# NOAA Technical Memorandum NMFS-SEFC-42



# NOAA/NMFS Annual report to epa

Environmental Assessment of Buccaneer Gas and Oil Field in the Northwestern Gulf of Mexico, 1978 - 1979

A report to the Environmental Protection Agency on work conducted under provisions of Interagency Agreement EPA-IAG-D5-E693-E0 during 1978 - 1979.

# SOUTHEAST FISHERIES CENTER GALVESTON LABORATORY

Volume VIII

TRACE METALS





# GALVESTON, TEXAS

U.S. DEPARTMENT OF COMMERCE National Oceanic and Atmospheric Administration National Marine Fisheries Service Southeast Fisheries Center Galveston Laboratory Galveston, Texas 77550



# NOAA Technical Memorandum NMFS-SEFC- 42

# Environmental Assessment of Buccaneer Gas and Oil Field In the Northwestern Gulf of Mexico, 1978-1979

# VOL. VIII - TRACE METALS

## ΒY

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A report to the Environmental Protection Agency on work conducted under provisions of Interagency Agreement EPA-IAG-D5-E693-E0 during 1978+1979.

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Tillery, J. B. 1980. Trace metals. Vol. VIII. In: Jackson, W. B. and E. P. Wilkens, (eds.). Environmental assessment of Buccaneer gas and oil field in the northwestern Gulf of Mexico, 1978-1979. NOAA Technical Memorandum NMFS-SEFC-42, 93 p. Available from: NTIS, Springfield, Virginia.

#### Volume VIII - TRACE METALS

## TABLE OF CONTENTS

Page

I. Editors' Section

Project Administration	v
List of Volumes	vii
Guide to Users of the Annual Report	x
Foreword	xi
List of Reports and Publications	xiii
Published Reports	xiii
Dissertations and Theses	xvii
Publications in Press or in Preparation	xvii
Introduction Location of Study Area Operation History of Buccaneer Field Fig. 1. Location of Buccaneer Field Fig. 2. Buccaneer Field Structures Fig. 3. Shell Oil Company's Alphanumerical Identification of Buccaneer Field Structures	xix xix xix xx xx xxii xxiii

II. Principal Investigators' Section

Work	Unit	2.4.	2 Trace	Metals	 xxiv

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#### LIST OF VOLUMES

#### This Annual Report is printed in ten separate volumes:

#### Volume I - SYNOPSIS/DATA MANAGEMENT

Work Unit 2.6.1 Synopsis

NMFS/SEFC Galveston Laboratory

Principal Investigators

Work Unit 2.2.3

Implement, Monitor, and Modify Data Management System

NMFS/SEFC National Fisheries Engineering Laboratory

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#### Volume II - SEDIMENTS AND PARTICULATES

Work Unit 2.3.2

Investigations of Surficial Sediments and Suspended Particulates at Buccaneer Field

Texas A&M University

J. Brooks, Ph.D. E. Estes, Ph.D. W. Huang, Ph.D.

#### Volume III - FISHES AND MACROCRUSTACEANS

Work Unit 2.3.5

Effect of Gas and Oil Field Structures and Effluents on Pelagic and Reef Fishes, Demersal Fishes, and Macrocrustaceans

LGL Ecological Research Associates, Inc.

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Work Unit 2.3.7

Bacterial Communities

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Volume V - FOULING COMMUNITY

Work Unit 2.3.8 Effects of Gas and Oil Field Structures and Effluents on Fouling Community Production and Function

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Volume VI - CURRENTS AND HYDROGRAPHY

Work Unit 2.3.9 Currents and Hydrography of the Buccaneer Field and Adjacent Waters

> Hazleton Environmental Sciences Corporation

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Volume VII - HYDROCARBONS

Work Unit 2.4.1 Hydrocarbons, Biocides, and Sulfur

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#### Volume VIII - TRACE METALS

Work Unit 2.4.2 Trace Metals

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#### Volume IX - FATE AND EFFECTS MODELING

Work Unit 2.5.1

Sources, Fate and Effects Modeling

Science Applications, Inc.

K. Fucik, Ph.D. I. Show, Ph.D.

#### Volume X - HYDRODYNAMIC MODELING

Work Unit 2.5.2

Hydrodynamic Modeling

Environmental Research and Technology, Inc.

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#### GUIDE TO USERS OF THE ANNUAL REPORT

Volume I (SYNOPSIS/DATA MANAGEMENT) of the Annual Report is designed to be used as a briefing document and as a key to more detailed scientific and technical information contained in Volumes II through X. Objectives, methods and results for each work unit are summarized in greatly abbreviated form within Volume I to facilitate dissemination of information. Thus, Volume I can be used alone or as a reference to companion Volumes II through X. Complete citations for literature cited in Volume I can be found in the Volumes II through X in which the detailed work unit reports are presented.

It is hoped that such an approach to environmental impact information dissemination will make the Annual Report a more useful and widely read document.

#### FOREWORD

Increased petroleum development of the outer continental shelf (OCS) of the United States is anticipated as the U.S. attempts to reduce its dependency on foreign petroleum supplies. To obtain information concerning the environmental consequences of such development, the Federal Government has supported major research efforts on the OCS to document environmental conditions before, during, and after oil and gas exploration, production, and transmission. Among these efforts is the Environmental Assessment of Buccaneer Gas and Oil Field Northwestern Gulf of Mexico, a project funded by the in the Environmental Protection Agency (EPA) through interagency agreement with the National Oceanic and Atomospheric Administration (NOAA) and managed by the National Marine Fisheries Service (NMFS), Southeast Fisheries Center (SEFC), Galveston Laboratory, in Galveston, Texas. Initiated in the autumn of 1975, the study is now in its last year. Its major products have been annual reports disseminated by the National Technical Information Service, data files archived and disseminated by NOAA's Environmental Data and Information Service, and research papers written by participating investigators and published in scientific or technical journals. Results have also been made available through EPA/NOAA/NMFS project reviews and workshops attended by project participants, and various governmental (Federal and State), private, and public user groups. The final products will be milestone reports summarizing the findings of the major investigative components of the study.

Objectives of the project are (1) to identify and document the types and extent of biological, chemical and physical alterations of the marine ecosystem associated with Buccaneer Gas and Oil Field, (2) to determine specific pollutants, their quantity and effects, and (3) to develop the capability to describe and predict fate and effects of Buccaneer Gas and Oil Field contaminants. The project uses historical and new data and includes investigations both in the field and in the laboratory. A brief Pilot Study was conducted in the autumn and winter of 1975-76. followed by an extensive biological/chemical/physical survey in 1976-77 comparing the Buccaneer Gas and Oil Field area with adjacent undeveloped or control areas. In 1977-78, investigations were intensified within Buccaneer Gas and Oil Field, comparing conditions around production platforms, which release various effluents including produced brine, with those around satellite structures (well jackets) which release no effluents. In 1978-79, studies around Buccaneer Gas and Oil Field structures focused on (1) concentrations and effects of pollutants in major components of

the marine ecosystem, including seawater, surficial sediments, suspended particulate matter, fouling community, bacterial community, and fishes and macro-crustaceans, (2) effects of circulation dynamics and hydrography on distribution of pollutants, and (3) mathematical modeling to describe and predict sources, fate and effects of pollutants. The final year, 1979-80, of study is continuing to focus on items (1) and (2) and on preparation of the milestone reports which will represent the final products of this study.

This project has provided a unique opportunity for a multiyear investigation of effects of chronic, low-level contamination of a marine ecosystem associated with gas and oil production in a longestablished field. In many respects, it represents a pioneering effort. It has been made possible through the cooporation of government agencies, Shell Oil Company (which owns and operates the field) and various contractors including universities and private companies. It is anticipated that the results of this project will impact in a significant way on future decisions regarding operations of gas and oil fields on the OCS.

> Charles W. Caillouet, Project Manager Chief, Environmental Research Division and William B. Jackson and E. Peter Wilkens, Editors

#### LIST OF REPORTS AND PUBLICATIONS

#### Published Reports

- Brooks, J. M., E. L. Estes and W. Huang. 1980. Investigations of surficial sediments and suspended particulates at Buccaneer field. Vol. II. In: Jackson, W. B. and E. P. Wilkens (eds.). Environmental assessment of Buccaneer gas and oil field in the northwestern Gulf of Mexico, 1978-1979. NOAA Technical Memorandum NMFS-SEFC-36, 261 p. Available from: NTIS, Springfield, Virginia.
- Danek, L. J. and M. S. Tomlinson. 1980. Currents and hydrography of the Buccaneer field and adjacent waters. Vol. VI. In: Jackson, W. B. and E. P. Wilkens, (eds.). Environmental assessment of Buccaneer gas and oil field in the northwestern Gulf of Mexico, 1978-1979. NOAA Technical Memorandum NMFS-SEFC-40, 33 p. Available from: NTIS, Springfield, Virginia.
- Finucane, J. H. 1977. Ichthyoplankton of the Buccaneer oil field off Galveston, Texas. Paper presented at the Fourth Biennial International Estuarine Research Conference, Mt. Pocono, Pa. (abstract published in proceedings).
- Fucik, K. and I. T. Show, Jr. 1980. Sources, fate and effects modeling. Vol. IX. In: Jackson, W. B. and E. P. Wilkens (eds.). Environmental assessment of Buccaneer gas and oil field in the northwestern Gulf of Mexico, 1978-1979. NOAA Technical Memorandum NMFS-SEFC-43, 105 p. Available from: NTIS, Springfield, Virginia.
- Gallaway, B. J., R. Howard, K. Green and L. Martin. 1976. A study plan for the Buccaneer oil field assessment program. A report to NMFS from LGL Limited-U.S., Inc., Bryan, Texas, 69 pp.
- Gallaway, B. J. and L. R. Martin. 1980. Effect of gas and oil field structures and effluents on pelagic and reef fishes, and demersal fishes and macrocrustaceans. Vol. III. In: Jackson, W. B. and E. P. Wilkens (eds.). Environmental assessment of Buccaneer gas and oil field in the northwestern Gulf of Mexico, 1978-1979. NOAA Technical Memorandum NMFS-SEFC-37, 49 p. Available from: NTIS, Springfield, Virginia.
- Harper, D. E., Jr., R. J. Scrudato and C. S. Giam. 1976. A preliminary environmental assessment of the Buccaneer oil/gas field (pilot study of the Buccaneer oil field (benthos and sediments).

A final report from Texas A&M University to the National Marine Fisheries Service, Galveston, Texas (Contract No. 03-6-042-35110), 63 pp.

- Hollaway, S. J., G. M. Faw, R. K. Sizemore. 1980. The bacterial community composition of an active oil field in the northwestern Gulf of Mexico. Mar. Poll. Bull. 11:153-156.
- Howard, R. L, G. S. Boland, B. J. Gallaway and G. D. Dennis. 1980. Effects of gas and oil field structures and effluents on fouling community production and function. Vol. V. In: Jackson, W. B. and E. P. Wilkens (eds.). Environmental assessment of Buccaneer gas and oil field in the northwestern Gulf of Mexico, 1978-1979. NOAA Technical Memorandum NMFS-SEFC-39, 60 p. Available from: NTIS, Springfield, Virginia.
- Jackson, W. B. (Editor). 1977. Environmental assessment of an active oil field in the northwestern Gulf of Mexico, 1976-1977. NOAA Annual Report to EPA, Project Number EPA-IAG-D5-E693-E0, 759 pp. Available from: NTIS, Springfield, Virginia, Accession No. PB283890.
- Jackson, W. B. (Editor). 1979. Environmental assessment of an active oil field in the northwestern Gulf of Mexico, 1977-1978. Volume I: Synopsis. NOAA Annual Report to EPA, Project Number EPA-IAG-D5-E693-E0. 62 pp. Available from: NTIS, Springfield, Virginia, Accession No. PB301339/AS.
- Jackson, W. B. (Editor). 1979. Environmental assessment of an active oil field in the northwestern Gulf of Mexico, 1977-1978.
  Volume III: Chemical and physical investigations. NOAA Annual Report to EPA, Project Number EPA-IAG-D5-E693-E0. 722 pp. Available from: NTIS, Springfield, Virginia, Accession No. PB80107899.
- Jackson, W. B. (Editor). 1979. Environmental assessment of an active oil field in the northwestern Gulf of Mexico, 1977-1978. Volume II: Data management and biological investigations. NOAA Annual Report to EPA, Project Number EPA-IAG-D5-E693-E0, 799 pp. Available from: NTIS, Springfield, Virginia, Accession No. PB80165970.
- Jackson W. B. and E. P. Wilkens. (Editors). 1980. Synopsis. Vol. I. In: Environmental assessment of Buccaneer gas and oil field in the northwestern Gulf of Mexico, 1978-1979. NOAA Technical Memorandum NMFS-SEFC-35, p. Available from: NTIS, Springfield, Virginia.

- Jackson, W. B., K. N. Baxter and C. W. Caillouet. 1978. Evironmental assessment of the Buccaneer oil and gas field off Galveston, Texas: An overview. Proceedings of the Offshore Technology Conference, May, 1978, Houston, Texas, OTC 3081:277-284.
- Jackson, W. B., K. N. Baxter, and C. W. Caillouet. 1979. Environmental assessment of an offshore oil field. Ecolibrium 8(1): 7-9.
- McCall, J. O. and R. K. Sizemore. 1979. Description of a bacteriocinogenic plasmid in <u>Beneckea harveyi</u>. Appl. Environ. Microbiol. 38(5):974-979.
- McKinney, L. 1979. Liljeborgiid amphiopods from the Gulf of Mexico and Caribbean Sea. Bull. Mar. Sci. 29(2):140-154.
- Middleditch, B. S. and B. Basile. 1976. Deuteriated analogs as internal standards for the quantitation of environmental alkanes by gas chromatography. Analyt. Letters 9(11):1031-1034.
- Middleditch, B. S. and B. Basile. 1979. Sulfur-34 as an internal standard for quantitation of environmental sulfur by combined gas chromatography-mass spectometry. Analyt. Letters 12(A7):777-781.
- Middleditch, B. S., B. Basile and E. S. Chang. 1977. Environmental effects of offshore oil production: alkanes in the region of the Buccaneer oilfield. J. Chromatography 142(1977):777-785.
- Middleditch, B. S., B. Basile and E. S. Chang. 1978. Alkanes in surficial sediments from the region of the Buccaneer oilfield. J. Chromatography 158:449-463.
- Middleditch, B. S., B. Basile and E. S. Chang. 1978. Discharge of alkanes during offshore oil production in the Buccaneer oilfield. Bull. Environ. Contam. Toxicol. 20:59-65.
- Middleditch, B. S., B. Basile and E. S. Chang. 1979. Alkanes in seawater in the vicinity of the Buccaneer oilfield. Bull. Environ. Contam. Toxicol. 21:413-420.
- Middleditch, B. S., E. S. Chang and B. Basile. 1979. Alkanes in barnacles (<u>Balanus tintinnabulum</u>) from the Buccaneer oilfield. Bull. Environ. Contam. Toxicol. 23:6-12.
- Middleditch, B. S., E. S. Chang and B. Basile. 1979. Alkanes in plankton from the Buccaneer oilfield. Bull. Environ. Contam. Toxicol. 21:421-427.

