

This is to certify that the
thesis entitled
BEHAVIOR OF SELECTED TRACE METALS IN SEDIMENTS
FROM THE CONTINENTAL SHELF OF THE AMAZON RIVER

presented by
Sandra M. Pelowski

has been accepted towards fulfillment
of the requirements for
M.S. degree in Geology

A handwritten signature in black ink, appearing to read "DAVID T. LONG". The signature is written over a horizontal line.

Major professor

David T. Long

Date August 8, 1983



RETURNING MATERIALS:
Place in book drop to
remove this checkout from
your record. FINES will
be charged if book is
returned after the date
stamped below.

ROOM USE ONLY

DO NOT CANCEL

BEHAVIOR OF SELECTED TRACE METALS IN SEDIMENTS FROM THE
CONTINENTAL SHELF OF THE AMAZON RIVER

By

Sandra M. Pelowski

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Geology

1983

Copyright by
SANDRA M. PELOWSKI
1983

ABSTRACT

BEHAVIOR OF SELECTED TRACE METALS IN SEDIMENTS FROM THE CONTINENTAL SHELF OF THE AMAZON RIVER

By

Sandra M. Pelowski

This research was to determine the chemical partitioning of Fe, Mn, Zn, Cu, Pb, Ni, Cr, Co, Ba and Al in sediments of the Amazon River Continental Shelf. Partitioning of metals was determined by a method of selective chemical attacks. The chemical data were studied in raw form and after reduction by R and Q-mode factor analysis. These data and previous studies on shelf hydrodynamics were used to conclude that: (1) the Amazon River is dominate over all other sources of trace metals to shelf sediments; (2) repartitioning of metals in sediments occurs between river and shelf environments; (3) the river sediment can be a potential source of metals to seawater, during passage to seawater. Importance as a source decreases as $Ni > Co > Fe > Cr$; (4) metal concentrations in the shelf sediments are dependent on grain-type; (5) Amazon Shelf Sediments remain oxic to a depth of 450 cm; (6) little repartitioning occurs with sediment depth.

Dedicated to my parents for all their loving support and encouragement.

ACKNOWLEDGEMENTS

I would like to express my sincere thanks to the members of my committee Dr. David T. Long, Chairman, Dr. Grahame Larson, and Dr. Duncan Sibley for their criticism, support and encouragement in completing this project. I would like to thank North Carolina State University, particularly Dr. David DeMaster for supplying the cores for analysis. I would also like to thank my friends and colleagues with whose help and support have made this project endurable.

This thesis was partially funded by a grant from Sigma Xi, the Research Society and a Research Scholarship from Marathon Oil Corporation.

TABLE OF CONTENTS

	Page
List of Tables	vi
List of Figures.	vii
Introduction	1
Significance and Research Goals.	3
Nature of Metals in Continental Shelf Environments	4
Sources of Metals to Shelf	4
Pathways and Sinks in Marine Systems	7
Diagenesis of Metals in Marine Sediments	11
Study Area	13
Methodology.	33
Results and Discussion	39
Chemical Partitioning of Metals in Amazon Shelf Sediments. .	39
Distribution of Metals on the Shelf.	52
Diagenesis of Metals in Amazon Shelf Sediments	73
Source	96
Conclusion	98
References	99
Appendices	
Appendix I Chemical Partitioning Data.	105
Appendix II Graphite Control Settings For Perkin Elmer 560 Atomic Adsorption Spectrophotometer with HGA:2200 Graphite Furnace	126
Appendix III B-Matrix of Weights from Q-mode and R-mode Factor Analysis.	130

LIST OF TABLES

Table	Page
1. Trace metal partitioning of Cr, Mn, Co, Cu, Fe, Ni, Zn in Amazon River suspended load and surficial shelf sediment as a function of sediment type.	41
2. Trace metal partitioning of Cr, Mn, Co, Cu, Fe, Ni, Zn in selected soils of the Amazon River Drainage Basin.	43

LIST OF FIGURES

Figure	Page
1. Study area and location of sampling stations	15
2. Morphostructural map of Amazon Drainage Basin (Stallard, 1980).	17
3. Typical surface-water salinities (0/00) during wet season conditions (April-May, 1968) and dry season conditions (November, 1967) of the surface waters off the Amazon. Profiles in the upper right hand corners show vertical salinity gradients in profiles taken directly seaward of the Amazon mouth. (Milliman <u>et al.</u> , 1975).	19
4. Map of Amazon River, showing locations on mainstream tributaries where sediment loads were measured in 1977 for the study by Meade <u>et al.</u> , 1979.	21
5. Distribution of grain-types at 0-2 depth on the Amazon Continental Shelf.	24
6. Areal distribution of mean grain size on the Amazon Continental Shelf (Nittrouer <u>et al.</u> , 1983)	26
7. Distribution of sediment accumulation rates on the Amazon Continental Shelf based on ²¹⁰ Pb geochronology (Kuehl <u>et al.</u> , 1982)	29
8. Clay mineral distribution along the Amazon Shelf from Nittrouer <u>et al.</u> (1983) and Gibbs (1977)	31
9. Flow chart of selective chemical attacks	35
10. Numerical representation of sediment type from Folk (1974) .	39
11. Contour map of zinc in the detrital fraction of the surface (0-5 cm) sediment of the Amazon Continental Shelf.	54
12. Contour map of zinc in the hydromorphic fraction of the surface (0-5 cm) sediment of the Amazon Continental Shelf. .	56
13. Contour map of total zinc in the surface (0-5 cm) sediment of the Amazon Continental Shelf.	58

Figure	Page
14. Plot of sediment type versus concentration of zinc total. Numbers refer to overlapped points	61
15. Plot of sediment type versus concentration of zinc in the detrital fraction. Numbers refer to overlapped points . . .	61
16. Plot of sediment type versus concentration of zinc in the hydromorphic fraction. Numbers refer to overlapped points .	63
17. Plot of sediment type versus concentration of zinc in the hydromorphic fraction plotted as ranked data	63
18. Contour map of the ratio zinc in the detrital fraction divided by aluminum in the detrital fraction in the surface (0-5 cm) sediments of the Amazon Continental Shelf	66
19. Contour map of the ratio total zinc concentration divided by total aluminum concentration in the surface (0-5 cm) sediments of the Amazon Continental Shelf.	68
20. Contour map of the ratio zinc in the oxide fraction divided by iron and manganese in the oxide fraction in the surface (0-5 cm) sediments of the Amazon Continental Shelf	70
21. Contour map of the ratio barium in the oxide fraction divided by iron and manganese in the oxide fraction in the surface (0-5 cm) sediments of the Amazon Continental Shelf	72
22. Contour map of the ratio zinc in the hydromorphic fraction divided by zinc in the detrital fraction in the surface (0-5 cm) sediments of the Amazon Continental Shelf	75
23. Contour map of the ratio barium in the hydromorphic fraction divided by barium in the detrital fraction	77
24. Sediment type with depth for core 10 (Nittrouer <u>et al.</u> , 1983).	79
25. Concentration of chromium with depth in core 10.	81
26. Concentration of iron with depth in core 10.	84
27. Concentration of manganese with depth in core 10	86
28. Concentration of zinc with depth in core 10.	88
29. Concentration of copper with depth in core 10.	91
30. Concentration of nickel with depth in core 10.	93
31. Concentration of barium with depth in core 10.	95

INTRODUCTION

The geochemical cycle of any trace metal is defined in terms of sources, pathways, and sinks. In continental shelf environments continental fresh water and marine waters mix. Upon mixing more than 95% of the terrigenous sediment contained in the freshwater settles out prior to 3 0/00 salinity (Milliman et al., 1975), thereby making continental shelf sediments a possible major sink for trace metals in exogenic systems.

Two major sources of trace metal influx into oceanic sediments exist; a river source and a hydrothermal source (Schutz and Turekian, 1965). Traditionally, continental runoff has been considered the major source of metals to seawater and marine sediments (Gibbs, 1965; Sholkovitz and Price, 1980). Recently, however, it has been suggested, and in part demonstrated, that hydrothermal activity associated with oceanic ridge systems could also be a significant source of metals to marine environments (Gordon and Corliss, 1979; Edmond et al., 1979; Windom et al., 1971; Brumsack, 1980; Dymond, 1981; Marchig et al., 1982; Bischoff and Dickson, 1975). The significance of this source, though, has as yet not been assessed.

The purpose of this research is to determine the controls on trace metal concentrations in continental shelf sediments as well as their source. The area for this study is the Amazon Continental Shelf which is a relatively contaminate free environment (Drever, 1982). The

working hypothesis for this study is that patterns of trace metal chemical partitioning among various chemical phases in shelf sediments should reflect the controls on their chemical behavior and sources of metals to the sediment (Loring, 1976; Loring, 1982; Luoma and Bryan, 1981).

SIGNIFICANCE AND RESEARCH GOALS

The Amazon River Continental Shelf was selected as a study area because it is an unpolluted system whose river source drains through diverse environments. Hence, it offers an excellent opportunity to study trace metal geochemical behaviors. It is also one of the major rivers of the world, supplying 18% of all river water to the ocean. Consequently, the study of the nature of trace metals in the associated shelf sediments should be particularly important in helping to understand the chemical processes occurring in shelf sediments.

The goals of this research are to:

- (1) Determine the partitioning fate of selected trace metals upon interaction with shelf sediments,
- (2) Determine the fate of selected trace metals during shelf sediment diagenesis,
- (3) Define trace metal sources to shelf sediments.

NATURE OF METALS IN MARINE AND CONTINENTAL SHELF ENVIRONMENTS

This section discusses previous work on the geochemical cycle of elements in marine environments. The geochemical cycles are defined in terms of sources, pathways, and sinks of the elements. Discussion is focused on those aspects of the marine environment that can be related to the geochemical behavior of metals in continental shelf environments. Trace metal diagenesis in marine sediments will also be discussed.

Sources of Metals to Shelf:

Sources of trace metals to marine and therefore continental shelf environments have been summarized by Schutz and Turekian (1965) as:

- (1) stream and river,
- (2) submarine volcanism,
- (3) submarine alteration or solution of non-volcanic material,
- (4) eolian,
- (5) glacial discharge, and
- (6) anthropogenic.

Eolian and glacial discharge are considered minor sources of trace metal input into the continental shelf (Schultz and Turekian, 1965). Submarine alteration and submarine volcanism on the other hand are difficult to distinguish as unique sources to shelf sediments and are therefore classified together as a ridge source. In the case of the Amazon River system, the anthropogenic input is considered negligible

(Drever, 1982). Ridge systems and river runoff can therefore be considered the two major sources of trace metal input into the shelf sediments.

Several marine environments have been studied (estuaries, deep ocean sediments, ridge systems, continental shelf and fjords) with regard to the delineation of separate trace metal sources. Factor analysis was used to define the relative importance of each source input (Imbrie and Van Andel, 1964). In this research two basic types of multivariant factor analysis were utilized, Q-mode and R-mode. Q-mode correlates two samples on the basis of the variables, whereas R-mode compares the relationships between the variables on the basis of the samples (Kerlinger, 1973; Nelson, 1981; Parks, 1970; Imbrie and Van Andel, 1964).

Mathematically, Q and R-mode factor analysis treat each sample or variable as a vector and resolves it into a small number of component vectors (Imbrie and Van Andel, 1964). Frequently, the original or raw data matrix must be transformed, but this transformation should in no way affect the accuracy of the program because relative proportions of variables are preserved (Bopp, 1981; Loring, 1982). This transformation of raw data allows every variable to have equal weight in the statistical program despite the ranges observed in variable's concentration.

The results of Q-mode factor analysis are written in two matrixes, the F_S -matrix and the B-matrix. The F_S -matrix is a table listing combinations of the variables that define the compositional end-members for each of the factors. The B-matrix is a matrix of the influence exerted by each end-member (i.e., matrix relates the intensity of

correlation between the factors) on each sample (Bopp, 1981; Bopp and Briggs, 1981). In the scaled varimax factor listing (F_S -matrix), if all variables were equally represented their varimax factor value would be 1.000. A strong positive value represents a positive correlation. A zero value represents no correlation and a strong negative value represents an inverse correlation with the matrix for that factor. A contour map of the matrix for each factor is generated and illustrates the distribution of factors in the study area (Bopp, 1981; Bopp and Biggs, 1981).

Most marine environments that have been studied have shown several source inputs. For example, Bopp and Biggs (1981) have identified three sources of metals to Delaware Bay sediments (representative of (1) a terrigenous natural background level source; (2) an oceanic source; and (3) a river source). Holmes and Martin (1978) on the other hand have determined two sources of trace metal origin to the continental shelf in the Gulf of Mexico (a natural background source and an anthropogenic source). In addition, Loring (1976, 1976b, 1979, 1982) has delineated two sources of trace metal input to the Saguenary Fjord; an industrial source and a natural source. Harding and Brown (1975) also investigated trace metal sources in the sediments of the Pamlico River Estuary, North Carolina. They found that the sources include a background (natural weathering) input source, and an industrial (anthropogenic) input source. Bender et al., (1971) studied sediments in the East Pacific Rise and found a seawater source and a ridge volcanism source. Edmond et al., (1982) dealt with sediments in the East Pacific Rise and concluded that the hydrothermal input in the oceans are substantial compared with fluvial transport. Heath and

Dymond (1981) identified 5 sources of input to Nazca plate sediments (a biogenic, detrital, hydrothermal, authigenic and solution residue). The detrital, hydrothermal and biogenic sources are the three dominate sources of trace metal input to the Plate sediments. The detrital component is the major input source for trace metals to the Plate sediments near the continental coast of South America, whereas the hydrothermal component is the major source of input to ocean sediments near the East Pacific Rise. The hydrothermal source is undetectable at 2500 km east of the East Pacific Rise (Heath and Dymond, 1981; Dymond, 1981).

The previous research cited above has shown that (1) when an anthropogenic source is present it is dominate; (2) when a study area is located near a ridge system, the hydrothermal source is dominate; (3) when a study area is located near a continental coast, the detrital input is dominate and (4) if 2500 km from a ridge source, ridge input is undetectable. Therefore, the concentrations and distributions of trace metals in a continental shelf environment should be able to be interpreted in terms of a single source.

Pathways and Sinks in Marine Systems:

The pathways of metals in exogenic systems can be defined in terms of five mechanisms of transport (Kharkar et al., 1968). They are:

- (1) in solution (free and complexed),
- (2) in the lattice of minerals of the suspended load,
- (3) associated with oxides of the suspended load,
- (4) adsorbed on the minerals of the suspended load, and
- (5) associated with solid organic material.

Trace metals can be removed from active transport in the marine environment by:

- (1) mechanical deposition of larger particles,

- (2) coagulation of the colloidal fraction,
- (3) humus colloids uptake
- (4) plankton microorganism extraction,
- (5) precipitation as oxide coatings,
- (6) adsorption in cation exchange sites, and
- (7) (in anaerobic conditions) forming insoluble sulfides
(Krauskopf, 1956; Morozov, 1979; Harding and Brown 1975).

These seven removal mechanisms would be the major sinks of trace metals in marine and therefore continental shelf systems.

The chemical nature of the pathways and sinks of metals are very similar as shown above and reflect whether or not the metal is in an active state of transport. The chemical nature of a metal in exogenic systems (independent of its state of transport) is defined then by the chemical state it is in:

- (1) dissolved (free and complexed),
- (2) adsorbed on or in exchange position in clays,
- (3) precipitated as hydroxides,
- (4) adsorbed on or co-precipitated with Fe and Mn oxides,
- (5) associated with organic matter,
- (6) precipitated as sulfides,
- (7) in lattice sites of minerals.

States of 2-6 are the states of the metal associated with the sediment. States 2-5 are collectively called the hydromorphic fraction or phase and state 6 is called the detrital or residual fraction. Metals in these fractions are normally differentiated by a series of selective chemical attacks on the sediment as discussed in the methods section. After the sediment has been chemically characterized, the metals are said to be partitioned among the different fractions of the sediment.

The following is a summary of work that has been done in defining these fractions for metals in marine sediments. Loring (1975, 1976, 1976b, 1979, 1982) studied trace metals in the sediments of the Saguenary Fjord. He found that the highest concentrations are found in mud (fine-grained) sediments and that the lowest concentrations occur

in the sandy (coarse) sediments (i.e. Co, Ni, Cr, Zn, Cu, and Pb concentrations increase with decreasing grain size). The detrital phase of Co, Ni, Cr, Zn, Cu, and Pb concentrations account for 71-98% of the total elemental concentrations in Fjord sediments. Holmes and Martin (1978) trace Cr, Cu, Fe, Mn, Ni, Zn, Ba and Pb migration in a continental shelf environment in the northwest Gulf of Mexico. They concluded that the most important factor affecting physical and chemical process within the sedimentary environment are variation in sediment accumulation rates. Brannon et al., (1979) researched Cu, Fe, Mn, and Zn in sediments from Mobil Bay, Alabama. They defined selective extraction phases investigated as adsorbed (ion exchangeable) on sediment material, reducible (solubility and migration controlled by oxidation-reduction reactions), bound in organic matter and residual. Iron in the reducible phase has a value of 68-79%. Of secondary importance to Fe is the organic phase (12-19%). Combined, the reducible and organic phases represent 90% of the total Fe concentration in the sediments. Manganese has 15-35% of total metal concentration in the reducible phase, 35-44% in the organically bound phase and 8-12% in the residual phase. Together, the organically bound, residual and reducible phases account for 78-80% of total Mn concentrations in the sediments. Copper has 51-61% of total metal retained in the residual phase. The organically bound phase is of secondary importance with 32-41% of total metal concentration. Combining the residual and organic phases, they represent 92% of total Cu in the sediments. Zinc has 52-59% of total metal concentration held in the organic phase and 38-44% in the residual phase. United, they equal 95% of total Zn concentration to the Bay sediments (Brannon et al., 1974). Harding and Brown (1975) studied Co,

Cr, Cu, Ni, Pb and Zn in the Pamlico River Estuary. They found that factors affecting trace metal uptake in sediments included an enrichment of trace metal concentrations in clays and organic matter. They stated that the surficial distribution of fine sediments appear to be due to the patterns of water circulation. Trace metal incorporation with clay sediments and organic matter in the estuary were dependent on temperature, pH, Eh and clay mineral type (the relative importance of each was undefined). Harding and Brown (1975) explain trace metal dispersal in the estuary based on the relative mobility of the elements. Cr is the most immobile element studied. It quickly drops out of the water column upon entering the estuary and is not dispersed throughout the Bay sediments. The moderately immobile trace elements, Co, Cu, Ni and Pb (relatively compared to the other elements studied) remain in solution, are circulated from their industrial source and are dispersed in clays and organic matter throughout the estuary sediments. Cosma et al. (1979) studied trace metals (Cr, Cu, Ni, Mn) in surface sediments in the continental shelf area between Arenzano and Capo Noli in the Ligurian Sea. Cr was controlled by pollution inputs. Nickel concentrations were accounted for by stream input of eroded basic rock outcrops. Copper concentrations are associated with the organic fraction. Manganese concentrations are related to sediment textures. Turekian and Imbrie (1966) researched deep sea sediments from the Atlantic Ocean. They found that the trace elements Ba, Co, Cu, Ni, Pb, Cr and Mn showed no correlation with clay mineralogy or depth of water. There was a strong correlation of metals Mn, Ni, Co with areas of low clay accumulation rates possibly due to a fine grained pelagic component. Morozov (1979) studied migration of Fe, Mn, Zn, Cu, Ni, Co, Cr,

and Pb around the mouths of several rivers. The general conclusions of this investigations were: Trace metal concentration in the suspended and dissolved forms decreased in the sequence river-estuary-sea-ocean; The portion of suspended Fe and Mn forms decrease from the river (97%) to ocean (7%); the mechanical deposition of the larger particles occurs near the mouth of a river; coagulation of the colloidal fraction and the humus colloids take up a large fraction of trace metals at the mouth of a river; and sea/fresh water zones show extensive plankton microorganism development which extract metals from the water column.

Summarizing past research these conclusions can be drawn: (1) trace metal concentrations increase with decreasing grain size; (2) there is no correlation with clay mineralogy or depth of water from the Atlantic deep-sea sediment core samples; (3) an important factor affecting processes in a basin is the variation in sediment accumulation rates; and (4) the relatively immobile elements will drop out of the water column upon entering an estuary from a river source.

Diagenesis of Metals in Marine Sediments:

Chemical conditions of sediments can change with depth as a result of compaction and age (Bonatti et al., 1971). Factors affecting the chemical conditions are: changes in Eh, sediment composition, temperature, bioturbation, and pH (Yen and Tang, 1977). Eh values normally decrease with depth in sediments (Addy et al., 1976). The relatively mobile elements should be enriched in the oxidized sediment zone (Ni, Fe, Mn, Co) (Addy et al., 1976; Holmes and Martin, 1978; Heath and Dymond, 1981); while less mobile elements like zinc and copper show little migration in the sediment column (Addy et al., 1976). Brooks et al., (1968), Bonatti et al., (1971) concluded that Fe and Cu are not

mobile elements and show no overall trend to increase with sediment depth, and Fe seems to show inconsistent behavior during diagenesis. Ba and Pb are also relatively immobile elements and according to Holmes and Martin (1978) show no overall trend with depth. Brannon et al., (1979) stated that no patterns of migration for the elements Fe, Mn, Cu and Zn could be conclusively drawn. Generally, if an environment is reducing, the elements with higher redox potentials should go into solution and if an environment is oxidizing they should precipitate. In this way the higher redox potential elements migrate up the sediment column, creating an enriched metal concentration on the top centimeters of the ocean floor (Addy et al., 1976).

In summary, these investigations show that: (1) Ni, Co, Mn should be enriched in the upper centimeters of the sediment column; (2) Ba, Pb, Zn, Cu should not be enriched nor depleted in the upper centimeters of the sediment column; and (3) Conflicting Fe behavior exists.

This summary shows that much research still needs to be done. No research involving source delineation in unpolluted continental shelf sediments has been reported. In this investigation, the chemical partitioning data on the Amazon Continental Shelf coupled with factor analysis can aid in the resolution of trace metal sources to shelf sediments. Chemical partitioning data with depth in Amazon Shelf sediments will help to eliminate conflicting diagenetic trace metal behavioral observations. Exploring trace metal behaviors encountered when fresh and oceanic waters merge will aid in the investigation of the controls or aid in determining the controls of geochemical cycling of trace metals.

STUDY AREA

The study area is located on the Continental Shelf at the mouth of the Amazon River (Figure 1) and extends from a latitude of 52°W to 46°E and a longitude of 2°S to 6°N. The Amazon River Basin lies entirely in the central equatorial area, extending from 5°N to 20°S longitude and from 50°W to 77°W latitude (Gibbs, 1967; Stallard, 1980). The Amazon River drains a diverse climatic area ranging from the arctic Andean Mountains to the tropical rain forests. Temperatures vary from less than 15°C in the Andes to 28°C in the tropical forests (Gibbs, 1967).

The Amazon River Drainage Basin is the largest in the world, draining an area $6.3 \times 10^6 \text{ km}^2$ (Keller, 1962). The river drains diverse geological environments (Figure 2) comprising active orogenic zones, epiorogenic uplift zones, stable cratonic zones and active sedimentary basin zones (Gibbs, 1967; Stallard, 1980). The Amazon River has an average discharge of $1.7 \times 10^5 \text{ m}^3/\text{sec}$, supplying 18% of all water from rivers into the ocean (Oltman, 1968; Drever, 1982). Sediment influx ranges from $8\text{--}9 \times 10^8$ tonnes/year; influx was measured at Óbidos a site marking 80% river flowage (Figure 4) (Holeman, 1968). The dissolved load is 2.9×10^8 tonnes/year (Meade et al., 1979). The clay content at the mouth of the river consists of 33% illite, 31% kaolinite, 27% montmorillite, and 2% chlorite (Milliman et al., 1975).

Precipitation in the Amazon River Basin ranges from less than 2000 mm/year to over 3500 mm/year (Stallard, 1980; Hoffman, 1968). The

Figure 1. Study area and location of sampling stations.

Figure 2. Morphostructural Map of Amazon Drainage Basin (Stallard, 1980).

1. Amazon Trough
2. Subandean Trough
3. Shields
4. Western Cordillera (Cordillera Occidental)
5. Intercordilleran Zone (includes the altiplano regions)
6. Eastern Cordillera (Cordillera Oriental)
7. Subandean Uplifts

Symbol key:

CONSTRUCTIVE STRUCTURAL RELIEF ELEMENTS

-  Trend of folded young mountain ranges of the Andean system.
-  Crest of horst mountains and monoclines.
-  Fault flexure.
-  Lithological. Step, escarpment.

DESTRUCTIVE NON-STRUCTURAL RELIEF ELEMENTS

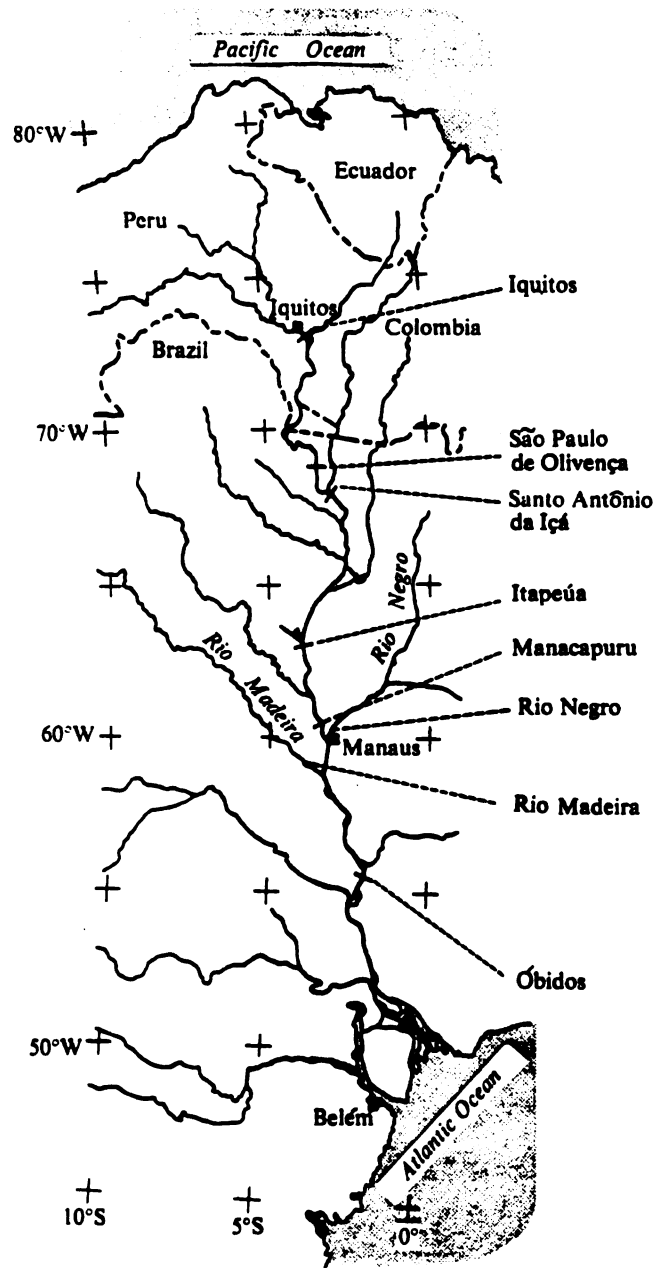
-  Old erosion. Surfaces of Mesozoic Tertiary age.
-  Occurrence of inselbergs.
-  Crest of residual relief.

ACCUMULATIVE RELIEF ELEMENTS

-  Quaternary fluvial. Alluvial or eolian deposits (in the Andes including glacio-fluvial and volcanic tectonic mudflow deposits).
-  Occurrence of Late-Tertiary and Quaternary lacustrine or marine deposits.
-  Pleistocene loess with ash-admixtures.
-  Sand dunes.
-  Pleistocene glacial deposits.
-  Occurrence of volcanoes.
-  Salt flat.
-  Lake.

Figure 3. Typical Surface-water salinities (0/00) during wet season conditions (April-May, 1968) and dry season conditions (November, 1967) of the surface waters off the Amazon. Profiles in the upper right hand corners show vertical salinity gradients in profiles taken directly seaward of the Amazon mouth. (Milliman et al., 1975).

Figure 4. Map of Amazon river, showing locations on mainstream tributaries where sediment loads were measured in 1977 for the study by Meade et al., 1979.



river has a low buffering capacity and pH values range from 6.5-7.5 throughout the year (Schmidt, 1972). The waters of the Amazon also appear thoroughly mixed vertically (Gibbs, 1967).

