

NOAA Technical Memorandum NMFS-SEFC-31



NOAA/NMFS FINAL REPORT TO DOE

Biological/Chemical Survey of Texoma and Capline Sector Salt Dome Brine Disposal Sites Off Louisiana, 1978-1979

A report to the Department of Energy on work conducted under provisions of Interagency Agreement EL-78-I-O-7146 during 1978-1979.

Volume VII

TRACE METALS



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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-31

**Biological/Chemical Survey of Texoma and
Capline Sector Salt Dome Brine Disposal
Sites Off Louisiana, 1978-1979**

**VOL. VII - DETERMINE TRACE METAL COMPOSITION
AND CONCENTRATION IN MAJOR
COMPONENTS OF THE ECOSYSTEM**

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of Interagency Agreement EL-78-I-0-7146 during 1978-1979.**

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Volume VII - TRACE METALS

TABLE OF CONTENTS

	<u>Page</u>
I. Editors' Section	
Project Administration	vi
List of Volumes	viii
Introduction	x
Fig. 1. Regions of Study for Brine Disposal Assessment-DOE/NOAA Interagency Agreement .	xiii
Fig. 2. Proposed Texoma Brine Disposal Site	xiv
Fig. 3. Proposed Capline Brine Disposal Site	xv
Fig. 4. Sampling Scheme for Proposed Brine Disposal Sites	xvi
List of Reports and Publications	xvii
II. Principal Investigators' Section	
Work Unit 3.3 Determine Trace Metal Composition and Con- centration in Major Components of the Marine Ecosystem	xx

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LIST OF VOLUMES

This Final Report is printed in nine separate volumes:

Volume I - BENTHOS

Work Unit 2.1 Describe Living and Dead Benthic (Macro- and Meio-) Communities

Coastal Ecosystems Management, Inc.

R. H. Parker, Ph.D.

A. L. Crowe

L. S. Bohme

Volume II - ZOOPLANKTON

Work Unit 2.2 Determine Seasonal Abundance, Distribution and Community Composition of Zooplankton

LGL Ecological Research Associates, Inc.

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Volume III - BACTERIA

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Volume IV - DEMERSAL FISHES AND MACRO-CRUSTACEANS

Work Unit 2.4 Determine Seasonal Abundance, Distribution and Community Composition of Demersal Finfishes and Macro-crustaceans

Texas A & M University

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Volume V - SEDIMENTS

Work Unit 3.1 Describe Surficial Sediments and Suspended
Particulate Matter

Energy Resources Company, Inc.

K. A. Hausknecht

Volume VI - HYDROCARBONS

Work Unit 3.2 Determine Hydrocarbon Composition and
Concentration in Major Components of the
Marine Ecosystem

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Volume VII- TRACE METALS

Work Unit 3.3 Determine Trace Metal Composition and
Concentration in Major Components of the
Marine Ecosystem

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Volume VIII - INORGANIC NUTRIENTS

Work Unit 3.4 Determine Seasonal Variations in Inorganic
Nutrients Composition and Concentrations in
the Water Column

Texas A & M University

J. M. Brooks, Ph.D.

Volume IX - SHRIMP DATA ANALYSIS

Work Unit 5.1 Analysis of Variance of Gulf Coast Shrimp Data

LGL Ecological Research Associates, Inc.

F. J. Margraf, Ph.D.

INTRODUCTION

In compliance with the Energy Policy and Conservation Act of 1975, Title 1, Part B (Public Law 94-163), the Department of Energy (DOE) implemented the Strategic Petroleum Reserve (SPR). The SPR program was implemented in August of 1977 with the goal of storing a minimum of one billion barrels of crude oil by December 22, 1982. After evaluating several physical storage possibilities, DOE determined that storage in commercially developed salt dome cavities through solution-mining processes was the most economically and environmentally advantageous option.

Six areas along the northwestern Gulf of Mexico were to be investigated as potential storage cavern sites. These areas are shown in Figure 1. This project, "Biological/Chemical Survey of Texoma and Capline Sector Salt Dome Brine Disposal Sites Off Louisiana", deals with proposed disposal sites associated with two of the cavern sites, West Hackberry and Weeks Island. The Biological/ Chemical Survey was initiated in April 1978 and was completed in December 1979. Its major products are Final Reports available through the National Technical Information Service (NTIS), Springfield, Virginia; data files available through the Environmental Data and Information Service (EDIS), Washington, D.C., and any research papers that may be written by participating principal investigators and published in scientific or technical journals. Preliminary results were also made available through DOE/NOAA/NMFS project reviews and workshops attended by project participants and various governmental, private and public user groups.

The objectives of the Biological/Chemical Survey were: (1) to describe the biological, physical and chemical components of the marine ecosystem for each disposal site; and (2) to assess, by analysis of Gulf Coast shrimp data, the importance of the Louisiana shrimping grounds in the vicinity of the proposed salt dome brine disposal sites. These objectives were achieved using historical and new data to describe and quantify the biological, chemical, and physical characteristics and the temporal variations of these characteristics in the environments of each proposed disposal site.

The two proposed disposal sites have been extensively examined, using available meteorological, oceanographic, bathymetric and ecological data, in the following two reports:

Environmental Data Service, DOC/NOAA. 1977.

Analysis of Brine Disposal in the Gulf of Mexico, #2 West Hackberry. Report to Federal Energy Administration Strategic Petroleum Reserve Program Salt Dome Storage. Center for Experiment Design and Data Analysis, NOAA, EDS, Marine Assessment Division, Washington, D.C.

Environmental Data Service, DOC/NOAA. 1977.

Analysis of Brine Disposal in the Gulf of Mexico, #3 Capline Sector. Report to Federal Energy Administration Strategic Petroleum Reserve Program Salt Dome Storage. Center for Experiment Design and Data Analysis, NOAA, EDS, Marine Assessment Division, Washington, D.C.

The above reports and other pertinent documents are available from the Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia, 22151.

Proposed locations of the West Hackberry (Texoma Sector) and Weeks Island (Capline Sector) brine disposal sites are shown in Figures 2 and 3, respectively. These sites are subject to change within the same geographic area pending results of baseline surveys presently underway.

The proposed West Hackberry disposal site is located approximately 9.7 km (6 miles) south off the coast from Mud Lake at Latitude $29^{\circ}40' N$ and Longitude $93^{\circ}28' W$ at a bottom depth of about 9 m (30 feet). Operational requirements and engineering limitations of the proposed brine diffuser at this site are as follows: length - 933.3 m (3070 feet); orientation -normal to coast; number of ports - 52; length between ports - 18 m (59 feet); port diameter - 7.6 cm (3 inches); orientation of port riser - 90° to bottom; and port exit velocity - 7.6 m/sec (25 ft/sec).

The proposed Weeks Island (Capline Sector) disposal site is located approximately 41.8 km (26 miles) off Marsh Island at Latitude $29^{\circ}04' N$ and Longitude $91^{\circ}45' W$ at a bottom depth of about 9 m (30 feet). Operational requirements and engineering limitations of the proposed brine diffuser at this site are as follows: length - 608 m (2000 feet); orientation -normal to coast; number of ports - 34; orientation to port riser - 90° to bottom, and port exit velocity - 7.6 m/sec (25 ft/sec).

The Biological/Chemical Surveys in the proposed salt dome brine disposal sites described seasonal abundance, distribution and community

composition of major benthic, planktonic, bacterial and demersal finfish and macro-crustacean ecosystem components; the sediments; the hydrocarbons and trace metals composition and concentration in the marine ecosystem; and the seasonal variations in inorganic nutrients composition and concentration of the water column. The sampling scheme used for sample collections around the two sites is shown in Figure 4. A separate data analysis assessed the importance of shrimp grounds in the vicinity of the proposed brine disposal sites in terms of historical data on species composition, marketing size categories and location of commercial shrimp catches within statistical reporting zones off the Louisiana coast.

Information concerning data from this project is available through the Program Data Manager: Mr. Jack Foreman, Environmental Data and Information Service, Page Building No. 2, 3300 Whitehaven Street, N.W., Washington, D.C.

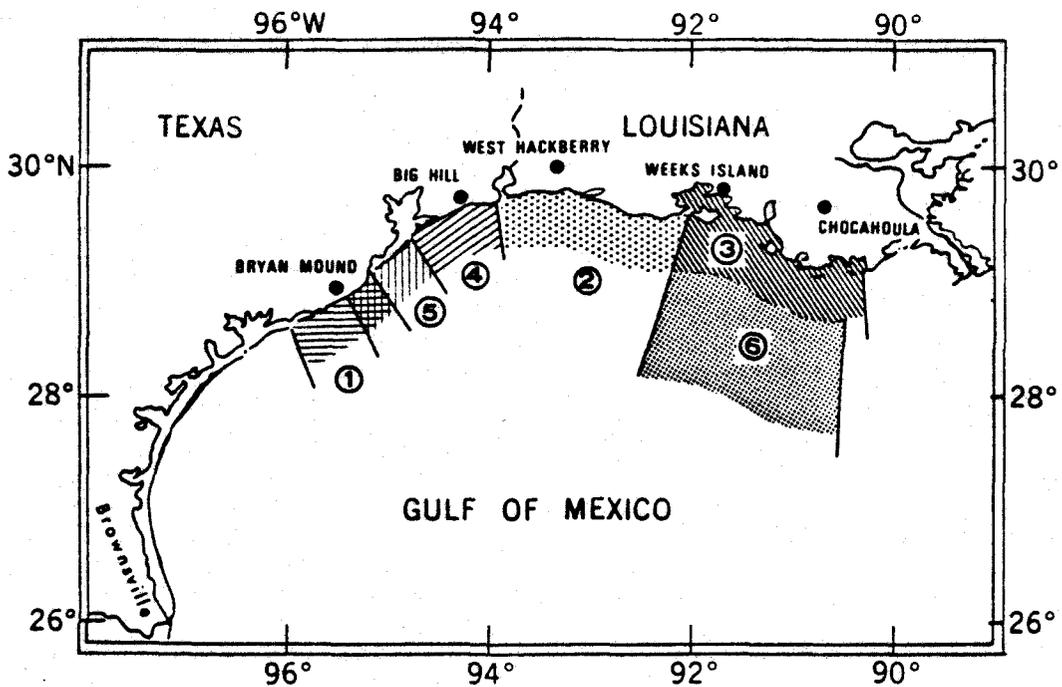


Figure 1. Regions of Study for Brine Disposal Assessment-DOE/NOAA Interagency Agreement (adapted from Environmental Data Service, DOC/NOAA. Analysis of Brine Disposal in the Gulf of Mexico, #2 West Hackberry. 1977.).

- 1 Texas Coastal Ocean, Colorado River to San Luis Pass (Bryan Mound)
- 2 Louisiana Coastal Ocean, Sabine Lake to S.W. Pass of Vermilion Bay (West Hackberry)
- 3 Louisiana Coastal Ocean, S.W. Pass, Vermilion Bay to Timbalier Island (Capline Sector)
- 4 Texas Coastal Ocean, Port Bolivar to Sabine Pass
- 5 Texas Coastal Ocean, Freeport Harbor to Galveston South Jetty
- 6 Louisiana Coastal Ocean, Offshore from Vermilion Bay to Terrebone Bay

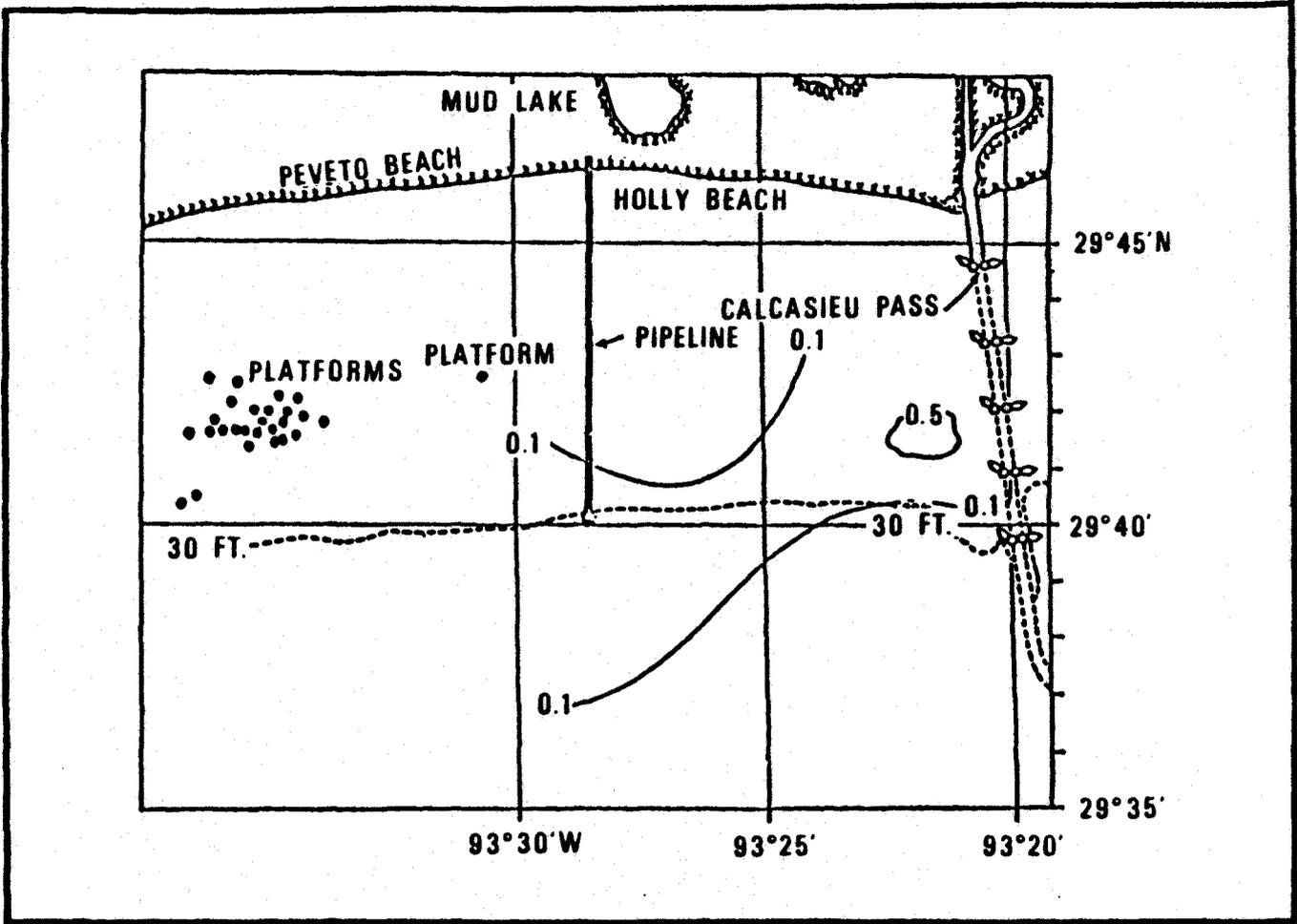


Figure 2. Proposed Texoma brine disposal site.

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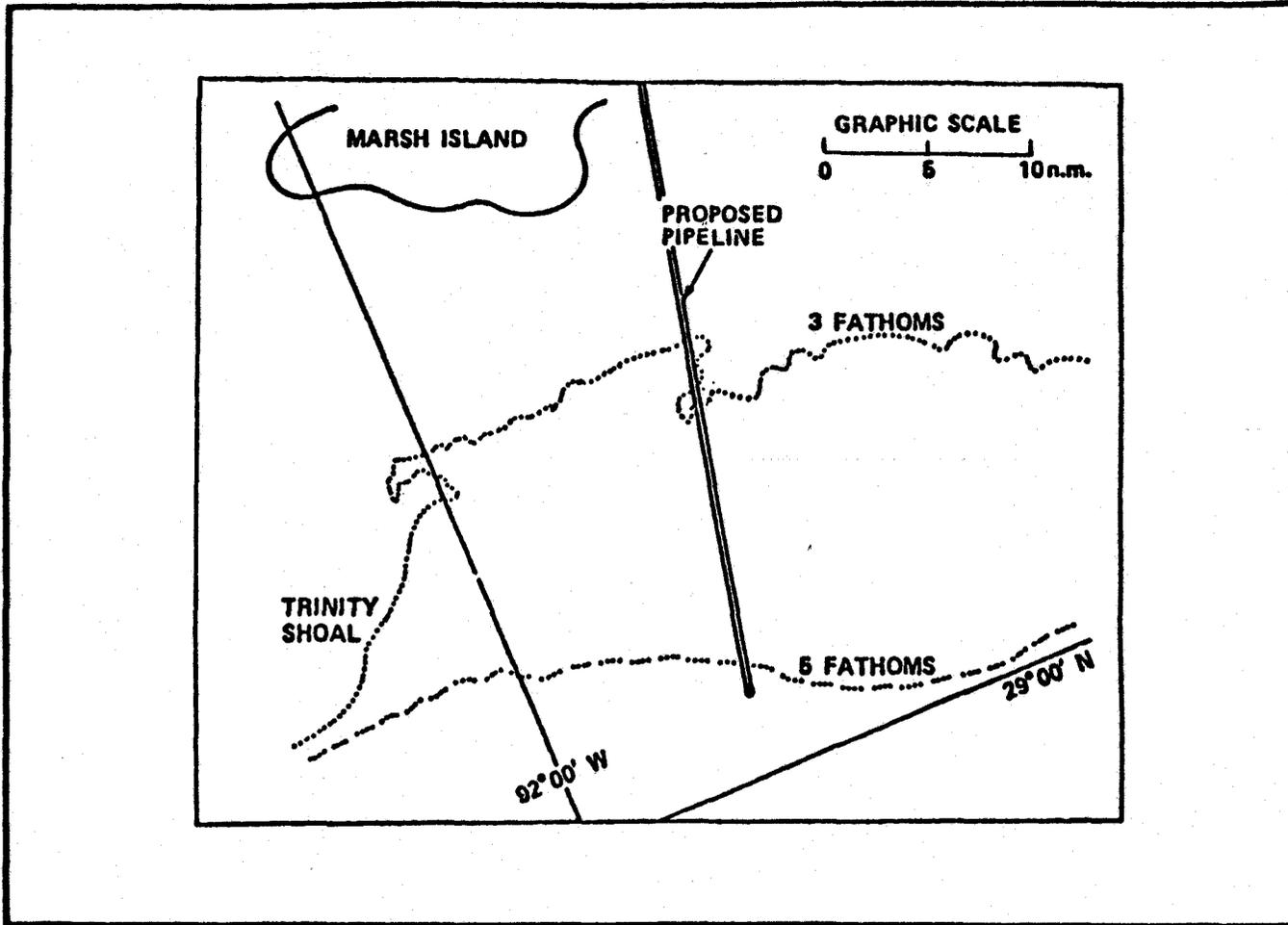


Figure 3. Proposed Capline brine disposal site.

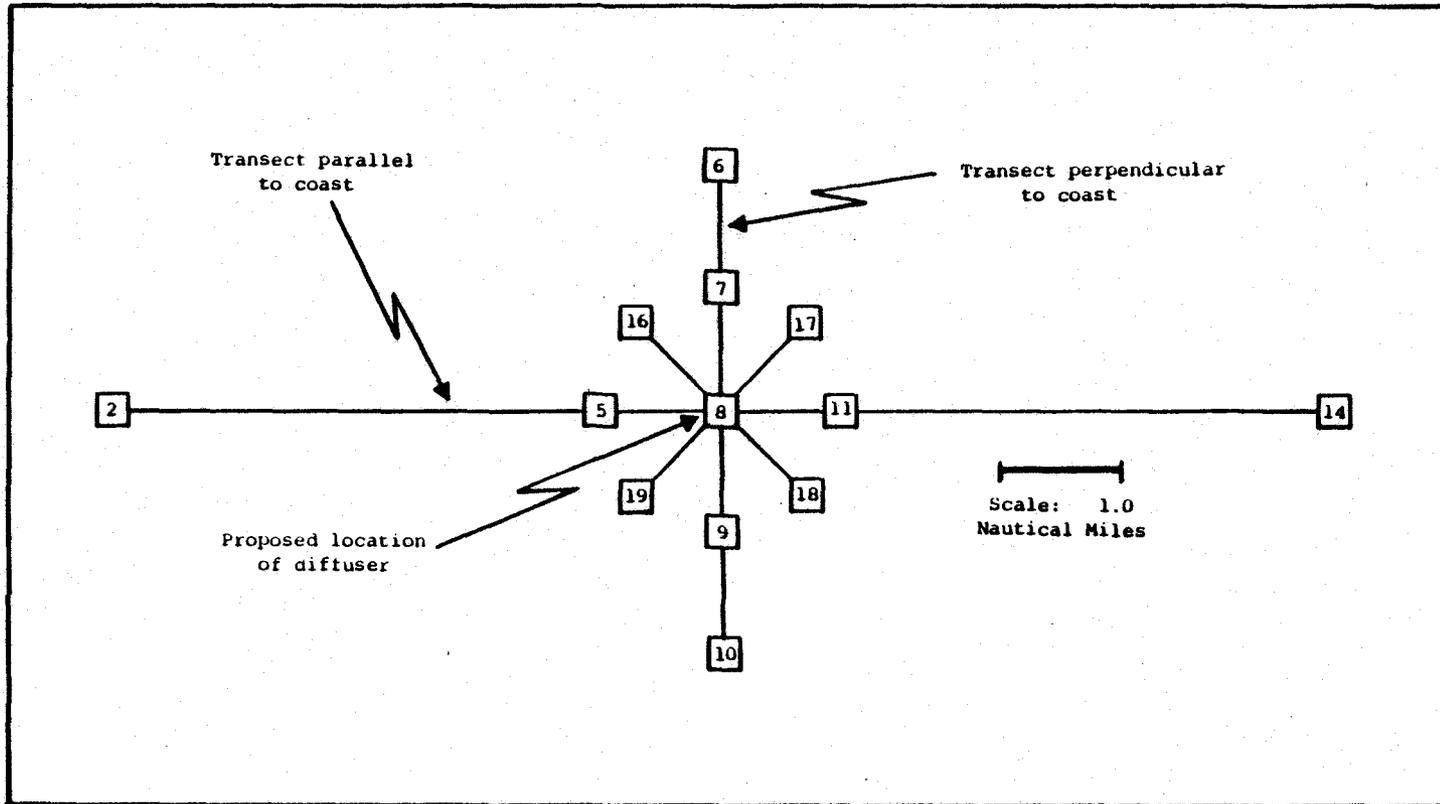


Figure 4. Sampling scheme for proposed salt dome brine disposal sites.

REPORTS AND PUBLICATIONS

- Boehm, P. D. and D. L. Fiest. 1980. Determine hydrocarbons composition and concentration in major components of the marine ecosystem. Vol. VI. In: Jackson, W. B. and G. M. Faw (eds.). Biological/chemical survey of Texoma and Capline sector salt dome brine disposal sites off Louisiana, 1978-1979. NOAA Technical Memorandum NMFS-SEFC-30, 136 p. Available from: NTIS, Springfield, Virginia.
- Brooks, J. M. 1980. Determine seasonal variations in inorganic nutrient composition and concentration of the water column. Vol. VIII. In: Jackson, W. B. and G. M. Faw (eds.). Biological/chemical survey of Texoma and Capline sector salt dome brine disposal sites off Louisiana, 1978-1979. NOAA Technical Memorandum NMFS-SEFC-32, 31 p. Available from: NTIS, Springfield, Virginia.
- Caillouet, C. W., F. J. Patella and W. B. Jackson. 1979. Relationship between marketing category (count) composition and ex-vessel value of reported annual catches of shrimp in the eastern Gulf of Mexico. *Marine Fisheries Review* 41(5-6):1-7.
- Caillouet, C. W., F. J. Patella and W. B. Jackson. 1980. Trends toward decreasing size of brown shrimp, Penaeus aztecus, and white shrimp, Penaeus setiferus, in reported annual catches from Texas and Louisiana. *NOAA/NMFS Fishery Bulletin* 77(4):985-989.
- Caillouet, C. W., D. B. Koi and W. B. Jackson. In press. Relationship between ex-vessel value and size composition of annual landings of shrimp from the Gulf and South Atlantic Coasts. *Marine Fisheries Review*.
- Caillouet, C. W. and D. B. Koi. In press. Trends in ex-vessel value and size composition of annual landings of brown, pink and white shrimp from the Gulf and South Atlantic coasts of the United States. *Marine Fisheries Review*.
- Hausknecht, K. A. 1980. Describe surficial sediments and suspended particulate matter. Vol. V. In: Jackson, W. B. and G. M. Faw (eds.). Biological/chemical survey of Texoma and Capline sector salt dome brine disposal sites off Louisiana, 1978-1979. NOAA Technical Memorandum NMFS-SEFC-29, 56 p. Available from: NTIS, Springfield, Virginia.