- Middleditch, B. S., E. S. Chang, B. Basile, and S. R. Missler. 1979. Alkanes in fish from the Buccaneer oilfield. Bull. Environ. Contam. Toxicol. 22:249-257.
- Middleditch, B. S. and D. L. West. 1979. Bicyclohexyl interference in the quantitation of environmental alkanes by gas chromatography. Analyt. Letters 12(A12):1279-1284.
- Middleditch, B. S. and D. L. West. 1980. Hydrocarbons, biocides, and sulfur. Vol. VII. In: Jackson, W. B. and E. P. Wilkens, (eds.). Environmental assessment of Buccaneer gas and oil field in the northwestern Gulf of Mexico, 1978-1979. NOAA Technical Memorandum NMFS-SEFC-41, p. Available from: NTIS, Springfield, Virginia.
- National Marine Fisheries Service. 1977. Environmental assessment of an active oil field in the northwestern Gulf of Mexico. A report of NMFS/LGL Workshop I, 1977-1978. NMFS Galveston Laboratory, Southeast Fisheries Center, NOAA, USDOC. Project Number EPA-IAG-D5-E693-E0.
- Savastano, K. and H. Holley. 1980. Implement, monitor, and modify data management system. Vol. I. In: Jackson, W. B. and E. P. Wilkens (eds.). Environmental assessment of Buccaneer gas and oil field in the northwestern Gulf of Mexico, 1978-1979. NOAA Technical Memorandum NMFS-SEFC-35. p. Available from: NTIS, Springfield, Virginia.
- Show, I. T., Jr. 1979. An application of compartmental models to mesoscale marine ecosystems, pages 73-97. In: J. H. Matis, B. C. Patten, and G. C. White (eds.). Compartmental analysis of ecosystem models. International Co-operative Publishing House, Fairland, Maryland, U.S.A.
- Sizemore, R. K. and K. Olsen. 1980. Bacterial communities. Vol. IV. <u>In</u>: Jackson, W. B. and E. P. Wilkens (eds.). Environmental assessment of Buccaneer gas and oil field in the northwestern Gulf of Mexico, 1978-1979. NOAA Technical Memorandum NMFS-SEFC-38, 32 p. Available from: NTIS, Springfield, Virginia.
- Smedes, G., J. Calman and J. Beebe. 1980. Hydrodynamic modeling. Vol. X. In: Jackson, W. B. and E. P. Wilkens (eds.). Environmental assessment of Buccaneer gas and oil field in the northwestern Gulf of Mexico, 1978-1979. NOAA Technical Memorandum NMFS-SEFC-44, 57 p. Available from: NTIS, Springfield, Virginia.
- Tillery, J. B. 1980. Trace metals. Vol. VIII. In: Jackson, W. B. and E. P. Wilkens, (eds.). Environmental assessment of Buccaneer

gas and oil field in the northwestern Gulf of Mexico, 1978-1979. NOAA Technical Memorandum NMFS-SEFC-42, 93 p. Available from: NTIS, Springfield, Virginia.

Wheeler, R. B., R. R. Schwarzer and J. B. Anderson. 1978. Assessment of environmental impact of offshore production in the Buccaneer oil field: sedimentologic and geochemical results. Proceedings of the Offshore Technology Conference, May 1978, Houston, Texas OTC 3082:285-290.

#### Dissertations and Theses

- Basile, B. 1978. Environmental effects of offshore oil production. Ph.D. Dissertation, University of Houston, Houston, Texas.
- Boland, G. S. 1980. Morphological parameters of the barnacle, <u>Balanus</u> <u>tintinnabulum antillensis</u>, as indicators of physiological and <u>environmental</u> conditions. M. S. Thesis, Texas A&M University, College Station, Texas.
- Chang, E. S. 1978. Sterols in the marine food web. M.S. Thesis, University Houston, Houston, Texas.
- McCall, J. O. 1979. Isolation and characterization of a bacteriocinogenic strain of the bioluminescent marine bacterium <u>Beneckea harveyi</u>. M.S. Thesis, University of Houston, Houston, Texas.
- West, D. L. 1979. Hydrocarbons, sulfur and acrolein in the marine ecosystem associated with offshore oil production. M.S. Thesis, University of Houston, Houston, Texas.
- Wheeler, R. B. 1979. Environmental trace metal geochemistry of the Buccaneer oil and gas field. M.S. Thesis, Rice University, Houston, Texas. 176 pp.

#### Publications in Press or in Preparation

Anderson, J. B., R. R. Schwarzer, B. S. Middleditch, and B. Basile. Trace metal and hydrocarbon distribution in the region of the Buccaneer oil field. M.S. in preparation.

- Devereux, R. and R. K. Sizemore. Incidence of degradative plasmids in hydrocarbon-utilizing bacteria. M.S. submitted to Developements in Industrial Microbiology.
- Hada, H. S. and R. K. Sizemore. A survey of the incidence of plasmids in marine <u>Vibrio</u> spp. M.S. submitted to Appl. Environ. Microbiol.
- McKinney, L. The genus <u>Photis</u> from the Texas coast with a description of a new species, <u>Photis</u> <u>melanicus</u>. Contrib. Mar. Sci. (in press).
- Middleditch, B. S. and B. Basile. 1980. Alkanes in shrimp from the Buccaneer oilfield. Bull. Environ. Contam. Toxicol. (in press).
- Middleditch, B. S. and B. Basile. 1980. Alkanes in benthic organisms from the Buccaneer oilfield. Bull. Environ. Contam. Toxicol. (in press).
- Middleditch, B. S. and B. Basile. 1980. Discharge of elemental sulfur and its distribution in the region of the Buccaneer oilfield. J. Chromatog. (in press).
- Olsen, K. D. and R. K. Sizemore. Effects of an established offshore oil platform on the autochthonous bacteria community. M. S. submitted to Developments in Industrial Microbiology.
- Rose, C. D. and T. J. Ward. Principles of aquatic hazard evaluation as applied to ocean-disposed wastes. M.S. in preparation; intended for publication as a report for Amer. Soc. Testing. Materials.
- Wheeler, R. B. 1980. Environmental trace metal geochemistry of the Buccaneer oil and gas field. Environ. Geol. (in press).

xviii

#### INTRODUCTION

#### Location of Study Area

The area selected for study is the operational Buccaneer Gas and Oil Field located approximately 49.6 kilometers (26.8 nautical miles) south southeast of the Galveston Sea Buoy off Galveston, Texas This field was selected in 1975 as the study area (Figure 1). (a) the field had been in production for about 15 years, because: which time had allowed full development of the associated marine communities; (b) it was isolated from other fields which facilitated the selection of an unaltered area (for comparison) within a reasonable distance of the field; (c) it produced both gas and oil that represented sources of pollutants from marine petroleum extraction; (d) its location simplified logistics and reduced the cost of the research; and (e) the Texas offshore area had not been fully developed for gas and oil production but was expected to experience accelerated exploitation in the future.

## Operation History of Buccaneer Field

Buccaneer Field was developed by Shell Oil Company in four offshore blocks leased in 1960 and 1968 as follows:

1960 G0709 288 2,790	1,129
1960 G0713 295 4,770	1,930
1960 G0714 296 4,501	1,821
1968 G1783 289 2,610	1,056

In development of the field, 17 structures were built; two are production platforms, two are quarters platforms, and 13 are satellite structures surrounding well jackets. Initial exploratory drilling began about mid-summer of 1960 with mobile drilling rigs. When (as the result of the exploratory drilling) proper locations for platforms were selected, the permanent production platforms were constructed.

There have been no reports of major oil spills from this field. There have been some reported losses of oil due to occasional mechanical failure of various pieces of equipment. The largest reported spill was three barrels in 1973. The reported oil spill chronology and quantity for Buccaneer Field is as follows:



FIGURE 1. LOCATION OF BUCCANEER FIELD

reported spill was three barrels in 1973. The reported oil spill chronology and quantity for Buccaneer Field is as follows:

		Amount		
Date	Source	Barrels	Liters	
September 1973	Platform 296-B	0.5	79	
November 1973	Unknown	3.0	477	
July 1974	Platform 296-B	0.5	79	
August 1974	Platform 296-B	1.7	265	
September 1975	Platform 288-A	0.2-0.4	38-56	
Totals		5.9-6.1	938-956	

Buccaneer Field first began operations with the production of oil. Later, when significant quantities of gas were found, the field began producing both oil and gas and has continued to do so to date.

The production platforms and satellites (well jackets) are connected by a number of pipelines with a 50.8 centimeters (20-inch) diameter main pipeline connecting the field to shore. All of the pipelines that are 25.4 centimeters (10 inches) or greater in diameter are buried. The Blue Dolphin Pipeline Company was granted a pipeline permit (No. G1381, Blocks 288 and 296) in 1965 and has operated the pipeline since its construction.

Buccaneer Field occupies a limited area (about 59.3 km<sup>2</sup>; 22.9 . statute miles) leased in the northwestern Gulf of Mexico. Four pes of structures are located in Buccaneer Field: production platyrms, quarters platforms, satellites (well jackets), and flare :acks. These are shown in Figure 2, which is an oblique aerial phoograph of production platform 288-A and vicinity within Buccaneer ield. A map of Buccaneer Field, (Figure 3) depicts the locations of platforms and satellites within the field.



FIGURE 2. BUCCANEER FIELD STRUCTURES



FIGURE 3. SHELL OIL COMPANY'S ALPHANUMERICAL IDENTIFICATION OF BUCCANEER GAS AND OIL FIELD STRUCTURES WORK UNIT 2.4.2 - TRACE METALS

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Southwest Research Institute

J. B. Tillery

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# TABLE OF CONTENTS

			Page
Ι.	INTE	RODUCTION	1
	Α. Β.	Background Purpose	1 2
II.	METH	OD AND MATERIALS	3
	A. B.	Instrumentation Sample Collection and Analysis	3
		<ol> <li>Sample Collection</li> <li>Surficial Sediments</li> </ol>	3 3
		a. Partial Digestion b. Total Digestion	3 4
		3. Sea Water and Produced Brine Discharge	5
		a. General b. Sea Water/Brine Extraction Procedure	5 5
		4. Suspended Particulate Matter	6
		a. Leach Procedure Using Weak Acid to Remove the Carbonate and Absorbed Elements b. Rigorous (Total) Digestion for the	6 8
		Refractory Elements	0
		<ol> <li>Dominant Fauna</li> <li>Macrocrustacea and Demersal Fish</li> </ol>	8 10
	с.	Analytical Parameters and Quality Assurance	11
		<ol> <li>Sediments</li> <li>Suspended Particulate Matter (SPM), Sea</li> <li>Water and Produced Princ</li> </ol>	11 11
		3. Biota	13
III.	RESU	ILTS AND DISCUSSION	15
	A. B.	Surficial Sediments Suspended Particulate Matter, Sea Water and Produced Princ	15 24
	C. D.	Fish and Shrimp Fouling Mat and Barnacles	29 38

## LIST OF TABLES

Numbe	er	Page
1.	Trace Metal Concentrations and Percent Recovery in NBS SRM 1645, River Sediment by Partial Digestion Procedure ( $\mu$ g/g dry wt)	12
2.	Trace Metal Concentrations and Percent Recoveries in NBS SRM 1577, Bovine Liver ( $\mug/g$ dry wt)	14
3.	Seasonal Comparison of Average Trace Metal Concentrations ( $\mu$ g/g dry wt) in Surficial Sediments from Platform 288-A	18
4.	Seasonal Comparison of Average Trace Metal Concentrations ( $\mu$ g/g dry wt) in Surficial Sediments from Platform 296-B	19
5.	Seasonal Comparison of Trace Metal Concentrations ( $\mug/g$ dry wt) in Surficial Sediments from Flare Stack and Well Jacket	20
6.	Comparison of Ambient Sediment Trace Metal Burdens $(\mug/g)$ Developed from Regression Equations (Metal Concentration vs Fe Concentrations) with Sediment Burden in Summer Cruise (I) Samples	23
7.	Average Seasonal Trace Metal Concentrations $({}_{\mu}g/g)$ in Suspended Particulate Matter	25
8.	Seasonal Comparison of Normalized (to Fe) Mean Concentrations in SPM with Normalized (to Fe) Mean Trace Metal Concentrations in Surficial Sediment	27
9.	Seasonal Concentrations ( $\mug/L)$ of Trace Metals in Sea Water and Produced Brine Samples	28
10.	Comparison of Seasonal Variations in Average Trace Metal Concentrations ( $_{\mu}g/g$ dry wt) in Archosargus probatocephalus (Sheepshead) Muscle Tissue with Other Gulf Studies	30
11.	Comparison of Seasonal Variations in Average Trace Metal Concentrations ( $_{\mu}g/g$ dry wt) in Chaetodipterus faber (Spadefish) Muscle Tissue with Other Gulf Studies	32
12.	Comparison of Seasonal Variations in Average Trace Metal Concentrations ( $_{\mu}$ g/g dry wt) in Stenotomus caprinus (Longspine Porgy) Muscle Tissue with Other Gulf Studies	33

#### Number

- Comparison of Average Trace Metal Concentrations in <u>Trachypenaeus</u> <u>similis</u> (Sugar Shrimp) Muscle Tissue by Season and Location
- 14. Comparison of Seasonal Variations in Average Trace Metal 37 Concentrations in Trachypanaeus similis (Sugar Shrimp) Muscle Tissue ( $_{u}g/g$  dry wt) with Other Gulf Studies
- 15. Seasonal Variation of Average Trace Metal Concentrations 39  $(\mu g/g dry wt)$  in Fouling Mat (8-Meter Depth)
- 16. Seasonal Variation of Average Trace Metal Concentrations 40  $(\mu g/g dry wt)$  in Barnacles (Predominantly, <u>Balanus</u> tintinnabulum) Soft Tissue

36

#### LIST OF FIGURES

Numb	ber de la companya de	Page
1.	Map of Study Area	47
2.	Temporal and Spacial Variation of Ba in Surficial Sediments at Platform 288-A	48
3.	Temporal and Spacial Variation of Cd in Surficial Sediments at Platform 288-A	49
4.	Temporal and Spacial Variation of Co in Surficial Sediments at Platform 288-A	50
5.	Temporal and Spacial Variation of Cr in Surficial Sediments at Platform 288-A	51
6.	Temporal and Spacial Variation of Cu in Surficial Sediments at Platform 288-A	52
7.	Temporal and Spacial Variation of Fe in Surficial Sediments at Platform 288-A	53
8.	Temporal and Spacial Variation of Hg in Surficial Sediments at Platform 288-A	54
9.	Temporal and Spacial Variation of Mn in Surficial Sediments at Platform 288-A	55
10.	Temporal and Spacial Variation of Ni in Surficial Sediments at Platform 288-A	56
11.	Temporal and Spacial Variation of Pb in Surficial Sediments at Platform 288-A	57
12.	Temporal and Spacial Variation of Sr in Surficial Sediments at Platform 288-A	58
13.	Temporal and Spacial Variation of Zn in Surficial Sediments at Platform 288-A	59
14.	Temporal and Spacial Variation of Ba in Surficial Sediments at Platform 296-B	60
15.	Temporal and Spacial Variation of Cd in Surficial Sediments at Platform 296-B	61
16.	Temporal and Spacial Variation of Co in Surficial Sediments at Platform 296-B	62