The Amazon River flows onto the shelf and into the Guiana Current. The Guiana Current is an extension of the South Equatorial Current which flows in a northwesterly direction along the east coast of South America (Ryther et al., 1967; Eisma et al., 1971). At the mouth of the river, 95% of the terrigenous sediment from surface waters settle out prior to 30‰ salinity (Milliman et al., 1975). Figure 3 shows surface water salinities for two seasons--the dry season, November, and the wet season, April-May.

The width of the Shelf ranges from 100 to 300 km. The bathymetric chart (Figure 1) of the Continental Shelf reveals a relatively flat inner shelf to the 40 meter isobath. There is an abrupt change at this point and a steepening in slope appears until the 60 meter isobath. The change of slope represents the foreset of a subaqueous prograding delta (Kuehl et al., 1982; Nittrouer et al., 1983). Surface grain size type distribution are shown in Figure 5. The upper two centimeters of shelf sediments are composed of (1) a mud (silt and clay) zone occupying the inner shelf seaward and northwestward of the Amazon River mouth and (2) a sand zone dominating the rest of the outer shelf region. Three detrital sedimentary deposits are observed from the surface sediment on the Amazon Continental Shelf (1) an outer shelf sand deposit; (2) an inner shelf mud deposit; and (3) mud interbedded with sand deposit (Kuehl et al., 1982; Nittrouer et al., 1983). The areal distribution of sediment grain size is in Figure 6. Outer shelf sands (median grain size 1.5-3.0 ϕ) show moderate to good sorting. Inner

Figure 5. Distribution of grain types at 0-2 cm depth on the Amazon Continental Shelf (Nittrouer et al., 1983).

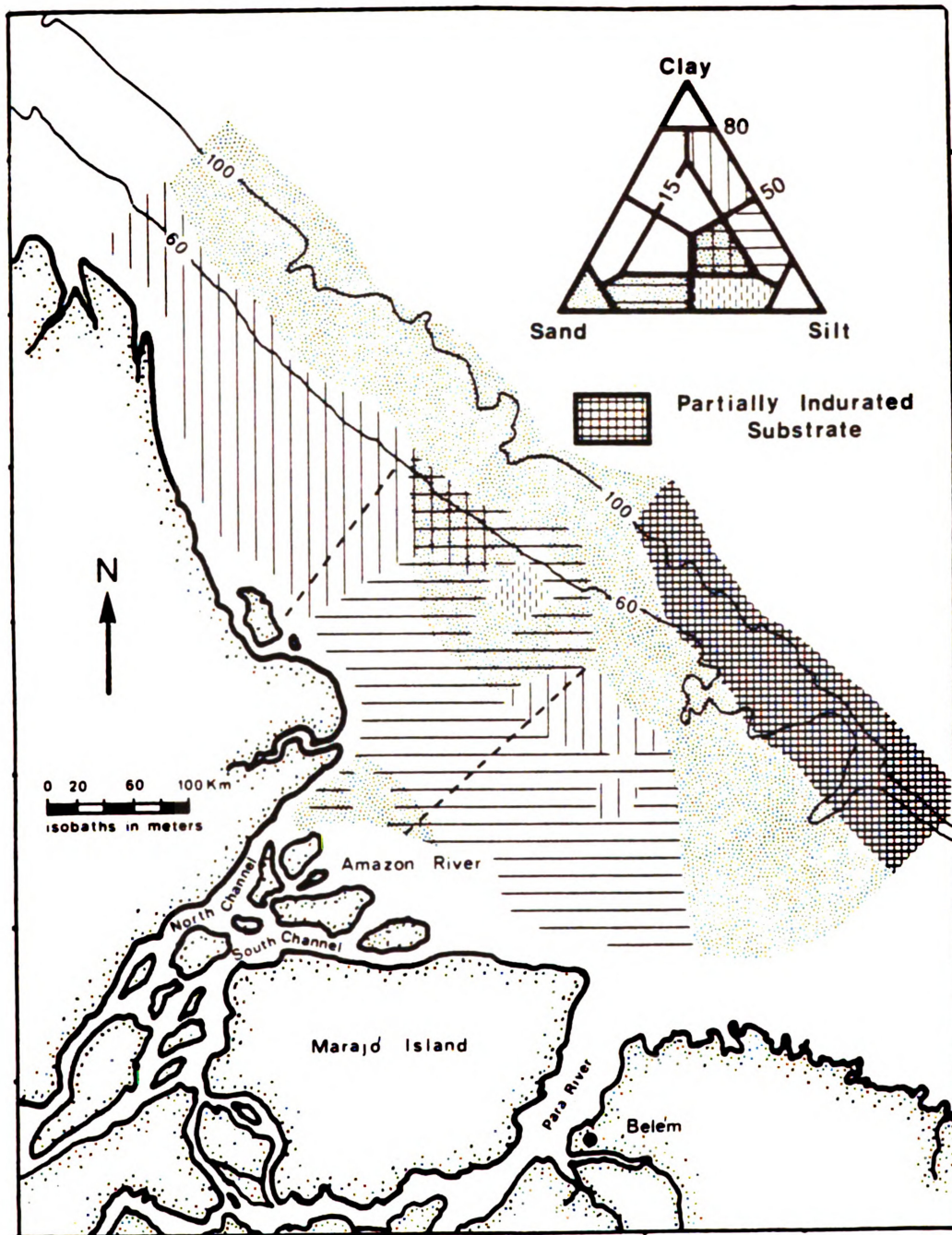
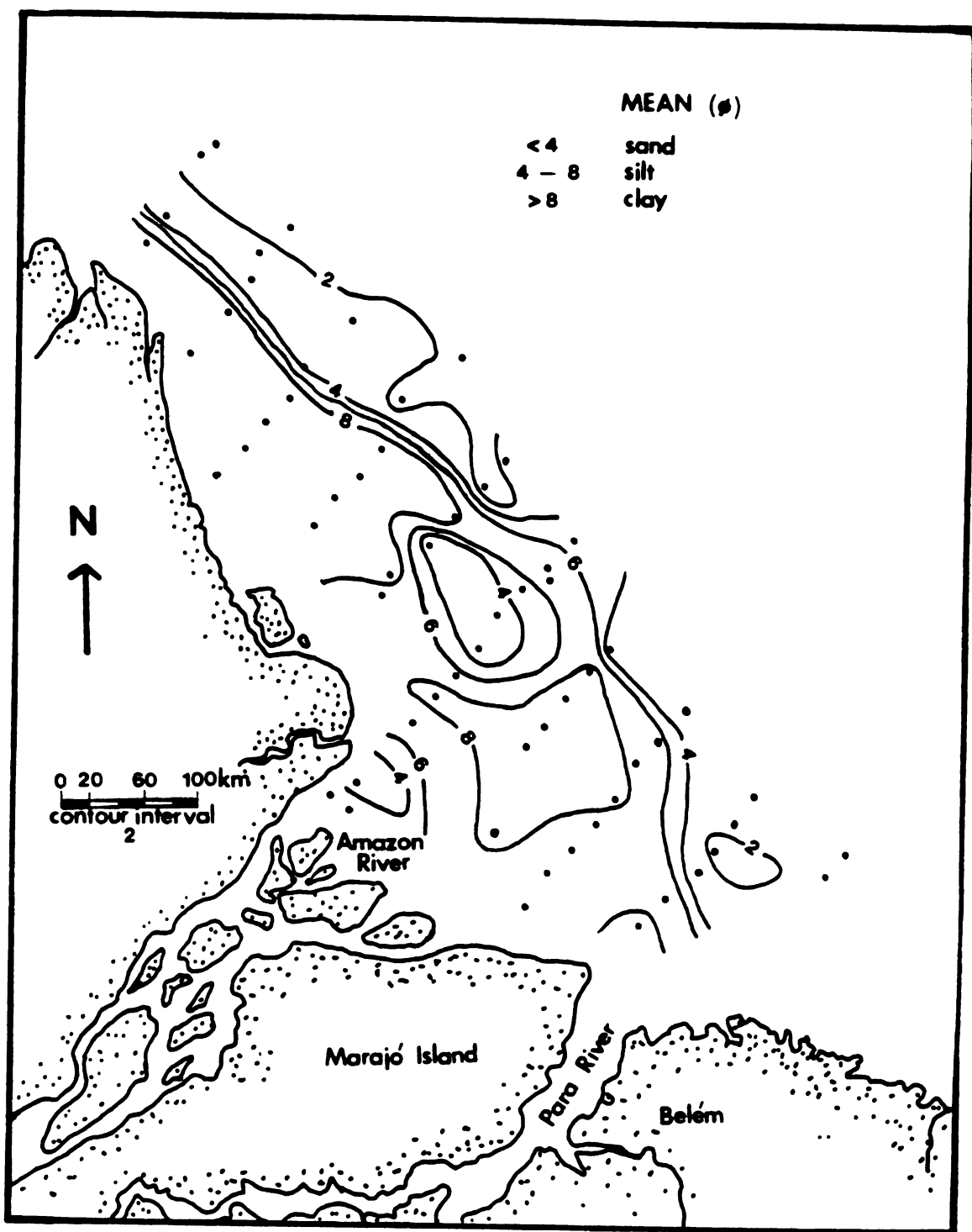


Figure 6. Areal distribution of mean grain size on the Amazon Continental Shelf (Nittrouer et al., 1983).



shelf muds (median grain size 6-9 ϕ) are poorly sorted (Nittrouer et al., 1983).

Several models have been proposed to explain the sedimentary structures and grain size distribution on the Amazon Continental Shelf (Milliman et al., 1975; Gibbs, 1976; Nittrouer et al., 1983). Milliman et al., (1975) hypothesizes that no modern muds are being deposited on the Amazon Shelf, except on a small nearshore zonal area. However, Milliman et al., (1975) states that two distinct periods of sedimentation have occurred in Quaternary time. One occurring at high sea level and the other at low sea level (60-80 meters below present sea level). During high sea level periods, inner shelf sediment accumulation occurs only in a narrow nearshore belt of mud. The majority of muds, however, are deposited at low sea levels. In direct opposition to Milliman et al., (1975) theory are Pb-210 data on shelf sediments. The Pb-210 dates indicate that modern mud accumulation is presently occurring (Figure 7) (Kuehl et al., 1982; Gibbs, 1976).

A second theory to explain the physical processes on the Amazon Continental Shelf was proposed by Gibbs (1976). Gibbs (1976) states that the Amazon River waters move offshore as a plume and is carried northwestward. Upon entry into the shelf, river particles settle out and are transported landward by bottom currents. A landward fining of particle size should result. Recent data, however, reveal an absence of reverse grading, contradicting the sedimentation model of Gibbs (1976) (Figure 8) (Nittrouer et al., 1983; DeMaster, personal communication 1982).

A recent model proposed by Nittrouer et al. (1983) suggests that modern sediment accumulation occurs as a result of a subaqueous delta

Figure 7. Distribution of sediment accumulation rates on the Amazon Continental Shelf based on ^{210}Pb geochronology. (Kuehl et al., 1982).

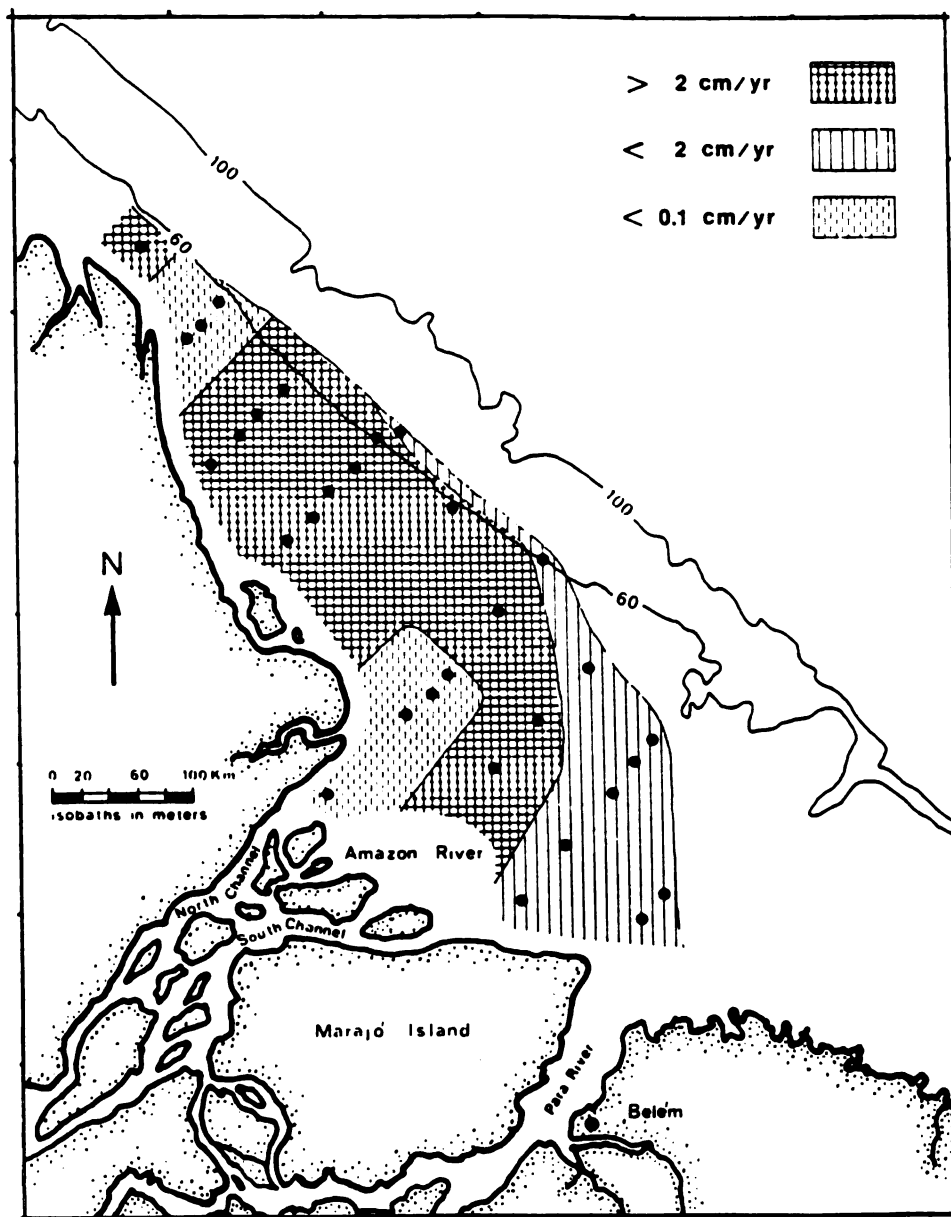
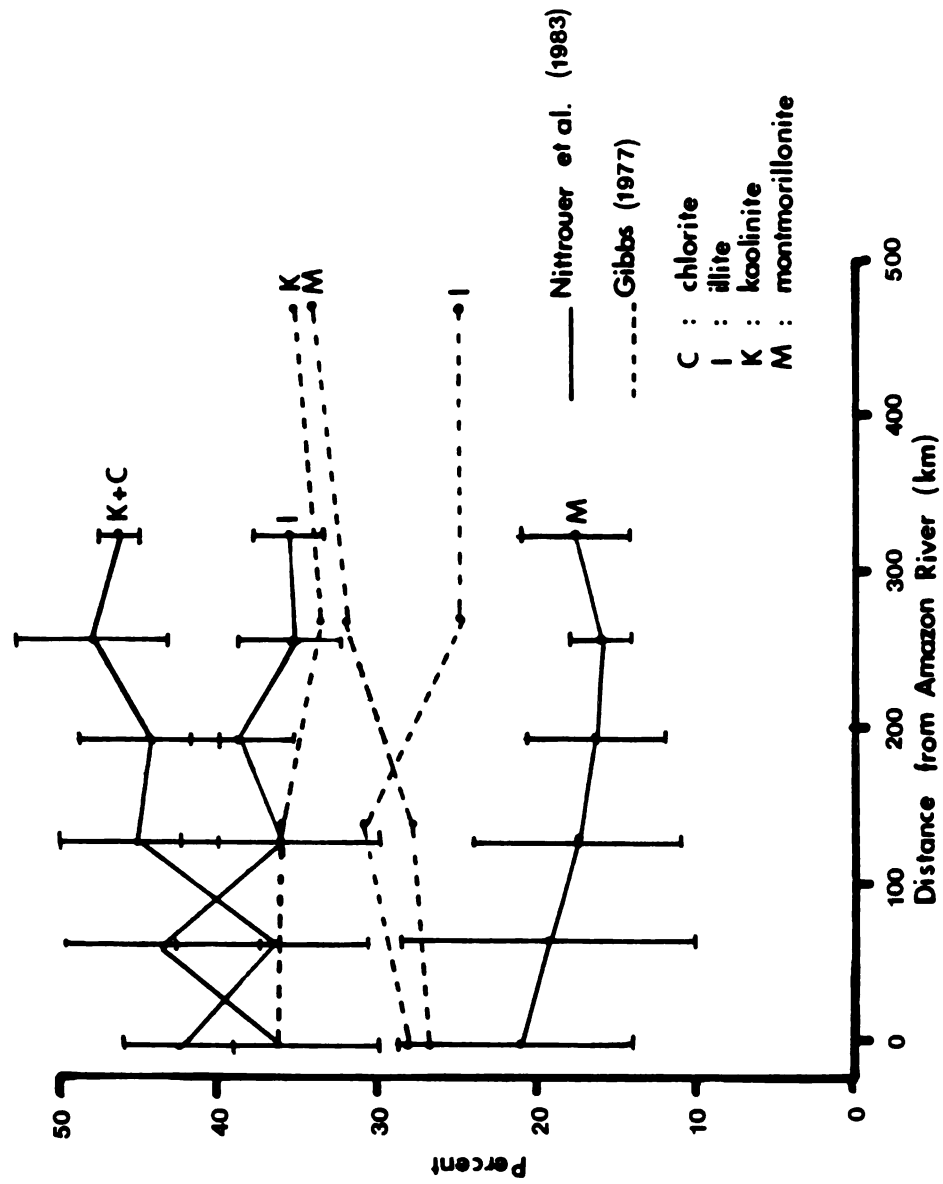


Figure 8. Clay mineral distribution along the Amazon Shelf from Nittrouer et al. (1983) and Gibbs (1977).



prograding over relict basal sands. Nittrouer et al., (1983) hypothesizes that a turbulent jet emanates from the river mouth and flows across the inner shelf. Their hypothesis is consistent with sediment accumulation rates based on Pb-210 data (Figure 7), sedimentary deposit data (Figure 5) and sediment grain distribution data (Figure 5).

At low sediment accumulation rates, the effects of bioturbation on the disruption of sedimentary structures increases (i.e., original stratification is preserved in areas of highest sediment accumulation rates with minimal bioturbation). A strong correlation therefore exists between accumulation rate and sedimentary structure (Kuehl et al., 1982). The model of Nittrouer et al., (1983) is the most consistent with present data and is therefore the accepted theory for use in this research.

METHODOLOGY

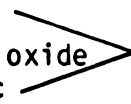
A research cruise to the Amazon Continental Shelf took place in October 1979. Shelf sediments (Figure 1) were sampled using an N.E.L.-Reineck type box corer (20 cm x 30 cm cross-sectional area), in order to maintain core stratigraphic integrity. These cores and soil samples from Belém (Figure 1) were immediately subsampled and shipped to North Carolina State University Laboratories. At North Carolina State University a series of analysis including grain-size analysis and Pb-210 analysis for sediment accumulation rate data were performed (Nitttrouer et al., 1983).

The cores were again subsampled for trace metal analysis in the Michigan State University Geochemistry Laboratory. The vials containing the Amazon sediments were placed in a 40°C oven for 96 hours, to completely dry the wet core samples. Each sample was dry sieved with a brass U.S. standard .212 mm sieve opening (65 mesh) sieve. After each sample, the sieve was placed in a sonic cleaner filled with distilled water for washing. After 10 minutes in the sonic cleaner, the sieve was rinsed with double distilled water and placed on its side to dry to prevent atmospheric or dust contamination (Bopp, 1981). To insure no contamination of the brass sieve on sediment samples, two identical samples were processed; one passing through the sieve, the second unsieved. Differences in the two samples were not statistically

different, therefore the sieve offered no significant source of contamination to the sample.

Each sample (5.000 grams dry weight of the less than .212 mm fraction) was weighed on a Mettler HL 52 scale and placed directly into pre-treated polyethylene centrifuge bottles. (Pre-treatment of the polyethylene centrifuge bottles included the following: (1) washing with soap and water, (2) rinsing with distilled water, (3) soaking in a 1:3 HCL solution overnight, (4) rinsing in double distilled water three times and (5) thoroughly drying).

A series of sequential chemical extractions were performed on each 5.000 gram sample (Figure 9). Extractions were performed in order to determine the partitioning of trace metals from four hypothesized fractions:

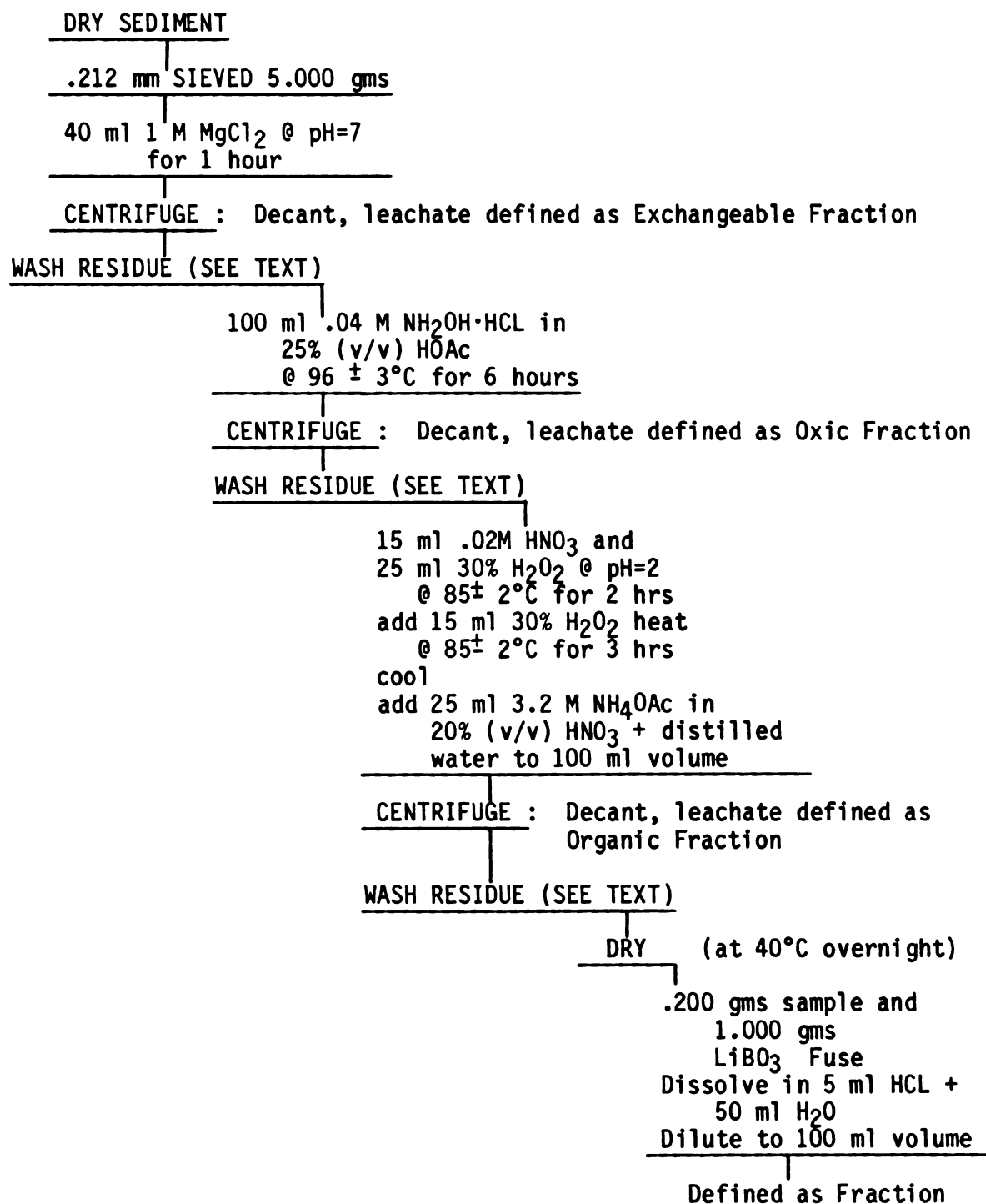
<u>Hypothesized sediment fraction</u>		<u>Chemical response of sediment to attack</u>
(1) Clay		Exchangeable
(2) Fe, Mn oxide		Easily and moderately reduced
(3) Organic		Oxidized
(4) Residual	Detrital	Resistent

(Gephart, 1982).

The procedure utilized is a combination of attacks performed by Tessier et al., (1979); Gibbs (1977); Gephart (1982); and Gupta and Chen (1975) and is summarized below:

(1) Exchangeable: 40 ml of 1 M $MgCl_2$, pH=7 were added to the 5.000 gram less than .212 mm dry sediment sample. The mixture was continuously agitated at room temperature for one hour (Tessier et al., 1979; Gibbs, 1977).

Figure 9. Flow chart of selective chemical attacks.



(2) Fe-Mn Oxide: The residue from (1) was leached with 100 ml of 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCL}$ in 25% (v/v) HOAc . This extraction was performed at $96 \pm 3^\circ\text{C}$ for six hours (Tessier et al., 1979; Gephart, 1982).

(3) Organic: The residue from (2) was extracted with 15 ml of 0.02 M HNO_3 and 25 ml of 30% H_2O_2 pH=2 (adjusted with HNO_3) heated to $85 \pm 2^\circ\text{C}$ for two hours with occasional agitation (every 15-20 minute agitation). At the conclusion of two hours a second aliquot of 15 ml 30% H_2O_2 was added. The sample was then returned to the water bath of $85 \pm 2^\circ\text{C}$ for three additional hours, occasionally agitating. After three hours, the sample was cooled to room temperature, at which time 25 ml of 3.2 M NH_4OAc in 20% (v/v) HNO_3 and double distilled water (diluting sample to 100 ml) were added. This mixture was stirred continuously at room temperature for 30 minutes (Gephart, 1982; Gupta and Chen, 1975).

(4) Residual: 0.200 grams of dry residue from (3) were fused with 1.000 gram of LiBO_3 at 1000°C in graphit crucibles for 15 minutes. The fused sample was removed from the furnace and immediately placed in a pre-prepared solution of 5 ml HCL and 50 ml double distilled water. Once dissolved, the sample was diluted to 100 ml with double distilled water. Duplicate fusions were run on each sample (Perkin Elmer Atomic Adsorption Instruction Manual, 1973; Gephart, 1982).

Upon completion of each attack, except the residual fraction, the sample was centrifuged for 12 minutes at 15,000 RPM. The supernate was drawn off and stored in pre-treated 250 ml polyethylene storage bottles. The residue sample was then rinsed with double distilled water and centrifuged at 15,000 RPM for 12 minutes, prior to subsequent extraction phases.

The supernate from each selective chemical extraction phase and the residual LiBO_3 fraction were analyzed by either a flame atomic adsorption 560 spectrophotometer or by a graphite furnace atomic adsorption HGA-2200 spectrophotometer. Atomic adsorption control settings for the elements analyzed by flame attachment in all matrixes were modified from conditions stated in the Perkin Elmer Atomic Adsorption Instruction Manual (1978). The Instruction Manual does not, however, offer optimized control settings for different matrixes when analyzing by graphite furnace. Optimization for each element analyzed by the graphite furnace for each of the four matrixes had to be performed. Optimization for each element in each matrix analyzed was in accordance with guidelines set forth in the Perkin Elmer Atomic Adsorption Instruction Manual for furnace (1978). Optimized control settings for the graphite furnace found in this study are summarized in Appendix II.

All sample sediments were also analyzed for total organic carbon content by a modified Walkley-Black titration method (Gaudette et al., 1974). A .200 gram dried, less than .212 mm sieved sediment sample was placed in a 500 ml Erlenmeyer flask. Precisely 10 ml of 1 N $\text{K}_2\text{Cr}_2\text{O}_7$ solution was added to each sample. The flask is then gently swirled to mix sediment and solution. Next, 20 ml of concentrated H_2SO_4 were added to the flask and again gently swirled for one minute. The mixture in the flask was allowed to stand at room temperature for 30 minutes. A standardization blank was run with each batch of samples. After standing 30 minutes, the solution was diluted to 200 ml volume with double distilled water and 10 ml 85% H_3PO_4 , .20 grams NaF and 15 drops of diphenylamine indicator were added to the flask.

