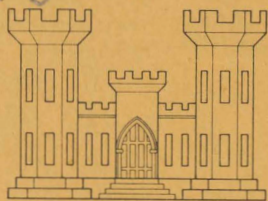


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DREDGED MATERIAL RESEARCH PROGRAM



MISCELLANEOUS PAPER D-76-18

DISTRIBUTION OF MANGANESE, NICKEL, ZINC, CADMIUM, AND ARSENIC IN SEDIMENTS AND IN THE STANDARD ELUTRIATE

by

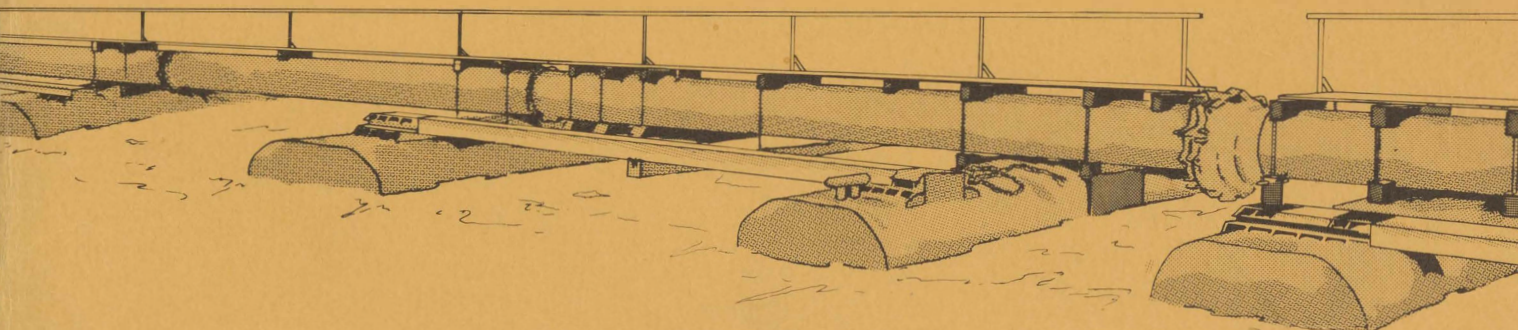
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June 1976

Final Report

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Distribution of manganese, nickel, zinc,



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20. ABSTRACT (Continued)

extractions using the Elutriate Test were also conducted. Manganese, nickel, cadmium, zinc, and arsenic concentrations were determined in each extractant. Nickel, cadmium, zinc, and arsenic concentrations were highest in fractions (e), (d), (d), and (c), respectively. Manganese concentration was highest in fraction (d) in sediments from Mobile Bay and Ashtabula and in fraction (e) in Bridgeport sediment. Manganese concentration determined in the standard elutriate was correlated with its concentration in sediment fractions (a), (b), and (c). Zinc concentration determined in the standard elutriate was correlated with its concentration in sediment fractions (c) and (d). However, nickel, cadmium, and arsenic concentrations were not correlated with their respective concentrations in any sediment fraction when all data were considered, although some site-specific correlations were noted for arsenic and nickel.

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PREFACE

This paper was prepared for publication in the "Journal of the Waterways and Harbors Division, Proceedings of the American Society of Civil Engineers."

The work was funded by the Department of the Army under the Environmental Impacts and Criteria Development Project of the Dredged Material Research Program (Dr. Robert M. Engler, Project Manager), sponsored by the Office, Chief of Engineers.

The work was conducted during the period July 1973 - August 1975 by the U. S. Army Engineer Waterways Experiment Station (WES), Vicksburg, Miss., by Messrs. J. M. Brannon and I. Smith, Ms. J. R. Rose, and Drs. R. M. Engler and P. G. Hunt of the Environmental Effects Laboratory (EEL). The study was under the general supervision of Dr. R. L. Eley, Chief, Ecosystem Research and Simulation Division and Dr. John Harrison, Chief, EEL.

Directors of WES during the conduct of this study and preparation of this paper were BG E. D. Peixotto, CE, and COL G. H. Hilt, CE. Technical Director was Mr. F. R. Brown.

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DISTRIBUTION OF MANGANESE, NICKEL, ZINC, CADMIUM, AND
ARSENIC IN SEDIMENTS AND IN THE STANDARD ELUTRIATE

By J. M. Brannon,¹ R. M. Engler,² J. R. Rose,³
P. G. Hunt,⁴ and I. Smith⁵

INTRODUCTION

The partitioning of trace metals in sediments among the various geochemical phases will determine the impact of the metals associated with the dredged material upon water quality and benthic organisms when the sediments are dredged (34,35). The abundance and distribution of the various geochemical forms of sediment-bound trace metals in sediments have, however, not been well documented. Where trace metal partitioning was conducted upon sediments, the procedure used subjected the sediment to drying and grinding prior to chemical fractionation (6,10,38,40) resulting in a complete loss of sample integrity and redistribution of constituents among the partitions. The oxidation and physical alteration of the sediment during drying and grinding will cause phase or fraction differentiation and redistribution of trace metals within the sediment, thereby invalidating the results (9).

Recently, a trend towards curtailment of open-water disposal of dredged material and use of confined land disposal has developed.

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Concerns about the effect of resuspended sediments on water quality have largely been due to the fear of the unknown and ignorance of the physico-chemical nature of sediments and, coupled with the unknown effect of deposited dredged material on benthic organisms, have been the leading factors initiating the trend towards curtailment of open-water disposal. Confined land disposal of dredged material, however, is not free of environmental problems and may represent a much more serious hazard to a smaller area.

To determine if open-water disposal of dredged material is environmentally acceptable, sediments must be tested prior to the start of dredging operations. The tests used must determine which chemical components of the sediments may be released at the time of dredging, during open-water disposal, and on a long-term basis after deposition at the open-water disposal site.

The only test available at the present time that can be used to evaluate the effects of dredged material disposal on water quality is the Elutriate Test. Interpretation and evaluation of Elutriate Test results have been hampered, however, by lack of basic information on the species and forms of contaminants in sediments that affect Elutriate Test results.

This article presents: (a) results of sequential selective extraction (partitioning) of freshwater and saltwater sediments, and (b) an examination of the relationship between trace metal concentrations in the standard elutriate resulting from the Elutriate Test and in the various chemically extracted sediment phases.

METHODS

Experimental methods

Sample Locations. The first location sampled was the Arlington Ship Channel in Mobile Bay, Alabama, a brackish estuarine area. The location of the three areas sampled is shown in Fig. 1.

The second location sampled was Ashtabula Harbor, a freshwater area located in northeast Ohio on the south shore of Lake Erie. The general locality and sampling areas are shown in Fig. 2. The Ashtabula River Basin has a small drainage area (137 sq miles or 220 sq km), but the

