Gulf of Mexico Produced Water Bioaccumulation Study

Executive Summaries

April 1997

(Reformatted for Microsoft Word in May 2009)

Prepared For:

Offshore Operators Committee
P.O. Box 50751
New Orleans, Louisiana 70150

Prepared By:

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

ACKNOWLEDGEMENTS
WE WOULD LIKE TO ACKNOWLEDGE THE OOC BIOACCUMULATION STUDY
CO-SPONSORS FOR THEIR SUPPORT OF THE PROJECT:

AEDC (USA), Inc.
Agip Petroleum Company, Inc.
Amerada Hess Corporation
American Exploration Company
Amoco Production Company
Anadarko Petroleum Company
ANR Production Company
Apache Corporation
(includes Aquila Energy Resources)
Ashland Exploration, Inc.
Ashlawn Energy, Inc.
Aviara Energy Corporation
(formerly Columbia Gas Development Corporation)
BHP Petroleum (Americas) Incorporated
Blue Dolphin Exploration Company
(includes Ivory Production Company)
BP Exploration
British-Borneo Exploration, Inc.
Chevron USA Prod. Company
CNG Producing Company, Inc.
Coastal Oil & Gas Corporation
Cockrell Oil Corporation
Conn Energy, Inc.
Conoco, Inc.
CXY Energy, Inc.
Elf Exploration Inc.
Enron Oil & Gas Company
Enserch Exploration Company
(includes DALEN Resources Oil & Gas
and EP Operating Ltd. Partnership)
Exxon Co., USA
Fina Oil & Chemical
Flores & Rucks, Inc.
Forcenergy Gas Exploration, Inc.
Forest Oil Corporation
Freeport-McMoran Oil & Gas Company
Greenhill Petroleum Corporation
Gulfstar Energy, Inc.
Gulfstream Resources, Inc.
Hall-Houston Oil Company
Houston Exploration Company
Howell Petroleum Company
Kerr-McGee Corporation

Louisiana Land & Exploration Company
Marathon Oil Company
Matrix Oil & Gas Company
Meridian Oil
Mesa Operating Ltd. Partnership
MidCon Offshore Corporation
Mitchell Energy Corporation
Mobil E & P Company
Murphy Exploration & Production Company
NCX Company, Inc.
Newfield Exploration Company
Nippon Oil Exploration USA (NOEX)
Norcen Explorer, Inc.
Oryx Energy Company
Oxy USA, Inc.
O.E.D.C. Partners
Panaco, Inc.
Pel Tex Oil Company
Pennzoil E & P Company
Phillips Petroleum Company
Pogo Producing Company
Samedan Oil Corporation
Santa Fe Energy Resources, Inc.
Seagull Energy Corporation
Shell Offshore Inc.
Sonat Exploration Company
Taylor Energy Company
Texaco Exploration & Production, Inc.
Torch Operating Company
Total Minatome Corporation
Trade & Development Corporation
UMC Petroleum Corporation
(includes General Atlantic Resources, Inc.)
Union Oil of California (UNOCAL)
Union Pacific Resources Company
Vastar Resources, Inc.
W & T Offshore
Zilkha Energy Company

THE CONTRACTORS FOR THIS STUDY WOULD LIKE TO ACKNOWLEDGE THE MEMBERS OF THE BIOACCUMULATION WORKING GROUP FOR THEIR SUPPORT AND COOPERATION DURING THIS PROJECT:

Dr. James P. Ray (Shell) - Chairman
Dr. R. C. Ayers (Robert Ayers & Associates)
Ms. Jan Farmer (BP Oil)
Mr. Brian E. Shannon (Arco)
Dr. Stanley Curtice (Texaco)
Dr. Andrew Glickman (Chevron)
Mr. Larry R. Henry (Chevron)
Dr. Bela M. James (Shell)
Mr. David J. LeBlanc (Texaco)
Dr. Lawrence A. Reitsema (Marathon)
Dr. Joseph P. Smith (Exxon Production Research Co.)
Dr. James E. O'Reilly (Exxon Production Research Co.)
Dr. Jerry Hall (Texaco)

THE CONTRACTOR WOULD ALSO LIKE TO ACKNOWLEDGE THE FOLLOWING INDIVIDUALS FOR THEIR CONTRIBUTION TO THIS PROJECT:

Dr. Woollcott Smith (Temple University)
Mr. Keith R. Parker (Data Analysis Group)
Dr. Dan D. Caudle (Sound Environmental Solutions, Inc.)

GULF OF MEXICO
PRODUCED WATER BIOACCUMULATION STUDY

TABLE OF CONTENTS

METALS AND ORGANIC CHEMICALS ASSOCIATED WITH OIL AND GAS WELL PRODUCED WATER: BIOACCUMULATION, FATES, AND EFFECTS IN THE MARINE ENVIRONMENT

EXECUTIVE SUMMARY

The current National Pollutant Discharge Elimination System (NPDES) General Permit (No. GMG290000) for discharges of 4,600 barrels/day or more of treated produced water from offshore oil and gas production platforms to offshore waters of the western Gulf of Mexico requires a site-specific bioaccumulation monitoring study. The offshore oil industry is participating in a U.S. Environmental Protection Agency-approved, generic bioaccumulation study that includes a more thorough evaluation of a smaller number of geographically distributed offshore produced water discharges. This report was prepared for the Gulf of Mexico Offshore Operators Committee to evaluate the scientific data concerning the bioaccumulation of chemicals commonly found in produced water to aid in interpreting the bioaccumulation monitoring data. This report evaluates the potential for bioaccumulation of the chemicals identified in the NPDES permit that require bioaccumulation evaluation and several other chemicals of environmental concern frequently found in treated produced water that is discharged to ocean waters of the Gulf of Mexico. The chemicals evaluated in this report include

- metals: arsenic, barium, cadmium, mercury, chromium, copper, lead, and zinc;
- naturally occurring radioactive material: radium-226 and radium-228;
- monocyclic aromatic hydrocarbons: benzene, toluene, ethylbenzene, and xylenes;
- polycyclic aromatic hydrocarbons (PAHs): fluorene, benzo(a)pyrene, total PAHs;
- miscellaneous organic chemicals: phenol and bis(2-ethylhexyl)phthalate (BEHP).