The solution in the flask was then back titrated with 0.5 N ferrous ammonium sulfate solution. The color progressed from an opaque green-brown to green upon the addition of the ferrous ammonium sulfate solution. The color continuously shifted upon further titration to a bluish-black-grey; at this point the addition of a few drops of ferrous solution shifted the color to a brilliant green end point (a one-drop end point) (Gaudette et al., 1974). The results of the analysis were calculated by the following equation:

$$\text{Organic Carbon} = 10(1-T/S)((.34)(.003)(100/.20))$$

T = sample titrated; S = standardization blank titration;
 .003 = meq weight of carbon; .34 = normality of $K_2Cr_4O_7$;
 W = weight of sediment sample; 10 = volume of $K_2Cr_4O_7$

(Gaudette et al., 1974).

The total organic carbon (TOC) content is presented in Appendix I.

The data from the chemical partitioning attacks were reduced by factor analysis, both R and Q-mode. Factor analysis can aid in revealing simple patterns from complex data sets. Data from the chemical partitioning attacks fulfills the three requirements of factor analysis utilization:

- (1) conveniently coded -- values in ppm,
- (2) large number of sample volume -- 84 samples, chemically fractionated into four phases, analyzed for 10 elements, and
- (3) prior knowledge of relationships is inadequate

(Kerlinger, 1973;
 Imbrie and Van Andel, 1964).

The data were factored by factor analysis in original (raw) form and after transformation of the data by natural log. The transformation of the data was done in order to see if any improvements on correlation could be made since geochemical data frequently does not have a normal distribution.

RESULTS AND DISCUSSION

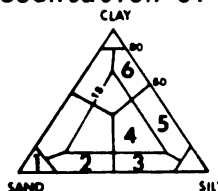
Results of the chemical partitioning studies for the metals are presented in Appendix I. These results will be discussed in three parts; general nature of partitioning of metals in the sediments, diagenesis of metals in the sediments in terms of metal partitioning, and source of trace metals to the sediments as interpreted from R and Q-mode factor analysis of the partitioning data.

Chemical Partitioning of Metals in Amazon Shelf Sediments

Two aspects of the chemical partitioning of the metals in the sediments are discussed: (1) a general summary of the nature of the partitioning in the sediments and (2) the nature of the partitioning over the shelf. In Table 1 the partitioning results from Appendix I are summarized as a function of sediment type. The sediments in the study area were classified by Nittrouer et al., (1983) as to type using the classification scheme of Folk (1974). Sediment types are defined as a function of where the sediment plots on a ternary diagram with respect to the three end-member compositions of clay-sand-silt. Numerical representation of sediment types found by Nittrouer et al., (1983) is shown below in Figure 10:

Figure 10. Numerical representation of sediment type from Folk (1974).

Type 1 = sand
Type 2 = sand-silt
Type 3 = silt-sand



Type 4 = sand-silt-clay
Type 5 = clayey-silt
Type 6 = silty-clay

Four chemically defined sediment fractions are shown on Table 1 (exchangeable, Fe-Mn oxide, organic matter, and detrital). The values are the average of the percent of the metal in a particular fraction. Since these values are averages of percents, the totals of a metal in a sediment type are not necessarily 100%.

Table 1 also present a summary of the work of Gibbs (1977) on the partitioning of selected metals in the suspended load of the Amazon River. Gibbs samples were taken off Macapa' Brazil and therefore would not be influenced by marine water (Gibbs, 1977). Although Gibbs samples were taken approximately five years before the present study samples were taken, little has happened climatically or environmentally that would change the nature of the partitioning of metals in the suspended load. It is suggested then that the results of Gibbs (1977) in general reflect the nature of metal partitioning in the suspended sediment today. Gibbs data can therefore be used to study gross differences in metal partitioning in the sediments between the freshwater environment of the Amazon River and the marine continental shelf environment. Table 2 is a summary of partitioning of metals in the soils. Soil samples were taken at Belém.

A summary of the behavior of each metal follows. Suspended load sediments refers to Gibbs (1977), shelf sediments refer to surficial (0-5cm) Continental Shelf sediments.

Chromium: Most of the Cr (usually greater than 90%) is associated in the residual fractions of the suspended load, shelf sediments, and soils and suggests that most of the Cr addition to the oceans is in the detrital phase of sediments. Of the hydromorphic phases in the shelf sediment, Fe-Mn oxides are the most important in sequestering Cr;

TABLE 2
Trace metal partitioning of Cr, Mn, Co, Cu, Fe, Ni, Zn in selected soils of the Amazon River Drainage Basin

	Soil				Core ⁷				Soil				Horizons ⁸			
	0-6 2.	2- 4.4	4.4 7.5	7.5 11.1	11.1- 15.	15- 23.	23- 31.	A ⁹ .	B .	C .	D .					
Cr	EX ¹ .	EX ¹ .	EX ¹ .	EX ¹ .	EX ¹ .	EX ¹ .	EX ¹ .	EX ¹ .	EX ¹ .	EX ¹ .	EX ¹ .	EX ¹ .	EX ¹ .	EX ¹ .	EX ¹ .	EX ¹ .
	OXD ² .17	OXD ² .17	OXD ² .17	OXD ² .17	OXD ² .17	OXD ² .17	OXD ² .17	OXD ² .17	OXD ² .17	OXD ² .17	OXD ² .17	OXD ² .17	OXD ² .17	OXD ² .17	OXD ² .17	OXD ² .17
	ORG ³ .26	ORG ³ .26	ORG ³ .26	ORG ³ .26	ORG ³ .26	ORG ³ .26	ORG ³ .26	ORG ³ .26	ORG ³ .26	ORG ³ .26	ORG ³ .26	ORG ³ .26	ORG ³ .26	ORG ³ .26	ORG ³ .26	ORG ³ .26
	RES ⁴ 5.44	RES ⁴ 5.44	RES ⁴ 5.44	RES ⁴ 5.44	RES ⁴ 5.44	RES ⁴ 5.44	RES ⁴ 5.44	RES ⁴ 5.44	RES ⁴ 5.44	RES ⁴ 5.44	RES ⁴ 5.44	RES ⁴ 5.44	RES ⁴ 5.44	RES ⁴ 5.44	RES ⁴ 5.44	RES ⁴ 5.44
	RES ⁴ 94.13	RES ⁴ 94.13	RES ⁴ 94.13	RES ⁴ 94.13	RES ⁴ 94.13	RES ⁴ 94.13	RES ⁴ 94.13	RES ⁴ 94.13	RES ⁴ 94.13	RES ⁴ 94.13	RES ⁴ 94.13	RES ⁴ 94.13	RES ⁴ 94.13	RES ⁴ 94.13	RES ⁴ 94.13	RES ⁴ 94.13
Mn	EX 9.71	EX 4.44	EX 8.00	EX 0	EX 0	EX 0	EX 0	EX 10.02	EX 2.98	EX 4.19	EX 3.82	EX 10.02	EX 2.98	EX 4.19	EX 3.82	EX 10.02
	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD .03	OXD .03	OXD .03	OXD .03	OXD .03	OXD .03	OXD .03	OXD .03	OXD .03
	ORG 2.04	ORG .14	ORG .35	ORG 2.17	ORG 1.37	ORG 1.69	ORG 2.41	ORG .30	ORG .71	ORG .99	ORG 1.43	ORG .30	ORG .71	ORG .99	ORG 1.43	ORG .30
	RES 88.26	RES 95.42	RES 91.65	RES 95.91	RES 97.67	RES 89.45	RES 92.91	RES 89.64	RES 96.29	RES 94.78	RES 94.65	RES 89.64	RES 96.29	RES 94.78	RES 94.65	RES 89.64
Co	EX 0	EX 0	EX 0	EX 0	EX 0	EX 0	EX 0	EX 0	EX 0	EX 0	EX 0	EX 0	EX 0	EX 0	EX 0	EX 0
	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0
	ORG 0	ORG 0	ORG 0	ORG 0	ORG 0	ORG 0	ORG 0	ORG 0	ORG 0	ORG 0	ORG 0	ORG 0	ORG 0	ORG 0	ORG 0	ORG 0
	RES 100	RES 100	RES 99.21	RES 99.98	RES 100	RES 100	RES 100	RES 100	RES 99.98	RES 99.86	RES 99.8	RES 100	RES 99.98	RES 99.86	RES 99.8	RES 100
Cu	EX 2.71	EX 5.54	EX 4.06	EX 10.96	EX 5.65	EX 9.86	EX 10.37	EX 1.99	EX 2.40	EX 0	EX 1.73	EX 1.99	EX 2.40	EX 0	EX 1.73	EX 1.99
	OXD 5.95	OXD 9.73	OXD 9.35	OXD 3.83	OXD 25.74	OXD 20.64	OXD 24.16	OXD 1.89	OXD 3.87	OXD 4.12	OXD 7.05	OXD 1.89	OXD 3.87	OXD 4.12	OXD 7.05	OXD 1.89
	ORG 36.96	ORG 65.21	ORG 63.11	ORG 69.71	ORG 36.81	ORG 13.93	ORG 16.41	ORG 20.02	ORG 11.45	ORG 6.72	ORG 8.46	ORG 20.02	ORG 11.45	ORG 6.72	ORG 8.46	ORG 20.02
	RES 54.38	RES 19.52	RES 23.47	RES 15.51	RES 31.81	RES 55.56	RES 49.06	RES 76.08	RES 82.28	RES 89.17	RES 82.76	RES 76.08	RES 82.28	RES 89.17	RES 82.76	RES 76.08
Fe	EX 3.13	EX 2.13	EX 2.26	EX 4.7	EX 1.91	EX 6.98	EX .66	EX .567	EX .246	EX .233	EX .091	EX .567	EX .246	EX .233	EX .091	EX .567
	OXD 16.19	OXD 14.84	OXD 20.53	OXD 40.16	OXD 26.17	OXD 28.67	OXD 3.42	OXD 11.35	OXD 12.94	OXD 13.589	OXD 13.47	OXD 11.35	OXD 12.94	OXD 13.589	OXD 13.47	OXD 11.35
	ORG .44	ORG .30	ORG .57	ORG .42	ORG .38	ORG .26	ORG 0	ORG .33	ORG .14	ORG .109	ORG .062	ORG .33	ORG .14	ORG .109	ORG .062	ORG .33
	RES 80.23	RES 82.72	RES 76.65	RES 54.71	RES 71.54	RES 64.09	RES 95.92	RES 87.75	RES 86.67	RES 86.07	RES 86.37	RES 87.75	RES 86.67	RES 86.07	RES 86.37	RES 87.75
Ni	EX .23	EX .35	EX 1.83	EX .086	EX .42	EX .58	EX .46	EX .738	EX .34	EX 1.17	EX .36	EX .738	EX .34	EX 1.17	EX .36	EX .738
	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0	OXD 0
	ORG .25	ORG .19	ORG .47	ORG 0	ORG 0	ORG .02	ORG .06	ORG .587	ORG .13	ORG 3.79	ORG .241	ORG .587	ORG .13	ORG 3.79	ORG .241	ORG .587
	RES 99.51	RES 99.45	RES 97.69	RES 99.91	RES 99.57	RES 99.39	RES 99.48	RES 98.67	RES 99.50	RES 95.02	RES 99.39	RES 98.67	RES 99.50	RES 95.02	RES 99.39	RES 98.67

Table 2. (cont'd.)

	Soil		Core ⁷		Soil		Horizons ⁸			
							A ⁹	B	C	D
Zn	0-6	2-4.4	7.5	11.1	15.1	23-31.	.	.	.	.
	2.									
	34.61	19.87	44.67	38.13	13.23	29.97	12.37	4.83	4.20	6.58
	OXD2	11.09	18.52	44.69	21.69	27.88	6.63	6.22	8.87	13.62
	ORG3	4.22	5.00	5.66	2.52	5.25	2.22	1.55	2.49	3.54
	RES4	64.81	31.80	11.51	62.75	36.90	78.76	87.40	84.40	76.20
1 Exchangeable/loosely adsorbed fraction										
2 Fe-Mn oxide fraction										
3 Organic fraction										
4 Residual fraction										
5 Average of percent metal in fraction										
6 Depth of core in cm										
7 Soil core depth in cm										
8 Soil horizon										
9 Soil horizon in core										

organic matter is second with the exchangeable fraction playing a relatively minor role. This nature of Cr partitioning in sediments is consistent with past work (Gephart, 1982).

The relative partitioning of Cr amount in the sediment fraction does not appear to be strongly dependent on grain-type in the shelf sediments. There is, however, significantly more Cr in the hydromorphic fraction of the sediments composed of sand (Type 1) than the other sediment types, with the Fe-Mn oxide fraction becoming very dominate in the sequestering of Cr. The nature of Cr partitioning in the sand sediment is consistent with the higher amount of hydromorphic Fe in this sediment type with respect to the other sediments (Table 1).

In general, there is slightly less metal in the hydromorphic fraction of the shelf sediments compared to the suspended load sediments. Organic matter is more important in sequestering Cr than Fe-Mn oxides in the suspended load. The hydromorphic fraction of the soil better reflects the partitioning in the suspended load rather than the shelf sediments, in that the organic fraction is dominate. The exchangeable and Fe-Mn oxide fractions have very minor roles in the sequestering of Cr in the soil samples.

The nature of Cr partitioning in the Amazon River environment suggests that Cr undergoes a repartitioning from river to shelf (e.g., organic fraction to Fe-Mn oxide fraction) and that the suspended sediment could be a source for dissolved Cr to seawater (e.g., less Cr in hydromorphic fraction of shelf sediments). The direction of repartitioning (organic matter to Fe-Mn oxide) suggests that organic matter could be a source of the dissolved Cr within the sediment.

Manganese: The Fe-Mn oxide fraction and residual fraction, combined account for the majority of Mn concentration in both suspended load and shelf sediments (approximately 80-95%). The amount of Mn in the Fe-Mn oxide fraction, the dominate fraction, decreases from suspended load to marine environment, whereas Mn in the detrital fraction in both suspended load and shelf remains similar (33%). The Mn organic fraction concentrations are of minor importance (5%) and are similar for shelf and suspended load sediments. The exchangeable fraction accounts for less than 1% total Mn in the suspended load sediments but increases in the shelf sediments to 15%. In general Mn can be quite mobile in this system since most of the Mn occurs in the hydromorphic phase.

Mn partitioning in the oxide, organic and detrital fractions of shelf sediments, appear to be influenced by grain-type. There is more Mn hydromorphics in clay sediments (Type 6) than in the other sediments. Within the hydromorphic fraction, the oxide fraction is dominate and increases from sand (Type 1) to clay (Type 6) sediments, 35% to 55% respectively. The organic fraction behaves similar to the oxide fraction (e.g., Type 1 at 1.8% increases to Type 6 at 55%). This Mn behavior is contrary to Cr hydromorphic behavior which decreases from sands (Type 1) to clays (Type 6) and Cr detrital fraction behavior which increases from sand (Type 1) to clay (Type 6) sediments.

The Mn in soils have a different distribution pattern among the four fractions than either the suspended load or shelf sediments. Of major importance in Mn sequestering in soils is the detrital fraction (at greater than 89%). The hydromorphic fraction is of minor importance with the oxide fraction being the most insignificant. This is a drastic change from shelf and suspended load sediments which had the

oxide fraction being of primary importance. In general, the data from Table 1 indicates that Mn undergoes repartitioning within the hydromorphic fraction from a river to a marine environment (e.g., oxide fraction to exchangeable fraction).

Cobalt: The detrital fraction is the fraction accounting for most of Co in shelf sediments and soils (90% and 99%, respectively). The dominance of the detrital fraction over the hydromorphic fractions has been found previously (Loring, 1979). The detrital fraction is also dominate (44%) versus the exchangeable, organic or oxide fractions. In the suspended load sediments, the hydromorphic fraction is the dominate fraction for Co concentration. Within the hydromorphic fraction for the suspended load sediments, the Fe-Mn oxide fraction dominates (28%), of secondary importance is the organic fraction (19%), and of least importance is the exchangeable fraction (8%).

The partitioning of Co in shelf sediments and soils are similar and differ from suspended load sediments. Shelf sediments and soils have 90-99% of Co sequestered in the detrital fraction with the hydromorphic fraction playing a minor role. However, in the suspended load (River) sediments the hydromorphic fraction dominates (e.g., 56%).

There are slight grain-type variations observed in Co. The hydromorphic fraction increases from sand (Type 1) to clay (Type 6) sediment. Co partitioning among various grain-types in shelf sediments is similar to Mn partitioning (e.g., the hydromorphic fraction increases from Type 1 to Type 6).

Generally, the nature of Co partitioning in this system suggests that Co goes through repartitioning from river to shelf (e.g., hydromorphic fraction to detrital fraction) and that the change in relative

importance of the hydromorphic fraction (56% to 6%) could be a source for dissolved cobalt to seawater.

Copper: Approximately 79% of the Cu is associated in the detrital fraction (suspended, shelf, and soil horizons). Therefore, most of the Cu in sediments brought into the ocean is in the detrital phase. The hydromorphic fraction (suspended and shelf) comprise the remaining 21% of Cu sequestered in sediments. Within the hydromorphic fraction, the oxide fraction is dominate (8-13%), followed by the organic fraction (6%) and the exchangeable fraction (2-5%). Comparing the organic and detrital fractions for suspended loads and shelf sediments, similar percent concentration values exist (6% organic fraction and 79% detrital fraction). However, the exchangeable fraction drops from 5% to 2% and the oxide fraction increases from 8% to 13% in suspended versus shelf sediments.

There is little significant change among the different grain-types (Types 1-6) in the detrital or hydromorphic fractions, although, there is a slight influence of grain-type on the exchangeable fraction. The exchangeable fraction decreases from Type 1 (2%) to Type 6 (.3%).

The nature of Cu partitioning between a soil core (sample from Belém) and soil horizons (A-D) are different. Soil horizons have a similar partitioning trend for Cu in shelf and suspended load sediments. The soil core has a residual fraction of Cu relative percent value of 23-55%. The hydromorphic fraction has a relative Cu concentration value of 21% for suspended load sediments, shelf sediments and soil horizons and increases to 45-77% for soil core.

In general, there is little repartitioning between the hydromorphic and detrital fractions from river to shelf environments. But,

within the hydromorphic fraction repartitioning occurs. Repartitioning of Cu from river to shelf environments is via the exchangeable fraction to the oxide fraction. This suggests that the oxide fraction is playing a greater role in sequestering Cu and that the exchangeable fraction may release Cu to seawater (i.e., be a source of Cu to seawater).

Iron: The major phases of Fe in the suspended sediments are the detrital fraction (46%) and oxide fraction (46%). There is a dramatic increase (46%-82%) in Fe detrital fraction and subsequent decrease in hydromorphic fraction from suspended load to shelf sediments. The dominant Fe fraction within the hydromorphic phase of the shelf sediments is the oxide fraction (17%). The organic and exchangeable phase are of minor significance.

Shelf sediments are slightly grain-type dependent. The detrital fraction in Type 1 is at a lower relative percent value than Type 6 (73% to 82%, respectively). There is a corresponding decrease in hydromorphic fraction from Type 1 to Type 6.

Soils (core and horizon) and shelf sediments have similar partitioning data. The detrital fraction dominates Fe partitioning with the oxide fraction of secondary importance. The organic fraction and exchangeable fraction are of minor importance.

Repartitioning does occur in Fe sediment concentrations between river and shelf sediments. The hydromorphic fraction decreases Fe concentration values while the residual fraction increases from river to shelf environments. This suggests that the suspended load can be a source of Fe to seawater.

Nickel. In the suspended load sediments the relative partitioning of Ni is dominated by the oxide fraction (45%) and the detrital fraction

(38%). Of minor importance are the organic fraction (13%) and the exchangeable fraction at 3%. The shelf sediments have different partitioning of Ni. Most of the Ni in the shelf sediments are in the detrital fraction (87%). Partitioning of Ni in the hydromorphic fraction of the shelf sediments is oxide fraction (7%), organic fraction (5%), exchangeable fraction 1%.

Shelf sediments appear slightly dependent on grain-type. The residual fraction has a slightly higher concentration percentage value in Type 1 grain-type (94%) as opposed to Type 6 (87%). Corresponding to this change, the hydromorphic fraction increases from Type 1 (6%) to Type 6 (13%).

Soils, both horizons and core samples, behave in a similar partitioning pattern as shelf sediments but not as suspended load sediments behave. Soils appear to have one dominate fraction (detrital 95-99%) for Ni. The hydromorphic fraction is minor and within this fraction, the oxide fraction is at undetectable levels.

The nature of Ni partitioning from suspended load to shelf environment suggests Ni repartitioning. The oxide fraction in the suspended load sediment repartitions to the detrital fraction in shelf sediments. This repartitioning of hydromorphic fraction (especially the oxide fraction) can be a potential source for Ni to seawater from suspended load sediments.

Zinc: Gibbs (1977) did not analyze for Zinc in suspended load sediments and therefore there will be no comparison between suspended load and shelf sediments for zinc. However, partitioning data for zinc is available for soil samples, shelf sediment and shelf sediment changes with grain-type (Table 1). The residual fraction (73% for shelf

sediments) is the dominate fraction of Zn in shelf sediments. The oxide fraction is of secondary importance at 21% with both organic (5%) and exchangeable (1%) fractions being of minor importance.

Grain-type dependency is observed in the residual as well as hydromorphic fractions. There is an increase in detrital Zn for Type 1 (64%) to Type 6 (77%). Corresponding to this increase, is a relative decrease in the hydromorphic fraction (Type 1 at 36% to Type 6 at 23%). All three individual phases (exchangeable, oxide, organic) within the hydromorphic fraction decrease from Type 1 (sand) to Type 6 (clay).

The soil horizons display a similar behavior as shelf sediments. The detrital phase is dominate (76-78%) and the hydromorphic is of lesser importance. However, soil core samples differ. They display two dominate fractions, the detrital and the oxide.

In summary:

- (1) Only Cr and Cu have the majority of their concentration in the residual fraction for all three environments (suspended load, shelf, soil).
- (2) Two fractions dominate the partitioning of Mn, Co, Ni, Fe in suspended load sediments (almost equal fractions): oxide and detrital.
- (3) In general, most metals (90%) are in a combination of residual and oxide fractions.
- (4) The hydromorphic fraction is dominate in controlling the behavior of Mn in both suspended and shelf environments.
- (5) All metals except for Mn and Cu show a decrease in the organic fraction from river to shelf environments.
- (6) All metals except for Mn and Cu show a decrease in the percentage of the metals in the hydromorphic fraction from river to shelf environments.
- (7) In general, the relative partitioning trends as a function of grain-type are preserved for all metals.

- (8) The hydromorphic fraction for Mn, Co, Cu, Ni all have grain-type trends which increase element concentrations from Type 1 and Type 6, Cr and Zn have a reverse trend.
- (9) The relative partitioning within the hydromorphic fraction is highly variable between soil and shelf environment, except for Cr, the relative partitioning of the metals between the soils and suspended material are not similar.
- (10) Cr, Co, Cu, Fe, Zn, Ni are partitioned similarly in shelf sediments (detrital 73-94%; oxide 4-27%; organic .2-6%; exchangeable 0-2%).
- (11) Relative partitioning of Mn, Cr, Cu in the sediment percent is the same in river and shelf environments.
- (12) Differences were observed in the relative partitioning of Fe, Co, and Ni between the sediments at the river and those of the shelf. The hydromorphic fraction (especially the oxide fraction) is much smaller in the shelf sediments.

The data can be interpreted to suggest that:

- (1) Significant repartitioning occurs between water and shelf environments.
- (2) Upon mixing with seawater the sediment could be a source of metals to seawater, the order of importance of this source decreases in the order Ni>Co>Fe>Cr.
- (3) Decay (oxidation) of organic matter could be the source of metal to seawater within the sediment.

Distribution of Metals on the Shelf:

The behavior of selected trace metals in this system were studied by the construction of contour maps of elemental concentrations in the surface sediment (Figures 11-13). Distribution maps were created for Zn and Ba. Zinc behavior was studied as a representative of a metal with both significant hydromorphic as well as residual partitioning.

Figure 11. Contour map of zinc in the detrital fraction of the surface (0-5 cm) sediment of the Amazon Continental Shelf.

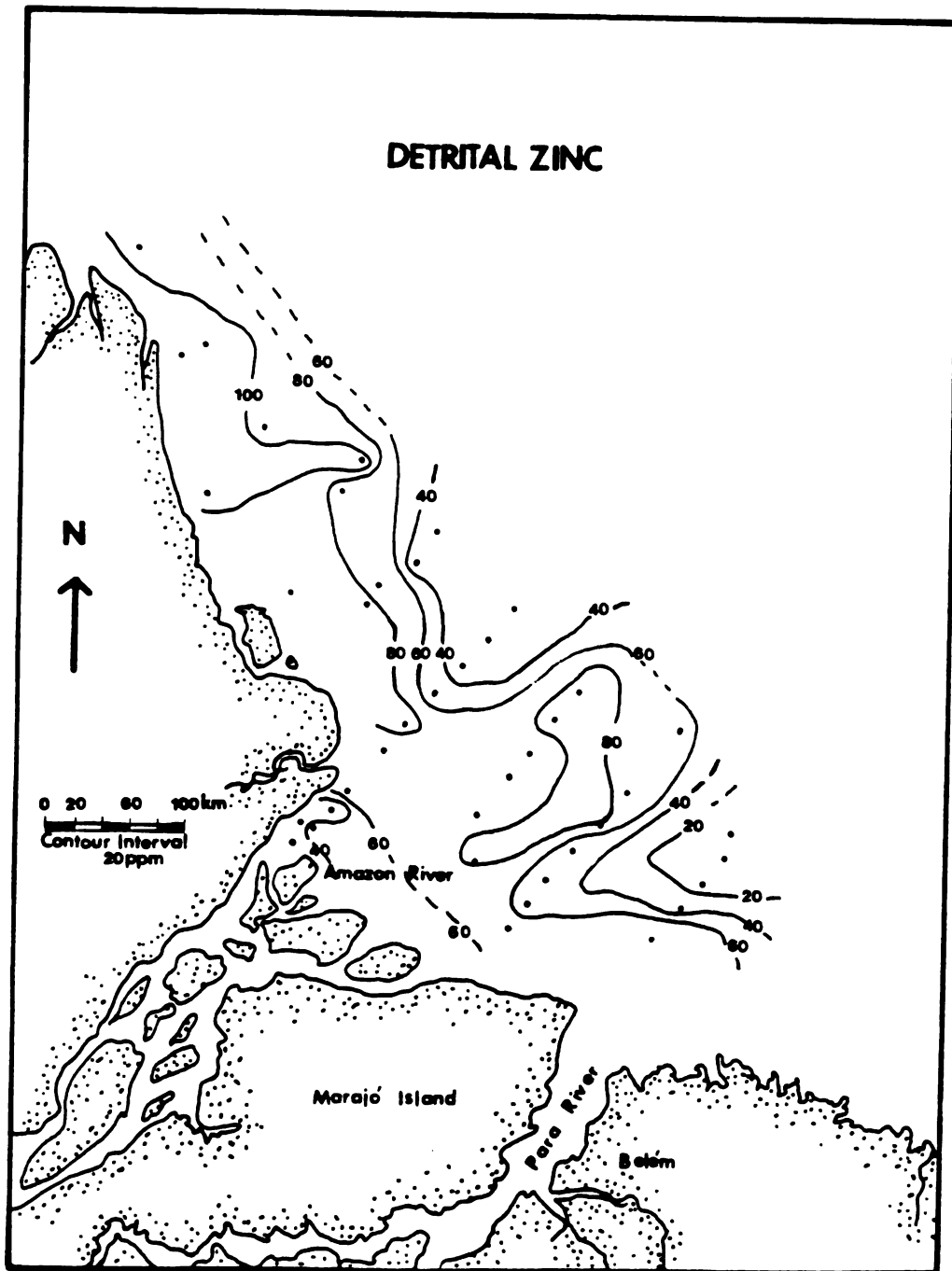


Figure 12. Contour map of zinc in the hydromorphic fraction of the surface (0-5 cm) sediment of the Amazon Continental Shelf.

