	20	1
5	3	24	1
6	1	25	2
10	3	30	1
15	1	50	1
20	3	150	1
25	13	200	1
50	2	250	1
60	1	<u>Speckled Trout</u>	
64	1	1	5
100	2	2	9
<u>Sheepshead</u>		3	7
1	16	4	7
2	22	5	8
3	17	6	3
4	4	7	2
5	5	8	6
6	7	10	17
7	1	11	2
8	2	12	12
9	2	13	1
10	18	15	17
12	6	16	4
15	5	20	24
18	1	24	1
20	5	25	18
25	2	26	1
30	1	28	1
40	1	30	23
100	1	32	1

Reference Figure 5.8. Average number of shellfish and finfish species caught by Louisiana recreational fishermen over a six month period.

NUMBER CAUGHT	RESPONSES	NUMBER CAUGHT	RESPONSES
<u>Speckled Trout</u>		<u>Tuna (continued)</u>	
35	7	120	1
40	8	150	1
43	2	<u>Vermilion Snapper</u>	
50	32	1	2
60	6	4	1
65	1	5	1
70	1	10	4
75	11	12	2
80	6	20	1
85	1	40	2
95	1	50	2
100	25	<u>Other</u>	
120	3	1	10
125	6	2	5
140	1	3	8
150	18	4	2
160	1	5	5
175	2	7	2
200	29	8	4
250	9	9	1
275	1	10	5
300	8	12	3
340	1	14	1
400	4	15	2
450	1	19	1
500	4	20	5
600	1	21	1
730	1	25	2
2000	1	30	3
<u>Tuna</u>		35	2
1	10	40	3
2	4	50	3
3	3	56	1
4	1	60	2
5	2	80	1
6	1	90	1
7	1	100	3
10	4	102	1
13	1	145	1
14	1	150	2
36	1	245	1
80	1		
100	1		

Reference Figure 5.9. Estimates of average weight of shellfish and finfish species caught by Louisiana recreational fishermen over a six month period.

POUNDS CAUGHT	RESPONSES	POUNDS CAUGHT	RESPONSES
<u>Shrimp</u>		<u>Dolphin (continued)</u>	
1	1	10	2
5	1	20	1
6	1	30	1
10	2	50	1
15	1	80	1
20	1	100	2
30	3	<u>Flounder</u>	
40	2	3	1
50	3	4	1
60	2	5	2
75	1	5	1
100	3	7	1
150	1	10	5
700	1	20	3
1000	2	28	1
2000	1	30	1
<u>Amberjack</u>		50	1
5	1	60	1
30	2	<u>Grouper</u>	
42	1	10	1
60	2	28	1
80	1	40	1
100	1	50	3
150	1	150	1
200	3	<u>Kingfish</u>	
300	1	150	1
400	1	<u>King Mackerel</u>	
600	1	20	1
<u>Black Drum</u>		25	1
10	2	30	1
20	1	35	1
25	2	100	2
40	1	125	1
50	1	150	1
100	2	200	1
<u>Croaker</u>		<u>Redfish</u>	
2	1	4	1
3	1	10	2
4	1	12	1
10	3	15	1
30	1	20	1
<u>Dolphin</u>		25	1
7	1	30	2

Reference Figure 5.9. Estimates of average weight of shellfish and finfish species caught by Louisiana recreational fishermen over a six month period.

POUNDS CAUGHT	RESPONSES	POUNDS CAUGHT	RESPONSES
40	1	<u>Spanish Mackerel</u>	
43	1	2	1
45	1	7	1
50	4	10	1
60	1	15	1
75	1	20	2
100	6	40	1
150	1	50	2
200	2	100	1
300	2	<u>Speckled Trout</u>	
<u>Red Snapper</u>		5	2
8	2	10	1
13	1	20	3
15	1	50	1
30	3	55	1
45	1	60	1
50	2	75	3
100	5	90	1
150	1	100	6
175	1	120	1
200	2	160	1
350	1	200	3
1000	2	251	1
8000	1	300	1
<u>Shark</u>		<u>Tuna</u>	
15	1	36	1
20	1	80	1
25	1	100	1
26	1	400	2
50	2	<u>Vermilion Snapper</u>	
60	1	3	1
75	1	10	1
100	2	20	3
<u>Sheepshead</u>		<u>Other</u>	
2	1	30	1
5	1	47	1
10	1	60	3
20	1	65	1
25	1	70	1
30	1	87	1
100	3	100	1
120	1	129	1
		300	1
		350	1

Reference Figure 5.9. Estimates of average weight of shellfish and finfish species caught by Louisiana recreational fishermen over a six month period.

POUNDS CAUGHT	RESPONSES	POUNDS CAUGHT	RESPONSES
400	1		
500	2		
2000	1		

Reference Figure 5.10. Average percentage of shellfish and finfish species kept for personal use by Louisiana recreational fishermen.

NUMBER KEPT	RESPONSES	NUMBER KEPT	RESPONSES
<u>Shrimp</u>		<u>Croaker</u> (continued)	
10	1	20	1
20	1	25	2
30	1	30	1
33	1	50	4
50	1	60	1
75	1	90	1
100	21	100	62
<u>Crab</u>		<u>Dolphin</u>	
50	1	25	2
100	16	50	7
<u>Oyster</u>		70	1
0	0	90	1
<u>Amberjack</u>		100	36
0	4	<u>Flounder</u>	
10	1	0	7
20	2	10	5
25	1	15	1
35	1	20	2
50	8	25	2
75	1	30	1
90	2	50	15
100	40	60	1
<u>Black Drum</u>		70	1
0	7	75	2
5	1	80	3
20	1	90	2
25	2	100	183
50	8	<u>Grouper</u>	
70	1	0	2
90	4	5	1
100	94	10	1
<u>Croaker</u>		25	1
0	7	35	1
5	1	50	4
10	2	60	1

Reference Figure 5.10. Average percentage of shellfish and finfish species kept for personal use (continued) by Louisiana recreational fishermen.

NUMBER KEPT	RESPONSES	NUMBER KEPT	RESPONSES
70	1	<u>Red Snapper (continued)</u>	
90	1	100	87
100	24	<u>Shark</u>	
<u>Kingfish</u>		5	1
50	1	25	1
100	8	35	1
<u>King Mackerel</u>		50	5
0	3	80	1
20	2	90	1
25	1	100	38
35	1	<u>Sheepshead</u>	
50	11	5	1
70	2	20	1
75	1	25	2
80	1	50	8
100	34	75	2
<u>Redfish</u>		80	1
0	6	100	98
5	1	<u>Spanish Mackerel</u>	
10	5	5	1
20	1	20	1
25	6	25	1
30	1	35	1
40	1	50	7
50	34	75	1
60	1	100	54
70	2	<u>Speckled Trout</u>	
75	9	5	3
80	8	10	3
90	7	15	1
100	293	20	5
<u>Red Snapper</u>		25	7
0	7	30	2
5	2	33	1
10	1	35	1
20	3	40	1
25	3	50	37
35	1	60	2
50	10	70	2
60	1	75	7
70	2	80	5
75	5	90	9
80	1	100	259
90	2		

Reference Figure 5.10. Average percentage of shellfish and finfish species kept for personal use (continued) by Louisiana recreational fishermen.

NUMBER KEPT	RESPONSES	NUMBER KEPT	RESPONSES
<u>Tuna</u>		<u>Other</u>	
5	1	1	1
15	1	3	1
20	1	5	1
25	1	20	4
50	8	25	1
70	1	35	1
80	1	50	6
100	21	60	1
<u>Vermilion Snapper</u>		75	1
5	1	90	1
25	1	100	67
50	5		
70	1		
100	10		

Reference Figure 5.11. Percentage of finfish parts consumed by Louisiana recreational fishermen.

FINFISH	# MEAT	# SKIN & MEAT	FINFISH	# MEAT	# SKIN & MEAT
Amberjack	61	3	Red Snapper	118	12
Black Drum	112	11	Shark	50	2
Croaker	73	12	Sheepshead	114	7
Dolphin	47	3	Spanish Mackerel	64	8
Flounder	222	30	Speckled Trout	349	36
Grouper	33	2	Tuna	38	1
Kingfish	8	0	Vermilion Snapper	20	1
King Mackerel	55	5	Other	73	4
Redfish	343	46			

Reference Figure 5.12. Frequency distribution of cooking methods used by Louisiana recreational fishermen.

COOKING METHOD	NUMBER	COOKING METHOD	NUMBER
Baked	268	Grilled	219
Barbecued	167	Smoked	36
Blackened	88	Stew/Soup	33
Boiled/Poached	25	Other	36
Fried	456		

Reference Figure 5.13. Frequency distribution of category fished for Texas recreational fishermen.

CATEGORY FISHED	NUMBER
Finfish	381
Shrimp	5
Crab	7
Oyster	1

Reference Figure 5.14. Frequency distribution of types of fishing licenses for Texas recreational fishermen.

TYPE OF FISHING LICENSE	NUMBER
In-State	350
Out-of-State	23
Both	3

Reference Figure 5.15. Frequency distribution of race for Texas recreational fishermen.

RACE	NUMBER	RACE	NUMBER
Black	4	Oriental	0
Hispanic	18	White	323
Native American	1	Other	0

Reference Figure 5.16. Frequency distribution of fishing mode for Texas recreational fishermen.