All these chemicals, except BEHP, are natural components of oil and gas well produced water and are natural trace ingredients of sea water.

The metals evaluated here are all, with the exception of mercury, nearly always found in produced water from the Gulf of Mexico. Mercury is only occasionally detected in produced water. These metals also are natural constituents of clean sea water. The metals most frequently found in produced water at concentrations substantially higher (1,000-fold or more) than their natural concentrations in clean sea water are barium, cadmium, chromium, copper, iron, lead, nickel, and zinc.

Some produced waters from the Gulf of Mexico contain concentrations of naturally occurring radioactivity higher than that encountered in sea water and brackish water. The most abundant radionuclides in produced water are radium-226 and radium-228. Concentrations in produced water may be up to 5,000 times higher than natural concentrations in sea water.

Monocyclic aromatic hydrocarbons (consisting primarily of benzene, toluene, ethylbenzene, and xylenes: BTEX) and PAHs are natural constituents of crude petroleum and dissolve from the oil into the produced water. Concentrations of BTEX are higher than those of PAHs in produced water and the relative concentration decreases with increasing molecular weight. High molecular weight, four- through six-ring PAHs are present at trace (sub-parts per billion) concentrations, when they can be detected at all. There are also traces of BTEX and PAHs in clean sea water, much of them derived from deposition of airborne hydrocarbons from combustion sources, and from natural oil and gas seeps that are abundant in the northwestern Gulf of Mexico.

Phenol often is present at high concentrations in produced water. BEHP is not a natural ingredient, nor is it added intentionally to produced water. It is a ubiquitous trace contaminant of the environment, being derived from leaching of plasticizers from plastics. Any traces detected in produced water probably are from this source.

For each of the chemicals, this report discusses the information available from the scientific literature on

- its occurrence in sea water;
- its occurrence in marine sediments;
- what is known about its tendency to bioaccumulate in tissues of marine organisms;
- concentrations in tissues of marine organisms in the Gulf of Mexico and in the other oceans of the world; and
- its toxicity to marine organisms.

Based on this information and information on the concentration of each chemical in Gulf of Mexico produced water, a judgement is made about the relative risk to the health of marine ecosystems and human consumers of fisheries products from these chemicals in produced water discharged to the ocean.

As a general rule, concentrations of metals in tissues of marine organisms in the Gulf of Mexico and in the immediate vicinity of offshore discharges of produced water are in the normal range and do not show evidence of bioaccumulation to potentially toxic levels for the organisms themselves or their consumers, including man. A review of the concentration of each metal in typical Gulf of Mexico produced water and its potential for bioaccumulation and toxicity reveals that only two metals have the potential to pose a health risk to marine organisms and their consumers. These metals are cadmium and copper. Any adverse effects of these metals, if they occur at all, are likely to be very localized in the immediate vicinity of the produced water discharge and affect mainly plants and animals living attached to submerged platform structures.

Radium isotopes, although often abundant in produced water, do not appear to bioaccumulate in the tissues of marine animals following discharge of produced water to the ocean. Radium is quantitatively removed from sea water by coprecipitation with barium as barium sulfate upon mixing of produced water (rich in barium) with sea water

(rich in sulfate). Radium is not toxic to marine organisms at the concentrations at which it occurs in produced water or in the receiving water environment of a produced water discharge. Therefore, it does not represent a hazard to marine organisms near produced water discharges, nor to human consumers of fishery products.

Phenol from produced water has a low potential to bioaccumulate and both phenol and BEHP are rapidly metabolized and excreted by marine animals. Therefore, these chemicals are not considered hazardous to marine organisms. BTEX are abundant in produced water, but disappear very rapidly from the receiving water environment through evaporation, dilution, and biodegradation. They are only moderately toxic and do not biaccumulate to high concentrations in tissues of marine animals. They are not transferred to man through consumption of fishery products. Therefore, BTEX in produced water does not pose a health risk to marine organisms or human consumers of fishery products.

PAHs in produced water, represented by the low molecular weight PAH, fluorene, and the high molecular weight PAH, benzo(a)pyrene, have a low or moderate potential risk to marine organisms and human consumers of fishery products. The low molecular weight two- and three-ring PAHs often are relatively abundant in produced water, concentrations decreasing with increasing molecular weight. They have a tendency to bioaccumulate and often are persistent in sediments near produced water discharges. Because they are toxic, they pose a moderate risk to organisms near the produced water discharge or in sediments near the outfall. High molecular weight four- through six-ring PAHs, on the other hand, are rarely present in produced water at greater than trace (sub-parts per billion) concentrations. Although some, such as benzo(a)pyrene, are known or suspected mammalian carcinogens and readily bioaccumulate, their extremely low concentrations in produced water renders them a low risk to marine ecosystems and human consumers of fishery products from the vicinity of produced water discharges. The major source of high molecular weigh PAHs in offshore waters of the Gulf of Mexico is soot from various combustion sources. PAHs associated with soot are tightly bound to the particles and are not readily bioavailable to marine organisms. These compounds are not accumulated efficiently from the food and are biodegraded rapidly in the tissues of most marine animals; therefore, they do not biomagnify in marine food webs and do not pose a potential hazard to fish that consume biofouling organisms from submerged platform structures.