Num	iber	Page
17.	Temporal and Spacial Variation of Cr in Surficial Sediments at Platform 296-B	63
18.	Temporal and Spacial Variation of Cu in Surficial Sediments at Platform 296-B	64
19.	Temporal and Spacial Variation of Fe in Surficial Sediments at Platform 296-B	65
20.	Temporal and Spacial Variation of Hg in Surficial Sediments at Platform 296-B	66
21.	Temporal and Spacial Variation of Mn in Surficial Sediments at Platform 296-B	67
22.	Temporal and Spacial Variation of Ni in Surficial Sediments at Platform 296-B	68
23.	Temporal and Spacial Variation of Pb in Surficial Sediments at Platform 296-B	69
24.	Temporal and Spacial Variation of Sr in Surficial Sediments at Platform 296-B	70
25.	Temporal and Spacial Variation of Zn in Surficial Sediments at Platform 296-B	71
26.	Scatter Plot of Ba versus Fe Concentration in Surficial Sediments During Cruise I and II	72
27.	Scatter Plot of Ba versus Fe Concentration in Surficial Sediments During Cruise III and IV	73
28.	Scatter Plot of Cd versus Fe Concentration in Surficial Sediments During Cruise I and II	74
29.	Scatter Plot of Cd versus Fe Concentration in Surficial Sediments During Cruise III and IV	75
30.	Scatter Plot of Co versus Fe Concentration in Surficial Sediments During Cruise I and II	76
31.	Scatter Plot of Co versus Fe Concentration in Surficial Sediments During Cruise III and IV	77
32.	Scatter Plot of Cr versus Fe Concentration in Surficial Sediments During Cruise I and II	78
33.	Scatter Plot of Cr versus Fe Concentration in Surficial Sediments During Cruise III and IV	79

# 2.4.2-vii

Numbe				Page
34.	Scatter Plot of Cu versus Fe Concentration Sediments During Cruise I and II	in	Surficial	80
35.	Scatter Plot of Cu versus Fe Concentration Sediments During Cruise III and IV	in	Surficial	81
36.	Scatter Plot of Hg versus Fe Concentration Sediments During Cruise I and II	in	Surficial	82
37.	Scatter Plot of Hg versus Fe Concentration Sediments During Cruise III and IV	in	Surficial	83
38.	Scatter Plot of Mn versus Fe Concentration Sediments During Cruise I and II	in	Surficial	84
39.	Scatter Plot of Mn versus Fe Concentration Sediments During Cruise III and IV	in	Surficial	85
40.	Scatter Plot of Ni versus Fe Concentration Sediments During Cruise I and II	in	Surficial	86
41.	Scatter Plot of Ni versus Fe Concentration Sediments During Cruise III and IV	in	Surficial	87
42.	Scatter Plot of Pb versus Fe Concentration Sediments During Cruise I and II	in	Surficial	88
43.	Scatter Plot of Pb versus Fe Concentration Sediments During Cruise III and IV	in	Surficial	89
44.	Scatter Plot of Sr versus Fe Concentration Sediments During Cruise I and II	in	Surficial	90
45.	Scatter Plot of Sr versus Fe Concentration Sediments During Cruise III and IV	in	Surficial	91
46.	Scatter Plot of Zn versus Fe Concentration Sediments During Cruise I and II	in	Surficial	92
47.	Scatter Plot of Zn versus Fe Concentration Sediments During Cruise III and IV	in	Surficial	93

# 2.4.2-viii

#### I. INTRODUCTION

#### A. Background

The "Environmental Assessment of the Buccaneer Gas and Oilfield in the Northwestern Gulf of Mexico" is a multidisciplinary program started in 1975 to examine what effect development of offshore oil and gas resources have on the marine environment and ecosystems existing on the Outer Continental Shelf (OCS) areas of Texas. This program is jointly sponsored by the Environmental Protection Agency (EPA) and the National Oceanic and Atmospheric Administration (NOAA). The Environmental Research Division of the National Marine Fisheries Service, Southeast Fisheries Center, Galveston Laboratory, have the management responsibilities for this program.

The objectives of this program as described in the "request for proposal" (RFP) are: (1) first year (1975) was a descriptive survey of environmental and ecosystem variables as compared to an adjacent unaltered area; (2) the second year was an intensive study of the environmental and ecosystem variables with the emphasis placed upon the comparison of production platforms (with discharges) with satellite structures (well jackets) having no discharges, and (3) in the third year the sources, fate and effects of oilfield pollutants in major ecosystem components, their mode of transport and bioaccumulation are to be investigated.

Only two other major studies funded by the government have directly investigated the effects of oil and gas drilling/production on the marine environment in the Gulf of Mexico. The 1975-76 Mississippi, Alabama, Florida (MAFLA) Rig Monitoring Study (Alexander et al., 1977) examined the impact of exploratory drilling operations on the marine environment and ecosystems before, during, and after the actual drilling operations. The other study is the 1978 Louisiana platform study (Bedinger et al., to be published

in 1980) which investigated the long-term fate and effect production platforms have on the marine environment and ecosystems operating on the OCS off the Louisiana coast. Both of these studies were funded by the Bureau of Land Management (BLM). These studies were to augment the larger "baseline" studies of the 1976-1977 South Texas Outer Continental Shelf (STOCS) and the 1977-78 baseline monitoring studies, Mississippi, Alabama, Florida Outer Continental Shelf (MAFLA), also sponsored by the BLM.

The Buccaneer Gas and Oilfield Study fulfills a unique position in relation to these other studies in that it provides long-term monitoring of a marine environment exposed to chronic, low level oilfield pollutants in an area free from other major pollutants sources.

## B. Purpose

The objective of this investigation was to determine the fate and effect, bioaccumulation and possible sources of 12 heavy metals that are associated with drilling and production activities on the marine environment and marine ecosystem in the Buccaneer gas and oilfield. This was accomplished by determining the concentrations of Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sr, and Zn in (1) surficial sediments, (2) suspended particulate matter, (3) sea water, (4) produced brine, (5) pelagic fish, (6) demersal fish, (7) macrocrustaceans, and (8) bioassay samples collected during four consecutive seasons from the area around two production platform structures (288-A, 296-B), a flare stack at 296-B, and a well jacket (288-5) (Figure 1, page 2.4.2-47).

The Buccaneer gas and oilfield is located approximately 50 km southeast of Galveston (Figure 1). It was developed by Shell Oil Company between 1960 and 1968.

### II. METHOD AND MATERIALS

#### A. Instrumentation

The following atomic absorption spectrophotometers were used for all metal analyses:

a Perkin-Elmer Model 5000 Atomic Absorption Spectrophotometer (AAS) with a HGA-500 Graphite Furnace and multigas flame capability. This system is completely automated and includes a Perkin-Elmer AS-3 Automatic Micro Sampler System for flame analysis and a Perkin-Elmer AS-1 Auto Sampling System for flameless analysis.

a Perkin-Elmer Model 560 Atomic Absorption Spectrophotometer with a HGA-500 Graphite Furnace and multigas flame capability.

a Perkin-Elmer Model 403 AAS with an Instrumentation Laboratory IL-455 Graphite Furnace.

a Perkin-Elmer Model 306 AAS with a HGA-2000 Graphite Furnace.

## B. <u>Sample Collection and Analysis</u>

1. Sample Collection

All surficial sediments, sea water, suspended particulates, produced brine, and biota samples for trace metal analyses were collected by other work groups (2.3.2, 2.3.4, 2.3.5, and 2.3.8) following instructions provided by 2.4.2.

Samples were collected using noncontaminating techniques and stored in preacid-washed polyethylene containers provided by Work Group 2.4.2. All samples were refrigerated after collection and were transported to the Galveston laboratory at which time they were frozen. Samples remained frozen until ready for preparation.

2. Surficial Sediments

A "partial" digestion was done on all sediment samples. On 25 percent of the total number of sediment samples, a "total" digestion was performed.

a. Partial Digestion

The sediment subsample was removed from the freezer and allowed to thaw completely and equilibrate with room temperature.

An acid-cleaned glass rod was used to thoroughly mix the wet sediment. Approximately 60-80 grams of the wet sediment was weighed into a tared polyethylene beaker and particles greater than, or equal to, 3 mm were removed with Teflon-coated forceps. The beaker was then covered with a thin sheet of tissue paper and placed in a drying oven (60°C) until sediment reached a constant dry weight. The sample was reweighed to determine water loss. The sample was then ground in a mortar and pestle and stored in an acid-cleaned polyethylene bottle.

A five-gram aliquot of the dried sediment was weighed into a 250-mL polyethylene screw-cap Erlenmeyer flask. Twenty-five milliliters of 5N  $\mathrm{HNO}_3$  was added to the sample. The flask was sealed and placed on a mechanical shaker at low speed for two hours. The leachate was quantitatively transferred to a 50-mL polyethylene centrifuge tube using three distilled water rinsings of the Erlenmeyer flask. The sample was then centrifuged at 2500-3000 RPM's for 20 minutes in order to separate the suspended silica material from the leach, thereby preventing an interference in the flame and flameless AAS determination of the analyte metals. The leachate was quantitatively transferred to a 50-mL polyethylene volumetric flask and made to volume with distilled water. This leachate was used for metal analysis. All metals, except Cd, were determined by flame AAS. Hg was determined on a one-gram aliquot of the original sample by cold vapor AAS.

### b. Total Digestion

A ten-gram subsample of the dried sediment (as prepared above for "partial" digestion) was sieved through a 100 mesh stainless steel (ATM Corporation, Milwaukee, Wisconsin) screen using an ATM Sonic Sifter. A five-gram subsample of the preground, presieved sample was weighed into a 250-mL Teflon beaker. Twenty-five mL of concentrated HCl was added to the sample and the beaker was covered with a Teflon watchglass. The sample was placed on a hot plate (90-100°C) for one hour to digest. Following the HCl digestion, the sample was allowed to cool in a clean bench and 15 mL of concentrated HNO<sub>3</sub> was added. The beaker was then returned to the hot plate for 45 minutes of heating (90-100°C). The beaker was removed and allowed to cool before adding 25 mL of 48 percent HF to disrupt the crystalline lattice of the sediment. The sample was returned to the hot plate for a third time and heated for two hours. After this final digestion, the sample was cooled and quantitatively transferred to a 50-mL polyethylene volumetric flask. The beaker was rinsed three times with distilled water and the flask brought to volume with distilled water.

All metals except Cd were determined by flame AAS. Cadmium was determined by flameless AAS. Hg was not to be determined on this total digestate. A nitrous oxide/acetylene flame was used to determine Ba, and Sr.

3. Sea Water and Produced Brine Discharge

a. General

The procedure for trace metal analysis of brines and sea water was an APDC-DDC/CHCl<sub>3</sub> (ammonium pyrollidine dithiocarbomatediethyldithiocarbamate/chloroform) extraction followed by a second extraction of the organic phase to stabilize the extracted metals (Jan and Young, 1978; De, et al., 1970). Barium and strontium were determined on the original acidified sample. All metal determinations were made by flame or flameless AAS except Hg for which cold vapor was used.

b. Sea Water/Brine Extraction Procedure

Frozen samples were allowed to thaw to room temperature and the total volume of sample collected determined. The samples
were then acidified with  $HNO_3$  (1 mL per 1000 mL of sample) and refrozen until ready for extraction.

Since the sea water samples could not be adequately filtered on board at the time of collection, acidified (pH <5) unfiltered samples were analyzed in the laboratory. This would allow recovery of any metals that would be lost to the polyethylene containers during shipment to the on-shore laboratory prior to acidifying.

A pH meter was used to adjust the pH of each solution to approximately 5.5 with dilute  $HNO_3$  or  $NH_4OH$ . Next, ammonium acetate ( $NH_4Ac$ ) buffer solution was added and the pH rechecked. Each solution was quantitatively transferred to a polyethylene separatory funnel and 2 mL of 2 percent APDC/DDC solution added. The solution was mixed well for 15 minutes then extracted twice with 10 mL of CHCl<sub>3</sub> (total of 20 mL). The organic and aqueous phases were allowed to separate and the organic extract was quantitatively transferred to a 50-mL extraction vessel. Both organic extracts (20 mL) were combined in the same extraction vessel. Next, 5 mL of 4N  $HNO_3$  was added to the extraction vessel and the sample shaken for 15 minutes. Phases were allowed to separate, and the aqueous phase was removed to a polyethylene vial for metal analysis by flameless AAS.

4. Suspended Particulate Matter

### a. Leach Procedure Using Weak Acid to Remove the Carbonate and Absorbed Elements

The Nucleopore filters (0.4  $\mu$ m, 47 mm polycarbonate membranes) were stored in a desiccator for at least twenty-four hours prior to use to maintain a constant weight. The Nucleopore Swin-Lok membrane filter holders were cleaned in 8N nitric acid for four hours, rinsed with distilled water, and dried. Each filter was then preweighed in a clean bench using Teflon-coated

forceps and loaded into the filter holder. The maximum volume (2 to 3 liters) of sea water was filtered through the Nucleopore filter to improve the detection limit of those metals that normally have low concentrations in suspended particulate samples (e.g., Cd and Hg).

After filtering the maximum amount (2 to 3 liters) of sea water, each Nucleopore filter was removed from its filter holder, in a clean bench, using Teflon-coated forceps. The filter was placed in a dessicator (over silica gel) for 48 hours to dry. Once it had dried to a constant weight, the filter was weighed on the microgram balance (four decimal places) so the mass of the suspended particulate matter could be determined.

In a clean bench, the dry Nucleopore filter was placed in a 125-mL polyethylene Erlenmeyer flask and 50 mL of 25 percent (v/v) acetic acid was added. The flask was sealed to prevent contamination and then placed on a shaker for two hours at a low speed to continue leaching. Using Teflon-coated forceps, the filter pad was removed from the Erlenmeyer flask and positioned over a 100-mL Teflon beaker. The leach acid was then poured over the Nucleopore filter and collected in the Teflon beaker. The Erlenmeyer flask was rinsed three times with distilled water and poured over the filter. The filter was then rinsed twice with distilled water and the rinse added to the Teflon beaker. The filter pad was then stored in a 2" x 6" "Zip-Lock" polyethylene bag for later digestion by the rigorous method (only 10 percent of samples underwent rigorous digestion). The Teflon beaker was placed on a hot plate with low heat (approximately 100°C) and the sample concentrated to less than 10 mL. The sample was cooled and quantitatively transferred to a 10-mL volumetric flask. Distilled water was used to make the flask to the mark after 0.050 mL (50  $\mu L)$  of Suprapur HNO3 was added to maintain the elements in solution.