FISHING MODE	NUMBER
Other than Boat	39
Private Boat Inshore	213
Private Boat Offshore	199
Charter Boat	25

Reference Figure 5.17. Frequency distribution of fishing zones for Texas recreational fishermen.

ZONE	NUMBER	ZONE	NUMBER
I	2	VI	22
II	1	VII	160
III	2	VIII	165
IV	1	IX	95
V	1		

Reference Figure 5.18. Frequency of distribution of fishing location for Texas recreational fishermen.

FREQUENCY OF FISHING LOCATION	NUMBER
Inshore	223
< 4.8 km (3 mi) Offshore	15
4.8 to 16 km (3 to 10 mi) Offshore	43
> 16 km (10 mi) Offshore	186

Reference Figure 5.19. Frequency distribution of trips in proximity to oilfield structures for Texas recreational fishermen.

PROXIMITY	NUMBER
< 300 m (1000 ft)	188
300 m to 0.8 km (1000 ft to 0.5 mi)	82
0.8 to 1.6 km (0.5 to 1 mi)	77
> 1.6 km (1 mi)	224

Reference Figure 5.20. Average number of shellfish and finfish species caught by Texas recreational fishermen over a six month period.

NUMBER CAUGHT	RESPONSES	NUMBER CAUGHT	RESPONSES
<u>Shrimp</u>		<u>Amberjack</u> (continued)	
0	0	70	1
<u>Crab</u>		75	2
48	2	150	2
84	1	<u>Black Drum</u>	
120	1	1	13
240	1	2	3
360	1	3	2
<u>Oyster</u>		4	5
48	1	5	2
<u>Amberjack</u>		6	3
1	10	10	3
2	7	12	4
3	2	19	1
4	2	20	1
5	2	25	1
6	1	<u>Croaker</u>	
7	1	1	1
10	1	2	3
11	1	3	1
12	1	4	1
12	1	5	4
15	1	6	4
20	3	10	3
25	1	15	1
50	2	20	1

Reference Figure 5.20. Average number of shellfish and finfish species caught by Texas recreational fishermen over a six month period.
(continued)

NUMBER CAUGHT	RESPONSES	NUMBER CAUGHT	RESPONSES
<u>Croaker</u>		<u>Grouper</u>	
30	3	1	4
40	2	3	2
90	1	4	1
100	1	5	3
<u>Dolphin</u>		30	1
1	10	<u>Kingfish</u>	
2	15	1	4
3	9	2	10
4	4	3	2
5	6	4	1
6	1	5	1
10	4	6	7
12	1	7	1
15	5	8	2
18	2	9	1
20	7	10	4
25	2	12	1
30	1	20	2
50	1	25	1
60	1	30	1
70	1	40	2
100	2	50	1
200	1	60	1
300	1	324	1
400	1	500	1
500	1	<u>King Mackerel</u>	
<u>Flounder</u>		1	4
1	12	2	7
2	16	3	6
3	12	4	6
4	5	5	5
5	7	6	9
6	14	8	2
7	5	9	1
8	3	10	6
10	10	12	1
15	4	15	2
18	1	20	2
20	9	30	1
25	2	40	3
30	1	50	3
40	3	72	1
80	1	100	1
100	2		

Reference Figure 5.20. Average number of shellfish and finfish species caught by Texas recreational fishermen over a six month period.

NUMBER CAUGHT	RESPONSES	NUMBER CAUGHT	RESPONSES
<u>King Mackerel</u>		<u>Red Snapper (continued)</u>	
250	1	17	1
500	1	20	5
<u>Redfish</u>		21	1
1	12	28	3
2	24	29	1
3	13	30	1
4	5	40	1
5	2	50	3
6	15	60	3
7	4	70	1
8	10	100	3
9	1	120	3
10	14	126	1
12	7	140	2
15	6	150	1
16	1	175	2
18	1	200	2
20	17	210	1
25	3	300	2
30	10	364	1
36	1	560	1
40	4	600	1
50	4	800	1
70	1	864	1
75	1	1000	2
80	2	2000	1
100	4	<u>Shark</u>	
150	2	1	16
350	1	2	12
<u>Red Snapper</u>		3	5
1	6	4	4
2	5	5	3
3	4	6	4
4	4	8	1
5	6	10	3
6	5	12	2
7	9	15	1
8	1	30	1
9	2	35	1
10	2	40	1
12	1	50	1
14	4	100	1
15	4		

Reference Figure 5.20. Average number of shellfish and finfish species caught by Texas recreational fishermen over a six month period.

NUMBER CAUGHT	RESPONSES	NUMBER CAUGHT	RESPONSES
<u>Sheepshead</u>		<u>Speckled Trout (continued)</u>	
1	8	26	1
3	2	30	11
4	1	35	2
5	2	36	3
6	1	40	9
10	1	50	2
12	1	55	1
20	2	60	3
<u>Spanish Mackerel</u>		65	1
1	6	70	1
2	2	75	2
3	1	80	1
4	3	90	1
5	2	100	5
10	4	120	1
15	1	130	2
20	1	150	1
30	1	200	4
35	1	300	1
40	1	400	3
50	1	500	2
80	1	<u>Tuna</u>	
<u>Speckled Trout</u>		1	5
1	7	2	2
2	2	3	1
3	3	4	3
4	4	5	2
5	6	6	2
6	14	7	2
7	3	8	7
8	9	9	1
9	1	10	2
10	15	12	1
12	10	15	2
13	1	20	1
14	1	50	1
15	8	<u>Vermilion Snapper</u>	
16	1	1	1
18	1	2	1
20	19	3	1
21	1	6	1
24	3	10	2
25	5	20	1

Reference Figure 5.20. Average number of shellfish and finfish species caught by Texas recreational fishermen over a six month period.

NUMBER CAUGHT	RESPONSES	NUMBER CAUGHT	RESPONSES
<u>Vermilion Snapper</u>		<u>Other (continued)</u>	
40	1	11	2
45	1	12	1
50	1	15	3
150	1	17	1
300	1	18	1
<u>Other</u>		20	1
1	19	25	1
2	7	30	1
3	5	36	2
4	2	40	1
5	5	50	1
6	6	90	1
7	1	100	1
8	5	700	1
10	3	1000	1

Reference Figure 5.21. Estimates of average weight of shellfish and finfish species caught by Texas recreational fishermen over a six month period.

POUNDS CAUGHT	RESPONSES	POUNDS CAUGHT	RESPONSES
<u>Shrimp</u>		<u>Amberjack (continued)</u>	
2	1	2500	1
25	1	<u>Black Drum</u>	
30	1	5	1
1500	1	6	1
<u>Amberjack</u>		10	1
3	1	50	1
10	1	200	1
20	1	400	2
23	1	<u>Croaker</u>	
35	1	2	1
50	2	5	3
65	1	10	2
125	1	12	1
150	2	60	1
200	1	<u>Dolphin</u>	
250	1	1.5	1
300	1	2	1
400	1	5	2
500	1	10	5
600	1	15	1
1000	1	20	2
1100	1	30	3

**Reference Figure 5.21. Estimates of average weight of shellfish and finfish species caught by
(continued) Texas recreational fishermen over a six month period.**

POUNDS CAUGHT	RESPONSES	POUNDS CAUGHT	RESPONSES
<u>Dolphin</u>		<u>Kingfish (continued)</u>	
50	3	240	1
60	3	300	1
75	1	350	1
80	1	500	1
100	2	<u>King Mackerel</u>	
110	1	10	1
150	1	12	1
160	1	30	1
200	3	45	1
300	1	50	2
400	1	100	3
1000	1	1000	3
<u>Flounder</u>		<u>Redfish</u>	
2	1	4	1
5	4	5	2
9	1	6	1
10	6	10	2
12	1	15	2
15	3	19	1
20	5	20	2
60	1	25	3
100	1	30	2
200	2	40	2
400	1	63	1
<u>Grouper</u>		100	6
10	2	120	2
20	1	150	1
30	1	200	2
50	3	300	2
100	1	400	1
200	1	<u>Red Snapper</u>	
<u>Kingfish</u>		7	1
8	1	10	2
10	1	20	3
15	1	30	1
20	1	35	1
25	1	40	1
30	2	50	3
40	1	60	1
50	1	75	1
75	1	85	1
100	3	100	4
200	1	150	3

Reference Figure 5.21. Estimates of average weight of shellfish and finfish species caught by (continued) Texas recreational fishermen over a six month period.

POUNDS CAUGHT	RESPONSES	POUNDS CAUGHT	RESPONSES
<u>Red Snapper</u>		<u>Speckled Trout (continued)</u>	
180	1	30	5
200	2	40	3
250	3	50	3
300	4	63	1
450	1	75	1
500	2	100	2
550	1	120	1
600	2	150	2
800	1	200	1
2500	1	400	1
17000	1		
<u>Shark</u>		<u>Tuna</u>	
10	1	14	1
14	1	20	2
30	1	25	1
35	1	30	1
80	1	50	1
100	2	100	5
126	1	160	1
150	1	200	3
300	1	250	1
		500	3
<u>Sheepshead</u>		<u>Vermilion Snapper</u>	
2	2	4	1
10	1	15	1
20	1	20	2
50	1	30	1
<u>Spanish Mackerel</u>		100	1
1	1	200	2
2	1	<u>Other</u>	
4	1	20	1
5	1	25	1
10	4	30	1
15	1	55	1
20	2	70	1
45	2	75	1
<u>Speckled Trout</u>		100	2
3	1	250	3
4	1	252	1
8	1	400	1
10	1	2100	1
15	1		
20	1		
25	1		

Reference Figure 5.22. Average percentage of shellfish and finfish species kept for personal use by Texas recreational fishermen.