GULF OF MEXICO PRODUCED WATER BIOACCUMULATION STUDY
DEFINITIVE COMPONENT

EXECUTIVE SUMMARY

The objectives of the Definitive Component of the Gulf of Mexico Produced Water Bioaccumulation Study were to

- determine whether statistically significant bioaccumulation of target chemicals in produced water occurs in the edible tissues of resident fishes and invertebrates at representative Gulf of Mexico offshore platforms that discharge more than 4,600 barrels per day (bbl/d) of produced water relative to non-discharging platforms; and

- evaluate the ecological and human health implications of observed concentrations of target chemicals in edible tissues of fishes and invertebrates collected near offshore platforms in the Gulf of Mexico.

The study was performed in response to a U.S. Environmental Protection Agency (EPA) Region VI National Pollutant Discharge Elimination System General Permit requirement and was funded through the Offshore Operators Committee. The Definitive Component was designed to compare concentrations of 60 target chemicals (metals, radium isotopes, phenol, bis(2-ethylhexyl)phthalate [BEHP], monocyclic aromatic hydrocarbons, and polycyclic aromatic hydrocarbons [PAHs]) in edible tissues of fish and bivalve mollusk species from two discharging/non-discharging platform pairs. The two discharging platforms discharged approximately 7,000 and 11,000 bbl/d of treated produced water. Samples of produced water, ambient seawater, and the selected fish and mollusk species were collected from the two platform pairs during two cruises, one in the spring and one in the fall. The samples were analyzed with state-of-the-art methods that included a rigorous quality assurance/quality control program. Low detection limits for the target chemicals were achieved that made it possible to determine if the target chemicals were present in edible tissues at concentrations of ecological and human health concern. Despite the low detection limits, the target organic chemicals were not present in most tissue samples at concentrations above the method detection limits. Radium isotopes were detected in 55% of the tissue samples, but at concentrations below EPA risk-based concentrations (RBCs). The four target metals were present in tissues at concentrations typical for marine animals from clean marine environments.

There was no evidence of bioaccumulation from produced water of mercury, BEHP, fluorene, and benzo(a)pyrene. The evidence for bioaccumulation from produced water was weak, inconclusive, doubtful, or contradictory for arsenic, barium, cadmium, radium isotopes, phenol, and total PAHs. Based on a review of the published literature, none of the EPA-specified target chemicals were present in edible tissues at concentrations that might be harmful to the fishes and mollusks. Two of the target chemicals (arsenic and cadmium) were present in a few edible tissue samples, particularly mollusks, at

concentrations slightly higher than RBCs. However, these chemicals were present in tissues in nontoxic forms and do not pose a health hazard to consumers of bivalve fishes and mollusks from the northwestern Gulf of Mexico.

GULF OF MEXICO PRODUCED WATER BIOACCUMULATION STUDY
DEFINITIVE COMPONENT

SYNOPSIS

Objectives

The objectives of the Definitive Component of the Gulf of Mexico Produced Water Bioaccumulation Study were to

- determine whether statistically significant bioaccumulation of target chemicals in produced water occurs in the edible tissues of resident fishes and invertebrates at representative Gulf of Mexico offshore platforms that discharge more than 4,600 barrels per day (bbl/d) of produced water relative to non-discharging platforms; and

- evaluate the ecological and human health significance of observed concentrations of target chemicals in edible tissues of fishes and invertebrates collected near offshore platforms in the Gulf of Mexico.

Background

In December 1993, the U.S. Environmental Protection Agency (EPA) Region VI published a modified version of the final National Pollutant Discharge Elimination System (NPDES) General Permit (GMG290000) for the Western Gulf of Mexico Outer Continental Shelf. The modified permit required that a site-specific bioaccumulation monitoring study be conducted by operators with existing facilities that discharge more than 4,600 bbl/d of produced water. The monitoring study design involved semiannual collections of tissues of mollusk, crustacean, and fish species at each platform discharging more than 4,600 bbl/d and analysis of these samples for volatile organic compounds (benzene, toluene, ethylbenzene), semivolatile organic compounds (phenol, fluorene, benzo[a]pyrene [BAP], bis(2-ethylhexyl)phthalate [BEHP]), metals (arsenic, cadmium, mercury), and radionuclides (^{226}Ra and ^{228}Ra). As an alternative to the preceding requirement, operators could participate in an EPA-approved, industry-wide, bioaccumulation monitoring study rather than conducting individual bioaccumulation monitoring studies. In response, the Offshore Operators Committee (OOC) proposed an industry-wide bioaccumulation study. After imposing additional requirements, EPA Region VI approved the industry-wide bioaccumulation study, which consisted of a Definitive Component and a Platform Survey Component. The Definitive Component involved intensive, statistically designed sampling to determine whether marine organisms at two locations, each representing a discharging and non-discharging platform pair, were bioaccumulating target chemicals from produced water. The Platform Survey Component met EPA requirements for sampling a broad geographic distribution of discharging and non-discharging platform sites to determine tissue concentrations of the target chemicals. Separate reports have been prepared for the Definitive and Platform Survey Components. In addition, a literature review on the

marine bioaccumulation, fate, and effects of produced water constituents has been prepared.

Study Design and Methods

The Definitive Component was designed to compare concentrations of target chemicals (12 NPDES permit chemicals plus 48 additional chemicals [barium, four monoaromatic hydrocarbons, and 43 polycyclic aromatic hydrocarbons] added to the study by the OOC) in the tissues of several fish and invertebrate species living at two platform pairs selected from four pairs that were initially sampled. The abundances of appropriate species and isolation of the platforms from other potential sources of the target chemicals (e.g., the Mississippi River) were the primary factors in the selection of the two platform pairs. One pair consisted of a platform discharging approximately 7,000 bbl/d of produced water and a reference platform and the other pair consisted of a platform discharging approximately 11,000 bbl/d and a reference platform.