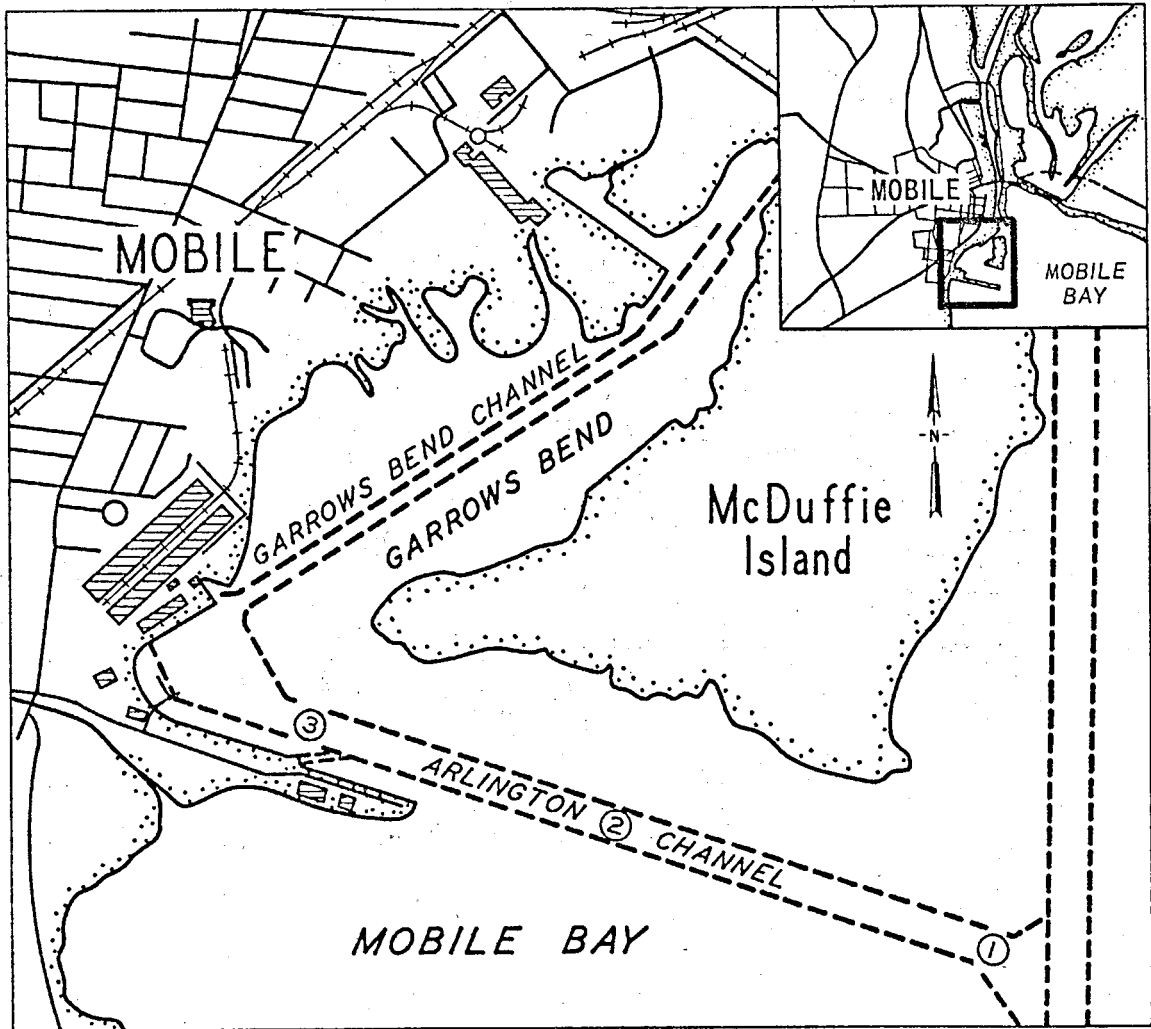


Figure 1. Location Map, Mobile Bay, Alabama

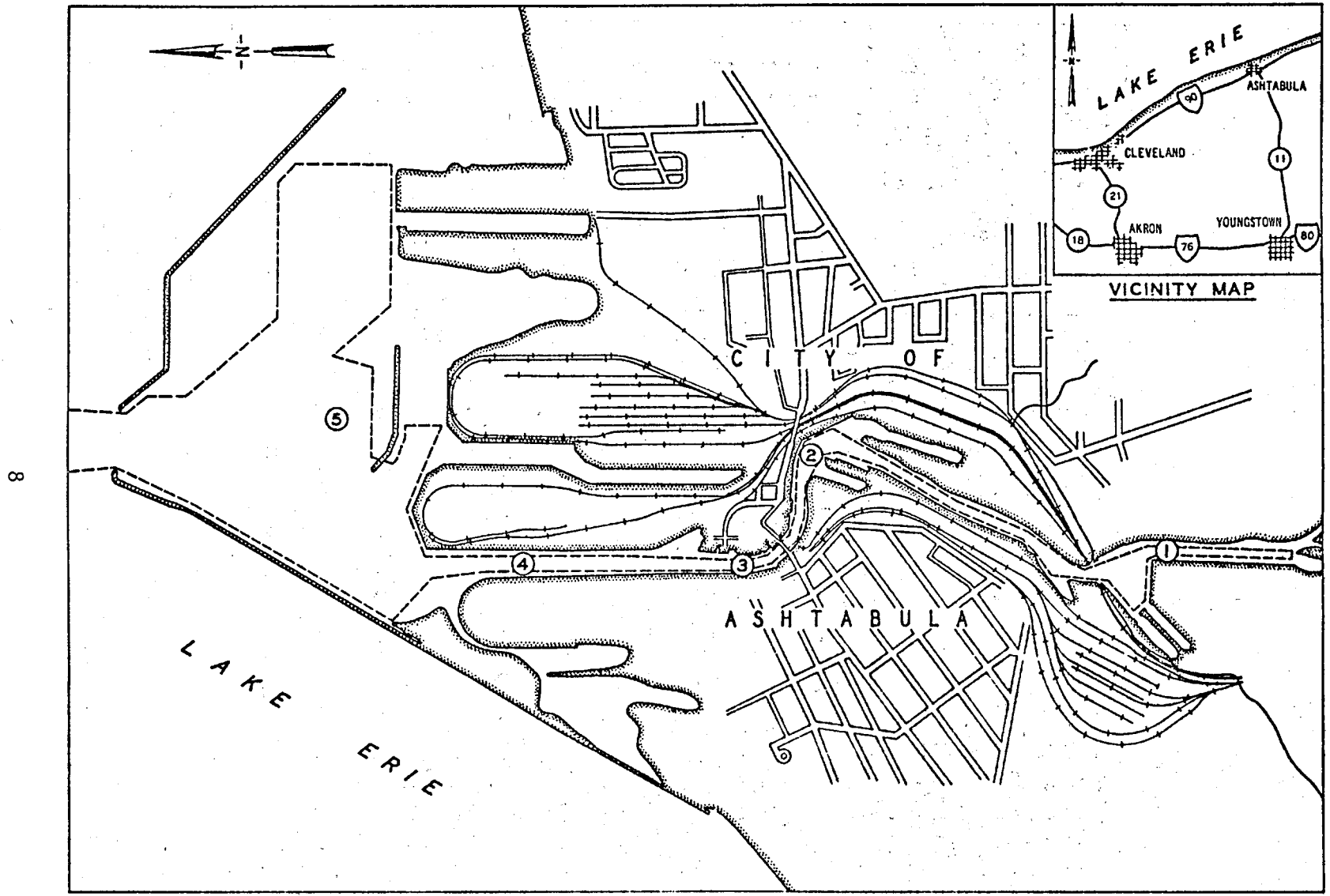


Figure 2. Location Map, Ashtabula, Ohio

harbor is a deep draft, inland commercial port.

Bridgeport Harbor, a small highly industrialized harbor located in southern Connecticut on Long Island Sound, was the third location sampled (Fig. 3). There is very little influx of fresh water into Bridgeport Harbor, resulting in saline water in the harbor.

Field Sampling Procedures. Five sediment cores, 60 cm in length and 7.5 cm in diameter, were taken in each of the three sampling sites located in the Arlington Ship Channel using a gravity sediment corer. Four sediment cores, similar to those taken in Mobile Bay, were taken in each of the five sampling sites located in Ashtabula and Bridgeport Harbors. The first three cores from each site were immediately sealed in their polycarbonate core liners with polycarbonate caps (all of which had been acid washed), stored upright in ice, transported to the Waterways Experiment Station (WES), and stored at 4°C. The two remaining cores from each site in Mobile Bay and the one remaining core from the Ashtabula and Bridgeport locations were measured for surface pH using a combination glass electrode and for redox potential (Eh) using a bright platinum electrode with a calomel reference electrode. Before Eh was measured, platinum electrodes were inserted lengthwise into each core to a depth of 6 cm; the core was sealed, and the electrodes were allowed to equilibrate for 12 hr before the calomel reference electrode was inserted just prior to the Eh measurement.

An unfiltered composite water sample consisting of equal parts surface, mid-level, and bottom water was taken at each site at Mobile Bay and Ashtabula, packed in ice for transport, and stored at 4°C until used in the Elutriate Test. Surface water from Long Island Sound (Eaton's Neck Disposal Area) was taken, stored in polypropylene bottles, packed in ice for transport, and stored at 4°C until used in the Bridgeport Elutriate Tests.

Selective extraction of sediments

The selective extraction procedure used in this investigation was published in a report entitled "A Practical Selective Extraction Procedure for Sediment Characterization" (18). However, since the report cited is not available to the general reader, the procedure is described