- Landry, A. M. and H. W. Armstrong. 1980. Determine seasonal abundance, distribution and community composition of demersal finfishes and macro-crustaceans. Vol. IV. In: Jackson, W. B. and G. M. Faw (eds.). Biological/chemical survey of Texoma and Capline sector salt dome brine disposal sites off Louisiana, 1978-1979. NOAA Technical Memorandum NMFS-SEFC-28, 180 p. Available from: NTIS, Springfield, Virginia.
- Margraf, F. J. 1980. -Analysis of Variance of Gulf Coast shrimp data. Vol. IX. In: Jackson, W. B. and G. M. Faw (eds.). Biological/chemical survey of Texoma and Capline sector salt dome brine disposal sites off Louisiana, 1978-1979. NOAA Technical Memorandum NMFS-SEFC-33, 293 p. Available from: NTIS, Springfield, Virginia.
- Parker, R. H. and A. L. Crowe. 1980. Describe living and dead benthic (macro- and meio-) communities. Vol. I. In: Jackson, W. B. and G. M. Faw (eds.). Biological/chemical survey of Texoma and Capline sector salt dome brine disposal sites off Louisiana, 1978-1979. NOAA Technical Memorandum NMFS-SEFC-25, 103 p. Available from: NTIS, Springfield, Virginia.
- Reitsema, L. A. 1980. Determine seasonal abundance, distribution and community composition of zooplankton. Vol. II. In: Jackson, W. B. and G. M. Faw (eds.). Biological/chemical survey of Texoma and Capline sector salt dome brine disposal sites off Louisiana, 1978-1979. NOAA Technical Memorandum NMFS-SEFC-26, 133 p. Available from: NTIS, Springfield, Virginia.
- Schwarz, J. R., S. K. Alexander, A. J. Schropp and V. L. Carpenter. 1980. Describe bacterial communities. Vol. III. In: Jackson, W. B. and G. M. Faw (eds.). Biological/chemical survey of Texoma and Capline sector salt dome brine disposal sites off Louisiana, 1978-1979. NOAA Technical Memorandum NMFS-SEFC-27, 48 p. Available from: NTIS, Springfield, Virginia.
- Tillery, J. B. 1980. Determine trace metal composition and concentration in major components of the marine ecosystem. Vol. VII. In: Jackson, W. B. and G. M. Faw (eds.). Biological/chemical survey of Texoma and Capline sector salt dome brine disposal sites off Louisiana, 1978-1979. NOAA Technical Memorandum NMFS-SEFC-31, 72 p. Available from: NTIS, Springfield, Virginia.

II. PRINCIPAL INVESTIGATORS' SECTION

WORK UNIT 3.2 - DETERMINE TRACE METAL COMPOSITION AND
CONCENTRATION IN MAJOR COMPONENTS OF THE
MARINE ECOSYSTEM

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ABSTRACT

This report is the result of the trace (or heavy) metal investigations at the West Hackberry (Texoma) and Weeks Island (Capline) proposed brine diffuser sites during four consecutive seasons (1978-79). Samples of suspended particulate matter, epibenthic organisms and macrocrustaceans were collected during all four seasons. Surficial sediments were collected during two seasons (summer and winter). The spacial and temporal distributions of 13 trace metals (Al, Ba, Cd, Cr, Cu, Co, Fe, Hg, Mn, Ni, Pb, Sr, and Zn) were determined in each sample matrix.

Higher metal concentrations in sediments from the West Hackberry site are in agreement with the higher amounts of silt, clay and organic carbon reported in these sediments. Lower metal concentrations in Weeks Island sediments are due to the higher amounts of silty sand and low organic carbon content.

There are seasonal variations in sediment Ba, Cd and Hg concentrations at the West Hackberry site. However, Ba, Sr and Cd concentrations in the summer (West Hackberry) did not correlate with other geochemical parameters and are suspected of coming from terrigenous sources and offshore oilfields. Sediment concentrations of Ni and Zn from the Weeks Island site did not correlate with other geochemical parameters (e.g., hydrous Fe fraction, % CaCO₃) and are thought to originate from the offshore oilfield to the southeast.

Seasonal concentrations of trace metals in suspended particulate matter were similar for both West Hackberry and Weeks Island. Concentrations of Al and Fe were high in the winter (season of highest loading) which suggest a significant amount of resuspension of bottom sediments.

The lack of adequate quantities of a single species of epibenthic organism through all seasons limited the use of these animals

as trace metal pollution indicators. Only Portunus gibbesii were available in sufficient numbers to determine seasonal and intraspecies variations. No seasonal variations were observed, but the intraspecies variation of Al, Cu, Fe, Hg, Mn, Sr, and Zn concentrations were high.

There are indications of seasonal variations of Ba, Cd and Hg in Penaeus setiferus (white shrimp) muscle tissues. No significant site differences in metal concentrations were observed in P. setiferus. Comparison of Trachypenaeus constrictus and Trachypenaeus similis trace metal burdens with other Gulf of Mexico studies indicates our concentrations of Cd, Pb and Sr are higher.

TABLE OF CONTENTS

	<u>Page</u>
Abstract	ii
List of Tables	vi
List of Figures	vii
I. INTRODUCTION	1
II. METHOD AND MATERIALS	6
A. Instrumentation	6
B. Sample Collection	6
C. Methodologies	6
1. Surficial Sediments	6
a. Partial Digestion	6
b. Total Digestion	7
2. Suspended Particulate Matter	8
a. Leach Procedure for Adsorbed Elements	8
b. Rigorous Digestion for Total Metals	9
3. Epibenthic	10
a. Microdigestion	10
b. Macrodigestion	11
c. Mercury in Epibenthic Tissue	12
4. Macrocrustacea	13
D. Analytical Parameters and Quality Assurance	13
1. Sediments	13
2. Suspended Particulate Matter (SPM)	13
3. Biota	14
III. RESULTS AND DISCUSSION	17
A. Surficial Sediments	17
B. Suspended Particulate Matter (SPM)	23
C. Biota	23
1. Macrocrustaceans	23
2. Epibenthic	30

	<u>Page</u>
IV. CONCLUSIONS	36
A. West Hackberry Disposal Site	36
B. Weeks Island Disposal Site	37
References	40
Appendix A - Figures	42
Appendix B - Sample and Data Inventories	71

LIST OF TABLES

<u>Number</u>		<u>Page</u>
1.	Trace Metal Concentrations and Percent Recovery in NBS SRM 1645 River Sediment	14
2.	Trace Metal Concentrations and Percent Recovery in NBS SRM 1577 Bovine Liver	16
3.	Seasonal Comparison of Average Trace Metal Concentrations in Surficial Sediments from West Hackberry (A) and Weeks Island (B) Disposal Sites	18
4.	Mean Trace Metal Concentrations ($\mu\text{g/L}$) and Mean Particulate (mg/L HOH) by Site in Suspended Particulate Matter	24
5.	Seasonal Trace Metal Concentrations ($\mu\text{g/g}$ dry weight) in Macrocrustacean from West Hackberry (A) Proposed Disposal Sites	25
6.	Seasonal Trace Metal concentrations ($\mu\text{g/g}$ dry weight) in Macrocrustacean from Weeks Island (B) Proposed Disposal Sites	26
7.	Comparison of Seasonal Variations in Average Trace Metal Concentrations in <i>Trachypenaeus similis</i> (Sugar Shrimp) and <i>T. constrictus</i> (Broken Neck Shrimp) Muscle Tissues ($\mu\text{g/g}$ dry weight) with Other Gulf Studies	29
8.	Species of Epibenthic Organisms Collected by Season at West Hackberry and Weeks Island Proposed Disposal Sites	31
9.	Trace Metal Concentrations ($\mu\text{g/g}$ wet weight) in Epibenthic Organisms by Season at the West Hackberry Proposed Disposal Site	32
10.	Trace Metal Concentrations ($\mu\text{g/g}$ wet weight) in Epibenthic Organisms by Season at Weeks Island Proposed Disposal Site	34

LIST OF FIGURES

<u>Number</u>	<u>Page</u>
1. Proposed Disposal Site at West Hackberry	43
2. Proposed Disposal Site at Weeks Island	44
3. Sampling Grid Used at West Hackberry and Weeks Island Proposed Disposal Sites	45
4. Al versus Fe in Surficial Sediments from West Hackberry; Summer (I) and Winter (III) Cruises	46
5. Ba versus Fe in Surficial Sediments from West Hackberry; Summer (I) and Winter (III) Cruises	47
6. Cd versus Fe in Surficial Sediments from West Hackberry; Summer (I) and Winter (III) Cruises	48
7. Co versus Fe in Surficial Sediments from West Hackberry; Summer (I) and Winter (III) Cruises	49
8. Cr versus Fe in Surficial Sediments from West Hackberry; Summer (I) and Winter (III) Cruises	50
9. Cu versus Fe in Surficial Sediments from West Hackberry; Summer (I) and Winter (III) Cruises	51
10. Hg versus Fe in Surficial Sediments from West Hackberry; Summer (I) and Winter (III) Cruises	52
11. Mn versus Fe in Surficial Sediments from West Hackberry; Summer (I) and Winter (III) Cruises	53
12. Ni versus Fe in Surficial Sediments from West Hackberry; Summer (I) and Winter (III) Cruises	54
13. Pb versus Fe in Surficial Sediments from West Hackberry; Summer (I) and Winter (III) Cruises	55
14. Sr versus Fe in Surficial Sediments from West Hackberry; Summer (I) and Winter (III) Cruises	56
15. Zn versus Fe in Surficial Sediments from West Hackberry; Summer (I) and Winter (III) Cruises	57
16. Al versus Fe in Surficial Sediments from Weeks Island; Summer (I) and Winter (III) Cruises	58

<u>Number</u>		<u>Page</u>
17.	Ba versus Fe in Surficial Sediments from Weeks Island; Summer (I) and Winter (III) Cruises	59
18.	Cd versus Fe in Surficial Sediments from Weeks Island; Summer (I) and Winter (III) Cruises	60
19.	Co versus Fe in Surficial Sediments from Weeks Island; Summer (I) and Winter (III) Cruises	61
20.	Cr versus Fe in Surficial Sediments from Weeks Island; Summer (I) and Winter (III) Cruises	62
21.	Cu versus Fe in Surficial Sediments from Weeks Island; Summer (I) and Winter (III) Cruises	63
22.	Hg versus Fe in Surficial Sediments from Weeks Island; Summer (I) and Winter (III) Cruises	64
23.	Mn versus Fe in Surficial Sediments from Weeks Island; Summer (I) and Winter (III) Cruises	65
24.	Ni versus Fe in Surficial Sediments from Weeks Island; Summer (I) and Winter (III) Cruises	66
25.	Pb versus Fe in Surficial Sediments from Weeks Island; Summer (I) and Winter (III) Cruises	67
26.	Sr versus Fe in Surficial Sediments from Weeks Island; Summer (I) and Winter (III) Cruises	68
27.	Zn versus Fe in Surficial Sediments from Weeks Island; Summer (I) and Winter (III) Cruises	69
28.	Fe versus % Clay in Surficial Sediments from West Hackberry (A) and Weeks Island (B) Sites for Summer (I) Cruise	70

I. INTRODUCTION

The Energy Policy and Conservation Act of 1975, Title I, Part B (P.L. 94-163) mandated the Department of Energy (DOE) to establish a Strategic Petroleum Reserve (SPR). In response to this mandate the DOE embarked upon a program to develop several natural salt dome formations along the Texas-Louisiana coast into underground storage cavities.

It was determined that existing salt dome cavities would not have sufficient volume to meet the goals of the SPR program and virgin salt domes would have to be leached to form new storage cavities. The estimated total volume of saturated brine solution (1.4-billion barrels per site) that will result from this program cannot be handled by current disposal methods (deep well injections and chemical feedstocks) (Bender 1978). The alternative is disposal offshore in the Gulf of Mexico. This requires a consideration of the effect this saturated brine solution will have on the marine environment and ecosystems at the disposal (diffuser) sites.

In the last decade, a number of multidisciplinary marine environmental studies have been conducted on the Outer Continental Shelf (OCS) of the Gulf of Mexico. Many of the larger studies have been sponsored by federal and state agencies, while a significant number of smaller studies have been conducted by universities, nonprofit organizations, and other research groups.

One objective of these studies has been to develop a better understanding of the trace metal chemistry involved in the marine environment and to delineate the natural fluxes and mechanisms that exist. This understanding is becoming more imperative as man's activities encroach further upon our coastal regions and OCS areas.

Information developed from these programs can be used to better understand the heavy metal data from the SPR program by providing a frame of reference from which evaluations and comparisons can be made.

Two of the larger studies were the environmental baseline studies on the Mississippi, Alabama and Florida (MAFLA) Outer Continental Shelf (Dames and Moore 1979) and the South Texas Outer Continental Shelf (STOCS) (Presley and Boothe 1979; Berryhill et al. 1979). These studies provided trace metal data on geochemical, water column, and biota samples from areas of the OCS not significantly impacted by man's activities (i.e., pollution). The objectives of the trace metal investigations were to delineate the ambient trace metal burdens and explain their seasonal and spacial variations and distributions in a selected population of marine samples.

This information would allow a background (baseline) from which future comparisons could be made if extensive utilization and development occurs in these areas. This information is also useful as a benchmark to which other trace metal environmental studies may be compared.

Perhaps the most significant study related to our investigation would be the earlier baseline survey at the West Hackberry proposed diffuser site (Shokes 1978). In the Shokes' study, samples for trace metal analyses were collected in the fall 1977 and the winter 1978. These included surficial sediments, selected macrobiota, suspended particulates, interstitial water, and filtered sea water. These samples were analyzed for ten trace metals (Fe, Al, Cu, Cr, Pb, Mn, Ni, Zn, Cd, Hg).

The objective of Shokes' (1978) survey was to describe the spacial and temporal variations of the ten trace metals in each sample type. The intraspecies variation in the biota samples

were also determined to allow estimations of sampling populations necessary to observe a percent change for a particular metal in a given species.

The trace metal burdens in the surficial sediments were strongly correlated with the sediment mineralogy and texture which were controlled by two factors: (1) current flows and storm fronts that dominated this relatively shallow offshore area and (2) the terrigenous inputs from the Calcasieu Pass (Shokes 1978).

Concentrations of Fe and Mn in Penaeus setiferus appeared to have a seasonal variation (Shokes 1978). Other metal concentrations in P. setiferus were similar to values obtained in other studies. Data from Shokes' study will be used later in this report.

A recently completed study which could impact the SPR program is the Bureau of Land Management's (BLM) fate and effects study of petroleum production platforms off the Louisiana coast (Tillery,¹ in preparation). Although the study area is to the southeast of the Weeks Island proposed diffuser site, there are longshore currents near the Louisiana-Texas coast that transport sediments and suspended particulate matter from this area into both the Weeks Island and West Hackberry sites.

Tillery's study (in preparation) has found sediment concentration gradients of Ba, Cd, Cu, Cr, Pb, Ni and Zn from the areas of several petroleum production platform structures that are not correlated to any geochemical parameters. These metals are suspected of being contaminants from the platform structures or petroleum production activities (past or present). The number of trace metals in surficial sediments that could be associated with platform structures increased with distance from the Mississippi River. This suggests that the sediment load of trace metals from the Mississippi River "masks" the effect of the platform structures. No evidence of bioaccumulation of trace metals in a number of different epibenthic, macrocrustacean, demersal and pelagic fish could be detected.

The findings from this BLM study (Tillery,¹ in preparation) appear to be supportive of three other studies conducted in the Gulf of Mexico. From 1972 to 1974 an Offshore Ecological Investigation (OEI) was conducted in Timbalier Bay, Louisiana, and the immediate offshore waters (Williams and Jones 1974; Montalvo and Brady 1974). These investigators concluded that Timbalier Bay sediments were contaminated with Ba from drilling fluids (barite) used in drilling operations, and there were higher concentrations of Hg, Pb, Cd, Zn and As in Timbalier Bay waters than in offshore waters. Also, the offshore water concentrations of Zn, Cd and Pb decreased with distance from production platform structures.

The second study is a four-year environmental evaluation of the Buccaneer gas/oilfield located 32 miles south of Galveston, Texas. Two active petroleum production platforms have been the center of this study. Results from the second year, 1977-1978, (Anderson and Schwarzer 1979) and the third year, 1978-1979, (Tillery,² 1980) indicate that sediment concentrations of Ba, Cd, Cr, Cu, Mn, Pb, Sr and Zn decrease with distance from the platforms and are not correlated to other geochemical parameters. It is believed these trace metals are coming from the platform structure, produced brine discharges, previous drilling operations, and boating activities around the platform structures.

The third study, which was a part of the MAFLA investigations mentioned earlier, is the Rig Monitoring Study (White, Turgon and Blizzard 1977) which examined an offshore drilling site prior to, during, and after drilling operations. Sediments and biota were analyzed for Cd, Cr, Cu, Fe, Pb, Ni and V. Bottom sediments showed an increase in Ba concentrations both "during" and "after" drilling operations. There were also increases in Fe concentration in epifauna but this could not be connected to the drilling activities. Storm passage, which increased the amount of resuspended sediments, may have been a causative factor.

Figure 1 shows the location of the West Hackberry disposal site. It is located approximately six miles off the coast from Mud Lake at 29°40'N and 93°28'W with a bottom depth of approximately 30 feet. This site is identified as site "A."

Figure 2 shows the location of the Weeks Island disposal site. It is approximately 26 miles from the south point off the coast of Marsh Island and is located at 29°04'N and 91°45'W with a depth of 30 feet. This site is identified as site "B."

Figure 3 illustrates the sampling grid used at both sites. Station 8 is located over the center of the proposed diffuser.

The purpose of this project is to conduct an environmental assessment of the West Hackberry and Weeks Island disposal sites. The objectives of the trace metal investigations are to characterize surficial sediments, suspended particulate matter, selected epibenthic organisms and macrocrustaceans, collected from the vicinity of the diffuser sites, for 13 trace (or heavy) metals (Al, Ba, Cd, Co, Cu, Cr, Fe, Hg, Mn, Ni, Pb, Sr, Zn) over four consecutive seasons.

These data, along with other trace metal data on these sites, will provide the ambient or "baseline" concentrations, seasonal variability, and intraspecies variability to which future monitoring efforts can be compared. This will provide information on the amount and affect of trace metal pollution added to the marine ecosystems at the brine diffusers once they become operational.

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 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 with an Instrumentation Laboratory IL-455 Graphite Furnace.
- * a Perkin-Elmer Model 306 with a HGA-2000 Graphite Furnace.

B. Sample Collection

All samples were collected using noncontaminating techniques and materials. Samples were placed in pre-acid washed polyethylene containers and frozen immediately after collection. Samples remained frozen until ready for analyses at the on-shore laboratory.

C. Methodologies

1. Surficial Sediments

The "partial" digestion was done on all sediment samples. On 25 percent 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 sediments before 60-80 grams of the wet sediment was weighed into a tared polyethylene beaker. 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 mL of 5N HNO₃ 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 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 analyzed for all metals (except Hg) using flame or flameless 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 screen (ATM Corporation, Milwaukee, Wisconsin) 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 on a clean bench and 15 mL of concentrated HNO₃ was added. The beaker was then returned to the hot plate and heated

(90-100°C) for 45 minutes. 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 Hg) were determined by flame or flameless AAS. Mercury (Hg) was not determined on this total digestate.

2. Suspended Particulate Matter

a. Leach Procedure for Adsorbed Elements

The Nucleopore filters (0.4 μm , 47 mm polycarbonate membranes) were stored in a desiccator for at least 24 hours to maintain a constant weight, and 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 on a clean bench using Teflon-coated forceps and loaded into the filter holder. The loaded filter holder was then sealed in a polyethylene bag for shipment to the collection site.

Upon arrival at the laboratory, each used Nucleopore filter was removed from its filter holder on a clean bench using Teflon-coated forceps. The filter was placed in a desiccator (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.

On 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 through the Nucleopore filter and collected in the Teflon beaker. The Erlenmeyer flask was rinsed three times with distilled water and poured through 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, 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 μ 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 analyses. A 1-mL aliquot of sample was removed for mercury determination.

b. Rigorous Digestion for Total Metals

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 μ 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 on a clean bench and 250 μ 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 on the clean bench, and 50 μL 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 make it to 10 mL.

The concentrations of analyte metals in this digestate were determined by flame or flameless AAS. Hg was not to be determined on this aliquot.

3. Epibenthic

a. Microdigestion

Due to the varied number and small quantity of some species collected, a microdigestion procedure using $\text{HNO}_3/\text{H}_2\text{O}_2$ was developed.

One gram (when available) of the wet tissue was weighed into a specially designed digestion tube (28-mm x 135-mm glass tube with a 24/40 ground glass joint). On a clean bench, three mL of Suprapur HNO_3 and one mL of H_2O_2 (30 percent) was slowly added to the digestion tube to prevent foaming. The tube was loosely sealed with a small polyethylene beaker to allow for escaping gases. The tube was placed in a water bath (95°C) and digested for six hours. Care was taken not to allow samples to evaporate to dryness by adding distilled water or HNO_3 as needed. The digestion tube was removed from the water bath and allowed to cool. The digestate was filtered into a 10-mL volumetric flask using a prerinsed (1 percent HNO_3) glass fiber filter (Reeve Angel). The digestion tube was rinsed twice with distilled water and rinses added to the 10-mL volumetric

flask. The flask was brought to the mark using distilled water. 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.

b. Macrodigestion

When a greater number of the same epibenthic species was collected, a multiash-digestion procedure was followed. Experience indicated that this procedure provided the optimum conditions for recovering both volatile (Cd, Pb, Zn) and nonvolatile (Fe, Cr, Ni, Ba, Cu) elements from biological tissues. The low temperature asher completely destroyed the sample matrix at temperatures (<150°C) compatible with retention of the volatile elements. Digestion of the ash in a closed Teflon bomb ensured the complete solubilization of the more refractory elements while retaining the more volatile.

Approximately 10 to 20 grams of the thawed epibenthic sample was weighed into a tared freeze-drying flask. The sample was freeze-dried and reweighed to determine the weight loss.

The sample was then placed into a homogenizing flask and homogenized using a Virtis "45" Homogenizer (The Virtis Company, Inc., Gardiner, New York) to ensure complete mixing of the sample. Approximately 0.5 grams of the finely ground sample was weighed into a tared Pyrex ashing boat. The boat was placed into the low temperature asher (LTA-505, LFE Corp., Waltham, Massachusetts) and ashed for 16 hours at 500 watts of forward power using an oxygen plasma. The ashing boats were removed from the asher and 1 mL of 70 percent Suprapur HNO₃ was added to solubilize the ash and retain it in the ashing boat during transfer to a clean bench. After allowing the ash to dissolve, it was quantitatively transferred to a Teflon bomb

using distilled water. After adding three additional milliliters of Suprapur HNO_3 to the Teflon bomb, it was sealed and placed in a steam bath at 90-100°C for two hours. Once the sample had been completely solubilized, the Teflon bomb was removed to a clean bench and the contents quantitatively rinsed into a 15-mL polyethylene centrifuge tube using two or three rinsings (both cap and cylinder) of distilled water. To remove suspended silica material that would seriously affect the atomic absorption analysis (flame or flameless), the sample was centrifuged at 2500 to 3000 RPM for 10 minutes. The supernatant was decanted into a 25-mL polyethylene volumetric flask without the precipitate. Then the precipitate was rinsed with 2 mL of distilled water and centrifuged again. The rinse was added to the volumetric flask and made up to volume with distilled water. This solution was used for all metal analyses except Hg.

c. Mercury in Epibenthic Tissue

A one-gram aliquot (when available) of the wet tissue sample was accurately weighed into a reaction vessel. Five mL of $\text{HClO}_4:\text{HNO}_3$ (5:1) and one mL of KMnO_4 (5 percent solution) were added to the vessel. The vessel was sealed, shaken for a few minutes, and placed in a water bath at 75°C overnight. After removing samples from the water bath, the samples are allowed to cool to room temperature. Next, 5 mL of Hg-free deionized water was added to the reaction vessel followed by one mL of 50 percent hydroxylamine hydrochloride. The sample was shaken, 5 percent stannous chloride was added, and the reaction vessel was 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 occurs relative to the concentration of Hg present. Hg was quantitated by the method of additions using spiked samples of the material being analyzed.

4. Macrocrustacea

Before dissecting, the shrimp and crab samples were weighed and measured. Only muscle tissue was used for the shrimp and crab samples. The tissue was removed with Teflon-coated 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 freeze-dried 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 epibenthic analyses (macrodigestion).

Hg was determined on a separate tissue aliquot by the cold vapor AAS method used for epibenthic samples.

The remaining metals were determined by flame or flameless AAS.

D. Analytical Parameters and Quality Assurance

1. Sediments

A standard reference material was prepared by the 5N HNO₃ "partial" digestion procedure and analyzed for the 13 analyte metals; National Bureau of Standards, Standard Reference Material 1645, River Sediment, was prepared and analyzed for the 13 metals even though Al, Ba, and Sr concentrations 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 homogeneous sediment sample that was prepared and routinely analyzed with the sediment samples as a quality control.

2. Suspended Particulate Matter (SPM)

Standard reference samples are not available for these sample matrices. Spiked membrane filters processed by the procedure

TABLE 1

TRACE METAL CONCENTRATIONS AND PERCENT RECOVERY IN NBS
SRM 1645 RIVER SEDIMENT* ($\mu\text{g/g}$ dry wt.)

		<u>Al</u>	<u>Ba</u>	<u>Cd</u>	<u>Cr**</u>	<u>Co</u>	<u>Cu</u>	<u>Fe**</u>	<u>Pb</u>	<u>Mn</u>	<u>Hg</u>	<u>Ni</u>	<u>Sr</u>	<u>Zn</u>
Reported Concentration	\bar{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 -	1720 169
Determined Concentration n = 7	\bar{x} sd	2624 45	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	23.7 1.0	586 31	1519 24
% Recovery		-	-	71	76	138	78	35	99	51	63	52	-	88

3.3-14

* by partial digestion procedure

** weight percent

***value not certified

NR = not reported

described for SPM were used to evaluate the procedure for SPM and as quality control samples.

3. Biota

National Bureau of Standards, Standard Research Material 1577, Bovine Liver, was prepared and analyzed using the methodologies described for macrocrustacean and epibenthic analyses to evaluate these procedures. A large homogeneous sample of shrimp tissue was prepared and periodically analyzed (spiked and unspiked) as a means to quantitate the macrocrustacean 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.

TABLE 2

TRACE METAL CONCENTRATIONS AND PERCENT RECOVERY IN NBS SRM 1577
BOVINE LIVER ($\mu\text{g/g}$ Dry wt.)

