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AN ASSESSMENT OF THE ENVIRONMENTAL EFFECTS OF DREDGED MATERIAL --ETC(U)
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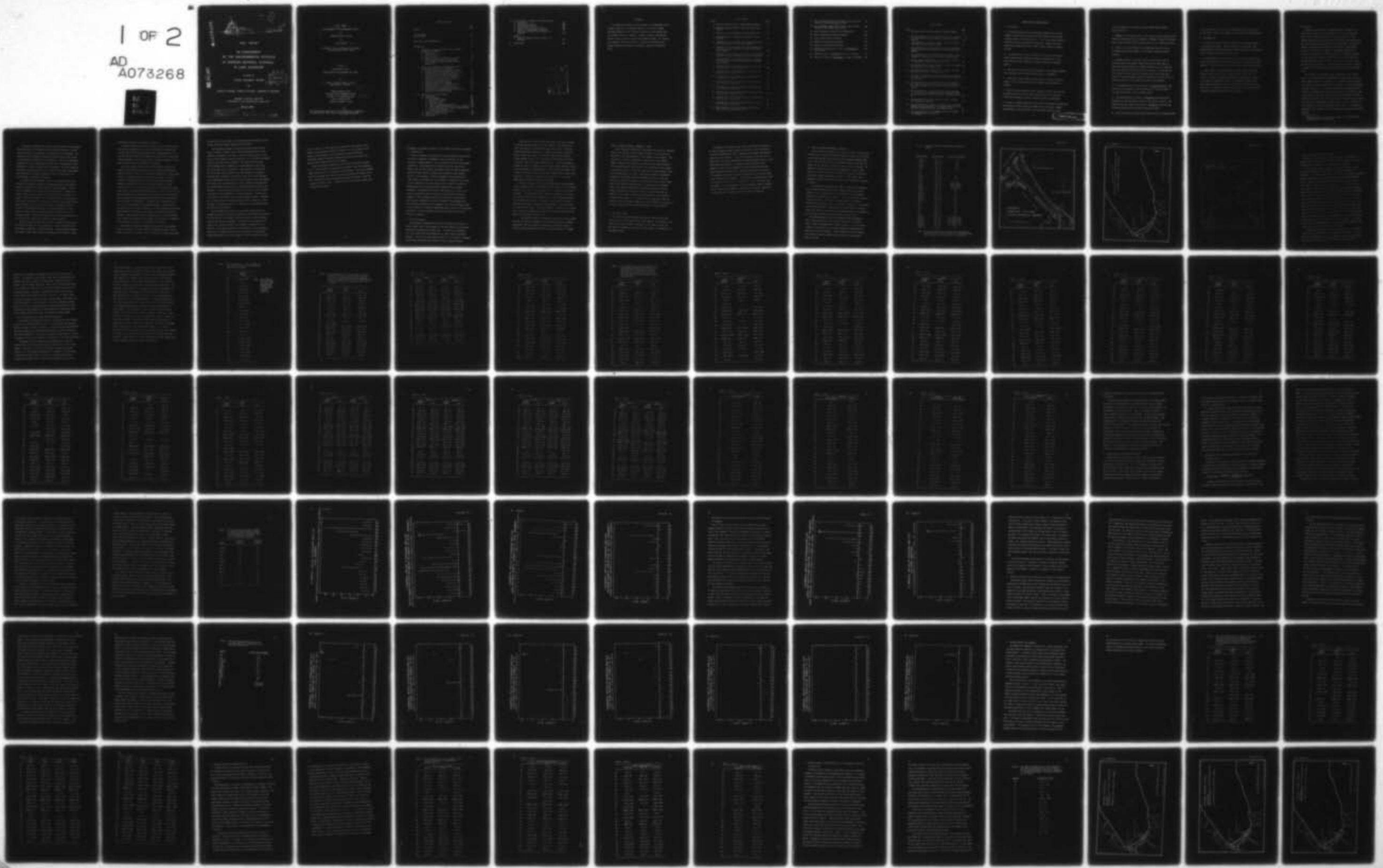

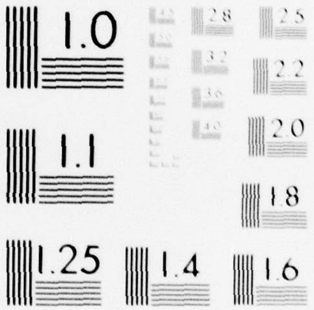

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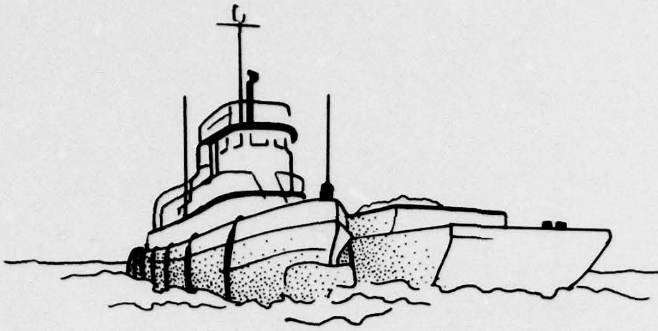

FINAL REPORT

AN ASSESSMENT OF THE ENVIRONMENTAL EFFECTS OF DREDGED MATERIAL DISPOSAL IN LAKE SUPERIOR

Volume 5

Trace Element Study

By

Philip A. Helmke, Robert D. Koons, Iskandar K. Iskandar

MARINE STUDIES CENTER
UNIVERSITY OF WISCONSIN, MADISON

March, 1976

(9) FINAL REPORT.

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A REPORT TO THE U.S. ARMY CORPS OF ENGINEERS
FROM THE MARINE STUDIES CENTER

Volume 5.

TRACE ELEMENT STUDY:
DULUTH-SUPERIOR AND KEWEENAW STUDY AREAS.

By

(10) Philip A./Helmke, Robert D./Koons
and Iskandar K./Iskandar

(11) Mar 76

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V. Appendix

THE AUTHORS

This study was conducted by three members of the Department of Soil Science, University of Wisconsin, Madison. Dr. Philip A. Helmke, Assistant Professor of Soil Science, directed the trace element study. His co-workers were Dr. Iskandar K. Iskandar, research associate, and Robert D. Koons, research assistant and graduate student. Dr. Iskander is currently on the staff of the U.S. Army Corps of Engineers Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, 03755.

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CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

1. In the Duluth-Superior area, background concentrations of trace elements in the clay-size fractions of lake sediments range from 65 to 88 ppm copper, 140 to 230 ppm zinc, 0.1 to 0.4 ppm mercury based on laboratory analysis of sediments and red clay. Sediments with concentrations exceeding the higher values of these ranges are probably polluted.

2. The concentrations of trace elements in the clay-size fraction of harbor sediments when compared to background concentrations in the same fraction of local sediments are useful indicators of sediment quality.

3. The results of analysis for trace elements in total sediment samples are of marginal value in determining the quality of sediments.

4. Correction of trace element concentrations in sediments for quartz content is not a satisfactory method for determining the quality of sediments.

5. Analysis of Duluth-Superior harbor sediments show that the clay-size fractions are derived from the same sources and are well mixed and distributed throughout the harbor before they settle to the bottom.

6. Analysis of samples collected in the lake at five sites 8-13 miles from Duluth-Superior harbor showed no evidence of zinc pollution. However, some evidence of copper enrichment from an unknown source was shown.

A high concentration of mercury at three of these sites indicated mercury pollution.

7. Sediments in the old dump sites in the lake and several sections of the harbor are polluted with zinc and copper. Sediments in areas of the harbor near the Duluth sewage outfall are polluted with zinc, copper and mercury.

8. Analysis of a single sediment core showed some signs of surface enrichment of some trace elements; this probably occurred by natural processes.

9. Laboratory analysis of sediment samples from different areas of the harbor and of one sediment sample from the lake showed that all samples had the same tendency to release soluble zinc, even though the total zinc concentrations varied from 69 to 250 ppm. We conclude from this that the in-lake disposal of dredged material from these harbor sites will not significantly affect the concentration of soluble zinc in the water column or in the interstitial water of the sediments.

10. The concentrations of zinc and copper in *Pontoporeia affinis* show little or no relationship to the concentrations of zinc and copper in the clay-size fraction or total sediment sample.

11. High concentrations of mercury in *Pontoporeia* were found where sediments also had high mercury values in the clay-size fraction. The highest values were found at one station: *Pontoporeia* contained 2 ppm of mercury and the clay-size fraction contained 4.2 ppm.

12. Analysis of mercury concentrations showed evidence of biomagnification

in the Lake Superior food chain from <u>Pontoporeia</u> through benthic fish to lake trout. There was no evidence of zinc or copper biomagnification.

B. Recommendations

1. The dumping of mercury-bearing sediments into Lake Superior needs to be monitored carefully. Evidence from our study indicates that dredged material containing more than 0.4 ppm of mercury in the clay-size fraction should not be dumped into the lake.

2. We recommend that the following values be used as approximate background concentrations in the clay-sized fraction of Duluth-Superior area sediments: 180 ppm for zinc, 75 ppm for copper, and 0.2 ppm for mercury.

3. Future studies of sediment quality in harbors other than Duluth-Superior should include a multi-element analysis of the clay-size fraction in sediment to determine background concentrations. Harbors should then be surveyed using faster, less expensive methods such as atomic absorption analysis to provide detailed maps of harbor areas in which there is evidence of heavy metal pollution. These surveys should include the element lead, which we did not measure.

Introduction

Dredging and the disposal of dredged material in waterways can create several problems of environmental quality if the dredged sediments contain significant amounts of chemical contaminants. Such problems can be divided into those that affect mainly water quality and those that affect mainly the character of the sediments. Both sets of problems are ultimately concerned with the effects of dredging and disposal on the biological community. This report summarizes the results of our research on sediment quality.[1] Our study was concerned with the impact of disposing dredged materials into Lake Superior on the concentrations of trace elements in sediments and, in turn, their possible impact on organisms. The problems of water quality as a result of dredging is being investigated by other researchers (Lee and Plumb, 1974).

Our studies of trace elements have concentrated on four related goals: 1) To establish suitable procedures to determine the status of trace element pollution of sediments; 2) to determine possible relationships of trace element concentrations in sediments to their concentrations in benthic organisms; 3) to study the accumulation of potentially toxic elements in different levels of the food chain; and 4) to determine some of the effects of sublethal concentrations of trace elements in benthic organisms (the results of this study are given in Volume 4 of this report). The study of zinc and mercury was emphasized in all of our studies, but much information was also collected for other elements. The procedures developed in this research can also be applied to other harbors and trace elements.

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[1] Sediment "quality" is used in this report to indicate inherent characteristics of the sediment.

The approach throughout this research was to emphasize new procedures and methods which will provide original information necessary to understand the impact of trace elements in sediments on the environment. This research was not an attempt to provide a detailed survey of the quality of the sediments or organisms in the study area. Some of the approaches explored early in our work produced results which indicated that further development of these procedures was not warranted. We have included our evaluation of these approaches in this report to aid future investigators. These approaches also provide valuable insight into the behavior of trace elements in the aquatic ecosystem.

The study of the environmental impact of potentially toxic trace elements on the aquatic ecosystem is complicated because every natural material contains some of every naturally occurring element. Thus, we were not concerned in our studies with the presence of an element in a sample; rather, we were concerned with how much of each element is in a sample. Some of the elements, such as copper and zinc, are essential to nutrition but can be toxic if present in sufficiently high concentrations. Other elements, such as mercury and cadmium, are believed to be nonessential to nutrition and are toxic at low concentrations. A third group of elements such as scandium, gallium and the rare earths are relatively benign. They are not essential for nutrition and generally do not provoke toxic effects when ingested in moderate amounts.

The main concern regarding heavy metals in sediments centers around the possibility that toxic trace elements may be made available to and assimilated by organisms -- including people. In some sediments, elements are present in such chemical forms or concentrations that toxic or other deleterious reactions are provoked in organisms.

Dredging and disposal activities disrupt pristine in-lake sites by the dumping of sediment that may have concentrations of heavy metals that are greater than those considered to be background values. It is possible that the processes of dredging and disposal will so alter the natural geochemical processes occurring in sediments and water so as to make the heavy metals more available to organisms.

Any test to determine the status of trace element pollution of sediments will ideally be able to clearly distinguish polluted from natural sediments, and will also predict the availability of toxic trace elements to organisms and their impact on the ecosystem. The EPA guidelines for determining the status of trace element pollution of sediments are based on the results of chemical analysis of total sediments (Boyd, 1972), and the elutriate test being studied by Lee and Plumb (1974). The current working guidelines for region V of the EPA are that concentrations of 1 ppm mercury and 50 ppm lead in the total sediment distinguish the boundary between unpolluted and polluted sediment classifications for these metals. Sediments having concentrations of zinc of less than 90 ppm are considered unpolluted. Sediments having concentrations of zinc from 90-200 ppm are considered moderately polluted. Concentrations of zinc greater than 200 ppm are recognized as heavily polluted. (Robert Bowden, personal communication). EPA also considers total sediment concentrations and elutriate concentrations in comparison to local natural conditions in the sediment and elutriate.

We propose an alternative procedure to the present total sediment analysis in section II of this volume to determine the status of trace element pollution of sediments. With this method, the natural background concentration of each element is considered and other objections to the results from total sediment analysis are eliminated.

The relationship between the effects and concentration of heavy metals in aquatic organisms and the forms and concentration of these elements in sediments is not known. Even such basic questions as the source of each element to aquatic organisms (i.e., from their food and/or water) has not been clearly answered. The composition and nature of the sediment must be important in the determination of the availability of heavy metals to organisms. Many organisms, some of which are at the base of the food chain, use the sediment as a substrate. Microorganisms, included in this benthic group, may have an important role in determining the availability of heavy metals to detritus feeders. The concentration of heavy metals in water is thought to be controlled by absorption-desorption processes on suspended particulate matter and sediments. The formation and dissolution of slightly soluble compounds is thought to be of secondary or of little importance. Sediments can act as both a source and a sink for trace elements in water. Therefore, even if the main route of uptake of heavy metals by organisms is from the water, the sediment still has an important role in determining the availability of heavy metals.

Any consideration of values of trace element concentrations in sediments that are to be used as guidelines to help determine the extent of pollution must also include the probable impact of these concentrations on the biological community. We report on the concentration of copper, zinc, mercury and other trace elements in organisms for two reasons: 1) to study the amounts of these elements in various trophic levels and 2) to examine the possible correlations and relationships between concentrations of trace elements in benthic organisms and sediments in section IV. These data, when combined with the results of the studies on trace element availability (section III, this volume) and the results of the laboratory bioassay (Volume 4) provide additional information needed to determine appropriate guidelines to evaluate the status of trace element pollution of sediments.

Neutron activation methods were used for determining the concentrations of trace elements in organisms and sediments. Most of the organism samples were too small to analyze by other techniques. Some of the elements present in organisms and sediments can only be measured by neutron activation. Because lead cannot be measured by neutron activation, it was not analyzed during this study. A description of the laboratory methods used in found in the Appendix.

ABSTRACT

I. Procedures to Evaluate the Status of Trace Element Pollution of Sediments

A. Introduction

Present procedures for evaluation of harbor sediments do not provide sufficient information to adequately assess alternatives for the disposal of dredged material. This is especially true for trace element evaluations. The elutriate test described later (also see Lee and Plumb, 1974) has been recently developed primarily to identify potential problems of water quality, although some information about sediment quality is also obtained. Existing knowledge of the relationship of trace elements in sediments to trace elements in organisms is too scarce to allow information from the elutriate test to predict the effect of dredged materials on the trace element concentrations in benthic organisms. The purpose of this part of ~~our~~ The study is to develop a procedure to accurately assess the extent of trace element pollution of sediments. Such a procedure must provide information about sediment quality which supplements the results provided by the elutirate test. The information provided by this procedure, along with the concentrations of trace elements in organisms ~~(section IV)~~ and the results of the bioassay experiment, is used to determine permissible concentrations of trace elements in sediments. ←

ABSTRACT

B. Present Procedures

Any procedure to determine the quality of sediments with respect to trace elements must be simple enough so that many samples can be analyzed quickly and accurately at a minimum cost. In addition, the procedure must also provide sufficient information to clearly identify polluted sediments. Most of the trace element criteria for the disposal of dredged material have been based on the results of total sediment analysis.

During the early 1970's the EPA guidelines classified a sediment as polluted and unsuitable for in-lake dumping if it contained more than 1 ppm mercury or 50 ppm lead or zinc (Boyd, 1972). The values chosen were based on the results of analyses of sediments collected during a Great Lakes survey. The US EPA, Region IX more recently listed proposed criteria of 0.5 ppm mercury, 50 ppm copper and lead, 75 ppm zinc, and 2 ppm cadmium (Windom, 1973). In 1973 an agreement between the Corps of Engineers and the EPA was reached defining criteria for ocean dumping of dredged material. These criteria are based on the release of dissolved solids from the spoil to water under standard test conditions. Actual water conditions at the disposal site were not taken into consideration (EPA, 1973 and 1973a).

A draft of proposed criteria for determination of the pollutional status of dredged material was proposed by EPA, Region V in 1975 (Federal Register, May 6, 1975). The elutriate test is to be used as an interim procedure. In the elutriate test, one part of sediment is mixed with four parts of water from the dredging site. After shaking the mixture for 30 minutes and allowing it to settle for 60 minutes, the water is withdrawn, centrifuged, filtered and then analyzed for the constituent of interest to the study. Restricted disposal is required if the results are 1.5 times the concentrations found for the same constituents in the water from the proposed disposal site.

The new EPA criteria for evaluating the status of trace element pollution of sediments considers the size distribution of the sediment, background of the trace element concentrations, and other factors in setting allowable concentration limits for certain elements in dredged material (Federal Register, September 5, 1975).

One of the major difficulties in evaluating the quality of sediments based on the results of total sediment analysis is the site-to-site variation in the concentrations of trace elements in the samples. This can occur as a result of variations in particle size distribution, mineral content, organic matter, or extent of trace element pollution. For most sediments, the major factor is the variability in the content of the mineral quartz. Quartz has relatively low concentrations of most trace elements, and it is a major constituent of almost all sediments. Variations in the quartz content of sediments can be such that two samples of sediment collected only a few feet apart may be quite different in their chemical characteristics. A suitable test of sediment quality must reduce the effects of the natural variations of trace element concentrations from site-to-site to such an extent that the degree of trace element pollution of the sediment can be determined by a simple chemical analysis. The results of our study demonstrate one method by which some external additions of trace elements to sediments can be easily identified from the natural background of trace elements.

C. The Area of Study

The cities of Duluth, Minnesota and Superior, Wisconsin and their joint harbor lie at the western end of Lake Superior. The geology of the region is described in detail in Volume 2 of this report so only that part which is important to the input of trace elements to sediments will be summarized here.

The bedrock of the western Lake Superior region consists primarily of Late Pre-Cambrian basalts, gabbros, and shales. These Pre-Cambrian rocks are typified by the cliffs of gabbro which dominate the Minnesota shoreline of Lake Superior. The cities and harbor lie at the foot of these cliffs on a plain formed where the submerged mouth of the St. Louis River enters Lake Superior. Along the Wisconsin shoreline thick deposits of red clay, the sediments of glacial Lake Duluth, lie atop earlier deposits of glacial till. These are mixed with a red, quartz rich sandstone to form the low bluffs characteristic of the south shore of this portion of Lake Superior. The red clay is carried by the rivers of the Wisconsin shore and by shoreline erosion into the present lake and harbor. It is an important, if not the dominant, input of sediment into this part of Lake Superior. The mineral and chemical contents of the lake and harbor sediments reflect this source of material.

D. Sample Collection and Methods of Analysis

In the period from October, 1973 to June, 1975 samples of the surface sediment were collected from the Duluth-Superior harbor, and from areas of Lake Superior near Duluth-Superior and the Keweenaw Waterway Upper Entry. One sediment core from the lake near Duluth-Superior and four samples of red clay from the Wisconsin shore were also collected. The methods of collection are described in Appendix A. Maps of sample locations are shown in Figures 1a, 1b and 2. The dates of collection and related information are shown in Table 1. These samples were packaged to prevent contamination and sent to our laboratory in Madison for analysis.

The sediments were analyzed for about 25 elements by instrumental and radiochemical neutron activation. Analyses were made on whole samples as well as various particle size fractions of the sediments. The method of separating the size fractions of the samples was a gravity settling procedure. The methods of sample separation and multi-element analysis are described in more detail in Appendix I. In addition to multielement analysis, determination of the mineralogy of selected samples was made by x-ray diffraction and determinations of the amount of quartz present were made using the methods of Jackson (1973).

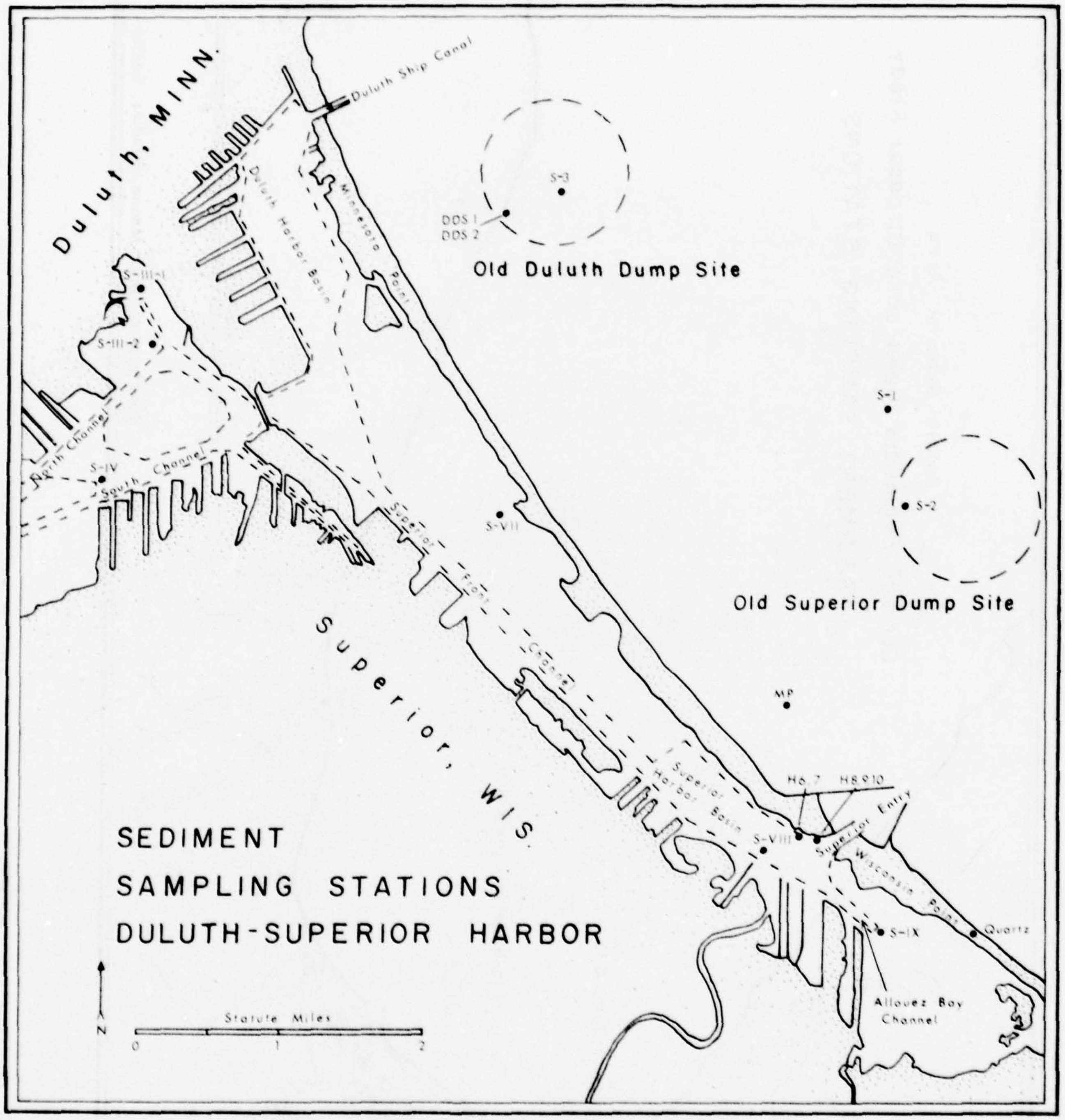
No attempt was made to collect and analyze enough sediments to make a complete map of our Lake Superior study sites; but rather, a smaller number of sediments were studied in detail in order to develop a general procedure which can be used to determine sediment quality with respect to trace elements. Other parameters of sediment quality such as oil and grease, phosphorus and nitrogen and oxygen demand were not studied.

Table 1. Collection Dates and Water Depths of Sediment Samples.

Sample Number	Date Collected	Water Depth (Meters)
S-III-1	Oct. 73	2.4
S-III-2	Oct. 73	2.1
S-IV	Oct. 73	7.6
S-VII	Oct. 73	2.4
S-VIII	Oct. 73	8.2
S-IX	Oct. 73	1.8
S-1	Oct. 73	-
S-2	Oct. 73	-
S-3	Oct. 73	-
DDS-1	Jul. 74	32
DDS-2	Jul. 74	30
A-30	Sep. 73	29
B-8-2	Sep. 73	8
DC-I	Jun. 74	Shore Sample
DC-II	Jun. 74	Shore Sample
AmB-R	Jun. 74	Shore Sample
AmB-G	Jun. 74	Shore Sample
Geo 19	Oct. 74	30
Geo 21	Oct. 74	32
Geo 43	Oct. 74	78
Geo 45	Oct. 74	75
Geo 46	Oct. 74	82
Geo 51	Oct. 74	84
Geo 59	Oct. 74	140
Geo MP	Oct. 74	14
K-1	Jun. 75	51
K-2	Jun. 75	39
K-3	Jun. 75	63
K-4	Jun. 75	84
K-5	Jun. 75	54
K-6	Jun. 75	32
K-7	Jun. 75	37
K-8	Jun. 75	41
Scow H6	May 75	from dredge scow
Scow H7	May 75	from dredge scow
Scow H8	May 75	from dredge scow
Scow H9	May 75	from dredge scow
Scow H10	May 75	from dredge scow
Core S2	Sep. 74	40
Core S4	Sep. 74	44

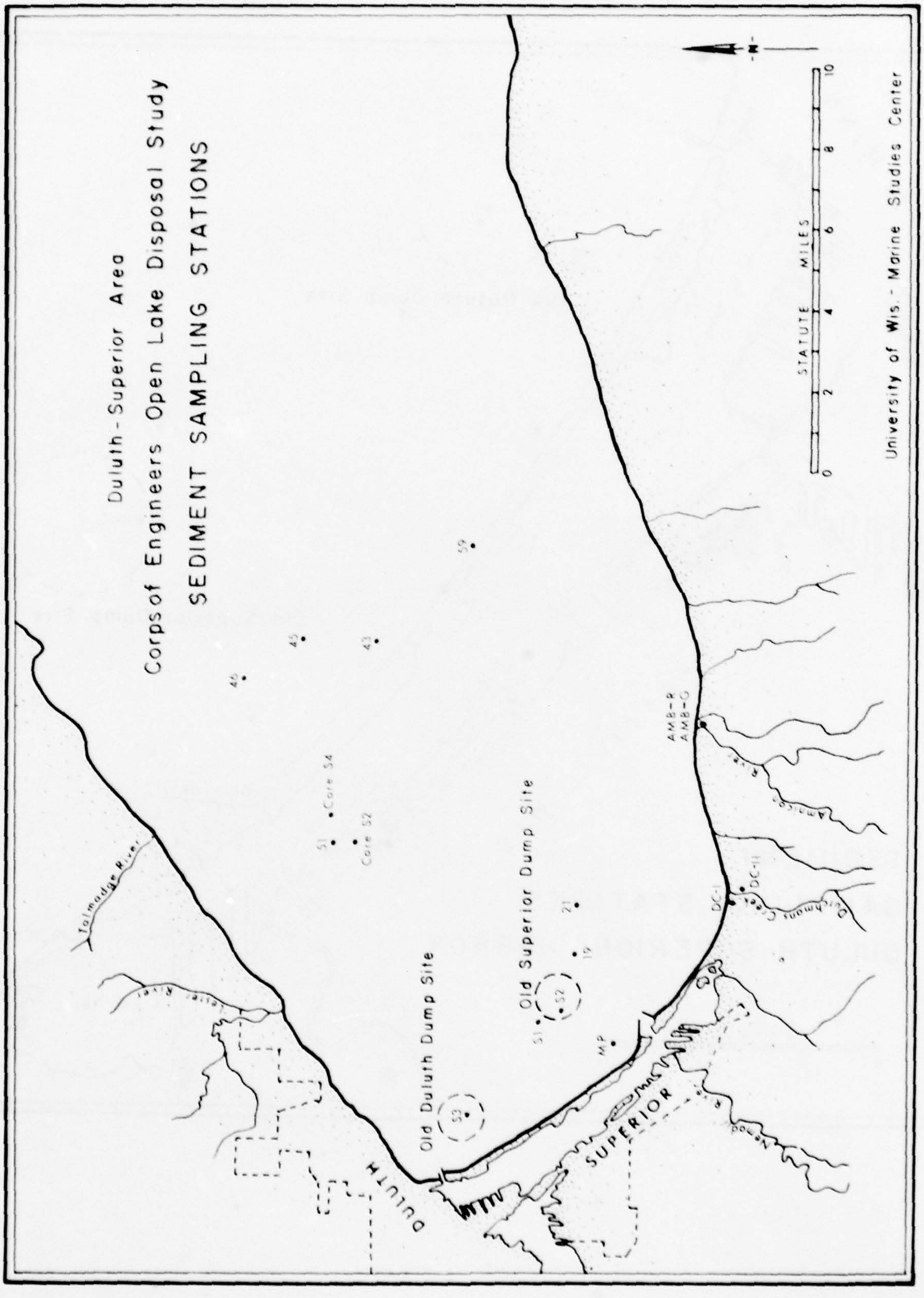
Note: All of the samples were collected by a Ponar dredge except the samples from the shore and the barges (scows). The core sample was collected by a gravity corer.

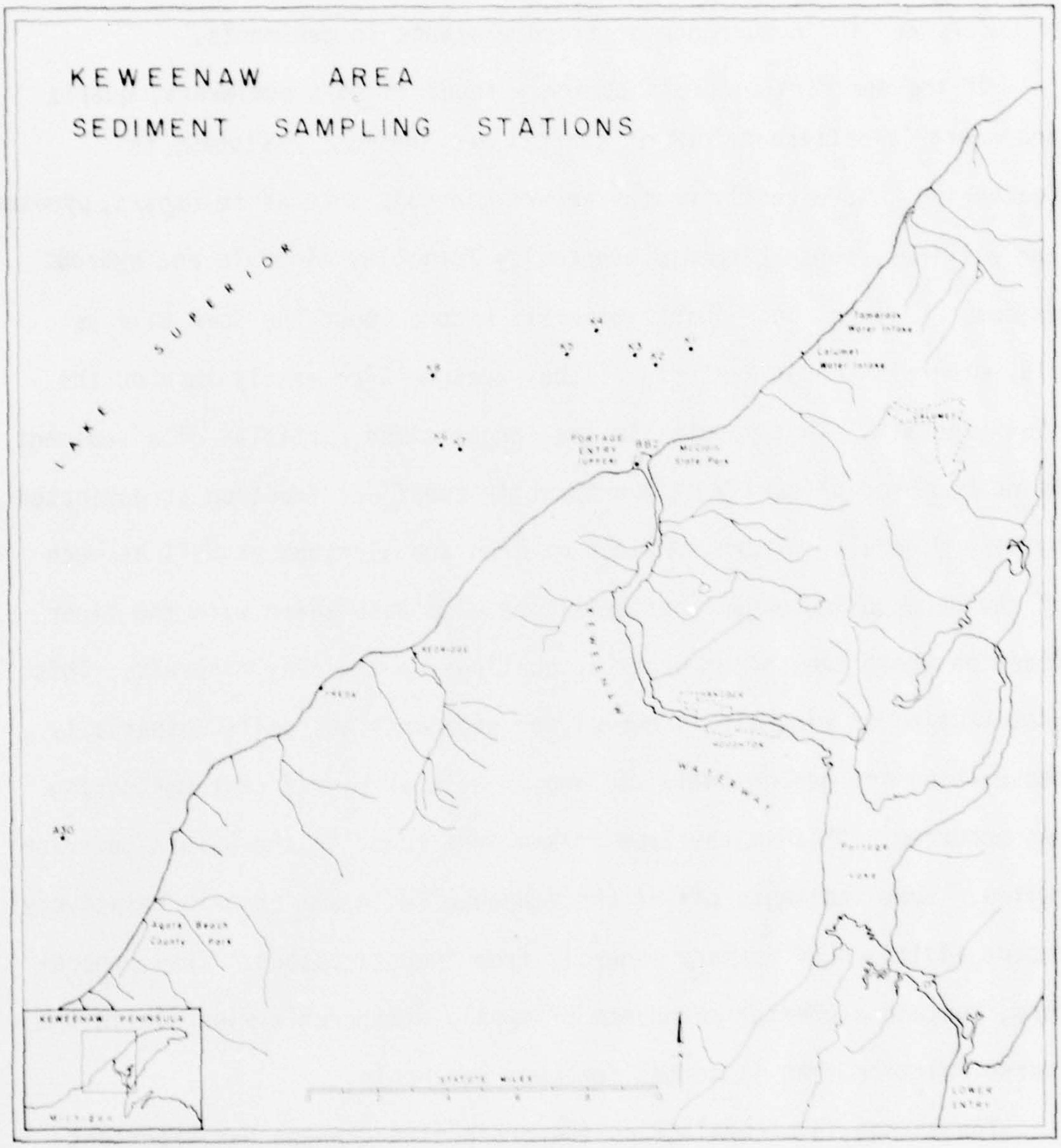
(figure 1a)



SEDIMENT
SAMPLING STATIONS
DULUTH-SUPERIOR HARBOR

(figure 1b)


Duluth - Superior Area
Corps of Engineers Open Lake Disposal Study
SEDIMENT SAMPLING STATIONS
STATUTE MILES
0
2
4
6
8
10
N
University of Wis. - Marine Studies Center
59
45
43
46
S1
Core S4
Core S2
Old Superior Dump Site
S2
21
19
S1
MP
Old Duluth Dump Site
S3
DULUTH
SUPERIOR
AMB-R
AMB-G
Amnicon River
DC-I
DC-II
Dutchmans Creek
Talmadge River
Lester River
Nemadji R.