PERCENT KEPT	RESPONSES	PERCENT KEPT	RESPONSES
<u>Shrimp</u>		<u>Dolphin (continued)</u>	
10	1	80	2
100	3	85	1
<u>Crab</u>		90	1
100	6	100	68
<u>Amberjack</u>		<u>Flounder</u>	
1	1	0	1
2	2	2	1
5	1	10	3
10	3	20	2
20	2	25	1
25	1	30	4
50	6	50	4
70	1	60	1
75	2	70	1
80	1	75	1
100	37	80	1
<u>Black Drum</u>		90	1
2	1	100	110
10	3	<u>Grouper</u>	
20	1	5	1
25	1	10	1
50	6	20	1
100	35	50	3
<u>Croaker</u>		100	13
0	2	<u>Kingfish</u>	
10	2	5	1
25	1	10	1
50	3	20	1
100	24	25	1
<u>Dolphin</u>		33	1
0	5	50	3
1	1	60	1
2	2	70	1
5	1	75	1
10	3	80	2
20	4	85	1
25	2	90	1
30	2	100	46
33	1	<u>King Mackerel</u>	
50	12	1	1
60	1	2	3
70	2	10	5
75	2	15	1

Reference Figure 5.22. Average percentage of shellfish and finfish species kept for personal use by Texas recreational fishermen.

PERCENT KEPT	RESPONSES	PERCENT KEPT	RESPONSES
<u>King Mackerel</u>		<u>Sheepshead</u>	
20	2	20	1
25	1	50	2
50	8	98	1
75	1	100	17
100	47	<u>Spanish Mackerel</u>	
<u>Redfish</u>		2	2
2	1	10	1
10	6	20	1
20	1	30	1
25	2	50	2
30	3	90	1
33	1	100	19
40	1	<u>Speckled Trout</u>	
50	11	2	2
60	1	10	6
70	175	20	3
75	1	25	3
80	1	30	3
90	2	33	1
100	152	40	1
<u>Red Snapper</u>		50	9
1	1	60	1
2	3	70	1
5	2	75	3
10	4	80	1
20	4	90	2
25	1	100	151
50	14	<u>Tuna</u>	
70	2	1	1
75	2	2	1
80	2	5	2
85	1	10	3
90	1	20	1
100	96	30	2
<u>Shark</u>		50	5
2	3	70	1
5	1	75	1
10	2	100	27
20	1	<u>Vermillion Snapper</u>	
50	7	2	1
75	1	10	1
85	1	20	1
100	46	50	3

Reference Figure 5.22. Average percentage of shellfish and finfish species kept for personal use by Texas recreational fishermen.

PERCENT KEPT	RESPONSES	PERCENT KEPT	RESPONSES
<u>Vermilion Snapper</u>		<u>Other (continued)</u>	
75	1	25	3
100	12	30	2
<u>Other</u>		40	1
2	2	50	3
5	1	80	1
10	2	90	1
20	2	100	66

Reference Figure 5.23. Percentage of finfish parts consumed by Texas recreational fishermen.

FINFISH	# MEAT	# SKIN & MEAT	FINFISH	# MEAT	# SKIN & MEAT
Amberjack	98	10	Red Snapper	112	25
Black Drum	33	10	Shark	50	13
Croaker	24	8	Sheepshead	14	5
Dolphin	90	18	Spanish Mackerel	25	7
Grouper	15	4	Speckled Trout	155	30
Kingfish	54	4	Tuna	30	10
King Mackerel	56	18	Vermilion Snapper	18	1
Redfish	141	39	Other	45	20

Reference Figure 5.24. Frequency distribution of cooking methods used by Texas recreational fishermen.

COOKING METHOD	NUMBER	COOKING METHOD	NUMBER
Baked	125	Fried	284
Barbecued	82	Grilled	178
Blackened	44	Smoked	28
Boiled/Poached	13	Stew/Soup	8
Broil	154	Other	15

Reference Figure 5.25. Frequency distribution of category fished for Louisiana and Texas commercial fishermen.

CATEGORY FISHED	NUMBER
Finfish	28
Shrimp	185
Crab	18
Oyster	9

Reference Figure 5.26. Frequency distribution of race for Louisiana and Texas commercial fishermen.

RACE	NUMBER	RACE	NUMBER
Black	6	Oriental	25
Hispanic	24	White	121
Native American	2	Other	9

Reference Figure 5.27. Frequency distribution of fishing zones for Louisiana and Texas commercial fishermen.

ZONE	NUMBER	ZONE	NUMBER
I	22	VI	41
II	37	VII	47
III	96	VIII	56
IV	77	IX	56
V	51		

Reference Figure 5.28. Frequency distribution of fishing location for Louisiana and Texas commercial fishermen.

FREQUENCY OF FISHING LOCATION	NUMBER
Inshore	104
< 4.8 km (3 mi) Offshore	33
4.8 to 16 km (3 to 10 mi) Offshore	55
> 16 km (10 mi) Offshore	73

Reference Figure 5.29. Frequency distribution of trips in proximity to oilfield structures for Louisiana and Texas commercial fishermen.

PROXIMITY	NUMBER
< 300 m (1000 ft)	89
300 m to 0.8 km (1000 ft to 0.5 mi)	66
0.8 to 1.6 km (0.5 to 1 mi)	57
> 1.6 km (1 mi)	60

Reference Figure 5.30. Average percentage of shellfish distribution for Louisiana and Texas commercial fishermen.

PERCENT	SHRIMP	BLUE CRAB	OYSTER
<u>Louisiana Wholesaler/Processor</u>			
6.0	1		
50.0	2	2	
70.0	1		
80.0	2		
90.0	4	2	
95.0	2		

Reference Figure 5.30. Average percentage of shellfish distribution for Louisiana and Texas commercial fishermen.
(continued)

PERCENT	SHRIMP	BLUE CRAB	OYSTER
<u>Louisiana Wholesaler/Processor</u>			
98.0	11	1	
98.5		1	
99.0	14		1
99.5	13	1	1
99.8	1		
99.9	12	2	
100.0	55	4	6
<u>Texas Wholesaler/Processor</u>			
4.5	1		
10.0	1		
50.0	2		
75.0	1		
80.0	1		
85.0	1		
90.0	1		
94.5	1		
95.0	1		
99.0	7		
99.1	1		
99.5	3		
99.9	18		
100.0	26		
<u>Total Wholesaler/Processor</u>			
4.5	1		
6.0	1		
10.0	1		
50.0	4	2	
70.0	1		
75.0	1		
80.0	3		
85.0	1		
90.0	5	2	
94.5	1		
95.0	3		
98.0	11	1	
98.5	1		
99.0	21		1
99.1	1		
99.5	16	1	1
99.8	1		
99.9	30	2	
100.0	81	4	6

**Reference Figure 5.30. Average percentage of shellfish distribution for Louisiana and Texas
(continued) commercial fishermen.**

PERCENT	SHRIMP	BLUE CRAB	OYSTER
<u>Louisiana Retail/Restaurant</u>			
4.5		1	
10.0	1		
15.0	1		
20.0	1		
50.0	1		
90.0		1	
100.0			1
<u>Texas Retail/Restaurant</u>			
0.5	2		
10.0	1		
20.0	1		
25.0	1		
50.0	1		
88.0	1		
90.0	2		
100.0	1	1	
<u>Total Retail/Restaurant</u>			
0.5	2		
4.5		1	
10.0	2		
15.0	1		
20.0	2		
25.0	1		
50.0	2		
88.0	1		
90.0	2	1	
100.0	1	1	1
<u>Louisiana Consumer</u>			
5.0		1	
9.5	1		
10.0		1	
<u>Texas Consumer</u>			
10.0	1		
15.0	1		
50.0	1		
<u>Total Consumer</u>			
5.0		1	
9.5	1		
10.0	1	1	
15.0	1		
50.0	1		

Reference Figure 5.30. Average percentage of shellfish distribution for Louisiana and Texas (continued) commercial fishermen.

PERCENT	SHRIMP	BLUE CRAB	OYSTER
<u>Louisiana Other</u>			
0.5		1	
30.0	1		
<u>Texas Other</u>			
0.1	1		
100.0	2		
<u>Total Other</u>			
0.1	1		
0.5		1	
30.0	1		
100.0	2		
<u>Louisiana Given Away</u>			
0.5	1		
1.0	2		
5.0	1		
10.0	1		
50.0		1	
60.0		1	
80.0		1	
100.0		1	
<u>Texas Given Away</u>			
0.0			
<u>Total Given Away</u>			
0.5	1		
1.0	2		
5.0	1		
10.0	1		
50.0		1	
60.0		1	
80.0		1	
100.0		1	
<u>Louisiana Kept</u>			
0.1	12	2	
0.2	1		
0.5	16	1	1
1.0	11		1
2.0	11	1	
5.0	2		
10.0	1	1	
20.0		1	
40.0		1	
50.0	1	3	
94.0	1		
100.0		16	

Reference Figure 5.30. Average percentage of shellfish distribution for Louisiana and Texas commercial fishermen.