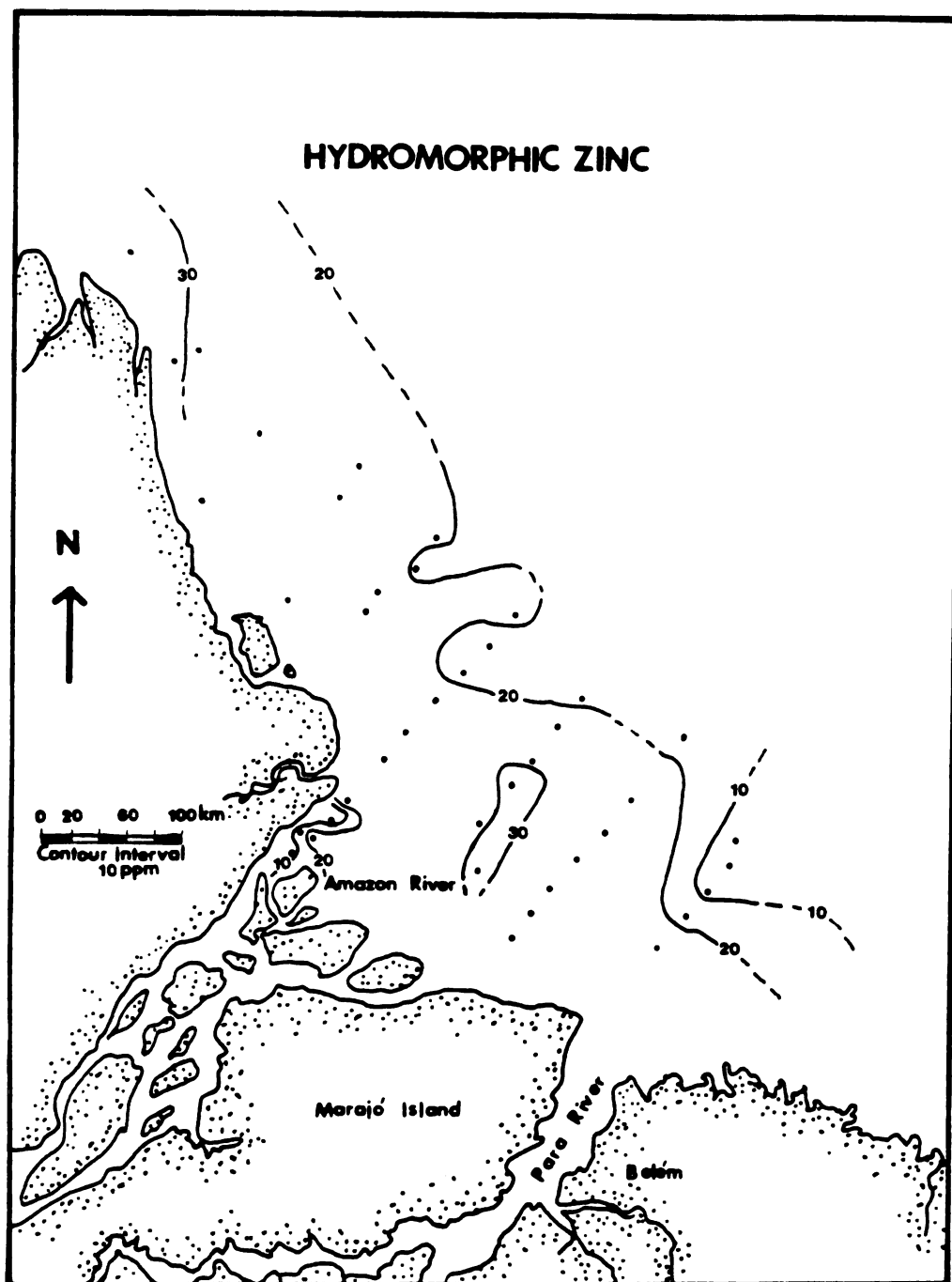
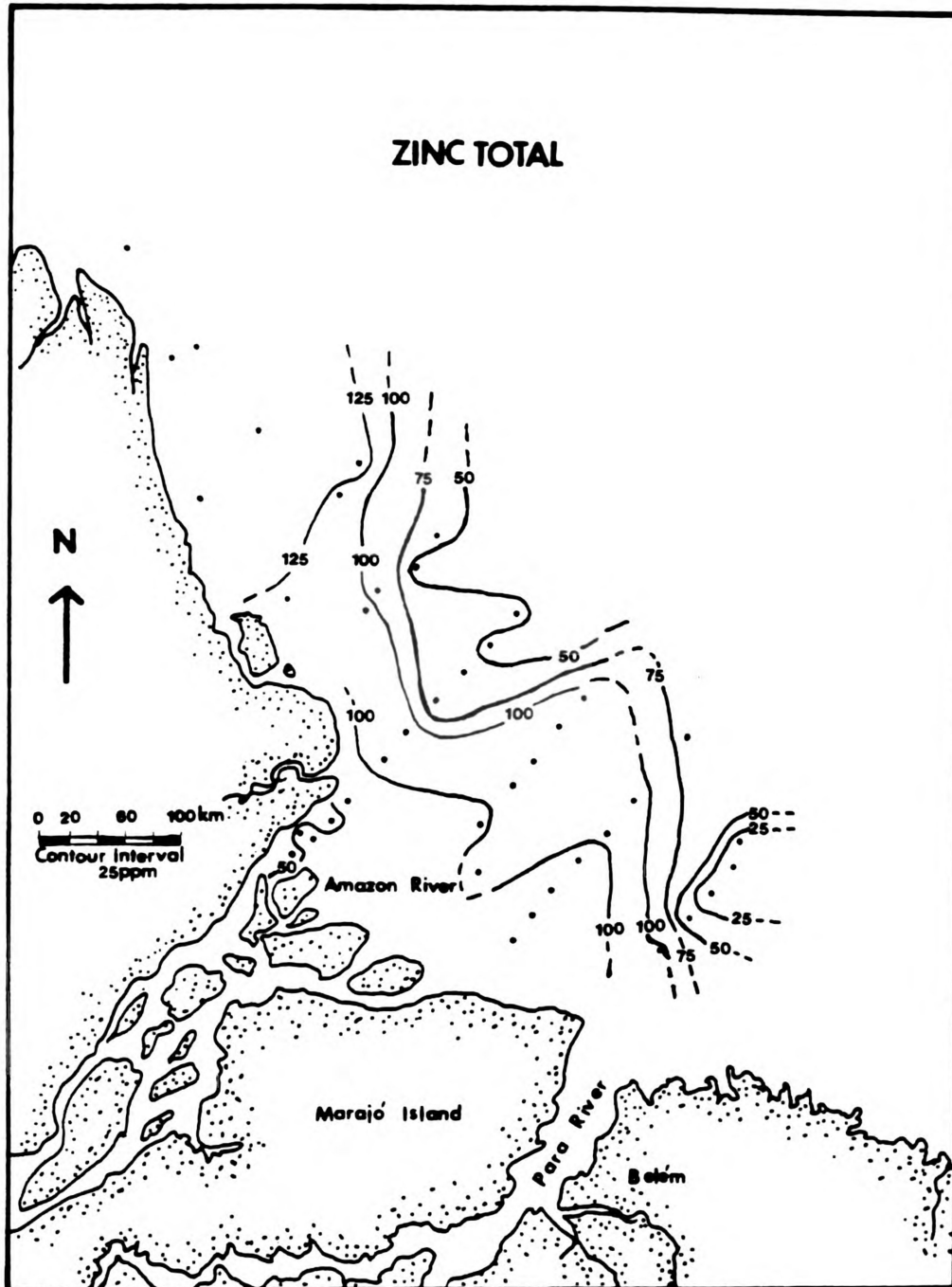


Figure 13. Contour map of total zinc in the surface (0-5 cm) sediment of the Amazon Continental Shelf.



Ba was chosen for study because it is an alkaline element and should behave differently than the transition metals studied.

Concentrations of zinc in the continental shelf sediments are shown in Figures 11, 12, and 13 representing absolute values of Zn in the detrital fraction, hydromorphic fraction and total sediment, respectively. The concentration patterns are similar in each figure and appear to reflect the distribution of sediment types on the shelf (Figure 5).

The concentration of Zn decreases from core location 2 (Type 6) to core locations 3,4,5,6 (Type 1). Core locations 30 and 33 (Type 1) have corresponding lower concentrations than core locations 31 and 32 (both of Type 5). Core locations 35, 29 and 28 all of similar type (Type 6) display similar concentrations. Cores 47-57, again reflect grain-type composition; they display similar grain-type compositions (Type 5) and therefore similar concentration values.

The dependency on grain-type for metal concentrations in the shelf sediments can be further demonstrated by plotting elemental concentration in the sediment versus grain-type. Figures 14, 15, and 16 are such plots for Zn-total, Zn-residual and Zn-hydromorphic, respectively. These Figures show distinct clusters of Zn concentrations depending on grain-type, with the biggest difference between Type 1 and Types 5 and 6 (sand and silt-clay, respectively). If the concentrations are plotted as ranked data, rather than as absolute data, the differences are made even clearer. For example, Figure 17 is a plot of sediment type versus Zn hydromorphic using ranked concentrations. One can clearly see that the concentration distribution of the Zn in the shelf sediment can be explained by the distribution of the various sediment

Figure 14. Plot of sediment type versus concentration of zinc total.
Numbers refer to overlapped points.

Figure 15. Plot of sediment type versus concentration of zinc in the
detrital fraction. Numbers refer to overlapped points.

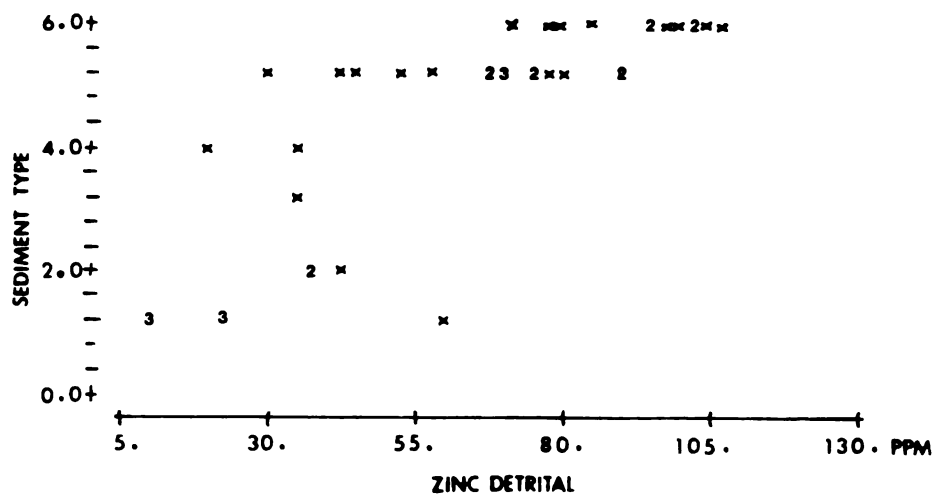
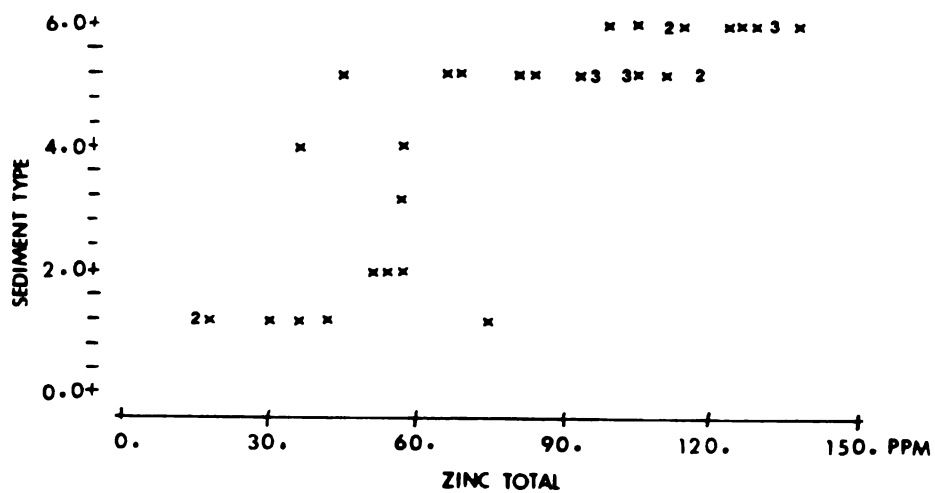
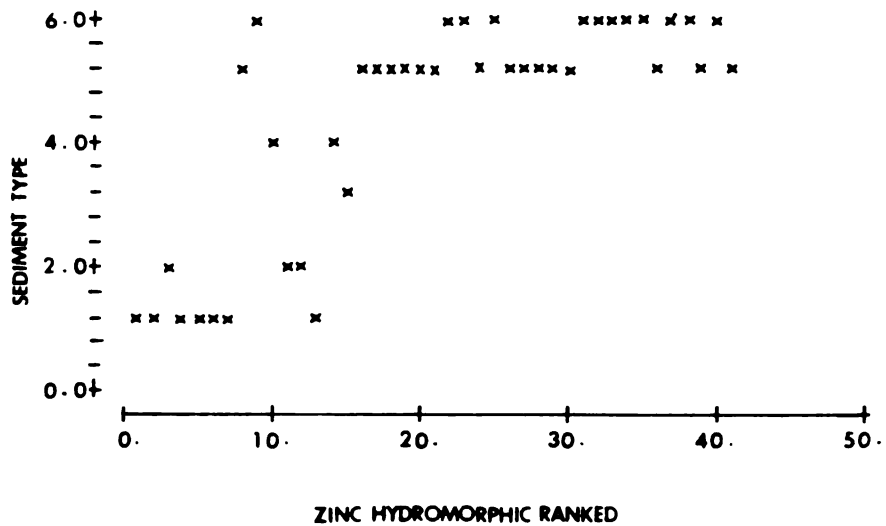
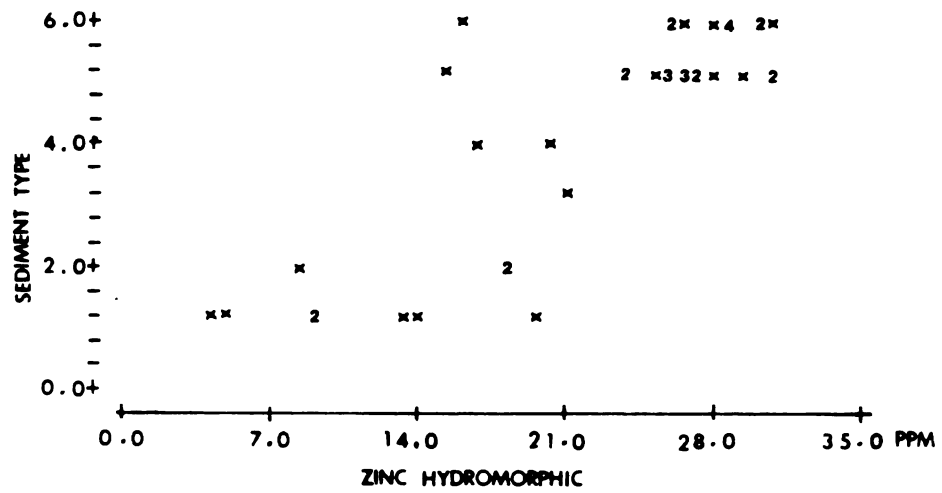


Figure 16. Plot of sediment type versus concentration of zinc in the hydromorphic fraction. Numbers refer to overlapped points.

Figure 17. Plot of sediment type versus concentration of zinc in the hydromorphic fraction plotted as ranked data.



type over the shelf. The dependency of metal concentration on grain-type is supported by the works of Gupta and Chen (1975), Loring (1979). On the Amazon Continental Shelf, grain-type appears to control metal concentration.

These results suggest that physical processes (mechanical deposition as a function of sediment type and shelf hydrodynamics) are mainly responsible for the distribution of metals on the shelf.

In an attempt to eliminate the effect of grain-type on metal concentrations when interpreting partitioning data, ratioed concentrations were studied. By using ratios, other possible controls (biogenic and geochemical) on metal distributions in shelf sediments can be deduced (Long and Gephart, 1982).

Ratios of metal concentration to Al were used to study metal distribution independent of biogenic effects (Sholkovitz and Price, 1980). Figures 18 and 19 are concentration maps of Zn residual/Al residual and Zn hydromorphic/Al total, respectively. Both maps show a strong dependency on grain-type and suggests that biogenic controls on the distribution of Zn in the shelf sediment is minor.

Zn, Ba/Fe + Mn oxide ratios were also utilized. The Fe + Mn oxide ratios were chosen because of the dependency of the oxide fraction on grain-type and by utilizing the ratio, normalization with respect to grain-type dependency was sought (Tessier et al., 1982). Figure 20 is a concentration map of Zn oxide/Fe + Mn oxide. The Zn oxide ratio has a uniform distribution across the shelf. Figure 21 is of Ba oxide/Fe + Mn oxide. The Ba oxide ratio has a high concentration (dump) at the mouth of the river and values decrease away from the coast. Figure 21 could be related to salinity, as the river waters mix with the oceans a

Figure 18. Contour map of the ratio zinc in the detrital fraction divided by aluminum in the detrital fraction in the surface (0-5 cm) sediments of the Amazon Continental Shelf.

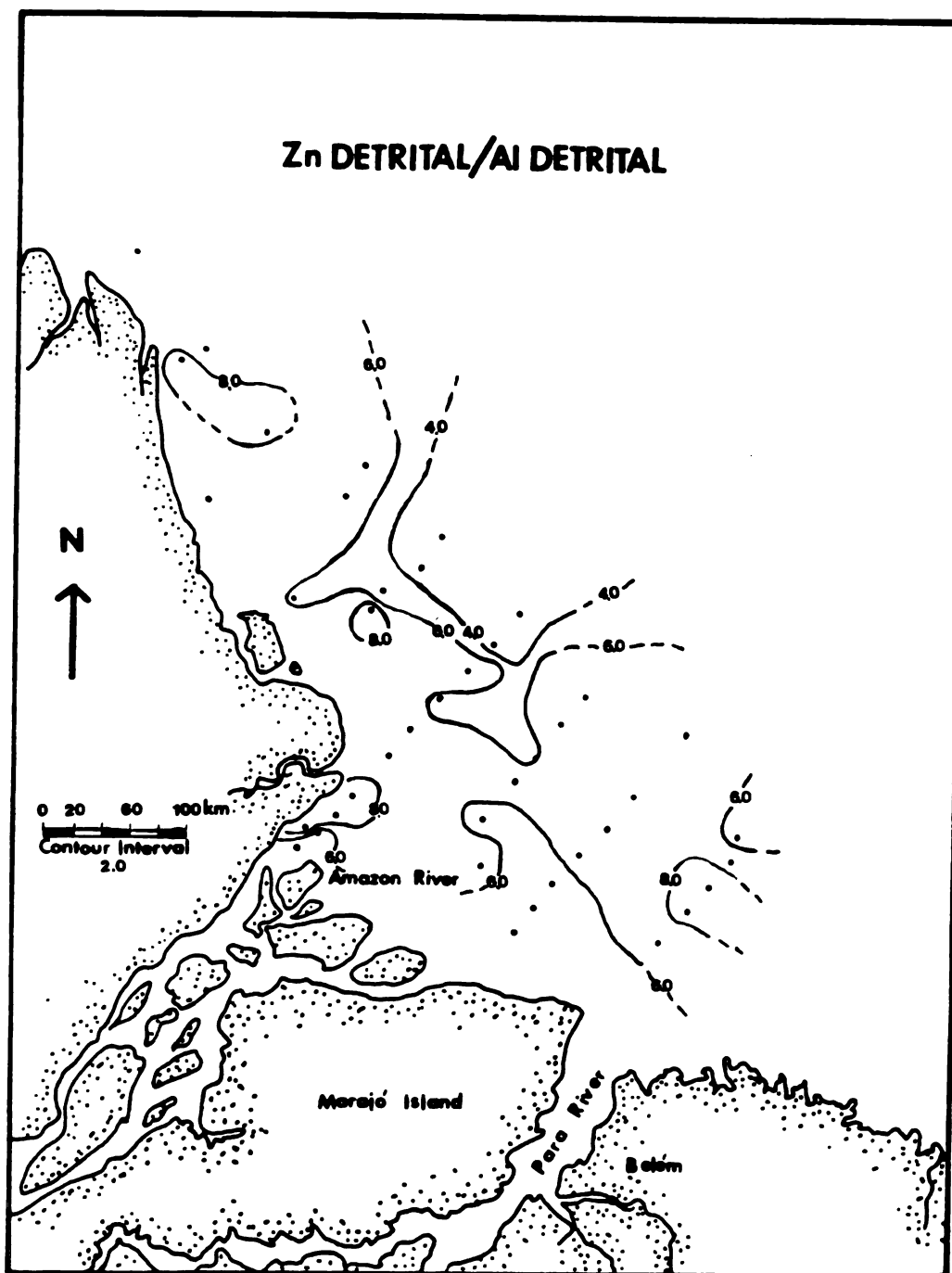


Figure 19. Contour map of the ratio hydromorphic zinc concentration divided by total aluminum concentration in the surface (0-5 cm) sediments of the Amazon Continental Shelf.

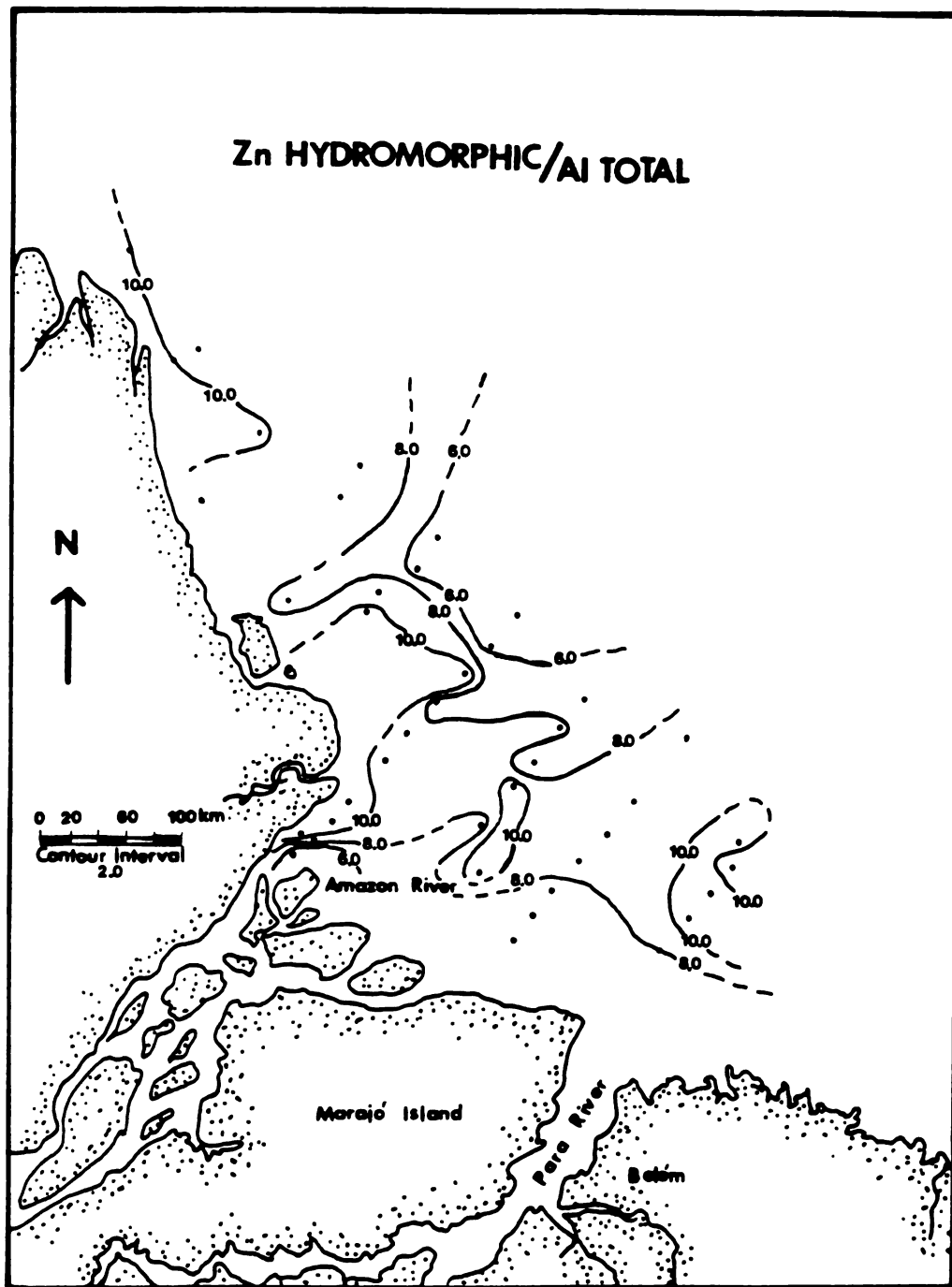


Figure 20. Contour map of the ratio zinc in the oxide fraction divided by iron and manganese in the oxide fraction in the surface (0-5 cm) sediments of the Amazon Continental Shelf.

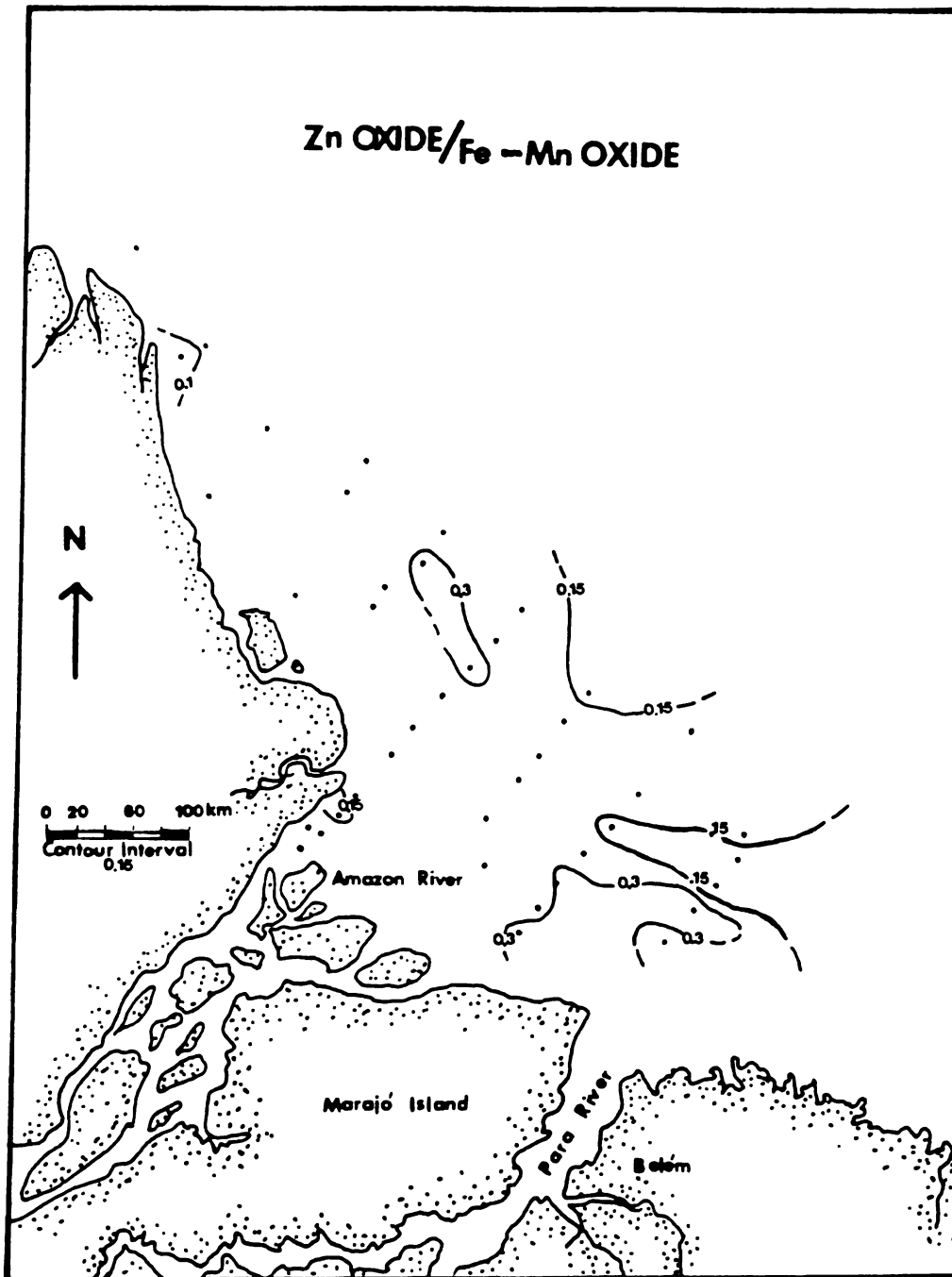
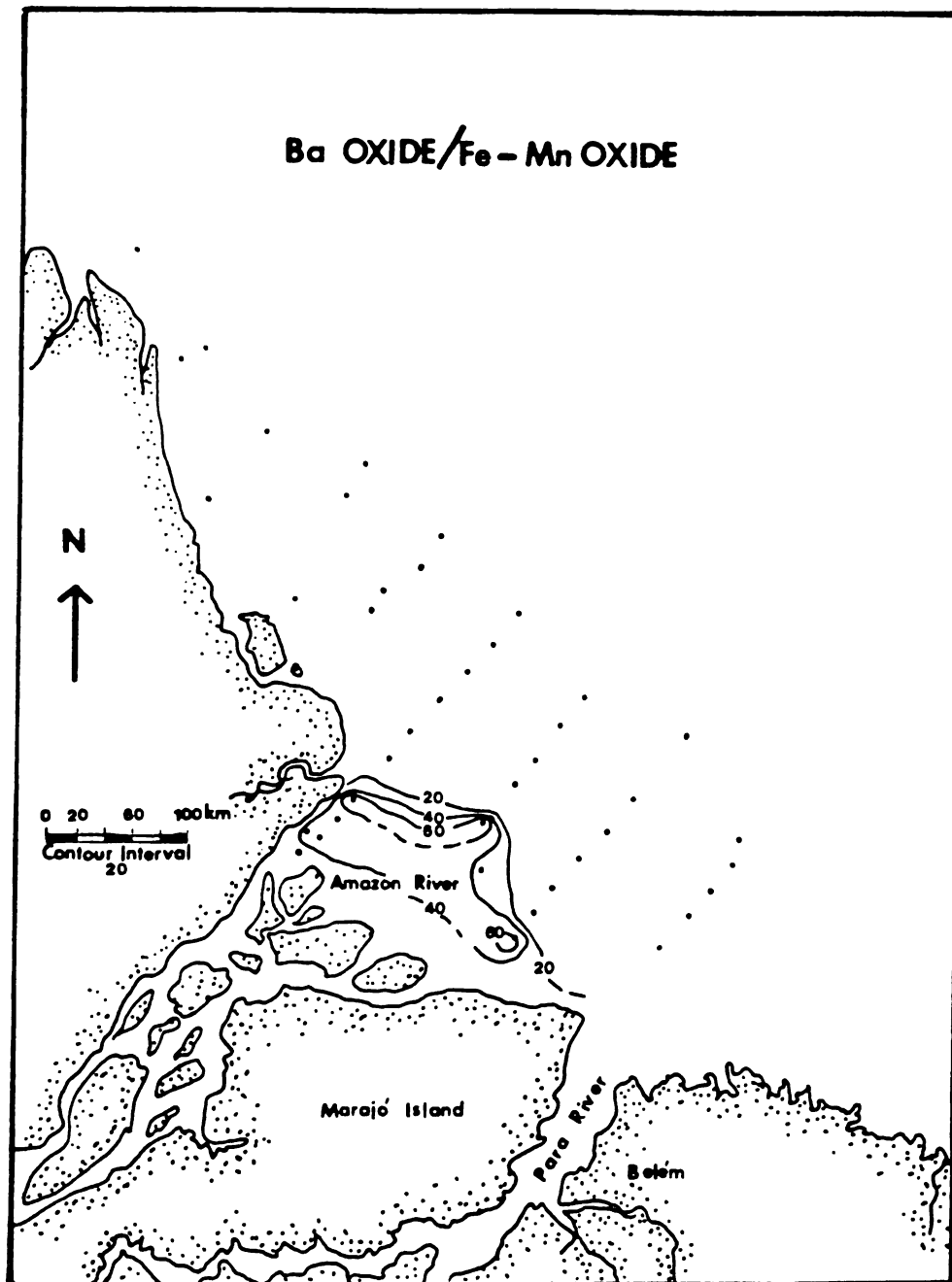


Figure 21. Contour map of the ratio barium in the oxide fraction divided by iron and manganese in the oxide fraction in the surface (0-5 cm) sediments of the Amazon Continental Shelf.



drop in terrigenous sediment load occurs before 3 0/00 salinity (Milliman et al., 1975) (Figure 3). Both maps (Figures 20 and 21) no longer show the strict grain-type dependency for the distribution of the metal in the sediment, each map having a slightly different distribution pattern.