KEWEENAW AREA
SEDIMENT SAMPLING STATIONS
LAKE SUPERIOR
K4
K3
K2
K1
K7
Tamarack Water Intake
Calumet Water Intake
CALUMET
PORTAGE ENTRY (UPPER)
BB2
McLain State Park
REDRIDGE
FREDA
KEWEENAW WATERWAY
HOUGHTON
Portage Lake
A30
Agate Beach County Park
KEWEENAW PENINSULA
MICHIGAN
STATUTE MILES
0
2
4
6
8
10
N
LOWER ENTRY

E. The Occurrence of Quartz in Sediments

The mineral quartz is one of the dominant minerals in sediments and some knowledge of its behavior in relation to other minerals is necessary to understand the occurrence of trace elements in sediments.

Of the dominant minerals commonly found in most sediments, quartz and chert (a different form of quartz) are the most resistant to weathering. More easily weathered are minerals such as feldspars, pyroxenes, and olivines, whose elements eventually form clay minerals and hydrous oxides. However, once quartz minerals become about the same size as clay minerals (about 2 microns), they weather more easily than do the clay minerals. This results in the larger sized particles of a sediment being composed primarily of quartz while the finer fraction is dominated by clay minerals. Hydrous oxides of iron and aluminum as well as much of the decomposing organic material are also associated with the finer fraction where they often occur as coatings on the clay minerals. This distribution of minerals is normal for sediments and soils, especially those which are geologically old enough so that significant weathering has occurred. This is the type of sediment found in the Duluth-Superior region. Some sediments off of the Keweenaw Peninsula contain relatively recent additions of primary minerals from the stampsands. They, therefore, contain a greater abundance of easily weatherable minerals in the coarse fraction than is normal for most sediments.

The change in mineralogy as the grain size changes has important implications on the content of trace elements in sediments. First of all, the concentration of most trace elements in quartz and chert are much lower than those found for most total sediments (Tables 2-4).

Apparently, most elements are excluded from the crystal structure of quartz. This compares to clay minerals which can incorporate some trace elements into their structure. Of even greater importance for clay minerals, and the organic matter and hydrous oxides associated with them, is the capacity of these materials to sorb and desorb metal ions by ion exchange phenomena. Feldspars, pyroxenes and olivines can also incorporate certain trace elements into their structure. The overall result is that the finest grain size fractions have the highest concentrations of each trace element in a mature sediment. Therefore, sediments composed mostly of silt and clay will generally have high concentrations of trace elements while those containing a larger proportion of quartz tend to be coarser grained and will have lower concentrations of each element.

F. Use of Element Ratios to Display Results Graphically.

The results of the elemental analysis of the harbor and lake sediments as well as four shore samples--one core, five scow samples and the quartz sample--are given in Tables 2 through 4. The uncertainties associated with each value represent one standard deviation based on counting statistics. The several methods which can be used to interpret these analytical results in regards to the status of pollution are discussed in the following section II.

The elements for which analyses were performed cover a range of concentrations, from 0.02 ppm for mercury to 50,000 ppm for iron in some samples. This makes it difficult to graphically represent the concentrations of all of the measured elements for a sample on a single figure. To reduce this range of values, a ratio to a standard value for each element was calculated and the result displayed graphically for each of the various elements. A single standard soil was used for all of the comparisons so that concentrations of each trace element in all samples can be compared to one another as a ratio to the same standard value for that element. The standard chosen was the clay-size (less than two micron) fraction of a sample taken from the red clay cliffs along the Wisconsin shoreline near the mouth of Dutchman Creek (Sample DC-I). This sample was chosen because it is thought to be fairly representative of the major input to the sediment in this portion of the lake and, it is undisturbed by man's activities in the area. If the standard chosen were a reflection of the combined effects of all natural inputs to the lake, then any sediment which contains the same mineral distribution as in the standard would likewise have about the same concentrations of every element. This would give a ratio to standard of one for every element. Such a standard for comparison purposes is difficult, if not impossible, to find so this was not attempted, but rather a standard was chosen which reflects a major input to the lake and, therefore, this standard can be used for purposes of comparison. Note that the standard chosen in no way affects the results which follow. It is merely a device to allow visual comparisons of the concentrations of trace elements in sediments. A sediment with external additions (including additions by man) of a given element will have a higher ratio for that element than a similar sediment which did not have such additions.

Table 2. The concentrations of trace elements in ppm for a sample of quartz isolated from Lake Superior sediment.

	Superior Quartz
As	0.58 ± 0.09
Ba	19 ± 2
Ce	6.2 ± 0.1
Co	0.09 ± 0.01
Cr	1.9 ± 0.1
Cs	0.20 ± 0.01
Cu	0.74 ± 0.03
Eu	0.063 ± 0.001
Fe	233 ± 7
Ga	1.07 ± 0.03
Hf	0.90 ± 0.03
K	1160 ± 50
La	2.59 ± 0.03
Lu	0.047 ± 0.002
Mn	5.6 ± 0.1
Na	698 ± 3
Rb	4.0 ± 0.3
Sc	0.268 ± 0.002
Sm	0.522 ± 0.003
Tb	0.078 ± 0.005
Th	1.28 ± 0.02
U	0.45 ± 0.04
Yb	0.31 ± 0.04
Zn	1.0 ± 0.3

Note: The uncertainties associated with each value represent one standard deviation based on counting statistics.

Table 3. The concentrations of trace elements in ppm for samples of "red clay" from the Wisconsin shore. The silt plus clay-size fraction is composed of particles smaller than 50 microns and the clay-size fraction is composed of particles smaller than 2 microns.

	DC-I		
	Total Sediment	Silt + Clay	Clay
As	10.2 ± 0.8	11 ± 1	13.2 ± 0.9
Ba	446 ± 25	570 ± 40	560 ± 30
Ce	76.1 ± 0.9	78.9 ± 0.9	95 ± 1
Co	17.8 ± 0.2	18.7 ± 0.2	19.3 ± 0.3
Cr	84 ± 2	94 ± 3	106 ± 2
Cs	4.2 ± 0.2	4.6 ± 0.2	4.8 ± 0.2
Cu	30 ± 2	52 ± 3	65 ± 5
Eu	1.29 ± 0.02	1.34 ± 0.02	1.56 ± 0.02
Fe	45400 ± 300	48700 ± 300	55500 ± 300
Ga	21 ± 1;	25 ± 1	25 ± 2
Hf	4.9 ± 0.2	4.6 ± 0.1	4.4 ± 0.2
Hg	0.02 ± 0.005	--	--
K	22400 ± 800	23500 ± 1000	28000 ± 1000
La	38.2 ± 0.3	41.9 ± 0.4	49.9 ± 0.3
Lu	0.52 ± 0.01	0.54 ± 0.02	0.62 ± 0.01
Na	6830 ± 30	7410 ± 30	7130 ± 30
Rb	85 ± 5	97 ± 5	107 ± 5
Sc	13.7 ± 0.1	14.8 ± 0.1	16.6 ± 0.1
Sm	6.81 ± 0.07	7.25 ± 0.07	8.47 ± 0.02
Tb	0.98 ± 0.05	1.02 ± 0.05	1.21 ± 0.06
Th	14.3 ± 0.2	15.1 ± 0.2	18.0 ± 0.2
U	1.9 ± 0.2	2.0 ± 0.3	2.4 ± 0.2
Yb	3.4 ± 0.1	3.6 ± 0.1	4.1 ± 0.1
Zn	104 ± 4	117 ± 4	127 ± 4

Table 3. (cont.)

	AmB-R		AmB-G	
	Total Sediment	Clay	Total Sediment	Clay
As	8.8 ± 0.9	10 ± 1	10 ± 1	9 ± 1
Ba	434 ± 21	600 ± 30	403 ± 21	590 ± 30
Ce	80.2 ± 0.7	102 ± 1	67.3 ± 0.6	143 ± 1
Co	18.6 ± 0.2	18.1 ± 0.2	15.9 ± 0.2	14.4 ± 0.3
Cr	90 ± 1	90 ± 2	86 ± 1	83 ± 2
Cs	3.9 ± 0.2	4.3 ± 0.2	4.4 ± 0.2	3.7 ± 0.2
Eu	1.34 ± 0.01	1.59 ± 0.02	1.13 ± 0.01	2.04 ± 0.09
Fe	48200 ± 200	48200 ± 500	40000 ± 200	35300 ± 200
Hf	5.30 ± 0.08	4.71 ± 0.09	4.02 ± 0.06	3.67 ± 0.08
K	25300 ± 700	33100 ± 900	20800 ± 600	29000 ± 1000
La	41.0 ± 0.8	51 ± 1	34.5 ± 0.8	76 ± 2
Lu	0.58 ± 0.01	0.58 ± 0.02	0.448 ± 0.009	0.54 ± 0.02
Na	7880 ± 80	11940 ± 40	7130 ± 20	16000 ± 200
Nd	42 ± 5	48 ± 6	30 ± 4	62 ± 8
Rb	98 ± 4	119 ± 5	84 ± 3	100 ± 5
Sb	X	X	1.0 ± 0.1	0.9 ± 0.1
Sc	14.6 ± 0.1	14.4 ± 0.1	12.6 ± 0.1	11.8 ± 0.2
Se	--	--	--	--
Sm	7.0 ± 0.1	9.0 ± 0.1	5.6 ± 0.3	11.8 ± 0.2
Tb	1.04 ± 0.03	1.09 ± 0.04	0.81 ± 0.02	1.34 ± 0.05
Th	15.6 ± 0.1	16.8 ± 0.2	12.9 ± 0.1	21.9 ± 0.2
Yb	3.6 ± 0.1	3.7 ± 0.2	2.8 ± 0.1	3.6 ± 0.2

Table 3. (cont.)

	DC-II		
	Total Sediment	Silt + Clay	Clay
As	10.5 ± 0.7	7.2 ± 0.5	11.3 ± 0.6
Ba	483 ± 30	519 ± 27	570 ± 30
Ce	78.7 ± 0.7	82.8 ± 0.9	77.3 ± 0.7
Co	19.0 ± 0.2	20.4 ± 0.2	21.6 ± 0.2
Cr	90 ± 2	99 ± 2	104 ± 2
Cs	4.4 ± 0.1	4.9 ± 0.2	5.3 ± 0.2
Eu	1.33 ± 0.01	1.39 ± 0.02	1.32 ± 0.01
Fe	47900 ± 300	53200 ± 300	57400 ± 300
Hf	4.8 ± 0.1	5.0 ± 0.1	4.9 ± 0.1
K	23600 ± 900	17600 ± 700	29000 ± 1000
La	40.2 ± 0.4	28.9 ± 0.2	42.8 ± 0.3
Lu	0.52 ± 0.01	0.52 ± 0.01	0.60 ± 0.01
Na	7000 ± 30	5060 ± 20	7090 ± 30
Rb	100 ± 5	108 ± 5	119 ± 5
Sc	14.5 ± 0.1	16.2 ± 0.1	17.3 ± 0.1
Sm	7.09 ± 0.07	5.15 ± 0.02	7.21 ± 0.02
Tb	0.98 ± 0.04	1.08 ± 0.04	1.03 ± 0.03
Th	14.6 ± 0.1	16.3 ± 0.3	16.4 ± 0.1
U	2.3 ± 0.2	2.1 ± 0.2	2.4 ± 0.2
Yb	3.3 ± 0.1	3.5 ± 0.1	3.7 ± 0.1
Zn	116 ± 2	134 ± 3	141 ± 3

Table 4. The concentrations of trace elements in ppm for samples of sediment from the Duluth-Superior Harbor and nearby Lake Superior. The silt plus clay fraction consists of particles smaller than 50 microns and the clay fraction consists of particles smaller than 2 microns.

	S-III-1		
	Total Sediment	Silt + Clay	Clay
As	5.4 ± 0.5	9 ± 1	21 ± 1
Ba	426 ± 22	428 ± 24	520 ± 70
Ce	39.6 ± 0.5	45.8 ± 0.6	100 ± 3
Co	7.92 ± 0.08	15.5 ± 0.2	25.5 ± 0.6
Cr	51 ± 1	95 ± 2	185 ± 5
Cs	1.8 ± 0.1	2.7 ± 0.1	6.2 ± 0.4
Cu	19.3 ± 0.4	89.8 ± 0.5	172 ± 2
Eu	0.81 ± 0.01	1.12 ± 0.01	1.62 ± 0.05
Fe	21300 ± 100	41100 ± 300	75700 ± 500
Ga	8.2 ± 0.1	16.0 ± 0.4	26.5 ± 0.7
Hf	4.5 ± 0.1	6.2 ± 0.1	5.0 ± 0.3
Hg	0.14 ± 0.02	--	0.99 ± 0.03
K	22500 ± 500	15100 ± 300	18100 ± 500
La	18.9 ± 0.5	26.8 ± 0.5	45 ± 1
Lu	0.287 ± 0.008	0.56 ± 0.01	0.92 ± 0.03
Na	8920 ± 60	11200 ± 100	6290 ± 60
Rb	63 ± 2	65 ± 4	108 ± 9
Sc	6.06 ± 0.02	11.4 ± 0.1	20.8 ± 0.3
Sm	3.78 ± 0.02	5.45 ± 0.02	8.23 ± 0.05
Tb	0.45 ± 0.02	0.72 ± 0.03	1.1 ± 0.1
Yb	1.96 ± 0.08	2.9 ± 0.1	3.4 ± 0.2
Zn	64 ± 5	180 ± 20	530 ± 60

Table 4. (cont.)

	S-III-2		
	Total Sediment	Silt + Clay	Clay
As	3 ± 2	6 ± 2	12 ± 2
Ba	410 ± 30	452 ± 23	460 ± 40
Ce	51.7 ± 0.5	74.8 ± 0.5	75.7 ± 0.6
Co	12.6 ± 0.2	14.1 ± 0.1	23.0 ± 0.2
Cr	78 ± 1	90 ± 1	134 ± 2
Cs	2.8 ± 0.2	--	--
Cu	40.8 ± 0.2	--	68.2 ± 0.4
Eu	0.96 ± 0.01	1.07 ± 0.01	1.19 ± 0.01
Fe	31800 ± 600	35900 ± 200	66200 ± 700
Ga	14.8 ± 0.5	--	26.3 ± 0.6
Hf	5.7 ± 0.1	5.6 ± 0.1	3.8 ± 0.1
Hg	0.24 ± 0.02	--	0.35 ± 0.01
K	15400 ± 900	13000 ± 1000	19400 ± 800
La	23.9 ± 0.2	23.8 ± 0.2	38.8 ± 0.4
Lu	0.326 ± 0.009	0.356 ± 0.009	0.41 ± 0.01
Na	11600 ± 50	11300 ± 50	8830 ± 40
Rb	60 ± 4	64 ± 3	106 ± 6
Sc	9.4 ± 0.2	10.9 ± 0.1	17.8 ± 0.3
Sm	4.5 ± 0.1	4.4 ± 0.1	6.5 ± 0.2
Tb	0.54 ± 0.03	--	0.86 ± 0.04
Yb	2.07 ± 0.09	2.22 ± 0.09	2.4 ± 0.1
Zn	98 ± 3	--	250 ± 30

Table 4. (cont.)

	S-IV		
	Total Sediment	Silt + Clay	Clay
As	4 ± 1	9 ± 1	19.1 ± 0.1
Ba	450 ± 27	460 ± 22	510 ± 40
Ce	54.4 ± 0.5	52.5 ± 0.3	70.4 ± 0.5
Co	12.2 ± 0.2	13.1 ± 0.1	20.7 ± 0.2
Cr	81 ± 1	88 ± 1	131 ± 2
Cs	3.2 ± 0.2	3.2 ± 0.1	5.8 ± 0.1
Cu	37.0 ± 0.2	40.3 ± 0.2	84.7 ± 0.7
Eu	0.97 ± 0.01	0.981 ± 0.009	1.12 ± 0.01
Fe	39700 ± 400	41600 ± 200	66300 ± 300
Ga	14.3 ± 0.4	15.2 ± 0.3	24.6 ± 0.7
Hf	5.5 ± 0.2	5.2 ± 0.1	3.6 ± 0.1
Hg	0.16 ± 0.02	--	0.53 ± 0.04
K	16000 ± 1000	16000 ± 1000	18300 ± 800
La	26.9 ± 0.3	26.7 ± 0.2	37.0 ± 0.3
Lu	0.33 ± 0.01	0.338 ± 0.009	0.40 ± 0.01
Na	11300 ± 50	11500 ± 60	5710 ± 20
Rb	60 ± 4	61 ± 3	90 ± 5
Sc	9.7 ± 0.1	10.5 ± 0.1	16.7 ± 0.3
Sm	4.6 ± 0.2	4.9 ± 0.1	6.2 ± 0.1
Tb	0.58 ± 0.03	0.61 ± 0.02	0.83 ± 0.03
Yb	2.2 ± 0.1	2.35 ± 0.09	2.6 ± 0.1
Zn	156 ± 5	195 ± 10	340 ± 10

Table 4. (cont.)

	S-VII		
	Total Sediment	Silt + Clay	Clay
As	5.1 ± 0.8	7.6 ± 0.9	16.4 ± 1.8
Ba	388 ± 21	480 ± 25	534 ± 30
Ce	49.2 ± 0.6	61.3 ± 0.7	88 ± 1
Co	10.8 ± 0.2	14.6 ± 0.2	26.3 ± 0.4
Cr	74 ± 1	98 ± 2	164 ± 3
Cs	2.5 ± 0.2	3.3 ± 0.2	6.8 ± 0.3
Cu	25.7 ± 0.1	31.0 ± 0.2	66.4 ± 0.4
Eu	0.90 ± 0.01	1.10 ± 0.01	1.38 ± 0.02
Fe	29000 ± 200	40100 ± 200	80800 ± 400
Ga	14.9 ± 0.5	15.0 ± 0.4	24.9 ± 0.6
Hf	4.7 ± 0.1	5.2 ± 0.1	4.3 ± 0.1
Hg	0.18 ± 0.02	--	0.42 ± 0.01
K	15300 ± 800	16800 ± 700	22000 ± 1000
La	23.8 ± 0.2	30.2 ± 0.3	45.1 ± 0.3
Lu	0.310 ± 0.008	0.360 ± 0.009	0.49 ± 0.01
Na	11300 ± 50	13400 ± 50	7100 ± 40
Rb	55 ± 4	66 ± 3	115 ± 5
Sc	8.86 ± 0.02	11.6 ± 0.1	20.9 ± 0.1
Sm	4.2 ± 0.1	5.4 ± 0.1	7.6 ± 0.2
Tb	0.53 ± 0.02	0.66 ± 0.02	1.05 ± 0.04
Yb	2.07 ± 0.07	2.34 ± 0.08	3.1 ± 0.1
Zn	104 ± 3	155 ± 3	350 ± 30

Table 4. (cont.)

	S-VIII		
	Total Sediment	Silt + Clay	Clay
As	3.7 ± 0.5	8.8 ± 0.9	16 ± 2
Ba	341 ± 15	438 ± 21	471 ± 25
Ce	31.9 ± 0.3	60.0 ± 0.7	85 ± 1
Co	4.82 ± 0.09	13.4 ± 0.2	23.8 ± 0.3
Cr	25 ± 1	78 ± 3	119 ± 2
Cs	0.98 ± 0.06	2.3 ± 0.2	6.1 ± 0.4
Cu	14.4 ± 0.1	41.9 ± 0.3	89.3 ± 0.8
Eu	0.637 ± 0.007	1.03 ± 0.01	1.32 ± 0.02
Fe	17100 ± 100	42800 ± 200	65800 ± 700
Ga	7.4 ± 0.2	15.2 ± 0.4	25.6 ± 0.7
Hf	4.1 ± 0.1	5.0 ± 0.1	4.3 ± 0.1
Hg	0.02 ± 0.005	--	0.274 ± 0.009
K	17500 ± 700	19300 ± 900	22700 ± 900
La	14.7 ± 0.2	30.1 ± 0.3	42.9 ± 0.3
Lu	0.287 ± 0.007	0.40 ± 0.01	0.52 ± 0.01
Na	4850 ± 20	9730 ± 40	3020 ± 20
Rb	53 ± 2	71 ± 3	105 ± 4
Sc	3.96 ± 0.01	10.7 ± 0.1	18.4 ± 0.1
Sm	3.02 ± 0.08	5.5 ± 0.1	7.3 ± 0.2
Tb	0.49 ± 0.02	0.71 ± 0.02	1.15 ± 0.04
Yb	1.93 ± 0.08	2.56 ± 0.08	3.4 ± 0.1
Zn	36 ± 3	103 ± 2	178 ± 4

Table 4. (cont.)

	S-IX		
	Total Sediment	Silt + Clay	Clay
As	6 ± 1	7 ± 2	10 ± 1
Ba	440 ± 23	460 ± 25	437 ± 30
Ce	63.4 ± 0.5	92.3 ± 0.7	77.3 ± 0.7
Co	12.7 ± 0.2	15.4 ± 0.1	21.7 ± 0.3
Cr	73 ± 1	88 ± 1	111 ± 2
Cs	2.9 ± 0.2	3.5 ± 0.1	5.7 ± 0.3
Cu	35.9 ± 0.2	--	57.6 ± 0.3
Eu	1.07 ± 0.01	1.24 ± 0.01	1.18 ± 0.01
Fe	31300 ± 200	34200 ± 200	52400 ± 400
Ga	13.9 ± 0.5	5.8 ± 0.1	28.4 ± 0.6
Hf	5.7 ± 0.2	5.7 ± 0.1	4.5 ± 0.2
Hg	0.05 ± 0.01	--	0.074 ± 0.005
K	18300 ± 800	21000 ± 1000	23000 ± 900
La	28.9 ± 0.3	35.3 ± 0.3	38.4 ± 0.4
Lu	0.46 ± 0.01	0.47 ± 0.01	0.49 ± 0.01
Na	7380 ± 30	9260 ± 50	4870 ± 20
Rb	76 ± 4	84 ± 4	110 ± 5
Sc	10.6 ± 0.1	12.6 ± 0.1	17.7 ± 0.1
Sm	5.3 ± 0.1	6.6 ± 0.1	6.5 ± 0.1
Tb	0.73 ± 0.03	0.85 ± 0.03	0.93 ± 0.04
Yb	3.1 ± 0.1	3.1 ± 0.1	3.2 ± 0.1
Zn	91 ± 3	110 ± 4	166 ± 5

Table 4. (cont.)

	S-1		
	Total Sediment	Silt + Clay	Clay
As	3.2 ± 0.8	8 ± 2	21 ± 2
Ba	420 ± 18	455 ± 23	530 ± 30
Ce	47.4 ± 0.4	58.3 ± 0.5	89.3 ± 0.8
Co	9.4 ± 0.1	12.9 ± 0.2	25.4 ± 0.4
Cr	57 ± 1	73 ± 1	119 ± 2
Cs	2.2 ± 0.1	2.8 ± 0.2	6.0 ± 0.4
Cu	18.6 ± 0.1	49.7 ± 0.4	96.6 ± 0.7
Eu	0.875 ± 0.009	1.03 ± 0.01	1.36 ± 0.02
Fe	27800 ± 100	35000 ± 700	67600 ± 300
Hf	6.3 ± 0.1	6.8 ± 0.1	4.7 ± 0.1
Hg	0.05 ± 0.01	--	--
K	20500 ± 2000	19100 ± 900	22800 ± 900
La	22.7 ± 0.2	29.6 ± 0.2	44.7 ± 0.3
Lu	0.378 ± 0.008	0.45 ± 0.01	0.52 ± 0.01
Na	7670 ± 60	10400 ± 100	5370 ± 30
Rb	74 ± 3	80 ± 3	111 ± 5
Sc	7.38 ± 0.07	10.0 ± 0.1	18.4 ± 0.1
Sm	4.4 ± 0.1	5.9 ± 0.1	8.3 ± 0.2
Tb	0.59 ± 0.02	0.71 ± 0.01	1.10 ± 0.04
Yb	2.6 ± 0.1	3.0 ± 0.1	3.6 ± 0.1
Zn	70 ± 4	91 ± 3	191 ± 5

Table 4. (cont.)

	S-2		
	Total Sediment	Silt + Clay	Clay
As	8 ± 1	8 ± 1	25 ± 3
Ce	33.0 ± 0.4	44.0 ± 0.4	80.6 ± 0.2
Co	8.25 ± 0.06	11.3 ± 0.1	29.3 ± 0.2
Cr	56 ± 6	71 ± 7	130 ± 13
Cs	1.9 ± 0.2	2.4 ± 0.3	7.3 ± 0.8
Cu	26 ± 1	--	--
Eu	0.99 ± 0.01	1.15 ± 0.01	1.57 ± 0.02
Fe	25800 ± 100	33700 ± 100	79300 ± 400
Ga	12.8 ± 0.3	--	--
Hf	8.6 ± 0.2	10.2 ± 0.3	4.9 ± 0.2
K	21000 ± 3000	22000 ± 2000	24000 ± 3000
La	21.7 ± 0.3	27.4 ± 0.3	43.8 ± 0.6
Lu	0.43 ± 0.01	0.470 ± 0.009	0.59 ± 0.02
Na	9820 ± 50	11300 ± 50	5030 ± 40
Rb	65 ± 7	75 ± 8	120 ± 14
Sc	6.86 ± 0.01	9.08 ± 0.01	20.6 ± 0.1
Sm	5.4 ± 0.3	5.85 ± 0.02	8.85 ± 0.03
Tb	0.80 ± 0.03	0.96 ± 0.03	1.51 ± 0.07
Yb	2.95 ± 0.09	3.31 ± 0.09	3.8 ± 0.2
Zn	40 ± 1	53 ± 1	166 ± 4

Table 4. (cont.)

	S-3		
	Total Sediment	Silt + Clay	Clay
As	8 ± 1	7.4 ± 0.5	35.4 ± 1.0
Ba	421 ± 22	450 ± 18	450 ± 60
Ce	48.5 ± 0.6	47.7 ± 0.5	97 ± 2
Co	12.1 ± 0.2	12.5 ± 0.2	31.3 ± 0.4
Cr	68 ± 1	68 ± 1	161 ± 4
Cs	2.2 ± 0.1	5.3 ± 0.1	6.1 ± 0.3
Cu	--	50.0 ± 0.3	91.7 ± 0.5
Eu	1.10 ± 0.01	1.11 ± 0.01	1.46 ± 0.03
Fe	32000 ± 2000	30100 ± 600	72700 ± 500
Ga	--	12.3 ± 0.3	25.6 ± 0.6
Hf	8.1 ± 0.1	7.7 ± 0.1	4.6 ± 0.1
Hg	0.09 ± 0.01	--	0.37 ± 0.03
K	19300 ± 500	20800 ± 400	22300 ± 500
La	25.0 ± 0.5	26.7 ± 0.4	46 ± 1
Lu	0.43 ± 0.01	0.468 ± 0.009	0.80 ± 0.03
Na	11700 ± 100	1.32 ± 0.03	6340 ± 20
Rb	68 ± 3	69 ± 2	104 ± 9
Sc	8.63 ± 0.03	8.99 ± 0.09	18.2 ± 0.1
Sm	5.21 ± 0.06	4.50 ± 0.05	7.96 ± 0.05
Tb	0.73 ± 0.03	0.70 ± 0.04	1.14 ± 0.06
Yb	2.9 ± 0.1	3.03 ± 0.08	3.9 ± 0.2
Zn	86 ± 2	104 ± 11	280 ± 24

Table 4. (cont.)

	DDS-1		
	Total Sediment	Silt + Clay	Clay
As	--	9 ± 2	29 ± 3
Ba	440 ± 30	470 ± 40	550 ± 60
Ce	40.8 ± 0.5	56.3 ± 0.5	94 ± 1
Co	4.7 ± 0.1	12.1 ± 0.2	25.8 ± 0.8
Cr	28 ± 1	65 ± 2	108 ± 3
Cs	1.3 ± 0.1	2.4 ± 0.2	6.1 ± 0.3
Cu	32.9 ± 0.6	51.3 ± 0.4	97.3 ± 0.8
Eu	0.722 ± 0.009	1.02 ± 0.01	1.35 ± 0.02
Fe	14000 ± 200	26200 ± 300	73300 ± 700
Ga	13.2 ± 0.3	--	--
Hf	5.0 ± 0.1	7.0 ± 0.1	4.6 ± 0.1
Hg	0.05	--	--
K	21000 ± 2000	23000 ± 1000	22600 ± 900
La	14.8 ± 0.2	26.1 ± 0.4	46.2 ± 0.7
Lu	0.287 ± 0.009	0.42 ± 0.01	0.53 ± 0.02
Na	--	11600 ± 100	5800 ± 100
Rb	77 ± 5	65 ± 1	96 ± 9
Sc	4.10 ± 0.02	9.00 ± 0.09	17.6 ± 0.2
Sm	3.05 ± 0.09	5.60 ± 0.15	8.9 ± 0.2
Tb	0.78 ± 0.04	--	1.10 ± 0.06
Yb	2.00 ± 0.09	2.8 ± 0.1	3.4 ± 0.2
Zn	30 ± 5	117 ± 11	279 ± 6

Table 4. (cont.)

	DDS-2		
	Total Sediment	Silt + Clay	Clay
As	6.5 ± 0.1	10 ± 2	32.3 ± 0.3
Ba	418 ± 17	500 ± 40	480 ± 40
Ce	40.3 ± 0.4	62.4 ± 0.7	94 ± 1
Co	4.07 ± 0.08	13.4 ± 0.3	26.9 ± 0.4
Cr	28 ± 0.5	75 ± 3	117 ± 2
Cs	1.3 ± 0.1	2.9 ± 0.2	6.6 ± 0.4
Cu	14.0 ± 0.1	31 ± 2	97.4 ± 0.9
Eu	0.682 ± 0.007	1.12 ± 0.02	1.43 ± 0.02
Fe	12600 ± 100	35900 ± 400	76600 ± 400
Ga	9.5 ± 0.3	12.0 ± 0.3	24.9 ± 0.7
Hf	4.4 ± 0.1	8.5 ± 0.2	4.9 ± 0.1
Hg	0.02 ± 0.005	--	--
K	27000 ± 2000	20000 ± 1000	22500 ± 1000
La	17.3 ± 0.2	28.6 ± 0.5	44.5 ± 0.4
Lu	0.276 ± 0.006	0.47 ± 0.02	0.55 ± 0.02
Na	7310 ± 70	12000 ± 100	6050 ± 40
Rb	76 ± 3	77 ± 7	102 ± 6
Sc	3.49 ± 0.01	10.3 ± 0.1	18.0 ± 0.2
Sm	3.09 ± 0.09	5.9 ± 0.1	8.4 ± 0.2
Tb	0.41 ± 0.01	0.72 ± 0.04	1.1 ± 0.05
Yb	1.97 ± 0.07	3.1 ± 0.1	3.4 ± 0.2
Zn	32 ± 2	110 ± 30	260 ± 10

Table 4. (cont.)

	Geo 19		Geo 21	
	Total Sediment	Clay	Total Sediment	Clay
As	6.1 ± 0.8	18 ± 2	6.2 ± 0.9	15 ± 2
Ba	460 ± 50	410 ± 30	470 ± 60	420 ± 30
Ce	50.6 ± 0.6	80.8 ± 0.9	62.3 ± 0.7	90 ± 1
Co	9.2 ± 0.1	24.6 ± 0.3	12.5 ± 0.1	27.4 ± 0.3
Cr	57 ± 2	112 ± 3	72 ± 2	124 ± 3
Cs	2.2 ± 0.1	6.2 ± 0.2	2.8 ± 0.1	6.6 ± 0.2
Cu	33 ± 1	76.5 ± 0.5	45.4 ± 0.5	72.6 ± 0.5
Eu	0.98 ± 0.01	1.28 ± 0.02	1.07 ± 0.01	1.43 ± 0.02
Fe	28000 ± 200	65000 ± 500	34400 ± 200	70500 ± 500
Ga	10.8 ± 0.3	26.7 ± 0.3	10.3 ± 0.3	23.0 ± 0.7
Hf	7.6 ± 0.2	4.4 ± 0.2	8.7 ± 0.2	5.0 ± 0.2
Hg	0.07 ± 0.02	1.23 ± 0.01	0.036 ± 0.004	1.37 ± 0.01
K	23200 ± 900	24400 ± 500	22100 ± 900	24000 ± 600
La	23.0 ± 0.6	39.4 ± 0.4	29.0 ± 0.8	43.7 ± 0.4
Lu	0.43 ± 0.02	0.52 ± 0.02	0.50 ± 0.02	0.58 ± 0.02
Na	10500 ± 40	5970 ± 20	9630 ± 40	5650 ± 20
Nd	--	--	--	54 ± 9
Rb	78 ± 8	125 ± 8	79 ± 9	118 ± 7
Sb	0.73 ± 0.09	1.3 ± 0.2	0.8 ± 0.1	1.3 ± 0.2
Sc	7.53 ± 0.02	17.5 ± 0.1	9.92 ± 0.07	19.6 ± 0.2
Se	--	--	--	--
Sm	4.6 ± 0.3	6.5 ± 0.3	5.6 ± 0.1	7.2 ± 0.2
Tb	0.65 ± 0.04	0.98 ± 0.05	0.74 ± 0.04	1.07 ± 0.05
Th	8.0 ± 0.2	15.6 ± 0.2	9.7 ± 0.2	16.2 ± 0.2
Yb	2.7 ± 0.2	3.2 ± 0.2	2.9 ± 0.2	3.7 ± 0.2
Zn	69 ± 6	238 ± 13	66 ± 6	190 ± 10

Table 4. (cont.)

