

NOAA Technical Memorandum NMFS-SEFC- 52



NOAA/NMFS MILESTONE REPORT TO EPA

Environmental Assessment of Buccaneer Gas and Oil Field in the Northwestern Gulf of Mexico, 1975-1980

A report to the Environmental Protection Agency on work conducted
under provisions of Interagency Agreement EPA-IAG-D5-E693-E0
during 1975-1980.

Volume VI

TRACE METALS



SOUTHEAST FISHERIES CENTER
GALVESTON LABORATORY



GALVESTON, TEXAS

NOVEMBER 1980

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-52

Environmental Assessment of Buccaneer Gas and Oil Field In the Northwestern Gulf of Mexico, 1975-1980.

VOL. VI - TRACE METALS

BY

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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 1975-1980.**

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Volume VI - TRACE METALS

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LIST OF VOLUMES

This Milestone Report is printed in six separate volumes:

Volume I - SEDIMENTS, PARTICULATES AND VOLATILE HYDROCARBONS

Work Unit 2.3.2 Investigations of Surficial Sediments,
Suspended Particulates and Volatile
Hydrocarbons at Buccaneer Gas and Oil
Field

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Volume II - FISHES AND MACRO-CRUSTACEANS

Work Unit 2.3.5/
2.3.8 Pelagic, Reef and Demersal Fishes, and
Macro-crustaceans/Biofouling Communities

LGL Ecological Research Associates, Inc.

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Volume III - BACTERIA

Work Unit 2.3.7 Bacteriology of a Gulf of Mexico
Gas and Oil Field

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Volume IV - CURRENTS AND HYDROGRAPHY

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

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Volume V - HYDROCARBONS

Work Unit 2.4.1 Hydrocarbons, Biocides and Sulfur

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Volume VI - TRACE METALS

Work Unit 2.4.2 Trace Metals

Southwest Research Institute

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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 in the Northwestern Gulf of Mexico, a project funded by the Environmental Protection Agency (EPA) through interagency agreement with the National Oceanic and Atmospheric 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 was completed in 1980. 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 product are these milestone reports summarizing the findings of the major investigative components of the study.

Objectives of the project were (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 used historical and new data and included 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 continued to focus on items (1) and (2) and on preparation of the milestone reports which represented the final products of this study.

This project has provided a unique opportunity for a multi-year investigation of effects of chronic, low-level contamination of a marine ecosystem associated with gas and oil production in a long-established field. In many respects, it represents a pioneering effort. It has been made possible through the cooperation 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
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Editors

LIST OF REPORTS AND PUBLICATIONS

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- 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.
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- Middleditch, B. S. and B. Basile. 1980. Discharge of elemental sulfur and its distribution in the region of the Buccaneer oil field. 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.
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LIST OF ARCHIVED DATA

Data available from U.S. Department of Commerce, NOAA, EDIS,
National Oceanographic Data Center, Washington, D.C. 20235

<u>Year</u>	<u>Data Type</u>	<u>NODC Accession Number</u>
1976-1977	Demersal Fish	78-0501
1976-1977	Sediment	78-0501
1976-1977	Birds	78-0501
1976-1977	Ichthyoplankton	78-0501
1976-1977	Pelagic Fish	78-0501
1976-1977	Plankton	78-0501
1976-1977	Sessile Fauna	78-0501
1976-1977	Total Organics	78-0501
1976-1977	Hydrocarbons	78-0501
1976-1977	Fish Determination	78-0501
1976-1977	Ocean Serial Stations	78-0501
1976-1977	Trace Metals	78-0501
1976-1977	Benthos	78-0501
1976-1977	Drift Bottle Releases	78-0501

<u>Year</u>	<u>Data Type</u>	<u>NODC Accession Number</u>
1977-1978	Brine Dye Release	80-0423
1977-1978	Fish Bioassay	80-0423
1977-1978	Ichthyoplankton	80-0423
1977-1978	Food Habits-Station	80-0423
1977-1978	Food Habits-Stomach	80-0423
1977-1978	Reef Fish Census	80-0423
1977-1978	Pelagic Fish Census	80-0423
1977-1978	Biofouling	80-0423
1977-1978	Transponding Buoy (2 Files)	80-0423
1977-1978	Drift Bottle Release/Recovery	80-0423
1977-1978	Dye Study-station	80-0423
1977-1978	Ocean Serial Stations	80-0423
1977-1978	Current Meter/Wind Records	80-0423
1977-1978	Non-Metal Analysis (Hydrocarbons)	80-0423
1977-1978	Bacteria - Behavior	80-0423
1977-1978	Bacteria - Degradation Rates	80-0423
1977-1978	Bacteria - Enumeration	80-0423
1977-1978	Bacteria - Enumeration	80-0423
1977-1978	Bacteria - Taxonomy/Physiological Diversity	80-0423

<u>Year</u>	<u>Data Type</u>	<u>NODC Accession Number</u>
1977-1978	Respirometry Experiment	80-0423
1977-1978	Trace Metals - Sediment (Diver Core)	80-0423
1977-1978	Sediment Size Analysis	80-0423
1977-1978	Stomach Contents	80-0423
1977-1978	Demersal Fish	80-0423
1977-1978	Shrimp Bioassay	80-0423
1977-1978	Trace Metals	80-0423
1977-1978	Trapped Suspended Sediment	80-0423
1977-1978	Non-Metal Analysis	80-0461
1977-1978	Bacteria - Behavior	80-0461
1977-1978	Bacteria - Degradation Rates	80-0461
1977-1978	Bacteria - Enumeration	80-0461
1977-1978	Bacteria - Taxonomy/Physiological Diversity	80-0461
1977-1978	Respirometry Experiment	80-0461
1977-1978	Trace Metals - Sediment (Diver Core)	80-0461
1977-1978	Sediment - Size Analysis	80-0461
1977-1978	Stomach Contents	80-0461
1977-1978	Demersal Fish	80-0461
1977-1978	Shrimp Bioassay	80-0461
1977-1978	Trace Metals	80-0461
1977-1978	Trapped Suspended Sediment	80-0461

<u>Year</u>	<u>Data Type</u>	<u>NODC Accession Number</u>
1978-1979	Stomach Contents	80-0416
1978-1979	Clay Mineralogy	80-0416
1978-1979	Bioassay (Toxicity)	80-0416
1978-1979	Algae	80-0416
1978-1979	Tagging	80-0416
1978-1979	Histopathology and Bacteriology	80-0416
1978-1979	Morphometric	80-0416
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<u>Year</u>	<u>Data Type</u>	NODC <u>Accession Number</u>
1978-1979	Pb - 210	80-0416
1978-1979	Bacteria - Enumeration	80-0416
1978-1979	Bacteria - Degradation Rates	80-0416
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1978-1979	Respirometry	80-0416

<u>Year</u>	<u>Data Type</u>	NODC <u>Accession Number</u>
1979-1980	Data being archived, will be available in late 1980	TBA

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 (Figure 1). This field was selected in 1975 as the study area because: (a) the field had been in production for about 15 years, 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:

<u>Year</u>	<u>Lease Number</u>	<u>Block Number</u>	<u>Acreage</u>	<u>Hectares</u>
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:

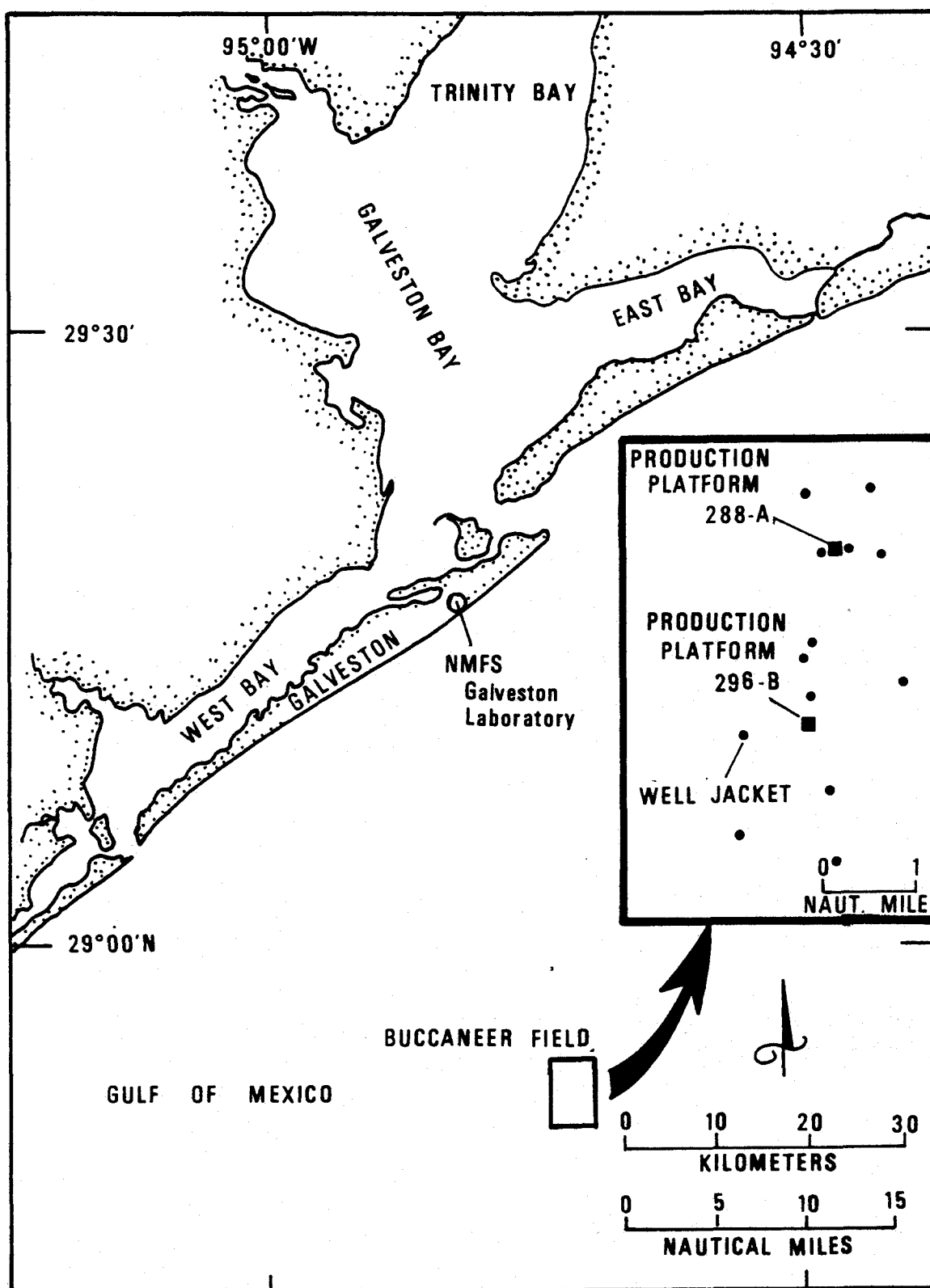


FIGURE 1. LOCATION OF BUCCANEER FIELD

<u>Date</u>	<u>Source</u>	<u>Amount</u>	
		<u>Barrels</u>	<u>Liters</u>
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 km²; 22.9 sq. statute miles) leased in the northwestern Gulf of Mexico. Four types of structures are located in Buccaneer Field: production platforms, quarters platforms, satellites (well jackets), and flare stacks. These are shown in Figure 2, which is an oblique aerial photograph of production platform 288-A and vicinity within Buccaneer Field. A map of Buccaneer Field, (Figure 3) depicts the locations of platforms and satellites within the field.