		<u>Al</u>	<u>Ba</u>	<u>Cd</u>	<u>Cr</u>	<u>Co</u>	<u>Cu</u>	<u>Fe</u>	<u>Pb</u>	<u>Mn</u>	<u>Hg</u>	<u>Ni</u>	<u>Sr</u>	<u>Zn</u>
Reported Concentration	\bar{x}	NR	NR	0.27	NR	(0.18)*	193	270	0.34	10.3	0.016	NR	(0.14)*	130
	sd	NR	NR	0.04	NR		10	20	0.08	1.0	0.002	NR		10
Determined Concentration n = 7	\bar{x}	6.9	4.78	0.43	1.19	0.18	188	252	0.31	9.48	0.015	0.19	0.15	138
	sd	1.5	0.16	0.05	0.12	0.00	3	26	0.08	0.00	0.001	0.00	0.00	5
% Recovery		-	-	119	-	(100)	97	93	91	92	94	-	(107)	106

*value not certified
NR=not reported

III. RESULTS AND DISCUSSION

A. Surficial Sediments

When performing baseline surveys for environmental monitoring to detect possible pollution events in the future, it is necessary to consider all possible inputs to the study area. This will allow a consideration of the natural variability that must be considered during the monitoring effort. The inputs may be from terrigenous sources which would include both natural and anthropogenic input (i.e., pollution of riverine inputs), or the inputs may be strictly from anthropogenic sources (i.e., offshore oilfields).

The West Hackberry brine disposal site can be influenced by the outfalls of the Mermentau, Atchafalaya and Mississippi Rivers. Major offshore oilfields to the east and southeast can also impact the disposal site since the longshore current generally flows from east to west in this area. The Weeks Island disposal site will be influenced by the Atchafalaya and Mississippi Rivers and the offshore oilfield to the south and east. Table 3 summarizes the seasonal trace metal character of the surficial sediments for the West Hackberry and Weeks Island disposal sites. Data from the West Hackberry site in fall 1977 and winter 1978 (Shokes 1978) are also included for comparison.

At the West Hackberry site, there are generally higher trace metal concentrations in the summer, but these appear significant only for Ba, Cd, and Hg. The higher Ba in the summer may result from a redistribution of sediments from the oilfields where $BaSO_4$ from drilling muds is present in the sediments. Cadmium and Hg may be from river pollution or from the proximity to Cameron, Louisiana with its sources of industrial pollution.

West Hackberry sediments appear to be relatively homogeneous (low coefficient of variation - CV) with respect to trace metals

TABLE 3. SEASONAL COMPARISON OF AVERAGE TRACE METAL CONCENTRATIONS IN SURFICIAL SEDIMENTS FROM WEST HACKBERRY (A) AND WEEKS ISLAND (B) DISPOSAL SITES

			µg/g dry weight												
			Al	Ba	Cd	Co	Cr	Cu	Fe ^a	Hg	Mn	Ni	Pb	Sr	Zn
Site A (W. Hackberry)	Summer n = 7	\bar{X}	2080	94	0.167	5.13	8.76	9.35	0.709	0.447	403	8.87	14.4	54	31
		CV%	22	14	17	10	29	24	19	27	27	15	25	47	13
	Winter n = 8	\bar{X}	2532	39	0.060	4.67	6.35	7.45	0.815	0.059	441	9.06	15.1	42	38
		CV%	23	8	28	6	24	34	16	21	31	18	24	20	16
Site B (W. Island)	Summer n = 7	\bar{X}	819	37	0.052	4.74	5.01	1.98	0.453	0.012	306	6.19	5.74	27	22
		CV%	15	45	37	5	17	40	10	39	12	8	22	39	8
	Winter n = 8	\bar{X}	1056	21	0.014	4.25	3.04	1.04	0.483	0.019	222	7.05	4.71	14	26
		CV%	11	18	16	8	7	31	12	33	3	9	21	17	6
Site A ⁽¹⁾ W. Hackberry	Fall 1977 n = 12	\bar{X}	1380	N/D	0.067	N/D	2.41	6.50	0.418	N/D	334	4.54	14.2	N/D	21.3
		CV%	15		13		17	23	13		19	11	16		10
	Winter 1978 n = 13	\bar{X}	885	N/D	0.058	N/D	2.14	5.71	0.390	.0163	314	5.18	13.8	N/D	19.9
		CV%	19		26		24	29	21	33	32	20	23		14

^a concentration in % dry weight

(1) Shokes, 1978 Table 3.3-2, p 3-25

in both the summer and winter. However, Sr is more variable in the summer even though its concentration is similar in both seasons. The higher concentrations of metals relative to the Weeks Island site are in line with the sediment texture. The West Hackberry site is mainly silt and clay with a high organic carbon content. Clays and organic materials tend to adsorb and complex metal ions and would be expected to have higher metal concentrations. Sediments from the Weeks Island site are predominately silty sand with a low organic carbon content. This is reflected in the lower metal concentrations observed in these samples.

A comparison of the West Hackberry data with that from Shokes indicates there are generally higher metal concentrations in our data. These differences appear to be significant for Al in the summer and winter and Cd in the summer. The more concentrated leaching solution (5N HNO₃) used in our study may account for the relatively high metal concentrations reported. However, this would not account for the higher Al and Cd concentrations.

Homogeneity of the sediment as measured by the %CV are very similar for our winter data and Shokes' winter data. The summer sediments appear to be slightly less homogeneous than what Shokes found in his fall sediment samples. Sediments from the Weeks Island disposal site do not show any significant seasonal variations in their trace metal composition. There is less homogeneity (higher CV) for Ba, Cd, Mn and Sr in the summer than the winter. This could be the result of less mixing of bottom sediments during the summer months as opposed to the more dynamic system caused by winter storms.

Another technique for determining future abnormal trace metal inputs to the brine disposal sites is to construct scatter plots of the ambient metal concentrations versus the Fe concentration in the surficial sediments. Since Fe is in relatively high concentration

when compared to the other transition metals, any pollution event would not seriously alter the Fe content of the sediments. It would however cause a significant increase in the other metal concentrations (i.e., pollution) relative to the Fe. Shokes (1978) has used this technique with 95 percent confidence intervals about the best-fit linear regression line to determine abnormal trace metal inputs to the proposed disposal areas.

Figures 4 through 15 are scatter plots for each of the metal concentrations versus the Fe concentrations for the West Hackberry disposal site during the summer and winter cruises. Figures 16 through 27 are similar scatter plots for the Weeks Island disposal site. Shokes' linear regression lines for his winter 1978 sampling have been included on some West Hackberry plots for comparison purposes.

Examination of Figures 4, 8, 9, 10, 11, 12, 13, and 15 for the West Hackberry site show there is good correlation for Al, Cr, Cu, Hg, Mn, Ni, Pb, and Zn in both the summer and winter seasons. There is good correlation for Cd (Figure 6) in the winter, but in the summer there is a group of samples whose Cd/Fe ratios are dissimilar to the other samples at this site. Elimination of this group improves the correlation coefficient ($Y = 0.21X - 0.02$, $r^2 = 0.997$). Elimination of 50 percent of the data points is justified because (1) a similar occurrence was noted at the original Weeks Island site (Shokes 1978) and (2) the slope of the new regression line is similar to Shokes. Also, it is interesting that the magnitude of this aberrant group is similar to that in Shokes' report even though the locations are different.

Barium and Sr did not correlate with Fe in the summer, but Sr had good correlation in the winter. These are Group IIA, alkaline earth metals, and would not necessarily be involved in the same geochemical mechanisms or fluxes the transition metals

would be. Both of these metals would be present in calcareous shell materials and also as potential pollutants from offshore petroleum drilling and production activities to the southeast of the West Hackberry disposal site. Longshore currents could be influxing contaminating sediment from the oilfield into the West Hackberry site.

Comparison with Shokes' sediment data from the winter of 1978 indicates close similarities in Al, Cd, Cr, Cu, Ni, and Zn (Figures 4, 6, 8, 9, 12, and 15, respectively). Lead (Figure 13), however, appears to be dissimilar in the summer and winter seasons as there is a difference in the slope of the regression lines compared to Shokes' data. This would suggest a different sediment texture since there is still good correlation with Fe.

Figures 16 through 27 for the Weeks Island disposal site show good correlation for all metals except Hg and Ni during the winter season. Generally, the correlation with Fe was poor during summer for all metals except Co and Cr. There were even negative correlations for Cd and Hg. Elimination of two high values improved the correlation ($r^2 = 0.634$) for Cd. Mercury correlation was not improved by selective removal of high values. These data suggest there are seasonal trace metal inputs to the Weeks Island site during the summer that disrupt the natural concentrations present in surficial sediments. This input would probably be from the Atchafalaya River, Mississippi River or the offshore oilfields to the south and east of the disposal site.

It is interesting that other investigators (Trefry and Presley 1976) have found significant inputs of Pb and Cd to the Gulf of Mexico by the Mississippi River but no significant increases in Mn, Co, Ni, Zn, Cr, or Cu. This leaves the offshore oilfields as suspect in causing the perturbations in the sediment trace

metal burdens during the summer.

Concentration of trace metals are related to the amount of fine grain (i.e., clay) materials in the sediments. Clay materials have naturally higher trace metal concentrations than courser sediment particles because the finer grain particles have larger surface areas and, therefore, more adsorption sites for binding metals. Abnormal trace metal inputs (i.e., pollution) to sediments also tend to be associated with the fine grain fraction of the sediments. The relationship between the grain size (%Clay) and the trace metal content of the sediment can be used to determine these abnormal trace metal inputs to the sediments. Figure 28 is a scatter plot of Fe versus %Clay in the Weeks Island samples during the summer season.

Iron should be representative of the other transition metals with respect to the relationship between metal content and %Clay in the sediment. Iron, being in relative higher concentration in the sediments, would not be influenced by anthropogenic inputs. However, Fe is a transition element and should have similar chemical behavior in the sediments as the other transition metals.

The Fe versus %Clay correlation is relatively weak ($r^2 = 0.322$) at the West Hackberry site. This is thought to be caused by the limited number of samples (i.e., data points) used in constructing the scatter plot and the homogeneity of the sediments with respect to the ambient Fe concentration. Other metals, except Ba, Cd and Sr, correlated well ($r^2 \geq 0.5$) with %Clay. This would be further evidence that there is an abnormal input of Ba, Cd, and Sr to the West Hackberry site during the summer.

Correlation of Fe versus %Clay at the Weeks Island site is low ($r^2 = 0.173$) but may be the result of a small sampling population since the scatter is minimal (i.e., very homogeneous). Cadmium, Al, and Mn have correlations similar to Fe. However,

Co, Ni, and Zn were not correlated (i.e., negative or weak correlations) with the clay fraction. The remaining metals (Ba, Cr, Cu, Pb, Sr, and Hg) appear to have good ($r^2 \geq 0.5$) correlation.

It was mentioned earlier that Co correlated well with the hydrous Fe fraction of the sediments (see Figure 19). This would leave Zn and Ni as being possible pollutants at the Weeks Island site during the summer.

B. Suspended Particulate Matter (SPM)

Table 4 summarizes the SPM trace metal concentrations by season.

The particulate loading (mg/L) appears to be similar in the summer, fall, and spring seasons. The winter season has a slightly higher loading at both the Weeks Island and West Hackberry sites. This would be expected because of the more dynamic system caused by winter storm fronts.

This higher winter loading is also reflected in the higher Al and Fe concentrations for this season. This is the only detectable trend noted in the SPM data. These higher Al and Fe concentrations would be indicative of resuspended surficial sediments during the winter.

No significant differences in trace metal concentrations were apparent for the West Hackberry and Weeks Island sites.

C. Biota

1. Macrocrustaceans

Five different species of shrimp were collected at the West Hackberry and Weeks Island proposed disposal sites during the four sampling seasons. The trace metal concentrations in the various species are summarized by season for the West Hackberry and Weeks Island disposal sites in Tables 5 and 6, respectively.

At the West Hackberry disposal site, there were adequate numbers of Penaeus setiferus in all four seasons to describe

TABLE 4. MEAN TRACE METAL CONCENTRATIONS ($\mu\text{g/L}$) AND MEAN PARTICULATE (mg/L HOH), BY SITE IN SUSPENDED PARTICULATE MATTER

Cruise	Site	Particulate		Al	Ba	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sr	Zn
		mg/L	HOH													
I Summer	A	6.86	\bar{X}	32	0.7	0.009	0.15	1.38	0.50	35.9	ND	12.8	3.5	0.84	ND	1.4
			CV%	102	65	265	55	96	125	130	—	52	193	102	—	98
	B	5.13	\bar{X}	36	0.2	0.011	0.17	0.95	0.16	3.9	ND	1.1	0.7	0.29	0.01	0.3
			CV%	103	109	178	60	108	138	123	—	67	100	228	171	265
II Fall	A	5.01	\bar{X}	18	0.2	ND	0.03	ND	0.64	30.2	0.39	6.9	0.3	0.21	0.23	ND
			CV%	215	101	—	138	—	135	220	190	62	211	114	76	—
	B	7.18	\bar{X}	5	0.3	0.009	0.02	ND	0.55	5.9	0.35	6.5	0.2	0.51	0.32	30.6
			CV%	30	63	265	78	—	152	147	70	28	77	98	57	231
III Winter	A	20.78	\bar{X}	63	0.5	0.046	0.12	0.65	0.19	127	ND	11.5	1.3	0.52	0.64	ND
			CV%	109	220	178	182	106	129	122	—	120	151	121	88	—
	B	13.17	\bar{X}	45	2.4	0.037	0.09	0.47	0.60	95.4	0.01	8.8	2.6	1.63	0.78	1.7
			CV%	33	120	75	123	146	163	58	265	40	83	155	39	265
IV Spring	A	7.00	\bar{X}	4	1.0	0.029	0.02	1.10	2.18	34.4	0.02	0.7	1.5	0.78	0.35	9.0
			CV%	124	151	96	185	105	196	209	100	180	121	243	39	265
	B	9.20	\bar{X}	2	5.2	0.295	ND	1.66	2.15	19.3	0.02	0.3	1.3	1.25	0.35	33.4
			CV%	145	82	227	—	86	265	41	133	265	130	247	58	129

N = number of samples averaged

ND = None Detected

TABLE 5. SEASONAL TRACE METAL CONCENTRATIONS ($\mu\text{g/g}$ dry weight) IN MACROCRUSTACEA FROM WEST HACKBERRY (A) PROPOSED DISPOSAL SITES

Cruise	Species		Al	Ba	Cd	Cr	Co	Cu	Fe	Pb	Mn	Hg	Ni	Sr	Zn
I Summer	<i>Penaeus aztecus</i>	\bar{X}	31	49	0.17	0.17	<0.30	26	48	<0.09	4.9	0.086	0.70	78	62
		CV%	62	75	33	56	—	18	57	—	50	27	38	24	20
		n = 5(23)*													
I Summer	<i>P. setiferus</i>	\bar{X}	21	1.6	0.11	0.17	0.37	34	41	0.10	4.9	0.109	1.30	50	70
		CV%	43	81	76	49	48	10	46	13	50	63	78	9	4
		n = 6(11)*													
II Fall	<i>P. aztecus</i>	\bar{X}	108	1.2	0.07	0.34	<0.30	27	146	<0.09	8.6	0.099	1.10	99	57
		CV%	—	—	—	—	—	—	—	—	—	—	—	—	—
		n = 1(6)*													
II Fall	<i>P. setiferus</i>	\bar{X}	37	62.1	0.05	0.34	<0.30	28	49	<0.09	4.1	0.084	0.78	62	63
		CV%	92	80	47	53	—	14	96	—	69	19	42	20	8
		n = 4(17)*													
III Winter	<i>P. setiferus</i>	\bar{X}	59	2.1	0.19	0.52	<0.30	36	45	0.61	1.7	0.093	0.85	128	40
		CV%	34	25	72	114	—	10	45	35	54	44	65	12	3
		n = 6(63)*													
III Winter	<i>Trachypenaeus similis</i>	\bar{X}	71	2.8	0.46	0.38	<0.30	22	47	3.19	2.7	0.018	1.62	198	43
		CV%	74	98	84	87	—	44	64	194	40	21	128	21	4
		n = 7(46)*													
III Winter	<i>Xiphopenaeus kroyeri</i>	\bar{X}	63	2.4	0.36	0.36	<0.30	28	37	0.91	2.9	0.080	0.47	215	41
		CV%	47	73	94	8.2	—	25	54	138	81	20	37	57	11
		n = 6(16)*													
IV Spring	<i>P. aztecus</i>	\bar{X}	54	1.3	0.32	0.34	<0.30	26	23	<0.09	1.3	0.040	1.01	156	44
		CV%	—	—	—	—	—	—	—	—	—	—	—	—	—
		n = 1(1)*													
IV Spring	<i>P. setiferus</i>	\bar{X}	64	1.1	0.47	0.33	<0.30	25	45	0.24	1.9	0.079	1.13	135	50
		CV%	29	37	123	25	—	11	63	60	54	36	87	10	2
		n = 5(21)*													

* n = number of samples analyzed () = number of individuals

TABLE 6. SEASONAL TRACE METAL CONCENTRATIONS ($\mu\text{g/g}$ dry weight) IN MACROCRUSTACEA FROM WEEKS ISLAND (B) PROPOSED DISPOSAL SITES

Cruise	Species		Al	Ba	Cd	Cr	Co	Cu	Fe	Pb	Mn	Hg	Ni	Sr	Zn	
I Summer	<i>Panopeus aztecus</i>	\bar{X}	25	13.2	0.17	0.11	<0.30	35	35	<0.09	4.9	0.072	0.84	75	62	
		CV% n = 6(17)*	69	221	37	46	—	12	68	—	67	32	53	27	3	
	<i>Panopeus setiferus</i>	\bar{X}	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS
		CV% n = 1(2)*	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	II Fall	<i>P. aztecus</i>	\bar{X}	19	22.3	0.03	0.19	<0.30	30	32	<0.09	4.4	0.081	1.46	72	62
			CV% n = 5(28)*	38	89	24	40	—	12	25	—	42	14	56	10	8
<i>Trachypanopeus constrictus</i>		\bar{X}	36	2.4	0.11	0.71	0.30	18	73	0.12	7.5	IS	2.57	100	67	
		CV% n = 1(3)*	—	—	—	—	—	—	—	—	—	—	—	—	—	
<i>P. aztecus</i>		\bar{X}	56	1.2	2.01	0.58	<0.30	52	34	0.29	1.8	IS	5.44	156	43	
		CV% n = 1(1)*	—	—	—	—	—	—	—	—	—	—	—	—	—	
<i>P. setiferus</i>	\bar{X}	42	2.0	0.37	0.69	<0.30	35	28	0.29	0.85	0.044	1.17	114	43		
	CV% n = 7(61)*	18	87	87	60	—	15	35	97	74	20	85	14	3		
III Winter	<i>T. constrictus</i>	\bar{X}	113	2.6	0.02	0.73	<0.30	27	79	8.36	<0.30	IS	<0.39	242	43.0	
		CV% n = 1(1)*	—	—	—	—	—	—	—	—	—	—	—	—	—	
	<i>T. similis</i>	\bar{X}	390	6.4	0.80	3.79	<0.30	62	122	5.84	<0.30	IS	2.98	315	47	
		CV% n = 1(1)*	—	—	—	—	—	—	—	—	—	—	—	—	—	
	<i>Xiphopenaeus kroyeri</i>	\bar{X}	78	2.4	0.32	0.60	<0.30	37	21	2.49	0.9	IS	2.57	179	39	
		CV% n = 3(3)*	100	80	57	90	—	14	24	115	59	—	95	42	11	
<i>Panopeus setiferus</i>	\bar{X}	52	1.3	0.13	0.50	<0.30	29	39	1.05	1.8	0.132	0.98	114	52		
	CV% n = 4(13)*	28	42	69	38	—	6	32	111	43	38	48	17	4		
IV Spring	<i>Trachypanopeus constrictus</i>	\bar{X}	66	2.8	1.30	0.35	<0.30	21	70	0.36	2.2	0.103	0.85	280	47	
		CV% n = 7(61)*	29	48	173	78	—	22	40	99	28	19	60	21	5	
	<i>Trachypanopeus similis</i>	\bar{X}	120	5.0	0.41	0.51	<0.30	17	94	0.86	2.6	<0.006	1.25	356	40	
		CV% n = 5(13)*	65	58	89	39	—	36	63	126	77	—	40	50	11	

IS = Insufficient sample
 * = number of samples analyzed () = number of individuals

the seasonal and intraspecies trace metal variability. Sufficient numbers of Penaeus aztecus were collected in the summer season to describe the intraspecies variability but not the seasonal variability. Adequate samples of Trachypenaeus similis and Xiphopenaeus kroyeri were collected at West Hackberry during the winter season. Five samples of T. similis were analyzed from the Weeks Island site in the spring allowing for a seasonal comparison with those from the West Hackberry site in the winter. However, this would include any site variability.

Table 5 shows an increase in Ba in P. setiferus during the fall season. This increase is an order of magnitude above the Ba concentration in the other three seasons and may be fine grain sediment contamination of the tissue. However, other metal concentrations are not increased in these fall samples. Also, there appears to be a significant increase in tissue Pb and Sr concentrations during the winter and spring seasons.

Trace metal concentrations in P. aztecus from the West Hackberry site during the summer season have concentrations similar to P. setiferus. Other samples of P. aztecus from the fall and spring seasons are not of sufficient sample size for evaluation and can only suggest possible trends.

Samples of T. similis and X. kroyeri (Table 5) collected in the winter at the West Hackberry site have similar trace metal concentrations as P. aztecus and P. setiferus except for a higher concentration of Pb and Hg in T. similis. The variability (%CV) of Pb in the T. similis is rather high (194 percent) and should be considered when evaluating this higher Pb concentration. Comparing these Pb and Hg concentrations with T. similis from the Weeks Island site during the spring (see later) suggests these are seasonal highs.

Evaluation of Table 6 for P. setiferus trace metal variability at the Weeks Island disposal site shows there are

significant seasonal variations with Cd and Hg. It should be kept in mind that both these elements are perhaps the most difficult to analyze in tissue samples; these seasonal differences may be more a reflection of the methodology than any real seasonal variation. Also, Pb appears to have a significant seasonal variation, but there is also high variability (%CV) within a season. The overall comparison with P. setiferus samples from Table 5 (West Hackberry) during the winter and spring indicates similar trace metal concentrations.

The trace metal data for P. aztecus from the Weeks Island site (Table 6) showed no seasonal differences between the summer and fall for any metal. Comparison with P. aztecus data from West Hackberry site (Table 5) indicates an increase in Ba during the summer at the Weeks Island site. However, the variability is high (CV = 221 percent) for this particular sample.

Trachypenaeus constrictus data at the Weeks Island site (Table 6) indicate that the sample size is sufficient only during the spring season (N=7). The variability (%CV) is high for Cd and Hg in this species.

A comparison of T. constrictus with P. setiferus shows the former to have a higher Fe and Sr content. This would have to be considered in using this species for monitoring tissue trace metal burdens.

The number of T. similis collected at the Weeks Island site was sufficient only during the spring season. A comparison of this data with T. similis data from the West Hackberry site (Table 5) was made earlier.

Table 7 is a comparison of trace metal concentrations in T. constrictus and T. similis with other studies performed in the Gulf of Mexico. There appears to be higher concentrations of Cd, Ni and Pb in our samples (T. similis) when compared to

TABLE 7. COMPARISON OF SEASONAL VARIATIONS IN AVERAGE TRACE METAL CONCENTRATIONS IN TRACHYPENEUS SIMILIS (SUGAR SHRIMP) AND T. CONSTRICTUS (BROKEN NECK SHRIMP) MUSCLE TISSUES ($\mu\text{g/g}$ DRY WT) WITH OTHER GULF STUDIES

	Crustae		Al	Ba	Li	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sr	Zn
SPR Brine	Fall	\bar{X}	38	2.4	0.11	<0.30	0.71	18	73	15	7.5	2.57	0.12	100	57
Disposal Texoma/ Capline Fall	n = 1(3) ^a	CV%	-	-	-	-	-	-	-	-	-	-	-	-	-
1978-Spring 1979	Winter	\bar{X}	113	2.6	<0.02	<0.30	0.73	27	79	15	<0.30	<0.39	8.36	242	43
(Trachypeneus constrictus)	n = 1(11) ^a	CV%	-	-	-	-	-	-	-	-	-	-	-	-	-
	Spring	\bar{X}	66	2.6	1.30	<0.30	0.36	21	70	0.103	2.2	0.85	0.36	280	47
	n = 7(6) ^a	CV%	29	48	173	-	78	22	40	29	26	60	99	21	5
	Winter	\bar{X}	110	3.3	0.50	<0.30	0.80	27	56	0.018	2.4	1.99	3.52	212	44
(Trachypeneus similis)	n = 8(47) ^a	CV%	111	87	75	-	155	62	69	21	55	103	165	27	6
	Spring	\bar{X}	120	5.0	0.41	<0.30	0.51	17	94	<0.006	2.5	1.25	0.86	356	46
	n = 5(13) ^a	CV%	85	58	89	-	39	36	83	-	77	40	126	50	11
Buccaneer ¹	Fall	\bar{X}	ND	2.9	2.46	0.35	0.43	28.7	53.8	0.119	4.41	1.13	0.37	30	51
	n = 11(83) ^a	CV%	-	89	161	26	34	34	33	19	46	40	47	24	5
(Trachypeneus similis)	Winter	\bar{X}	ND	1.7	0.84	0.68	0.59	27.2	49.2	0.128	3.90	2.32	0.49	44	48
	n = 23(191) ^a	CV%	-	27	218	66	71	20	19	14	72	68	118	25	6
	Spring	\bar{X}	ND	4.3	2.03	0.37	1.04	33.4	58.3	0.154	3.95	0.608	0.23	24	54
	n = 11(58) ^a	CV%	-	9	218	23	55	17	32	19	39	52	27	16	3
MAFLA Rig ²	Before	\bar{X}	ND	ND	0.03	ND	1.0	23	31	ND	ND	0.4	0.8	ND	ND
Monitoring	CV%	-	-	100	-	50	13	110	-	-	75	22	-	-	-
(Trachypeneus similis)	During	\bar{X}	ND	ND	0.04	ND	0.7	25	57	ND	ND	0.5	0.6	ND	ND
	CV%	-	-	150	-	57	12	42	-	-	80	87	-	-	-
	After	\bar{X}	ND	ND	0.03	ND	0.2	19	23	ND	ND	0.5	0.1	ND	ND
	CV%	-	-	87	-	50	16	87	-	-	260	40	-	-	-
SPR Brine ³		\bar{X}	45	ND	0.017**	ND	0.131	16.8	65.8	ND	5.09	0.217	0.285	ND	60.2
Disposal Texoma Group Fall 1977- Winter 1978 (Trachypeneus sp.)		CV%	62	-	-	-	24	19	42	-	24	44	42	-	6

1. Tillery, 1979.

2. Alexander, 1977, before, during and after refer to drilling operations; from Table 13, p 66.

3. Shokes, 1978, summary of data for West Hackberry Control II, Table 3.3.6, p 3-47.

^a "n" is number of pooled samples; number in () is total individuals sampled.