The selected platforms (**Figure S-1**) were visited during May and October-December 1995. Three samples of produced water were collected at each discharging platform. Three samples of ambient seawater, and multiple specimens of two bivalve mollusks and three fish species (**Table S-1**) were collected at each platform. Fish tissue samples consisted of muscle (edible fillet) only, while bivalve samples included the whole soft tissue. The samples were analyzed using state-of-the-art instrumentation and methods following a rigorous quality assurance/quality control program to determine the concentrations of the target chemicals. Low method detection limits (MDLs) comparable to or below risk-based concentrations (RBCs) were achieved through this effort (**Table S-2**). This made it possible to determine if target chemicals were present at concentrations of ecological and human health concern.

Data on concentrations of target chemicals in produced water and ambient seawater were used to estimate the potential exposure of marine animals to elevated concentrations of target chemicals. Statistical comparisons of concentrations of target produced water chemicals in fishes and bivalves from the discharging/reference platform pairs were used to determine if animals from discharging platforms are bioaccumulating the target chemicals from the produced water discharges. When a statistically significant difference was detected, the tissue residues were compared with the tissue residue data for the same or closely related taxa in the scientific literature. The results of this evaluation for each species and target chemical were classified based on the criteria in **Table S-3** into one of four categories: 1) strong evidence for bioaccumulation; 2) weak or inconclusive evidence for bioaccumulation; 3) doubtful or contradictory evidence for bioaccumulation; and 4) no evidence for bioaccumulation.

Results

Bioaccumulation

All but two of the target chemicals were found at higher concentrations in produced water than in seawater. The first exception was mercury which was not present at

concentrations above the MDL. The second exception, BEHP, is not a natural or intentionally-added component of produced water and when detected in produced water probably is due to contamination of the sample during collection, processing, or analysis. Most of the volatile and semivolatile organic compounds except BAP were present in produced water at concentrations above their MDLs, while concentrations of the same compounds in seawater and tissues were nearly all below their MDLs (**Table S-4**).

The probability of bioaccumulation from produced water was assessed for arsenic, barium, cadmium, and mercury; ^{226}Ra and ^{228}Ra; phenol; BEHP; fluorene; BAP; and total polycyclic aromatic hydrocarbons (PAHs) (**Table S-5**). The volatile organics were excluded from this assessment since more than 96% of the tissue concentrations were less than the MDLs, indicating that bioaccumulation of volatile organics from produced water or any other source is not a significant concern for fishes and bivalves near offshore oil platforms.

There was no strong evidence for bioaccumulation (as defined by the criteria for Category 1 in **Table S-3**) for any of the chemicals assessed. There was no evidence at all for bioaccumulation (as defined by the criteria for Category 4 in **Table S-3**) for mercury, BEHP, fluorene, and BAP. Evidence for bioaccumulation of the other assessed chemicals was either Category 2 (weak or inconclusive) or Category 3 (doubtful and contradictory).

Evidence for bioaccumulation of arsenic in fishes was considered "weak or inconclusive" because tissue concentrations were statistically significantly higher at discharging than at reference platforms in only 3 out of 12 cases.

At one platform pair during one cruise thorny oyster from the discharging platform contained statistically significantly higher concentrations of several PAHs than thorny oyster from the paired reference site. The PAH assemblage in the thorny oyster tissues resembled that of a light refined product or produced water. Concentrations of individual PAHs generally were low and not unusual for soft tissues of bivalves. Therefore, thorny oyster was placed in Category 2 because bioaccumulation of petroleum-derived PAHs was demonstrated in only one instance, and the source(s) of the PAHs was unclear.

Ecological Risk

Based on a review of the published literature on relationships between toxic response and tissue residues of metals, radium isotopes, and organics in freshwater and marine organisms, none of the EPA-specified target chemicals were present at concentrations that might be harmful to the fishes and bivalves. The only possible exception is cadmium in thorny oysters. However, natural concentrations of cadmium are elevated in soft tissues of oysters and scallops from uncontaminated marine environments world-wide. These cadmium residues are tightly bound to solid concretions, mostly in the kidneys, and are not toxic to the bivalves. It is probable that thorny oysters also naturally sequester large amounts of cadmium in inert tissue granules.

Human Health Assessment

The method used to assess if fishes and bivalves harvested near offshore produced water discharges pose a health risk to human consumers was to compare tissue concentrations of the target chemicals in fishes and bivalves with RBCs. It should be noted that the bivalves and three of the fish species (creole-fish, yellow chub, and sergeant major) are not normally consumed by humans. Concentrations of most target chemicals in edible fish and bivalve tissues were substantially lower than the RBCs. Arsenic exceeded the RBC in all fish and bivalve species, and cadmium exceeded the RBC in the thorny oyster. However, the RBC for arsenic is believed to be overly conservative, because the arsenic present in marine organisms is present in non-toxic organic forms. As discussed above, several species of bivalves contain naturally high concentrations of cadmium (above RBC) in their tissues in inert granules; in this form it is not bioavailable to consumers of fishery products, including humans. It is therefore highly likely that the cadmium in thorny oysters is natural and does not pose a health hazard to human consumers of shellfish products. The other target chemical concentrations in fish and bivalve tissues were well below the applicable RBC values and do not pose any health risk to human consumers of fishery products harvested near produced water discharges.