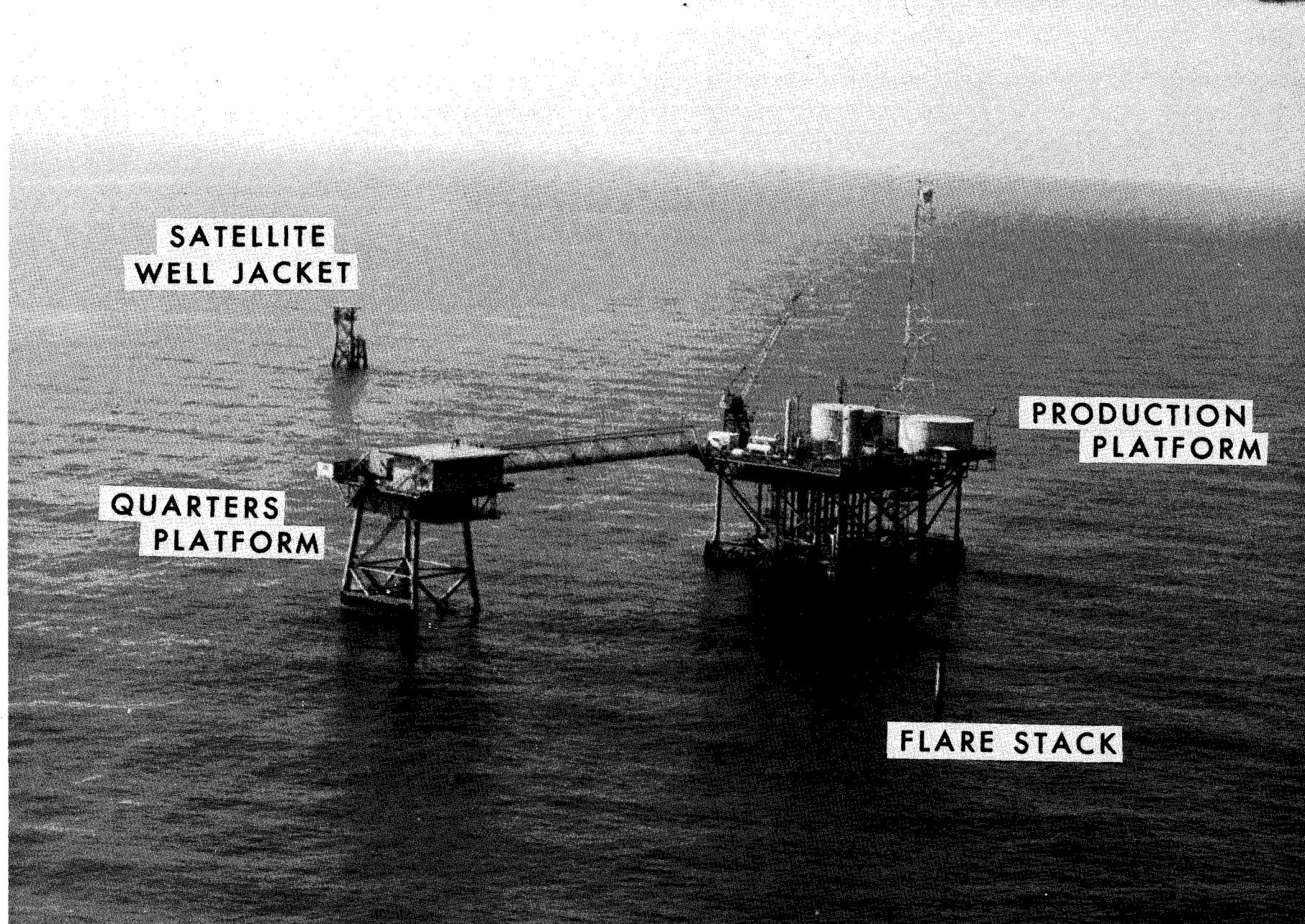


FIGURE 2. BUCCANEER FIELD STRUCTURES

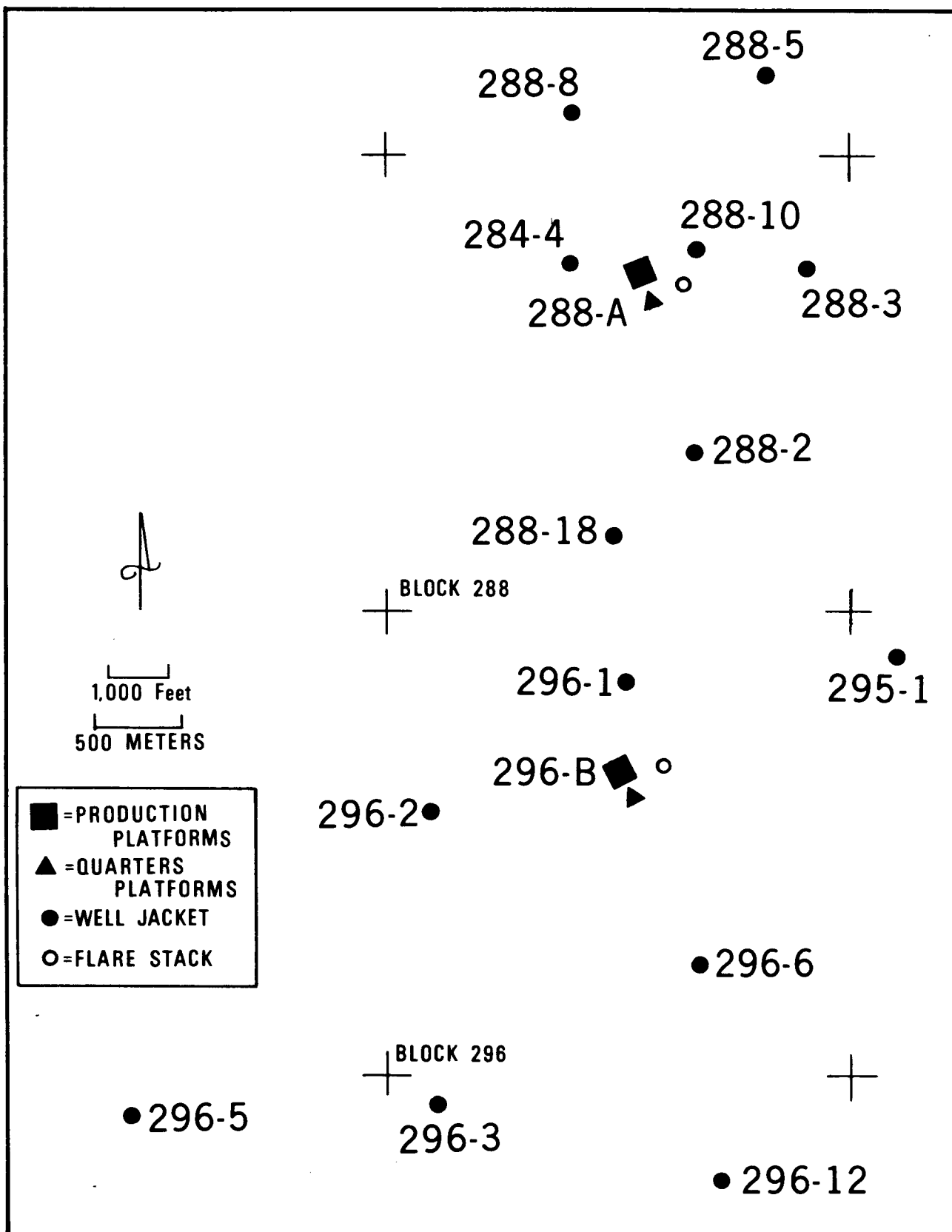


FIGURE 3. SHELL OIL COMPANY'S ALPHANUMERICAL IDENTIFICATION OF BUCCANEER GAS AND OIL FIELD STRUCTURES

WORK UNIT 2.4.2 - TRACE METALS

Southwest Research Institute

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ABSTRACT

This report provides an overview of four years (1976-1980) of trace metal investigations conducted as a part of a larger multidisciplinary, marine, environmental assessment program of the Buccaneer gas and oil field. Concentrations of Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Hg, Fe, Mn, Ni, Pb, Sb, Se, Sr, Tl and Zn have been determined in surficial sediments, subsurface sediments, suspended particulate matter, seawater, produced brine, crude oil and various tissues of biological organisms collected seasonally near two petroleum production platforms. Concentrations of Ba, Cd, Cr, Co, Cu, Mn, Pb, Sr, Hg and Zn in surficial sediments have been related to the platforms or activities on them. Trace metal concentrations in suspended particulate matter are higher than in bottom sediments. Seawater trace metal concentrations are within the range reported for shelf waters. Produced brine discharge have concentrations of Ba, Cd, Cr, Fe, Hg, Mn, Sr, Tl and Zn that are higher than seawater and vary with time. No evidence of excessive bioaccumulation of trace metals in marine organisms from the area around the production platforms was established. Seasonal variations of trace metals were observed in various marine organisms.

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SECTION 1

INTRODUCTION

With rising costs and diminishing supplies of petroleum, the next decade will see an increase in the development of offshore and nearshore petroleum resources. The impact this will have on the marine environment and ecology can be minimized with adequate planning and realistic regulations (1). However, the formulation of these plans and regulations will require a sound, technical data base.

This milestone report is an overview of the four years (1976-1980) of trace metal investigations (Work Group 2.4.2) performed on the "Environmental Assessment of the Buccaneer Gas and Oilfield in the Northwestern Gulf of Mexico" (BGOF).

Funding for this program has come from the Environmental Protection Agency (EPA) and the National Oceanic and Atmospheric Administration (NOAA). Management responsibilities are with the Environmental Research Division of the National Marine Fisheries Service, Southeast Fisheries Center, Galveston Laboratory, Galveston, Texas.

This study has a unique place in relation to the other studies funded by the Federal government that deal with the environmental effects of offshore petroleum production. The Buccaneer Gas and Oilfield study was designed to provide data on the chronic, low-level pollution associated with active petroleum production platforms located in the offshore environment. Results from this (BGOF) program along with the MAFLA Rig Monitoring study (2) and the Louisiana Platform study (3), augmented by data from the BLM-STOCS study (4), the MAFLA Baseline study (5) and the OEI studies (6a,6b) should provide a relatively strong data base from which intelligent plans and regulations can be formulated.

The overall objectives of the Trace Metal Work Groups (2.4.2) were to 1) identify the types and extent of environmental and ecosystems alterations associated with development and release of specific trace metal contaminants from an active gas and oilfield, 2) determine the spatial and temporal distribution of 19 trace metals in the Buccaneer gas and oilfield and the effects they have on the various components of the marine ecosystems, and 3) provide data on trace metal concentrations in various components of the marine ecosystem such that capabilities to describe and predict sources, fate and effects of gas and oilfield trace metal contaminants can be developed.

The BGOF is located approximately 49.6 km south/southeast from the Galveston Sea Buoy off Galveston, Texas. The development and operational history of the BGOF are given elsewhere (7).

The first (1976-1977) and second (1977-1978) years of trace metal investigations of the BGOF were performed by Drs. J. B. Anderson (Rice University, Houston, Texas) and R. R. Schwarzer (Texas Southern University, Houston, Texas).

Drs. Anderson and Schwarzer studied 12 trace metals (Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sr, and Zn) in 1) surficial sediments, suspended sediments and downcore sediments from a) the BGOF study area, b) near petroleum production platform 288-A, c) satellite structure 288-3, and d) from Galveston Bay to the BGOF at 8-km intervals; 2) produced brine from platforms 288-A and 296-B; 3) fouling organisms and barnacles from the legs of platform 288-A and satellite structure 288-3; and 4) various marine organisms from the vicinity of platform 288-A. Along with these trace metal studies, they also did geophysical studies of the bottom and sediment texture analyses.

The objectives of these first two years of study were to 1) characterize bottom sediments throughout the BGOF, 2) determine if trace metal pollution is present in the BGOF, 3) examine possible sources of metal pollution within the BGOF, and 4) determine the concentrations of trace metals in marine organisms that inhabit the BGOF so estimates of bioaccumulation could be made.