** only one value given, others were "not detected."

ND = not determined.

IS = insufficient sample.

the SPR fall 1977-winter 1978 data. The intraspecies variability is similar except for Pb in our study, which is higher.

Our Cd concentrations are higher than what was found in the MAFLA Rig Monitoring Study (White et al. 1977), but the other metal concentrations agree reasonably well.

Comparison with data from the third year Buccaneer Oilfield (BOF) Study (Tillery² 1980) shows that Hg is lower in our samples but Pb and Sr are higher. Also, the overall Fe concentration may be slightly higher in our samples.

The higher Cd concentration in our samples may be due to spacial or seasonal differences or possible contaminants. The recoveries obtained from NBS Bovine Liver (Table 2) and the daily quality assurance program followed would suggest contamination is not the problem unless it occurred during sampling.

2. Epibenthic

Two species of epibenthic organisms were to be sampled at the West Hackberry and Weeks Island disposal sites. The sea onion, Paranthus rapiformis, and the sea worm, Chaetotterus sp., were selected because of their availability at the proposed disposal sites during previous sampling efforts.

Neither of these species nor any other epibenthic organisms were found at the West Hackberry site during the summer season. At the Weeks Island site, five different epibenthic samples were collected during the summer. However, the numbers of each species collected were low and none were sea onions or sea worms (see Table 8 for epibenthic organisms collected by season).

Table 9 is a summary, by season, of the mean trace metal burdens in the various epibenthic organisms collected at the West Hackberry disposal site. Portunus gibbesii was the only species common to more than one season. Comparison of the summer and winter data for this species shows higher concentrations

TABLE 8. SPECIES OF EPIBENTHIC ORGANISMS COLLECTED BY SEASON AT WEST HACKBERRY AND WEEKS ISLAND PROPOSED DISPOSAL SITES

<u>SITE A - W. HACKBERRY</u>			
<u>Summer (I)</u>	<u>Fall (II)</u>	<u>Winter (III)</u>	<u>Spring (IV)</u>
(None collected)	Portunus gibbesii Polinicies duplicatus Busycon contrarium Thais haemostoma Cantharus cancellarius	Portunus gibbesii	Callinectes sapidus
<u>SITE B-WEEKS ISLAND</u>			
Dinocardium robustum Persephona aquilonaris Echinodermata sp. Pagurus pollicaris Polinicies duplicatus	Portunus gibbesii Callinectes similis	Portunus gibbesii Persophona aquilonaris	Portunus gibbesii Callinectes similis Callinectes sapidus

TABLE 9. TRACE METAL CONCENTRATIONS ($\mu\text{g/g}$ wet weight) IN EPIBENTHIC ORGANISMS BY SEASON AT THE WEST HACKBERRY PROPOSED DISPOSAL SITE

Season	Species		Al	Ba	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sr	Zn
Summer (II)	(none collected)	\bar{X}	—	—	—	—	—	—	—	—	—	—	—	—	—
		CV%	—	—	—	—	—	—	—	—	—	—	—	—	—
	<u>Portunus gibbesii</u>	\bar{X}	347	115	0.46	2.57	1.12	6.00	182	IS	18.0	2.87	2.33	20.2	14
	n = 2 (10)*	CV%	15	56	11	90	29	23	34	—	72	60	76	141	8
	<u>Polinicies duplicatus</u>	\bar{X}	31.6	12.5	0.13	<0.14	0.27	10.6	37	0.011	3.6	0.45	0.14	0.37	19
n = 1 (6)*	CV%	—	—	—	—	—	—	—	—	—	—	—	—	—	
Fall (III)	<u>Busycon contrarium</u>	\bar{X}	80.5	12.1	0.70	0.30	0.39	4.98	88	<0.006	2.8	0.39	0.34	<0.12	28
	n = 1 (2)*	CV%	—	—	—	—	—	—	—	—	—	—	—	—	—
	<u>Thais haemostoma</u>	\bar{X}	93	19	0.86	0.38	0.74	5.07	137	0.014	6.04	0.67	0.44	3.96	33
	n = 4 (19)*	CV%	20	16	59	10	51	12	17	35	16	28	20	12	5
	<u>Cantharus cancellarius</u>	\bar{X}	60	32	1.53	0.40	0.74	17.0	75	IS	8.54	0.52	0.33	<0.12	21
n = 2 (2)*	CV%	3	33	15	46	50	134	7	—	7	19	24	—	55	
Winter (III)	<u>Portunus gibbesii</u>	\bar{X}	13	9.9	0.85	0.57	0.77	17.8	52	0.015	11.8	1.06	1.31	54	9.1
	n = 8 (125)*	CV%	43	33	36	28	94	28	62	66	32	100	80	9	35
Spring (IV)	<u>Callinectes sapidus**</u>	\bar{X}	640	157	2.17	0.62	1.20	244	893	0.044	99.4	3.31	2.65	580	81
	n = 7 (31)*	CV%	23	33	30	59	32	17	36	12	71	44	21	6	10

* n = number of samples analyzed () = number of individuals

** concentration in dry weight

IS = insufficient sample

of Al, Ba, Co, and Fe during the summer. These differences may be due to incorporation of fine grains of sediment into the tissues rather than actual biochemical uptake.

Examination of the mean trace metal concentrations in the other species listed in Table 9 indicates there are wide ranges of various metals in these different species. Since the total number of individual species analyzed are low, these concentrations only suggest what the normal ambient levels should be. A larger sample pool for each species is needed before statistical evaluations, that would adequately describe the burden and normal intraspecies variations of trace metals in these organisms, can be performed.

Table 10 is a seasonal summary of the trace metal concentrations in the epibenthic organisms from the Weeks Island disposal site. The summer seasons did not produce large numbers of any epibenthic organisms suitable for monitoring trace metal burdens. Five different organisms were sampled during this season, but the total number of individuals analyzed were insufficient for adequate statistical treatment. The mean concentrations of the 13 analyte trace metals for each species are given in Table 10 as indicating what levels can be expected in each species.

In the fall, winter and spring seasons, sufficient numbers of P. gibbesii were collected at the Weeks Island site to give some idea as to the suitability of this organism for monitoring trace metal burdens. There does not appear to be any large seasonal variations in the trace metal concentrations in this species, but the variability (%CV) is higher for Al, Cu, Fe, Hg, Mn, Sr and Zn during the fall season.

Comparison of the trace metal concentrations in P. gibbesii from the winter cruise of the West Hackberry and Weeks Island disposal sites (Tables 9 and 10) shows very similar values for all trace metals analyzed. This is also true for Callinectes sapidus at both sites in the spring.

TABLE 10. TRACE METAL CONCENTRATIONS ($\mu\text{g/g}$ wet weight) IN EPIBENTHIC ORGANISMS BY SEASON AT WEEKS ISLAND PROPOSED DISPOSAL SITE

Season	Species		Al	Ba	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sr	Zn
Summer (I)	<i>Dinocardium robustum</i> n = 1 (1)*	\bar{x}	322	50	0.18	0.83	1.08	2.15	379	0.006	24.5	1.33	0.98	1.5	12
		CV%	—	—	—	—	—	—	—	—	—	—	—	—	—
	<i>Persephona aquilonaris</i> n = 1 (1)*	\bar{x}	49	38	0.89	0.75	0.44	7.68	119	<0.006	23.9	0.85	0.33	28.0	27
		CV%	—	—	—	—	—	—	—	—	—	—	—	—	—
	<i>Echinodermata</i> n = 1 (1)*	\bar{x}	IS	43	0.07	1.00	1.62	0.60	1218	<0.006	15.0	1.49	2.13	0.5	10
		CV%	—	—	—	—	—	—	—	—	—	—	—	—	—
	<i>Paqurus pollicaris</i> n = 2 (7)*	\bar{x}	386	28	0.60	0.94	1.18	59.8	483	0.013**	36.1	1.13	0.58	15.3	
		CV%	24	47	41	4	17	21	38	—	67	19	43	12	
	<i>Polinicies duplicatus</i> n = 1 (3)*	\bar{x}	134	25	0.82	0.63	0.52	7.43	282	0.14	18.9	0.70	0.27	0.2	21
		CV%	—	—	—	—	—	—	—	—	—	—	—	—	—
Fall (II)	<i>Portunus gibbesii</i> n = 7 (38)*	\bar{x}	44	24	0.42	0.29	0.38	25.0	40	0.036***	7.66	0.62	0.24	12.3	19.6
		CV%	47	30	44	11	30	45	94	134	70	18	28	36	57
	<i>Callinectes similis</i> n = 2 (11)*	\bar{x}	59	48	0.85	0.60	0.50	53.0	42	IS	13.0	1.15	0.81	16.4	50.9
		CV%	28	8	32	61	16	8	44	—	38	30	6	34	33
	<i>Portunus gibbesii</i> n = 7 (123)*	\bar{x}	11	11	0.75	0.50	0.71	16.7	48	0.014****	8.89	0.77	0.75	51	8.5
		CV%	13	23	21	19	46	22	61	45	36	40	13	10	27
Winter (III)	<i>Persephona aquilonaris</i> n = 1 (1)*	\bar{x}	71	33	2.39	2.77	4.09	6.98	182	IS	15.4	<0.13	7.13	24	<3.2
		CV%	—	—	—	—	—	—	—	—	—	—	—	—	—
	<i>Poctonus gibbesii</i> n = 6 (52)*	\bar{x}	8.8	5.9	0.87	0.50	0.45	17.4	37	IS	4.96	0.62	0.80	31	5.4
		CV%	18	38	53	18	14	25	21	—	20	61	38	14	31
Spring (IV)	<i>Callinectes similis</i> n = 1 (2)*	\bar{x}	7.0	4.5	0.84	0.40	0.25	10.8	29	IS	2.79	0.97	0.05	20	9.2
		CV%	—	—	—	—	—	—	—	—	—	—	—	—	—
	<i>Callinectes sapidus</i> n = 1 (3)*	\bar{x}	918	202	2.48	0.60	2.33	217	1350	0.055	119	5.66	1.11	734	96
		CV%	—	—	—	—	—	—	—	—	—	—	—	—	—

*n = number of samples analyzed () = number of individuals
 **1 sample (6 individuals) analyzed
 IS = Insufficient sample

***based on n = 5 (32)
 ****based on n = 3 (54)

Comparison of the trace metal concentrations in P. gibbesii from the winter cruise of the West Hackberry and Weeks Island disposal sites (Tables 9 and 10) shows very similar values for all trace metals analyzed. This is also true for Callinectes sapidus at both sites in the spring.

The use of epibenthic organisms as monitors for trace metal burdens at the disposal sites will be limited more by their availability than any intraspecies variability in trace metal burdens. Intraspecies variability may be adjusted by increasing the number of samples analyzed (but only if they are available). Mixing of different species will not be acceptable for making up adequate sample sizes due to the high variability for certain metals between species.

IV. CONCLUSIONS

A. West Hackberry Disposal Site

Surficial sediments from the West Hackberry site are relatively homogeneous with respect to trace metals in both the summer and winter seasons. There is an apparent input of Cd, Ba and Sr during the summer season that does not correlate with the hydrous Fe fraction (at three sampling stations for Cd) or the clay fraction of the sediments. Cadmium may be influxing from riverine or coastal sources, while Ba and Sr are thought to be from the offshore oilfields to the southeast of the proposed disposal site. These possible sources of Ba, Cd, and Sr would have to be considered in any future monitoring activities.

Comparison of our sediment data with previous sampling activities shows our results to be slightly higher for most analyte metals. This is thought to be caused by a strong leaching solution we used and not to any overall increase in sediment trace metal burdens. There does appear to be some changes in sediment texture since the previous sampling program (winter 1977-78) was conducted.

Suspended particulate matter loading was high in the winter but lower in the other three seasons. Increased concentrations of Al and Fe in the winter SPM suggest the increase is from resuspended sediments. No other seasonal trends were apparent in the trace metal SPM data.

Only P. setiferus was collected in sufficient numbers in all four seasons to describe both the intraspecies and seasonal variabilities. There were increased concentrations of Ba in the fall and Pb and Sr in the winter and spring. These seasonal variations would have to be considered in using P. setiferus in a monitoring program.

Other species examined showed that T. similis had higher concentrations of Pb and Hg than P. setiferus. These may be

seasonally related. P. aztecus and X. kroyeri have trace metal concentrations similar to P. setiferus.

No epibenthic samples were available at the West Hackberry site during the summer. Five different species of epibenthic organisms were collected in the fall but only P. gibbesii were common to another season sampling (winter). The number of samples from these five species were not sufficient for adequate statistical treatment. P. gibbesii appears to contain higher concentrations of Al, Ba, Co and Fe during the summer. This is based on only two samples (10 individuals) collected during the summer season. These higher metal concentrations may be due to fine grain sediment particles in the tissues rather than biochemical uptake.

The availability of epibenthic organisms at this site will limit their usefulness as organisms for monitoring trace metal accumulations.

B. Weeks Island Disposal Site

Surficial sediments from the Weeks Island site do not show any significant trace metal variation between the summer and winter seasons. However, there is less sediment homogeneity for Ba, Cd, Mn and Sr in the summer season.

Correlation of metals with the hydrous Fe fractions in the sediments was good ($r^2 \geq 0.5$) for all metals except Hg and Ni in the winter. In the summer, correlation was poor for all metals except Co and Cr. However, the correlation with the clay fraction of the sediments (summer) was good for all metals except Co, Ni and Zn. This would leave Zn and Ni as possible contaminants in the sediments during the summer season. The offshore oilfields to the east and south of the proposed disposal site would be a possible source of this Zn and Ni influx.

Suspended particulate matter loading was higher in the winter than the other seasons. Concentrations of Al and Fe were significantly

increased in the winter, which suggests the increase in SPM loading is from resuspended sediments. No other patterns in the trace metal data were noted.

There are seasonal variations in Cd, Pb and Hg concentrations in P. setiferus, but high intraspecies variation for these metals makes seasonal variations suspect. Overall comparison of trace metal burden for the winter and spring in P. setiferus with the West Hackberry data shows the concentrations are similar.

Trace metal concentrations in P. aztecus showed no seasonal differences between the summer and fall seasons. These were the only seasons adequate samples were collected.

T. constrictus samples were adequate only in the spring season. The intraspecies variability of Cd and Hg were high for this species.

Comparison of T. constrictus with P. setiferus shows the former to have higher Fe and Sr, which would have to be considered when using T. constrictus in a monitoring program.

Comparison of T. similis and T. constrictus data from both disposal sites with data from other recent studies in the Gulf indicates our data are comparable with what other investigators have found in these species except for Cd, Hg, Pb and Sr. Concentrations of Hg are lower in our samples (T. similis) than other studies while concentrations of Cd, Pb and Sr are higher. These differences are thought to be caused by spacial and/or seasonal differences.

The number of epibenthic organisms collected during the summer were very minimal and dispersed over five different species - only one of which, Persephona aquilonaris, was sampled in another season.

P. gibbesii were collected in sufficient numbers in the fall, winter and spring to determine its intraspecies and seasonal variability. There were no apparent seasonal variations in any

metal analyzed, but the intraspecies variability in the fall was high for Al, Cu, Fe, Hg, Sr and Zn. This would limit the usefulness of this species for monitoring efforts unless larger numbers were analyzed.

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.
- 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, 1977-1979," Volume III, Physical and Chemical Investigations.
- Bender, E., "NOAA Analyses Brine Disposal at Gulf of Mexico Sites", Sea Technology, 19, 44, 1978.
- Berryhill, H. L. et al. In: "Environmental Studies, South Texas. Outer Continental Shelf, 1975"; Geology, prepared by U.S. Geological Survey for Bureau of Land Management, Contract 08550-MY 5-20, 1979.
- Dames and Moore, "The Mississippi, Alabama, Florida, Outer Continental Shelf Baseline Environmental Survey, 1977-1978", Final Report, Volume I-A, Program Synthesis Report, prepared for for Bureau of Land Management, Contract AA550-CT7-34, January 1979.
- Montalva, J. G. and D. V. Brady, Part 1: Toxic Metal Determinations in Timbalier Bay Water Samples. In: Offshore Ecology Investigations, Gulf University Research Consortium, 1974.
- Montalvo, J. G. and D. V. Brady, Part 2: Toxic Metal Determinations in Offshore Water Samples. In: Offshore Ecology Investigations, Gulf University Research Consortium, 1974.
- Shokes, F. F., "Characterization of Baseline Conditions at the West Hackberry Offshore Brine Disposal Site - Texoma Group Strategic Petroleum Reserve Program," Science Applications, Inc. Department of Energy, Contract EL-77-C-01.
- ¹Tillery, 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).
- ²Tillery, J. B., Work Unit 2.4.2-Trace Metals. In: W. B. Jackson [Ed.], 1980, "NOAA/NMFS Annual Report to EPA, Environmental Assessment of an Active Gas and Oilfield in the Northwestern Gulf of Mexico, 1978-1979", under Interagency Agreement EPA-IAG-D5-E693-EO.

Trefry, J. G. and B. J. Presley, "Heavy Metal Transport From the Mississippi River to the Gulf of Mexico." In: H. L. Windom and R. A. Duce [Eds.], Marine Pollutant Transfer, Lexington Books, Lexington, Massachusetts, 1976.

White, T. T., K. E. Turgon and A. W. Blizzard. In: "Baseline Monitoring Studies, Mississippi, Alabama, Florida, Outer Continental Shelf, 1975-1976", Volume VI, Rig Monitoring, Project Manager J. E. Alexander, prepared by State University System of Florida Institute of Oceanography for the Bureau of Land Management, Contract 08550-CI5-30, June 1977.

Williams, S. E. and J. J. Jones. "The Distribution and Origin of Bottom Sediments in Timbalier Bay, Louisiana." In: Offshore Ecology Investigations, Gulf University Research Consortium, 1974.