This solution was then used to determine the different analyte metals using flame, flameless, or cold vapor (Hg) AAS. The concentration of the different elements determined the method of AAS analysis. A 1-mL aliquot of sample was removed for mercury determination.

### b. <u>Rigorous (Total) Digestion for the</u> Refractory Elements

After the above leaching procedure, the refractory matter remaining on the Nucleopore filter was removed by placing the filter pad (using Teflon-coated forceps) into an all-Teflon bomb, adding 750  $\mu$ L of concentrated Suprapur HCl and sealing. After digestion of the sample for two hours in a steam bath (90-100°C), the sample was cooled and the bomb opened in a clean bench and 250  $_{\mu}L$  of concentrated Suprapur HNO3 was added. The bomb was resealed and returned to the steam bath for 30 minutes. The bomb was again removed from the water bath, cooled, opened in the clean bench, and 50  $\mu$ L of concentrated HF was added. The bomb was resealed and returned to the steam bath for one hour. After allowing the bomb to cool, the digestate was quantitatively transferred to a 10-mL volumetric flask. The bomb (cap and cylinder) was rinsed three times with distilled water. The rinsings were added to the volumetric flask and distilled water was used to bring the volume to 10 milliliters.

The concentration of analyte metals in this digestate were in the range of flameless AAS except for Fe, Mn, and Zn which were analyzed by flame AAS. Hg was not determined on this aliquot.

#### 5. Dominant Fauna

Upon arrival at the on-shore laboratory for trace metal analysis, the samples were thawed and prepared on a clean bench using Teflon-coated and stainless steel surgical instruments.

During the dissection, separate instruments were used for separate species and individuals in order to prevent cross-contamination. Between use, all dissecting instruments were cleaned according to normal laboratory procedures, washed with 0.1N nitric acid and rinsed with distilled water.

Each specimen was worked up individually with filets from left and right sides placed in an acid-washed, preweighed, 250-mL polyethylene beaker. The beakers were weighed to determine the wet weight of the muscle tissue. The sample was then frozen, freeze dried, and reweighed to determine the water loss. Next, the freeze-dried sample was ground in a Virtis "45" Homogenizer (The Virtis Company, Inc., Gardiner, New York) using stainless steel blades. This ensured complete mixing of the sample.

The finely ground sample (0.5 grams) was then weighed into a tared Pyrex ashing boat. The boat was placed into the low temperature asher (LTA-505, LFE Corporation, Waltham, Massachusetts) and the sample was ashed for 16 hours at 450 watts of forward power using an oxygen plasma. The ashing boats were removed from the asher and 1 mL of 70 percent HNO3 (Suprapur) was added to solubilize the ash and retain it in the ashing boat during the transfer to a clean bench. The ash was quantitatively transferred into a Teflon bomb with distilled water and 3 mL of 70 percent HNO3 (Suprapur) was added. The Teflon bomb was then sealed and placed in a steam bath (90-100°C) for two hours. The bomb was allowed to cool and the digestate was quantitatively rinsed into a 15-mL polyethylene centrifuge tube using three rinsings (both cap and cylinder) of distilled water. The sample was then centrifuged for 10 minutes at 3000 RPM. The supernatant was decanted into a 25-mL volumetric flask without disturbing the precipitate. The precipitate was then rinsed with 2 mL of distilled water and recentrifuged for 10 minutes. This rinse was then decanted into the volumetric flask and brought to volume with distilled water.

The concentrations of Cu, Fe, and Zn were great enough that aspiration into an air/acetylene flame (AAS) was used to quantitate them. Barium, Cd, Cr, Co, Pb, Mn, and Ni were quantitated using flameless AAS. Strontium was analyzed using a nitrous oxide/acetylene flame.

Because of the volatility of Hq, a special procedure was used to determine Hg in the fish tissue. A one-gram aliquot of the finely ground, freeze-dried sample was weighed into a reaction vessel. Five mL of  $HC10_4$ : HNO3 (5:1) and 1 mL of KMnO4 (5 percent solution) were added to the vessel. The vessel was shaken for five minutes, then placed in a water bath  $(75^{\circ}C)$  for 30 minutes. After removing the samples from the water bath, the samples were cooled to room temperature. Next, 5 mL of distilled (Hg-free) water was added followed by 1 mL of hydroxylamine hydrochloride (50 percent). The sample was then shaken. Stannous chloride (5 percent) was added to the sample and the reaction vessel connected to the cold vapor analytical train. The Hg was purged  $(N_2)$  out of the sample and into a chamber where the light absorption occurred relative to the concentration of Hq present. Hq was quantitated by the method-of-additions using spiked samples of the material analyzed.

#### 6. Macrocrustacea and Demersal Fish

Before dissecting, the longspine porgy and broken neck shrimp samples were weighed and measured. Only muscle tissue was used for the samples. The tissue was removed with Tefloncoated forceps and stainless steel surgical scissors after the specimen had been thawed. The excised tissue was placed in a tared freeze-drying flask and weighed. The sample was then freezedried and reweighed to determine weight loss. The freeze-dried tissue was thoroughly ground in a Virtis homogenizer and stored in a polyethylene bottle. A 0.5-gram aliquot of the finely ground

homogenized sample was weighed into a Pyrex ashing boat. From this point, the sample was ashed, digested, and analyzed according to the procedure given for dominant fauna analyses.

Hg was determined on a separate tissue aliquot by the cold vapor AAS method used for dominant fauna analyses. All other metals except Cu, Fe, and Zn required flameless AAS because of low concentrations.

#### C. Analytical Parameters and Quality Assurance

#### 1. Sediments

A standard reference material was prepared by the 5N HNO<sub>3</sub> "partial" digestion procedure and analyzed for the 12 analyte metals; National Bureau of Standards, Standard Reference Material 1645, River Sediment, was prepared and analyzed for the 12 metals even though Ba and Sr were not reported for the NBS SRM River Sediment.

Table 1 summarizes the results of the analyses of NBS SRM River Sediment using the partial digestion procedure.

The NBS SRM, River Sediment, was used to calibrate a homogenous sediment sample that was prepared and routinely analyzed with the sediment samples as a quality control.

#### 2. Suspended Particulate Matter (SPM), Sea Water and Produced Brine

Standard reference samples are not available for these sample matrices. Spiked membrane filters processed by the procedure described for SPM were used to evaluate the procedure for SPM and as quality control samples.

Artificial sea water (Riley and Skirrow, 1975) was spiked with known quantities of analyte metals and extracted using the procedure described for sea water and produced brine samples. These spiked samples were used to evaluate the extraction procedure and were periodically run as quality control samples for the sea water and produced brine analyses.

		<u>Ba</u>	Cd	<u>Cr*</u>	Co	Cu	Fe*	Pb	Mn	Hg	<u>Ni</u>	Sr	Zn
Reported Concentration	x sd	NR NR	10.2 1.5	2.96 0.28	(8)** NR	109 19	11.3 1.2	714 28	785 97	1.1 0.5	45.8 2.9	NR NR	1720 169
Determined Concentration n = 7	x sd	20.2 6.7	7.23 0.44	2.26 0.06	11.1 $1.1$	84.2 2.8	3.94 0.16	710 30	398 8	0.69 0.05	23.6 1.0	586 31	1519 24
% Recovery		-	71	76	(139)	77	35	99	51	63	52	-	· 88

TABLE 1TRACE METAL CONCENTRATIONS AND PERCENT RECOVERY IN NBS SRM 1645 RIVER<br/>SEDIMENT BY PARTIAL DIGESTION PROCEDURE (µg/g Dry wt.)

\* weight %

2.4.2-12

**\*\*** value not certified

NR = not reported

#### 3. Biota

National Bureau of Standards, Standard Research Material 1577, Bovine Liver, was prepared and analyzed using the methodology described for dominate fauna analyses to evaluate the procedure. A large homogenous sample of fish muscle tissue was prepared and periodically analyzed (spiked and unspiked) as a means to quantitate the biota data ("method of additions") and to act as a routine quality control.

Table 2 summarizes the results of the analyses of NBS SRM 1577, Bovine Liver.

		Ba	_Cd	<u>Cr</u>	Co	_Cu_	_Fe_	Pb	Mn	Hg	Ni	Sr	Zn
Reported Concentration	x sd	NR NR	0.27 0.04	NR NR	(0.18)*	193 10	270 20	0.34 0.08	$\begin{array}{c} 10.3 \\ 1.0 \end{array}$	0.016 0.002	NR NR	(0.14)*	130 10
Determined Concentration n = 7	x st	4.78 0.16	0.43 0.05	1.19 0.12	$\begin{array}{c} 0.18\\ 0.00\end{array}$	188 3	252 26	0.31 0.08	9.48 0.00	0.015 0.001	0.19 0.00	0.15 0.00	138 5
% Recovery		-	119	-	(100)	97	93	91	92	94	. –	(107)	106

TABLE 2

TRACE METAL CONCENTRATIONS AND PERCENT RECOVERY IN NBS SRM 1577 BOVINE LIVER (µg/g Dry wt.)

\* value not certified

NR = not reported

#### III. RESULTS AND DISCUSSION

#### A. Surficial Sediments

Sediments are the final repository of all trace metals in the marine environment. Sediment trace metal burdens can provide important information on what influence man's activities have had on the marine environment and ecology.

Anderson and Schwarzer (1979) have shown that surficial sediment concentrations of Ba, Pb, Sr and Zn are significantly above background levels within 180 meters of the platform structures. They determined these increases by comparing the surficial sediment concentrations with downcore sediments concentrations at a core depth that would reflect the predevelopment era of the Buccaneer Oilfield and by comparing with surficial sediment concentrations from an undeveloped area (South Texas Outer Continental Shelf Study)(Berryhill, 1975).

This year's sediment investigations have been concentrated on the near-field environment of the Buccaneer oilfield. Since the platforms have produced brine discharges and more activities that could add metal pollution to the marine environment, a well jacket (288-5) (see Figure 1, page 2.4.2-47) was selected as a control station to which comparisons could be made. The well jacket is not an ideal control, but it can simulate the platform structures and it does not have the discharges the platforms have. Also, it is relatively close to the platforms and would be subjected to the same natural variances (winds, currents, storm fronts, etc.) that would effect the sediment trace metal burdens at the platforms.

Surficial sediments from the area of platforms 288-A and 296-B show distinct concentration gradients for several trace metals (Ba, Cd, Cr, Cu, Mn, Pb, Sr, Zn). There appears to be

a strong seasonal effect on both the concentration gradients and the overall trace metal concentration at both platforms.

Figures 2 through 13 and 14 through 25 are graphical representations of the concentration gradients and seasonal variability at platforms 288-A and 296-B, respectively. In the fall season (Cruise II) and spring season (Cruise IV), a reduced sampling effort was conducted at the 25-meter stations only. Therefore, no statement can be made about concentration gradients during these two seasons. However, the overall seasonal variability of trace metals in surficial sediments can be estimated based on the available data.

At platform 288-A, there appears to be a strong seasonal variation in Ba, Cd, Cu, Pb, Ni, and Zn (Figures 2, 3, 6, 11, 10, 13). There is a suggestion of seasonal variability in Hg at platform 288-A (Figure 8). The remaining metals (Co, Fe, Mn) appear to be relatively consistent through all seasons with occasional high values.

Summer (Cruise I) season sediments have the highest metal concentrations and the strongest suggestion of concentration gradients, while the winter samples (Cruise III) have the lowest concentrations of Ba, Co, Cu, and Hg.

At platform 296-B, there are seasonal variations in Ba, Cr, Pb, Sr, and Zn (Figures 14, 17, 23, 24, and 25). The remaining metal (Cd, Co, Cu, Fe, Mn, Hg, Ni) concentrations appear not to vary seasonally.

Seasonal variations in the sediment trace metal burdens are probably due to the very dynamic bottom caused by the strong currents and wave action around the platform structures (Anderson and Schwarzer, 1979; Brooks, Estes and Huang, in preparation). These currents and wave actions cause a significant amount of continuous scouring and resuspension of bottom sediments which causes changes in sediment texture and characteristics that can affect the trace metal composition.

Tables 3, 4, and 5 are the average trace metal concentrations, by season, for platforms 288-A, 296-B, and flare stack 296-B/well jacket 288-5, respectively.

At platforms 288-A and 296-B (Tables 3 and 4) there appears to be less overall variability in metal concentrations during the winter sampling (Cruise III). The highest variability is in Cd, Hg, and Zn. There are high seasonal variabilities for metals which are due to one or two unusually high samples for that season. Examples of these are Cu and Pb in the summer at 288-A (Table 3), Sr in the fall and Cr during the spring at 296-B (Table 4).

Comparison of the overall seasonal mean concentrations with the 288-5 well jacket "control" (Table 5) does not show any significant trends; however, there are consistently higher Cu and Zn concentrations at the well jacket than at the platforms or flare stack.

A means of assessing the trace metal concentration gradients at the platforms is to construct scatter plots of the metal concentrations versus the Fe concentration (Trefrey and Presley, 1977). Since Fe, as compared to other transition elements, is in relatively high concentration in the sediments, only catastrophic inputs would seriously effect its concentration. Therefore, in unaltered sediments, correlation between the Fe values and other transition metal values should be very good. By plotting these metal values versus Fe values and determining the best-fit linear equations and correlation coefficients ( $R^2$ ), any abnormal metal inputs to the sediments can be identified.

Figures 26 through 47 are scatter plots of the sediment metal concentrations versus the Fe concentration by season. These plots include all sediment samples analyzed during a season. Best-fit linear regression equations with their  $R^2$  value are given for each season.