PERCENT	SHRIMP	BLUE CRAB	OYSTER
<u>Texas Kept</u>			
0.1	22		
0.5	5		
1.0	7		
2.0	1		
<u>Total Kept</u>			
0.1	34	2	
0.2	1		
0.5	21	1	1
1.0	18		1
2.0	12	1	
5.0	2		
10.0	1	1	
20.0		1	
40.0		1	
50.0	1	3	
94.0	1		
100.0		16	

Reference Figure 5.31. Average percentage of finfish distribution for Louisiana and Texas commercial fishermen.

PERCENT	LOUISIANA	TEXAS	TOTAL
<u>WHOLESALE/PROCESSOR</u>			
<u>Amberjack</u>			
90.0	1		1
100.0	1		1
<u>Black Drum</u>			
95.0	1		1
99.0	1		1
99.9		2	2
100.0	4	1	5
<u>Croaker</u>			
100.0	2		2
<u>Dolphin</u>			
100.0	6		6
<u>Flounder</u>			
95.0	1		1
99.0	2		2
99.5	1		1
99.9	2	2	4
100.0	6	1	7

Reference Figure 5.31. Average percentage of finfish distribution for Louisiana and Texas commercial fishermen.
(continued)

PERCENT	LOUISIANA	TEXAS	TOTAL
<u>WHOLESALE/PROCESSOR</u>			
<u>Grouper</u>			
50.0	1		1
90.0	1		1
99.0	1	1	2
100.0		1	1
<u>Kingfish</u>			
0.0			0
<u>King Mackerel</u>			
100.0	4	1	5
<u>Red Snapper</u>			
99.0		1	1
100.0	2	1	3
<u>Shark</u>			
60.0	1		
99.5	1		
100.0	5	1	6
<u>Sheepshead</u>			
99.0	1		1
99.9		2	2
100.0	11	1	12
<u>Spanish Mackerel</u>			
100.0	1		1
<u>Speckled Trout</u>			
95.0	1		1
99.5	1		1
100.0	1		1
<u>Tuna</u>			
99.0	1		1
99.5	1		1
100.0	6		6
<u>Vermilion Snapper</u>			
90.0	1		1
100.0		1	1
<u>Other</u>			
90.0	1		1
99.0	1		1
100.0	5		5
<u>RETAIL/RESTAURANT</u>			
<u>Amberjack</u>			
0.0			0
<u>Black Drum</u>			
0.0			0

Reference Figure 5.31. Average percentage of finfish distribution for Louisiana and Texas
(continued) commercial fishermen.

PERCENT	LOUISIANA	TEXAS	TOTAL
<u>RETAIL/RESTAURANT</u>			
<u>Croaker</u> 0.0			0
<u>Dolphin</u> 0.0			0
<u>Flounder</u> 100.0		2	2
<u>Grouper</u> 0.0			0
<u>Kingfish</u> 0.0			0
<u>King Mackerel</u> 0.0			0
<u>Red Snapper</u> 0.0			0
<u>Shark</u> 0.0			0
<u>Sheepshead</u> 0.0			0
<u>Spanish Mackerel</u> 0.0			0
<u>Speckled Trout</u> 0.0			0
<u>Tuna</u> 0.0			0
<u>Vermilion Snapper</u> 0.0			0
<u>Other</u> 0.0			0
<u>CONSUMER</u>			
<u>Amberjack</u> 0.0			0
<u>Black Drum</u> 0.0			0
<u>Croaker</u> 0.0			0
<u>Dolphin</u> 0.0			0
<u>Flounder</u> 0.0			0
<u>Grouper</u> 0.0			0
<u>Kingfish</u> 0.0			0

Reference Figure 5.31. Average percentage of finfish distribution for Louisiana and Texas
(continued) commercial fishermen.

PERCENT	LOUISIANA	TEXAS	TOTAL
<u>CONSUMER</u>			
<u>King Mackerel</u>			
0.0			0
<u>Shark</u>			
0.0			0
<u>Sheepshead</u>			
0.0			0
<u>Spanish Mackerel</u>			
0.0			0
<u>Speckled Trout</u>			
0.0			0
<u>Tuna</u>			
0.0			0
<u>Vermilion Snapper</u>			
0.0			0
<u>Other</u>			
0.0			0
<u>OTHER</u>			
<u>Amberjack</u>			
0.0			0
<u>Black Drum</u>			
0.0			0
<u>Croaker</u>			
100.0		1	1
<u>Dolphin</u>			
0.0			0
<u>Flounder</u>			
0.0			0
<u>Grouper</u>			
0.0			0
<u>Kingfish</u>			
0.0			0
<u>King Mackerel</u>			
0.0			0
<u>Red Snapper</u>			
0.0			0
<u>Shark</u>			
0.0			0
<u>Sheepshead</u>			
0.0			0
<u>Spanish Mackerel</u>			
0.0			0
<u>Speckled Trout</u>			
0.0			0

Reference Figure 5.31. Average percentage of finfish distribution for Louisiana and Texas commercial fishermen.
(continued)

PERCENT	LOUISIANA	TEXAS	TOTAL
<u>OTHER</u>			
<u>Tuna</u>			
0.0			0
<u>Vermilion Snapper</u>			
0.0			0
<u>Other</u>			
0.0			0
<u>GIVEN AWAY</u>			
<u>Amberjack</u>			
10.0	1		1
<u>Black Drum</u>			
0.0			0
<u>Croaker</u>			
0.0			0
<u>Dolphin</u>			
0.0			0
<u>Flounder</u>			
0.0			0
<u>Grouper</u>			
0.0			0
<u>Kingfish</u>			
0.0			0
<u>King Mackerel</u>			
0.0			0
<u>Shark</u>			
0.0			0
<u>Sheepshead</u>			
0.0			0
<u>Spanish Mackerel</u>			
0.0			0
<u>Speckled Trout</u>			
100.0	1		1
<u>Tuna</u>			
0.0			0
<u>Vermilion Snapper</u>			
0.0			0
<u>Other</u>			
10.0	1		1
<u>KEPT</u>			
<u>Amberjack</u>			
100.0	1		1

Reference Figure 5.31. Average percentage of finfish distribution for Louisiana and Texas (continued) commercial fishermen.

PERCENT	LOUISIANA	TEXAS	TOTAL
<u>KEPT</u>			
<u>Black Drum</u>			
0.1		2	2
1.0	1		1
5.0	1		1
100.0		1	1
<u>Croaker</u>			
100.0		1	1
<u>Dolphin</u>			
0.0			0
<u>Flounder</u>			
0.1	2	2	4
0.5	1		1
1.0	2		2
5.0	1		1
100.0	8	7	15
<u>Grouper</u>			
1.0	1	1	2
10.0	1		1
50.0	1		1
100.0		1	1
<u>Kingfish</u>			
0.0			0
<u>King Mackerel</u>			
100.0	1		1
<u>Red Snapper</u>			
1.0		1	1
100.0		3	3
<u>Shark</u>			
0.5	1		1
40.0	1		1
100.0		3	3
<u>Sheepshead</u>			
0.1		2	2
1.0	1		1
100.0	1	2	3
<u>Spanish Mackerel</u>			
0.0			0
<u>Speckled Trout</u>			
0.5	1		1
5.0	1		1
100.0	4	1	5

Reference Figure 5.31. Average percentage of finfish distribution for Louisiana and Texas commercial fishermen.
(continued)

PERCENT	LOUISIANA	TEXAS	TOTAL
<u>KEPT</u>			
<u>Tuna</u>			
0.5	1		1
1.0	1		1
<u>Vermilion Snapper</u>			
10.0	1		1
<u>Other</u>			
1.0	1		1
100.0	4	3	7

Reference Figure 5.32. Percentage of finfish parts consumed by Louisiana and Texas commercial fishermen.

FINFISH	LOUISIANA	TEXAS	TOTAL
<u>Meat Only</u>			
Amberjack	0	0	0
Black Drum	1	3	4
Croaker	0	1	1
Dolphin	0	0	0
Flounder	8	9	17
Grouper	1	1	2
Kingfish	0	0	0
King Mackerel	0	0	0
Redfish	3	0	3
Red Snapper	0	4	4
Shark	3	3	6
Sheepshead	1	4	5
Spanish Mackerel	0	0	0
Speckled Trout	6	1	7
Tuna	1	0	1
Vermilion Snapper	0	0	0
Other	1	2	3
<u>Skin & Meat</u>			
Amberjack	1	0	1
Black Drum	2	0	2
Croaker	0	0	0
Dolphin	0	0	0
Flounder	5	2	7
Grouper	2	0	2
Kingfish	0	0	0
King Mackerel	1	0	1
Redfish	0	0	0
Red Snapper	0	0	0
Shark	0	0	0

Reference Figure 5.32. Percentage of finfish parts consumed by Louisiana and Texas commercial fishermen.

FINFISH	LOUISIANA	TEXAS	TOTAL
Skin & Meat			
Sheepshead	1	0	1
Spanish Mackerel	0	0	0
Speckled Trout	1	0	1
Tuna	1	0	1
Vermilion Snapper	0	0	0
Other	1	0	1

Reference Figure 5.33. Frequency distribution of cooking methods used by Louisiana and Texas commercial fishermen.