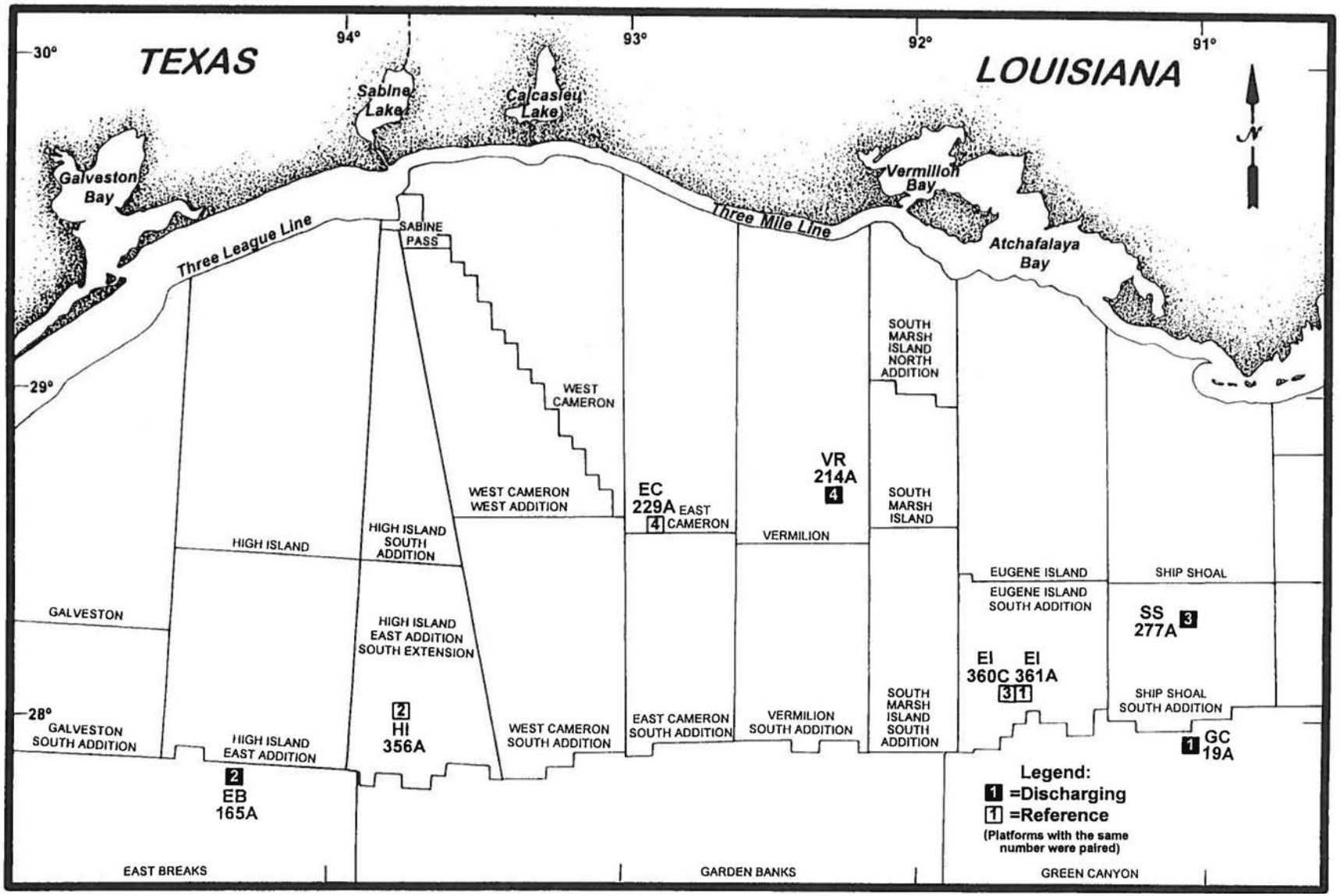

Figure S-1. Platforms sampled during Cruise 1 of the Definitive Component of the OOC Gulf of Mexico Produced Water Bioaccumulation Study.

Table S-1. Platforms sampled and species collected for the Definitive Component.

Platform Pair	Sampling Period	Species
East Breaks 165A High Island A 356A	Spring 1995	Jewel box (mollusk) Thorny oyster (mollusk) Yellow chub (fish) Creole-fish (fish) Rockhind (fish)
	Fall 1995	Jewel box (mollusk) Thorny oyster (mollusk) Yellow chub (fish) Creole-fish (fish) Sergeant major (fish)
Green Canyon 19A Eugene Island 361A	Spring 1995	Jewel box (mollusk) Thorny oyster (mollusk) Yellow chub (fish) Creole-fish (fish) Gray triggerfish (fish)
	Fall 1995	Jewel box (mollusk) Thorny oyster (mollusk) Yellow chub (fish) Creole-fish (fish) Gray triggerfish (fish)

Table S-2. Method detection limits for the Definitive Component Study.

Target Chemical Class	Produced Water (ng/L)	Ambient Seawater (ng/L)[d]	Tissue (ng/g - dry weight)
Volatile Organic Compounds	90 to 310	90 to 310	2.4 to 4.1
Semivolatile Organic Compounds [a]	1.0 to 11	1.0 to 11	1.3 to 16
Metals [b]	10 to 620	5 to 30	1 to 50
Radium Isotopes [c]	0.01 to 0.75	0.007 to 0.070	0.001 to 0.03

[a] Not included in range are bis(2-ethylhexyl)phthalate (90 ng/L in water and 140 ng/g in tissues) and phenol (38 ng/g in tissues).
[b] Not included in range is barium (240 µg/L in produced water and 140 ng/L in ambient seawater).
[c] pCi/L and pCi/g wet weight.
[d] ng/L and ng/g are approximately the same as parts per billion (ppb).

Table S-3. Criteria for produced water bioaccumulation classification for species and target chemicals.

Category 1: Strong evidence for bioaccumulation to biologically significant tissue concentrations.

A. Tissue concentrations significantly higher at the discharging platform of both platform pairs and both surveys; and

B. Tissue residues for chemical at discharging platforms exceed the "typical" range for the chemical in marine animals from uncontaminated environments.

Category 2: Weak or inconclusive evidence for bioaccumulation.

A. Tissue concentrations significantly greater at one discharging platform (compared to the paired reference platform) on both surveys, but no significant differences at the other platform pair; or

B. Tissue concentrations significantly greater at one or both discharging platforms in comparison to their paired reference platforms, but only on one survey; and

C. Differences in concentrations in tissues of marine animals from discharge and reference platforms are small and within the "typical" range for marine animals from uncontaminated marine environments.

Category 3: Doubtful or contradictory evidence for bioaccumulation.