Trace metal investigations during the third (1978-1979) and fourth (1979-1980) years of the BGOF environmental study were performed by the author at Southwest Research Institute, San Antonio, Texas.

The same set of 12 trace metals previously examined were continued in the third year in the following samples: surficial sediments, suspended particulate matter, seawater, produced brine, fouling mat, barnacles, and muscle tissue from selected species of demersal and pelagic fishes and macrocrustaceans.

The objectives of the third year were similar to those listed earlier for the previous years, however, the program was designed so a more detailed examination of the temporal and spatial variations of these 12 trace metals could be delineated. Four consecutive seasons (summer, fall, winter and spring) were sampled.

The fourth and final year of the BGOF study saw a change in the suit of trace metals investigated. Eleven of the original 12 trace metals (Co deleted) were retained and augmented by another seven trace metals (Ag, Al, As, Be, Sb, Se, and Tl) which allowed all 13 priority pollutant metals (8) to be examined.

This limited the objectives of the fourth year to those of the previous year since no data base existed for the new metals added. Only two seasons (summer and winter) were sampled during this final year.

The samples analyzed during the fourth year included: surficial sediments, suspended particulate matter, seawater, produced brine, crude oil, and three tissues from three species of dominate fauna that inhabit the area around the platform structures.

SECTION 2

METHODS AND MATERIALS

Details of the sampling and analytical methodologies used in the first and second years are given by Anderson and Schwarzer (9a). Sampling and analytical methodologies for the third year are given elsewhere (10). Fourth year sampling and analytical methodologies were those of the third year with some exceptions. Details of these exceptions are provided in Appendix A.

Analytical and sampling variability for the first and second years of the BGOF are provided elsewhere (9b).

Tables 1 and 3 give the analytical error for sediments and biota, respectively, for the third and fourth years. The larger variability for As, Ba, Be, Cr, Hg, Ni, Sb, and Tl are due to the higher variability of the more sensitive graphite furnace AAS technique and the low concentrations present.

Table 2 is an estimate of the sampling variability expressed as the average of the coefficient of variation ($1 \text{ SD} \times 100/\bar{x}$) from two sets of duplicate surficial sediments collected during the summer and winter of the third year (1978-1979). This would include the analytical error from Table 1.

All biological samples consisted of pooled samples and no estimate of sampling error is available on individual organisms for the third (1978-1979) and fourth (1979-1980) years.

Figures 1, 2, and 3 illustrate the sampling grid used at the indicated platforms during the second, third, and fourth years, respectively.

TABLE 1. ESTIMATE OF ANALYTICAL ERROR FOR
THIRD AND FOURTH YEARS SEDIMENT SAMPLES

Metal	Analytical Error* %
Ag	27
As	25
Ba	27
Be	15
Cd	24
Cr	10
Cu	5
Fe	18
Hg	7
Mn	28
Ni	5
Pb	3
Sb	16
Se	20
Sr	4
Tl	20
Zn	10

* $\frac{SD \times 100}{\bar{x}}$

n = 7

TABLE 2. ESTIMATE OF SAMPLING VARIABILITY FOR
THIRD YEAR SEDIMENT SAMPLES. REPORTED AS AVERAGE
PERCENT COEFFICIENT OF VARIATION*

Metal	Cruise 1 (Summer)	Cruise 3 (Winter)
Ba	96	8
Cd	5	9
Cr	79	30
Co	79	33
Cu	129	30
Fe	67	35
Pb	60	104
Mn	66	18
Hg	132	127
Ni	49	72
Sr	27	6
Zn	7	131

* Analyses of two sets of duplicate surficial
sediment samples taken at same sample station.

TABLE 3. ESTIMATE OF ANALYTICAL ERROR FOR
THIRD AND FOURTH YEARS BIOLOGICAL SAMPLES

Metal	Analytical Error* %
Ag	19
As	107
Ba	34
Be	43
Cd	15
Cr	42
Cu	10
Fe	10
Hg	42
Mn	26
Ni	31
Pb	12
Sb	94
Se	3
Sr	7
Tl	175
Zn	2

* $\frac{SD \times 100}{\bar{x}}$

n = 5

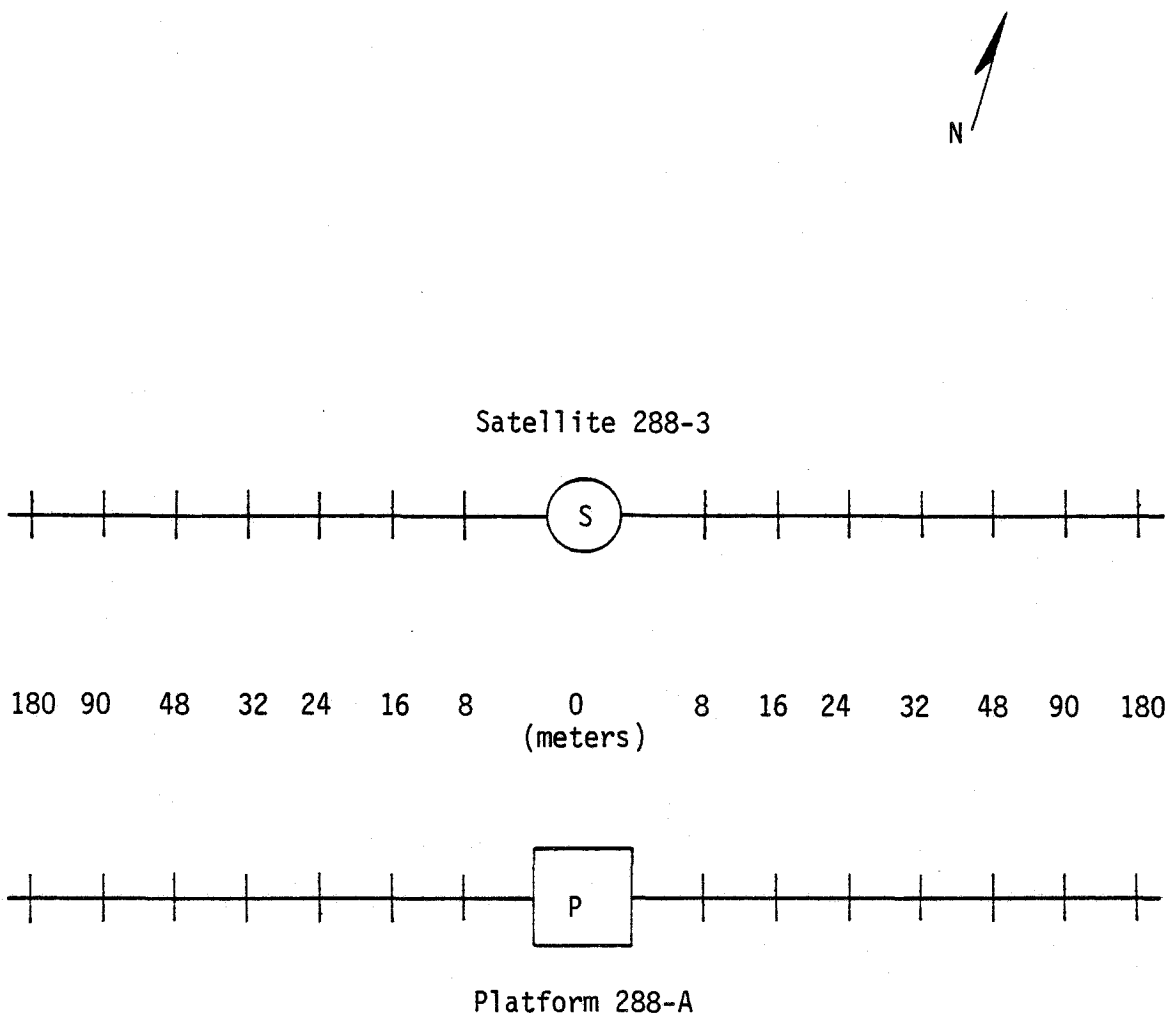


Figure 1. Sampling diagram for sediments. Second year (1977-1978)*

*Anderson and Schwarzer, 1979.

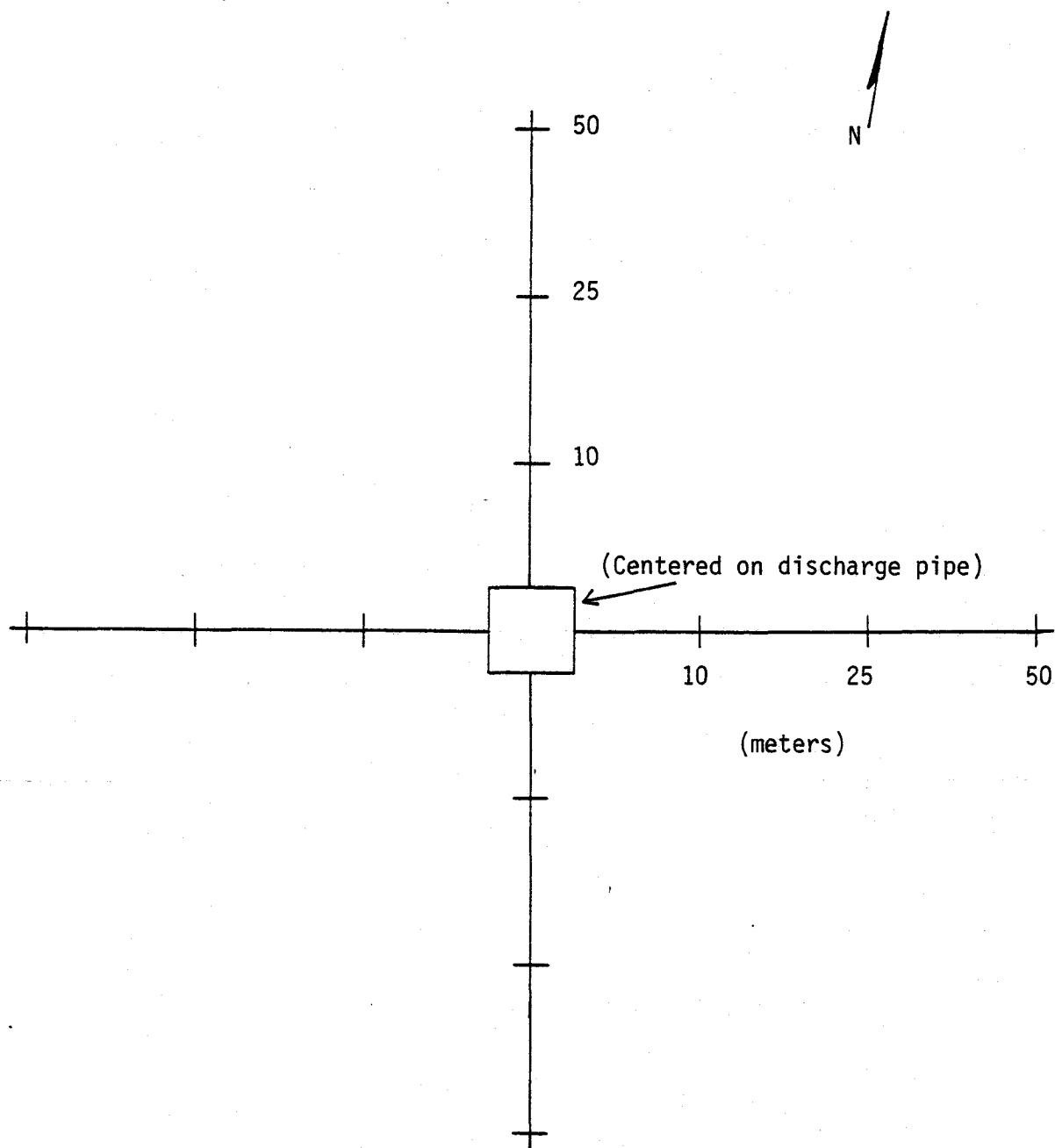


Figure 2. Sampling grid for third year (1978-1979) surficial sediments at platforms 288-A and 296-B.