Figures 22 and 23 show Zn hydromorphic/Zn residual and Ba hydromorphic/Ba residual, respectively. Both Figures (22 and 23) display an increase in hydromorphic/detrital ratios as one moves in a direction across the shelf, away from the coast. Also observed in Figure 22 is the high ratio Zn values associated with sediments of Types 1 and 2 (sands). These Figures suggest that either the hydromorphic fraction is a source for metals to seawater resulting in a decrease in hydromorphic fraction or that metal is repartitioned from the hydromorphic fraction to the detrital resulting in an increase in residual fraction to account for observed ratio trends.

Diagenesis of Metals in Amazon Shelf Sediments:

Sediment samples were taken as a function of depth at locations 10 and 42 (Figure 1). Core 42 and core 10 were found to have similar trends and therefore only core 10 will be discussed. Metal concentrations versus depth profiles are in Figures 24-31 for core 10. Figure 24 shows sediment type for samples with depth. Figure 25 is a plot of Cr concentration with depth and shows that the organic and oxide phases are of minor importance in controlling Cr concentration and have a constant value throughout the core. Chromium concentrations in the detrital phase, however, show several fluctuations. There is a decrease at 50 cm (silt composition), an increase at 220 cm (clay composition), a

Figure 22. Contour map of the ratio zinc in the hydromorphic fraction divided by zinc in the detrital fraction in the surface (0-5 cm) sediments of the Amazon Continental Shelf.

Zn HYDROMORPHIC/Zn DETRITAL

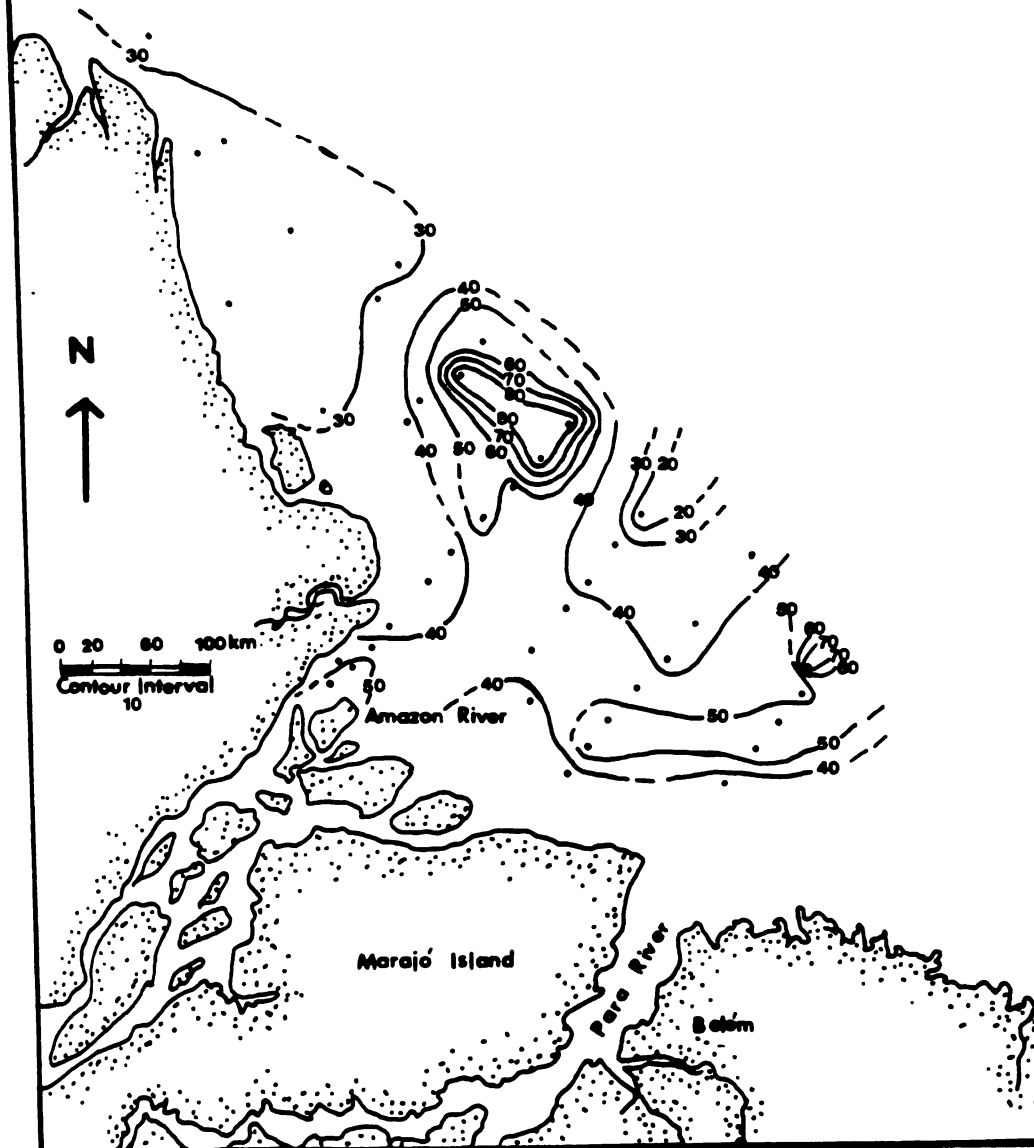


Figure 23. Contour map of the ratio barium in the hydromorphic fraction divided by barium in the detrital fraction.

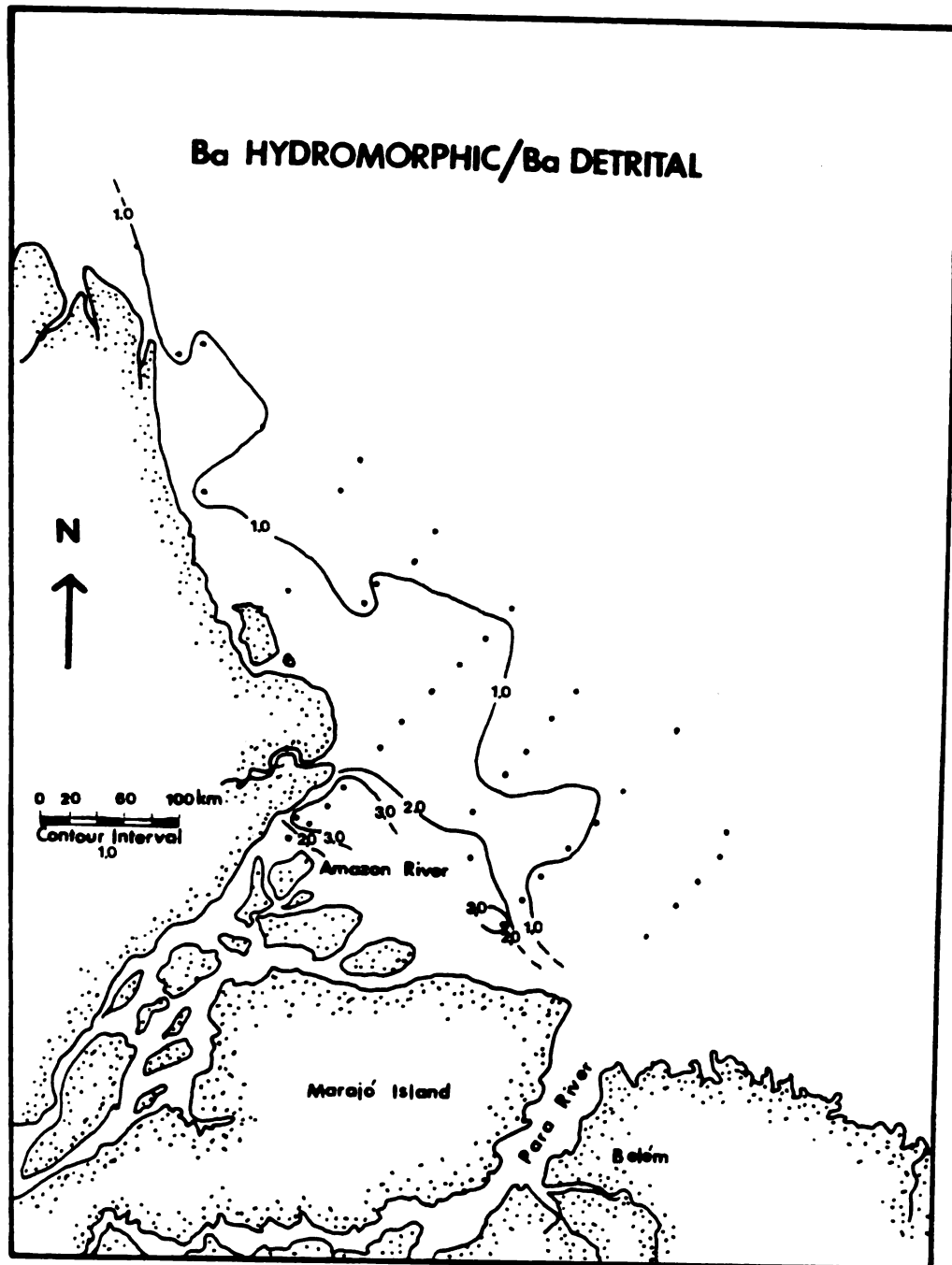


Figure 24. Sediment type with depth for core 10 (Nittrouer et al., 1983).

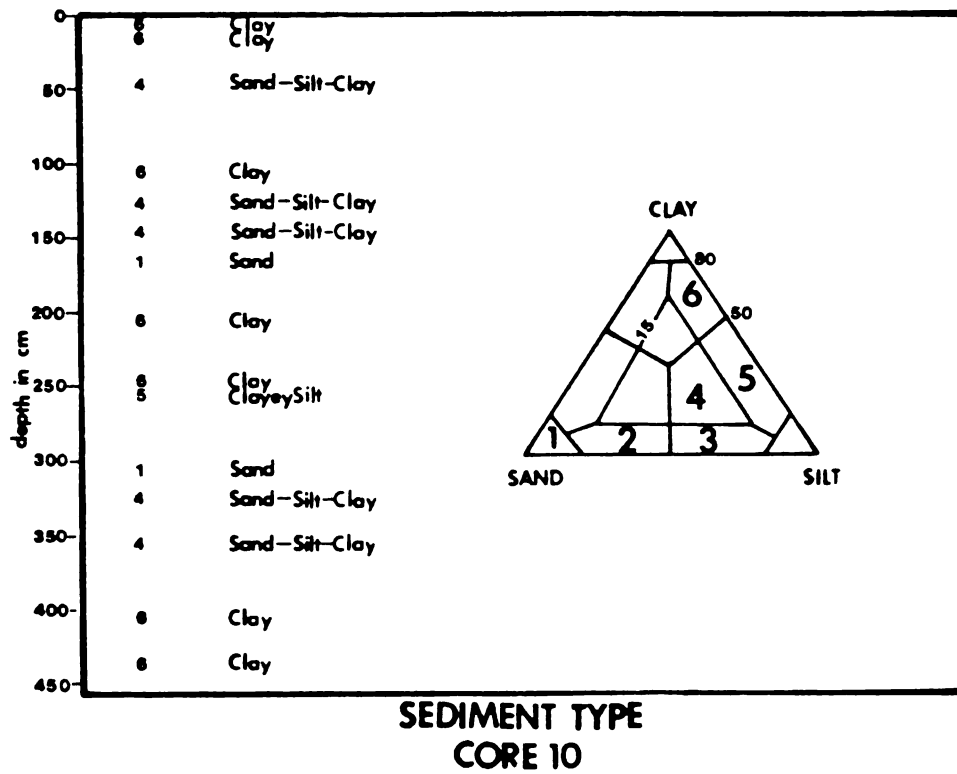
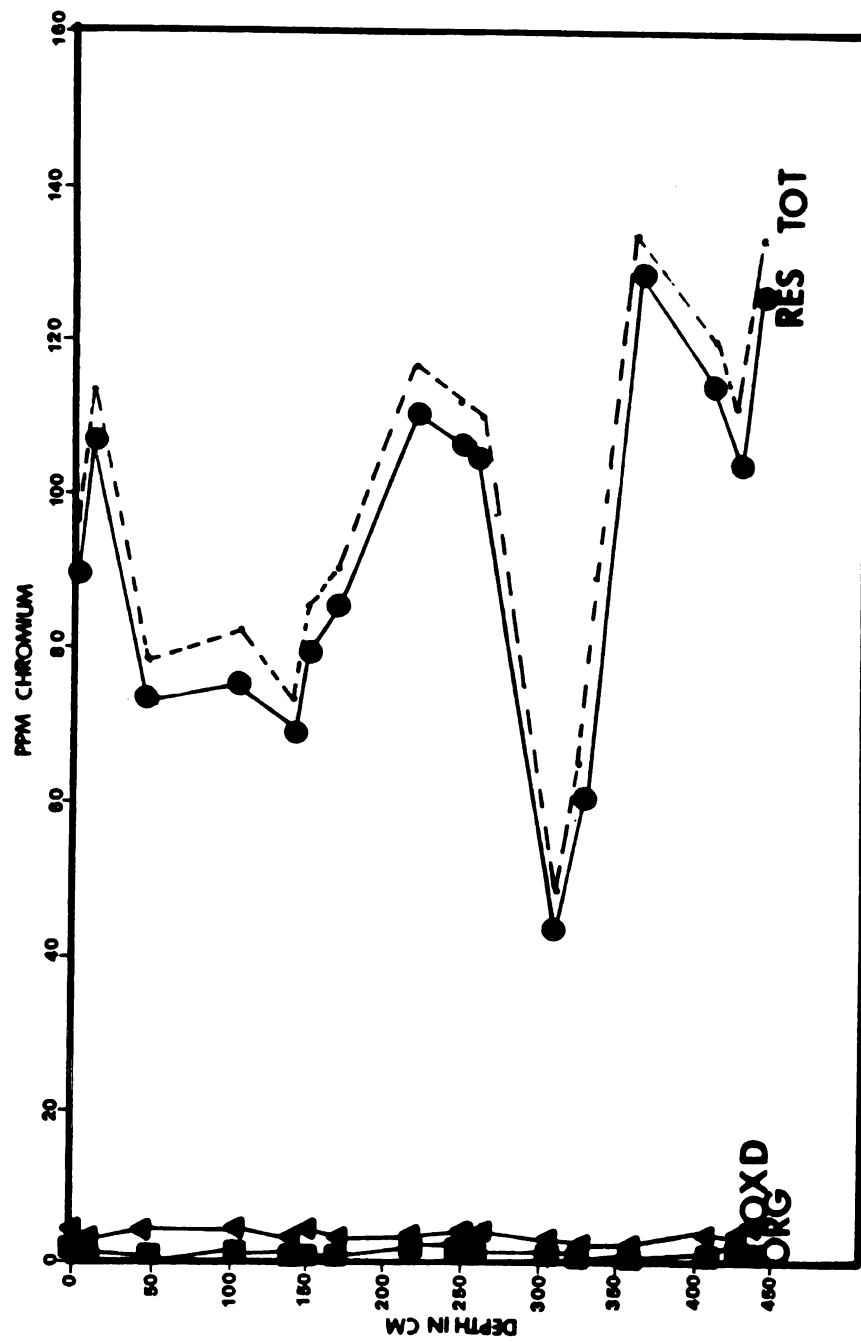


Figure 25. Concentration of chromium with depth in core 10.

Symbol key:

- ORG - organic fraction
- ▲ OXD - oxide fraction
- RES - detrital fraction
- TOT - total Cr concentration



CORE 10 CHROMIUM

decrease at 310 cm (sand), and an increase at 350 cm (silt composition). This suggests for Cr that the detrital fraction is grain-type dependent.

Iron concentration versus depth (Figure 26) shows relatively constant concentration values for Fe in the oxide and detrital phases. However, a slight decrease of Fe in these fractions is observed at 360 cm where a compositional change from sand-silt-clay to silty-clay occurs. The exchangeable, and organic phases show a fluctuation in Fe concentration at 100 cm; the exchangeable phase increases while the organic phase decreases. At 200 cm there is a decrease in Fe concentration and at 350 cm, another decrease in both exchangeable and organic phases. These changes in concentration reflect changes in composition. (Type 4 has a higher concentration value than Type 6). This suggests that for Fe, grain-type plays a significant part in metal concentration.

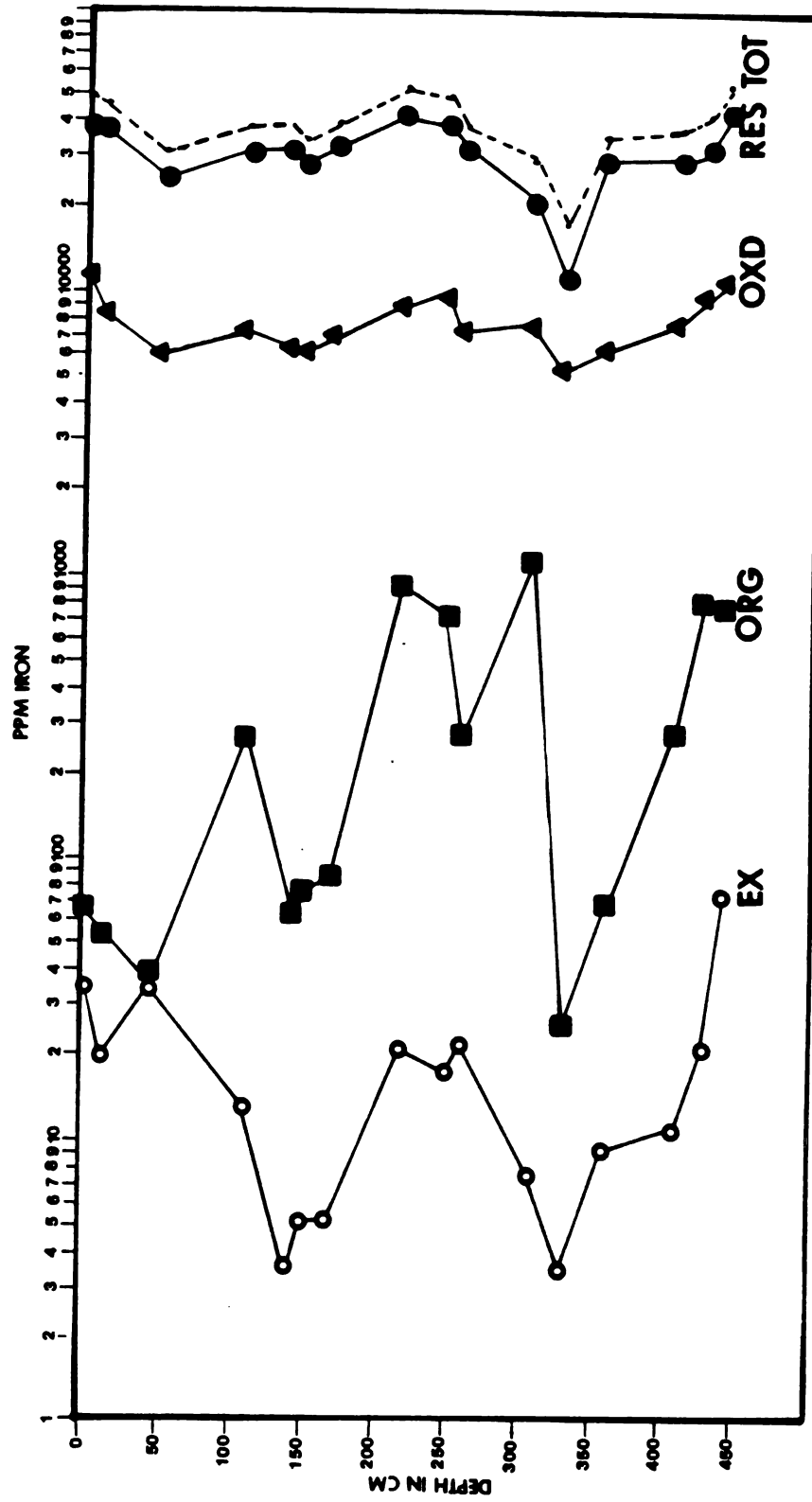
Mn concentration with depth (Figure 27) shows that the amount of Mn in the exchangeable, residual and organic fractions is fairly constant with depth. Manganese in the oxide fraction (the major phase of Mn in the sediment) changes with depth as a function of sediment type. The highest concentration values are in the sand-silty-clay composition, the lower concentrations appear in the sand and silty-clay compositions. Thus, for Mn, the concentration changes with depth and nature of its partitioning suggests that Mn concentration is grain-type dependent and that the total Mn concentration pattern reflects the Mn oxide pattern.

Figure 28 is a plot of Zn concentration versus depth. The Zn plot shows that concentrations in the organic and oxide phases are constant

Figure 26. Concentration of iron with depth in core 10.

Symbol key:

- EX - exchangeable fraction
- ORG - organic fraction
- ▲ OXD - oxide fraction
- RES - detrital fraction
- TOT - total Fe concentration

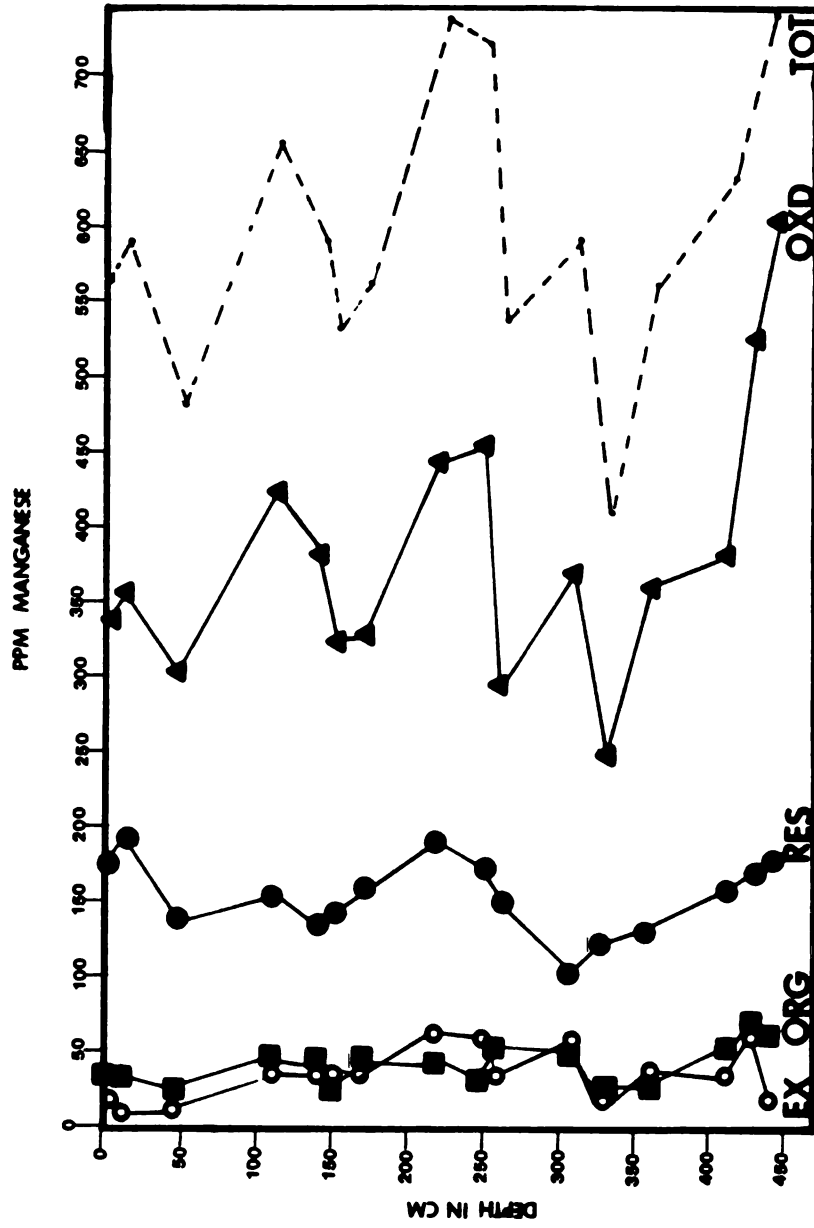


CORE 10 IRON

Figure 27. Concentration of manganese with depth in core 10.