	Geo 43		Geo 45	
	Total Sediment	Clay	Total Sediment	Clay
As	25 ± 2	31 ± 2	19 ± 2	21 ± 2
Ba	530 ± 60	530 ± 29	455 ± 29	510 ± 40
Ce	80.2 ± 0.9	71.0 ± 0.7	76 ± 1	75 ± 1
Co	18.2 ± 0.2	23.3 ± 0.2	17.4 ± 0.2	23.6 ± 0.3
Cr	95 ± 3	112 ± 2	90 ± 2	107 ± 3
Cs	4.2 ± 0.2	5.6 ± 0.4	3.9 ± 0.1	6.0 ± 0.2
Cu	90.8 ± 0.9	125.5 ± 0.5	101 ± 1	91.1 ± 0.7
Eu	1.33 ± 0.01	1.19 ± 0.01	1.34 ± 0.02	1.26 ± 0.06
Fe	55600 ± 300	66500 ± 300	51400 ± 300	65900 ± 500
Ga	14.5 ± 0.3	19.2 ± 0.5	15.5 ± 0.5	24.5 ± 0.3
Hf	5.8 ± 0.1	4.1 ± 0.1	5.7 ± 0.1	4.0 ± 0.2
Hg	0.13 ± 0.01	0.67 ± 0.01	0.24 + 0.15	2.7 ± 0.1
K	20300 ± 800	27000 ± 1000	19600 ± 500	25200 ± 600
La	38.7 ± 0.9	37 ± 1	35.8 ± 0.4	37.3 ± 0.4
Lu	0.51 ± 0.02	0.47 ± 0.02	0.49 ± 0.02	0.47 ± 0.02
Na	9290 ± 40	7600 ± 70	9210 ± 30	7780 ± 20
Nd	--	25 ± 4	41 ± 7	34 ± 8
Rb	91 ± 8	114 ± 5	88 ± 5	128 ± 9
Sb	1.4 ± 0.2	1.2 ± 0.2	1.3 ± 0.2	2.1 ± 0.3
Sc	14.0 ± 0.7	17.0 ± 0.1	13.4 ± 0.1	17.2 ± 0.1
Se	--	--	--	--
Sm	6.8 ± 0.2	7.2 ± 0.5	6.5 ± 0.2	6.4 ± 0.2
Tb	0.93 ± 0.04	0.85 ± 0.04	0.85 ± 0.04	0.86 ± 0.05
Th	13.6 ± 0.3	13.7 ± 0.1	12.3 ± 0.2	13.8 ± 0.2
Yb	3.3 ± 0.2	2.8 ± 0.1	3.2 ± 0.2	3.0 ± 0.2
Zn	131 ± 10	210 ± 20	144 ± 6	216 ± 12

Table 4. (cont.)

	Geo 46		Geo 51	
	Total Sediment	Clay	Total Sediment	Clay
As	19 ± 2	19 ± 3	12 ± 2	15 ± 2
Ba	460 ± 50	460 ± 30	500 ± 60	440 ± 30
Ce	74.8 ± 0.8	70.1 ± 0.8	72.3 ± 0.9	77.9 ± 0.9
Co	17.7 ± 0.2	22.6 ± 0.5	15.4 ± 0.2	24.3 ± 0.5
Cr	95 ± 3	101 ± 3	88 ± 3	112 ± 3
Cs	3.8 ± 0.1	5.8 ± 0.2	3.4 ± 0.1	5.8 ± 0.2
Cu	92 ± 1	95 ± 3	83 ± 3	135 ± 1
Eu	1.32 ± 0.01	1.16 ± 0.02	1.27 ± 0.02	1.20 ± 0.02
Fe	51300 ± 300	60900 ± 600	42200 ± 300	62300 ± 400
Ga	17.7 ± 0.3	19.2 ± 0.5	14.8 ± 0.5	17.9 ± 0.4
Hf	5.8 ± 0.1	3.7 ± 0.2	6.7 ± 0.2	4.5 ± 0.2
Hg	0.11 ± 0.02	0.172 ± 0.004	0.11 + 0.01	0.6 + 0.1
K	19700 ± 900	24900 ± 700	19900 ± 900	24700 ± 600
La	36.0 ± 0.8	35.0 ± 0.4	34.9 ± 0.9	38.5 ± 0.4
Lu	0.50 ± 0.02	0.44 ± 0.02	0.49 ± 0.02	0.50 ± 0.02
Na	10100 ± 40	8420 ± 30	11100 ± 500	6990 ± 20
Nd	--	35 ± 7	--	48 ± 10
Rb	82 ± 7	122 ± 8	84 ± 9	103 ± 7
Sb	1.1 ± 0.1	1.8 ± 0.3	1.2 ± 0.2	1.7 ± 0.2
Sc	13.7 ± 0.1	16.0 ± 0.1	12.2 ± 0.1	17.5 ± 0.1
Se	--	--	--	--
Sm	6.7 ± 0.2	5.5 ± 0.2	6.3 ± 0.1	6.5 ± 0.2
Tb	0.89 ± 0.05	0.80 ± 0.04	0.84 ± 0.04	0.92 ± 0.05
Th	12.1 ± 0.2	12.9 ± 0.2	11.5 ± 0.2	14.5 ± 0.2
Yb	3.2 ± 0.2	2.8 ± 0.2	3.2 ± 0.2	3.2 ± 0.2
Zn	145 ± 5	178 ± 15	131 ± 9	181 ± 13

Table 4. (cont.)

	Geo 59		Geo MP	
	Total Sediment	Clay	Total Sediment	Clay
As	10 ± 1	18 ± 2	5.9 ± 0.6	28 ± 3
Ba	460 ± 60	413 ± 29	430 ± 40	570 ± 60
Ce	63.4 ± 0.7	99 ± 1	37.1 ± 0.9	144 ± 2
Co	13.1 ± 0.1	25.0 ± 0.2	4.96 ± 0.07	38.4 ± 0.7
Cr	71 ± 2	127 ± 3	33 ± 1	150 ± 4
Cs	3.1 ± 0.1	6.3 ± 0.2	1.2 ± 0.1	80 ± 6
Cu	49.4 ± 0.6	66.7 ± 0.5	12.7 ± 0.4	185 ± 1
Eu	1.04 ± 0.01	1.59 ± 0.02	0.750 ± 0.009	1.89 ± 0.03
Fe	36900 ± 200	71100 ± 400	18100 ± 100	80400 ± 600
Ga	14.3 ± 0.3	25.2 ± 0.3	7.6 ± 0.4	31.8 ± 0.7
Hf	4.9 ± 0.1	5.3 ± 0.2	7.7 ± 0.2	5.3 ± 0.2
Hg	0.024 ± 0.004	0.20 ± 0.02	X	4.22 ± 0.05
K	20000 ± 1000	24200 ± 500	24400 ± 800	27000 ± 1000
La	31.5 ± 0.8	49.9 ± 0.5	18.6 ± 0.4	60 ± 2
Lu	0.42 ± 0.02	0.62 ± 0.02	0.39 ± 0.01	0.71 ± 0.03
Na	7170 ± 40	5490 ± 20	6810 ± 30	6980 ± 40
Nd	--	55 ± 10	--	43 ± 8
Rb	67 ± 8	114 ± 6	78 ± 5	129 ± 10
Sb	0.8 ± 0.1	1.3 ± 0.2	0.67 ± 0.09	2.5 + 0.5
Sc	10.5 ± 0.1	20.4 ± 0.1	4.40 ± 0.01	21.6 ± 0.1
Se	--	--	--	--
Sm	5.3 ± 0.1	8.5 ± 0.2	3.67 ± 0.07	10.3 ± 0.2
Tb	0.73 ± 0.03	1.17 ± 0.05	0.48 ± 0.02	1.41 ± 0.08
Th	10.2 ± 0.2	18.2 ± 0.2	5.6 ± 0.1	21.5 ± 0.3
Yb	2.9 ± 0.2	4.1 ± 0.2	2.4 ± 0.2	4.5 ± 0.3
Zn	76 ± 3	177 ± 8	38 ± 4	360 ± 20

Table 4. (cont.)

	SCOW H6	
	Total sediment	Clay
As	7 ± 1	16 ± 2
Ba	423 ± 16	480 ± 30
Ce	49.1 ± 0.3	87.2 ± 0.5
Co	10.2 ± 0.1	24.6 ± 0.2
Cr	58.5 ± 0.9	118 ± 2
Cs	2.29 ± 0.07	5.9 ± 0.2
Cu	28.3 ± 0.2	75.8 ± 0.5
Eu	0.913 ± 0.008	1.33 ± 0.01
Fe	30400 ± 100	66000 ± 300
Ga	12.0 ± 0.3	18 ± 3
Hf	6.9 ± 0.1	4.9 ± 0.1
Hg	0.058 ± 0.003	0.829 ± 0.006
K	20700 ± 900	23700 ± 900
La	24.6 ± 0.3	42.9 ± 0.3
Lu	0.404 ± 0.006	0.54 ± 0.01
Na	8900 ± 40	5670 ± 20
Nd	26 ± 3	37 ± 5
Rb	71 ± 2	119 ± 7
Sb	0.81 ± 0.03	1.43 ± 0.07
Sc	8.11 ± 0.09	18.4 ± 0.05
Sm	4.8 ± 0.1	7.6 ± 0.3
Tb	0.60 ± 0.02	1.02 ± 0.03
Th	8.33 ± 0.06	16.7 ± 0.2
Yb	2.68 ± 0.07	3.4 ± 0.1
Zn	71 ± 3	194 ± 3

Table 4. (cont.)

	SCOW H7	
	Total sediment	Clay
As	8 ± 1	16 ± 2
Ba	399 ± 16	470 ± 20
Ce	47.1 ± 0.3	87.7 ± 0.5
Co	10.0 ± 0.1	25.6 ± 0.2
Cr	59.3 ± 0.8	121 ± 1
Cs	2.26 ± 0.06	6.1 ± 0.2
Cu	26.6 ± 0.2	71.3 ± 0.5
Eu	0.891 ± 0.008	1.38 ± 0.01
Fe	30000 ± 100	68000 ± 1000
Ga	12.5 ± 0.7	18 ± 3
Hf	5.8 ± 0.1	5.09 ± 0.08
Hg	0.038 ± 0.007	0.58 ± 0.02
K	19600 ± 800	25000 ± 1000
La	23.5 ± 0.2	44.2 ± 0.4
Lu	0.379 ± 0.006	0.57 ± 0.01
Na	8850 ± 40	5820 ± 20
Nd	21 ± 2	39 ± 4
Rb	68 ± 2	115 ± 4
Sb	0.74 ± 0.07	1.41 ± 0.05
Sc	7.89 ± 0.04	19.1 ± 0.05
Sm	4.54 ± 0.01	7.96 ± 0.02
Tb	0.57 ± 0.02	1.09 ± 0.03
Th	8.01 ± 0.06	17.4 ± 0.1
Yb	2.41 ± 0.06	3.6 ± 0.1
Zn	70 ± 1	180 ± 12

Table 4. (cont.)

	SCOW H8 Total sediment	SCOW H9 Total sediment
As	--	--
Ba	275 ± 12	270 ± 11
Ce	32.6 ± 0.2	32.7 ± 0.2
Co	5.98 ± 0.06	5.49 ± 0.05
Cr	28.3 ± 0.5	24.7 ± 0.5
Cs	7.3 ± 0.5	0.75 ± 0.04
Cu	12.3 ± 0.1	12.5 ± 0.1
Eu	0.580 ± 0.005	0.585 ± 0.005
Fe	15850 ± 60	15270 ± 60
Ga	6.6 ± 0.3	5.9 ± 0.1
Hf	3.15 ± 0.07	3.64 ± 0.05
Hg	<0.01	<0.01
K	13800 ± 600	15000 ± 700
La	15.5 ± 0.2	16.0 ± 0.1
Lu	0.225 ± 0.004	0.273 ± 0.005
Na	6420 ± 30	5540 ± 20
Nd	15 ± 2	17 ± 2
Rb	46 ± 2	45 ± 2
Sb	0.23 ± 0.02	0.44 ± 0.02
Sc	5.00 ± 0.04	4.41 ± 0.04
Sm	3.0 ± 0.1	3.1 ± 0.1
Tb	0.32 ± 0.01	0.36 ± 0.01
Th	3.94 ± 0.04	4.58 ± 0.05
Yb	1.49 ± 0.04	1.76 ± 0.05
Zn	32.3 ± 0.8	24 ± 1

Table 4. (cont.)

	SCOW H10	
	Total sediment	Clay
As	5 ± 1	--
Ba	314 ± 14	470 ± 25
Ce	35.1 ± 0.2	89.6 ± 0.6
Co	5.90 ± 0.06	25.4 ± 0.3
Cr	30 ± 1	117 ± 2
Cs	1.12 ± 0.05	6.0 ± 0.2
Cu	11.6 ± 0.1	78.5 ± 0.6
Eu	0.627 ± 0.006	1.42 ± 0.05
Fe	17370 ± 70	69300 ± 300
Ga	6.8 ± 0.4	18 ± 3
Hf	3.89 ± 0.05	4.9 ± 0.1
Hg	0.02 ± 0.01	0.97 ± 0.01
K	15900 ± 700	31000 ± 1000
La	17.4 ± 0.1	45.0 ± 0.5
Lu	0.267 ± 0.005	0.57 ± 0.01
Na	6170 ± 20	5890 ± 30
Nd	15 ± 2	42 ± 5
Rb	53 ± 2	119 ± 5
Sb	0.46 ± 0.02	1.52 ± 0.08
Sc	4.99 ± 0.02	18.7 ± 0.2
Sm	3.4 ± 0.1	8.0 ± 0.4
Tb	0.40 ± 0.01	1.12 ± 0.04
Th	5.36 ± 0.05	17.5 ± 0.1
Yb	1.67 ± 0.09	3.6 ± 0.1
Zn	32 ± 3	195 ± 5

II. Comparison of Methods to Evaluate the Status of Trace Element Pollution of Sediments

We explored two approaches to reduce the effects of variable amounts of quartz in sediment samples on the concentrations of trace elements. One approach is to correct the results of the total sediment analysis for the effects of dilution by quartz. That is, the effect of quartz is made a constant factor for all of the samples. Obviously, this approach requires that the samples be analyzed for their content of quartz. The second approach is to separate and analyze the less-than-two-micron fraction of the sediments. The proportion of quartz in the clay-size fraction should be less than in the total sediment. Also, the proportion of quartz found in this size fraction should be more nearly constant than in the total sediments because particles of this size can be easily suspended and transported in water. Therefore, samples of this size fraction have more uniform minerology than do samples of total sediments. The results of both approaches are compared to the results based on the analysis of total sediments in the following sections.

A. Results Based on Total Sediment Analysis

Comparison of the results given in Table 4 shows that the concentrations of most elements in the total sediments vary from sample to sample by more than a factor of four. This is illustrated in Figure 3 which shows the range of ratios obtained when the values are compared to those of the red clay. In all cases those sediments that contain the lowest concentrations of trace elements,contain the highest concentrations of coarser grained material , therefore, quartz. (Textural analyses of these sediments are presented in Volume 2). Further, the sediments with the highest concentrations of trace elements contain the greatest proportion of fine grained material.

The extent of any trace element pollution of the samples is almost impossible to determine because the trace element concentrations vary by more than a factor of two due to the effects of dilution by quartz. It is almost impossible to separate this variation from the variability expected as a result of pollution. Some indication of which sediments are polluted can be made by comparing the concentrations of elements used by man, such as zinc and mercury, to those not used, such as scandium and lanthanum. However, this is not satisfactory for general use because of the special techniques needed to analyze for the latter elements. The procedures discussed in the following sections are better than this method. We conclude that although analysis of total sediment concentrations are easily done in the laboratory, the results are of marginal value to evaluate the status of trace element pollution of sediments.

B. Correction of Total Sediment Concentrations for the Effects of Dilution by Quartz

To adjust for the variations in quartz content for different sediments, a correction to the concentrations of trace elements in the total sediment can be made to find the concentration of each element in the non-quartz fraction. The formula used to make this correction is:

$$\text{ppm(corrected)} = \frac{\text{ppm(total) - fraction qtz x ppm (qtz)}}{\text{1 - fraction qtz}}$$

For eight of the samples from the harbor and old dump site areas, the quartz content was determined by the method of Jackson (1973). The results are listed as percent measured quartz in the second column of Table 5. Using these quartz concentrations and the measured values of the elements measured in quartz (Table 2) the elemental ratios to standard red clay were computed using this formula. To complete the suite of elements, it was assumed that the concentration of mercury in quartz is zero. It is below our detection limit of 0.001 ppm. This will not over estimate the corrected values of mercury in sediments because the concentration of mercury in quartz is so low as compared to sediments that the last term in the numerator of the preceding equation can be ignored. The ranges for the eight samples for these quartz corrected concentrations expressed as a ratio to the standard clay for each element are shown in Figure 4. The ranges in values for some elements in the eight sediments are smaller than the ranges for the uncorrected total sediment values (Figure 3); however, they are still too large to be acceptable. For instance, although a rare earth element such as lanthanum is rarely subject to human input to the sediment, its ratios normally vary from 0.90 to 1.92. Similar ranges are found for most of the other elements. Of note is that copper, an element whose concentration may be expected to be influenced by human activity, has one of the smallest ranges of any element.

The method of Jackson (1973), although commonly used in some applications with good results (Thomas, 1975), may give variable results here because it only takes into account correction of the sample for quartz. This procedure does not account for other accessory minerals such as illmenite, magnetite, etc., which can have very high concentrations of some trace elements (Paster et al., 1974) and which are expected to have variable concentrations in sediments analogous to the case for quartz.

The method described above requires values of concentration of quartz in the samples but the analytical method used to determine quartz is not entirely satisfactory. It is difficult to perform and gives only approximate values of the concentration of quartz. Perhaps some of the variation in the ratios found above could be due to analytical errors in determining the quartz content. To check this, a quartz content was calculated for each sediment which we will call the optimum quartz content. This is done by calculating the percentage of quartz needed in a sediment so that the ratio for scandium is exactly 1.00 for that sediment. Scandium was chosen as the element to use in the process of normalization for three reasons: its concentration is very low in quartz; it is an element which is not thought to be added to the sediment by man's activities; and it is an element for which our analyses are unusually precise. The percentages of quartz calculated in this manner for 11 harbor and dump site sediments are shown in column 3 of Table 5. The values of quartz calculated by this procedure show fair agreement with those measured experimentally. The differences may be due to the poor accuracy of the analysis of quartz or to the inclusion of scandium in minor mineral phases of the sediment. We suspect that both are important, but additional information is not available.

The ratios to standard clay for each element were again calculated for 11 samples using the optimum values for quartz. The ranges for these ratios are plotted in Figure 5. The ranges are smaller than those for the measured quartz correction, especially when it is considered that there are three more samples used for this diagram than for Figures 3 and 4. However, the ranges are still too large for elements which are not subject to human input to be very informative when trying to determine sediment quality. The same approach of optimum quartz correction is applied to seven in-lake sediments in Figure 6. These sediments were collected from locations in the lake which are expected to be relatively unaffected by man's activities in the harbor except for previous disposal of dredged material. They may represent natural background conditions which exist at the present time in the lake. The ranges in elemental ratios for these sediments are found to be significantly smaller, especially for the rare earth elements. The small range for zinc and its ratio of approximately one is an indication that these sediments may be unaffected by man. However, the ranges are still larger than desired if this procedure is to be of much use in judging the quality of the harbor sediments. The smaller ranges of concentrations for the sediments from the open lake compared to those from the harbor may be the result of the greater efficiency of mixing in the lake and/or the lack of man's impact on these sediments. If mixing of sediments is more thorough in the lake, the sediments should have the same proportions of the different minerals and, therefore, about the same concentrations of trace elements.

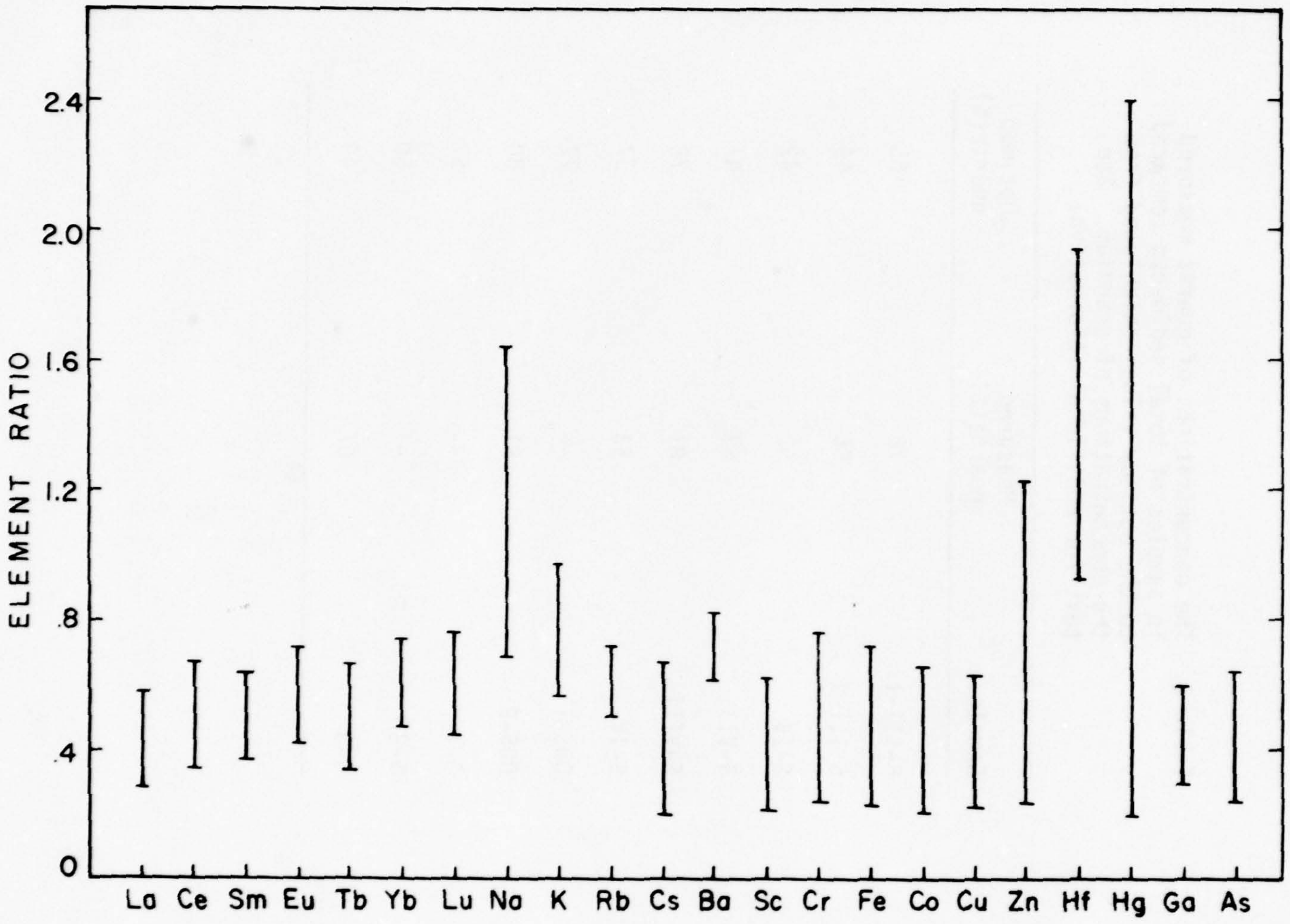
As a result of these analyses it appears that the method of using a measured value of quartz to correct elemental concentrations is only slightly better than using the results of total sediment analysis for detecting trace element pollution of sediments. The interpretation of the data on the clay-size fraction of the sediments described in the next section provides such clear information about sediment quality that attempts to glean such information by the procedures described above are thought to be not justified.

Table 5. The concentrations of quartz measured in samples of total sediments compared to the optimum values calculated from the concentrations of scandium. See text for additional information.

Sample	Measured quartz(%)	Optimum quartz(%)
S-III-1	78	65
S-III-2	56	44
S-IV	52	42
S-VII	63	47
S-VIII	87	78
S-IX	53	37
DDS-1	--	77
DDS-2	81	80
S-1	--	57
S-2	--	60
S-3	67	49

(figure 3)

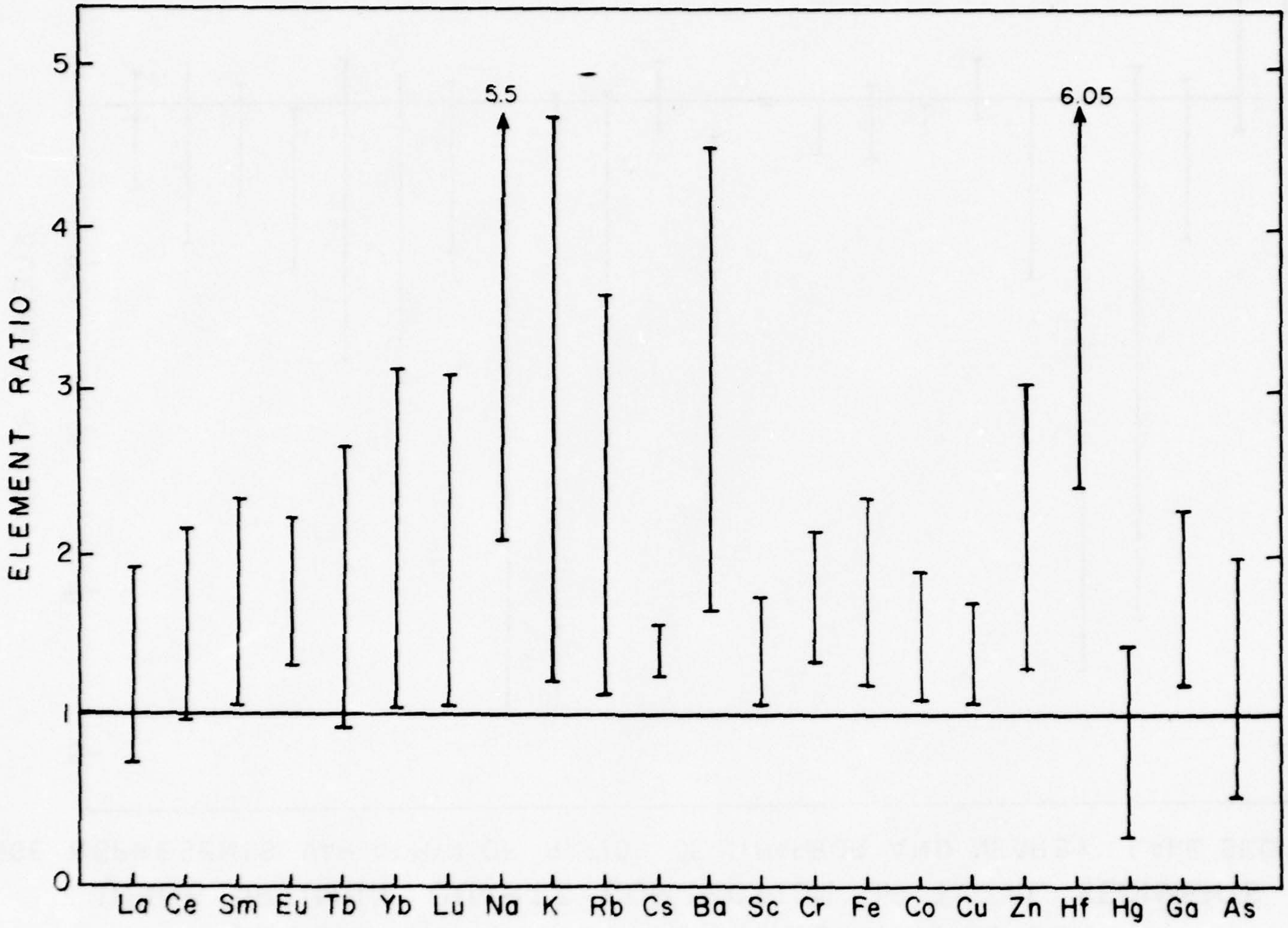
ELEMENTAL RATIOS TO STANDARD RED CLAY
TOTAL SEDIMENT
RANGE REPRESENTS VARIATION OF RATIOS OF 13 HARBOR AND NEARBY LAKE SEDIMENTS



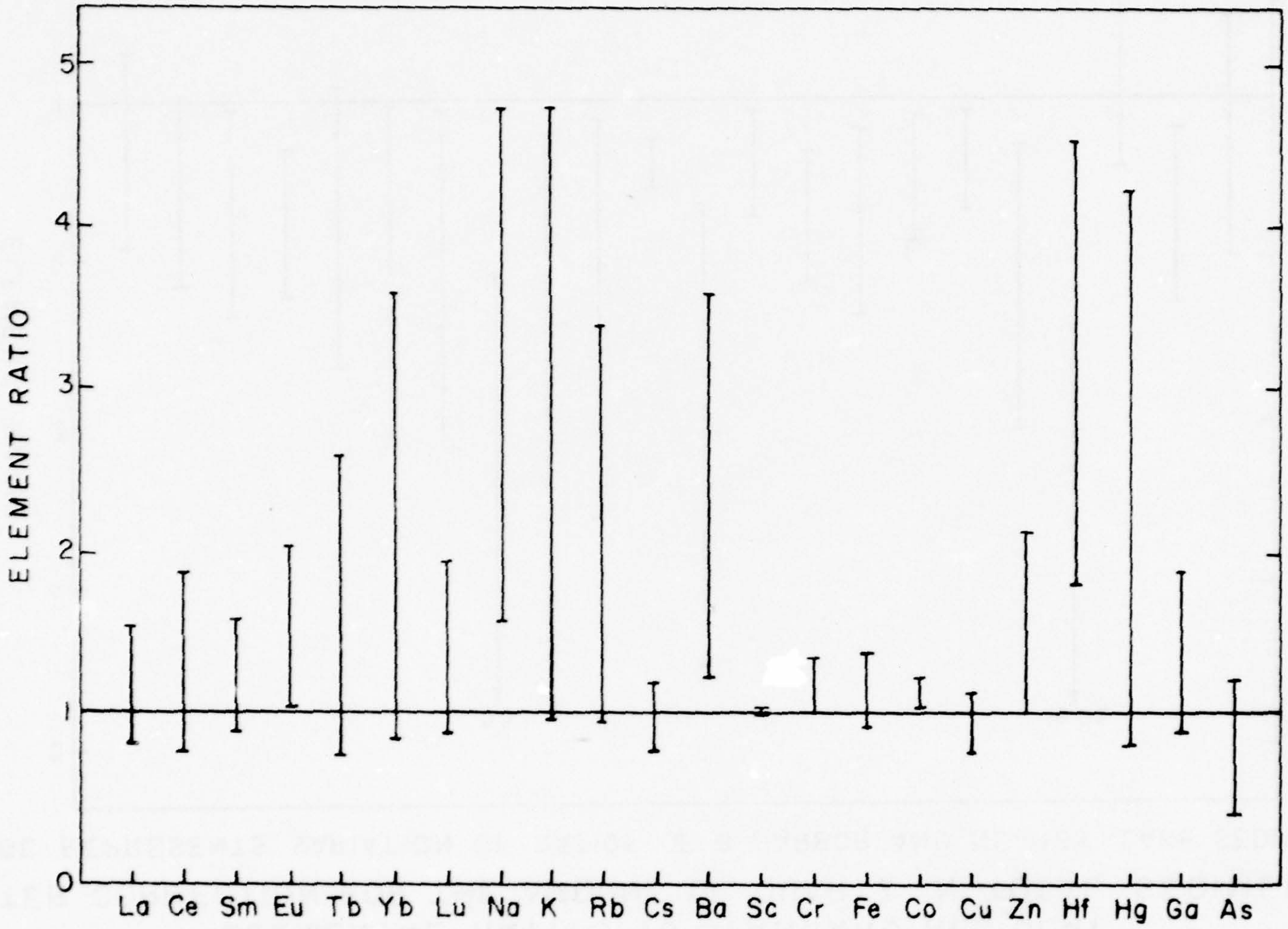
(figure 4)