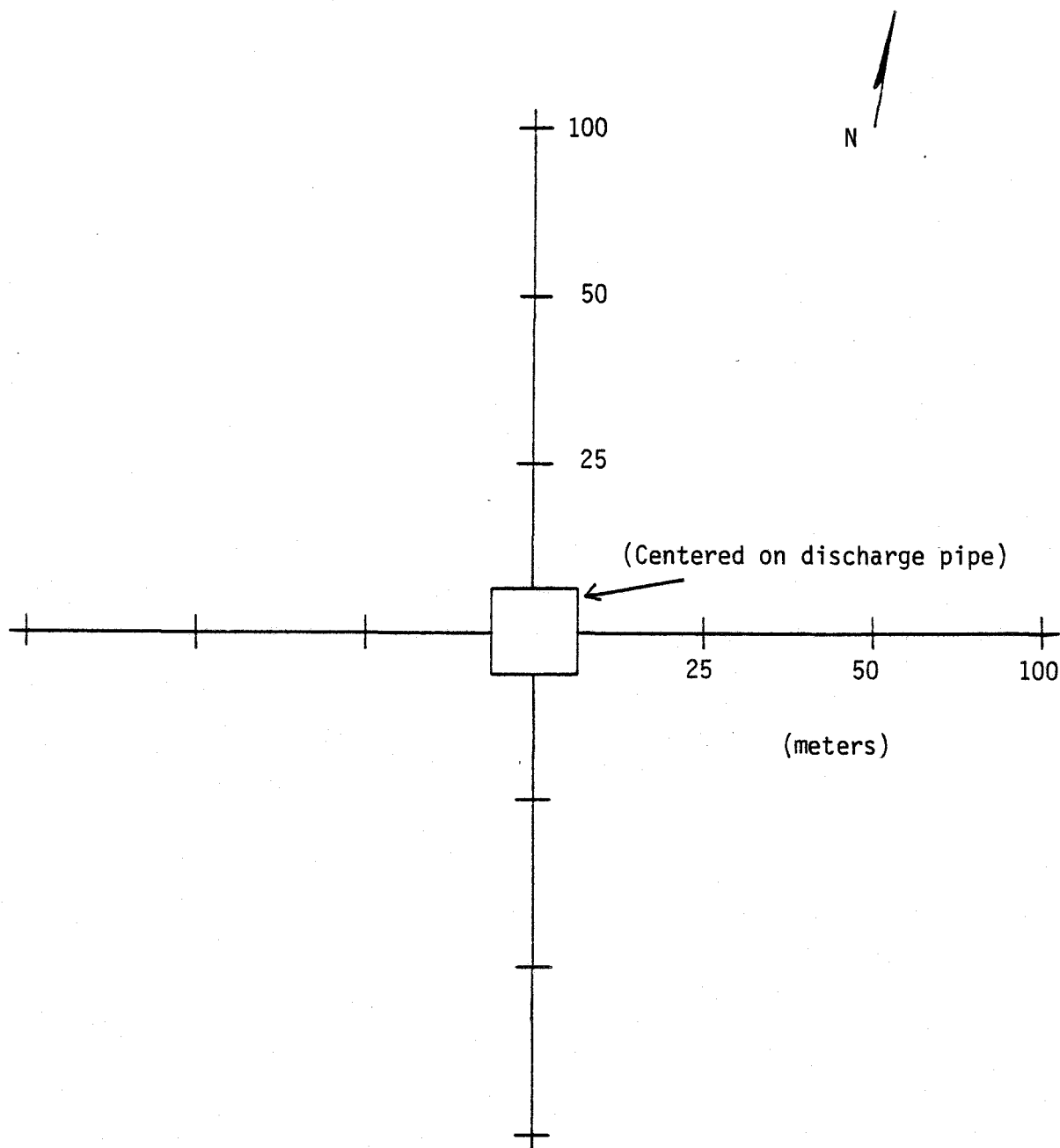


Figure 3. Sampling grid for fourth year (1979-1980) surficial sediments at platforms 288-A and 296-B.

SECTION 3

RESULTS AND DISCUSSION

SEDIMENTS

Early investigations of trace metals in surficial sediments from the BGOF indicated there were higher concentrations within 180 meters of the platform structures (9b).

Anderson and Schwarzer (9b) determined there were accumulations of Ba, Pb, Sr, Hg and Zn in surficial sediments within 180 meters of platform 288-A and well jacket 288-3. Control sediments used for comparison were subsurface sediments taken at the same locations as the surficial sediments. These subsurface sediments represented ambient trace metal concentrations prior to the development of the BGOF. Surficial sediments from the BLM-STOCS study (11) were also used as controls since they represented a relative pristine area of the Gulf of Mexico.

There were higher concentrations of Ba, Pb, Sr, and Zn near the platform (288-A) than well jacket (288-3). This was attributed to the size of the platform relative to the well jacket and the fact that no discharges were associated with the well jacket (9b).

The earlier trace metal investigations of Anderson and Schwarzer (9a,9b) of the BGOF study did not attempt to integrate the sediment geochemical parameters that could cause natural variations in trace metal concentrations. However, this was done later (12) using Q-mode cluster analysis to group sediments with similar characteristics and compare their trace metal concentrations. This revealed an accumulation of Ba, Sr, Cd, Co and Pb in surficial sediments near platform 288-A when compared to "pristine" sediments from 1) BLM-STOCS, 2) BGOF far-field samples, and 3) BGOF subsurface samples.

Sources of these sediment trace metal near the platform structure were suspected of coming from 1) corrosion of platform structures 2) sacrificial cathodes, 3) activities on the platform structures, 4) produced brine discharges, 5) corrosion of metallic debris on the bottom, and 6) engine exhaust from pleasure boats (Pb) (9b).

Based upon the finding from the first and second years, the third and fourth years of the BGOF study concentrated upon the "near-field" (within 100 meters) effect of the platform structures 288-A and 296-B.

Samples of surficial sediments were collected during four consecutive seasons during the third year and two seasons (summer and winter) during the fourth and final year. Samples were taken from the vicinity of platforms 288-A and 296-B during the third and fourth years and also at well jacket 288-5 and flare stack 296-B during the third year.

Concentration gradients of Ba, Cd, Cr, Cu, Mn, Pb, Sr, and Zn that decreased with distance from platforms 288-A and 296-B were observed in the third year (1978-1979). In the fourth year (1979-1980), similar gradients were observed for these same trace metals plus Ag and Hg. Table 4 illustrates these gradients identified during the fourth year sampling at platform 296-B. Each of the axis (north, east, south and west) consists of three samples with the arithmetic mean given. The "structure" station consist of one sample directly under the produced brine discharge pipe. The arithmetic mean (\bar{x}), standard deviation (SD) and coefficient of variation (CV%) are given for all samples collected at the platform.

Since these concentration gradients could be caused by natural geochemical variations in the sediments, a technique to distinguish between the natural variability and pollution events is needed. One such technique that has been used successfully (13,14) is to normalize the trace metal concentrations to the hydrated Fe oxide fraction of the sediments. The Fe content of the sediments is high (percent range) when compared to the other trace metals (ppm range) and any abnormal input of trace metals to the sediments would have minimal effect on the Fe content but would have a large impact on the other trace metals. Also, Fe being a transition metal would behave chemically like the other transition metals.

The input of abnormal amounts of trace metals to the sediments would be identified as an enriched ratio of metal concentration to Fe concentration. This is also easy to recognize visually by making a scatter plot of the metal concentration versus Fe concentration and identifying pollution as increased scatter along the Y-axis.

Figures 4, 5, 6 and 7 are examples of these scatter plots for Ni, Cd, Pb and Zn from the third year. These plots consist of all the sediment samples collected during a season. Included on the plots are the regression equation and r^2 value (goodness of fit) for each season. As a point of comparison, the regression equation with a 95% confidence interval of sediment data from the STOCS study (11) are included. The STOCS sediments can be considered as coming from a pristine area and representative of ambient trace metal concentrations. Examination of Figure 4 shows that Ni is within the limits of the STOCS Ni data and therefore at ambient concentration in the BGOF sediments. Figures 5, 6 and 7 show there is considerable scatter along the Y-axis for Cd, Pb and Zn as compared to the STOCS confidence limits ($p=0.05$). This indicates there is an abnormal input of Cd, Pb and Zn to the sediments. Generally, the farthestest points out on the Y-axis (i.e., pollution) are those stations closest to the platform structures.

TABLE 4. SEASONAL COMPARISON OF AVERAGE TRACE METAL CONCENTRATIONS
($\mu\text{g/g}$ dry wt) IN SURFICIAL SEDIMENTS FROM PLATFORM 296-B

Cruise	Axis	Ag	Ba	Cd	Cr	Cu	Hg	Fe*	Mn	Pb	Sr	Zn
I (Summer 1979)	N	0.04	57.2	0.50	8.6	6.6	0.13	0.50	165	136	2188	1183
	S	0.01	33.9	0.99	3.4	4.6	0.24	0.51	178	18	147	108
	E	0.03	110	0.64	9.3	8.5	0.10	0.46	126	162	759	1088
	W	0.01	37.3	0.35	6.9	6.9	0.37	0.59	206	66	139	273
	Structure	0.06	88.4	0.55	10.3	40.5	0.27	0.68	194	201	627	928
	\bar{x}	0.03	62.0	0.61	7.3	9.3	0.21	0.53	171	104	794	683
	SD	0.03	47.7	0.73	5.3	10.1	0.23	0.16	41	115	1548	755
	CV%	93	76	119	73	109	107	30	24	111	195	111

II (Winter 1979)	N	0.02	74.4	0.47	13.5	8.1	0.28	0.43	187	69	2155	1423
	S	0.01	23.2	0.14	3.6	5.1	0.05	0.39	187	12	89	173
	E	0.03	63.7	0.46	8.3	11.2	0.13	0.55	203	48	331	1266
	W	0.02	30.5	0.63	5.3	17.6	0.05	0.39	162	63	121	487
	Structure	0.09	118.0	1.21	47.9	28.0	0.24	12.07	215	276	390	2289
	\bar{x}	0.03	53.3	0.48	10.7	11.9	0.14	0.50	187	66	652	949
	SD	0.02	43.1	0.56	12.7	12.4	0.19	0.25	36	84	1665	1280
	CV%	85	81	116	119	104	140	50	19	127	255	135

* Concentration in percent.