Symbol key:

- EX - exchangeable fraction
- ORG - organic fraction
- ▲ OXD - oxide fraction
- RES - detrital fraction
- TOT - total Mn concentration

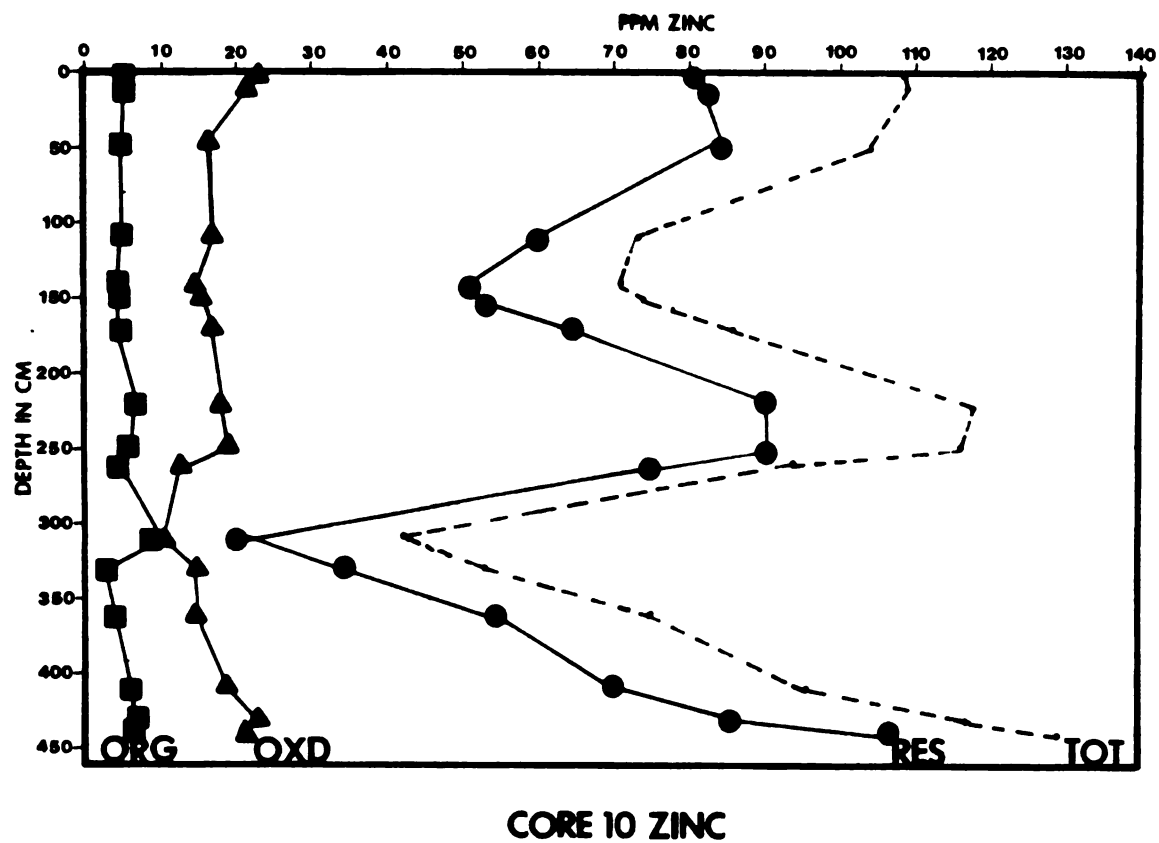


CORE 10 MANGANESE

Figure 28. Concentration of zinc with depth in core 10.

Symbol key:

- ORG - organic fraction
- ▲ OXD - oxide fraction
- RES - detrital fraction
- TOT - total Zn concentration



with depth except at 330 cm. There is a decrease of Zn in the organic phase and an increase of Zn in the oxide phase. There are two fluctuations of Zn in the residual phase with depth: at 150 cm and at 310 cm. Both depths show a decrease in detrital concentration of Zn. At 150 cm and 310 cm depths the sediment composition changes to the sand (Type 1). Other compositional changes (sand-silty-clay and silty-clays) appear to have no discernable effect on concentrations of Zn in the sediment.

Figure 29 is a plot of Cu concentration with depth. Copper in the oxide fraction appears constant with depth and is relatively small. The organic fraction also is constant with depth except for an increase at 300 cm. The organic fraction increases drastically due to encountering a grain-type compositional change at this point. Copper in the detrital fraction is of dominate control on its concentration in these sediments and fluctuates throughout the sediment core. The Cu detrital fraction appear to be controlled by the sediment type (higher concentration values are associated with clay type sediment and lower concentration values are associated with sand type composition).

Figures 30 and 31, nickel and barium concentrations with depth, respectively, show similar grain-type dependencies. The organic and oxide fraction are relatively unimportant and remain constant with depth. Little repartitioning occurs with depth. The detrital fraction has two major low level concentration points at 150 cm and 300 cm for both barium and nickel profiles. These low level concentration points correspond to a sand grain-type (Type 1). High concentration levels correspond to a clay grain-type (Type 5 and Type 6). Nickel and barium

Figure 29. Concentration of copper with depth in core 10.

Symbol key:

- ORG - organic fraction
- ▲ OXD - oxide fraction
- RES - detrital fraction
- TOT - total Cu concentration

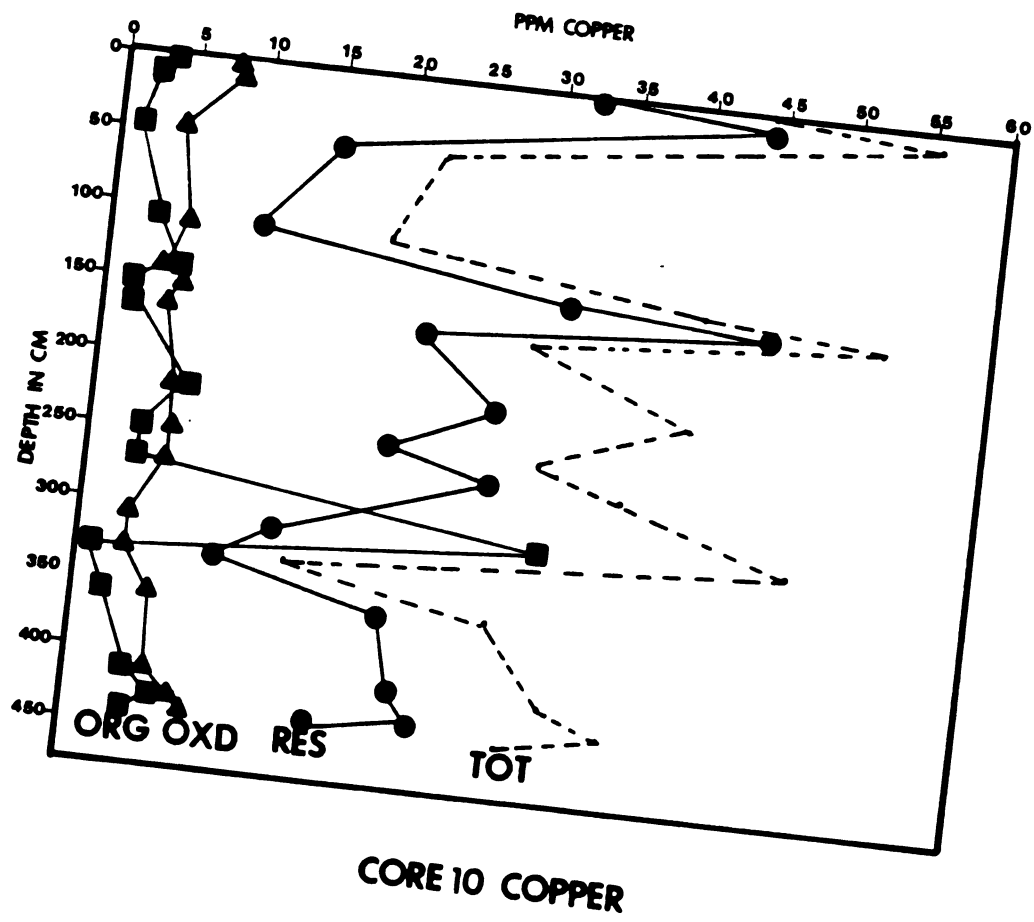


Figure 30. Concentration of nickel with depth in core 10.

Symbol key:

■ ORG - organic fraction

▲ OXD - oxide fraction

● RES - detrital fraction

- TOT - total Ni concentration

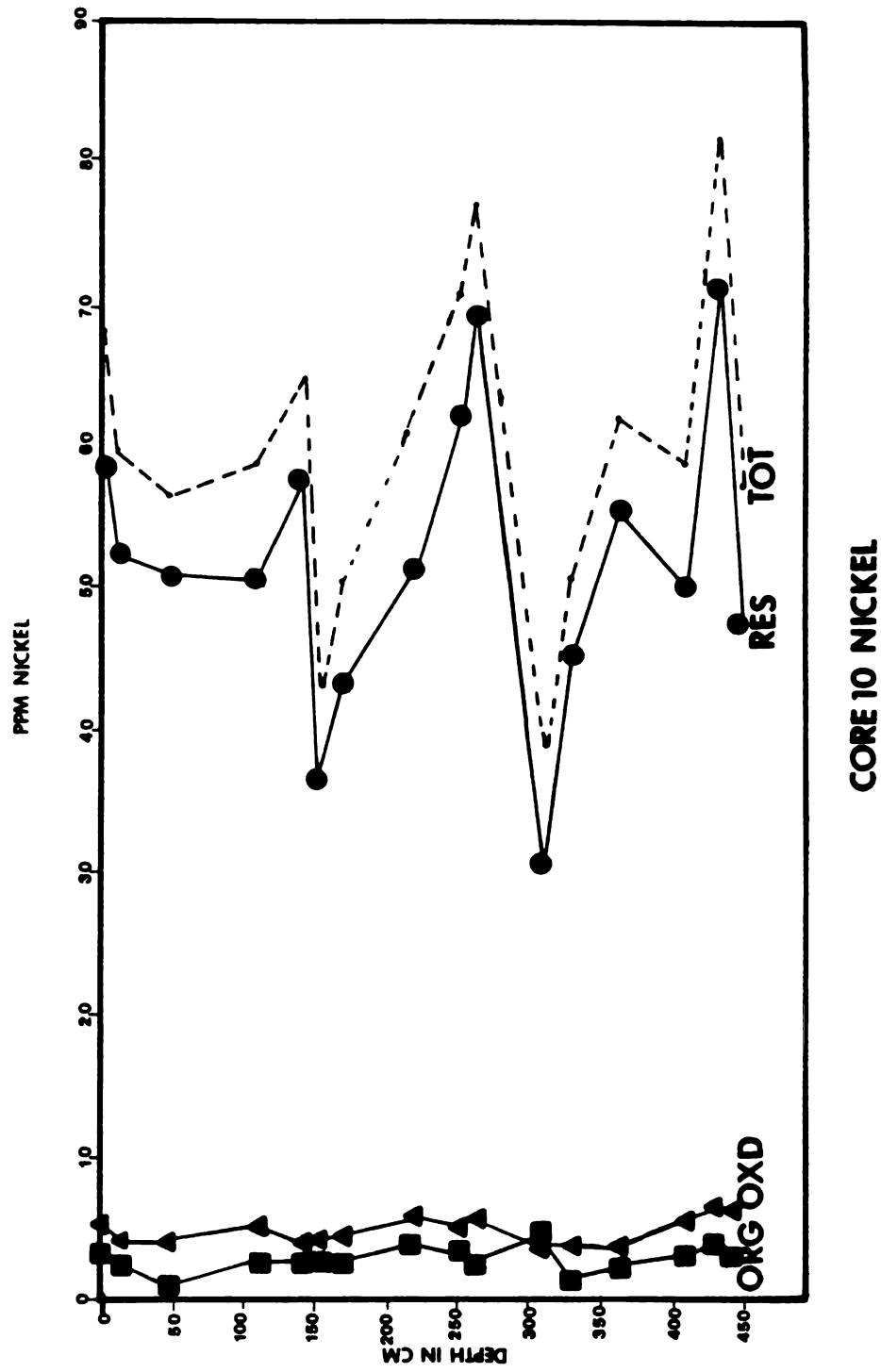
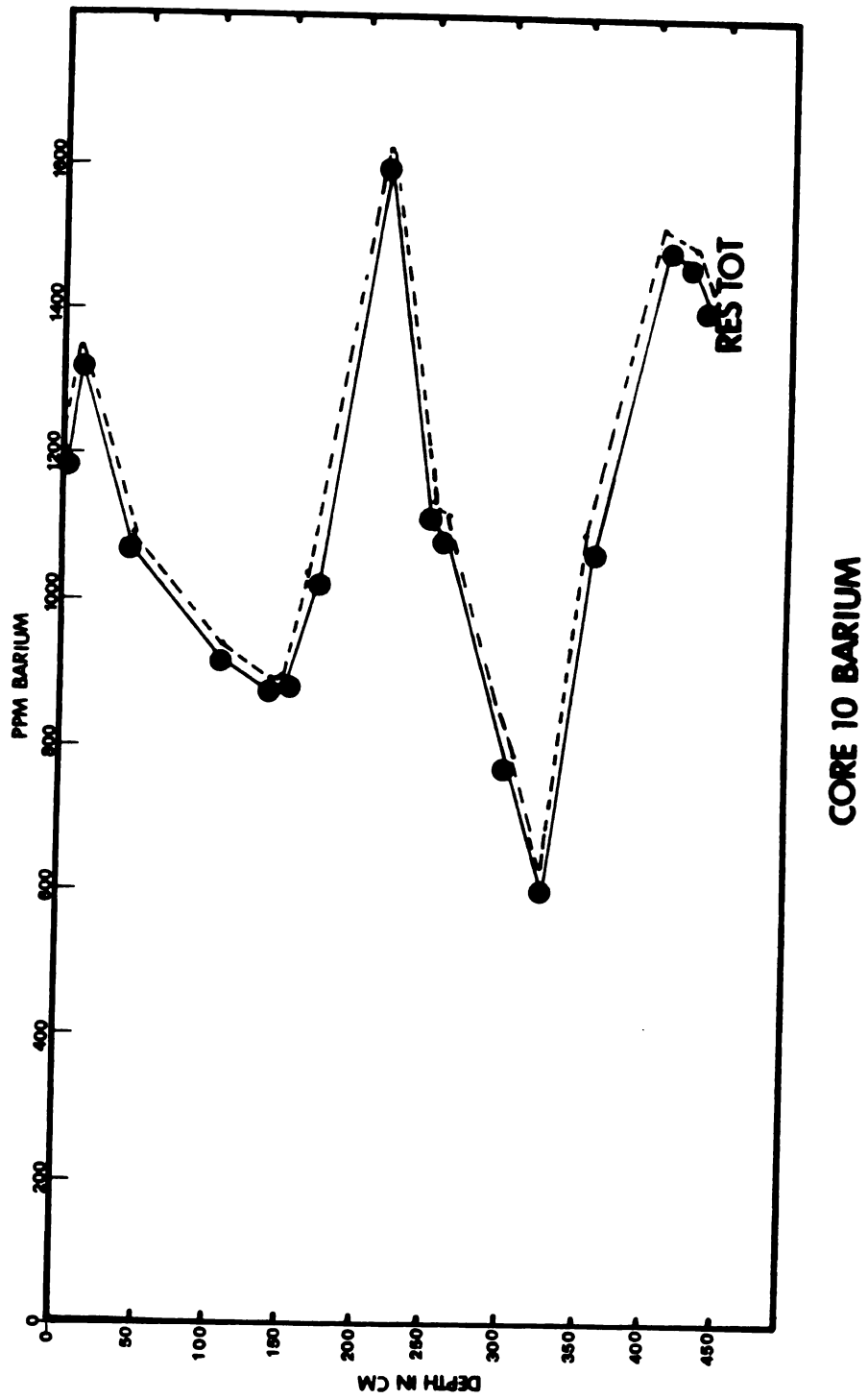


Figure 31. Concentration of barium with depth in core 10.

Symbol key:

- RES - detrital fraction
- TOT - total Ba concentration



concentrations with depth are, therefore, grain-type dependent and show little repartitioning.

In general, there exists a relationship between sediment type and concentration of the detrital fraction. The hydromorphic phase is more independent of sediment type with depth than they are at the surface (excluding Mn oxide fraction). The relative importance of the hydromorphic phases in sequestering metal does not indicate major repartitioning of the metals with depth within the hydromorphic fraction.

These observations can be interpreted to indicate that to a depth of 450 cm on the shelf, the metal concentrations in the sediment are dependent on sediment type. However, the relatively high amount of Mn in the Fe-Mn oxide fraction results in the profile of total Mn concentration with depth to be independent of sediment type as the Mn in the oxide fraction gets redistributed.

Core 10 sediments are also considered oxic throughout the core length. The lack of decreasing metal concentration in the oxide phase and no observable oxidized sediment zone enrichment for Ni, Fe, Mn, and Co which is expected when reducing conditions are encountered [Addy et al., 1976; Holmes and Martin, 1978; Heath and Dymond, 1981]. These observations lead to the conclusion that core 10 does not encounter a reducing environment and is therefore considered oxic throughout the core.

Source:

Partitioning data for the surface (0-5 cm) shelf sediments were arranged in a Q-mode and R-mode factor analysis array. The data was factored in raw form and in transformed form (i.e., natural log matrix) (Loring, 1982). The B-matrix for factor analysis of raw R-mode,

transformed R-mode, transformed R-mode PA1, raw Q-mode, and transformed Q-mode PA1 appear in Appendix III. Q-mode will be discussed below. The results of R-mode factor analysis will not be discussed, however the data appears in Appendix III. PA1 (principal factoring iteration) was employed because one factor dominated. PA1 may extract other variables which cannot be determined by other factor methods (Statistical Package for the Social Sciences, 1975).

The B-matrix is the influence of each end member on the total metals found in each sediment sample (Bopp and Biggs, 1981). Q-mode factor analysis, both raw and transformed PA1 forms, show high communality (i.e., squared multiple correlation) of about .9 and has one factor accounting for greater than 90% factor influence on the shelf. In conclusion, only one factor appears to be controlling the source of trace metals to the shelf sediments. This factor is interpreted to indicate that the Amazon River is the dominant source. Other factors accounting for an anthropogenic source or a biogenic source are undetectable. A hydrothermal source is also undetectable, which is in support with past work (Dymond and Heath, 1982).

CONCLUSIONS

This research examined the chemical partitioning of Fe, Mn, Zn, Cu, Pb, Ni, Cr, Co, Ba and Al among four theoretical phases within continental shelf sediments and soils from Belém. The conclusions of this study are:

- (1) The Amazon River is dominate over all other sources of trace metals to shelf sediments.
- (2) Significant repartitioning of metals in sediment occurs when sediments move from a river to an ocean environment.
- (3) The suspended load sediment of the river can be a potential source of metals to seawater, when the sediment enter seawater. The order of importance for this source decreases in the sequence Ni>Co>Fe>Cr.
- (4) Metal concentrations and distribution in and on the shelf are mainly dependent on the grain-type of the sediment.
- (5) Amazon shelf sediments do not encounter reducing conditions to a depth of 450 cm.
- (6) Little repartitioning of metals in the sediment occurs with depth.

REFERENCES

Figure 29. Concentration of copper with depth in core 10.

Symbol key:

- ORG - organic fraction
- ▲ OXD - oxide fraction
- RES - detrital fraction
- TOT - total Cu concentration

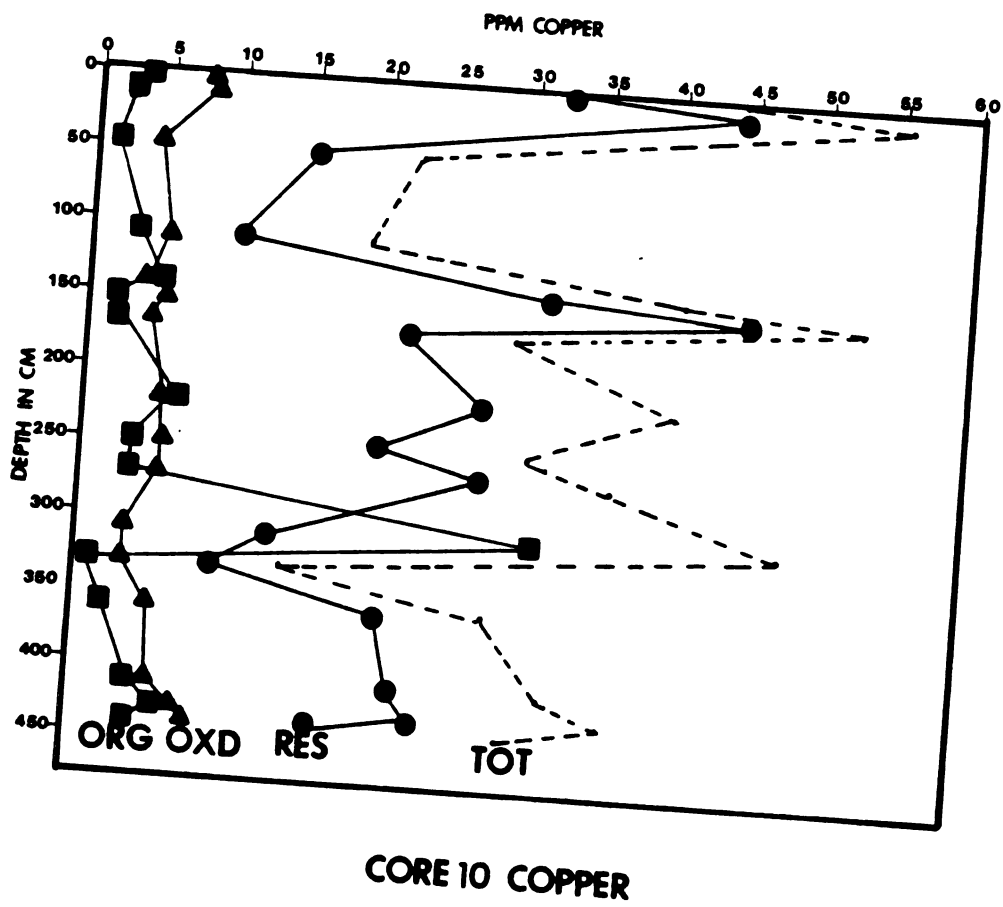
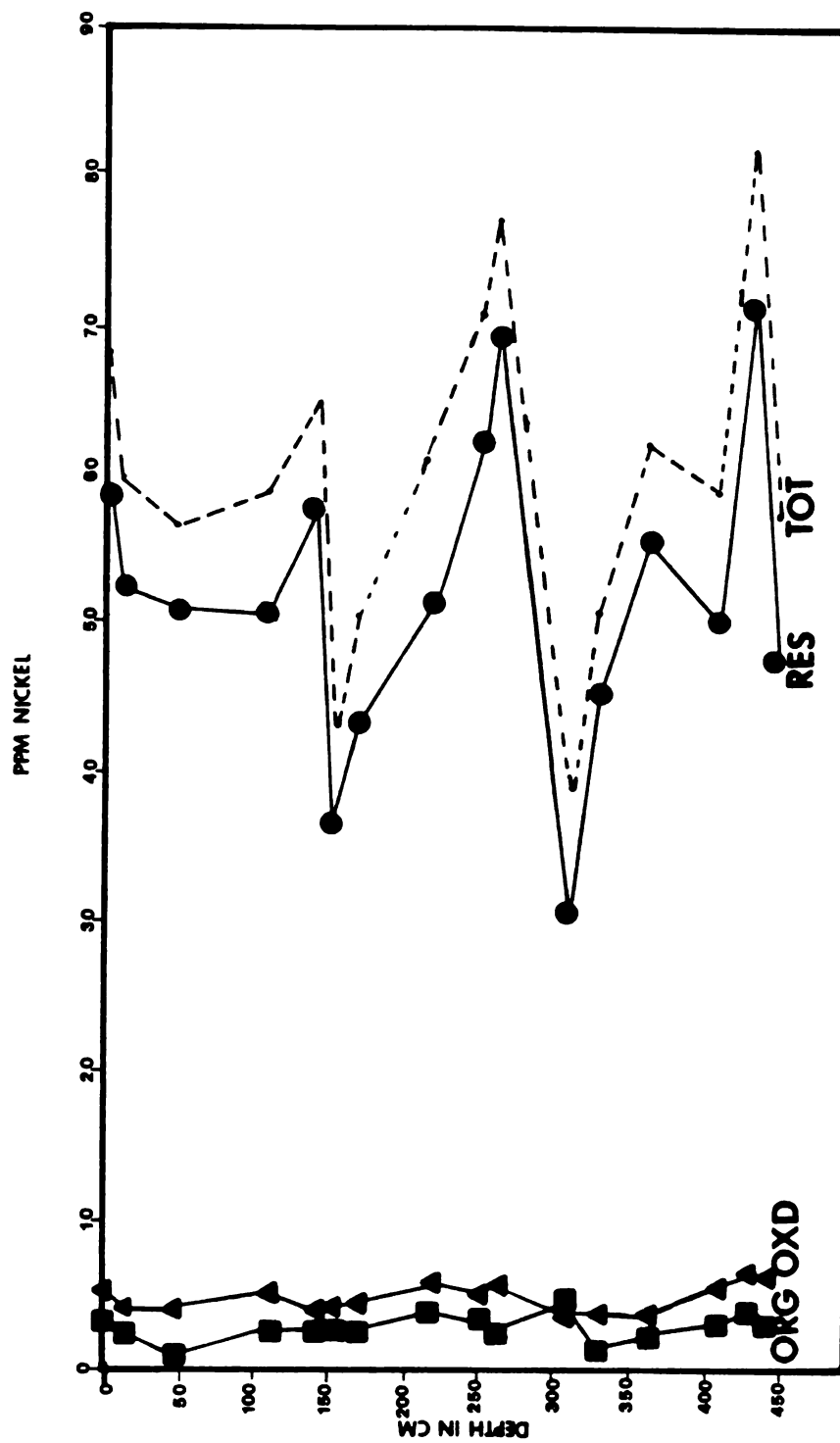


Figure 30. Concentration of nickel with depth in core 10.

Symbol key:

- ORG - organic fraction
- ▲ OXD - oxide fraction
- RES - detrital fraction
- TOT - total Ni concentration

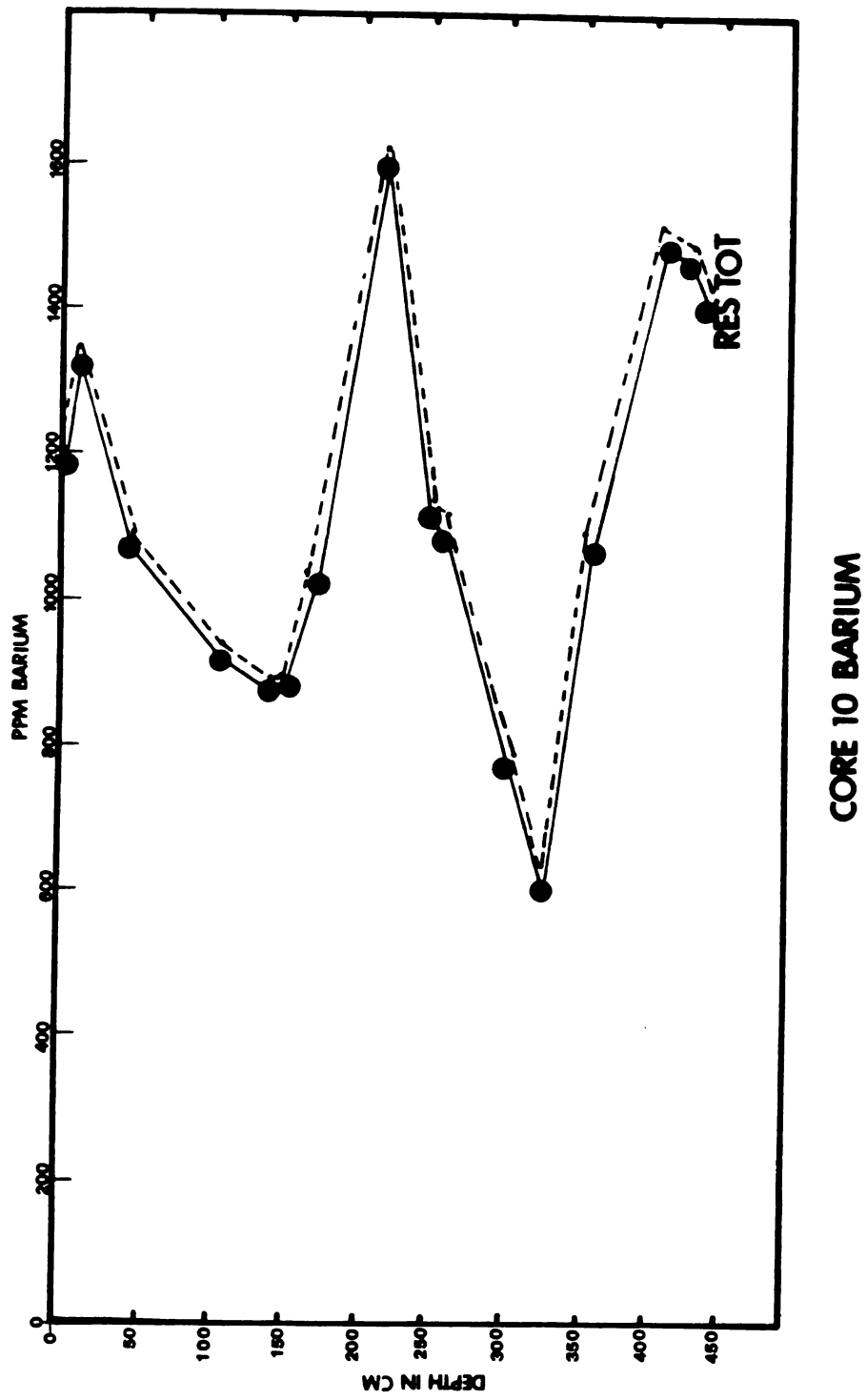


CORE 10 NICKEL

Figure 31. Concentration of barium with depth in core 10.