A. Tissue concentrations significantly higher at one discharging platform on one occasion (compared to the paired reference platform); and

B. Tissue concentrations significantly higher at one or both reference platforms than at the paired discharging platform on one or both cruises; and

C. Differences in concentrations in tissues of marine animals from discharge and reference platforms are small and within the "typical" range for marine animals from uncontaminated marine environments.

Category 4: No evidence of bioaccumulation.

A. No significant differences between paired produced water discharging and reference platforms for either cruise or concentrations significantly higher more frequently in marine animals from the reference than from the discharging platform; and

B. All concentrations within the "typical" range for uncontaminated marine environments.

Table S-4. Percentage of analysis values (dry weight basis) below method detection limit (MDL) and practical quantitation level (PQL) (defined as five times MDL). There is a reduced confidence in the reported magnitude of a value that is below the PQL.

Target Chemical Class	Produced Water		Ambient Seawater		Tissues	
	MDL	PQL	MDL	PQL	MDL	PQL
Volatile Organic Compounds	5	5	98	100	96	99
Semivolatile Organic Compounds	30	34	88	97	87	98
Metals	40	43	33	36	1	12
Radium Isotopes	0	0	52	52	45[a]	45

[a] Includes values below PQL defined in this study.

Table S-5. Ranking of the evidence for bioaccumulation from produced water by marine bivalves and fish from the vicinity of offshore, high-volume produced water discharges. The ranking categories are 1) strong evidence for bioaccumulation; 2) weak or inconclusive evidence for bioaccumulation; 3) doubtful or contradictory evidence for bioaccumulation; and 4) no evidence for bioaccumulation. Volatile organic compounds were not included in this analysis because they were not detected in 96% of the samples and were therefore Category 4.

Chemical	Jewel Box	Thorny Oyster	Fish
Arsenic	4	3	2
Barium	3	4	4
Cadmium	4	3	4 (YC, CF, RH) 3 (GT, SM)
Mercury	4	4	4
Radium Isotopes	3	4	4
Phenol	3	3	3 (GT) 4 (YC, CF, RH, SM)
Bis(2-ethylhexyl)phthalate	4	4	4
Fluorene	4	4	4
Benzo(a)pyrene	4	4	4
Total Polycyclic Aromatic Hydrocarbons	3	2	4

CF = Creole-fish.
RH = Rockhind.
SM = Sergeant major.
GT = Gray triggerfish.
YC = Yellow chub.

GULF OF MEXICO PRODUCED WATER BIOACCUMULATION STUDY
PLATFORM SURVEY COMPONENT

EXECUTIVE SUMMARY

The National Pollutant Discharge Elimination System General Permit for the Western Gulf of Mexico Outer Continental Shelf (GMG 290000) requires bioaccumulation monitoring for facilities discharging more than 4,600 barrels/day (bbl/d) of treated produced water. The objective of the Platform Survey Component of the bioaccumulation study was to determine the concentrations of 12 U.S. Environmental Protection Agency (EPA)-specified target chemicals in edible tissues of fishes and invertebrates collected in the immediate vicinity of produced water discharging and non-discharging platforms from different regions of the western Gulf of Mexico. Two species of fish were sampled from 11 discharging/non-discharging platform pairs, and oysters, blue crabs, and 1 species of fish were collected for analysis from 1 discharging/non-discharging platform pair. The platform pairs consisted of Definitive Component Platforms and platforms located in four areas: high platform density; influenced by the Mississippi River; water depths less than 10 m; and off the Texas coast. Edible tissues of oysters, crabs, and fishes were analyzed by advanced, sensitive methods for arsenic, cadmium, mercury, ^{226}Ra and ^{228}Ra, benzene, toluene, ethylbenzene, phenol, bis(2-ethylhexyl)phthalate (BEHP), fluorene, and benzo(a)pyrene (BAP). The target metals were measured in 496 tissue samples; target volatile organic chemicals were measured in 494 tissue samples, target semivolatile organic chemicals were measured in 495 tissue samples; and target radionuclides were measured in 495 tissue samples. This represents the largest existing database of chemical residues in tissues of marine animals from the western Gulf of Mexico.

The analytical methods provided method detection limits (MDLs) well below screening level risk-based concentrations (RBCs) for protection of human consumers of fishery products. Nevertheless, most of the analytical results for organic chemicals in tissues were below the MDLs. The volatile aromatic hydrocarbons, benzene, toluene, and ethylbenzene were not detected in 97% of tissue samples. In the few samples in which a volatile aromatic hydrocarbon was detected, the concentration was orders of magnitude below the RBC. Fluorene was not detected in 89% of tissue samples. The highest measured concentration was 0.03% of the RBC. BAP was not detected in over 97% of 494 tissue samples. Phenol was not detected in 86% of tissue samples. Most of the other tissue samples in which phenol was detected were collected from non-discharging platforms and contained phenol concentrations 50% or less of the RBC. BEHP was not detected in 90% of tissue samples. It was found in some blank samples, indicating that, when present, it may be the result of sample contamination during collection, processing, and analysis. Tissues containing detectable concentrations of BEHP were collected about equally from discharging and non-discharging platforms. The tissue BEHP, if not an artifact, was derived from a source other than produced water, because BEHP is not a known component of produced water. Arsenic and mercury were detected in all tissue samples. Concentrations were typical of those in tissues of marine animals from clean marine

environments throughout the world. All tissue samples contained arsenic concentrations higher than the RBC. Arsenic is abundant in edible tissues of all marine animals and is present in non-toxic organic forms. There was no apparent difference in mercury and arsenic concentrations in tissues of marine animals from discharging and non-discharging platform sites. Cadmium was detected in 82% of 496 tissue samples. Cadmium concentrations were comparable in edible tissues of marine animals from discharging and non-discharging platforms. Total radium (sum of ^{226}Ra and ^{228}Ra) was detected in less than half of the tissue samples.