COOKING METHOD	LOUISIANA	TEXAS	TOTAL
Baked	32	11	43
Barbecued	26	7	33
Blackened	15	2	17
Boiled/Poached	89	28	117
Broiled	42	15	57
Fried	135	58	193
Grilled	41	10	51
Smoked	8	2	10
Stew/Soup	56	14	70
Other	64	6	70

Reference Figure 5.34. Frequency distribution of race for Louisiana oystermen.

RACE	NUMBER	RACE	NUMBER
Black	0	Oriental	0
Hispanic	1	White	10
Native American	0	Other	0

Reference Figure 5.35. Frequency distribution of fishing zones used by Louisiana oystermen.

ZONE	NUMBER	ZONE	NUMBER
I	15	VI	0
II	0	VII	0
III	2	VIII	0
IV	2	IX	0
V	0		

Reference Figure 5.36. Frequency distribution of fishing location for Louisiana oystermen.

FREQUENCY OF FISHING LOCATION	NUMBER
Inshore	16
< 4.8 km (3 mi) Offshore	0
4.8 to 16 km (3 to 10 mi) Offshore	1

Reference Figure 5.37. Frequency distribution of trips in proximity to oilfield structures for Louisiana oystermen.

PROXIMITY	NUMBER
< 300 m (1000 ft)	8
300 m to 0.8 km (1000 ft to 0.5 mi)	8
0.8 to 1.6 km (0.5 to 1 mi)	6
> 1.6 km (1 mi)	5

Reference Figure 5.38. Frequency distribution of methods of cooking oysters for consumption by Louisiana oystermen.

COOKING METHOD	NUMBER	COOKING METHOD	NUMBER
Raw	15	Fried	16
Baked	0	Grilled	1
Barbecued	0	Smoked	0
Blackened	0	Stew/Soup	14
Boiled/Poached	2	Other	5
Broiled	1		

Reference Figure 5.39. Frequency distribution of race for Texas oystermen.

RACE	NUMBER	RACE	NUMBER
Black	2	Oriental	0
Hispanic	9	White	2
Native American	2	Other	0

Reference Figure 5.40. Frequency distribution of fishing zones used by Texas oystermen.

ZONE	NUMBER	ZONE	NUMBER
I	0	VI	0
II	1	VII	16
III	1	VIII	0
IV	0	IX	0
V	0		

Reference Figure 5.41. Frequency distribution of trips in proximity to oilfield structures for Texas oystermen.

PROXIMITY	NUMBER
< 300 m (1000 ft)	1
300 m to 0.8 km (1000 ft to 0.5 mi)	0
0.8 to 1.6 km (0.5 to 1 mi)	7
> 1.6 km (1 mi)	11

Reference Figure 5.42. Frequency distribution of methods of cooking oysters for consumption by Texas oystermen.

COOKING METHOD	NUMBER	COOKING METHOD	NUMBER
Raw	13	Fried	15
Baked	1	Grilled	1
Barbecued	1	Smoked	0
Blackened	0	Stew/Soup	7
Boiled/Poached	2	Other	2
Broiled	0		

Reference Figure 5.43. Frequency distribution of sources of seafood for Louisiana wholesalers/processors.

PERCENT	FINFISH	SHRIMP	OYSTER	BLUE CRAB
<u>In-State Commercial</u>				
10	1	1	2	
25	1			
32		1		
50				1
65		1		
70	1	3		
75			2	
80		2		1
90	1			1
95		2		
100	9	14	7	12
<u>In-State Wholesalers</u>				
5		1		
10		3	1	
20				1
25	2		1	
30	1	3	1	
35		1		
50	1	1		1
60	1			
68		1		
70		2		
75		1		

**Reference Figure 5.43. Frequency distribution of sources of seafood for Louisiana
(continued) wholesalers/processors.**

PERCENT	FINFISH	SHRIMP	OYSTER	BLUE CRAB
<u>In-State Wholesalers</u>				
80	1			
90		2	1	2
99			1	
100	3	3	4	2
<u>In-State Processors</u>				
3				1
5			1	
10		1		
20		1		
40	1			
42	1			
43	1			
60			1	
80		1		
90		1		
92				1
100		3	5	2
<u>Out-of-State</u>				
1			1	
5		2		
7	1			1
8				1
10	2	2	1	2
15		1		
20	1			
25		1	1	
30	1	1		
40	1			
50		1		
52		1		
60		1		
75	1			
90		1	1	
100	1	1	1	
<u>Out-of-Country</u>				
5		1		
6		1		
10	1			
30	1			
50	1			
100		1	1	1

Reference Figure 5.6. Frequency distribution of fishing location for Louisiana recreational fishermen.

FREQUENCY OF FISHING LOCATION	NUMBER
Inshore	403
< 4.8 km (3 mi) Offshore	44
4.8 to 16 km (3 to 10 mi) Offshore	77
> 16 km (10 mi) Offshore	152

Reference Figure 5.7. Frequency distribution of trips in proximity to oilfield structures for Louisiana recreational fishermen.

PROXIMITY	NUMBER
< 300 m (1000 ft)	262
300 m to 0.8 km (1000 ft to 0.5 mi)	82
0.8 to 1.6 km (0.5 to 1 mi)	93
> 1.6 km (1 mi)	249

Reference Figure 5.8. Average number of shellfish and finfish species caught by Louisiana recreational fishermen over a six month period.

NUMBER CAUGHT	RESPONSES	NUMBER CAUGHT	RESPONSES
<u>Shrimp</u>		<u>Black Drum</u>	
600	1	1	31
<u>Crab</u>		2	16
10	1	3	13
<u>Oyster</u>		4	9
0	0	5	13
<u>Amberjack</u>		6	10
1	5	8	1
2	8	10	10
3	7	12	1
4	1	15	4
5	1	20	1
6	4	30	5
8	1	40	1
9	1	45	1
10	6	50	1
12	2	1000	1
15	1	<u>Croaker</u>	
17	1	1	7
20	3	2	7
21	1	3	6
25	1	4	3
28	1	5	5
40	1	6	8
50	1	8	1
200	1	10	12

Reference Figure 5.44. Average percentage of suppliers' fishing location for Louisiana wholesalers/processors.

PERCENT	RESPONSES	PERCENT	RESPONSES
<u>Inshore</u>		<u>Inshore-Near Platform (continued)</u>	
5	1	90	1
15	1	100	5
20	1	<u>Offshore</u>	
30	2	5	1
50	2	10	1
70	3	25	2
75	3	30	3
90	2	50	3
95	1	70	2
98	1	80	1
100	17	85	1
<u>Inshore-Near Platform</u>		95	1
5	1	100	6
10	2	<u>Offshore-Near Platform</u>	
15	1	20	1
20	2	25	1
30	3	50	4
50	2	60	1
60	1	80	1
70	1	95	1
75	2	100	6
80	1		

Reference Figure 5.45. Frequency distribution of suppliers' fishing zones for Louisiana wholesalers/processors.

ZONE	NUMBER	ZONE	NUMBER
I	6	VI	18
II	12	VII	10
III	13	VIII	7
IV	61	IX	2
V	15		

Reference Figure 5.46. Frequency distribution of shellfish destinations from Louisiana wholesalers/processors.

PERCENT	WHOLESALE/DEALER	PROCESSING PLANT	RETAILER/RESTAURANT	OTHER	OUT-OF-STATE
<u>Shrimp</u>					
1	1				1
3	1				
5	2		3	1	
8					1

**Reference Figure 5.46. Frequency distribution of shellfish destinations from Louisiana
(continued) wholesalers/processors.**

PERCENT	WHOLESALE/DEALER	PROCESSING PLANT	RETAILER/RESTAURANT	OTHER	OUT-OF-STATE
Shrimp					
10		1	4	1	2
15	1				
20	1		1	1	
25		1		1	
30			1		1
35	1				
40					1
50	2		1		1
60		2			1
70		1			2
75	1		1		1
79					1
80	1				1
90	1	1	1		
92			1		
95		1			1
97					1
99		1			1
100		4	7	1	2
Oyster					
.02		1			
5	1		2		1
10			1	1	1
20			1		
40	1				
60					1
75	1				
80	1				
90	1	1	2		1
95			1		
98					1
100	3	2	4		1
Blue Crab (Hard Shell)					
2					1
10		1	2	1	1
20		1	1		
30			1		
70	1				1
80	1				1
90		2	1		2
98			1		
100	1	2	3		3

Reference Figure 5.46. Frequency distribution of shellfish destinations from Louisiana wholesalers/processors.
(continued)

PERCENT	WHOLESALER/ DEALER	PROCESSING PLANT	RETAILER/ RESTAURANT	OTHER	OUT-OF- STATE
Blue Crab (Soft Shell)					
6					1
10				1	1
20			1		
25			1		
30			1		
70	1				
75	2				
80	1				
90			2		
94			1		
100			2		
Blue Crab (Meat)					
1				1	
12					1
30	1		1		1
70	2		1		2
75	1				
88			1		
99					1
100			6		1

Reference Figure 5.47. Frequency distribution of saltwater finfish destinations from Louisiana wholesalers/processors.