Symbol key:

- RES - detrital fraction
- TOT - total Ba concentration



concentrations with depth are, therefore, grain-type dependent and show little repartitioning.

In general, there exists a relationship between sediment type and concentration of the detrital fraction. The hydromorphic phase is more independent of sediment type with depth than they are at the surface (excluding Mn oxide fraction). The relative importance of the hydromorphic phases in sequestering metal does not indicate major repartitioning of the metals with depth within the hydromorphic fraction.

These observations can be interpreted to indicate that to a depth of 450 cm on the shelf, the metal concentrations in the sediment are dependent on sediment type. However, the relatively high amount of Mn in the Fe-Mn oxide fraction results in the profile of total Mn concentration with depth to be independent of sediment type as the Mn in the oxide fraction gets redistributed.

Core 10 sediments are also considered oxic throughout the core length. The lack of decreasing metal concentration in the oxide phase and no observable oxidized sediment zone enrichment for Ni, Fe, Mn, and Co which is expected when reducing conditions are encountered [Addy et al., 1976; Holmes and Martin, 1978; Heath and Dymond, 1981]. These observations lead to the conclusion that core 10 does not encounter a reducing environment and is therefore considered oxic throughout the core.

Source:

Partitioning data for the surface (0-5 cm) shelf sediments were arranged in a Q-mode and R-mode factor analysis array. The data was factored in raw form and in transformed form (i.e., natural log matrix) (Loring, 1982). The B-matrix for factor analysis of raw R-mode,

transformed R-mode, transformed R-mode PA1, raw Q-mode, and transformed Q-mode PA1 appear in Appendix III. Q-mode will be discussed below. The results of R-mode factor analysis will not be discussed, however the data appears in Appendix III. PA1 (principal factoring iteration) was employed because one factor dominated. PA1 may extract other variables which cannot be determined by other factor methods (Statistical Package for the Social Sciences, 1975).

The B-matrix is the influence of each end member on the total metals found in each sediment sample (Bopp and Biggs, 1981). Q-mode factor analysis, both raw and transformed PA1 forms, show high communality (i.e., squared multiple correlation) of about .9 and has one factor accounting for greater than 90% factor influence on the shelf. In conclusion, only one factor appears to be controlling the source of trace metals to the shelf sediments. This factor is interpreted to indicate that the Amazon River is the dominant source. Other factors accounting for an anthropogenic source or a biogenic source are undetectable. A hydrothermal source is also undetectable, which is in support with past work (Dymond and Heath, 1982).

CONCLUSIONS

This research examined the chemical partitioning of Fe, Mn, Zn, Cu, Pb, Ni, Cr, Co, Ba and Al among four theoretical phases within continental shelf sediments and soils from Belém. The conclusions of this study are:

- (1) The Amazon River is dominate over all other sources of trace metals to shelf sediments.
- (2) Significant repartitioning of metals in sediment occurs when sediments move from a river to an ocean environment.
- (3) The suspended load sediment of the river can be a potential source of metals to seawater, when the sediment enter seawater. The order of importance for this source decreases in the sequence Ni>Co>Fe>Cr.
- (4) Metal concentrations and distribution in and on the shelf are mainly dependent on the grain-type of the sediment.
- (5) Amazon shelf sediments do not encounter reducing conditions to a depth of 450 cm.
- (6) Little repartitioning of metals in the sediment occurs with depth.

REFERENCES

REFERENCES

- Addy S. K., Presley B.J. and Ewing M. (1976) Distribution of manganese, iron and other trace elements in a core from the Northwest Atlantic. *J. Sed. Pet.* 46, (4), 813-818.
- Bender M., Broecker W., Gornitz V., Middel U., Kay R., Sun S.S. and Biscaye P. (1971) Geochemistry of 3 cores from the East Pacific Rise. *Earth and Planet. Sci. Lett.* 12, 425-433.
- Bischoff J.L. and Dickson F.W. (1975) Seawater-basalt interaction at 200°C and 500 bars: Implications for origin of seafloor heavy-metal deposits and regulation of seawater chemistry. *Earth and Planet. Sci. Lett.* 25, 385-397.
- Bonatti E., Fisher D.E., Joensuu O. and Rydell H.S. (1971) Post depositional mobility of some transition elements, phosphorus, uranium, and thorium in deep sea sediments. *Geochim. Cosmochim. Acta* 35, 189-201.
- Bopp F. III and Biggs R.B. (1981) Metals in estuarine sediments: Factor analysis and its environmental significance. *Science* 214, 441-443.
- Bopp F. III (1981) Ph.D. Thesis: University of Delaware, 1-179.
- Brannon J.M., Rose J.R., Engler R.M. and Smith I. (1977) The distribution of heavy metals in sediment fractions from Mobil Bay, Alabama. *Chemistry of Marine Sediments*, (ed. T.F. Yen), 125-149.
- Brooks R.R., Presley B.J. and Kaplan I.P. (1968) Trace elements in the interstitial waters of marine sediments. *Geochim. Cosmochim. Acta* 32, 397-414.
- Brumsack H.J. (1980) Geochemistry of cretaceous black shales from the Atlantic Ocean. *Chem. Geol.* 31, 1-25.
- Corliss J.B., Dymond J., Gordon L.I., Edmond J.M., Von Herzen R.P., Ballard R.D., Green K., Williams D., Bainbridge A., Crane K., and Van Andel T.H. (1979) Submarine thermal springs on the Galapagos rift. *Science* 203, (4385), 1073-1083.

- Cosma B., Drago M., Tucci S., Piccazzo M. and Scarponi G. (1979) Heavy metals in Ligurian Sea sediments: Distribution of Cr, Cu, Ni and Mn in superficial sediments. *Mar. Chem.* 8, 125-142.
- DeMaster D. (1982) Personal communication. North Carolina State University.
- Demina L.L., Gordeyev V.V. and Formina L.S. (1978) Forms of occurrence of Fe, Mn, Zn, and Cu in river water and suspended matter, and their variation in the zone of mixing of river and seawater. (As exemplified by Rivers of the Black Sea, Sea of Azov, and Caspian Sea Basins). *Geochem. Intl.* 15, (4), 146-163.
- Drever J.I. (1982) *The Geochemistry of National Waters*, Prentice-Hall, Inc., 163-165.
- Dymond J. (1981) Geochemistry of nazca plate surface sediments: An evaluation of hydrothermal, biogenic, detrital, and hydrogenous sources. *Geol. Soc. Amer.* 154, 133-173.
- Dymond J., Corliss J.B., Cobler R., Muratii C.M., Chou C. and Conard R. Composition and origin of sediments recovered by deep drilling of sediment mounds, Galapagos Spreading Center. 377-385.
- Edmond J.M. (1981) Hydrothermal activity at mid-ocean ridge axes. *Nature* 290, (5802) 87-88.
- Edmond J.M., Craig H., Gordon L.I. and Holland H.D. (1979) Chemistry of hydrothermal waters at 21°N on the East Pacific Rise. *EOS* 60, (46), 864.
- Edmond J.M., Measures C., McDuff R.E., Chan L.H., Collier R., Grant B., Gordon L.I. and Corliss J.B. (1979) Ridge crest hydrothermal activity and the balances of the major and minor elements in the ocean: The Galapagos data. *Earth Planet. Sci. Lett.* 46, 1-18.
- Edmond J.M., Von Damm K.L., McDuff R.E. and Measures C.I. (1982) Chemistry of hot springs on the East Pacific Rise and their effluent disposal. *Nature* 297, 187-191.
- Eisma D. and Van Der Mavel H.W. (1971) Marine muds along the Guyana Coast and their origin from the Amazon Basin. *Contrib. Mineralogy and Petrology* 31, 321-334.
- Folk R.L. (1974) *Petrology of sedimentary rocks*. Hemphill Publ. Co. 182.
- Gaudette H.E., Flight, W.R., Toner, L. and Floger, D.W. (1974) An inexpensive titration method for the determination of organic carbon in recent sediments. *J. Sed. Pet.* 44, (1), 249-253.

- Gephart C.J. (1982) Relative importance of iron-oxide, manganese-oxide, and organic material on the adsorption of chromium in natural water sediment systems. MS Thesis, Michigan State University.
- Gibbs R.J. (1965) The Geochemistry of the Amazon River Basin. Ph.D. Thesis, University of California, San Diego.
- Gibbs R.J. (1967) The geochemistry of the Amazon River system: Part I the factors that control the salinity and the composition and concentration of the suspended solids. *Geol. Soc. Amer. Bull.* 78, 1203-1232.
- Gibbs R.J. (1976) Amazon River sediment transport in the Atlantic Ocean. *Geology* 4, 45-48.
- Gibbs R.J. (1977) Transport phases of transition metals in the Amazon and Yukon Rivers. *Geol. Soc. Amer. Bull.* 88, 829-843.
- Grupta S.K. and Chen K.Y. (1975) Partitioning of trace metals in selective chemical fractions on nearshore sediments. *Environ. Letters* 10, (2), 129-158.
- Harding S.C. and Brown H.S. (1976) Distribution of selected trace elements in sediments of Pamlico River, Estuary, North Carolina. *Environ. Geol.* 1, (3), 181-190.
- Heath G.R. and Dymond J. (1981) Metalliferous-sediment deposition in time and space: East Pacific Rise and Bauer Basin Northern Nazca Plate. *Nazca Plate: Crustal Formation and Andean Convergence.* 175-197.
- Hoffmann J.A.J. (1975) Climatic Atlas of South America WMO: Hungary.
- Holeman J.N. (1968) The sediment yield of major rivers of the world. *Water Resources Research* 4, 737-747.
- Holmes C.W. and Martin E.A. (1978) Migration of anthropogenically induced trace metals (barium and lead) in a continental shelf environment. *Amer. Chem. Society* 672-676.
- Imbrie J. and Van Andel T.H. (1964) Factor analysis of heavy-mineral data. *Geol. Soc. Amer. Bull.* 75, 1131-1156.
- Kerlinger F.N. (1973) Foundations of behavioral research. Holt, Rinehart and Winston, Inc., New York. 582-692.
- Kharkar D.P., Turekian K.L. and Bertine K.K. (1968) Stream supply of dissolved silver, molybdenum, antimony, selenium, chromium, cobalt, rubidium and cesium to the oceans. *Geochim. Cosmochim. Acta* 32, 285-298.

- Kitano Y., Sakata M. and Matsumoto E. (1980) Partitioning of heavy metals into mineral and organic fractions in a sediment core from Tokyo Bay. *Geochim. Cosmochim. Acta* 44, 1279-1285.
- Krauskopf K.B. (1956) Factors controlling the concentration of 13 rare metals in seawater. *Geochim. Cosmochim. Acta* 9, 1-32B.
- Kuehl S.A., Nittrouer C.A. and DeMaster D.J. (1982) Modern sediment accumulation and strata formation on the Amazon Continental Shelf. *Marine Geology* 49, 279-300.
- Long D.T. and Gephart C.J. (1982) Relative importance of iron-oxide, manganese-oxide, and organic material on the adsorption of chromium in natural water sediment systems. *Proceeding from October Geological Society of America National Conference.*
- Loring D.H. (1976) The distribution and partition of zinc, copper, and lead in the sediments of the Saguenary Fjord. *Can. J. Earth Sci.* 13, 960-971.
- Loring D.H. (1976b) Distribution and partition of cobalt, nickel, chromium, and vanadium in the sediments of the Saguenary Fjord. *Can. J. Earth Sci.* 13, 1706-1718.
- Loring D.H. (1979) Geochemistry of cobalt, nickel, chromium and vanadium in the sediments of the estuary and open Gulf of St. Lawrence. *Can. J. Earth Sci.* 16, 1197-1209.
- Loring D.H. (1982) Geochemical factors controlling the accumulation and dispersal of heavy metals in the Bay of Fundy Sediments. *Can. J. Earth Sci.* 19, (5), 930-944.
- Luoma S.M. and Bryan G.W. (1981) A statistical assessment of the form of trace metals in oxidized estuarine sediments employing chemical extractants. *The Science of the Total Environment* 17, 165-196.
- Marchig V. and Gundlach H. (1982) Iron-rich metalliferous sediments on the East Pacific Rise: Prototype of undifferentiated metalliferous sediments on divergent plate boundaries. *Earth Planet. Sci. Lett.* 58, 361-382.
- Martin J.M. and Meybeck M. (1979) Elemental mass-balance of material carried by major world rivers. *Marine Chem.* 7, 173-206.
- Meade R.H., Curtis W., DeVale C.M., Edmond J.M., Nordin C.F. Jr. and Rodrigues F.M. Costa. (1979) Sediment loads in the Amazon River. *Nature* 278, 161-163.
- Milliman J.D., Summerhayes C.P. and Barretto H.T. (1975) Oceanography and suspended matters off the Amazon River February - March 1973. *J. Sed. Petrol.* 45, 189-206.
- Morozov N.P. (1979) Trace-element migration - form relationships for rivers, estuaries, seas, and oceans. *Geochem. Intl.* 16, (4), 161-164.

- Nelsen T.A. (1981) The application of Q-mode factor analysis to suspended particulate matter studies: Examples from the New York Bright Apex. *Marine Geology* 39, 15-31.
- Nittrouer C.A., DeMaster D.J. and Kowsmann R.O. (1981) The deltaic nature of Amazon shelf sedimentation as revealed by high resolution seismic reflection studies. *EOS* 62, (17), 303.
- Nittrouer C.A., Sharara M.T. and DeMaster D.J. (1983) Variations of sediment texture on the Amazon Continental Shelf. *J. Sed. Pet.* 53, (1), 179-191.
- Ottman R.E. (1968) Reconnaissance investigations of the discharge and water quality of the Amazon River. *U.S.G.S. Circ.* 552, 16.
- Parks J.M. (1970) Fortran IV Program for Q-Mode cluster analysis on distance function with printed dendrogram. *Computer Contribution* 46. State Geological Survey, The University of Kansas.
- Perkin Elmer Atomic Absorption Spectroscopy Instruction Book (1973).
- Ryther J.J., Menzel D.W., Corwin N. (1967) Influence of the Amazon River outflow on the ecology of the western Tropical Atlantic I. hydrography and nutrient chemistry. *J. Mar. Res.* 25, 69-83.
- Schmidt G.F. (1972) Amounts of suspended solids and dissolved substances in the middle reaches of the Amazon over the course of one year. *Amazoniana* 3, (11) 208-223.
- Schultz D.J. and Turekian K.K. (1965) The investigation of the geographical and vertical distribution of several trace elements in seawater using neutron activation analysis. *Geochim. Cosmochim. Acta* 29, 259-313.
- Sholkovitz E.R. (1976) Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater. *Geochim. Cosmochim. Acta* 40, 831-845.
- Sholkovitz E.R. and Price N.B. (1980) The major element chemistry of suspended matter in the Amazon Estuary. *Geochim. Cosmochim. Acta* 44, 163-171.
- Stallard R.F. (1980) Major element geochemistry of the Amazon River system. PhD. Thesis: Woods Hole Oceanographic Institution and Massachusetts Inst. of Technology, 1-366.
- Statistical package for the social sciences (1975) (eds. Nie H.H., Hull C.H., Jenkins J.G., Steinbrenner K. and Bent D.H.) McGraw-Hill Book Co. 468-508.
- Tessier A., Campbell P.G.C. and Bisson M. (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* 51, (7).

- Tessier A., Campbell P.G.C. and Bisson M. (1982) Particulate trace metal speciation in stream sediments and relationships by grain size: Implications for geochemical exploration. *J. Chem. Exp.* 16, 77-104.
- Turekian K.K. and Imbric J. (1966) The distribution of trace elements in deep-sea sediments of the Atlantic Ocean. *Earth Planet. Sci. Lett.* 1, 161-168.
- Walkley A. and Black I.A. (1934) An examination of the Degthareff method for determining soil organic matter and a proposed modification of the chronic acid titration method. *Soil Sci.* 27, 29-38.
- Windom H.L., Beck K.C. and Smith R. (1971) Transport of trace metals to the Atlantic Ocean by Three Southeastern Rivers. *Southeastern Geology* 12, (3), 169-181.
- Yen T.F. and Tang J.I.S. (1977) Chemical aspects of marine sediments. In *Chemistry of Marine Sediments* (ed. T.F. Yen), 1-38.

APPENDICES

APPENDIX I
CHEMICAL PARTITIONING DATA

APPENDIX I

A = Sample Location

B = Processed prior to receiving sample (1 = yes; 2 = no)

C = Bioturbated (1 = yes; 2 = no)

D = Sample sediment type (Type 1-6 see triangular diagram) (Nitttrouer et al., 1983).

E = Sediment accumulate rate based on Pb-210 data (Nitttrouer et al., 1983).

F = Depth in cm (low)

G = Depth in cm (high)

H = Total organic carbon

I = Exchangable fraction in ppm

J = Fe-Mn oxide fraction in ppm

K = Organic fraction in ppm

L = Residual fraction in ppm

M = Total metal concentration in ppm (Addition of I - L values)

-- = Missing data

99 = Missing data

80 = Soils taken at Belem'

81-85 = Soil horizons

All samples sieved in less than .212 mm sieve prior to analysis.

[illegible]

COPPER (cont'd)

A	B	C	D	E	F	G	H	I	J	K	L	M
46.	22	99	6.	3.	0.	5.	0.	.300	6.973	3.733	31.167	42.173
46.	22	99	99	99	05	10	.250	.110	7.487	3.280	24.667	35.544
46.	22	99	99	99	10	15	.270	.080	9.247	3.027	23.167	35.521
46.	22	99	99	99	15	20	.150	0.000	7.660	3.027	31.167	41.854
46.	22	99	99	99	20	25	.250	.250	8.387	3.367	215.500	227.500
46.	22	99	99	99	25	30	.050	.040	6.787	3.013	36.917	46.757
46.	22	99	99	99	30	35	.200	0.000	6.240	2.660	21.333	30.233
46.	22	99	99	99	35	40	.150	.290	7.647	4.720	167.830	180.490
46.	22	99	99	99	40	45	.190	.047	8.507	5.740	16.250	30.544
46.	22	99	99	99	45	50	.240	.073	8.233	4.327	67.000	79.633
47.	22	99	99	99	50	55	.260	0.000	10.687	4.400	30.000	45.087
50.	22	99	99	99	55	60	.260	.343	17.953	4.747	135.330	158.380
55.	22	99	99	99	60	65	.200	0.000	9.700	5.780	60.833	76.313
56.	22	99	99	99	65	70	.100	.300	9.960	5.140	35.667	51.067
57.	22	99	99	99	70	75	.000	.323	25.420	22.353	40.083	88.179
80.	22	99	99	99	75	80	.300	.907	1.987	12.347	18.167	33.408
80.	22	99	99	99	80	85	.710	.710	1.247	8.353	2.500	12.810
80.	22	99	99	99	85	90	.500	.577	1.327	8.960	3.333	14.197
80.	22	99	99	99	90	95	.050	2.827	1.987	17.980	4.000	25.794
80.	22	99	99	99	95	100	.150	1.553	7.080	10.127	8.750	27.510
80.	22	99	99	99	100	105	.100	7.780	16.287	10.993	43.833	78.893
80.	22	99	99	99	105	110	.100	1.310	3.053	2.073	6.200	12.635
81.	22	99	99	99	110	115	.970	.203	.193	2.040	7.750	10.186
82.	22	99	99	99	115	120	.940	.253	.633	1.247	12.200	14.333
83.	22	99	99	99	120	125	.890	.367	.593	1.753	12.600	15.313
84.	22	99	99	99	125	130	.140	0.000	.650	1.060	14.083	15.793
85.	22	99	99	99	130	135	.660	.310	1.260	1.513	14.800	17.883

IRON

A	B	C	D	E	F	G	H	I	J	K	L	M
23	2	1	5	2	0	2	0	4	6800	56	33900	40760
4	1	1	5	2	0	1	0	5	2780	16	10275	13077
5	1	1	1	2	0	5	0	6	1953	17	2716	4692
7	1	1	1	2	0	1	0	1	2120	24	2983	5129
9	1	1	1	2	0	1	0	7	3466	7	5990	9491
10	1	1	1	2	0	1	0	7	1814	7	41592	43420
10	1	1	1	2	0	1	0	7	6980	47	34217	41273
10	1	1	1	2	0	1	0	9	11840	64	37508	49548
10	1	1	1	2	0	1	0	10	8600	56	37717	46393
10	1	1	1	2	0	1	0	10	6026	35	25842	31938
10	1	1	1	2	0	1	0	13	7100	266	31017	38397
10	1	1	1	2	0	1	0	13	6493	64	31775	38337
10	1	1	1	2	0	1	0	15	6120	78	28600	38304
10	1	1	1	2	0	1	0	15	7020	85	32400	39511
10	1	1	1	2	0	1	0	16	9353	916	41048	51339
10	1	1	1	2	0	1	0	17	9900	713	39717	50348
10	1	1	1	2	0	1	0	17	7480	278	32117	39898
10	1	1	1	2	0	1	0	22	7806	11	20800	29726
10	1	1	1	2	0	1	0	22	5256	11	19500	17245
10	1	1	1	2	0	1	0	3	5280	25	29500	35558
10	1	1	1	2	0	1	0	9	7960	288	29783	38043
10	1	1	1	2	0	1	0	11	9900	826	31767	43415
10	1	1	1	2	0	1	0	21	10907	796	41683	53459
10	1	1	1	2	0	1	0	21	6793	44	27550	34393
10	1	1	1	2	0	1	0	21	5453	50	24875	30400
10	1	1	1	2	0	1	0	21	6086	49	24142	30288
10	1	1	1	2	0	1	0	10	5133	89	29933	35556
10	1	1	1	2	0	1	0	28	9360	82	37433	48504
10	1	1	1	2	0	1	0	28	957	82	34883	45911
10	1	1	1	2	0	1	0	13	957	58	34450	42455
10	1	1	1	2	0	1	0	26	7920	59	33925	41589
10	1	1	1	2	0	1	0	10	7593	56	39175	47405
10	1	1	1	2	0	1	0	13	8160	64	44558	52339
10	1	1	1	2	0	1	0	22	7693	37	23133	29013
10	1	1	1	2	0	1	0	22	5840	29	19333	26559
10	1	1	1	2	0	1	0	1	5286	13	26550	30250
10	1	1	1	2	0	1	0	9	3786	27	22992	29130
10	1	1	1	2	0	1	0	4	6706	81	39317	47240
10	1	1	1	2	0	1	0	15	3266	11	16367	19880
10	1	1	1	2	0	1	0	35	5380	90	27875	33348
10	1	1	1	2	0	1	0	22	6666	258	29367	35314
10	1	1	1	2	0	1	0	22	3451	9	12558	15028
10	1	1	1	2	0	1	0	27	7566	9	35625	43288
10	1	1	1	2	0	1	0	27	7246	59	32900	40217
10	1	1	1	2	0	1	0	11	7653	59	39667	47392
10	1	1	1	2	0	1	0	12	7733	94	34594	42456
10	1	1	1	2	0	1	0	33	3473	13	17783	21276
10	1	1	1	2	0	1	0	6	5100	33	22700	27843
10	1	1	1	2	0	1	0	9	8306	77	46192	55551
10	1	1	1	2	0	1	0	8	8145	72	47900	55528
10	1	1	1	2	0	1	0	24	8826	249	45017	54127
10	1	1	1	2	0	1	0	34	9113	682	45083	55899
10	1	1	1	2	0	1	0	19	1458	720	46542	56157
10	1	1	1	2	0	1	0	36	767	49	39583	44690
10	1	1	1	2	0	1	0	10	655	273	27317	30450
10	1	1	1	2	0	1	0	3	643	319	29192	37493
10	1	1	1	2	0	1	0	86	713	64	38192	45556

COBALT (cont'd.)

A	B	C	D	E	F	G	H	I	J	K	L	M
46.	22	99	99	99	05	00	0.000	.035	1.711	1.920	43.375	45.241
46.	22	99	99	99	10	00	.250	0.000	4.060	1.420	44.375	45.855
46.	22	99	99	99	20	00	.150	.040	1.825	1.230	53.700	56.795
46.	22	99	99	99	30	00	.250	.035	.914	1.750	52.250	54.949
46.	22	99	99	99	40	00	.050	0.000	1.007	1.547	45.400	47.954
46.	22	99	99	99	50	00	.200	0.000	1.870	1.710	50.500	54.080
46.	22	99	99	99	60	00	.150	0.000	1.876	1.800	48.375	51.051
46.	22	99	99	99	70	00	.200	0.000	1.576	2.067	48.500	52.143
46.	22	99	99	99	80	00	.190	0.000	2.638	1.840	58.500	62.978
46.	22	99	99	99	90	00	.240	0.000	2.060	1.893	50.200	57.153
47.	22	99	99	99	00	00	.260	0.000	2.063	1.455	57.750	61.268
50.	22	99	99	99	10	00	.260	.180	1.604	1.207	49.500	52.491
55.	22	99	99	99	20	00	.200	.743	1.169	1.420	48.500	51.832
57.	22	99	99	99	30	00	.100	0.000	6.633	1.767	57.250	60.420
80.	22	99	99	99	40	00	.300	0.000	1.680	1.490	48.750	48.750
80.	22	99	99	99	50	00	.710	0.000	0.000	0.000	41.625	41.625
80.	22	99	99	99	60	00	.500	.400	0.000	0.000	50.250	50.650
80.	22	99	99	99	70	00	.050	.010	0.000	0.000	49.000	49.010
80.	22	99	99	99	80	00	.150	0.000	0.000	0.000	45.250	45.250
80.	22	99	99	99	90	00	.100	0.000	0.000	0.000	45.625	45.625
80.	22	99	99	99	00	00	.300	0.000	0.000	0.000	38.667	38.667
81.	22	99	99	99	10	00	.970	0.000	0.000	0.000	38.000	38.000
82.	22	99	99	99	20	00	.940	0.000	0.000	0.000	37.800	37.800
83.	22	99	99	99	30	00	.890	0.000	.020	.030	30.500	30.550
84.	22	99	99	99	40	00	.140	0.000	.040	.010	35.500	35.603
85.	22	99	99	99	50	00	.660	0.000	.103	0.000	50.500	50.603