The results of this study indicate that there is no relationship between the proximity of marine animals to offshore produced water discharges and concentrations in their edible tissues of the 12 EPA-targeted chemicals. The concentrations of the chemicals in edible tissues of marine animals from the western Gulf of Mexico are below concentrations that might represent a hazard to the marine animals themselves or their consumers, including man.

GULF OF MEXICO PRODUCED WATER BIOACCUMULATION STUDY
PLATFORM SURVEY COMPONENT

SYNOPSIS

Introduction

The National Pollutant Discharge Elimination System General Permit for the Western Gulf of Mexico Outer Continental Shelf (GMG 290000) requires bioaccumulation monitoring for facilities discharging more than 4,600 barrels/day (bbl/d) of produced water. The monitoring required by the permit was to be carried out according to a U.S. Environmental Protection Agency (EPA) defined sampling plan. As an alternative to sampling at each facility discharging in excess of 4,600 bbl/d, the permit allowed operators to participate in an EPA-approved, industry-wide, bioaccumulation monitoring program. The EPA approved an industry-wide study design proposed by the Offshore Operators Committee (OOC). The study consisted of two parts: the OOC-designed Definitive Component, which involved intensive, statistically designed sampling at a limited number of sites, and the EPA-specified Platform Survey Component, which involved sampling at a broad cross-section of locations in the central and western Gulf of Mexico.

Objective

The objective of the Platform Survey Component was to determine the concentrations of EPA-specified target chemicals in the edible tissue of marine organisms collected in the immediate vicinity of discharging and non-discharging platforms from different regions in the Gulf of Mexico. To meet this objective, biological specimens were collected at 12 platform pairs (1 discharging platform and 1 non-discharging platform in each pair). The EPA required that two platform pairs be located in each of the following areas: high platform density; influenced by the Mississippi River; less than 10 m water depths; and off the Texas coast. To reach the required total of 12 platform pairs, the 4 platform pairs that were candidate study sites for the Definitive Component were also included. **Figure S-1** shows the geographic locations of the platforms.

Sampling Design

At 11 platform pairs two species of fish were to be collected, and at 1 platform pair fish, mollusk, and crustacean species were to be collected. Sampling was conducted during the fall and spring at each platform pair. The edible tissues were analyzed to determine the concentrations of selected volatile organic compounds (VOCs) (benzene, toluene, and ethylbenzene), semivolatile organic compounds (SVOCs) (phenol, fluorene, benzo[a]pyrene [BAP], and bis[2-ethylhexyl]phthalate [BEHP]), metals (arsenic, cadmium, and mercury), and radionuclides (^{226}Ra and ^{228}Ra).

Results

The results of this investigation represent the largest existing database on contaminant residues in tissues of marine animals, particularly fishes, from the northwestern Gulf of Mexico. The target metals were measured in 496 tissue samples; target volatile organic chemicals were measured in 494 tissue samples, target semivolatile organic chemicals were measured in 495 tissue samples; and target radionuclides were measured in 495 tissue samples.

One would expect that concentrations of the chemicals would be significantly higher in tissues of marine animals from platforms with large-volume produced water discharges than in tissues of marine animals from nearby offshore platforms with no produced water discharge. This was not found to be the case in this study. Highly specific and sensitive analytical methods were used in this investigation to quantify traces of the target chemicals in marine organisms. Method detection limits (MDLs) were well below risk-based concentrations (RBCs) (MDLs averaged 6.0% of corresponding RBCs) of the analytes in tissues of fishes consumed by man. Thus, very low tissue concentrations and small differences among sampling sites could be detected. Nevertheless, no consistent trends in concentrations of the different target chemicals were detected in tissues of marine mammals from different regions of the northwestern Gulf of Mexico and between produced water discharging and non-discharging sites.

The results for VOCs, SVOCs, metals, and radium are discussed below.

Volatiles

Benzene, toluene, and ethylbenzene were not detectable in 96.8% of the tissue samples analyzed for this study. The MDLs were orders of magnitude below RBCs for benzene and toluene. These results show that the concentrations of volatile aromatic hydrocarbons in Gulf of Mexico marine organisms living near offshore platforms are well below levels of environmental concern. The presence of benzene, toluene, and ethylbenzene from produced water or any other source in marine organisms living near offshore platforms is not a significant environmental problem.

Semivolatiles

Fluorene was not detectable in 89% of the samples analyzed for this study. The highest concentration measured in any sample was only 0.03% of the RBC. These results show that contamination of Gulf of Mexico organisms living near offshore platforms by fluorene from produced water or any other source is not a significant environmental problem.

Phenol was not detectable in 86% of the samples analyzed for this study. In the remaining samples, the highest concentrations (less than of the RBC) were found in samples collected near platforms that were not discharging produced water. These results show that phenol is not found at levels of concern in Gulf of Mexico marine organisms living near offshore platforms and that there is no indication

that the presence of phenol is correlated with the practice of discharging produced water.

BAP was not detectable in 97% of the 494 samples analyzed for this study. The results of this study show that BAP is not found at levels of concern in the Gulf of Mexico marine organisms living near offshore platforms. BAP usually is not detected in produced water; it is primarily from combustion sources. There is no indication that the presence of BAP is correlated with the practice of discharging produced water.

BEHP was not detectable in 90% of the samples analyzed for this study. The remaining 11% of samples in which BEHP was detectable were about equally divided between discharging and non-discharging sites. BEHP is not a natural or intentionally added component of produced water so one would not expect it to be present at elevated concentrations in tissues of marine animals near produced water discharges. It is recognized that BEHP is frequently present as an artifact in environmental samples. The results of this study were consistent with this view in that BEHP was found in concentrations exceeding the RBC in some samples at about the same number of discharging platforms and non-discharging platforms. There is no indication that the presence of BEHP is correlated with the practice of discharging produced water.