ELEMENTAL RATIOS TO STANDARD RED CLAY
AFTER CORRECTION FOR THE AMOUNT OF QUARTZ IN TOTAL SEDIMENT

RANGE REPRESENTS VARIATION OF RATIOS OF 8 HARBOR AND NEARBY LAKE SEDIMENTS

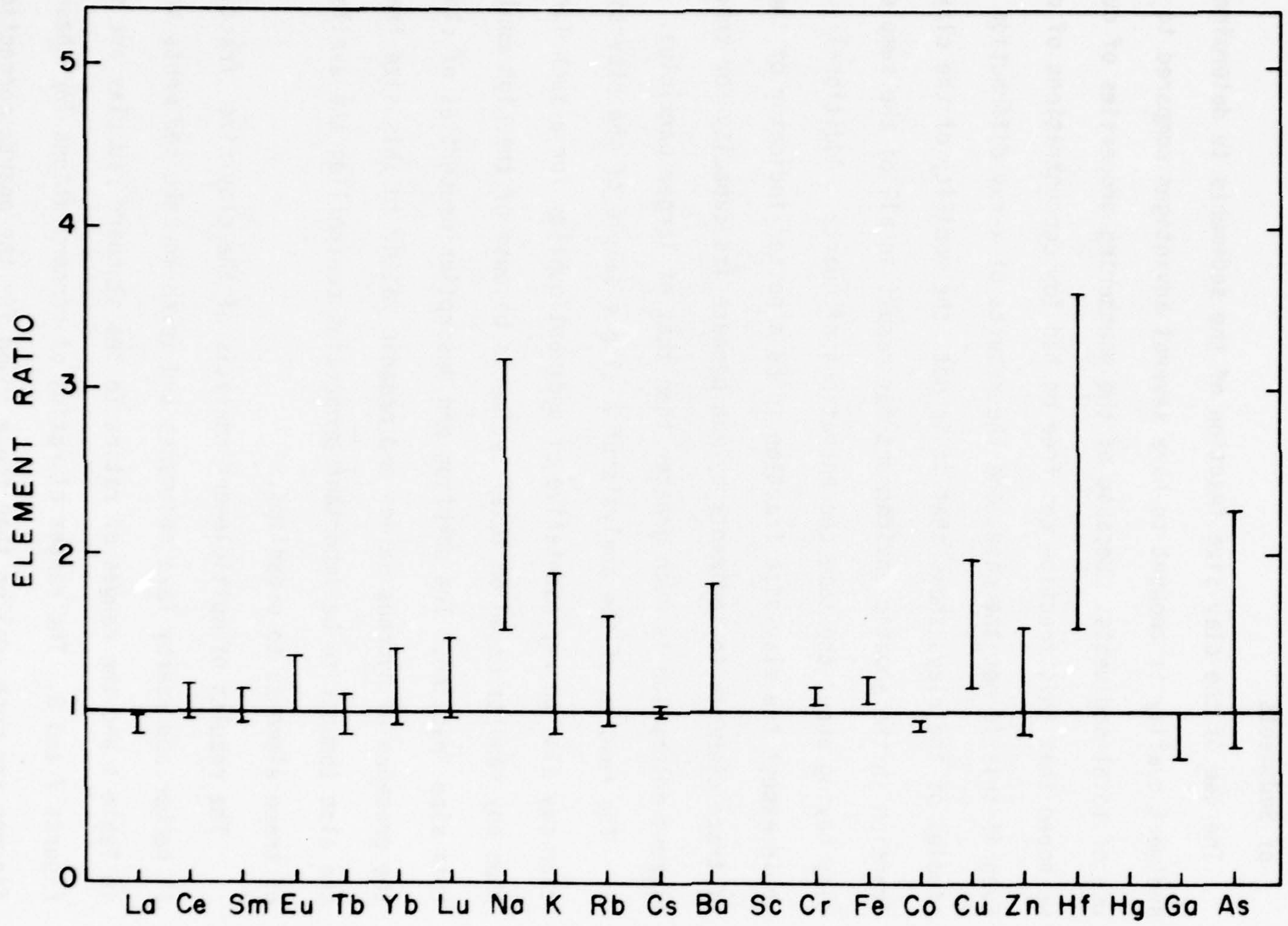


ELEMENTAL RATIOS TO STANDARD RED CLAY
USING OPTIMUM QUARTZ CORRECTION OF TOTAL SEDIMENTS
RANGE REPRESENTS VARIATION OF RATIOS OF 11 HARBOR AND NEARBY LAKE SEDIMENTS



(figure 6)

ELEMENTAL RATIOS TO STANDARD RED CLAY
OPTIMUM QUARTZ CORRECTION OF TOTAL SEDIMENTS
RANGE REPRESENTS VARIATION OF RATIOS OF 7 OPEN LAKE SEDIMENTS



C. Comparison of Trace Element Concentrations in the Clay-Size Fraction of Sediments

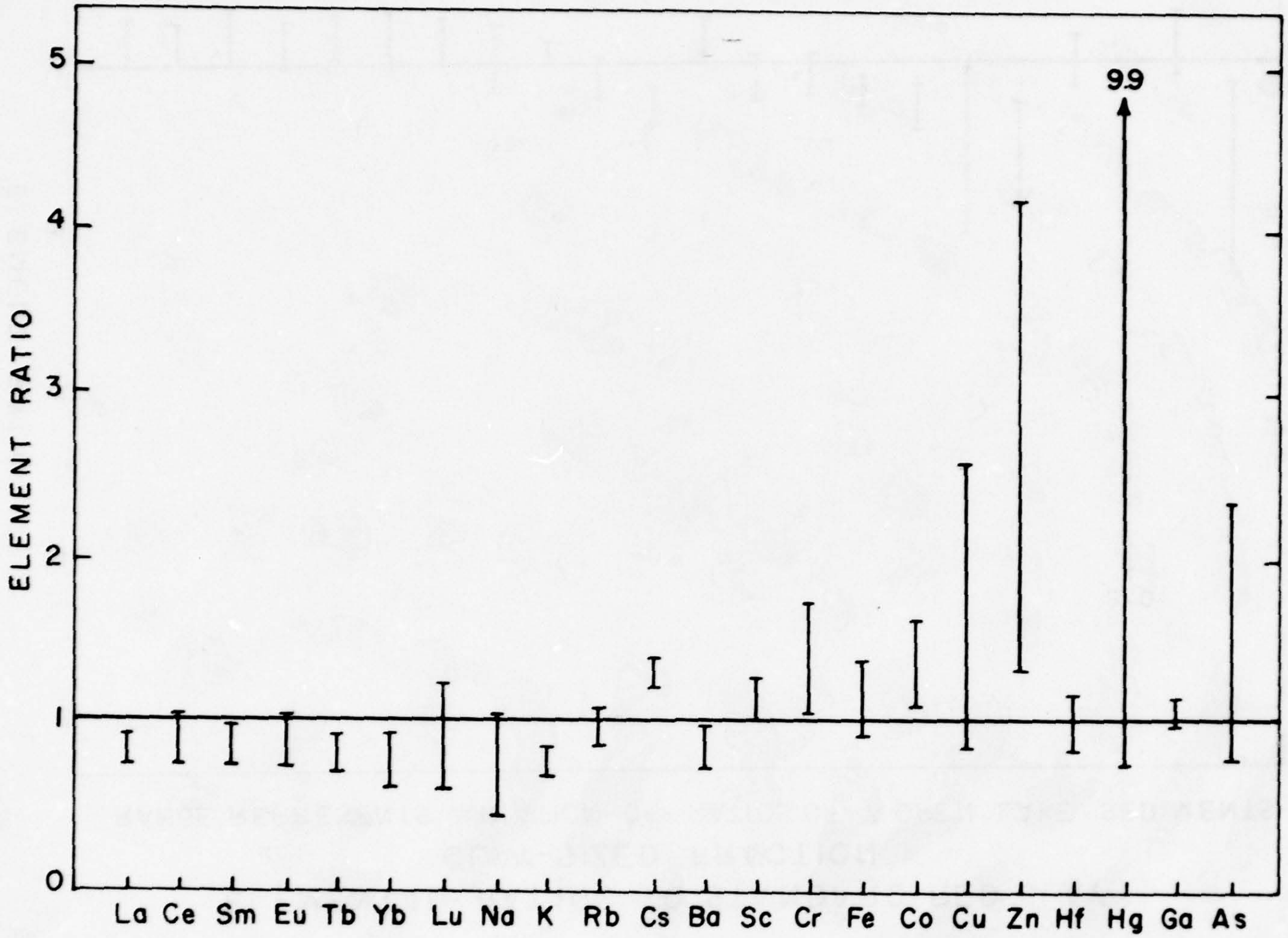
The use of the clay-size fraction of the sediments to determine sediment quality is thought to have several advantages compared to the use of total sediments. Because of the weathering properties of quartz, we hoped that this fraction was free or had low concentrations of quartz. Even if this is not the case, and the results of x-ray diffraction studies of the clays shows that it is not, the mobility of the clay-size fraction in the aquatic environment may result in all of the samples of clay having about the same concentrations of quartz. Additionally, one would expect the clay-size fraction to be a better indicator of the input of trace elements to sediments by man because its capacity for trace element adsorption is much greater than that of larger particles.

The results of the analysis of a single sample of the clay-size fraction may also be representative of sediment quality for a much larger area than any results based on total sediments because of the high mobility of this size fraction. The sorption and desorption properties of clays and the presence of hydrous oxides and organic matter in this size fraction are also thought to be important properties controlling the availability of trace elements to organisms.

The results of multielement analysis of the clay-size fraction of 11 harbor and nearby lake sediments and seven in-lake sediments are given in Table 4 and the ranges of ratios to the standard red clay are shown in Figures 7 and 8. The ranges of ratios of concentrations for these two figures are much smaller than those found for the quartz correction method (Figures 4-6). This is especially true for those elements which are not

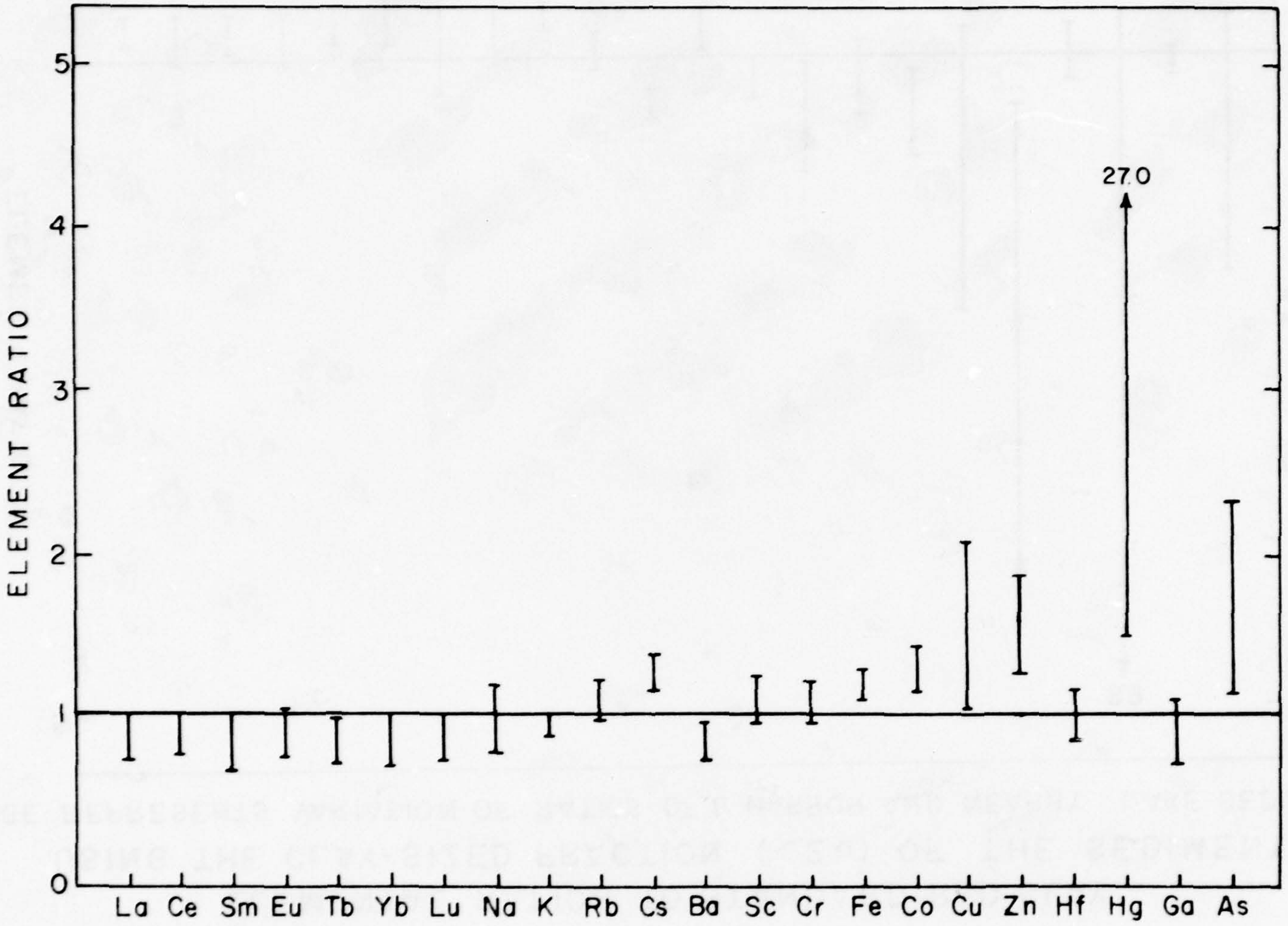
ELEMENTAL RATIOS TO STANDARD RED CLAY USING THE CLAY-SIZED FRACTION (<2μ) OF THE SEDIMENTS

RANGE REPRESENTS VARIATION OF RATIOS OF 8 HARBOR AND NEARBY LAKE SEDIMENTS



ELEMENTAL RATIOS TO STANDARD RED CLAY
CLAY-SIZED FRACTION

RANGE REPRESENTS VARIATION OF RATIOS OF 7 OPEN LAKE SEDIMENTS



used by man such as those listed in Figures 4-6 -- lanthanum (La) through scandium (Sc). In the seven in-lake sediments, the ranges are quite small for every element except arsenic, copper and mercury (Figure 8). Arsenic is quite mobile in the sediment environment so variations in concentrations of this element can be expected as a result of natural processes. The situation for mercury is discussed later. In contrast, the harbor and nearby lake sediments show a large range of values for copper, zinc, chromium, mercury and arsenic. These elements are commonly associated with industrial processes and ore handling activities such as those occurring in the Duluth-Superior harbor. The range of values for these elements suggests that some of the harbor sediments are affected by man.

Of the three methods of data analysis, it appears that the approach of using the clay-size fraction of a sediment to determine sediment quality with respect to trace elements is the best method, and the procedure for this method is examined in more detail in the following section.

D. The Use of the Clay-Size Fraction as an Indicator of Sediment Quality

The previous figures used to evaluate the usefulness of the different approaches of interpreting the results showed only the range of ratios for a set of samples. More detailed information about the character of the sediments at each sampling station is obtained when the results of single samples are shown in a similar fashion. Figures 9 through 15 show element ratios at individual sample locations for comparison of various sediments within the harbor. The ratios for almost all of the elements in most of the samples are about one. The uniformity of the ratios and their values of near unity for as many as 22 elements provide good evidence that the clay-size fraction of all of the samples have almost identical compositions. This is especially significant because many of the elements are associated with mineral phases that weather and react chemically by different mechanisms and rates. The relative uniformity of the trace element concentrations shows that all of the samples are derived from the same materials and that the clay-size fraction is well mixed before it is deposited as sediment.

The similarity of the concentrations of trace elements in the red clay to those of the sediments does not necessarily prove that most of the fine sediment is derived from the red clay deposits. In fact, some of the elements show consistent trends in their concentrations in the red clay and the clay-size fraction of the sediments that indicate there are other sources of these elements: natural or man-made. The best example is the element zinc which has higher concentrations in all of the clay samples from the sediment, including those from the core, than in the red clay. Additional research is needed to determine what fraction of the present sediments results from the red clay. However, this information is not needed in order to use the results of chemical analysis of the clay-size fraction to determine which sediments are polluted. The important requirement is that this size fraction has uniform concentrations of trace elements throughout the study area so that additions of individual elements to the sediments can be detected. For example, comparison of the results shown in Figures 9 (sample S-III-1) and 14 (sample S-IX) show that the sediment of sample S-III-1 has received additions of copper, zinc and mercury. The uniformity of all of the other element ratios indicates that these three elements are the result of one or more separate sources. Such a pattern is expected if these elements were added to the sediment by man's activities. In effect then, the results from clay-size fraction analysis can be used to determine the background concentrations of the various elements in the study area. The concentrations found in the red clay are only one factor that must be considered when selecting these values. Other sediment sources must also be taken into account.

Apparently the clay-size fraction yields almost constant concentrations of trace elements as a result of the fraction being very mobile in the aquatic environment rather than its being free of quartz. Results of x-ray diffraction studies show that all of the samples of clay contain some quartz. We cannot determine the exact amount present because the procedures used do not lend themselves to quantative results. The major input of sediment to the harbor is suspended sediment from the Nemadji and St. Louis Rivers. Another major input to the entire southwest corner of Lake Superior is red clay either washed from the cliffs along the Wisconsin shoreline or carried as suspended matter in the rivers on that shore. Recent evidence indicates that 86,000 tons of suspended sediment per year are contributed to Lake Superior from the rivers along the Wisconsin shore during the period of open flow (Roubal et al., 1974). This input combined with its relatively high mobility in the aquatic system creates a consistent background concentration of trace elements throughout this portion of Lake Superior and the Duluth-Superior harbor. Thus, an external addition of an element can be detected if a chemical analysis is made of this size fraction. Also of major importance is that any ions of trace elements that enter the harbor in aqueous solution, such as in sewage effluent, will be absorbed predominantly onto this size fraction.

For the harbor and nearby lake sediments the less than 50 micron fraction (silt-plus-clay) was also collected. The results of elemental analysis of this fraction are shown in Table 4. With the exception of hafnium, the concentrations of all trace elements measured in the silt-plus-clay fraction are higher than the concentrations in the total sediment and lower than those in the clay-size fraction. This probably results because minerals of low trace element content, such as quartz, are predominant in the larger size fractions and minerals of higher trace element content are predominant in the clay-size fraction. It appears that the silt-plus-clay fraction is composed of a mixture of the minerals found in both the larger and smaller fractions. The trace element hafnium and the major elements sodium and potassium are of highest concentrations in the sand-sized fractions of most samples. The concentration of hafnium in quartz is approximately 20 percent of the value found in most total sediments. The concentrations of sodium and potassium in quartz are also relatively high and even higher in feldspars. Hafnium is also known to be included in the lattice structure of zircon in quite high concentrations. Zircon is a mineral that is resistant to weathering so it remains predominantly in the sand-sized fraction of the sediment. Sodium, potassium and hafnium tend to be more concentrated in the larger size fractions where minerals that concentrate these elements are more abundant.

A comparison of the results for two samples (sample S-III-1 and sample S-IX) representing the extreme cases of high and low trace element concentrations, illustrates the usefulness of analyzing the clay-size fraction. Sample S-III-1 was taken from the backwater area adjacent to the 21st Avenue dock and the Duluth sewage treatment plant and sample S-IX was taken from the entrance to Allouez Bay. Sample S-III-1 has a high ratio to standard clay for the elements zinc, copper, mercury, chromium, arsenic, and to a lesser extent, iron (Figure 9). This may result from its proximity to the effluent discharge from the sewage treatment plant combined with the use of the area as a dump site for harbor spoil and for refuse from land sites. The sediment from the entrance to Allouez Bay, S-IX (Figure 14), has ratios near one for these elements, and it closely resembles the sediments taken from the open lake and red clay. The elimination of the large variations in element ratios from site-to-site by use of the clay fraction is a significant improvement over the results which are obtained by total sediment analysis. For example, the concentrations of most trace elements in the total sediment are greater in sample S-IX than in S-III-1, suggesting that the sample from Allouez Bay (S-IX) is more polluted than the sample from near the sewage outfall (S-III-1); however, the results based on the clay-size fraction show that the reverse is correct. This results from the fact that the sediment from station S-III-1 is coarser grained than the sediment from station S-IX, and therefore, it contains more quartz which effectively dilutes the concentrations of trace elements when the total sediment is analyzed.

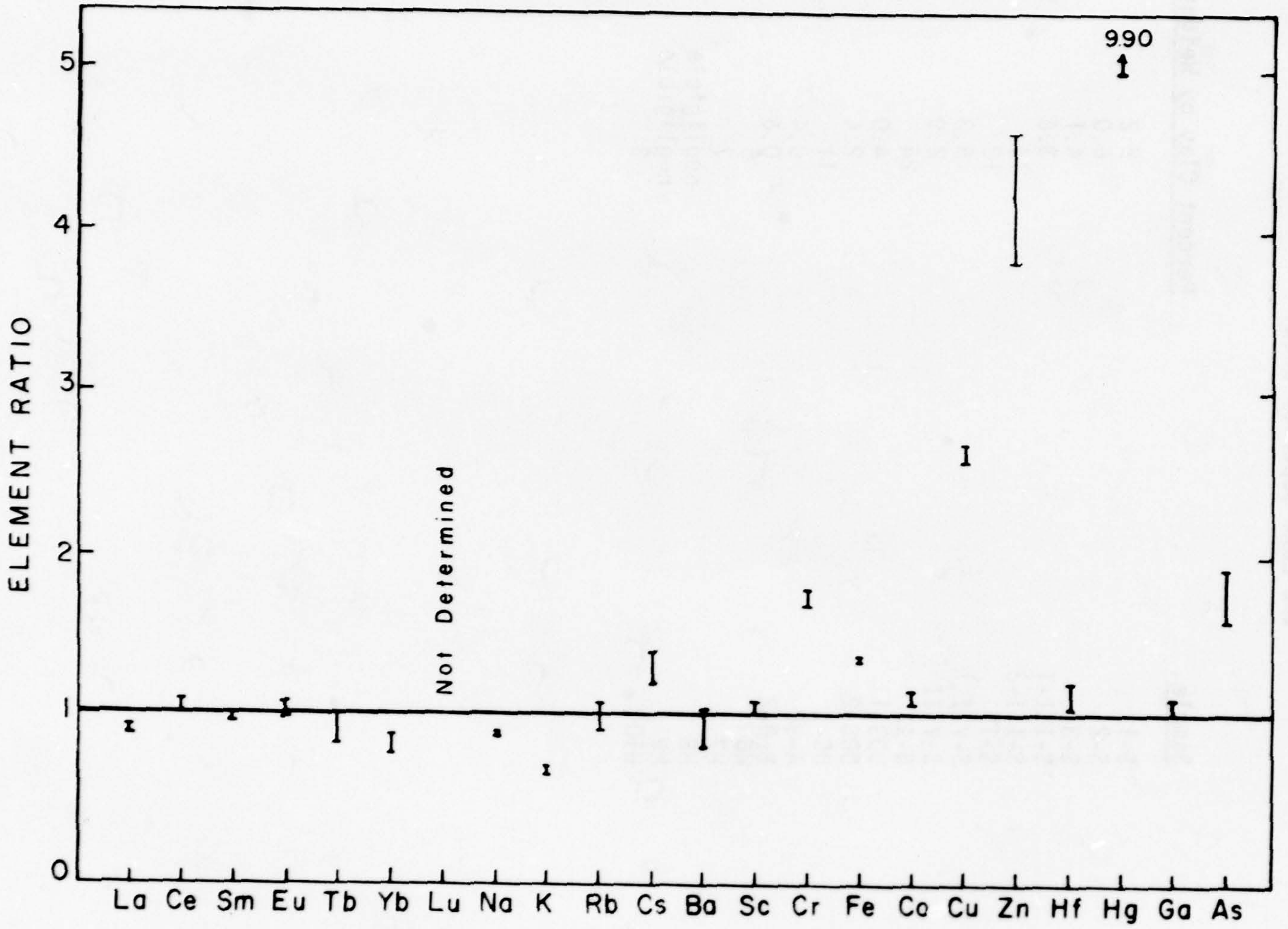
A survey of the harbor area using the results of trace element analysis of the clay-size fraction is needed to provide a detailed map of the extent of heavy metal pollution in the harbor sediments. Such a survey should include the element lead. We did not determine this element because it cannot be measured by neutron activation analysis. Future work using the clay-size fraction of a sediment can be done by a commercial or control agency laboratory. The use of neutron activation analysis is not required once the basis of comparison is established as it has been in the case for the Duluth-Superior Harbor. A multi-element technique of analysis is initially needed at other harbors in order to establish the concentration of any trace elements in the natural sediment to provide evidence of the uniformity of the sediments. An agency concerned with the quality of sediment or dredge spoil can then look at one or several elements of interest by their standard method, such as atomic absorption analysis, after the clay-size fractions have been separated from the samples. If the elemental ratio of interest in the clay-size fraction is within a range determined to represent polluted sediment, appropriate disposition of the dredge spoil can be effected. Approximate values of concentrations of mercury, zinc and copper representing background levels are suggested in section II, G.

The use of the clay-size fraction is obviously not practical when a sediment sample contains so little clay that a sample large enough to analyze cannot be isolated. This was not a problem for most of the samples from the Duluth-Superior area except for samples collected near sandy beaches. However, most of the samples from the lake near the Keweenaw area are so sandy that it is almost impossible to separate a reasonable sized clay sample. This is shown in Table 6 which reports the approximate concentrations of the clay-size fraction in some of the samples studied.

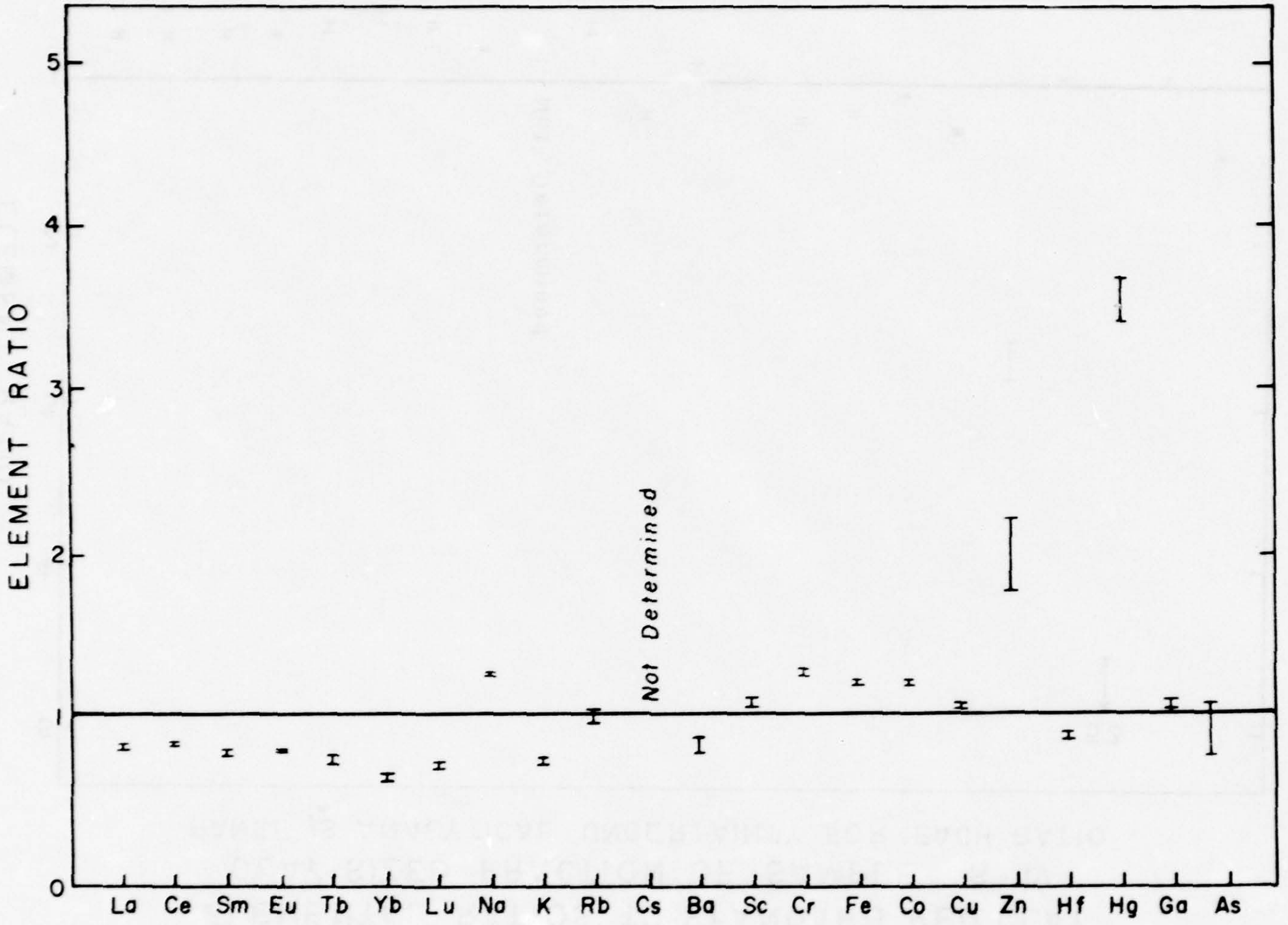
Table 6. The approximate concentrations of the clay-size fraction in some samples from the Lake Superior area.

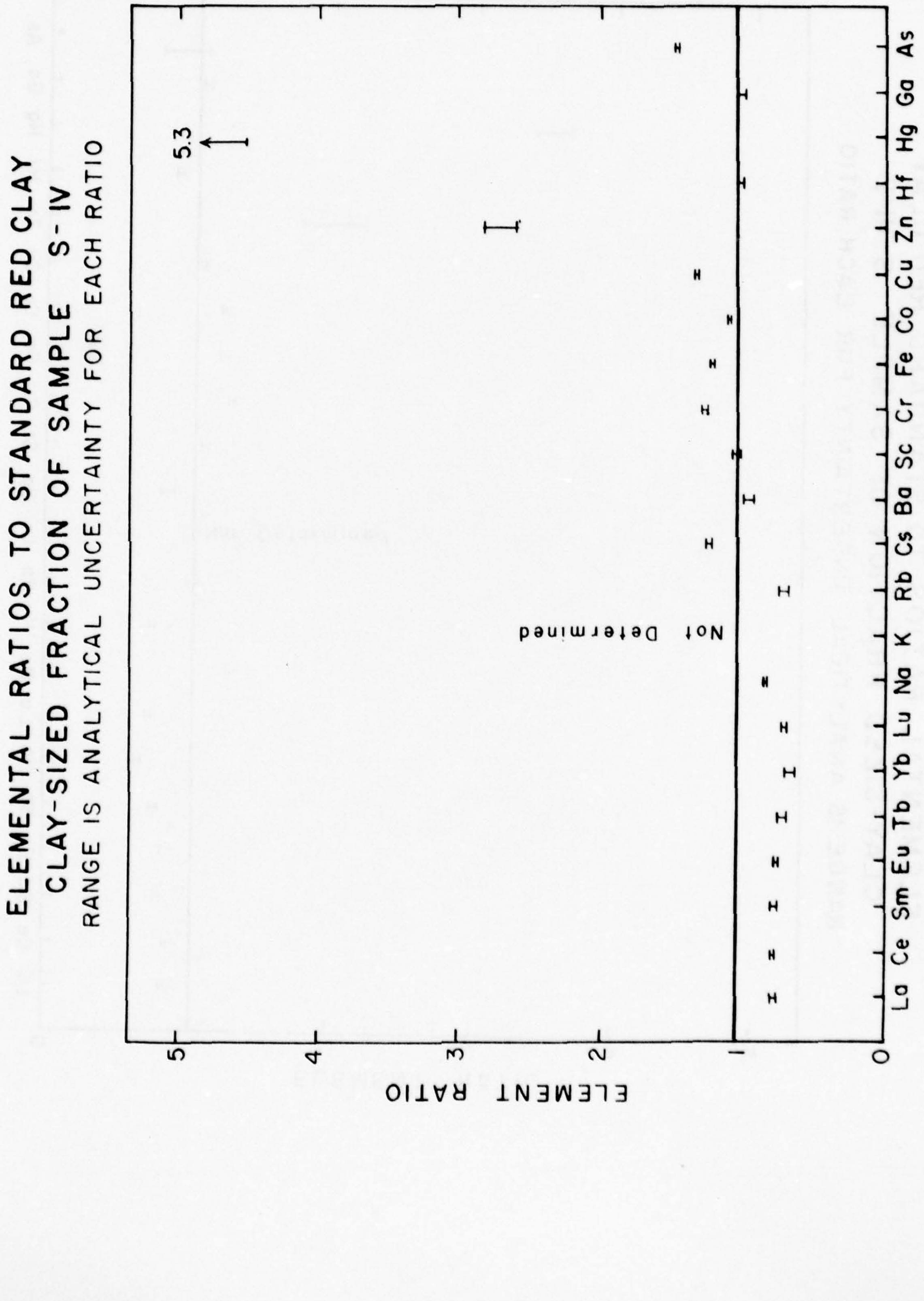
Sample	Percent Clay by Weight
S-1	8.2
S-2	6.0
S-3	4.1
S-III-1	3.6
S-III-2	14
S-IV	13
S-VII	8.3
S-VIII	2.9
S-IX	24
DDS-1	4.0
DDS-2	2.4
DC-I	11
A-30	0.4
B-8-2	0.6
H6	6
H7	7
H8	negligible
H9	negligible
H10	3

ELEMENTAL RATIOS TO STANDARD RED CLAY
CLAY-SIZED FRACTION OF SAMPLE S-III-1
RANGE IS ANALYTICAL UNCERTAINTY FOR EACH RATIO