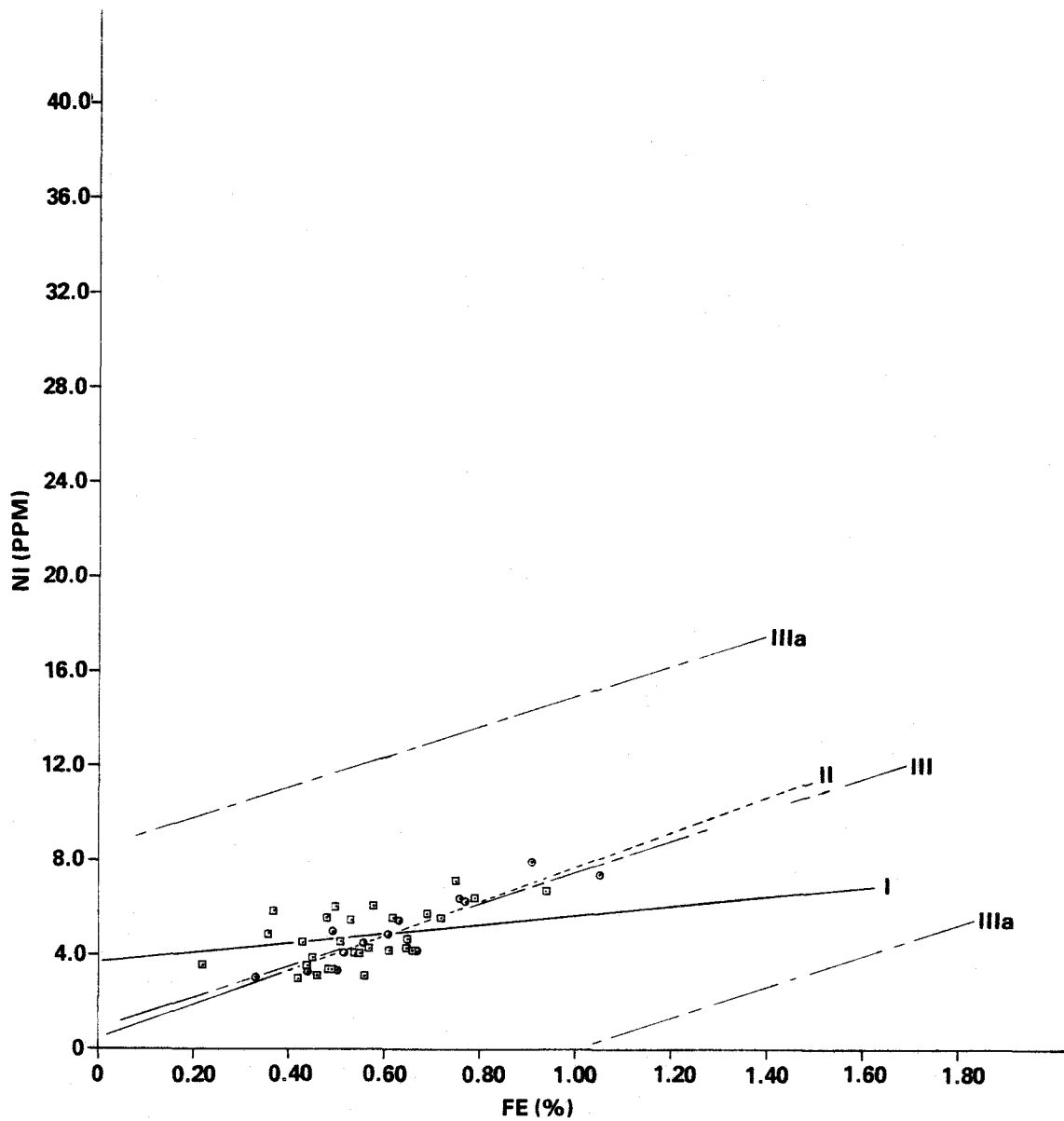
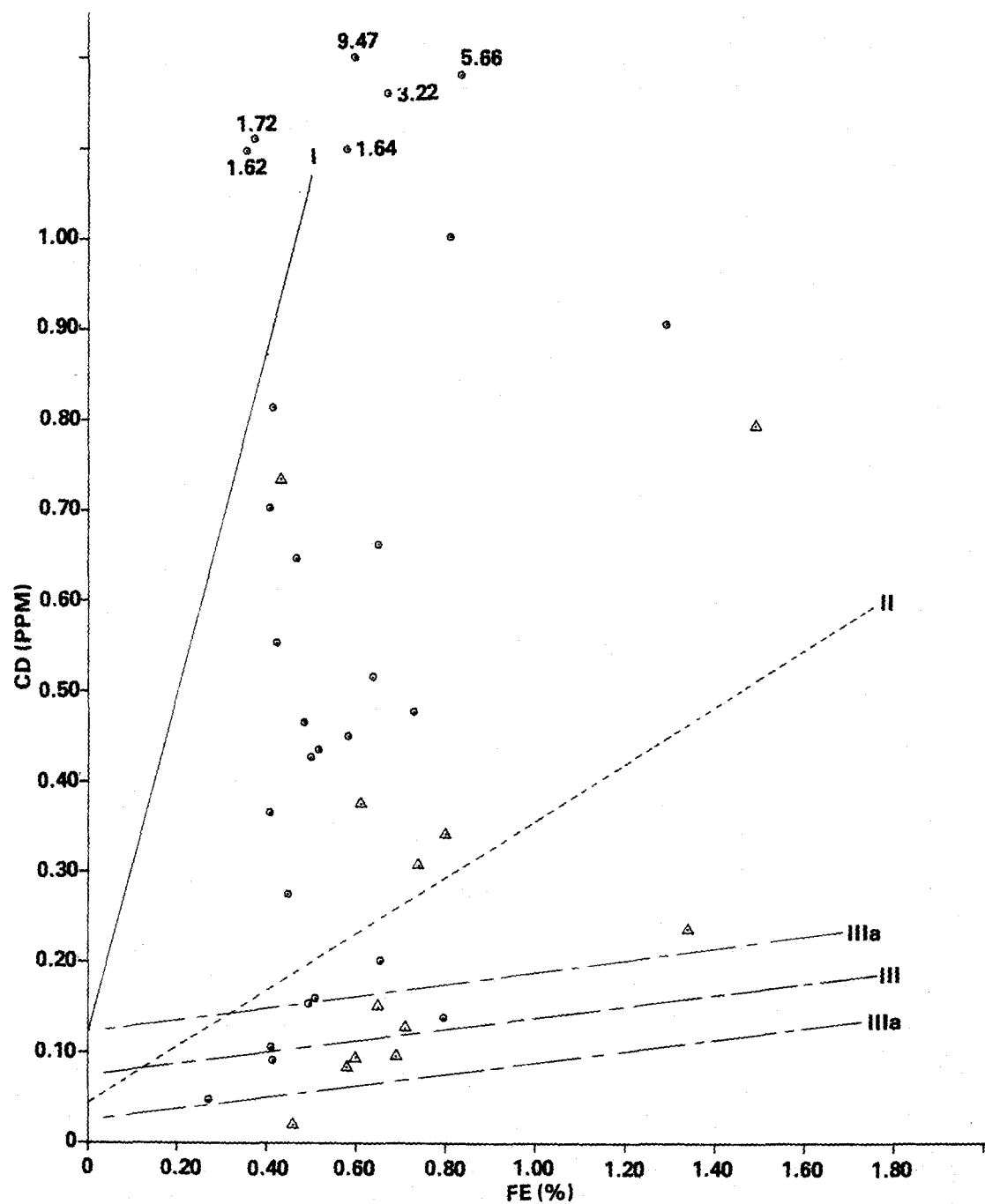


Figure 4. Scatter plot of surficial sediments NI concentration versus Fe concentration from 5N HNO₃ leach (summer and fall samplings 1978-1979).



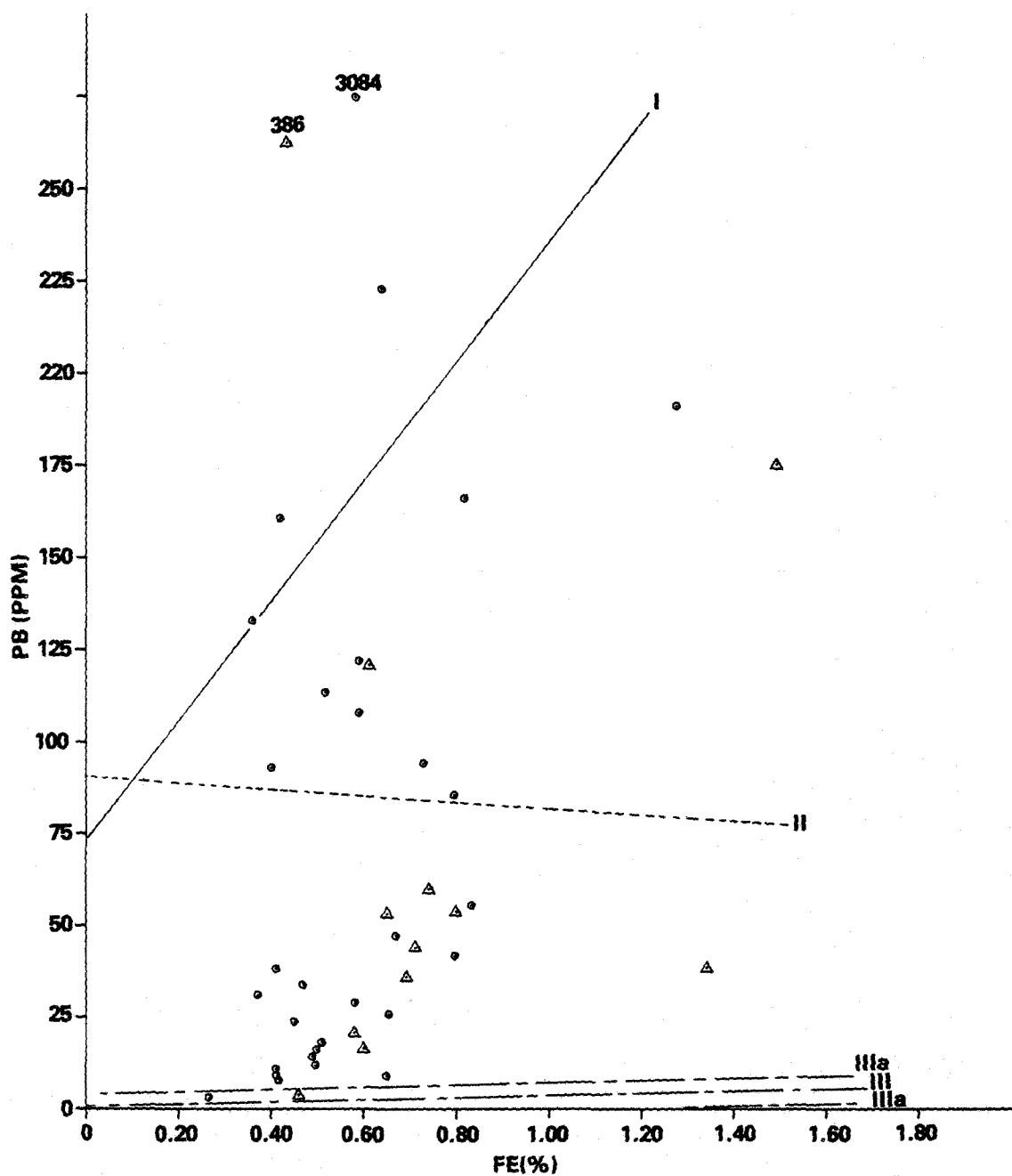
I = \circ ; $y = 1.87x + 0.124$, $R^2 = 0.0367$, Summer

II = \triangle ; $y = 0.31x + 0.045$, $R^2 = 0.1614$, Fall

III = STOCs regression, $y = 0.063x + 0.075$, $R^2 = 0.8195$

IIIa = STOCs regression, confidence limit at 95%

Figure 5. Scatter plot of surficial sediments Cd concentration versus Fe concentration from 5N HNO₃ leach (summer and fall samplings 1978-1979).