Cruise	Axis	Ba	Cd	Co	Cr	Cu	Fe**	llg	Mn	NI	РЬ	Sr	Zn
I (Summor)	N E S	136 81 83	1.42 0.50 0.55	4.48 4.55 5.45	10.6 10.5 7.45	21.3 48.2 8.6	0.82 0.54 0.59	0.330 0.098 0.482	336 214 297	8.78 13.6 7.44	84.8 45.8 82.5	630 418 212	1680 301 341
(Same)	W	90	0.45	4.33	9.06	12.2	0.66	0.027	263	7.76	69.6	373	1801
	Structure	179	1.17	4.39	17.1	20.7	0.49	0.101	566	8.20	1588	754	2356
	Mean	109	0.80	4.70	10.5	22.3	0.63	0.215	319	9.22	287	464	1220
	SD	58	0.83	0.85	4.9	23.0	0.23	0.274	195	5.41	808	322	1635
	C¥ %	52.3%	104%	18.1%	46.7%	103%	36.5%	127%	61.1%	58.7%	282%	69.4%	134%
11 (Fall)	N E S W Structure	22 15 43* 28 31*	0.10 0.15 0.79* 0.34 0.38*	3.94 4.27 3.15* 4.39 2.47*	5.50 6.78 15.5* 6.93 11.5*	9.78 8.83 10.3* 12.5 34.9*	0.69 0.65 1.49* 0.80 0.61*	0.135 0.144 0.164* 0.163 0.123*	221 133 295* 175 180*	7.24 9.29 7.10* 9.83 6.28*	36.4 52.7 176* 53.5 120*	163 72.7 499* 130 936*	486 593 3521* 291 1420*
	Mean	28	0.35	3.64	9.24	15.3	0.85	0.146	201	7.95	87.7	360	1262
	SD	10	0.27	0.82	4.17	11.1	0.37	0.018	61	1.53	58.9	362	1334
	CV %	37.7%	77.4%	22.43	45.2%	72.5%	43.1%	12.2%	30%	19.2%	67.1%	101%	106%
III (Winter)	N E S W Structure	7.8 12 12 10 20	0.13 0.18 0.09 0.07 0.40	5.07 3.07 2.73 3.80 5.34	6.08 8.23 8.13 5.92 11.1	8.20 6.47 7.38 5.55 9.06	0.46 0.61 0.51 0.57 0.65	0.390 0.062 0.114 0.035 1.223	163 204 196 223 205	4.46 5.28 5.07 4.66 4.33	46.0 189 33.6 51.5 109	307 509 201 169 168	444 1129 311 312 697
	Mean	12	0.17	4.00	7.89	7.33	0.56	0.365	198	4.76	87.7	271	579
	SD	4.4	0.13	1.17	2.10	1.38	0.08	0.500	22.0	0.40	63.2	145	346
	CV %	35.9%	76.5%	29.2%	26.6%	18.9%	13.5%	137%	11.1%	8.48%	72.1%	53.5%	59.71
l¥ (Spring)	N E S W Structure	11 22 35 19 29	0.29 0.30 0.22 0.09 0.16	3.52 2.95 4.66 4.54 4.32	23.6 11.4 16.1 6.51 6.85	10.2 9.68 23.4 4.86 20.9	0.52 0.63 0.91 0.67 0.76	0.210 0.152 0.051 0.024 0.201	215 281 262 234 243	4.07 5.50 7.95 4.20 6.40	129 118 137 67.1 62.1	226 366 221 146 181	638 1439 972 166 510
	Mean	23	0.21	4.00	12.9	13.8	0.70	0.128	247	4.62	102	228	745
	SD	9.1	0.09	0.74	7.15	7.94	0.15	0.086	25.5	1.62	35.4	83.7	484
	CV %	39.4%	41.8%	18.4%	55.5%	57.5%	21.1%	67.2%	10.3%	28.8%	34.5%	36.7%	64.9%

Table 3

SEASONAL COMPARISON OF AVERAGE TRACE METAL CONCENTRATIONS (µg/g DRY WT) IN SURFICIAL SEDIMENTS FROM PLATFORM 288-A

\* shell hash

\*\* concentration in %

					FROM	PLATFUR	M 296-E	5					
Cruise	Axis	Ba	Cd	Co	Cr	Cu	Fe**	llg	Mn	NI	Pb	Sr	Zn
I (Summer)	N E S W Structure	44 100 77 81 187	1.08 0.64 0.35 3.45 5.66	4.59 4.10 4.11 4.20 4.39	6.87 7.46 8.60 9.83 16.8	4.9 5.0 13.9 8.7 20.5	0.44 0.41 0.54 0.56 0.83	0.050 0.032 0.123 0.103 0.049	169 170 167 172 190	5.90 5.83 7.23 6.44 9.43	21.7 82.1 29.0 88.3 55.6	212 335 251 172 729	259 574 300 429 1746
	Mean SD CV %	88 55 62.5%	1.67 2.78 166%	4.22 0.44 10.43	8.90 2.98 33.5%	9.1 7.5 82.4%	0.51 0.15 29.4%	0.073 0.084 115%	171 15 8.8%	6.58 1.72 26.1%	60.0 52.7 87.8%	289 219 75.8%	519 552 106%
11 (Fall)	N E S W Structure	43 111* 37 15 15	0.31 0.74* 0.13 0.08 0.09	4.50 2.14* 3.37 3.71 4.05	7.91 6.48* 7.68 3.99 4.44	11.1 6.95* 6.32 2.64 3.69	0.74 0.43* 0.71 0.58 0.60	0.106 0.015* 0.153 0.032 0.054	169 107* 207 169 177	8.06 4.51* 6.96 7.24 5.33	60.2 386* 44.3 21.3 16.7	186 2558* 625 270 55.1	1478 2120* 428 196 195
	Mean SD CV %	42 41 98.3%	0.27 0.28 103%	3.55 0.89 25.2%	6.10 1.81 29.7%	6.14 3.30 53.7%	0.61 0.12 20.1%	0.072 0.057 78.8%	166 36 22%	6.42 1.46 22.7%	106 158 149%	739 1039 141%	883 871 98.6%
llI (Winter)	N E S W Structure	23 25 24 25 41	0.07 0.11 0.19 0.07 0.22	4.35 4.01 4.20 3.52 4.54	6.85 9.76 6.18 6.49 11.8	5.44 4.17 3.47 6.09 8.03	0.55 0.57 0.53 0.55 0.61	0.137 0.096 0.168 0.092 0.036	180 180 171 183 195	4.76 4.29 4.66 4.85 4.20	66.9 90.1 33.6 45.0 60.9	145 260 134 129 267	211 498 967 123 859
	Mean SD CV %	27 7.4 27.2%	0.13 0.07 52.6%	4.12 0.39 9.45%	8.22 2.46 30.0%	5.44 1.78 32.7%	0.56 0.03 5.35%	0.106 0.050 47.2%	182 8.64 4.75%	4.55 0.29 6.37%	59.3 21.6 36.5%	187 70.1 37.5%	532 377 70.9%
IV (Spring)	N E S W Structure	14 19 14 30 75	0.04 0.12 0.06 0.04 0.53	2.06 4.56 5.51 4.80 4.20	2.58 5.01 5.44 5.19 35.8	1.70 14.8 6.92 3.59 21.7	0.33 0.53 0.61 0.49 1.05	0.012 0.222 0.188 0.056 0.217	104 187 238 179 231	3.04 4.72 4.85 3.43 7.44	< 2.16 22.8 57.8 40.0 403	48.2 101 140 81.0 404	170 276 151 96.7 3692
	Mean SÐ CV %	31 26 84.3%	0.16 0.21 133%	4.23 1.30 30.8%	10.8 14.0 130%	9.74 8.35 85.7%	0.60 0.27 44.9%	0.139 0.098 70.5%	188 53.6 28.5%	4.70 1.72 36.7%	105 168 160%	155 143 92,5%	877 1575 180%

Table 4 SEASONAL COMPARISON OF AVERAGE TRACE METAL CONCENTRATIONS (µg/g DRY WT) IN SURFICIAL SEDIMENTS FROM PLATFORM 296-B

\* shell hash

\*\* concentration in %

			1 14	UN TEAK	L JINUK	AND WL	LL UNCK					
Cruise	Ba	Cđ	Co	Cr	Cu	Fe**	Hg	Mn	NI	Pb	Sr	Zn
Flare Stack												
I - Summer 11 - Fall 111 - Winter IV - Spring	24.3 12 <4.2 8.1	0.05 0.02 0.004 0.03	3.90 3.71 4.32 3.63	3.94 3.47 4.30 3.17	1.77 1.70 1.95 1.96	0.27 0.46 0.45 0.44	0.008 0.014 <0.009 <0.009	210 178 182 206	3.18 4.23 3.94 3.30	2.88 3.35 12.5 4.73	67.8 52.6 154 138	22.2 22.2 17.4 19.3
Well Jacket												
I - Summer II - Fall III - Winter IV - Spring	240 43* 28 35	0.70 0.24* 0.13 0.08	4.14 360* 6.25 2.50	13.8 6.63* 6.54 8.78	14.6 7.57* 41.2 11.8	0.40 1.34* 0.94 0.77	0.049 0.752* 0.039 0.042	891 400* 401 314	5.50 7.37* 6.79 6.27	96.6 38.9* 60.9 44.4	1017 1404* 300 236	1094 2781* 1464 751

Table 5 SEASONAL COMPARISON OF TRACE METAL CONCENTRATIONS (µg/g DRY WT) IN SURFICIAL SEDIMENTS FROM FLARE STACK AND WELL JACKET

\* shell hash

\*\* concentration in %

There are two samples with unusually high Fe concentrations in the fall season which tend to distort the regression lines for Ba, Co, Cu, Ni, and Pb (Figures 26, 30, 34, 40, and 42, respectively).

Examination of the scatter plots shows some interesting trends. The summer season showed more scatter for Ba, Cd, Cr, Cu, Mn, Pb, Sr, and Zn. There is also a moderate amount of scatter in Cd, Cr, Sr, Mn, and Zn during the fall season. Mercury has relatively little scatter during the summer and fall but significantly more during the winter and spring.

Scatter plots of Ba, Cd, Cr, Cu, Mn, Pb, Sr, and Zn for the winter and spring show less scatter as compared to the summer and fall.

Nickel and Co show little scatter through all four seasons.

The regression equations and correlation coefficients  $(R^2)$ for the fall, winter, and spring seasons can be improved by elimination of one or more unusually high values. For example, in Figure 45 for Sr, the negative slope of the regression line is reversed and the  $R^2$  value increases to 0.1687 by elimination of the two values above 1000 ppm Sr.

It is important to note that the majority of data points with an unusally high Y-axis scatter are at those stations near (0 and 25 meters) the platform structures. This would suggest that the source of these increased metal concentrations could be related to the platform structures or the petroleum production activities on them.

Comparison of these scatter plots with others from areas of the Gulf that are not considered to be contaminated (Trefry and Presley, 1976; Shokes, 1978; Tillery, in preparation) illustrate the abnormality of the situation near these platform structures. Comparison of these linear regression equations with those from noncontaminated areas can give an estimate of the natural concentrations

of trace metals in sediments and indicate if there are significant increases in sediment trace metal concentrations near the platform structures.

Table 6 is a comparison of the normal trace metal concentration in sediments, developed from linear regression equations (metal concentration versus Fe concentrations), from two studies, representative of noncontaminated areas of the Gulf, with concentrations derived from the summer cruise samples (Cruise I). A third comparison is made to the normal concentrations developed from plots of trace metal concentrations from diver-collected core samples taken during the second year (1977-1978) of the BOF study. These sediment core samples were collected at platform 288-A and satellite structure. Only the bottom core samples were used since Anderson and Schwarzer (1979) indicated these were representative of the predevelopment period of the BOF.

There is an apparent accumulation of Cr, Hg, Pb, Sr and Zn in sediment when compared to the ambient levels developed from the core samples (second year BOF). Compared to the Louisiana Platform Study values, Pb would not be accumulating in the BOF sediments. However, the Louisiana Platform Study samples were collected in the offshore oilfields and may actually show some accumulation from this source.

Sediment characteristics can cause variations in the trace metal content of sediments. Trace metal concentrations and sediment grain size have an inverse relationship which is thought to be caused by the increased surface area (i.e., adsorption sites) available for metal binding. Unaltered sediments should have a positive regression slope and good correlation in a scatter plot of grain size (Ø) versus metal concentration.

Figures 48 and 49 are seasonal scatter plots of sediment Fe concentration versus grain size ( $\emptyset$ ) showing the best fit linear

### Table 6

## 

	1978-79 BOF		BLM-1978-79	1977-78 BOF
Metal	Summer Cruise	Trefry & Presley 1976	Louisiana Platform Study Tillery inpreparation	Core Samples <sup>(1)</sup> Anderson & Schwarzer 1979
Ba	51	ND	39.5	112 (2)
Cd	0.124	0.056	0.131	5.46 <sup>(2)</sup>
Co	3.74	NR	ND	-2.35
Cr	2.5	NR	1.68	0.53
Cu	0.5	1.41	2.79	0.47
Hg	-0.174	ND	ND	0.067
Mn ·	123	NR	ND	177
Ni	1.19	1.72	4.40	-2.82
РЬ	7.37	2.03	8.63	0.83
Sr	187	ND	ND	25
Zn	-826	-2.40	22.8	20.8

(1) only bottom core samples used

(2) only 3 data points used to develop this value;  $\leq$  values not used

ND = metal not determined

NR = data not reported

equation and correlation coefficient. There is very poor correlation in any season. Other metals (except Co) had poor correlation with sediment grain size through all four seasons. However, there was good correlation of Co during the summer ( $R^2 = 0.54$ ) and fall ( $R^2 = 0.57$ ) seasons.

This lack of correlation with sediment grain size (Brooks et al., in preparation) is further evidence that the trace metal gradients of Ba, Cd, Cr, Cu, Mn, Pb, Sr, and Zn observed at the platform structures are related to the structures or the petroleum production activities on them. These metals include those (Ba, Sr, Cd, Co, Pb) that Wheeler (1979) found by cluster analysis to be associated with anthropogenic inputs.

#### B. Suspended Particulate Matter, Sea Water and Produced Brine

Platform 296-B was actively discharging production waters (brine) to the marine water column during this year's investigation. Platform 288-A was not discharging production brine during this year's sampling but has been actively discharging in the recent past. Previous investigations of these production brines (Anderson and Schwarzer, 1979) has shown that the average concentrations of Sr and Ba from platform 296-B were 33.5 ppm and 3.5 ppm, respectively. By examining these production brines, sea water and suspended particulate matter (SPM), the transport and fate of the trace metals introduced to the marine environment from this source may be determined.