PERCENT	WHOLESALER/ DEALER	PROCESSING PLANT	RETAILER/ RESTAURANT	OTHER	OUT-OF- STATE
Black Drum					
1					1
5	1				
9					1
20			1		
50	1	1			
80	1				
91			1		
95					1
99			1		
100		1	1		
Flounder					
7					1
10					1
20			1		
50	1	1	1		1

**Reference Figure 5.47. Frequency distribution of saltwater finfish destinations from Louisiana
(continued) wholesalers/processors.**

PERCENT	WHOLESALE/ DEALER	PROCESSING PLANT	RETAILER/ RESTAURANT	OTHER	OUT-OF- STATE
<u>Flounder</u>					
80	1				
90	1		1		
93			1		
100		1	3		
<u>Red Snapper</u>					
20	1				
80					1
100	1		1		
<u>Sheepshead</u>					
1					1
20			1		1
29					1
30	1	1			
40	1				1
50	1		1		
60					1
71			1		
80	1		1		
99			1		
100		1			
<u>Speckled Trout</u>					
5					1
9					1
10	1				
30					1
70	1				
90			1		
91			1		
95			1		
100	1	1	2		
<u>Tuna</u>					
5	1				
6					1
20					1
40	1	1			
94			1		
5					1
100	2		1		
<u>Vermilion Snapper</u>					
10	1				
90					1
100	1		1		1

Reference Figure 5.48. Frequency distribution of shellfish product sold by Louisiana wholesalers/processors.

PRODUCT FORM	NUMBER	PRODUCT FORM	NUMBER
<u>Oyster</u>		<u>Shrimp</u>	
In Shell	12	Heads-On	24
Shucked	17	Heads-Off	23
Prepared	2	Peeled/Undeveined	16
<u>Crab</u>		Peeled/Deveined	9
Whole	17	Prepared	4
Meat	16		
Prepared	3		

Reference Figure 5.49. Frequency distribution of finfish product sold by Louisiana wholesalers/processors.

PRODUCT FORM	WHOLE	FILET WITH SKIN	FILET NO SKIN	OTHER
Black Drum	7	0	3	1
Flounder	11	0	2	1
Red Snapper	6	0	2	1
Sheepshead	6	0	3	1
Speckled Trout	9	1	5	1
Tuna	5	0	1	1
Vermilion Snapper	3	0	1	1
Other	6	0	1	1

Reference Figure 5.50. Frequency distribution of sources of seafood for Texas wholesalers/processors.

PERCENT	FINFISH	SHRIMP	OYSTER	BLUE CRAB
<u>In-State Commercial</u>				
10		2		
15	1			
75	1			
80	1	2		1
90		2	1	
99		1		
100	3	2	1	3
<u>In-State Wholesalers</u>				
1		1		
5	1			
10	1	2	1	
20	1	3		
45			1	
50		1		
80		1		1
85	1			

Reference Figure 5.50. Frequency distribution of sources of seafood for Texas wholesalers/processors.

PERCENT	FINFISH	SHRIMP	OYSTER	BLUE CRAB
<u>In-State Wholesalers</u>				
90		1		
100	1	1	2	1
<u>In-State Processors</u>				
5	1	2		
10	1	1		
20				1
50		1		
70		1		
85		1		
100		1	2	1
<u>Out-Of-State</u>				
5	1			
10		1		
20	1			
50	1			
70		1		
85			1	
100	1			
<u>Out-Of-Country</u>				
5		1		
10	1	1		
30	1	1		
80	1			
100	1	1		

Reference Figure 5.51. Average percentage of suppliers' fishing location for Texas wholesalers/processors.

PERCENT	RESPONSES	PERCENT	RESPONSES
<u>Inshore</u>		<u>Offshore</u>	
0.05	1	20	2
70	1	30	1
75	1	90	1
80	1	100	1
100	3	<u>Offshore-Near Platform</u>	
<u>Inshore-Near Platform</u>		5	1
0.05	1	10	1
10	2	100	2
100	1		

Reference Figure 5.52. Frequency distribution of suppliers' fishing zones for Texas wholesalers/processors.

ZONE	NUMBER	ZONE	NUMBER
I	0	VI	2
II	0	VII	20
III	0	VIII	18
IV	6	IX	12
V	0		

Reference Figure 5.53. Frequency distribution of shellfish destinations from Texas wholesalers/processors.

PERCENT	WHOLESALE DEALER	PROCESSING PLANT	RETAILER/ RESTAURANT	OTHER	OUT-OF- STATE
<u>Shrimp</u>					
5	1			2	
10	1		1		2
15	1				
16	1				
20	1		2		
25					1
50		1			1
70		1			
75	1				
80		1	2		1
85		1			
90			1		1
100	2	1	2		
<u>Oyster</u>					
2				1	
10			1		
25		1			
30					1
70			1		
75					1
100			1		
<u>Blue Crab (Hard Shell)</u>					
90				1	
100			2		
<u>Blue Crab (Soft Shell)</u>					
100			2		
<u>Blue Crab (Meat)</u>					
1				1	
80			1		
100				1	

Reference Figure 5.54. Frequency distribution of saltwater finfish destinations from Texas wholesalers/processors.

PERCENT	WHOLESALE DEALER	PROCESSING PLANT	RETAILER/ RESTAURANT	OTHER	OUT-OF- STATE
<u>Black Drum</u>					
20					1
30			1		
50			1	1	
70	1				
80	1				
100	1		1		
<u>Flounder</u>					
10			1		
20	1				
25				1	
40			1		
50	1				
70					1
75			1		
95			1		
100			3		
<u>Red Snapper</u>					
10			1		
20	1		1		
25				1	
70					1
75			1		
80	1				
95			1		
100			2		
<u>Sheepshead</u>					
25			1		
75				1	
95			1		
100			2		
<u>Speckled Trout</u>					
100			2		
<u>Tuna</u>					
90			1		
100			2		
<u>Vermilion Snapper</u>					
100			2	1	

Reference Figure 5.55. Frequency distribution of shellfish product sold by Texas wholesalers/processors.

PRODUCT FORM	NUMBER	PRODUCT FORM	NUMBER
<u>Oyster</u>		<u>Shrimp</u>	
In Shell	7	Heads-On	13
Shucked	5	Heads-Off	15
Prepared	1	Peeled/Undeined	4
<u>Crab</u>		Peeled/Deined	6
Whole	6	Prepared	2
Meat	4		
Prepared	2		

Reference Figure 5.56. Frequency distribution of finfish product sold by Texas wholesalers/processors.

PRODUCT FORM	WHOLE	FILET WITH SKIN	FILET NO SKIN	OTHER
Black Drum	5	0	3	0
Flounder	6	0	2	0
Red Snapper	5	1	1	0
Sheepshead	4	0	1	0
Speckled Trout	3	0	1	0
Tuna	2	0	1	0
Vermilion Snapper	3	0	1	0
Other	4	0	3	1

Reference Figure 5.57. Frequency distribution of shellfish product sold by Louisiana retailers.

SHELLFISH	UNCOOKED/ UNPREPARED	COOKED/ PREPARED
Crab Hard	104	95
Crab Soft	67	4
Crab Meat	54	26
Oysters Whole	44	0
Oysters Meat	115	13
Shrimp Heads-On	152	89
Shrimp Heads-Off	45	3
Shrimp Peeled	48	14

Reference Figure 5.58. Frequency distribution of finfish product sold by Louisiana retailers.

FINFISH	WHOLE SKIN	WHOLE NO SKIN	FILLET SKIN	FILLET NO SKIN	COOKED/ PREPARED
Amberjack	2	1	1	2	0
Black Drum	10	0	1	3	0
Croaker	4	0	0	0	0

Reference Figure 5.58. Frequency distribution of finfish product sold by Louisiana retailers.
(continued)

FINFISH	WHOLE SKIN	WHOLE NO SKIN	FILLET SKIN	FILLET NO SKIN	PARTS	COOKED/ PREPARED
Dolphin	5	0	4	5	0	0
Flounder	48	0	6	11	0	1
Grouper	3	0	1	4	0	0
Kingfish	0	0	0	0	0	0
King Mackerel	1	0	0	0	0	0
Red Snapper	24	0	11	12	0	0
Shark	2	0	2	5	0	0
Sheepshead	12	0	0	2	0	0
Spanish Mackerel	12	0	0	0	0	0
Speckled Trout	38	1	7	20	0	2
Tuna	2	0	13	9	0	0
Other	13	0	5	11	0	7

Reference Figure 5.59. Frequency distribution of shellfish product sold by Texas retailers.

SHELLFISH	UNCOOKED/ UNPREPARED	COOKED/ PREPARED
Crab Hard	54	9
Crab Soft	19	2
Crab Meat	29	16
Oysters Whole	12	0
Oysters Meat	67	36
Shrimp Heads-On	52	3
Shrimp Heads-Off	94	3
Shrimp Peeled	20	43

Reference Figure 5.60. Frequency distribution of finfish product sold by Texas retailers.

FINFISH	WHOLE SKIN	WHOLE NO SKIN	FILLET SKIN	FILLET NO SKIN	PARTS	COOKED/ PREPARED
Amberjack	1	0	0	3	0	0
Black Drum	48	0	3	5	0	7
Croaker	7	0	0	0	0	0
Dolphin	0	0	0	1	0	0
Flounder	50	0	3	8	0	3
Grouper	4	0	0	2	2	0
Kingfish	3	0	0	0	0	0
King Mackerel	0	0	0	0	0	0
Red Snapper	44	0	11	9	1	3
Shark	3	0	2	6	0	0
Sheepshead	38	1	2	3	0	2
Spanish Mackerel	4	0	1	2	0	0
Speckled Trout	26	0	8	8	0	13

Reference Figure 5.60. Frequency distribution of finfish product sold by Texas retailers.
(continued)

FINFISH	WHOLE SKIN	WHOLE NO SKIN	FILLET SKIN	FILLET NO SKIN	PARTS	COOKED/ PREPARED
Tuna	4	0	3	4	3	0
Other	19	0	0	1	0	3

Reference Figure 5.61. Average percentage of types of seafood dishes served in 1992 by Louisiana restaurants.