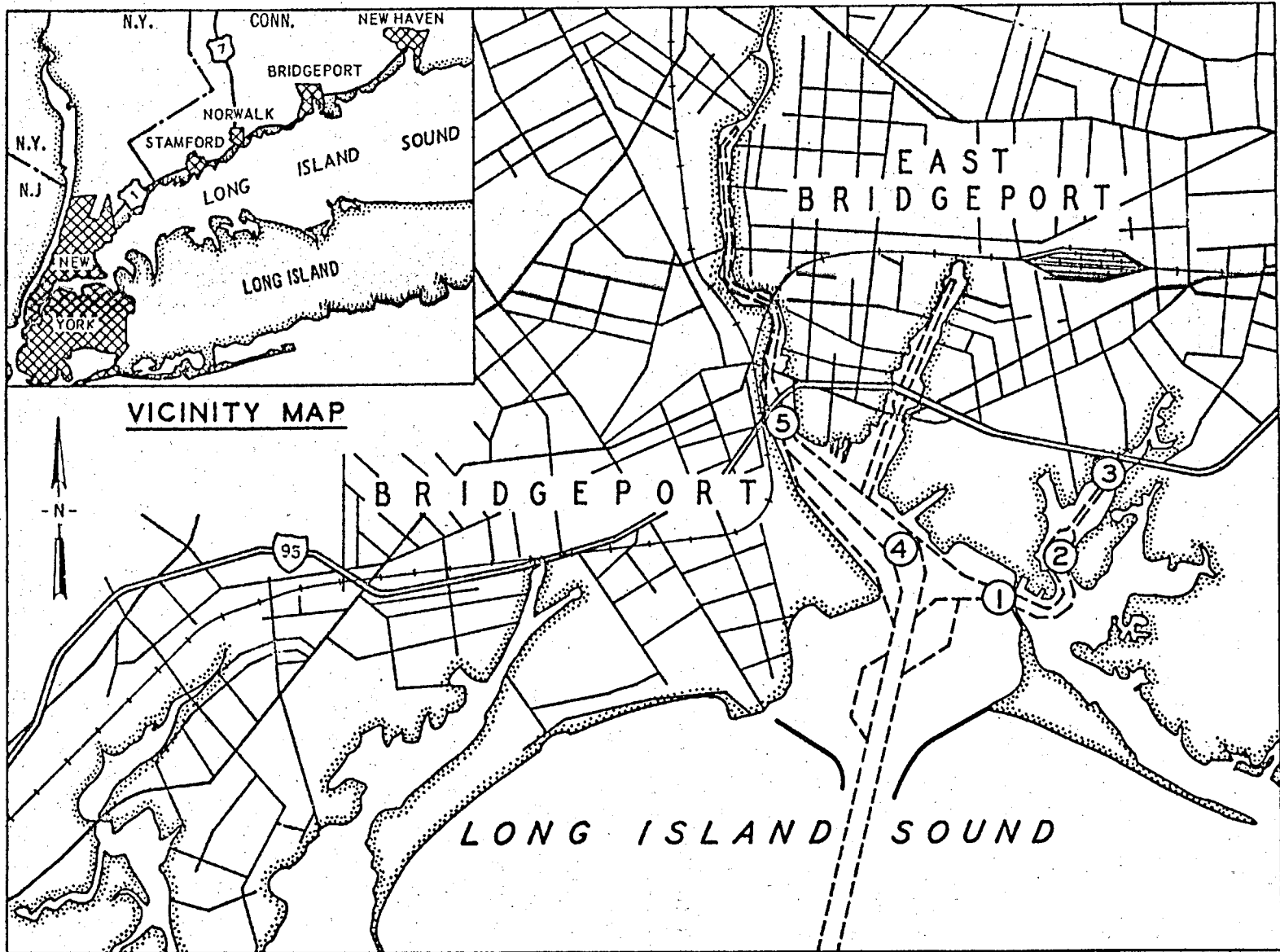


Figure 3. Location Map, Bridgeport, Connecticut

in the following paragraphs, and a schematic representation is presented in Fig. 4.

Prior to sample processing, a disposable glove bag containing a nitrogen atmosphere under positive pressure was prepared. Oxygen-free conditions in the glove bag were verified with a polarographic oxygen analyzer. Sample handling and all steps in the interstitial water and ammonium acetate (exchangeable phase) extractions were conducted under a nitrogen atmosphere. All hardware used in the extractions was acid washed with 6 N hydrochloric acid prior to use.

Interstitial Water (IW). The sediment core was first extruded from its liner into a flat plastic container in the glove bag. The core was then divided into four sections 15 cm in length. Each section was then split into halves with one half (approximately 300 cc) being used for the IW and the remaining half for all other analyses. The half section used to obtain IW was placed into an oxygen-free, polycarbonate 500-ml centrifuge bottle in the glove bag, followed by centrifugation in a refrigerated centrifuge (4°C) at 9000 rpm (13,000 x g) for 5 min. This was sufficient to obtain approximately 40 percent of the total sediment water. Following centrifugation the IW was vacuum filtered under nitrogen through a 0.45- μ m pore-size membrane filter and immediately acidified to pH 1 with hydrochloric acid. The IW was then stored in polyethylene bottles for subsequent analysis.

Exchangeable Phase (EP). The other remaining section half of each depth segment of wet sediment was blended with an electrically driven polyethylene stirrer contained in the glove bag. A subsample (approximately 20-g dry weight) of each homogenized sediment section was then weighed into an oxygen-free, tared, 250-ml centrifuge tube containing 100-ml deoxygenated 1 N ammonium acetate (27) adjusted to the pH of the surface sediment at that site. The ratio of sediment to extractant was approximately 1:5. Other subsamples of the homogenized sediment were removed for determination of percent solids. The sediment suspensions were removed for determination of percent solids. The sediment suspensions were shaken for 1 hr. The suspensions were centrifuged and then vacuum filtered under oxygen-free conditions. The filtrates were then

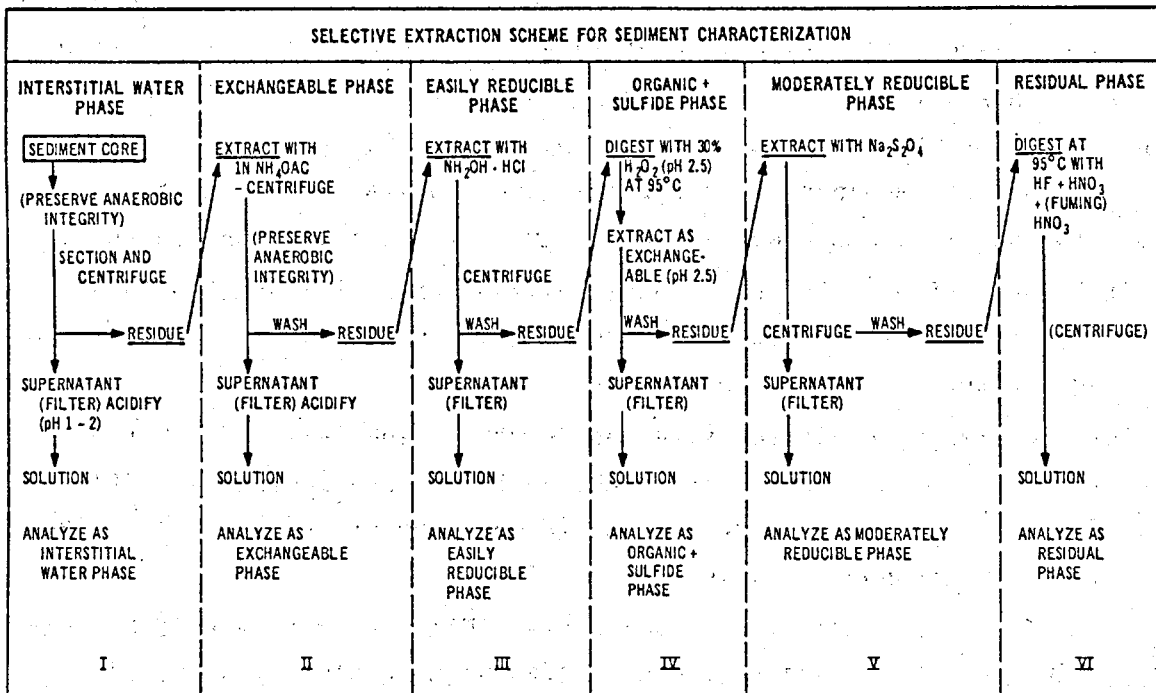


Figure 4. Selective Extraction Scheme for Sediment Characterization

acidified and subsequently stored as previously described for the IW. This extractant also included metals from the IW. Specific concentrations of constituents in this extract were therefore corrected for the mass of material found in the IW.

Additional subsamples from the blended half of the depth segments were set aside for determination of total metals, total Kjeldahl nitrogen, total organic and inorganic carbon, total sulfides, and free sulfides.

Easily Reducible Phase (ERP). The residue from the 1 N ammonium acetate extraction was washed once with 50 ml of nitrogen sparged distilled deionized water and centrifuged at 6000 rpm for 5 min, and the liquid phase discarded. The remaining sediment residue was then blended and a 2-g (dry weight) subsample removed and 100 ml of 0.1 M hydroxylamine hydrochloride-0.01 M nitric acid solution added. The solids-to-extractant ratio was approximately 1:50. The mixture was mechanically shaken for 30 min and then centrifuged; the extract was then filtered through 0.45- μ m pore-size membrane filters (7).

Organic + Sulfide Phase (OSP). The residue from the ERP was washed once with distilled water and centrifuged. The supernate was then discarded. Each of the residue samples was then digested at 95°C with 30 percent hydrogen peroxide acidified to pH 2.5 (27). The digest was kept acidic to keep any metals released in solution. The residue remaining after digestion was mechanically shaken for 1 hr with 100 ml of 1 N ammonium acetate buffered at pH 2.5. The extract was separated as previously described; the residue washed once with distilled water and centrifuged; and the supernate discarded.

Moderately Reducible Phase (MRP). The washed residue from the OSP was extracted with 100 ml of a solution containing 16 g of sodium citrate and 1.67 g of sodium dithionite in H₂O. The mixture was then mechanically shaken for 17 hr (25). The extract was separated by centrifugation and filtration through 0.45 μ m pore-size membrane filters. This extract contains reduced iron and metals that may have been associated with the hydrous iron oxides. The residue was washed once with distilled water and the supernate discarded.

Residual Phase (RP). A 0.5-g (oven-dry weight) subsample of the residue from the MRP was digested with a solution of 15 ml of hydrofluoric acid and 10 ml of concentrated nitric acid in a covered Teflon beaker at approximately 175°C. After evaporation to near dryness, 8 ml of fuming nitric acid was added stepwise in 2-ml increments, and the sample was again evaporated to near dryness. The residue was dissolved in hot 6 N hydrochloric acid and diluted to 50 ml in a volumetric flask. This digestion is a modification of the total digestion method of Smith and Windom (44), and uses fuming nitric acid in place of perchloric acid.

Total Digestion of Sediment. The sediment subsample set aside for total metal analyses was dried and ground using an agate mortar. A 0.5-g subsample of sediment was then weighed into a Teflon beaker, digested, and brought to volume in the same manner as the RP digestion.