Metals

Mercury was detectable in all samples analyzed for this study. Mean mercury concentrations were equally likely to be higher in tissues of particular species from a produced water discharge site as from a non-discharging platform. This supports the results of this study that show fishes and invertebrates are not bioaccumulating mercury from offshore produced water discharges.

Arsenic was detectable in all tissue samples analyzed for this study. As is the case with essentially all seafood, average levels of arsenic in tissues analyzed for this study were in excess of the RBC at both discharging and non-discharging platforms. Arsenic concentrations in edible tissues of marine animals analyzed in this study are within the natural range for marine animals world-wide. Average levels of arsenic in the tissues of a given species were no more likely to be higher for organisms collected near discharging platforms than for organisms collected near non-discharging platforms. This suggests that factors other than proximity to a produced water discharge are the main determinants of tissue arsenic levels. Arsenic concentrations measured in tissues of marine fishes and invertebrates from the vicinity of platforms in the northwestern Gulf of Mexico are within the range typical for animals living in the Gulf of Mexico. Therefore, there is no indication that marine animals were bioaccumulating arsenic from produced water.

Cadmium was detectable in 82% of the 496 samples analyzed for this study. Oysters world-wide contain naturally high concentrations of cadmium in soft

tissues, mostly the kidneys. Mean cadmium concentrations in oyster tissues in this study were comparable at the nearshore produced water discharging and non-discharging platforms, but were higher in the fall than in the spring, possibly reflecting seasonal changes in cadmium concentrations in the ambient seawater.

There was no consistent trend of geographic, seasonal, or discharge/non-discharge differences in concentrations of cadmium in tissues of marine fishes and crabs. This study indicates that cadmium was not bioaccumulated from produced water by the marine fishes and crabs.

Radium

Radium was detectable in less than half of the samples analyzed for this study. The highest concentration was less than one-third the RBC. The results of this study do not indicate that contamination of organisms found near Gulf of Mexico platforms with radium from produced water or any other source is a significant environmental concern.

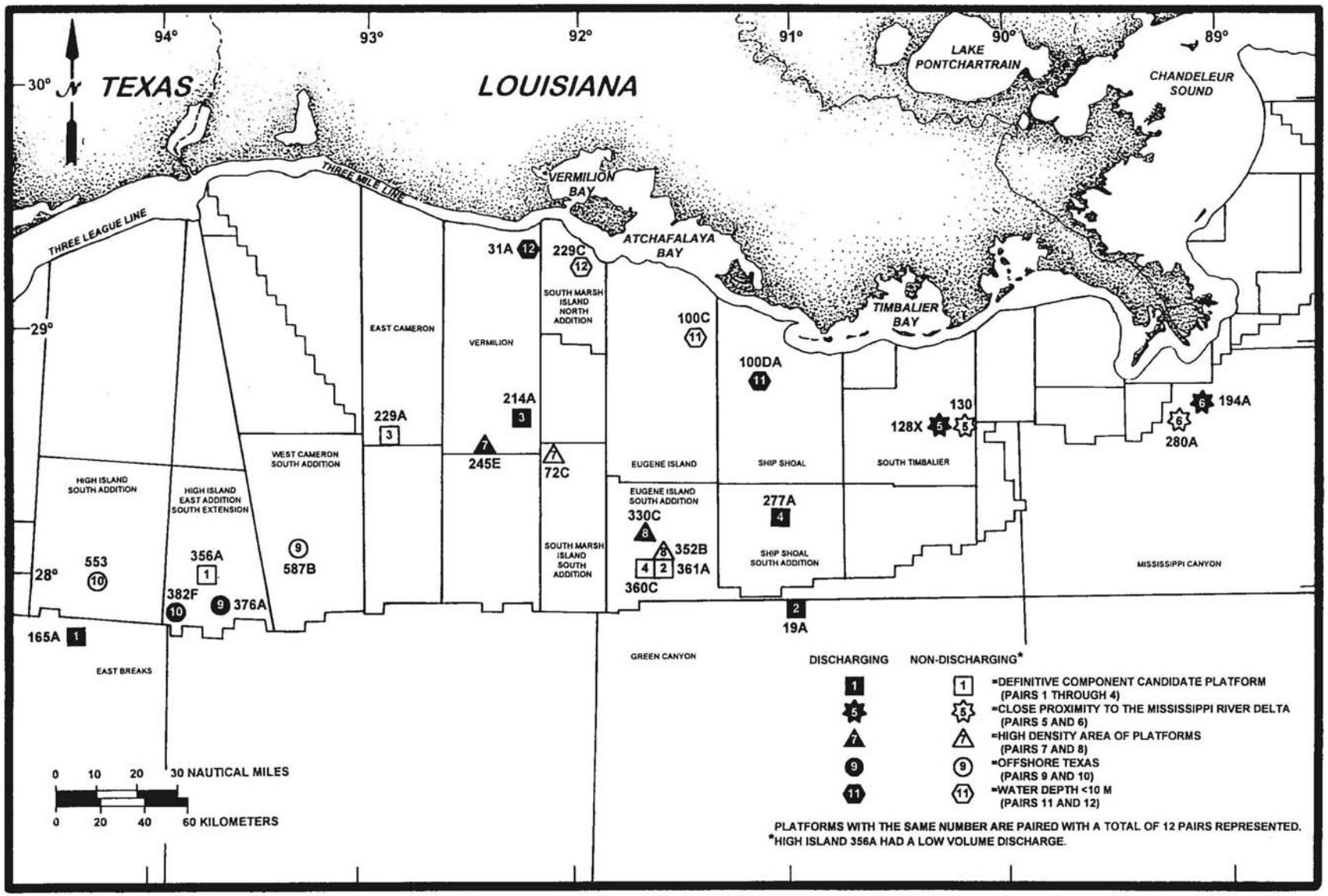

Figure S-1. Platforms sampled during the Platform Survey Component of the OOC Gulf of Mexico Produced Water Bioaccumulation Study.