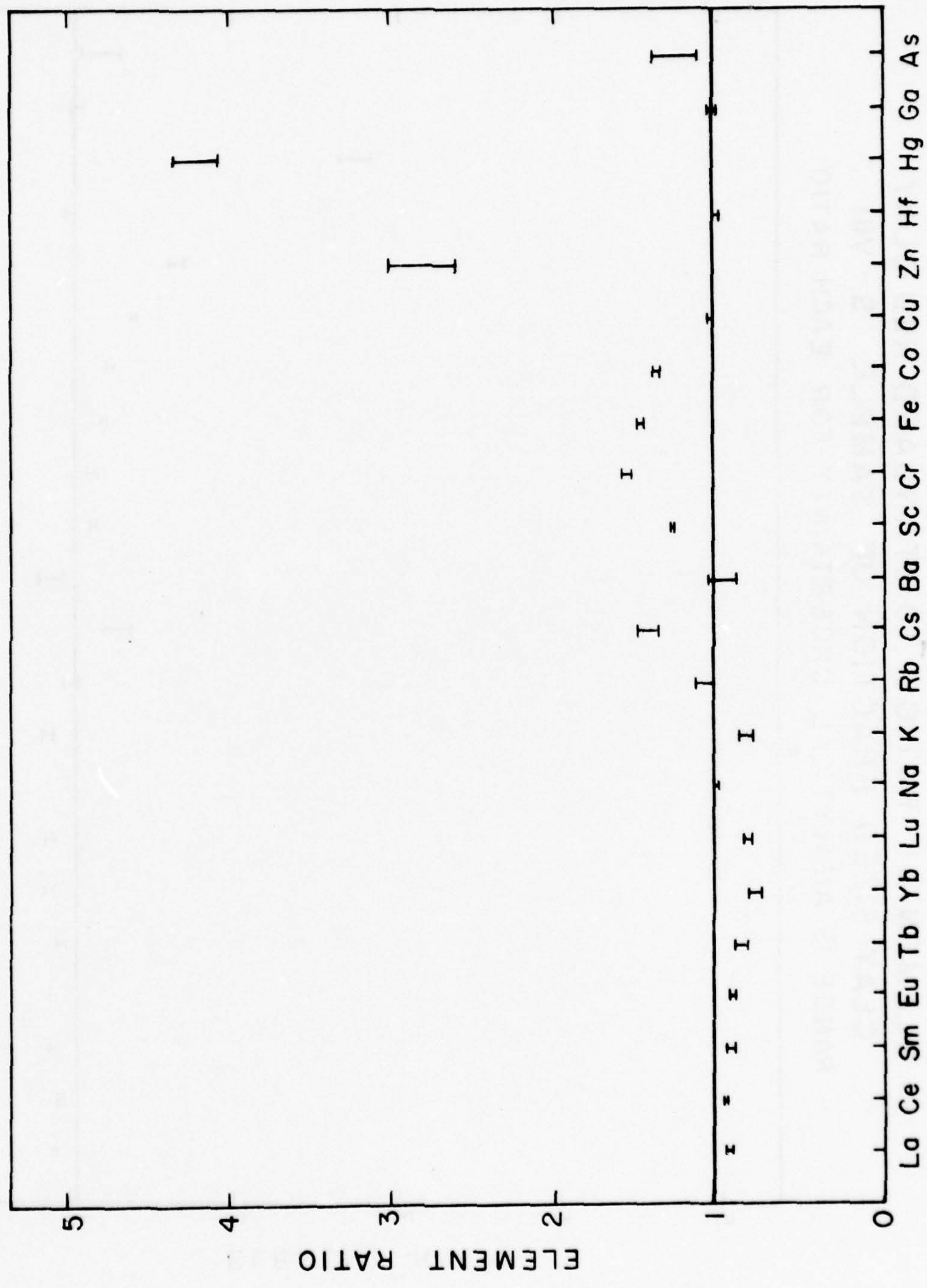
ELEMENTAL RATIOS TO STANDARD RED CLAY
CLAY-SIZED FRACTION OF SAMPLE S-III-2
RANGE IS ANALYTICAL UNCERTAINTY FOR EACH RATIO





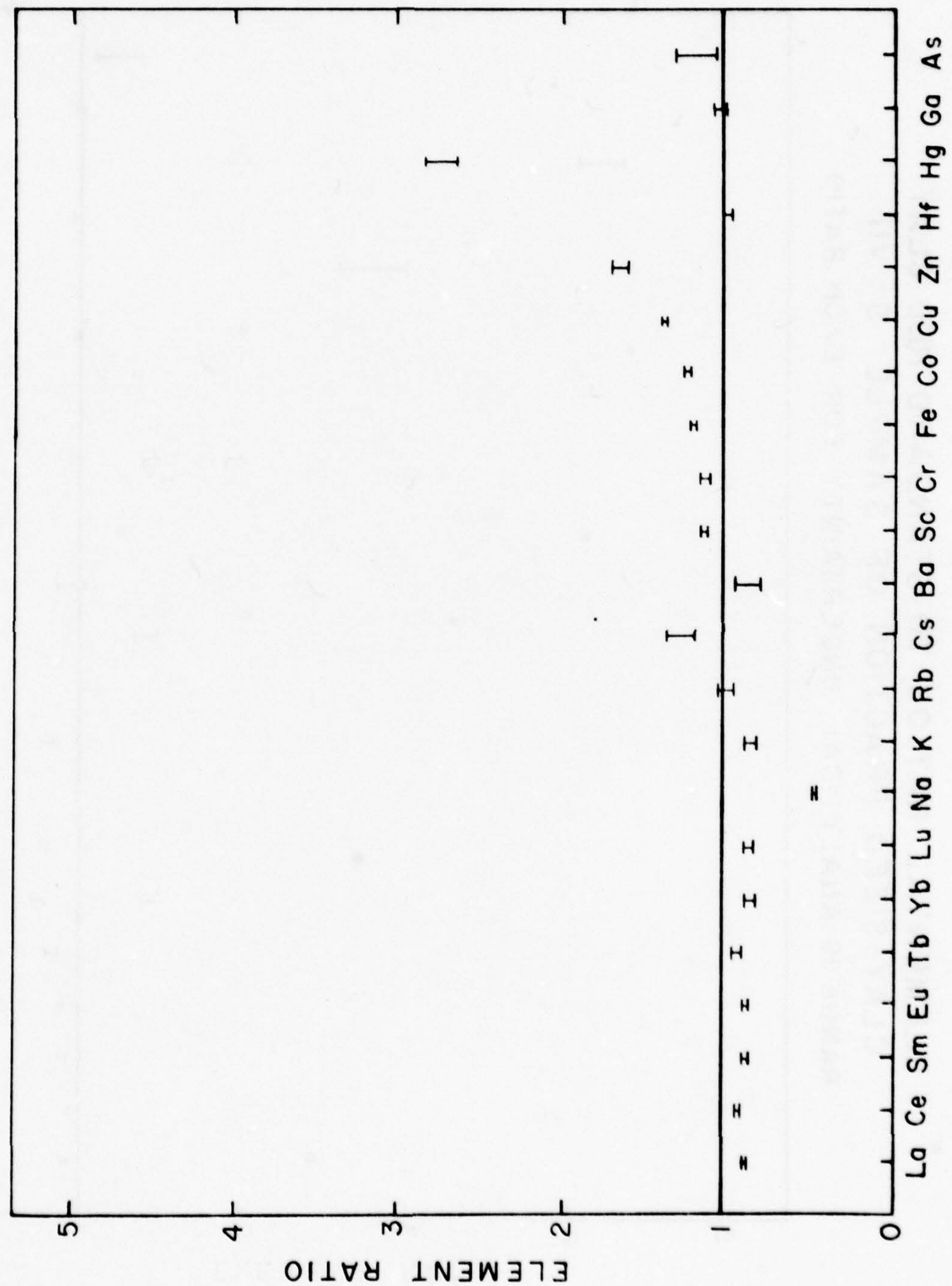
ELEMENTAL RATIOS TO STANDARD RED CLAY
CLAY-SIZED FRACTION OF SAMPLE S-IV
RANGE IS ANALYTICAL UNCERTAINTY FOR EACH RATIO

(figure 12)



ELEMENTAL RATIOS TO STANDARD RED CLAY
CLAY-SIZED FRACTION OF SAMPLE S-VII
RANGE IS ANALYTICAL UNCERTAINTY FOR EACH RATIO

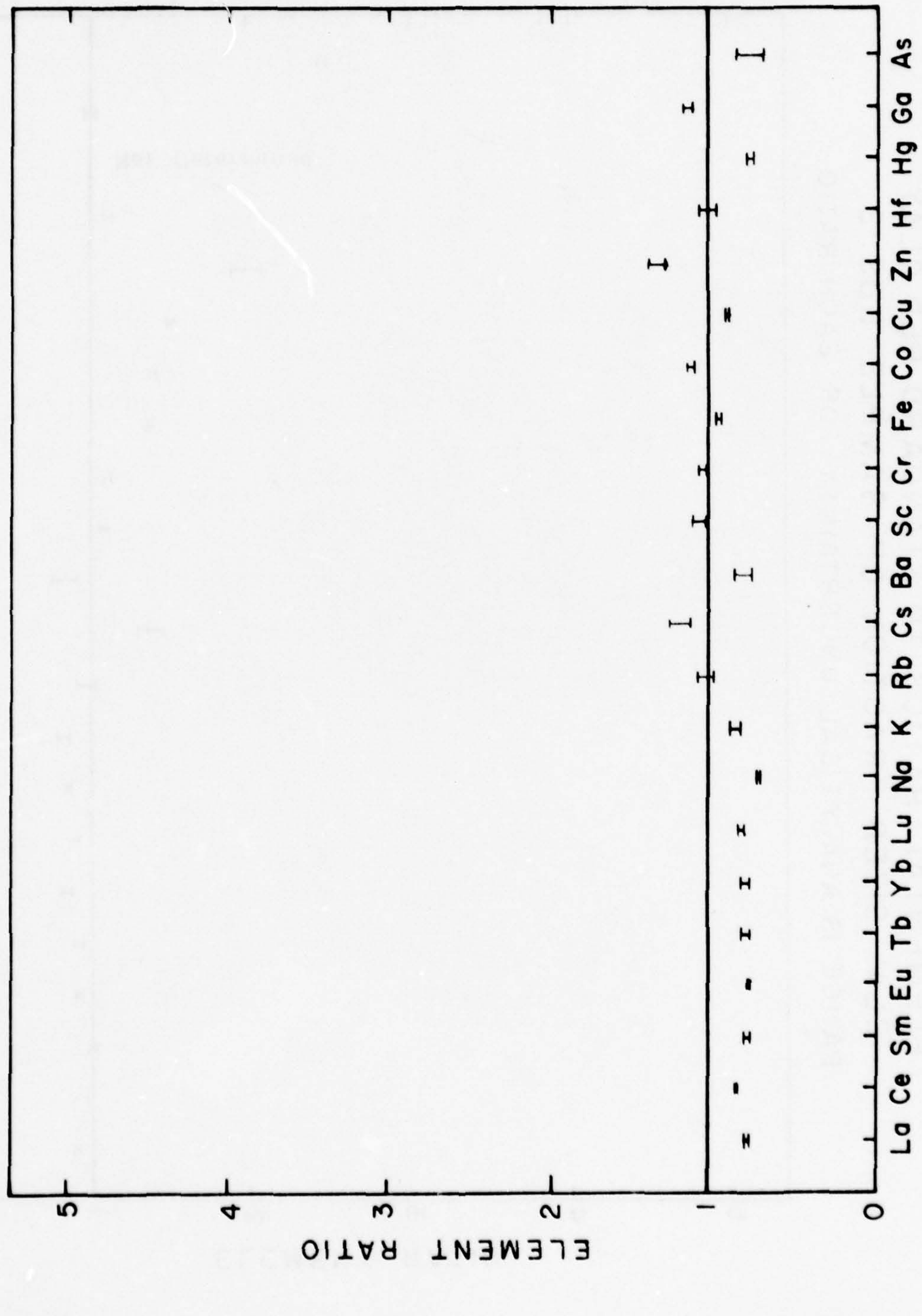
(figure 13)



ELEMENTAL RATIOS TO STANDARD RED CLAY

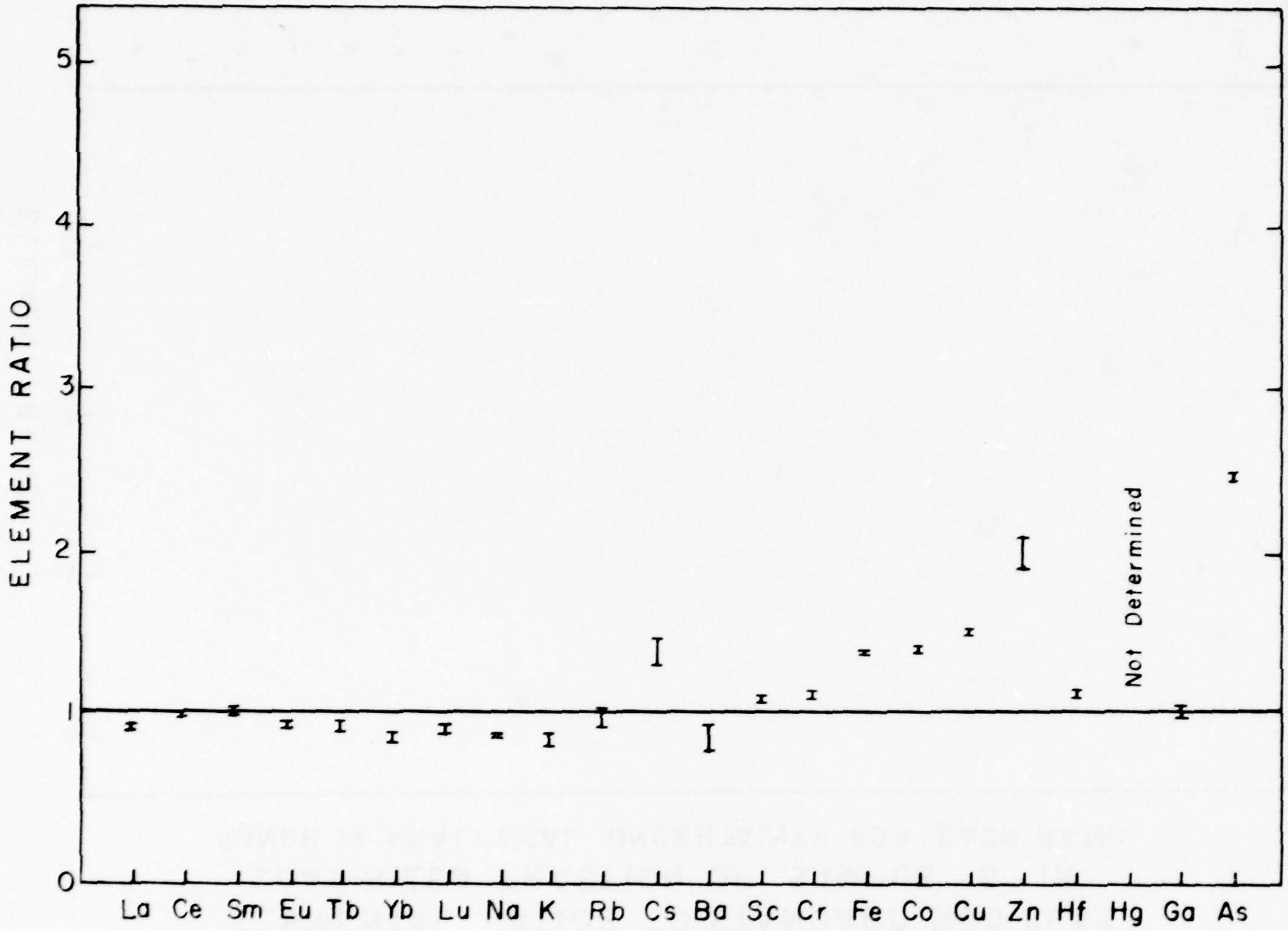
CLAY-SIZED FRACTION OF SAMPLE S-VIII

RANGE IS ANALYTICAL UNCERTAINTY FOR EACH RATIO



ELEMENTAL RATIOS TO STANDARD RED CLAY
CLAY-SIZED FRACTION OF SAMPLE S - IX
RANGE IS ANALYTICAL UNCERTAINTY FOR EACH RATIO

ELEMENTAL RATIOS TO STANDARD RED CLAY
CLAY-SIZED FRACTION OF SAMPLE DDS-2
RANGE IS ANALYTICAL UNCERTAINTY FOR EACH RATIO



E. Sediment Samples from Keweenaw

Two samples from Keweenaw: A-30 and B-8-2, contain only about 0.5% clay-sized materials compared to as much as 24% for the samples from Duluth-Superior. In addition, these values from the Keweenaw samples are possibly high because to collect even the percentages reported in Table 6 required 12 hours of shaking the sediment-water mixture. This compares to one hour of shaking for the Duluth-Superior sediments. We suspect that prolonged shaking produces a portion of the fine material collected from the Keweenaw samples by grinding the sand-sized particles. A sample produced by this mechanism will probably give little information about sediment quality.

The concentrations of trace elements in the samples collected from Keweenaw are given in Table 7. In the K series of samples, the concentrations of some elements vary by more than a factor of 20. There is a progressive decrease in the concentrations of most elements in the samples collected offshore from near the stampsands (K-1) to the samples collected offshore from the waterway entry (K-8). This is especially so for copper, 98 to 4.3 ppm, and zinc, 47 to 8.0 ppm in the total sediments. This trend is probably the result of increasing proportions of quartz and decreasing proportions of lithic fragments from sample number K1 to K8.

The current and wave action is apparently so strong at the Keweenaw area that most of the fine material is removed from the near-shore sediments. Environmental compartments other than the clay-size fraction need to be studied in this area to obtain information about the quality of the lake sediments. The presence of clay in the sediments of the Keweenaw Waterway suggests that procedures similar to those developed for the

Duluth-Superior area will be useful to determine the extent of trace element pollution in the areas to be dredged. We did not do additional studies of the Keweenaw sediments because of the intensive efforts of Michigan Technological Institute at Houghton.

Table 7. The concentrations of trace elements in ppm for samples of sediment from the Keweenaw area. The sample of silt-plus-clay consists of particles smaller than 50 microns and the sample of clay consists of particles smaller than 2 microns.

	A-30		
	Total Sediment	Silt + Clay	Clay
As	--	8 ± 3	44 ± 10
Ce	12.8 ± 0.3	43 ± 1	145 ± 4
Co	2.58 ± 0.04	15.1 ± 0.2	39.2 ± 0.7
Cr	15 ± 2	74 ± 7	186 ± 20
Cs	0.61 ± 0.08	2.6 ± 0.3	8 ± 2
Eu	0.37 ± 0.01	1.17 ± 0.01	2.66 ± 0.08
Fe	7200 ± 100	36100 ± 200	74000 ± 1000
Hf	2.4 ± 0.1	6.6 ± 0.3	5.8 ± 0.8
K	13000 ± 2000	18000 ± 3000	30000 ± 3000
La	9.4 ± 0.2	25.9 ± 0.5	54 ± 1
Lu	0.145 ± 0.007	0.41 ± 0.01	--
Mn	--	360 ± 250	1500 ± 700
Na	4680 ± 50	12600 ± 100	6100 ± 200
Rb	37 ± 4	70 ± 8	120 ± 30
Sc	1.95 ± 0.01	10.4 ± 0.1	27.2 ± 0.1
Sm	1.8 ± 0.1	5.5 ± 0.1	11.4 ± 0.8
Tb	0.27 ± 0.02	0.85 ± 0.05	2.1 ± 0.2
Yb	0.91 ± 0.05	2.8 ± 0.1	4.5 ± 0.5
Zn	12.1 ± 0.7	59 ± 2	308 ± 10

Table 7. (cont.)

	B-8-2		
	Total Sediment	Silt + Clay	Clay
As	--	8 ± 2	41 ± 9
Ce	19.6 ± 0.5	41.9 ± 0.7	70 ± 5
Co	11.9 ± 0.1	24.0 ± 0.2	49.1 ± 0.9
Cr	53 ± 5	112 ± 12	212 ± 25
Cs	1.1 ± 0.2	2.2 ± 0.3	5.7 ± 0.9
Eu	0.75 ± 0.01	1.31 ± 0.01	2.0 ± 0.1
Fe	25500 ± 200	52700 ± 200	78000 ± 1000
Hf	3.0 ± 0.2	7.1 ± 0.2	4.0 ± 0.9
K	17000 ± 2000	17000 ± 2000	25000 ± 3000
La	15.7 ± 0.3	21.7 ± 0.3	--
Lu	0.236 ± 0.006	0.40 ± 0.01	0.68 ± 0.06
Mn	--	640 ± 180	1100 ± 500
Na	9990 ± 50	14900 ± 70	6400 ± 100
Rb	52 ± 6	55 ± 6	110 ± 25
Sc	7.83 ± 0.02	16.7 ± 0.1	31.2 ± 0.2
Sm	3.1 ± 0.2	5.9 ± 0.1	8.3 ± 0.8
Tb	0.45 ± 0.04	0.89 ± 0.04	1.4 ± 0.3
Yb	1.64 ± 0.06	3.1 ± 0.1	4.0 ± 0.4
Zn	33 ± 2	67 ± 2	233 ± 12

Table 7. (cont.)

	K-1 Total	K-2 Total	K-3 Total	K-4 Total
Ba	392 ± 16	395 ± 11	402 ± 12	324 ± 13
Ce	28.8 ± 0.2	19.8 ± 0.2	26.6 ± 0.1	31.4 ± 0.2
Co	9.61 ± 0.07	3.89 ± 0.04	5.81 ± 0.04	5.35 ± 0.05
Cr	45.1 ± 0.7	20.8 ± 0.4	29.1 ± 0.5	31.4 ± 0.7
Cs	0.89 ± 0.05	0.75 ± 0.03	0.99 ± 0.04	1.25 ± 0.05
Cu	97.6 ± 0.7	28.4 ± 0.2	41.1 ± 0.3	41.8 ± 0.3
Eu	0.708 ± 0.006	0.517 ± 0.005	0.618 ± 0.005	0.635 ± 0.008
Fe	22300 ± 100	11550 ± 60	15040 ± 60	15160 ± 80
Ga	9.8 ± 0.2	6.2 ± 0.2	7.5 ± 0.2	7.2 ± 0.3
Hf	3.53 ± 0.06	3.76 ± 0.05	3.78 ± 0.06	4.98 ± 0.07
K	19400 ± 700	20300 ± 400	20200 ± 600	16200 ± 500
La	14.0 ± 0.1	11.3 ± 0.1	13.1 ± 0.6	15.7 ± 0.1
Lu	0.235 ± 0.006	0.193 ± 0.003	0.225 ± 0.004	0.252 ± 0.005
Na	10700 ± 20	5880 ± 10	8950 ± 20	8150 ± 20
Nd	12 ± 2	10 ± 1	X	X
Rb	56 ± 2	57 ± 1	56 ± 3	53 ± 2
Sb	0.52 ± 0.08	0.45 ± 0.04	0.61 ± 0.06	0.52 ± 0.06
Sc	6.42 ± 0.01	3.03 ± 0.01	4.38 ± 0.01	4.38 ± 0.01
Sm	2.77 ± 0.08	2.02 ± 0.04	2.51 ± 0.07	3.03 ± 0.02
Tb	0.26 ± 0.01	0.234 ± 0.008	0.31 ± 0.01	0.38 ± 0.01
Th	3.25 ± 0.05	2.85 ± 0.03	3.72 ± 0.04	5.06 ± 0.05
Yb	1.50 ± 0.06	1.24 ± 0.03	1.47 ± 0.05	1.71 ± 0.07
Zn	47 ± 1	20.8 ± 0.6	33.2 ± 0.6	37 ± 1

Table 7. (cont.)

	K-5 Total	K-6 Total	K-7 Total	K-8 Total
Ba	266 ± 10	290 ± 12	213 ± 8	215 ± 7
Ce	20.1 ± 0.1	21.5 ± 0.2	15.6 ± 0.1	14.2 ± 0.2
Co	2.02 ± 0.02	2.60 ± 0.04	1.36 ± 0.02	0.96 ± 0.02
Cr	13.7 ± 0.2	13.0 ± 0.5	10.7 ± 0.3	6.3 ± 0.2
Cs	6.4 ± 0.2	0.65 ± 0.05	0.54 ± 0.02	4.5 ± 0.2
Cu	7.35 ± 0.07	16.1 ± 0.2	5.62 ± 0.06	4.25 ± 0.04
Eu	0.38 ± 0.01	0.544 ± 0.005	0.283 ± 0.003	0.255 ± 0.008
Fe	10830 ± 50	8710 ± 60	7020 ± 40	3480 ± 30
Ga	4.2 ± 0.1	5.4 ± 0.1	3.3 ± 0.1	3.2 ± 0.1
Hf	1.97 ± 0.03	2.90 ± 0.05	2.08 ± 0.03	1.44 ± 0.03
K	13500 ± 300	14700 ± 500	9700 ± 300	9800 ± 400
La	11.5 ± 0.1	11.2 ± 0.2	9.45 ± 0.09	7.33 ± 0.07
Lu	0.153 ± 0.003	0.242 ± 0.005	0.148 ± 0.003	0.432 ± 0.009
Na	4330 ± 10	6210 ± 10	3480 ± 10	4300 ± 10
Nd	12 ± 1	13 ± 2	7.0 ± 0.8	6.2 ± 0.8
Rb	41 ± 1	40 ± 3	30 ± 1	29.0 ± 0.9
Sb	0.42 ± 0.04	0.34 ± 0.05	0.41 ± 0.04	0.24 ± 0.02
Sc	1.82 ± 0.005	2.17 ± 0.01	1.54 ± 0.005	0.917 ± 0.005
Sm	1.94 ± 0.05	2.23 ± 0.01	1.38 ± 0.01	1.14 ± 0.01
Tb	0.239 ± 0.006	0.32 ± 0.01	0.184 ± 0.008	0.137 ± 0.005
Th	3.79 ± 0.03	2.96 ± 0.05	2.36 ± 0.03	1.82 ± 0.02
Yb	1.01 ± 0.03	1.68 ± 0.07	1.03 ± 0.07	0.65 ± 0.03
Zn	13.5 ± 0.5	16.7 ± 0.8	10.6 ± 0.5	8.0 ± 0.4

F. Analytical Results for Sediment Core S-2

A sediment core 33 cm long was collected from a depth of 40 meters. The location of the sample site is shown in Figure 1b. Except for the top 1 cm, the core sample was sectioned at intervals of 2 or 4 cm. The analytical results for the clay-size fraction of these samples are given in Table 8.

The concentrations of elements are independent of the depth in the core from which the sample was taken--except those of arsenic, copper, iron, mercury and zinc which are higher in the upper sections of the core. The almost identical concentrations of most of the elements in the core samples indicate that the composition and proportions of materials deposited as sediment have remained constant for the period of time represented by the core. Some of the observed enrichment of the above elements may be due to natural processes of diagensis. The surface enrichment of these elements is thought to result from processes of dissolution involving reduction of the oxides of iron and manganese in the buried sediment, upward diffusion, and precipitation at levels higher in the sediment column as the result of an increase in the oxidation potential. This process is well documented in the oceanographic literature.

A portion of the surface enrichment may also be the result of pollution. Accurate values of the sedimentation rate are needed to determine if this is so. However, it is difficult and expensive to do, and this information is not available for the Duluth-Superior portion of the lake. The average rates of sedimentation indicated by analysis of cores collected from about 50 km from Grand Marais, MI at a depth of

141 m and about 10 km offshore from Wisconsin's Sand Island at a depth of 61 m ranged from 0.13 to 0.30 mm/year as determined by two independent methods (Bruland et al., 1974). With an assumed sedimentation rate of 0.3 mm/year for core S-2, material deeper than about 3 cm should be old enough to not be significantly affected by pollution. However, inspection of the results in Table 8 show that the sample from 3 to 5 cm is enriched in mercury and the sample from 7 to 9 cm is enriched in zinc and arsenic. The rate of sedimentation must be about 0.6 to 0.8 mm/year if the sample from 5 to 7 cm is enriched by pollution. This is clearly possible and even probable when one considers that the core came from an area which is characterized by frequent turbidity from stream run-off, shore erosion and re-suspension. Therefore, we cannot determine if the enrichment of some elements in the surface portions of the sediment is the result of pollution or natural processes. This predicament complicates somewhat the interpretation of the status of pollution of sediment samples, but a satisfactory approach is explained in section II, G of this report. The problems of interpretation of results introduced by diagensis is thought to be minimal for the harbor sediments because the rate of sedimentation is so high that there is no time for the necessary reactions to occur. This is fortunate because the most precise knowledge of the status of pollution is needed only for the areas to be dredged.

Table 8. The concentrations of trace elements in ppm for the clay fraction (< 2 microns) of sediment core S-2.

	Core S-2 Clay Fractions		
	0-1 cm	1-3 cm	3-5 cm
As	30 ± 3	31 ± 3	21 ± 2
Ba	390 ± 30	400 ± 30	460 ± 30
Ce	86.5 ± 0.5	91.6 ± 0.5	94.5 ± 0.6
Co	23.7 ± 0.5	25.3 ± 0.2	24.9 ± 0.5
Cr	111 ± 2	113 ± 2	118 ± 2
Cs	7.0 ± 0.2	6.9 ± 0.2	6.3 ± 0.2
Cu	88 ± 1	--	69 ± 1
Eu	1.37 ± 0.02	1.44 ± 0.02	1.43 ± 0.02
Fe	75500 ± 300	81000 ± 300	70800 ± 300
Hf	4.84 ± 0.07	5.0 ± 0.1	4.91 ± 0.07
Hg	0.41 ± 0.02	--	0.40 ± 0.02
K	21600 ± 800	22800 ± 900	24000 ± 1000
La	43.6 ± 0.4	44.4 ± 0.4	45.2 ± 0.4
Lu	0.54 ± 0.02	0.56 ± 0.02	0.58 ± 0.02
Mn	2320 ± 40	1440 ± 10	964 ± 6
Na	5000 ± 20	5070 ± 30	5520 ± 20
Nd	39 ± 7	32 ± 6	33 ± 5
Rb	99 ± 7	101 ± 4	110 ± 6
Sb	1.5 ± 0.1	1.6 ± 0.1	1.8 ± 0.1
Sc	18.1 ± 0.1	18.3 ± 0.1	19.3 ± 0.1
Sm	7.66 ± 0.05	7.93 ± 0.05	8.04 ± 0.05
Tb	1.06 ± 0.03	1.08 ± 0.04	1.11 ± 0.04
Th	16.2 ± 0.2	17.2 ± 0.2	17.4 ± 0.2
Yb	3.6 ± 0.2	3.7 ± 0.2	3.6 ± 0.2
Zn	201 ± 3	231 ± 4	233 ± 5

Table 8. (cont.)

	Core S-2 Clay Fractions		
	5-7 cm	7-9 cm	9-13 cm
As	21 ± 2	19 ± 2	15 ± 2
Ba	440 ± 40	450 ± 30	480 ± 30
Ce	93.1 ± 0.6	93.2 ± 0.5	104 ± 1
Co	23.8 ± 0.5	25.8 ± 0.5	27.1 ± 0.3
Cr	118 ± 2	123 ± 2	126 ± 2
Cs	6.3 ± 0.2	6.3 ± 0.2	6.3 ± 0.2
Cu	--	69 ± 1	--
Eu	1.40 ± 0.05	1.49 ± 0.04	1.57 ± 0.05
Fe	67100 ± 400	70900 ± 300	74500 ± 400
Hf	5.04 ± 0.08	5.3 ± 0.1	5.29 ± 0.08
Hg	--	0.10 ± 0.01	--
K	23000 ± 1000	23500 ± 900	25000 ± 1000
La	43.7 ± 0.5	47.3 ± 0.5	49 ± 1
Lu	0.56 ± 0.02	0.60 ± 0.02	0.63 ± 0.02
Mn	810 ± 20	906 ± 5	830 ± 10
Na	5410 ± 30	5260 ± 20	5680 ± 90
Nd	38 ± 6	41 ± 6	52 ± 8
Rb	111 ± 6	119 ± 6	114 ± 5
Sb	1.9 ± 0.1	1.5 ± 0.1	1.6 ± 0.1
Sc	19.3 ± 0.1	20.0 ± 0.1	20.9 ± 0.1
Sm	7.78 ± 0.05	7.85 ± 0.05	8.9 ± 0.2
Tb	1.13 ± 0.04	1.14 ± 0.03	1.21 ± 0.04
Th	17.4 ± 0.2	17.7 ± 0.2	19.0 ± 0.2
Yb	3.7 ± 0.2	3.8 ± 0.2	4.2 ± 0.2
Zn	222 ± 5	186 ± 3	162 ± 4

Table 8. (cont.)

	Core S-2 Clay Fractions		
	13-17 cm	17-21 cm	21-25 cm
As	12 ± 2	13 ± 1	12 ± 2
Ba	460 ± 30	530 ± 40	430 ± 30
Ce	101 ± 1	92.1 ± 0.6	91.9 ± 0.5
Co	24.1 ± 0.1	24.2 ± 0.2	25.0 ± 0.5
Cr	123 ± 2	125 ± 2	122 + 2
Cs	6.4 ± 0.2	6.3 ± 0.2	6.1 ± 0.2
Cu	64 ± 1	--	63 ± 1
Eu	1.50 ± 0.02	1.48 ± 0.01	1.45 ± 0.04
Fe	70700 ± 400	69700 ± 200	70500 ± 300
Hf	5.36 ± 0.08	5.5 ± 0.1	5.38 ± 0.09
Hg	0.60 ± 0.02	--	0.18 ± 0.01
K	24000 ± 1000	24400 ± 900	25000 ± 1000
La	47.3 ± 0.4	47.9 ± 0.5	46 ± 1
Lu	0.63 ± 0.02	0.60 ± 0.02	0.61 ± 0.02
Mn	663 ± 4	672 ± 4	697 ± 13
Na	5480 + 30	5620 ± 90	05460 ± 30
Nd	48 ± 8	36 ± 6	41 ± 6
Rb	115 + 8	127 ± 6	118 ± 6
Sb	1.3 ± 0.1	1.2 ± 0.1	1.3 ± 0.1
Sc	20.3 ± 0.2	20.5 ± 0.1	19.9 ± 0.1
Sm	8.4 ± 0.2	8.36 ± 0.05	8.5 ± 0.2
Tb	1.18 ± 0.04	1.20 ± 0.04	1.17 ± 0.03
Th	18.9 ± 0.2	18.7 ± 0.2	18.2 ± 0.2
Yb	4.1 ± 0.2	4.0 ± 0.2	3.9 ± 0.2
Zn	164 ± 10	176 ± 3	176 ± 6

Table 8. (cont.)