Elutriate Test. The Elutriate Test (30) was conducted in duplicate upon each depth segment of one core from each site at a location. The procedure consisted of 30 min of vigorous shaking of one part sediment with four parts dredging or disposal site water (volume/volume), followed by 1 hr of settling and centrifugation and filtration through a 0.45- μ m pore-size membrane filter.

Analytical methods

A Perkin-Elmer Model 503 atomic absorption spectrophotometer was used in all metal determinations. Direct flame aspiration with a deuterium arc background corrector was used when concentrations exceeded instrument detection limits. For lower concentrations, extracts were analyzed by the method of standard additions using a Perkin-Elmer Model 2100 heated graphite atomic absorption spectrophotometer. Arsenic was determined using a Perkin-Elmer Model 503 atomic absorption spectrophotometer and a hydride generator. When this method gave poor recovery of spiked samples, the Perkin-Elmer Model 2100 heated graphite atomizer was used.

Dispersed particle-size distribution (39) and cation exchange capacity (27) were determined on wet sediment samples from each segment of all cores. The cation exchange capacity procedure included saturating wet sediment samples with ammonium, removing excess ammonium with

isopropyl alcohol, and extracting the sediments with a series of 2 N potassium chloride solutions (5). Ammonium in the cation exchange extract was determined by nesslerization after steam distillation with magnesium oxide (5).

Total organic carbon was determined by dry combustion (2). Inorganic carbon content was estimated by dry combustion without sample pretreatment with sulfurous acid (3).

Total and free sulfides were determined by the Connell (12) modification of the Farber (20) method.

Statistical methods

Simple linear correlations were calculated to determine what relationship, if any, existed among the various parameters studied.

RESULTS

The data presented herein are mean values for each parameter measured at a specific location. Correlation coefficient values were obtained using individual numbers, not average values. Should the reader desire a more detailed description of the chemical trends observed in any of the three locations studied, refer to Brannon et al. (4).

When examining these results, or the results of any other selective extraction scheme, the reader should keep a number of points in mind:

- a. Labeling of the various chemically extracted phases is a matter of convenience. Metals extracted in these phases are related in some unknown way to certain forms of chemicals that are expected to be extracted by the reagents used (G. F. Lee, 1975, Personal Communication).
- b. Trace metal distribution in any extraction scheme is operationally defined by the method of extraction rather than any fundamental properties of the system (28).
- c. The best approach to sediment fractionation is to analyze separately each mineral phase in the sediments. Sediment chemistry has not advanced to the point where such an approach is feasible. At the present time, the best approach to sediment fractionation is to use an empirical sequential selective extraction scheme.

In the interest of brevity, designations of the various chemically extracted phases have been abbreviated throughout the text as shown below:

Interstitial Water (IW)	Exchangeable Phase (EP)
Easily Reducible Phase (ERP)	Organic + Sulfide Phase (OSP)
Moderately Reducible Phase (MRP)	Residual Phase (RP)

The term "standard elutriate" will be used to designate the supernate resulting from the Elutriate Test procedure.

Sediment Physical and Chemical Characteristics. The sediments differed between locations in nearly all physical and chemical parameters measured. Mean values of the physical and chemical parameters measured in the sediments are presented in Table 1.

Results of particle-size analysis indicated that the <2- μm particle-size fraction (clay) was predominant in sediments from Mobile Bay, constituting 52.7 percent of the sediments. Sediments from Ashtabula and Bridgeport were composed predominately of the silt-size fraction (2-50 μm), constituting 62.7 percent and 58.2 percent of these sediments, respectively.

Cation exchange capacity was highest in sediments from Mobile Bay where clay content was highest, averaging 46.3 meq/100 g compared to values of less than 24 meq/100 g in the two remaining locations.

Organic carbon content differences between locations were slight. Inorganic carbon content showed greater differences, averaging 2.19 percent in sediments from Bridgeport compared to 0.07 percent in sediments from Mobile Bay. Total sulfide concentration ranged between 2680 $\mu\text{g/g}$ in sediments from Bridgeport and 240 $\mu\text{g/g}$ in sediments from Ashtabula. Free sulfides averaging 81 $\mu\text{g/g}$ were also found in sediments from Bridgeport.

Total heavy metal concentrations were different between locations. Sediments from Bridgeport were generally highest in heavy metals with the exception of manganese and nickel. Cadmium and zinc concentrations in sediments from Bridgeport averaged 17.6 $\mu\text{g/g}$ and 1067 $\mu\text{g/g}$, respectively. This greatly exceeded concentrations found in sediments from the other two locations.

TABLE 1. Average Physical and Chemical Sediment Characteristics

Parameter (1)	Location		
	Mobile Bay, Alabama (2)	Ashtabula, Ohio (3)	Bridgeport, Connecticut (4)
Particle size distribution, percent			
<2 micrometers	52.7	36.0	38.3
2-50 micrometers	32.5	62.7	58.2
>50 micrometers	14.8	1.3	3.5
Cation exchange capacity, milliequivalent per 100 grams	46.3	16.9	23.9
Total organic carbon, percent	2.03	2.42	2.69
Total inorganic carbon, percent	0.07	0.56	2.19
Total sulfides, micrograms per gram	903	240	2680
Total nitrogen, micrograms per gram	1900	1390	2680
Total metals, micrograms per gram			
Manganese	746	642	531
Nickel	156	213	203
Cadmium	3.62	4.14	17.60
Zinc	243	444	1067
Arsenic	4.08	6.50	6.90

The redox potential (Eh) of the sediments indicated reduced conditions (Eh = < -100 mv) in all locations. The pH measurements showed a pH near neutrality for surface sediments at all locations.

Manganese (Mn). The three locations studied showed different Mn concentrations in each chemically extracted phase. Fig. 5 shows the average concentrations of Mn found in the various sediment fractions and in the standard elutriate. The OSP showed the highest concentration of sediment Mn in the Mobile Bay and Ashtabula locations, averaging 338 µg/g and 267 µg/g, respectively. The concentration of RP Mn averaged 363 µg/g in Bridgeport sediments which was the highest concentration of any phase extracted in that location.

Interstitial water concentrations of Mn ranged from an average of 9.75 mg/l in sediments from Mobile Bay to an average of 0.29 mg/l in sediments from Bridgeport. The IW Mn concentration was correlated with EP Mn concentration ($r = 0.904$) and ERP Mn concentration ($r = 0.749$) where r is the degree of correlation. Exchangeable phase Mn was also correlated with ERP Mn concentration ($r = 0.838$). Manganese concentration in the MRP and RP was not correlated with any of the physical or chemical sediment parameters determined.

Manganese concentration in the standard elutriate ranged from an average of 1.28 mg/l in the Mobile Bay location to an average of 0.16 mg/l in the Bridgeport location. Background level of Mn in the water used in the Elutriate Test did not exceed 0.08 mg/l in any location. Manganese concentration in the standard elutriate was correlated with Mn concentration in the IW ($r = 0.849$), EP ($r = 0.755$), and ERP ($r = 0.633$).

Nickel (Ni). Sediment nickel was concentrated in the RP in all locations (Fig. 6). Nickel concentration of the RP ranged between 116 µg/g and 128 µg/g. The OSP also contained significant amounts of Ni. Average Ni concentration in the OSP ranged from 8.17 µg/g in sediments from Mobile Bay to 46.65 µg/g in sediments from Bridgeport. Nickel concentration in the OSP was correlated with total sulfide concentration in sediments from Ashtabula ($r = 0.475$) and Bridgeport ($r = 0.685$).