APPENDIX A

Figures

3.3-43

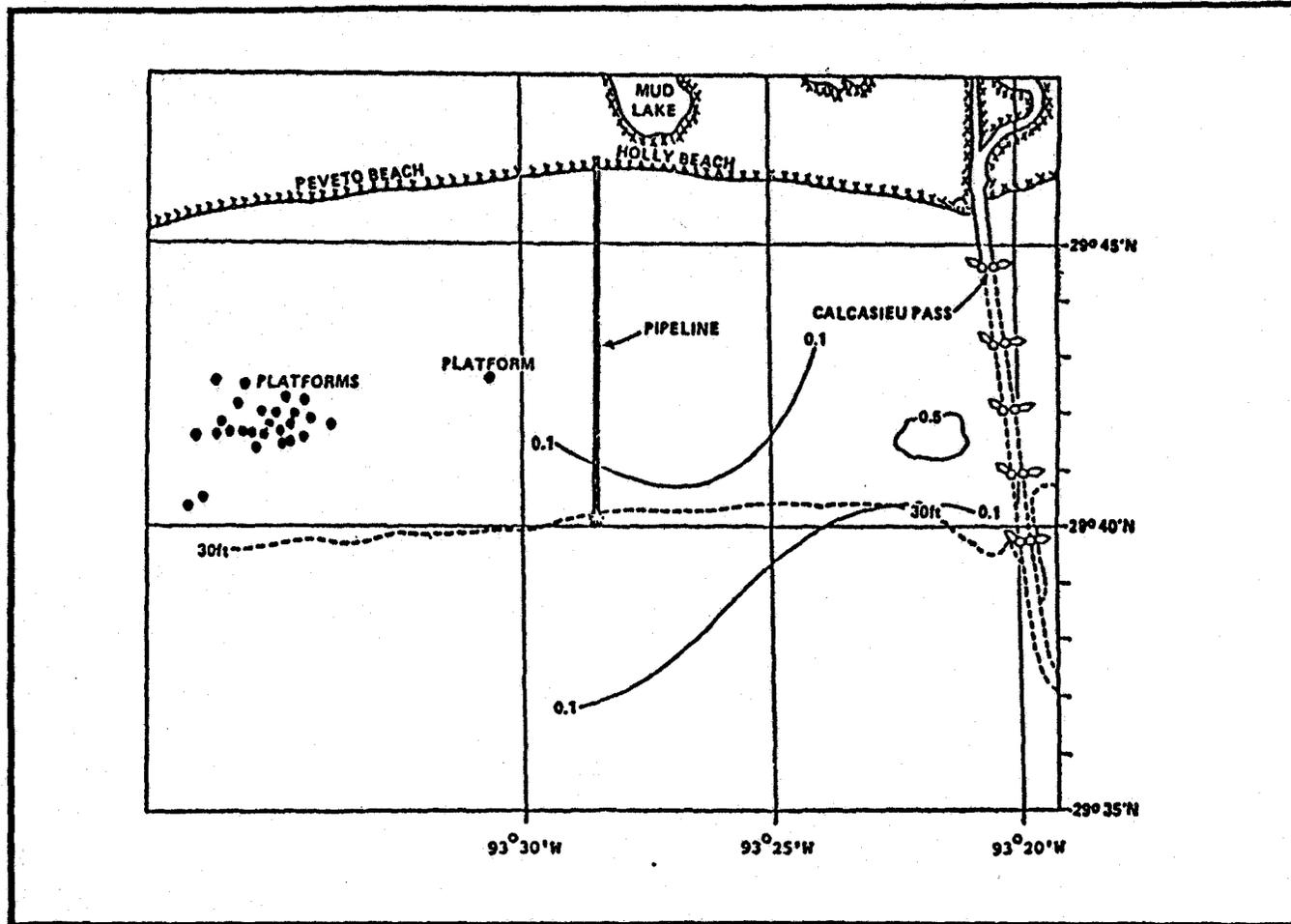


Figure 1. Proposed Disposal Site at West Hackberry

3.3-44

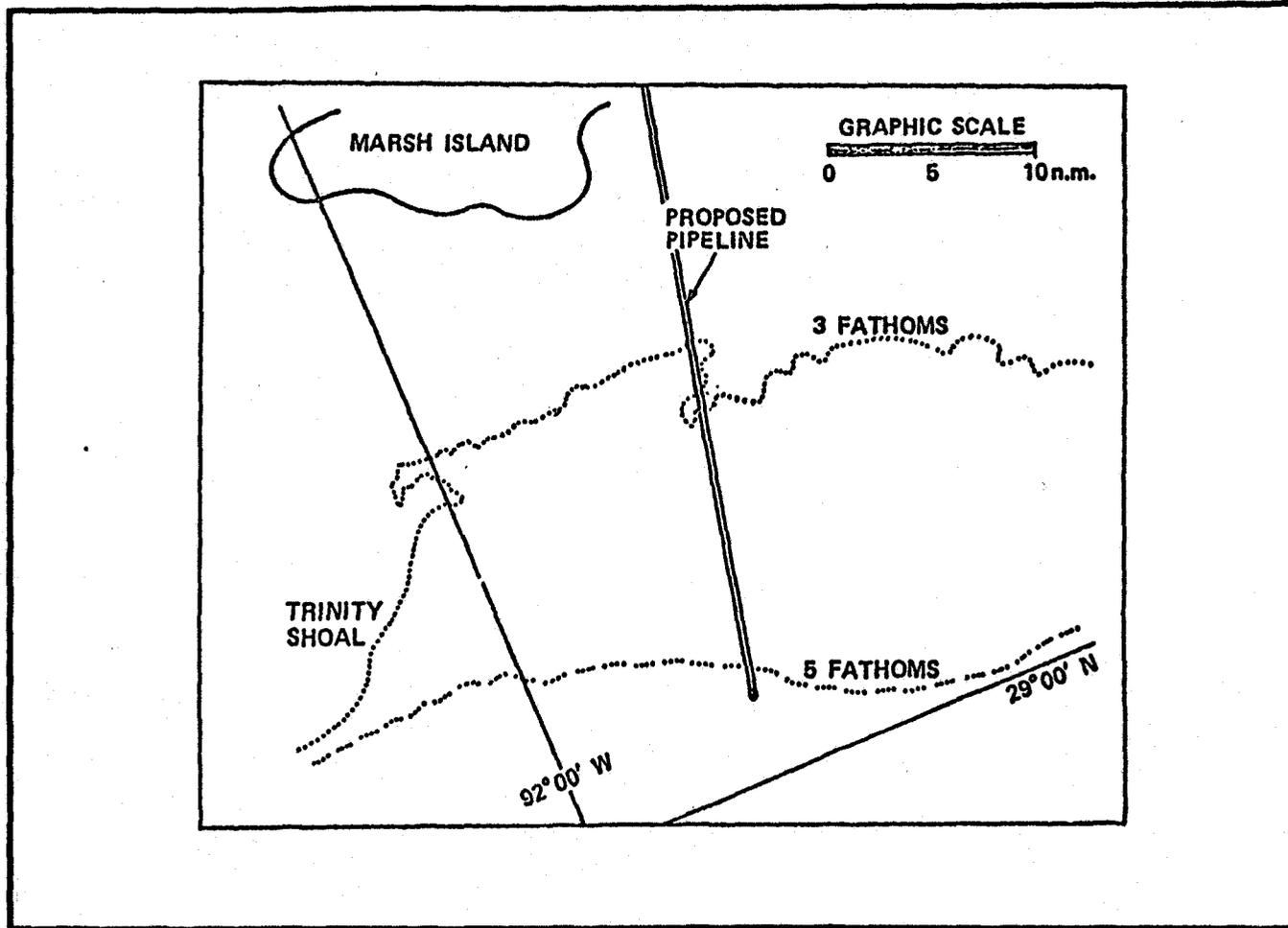


Figure 2. Proposed Disposal Site at Weeks Island

3.3-45

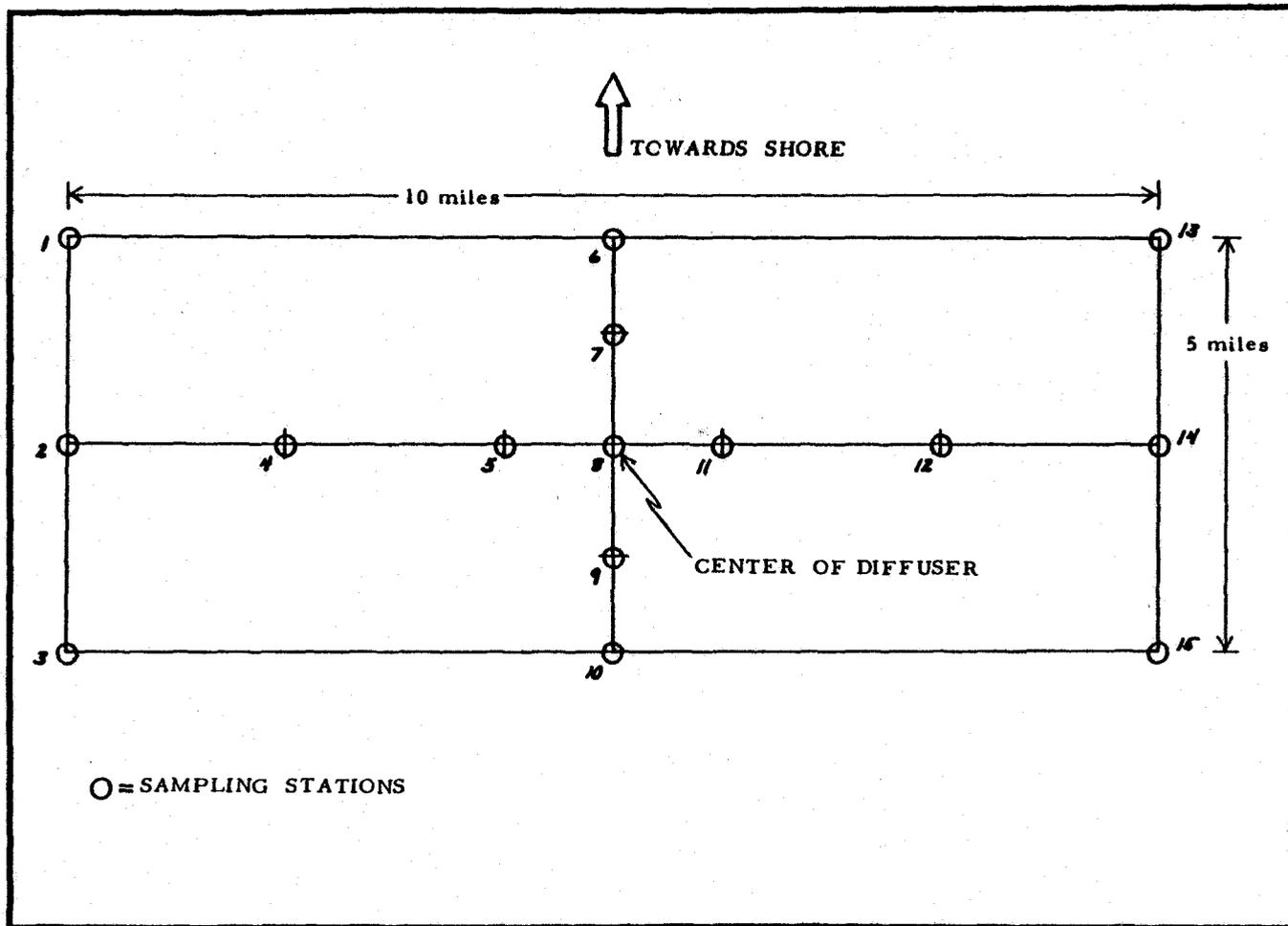


Figure 3. Sampling Grid Used at West Hackberry and Weeks Island Proposed Disposal Sites

3.3-46

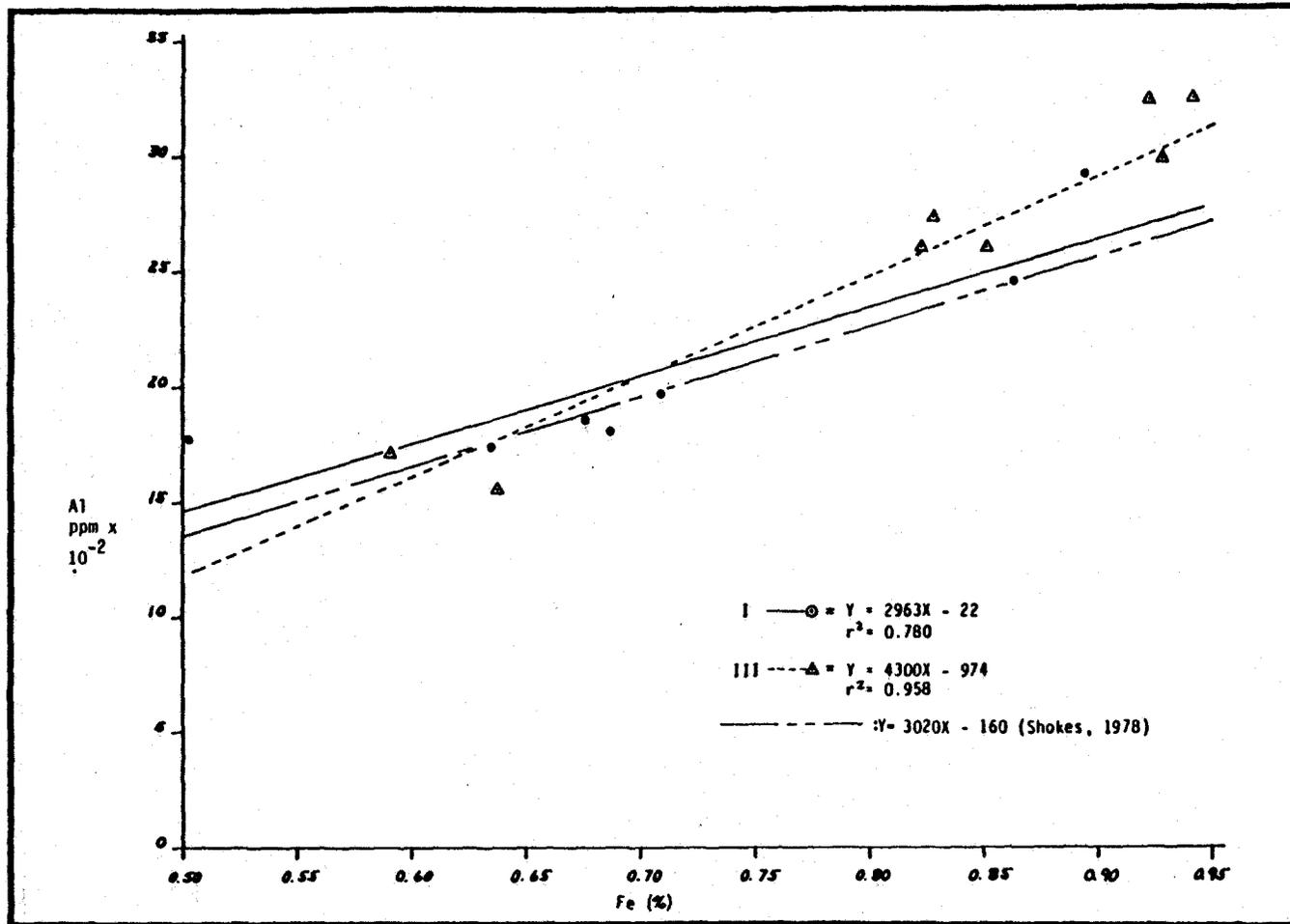


Figure 4. Al versus Fe in Surficial Sediments from West Hackberry;
Summer (I) and Winter (III) Cruises

3.3-47

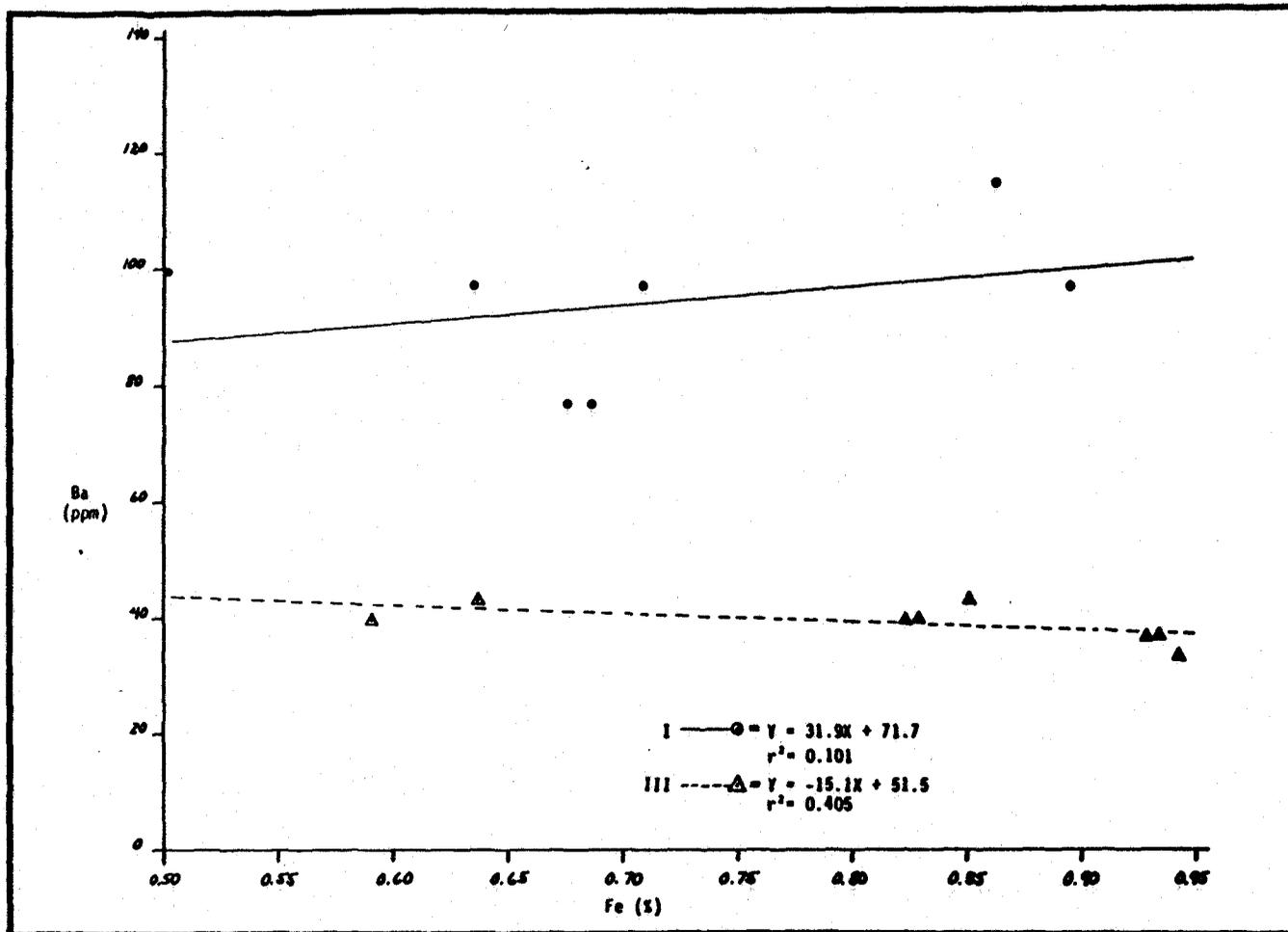


Figure 5. Ba versus Fe in Surficial Sediments from West Hackberry; Summer (I) and Winter (III) Cruises

3.3-48

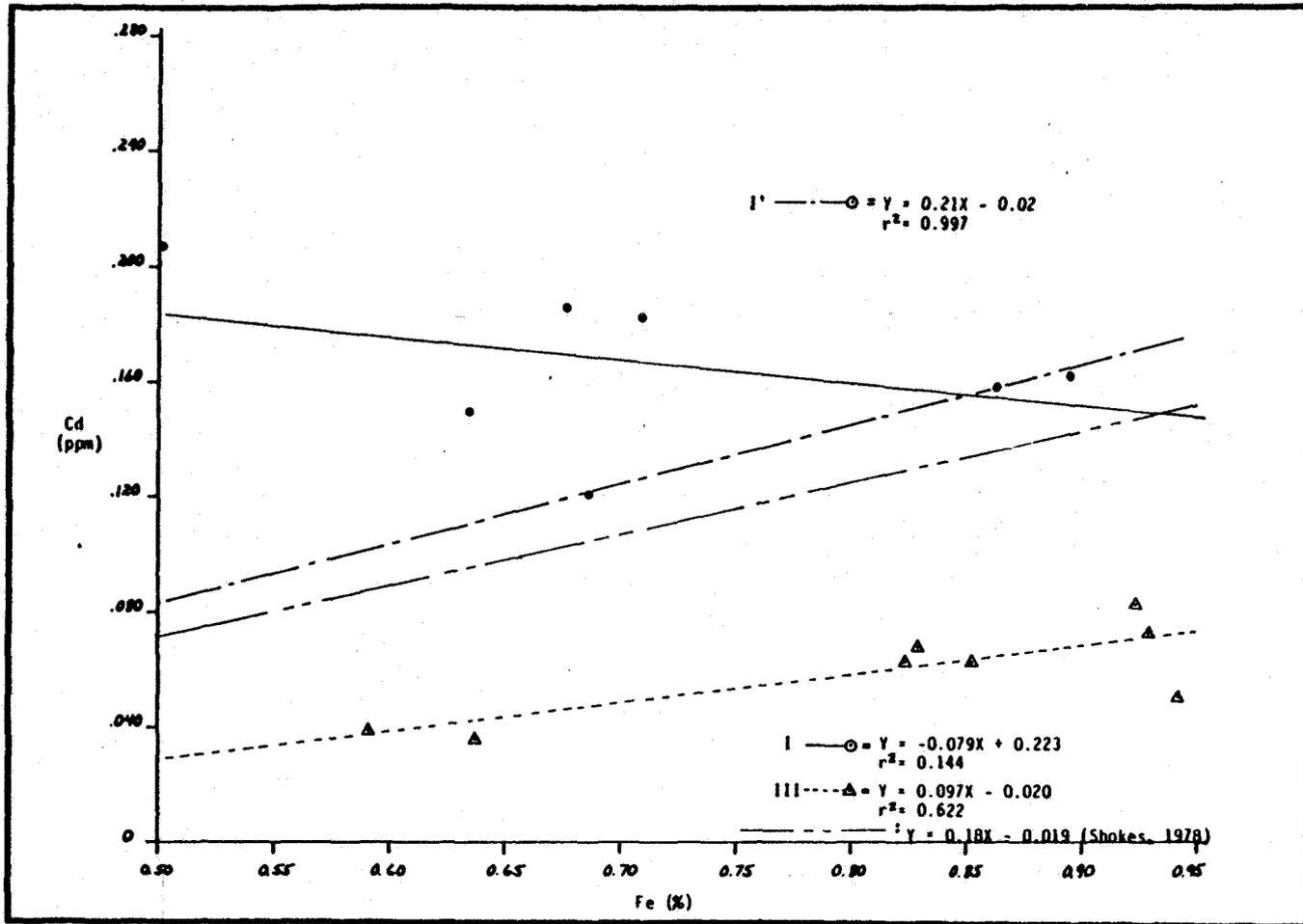


Figure 6. Cd versus Fe in Surficial Sediments from West Hackberry; Summer (I) and Winter (III) Cruises

3.3-49

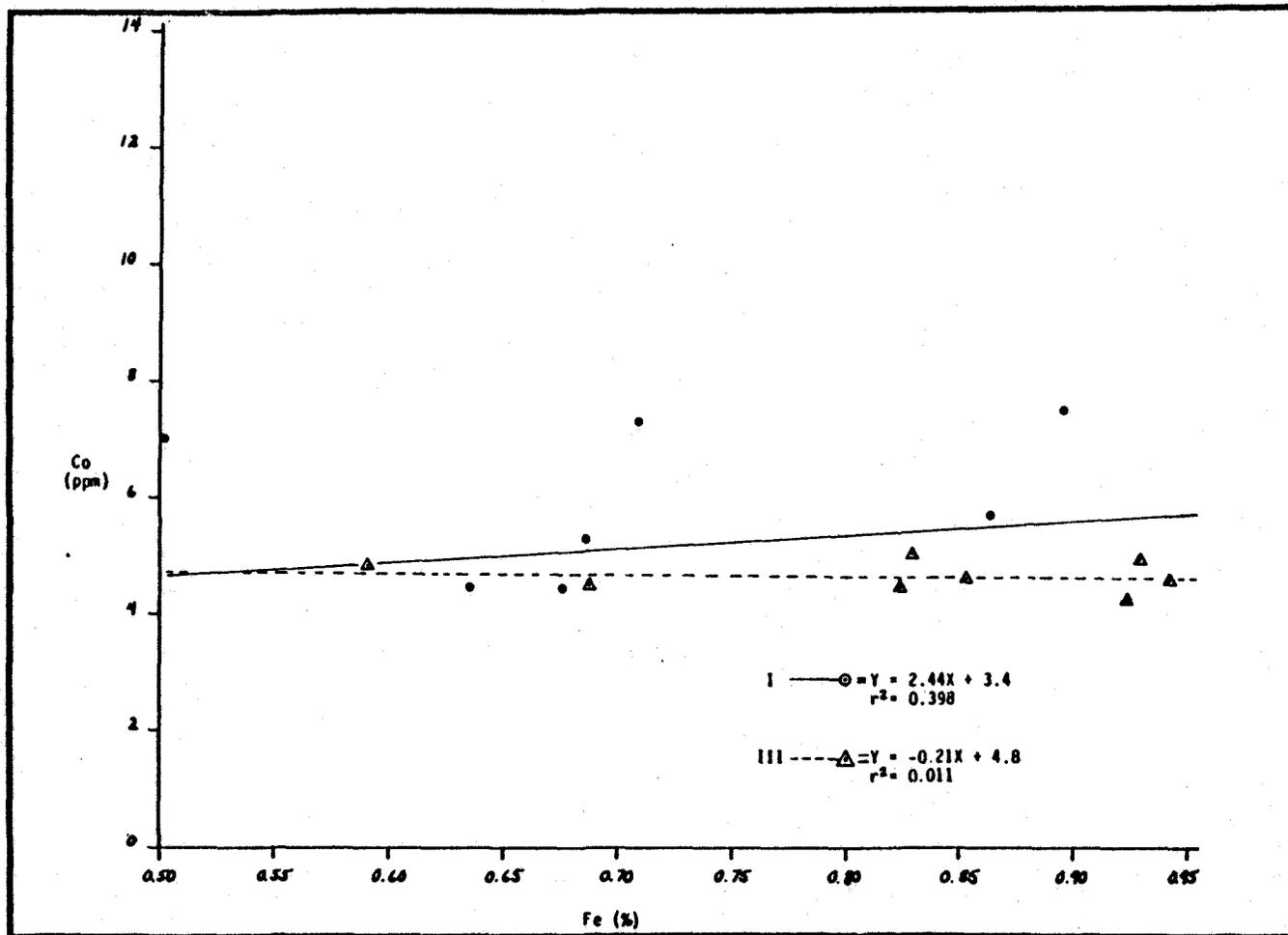


Figure 7. Co versus Fe in Surficial Sediments from West Hackberry; Summer (I) and Winter (III) Cruises

3.3-50

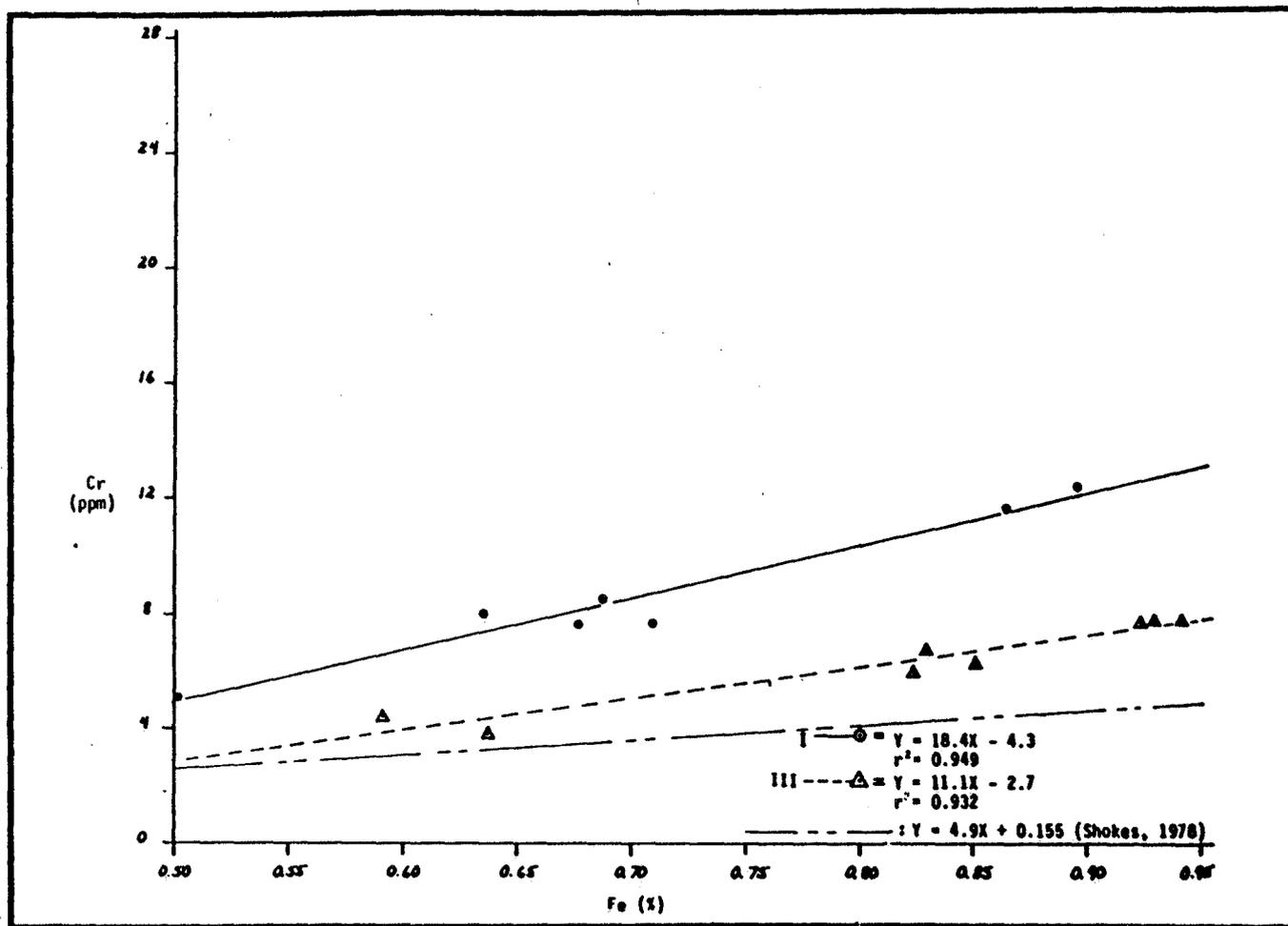


Figure 8. Cr versus Fe in Surficial Sediments from West Hackberry; Summer (I) and Winter (III) Cruises