	Core S-2 Clay Fraction	
	25-29 cm	29-33 cm
As	10 ± 1	13 ± 1
Ba	470 ± 30	430 ± 30
Ce	96.3 ± 0.6	100 ± 1
Co	24.3 ± 0.2	27.5 ± 0.5
Cr	123 ± 2	125 ± 2
Cs	6.5 ± 0.2	6.3 ± 0.2
Cu	--	64 ± 1
Eu	1.45 ± 0.04	1.60 ± 0.04
Fe	69900 ± 400	71500 ± 300
Hf	5.17 ± 0.07	5.5 ± 0.1
Hg	--	<0.20
K	21000 ± 800	24100 ± 900
La	45.4 ± 0.4	50.0 ± 0.5
Lu	0.60 ± 0.02	0.62 ± 0.02
Mn	677 ± 4	820 ± 10
Na	4530 ± 20	5430 ± 20
Nd	49 ± 8	50 ± 8
Rb	104 ± 5	113 ± 5
Sb	1.2 ± 0.1	1.5 ± 0.1
Sc	20.1 ± 0.2	20.5 ± 0.1
Sm	8.26 ± 0.05	8.91 ± 0.06
Tb	1.14 ± 0.03	1.20 ± 0.04
Th	18.2 ± 0.2	18.7 ± 0.2
Yb	4.0 ± 0.3	4.0 ± 0.2
Zn	154 ± 9	191 ± 6

G. Guideline Values of Concentrations of Trace Elements in the Clay-Size Fraction

The quality of the sediment in the disposal area can be enhanced, degraded, or unchanged by the dredged material dumped on it. Disposal of sediment into the lake may result in the new sediment having higher, lower, or the same concentrations of trace elements as the original sediment. The guideline values developed in this section are based on the assumption that the disposal of dredged materials should not change the quality of the present sediments in the lake with respect to trace elements. These initial guidelines will then be evaluated further in later sections of this report which deal with results found in the study of trace elements in organisms and their relationship to sediments.

The approximate background values for the clay-size fraction from the Duluth-Superior area are 180 ppm zinc, 75 ppm copper and 0.2 ppm mercury. These values are suggested by three pieces of evidence. First of all, they approximate the values found for the clay-size fraction from sediment core S-2 (Table 8). Second, the above values are the most common values found when all of the results are considered. There are no samples with values significantly lower than the above results. The third bit of evidence is provided by the results found for a core sample of sediment reported by Korda et al. (1976). This core sample was collected 14 km offshore from Tofte, Minnesota at a depth of about 180 meters. Although this sample was collected several hundred km from our study site and only the total sediment was analyzed, the results for the prehistoric portion of the core (Table 9) are very similar to the values we found in the clay-size fraction from the Duluth-Superior area. The sediment in the region from which the Tofte core was collected probably consisted of mostly small particles because of the core's depth and distance from shore; therefore, the results can be compared with some confidence. The values of 65-72 ppm copper and 140 to 160 ppm zinc found for the prehistoric portion of the Tofte core are only slightly lower than those suggested by the other two lines of evidence.

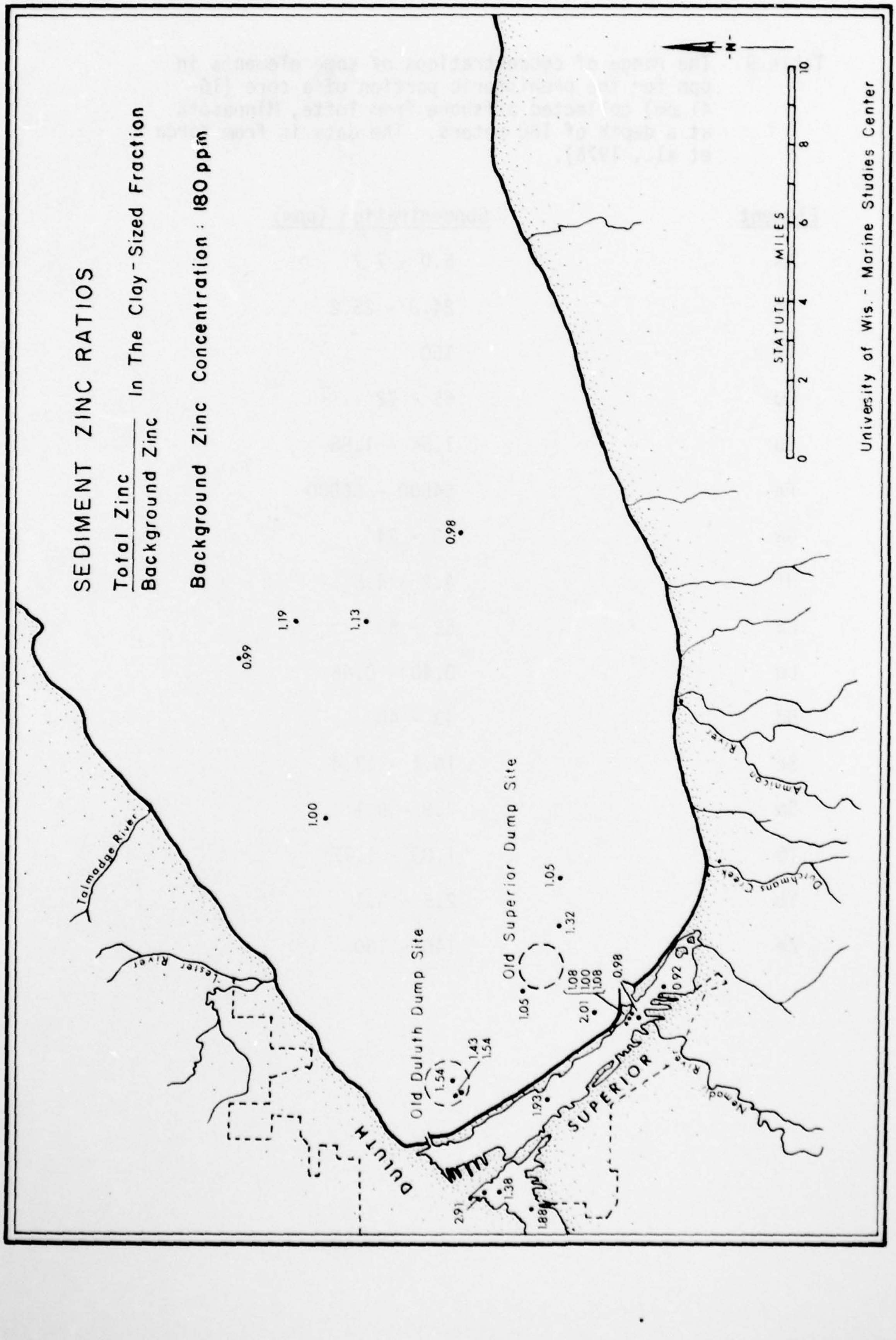
The background values suggested above are slightly higher than the lowest values found for these elements in the red clay and the deeper portions of the sediment core. However, they are representative of the values found for much of the sediment from this portion of the lake. The minimum values suggested by the concentrations found in the red clay and the sediment core are about 65 ppm copper, 140 ppm zinc and 0.1 ppm mercury.

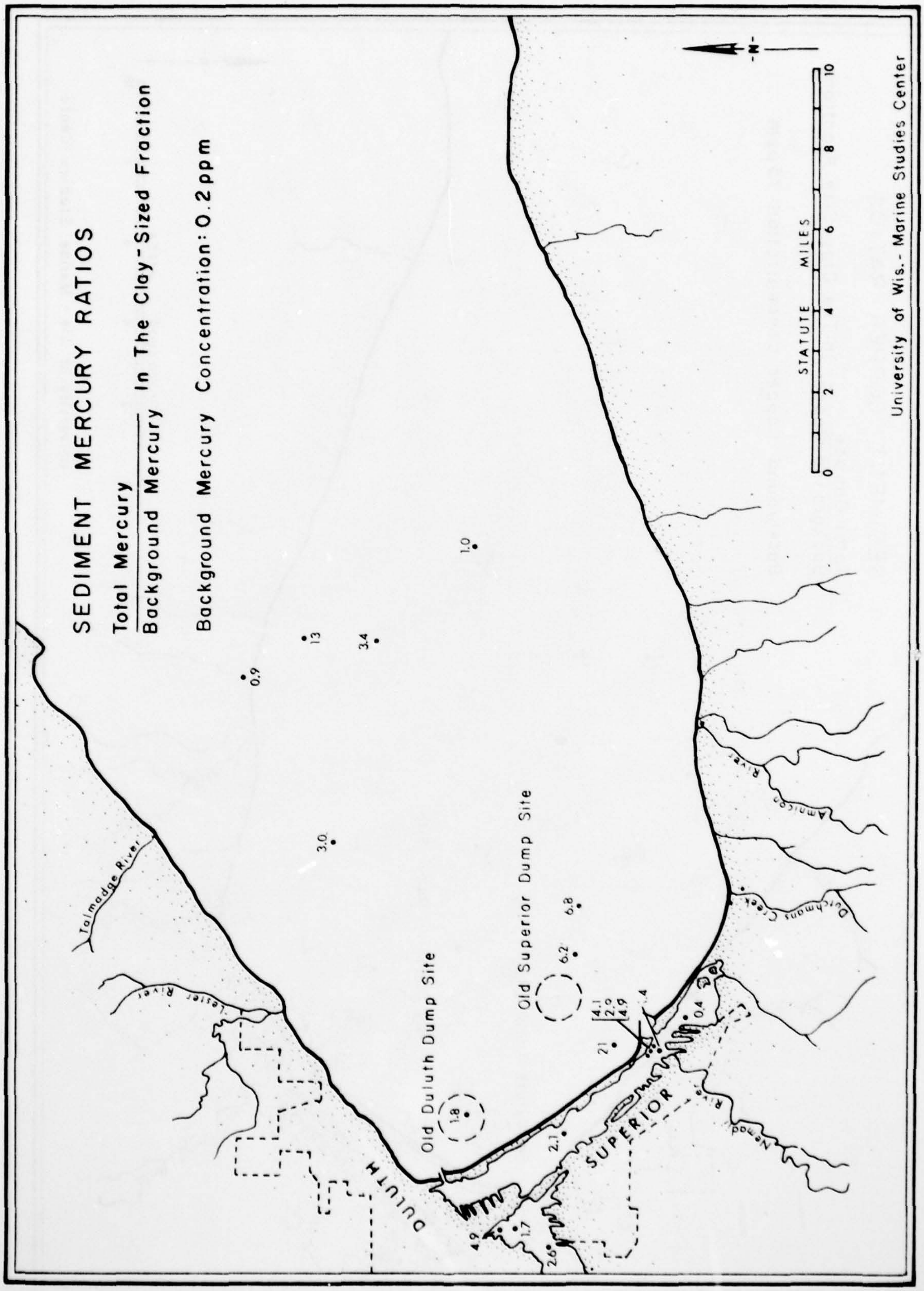
The extent of enrichment of zinc, copper and mercury in the sediments from the Duluth-Superior harbor and nearby Lake Superior is shown in Figures 16-18. The values shown in these figures are the ratios of the concentration of each element in the clay-size fraction to the background values of 75 ppm copper, 180 ppm zinc and 0.2 ppm mercury. A value of near one shows that the concentration of that element in the clay-size fraction is near the background value.

The values for zinc in the deeper portions of the lake are all near one (Figure 16). The values are higher in the areas of the old dump sites, reaching a value of 1.54 at the Duluth dump site. The highest value found for the samples from the lake is 2.01 near Minnesota Point. For the harbor, all of the samples from near Superior Entry have values of about one. The sample with the highest value (2.91) is from near the Duluth sewage outfall.

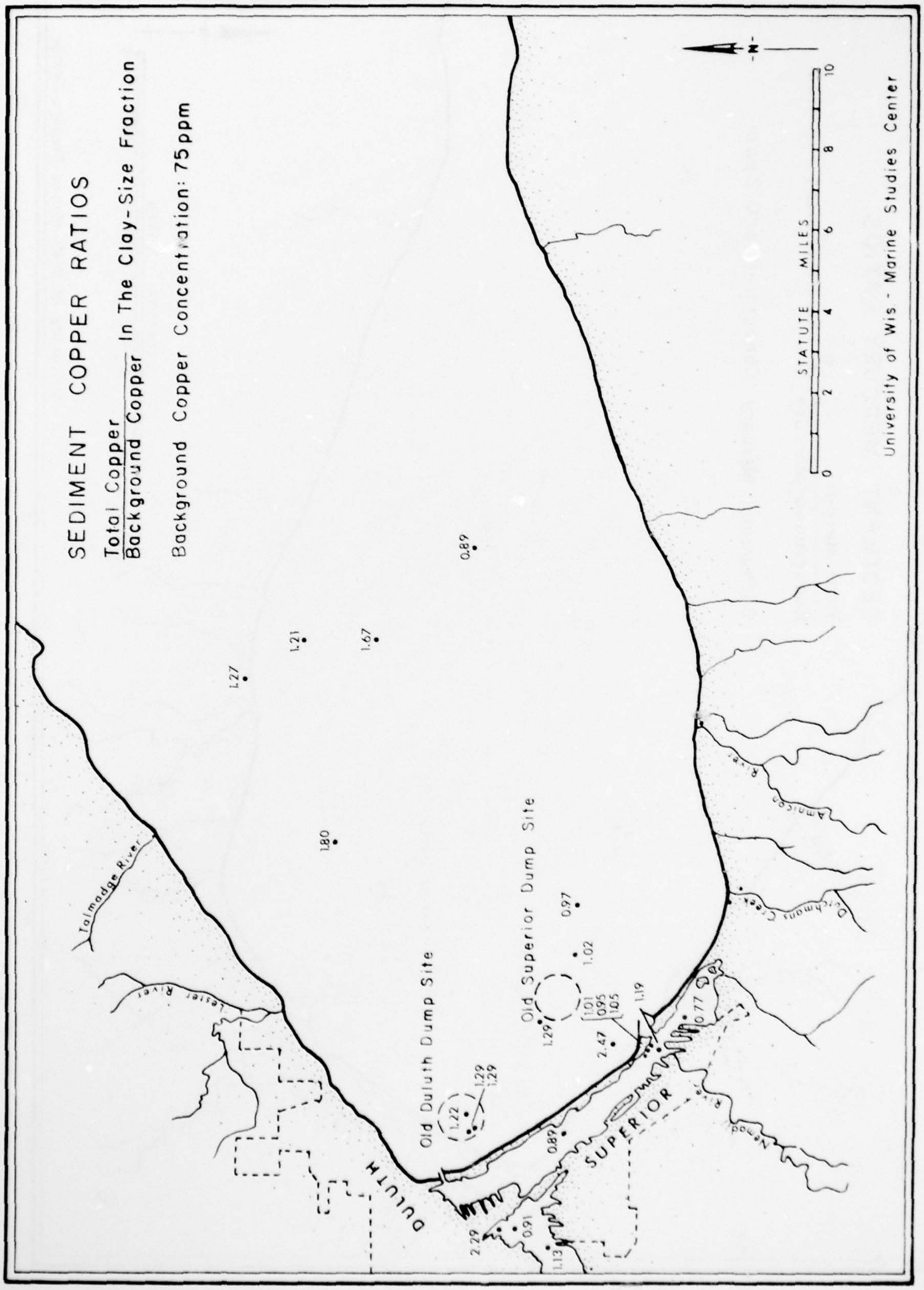
Table 9. The range of concentrations of some elements in ppm for the prehistoric portion of a core (16-41 cm) collected offshore from Tofte, Minnesota at a depth of 180 meters. The data is from Korda et al., 1976).

Element	Concentration (ppm)
As	6.0 - 7.7
Co	24.3 - 25.2
Cr	150
Cu	65 - 72
Eu	1.54 - 1.88
Fe	54500 - 56000
Ga	23 - 24
Hf	4.2 - 4.5
La	52 - 59
Lu	0.40 - 0.46
Nd	43 - 49
Sc	16.1 - 17.4
Sm	7.9 - 9.1
Tb	1.09 - 1.17
Yb	2.5 - 3.1
Zn	140 - 160


SEDIMENT ZINC RATIOS
Total Zinc / Background Zinc In The Clay-Sized Fraction
Background Zinc Concentration: 180 ppm
0.99
1.19
1.13
0.98
1.00
1.05
1.32
1.05
1.08
1.00
1.08
2.01
0.98
0.92
1.54
1.43
1.54
1.93
1.38
2.91
1.88
Old Duluth Dump Site
Old Superior Dump Site
Talmadge River
Lester River
Amnicon River
Dutchmans Creek
Nemadji River
DULUTH
SUPERIOR
N
0 2 4 6 8 10
STATUTE MILES
University of Wis. - Marine Studies Center


SEDIMENT MERCURY RATIOS
Total Mercury / Background Mercury In The Clay-Sized Fraction
Background Mercury Concentration: 0.2 ppm
STATUTE MILES
0
2
4
6
8
10
N
University of Wis.- Marine Studies Center
Talmadge River
Lester River
Amnicon River
Dutchmans Creek
Nemadji River
DULUTH
SUPERIOR
Old Duluth Dump Site
Old Superior Dump Site
1.8
2.1
4.9
1.7
2.6
21
4.1
2.0
4.9
.4
0.4
6.2
6.8
3.0
0.9
13
3.4
1.0

(figure 18)


SEDIMENT COPPER RATIOS
Total Copper / Background Copper In The Clay-Size Fraction
Background Copper Concentration: 75ppm
N
STATUTE MILES
0
2
4
6
8
10
University of Wis - Marine Studies Center
0.89
1.27
1.21
1.67
1.80
0.97
1.02
Old Superior Dump Site
Old Duluth Dump Site
1.29
1.01
0.95
1.05
1.19
2.47
1.22
1.29
1.29
0.89
0.77
2.29
0.91
1.13
DULUTH
SUPERIOR
Talmadge River
Lester River
Amnicon River
Nemadji River
Dutchmans Creek

AD-A073 268 WISCONSIN UNIV-MADISON MARINE STUDIES CENTER F/G 13/2
AN ASSESSMENT OF THE ENVIRONMENTAL EFFECTS OF DREDGED MATERIAL --ETC(U)
MAR 76 P A HELMKE, R D KOONS, I K ISKANDAR DACW37-74-C-0013

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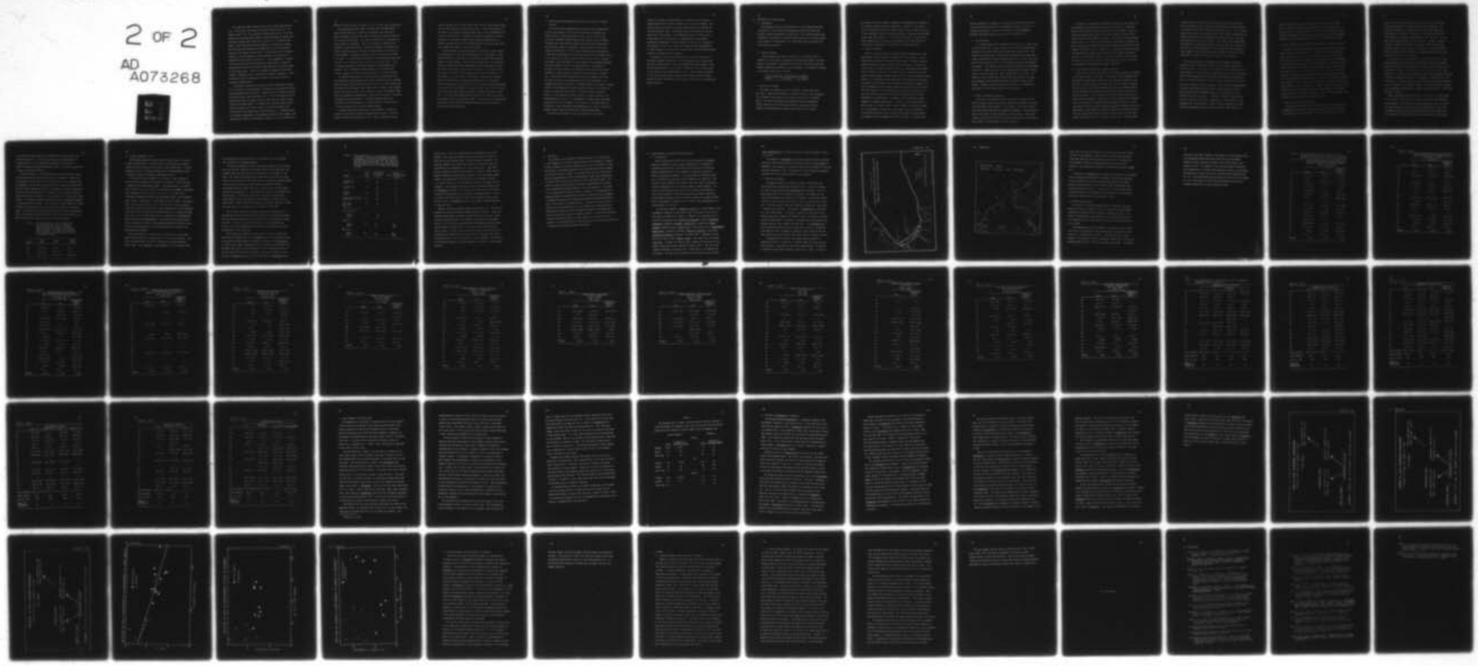

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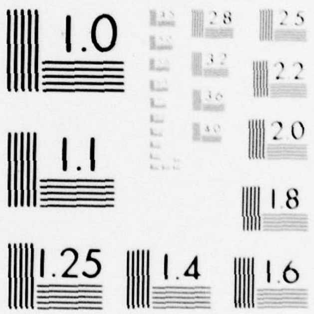

MICROCOPY RESOLUTION TEST CHART
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The values for copper (Figure 18) are more variable than those of zinc. All but two of the samples have values greater than one. The highest value is 2.47 for the sample from Minnesota Point. All of the samples from the harbor have values of about one except the sample from the Duluth sewage outfall which has a value of 2.3. Except for this sample, none of the harbor samples appear to be polluted with copper. We do not know what processes are responsible for the high values of copper for the samples from the lake. It may be the result of natural processes, such as diagensis as discussed earlier in section II, G, combined with the results of pollution. If this hypothesis is correct, some of the variability of the values for copper shown in Figure 18 are probably the result of the Ponar dredge sampling to different depths at the various sites. There is no evidence to suggest that any such process of diagensis occurs in the harbor sediments; therefore, it does not detract from the usefulness of using the clay-size fraction to determine sediment quality.

The values for mercury are even more variable than those of copper. As is the case for zinc and copper, the sample from Minnesota Point also has the highest ratio for mercury. Sample 45 from the deeper portions of the lake also has a very high ratio of 13. All of the samples from the harbor have values for mercury that are lower than the highest values found for the lake samples. The sample from the Duluth sewage outfall shows the highest ratio with a value of 4.9 while the sample from Allouez Bay has the lowest with a value of about 0.4. Although mercury is also more concentrated in the uppermost portions of the sediment core (see Table 8), there is no evidence to indicate if this is produced by a mechanism similar to that for copper, or if it is the result of pollution.

The preceding discussion makes it evident that the magnitude of trace element pollution is difficult to determine even after gross sample to sample variations are largely eliminated by using the results for the clay-size fraction. The status of pollution by zinc appears to be the easiest to determine. Some of the variability found for the elements of copper and mercury in the lake sediments are probably the result of natural processes that enrich these elements in the surface of the sediment. Additional evidence for this is found in the results for arsenic. It is enriched in the surface of the sediment by more than a factor of two as shown by the results for the sediment core. Also, like copper and mercury, the values found for the lake samples are variable. This is expected if these elements are enriched in the surface sediment and if the Ponar dredge samples to different depths.

An important observation is that the range of concentrations for the elements not used commonly by man, such as the rare earths, scandium, gallium, barium, hafnium and cobalt are small for all of the samples from the lake and from the harbor (see Figures 9-15). However, those elements used by man, such as copper, zinc and mercury, show a considerable range above the background concentrations in the clay-size fraction. Pollution of sediments by these elements is indicated although some of the variability in the concentrations of these elements may be the result of natural processes such as those discussed above.

A maximum background concentration of each element is needed to account for the natural surface enrichment which can occur. The core samples contained concentrations of zinc, copper, and mercury in the surface sediments (0-5 cm) which are higher than the concentrations found for the lower portions of the core (21-33 cm). These concentrations in the lowest core sections are approximately equal to the concentrations in the local red clay soils. Therefore, this core is assumed to be representative of the range of natural trace element concentrations in a vertical sediment section for the Duluth-Superior area of the lake, with trace element enrichment in the surface layers.

An approximation to the minimum extent of pollution of these samples can be determined if the maximum concentrations of the elements in the surface sediment of core sample S-2 are used to represent the background values for these elements. Based on this sediment core, our estimate of maximum, natural trace metal concentrations are 88 ppm copper, 230 ppm zinc and 0.4 ppm mercury in the clay-size fraction. For Figures 16-18, the values of the ratios that represent the maximum background are 1.2 for copper, 1.3 for zinc and 2.0 for mercury. These results indicate that the old dump sites in the lake and several areas in the Duluth portion of the harbor are enriched in zinc and pollution must be suspected as a source of this enrichment. For copper, three areas of the lake have values well above the maximum background, indicating pollution at these sites. The only harbor sample with a high ratio for copper and mercury is from the vicinity of the sewage outfall. Several areas of the lake have ratios that are well above the maximum background values for mercury, indicating pollution by mercury.

H. Conclusions and Recommendations Based on the Results of Sediment Studies.

The results of multielement analysis show that the concentrations of most trace elements in the clay-size fraction of sediments are almost uniform in the Duluth-Superior area. The use of this size fraction to determine sediment quality with respect to trace elements eliminates the large sample-to-sample variations often obtained when total sediment samples are analyzed. Some variability of the trace element concentrations is still present because natural processes can enrich some trace elements in the surface portions of the sediment, such as was shown by the results obtained from the sediment core. However, the extent of this enrichment is small enough so that sediments polluted with trace elements can still be detected easily. We consider it unlikely that trace elements are enriched in the surface of the harbor sediments by natural processes because of the high rate of sedimentation. Future work should include the analysis of sediment cores from the harbor to verify the assumed absence of surface enrichment. We recommend that future evaluations of sediment quality with respect to trace elements in Duluth-Superior and other harbors be based on the results of analysis of the clay-size fraction. The use of neutron activation analysis is not required for future studies of sediment quality in the Duluth-Superior area, but it is recommended for harbors where background concentrations of trace elements are not known. We recommend that the technique of atomic absorption spectrophotometry be used for analysis of sediment quality where background levels have been determined.

The possible enrichment of some trace elements in the surface sediments precludes the determination of a single value for the background concentrations of these elements in the clay-size fraction. The minimum values are 140 ppm zinc, 65 ppm copper and 0.1 ppm mercury for the Duluth-Superior area. The maximum values are 230 ppm zinc, 88 ppm copper and 0.4 ppm mercury. We recommend the values of 180 ppm zinc, 75 ppm copper and 0.2 ppm mercury as representing the approximate background concentrations of these elements in the clay-size fraction of the sediments in this area. Samples of sediment having concentrations of these elements in the clay-size fraction higher than the maximum values, should be suspected of being polluted.

Evaluation of the results obtained from the clay-size fraction of the harbor sediments shows that of all the sampled sites, the area near the Duluth sewage outfall is the most polluted with trace elements, while the area near Allouez Bay is pristine. Sediment from the old dump sites in the lake have high concentrations of zinc. A map showing the quality of the harbor sediments with respect to trace elements should be made using the results of analysis of the clay-size fraction and a comprehensive sampling program.

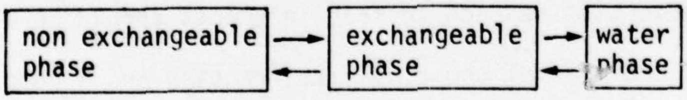
III. Availability of Trace Elements

A. Introduction

The background values of concentrations of trace elements described in section II of this report were determined without considering the effects of these concentrations on the biota. This section provides some information on procedures to determine what proportion of the total amount of any element in the sediment is in a form that might be available for assimilation by organisms.

B. Present Knowledge

A large proportion of the total content of any element found in a sediment is not available to organisms or to the water column. The total amount of any element in sediments or soils can be classified into three general categories according to current knowledge. The categories (phases) are related to each other as follows:



1. Definition of Phases

The phases are thought to be in a condition of steady state with each other. Generally, the phases are defined in terms of the time needed for an element in one phase to react and be classified in a different phase. The reactions between the exchangeable and non-exchangeable (fixed) phases are slow, often requiring years, while the reactions between the exchangeable and soluble phases require hours or days.

Any element in the fixed phase is thought to be unavailable to organisms or to the water column under normal conditions. Elements in the soluble phase are probably available to organisms and the water column, and those in the exchangeable phase can be made available to organisms and the water column under many conditions. The relative proportions of each of the phases depends upon the methods of measurement, which make difficult a quantitative interpretation of availability in laboratory tests.

2. Analytical Methods

There is no single analytical method suitable to define each of the above phases. Most procedures to determine the availability of trace elements are the result of research in agriculture. The most successful approach has been to leach a sample of soil with water or a solution of acids, salts or complexing reagents (EDTA, etc.) and analyze the leachate for the element of interest. The results are then correlated with the uptake of that element by plants grown in the soil and other quality factors. However, it is important to note that none of the procedures can predict the uptake of trace elements (and presumably availability) _a priori_. All of the procedures require extensive calibration experiments in the field. Often the uptake of trace elements varies according to the type of soil and plants which then require field calibration experiments for each combination of circumstances. The uptake of trace elements by aquatic organisms is probably more complex. In fact, it is not known whether food or water is the major source of trace elements to aquatic organisms. It is unreasonable to expect any simple chemical test of sediments to yield results that can be used to predict the uptake of trace elements by organisms with the knowledge available at present. We propose that the best approach is to develop a test that yields results which can be correlated with the uptake of trace elements by organisms in field or laboratory experiments. Some of this research is being funded by Waterway Experiment Station using results of elutriate tests.

3. Elutriate Tests

In a recent study of the elutriate test by Lee, et al. (1975), they concluded that copper, cadmium, lead, and zinc were not released from sediments to the water under aerated conditions (pages 176-181, their report) even though some of their sediments contained much higher than normal concentrations of these elements (page 125). In fact, they found that the concentrations of Zn in the water were reduced by the presence of sediment. The elements iron and lead were released from the sediments under anoxic (reducing) conditions and manganese was released in either anoxic or aerated conditions. Other elements were not studied. The results of the elutriate study indicate that the transfer of soluble trace elements from disturbed sediments to the water column can be minimal. However, the same results give little or no information on the extent of trace element pollution of the sediment.

4. Effect of Dredging and Dumping

There are two situations during the disposal of dredge spoil in which it appears useful to have data concerning the content of exchangeable and soluble trace elements in the sediment. The first situation occurs during the operations of dredging and dumping. The main concern here is the effect of these operations on water quality. The second concern is the long-term effects of dumping dredge spoil in the lake on the content of trace elements in benthic organisms.

The effects of the dumping and dredging operations on the content of trace elements in water were not included in this study. A literature survey of such effects has been done by Lee and Plumb (1974). They concluded that these effects tend to be of short duration in most circumstances because of the effects of dilution. The results of the elutriate study by Lee, et al (1975) also indicate that the effects of dredging and spoil disposal have minimal effects on the soluble concentrations of trace elements in the water column. However, it is important to note that short-term observations of water quality changes during dredging and dumping operations, and laboratory analysis of sediment elutriate cannot be used to predict the long-term effects of dumping dredge material in the lake on the uptake of trace elements by aquatic organisms.

5. Trace Element Availability to Aquatic Organisms

There are at least two mechanisms by which trace elements in sediments can be made available to organisms. The release of trace elements from the sediment to water where they may be assimilated by organisms is one mechanism. This has been studied intensively for Lake Superior samples by Glass (1973). He collected sediment cores and water samples from an area of 400 square miles where the bottom of the lake was covered with taconite tailings. A set of samples was also collected from 3 cm to 30 meters above the sediment. Samples of interstitial water were collected from 1.3, 3.8 and 6.3 cm below the sediment-water interface. The concentrations of calcium, copper, maganese, magnesium, potassium and silica were higher in the samples of interstitial water from the tailings than from the corresponding samples from the sediment, which, in turn, were higher than those found for the samples of lake water. Although higher concentrations were found in the interstitial water from the tailings area, no differences were found in the concentrations of these elements in the water column from the affected and central sites. In a literature survey of this and other studies, Lee and Plumb (1974) concluded that the chemical characteristics of interstitial water has little or no effect on the quality of the overlying water. Any soluble forms released from the sediment are apparently diluted to such an extent that the impact on water quality cannot be measured. This indicates that the transfer of trace elements from interstitial water to the water column is of minor importance to organisms in the water column for the short-term.

The second mechanism is the uptake of trace elements by benthic organisms from the interstitial water (the exchangeable phase) and/or from their food in the sediment. The generally higher concentrations of trace elements in the interstitial water combined with the microbiological activity and scavenging of food by benthic macroorganisms indicates this may be an important pathway by which those trace elements can enter the food chain. However, virtually nothing is known about the feeding habits of benthic macroorganisms and even less is known about the uptake or mobilization from the exchangeable phase of trace elements by microorganismsand gastric chemicals. Bacteria are known to convert ionic mercury to the more toxic form: methylmercury. Methylmercury is also biomagnified in the food chain. However, we are not aware of any data that indicates whether the major source of this or other elements to benthic macroorganisms is from the interstitial water, food or other sources. While the effects of microorganisms on the availability of trace elements is a promising area of research, the limitations of time, personnel and equipment permitted us to only investigate a few parameters thought to control the concentration of zinc in the interstitial water.