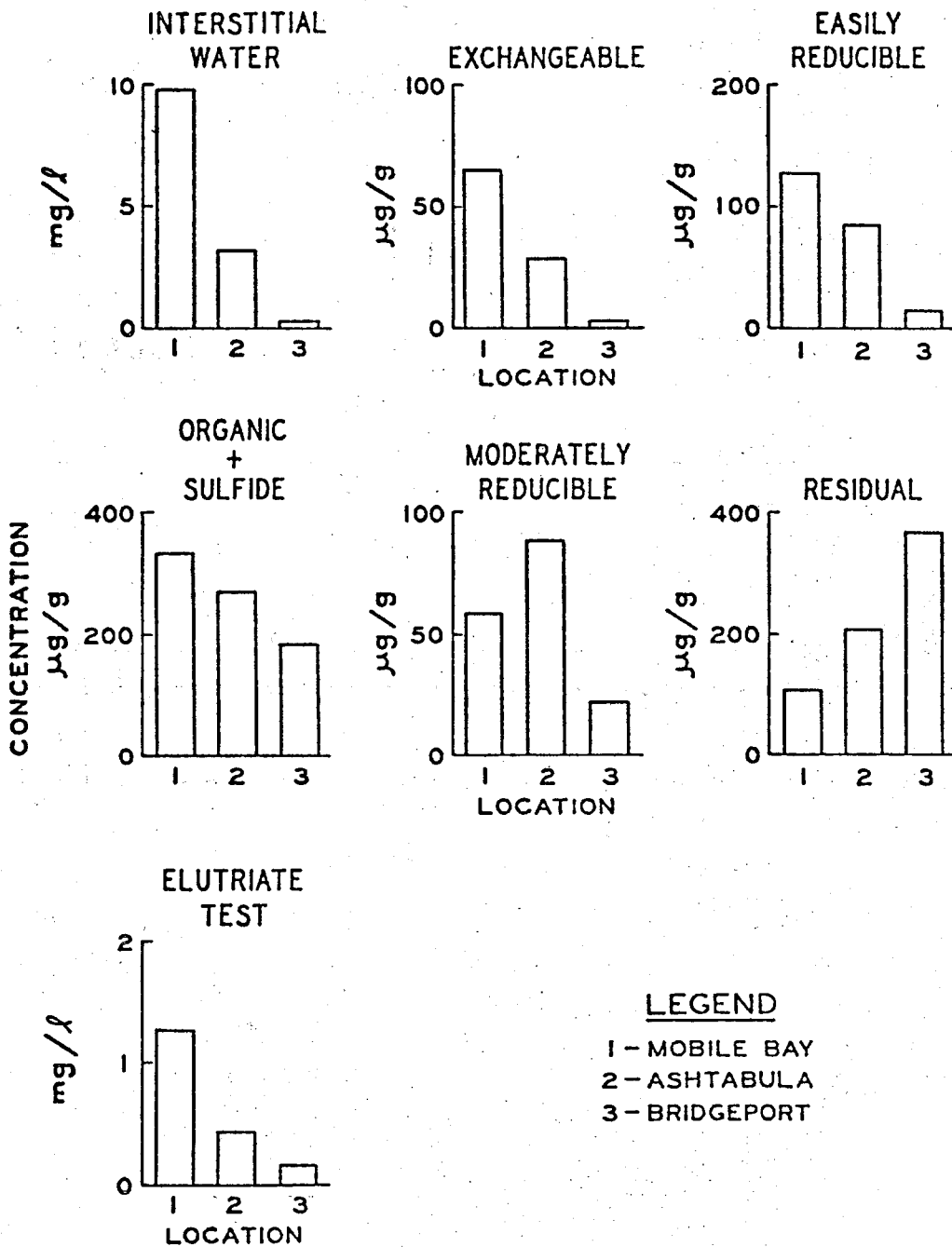


Figure 5. Distribution of Manganese in the Various Chemical Fractions

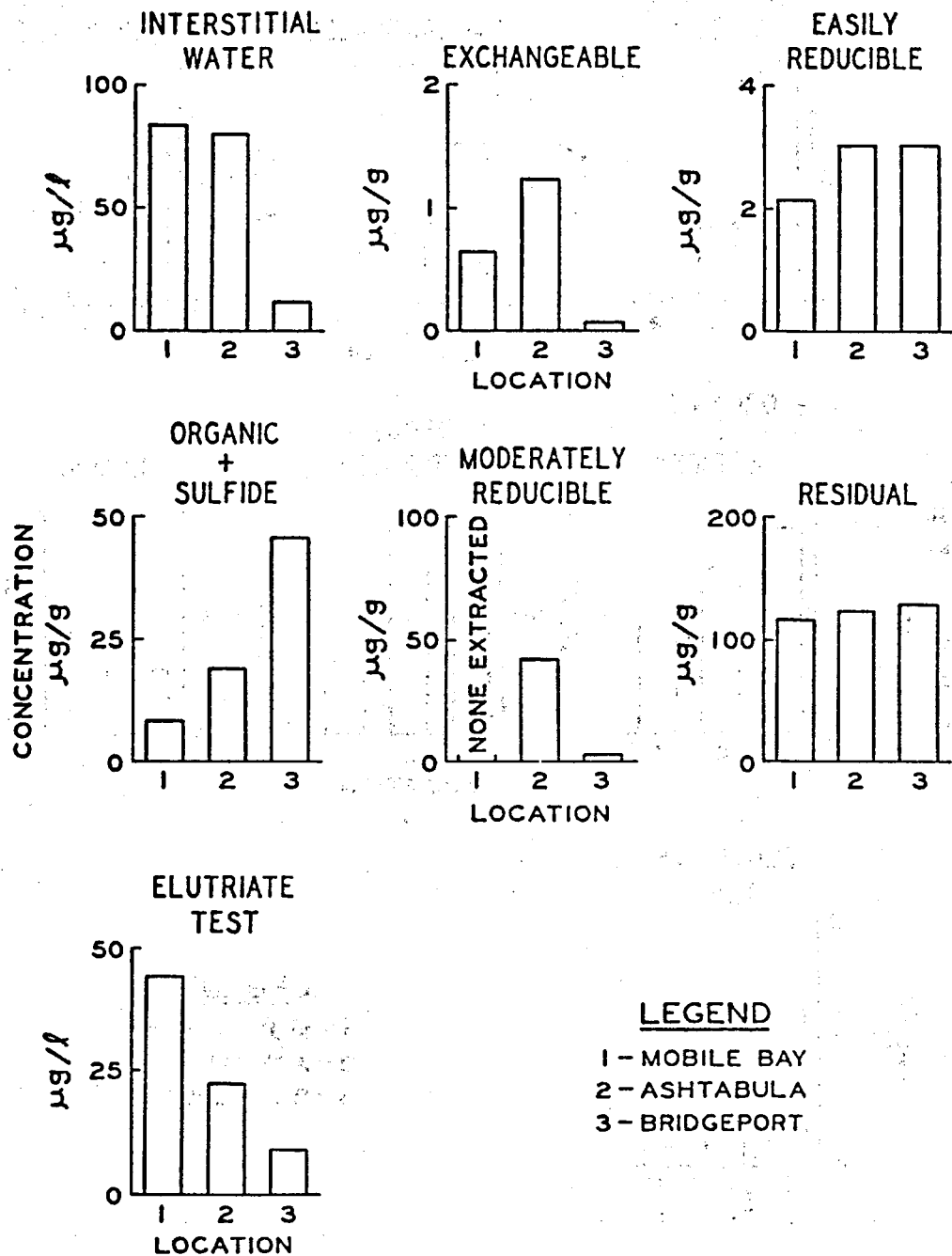


Figure 6. Distribution of Nickel in the Various Chemical Fractions

Nickel concentration in the OSP was also correlated with total sediment organic carbon ($r = 0.418$).

Nickel concentration in the standard elutriate ranged from 44.2 $\mu\text{g}/\ell$ in Mobile Bay to 9.05 $\mu\text{g}/\ell$ in Bridgeport. Nickel concentration in the standard elutriate was correlated with Ni concentration in different sediment phases in each location. The sediment phases whose Ni concentrations were correlated with Ni concentration in the standard elutriate are listed in Table 2 with the degree of correlation (r).

Table 2. Degree of Correlation of Nickel Concentration in Sediment and Standard Elutriate

Location (1)	Sediment Phase (2)	Degree of Correlation (r) (3)
Mobile Bay	ERP	0.506
Ashtabula	OSP	0.436
Bridgeport	OSP	0.553
	ERP	0.410
	IW	0.394

Cadmium (Cd). Cadmium concentration in the RP was highest in sediments from Mobile Bay, but OSP Cd was highest in sediments from Ashtabula and Bridgeport (Fig. 7). Cadmium concentration in the RP ranged from undetectable levels ($<0.1 \mu\text{g}/\text{g}$) in sediments from Bridgeport to an average of 2.86 $\mu\text{g}/\text{g}$ in sediments from Mobile Bay. Average Cd concentration in the OSP ranged from 0.60 $\mu\text{g}/\text{g}$ in sediments from Mobile Bay to 14.58 $\mu\text{g}/\text{g}$ in sediments from Bridgeport. No Cd was found in the MRP in any location. Cadmium concentration in the OSP was correlated with total sediment sulfide concentration in sediments from Ashtabula ($r = 0.512$) and Bridgeport ($r = 0.501$).