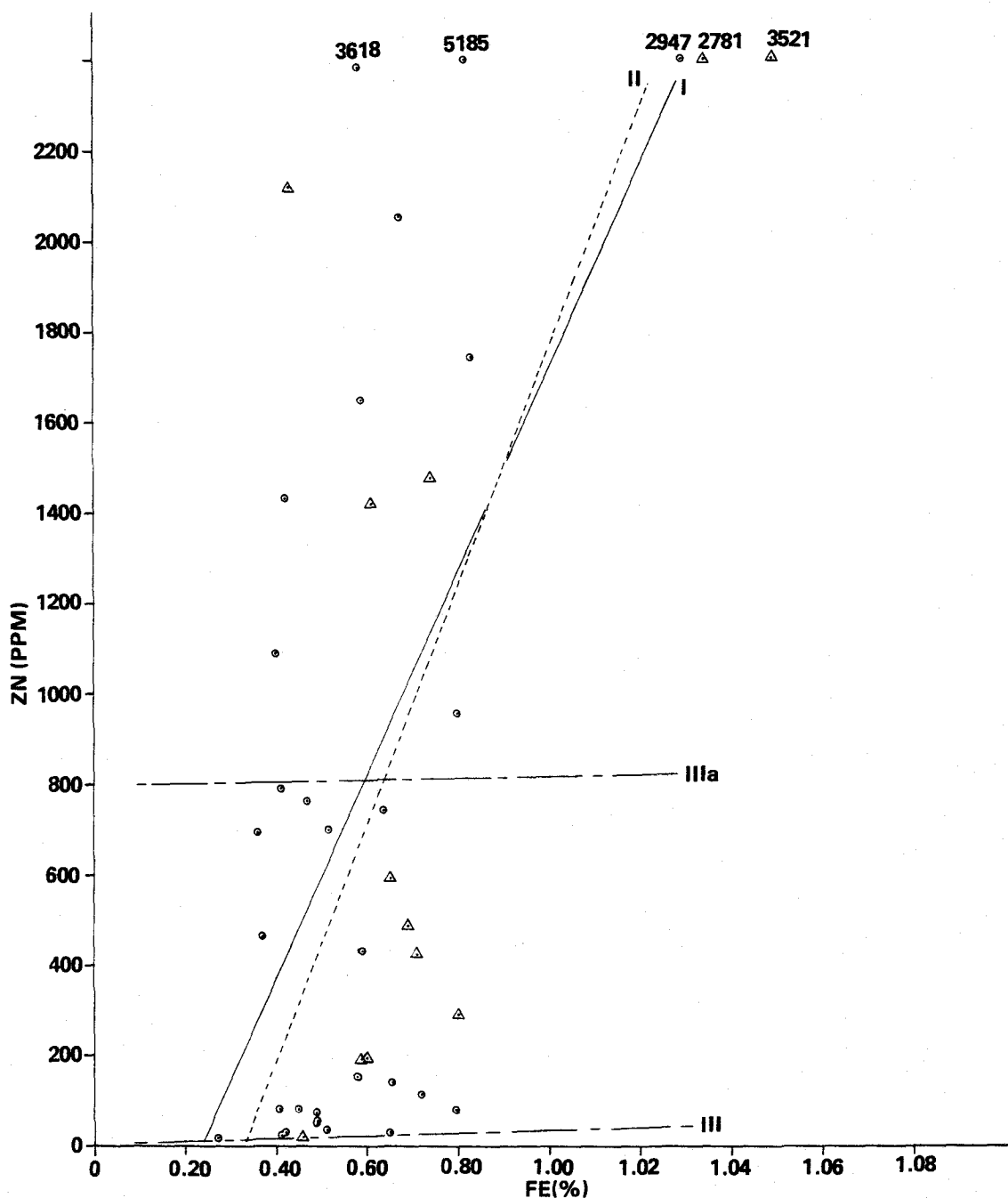
I = \circ ; $y = 163x + 74$, $R^2 = 0.0035$, Summer

II = Δ ; $y = -8.8x + 91$, $R^2 = 0.0007$, Fall

III = STOCs regression, $y = 2.9x + 0.7$, $R^2 = 0.8139$

IIIa = STOCs regression, confidence limit at 95%

Figure 6. Scatter plot of surficial sediments PB concentration versus Fe concentration from 5N HNO₃ leach (summer and fall samplings 1978-1979).



I = \circ ; $y = 2994x - 826$, $R^2 = 0.2454$, Summer

II = \triangle ; $y = 2634x - 870$, $R^2 = 0.5596$, Fall

III = STOCS regression, $y = 30x + 2.5$, $R^2 = 0.9754$

IIIa = STOCS regression, confidence limit at 95%

Figure 7. Scatter plot of surficial sediments ZN concentration versus Fe concentration from 5N HNO_3 leach (summer and fall samplings 1978-1979).

Trace metals tend to be complexed by the organics materials present in sediments (15), and there is a positive correlation between the amount of organic material (as measured by TOC) and the amount of trace metals present. This relationship can be used like the one described above for trace metal versus Fe ratios. Enriched ratios indicate abnormal trace metal inputs.

A third parameter can also be used to show trace metal pollution of sediments similar to those described above. It is known that as the grain size of the sediments get smaller, the trace metal concentrations increase. This is caused by the larger surface area available on the smaller sediment particles which afford more binding sites for the metals. This phenomena not only affects the natural levels of trace metals in sediments but also the abnormal inputs (i.e., pollution). Plotting the metal concentration versus the ϕ (phi) value (i.e., particle size) of the sediments can be used to identify trace metal pollution as was illustrated earlier for metal-Fe plots.

The metal versus TOC plot and metal versus ϕ plots from the third and fourth years have followed the same trends as those illustrated in Figures 4, 5, 6 and 7 for metals versus Fe plots.

The normalizing of the sediment trace metal concentrations to Fe, TOC and ϕ indicate that the concentration gradients of Ba, Cd, Cr, Cu, Mn, Pb, Sr, and Zn cannot be attributed to natural variations and are suspected of originating from the platform structures or activities on the platforms. These platform sources may include those listed earlier by Anderson and Schwarzer (9b).

It is interesting that Gallaway et al. (16) has shown that a significant amount of sport fishing occurs at these platforms which reinforces the theory that pleasure boat exhaust are an important source of Pb to the marine sediments near the platforms.

The distribution of trace metals in sediments around the platforms generally follows the seasonal current patterns (9b,10). Currents, wave action and turbulence around the platforms (17) tend to continually redistribute the bottom sediments away from the platforms (18) which effectively prevents any long-term buildup of contaminated sediments near the platform structures.

Estimations of the amounts of trace metals accumulating in the surficial sediments within 180 meters of platforms 288-A and 296-B were made by using mean sediment metal concentrations normalized to Fe. Correction for ambient levels of trace metals in the surficial sediments was made by normalizing (to Fe) the mean trace metal concentrations in the bottom samples of sediment cores taken in the second year (1977-1978) BGOF study. According to Anderson and Schwarzer (9b), these sediments represent the predevelopment period of the BGOF and should be representative of ambient trace metal concentrations for this area of the Gulf.

The mean metal to Fe ratios of the bottom cores were used to adjust the mean Fe concentrations of the surficial sediments to give an estimated ambient level of the metal:

$$\left(\frac{M}{Fe}\right)_{core} \times Fe_{surf} = M_{surf-amb}$$

$$M_{surf-detn} - M_{surf-amb} = M_{surf-accum}$$

where $\left(\frac{M}{Fe}\right)_{core}$ = mean $\frac{\text{metal concentration}}{\text{Fe concentration}}$ in the bottom core samples

Fe_{surf} = mean Fe concentration in the surficial sediments

$M_{surf-amb}$ = mean ambient metal concentration in the surficial sediments

$M_{surf-detn}$ = mean metal concentration determined in the surficial sediments

$M_{surf-accum}$ = estimated mean metal concentration accumulating in the surficial sediments

The arithmetic mean concentration of each metal was determined from all sampling points and used along with the standard deviation to calculate a lower confidence limit (LCL) at the 95 percent confidence level. The LCL is calculated as

$$LCL_{0.95} = \bar{x} - t_{0.05} (n-1) \frac{s}{\sqrt{n}}$$

where \bar{x} = arithmetic mean

$t_{0.05} (n-1)$ = Student's t value with n-1 degrees of freedom at the 0.05 significance level

s = estimated standard deviation

n = sample size.

This value represents the minimum trace mean concentration of that metal in the study area, at the 95-percent confidence level and was used as $M_{surf-detn}$. A similar calculation was used to determine an upper confidence limit (UCL) on the ambient concentration as

$$UCL_{0.95} = \bar{x} + t_{0.05} (n-1) \frac{s}{\sqrt{n}}$$

This represents the maximum mean concentration of ambient mean metal concentration in the surficial sediments and was used for $M_{\text{surf-amb}}$. Substituting these into the equation above gives a value which, if positive, implies that a significant accumulation of a particular metal occurred in the surficial sediments.

This exercise was also performed using sediment data from STOCS study (11) as representative of ambient trace metal concentrations in sediments. These results are also given in Table 5.

Table 5 shows similar results when using the BGOF bottom core samples and the STOCS data. There are significant ($p=0.05$) short-term accumulations of Ba, Co, Cr, Cu, and Pb in the sediments near the platform structures. The accumulations of Hg, Mn, Sr and Zn appear to be more persistent with time.

SUSPENDED PARTICULATE MATTER

Examination of trace metal concentrations in suspended particulate matter (SPM) are important because 1) they provide an important transport medium for trace metals in the marine environment and 2) they are an important food source for filter-feeding organisms. Detritus materials in the SPM can absorb or adsorb large amounts of trace metals from the water column. The organic materials in SPM can also complex trace metal (15).

Eventually the trace metals associated with SPM will be deposited in bottom sediment, but before that occurs the SPM can be moved over great distances by wave and wind action and currents.

Anderson and Schwarzer (9a) showed that SPM from the vicinity of platform 288-A contain larger amounts of detritus and organic material from the platform structure or the biota associated with it. These investigators also found a significant amount of metal flakes from the platform structure contaminating their sediment trap samples. Material in these sediment traps indicated that most of it was large enough that it would be deposited close to the platform structures. However, in those sediment traps closest to the bottom about 10% of the material was fine grain sediments. This material was from the nephroid layer normally present near the bottom (except the winter season). This nephroid layer is suspected of being from resuspended bottom sediments (9a,18).

Variability in trace metal concentration of SPM (9a,10) did not allow the identification of trace metals emanating from the platform structures or the produced brine discharges.

Seasonal and sample variability of SPM trace metals from the fourth year are illustrated in Table 6. Trace metal concentrations in SPM are usually higher than the concentration in the bottom sediments (9a,10).

TABLE 5. SIGNIFICANT (95% LEVEL) ACCUMULATIONS OF TRACE METALS ($\mu\text{g/g}$ dry wt) IN SURFICIAL SEDIMENTS AT PLATFORM 288-A

Trace Metal	Second Year	Third Year				Fourth Year Summer
		Summer	Fall	Winter	Spring	
BGOF Bottom Core Sediments Representative of Ambient ^a						
Ba	236	45	NS ^b	NS	NS	8
Cd ^c	NS	NS	NS	NS	NS	NS ^d
Co	2	1	NS	NS	1	ND ^d
Cr	NS	2	NS	NS	NS	NS
Cu ^c	NS	7	NS	1	NS	NS
Hg ^c	NS	0.04	NS	0.03	0.02	0.02
Mn	81	155	67	107	93	137
Ni	NS	NS	NS	NS	NS	NS
Pb	30	NS	NS	45	NS	43
Sr	61	298	NS	144	14	393
Zn	71	390	31	332	NS	522

STOCS Surficial Sediments Representative of Ambient ^e						
Ba	252	55	NS	NS	NS	17
Cd	NS	NS	NS	NS	NS	NS
Cr	2.2	3	NS	1	NS	1
Cu	4.1	9	2	3	1	NS
Mn	47	136	48	86	80	115
Ni	2	2	1	NS	NS	NS
Pb	32	NS	NS	46	NS	45
Zn	84	398	38	340	NS	530

a. BGOF Second Year (Anderson and Schwarzer, 1979). See text for explanation.

b. NS - not significant.

c. Many < values in concentration data from core samples and surficial sediment from second year.

d. ND - not determined.

e. STOCS 1975 Season II (Martin and Holmes, 1976). See text for explanation.