6. Factors Affecting Trace Element Concentrations in Interstitial Water

A number of factors significantly affect the concentrations of trace elements in the interstitial water of sediments. These include the pH, redox potential, particle size, types of minerals and possibly others. All analytical procedures to determine the availability of trace elements are also affected by these,plus the following factors: ratio of solid to liquid; separation of solid and liquid, agitation, time of contact; and the characteristics of the leaching reagent. It should be possible to develop a procedure that will standardize all of these factors and that will provide qualitative data about the abilities of sediments to release trace elements. This information could be used to evaluate the status of trace element pollution of sediments. However, the results of such a test could not be used to predict the uptake of trace elements by organisms without extensive calibration experiments. These would be expensive, and therefore, they may not be economically feasible.

C. Effect of Solid-Liquid Separation

The separation of the solid and liquid phases must be complete and reproducible in any testing procedure involving leaching of sediments. The concentrations of most elements in the solid phase are many times those found for the water phase but only the portion of the elements found as dissolved forms (soluble phase) should be measured. The traditional procedures to separate the solid and liquid phases are centrifuging or filtering. Centrifuging is most efficient when the liquid phase has a suitable concentration of ionic species. It is not very effective when working with natural water. Instead, filtering is preferred. Modern filters come in a variety of pore sizes but the smallest, practical size is about 0.45 microns. Filters with smaller pores require a long time to filter a reasonable volume of water, and therefore, their use is not practical.

The results of a simple experiment illustrate the effects of incomplete separation of the solid and liquid phases. Samples of sediments weighing 50 grams were mixed with 900 ml of water from Lake Superior and agitated for 24 hours. No attempt was made to control the pH or other variables. An aliquot of the solution was then filtered through a Millipore, 0.45 micron, washed filter and 15 ml collected in a cleaned plastic vial for analysis. A sample of the Lake Superior water used for the experiment was also filtered in an identical fashion. The samples were then analyzed by our procedures of radiochemical neutron activation analysis. The results are given in Table 10.

Other investigators report values of 1 to 5 ppb zinc, 0.2 ppb copper and less than 0.01 ppb mercury for water from the open lake (Biesinger and Christensen, 1972; Gary Glass, personal communication). Our values for copper and mercury are about ten times these values. Some of the discrepancy may result from the different analytical techniques used. Our technique of neutron activation analysis measures the total amount of any element present and does not differentiate between soluble and particulate species. The values quoted above are concentrations of soluble species. This is especially important here because our sample of water was collected immediately after a storm and the water was visibly turbid before filtering.

Of more importance is the significantly higher concentrations found for the water samples that were mixed with the sediments. Some of the difference may be the result of the release of some of each element from the sediment. The results of the analysis also indicate that some solid material passed through the filter as the elements, scandium, gallium and the rare earths were detected in the samples, but the results cannot be quantified because no standard for these elements was irradiated for these samples. The elements mentioned above are present in undetectable amounts as dissolved species in water. Their detection in these samples is strong evidence of the presence of finely divided solid material in the water phase. The situation might be improved with better filtering techniques, such as high pressure filtration with filters having smaller pore sizes, but we did not have sufficient time to refine our procedures.

Table 10. The concentrations of trace elements in ppb (microgram per liter) in samples of open water from Lake Superior and from water agitated with sediments from Duluth-Superior harbor. The analytical uncertainties represent one standard deviation based on counting statistics.

Element	Lake Water	Sample S-VII	Sample S-III-1
Cu	2.3 ± 0.1	44 ± 1	42 ± 1
Zn	2.8 ± 0.3	200 ± 10	43 ± 3
Hg	0.16 ± 0.01	0.88 ± 0.04	0.20 ± 0.01

D. Isotopic Exchange of Zinc

An alternate approach to determining the soluble phase is to use an analytical method that is sensitive only to dissolved species and not neutron activation analysis which measures total amounts only. A second procedure we used is isotopic exchange which is being developed in our laboratories (Checkai and Helmke, unpublished results).

The principle of the procedure is as follows. A small amount of carrier-free radioisotope of the element of interest, in this case zinc, is added to the sediment-water mixture. The aqueous phase is a 0.0005 molar solution of calcium chloride. The amount of zinc added is negligibly small compared to the total zinc in the mixture. The added zinc is distributed between the soluble and exchangeable phases of the sediment-water mixture. The mixture is centrifuged and then filtered. The aqueous phase is then passed through a small column of chelex 100 ion exchange resin which removes the soluble zinc ions quantitatively from the solution. After the column is rinsed with pure water, the zinc is stripped from the resin by 2 ml of 0.01 molar EDTA, and its concentration is determined by atomic adsorption spectrophotometry. The yields in each step are monitored, and they are found to be consistently between 95 and 100 per cent. The details of the procedure and its application to soil analysis are being published elsewhere.

While the procedure is reliable for soil analysis, we did not have enough time to explore all of the aspects of its use with sediments. However, the results shown in Table 11 indicate that the method deserves further study. The advantages of the procedure is that it measures both the exchangeable and soluble phases in one experiment, and it measures only soluble zinc in the aqueous phase.

The results presented in Table 11 (duplicate analyses of each sample) show that the zinc released to the soluble phase from the harbor and lake sediment sample has about the same concentrations as was found for lake water. This observation should not be interpreted to mean that the same results will be obtained if pure lake water is used because we used 0.0005 m calcium chloride solution and many factors may affect the results. The sediment with the highest total zinc, sample S-III-1, has the lowest content of exchangeable zinc. The results show that all of the harbor and lake sediments, including the sample with the highest measured total concentration of zinc, have about the same tendency to release zinc in a soluble form. These results are consistent with those of Lee et al. (1975) who found that zinc in sediments is not released to the water.

The sediments used for the bioassay experiments released zinc at concentrations several hundred times those found for the natural sediments. This was expected because the bioassay sediments were treated with soluble zinc salts. There is a progressive increase in the exchangeable and soluble zinc in the sediments from the bioassay experiments as the total concentration of zinc increased.

Some information relating the values given in Table 11 and the bioavailability and uptake of zinc by Pontoporeia can be derived from the data of bioassay experiment number 16, reported in Volume 3. The Pontoporeia in control tanks 3 and 4 contained from 94 to 99 ppm zinc while those from the tanks with high and low concentrations of zinc contained from 135 to 155 ppm zinc at the end of the experiment. The concentrations of zinc in the control Pontoporeia were similar to those found in Pontoporeia taken

Table 11. The concentrations of zinc obtained by isotopic exchange in the soluble and exchangeable phases of sediments from the Duluth-Superior harbor and from the bioassay experiment 16. Four grams of undried sediment (dry weight basis) were agitated for two hours with 35 ml of 0.0005 molar calcium chloride.

Sample	Total zinc (ppm)	Exchangeable ppm dry wt. (± 20%)	Soluble ppb in aqueous phase (± 20%)
Allouez Bay	78	22	7
(S-IX)		15	4
Old Dump Site	87	38	5
(S-3)		49	4
Harbor	143	30	8
(S-VII)		31	7
Duluth-Sewage Outfall	250	14	4
(S-III-1)		12	2
Open Lake (Geo. 19)	69	20	2
Exp. 16 control			
Tank 3	12	2.3	3
Tank 4		0.7	2
Low zinc			
Tank 5	67	15	160
Tank 6		16	190
High zinc			
Tank 1	127	39	1800
Tank 2		35	1100

from the lake. Also, the concentrations of exchangeable zinc in the sediment of the tanks with high and low zinc were about the same as found for the lake sediment (Geo. 19) and some harbor sediments. The bioassay sediments were almost pure sand, which accounts for the low concentration of exchangeable zinc in the control tanks. Sand sized particles generally have very low capacities to adsorb soluble forms of elements compared to clay particles, hydrous oxides and organic matter. However, the concentration of soluble zinc is much higher for tanks 1, 2, 5 and 6 than it is for the controls or any of the harbor and lake sediments. This indicates that the increase in the body burden of zinc for Pontoporeia in tanks 1, 2, 5 and 6 is the result of the increase of soluble zinc and not due to the increase of exchangeable zinc. If this is correct, the results given in Table 11 then suggest that the availability of zinc to Pontoporeia in all of the natural sediments analyzed is about the same.

However, the above procedures measure only soluble zinc. They did not measure the zinc associated with organic matter and detritus. These are important food sources for benthic organisms,and the zinc may be sorbed across the intestinal walls. For example, the sample from the sewage outfall (S-III-1) has low concentrations of exchangeable and near normal concentrations of soluble zinc. It also has a high concentration of organic matter. Any zinc associated with the organic matter may not be exchangeable or soluble but still be available to organisms that ingest the organic matter. Also, zinc present in the exchangeable phase may be assimilated by organisms if gastric chemicals can remove it from ingested particles.

E. Conclusions

The results of our study and the report by Lee, et al (1975), show: 1) the inadequacy of using the concentrations of trace elements in samples of total sediments to evaluate sediment quality, and 2) the effect of some trace metals in disturbed sediments on the concentration of these elements in the water column is minimal. We conclude from our study that the disposal of dredged material will not significantly affect the concentration of soluble zinc in the water column and in the interstitial water. Evidence from the bioassay indicates that higher concentrations of soluble zinc correlate with increased uptake of zinc by Pontoporeia. The uptake of zinc associated with organic matter is unknown. The incompleteness of knowledge about the relationships of benthic organisms and trace elements in sediments indicates that a prudent and conservative approach should be used in the disposal of dredged material: disposal should be limited to material having concentrations of trace elements near background values. This approach requires reliable and simple procedures to determine background values and the extent of sediment pollution. Of the three procedures currently available; analysis of total sediments, elutriate tests, or analysis of clay-sized fraction, only the analysis of the clay-sized fraction is capable of providing the needed information.

IV. Trace Elements in Organisms From Lake Superior

A. Introduction

Benthic organisms and fishes from the Duluth-Superior and Keweenaw areas were analyzed to study possible concentration of elements at different trophic levels in the food chain and possible correlations between concentrations of trace elements in organisms, especially benthic organisms, and sediments. The large number of variables (difficult or impossible to measure) that are thought to be important in the release of trace elements from sediments, and their uptake by organisms requires knowledge of the net result of uptake of trace elements. The results of these analyses give the extent of uptake and biomagnification of trace elements in the food chain under the present conditions of Lake Superior, and they serve as a base to predict the probable effects that in-lake dumping of dredge spoil will have on the concentrations of trace elements in the biota.

The burrowing amphipod, Pontoporeia affinis, is a major member of the macrobenthic community in Lake Superior and is an important part of the food supply of numerous fish species. Amphipods are a dominant part of the diet of young lake trout (Salvelinus namaycush), suckers (Catostomus catostomus), whitefish (Coregonus clupeaformis), slimysculpin (Cottus cognatus), mottled sculpin (Cottus bairdi), four-horned sculpin (Myoxocephalus quadricornis), ninespine stickleback (Pungitius pungitius), trout perch (percopsis omiscomaycus) (Anderson and Smith, 1971). Amphipods also are part of the diet of smelt (Osmerus mordax), large lake trout, and burbot (Lota lota). Of these fish species, smelt, burbot and lake trout are consumers of smelt and sculpin (Anderson and Smith, 1971). Lake trout also consume sticklebacks and yellow perch. Burbot feed on sticklebacks and trout perch. The diet of adult whitefish also includes sculpin, alewife

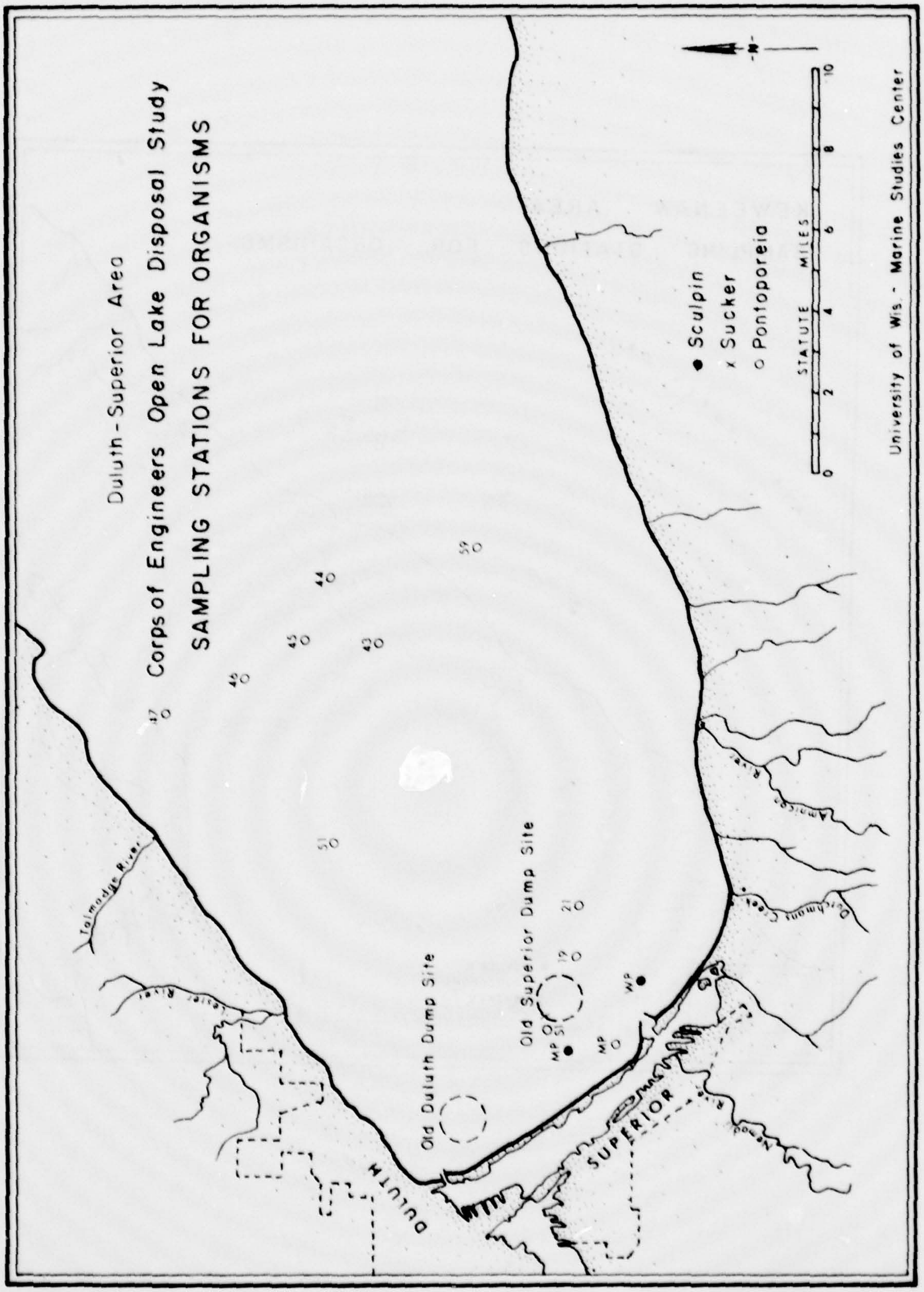
(Alosa pseudoharengus), and several species of minnow and darter (Scott, et al, 1973).

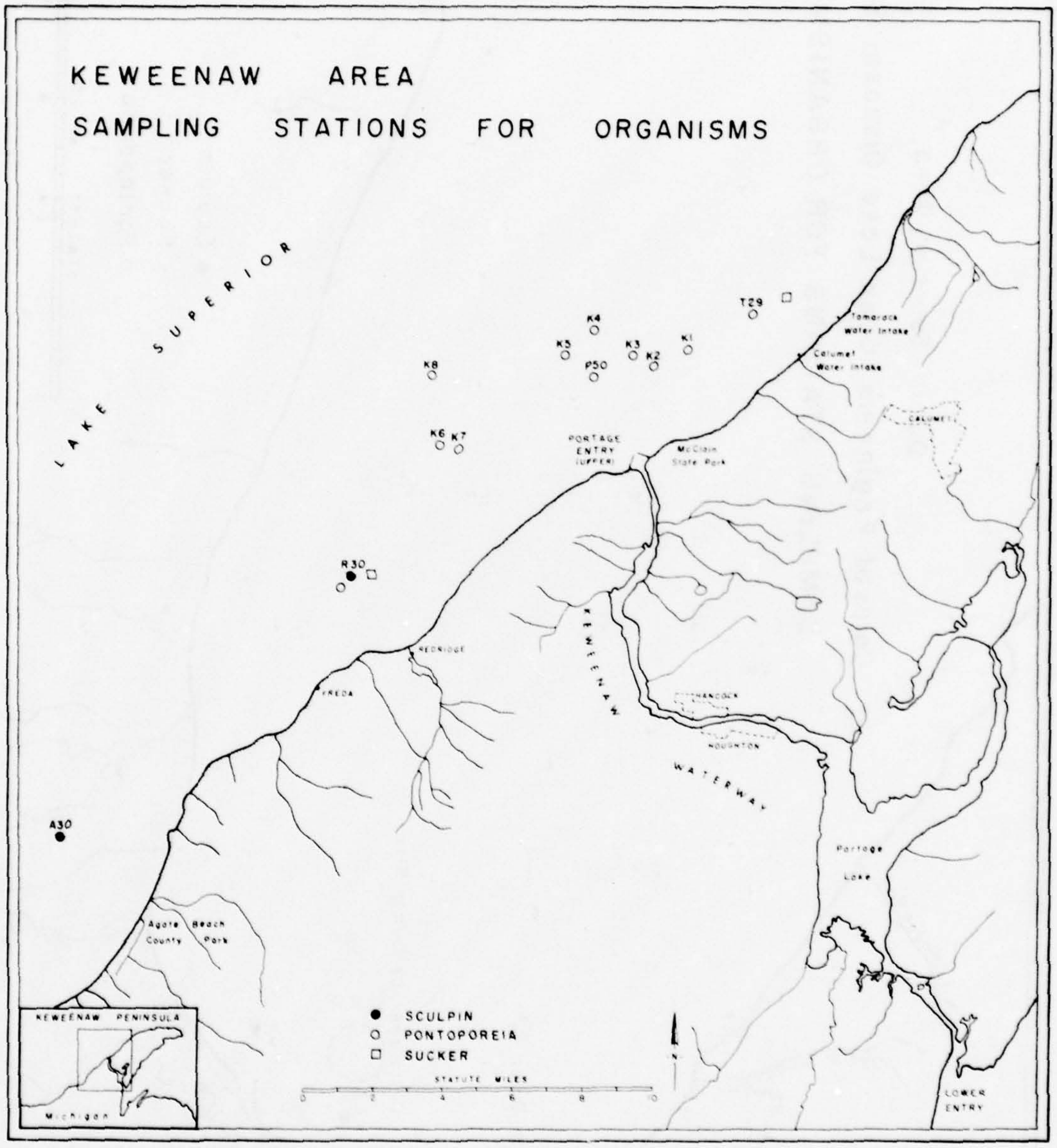
The proximity of Pontoporeia to sediment suggests that this organism may be one organism that reflects the concentrations of trace elements in sediments, and a pathway for transfer of metals from sediments to fish, and the human consumers of fish. The species of fish collected and analyzed represent the various trophic levels in Lake Superior.

B. Collection of Samples

The sampling locations are shown in Figures 19 and 20 for the Duluth-Superior and Keweenaw areas respectively. A sample of sediment was taken at each station where Pontoporeia were collected. The fish were caught either by gill netting or trawling. The samples of lake trout were purchased from commercial gill netters. The fresh fish were removed from the nets and frozen whole as soon as possible after collection. The frozen samples were then returned to Madison, WI. and stored in freezers until analysis. The samples of Pontoporeia were collected by a 9"x9" Ponar dredge. The dredge is made of cast iron and all non-ferrous parts were replaced with stainless steel or aluminum to minimize possible contamination. The samples of sediment were sieved aboard ship through stainless steel screens with lake water. The Pontoporeia were then collected from the sieves and frozen until analysis. Information concerning the size, the number of organisms used for analysis and the date collected are given with the analytical results in Tables 12 and 14.

In preparation for analysis, the samples were dissected in a laminar flow hood in a clean room. Stainless steel tools were used for the dissection. Experience has shown that contamination of the samples is negligible under these conditions (Korda et al., 1976). A filet of


Duluth-Superior Area
Corps of Engineers Open Lake Disposal Study
SAMPLING STATIONS FOR ORGANISMS
47
46
45
44
43
50
51
21
12
Old Duluth Dump Site
Old Superior Dump Site
MP
SI
MP
WP
Talmadge River
Lester River
Amnicon River
Dutchmans Creek
Nemadji River
DULUTH
SUPERIOR
● Sculpin
x Sucker
o Pontoporeia
STATUTE MILES
0
2
4
6
8
10
N
University of Wis. - Marine Studies Center


KEWEENAW AREA
SAMPLING STATIONS FOR ORGANISMS
LAKE SUPERIOR
T29
K4
K5
K3
K2
K1
P50
K8
K6
K7
Tamarack Water Intake
Calumet Water Intake
CALUMET
PORTAGE ENTRY (UPPER)
McClain State Park
R30
KEWEENAW WATERWAY
REDRIDGE
FREDA
HANCOCK
HOUGHTON
A30
Portage Lake
Agate Beach County Park
KEWEENAW PENINSULA
Michigan
● SCULPIN
○ PONTOPOREIA
□ SUCKER
STATUTE MILES
0
2
4
6
8
10
N
LOWER ENTRY

flesh, the liver and the contents of the alimentary canal were removed from the fish for analysis. When possible, to reduce the variations found when individual fish are analyzed, portions of individual fish were combined to produce a composite sample for each species for analysis. The samples were weighed wet, freeze-dried, and then weighed dry.

The samples of Pontoporeia were thawed and washed twice in deionized water to remove the small amount of sediment mixed with the organisms. It was not possible to obtain an accurate wet weight of the samples because they were usually so small that any water included with the sample produced high results. All of the trace element analyses were by modifications of our procedures for radiochemical and instrumental neutron activation analysis (Henzler et al., 1974).

C. Results and Discussion

The results of the trace element analysis of organisms from Lake Superior are given in Tables 12 and 14. The analytical uncertainties represent one standard deviation based on counting statistics. The values of concentrations are expressed on the freeze-dried weight but the information given in each table can be used to convert the results to wet weight.

The concentrations of trace elements in the samples of fish flesh are similar to those found by other investigators studying fresh water fishes (e.g., Copeland et al., 1973). The concentrations of trace elements in the samples of liver are generally higher than in the corresponding samples of flesh. This is considered to be normal. The concentrations of most trace elements in the contents of the alimentary canal are considerably greater than those found for the corresponding samples of flesh, and they are similar to the levels found in the samples of liver. The samples of flesh from lake trout and whitefish have concentrations of mercury, when expressed correctly as wet weights, that exceed the 0.5 ppm limit set by the Food and Drug Administration for fish. The United States has published no official limit for arsenic, but all of the samples of flesh have concentrations that are significantly below the limit set by Canada of 5 ppm.

Table 12. The concentrations of trace elements in ppm for samples of fish from Lake Superior. The values are expressed on the weight of the freeze-dried samples.

	SCULPIN (Duluth-Superior, Wisconsin Point) Composite of Eight Fish, Mixture of Slimy & 4-Horn, July 5, 1974 2-7 cm long		
	Flesh	Liver	Contents of Alimentary Canal
As	1.0 ± 0.2	1.5 ± 0.3	1.7 ± 0.1
Br	36 ± 1	58 ± 2	177 ± 6
Co	0.18 ± 0.02	0.17 ± 0.02	1.1 ± 0.1
Cr	1.9 ± 0.5	< 1	5 ± 1
Cu	2.43 ± 0.06	41 ± 2	50 ± 1
Eu	< 0.005	< 0.002	0.08 ± 0.01
Fe	40 ± 10	120 ± 20	3000 ± 100
Ga	--	--	--
Hg	0.7 ± 0.1	0.4 ± 0.1	0.32 ± 0.03
La	< 0.008	< 0.006	1.5 ± 0.2
Na	1630 ± 30	2330 ± 40	3110 ± 40
Rb	16.7 ± 0.4	14 ± 1	45 ± 3
Sb	0.10 ± 0.02	--	--
Sc	0.004 ± 0.001	< 0.001	0.79 ± 0.01
Se	1.5 ± 0.3	3.2 ± 0.7	1.8 ± 0.5
Sm	< 0.004	< 0.004	0.43 ± 0.05
Zn	23 ± 1	64 ± 2	74 ± 2
Dry/Wet	0.266	0.340	0.273

Table 12. (cont.)

	SCULPIN (Duluth-Superior, Minnesota Point) Composite of Eight Fish, Mixture of Slimy & 4-Horn, Sept. 28, 1973 3-8 cm long		
	Flesh	Liver	Contents of Alimentary Canal
As	--	2.6 ± 0.4	1.3 ± 0.3
Br	44 ± 2	77 ± 2	142 ± 5
Co	0.05 ± 0.01	0.17 ± 0.02	1.28 ± 0.04
Cr	< 1	< 1	7 ± 1
Cu	2.68 ± 0.07	52 ± 3	73 ± 3
Eu	< 0.02	< 0.01	0.14 ± 0.01
Fe	40 ± 10	120 ± 10	5500 ± 80
Ga	--	--	--
Hg	0.48 ± 0.05	0.37 ± 0.06	0.4 ± 0.1
La	< 0.007	--	2.2 ± 0.1
Na	2400 ± 100	2800 ± 100	1200 ± 70
Rb	22 ± 2	17 ± 3	26 ± 4
Sb	--	--	--
Sc	0.007 ± 0.001	< 0.001	1.00 ± 0.02
Se	1.4 ± 0.3	3.4 ± 0.8	2.6 ± 0.6
Sm	< 0.008	< 0.007	0.45 ± 0.01
Zn	33 ± 1	65 ± 2	114 ± 2
Dry/Wet	0.242	0.356	0.295

Table 12. (cont.)

	SCULPIN (Keweenaw, Redridge) Composite of 20 Fish, Mixture of Mottled & Slimy, Sept. 20, 1973 3-6 cm long		
	Flesh	Liver	Contents of Alimentary Canal
As	2.2 ± 0.8	< 1.0	3.2 ± 0.3
Br	110 ± 4	149 ± 6	238 ± 10
Cd	--	3.6 ± 0.4	2.1 ± 0.3
Co	0.36 ± 0.03	0.62 ± 0.04	1.5 ± 0.1
Cr	1.1 ± 0.3	--	8 ± 1
Cu	3.07 ± 0.04	63 ± 1	70 ± 1
Eu	0.012 ± 0.002	0.022 ± 0.002	0.31 ± 0.01
Fe	26 ± 9	140 ± 20	2570 ± 40
Ga	< 0.003	--	0.21 ± 0.02
Hg	0.76 ± 0.02	0.73 ± 0.02	1.8 ± 0.1
La	< 0.008	< 0.002	8.4 ± 0.2
Na	3430 ± 50	4040 ± 50	4440 ± 50
Rb	23 ± 2	20 ± 2	21 ± 2
Sb	0.14 ± 0.02	--	0.29 ± 0.05
Sc	0.012 ± 0.002	< 0.001	1.03 ± 0.01
Se	2.7 ± 0.4	6.0 ± 0.8	3.9 ± 0.5
Sm	< 0.004	< 0.004	1.92 ± 0.03
Zn	34 ± 1	114 ± 4	85 ± 3
Dry/Wet	0.354	0.394	0.594

Table 12. (cont.)

	SCULPIN (Keweenaw, Agate Beach) Composite of 20 Fish, Mixture of Mottled & Slimy, Sept. 20, 1973 3-6 cm long		
	Flesh	Liver	Contents of Alimentary Canal
As	2.60 ± 0.02	5.2 ± 0.1	11.4 ± 0.1
Br	--	--	--
Cd	--	7.5 ± 0.2	7.1 ± 0.3
Co	--	--	--
Cr	--	--	--
Cu	2.54 ± 0.06	33.1 ± 0.4	126 ± 2
Eu	--	--	--
Fe	--	--	--
Ga	< 0.003	< 0.01	0.63 ± 0.02
Hg	0.96 ± 0.06	0.30 ± 0.01	0.35 ± 0.01
La	--	--	--
Na	--	--	--
Rb	--	--	--
Sb	0.16 ± 0.01	0.26 ± 0.02	0.58 ± 0.02
Sc	--	--	--
Se	--	--	--
Sm	--	--	--
Zn	32 ± 2	139 ± 10	102 ± 8
Dry/Wet	0.234	0.355	0.476

Table 12. (cont.)

	SUCKER (Duluth-Superior) Composite of Four Fish Oct. 15, 1973 31-37 cm long		
	Flesh	Liver	Contents of Alimentary Canal
As	< 1	3.5 ± 0.7	3 ± 1
Cd	< 0.2	2.8 ± 0.3	3.0 ± 0.2
Co	< 0.1	< 0.2	2.4 ± 0.1
Cr	< 1	< 1	11 ± 2
Cu	1.99 ± 0.03	24.4 ± 0.4	104 ± 2
Eu	0.01	0.02	0.23 ± 0.01
Fe	21 ± 5	--	6700 ± 200
Ga	< 0.006	< 0.001	0.75 ± 0.04
Hg	1.48 ± 0.04	0.32 ± 0.01	0.24 ± 0.01
La	< 0.01	< 0.04	5.5 ± 0.2
Na	2320 ± 40	4890 ± 60	10100 ± 100
Rb	25 ± 3	17 ± 2	34 ± 3
Sb	0.036 ± 0.006	0.043 ± 0.007	0.05 ± 0.02
Sc	0.015 ± 0.002	0.015 ± 0.002	1.70 ± 0.02
Se	2.5 ± 0.6	4.3 ± 0.4	3.3 ± 0.2
Sm	< 0.01	< 0.01	1.04 ± 0.04
Zn	20 ± 1	70 ± 2	110 ± 4
Dry/Wet	0.191	0.251	0.193

Table 12. (cont.)

	SUCKER (Duluth-Superior) One Fish, Female Oct. 15, 1973 31 cm long		
	Flesh	Liver	Contents of Alimentary Canal
As	1.6 ± 0.1	1.2 ± 0.1	4.5 ± 0.1
Cd	--	--	1.4 ± 0.5
Cu	3.3 ± 0.1	19.0 ± 0.5	70 ± 2
Ga	<0.01	<0.01	0.13 ± 0.02
Hg	1.03 ± 0.06	0.20 ± 0.01	
Sb	0.13 ± 0.01	0.10 ± 0.01	0.41 ± 0.04
Sc	--	--	--
Se	1.1 ± 0.1	3.3 ± 0.1	3.8 ± 0.2
Zn	15 ± 1	67 ± 3	137 ± 4
Dry/Wet	0.191	0.251	0.193

Table 12. (cont.)

SUCKER (Keweenaw, Calumet-Tamarack)
Composite of Eight Fish
Sept. 12, 1973
35-44 cm long

	Flesh	Liver	Contents of Alimentary Canal
As	0.7 ± 0.2	1.3 ± 0.4	3 ± 1
Cd	< 0.1	3.5 ± 0.1	9.4 ± 0.3
Co	< 0.05	0.11 ± 0.01	1.2 ± 0.1
Cr	< 1	< 1	4 ± 1
Cu	2.33 ± 0.06	72 ± 1	137 ± 2
Eu	< 0.01	< 0.01	0.085 ± 0.003
Fe	20 ± 10	240 ± 30	3040 ± 80
Ga	< 0.05	< 0.01	< 0.02
Hg	1.55 ± 0.02	0.39 ± 0.01	0.44 ± 0.01
La	< 0.008	< 0.008	1.5 ± 0.1
Na	2420 ± 40	13800 ± 200	7900 ± 100
Rb	23 ± 2	10 ± 1	24 ± 2
Sb	0.075 ± 0.007	0.06 ± 0.01	0.14 ± 0.02
Sc	0.015 ± 0.002	0.014 ± 0.002	0.80 ± 0.01
Se	1.4 ± 0.1	4.7 ± 0.2	2.6 ± 0.2
Sm	0.004	< 0.005	0.26 ± 0.01
Zn	26 ± 1	104 ± 3	103 ± 7
Dry/Wet	0.193	0.225	0.189

Table 12. (cont.)

	SUCKER (Keweenaw, Redridge) One Fish, Female Sept. 9, 1973 38 cm long		
	Flesh	Liver	Contents of Alimentary Canal
As	0.74 ± 0.03	2.4 ± 0.3	0.91 ± 0.03
Cd	< 0.5	10.0 ± 0.5	--
Cu	1.41 ± 0.02	83 ± 1	10.2 ± 0.1
Hg	2.0 ± 0.1	0.62 ± 0.03	0.13 ± 0.01
Sb	0.14 ± 0.01	0.20 ± 0.02	0.17 ± 0.02
Sc	0.020 ± 0.003	0.008 ± 0.003	< 0.001
Se	1.2 ± 0.1	5.6 ± 0.2	2.6 ± 0.1
Zn	31 ± 9	150 ± 18	170 ± 25
Dry/Wet	0.189	0.211	0.235

Table 12. (cont.)