Cadmium concentration in the standard elutriate was below

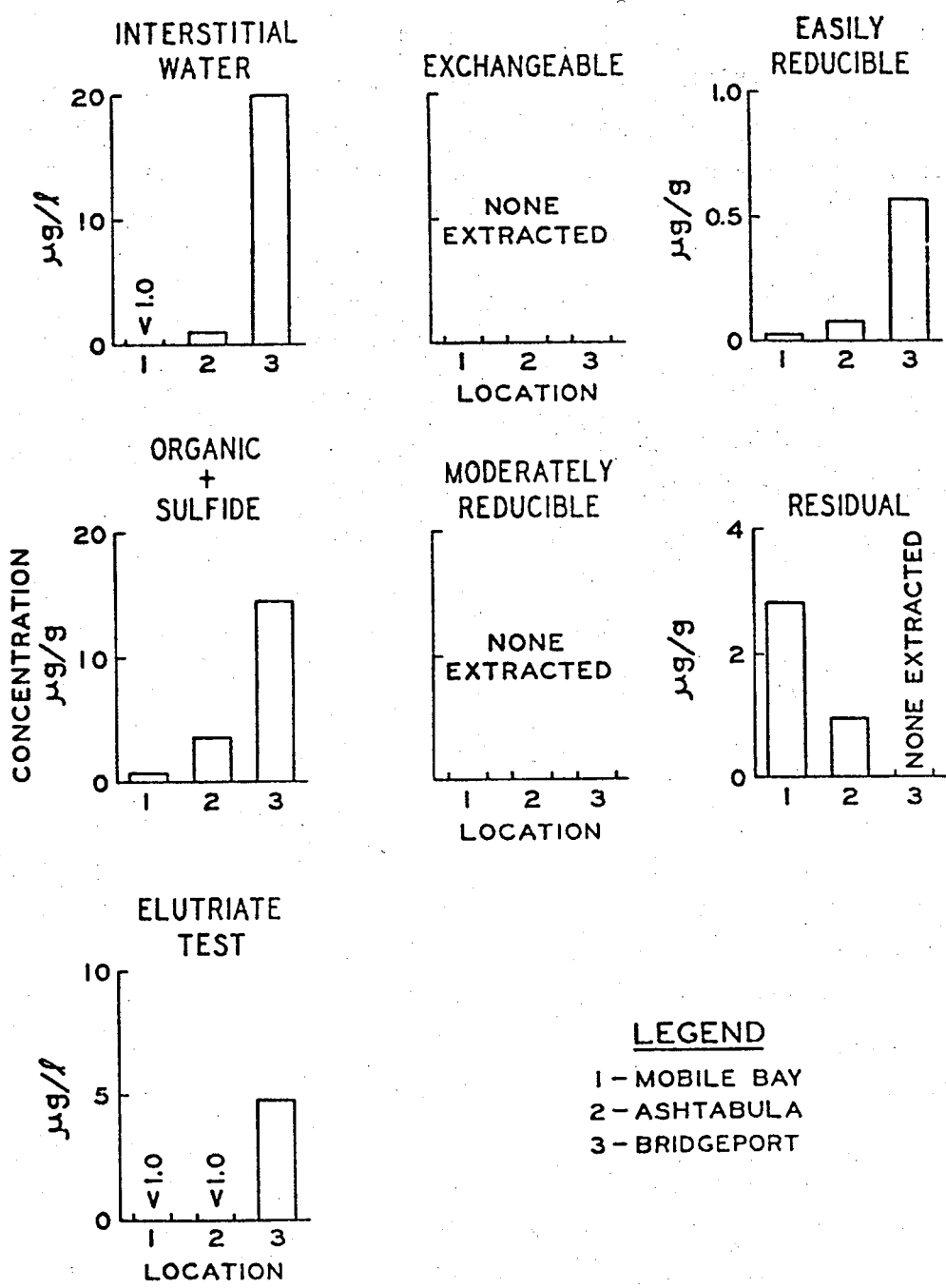


Figure 7. Distribution of Cadmium in the Various Chemical Fractions

instrument detection limits in the Mobile Bay and Ashtabula locations. Cadmium concentration in the Bridgeport standard elutriate averaged $4.9 \mu\text{g}/\ell$, which was equal to background Cd levels in the water used in the Elutriate Test. No correlation was seen between Cd concentration in the standard elutriate and Cd concentration in any of the various chemically extracted sediment phases.

Zinc (Zn). The highest Zn concentrations in the fractions analyzed occurred in the OSP in all locations (Fig. 8). However, the RP was not determined. Average Zn concentration in the OSP ranged from $123.8 \mu\text{g}/\text{g}$ in sediments from Mobile Bay to $568.0 \mu\text{g}/\text{g}$ in sediments from Bridgeport. Zinc concentration in the OSP was correlated with total sulfide concentration ($r = 0.526$) in sediments from Bridgeport. No Zn was extracted in the EP in sediments from Mobile Bay. Average Zn concentration in the IW ranged from $0.035 \text{ mg}/\ell$ in sediments from Mobile Bay to $0.92 \text{ mg}/\ell$ in sediments from Ashtabula.

Sodium dithionite used in the MRP extraction was contaminated with Zn. This Zn contamination carried over into the RP, necessitating calculation of RP Zn concentration by the difference between the analytical total and the sum of the remaining Zn phases.

Zinc concentration in the standard elutriate ranged from $0.005 \text{ mg}/\ell$ in Mobile Bay location to $1.13 \text{ mg}/\ell$ in the Bridgeport location. Zinc concentration in the standard elutriate was correlated with ERP Zn ($r = 0.466$) and OSP Zn ($r = 0.516$).

Arsenic (As). Arsenic concentration was highest in the MRP in all locations studied (Fig. 9). Average As concentration in the MRP ranged from $4.45 \mu\text{g}/\text{g}$ in Bridgeport sediments to $5.55 \mu\text{g}/\text{g}$ in Ashtabula sediments. No OSP As was extracted in any location. Average IW As concentration ranged from $4.6 \mu\text{g}/\ell$ in sediments from Mobile Bay to $34.5 \mu\text{g}/\ell$ in sediments from Bridgeport. Exchangeable phase As was found only in the sediments from Ashtabula and was correlated with IW As ($r = 0.659$) and ERP As ($r = 0.446$) in this location.

Average As concentration in the standard elutriate ranged from $1.72 \mu\text{g}/\ell$ in the Mobile Bay location to $3.32 \mu\text{g}/\ell$ in the Bridgeport