Table 7 is the seasonal average trace metal concentrations in SPM from Platforms 288-A, 296-B, well jacket 288-5, and flare stack 296-B. The trace metal burdens in SPM samples are known to be highly variable. However, by comparing to a control sample (well jacket), an estimation of the trace metal input from the produced brine discharge may be made. Also, by normalizing the

Cruise	Location	Ba	Cd	<u>Cr</u>	Co	Cu	Fe	Pb	Mn	Hg	Ni	<u>Sr</u>	Zn
	288-A	357	41.9	435	29.1	324	4301	294	670	38.1	537	140	1012
	296-B	319	34.2	185	31.2	135	3446	149	354	40.8	301	159	1001
I	Well Jacket *	31	10.8	81	7.4	39	1670	14	444	9.7	50	104	238
Summer	Flare Stack **	172	24.2	14	16.6	79	1792	31	597	2.4	18	91	534
	X	317	36.1	335	28.6	210	3668	201	506	36.6	380	145	952
	sd.	309	17.0	492	12.8	251	4733	388	304	18.0	382	58	464
	RSD(%)	97	47	147	45	120	129	193	60	49	101	40	49
	n=23												
	288-1	86	9.1	42	7.8	57	1235	42	843	6.2	287	131	251
	296-8	83	70.0	67	9.5	73	1053	17	361	11.1	135	77	262
11	Well Jacket *	58	9.7	77	6.7	29	130	12	3	8.8	61	47	215
Fall	Flare Stack **	55	12.8	42	9.4	42	458	6	257	12.3	97	153	302
	X	77.	35.1	55	8.7	59	938	23	475	9.5	173	105	261
	sd.	34	59.8	44	3.6	37	488	22	410	6.8	293	55	128
	RSD(%)	44	170	80	41	63	52	96	86	72	169	52	49
	n≈12												
	288-A	20	16.0	22	11.2	91	885	35	1170	14.7	128	160	272
	296-В	56	33.6	47	9.8	69	1375	15	1064	13.1	85	156	321
111	Well Jacket	37	17.3	12	11.9	26	115	22	3751	15.5	101	182	381
Winter	Elare Stack ""	- 74 .	11.4	8	7.9	17	838	15	380	10.3	66	108	252
	×	43	25.4	35	10.3	73	1115	23	1193	13.7	101	156	303
	Sd.	67	51.3	42	4.0	93	782	17	849	3.9	72	25	187
	K2D(%)	156	202	120	39	127	70	74	Л	28	1	16	62
	N=22												
	288-A	74	5.4	14	7.8	230	3417	12	1786	6.6	42	68	141
	296-B	67	10.4	11	9.8	344	2963	27	1514	11.1	83	88	269
17	Well Jacket *	136	11.6	8	8.4	134	4386	19	1365	10.5	68	63	39
Spring	Flare Stack **	58	0.2	9	19.7	15	3693	16	1222	0.4	54	96	284
	x	75	7.6	12	9.7	252	3415	20	1590	8.3	62	79	198
	sd.	30	7.4	11	5.3	228	558	10	528	7.2	40	20	143
	RSD(%)	40	97	92	55	90	16	50	33	87	65	25	72
	n=12												

Table 7 AVERAGE SEASONAL TRACE METAL CONCENTRATIONS ( $\mu$ g/g) IN SUSPENDED PARTICULATE MATTER

\* Well Jacket 288-5

\*\* Flare Stack 296-B

SPM trace metal concentrations to their hydrous Fe concentration and comparing to sediment data similarly normalized, the amount of SPM from resuspension of fine grain sediments can be estimated.

Examination of Table 7 shows that well jacket samples during the summer have lower trace metal concentrations except for Mn, which is similar to the other structures. The fall samples have similar concentration of metals except for Fe, Pb, Mn, Ni and Sr which are lower at the well jacket station. The winter and spring sample concentrations are similar except for a high Mn concentration at the well jacket during the winter. Since there are similar trace metal concentrations at both platforms and the flare stack, the inputs from the produced brine discharge cannot be determined.

Table 8 is the mean trace metal concentrations from Table 4 (sediments) and Table 7 (SPM) normalized with the hydrous Fe concentrations. This allows a comparison between the normalized sediment and SPM trace metal concentrations such that the contribution from resuspension of bottom sediment can be determined. In the summer, fall and winter, only Pb appears to be associated with resuspended sediments. In the spring, Sr in the SPM may come from resuspended sediments.

Table 8 also shows there are similar concentrations of all metals at platforms 288-A and 296-B. The higher concentrations of metals in the SPM may be from (1) the smaller size particles, (2) the organic materials present in the SPM, or (3) from the platform structures.

The average seasonal trace metal concentrations in sea water and produced brine are given in Table 9. There does not appear to be any seasonal trends in the metal concentrations of the produced brine samples. However, there does appear to be a higher concentration of Cd, Pb and Zn in the samples taken in the summer.

	Cruise	1	Ba	<u>Cd</u>	Cr	Co	<u>Cu</u>	Pb	Mn	Hg	Ni	Sr	Zn
	Summer	•	864.2	98.15	913.3	77.97	572.5	548.0	1379	99.78	1036	395.3	2595
	Fall 11		820.9	374.2	586.4	92.75	629.0	245.2	5064	101.28	1844	1119	2783
SPM													
	Winter III	•	385.7	227.8	313.9	92.38	654.7	206.3	10700	122.9	905.8	1399	2717
	Spring IV		219.6	22.54	35.14	28.40	737.9	58.57	4656	24.30	181.6	231.3	579.8
	Summer I	A* B*	173.1 172.5	1.270 3.275	16.67 17.45	7.460 8.275	35.40 17.84	455.6 117.6	506.3 335.3	0.3413 0.143	14.63 12.90	736.5 566.7	1937 1018
	Fall II	A* B*	32.94 68.85	0.4118 0.4426	10.87 10.00	4.282 5.820	18.00 10.07	103.2 173.8	236.5 272.1	0.172 0.118	9.353 10.525	423.5 1211	1485 1448
Sediments													
	Winter III	А* В*	21.43 48.21	0.3036 0.2321	14.09 14.68	7.143 7.357	13.09 9.714	156.6 105.9	353.6 325.0	0.6518 0.1893	8.500 8.125	483.9 333.9	1034 950
	Spring IV	A* B*	32.86 51.67	0.3000 0.2667	18.43 18.00	5.714 7.050	19.71 16.23	145.7 175.0	352.9 313.3	0.1829 0.2317	6.600 7.833	325.7 258.3	1064 1462

Table 8 SEASONAL COMPARISON OF NORMALIZED (TO FE) MEAN CONCENTRATIONS IN SPM WITH NORMALIZED (TO FE) MEAN TRACE METAL CONCENTRATIONS IN SURFICIAL SEDIMENT

\* Platform

Table 9 SEASONAL CONCENTRATIONS ( ${\tt ug/L}$ ) OF TRACE METALS IN SEA WATER AND PRODUCED BRINE SAMPLES

<u>Cruise</u>	Site	(m) Distance	Number of Samples Averaged	Ba	दव	<u>Co</u>	<u>(r</u>	Cu	fe	Hq	Mn	NI	Pb	<u>Sr</u> *	Zn	
	A	0	1	21	0.005	<0.07	0.03	0.52	<0.51	0.056	0.17	0.07	0.59	12.3	3.2	
I (Summer)	B	0 25 100	1 4	26 21 16	<0.002 0.031 0.016	<0.07 <0.07 0.07	0.03 0.02 0.03	0.18 0.77 0.43	2.20 2.55 1.38	0.072 0.058 0.059	0.02 0.07 0.02	0.10 0.12 0.02	0.27 1.22 0.21	11.1 11.2 9.7	0.8 3.3 3.9	
	Flare	25	1	21	0.018	<0.07	0.01	0.54	4.13	0.033	<0.01	0.02	0.49	12.6	3.0	
	Well Jacket	t 0 25	1	25 16	0.009	<0.07 <0.07	0.01 0.26	0.49 0.43	2.62 4.82	0.069	<0.01 0.23	0.04 0.18	1.21	10.9 12.9	1.8 3.5	
	8-Produced Brine	0	2	1548	0.167	<0.07	1.03	0.59	339.50	0.121	0.68	0.29	2.93	58.1	47.7	
	A	0 25	1	13 19	0.006 0.011	<0.07 <0.07	0.02 0.02	0.40 0.54	<0.51 0.96	0.049 0.062	<0.01 0.02	0.05	0.38 0.55	13.2 9.9	1.2 2.8	
11	8	0 25	1	17 17	0.005 0.007	<0.07 <0.07	0.02 0.01	0.22 0.36	<0.51 <0.51	<0.027 0.069	0.04 <0.01	0.32 0.02	2.85 0.67	11.1 10.5	1.6 4.6	
(Spring)	Flare	25	1	17	0.010	<0.07	0.01	0.47	<0.51	0.046	<0.01	0.05	0.64	9.0	7.9	
	Well Jacket	L 0	1	17	<0.002	<0.07	0.09	0.55	<0.51	<0.027	0.06	0.03	0.91	13.4	1.6	
	8-Produced Brine	0	1	1542	0.003	<0.07	0.73	0.14	203.00	0.086	0.65	0.41	0.42	64.1	1.6	
	A	0 25	1	23 22	0.023	0.08 <0.07	0.04	0.51	5.37 <0.51	0.056	0.07	0.98	2.35	13.2	3.4 2.3	
	D	0	1	25	0.009	<0.07	0.03	0.52	16.40	0.038	0.02	0.05	1.83	11.3	5.4	
(Winter)	ь	100	i	23	0.007	(0.07	0.04	2.20	1.24	0.036	0.01	0.12	5.24	12.2	4.8	
	Flare	25	1	26	<0.002	0.18	0.72	0.37	1.51	0.056	0.01	0.09	0.37	12.1	1.6	
	Well Jacket	25	1	19 23	0.003 0.004	<0.07 <0.07	0.03	0.52	3.58	0.056 0.027	0.01 0.03	0.04	0.50	12.2	1.6	
	8-Produced Brine	0	2	1029	0.014	<0.07	1.45	1.01	379.50	0.110	1.27	0.62	0.93	67.0	3.5	
	A	0	ł	27	0.008	<0.07	0.02	0.38	0.69	<0.027	0.02	0.09	0.48	12.4	2.3	
	8	0 25	1	23 24	0.013	<0.07	0.01	0.40	1.38	<0.027	0.38	0.03	0.72	11.7	10.3	
IV	Flare	25	•	26	0.019	0.08	0 15	0.41	10.50	(0.027	0.07	0.24	0.78	10.9	5.2	
(FALI)	Well Jacket	0	1	20	0.007	<0.07	65.10	0.56	0.55	0.072	0.04	0.03	168.0	12.5	2.7	
	8-Produced Brine	25 0	1	15 1056	0.005 0.045	0.10 <0.07	0.02 0.09	0.35 0.47	1.51 118.00	<0.027 0.424	0.08 0.76	<0.01 0.09	0.32 0.54	6.6 93.6	4.1	

\* Strontium reported in µg/mL (ppm).

No cause for a seasonal difference in the produced brine waters is known.

Comparing the trace metal concentrations in produced brine discharge from platform 296-B with the sea water collected from around 296-B (Table 9) indicates an enrichment of Cd, Cr, Fe, Hg, Mn, Ni, Pb, Sr and Zn in the produced brine during the summer. However, only Cr, Fe and Mn continue to be enriched through the other three seasons. Barium and Sr are higher through all seasons.

These higher concentrations of Cr, Fe, Mn, Ba and Sr in produced brine can be a significant source of these metals to the sediments and SPM. Also, our Ba concentrations in produced brine from platform 296-B are similar to the average concentration reported last year (3.5 ppm)(Anderson and Schwarzer, 1979). Our Sr concentrations are about twice the average concentration reported last year (33.5 ppm)(Anderson and Schwarzer, 1979).

Trace metal concentrations in sea water are low (for unfiltered sea water) and no seasonal trends were observed. There are no apparent correlations in sea water metal concentrations and the platform or satellite structures.

#### C. Fish and Shrimp

Pelagic fish were collected in four consecutive seasons from the vicinity of platforms 288-A, 296-B and well jacket 288-5. Two species were sampled, <u>Archosargus probatocephalus</u> (sheepshead) and <u>Chaetodipterus faber</u> (spadefish). One species of demersal fish, <u>Stenotomus caprinus</u> (longspine porgy), was substituted for macrocrustacean samples during the summer cruise. Macrocrustacean samples collected in the fall, winter, and spring seasons were Trachypenaeus similis (sugar shrimp).

Only muscle tissue of fish and shrimp were analyzed for trace metals. Comparison of the seasonal mean trace metal concentrations in sheepshead, spadefish and longspine porgy with other Gulf studies are presented in Tables 10, 11, and 12, respectively.

	In <u>mon</u>	05/11/00/	2 1.101	moourn	<u>mr og</u>	(Shirri Si			110000		Unich	GOLI JI	ODILJ	
	Cruise		Ba	Cd	<u>Co</u>	Cr	Cu	Fe	Hg	Mn	NI	Pb	Sr	<u>Zn</u>
	Summer n=8	⊼* sd. RSD%	<0.88  	0.031 0.032 103	<0.30 	0.245 0.055 22	0.59 0.17 29	8.5 2.8 33	0.354 0.155 44	0.37 0.07 20	0.561 0.257 46	0.129 0.034 26	19.9 3.5 18	13.5 1.1 8
Виссалее	Fall n=12	⊼* sd. RSD%	1.1 0.51 46	0.146 0.103 71	0.32 0.05 16	0.890 0.566 64	1.51 0.62 41	9.6 6.4 67	0.170 0.120 70	0.47 0.10 21	0.625 0.193 31	0.501 0.644 129	2.0 2.3 115	12.1 1.5 12
Oilfield	Winter n=19	R* sd. RSD%	1.3 0.66 51	0.376 0.964 256	0.62 0.46 75	0.606 0.483 80	1.40 0.68 49	12.5 3.8 30	0.426 0.217 51	0.59 0.16 26	0.978 0.529 54	0.757 0.899 119	4.6 5.3 115	14.7 3.4 23
	Spring n=12	x̃* sd RSD%	3.4 1.6 47	0.240 0.280 117	0.37 0.09 23	2.65 2.92 110	0.99 0.19 19	27.3 16.1 59	0.672 0.594 88	0.51 0.12 23	0.532 0.242 45	0.185 0.096 52	3.8 1.5 39	27.3 16.1 59
Louisiana	1	Range		<0.011-		<0.20-	0.57-	12.4-			<0.38-	<0.110-		9.2-
Study		₹* RSD%	NA	0.052 8.8	ND	1.04 70	1.13	20.6 43	ND	ND	2.33 1.17 54	0.210 0.128 30	ND	18.1 13.9 18

Table 10 COMPARISON OF SEASONAL VARIATIONS IN AVERAGE TRACE METAL CONCENTRATIONS (µg/g DRY WT) IN ARCHOSARGUS PROBATOCEPHALUS (SHEEPSHEAD) MUSCLE TISSUE WITH OTHER GULF STUDIES

1. Tillery, 1979

\* Those samples at or below detection limit included as detection limit value.