MANGANESE

A	B	C	D	E	F	G	H	I	J	K	L	M
23	21	11	55	22	00	21	190	257	309	31	176	519
44	21	11	55	22	00	15	000	537	97	4	27	330
56	11	11	11	22	00	11	000	537	867	.8120	26	190
79	11	11	56	22	00	11	000	2630	28	.767	33	293
10	11	11	56	22	00	11	000	1647	23	1.287	98	54
00	11	11	56	22	00	11	000	2247	000	1.340	080	183
10	11	11	56	22	00	11	000	2533	23	.940	080	600
00	11	11	56	22	00	11	000	17587	245	27.513	184	1024
00	11	11	56	22	00	11	000	17210	342	35.107	830	462
00	11	11	56	22	00	11	000	10917	357	34.973	730	567
00	11	11	56	22	00	11	000	16063	305	26.460	800	590
00	11	11	56	22	00	11	000	35233	325	43.260	730	482
00	11	11	56	22	00	11	000	34023	425	32.727	410	559
00	11	11	56	22	00	11	000	34467	384	28.767	270	591
00	11	11	56	22	00	11	000	38733	326	33.460	570	532
00	11	11	56	22	00	11	000	46633	330	61.527	670	563
00	11	11	56	22	00	11	000	53733	445	60.887	170	745
00	11	11	56	22	00	11	000	53700	458	32.460	000	730
00	11	11	56	22	00	11	000	51833	398	60.760	500	540
00	11	11	56	22	00	11	000	16127	372	50.760	400	535
00	11	11	56	22	00	11	000	31133	251	16.907	130	565
00	11	11	56	22	00	11	000	51900	363	36.460	130	565
00	11	11	56	22	00	11	000	67600	386	39.847	670	638
00	11	11	56	22	00	11	000	20937	528	64.787	580	838
00	11	11	56	22	00	11	000	81100	606	62.747	170	870
00	11	11	56	22	00	11	000	68100	220	21.387	080	489
00	11	11	56	22	00	11	000	56867	250	21.967	520	469
00	11	11	56	22	00	11	000	18870	229	18.940	580	513
00	11	11	56	22	00	11	000	80267	391	40.470	770	470
00	11	11	56	22	00	11	000	135130	391	36.087	000	645
00	11	11	56	22	00	11	000	101070	355	31.413	570	683
00	11	11	56	22	00	11	000	225720	269	21.067	580	713
00	11	11	56	22	00	11	000	48300	322	34.360	580	589
00	11	11	56	22	00	11	000	35400	323	33.340	330	589
00	11	11	56	22	00	11	000	99000	323	46.467	330	722
00	11	11	56	22	00	11	000	103730	366	18.413	580	641
00	11	11	56	22	00	11	000	22393	188	13.687	200	432
00	11	11	56	22	00	11	000	46800	185	13.993	920	353
00	11	11	56	22	00	11	000	17590	129	6.993	000	455
00	11	11	56	22	00	11	000	345990	139	11.933	520	399
00	11	11	56	22	00	11	000	105037	427	58.247	920	691
00	11	11	56	22	00	11	000	815970	200	12.373	500	243
00	11	11	56	22	00	11	000	148930	42	15.053	250	619
00	11	11	56	22	00	11	000	165830	200	5.660	250	752
00	11	11	56	22	00	11	000	122853	351	24.380	670	333
00	11	11	56	22	00	11	000	29933	111	5.533	250	252
00	11	11	56	22	00	11	000	18970	231	17.840	200	421
00	11	11	56	22	00	11	000	33233	409	55.533	580	670
00	11	11	56	22	00	11	000	66600	525	18.340	500	816
00	11	11	56	22	00	11	000	559533	671	87.895	750	1014
00	11	11	56	22	00	11	000	559567	591	86.880	170	1017
00	11	11	56	22	00	11	000	2718	658	55.567	500	935
00	11	11	56	22	00	11	000	27103	188	11.440	500	935
00	11	11	56	22	00	11	000	117.03	168	8.587	750	315
00	11	11	56	22	00	11	000	43.033	318	35.320	830	620
00	11	11	56	22	00	11	000	511.130	511	63.287	670	802

NICKEL

A	B	C	D	E	F	G	H	I	J	K	L	M
2	2	1	5	2	0	2	190	.030	4	2	64	71
3	2	1	1	2	0	5	.000	.087	1	.030	23	27
4	2	1	1	2	0	0	.000	.110	1	.293	38	40
5	2	1	1	2	0	0	.000	.055	1	.360	700	94
6	2	1	1	2	0	0	.000	.060	1	.490	33	34
7	2	1	1	2	0	0	.000	.098	1	.727	41	43
8	2	1	1	2	0	0	.000	.283	5	2	22	24
9	2	1	1	2	0	0	.000	0	5	2	48	57
10	2	1	1	2	0	0	.000	.142	5	2	58	67
10	2	1	1	2	0	0	.000	.150	4	2	52	59
10	2	1	1	2	0	0	.000	.055	4	2	51	55
10	2	1	1	2	0	0	.100	.025	5	2	50	56
10	2	1	1	2	0	0	.250	.248	4	2	57	58
10	2	1	1	2	0	0	.100	.036	4	2	43	64
10	2	1	1	2	0	0	.150	.090	4	2	36	43
10	2	1	1	2	0	0	.220	.098	5	2	50	50
10	2	1	1	2	0	0	.190	.050	5	2	61	61
10	2	1	1	2	0	0	.000	.046	3	2	70	77
10	2	1	1	2	0	0	.000	.052	3	2	69	77
10	2	1	1	2	0	0	.000	.182	3	2	30	38
10	2	1	1	2	0	0	.100	.100	3	2	45	50
10	2	1	1	2	0	0	.100	.024	3	2	55	62
10	2	1	1	2	0	0	.000	.062	3	2	50	58
11	2	1	1	2	0	0	.310	.108	3	2	47	81
12	2	1	1	2	0	0	.050	0	4	2	55	57
13	2	1	1	2	0	0	.200	.076	3	2	71	83
14	2	1	1	2	0	0	.150	.088	3	2	49	61
15	2	1	1	2	0	0	.200	.495	3	2	45	51
16	2	1	1	2	0	0	.150	.025	3	2	52	60
17	2	1	1	2	0	0	.200	.125	3	2	46	55
18	2	1	1	2	0	0	.150	.092	3	2	58	55
19	2	1	1	2	0	0	.260	.330	3	2	82	76
20	2	1	1	2	0	0	.000	.184	3	2	51	89
25	2	1	1	2	0	0	.000	.012	4	2	70	78
26	2	1	1	2	0	0	.000	.092	4	2	46	56
27	2	1	1	2	0	0	.000	0	4	2	44	51
28	2	1	1	2	0	0	.000	.384	3	2	44	60
29	2	1	1	2	0	0	.100	.000	3	2	51	56
30	2	1	1	2	0	0	.000	.005	3	2	52	61
31	2	1	1	2	0	0	.000	.340	1	2	53	56
32	2	1	1	2	0	0	.000	.157	3	2	44	50
33	2	1	1	2	0	0	.000	.927	6	2	39	49
34	2	1	1	2	0	0	.000	.260	1	2	35	37
35	2	1	1	2	0	0	.000	.490	5	2	58	67
36	2	1	1	2	0	0	.050	.107	7	2	76	87
37	2	1	1	2	0	0	.200	.416	4	2	56	64
38	2	1	1	2	0	0	.000	.357	3	2	51	61
39	2	1	1	2	0	0	.000	.097	3	2	45	52
42	2	1	1	2	0	0	.290	.105	4	2	43	50
42	2	1	1	2	0	0	.230	.878	4	2	47	55
42	2	1	1	2	0	0	.150	.508	4	2	54	63
42	2	1	1	2	0	0	.000	.012	4	2	52	63
42	2	1	1	2	0	0	.000	.190	6	2	66	76
42	2	1	1	2	0	0	.240	.096	8	2	49	58
42	2	1	1	2	0	0	.000	.072	7	2	68	89
42	2	1	1	2	0	0	.190	.080	18	2	49	57
43	2	1	1	2	0	0	.100	.050	10	2	76	89

NICKEL (cont'd.)

A	B	C	D	E	F	G	H	I	J	K	L	M
46.	2.	99.	6.	3.	0.	5.	0.	.485	5.247	3.870	67.500	77.102
46.	2.	99.	99.	99.	5.	10.	.250	.144	16.150	6.470	51.500	74.274
46.	2.	99.	99.	99.	10.	15.	.270	.344	4.355	3.067	45.875	53.641
46.	2.	99.	99.	99.	15.	20.	.150	.122	4.447	3.750	54.000	62.319
46.	2.	99.	99.	99.	20.	25.	.250	.037	5.340	3.413	64.700	73.490
46.	2.	99.	99.	99.	25.	30.	.050	.008	11.524	7.260	73.625	92.417
46.	2.	99.	99.	99.	30.	35.	.200	.025	4.170	3.570	46.000	53.765
46.	2.	99.	99.	99.	35.	40.	.150	.223	6.730	5.770	56.375	69.098
46.	2.	99.	99.	99.	40.	45.	.190	.245	7.287	3.480	60.500	71.512
46.	2.	99.	99.	99.	45.	50.	.240	.098	6.600	4.040	95.250	105.990
47.	2.	99.	6.	3.	0.	50.	.260	.566	8.096	3.293	74.750	86.705
50.	1.	1.	6.	3.	0.	1.	.260	.410	4.880	3.193	56.625	65.108
55.	1.	1.	6.	1.	0.	1.	.200	.532	4.800	4.547	83.250	93.129
55.	1.	2.	6.	1.	0.	2.	.100	.167	9.580	3.320	78.500	91.557
57.	2.	1.	6.	1.	0.	2.	0.	.310	5.730	3.480	46.300	55.820
80.	2.	99.	99.	99.	0.	2.	.300	.075	0.000	.080	31.375	31.530
80.	2.	99.	99.	99.	0.	2.	.710	.122	0.000	.067	34.250	34.439
80.	2.	99.	99.	99.	4.	7.	.500	.472	0.000	.120	25.125	25.719
80.	2.	99.	99.	99.	7.	11.	.050	.040	0.000	0.000	46.333	46.373
80.	2.	99.	99.	99.	11.	15.	.150	.192	0.000	0.000	45.500	45.592
80.	2.	99.	99.	99.	15.	20.	.100	.226	0.000	.007	38.250	38.483
81.	2.	99.	99.	99.	23.	23.	.277	.232	0.000	.030	50.250	50.512
82.	2.	99.	99.	99.	99.	99.	.970	.277	0.000	.220	37.000	37.497
83.	2.	99.	99.	99.	99.	99.	.890	.066	0.000	.140	43.833	44.039
84.	2.	99.	99.	99.	99.	99.	1.140	.182	0.000	.070	53.250	53.502
85.	2.	99.	99.	99.	99.	99.	1.660	.255	0.000	.853	21.375	22.493
								.140	0.000	.093	38.250	38.483

LEAD										
A	23	45	67	9	10	10	10	10	10	10
B	2	2	1	1	2	2	2	2	2	2
C	1	1	1	1	1	1	1	1	1	1
D	5	5	1	1	1	5	6	6	4	4
E	2	2	2	2	2	2	2	2	2	2
F	0	0	0	0	0	0	0	0	0	0
G	2	1	1	1	1	1	1	1	1	1
H	1900	0000	0000	0000	0000	0000	0000	0000	0000	0000
I	0	0	0	0	0	0	0	0	0	0
J	0	0	0	0	0	0	0	0	0	0
K	860	920	060	040	170	170	170	170	170	170
L	0	0	0	0	0	0	0	0	0	0
M	860	1045	16060	16300	16010	16500	16520	16520	16520	16520

LEAD (cont'd.)

A	B	C	D	E	F	G	H	I	J	K	L	M
46.	22	22	6.	3.	0.	5.	0.	0.	0.	1.	6.	8.
46.	22	22	99	99	5.	0.	2500	0.	0.	730	700	730
46.	22	22	99	99	10	15	2700	0.	0.	080	000	080
46.	22	22	99	99	25	20	1500	0.	0.	1450	000	1450
46.	22	22	99	99	30	25	2500	0.	0.	1690	000	1690
46.	22	22	99	99	35	30	0500	0.	0.	1970	000	1970
46.	22	22	99	99	40	35	1900	0.	0.	1320	665	985
46.	22	22	99	99	45	40	2400	0.	0.	1880	515	120
47.	22	22	99	99	50	45	2600	0.	0.	1630	500	830
45	22	22	99	99	55	50	2600	0.	0.	1830	250	230
50	22	22	99	99	60	55	2000	0.	0.	2800	1400	200
55	22	22	99	99	65	60	1000	0.	0.	1230	415	745
57.	22	22	99	99	70	65	3000	0.	0.	1740	000	800
80	22	22	99	99	75	70	7100	0.	0.	5010	000	139
80	22	22	99	99	80	75	5000	0.	2.	4950	000	230
80	22	22	99	99	85	80	5000	0.	2.	5100	000	813
80	22	22	99	99	90	85	1500	0.	4.	5247	000	707
80	22	22	99	99	95	90	1500	0.	4.	5247	000	343
80	22	22	99	99	100	95	1000	0.	2.	5500	000	826
80	22	22	99	99	105	100	9700	0.	3.	2800	145	845
81.	22	22	99	99	110	105	9400	0.	3.	3600	000	660
82.	22	22	99	99	115	110	8900	0.	0.	640	000	640
82.	22	22	99	99	120	115	8900	0.	0.	850	335	195
83.	22	22	99	99	125	120	11400	0.	0.	910	000	910
84.	22	22	99	99	130	125	6600	0.	0.	920	000	950

ALUMINUM (cont'd.)

A	B	C	D	E	F	G	H	I	J	K	L	M
46.	22	22	6.	3.	0.	5.	0.	76.	1496.	2863.	157630.	162060.
46.	22	22	99.	99.	0.	10.	000	24.	1469.	2789.	99631.	103920.
46.	22	22	99.	99.	15.	000	270	35.	1770.	2791.	107540.	112130.
46.	22	22	99.	99.	20.	000	150	76.	2423.	2245.	137970.	142110.
46.	22	22	99.	99.	25.	000	250	66.	1872.	2205.	148130.	152380.
46.	22	22	99.	99.	30.	000	050	47.	1649.	2696.	111430.	15820.
46.	22	22	99.	99.	35.	000	200	46.	1959.	2763.	138820.	143590.
46.	22	22	99.	99.	40.	000	150	77.	1881.	3069.	124440.	129470.
46.	22	22	99.	99.	45.	000	190	77.	2232.	3845.	154900.	161050.
47.	22	22	99.	99.	50.	000	240	20.	1550.	3091.	120610.	125270.
47.	22	22	99.	99.	55.	000	260	43.	1545.	2220.	152660.	156470.
50.	22	22	99.	99.	60.	000	260	27.	1646.	2480.	90554.	94818.
50.	22	22	99.	99.	65.	000	200	78.	2011.	2371.	157680.	162140.
50.	22	22	99.	99.	70.	000	1000	30.	1847.	3118.	131500.	136500.
50.	22	22	99.	99.	75.	000	000	51.	1566.	2769.	122110.	126500.
80.	22	22	99.	99.	80.	000	300	159.	1116.	1388.	16615.	19379.
80.	22	22	99.	99.	85.	000	710	895.	1040.	1524.	25859.	29319.
80.	22	22	99.	99.	90.	000	500	646.	943.	1499.	33128.	36217.
80.	22	22	99.	99.	95.	000	050	86.	806.	928.	30216.	32038.
80.	22	22	99.	99.	100.	000	150	479.	765.	696.	29205.	31147.
80.	22	22	99.	99.	105.	000	100	274.	659.	323.	12878.	14135.
80.	22	22	99.	99.	110.	000	100	289.	399.	102.	14325.	15116.
81.	22	22	99.	99.	115.	000	970	1297.	2742.	3103.	51737.	58880.
82.	22	22	99.	99.	120.	000	800	2337.	2337.	4103.	99385.	108110.
82.	22	22	99.	99.	125.	000	800	2028.	2425.	3655.	65855.	74016.
84.	22	22	99.	99.	130.	000	140	1111.	2702.	3685.	84320.	91818.
84.	22	22	99.	99.	135.	000	160	984.	2838.	3792.	83800.	91415.

APPENDIX II
GRAPHITE CONTROL SETTINGS
FOR PERKIN ELMER 560
ATOMIC ADSORPTION SPECTROPHOTOMETER
WITH HGA:2200 GRAPHITE FURNACE

MATRIX: MgCl_2 (Exchangeable Fraction)

Signal = concentration (conc)

Mode = peak height (pk ht)

Recorder = TIC

Gas Flow = 7 normal:33 on Argon flow meter

Volume = 20 μl

Chromium: atm 2700°C at 14 seconds
char 1100°C at 30 seconds
dry 100°C at 60 seconds
mode AA only
time = 8.0 seconds reading

Cobalt: atm 2700°C at 8 seconds
char 1000°C at 40 seconds
dry 100°C at 60 seconds
mode AA-BG
time = 6.0 seconds reading

Nickel: atm 2700°C at 10 seconds
char 1000°C at 30 seconds
dry 100°C at 60 seconds
mode AA-BG
time = 6.0 seconds reading

Aluminum: atm 2700°C at 11 seconds
char 1300°C at 20 seconds
dry 100°C at 60 seconds
mode AA-BG
time = 4.0 seconds reading

Barium: atm 2800°C at 13 seconds
char 1500°C at 30 seconds
dry 100°C at 60 seconds
mode AA only
time = 4.0 seconds reading
Gas Flow increased for Ba

Lead: atm 2300°C at 10 seconds
char 700°C at 10 seconds
dry 100°C at 60 seconds
mode AA-BG
time = 6.0 seconds reading
Gas Flow = 30

MATRIX: .04 M $\text{NH}_2\text{OH}\cdot\text{HCL}$ in 25% (v/v) HOAc (Oxide Fraction)

Signal = concentration (conc)

Mode = peak height (pk ht)

Recorder = TIC

Gas Flow = 7 normal:33 on Argon flow meter

Volume = 20 μl

Chromium: atm 2700°C at 12 seconds
char 1100°C at 10 seconds
dry 100°C at 20 seconds
mode AA only
time = 6.0 seconds reading

Cobalt: atm 2700°C at 12 seconds
char 1000°C at 20 seconds
dry 100°C at 20 seconds
mode AA-BG
time = 8.0 seconds reading

Nickel: atm 2700°C at 12 seconds
char 1000°C at 20 seconds
dry 100°C at 20 seconds
mode AA-BG
time = 6.0 seconds reading

Aluminum: atm 2700°C at 12 seconds
char 1400°C at 20 seconds
dry 100°C at 20 seconds
mode AA-BG
time = 6.0 seconds reading
Gas Flow increase for Al

Barium: atm 2800°C at 14 seconds
char 1600°C at 20 seconds
dry 100°C at 20 seconds
mode AA only
time = 10.0 seconds reading
Gas Flow increase for Ba

Lead: atm 2300°C at 8 seconds
char 600°C at 16 seconds
dry 100°C at 20 seconds
mode AA-BG
time = 6.0 seconds reading
Gas Flow = 7N:30

MATRIX: 3.5 ratio .02HNO₃:3.2 NH₄OAc in 20% (v/v) HNO₃ (Organic Fraction)

Signal = concentration (conc)

Mode = peak height (pk ht)

Recorder = TIC

Gas Flow = 7 normal:33 on Argon flow meter

Volume = 20 µl

Chromium: atm 2700°C at 12 seconds
char 1100°C at 20 seconds
dry 100°C at 20 seconds
mode AA only
time = 10.0 seconds reading

Cobalt: atm 2700°C at 12 seconds
char 1000°C at 20 seconds
dry 100°C at 20 seconds
mode AA-BG
time = 6.0 seconds reading

Nickel: atm 2700°C at 12 seconds
char 1000°C at 20 seconds
dry 100°C at 20 seconds
mode AA-BG
time = 6.0 seconds reading

Aluminum: atm 2700°C at 12 seconds
char 1400°C at 30 seconds
dry 100°C at 20 seconds
mode AA-BG
time = 4.0 seconds reading

Barium: atm 2800°C at 12 seconds
char 1500°C at 10 seconds
dry 100°C at 20 seconds
mode AA only
time = 6.0 seconds reading
Gas Flow increased for Ba

Lead: atm 2300°C at 10 seconds
char 700°C at 20 seconds
dry 100°C at 20 seconds
mode AA-BG
time = 8.0 seconds reading
Gas Flow = 7N:30

MATRIX: LiBO_3 (Residual Fraction)

Signal = concentration (conc)

Mode = peak height (pk ht)

Recorder = TIC

Gas Flow = 7 normal:33 on Argon flow meter

Volume = 20 μl

Chromium: atm 2700°C at 13 seconds
char 1100°C at 30 seconds
dry 100°C at 25 seconds
mode AA only
time = 4.0 seconds reading

Cobalt: atm 2700°C at 12 seconds
char 1000°C at 30 seconds
dry 100°C at 25 seconds
mode AA-BG
time = 6.0 seconds reading

Nickel: atm 2700°C at 12 seconds
char 1000°C at 30 seconds
dry 100°C at 25 seconds
mode AA-BG
time = 8.0 seconds reading

Aluminum: atm 2600°C at 15 seconds
char 1400°C at 30 seconds
dry 100°C at 25 seconds
mode AA-BG
time = 6.0 seconds reading

Barium: atm 2700°C at 14 seconds
char 1600°C at 30 seconds
dry 100°C at 25 seconds
mode AA only
time = 6.0 seconds reading
Gas Flow increased for Ba

Lead: atm 2300°C at 12 seconds
char 600°C at 10 seconds
dry 100°C at 25 seconds
mode AA-BG
time = 6.0 seconds reading
Gas Flow = 7N:30

APPENDIX III
B-MATRIX OF WEIGHTS FROM Q-MODE
AND R-MODE FACTOR ANALYSIS

Raw Q-Mode Factor Analysis

PA1*

<u>Sample Location</u>	<u>Communality</u>	<u>Factor 1</u>
2	.99870	.02474
3	.99849	.02474
4	.83878	.02267
5	.84175	.02271
6	.90706	.02358
7	.96277	.02429
9	.99887	.02474
10	.99396	.02468
11	.99982	.02475
12	.99919	.02474
13	.99914	.02474
14	.99875	.02474
15	.99977	.02475
16	.95771	.02423
17	.99978	.02475
18	.99985	.02475
19	.99924	.02475
20	.99616	.02471
25	.99972	.02475
26	.99865	.02474
27	.99119	.02465
28	.99713	.02472
29	.99874	.02474
30	.99845	.02474
31	.99819	.02473
32	.99997	.02475
33	.99856	.02474
34	.99911	.02474
35	.99972	.02475
36	.99821	.02473
37	.99986	.02475
38	.99830	.02473
39	.99967	.02475
42	.94691	.02409
43	.99826	.02473
46	.99945	.02475
47	.99562	.02470
50	.99634	.02470
55	.99945	.02475
56	.99642	.02471
57	.99929	.02475

Variance 98.5

Cum. Variance 98.5

*PA1 = Principal factoring without Iteration.

Transformed Q-Mode Factor Analysis

		Factor Score Coefficients	
<u>Sample Location</u>	<u>Communality</u>	<u>Factor 1</u>	<u>Factor 2</u>
2	.99904	-.03359	.07694
3	.97704	-.03402	.07687
4	.92040	.07805	-.05198
5	.84777	.05564	-.02497
6	.90567	.05313	-.02037
7	.90804	.06597	-.03645
9	.99404	.05992	-.02662
10	.99185	.06286	-.03036
11	.97462	.05409	-.01988
12	.99086	-.03125	.07446
13	.99054	-.03534	.07846
14	.99691	-.03669	.07991
15	.99727	-.03507	.07834
16	.97502	.05969	-.02680
17	.98611	.06046	-.02749
18	.99111	-.03392	.07726
19	.99415	.05386	-.01921
20	.98920	.05922	-.02574
25	.98732	.05845	-.02491
26	.97539	.04880	-.01313
27	.99882	.03942	-.00221
28	.99944	-.03371	.07705
29	.98462	-.03521	.07852
30	.97495	-.03222	.07527
31	.97432	.05991	-.02705
32	.99187	.03895	-.00169
33	.99489	-.03385	.07703
34	.98747	-.03696	.08012
35	.99507	.05740	-.02365
36	.99888	.05407	-.01936
37	.99515	-.03465	.07797
38	.99797	-.03597	.07917
39	.92482	-.03141	.07478
42	.99482	.05970	-.02806
43	.99562	-.03591	.07912
46	.99267	.06062	-.02753
47	.99454	.05369	-.01892
50	.98836	.06301	-.03063
55	.99431	.06457	-.03246
56	.99637	-.03471	.07797
57	.98825	.04442	-.00786
Variance		85.1	12.9
Cum. Variance		85.1	98.0

Transformed R-Mode Factor Analysis

Factor Score Coefficients

<u>Variable</u>	<u>Communality</u>	<u>Factor 1</u>	<u>Factor 2</u>	<u>Factor 3</u>
Ba hydromorphic	.97813	.43968	.42335	-.73635
Ba detrital	.82681	-.44567	.51495	-.29946
Cu hydromorphic	.47255	-.03200	-.07351	-.02796
Cu detrital	.69516	.08458	-.39477	.06976
Fe hydromorphic	.99442	-1.99033	3.68699	1.24704
Fe detrital	.29146	.04400	-.02217	.09278
Co hydromorphic	.43779	.08092	-.01364	-.14581
Co detrital	.77044	.33520	-.33985	-.07342
Mn hydromorphic	.83414	.45541	-.92104	-.49177
Mn detrital	.89422	1.05746	-.88667	-.13179
Zn hydromorphic	.88380	.23477	-1.20147	.15529
Zn detrital	.83561	.34932	-.37750	.23755
Ni hydromorphic	.64380	.14875	-.22425	-.11346
Ni detrital	.82108	-.27355	.03840	.52969
Pb hydromorphic	.53736	.09078	-.09969	-.03383
Pb detrital	.60302	.16213	-.00120	-.24376
Cr hydromorphic	.89696	.18542	.46088	-.02429
Cr detrital	.54842	-.10497	.14161	.18548
Al hydromorphic	.85187	.25574	-.48270	-.34914
Al detrital	.81213	.13346	-.13397	.16588
Variance		72.3	10.5	7.3
Cum. Variance		72.3	82.8	90.1

Raw R-Mode Factor Analysis

PA1*

<u>Variable</u>	<u>Communality</u>	<u>Factor Score Coefficients</u>				
		<u>Factor 1</u>	<u>Factor 2</u>	<u>Factor 3</u>	<u>Factor 4</u>	<u>Factor 5</u>
Ba hydromorphic	.81095	.08720	.10476	-.03189	-.00251	-.13321
Ba detrital	.61631	-.03375	.41834	.18971	-.00334	-.07891
Cu hydromorphic	.69970	-.00150	-.05572	-.02903	.66590	.01868
Cu detrital	.58442	.02092	-.13135	.28220	-.00904	.21053
Fe hydromorphic	.94517	.05526	-.00047	.26001	.05483	.02307
Fe detrital	.64126	.11785	-.06084	-.11879	-.12587	.03125
Co hydromorphic	.74976	.04969	.21432	.05221	.27663	.41244
Co detrital	.64514	.06260	.24298	-.01958	-.23285	.01130
Mn hydromorphic	.82285	-.10605	.13254	.59668	-.04542	-.09965
Mn detrital	.78229	.08168	.11101	.05630	.04908	.11482
Zn hydromorphic	.91678	.08660	-.07337	.12930	.07550	.06580
Zn detrital	.79788	.10335	-.08994	-.02701	.03795	-.10587
Ni hydromorphic	.69948	.12661	-.08506	-.17530	-.06601	-.02897
Ni detrital	.64504	.09712	.02494	-.00823	-.29052	.11907
Pb hydromorphic	.55320	-.00218	-.33903	.13507	.12742	-.10807
Pb detrital	.80457	.00408	.00085	-.01145	.00463	.74933
Cr hydromorphic	.83955	.09248	-.01746	.05542	.03868	-.01126
Cr detrital	.60013	.09334	-.31387	-.05507	-.31201	.02555
Al hydromorphic	.76383	.11654	-.06544	-.14313	.04647	-.09746
Al detrital	.79544	.10258	-.01981	-.11538	.13008	-.14066
Variance	45.2	10.2	6.7	6.2	5.2	
Cum. Variance	45.2	55.5	62.1	68.4	73.6	

*PA1 = Principal factoring without Iteration

Raw R-Mode Factor Analysis

Variable	Communality	Factor Score Coefficients				
		Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Total organic carbon	.76101	-.02520	.42397	-.03968	-.02519	.05073
Ba hydromorphic	.80949	.08581	.00635	.10451	-.02968	-.12831
Ba detrital	.60894	-.02358	.00181	.41687	.18904	-.06515
Cu hydromorphic	.71319	-.09710	.52394	.04369	-.00745	.01430
Cu detrital	.58316	.02377	-.02693	-.12903	.28443	.20548
Fe hydromorphic	.94390	.04876	.03083	.00648	.26128	.01629
Fe detrital	.65335	.14101	-.13975	-.07896	-.11863	.02095
Co hydromorphic	.68029	.04043	.12874	.24639	.05574	.38054
Co detrital	.64343	.10452	-.19412	.20525	-.02750	.01226
Mn hydromorphic	.81433	-.09960	-.02950	.12763	.59370	-.09018
Mn detrital	.78213	.08149	.02447	.11610	.05769	.10929
Zn hydromorphic	.91202	.07607	.04561	-.06312	.13205	.05603
Zn detrital	.80201	.08770	.05250	-.08072	-.02121	-.09940
Ni hydromorphic	.70685	.13882	-.08303	-.10005	-.17840	-.04748
Ni detrital	.61326	.13175	-.18999	-.01445	-.01393	.13243
Pb hydromorphic	.52819	-.02434	.06273	-.32343	.13624	-.13225
Pb detrital	.82147	.00775	.03574	.00936	-.00808	.76075
Cr hydromorphic	.83804	.08631	.02372	-.01246	.05765	-.01659
Cr detrital	.55398	.10928	-.15846	-.34531	-.05353	.05706
Al hydromorphic	.76387	.10760	.02896	-.06225	-.14210	-.10825
Al detrital	.80751	.07632	.12318	.00076	-.10814	-.13603
Variance	44.4	44.4	9.8	7.6	6.2	5.0
Cum. Variance	44.4	44.4	54.2	61.9	68.0	73.0

MICHIGAN STATE UNIVERSITY LIBRARIES



3 1293 03142 8570