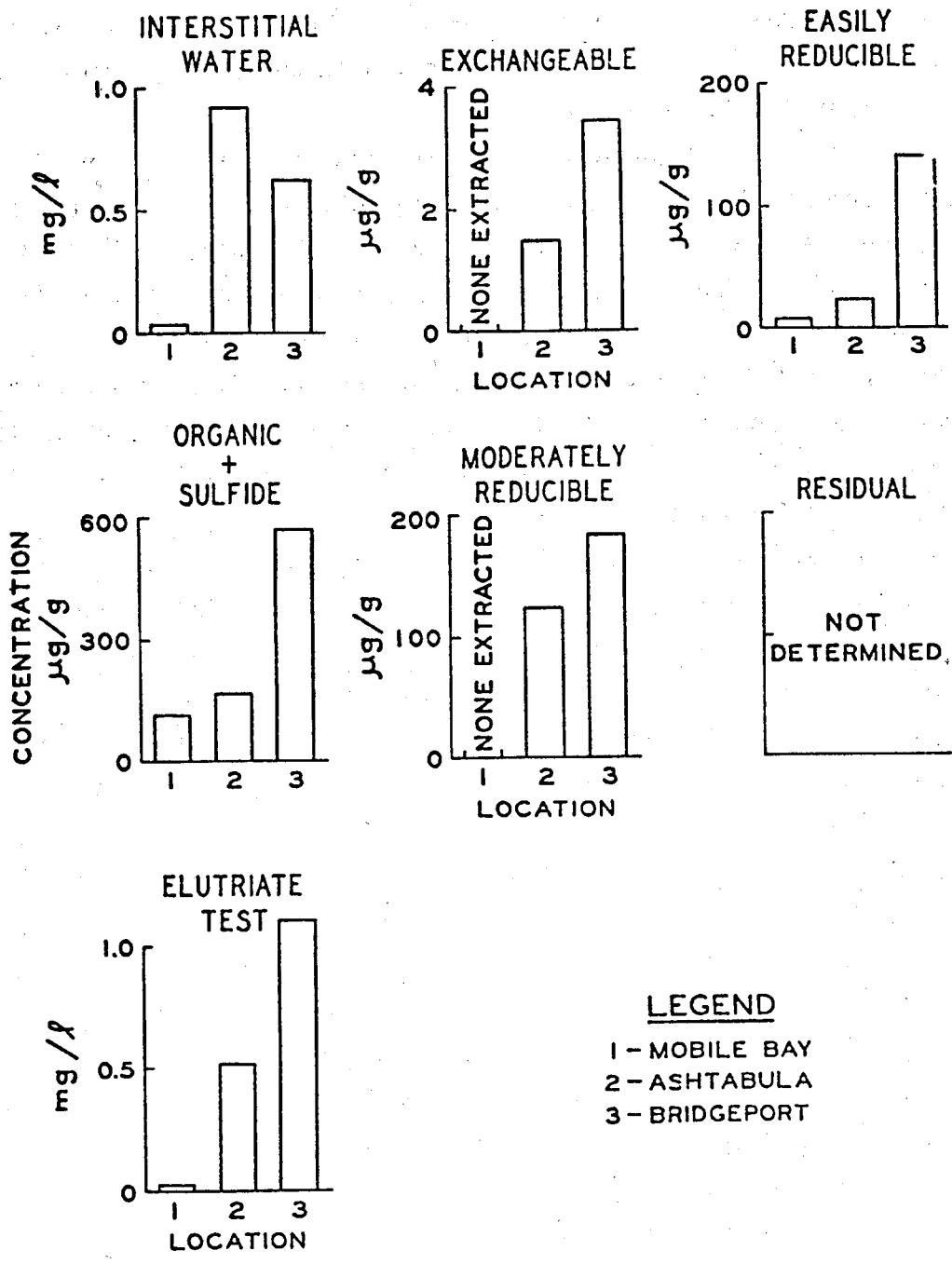


Figure 8. Distribution of Zinc in the Various Chemical Fractions

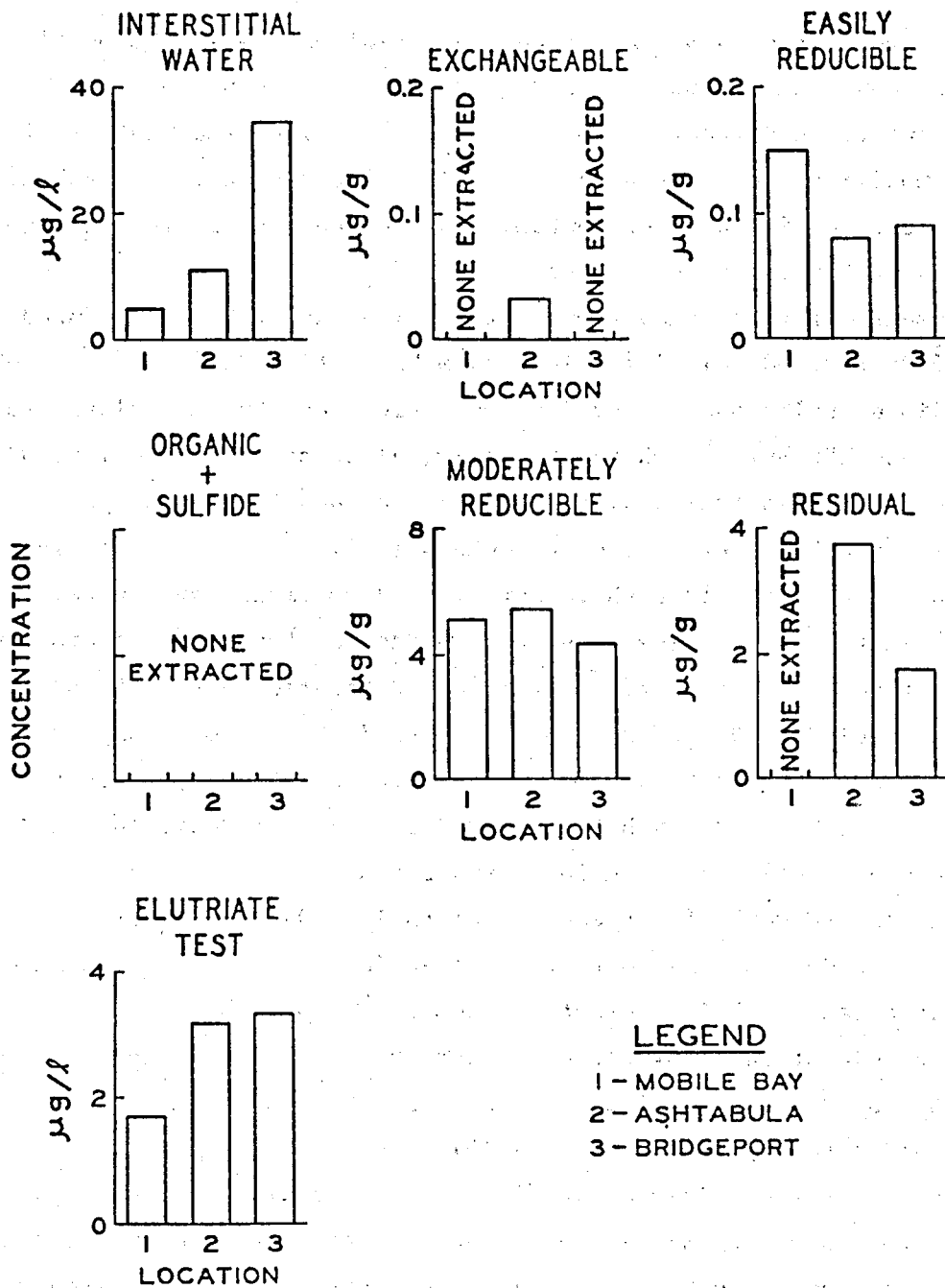


Figure 9. Distribution of Arsenic in the Various Chemical Fractions

sediments. Arsenic concentration in the standard elutriate was correlated with EP As ($r = 0.477$) in the sediments from Ashtabula.

Discussion

Sediment Trace Metal Distribution. Sediment IW is the mobile, non-adsorbed fluid component of sediments and can represent from 31 percent to 70 percent of the weight of "in situ" sediments (4). Due to the mobility and apparent availability of contaminants dissolved in the IW, the partitioning of contaminants between the solid and liquid phase is of considerable interest.

Results of this study show that sediment anaerobic or reduced conditions favored solubilization and mobilization of Mn and As from the sediment solid phase. Easily reducible phase Mn was related to both EP and ERP Mn. Gotoh and Patrick (24) found that in soils, water soluble + EP Mn increased with decreasing pH and Eh at the expense of ERP Mn. In 1931 Piper, cited in Jackson (27), published a similar relationship to those given above for reduced sediments and soils.

Similar relationships were seen in the As results for sediments from Ashtabula. Interstitial water As was related only to EP As. The EP As was related to ERP As. This suggested that a more complex relation existed among the IW, EP, and ERP. One possibility is that the EP served as an intermediary between ERP and IW As. No correlation was seen in any location between IW As and ERP As.

Similar to work of Johnson and Hiltholt (29) As was not associated with the sediment organic matter. Extraction of the sediments resulted in no detectable OSP As; detection limits were $0.05 \mu\text{g/g}$.

The role of As in oxidation reduction reactions is unclear. However, As is subject to oxidation and reduction, having an oxidized state (As^{+5}) and a reduced state (As^{+3}) (15). The reduced state (As^{+3}) is more soluble than the oxidized state (As^{+5}) and is similar to the situation encountered with the oxidized and reduced states of iron (Fe) and Mn. The data of Deuel and Swoboda (15) showed that a reduced environment resulted in a greater water-soluble As concentration. These researchers concluded that the solubilization of As at lower redox potentials was due to the reduction of Fe and release of adsorbed As rather than the

reduction of As itself. However, intensive reducing conditions were not attained under the experimental conditions of Deuel and Swoboda (15). Brannon et al. (4) found no relationship between As and Fe released in the ERP; indicating that reduction as As^{+5} to As^{+3} may be occurring under the reduced environment of sediments independent of Fe^{+3} reduction and subsequent release of occluded As.

The sediments studied were in a reduced state and contained high levels of sulfides leading to the assumption that metal concentration in the sediment IW would be governed by metal sulfide salt solubility. Results of this study, however, indicated that some mechanism involving the sediment IW resulted in Ni and Zn concentrations in the IW greater than would be expected if only the solubility of their simple sulfides were considered.

Zinc and Ni concentrations of sediment IW should be severely limited where sediment IW has a sulfide activity of 10^{-10} M or greater and should be limited to concentrations of 1.04×10^{-6} $\mu\text{g}/\ell$ and 0.18 $\mu\text{g}/\ell$, respectively (17). Assuming that 10^{-10} M was a reasonable approximation of sulfide activity in the sediment IW, then Zn exceeded sulfide solubility in the IW of sediments from all locations. The high Zn concentrations in Bridgeport sediment IW occurred despite the presence of average free sulfide concentrations of 81 $\mu\text{g}/\text{g}$ in the sediments.

Organic chelation of metals in sediment IW has been implicated as a mechanism for stabilization of soluble metal ions under conditions which should cause them to precipitate (17,40,42). Nickel complexes with soil humic acids (26), soil fulvic acids (43), or sediment organic matter (17) should be more stable than comparable Zn complexes. Nickel concentration was 2.5 times higher than Zn concentration in the IW of sediments from Mobile Bay, which would indicate that organic Ni complexes were more stable than organic Zn complexes. Zinc concentrations in the IW of sediments from Bridgeport and Ashtabula were much higher than Ni concentrations in the IW of these locations. These results indicated that some mechanism other than metal organic complex formation, possibly the presence of polysulfide complexes and sulfide salts of much greater

solubilities (8), was at work in the sediment IW of Bridgeport and Ashtabula.

These results demonstrate that high concentrations of metals can develop in the IW of sediments rich in sulfides but that the responsible mechanisms are often unknown. Contrary to popular argument, the formation of metal organic complexes in the sediment IW was not responsible for elevated trace metal concentrations in the sediment IW in all cases.

Duchart et al. (16) advanced the argument that reduction of hydrous oxides in sediments may release trace metals into the IW. No correlation was seen, however, between Mn or Fe (4) concentration in the IW and the other metals analyzed. This does not preclude the release of trace metals from hydrous oxides upon reduction, but may be indicative of different control mechanisms, such as differing sulfide solubility and differing stability of metal-organic complexes and chelates for Mn, Fe, and the other trace metals in the IW.

The 1 N ammonium acetate extractant (EP) was selected to remove cations sorbed on mineral and organic exchange sites. The results indicated, however, that sorption of Cd and Zn by the sediments from the extract was occurring. Reagent Zn contamination was reduced following extraction of sediments from Mobile Bay. No Cd was extracted from sediments by 1 N ammonium acetate in any location. Sorption of Zn and Cd by the sediment solid phase was indicated from these results. Ammonium acetate will also extensively dissolve calcium (Ca) and magnesium (Mg) from CaCO_3 (calcite) or $\text{CaCO}_3 \cdot \text{MgCO}_3$ (dolomite) (27), which may present problems when adapting this selective extraction procedure to calcareous sediments.