TABLE 6. 1979-1980 SEASONAL COMPARISON OF TRACE METAL CONCENTRATIONS ($\mu\text{g/g}$ dry wt) IN SUSPENDED PARTICULATE MATTER FROM MID-DEPTH AND BOTTOM SAMPLES TAKEN AT PLATFORM 296-B

Depth	Parameter	Ag	Ba	Cd	Cr	Cu	Hg	Fe	Mn	Pb	Sr	Zn
<u>CRUISE I - Summer 1979</u>												
Mid-depth	\bar{x}	28.2	103	<62.2	59	106	0.56	1625	510	134	691	666
	SD	81.3	79	--	67	143	0.04	2060	423	173	879	911
	CV%	288	76	--	113	134	6	127	83	129	127	137
	n = 13											
Bottom	\bar{x}	3.7	157	<62.2	76	96	1.25	1111	884	124	586	669
	SD	0.7	149	--	119	115	2.07	1171	1071	242	872	1414
	CV%	18	95	--	156	120	166	105	121	195	149	211
	n = 12											

<u>CRUISE II - Winter 1979</u>												
Mid-depth	\bar{x}	1.2	748	13.6	155	74	2.17	700	453	34	174	64
	SD	2.9	1069	16.7	255	60	1.20	519	576	--	144	44
	CV%	252	143	123	145	82	55	74	127	--	83	69
	n = 12											
Bottom	\bar{x}	0.3	393	7.4	126	126	1.00	2152	1380	43	199	150
	SD	0.3	390	8.6	264	164	0.68	1393	1524	24	204	298
	CV%	97	99	117	209	131	68	65	118	54	102	199
	n = 12											

This is probably a function of the dominant amount of clay in the SPM and the higher amount of organic material present (18).

SEAWATER AND PRODUCED BRINE

Like the SPM, seawater is an important transport medium of dissolved trace metals. Produced brine discharged into the marine environment can be a potential hazard to marine life if significant quantities of toxic metals are present (19).

Anderson and Schwarzer (9b) reported only Ba and Sr to be in sufficient concentration in produced brine to effect the marine environment. However, the analytical technique used did not allow an accurate determination of the transition metals present.

Results from the third and fourth years of the BGOF study indicate the produced brine discharge have concentrations of Ba, Cd, Cr, Fe, Hg, Mn, Sr, Tl and Zn significantly greater than the seawater to which it is discharged (10) (see Table 7). This could result in an increase of trace metals in the vicinity of the platforms. There are significant seasonal differences in certain metals concentrations in the produced brine discharge that may be the result of discharging from different wells or contamination from the discharge stand pipe. These seasonal differences are shown in Table 8.

Seawater trace metal concentrations from the area around platforms 288-A and 296-B were within the range of noncontaminated shelf waters (20). Concentrations of trace metals in seawater and produced brine samples are given in Table 7.

BIOFOULING

Barnacles and other marine organisms that attach themselves to the platform structures are a food source for "grazing" fish (16). Any accumulation of trace metals in the fouling organisms could be passed along to other animals higher in the food web. Also these fouling organism would have the most consistent exposure to trace metals from the platform structures.

No excessive accumulation of trace metal has occurred in the fouling organisms (9b,10). Also there is no evidence that fouling organisms close to the produced brine discharge have accumulated more trace metals than other fouling organisms (10).

DOMINANT FAUNA

Marine organisms that inhabit the waters near sources of trace metal pollution have been used as "pollution indicators" to quantify the type and extent of trace metal pollution (21). It is preferable to use sessile organisms even if they have to be transposed to the

TABLE 7. MEAN TRACE METAL CONCENTRATIONS ($\mu\text{g/L}$) SEAWATER (UNFILTERED) AND PRODUCED BRINE FROM PLATFORM 296-B DURING 1979-1980

Sample	Cruise		Ag	As	Ba	Be	Cd	Cr	Cu	Fe	Hg
Seawater	Summer 1979	\bar{x}	0.033	<0.037	0.121	<0.002	0.050	0.051	0.340	1.24	0.032
		Sd	0.028	-	0.068	-	0.049	0.029	0.174	0.33	0.004
		CV % n = 5	85	-	56	0	98	57	51	27	13
	Winter 1979	\bar{x}	0.006	0.076	0.259	0.038	0.037	0.106	1.10	5.14	0.094
		Sd	0.001	0.050	0.161	0.002	0.018	0.020	0.43	1.94	0.019
		CV % n = 4	17	66	62	6	50	19	40	38	21
Produced Brine	Summer 1979	\bar{x}	0.049	0.091	2.40	<0.002	2.06	0.879	1.83	2901	0.076
		Sd	0.018	0.041	1.62	-	1.92	0.761	1.76	772	0.020
		CV % n = 2	37	45	68	-	93	87	97	27	27
	Winter 1979	\bar{x}	0.007	0.551	10.4	0.025	0.160	0.970	1.41	2874	0.239
		Sd	0.002	0.058	0.6	0.005	0.004	0.392	0.72	461	0.160
		CV % n = 2	27	11	6	20	3	40	51	16	67

Sample	Cruise		Mn	Ni	Pb	Sb	Se	Sr	Tl	Zn
Seawater	Summer 1979	\bar{x}	0.064	0.148	0.225	0.111	<0.027	46.5	0.053	2.59
		Sd	0.045	0.080	0.140	0.019	-	5.3	0.027	1.27
		CV % n = 5	71	54	62	17	-	11	51	49
	Winter 1979	\bar{x}	0.073	0.648	0.728	0.051	0.057	53.7	<0.050	3.43
		Sd	0.032	0.192	0.239	0.035	0.044	4.6	-	1.11
		CV % n = 4	43	30	33	68	77	9	-	32
Produced Brine	Summer 1979	\bar{x}	2.69	0.354	0.610	0.087	<0.027	191	0.225	93.7
		Sd	0.48	0.165	0.459	0.001	-	151	0.088	102
		CV % n = 2	18	47	75	1.1	-	79	39	109
	Winter 1979	\bar{x}	5.90	1.10	0.959	0.034	<0.027	269	0.425	28.1
		Sd	1.49	0.11	0.210	0.001	-	3	0.047	23.8
		CV % n = 2	25	10	22	2	-	1	11	85

TABLE 8. MEAN TRACE METAL CONCENTRATION ($\mu\text{g/mL}$) IN PRODUCED BRINE SAMPLES

Year	Cruise	Ba	Fe	Sr
Second (1977-78)	Summer	3.5	10.0	33.5
	Summer	1548	340	58
Third (1978-79)	Fall	1542	203	64
	Winter	1029	380	67
	Spring	1056	118	94
Fourth (1979-80)	Summer	2	2901	191
	Winter	10	2874	269

study area. This is not always possible because of technical problems and cost considerations. Other free-moving organisms can be used as indicators of pollution if their life-cycle is limited to a restricted area. Gallaway et al. (16) have shown that spadefish (Chaetodipterus faber) are "habitat faithful" to a particular platform structure and, therefore, may be used as a pollution indicator.

Various marine biota have been collected and analyzed for trace metals over the four years of the BGOF study (9a,10). Perhaps the most important limiting factors in using these various species of biota as pollution indicators is their availability and their natural habitat range. In regards to availability, spadefish (Chaetodipterus faber), sheepshead (Archosargus probatocephalus), sugar shrimp (Trachypenaeus similis) and stone crabs (Menippe mercenaria) appear to be the better candidates. Each of those organisms have been collected at various times during the BGOF study.

Another limiting feature is how to determine bioaccumulation of trace metals in a free-living population of marine animals. Comparison to a similar population in a pristine area or to a population under controlled laboratory conditions are the only technique available. This immediately limits the available organisms to those with a sufficient data base in the literature.

Anderson and Schwarzer (9b) analyzed tissues from several different species of biota during the first and second years of the BGOF study. However, because of a lack of sensitivity for most metals and instrument problems, much of the muscle tissue (i.e., low concentrations) data is of limited value because of the large numbers of data points below the limit of detection.

Comparisons of the first year's trace metal concentrations of Cd, Cr, Cu, Mn, Pb and Zn in shrimp, fish muscle and fish livers with similar data from the STOCS (22) study was presented by Anderson and Schwarzer (9b). The average concentrations of Cd and Cr in shrimp were lower than the STOCS data; the average concentration of Pb and Zn were higher. The average concentrations of Cr, Cu, and Zn were higher in fish muscle tissue than the STOCS averages; Cd, Mn and Pb were lower than the STOCS data. Concentrations of Cd, Cr, Cu, Mn and Pb in fish liver tissues were higher than the average concentrations of the STOCS data; Zn concentrations were lower. No comparisons of the biota trace metal data from the second year were made.

Spadefish (C. faber), sheepshead (A. probatocephalus) and longspine porgy (S. caprinus) muscle tissues were analyzed during the third year. During the fourth year, spadefish (C. faber), sheepshead (A. probatocephalus) and stone crab (M. mercenaria) were analyzed. Also during the fourth year, three different tissues of spadefish (C. faber) and sheepshead (A. probatocephalus) were analyzed: gills, kidney, and muscle. Gonads were to be analyzed but the fish collected did not have sufficiently

developed gonads to sample. Diseased fish and healthy fish were also analyzed (fourth year) to determine if correlation of trace metal concentrations and occurrence of fin rot disease could be established.

Seasonal trace metal concentrations in spadefish (C. faber) muscle tissue from the third (1978-1979) and fourth (1979-1980) years are presented in Table 9. There are significant ($p=0.05$) seasonal differences in the trace metal concentrations of Fe and Pb. Comparison of the third year (1978-1979) summer data to the data from the Louisiana Platform Study indicates there are significantly ($p=0.05$) higher concentrations of Cd, Cr, and Cu from the latter study. Considering the other sampling periods, the differences are not significant ($p=0.05$). This suggests that to determine if bioaccumulation of trace metals has occurred in spadefish (C. faber), consideration of the seasonal variability and possibly the spatial variability will have to be made. Also, a larger sampling population will be needed.

Table 10 is a comparison of the trace metal concentrations in spadefish (C. faber) liver tissue from three years of the BGOF compared to red snapper (L. campechanus) liver data from the STOCS (22). There is significant ($p=0.05$) seasonal difference for Cu between the second year (1977-1978) and the summer season of the fourth year (1979-1980). There are no significant ($p=0.05$) differences between the BGOF data and the STOCS data.

Table 11 is a comparison of the seasonal variability (third year) of trace metals in muscle tissue of sheepshead (A. probatocephalus) with similar data from the Louisiana Platform Study (23). There are significant ($p=0.05$) differences between the summer Cr, Cu, Fe, and Ni concentrations and the Louisiana Platform concentrations. However, the concentrations of these metals from the other seasons are not significantly different than the Louisiana Platform Study concentrations. This suggests the same precautions given earlier about determining bioaccumulations in spadefish (C. faber) should also apply to sheepshead (A. probatocephalus) muscle tissue.

Comparison of diseased and healthy spadefish (C. faber) during the fourth year (1979-1980) indicated only Ba in gills tissue was significantly ($p=0.05$) higher when compared to healthy gills. This higher Ba concentration ($4.1 \mu\text{g/g}$) in the gills may be caused by fine grain sediments trapped in the gill tissue rather than bioaccumulation of Ba by the spadefish. The relationship of the higher Ba in the diseased gill tissues should be investigated further to determine if it is a causative factor of the disease or possibly a symptom of it.