ND = Not determined

NA = Data not available

	CHA	EIUUII	TERUS	FADER	( SPAUE	risnj	MUSULE	112200	- WIIII	UTILK	GOLL 3	TUDILS		
	Cruise		Ba	<u>C4</u>	Co	<u>Cr</u>	Cu	<u>Fe</u>	. Hg	Mn	<u>N1</u>	Pb	Sr	Zn
	Summer n=8	就* sd. RSD%	<0.88  	0.032 0.022 69	<0.30 	0.223 0.061 27	0.53 0.08 15	8.8 3.3 38	0.222 0.076 34	0.52 0.27 52	1.04 0.75 72	0.130 0.040 31	22.4 2.5 11	17.7 2.0 11
	Fall n=12	īč* sd. RSD%	1.2 0.5 45	0.158 0.067 42	0.39 0.22 56	0.966 0.533 55	1.72 0.62 36	10.8 6.8 63	0.140 0.074 53	0.38 0.08 21	0.88 0.72 82	0.300 0.132 44	1.35 1.20 89	16.2 4.3 26
Buccaneer Oilfield	Winter n=18	₹* sd. RSD%	1.2 0.5 45	0.132 0.048 36	0.67 0.56 83	0.764 0.825 108	3.25 4.87 150	13.3 5.5 42	0.283 0.091 32	0.49 0.12 25	1.32 0.65 49	0.531 0.383 72	3.49 1.95 56	17.8 3.0 17
	Spring n=12	₹* sd. RSD%	3.6 1.4 39	0.186 0.232 125	0.39 0.18 47	1.17 1.15 98	1.02 0.20 20	22.0 10.6 48	0.274 0.077 28	0.56 0.08 14	0.46 0.19 41	0.249 0.224 90	2.35 0.73 31	22.0 10.6 48
Louisiana Platform Study <sup>I</sup>		Range	NA	<0.011- 0.158 0.068 0.070 102	ND	<0.20- 3.12 0.71 0.91 127	0.37- 1.83 1.14 0.34 30	8.6 42.8 18.2 8.3 45.4	ND	ND	<0.38- 2.32 0.86 0.64 74	<0.11 0.37 0.23 0.31 133	ND	11.3- 21.4 17.3 2.7 16

Table 11 COMPARISON OF SEASONAL VARIATIONS IN AVERAGE TRACE METAL CONCENTRATIONS (µg/g DRY WT) IN CHAFTODIPTERUS FABER (SPADEFISH) MUSCLE TISSUE WITH OTHER GULF STUDIES

1. Tillery, 1980

\* Those samples at or below detection limit included as detection limit value.

ND = not determined NA = data not available

COMPARISON	OF AVE	RAGE	TRACE	METAL (µg/g	CONCENT DRY WT)	RATIO WITH	Table 1 N IN <u>ST</u> OTHER	2 Enotoml Gulf Of	IS CAPRI MEXICO	NUS (I	_ONGSP1 [ES	INE PORG	GY) MUS	CLE TI	SSUE
			Ba	<u>Cd</u>	<u>Co</u>	<u>Cr</u>	Cu	Fe	Hg	Mn	NI	Pb	Sr	Zn	
Buccaneer <sup>1</sup>	Summer 1978	R RSDX n=23	0.91 9	0.037 62	<0.30 	0.58 110	1.82 52	22.3 27	0.027 56	1.81 31	1.63 37	0.14 36	32.5 13	16.1 7	
exocc?	1977	x RSD% n=11	ND	<0.01 0	ND	0.04 25	1.0 30	4.9 18	ND	ND	<0.07 29	<0.05 20	ND	12 10	
51005-	1976	ž RSD% n=9	ND	0.02 50	NÐ	0.03 33	0.9 22	4.6 41	ND	ND	0.10 30	0.05 80	ND	11 34	

1. Stenotomus caprinus substituted when no macrocrustacean samples were available. 2. Presley and Booth, 1979, Table 6.8, p 6-42.

There are no significant differences in trace metal burdens of sheepshead, spadefish or longspine porgy collected from the vicinity of the platforms with those from the well jacket (control).

To determine if there are significant seasonal differences in the trace metal concentrations in sheepshead and spadefish muscle tissues, an analysis of variance followed by a least significant difference means operation was performed on the data in Tables 10 and 11.

There were significant seasonal differences for all metals, except Cd, in sheepshead tissue (Table 10). There were significantly higher concentrations of Ba, Cr, Fe and Hg in the tissues during the spring. Winter season concentrations of Co, Cu, Pb, Mn, Ni and Zn were higher and, during the fall, Cu was also high. Sr concentrations were higher in the summer. Concentrations of Ba, Cr, Fe, and Hg were lower and more similar during the summer, fall and winter. Concentrations of Co, Mn, and Ni were lower and more similar during the summer, fall and spring. Summer and spring concentrations of Cu and Pb were lower and more similar while the fall, winter and spring concentrations of Sr are low and similar to each other. Zinc concentrations were generally lower in the fall, summer and spring seasons.

The Pb concentrations in the fall and the Mn concentrations in the spring were between the high concentrations in the winter and the lower concentrations in the spring (Pb) and fall (Mn). The Zn concentrations in the summer and spring are also in between the higher concentration in the winter and the lower concentration in the fall.

No seasonal differences were observed for Cd, Cr, Co, Cu and Zn in spadefish tissues (Table 11). However, there were significant seasonal differences for the remaining metals. Concentrations of Ba and Fe were highest in the spring. Lead concentrations

were higher in the winter. Concentrations of Mn and Hg were higher and more similar during the summer, winter and spring. Nickel tended to increase in concentration in the order of spring, fall, winter and summer with the spring and fall values being similar (and lower) and the fall, winter and summer being similar. The Ni concentrations in the fall are between the lower and higher concentrations.

Barium and Fe concentrations are lower and more similar in the summer, fall and winter. Lead concentrations tend to be lower and more similar in the summer, fall and spring. Fall concentrations of Mn and Hg are lower. Strontium concentrations increase in the order of fall, spring, winter and summer. The fall and spring Sr concentrations are more similar as are the spring and winter. Spring Sr concentrations are between the fall and winter concentrations in similarity.

To determine if bioaccumulation of any trace metals has occurred in sheepshead, spadefish or longspine porgy, a confidence interval was constructed around the summer mean values (Tables 10, 11 and 12) at a 95 percent confidence level, and the mean concentrations from the other studies tested to see if they were within this confidence interval. The summer data was selected for the sheepshead and spadefish since the time frame of collection closely matched the other study.

There were no significant differences in Cd, Pb and Zn concentrations in sheepshead tissue (Table 10) when compared to the Louisiana Platform data. There were significantly higher concentrations of Cr, Cu, Fe and Ni in the sheepshead from the Louisiana study.

Comparison of the spadefish data (Table 11) with the Louisiana study showed no significant difference in Ni and Zn concentrations. However, there were significant higher concentrations of the remaining metal (Cd, Cr, Cu, Fe and Pb) in the Louisiana samples. All metals showed a significantly higher concentration in longspine porgy when compared to data from the STOCS study. This would suggest that bioaccumulation of trace metals has occurred in the longspine porgy from the Buccaneer oilfield. The production platform may be one source of these metals. However, since there were also high SPM trace metal concentrations during the summer, the possibility that this is a seasonal high rather than irreversible bioaccumulation cannot be ruled out. More information is needed on the seasonal variabilities of trace metals in this species.

The seasonal variations of trace metals in sheepshead and spadefish do not appear to be related to the platforms or satellite structures. Also, the seasonal highs do not correspond to the seasonal variations in the trace metal content of the sediments or SPM. There does not appear to be any bioaccumulation of trace metals in either sheepshead or spadefish muscle tissues.

Table 13 is a seasonal comparison of the trace metal concentrations in <u>Trachypenaeus similis</u> (sugar shrimp) by sampling location. Comparing the platform samples with the well jacket (control) samples show there are some higher concentrations of Cd. However, the high values at 296-B in the fall, 288-A in the winter and spring, and the well jacket (288-5) in the spring are due to one high sample in the groups analyzed. This is reflected in the high Relative Standard Deviation  $[RSD(%) = \frac{1 \text{ std. dev.}}{\text{mean}} \times 100]$ for those samples with n>1. One high sample at 288-A in the winter caused the high RSD(%) for Ni.

Other investigators have analyzed sugar shrimp from various areas of the Gulf. Table 14 is a comparison of our seasonal results with these other studies. Data from this table is a summary of the results presented in Table 13.

Concentrations of Cd are higher by a factor of one or two than what was reported in the MAFLA rig monitoring study (Presley and Booth, 1979) and the SPR monitoring program (Shokes, 1979).

	•	- 15(25)+	<u>Ba</u>	Cd	Co	<u>Cr</u>	<u>Cu</u>	Fe	Hg	Mn	<u>N1</u> .	Pb	Sr	Zn
	288-A	n=15(35)* X RSD%	1.6 16	0.235 54	0.33 23	0.30 19	28.5 52	40.0 24	0.105 22	3.87 58	1.06	0.28	27	51
Fall	296-B	n=5(40)* R RSD%	2.9 133	5.13 93	0.37 31	0.56 14	29.4 14	67.8 21	0.133 14	4.97 32	1.25 23	0.47	30 22	3 52
	288-5 Well Jacket	n=1(8)* X RSD%	9.4 	0.22	<0.30 	0.45	26.2	52.4	0.114	3.30	0.93	0.28	45	45
	<sup>-</sup> 288-A	n=11(93)* RSD%	1.6 21	0.862 232	0.53 49	0.52 28	25.6 28	48.8 19	0.123 9	4.91 78	1.66	0.33	39	46
Winter	296-B	n=11(90)* X RSD%	1.8 25	0.378 89	0.84 68	0.67 88	28.1 9	50.5 19	0.136	3.03	2.91	0.65	20 50	4 50
	288-5 Well Jacket	n=1(8)* X RSD%	2.9	0.507	0.61	0.43	34.2	38.7	0.113	2.31	2.78	0.53	30	5
	288-A	n=5(27)* X RSD% n=5(25)*	4.4 7	1.36 173	0.39 23	1.07 79	34.6 20	66.1 15	0.155 16	5.09 28	0.45 20	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	24 21	54 3
Spring	296-B	X RSD% n=1(6)*	<b>4.1</b> 10	0.207 22	0.36 25	1.11 9	33.3 14	53.7 22	0.160 22	2.68 19	0.74 57	0.22 32	23 11	54 3
	288-5 Well Jacket	x RSD2	4.8	14.5	<0.30	0.51	28.0	82.9 	0.118	4.55	<0.38	0.20	23	52

Table 13COMPARISON OF AVERAGE TRACE METAL CONCENTRATIONS IN TRACHYPENAEUS SIMILIS(SUGAR SHRIMP) MUSCLE TISSUES BY SEASON AND LOCATION

\* n = number of pooled samples analyzed; ( ) indicates number of individuals pooled.

						Table 14				
COMPARISON	0F	SEASONAL	VARIATIONS	IN A	AVERAGE	TRACE METAL	CONCENTRATIONS	IN	TRACHYPENAEUS	<u>SIMILIS</u>
		(SUG/	\R SHRIMP) N	1USCI	LE TISS	UE (µg/g DRY	WT) WITH OTHER	GUL	F STUDIES	

	Cruise		Ba	Cd	<u>Co</u>	Cr	<u>Cu</u>	Fe	Hg	Mn	Ni	РЬ	Sr	Zn
Dursenson	Fall n=11(83)*	X RSD%	2.9 89	2.46 161	0.35 26	0.43 34	28.7 34	53.8 33	0.119 19	4.41 46	1.13 40	0.37 47	30 24	51 5
( <u>T. similis</u> )	Winter n=23(191)*	X RSD%	1.7 27	0.64 218	0-68 66	0.59 71	27.2 20	49.2 19	0.128 14	3.90 72	2.32 88	0.49 118	44 25	48 6
	Spring n=11(58)*	X RSD%	4.3 9	2.03 218	0.37 23	1.04 55	33.4 17	58.3 32	0.154 19	3.95 39	0.608 52	0.23 27	24 15	54 3
NASIA 04-1	Before	ž RSD%	ND	0.03 100	ND	1.0 50	23 13	31 110	ND	ND	0.4	0.9 22	ND	ND
MAFLA RTG Monitoring	During	X RSD%	ND	0.04 150	ND	0.7 57	25 12	57 42	ND	ND	0.5 80	0.6 67	ND	ND
( <u>1. \$1m1(15</u> )	After	₹ RSD%	ND	0.03 67	ND	0.2 50	19 16	23 87	ND	ND	0.5 260	0.1 40	ND	ND
SPR Brine Disposal Texoma Group Fall 1977-Winter 1978 <sup>2</sup>		RSD%	ND	, 0.017 ** 	ND	0.131 24	16.8 19	65.8 42	ND	5.09 24	0.217 44	0.265 42	ND	60.2 6

(Trachypenaeus sp.)

Alexander, 1977, before, during and after refer to drilling operations; from Table 13, p 66.
Shokes, 1978, summary of data for West Hackberry Control II, Table 3.3-6, p 3-47.

\* "n" is number of pooled samples; number in ( ) is total individuals sampled. \*\* only one value given, others were "not detected". ND = not determined.

The Ni concentrations during the summer and fall cruises were higher than what other investigators have reported, but the spring season data were similar.

These higher concentrations of Cd and Ni may be related to the platform structures; however, there were no abnormalities found in the sediment-Ni concentrations. Elimination of the high samples for Cd at the platforms would still give a mean concentration higher than that reported by other investigators. The high concentrations of Ba, Cd, and Pb in the sediments during the summer may have some relations to the fact that no shrimp samples were available around the platforms during this season.

#### D. Fouling Mat and Barnacles

Examination of fouling mat and barnacle samples for trace metals will provide information on what concentrations of these metals "grazing" fish are exposed to that inhabit the platform structures. It will also give some indication if there is metal contamination from the platform discharges. This will be reflected in an increase in certain metal concentrations near the source of discharge. Seasonal samples of fouling mat and barnacles were collected from the legs of platforms 288-A, 296-B, 296-B quarters, 296-B flare stack, and well jacket 288-5 at a water depth of eight meters. The 288-5 well jacket sample was used as a control.

Tables 15 and 16 summarize the seasonal trace metal concentrations in fouling mat and barnacles, respectively. One general observation of Table 15 for fouling mat is the low variation (RSD %) in the metal content considering the various flora and fauna that compose the fouling mat samples.

Comparison of the annual average concentrations of metals does not show any significant seasonal trends. However, there is a tendency for the well jacket (control) samples to have lower metal levels than the other samples through all seasons.