The hydroxylamine hydrochloride solution primarily extracted the hydrous oxides of Mn and coprecipitated trace elements (7). Except for Zn in the sediments from Mobile Bay, there was no correlation between Mn and trace metal concentration in the ERP. Results did indicate, however, that some trace metals were extracted in the ERP. This indicated that sorption or occlusion of trace metals by a mixed system of hydrous Fe and Mn oxides and hydroxides may be more complex than simple sorption by discrete phases. The sorption or occlusion of trace metals

by hydrous oxides may be similar to that proposed for copper (Cu) by McLaren and Crawford (36). Their data indicated that Mn has a greater effect than Fe on the amount of Cu occluded. Since Cu associated with the oxide phase is a function of both initial sorption and retention, McLaren and Crawford (36) felt that Mn oxides sorbed the Cu. Due to their greater abundance, the Fe oxides were implicated as responsible for the occlusion of Cu into the oxides.

Nickel was the only metal extracted from the OSP that correlated with the total organic carbon content of the sediments. The lack of correlation of the other trace metals with the total organic carbon content of the sediments was not surprising when the number of factors that can contribute to metal concentration in this phase is considered.

Organic partitioning as determined by the acidified hydrogen peroxide (H_2O_2) digestion represents a less than complete oxidation of the sediment organic matter (27). Elemental carbon and resistant, paraffin-like organic material is not decomposed by the H_2O_2 and to some extent structural (nonhumified) organic matter is not attacked (27). Alexander and Byers, as cited in Jackson (27), found as much as 16 percent of the original carbon content of soils in the residue of the H_2O_2 digest. However, the residual organic material is considered very stable and resistant to decomposition.

The large amounts of Mn extracted in the OSP were indicative of another feature of the H_2O_2 digestion. Free manganese dioxide (MnO_2) remaining after extraction of the ERP is changed by the procedure to Mn^{++} and brought into solution during the digestion along with any calcite ($CaCO_3$) remaining in the sediment (27). In the original procedure of Jackson (27), the soluble Mn^{++} is eventually converted to insoluble Mn_3O_4 during drying of the digest residue at $110^\circ C$ for weight loss determination. The procedure used in this study involved extraction of the wet H_2O_2 digest residue rather than drying, maintaining released Mn in the soluble Mn^{++} form.

Metal-sulfide salts were apparently a source of trace metals extracted in the OSP as evidenced by the numerous positive correlations

between metal concentration in the OSP and total sediment sulfide concentration. Fixation of heavy metals by sulfides has been observed by other workers in reduced environments (21,22,31). Decomposition of sulfide salts under oxidizing conditions has also been noted (19).

Arsenic distribution in the MRP as observed in this study agreed with the data of Crecelius et al. (14). These workers found 34 to 66 percent of total As in sediments from Puget Sound to be extractable with citrate-dithionite or oxlate. Citrate-dithionite primarily extracts the hydrous oxides of Fe and Mn (25,37). Use of the citrate chelating agent with the dithionite aids Fe extraction and removes some coatings of alumina (1,37).

Trace metals associated with the hydrous oxides and hydroxides of Fe would probably have little effect on benthic organisms. Luoma and Jenne (34,35) showed that there was little uptake of Cd, Zn, or cobalt (Co) by deposit-feeding clams (Macoma balthica) when these metals were coprecipitated with amorphous Fe oxides or Mn oxides. There is little reason to believe that trace metals associated with older Fe oxides in sediments would be more available to benthic clams. Lee (32) reviewed the literature on the role of Fe oxides in the aquatic environment. He found that the crystallinity of hydrous Fe oxide precipitates increased with time. The aggregation of primary particles results in the surface area decreasing with time and is responsible for the decreasing sorption capacity of hydrous oxides with time (32).

The only trace metal not associated with the hydrous Fe oxides to some extent was Cd. This indicated that although the hydrous oxides may adsorb Cd, very little adsorbed Cd was retained by the hydrous oxide fraction. Nickel was associated with the MRP only in sediments from Ashtabula. The data indicated that Ni extracted in the MRP was associated with Mn oxides rather than the more plentiful Fe oxides. It is probable that the Mn extracted in the MRP was occluded by Fe oxides since hydroxylamine hydrochloride and acidified H_2O_2 are both efficient extractors of free Mn oxides. This further supports the contention of McLaren and Crawford (36) that Fe oxides are responsible for the occlusion of trace metals adsorbed by hydrous Mn oxides.

The RP trace metals are those associated with mineral lattices and metals in this phase are stable and biologically inactive. The results of this investigation indicated that Ni was associated primarily with the RP. These findings agreed with the findings of Chester et al. (11), who found that the majority of Ni near continents was in the residual fraction. The percentage of Ni in the RP decreased toward mid-ocean, with those sediments which contained the minimum RP Ni having the highest total Ni concentration (11).

Particle size was not implicated as a universal source of RP Ni. The clay-size fraction ($<2 \mu\text{m}$) was the source of RP Ni in sediments from Ashtabula, which is contrary to what would be expected from the findings of Chester et al. (11). The decrease in RP Ni with distance from the continents implicated the larger sediment particles as the source of RP Ni. Larger sedimentary particles should settle closer to the continents with the smaller particles carried farther out into the oceans by the currents.

Heavy Metals in the Standard Elutriate. The results indicated that metal concentrations in the sediment phases thought to be the most mobile were related to their respective concentrations in the standard elutriate. No relationship existed between trace metal concentrations in the standard elutriate and total sediment metal concentrations for Mn, Ni, As, Cd, and Zn. Trace metal concentrations in the MRP and RP were also not related to trace metal concentrations in the standard elutriate. This occurred despite the fact that the majority of sediment As and Ni were extracted in the MRP and RP, respectively. The mobility of the more easily extracted phases, coupled with the immobility of metals in the MRP and RP, demonstrated that the physical-chemical form of bound metals was a greater factor than total metal concentrations in determining the mobility of metals into the standard elutriate.

The relationship between metal physical-chemical form and mobility into the standard elutriate was well illustrated in the Mn results. Interstitial water Mn, which would be expected to be immediately mobile, showed the highest degree of correlation with Mn concentration in the

standard elutriate. Manganese in the EP and ERP, initially not in solution in the sediments, showed lesser degrees of correlation with Mn concentration in the standard elutriate. This indicated a lower degree of mobility for EP and ERP Mn than for IW Mn, even though actual Mn concentration increased in the order of ERP > EP > IW.

Metals associated with the OSP would be expected to be relatively immobile due to the harshness of the acidified H_2O_2 digest used to obtain this phase. However, the results indicated that Zn and Ni in this phase were somewhat mobile. Metal mobilization from the OSP into the standard elutriate could be traced to metal sulfide oxidation and release of sulfide-bound metals into solution during the Elutriate Test procedure.

Zinc and Ni concentrations in the OSP, in addition to being related to their concentrations in the standard elutriate, were related to total sediment sulfide concentration. This indicated that Zn and Ni sulfides were being extracted in the OSP. Sulfide oxidation can proceed rapidly when oxygen (O_2) is present (13), but metals released into solution would be expected to be rapidly adsorbed by sediment solid phases (21). However, significant amounts of Zn were not adsorbed by the sediment as evidenced by the high Zn concentrations found in the standard elutriate. The cation exchange capacity data also indicated a low cation adsorption capacity for the sediments from Ashtabula and Bridgeport. These high Zn concentrations were not seen by Lee et al. (33) in the standard elutriate of sediments from the same locations. However, the Elutriate Test as used by Lee et al. (33) was modified to include air agitation of the sediment-water mixture. This ensured the presence of O_2 throughout the half-hour agitation period, and resulted in greater precipitation of Fe oxides and hydroxides than would have been the case if O_2 became depleted during the Elutriate Test procedure. This would hold true for Elutriate Tests at the same pH, because the precipitation of Fe oxides and hydroxides becomes much slower as the pH decreases (45). The increased rate of Fe precipitation would result in increased adsorption of trace metals (23,28,31) from solution during the course of the Elutriate Test.

When organic complexes migrate from an environment that is reducing in character into one that is oxidizing, the metals in the complexes will tend to precipitate. The extent to which metals in organic complexes will precipitate from solution depends on the stability of their complexes (41). This may have affected the Elutriate Test Zn results in sediments from Bridgeport in view of the unusual behavior of IW Zn previously discussed.

Conclusions

The main findings of this study of Mn, Cd, As, Zn, and Ni distribution in freshwater and marine sediments and the relationship these distributions have with metal concentrations in the standard elutriate are as follows:

- a. No relationship existed between trace metal concentration in the standard elutriate and total metal concentration in the sediment.
- b. Trace metals extracted in the MRP and bound in mineral lattices (RP) were not related to trace metal concentrations in the standard elutriate. This occurred despite the fact that the majority of sediment As and Ni were extracted in the MRP and RP, respectively.
- c. Trace metal concentrations in the sediment phases thought to be the most mobile were related to their respective concentrations in the standard elutriate.
- d. The selective extraction procedures can be used successfully in determining the distribution of metals in the various operationally defined phases in a sediment. The metals extracted in any particular phase are not discrete forms of the metal, but are operationally defined by the method of extraction.
- e. Manganese concentration in the standard elutriate can be used to predict Mn concentration in the IW, EP, and ERP. Zinc concentration in the standard elutriate can be used to predict Zn concentration in the ERP and OSP. Arsenic and Ni did not show any general relationship between their concentrations in

the standard elutriate and in the various chemically extracted phases. Any predictive capability for As and Ni would be site specific.

APPENDIX I.-REFERENCES

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