PERCENT SERVED	RESPONSES	PERCENT SERVED	RESPONSES
<u>Shellfish</u>		<u>Finfish</u> (continued)	
10	4	48	1
15	2	50	16
16	1	60	2
20	2	65	1
25	4	70	2
30	8	75	1
35	2	80	1
36	1	82	1
40	4	85	2
44	1	90	2
48	1	100	3
50	11	<u>Both</u>	
55	1	2	2
60	10	5	4
70	5	6	1
75	1	10	6
80	3	15	2
90	1	16	1
100	4	20	6
<u>Finfish</u>		25	2
1	1	29	1
10	3	30	2
15	1	40	1
20	3	45	1
25	5	50	2
30	9	59	1
35	1	75	1
38	1	80	2
40	7	100	2
45	2		

Reference Figure 5.62. Average percentage of shellfish dishes served per week in 1992 by Louisiana restaurants.

PERCENT SERVED	RESPONSES	PERCENT SERVED	RESPONSES
<u>Blue Crab - Soft Shell</u>		<u>Oyster - Meat (continued)</u>	
1	2	20	8
3	1	21	1
4	1	23	2
5	6	25	4
8	2	30	4
10	16	35	1
15	1	40	1
20	6	50	2
25	1	<u>Shrimp</u>	
38	1	5	1
80	1	10	1
<u>Blue Crab - Other</u>		15	2
2	2	20	2
5	5	25	4
8	2	30	9
10	6	35	3
15	1	40	8
20	5	45	1
30	5	46	1
40	3	50	12
45	1	60	4
50	4	70	5
<u>Oyster - Half Shell</u>		75	2
2	3	80	5
3	1	82	1
4	2	90	2
5	5	95	1
10	4	97	1
15	1	100	5
20	1	<u>Other</u>	
30	2	1	1
50	1	2	1
95	1	5	3
<u>Oyster - Meat</u>		8	2
1	1	9	1
3	2	10	5
4	1	12	2
5	3	15	2
6	1	17	1
8	2	20	6
10	11	25	1
15	3	28	1
18	1	30	2

Reference Figure 5.62. Average percentage of shellfish dishes served per week in 1992 by Louisiana restaurants.

PERCENT SERVED	RESPONSES	PERCENT SERVED	RESPONSES
<u>Other</u>			
35	2		
40	2		
45	1		
50	1		
62	1		
65	1		

Reference Figure 5.63. Average percentage of finfish dishes served per week in 1992 by Louisiana restaurants.

PERCENT SERVED	RESPONSES	PERCENT SERVED	RESPONSES
<u>Amberjack</u>		<u>Flounder (continued)</u>	
0.5	1	2	2
2	1	3	1
5	5	5	3
10	6	10	6
15	3	15	3
20	2	20	4
30	1	30	1
<u>Black Drum</u>		40	3
1	1	50	1
2	2	54	1
10	6	<u>Grouper</u>	
15	2	1	1
20	2	3	1
25	1	5	5
30	1	10	5
50	1	100	1
60	1	<u>Kingfish</u>	
<u>Croaker</u>		0	0
1	1	<u>King Mackerel</u>	
<u>Dolphin</u>		2	1
3	1	<u>Red Fish</u>	
5	6	5	2
10	4	8	1
15	2	10	4
20	3	15	1
25	1	25	1
30	3	40	1
<u>Flounder</u>		<u>Red Snapper</u>	
0.5	1	2	1
1	1	5	9

Reference Figure 5.63. Average percentage of finfish dishes served per week in 1992 by Louisiana restaurants.

PERCENT SERVED	RESPONSES	PERCENT SERVED	RESPONSES
<u>Red Snapper</u>		<u>Speckled Trout (continued)</u>	
8	1	60	1
10	6	70	1
15	5	<u>Tuna</u>	
20	6	2	1
25	1	5	4
30	4	10	7
40	1	20	8
50	4	40	5
60	1	50	3
80	1	60	1
<u>Shark</u>		70	1
5	1	100	2
15	1	<u>Vermilion Snapper</u>	
<u>Sheepshead</u>		5	2
2	1	10	1
5	1	20	1
10	4	<u>Other</u>	
20	1	0.5	1
30	2	3	1
<u>Spanish Mackerel</u>		5	4
0	0	6	1
<u>Speckled Trout</u>		10	4
0.75	1	15	3
2	1	20	4
5	1	30	3
10	8	40	1
15	1	45	1
20	5	50	2
25	1	60	1
30	3	80	1
35	3	90	2
40	1	95	2
46	1	98	1
50	2	100	8

Reference Figure 5.64. Average number of meals served in 1992 by Louisiana restaurants which included seafood stock.

NUMBER OF MEALS	RESPONSES	NUMBER OF MEALS	RESPONSES
<u>Shellfish Stock</u>		<u>Finfish Stock</u>	
1	3	1	1
2	1	5	1
10	3	10	3
15	1	15	2
20	6	20	1
30	2	30	4
40	1	50	1
60	3	80	1
70	1	300	1
75	1	500	1
80	1	765	1
100	2	3000	1
150	2	<u>Both</u>	
200	2	5	1
300	1	10	1
400	1	15	1
500	1	20	3
600	1	30	1
900	2	40	1
1000	1	50	1
1200	1	100	1
1500	1	128	1
1530	1	200	1
3000	1	255	1
		300	2
		500	1
		800	1

Reference Figure 5.65. Frequency distribution of shellfish used in stock by Louisiana restaurants in 1992.

TYPE OF SHELLFISH	NUMBER
Blue Crab	25
Shrimp	49
Oyster	14

Reference Figure 5.66. Average percentage of sources of seafood for Louisiana restaurants in 1992.

PERCENT	RESPONSES	PERCENT	RESPONSES
<u>Commercial Fishermen</u>		<u>Wholesalers/Processors (continued)</u>	
5	1	90	7
10	4	95	2
20	2	98	2
25	1	100	41
30	1	<u>Retailers</u>	
40	1	2	1
50	1	5	2
70	1	10	4
75	1	15	2
80	2	20	1
<u>Wholesalers/Processors</u>		25	1
20	2	40	1
25	1	50	3
30	2	60	1
40	1	100	3
50	6	<u>Other</u>	
60	1	2	1
70	1	5	1
80	2	10	1
85	2	30	1

Reference Figure 5.67. Percentage of finfish parts served in 1992 by Louisiana restaurants.

FINFISH	MEAT ONLY	SKIN & MEAT
Amberjack	21	0
Black Drum	20	1
Croaker	1	1
Dolphin	20	1
Flounder	25	11
Grouper	16	2
Kingfish	1	0
King Mackerel	1	2
Redfish	12	2
Red Snapper	35	7
Shark	5	0
Sheepshead	12	0
Spanish Mackerel	1	0
Speckled Trout	27	7
Tuna	30	2
Vermilion Snapper	5	1
Other	124	0

Reference Figure 5.68. Percentage of finfish species used in stock by Louisiana restaurants in 1992.

FINFISH	NUMBER	FINFISH	NUMBER
Amberjack	4	Red Snapper	9
Black Drum	1	Shark	0
Croaker	0	Sheepshead	4
Dolphin	1	Spanish Mackerel	0
Flounder	4	Speckled Trout	7
Grouper	5	Tuna	3
Kingfish	0	Vermilion Snapper	0
King Mackerel	2	Other	4
Redfish	1		

Reference Figure 5.69. Frequency distribution of cooking methods of seafood served in Louisiana restaurants in 1992.

COOKING METHOD	NUMBER	COOKING METHOD	NUMBER
Baked	90	Fried	62
Barbecued	30	Grilled	51
Blackened	72	Smoked	12
Boiled/Poached	28	Stew/Soup	39
Broiled	50	Other	7

Reference Figure 5.70. Average percentage of types of seafood dishes served in 1992 by Texas restaurants..

PERCENT SERVED	RESPONSES	PERCENT SERVED	RESPONSES
<u>Shellfish</u>		<u>Shellfish</u> (continued)	
1	1	95	1
2	1	98	1
5	2	99	1
10	5	100	8
12	1	<u>Finfish</u>	
15	1	1	1
20	2	2	1
25	2	5	2
30	4	10	2
35	1	15	3
40	4	20	4
50	5	25	3
55	1	30	4
60	6	35	1
66	1	40	5
70	1	45	2
75	2	50	8
80	3	60	2
85	3	65	1
90	2	70	1

Reference Figure 5.70. Average percentage of types of seafood dishes served in 1992 by Texas restaurants..

PERCENT SERVED	RESPONSES	PERCENT SERVED	RESPONSES
<u>Finfish</u>		<u>Both</u>	
75	1	4	1
80	2	5	3
85	1	10	4
88	1	25	4
90	2	30	3
95	1	75	1
99	1	90	1
100	2	100	3

Reference Figure 5.71. Average percentage of shellfish dishes served per week in 1992 by Texas restaurants.