During the summer (1978-1979) sampling, no macrocrustacean samples were available at the platform and longspine porgy (Stenotomus caprinus) was substituted. The results of the trace metal analysis of these fish are presented in Table 12. The concentrations of Cr, Fe, Ni, and Pb were significantly ($p=0.05$) higher than similar data on longspine

TABLE 9. COMPARISON OF SEASONAL VARIATIONS IN AVERAGE TRACE METAL CONCENTRATIONS ($\mu\text{g/g}$ dry wt) IN CHAETODIPTERUS FABER (SPADEFISH) MUSCLE TISSUE WITH OTHER GULF STUDIES

Year	Cruise	Parameter	Cd ^a	Cr ^a	Cu ^a	Fe ^a	Pb ^a
Buccaneer Oilfield	Summer n = 8	\bar{x}	0.032	0.223	0.53	8.8	0.13
		SD	0.022	0.061	0.08	3.3	0.04
		RSD%	69	27	15	38	31
	Fall n = 12	\bar{x}	0.158	0.966	1.72	10.8	0.30
		SD	0.067	0.533	0.62	6.8	0.13
		RSD%	42	55	36	63	44
	Winter n = 18	\bar{x}	0.132	0.764	3.25	13.3	0.53
		SD	0.048	0.825	4.87	5.5	0.38
		RSD%	36	108	150	42	72
	Spring n = 12	\bar{x}	0.186	1.17	1.02	22.0	0.25
		SD	0.232	1.15	0.20	10.6	0.22
		RSD%	125	98	20	48	90
	Summer n = 5	\bar{x}	0.082	0.236	0.65	8	0.32
		SD	0.062	0.007	0.15	3	0.27
		RSD%	76	3	23	36	84
Louisiana Platform Study ^b	1978	\bar{x}	0.019	0.201	3.14	13	0.25
		SD	0.017	0.004	0.25	3	0.11
		RSD%	93	2	8	21	43
	1978	Range	<0.011- 0.158	<0.20- 3.12	0.37- 1.83	8.6- 42.8	<0.11 0.37
		\bar{x}	0.068	0.71	1.14	18.2	0.23
		SD	0.070	0.91	0.34	8.3	0.31
		RSD%	102	127	30	45.4	133

a. Those samples at or below detection limit included as detection limit value.

b. Tillery, 1980.

TABLE 10. SEASONAL COMPARISON OF CHAETODIPTERUS FABER (SPADEFISH) LIVER TRACE METAL CONCENTRATIONS ($\mu\text{g/g}$ dry wt) WITH L. CAMPECHANUS LIVER TISSUE FROM STOCS

Year	Cruise	Para- meter	Ba	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sr	Z
First (1976- 77)	Summer	\bar{x}	NR ¹	6.4	6.6	72.8	NR	NR	4.8	NR	9.1	NR	86.8
Second (1977- 78)	Summer	\bar{x}	2.0	24.4	2.5	48.7	2198	0.2	8.7	1.9	4.9	1.8	131
		SD	1.04	19.4	4.2	43.9	829	0.12	2.4	2.98	3.5	0.8	22
		CV% n=12	52	79	167	90	38	60	28	155	71	45	17
Fourth (1979- 80)	Summer	\bar{x}	0.41	36.8	0.31	19.3	1055	0.151	8.54	1.48	0.64	3.55	177
		SD	0.14	33.6	0.17	4.2	455	0.075	2.44	1.49	0.53	1.15	163
		CV% n=5	35	92	56	22	43	50	29	101	83	32	92
	Winter	\bar{x}	0.37	1.42	0.19	40.0	1490	0.163	3.44	0.38	0.34	4.99	68
		SD	0.99	1.32	0.02	11.6	466	0.117	1.44	0.13	0.12	8.01	32
		CV% n=5	24	93	12	29	31	72	33	34	35	161	47
STOCS ³ (1976- 77)	Winter	\bar{x}	NR	3.70	2.20	14.7	NR	NR	3.40	NR	2.80	NR	146.4
	Spring												
	Summer	Range		0.7- 6.10	2.0- 2.2	9.0- 15.0			3.00- 4.70		1.0- 7.60		100- 268
		n=22											

1. NR = not determined.

2. Presley, B. J. and P. N. Booth, 1979, Vol. III, p. E-3.

TABLE 11. COMPARISON OF SEASONAL VARIATIONS IN AVERAGE TRACE METAL CONCENTRATIONS ($\mu\text{g/g}$ dry wt) IN ARCHOSARGUS PROBATOCEPHALUS (SHEEPSHEAD) MUSCLE TISSUE WITH OTHER GULF STUDIES

Cruise		Parameter	Cr	Cu	Fe	Ni
Buccaneer Oilfield (1978- 1979)	Summer	\bar{x}^a	0.245 ^b	0.59 ^b	8.5 ^b	0.561 ^b
		SD	0.055	0.17	2.8	0.257
		RSD%	22	29	33	46
		n=8				
	Fall	\bar{x}	0.890	1.51	9.6	0.625
		SD	0.566	0.62	6.4	0.193
		RSD%	64	41	67	31
		n=12				
	Winter	\bar{x}	0.606	1.40	12.5	0.978
		SD	0.483	0.68	3.8	0.529
		RSD%	80	49	30	54
		n=19				
	Spring	\bar{x}	2.65	0.99	27.3	0.532
		SD	2.92	0.19	16.1	0.242
		RSD%	110	19	59	45
		n=12				
<hr/>						
Louisiana Platform Study ^c		Range	<0.20- 2.03	0.57- 2.18	12.4- 35.7	<0.38- 2.33
		\bar{x}	1.04 ^b	1.13 ^b	20.6 ^b	1.17 ^b
		RSD%	70	46	43	54

- a. Those samples at or below detection limit included as detection limit value.
b. Significant ($p = 0.05$) difference.
c. Tillery, 1979.

TABLE 12. COMPARISON OF AVERAGE TRACE METAL CONCENTRATION IN STENOTOMUS CAPRINUS (LONGSPINE PORGY) MUSCLE TISSUE ($\mu\text{g/g}$ dry wt) WITH OTHER GULF OF MEXICO STUDIES

	Cruise	Parameter	Cr ^a	Fe ^a	Ni ^a	Pb ^a
Buccaneer ^b	Summer 1978	\bar{x}	0.58	22.3	1.63	0.14
		RSD%	110	27	37	36
		n=23				
<hr/>						
STOCS ^c	1977	\bar{x}	0.04	4.9	<0.07	<0.05
		RSD%	25	18	29	20
		n=11				
STOCS ^c	1976	\bar{x}	0.03	4.6	0.10	0.05
		RSD%	33	41	30	80
		n=9				

a. Significant ($p = 0.05$) difference.

b. Stenotomus caprinus substituted when no macrocrustacean samples were available.

c. Presley and Booth, 1979, Table 6.8, p. 6-42.

porgy from the STOCS study (22). However, longspine porgy was only sampled this one season and determination of long-term bioaccumulation of these metals is not possible on this limited data.

Sugar shrimp (I. similis) analyzed in the third year had higher Cd-tissue levels than a similar population from the MAFLA Rig Monitoring Study (2) and the SPR program (13). However, the variability in these Cd data from the BGOF make this high Cd data suspect. The high Cd variability comes from one or two pooled samples that have an unusually high Cd content.

Other investigations have identified higher concentrations of Ca in kidneys along with suppressed levels of Cu and Mg in gonads in Dover sole (Microstomus pacificus) with fin erosion disease (21). The lack of developed gonad tissues in our samples from the winter season prevented this observation from being made in the BGOF study.

CRUDE OIL

Trace metal content of crude oil produced in the BGOF was determined in the fourth year. Table 13 gives the results of this analysis. The only metal that may impact the marine environment in the event of a major oil spill would be Ni. From this data and the reported volume of oil lost to the marine environment in the BGOF (7), crude oil is an insignificant source of trace metals to the BGOF marine environment.

TABLE 13. TRACE METAL CONCENTRATIONS ($\mu\text{g/g}$) IN
BUCCANEER CRUDE OIL*

Metal	Concentration
Ag	<0.011
Al	<0.07
As	0.116
Ba	0.001
Be	<0.0001
Cd	<0.002
Cr	0.002
Cu	0.014
Fe	0.057
Hg	0.055
Mn	0.002
Ni	1.34
Pb	<0.02
Sb	0.012
Se	0.0001
Sr	0.02
Tl	0.0003
Zn	0.04

* Sample collected from on-shore facility by
Work Group 3.7 in Spring 1980.

SECTION 4

CONCLUSIONS

1. There are seasonal concentration gradients in surficial sediments of Ag, Ba, Be, Cd, Cr, Co, Cu, Mn, Pb, Sr, Hg and Zn within 180 meters of the platform structures.
2. Various normalizing and statistical techniques to eliminate the natural variability of trace metals in surficial sediments indicates an input of Ba, Cd, Cr, Co, Cu, Mn, Pb, Sr, Hg and Zn from the platform structures, activities on or about the structures or engine exhaust from pleasure/service boats.
3. A comparison with other sediments from the Gulf of Mexico shows there have been short-term accumulations of Ba, Co, Cr, Cu, and Pb in the BGOF sediments near the platforms, and more persistent accumulations of Hg, Mn, Sr and Zn have occurred.
4. Distribution of sediments with trace metal accumulations generally follow the seasonal current patterns near the platform structures.
5. Wave action, currents and turbulence around platform structures tend to disperse bottom sediment and prevents a long-term buildup of contaminated sediments at the platforms except those metals noted in 3.
6. Suspended particulate matter have higher trace metal concentrations than bottom sediments.
7. Variability in trace metal concentrations in suspended particulate matter are too great to identify any anthropogenic inputs related to the BGOF.
8. Trace metal concentrations in seawater are within the range reported for nonpolluted shelf waters (unfiltered).
9. There are seasonal variations in the trace metal concentrations in produced brine.
10. Produced brine discharges have concentrations of Ba, Cd, Cr, Fe, Hg, Mn, Sr, Tl and Zn that are significantly higher than the seawater they are discharged into.

11. Large volumes of produced brine could add a significant amount of trace metals to the marine environment but currents and wave action would tend to dilute and move them away from the platforms.
12. There has been no accumulation of trace metals in biofouling communities from the produced brine discharge.
13. Metal concentrations in fish tissues from the first and second years are much higher than those reported in the BLM-STOCS study and the third and fourth years. Lack of sensitivity and analytical problems in the first and second years limits the usefulness of this data.
14. Comparison of data from spadefish and sheepshead tissue (third and fourth years) with similar data from other areas of the Gulf indicate no bioaccumulation has occurred in these species.
15. Indications of bioaccumulation of Cd in longspine porgy tissue (third year) are questionable because of the high variability and will need further study.
16. Bioaccumulation of trace metals in sugar shrimp cannot be confirmed because seasonal variations are unknown.
17. Comparison of diseased and healthy spadefish trace metal burdens (fourth year) indicates Ba levels in gill tissue of diseased fish are higher. Relation of this finding to the disease state are unknown and will require further laboratory investigations.
18. Trace metal concentrations in spadefish and sheepshead muscle tissue (third year) correlate with the suspended particulate trace metal concentrations, i.e., higher in winter season.
19. Crude oil from the BGOF (fourth year) is low in trace metal content. Only Ni is above 1 ppm.

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APPENDIX A

ANALYTICAL METHODOLOGIES FOR THE FOURTH YEAR BGOF STUDY

1. Sediments - no change from third year.
2. SPM - no change from third year.
3. Seawater and Produced Brine - same extraction procedure used in third year was used for: Ag, As, Cd, Cr, Cu, Hg, Fe, Mn, Ni, Pb, Sb, Se, Tl and Zn.

The following elements were determined on the raw seawater and produced brine samples by injecting an aliquot into the graphite tube furnace: Al, Ba, Be and Sr.

4. Crude oil - A 78.6 gram (100 mL) sample was digested with H_2SO_4 then ashed in a muffle furnace at 350°C . The resulting ash was solubilized with HNO_3 (Suprapur) and quantitatively transferred to a 10-mL volumetric flask. Milli-Q water was used to make the sample to volume. The sample was then analyzed by AAS.
5. Biota - all tissue samples were prepared and analyzed by the low-temperature ashing (AAS) technique used for muscle tissue in the third year.

Stone crab (Menippe mercenaria) samples consisted only of the soft-tissue parts.