3.3-51

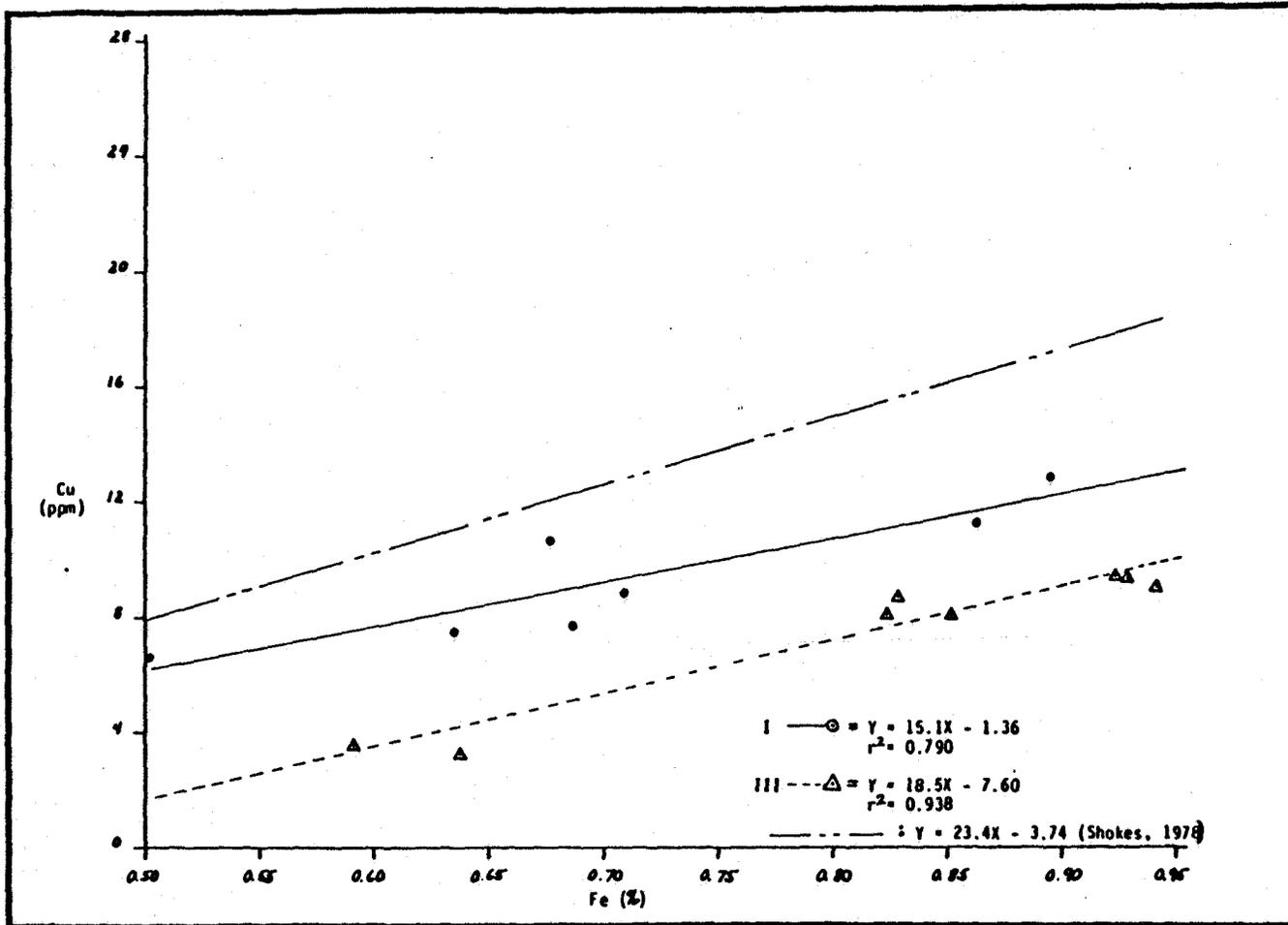


Figure 9. Cu versus Fe in Surficial Sediments from West Hackberry; Summer (I) and Winter (III) Cruises

3.3-52

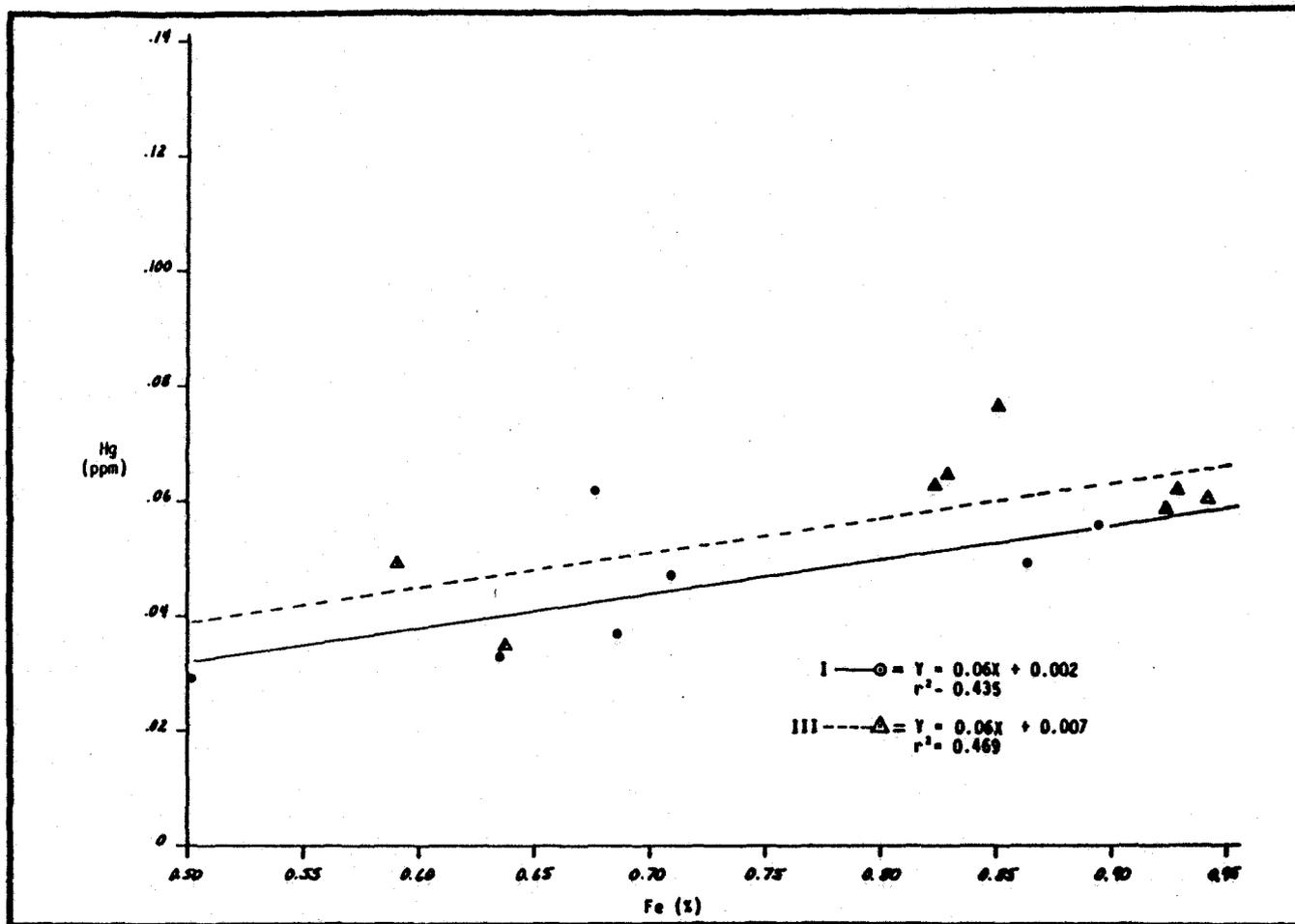


Figure 10. Hg versus Fe in Surficial Sediments from West Hackberry; Summer (I) and Winter (III) Cruises

3.3-53

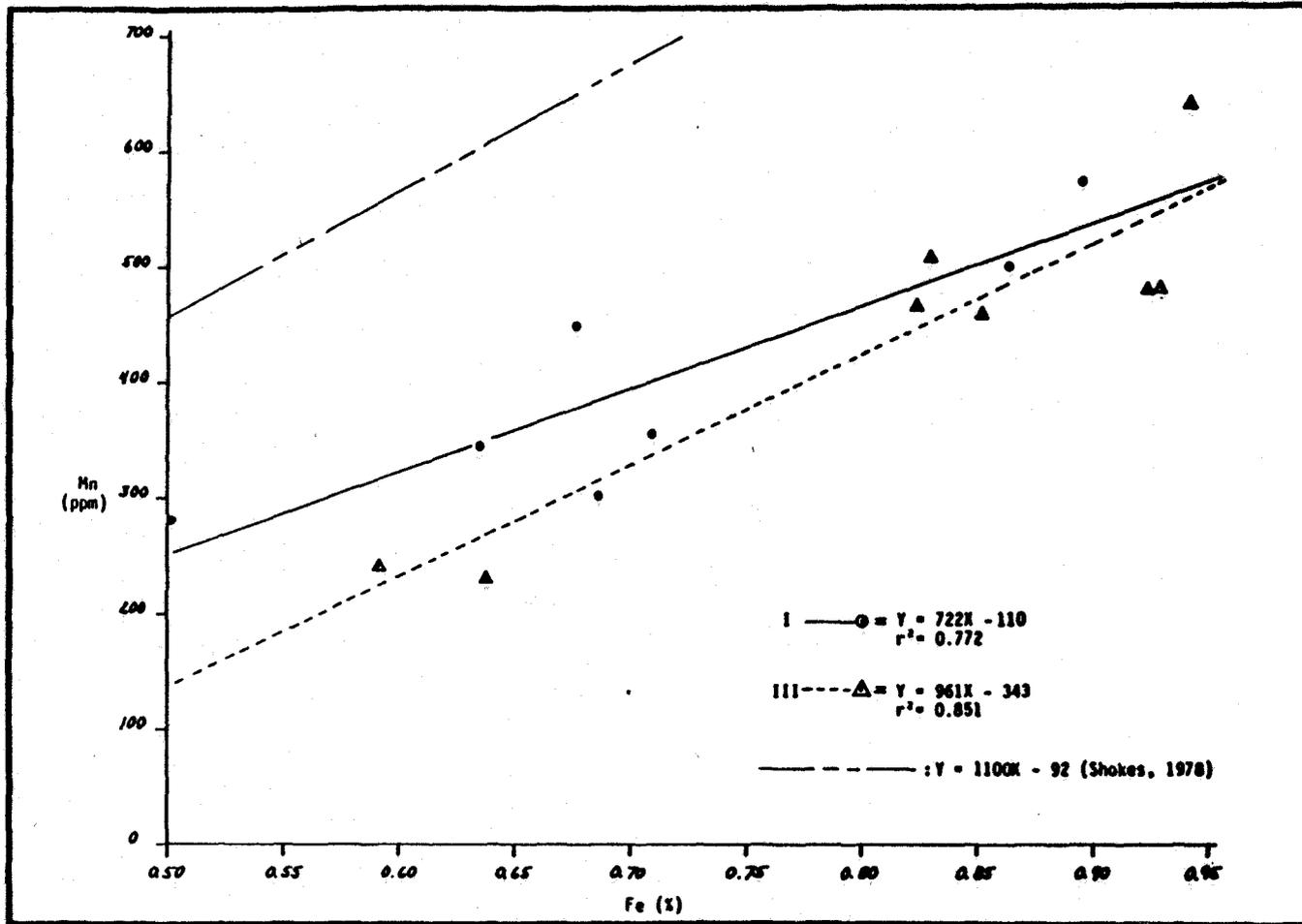


Figure 11. Mn versus Fe in Surficial Sediments from West Hackberry; Summer (I) and Winter (III) Cruises

3.3-54

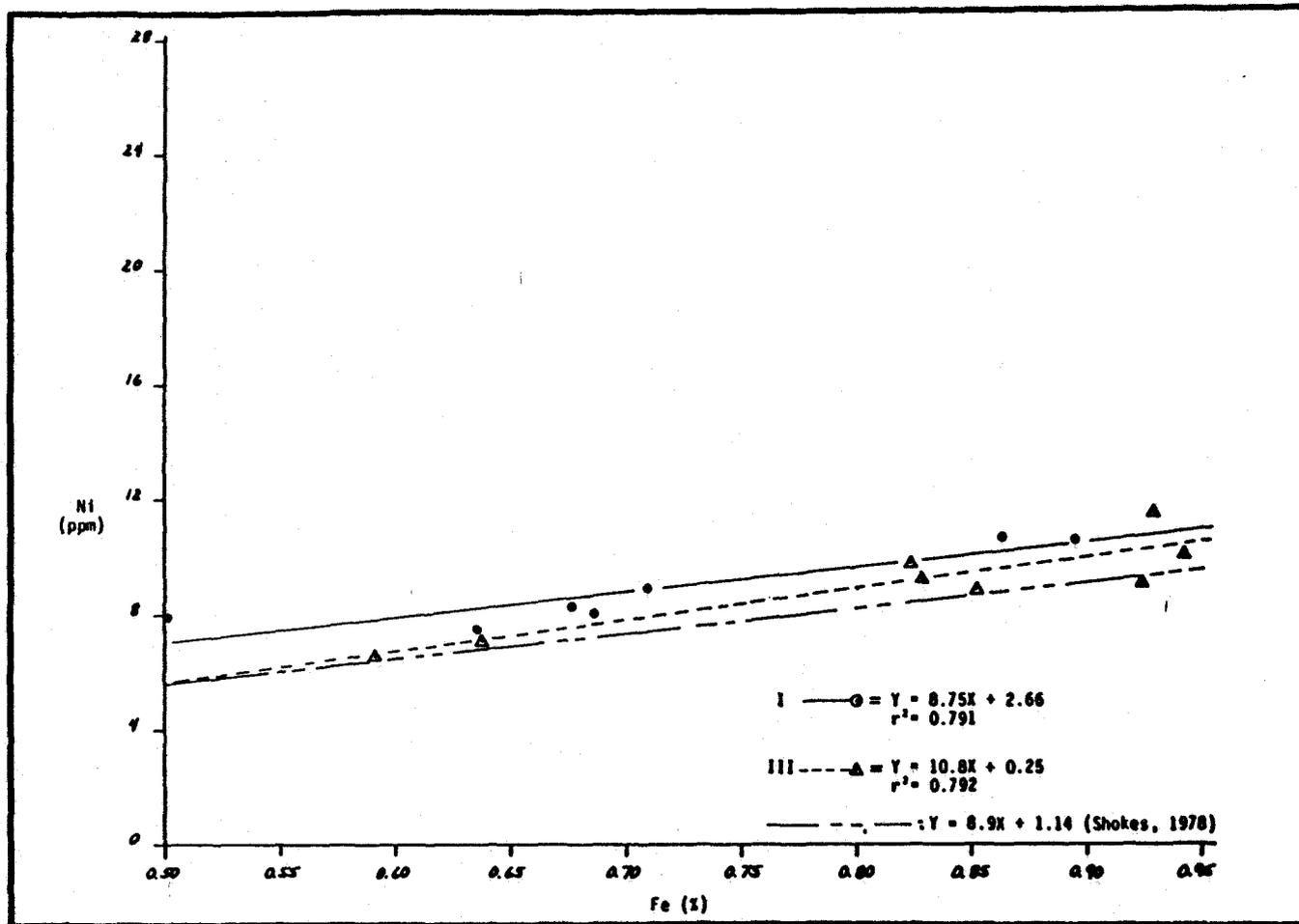


Figure 12. Ni versus Fe in Surficial Sediments from West Hackberry; Summer (I) and Winter (III) Cruises

3.3-55

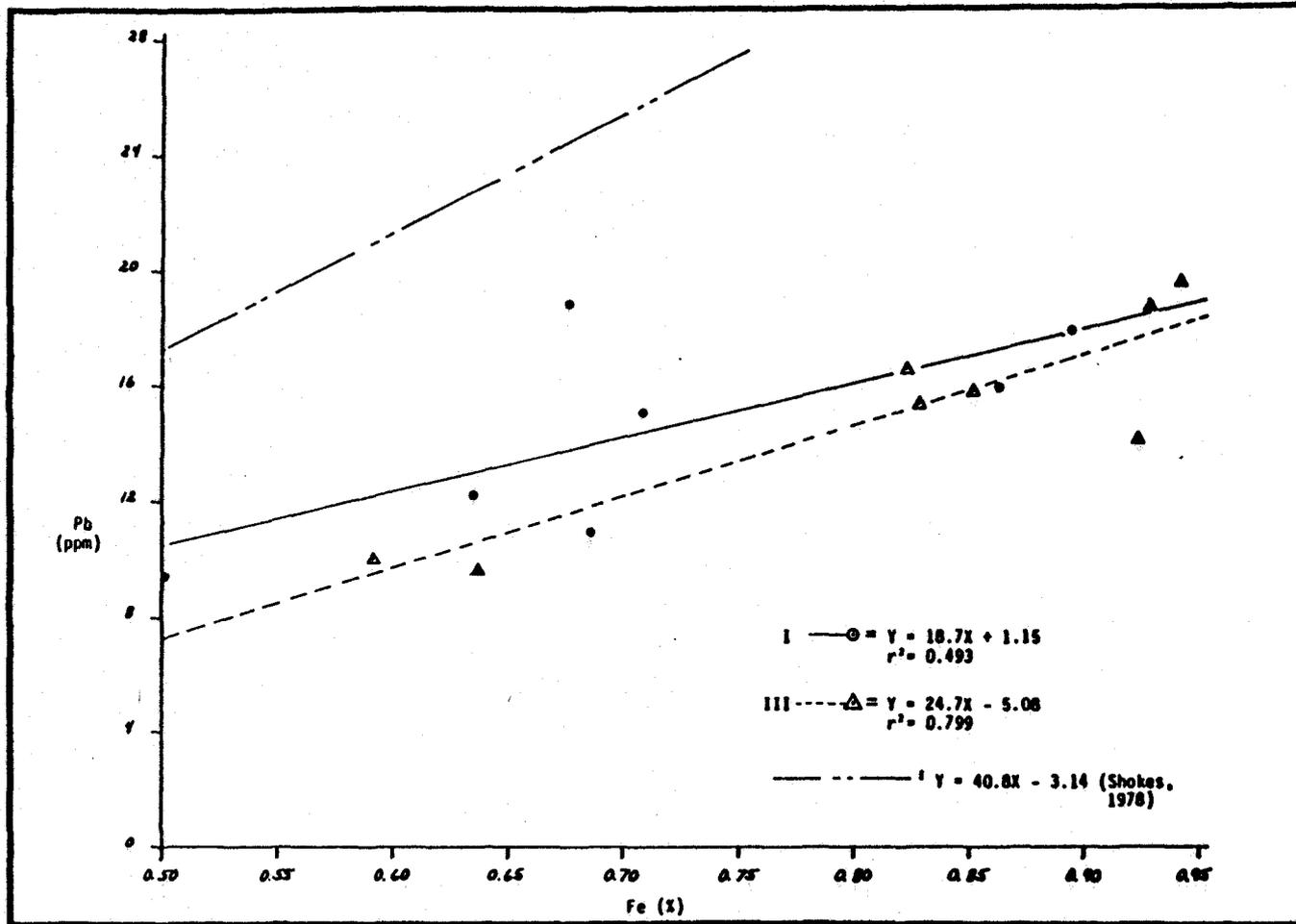


Figure 13. Pb versus Fe Surficial Sediments from West Hackberry; Summer (I) and Winter (III) Cruises

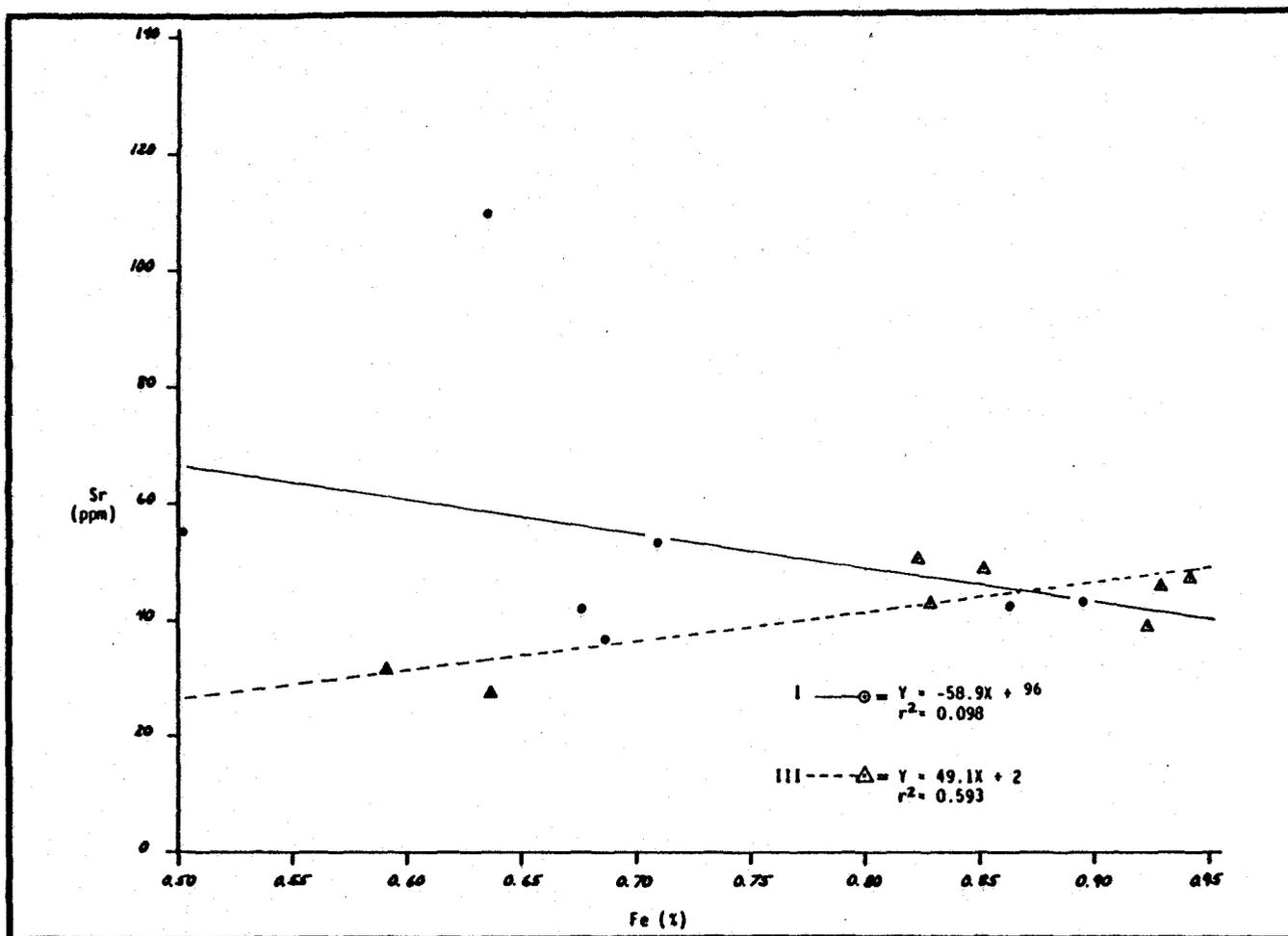


Figure 14. Sr versus Fe in Surficial Sediments from West Hackberry; Summer (I) and Winter (III) Cruises

3.3-57

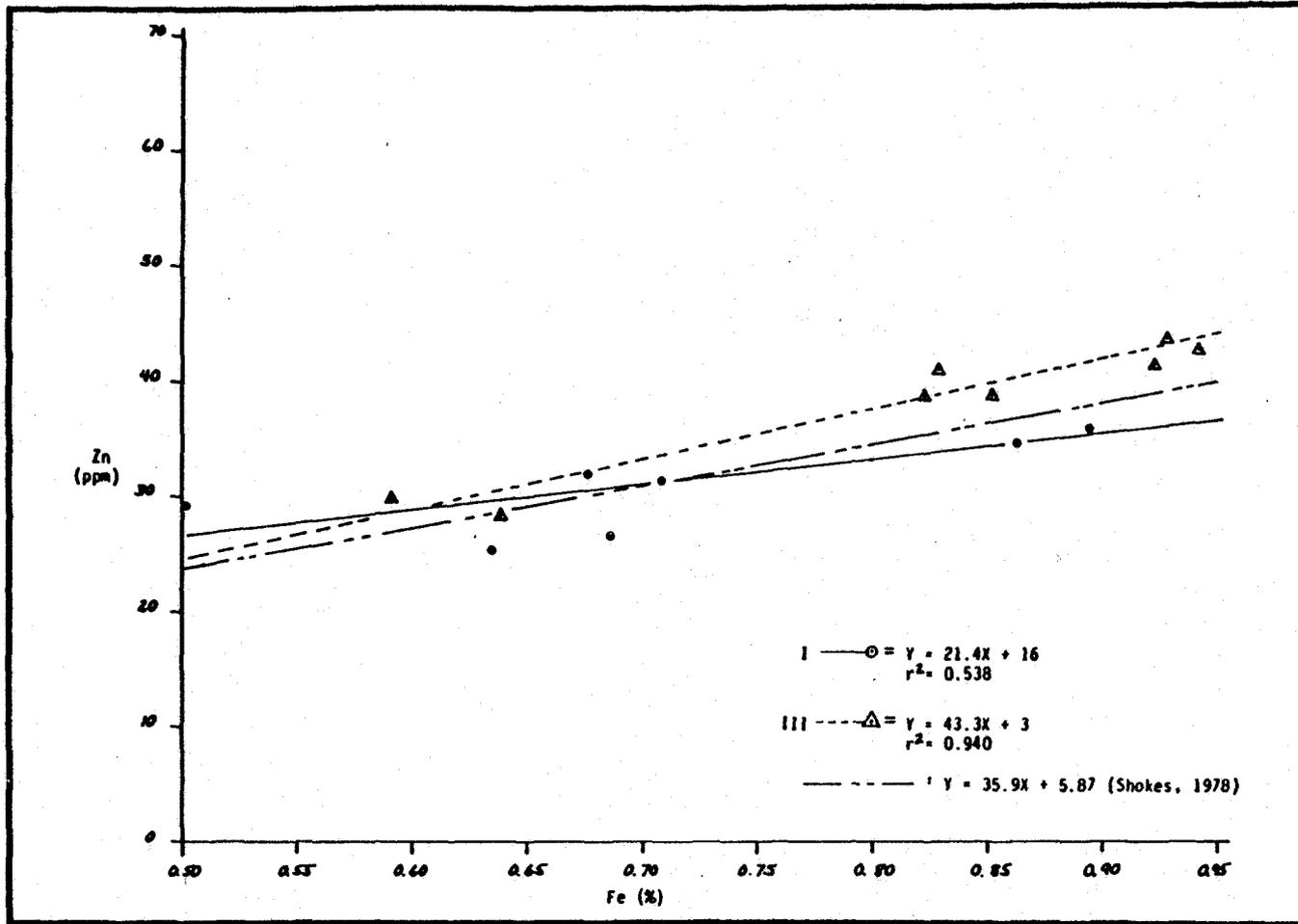


Figure 15. Zn versus Fe in Surficial Sediments from West Hackberry; Summer (I) and Winter (III) Cruises