Cruise	Sampling Location	Ba	Cd	Co	Cr	Cu	<u>Fe</u> *	Hg	Mn	NI	Pb	<u>Sr</u> *	Zn
Summer	288-A 296-B** 296-B Quarters 296-B Flare Stack 288 6 Kall Laket	630 675/698 570 731	0.86 <0.01/1.11 0.82 2.14	3.97 4.79/4.69 1.53 1.22	26.6 20.1/26.8 3.79 2.99	14.7 22.0/30.9 10.6 71.0	35.40 5.80/9.49 0.42 0.47	<0.008 " "	318 49/335 109 110	39.0 16.2/19. 8.8 10.2	18.8 19.7/5.9 1.9 0.9	2.2 0.70/0.51 0.7 1.9	167 207/570 40 .33
	z88-5 Well Jacket X RSD% n=6	749 30	0.56 0.92 77	2.55 3.13 50	9.43 15.0 73	27.6 81	3.59 99	<0.008 	302 304 65	19.4 18.8 58	7.5 7.5 87	3.1 1.5 70	99 186 108
Fall	288-A 296-B** 296-B Quarters 296-B Flare Stack 288-5 Well Jacket R RSD% n=6	873 776/870 792 1040 1074 904 14	2.27 2.45/3.47 2.66 2.36 1.63 2.47 24	3.36 2.25/2.96 1.73 2.14 3.88 2.72 30	24.6 14.6/559 9.68 10.3 11.7 105 21	14.1 9.4/60 8.3 11.9 7.5 18.6 111	5.93 4.19/10.0 2.11 2.53 3.28 4.68 63	<0.008 " " <0.008	274 64/157 143 96 128 160 38	16.7 13.9/32.2 13.5 12.0 14.4 17.1 44	15.3 3.3/4.9 2.7 3.1 2.4 5.3 94	1.7 0.37/0.25 0.4 0.3 0.7 0.7 89	104 231/104 51 54 44 98 72
Winter	288-A 296-B** 296-B Quarters 296-B Flare Stack 288-5 Well Jacket R RSD% n=6	192 473/152 222 192 122 226 56	2.00 1.52/2.47 1.02 3.61 0.58 1.87 58	3.15 4.79/4.45 3.12 3.36 2.46 3.56 25	5.72 25.6/10.6 8.23 6.72 6.87 10.6 71	11.7 12.4/13.1 11.2 11.3 11.9 11.9 6	3.54 7.29/5.65 3.52 4.32 3.72 4.67 32	<0.008 "" " " <0.008	288 484/246 191 226 195 272 41	6.5 12.1/8.7 7.3 8.2 7.2 8.3 24	8.62 15.3/11.4 8.75 9.26 10.5 10.6 24	2.6 4.0/3.3 2.2 1.4 2.6 2.7 33	137 92/68 65 60 61 81 37
Spring	288-A 296-B** 296-B Quarters 296-B Flare Stack 288-5 Well Jacket R RSD3 n=6	276 151/382 232 512 99 275 55	1.41 1.65/1.03 4.14 3.15 0.96 2.06 63	2.58 4.71/8.20 4.49 2.49 2.46 4.16 54	11.2 10.5/12.1 10.0 8.9 5.6 9.7 24	13.1 13.2/14.4 14.7 15.7 11.8 13.8 10	3.59 4.47/6.59 5.32 3.93 2.73 4.44 31	<0.008 " " " " <0.008	255 373/503 330 285 262 335 28	5.9 7.8/10.8 9.2 7.5 5.9 7.9 24	6.04 8 3.9/8.5 10.5 9.10 2.43 6.75 47	3.1 4.2/4.0 1.3 1.7 3.7 3.0 41	102 107/73 53 55 63 76 31

Table 15 SEASONAL VARIATION OF AVERAGE TRACE METAL CONCENTRATIONS ( $\mu$ g/g DRY WT) IN FOULING MAT (8 METER DEPTH)

concentration in mg/g duplicate samples \*

\*\*

# Table 16 SEASONAL VARIATIONS OF AVERAGE TRACE METAL CONCENTRATIONS (µg/g DRY WT) IN BARNACLE (PREDOMINANTLY, <u>BALANUS TINTINNABULUM</u>) SOFT TISSUE

truise	Sampling Location	Ba	<u>Cd</u>	Co	Cr	Cu	Fe	Hg	Mn	<u>N1</u>	Pb	<u>Sr</u>	Zn
Summer	288-A 296-B* 296-B Quarters 296-B Flare Stack 288-5 Well Jacket R RSD% n=6	5.4 3.6/6.0 6.6 6.5 4.2 5.4 23	12.5 13.5/9.8 10.3 9.9 8.8 10.8 17	0.92 2.39/0.95 1.0 0.82 1.0 1.18 51	2.2 1.9/1.3 2.2 1.5 1.7 1.8 21	22.2 17.6/16.3 17.7 17.1 17.9 18.1 11	107 100/99 120 108 122 109 9	0.020 0.012/0.028 0.014 0.013 0.029 0.019 42	18.0 15.5/15.0 17.0 17.0 16.5 16.5 7	25.3 8.7/9.2 4.5 6.9 4.7 9.9 79	0.71 0.17/0.69 0.51 0.42 0.37 0.48 43	122 92/93 153 185 105 125 30	449 417/346 369 332 341 376 13
Fall	288-A 296-8* 296-8 Quarters 296-B Flare Stack 288-5 Well Jacket R RSD% n=6	9.4 12.0/10.6 6.8 8.5 4.3 8.6 32	11.3 12.0/11.9 11.1 14.1 7.4 11.3 19	1.4 1.1/1.6 1.8 1.2 0.7 1.3 30	2.7 2.9/2.7 1.8 1.6 1.4 2.2 30	13.4 14.5/17.4 13.8 15.0 7.3 13.6 25	437 468/449 333 447 259 399 21	<0.008 0.015/0.012 0.021 0.026 0.016 44	24.5 24.5/25.0 21.5 24.0 16.5 22.7 14	10.2 8.2/10.0 8.1 10.8 8.6 9.3 13	1.57 1.47/0.60 0.43 2.20 0.67 1.16 60	109 189/222 103 144 80 141 39	341 342/339 243 258 136 277 30
Winter	288-A 296-B* 296-B Quarters 296-B Flare Stack 288-5 Well Jacket R RSD% n=6	6.5 3.9/4.9 6.2 8.6 8.7 6.5 30	25.0 23.6/21.5 23.6 28.5 18.1 23.4 15	0.92 0.55/0.50 0.60 0.33 <0.30 0.53 42	8.1 2.3/9.3 2.5 1.8 4.7 4.8 68	27.8 23.1/24.3 27.1 32.7 17.4 25.4 20	259 157/155 194 173 168 184 21	0.035 0.032/0.034 0.040 0.041 0.039 0.037 11	22.6 8.84/9.97 14.1 12.3 12.7 13.4 36	5.6 4.8/10.0 3.2 1.7 2.1 4.5 68	0.33 1.92/0.43 0.39 0.86 0.81 0.79 76	233 115/138 236 382 103 201 53	661 588/415 511 469 403 508 20
Spring	288-A 296-B* 296-B Quarters 296-B Flare Stack 288-5 Well Jacket RSD% n=6	3.8 4.6/4.2 7.2 3.1 7.8 5.1 38	14.2 14.0/15.7 11.6 13.6 9.8 13.1 16	1.30 0.92/0.35 4.6 0.46 0.30 1.3 125	1.3 0.9/1.4 2.1 0.8 0.9 1.2 40	11.8 13.2/16.5 13.2 16.7 14.0 14.3 14	82 121/78 107 87 114 98 19	0.016 0.010/0.029 0.017 0.017 0.016 0.018 33	15.3 11.7/11.1 11.4 12.9 16.4 13.1 17	4.4 4.8/5.9 2.2 6.0 2.1 4.2 40	<0.11 <0.11/0.21 0.30 <0.11 0.20 0.17 45	107 2560/951 258 114 265 709 135	329 282/207 255 333 266 279 17

\* duplicate samples

Table 16 for barnacles does not show any significant seasonal trends. There appears to be slightly lower values for the well jacket (control) samples but analytical variability makes this difficult to determine. The predominant species sampled was Balanus tintinnabulum.

There is no indication of higher concentrations of Ba and Sr from the produced brine discharges accumulating in either the fouling mat or barnacle samples.
#### IV. CONCLUSIONS

Concentrations gradients of Ba, Cd, Cr, Cu, Mn, Pb, Sr, and Zn in surficial sediments at platform structures 288-A and 296-B are not related to the hydrated iron fraction of the sediments or the sediment grain size. This suggests these metals have an input that is related to the platform structures or petroleum production activities.

There are seasonal variation in the concentration and distribution of these metals in the sediments near the platform structures. Generally, the summer and fall seasons have higher and more variable concentrations while the winter and spring are lower and less variable.

There is a significant accumulation of Cr, Hg, Pb, Sr and Zn in the sediments around the platform structures.

Suspended particulate matter trace metal concentrations are highly variable with the higher concentrations present in the summer. Due to the variability, SPM trace metal concentrations cannot be related to the platform discharges. Comparison of normalized SPM and surficial sediment data suggest resuspended sediments as a source of Pb during the summer, fall and winter, and of Sr in the spring.

Produced brine samples contain higher concentrations of Ba, Cr, Fe, Mn and Sr relative to sea water. The average concentration of Ba was 1.39 ppm. This is similar to last year's reported concentration. The average Sr concentration (70.7 ppm) is about twice last year's average concentration.

There are significant seasonal variations in all metals except Cd in <u>Archosargus probatocephalus</u> (sheepshead) and Ba, Fe, Pb, Mn, Hg, Ni, Sr and Zn in <u>Chaetodipterus faber</u> (spadefish) tissues. Seasonal variations in heavy metal concentrations in sheepshead and spadefish are not necessarily related to the platform structures. Bioaccumulations of Cd, Cr, Cu, Fe, Ni, Pb and Zn has not occurred in either sheepshead or spadefish.

Comparison of the heavy metal concentrations from <u>Stenostomus</u> <u>caprinus</u> (longspine porgy) with data from other studies indicate bioaccumulation of Cd, Cr, Cu, Fe, Ni, Pb and Zn has occurred. Lack of sensitivity for Cr and Ni may cause a bias towards higher mean concentrations for these metals. The higher metal concentrations in the longspine porgy may be related to the higher (and more variable) metal concentration in the surficial sediments near the platforms during the summer. Insufficient data on the seasonal variation of these metals in longspine porgy prevents confirmation of irreversible bioaccumulation.

There were higher concentrations of Cd in <u>Trachypenaeus</u> <u>similis</u> (sugar shrimp) than what other investigators have found in this species. Higher Ni concentrations were found in the fall and winter but had returned to normal by spring.

No significant trends or increases were noted for heavy metal concentrations in fouling mat or barnacles in any season.

#### REFERENCES

- Alexander, J. E., Program Manager, Baseline Monitoring Studies, Mississippi, Alabama, Florida, Outer Continental Shelf 1975-76, Vol. VI, Rig Monitoring. (Assessment of the Environmental Impact of Exploratory Oil Drilling.) Bureau of Land Management, Contract 08550-CT5-30, June 1977.
- 2. Anderson, J. B. and R. R. Schwarzer, Work Unit 2.3.2-2.4.2, Sedimentology and Trace Metal Concentrations in Sediments and Organisms. In: W B. Jackson [Ed.], 1979 NOAA/NMFS Annual Report to EPA, "Environmental Assessment of an Active Oilfield in the Northwestern Gulf of Mexico, 1977-1978," Volume III, Physical and Chemical Investigations.
- 3. Bedinger, C. A., Project Manager, Ecological Investigations of Petroleum Production Platforms in the Central Gulf of Mexico, Final Report. Bureau of Land Management, Contract AA551-CT8-17 (to be published in 1979).
- 4. Berryhill, H. L., Environmental Studies, South Texas Outer Continental Shelf, Geology, Final Report, 1975. Bureau of Land Management, Contract 08550-MU5-20, February 1976.
- Brooks, J. M., E. L. Estes and W. H. Huang, Work Unit 3.2, Surficial Sediments and Suspended Particulates. In: W. B. Jackson [Ed.], 1980 NOAA/NMFS Annual Report to EPA, "Environmental Assessment of an Active Oilfield in the Northwestern Gulf of Mexico, 1978-1979." (in preparation).
- De, Anil K., Shripad M. Khopkar and Robert A. Chalmers, Solent Extraction of Metals, Van Nostrand Reinhold, London, pp. 141-148, 1970.
- Jan, Tsu K. and David R. Young, Determination of Microgram Amounts of Some Transition Metals in Seawater by Methyl Isobutyl Ketone-Nitric Acid Successive Extraction and Flameless Atomic Absorption Spectrophotometry. <u>Anal. Chem.</u>, 50:9, 1250-1253, 1978.
- 8. Presley, B. J. and P. N. Booth, Trace Metals in Epifauna, Zooplankton and Macronekton, Chap. 6, in Environmental Studies, South Texas Outer Continental Shelf, Biology and Chemistry, Final Report, 1977. Bureau of Land Management, Contract AA550-CT7-11, January 1979.
- Riley, J. P. and G. Skirrow, Chemical Oceanography, Vol. 3, 2nd Ed., p. 517 (method of Lyman and Fleming), 1975.

- Shokes, R. A., Characterization of Baseline Conditions at the West Hackberry Offshore Brine Disposal Site - Texoma Group Strategic Petroleum Reserve Program. Sciences Applications, Inc., Department of Energy, Contract EL-77-C-01-8788, November 1, 1978.
- Tillery, J. B., Work Group 700, Trace Metals. In: C. A Bedinger (Project Manager), "Ecological Investigations of Petroleum Production Platforms in the Central Gulf of Mexico." Final Report, Bureau of Land Management, Contract AA551-CT8-17 (in preparation).
- Trefry, J. H. and B. J. Presley, Heavy Metal Transport of the Mississippi River to the Gulf of Mexico in Marine Pollutant Transfer, H. L. Windom and R. A. Duce [Ed.], Lexington Books, Massachusetts, pp. 39-75, 1976.
- Wheeler, R. B., Environmental Geochemistry of Sediments in the Buccaneer Oilfield: Factors Controlling Concentrations of Trace Metals in Sediments, Master of Science Thesis, Rice University, Houston, Texas, May 1979.

APPENDIX Figures



Figure 1. Map of Study Area



26-+ SPRING - IV ppm 25 2.5 25 -WINTER - III ppm 12.5 2.5 25-FALL -II ppm 12.5 (NA) 2.5 25 SuitiMER - I ppm 2.5 10 25 Meters NORTH 0 25 Meters EAST 10 25 3 Meters WEST 0 50 10 50 10 25 50 50 Meters SOUTH DISCHARGE Figure 3. Temporal and Spacial Variation of Cd in Surficial Sediments at Platform 288-A

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**Z**0-SPRING - IV ppm 10 2 20 WINTER - 111 ppm 10 z Zo FALL - II ppm 10 (NA) Z 20. SUMMER - I ppm 10 Ż 10 25 Meters NORTH 0 25 Meters EAST 10 25 50 Meters SOUTH 10 25 50 Meters WEST 0 50 10 50 2 DISCHARGE Temporal and Spacial Variation of Cr in Surficial Sediments at Platform 288-A Figure 5.







500 SPRING - IV ppm 50 50 500 WINTER - 111 ppm ss 50 500 FALL - 11 ppm & (NA) 50 500 SUMMER - I ppm 250 50 10 25 50 Meters NORTH 10 25 50 Meters EAST 10 25 50 Meters SOUTH 10 25 50 Meters WEST 0 DISCHARGE Temporal and Spacial Variation of Mn in Surficial Sediments at Platform 288-A Figure 9.





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Figure 11. Temporal and Spacial Variation of Pb in Surficial Sediments at Platform 288-A







Figure 14. Temporal and Spacial Variation of Ba in Surficial Sediments at Platform 296-B









25 -SPRING - IV ppm 2.5 25 -MINTER - III ppm 5:2-2.5 25 FALL - 11 ppn ä (NA) 2.5 27.9 A 25 summer - I ppm - I 2.5 10 25 S Meters NORTH 0 25 50 Meters EAST 10 25 5 Meters SOUTH 0 50 10 0 25 9 Meters WEST 50 10 50 DISCHARGE

Figure 18. Temporal and Spacial Variation of Cu in Surficial Sediments at Platform 296-B





Temporal and Spacial Variation of Hg in Surficial Sediments at Platform 296-B





















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2.4.2-85