PERCENT SERVED	RESPONSES	PERCENT SERVED	RESPONSES
<u>Blue Crab - Soft Shell</u>		<u>Oyster - Meat (continued)</u>	
1	1	15	4
2	2	20	2
3	3	25	2
5	6	45	1
10	4	100	1
15	2	<u>Shrimp</u>	
<u>Blue Crab - Other</u>		3	1
5	3	5	1
8	1	10	1
10	8	20	2
19	1	30	3
20	2	40	1
25	1	45	2
30	2	50	3
<u>Oyster - Half Shell</u>		55	1
1	1	60	8
3	1	65	1
5	2	70	5
10	3	72	1
12	1	75	4
15	3	80	6
18	1	85	2
20	4	86	1
35	1	90	3
100	1	95	5
<u>Oyster - Meat</u>		98	1
2	1	99	1
5	2	100	19
10	3		

Reference Figure 5.71. Average percentage of shellfish dishes served per week in 1992 by Texas (continued) restaurants.

PERCENT SERVED	RESPONSES	PERCENT SERVED	RESPONSES
<u>Other</u>		<u>Other (continued)</u>	
1	1	20	5
2	1	25	4
3	1	30	1
5	2	50	2
10	4	80	1
12	1	100	1
15	2		

Reference Figure 5.72. Average percentage of finfish dishes served per week in 1992 by Texas restaurants.

PERCENT SERVED	RESPONSES	PERCENT SERVED	RESPONSES
<u>Amberjack</u>		<u>Flounder (continued)</u>	
5	4	60	1
10	2	80	1
30	1	100	1
38	1	<u>Grouper</u>	
<u>Black Drum</u>		5	6
2	1	10	2
5	3	25	1
10	1	50	1
20	2	<u>Kingfish</u>	
50	1	1	1
60	1	5	1
<u>Croaker</u>		<u>King Mackerel</u>	
1	1	1	1
<u>Dolphin</u>		<u>Redfish</u>	
3	2	5	2
5	2	10	2
15	1	15	1
20	1	20	2
<u>Flounder</u>		30	1
1	1	<u>Red Snapper</u>	
2	2	2	1
5	5	3	1
10	2	5	4
15	4	10	6
20	3	15	3
22	1	19	1
25	3	20	2
30	3	25	1
35	1	30	2
40	1	35	1

Reference Figure 5.72. Average percentage of finfish dishes served per week in 1992 by Texas restaurants.

PERCENT SERVED	RESPONSES	PERCENT SERVED	RESPONSES
<u>Red Snapper</u>		<u>Speckled Trout (continued)</u>	
40	2	40	1
50	2	100	2
65	1	<u>Tuna</u>	
70	1	2	1
75	2	5	7
90	2	15	3
<u>Shark</u>		16	1
1	1	20	1
2	1	25	1
5	3	30	1
10	2	40	3
38	1	50	1
<u>Sheepshead</u>		<u>Vermilion Snapper</u>	
5	1	5	1
9	1	15	1
10	3	20	4
20	3	30	2
<u>Spanish Mackerel</u>		40	2
10	1	50	1
<u>Speckled Trout</u>		51	1
1	1	55	1
2	1	60	1
3	1	70	1
5	2	80	2
10	2	85	1
15	1	90	2
20	2	95	1
25	1	100	12
30	1		

Reference Figure 5.73. Average number of meals served in 1992 by Texas restaurants which included seafood stock.

NUMBER OF MEALS	RESPONSES	NUMBER OF MEALS	RESPONSES
<u>Shellfish Stock</u>		<u>Shellfish Stock (continued)</u>	
1	1	100	3
10	1	120	1
14	1	175	1
15	1	200	2
20	4	210	1
40	1	420	1
50	2	961	1
60	1		

Reference Figure 5.73. Average number of meals served in 1992 by Texas restaurants which included seafood stock.

NUMBER OF MEALS	RESPONSES	NUMBER OF MEALS	RESPONSES
<u>Finfish Stock</u>		<u>Both</u>	
5	1	1	1
8	1	10	2
14	1	20	1
40	1	30	1
50	3	75	1
100	2	100	1
175	1	200	1
192	1	300	2
200	1	325	1
2000	1	384	1
		800	1

Reference Figure 5.74. Frequency distribution of shellfish used in stock by Texas restaurants in 1992.

TYPE OF SHELLFISH	NUMBER
Blue Crab	10
Shrimp	36
Oyster	6

Reference Figure 5.75. Average percentage of sources of seafood for Texas restaurants in 1992.

PERCENT	RESPONSES	PERCENT	RESPONSES
<u>Commercial Fishermen</u>		<u>Wholesalers/Processors (continued)</u>	
5	1	95	6
10	3	99	1
20	2	100	43
50	1	<u>Retailers</u>	
60	2	5	3
90	1	10	2
100	1	20	2
<u>Wholesalers/Processors</u>		40	1
10	1	50	1
20	2	75	1
25	1	100	5
40	2	<u>Other</u>	
75	1	1	1
80	2	5	1
85	1	10	2
90	2	15	1
		50	1

Reference Figure 5.76. Percentage of finfish parts served in 1992 by Texas restaurants.

FINFISH	MEAT ONLY	SKIN & MEAT
Amberjack	8	2
Black Drum	56	0
Croaker	14	0
Dolphin	42	0
Flounder	154	77
Grouper	63	7
Kingfish	14	0
King Mackerel	14	0
Redfish	49	21
Red Snapper	168	70
Shark	56	7
Sheepshead	49	7
Spanish Mackerel	21	0
Speckled Trout	91	35
Tuna	133	0
Vermilion Snapper	0	0
Other	147	21

Reference Figure 5.77. Percentage of finfish species used in stock by Texas restaurants in 1992.

FINFISH	NUMBER	FINFISH	NUMBER
Amberjack	14	Red Snapper	49
Black Drum	7	Shark	7
Croaker	0	Sheepshead	7
Dolphin	7	Spanish Mackerel	0
Flounder	21	Speckled Trout	7
Grouper	7	Tuna	0
Kingfish	0	Vermilion Snapper	0
King Mackerel	0	Other	35
Redfish	7		

Reference Figure 5.78. Frequency distribution of cooking methods of seafood served in Texas restaurants in 1992.

COOKING METHOD	NUMBER	COOKING METHOD	NUMBER
Baked	203	Fried	420
Barbecued	56	Grilled	273
Blackened	175	Smoked	70
Boiled/Poached	210	Stew/Soup	217
Broiled	238	Other	70

Reference Figure 6.1. Frequency distribution of finfish species caught in proximity to oilfield structures in the summer and fall of 1992 in Louisiana.

SPECIES	PERCENTAGE CAUGHT	PERCENTAGE CAUGHT
	< 1000 FT	> 1 MI
Amberjack	4.75	2.23
Black Drum	5.18	6.06
Croaker	4.06	4.79
Dolphin	3.36	2.23
Flounder	9.66	13.83
Grouper	2.59	1.28
Kingfish	0.69	0.43
King Mackerel	4.23	2.23
Redfish	16.74	22.23
Red Snapper	9.49	4.68
Shark	3.97	2.45
Sheepshead	4.06	6.81
Spanish Mackerel	5.00	3.51
Speckled Trout	16.57	20.32
Tuna	2.76	1.28
Vermilion Snapper	1.21	0.85
Other	5.69	4.79

Reference Figure 6.2. Frequency distribution of finfish species caught in proximity to oilfield structures in the summer and fall of 1992 in Texas.

SPECIES	PERCENTAGE CAUGHT	PERCENTAGE CAUGHT
	< 1000 FT	> 1 MI
Amberjack	6.09	4.43
Black Drum	2.30	4.18
Croaker	2.30	2.09
Dolphin	11.23	7.63
Flounder	6.22	10.46
Grouper	1.89	1.72
Kingfish	7.58	3.08
King Mackerel	5.95	5.54
Redfish	10.15	14.51
Red Snapper	14.75	8.24
Shark	6.09	4.55
Sheepshead	0.68	1.85
Spanish Mackerel	2.98	2.83
Speckled Trout	9.47	15.25
Tuna	4.06	4.67
Vermilion Snapper	2.44	1.85
Other	5.82	7.13

Reference Figure 6.3. Frequency distribution of finfish species caught in summer and fall of 1992 in Louisiana.

SPECIES	SUMMER NUMBER	FALL NUMBER
Amberjack	55	7
Black Drum	63	63
Croaker	45	48
Dolphin	44	7
Flounder	121	134
Grouper	33	4
Kingfish	7	3
King Mackerel	54	8
Redfish	180	230
Red Snapper	111	23
Shark	44	12
Sheepshead	73	54
Spanish Mackerel	57	18
Speckled Trout	184	204
Tuna	30	8
Vermilion Snapper	16	4
Other	69	29

Reference Figure 6.4. Frequency distribution of finfish species caught in summer and fall of 1992 in Texas.

SPECIES	SUMMER NUMBER	FALL NUMBER
Amberjack	51	10
Black Drum	41	8
Croaker	25	9
Dolphin	92	20
Flounder	74	56
Grouper	20	2
Kingfish	59	5
King Mackerel	61	14
Redfish	116	76
Red Snapper	112	28
Shark	54	14
Sheepshead	15	7
Spanish Mackerel	24	14
Speckled Trout	118	75
Tuna	43	11
Vermilion Snapper	20	1
Other	71	18