3.3-58

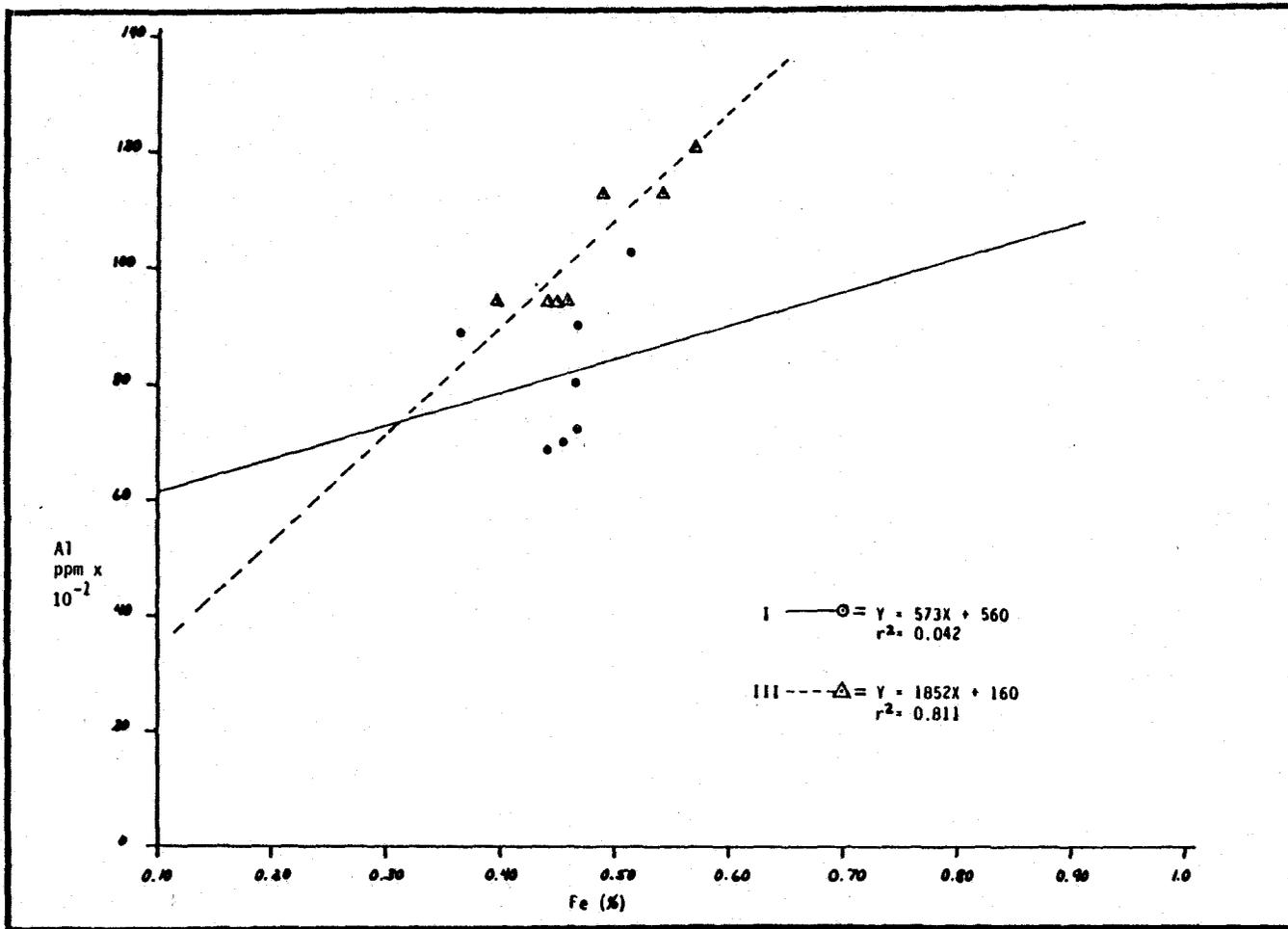


Figure 16. Al versus Fe in Surficial Sediments from Weeks Island; Summer (I) and Winter (III) Cruises

3.3-59

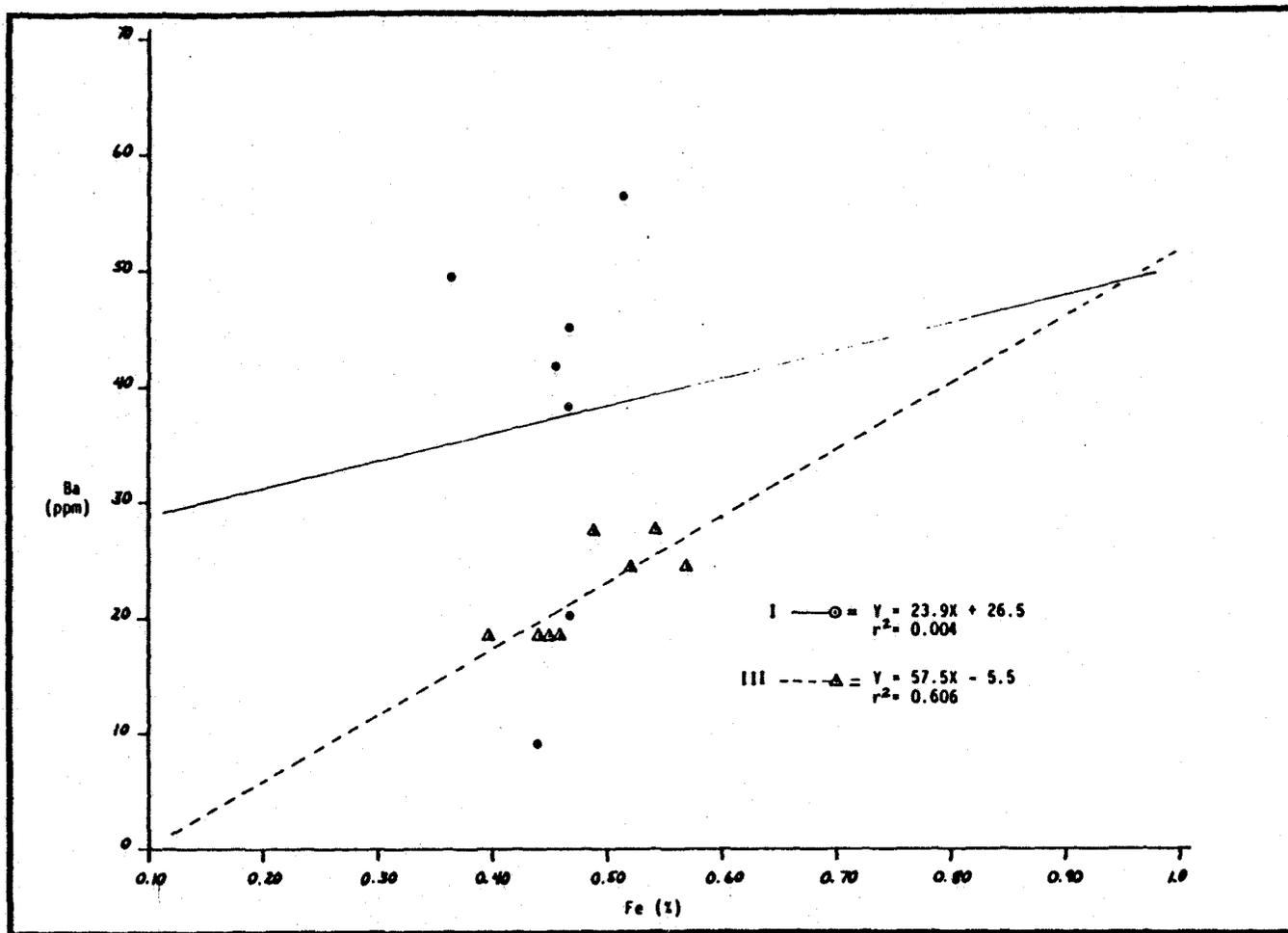


Figure 17. Ba versus Fe in Surficial Sediment from Weeks Island; Summer (I) and Winter (III) Cruises

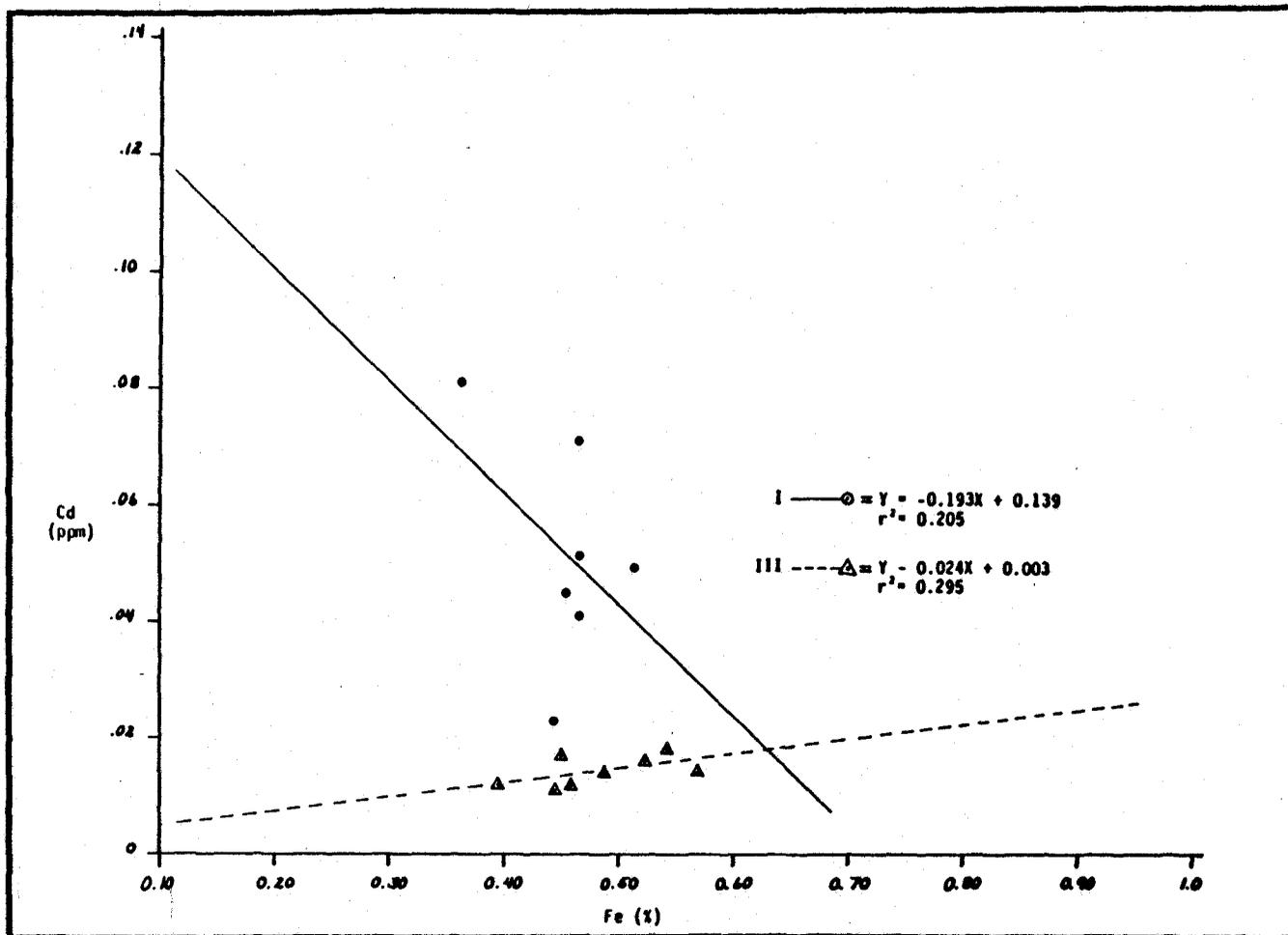


Figure 18. Cd versus Fe in Surficial Sediments from Weeks Island; Summer (I) and Winter (III) Cruises

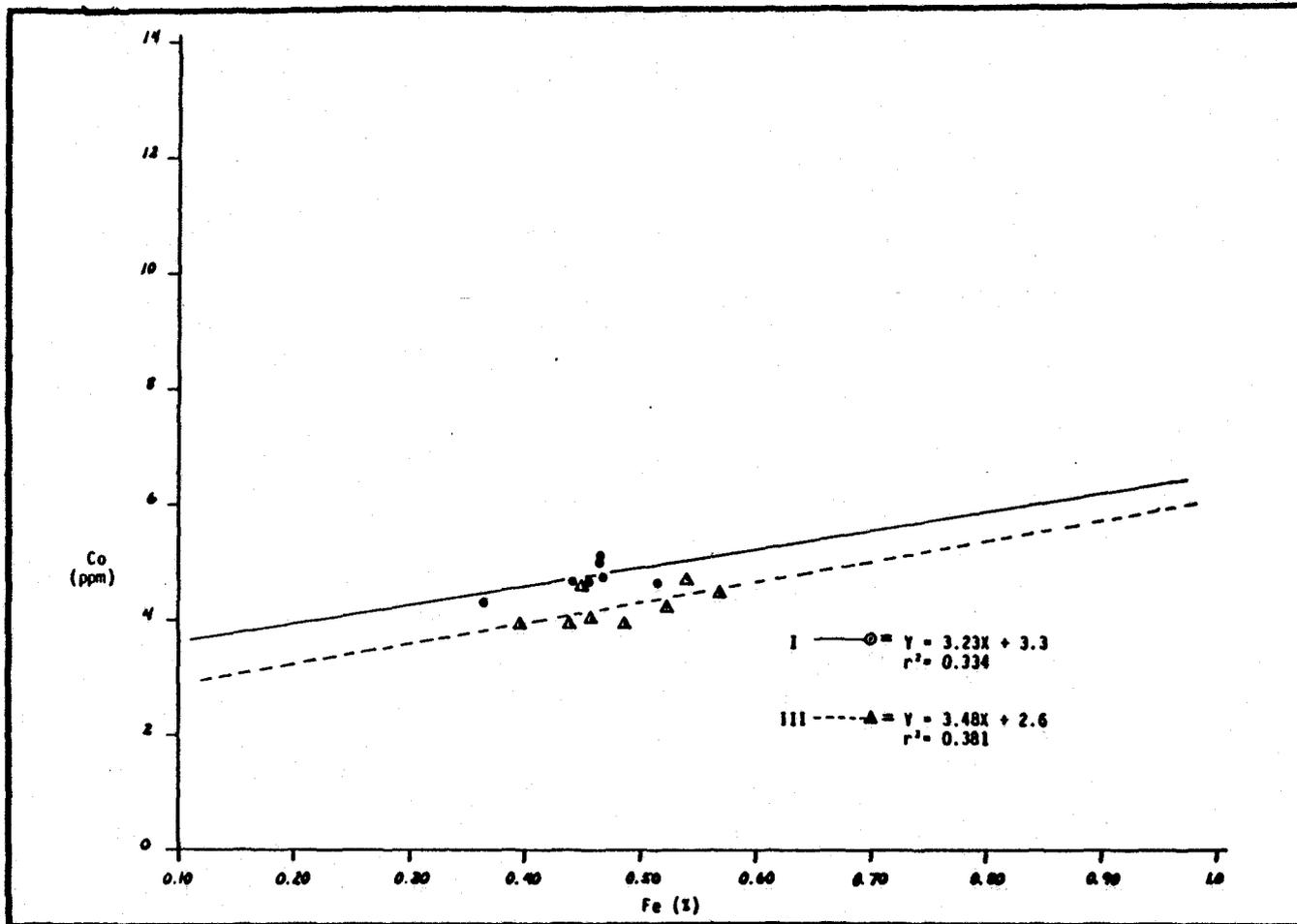


Figure 19. Co versus Fe in Surficial Sediments from Weeks Island; Summer (I) and Winter (III) Cruises

3.3-62

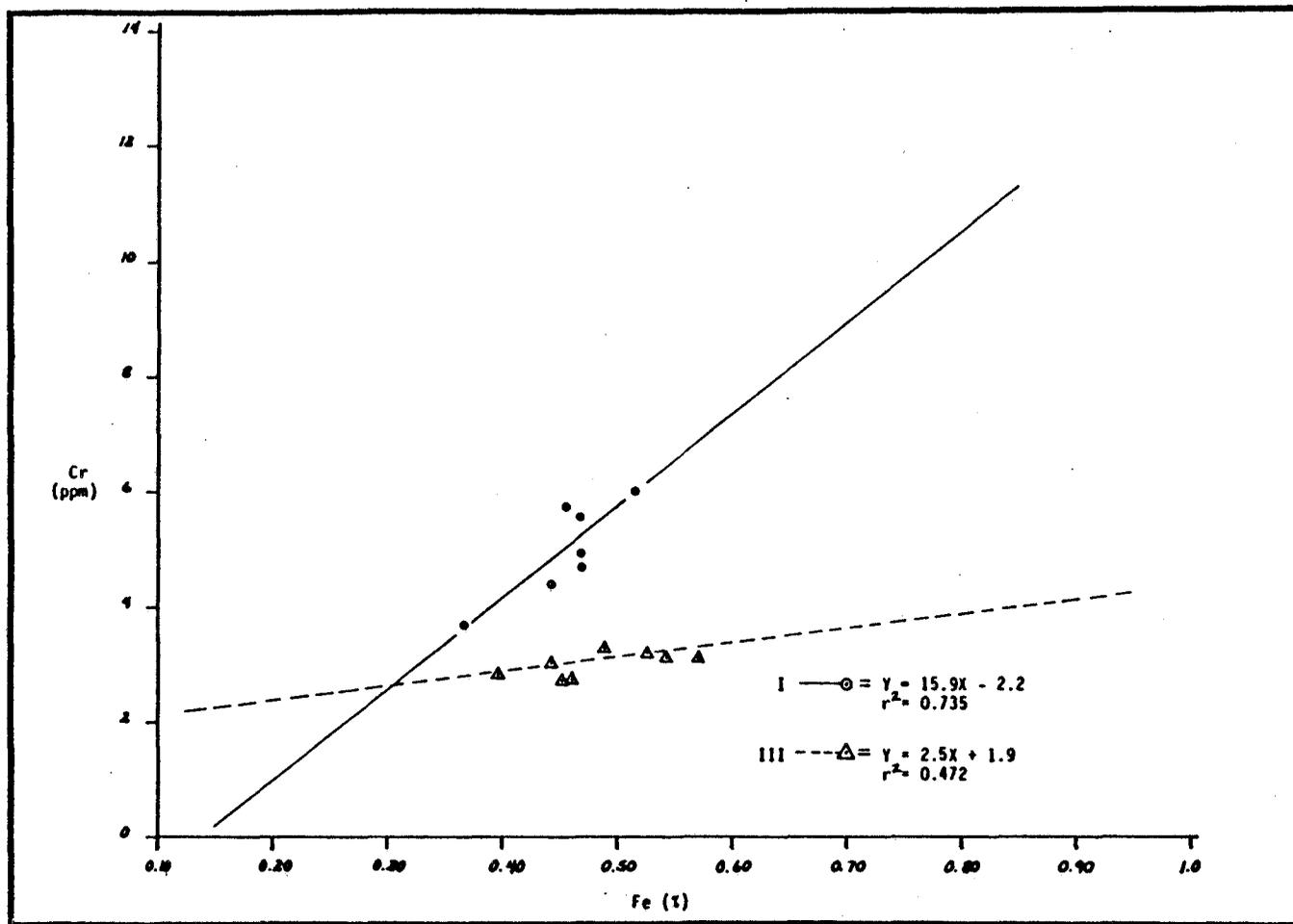


Figure 20. Cr versus Fe in Surficial Sediments from Weeks Island; Summer (I) and Winter (III) Cruises

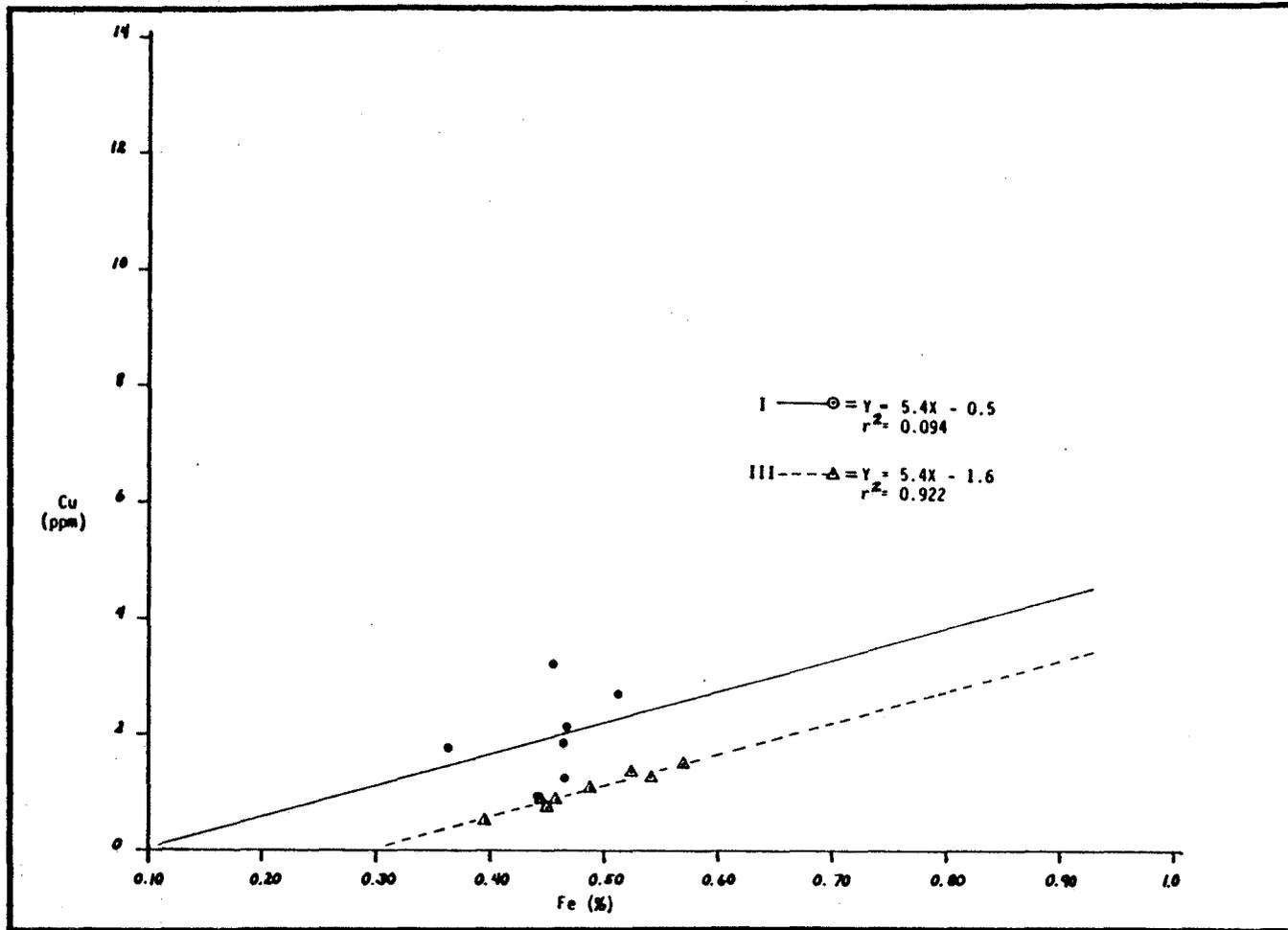


Figure 21. Cu versus Fe in Surficial Sediments from Weeks Island; Summer (I) and Winter (III) Cruises

3.3-64

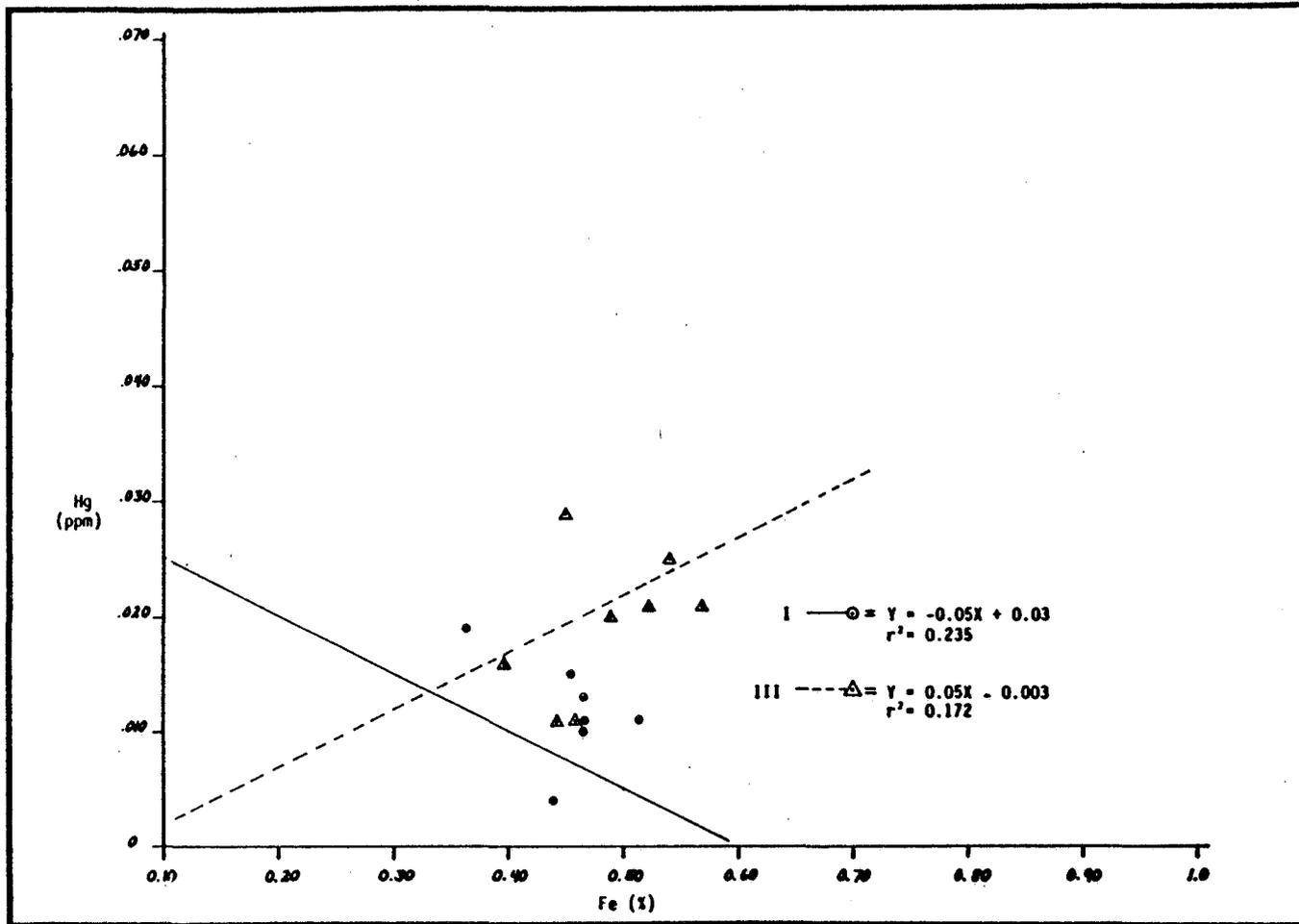


Figure 22. Hg versus Fe in Surficial Sediments from Weeks Island; Summer (I) and Winter (III) Cruises

3.3-65

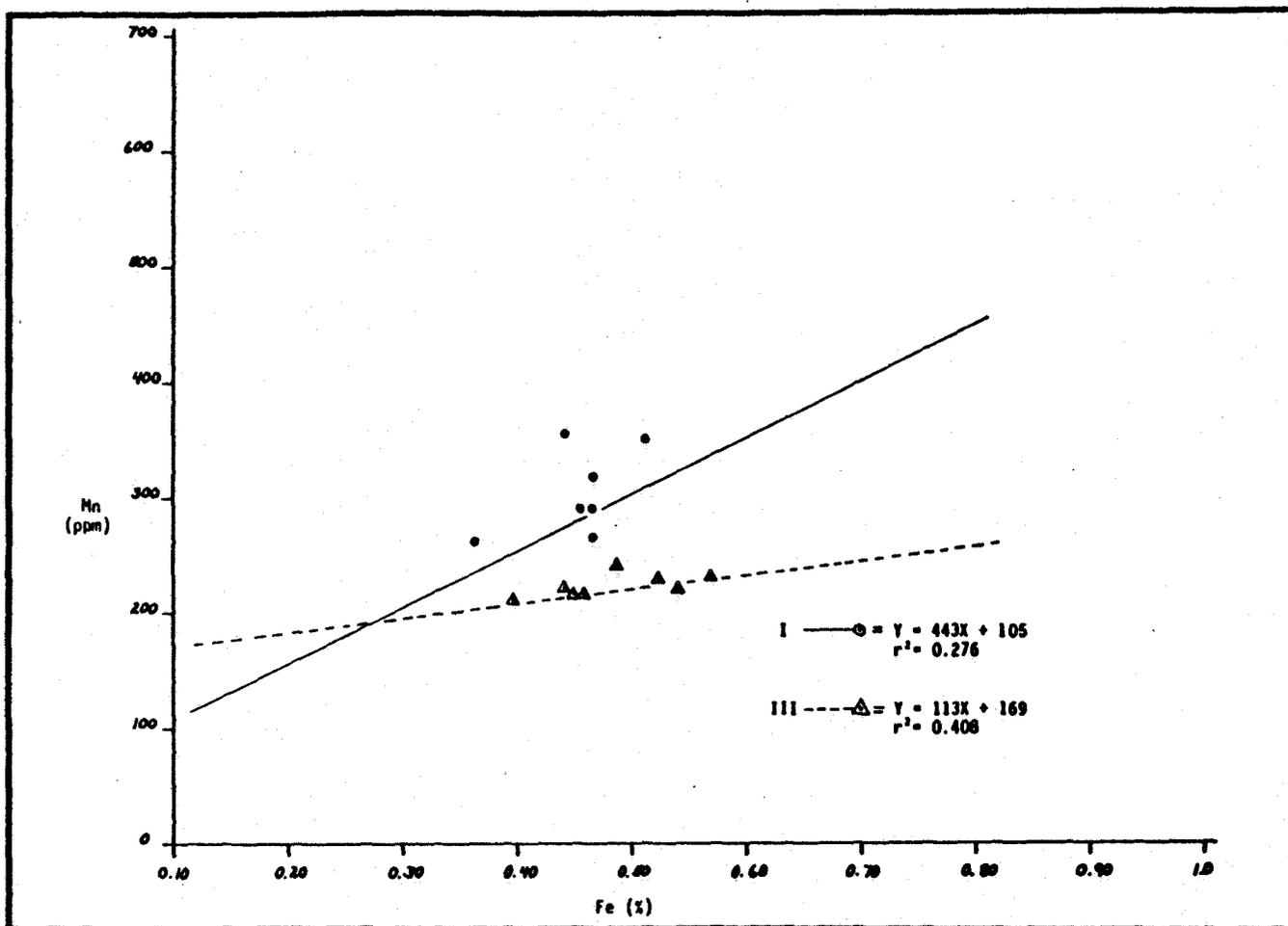


Figure 23. Mn versus Fe in Surficial Sediments from Weeks Island; Summer (I) and Winter (III) Cruises

3.3-66

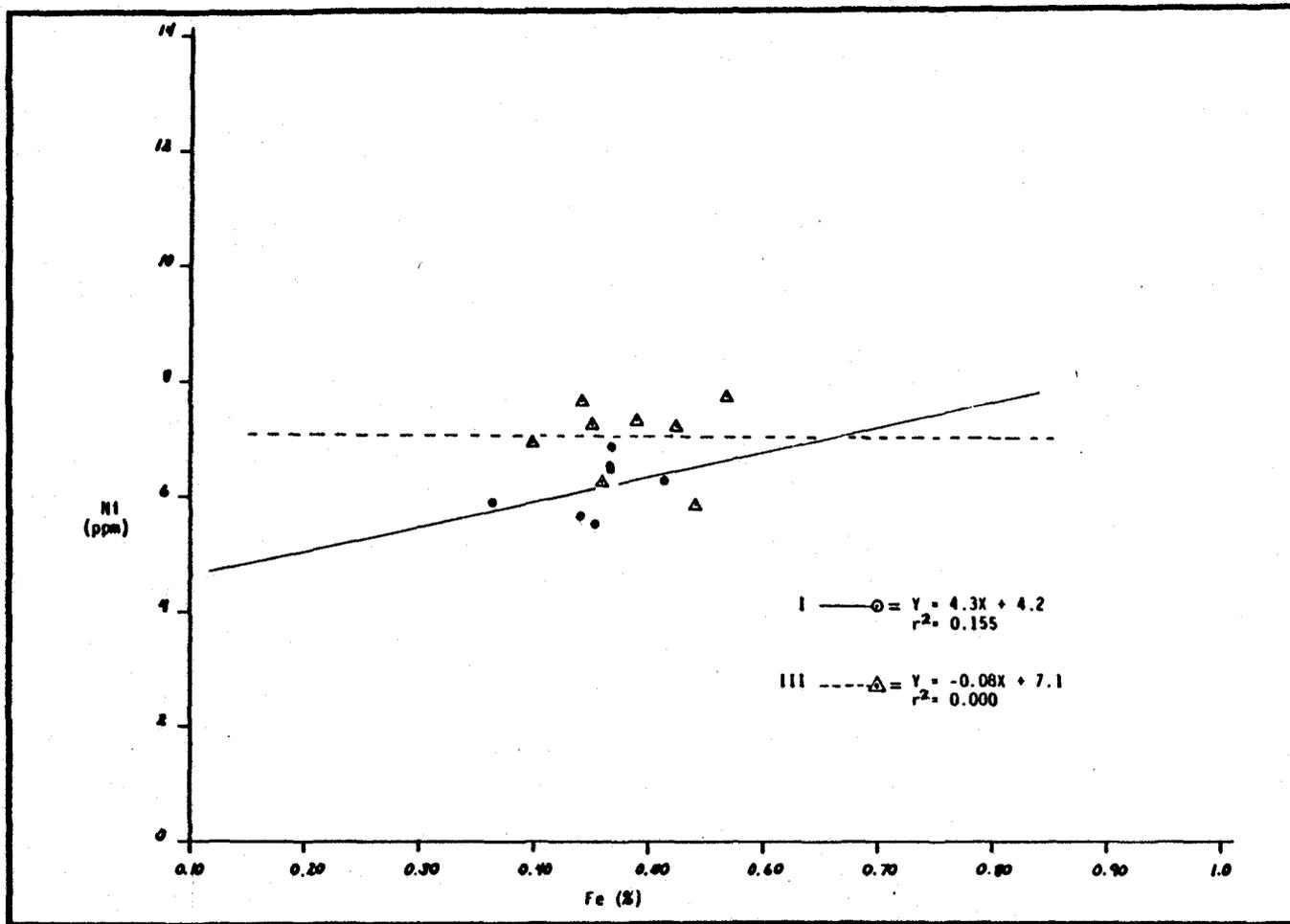


Figure 24. Ni versus Fe in Surficial Sediments from Weeks Island; Summer (I) and Winter (II) Cruises.

3.3-67

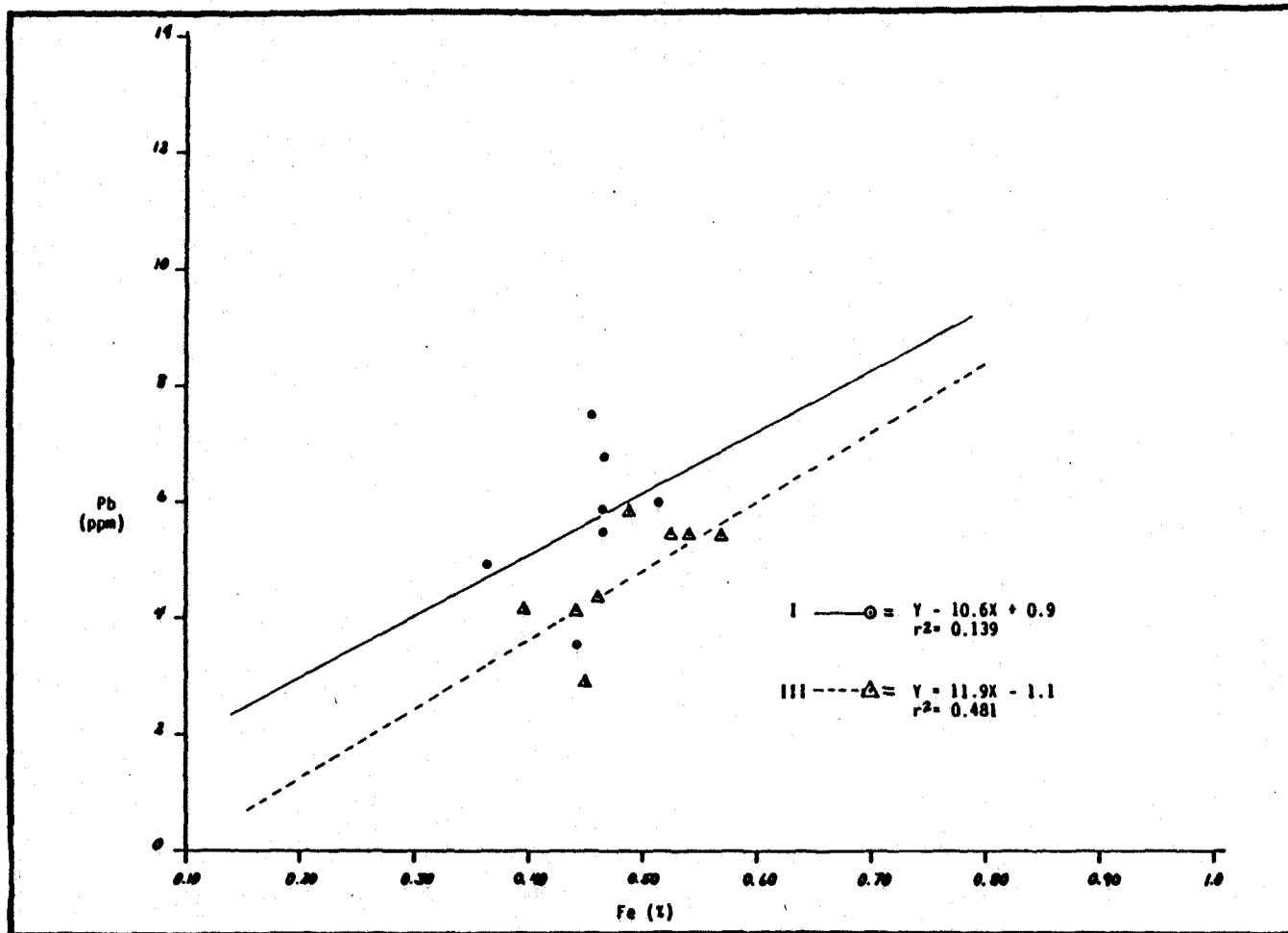


Figure 25. Pb versus Fe in Surficial Sediments from Weeks Island; Summer (I) and Winter (III) Cruises

3.3-68

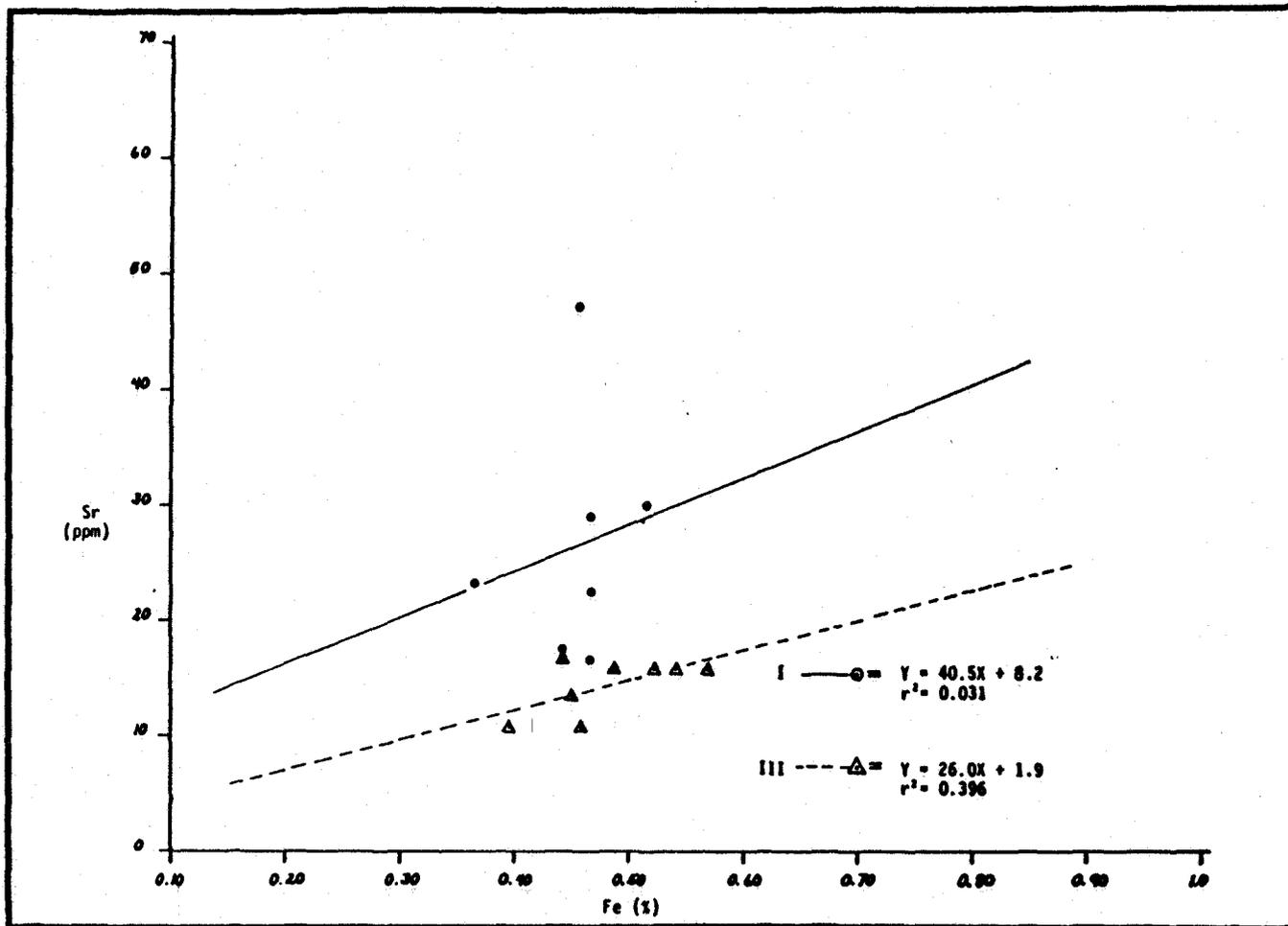


Figure 26. Sr versus Fe in Surficial Sediments from Weeks Island; Summer (I) and Winter (III) Cruises

3.3-69

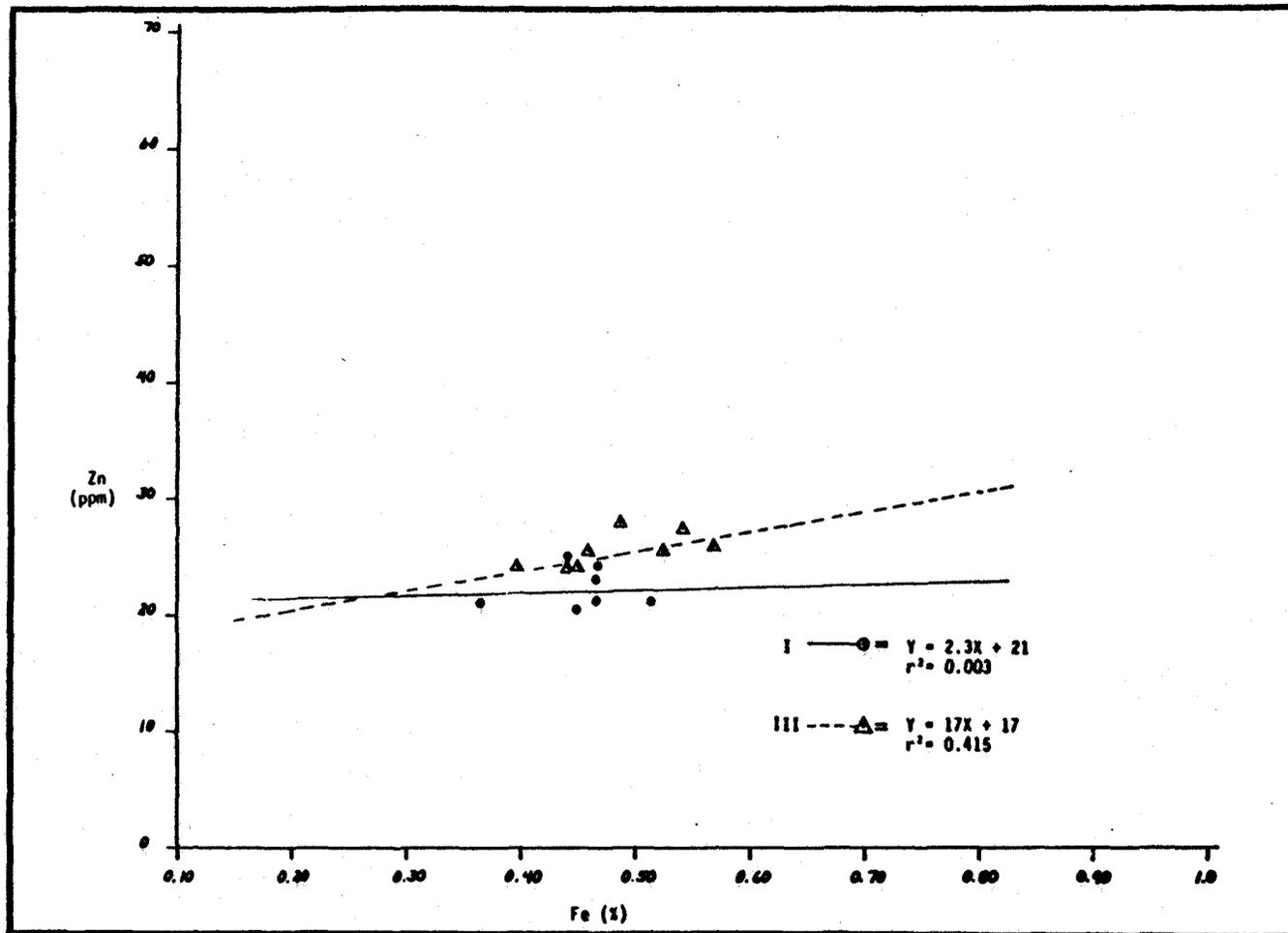


Figure 27. Zn versus Fe in Surficial Sediments from Weeks Island; Summer (I) and Winter (III) Cruises

3.3-70

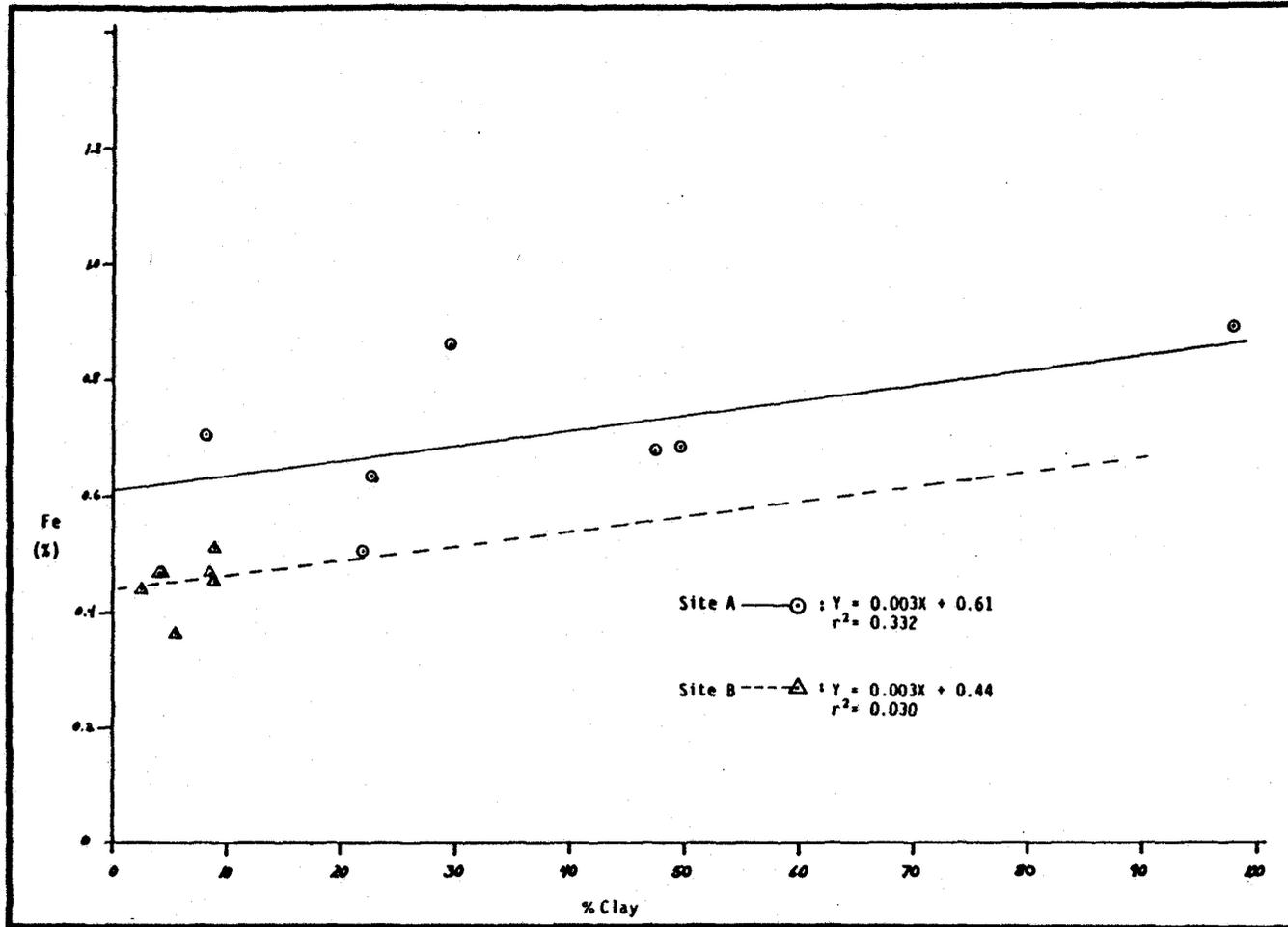


Figure 28. Fe versus % Clay in Surficial Sediments from West Hackberry (A) and Weeks Island (B) Site for Summer (I) Cruise

APPENDIX B
Sample and Data Inventories

Sample and Data Inventories

<u>Sample Type</u>	<u>Number Contracted</u>	<u>Number Collected</u>	<u>Number Analyzed</u>
Epibenthic	56	56	56
Macrocrustacean	56	56	56
Suspended Particulate Matter	56	56	56
Surficial Sediments	36	36	36

3.3-72