	SUCKER (Keweenaw, Calumet-Tamarack) One Fish, Female Sept. 12, 1973 35 cm long		
	Flesh	Liver	Contents of Alimentary Canal
As	0.42 ± 0.01	0.54 ± 0.01	0.12 ± 0.01
Cd	--	2.8 ± 0.2	6.9 ± 0.3
Cu	1.32 ± 0.02	84 ± 1	213 ± 2
Hg	1.06 ± 0.07	0.24 ± 0.01	0.30 ± 0.01
Sb	0.04 ± 0.01	0.2 ± 0.1	0.3 ± 0.1
Sc	--	0.006 ± 0.002	--
Se	--	17.6 ± 0.4	16 ± 1
Zn	24 ± 4	158 ± 18	125 ± 9
Dry/Wet	0.186	0.164	0.151

Table 12. (cont.)

	WHITEFISH (Keweenaw area) One Fish May, 1974 52 cm long		
	Flesh	Liver	Contents of Alimentary Canal
As	1.2 ± 0.2	3.7 ± 0.7	8 ± 1
Br	32 ± 2	41 ± 2	108 ± 3
Cd	--	--	--
Co	0.12 ± 0.02	0.3 ± 0.1	0.14 ± 0.03
Cr	< 1	< 1	< 1
Cu	2.69 ± 0.06	42 ± 1	12.1 ± 0.2
Eu	0.007 ± 0.001	0.03 ± 0.01	0.025 ± 0.004
Fe	< 50	220 ± 30	120 ± 20
Ga	--	--	--
Hg	4.36 ± 0.07	1.54 ± 0.04	6.9 ± 0.6
La	< 0.02	< 0.02	< 0.07
Na	1740 ± 50	3360 ± 100	8500 ± 100
Rb	25 ± 2	19 ± 1	43 ± 3
Sb	< 0.1	< 0.2	< 0.3
Sc	< 0.006	0.004 ± 0.002	0.012 ± 0.006
Se	2.2 ± 0.3	4.7 ± 0.4	6 ± 1
Sm	< 0.002	< 0.01	0.2 ± 0.1
Zn	12 ± 1	60 ± 2	162 ± 6
Dry/Wet	0.290	0.372	0.216

Table 12. (cont.)

	BURBOT (Duluth-Superior area) One Fish Sept. 14, 1973 35 cm long	
	Flesh	Contents of Alimentary Canal
As	<1.5	3 ± 1
Br	--	--
Cd	--	0.3 ± 0.1
Co	<0.03	0.35 ± 0.02
Cr	<1	2.5 ± 0.8
Cu	2.96 ± 0.06	5.30 ± 0.08
Eu	0.005 ± 0.001	0.051 ± 0.003
Fe	--	1200 ± 70
Ga	<0.01	0.33 ± 0.05
Hg	2.20 ± 0.04	0.49 ± 0.02
La	<0.04	0.8 ± 0.1
Na	3230 ± 50	12400 ± 200
Rb	30 ± 2	42 ± 4
Sb	--	0.26 ± 0.01
Sc	0.012 ± 0.001	0.27 ± 0.01
Se	1.6 ± 0.2	1.8 ± 0.2
Sm	<0.06	0.20 ± 0.02
Zn	27 ± 1	251 ± 6
Dry/Wet	0.184	0.0945

Table 12. (cont.)

	LAKE TROUT (Western Lake Superior) Composite of Three Fish Jan. 15, 1975 44, 45 & 46 cm long		
	Flesh	Liver	Contents of Alimentary Canal
As	0.67 ± 0.07	1.3 ± 0.2	3.1 ± 0.7
Br	17.4 ± 0.5	50 ± 1	81 ± 2
Co	< 0.03	0.14 ± 0.02	0.10 ± 0.01
Cr	< 1	< 1	< 1
Cu	1.94 ± 0.06	67 ± 2	98 ± 2
Eu	< 0.01	< 0.02	< 0.02
Fe	--	300 ± 20	60 ± 10
Hg	2.9 ± 0.2	3.9 ± 0.1	--
La	< 0.06	< 0.08	< 0.1
Na	1340 ± 10	4100 ± 50	7850 ± 80
Rb	26 ± 1	22 ± 1	39 ± 2
Sc	< 0.001	< 0.001	< 0.002
Se	1.5 ± 0.5	10 ± 1	2 ± 0.5
Sm	< 0.08	< 0.1	< 0.1
Zn	11.6 ± 0.8	128 ± 3	161 ± 4
Dry/Wet	0.218	0.253	0.173

Table 12. (cont.)

LAKE TROUT (Keweenaw area)
Composite of Three Fish
May, 1974
42, 58 & 61 cm long

	Flesh	Liver	Contents of Alimentary Canal
As	0.7 ± 0.1	2.8 ± 0.5	--
Br	19 ± 1	99 ± 2	--
Co	0.02 ± 0.01	0.17 ± 0.04	1.2 ± 0.1
Cr	< 1	< 1	3.3 ± 0.6
Cu	2.25 ± 0.04	101 ± 2	111 ± 1
Eu	< 0.01	0.08 ± 0.01	0.06 ± 0.01
Fe	10 ± 1	210 ± 30	2000 ± 100
Hg	4.4 ± 0.1	4.2 ± 0.1	2.3 ± 0.1
La	< 0.08	< 0.06	< 0.08
Na	--	--	--
Rb	33 ± 3	30 ± 2	41 ± 4
Sc	< 0.007	< 0.002	< 0.002
Se	2.1 ± 0.2	11 ± 1	4.7 ± 0.5
Sm	0.05 ± 0.02	< 0.03	< 0.02
Zn	14 ± 1	98 ± 3	260 ± 10
Dry/Wet	0.249	0.292	0.210

Table 14. The concentrations of trace elements in ppm for samples of *Pontoporeia* from Lake Superior.

	Pontoporeia (Duluth-Superior)			
	19	21	Minnesota Point	43
As	3.7 ± 0.4	2.9 ± 0.4	5.2 ± 0.5	4.3 ± 0.5
Br	550 ± 10	500 ± 10	392 ± 8	--
Co	1.2 ± 0.1	2.0 ± 0.1	1.3 ± 0.1	2.0 ± 0.1
Cr	101 ± 5	10 ± 2	10 ± 1	10 ± 2
Cu	59 ± 1	67 ± 2	116 ± 1	93 ± 2
Eu	0.11 ± 0.02	0.13 ± 0.02	0.10 ± 0.01	0.14 ± 0.02
Fe	3800 ± 100	5400 ± 200	3700 ± 300	7800 ± 100
Ga	--	--	0.50 ± 0.07	--
Hg	0.09 ± 0.02	0.10 ± 0.01	2.0 ± 0.2	--
K	--	2300 ± 200	2000 ± 200	--
La	2.9 ± 0.2	4.1 ± 0.1	2.8 ± 0.3	4.5 ± 0.1
Na	812 ± 5	1050 ± 10	1270 ± 10	1050 ± 20
Sb	--	--	--	--
Sc	0.95 ± 0.02	1.45 ± 0.02	0.96 ± 0.02	1.52 ± 0.03
Sm	0.52 ± 0.02	0.75 ± 0.02	0.62 ± 0.02	0.76 ± 0.02
Zn	83 ± 4	74 ± 5	87 ± 4	70 ± 6
Date Collected	Sept. 10 to 17, 1974 →			
Depth (meters)	30.0	32.0	14.0	78.0
Avg. wt. (mg)	0.74	0.69	0.58	0.86
Number of *Pontoporeia*	20	29	40	13

Table 14. (cont.)

	Pontoporeia (Duluth-Superior)		
	44	45	46
As	3.9 ± 0.2	3.7 ± 0.1	4.1 ± 0.3
Br	450 ± 10	296 ± 6	486 ± 8
Co	1.3 ± 0.1	1.8 ± 0.1	2.2 ± 0.1
Cr	7 ± 1	10 ± 2	12 ± 2
Cu	97 ± 1	178 ± 2	144 ± 2
Eu	0.09 ± 0.01	0.10 ± 0.01	0.16 ± 0.01
Fe	5300 ± 100	7500 ± 200	10300 ± 300
Ga	1.6 ± 0.1	0.9 ± 0.1	0.6 ± 0.1
Hg	0.34 ± 0.05	1.7 ± 0.6	0.26 ± 0.04
K	610 ± 40	--	590 ± 40
La	2.3 ± 0.1	3.5 ± 0.3	2.6 ± 0.2
Na	370 ± 10	970 ± 20	410 ± 10
Sb	0.24 ± 0.02	0.20 ± 0.01	0.22 ± 0.03
Sc	0.97 ± 0.01	1.40 ± 0.02	1.51 ± 0.02
Sm	0.46 ± 0.01	0.72 ± 0.02	0.55 ± 0.01
Zn	56 ± 3	85 ± 4	80 ± 4
Date Collected	Sept. 10 to 17, 1974 ⟶		
Depth (meters)	78.0	75.0	82.0
Avg. wt. (mg)	0.94	0.98	0.71
Number of *Pontoporeia*	15	10	18

Table 14. (cont.)

	Pontoporeia (Duluth-Superior)			
	47	51	59	Superior Dump Site
As	8.7 ± 0.5	4.3 ± 0.2	1.5 ± 0.2	3.4 ± 0.3
Br	330 ± 10	500 ± 10	280 ± 10	--
Co	3.0 ± 0.2	2.3 ± 0.1	0.98 ± 0.07	2.1 ± 0.1
Cr	10 ± 2	12 ± 2	5 ± 1	14 ± 2
Cu	130 ± 1	113 ± 1	44 ± 1	113 ± 1
Eu	0.19 ± 0.02	0.18 ± 0.02	0.07 ± 0.01	0.17 ± 0.01
Fe	18800 ± 300	8700 ± 200	3500 ± 100	5700 ± 200
Ga	--	1.0 ± 0.1	--	0.68 ± 0.04
Hg	1.2 ± 0.2	0.97 ± 0.07	0.024 ± 0.005	0.13 ± 0.01
K	1500 ± 200	790 ± 40	1400 ± 200	--
La	4.5 ± 0.3	3.3 ± 0.2	2.5 ± 0.1	4.1 ± 0.1
Na	1300 ± 20	550 ± 10	510 ± 10	3000 ± 100
Sb	0.32 ± 0.03	0.19 ± 0.01	--	0.25 ± 0.03
Sc	1.86 ± 0.03	1.69 ± 0.02	0.79 ± 0.01	1.49 ± 0.02
Sm	0.98 ± 0.03	0.63 ± 0.05	0.41 ± 0.01	0.81 ± 0.01
Zn	90 ± 6	83 ± 5	60 ± 4	73 ± 4
Date Collected	Sept. 10 to 17, 1974 ⟶			Oct. 14, 1973
Depth (meters)	120.0	84.0	140.0	24.0
Avg. wt. (mg)	0.74	0.91	0.93	1.23
Number of *Pontoporeia*	16	20	22	70

Table 14. (cont.)

	Pontoporeia (Keweenaw)			
	K1	K2	K3	K4
As	6.6 ± 0.8	7 ± 1	5.5 ± 0.8	7.1 ± 0.8
Br	950 ± 50	860 ± 40	930 ± 40	990 ± 40
Co	1.7 ± 0.1	1.33 ± 0.06	1.1 ± 0.1	2.0 ± 0.1
Cr	10 ± 1	6 ± 1	7 ± 2	9 ± 2
Cu	202 ± 2	238 ± 2	154 ± 2	194 ± 4
Eu	0.13 ± 0.02	0.13 ± 0.02	0.08 ± 0.01	0.13 ± 0.03
Fe	4300 ± 100	3600 ± 100	2500 ± 100	5900 ± 200
Ga	--	--	--	--
Hg	0.38 ± 0.03	0.36 ± 0.04	0.21 ± 0.02	--
K	--	--	--	--
La	2.8 ± 0.4	2.3 ± 0.3	1.8 ± 0.2	4.1 ± 0.4
Na	1430 ± 20	1320 ± 20	1150 ± 20	1530 ± 30
Sb	--	--	--	--
Sc	1.26 ± 0.02	1.02 ± 0.02	0.81 ± 0.01	1.60 ± 0.03
Sm	0.66 ± 0.03	0.52 ± 0.03	0.37 ± 0.02	0.84 ± 0.03
Zn	101 ± 4	104 ± 4	95 ± 5	127 ± 7
Date Collected	June 7 to 10, 1975 →			
Depth (meters)	51.2	39.6	63.4	84.4
Avg. wt. (mg)	0.37	0.38	0.38	0.17
Number of *Pontoporeia*	43	47	27	19

Table 14. (cont.)

	Pontoporeia (Keweenaw)		
	K5	K6	K7
As	6 ± 1	4.9 ± 0.7	8.7 ± 0.9
Br	920 ± 40	740 ± 30	1090 ± 50
Co	0.5 ± 0.1	0.66 ± 0.06	2.7 ± 0.1
Cr	--	2.4 ± 0.6	--
Cu	177 ± 2	193 ± 2	229 ± 2
Eu	--	0.028 ± 0.008	0.10 ± 0.02
Fe	760 ± 50	1110 ± 60	3100 ± 100
Ga	--	--	--
Hg	0.28 ± 0.02	0.18 ± 0.02	0.28 ± 0.04
K	--	--	--
La	--	1.0 ± 0.2	1.7 ± 0.3
Na	360 ± 20	1790 ± 20	810 ± 20
Sb	--	--	--
Sc	0.26 ± 0.01	0.34 ± 0.01	0.43 ± 0.02
Sm	0.12 ± 0.01	0.21 ± 0.03	0.29 ± 0.02
Zn	103 ± 5	79 ± 3	142 ± 7
Date Collected	June 7 to 10, 1975 →		
Depth (meters)	53.6	32.3	37.2
Avg. wt. (mg)	0.32	0.71	0.27
Number of Pontoporeia	28	20	22

Table 14. (cont.)

	Pontoporeia (Keweenaw)			
	K8	Portage Entry (P50)	Tamarack (T29)	Redridge (R30)
As	7 ± 1			<2
Br	920 ± 40	710 ± 20	620 ± 30	--
Co	0.8 ± 0.1	3.2 ± 0.1	2.1 ± 0.2	0.8 ± 0.1
Cr	18 ± 3	7 ± 1	4 ± 1	<3
Cu	140 ± 2	212 ± 4	158 ± 2	206 ± 2
Eu	--	0.13 ± 0.01	0.08 ± 0.01	0.08 ± 0.01
Fe	1600 ± 100	4400 ± 300	2600 ± 200	1200 ± 100
Ga	--	0.8 ± 0.1	0.6 ± 0.2	0.78 ± 0.04
Hg	0.19 ± 0.02	1.0 ± 0.1	0.30 ± 0.03	0.14 ± 0.03
K	--	2300 ± 400	1600 ± 300	--
La	--	2.1 ± 0.1	2.0 ± 0.2	1.6 ± 0.1
Na	780 ± 30	1780 ± 40	940 ± 30	2910 ± 50
Sb	--	--	--	--
Sc	0.43 ± 0.02	1.27 ± 0.03	0.86 ± 0.02	0.44 ± 0.01
Sm	0.18 ± 0.02	0.78 ± 0.05	0.46 ± 0.03	0.34 ± 0.02
Zn	107 ± 6	85 ± 4	72 ± 4	63 ± 5
Date Collected	June 7-10, 1975	May 27, 1974	⟶	Sept. 8, 1974
Depth (meters)	40.8	48.8	28.3	20.0 - 30.0
Avg. wt. (mg)	0.28	0.83	0.81	1.22
Number of Pontoporeia	27	85	80	58

D. Trace Elements in the Food Chain

The beginnings of the concept of biomagnification of trace elements in the food chain are nebulous but the concept must have been influenced by analogy with the observed biomagnification of pesticides. Recent investigations have shown that trace elements, in general, do not become more concentrated at the higher trophic levels of the aquatic food chain -- with the possible exception of mercury, cesium, and arsenic (e.g., Copeland et al., 1973). These conclusions are supported by the results of this study.

The concentrations of copper, zinc and mercury in organisms from three trophic levels from Lake Superior are shown in Figures 21 to 23. The concentrations of zinc actually decrease in the higher levels of the food chain. The concentrations of copper in the Pontoporeia have relatively high values,but the values in the fish are much lower and are almost the same for all of the species. The results for mercury indicate clearly that its concentration increases in the food chain. The values for lake trout, a predator species, are significantly higher than those found for the benthos eaters, which, in turn, are greater than the most common values found for Pontoporeia. The value for the single adult whitefish is 4.3 ppm or close to that of the lake trout. When young, the whitefish's diet consists of Pontoporeia, but as the fish approaches adulthood, its diet also includes smaller fish.[1] The value for the single burbot of 2.2 ppm mercury is similar to that found for suckers and sculpin.

The data for the fish livers show the same trend as do those for the samples of flesh. The concentrations of mercury in the liver samples from lake trout are greater than for any of the other fish species. The

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[1] Scott, et al, 1973.

concentrations of copper and zinc in the liver samples are not as uniform as those for the flesh samples, but there is no clear trend of either element being concentrated into the livers of the fish at the higher trophic levels. The elements arsenic, cobalt, chromium and selenuim are not a focal point of this study, but the data available indicate that none of these elements are biomagnified in the food chain.

Fish are probably so mobile and the sources of trace elements so numerous that their body burden of trace elements cannot be easily correlated with the presence of a small area of sediment with anomalous concentrations of trace elements. However, the data in Table 12 do indicate that the concentrations of trace elements in fish can be dependent on regional location. The necessary information is collected in Table 13 which compares the concentrations of copper, zinc and mercury in the composite samples of liver for fish from the Duluth-Superior and Keweenaw area. In every case for these species, the concentrations of copper and zinc in the livers of fish from the Keweenaw area are higher than those found for similar samples from Duluth-Superior. Except for sculpin, the concentrations of mercury in the two sets of samples are nearly the same. No such differences are found for the samples of flesh. These observations indicate that the concentrations of trace elements in samples of fish, especially samples of liver, are not controlled at a constant level by biochemical reactions but are influenced by trace elements in the environment of the organisms.

The relatively high concentrations of zinc and copper in the livers of the Keweenaw fish may be a result of their food. The concentrations of these elements in the contents of the alimentary canal are about the same to slightly higher for the Keweenaw samples compared to those from the Duluth-Superior area (See Table 13). A later section also shows that the concentrations of copper and zinc in samples of Pontoporeia from Keweenaw are higher than those from Duluth-Superior. Also, biologists commonly assume that about 10 grams of food must be ingested for each gram of body weight gained. This value, when combined with the concentrations of trace elements found in the contents of the alimentary canal, shows that the efficiency of transfer of copper, zinc and mercury through the gut wall of these fish must be low. The entire body burden of these elements can be accounted for if only a small fraction (1-20%) of the elements found in the food is assimilated.

Although the evidence indicates that copper and zinc are not biomagnified in the food chain, their concentrations in the liver do reflect their concentrations in the food. Not enough is known of the normal concentrations of these elements in samples of fish liver to determine if the values found for the Keweenaw samples are excessive or if those from Duluth-Superior are deficient. Most previous studies have analyzed whole fish only. The results of this study show clearly the value of analyzing the different parts of organisms separately.

We conclude that the effects of regional environments on the concentrations of copper and zinc in these fish are most evident in liver samples while mercury is most easily detected in samples of flesh. There is no evidence that copper and zinc are biomagnified in the flesh of fish. Mercury is biomagnified in the food chain.

Table 13

The concentrations of copper, zinc and mercury in ppm for samples of liver and contents of alimentary canal from fish collected from the Duluth-Superior area are compared to similar samples from the Keweenaw area.

	Duluth-Superior		Keweenaw	
	Liver	Contents of Alimentary Canal	Liver	Contents of Alimentary Canal
Copper				
Sculpin	41-52	50-73	63	70
Sucker	24	104	72	137
Lake Trout	67	98	101	111
Zinc				
Sculpin	65	74-114	114	85
Sucker	70	110	104	103
Lake Trout	28	161	98	260
Mercury				
Sculpin	0.4	0.3-0.4	0.7	1.8
Sucker	0.3	0.2	0.4	0.4
Lake Trout	3.9	-	4.2	2.3

E. Relation of Pontoporeia to Sediments

The burrowing amphipod Pontoporeia is a predominant member of the macrobenthic community in Lake Superior and is in the lower part of the food chain for numerous fishes. Pontoporeia spend most of their time in the sediment which is also thought to contain their prime source of food. They generally feed upon detritus and associated microorganisms (Marzolf, 1965). It is generally thought that they move much shorter distances than do fish. All of these factors indicate that the concentrations of trace elements in Pontoporeia may be a valuable indicator of sediment quality with respect to trace elements.

Twenty-two samples of Pontoporeia were collected from the Duluth-Superior and Keweenaw areas. The results of the analysis, the depth from which they were collected, the date of collection and their average dry weight are presented in Table 14. The number of organisms per sample has only an approximate relationship to the population density at each site because the methods of collection were not completely quantitative.

No attempt was made to clear the alimentary canal of the Pontoporeia. They were frozen immediately after collection. The results, therefore, have values of concentrations of scandium, gallium and the rare earths that are significantly higher than found for the samples of fish (Table 12). This is a result of these elements being associated with the inorganic portion of the sediment which is ingested by Pontoporeia along with their food. A sample of sediment was also collected from most of the sites. The results of the sediment analysis corresponding to the samples of Pontoporeia are given in Tables 4 and 7. The samples of sediment from the Keweenaw area are unusually sandy and it was impractical to separate a clay-size fraction from these samples.

Several observations pertinent to the impact of the disposal of dredge spoil polluted with trace elements on the concentrations of trace elements in Pontoporeia can be made from the data presented in Tables 12, 4 and 7. The element zinc is present in higher concentrations in the Pontoporeia from Keweenaw (mean 107 ± 19 ppm, range 79 to 142 ppm) than in the samples from Duluth-Superior (Mean 75 ± 14 ppm, range 43 to 90 ppm). However, inspection of the data for the corresponding samples of sediment shows that the Keweenaw area has lower values of zinc (mean 24 ± 14 ppm, range 8 to 47 ppm) than does the Duluth-Superior area (mean 100 ± 44 ppm, range 66 to 145 ppm). This indicates again how poorly values of trace element concentrations in total sediments predict the uptake of trace elements by organisms.

This apparent contradiction may be a result of the generally smaller size of the Pontoporeia from Keweenaw. Figure 24 shows the relationship between the concentration of zinc in Pontoporeia and the average weight of the organisms in each sample. The line represents a least squares analysis of the data points. The average weight of Pontoporeia in four of the samples from Keweenaw fall within the range found for the Duluth-Superior samples, and it is important to note that the concentrations of zinc in these samples are also about the same as those found for the Duluth-Superior samples. We conclude that the high concentrations of zinc in most of the Keweenaw samples are due to the smaller size of the organisms. The smaller average weight of the Pontoporeia from Keweenaw is not the result of our sample handling and freeze-drying procedures. The organisms were noted to be small during collection.

The smaller organisms from Keweenaw tend to be found in deeper water, but this relationship is not consistent. The sample from Portage Entry was collected in 1974 at 48.8 meters and the average weight of the Pontoporeia is 0.83 mg while samples K2 and K8 were collected in 1975 at about 40 meters; however, the Pontoporeia in these samples have an average weight of less than 0.38 mg. Probably, the variations are a result of seasonal variations in the populations combined with other variables such as water temperature and supply of food.

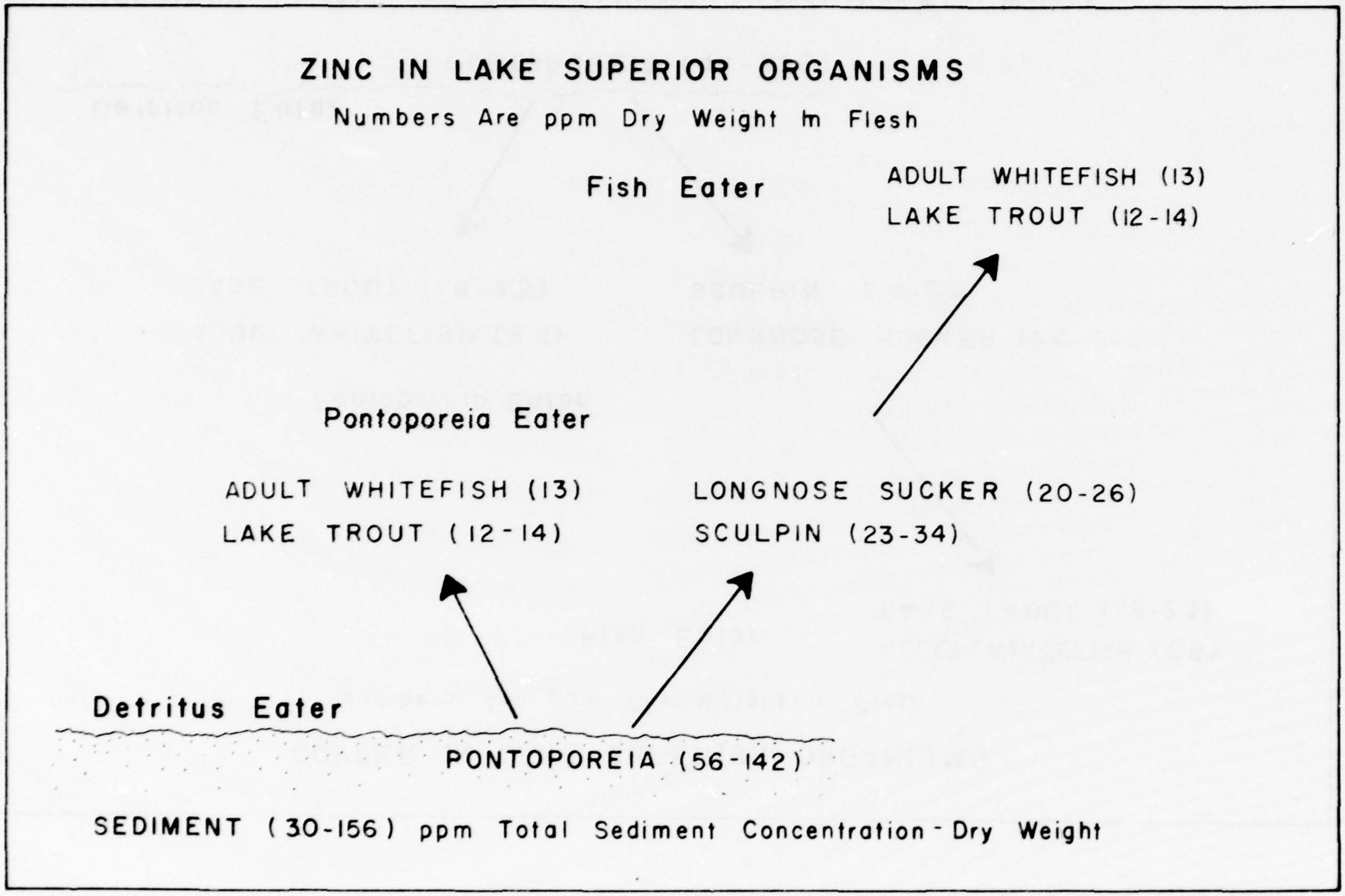
There is no evidence that the smaller size of the Keweenaw Pontoporeia is a result of their higher content of zinc. Some of the zinc in the sample of Pontoporeia are a result of sediment contained in their alimentary canal. An approximate correction for this portion of the total zinc can be made from the ratios of concentrations of zinc and scandium in the Pontoporeia and sediment. This assumes that the ratio of zinc to scandium in the bulk sediment is the same as in the sediment contained in the alimentary canal, and that no scandium is contained in the flesh or shell of the organisms. The results of these types of calculations show that about 10% of the total zinc in the Pontoporeia is the result of the presence of sediment in their alimentary canal. The samples from Keweenaw have a smaller correction which tends to amplify the differences between the samples from Duluth-Superior and Keweenaw. We conclude that the high concentrations of zinc in the Pontoporeia from Keweenaw as compared to those from Duluth-Superior correctly represent a higher body burden of this element in the

Keweenaw organisms. The high zinc concentrations probably result from a greater ratio of exoskeleton to flesh for the smaller organisms as compared to larger organisms because the hard parts of crustaceans can contain up to 200 ppm zinc (Bowen, 1966). Therefore, the concentrations of zinc in different samples of Pontoporeia can be compared only when the organisms within each sample are about the same size.

For the range of concentrations found in this study, the concentrations of zinc in Pontoporeia show little or no relationship to the concentrations of zinc in the total sediment (Figure 25). The same is true for the clay-size fraction.

The concentrations of copper in Pontoporeia from Keweenaw are higher (mean 191 ± 31 ppm, range 154-238 ppm) than those for Duluth-Superior (mean 105 ± 39 ppm, range 44-178 ppm). However, unlike the case for zinc, there is no clear relationship between the sizes of the Pontoporeia and their concentrations of copper. All of the Pontoporeia from Keweenaw, including the samples of large organisms, have high concentrations of copper. There is no simple relationship between the concentrations of copper in Pontoporeia and sediment (Figure 26).

We have too few data points to describe any clear relationship between the concentrations of mercury in Pontoporeia and sediment. However, it is important to note that the clay-size fraction of sample MP has the highest concentration of mercury found in the lake (4.3 ppm) and the Pontoporeia from this station also have the highest concentration found (2.0 ppm). Sample 45 has the second highest values, 2.7 ppm in the clay and 1.7 ppm in Pontoporeia. This apparent relationship is not perfect because sample 21 contains 1.4 ppm mercury but the Pontoporeia have only 0.1 ppm. Comparison of the other values shows that all of the samples of Pontoporeia containing high concentrations of mercury come from stations having high concentrations of mercury in the clay-size fraction but that some stations having high concentrations in the clay-size fraction have low concentrations in the Pontoporeia. All of the samples of Pontoporeia from the Keweenaw area have low and almost constant concentrations of mercury (0.14 to 0.38 ppm) except sample P 50 which contains 1.0 ppm mercury.



ZINC IN LAKE SUPERIOR ORGANISMS

Numbers Are ppm Dry Weight In Flesh

Fish Eater

ADULT WHITEFISH (13)
LAKE TROUT (12-14)

Pontoporeia Eater

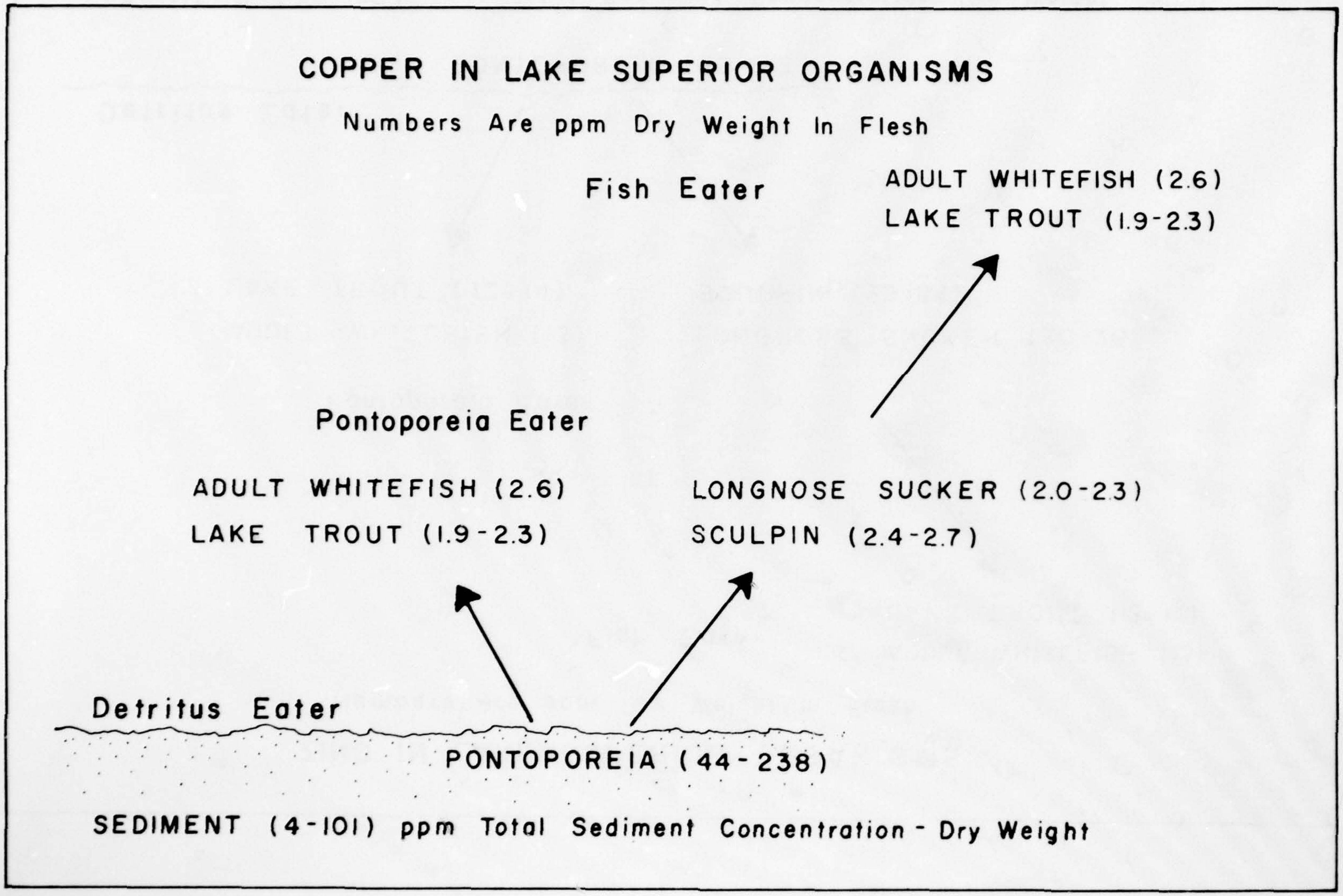
ADULT WHITEFISH (13)
LAKE TROUT (12-14)

LONGNOSE SUCKER (20-26)
SCULPIN (23-34)

Detritus Eater

PONTOPOREIA (56-142)

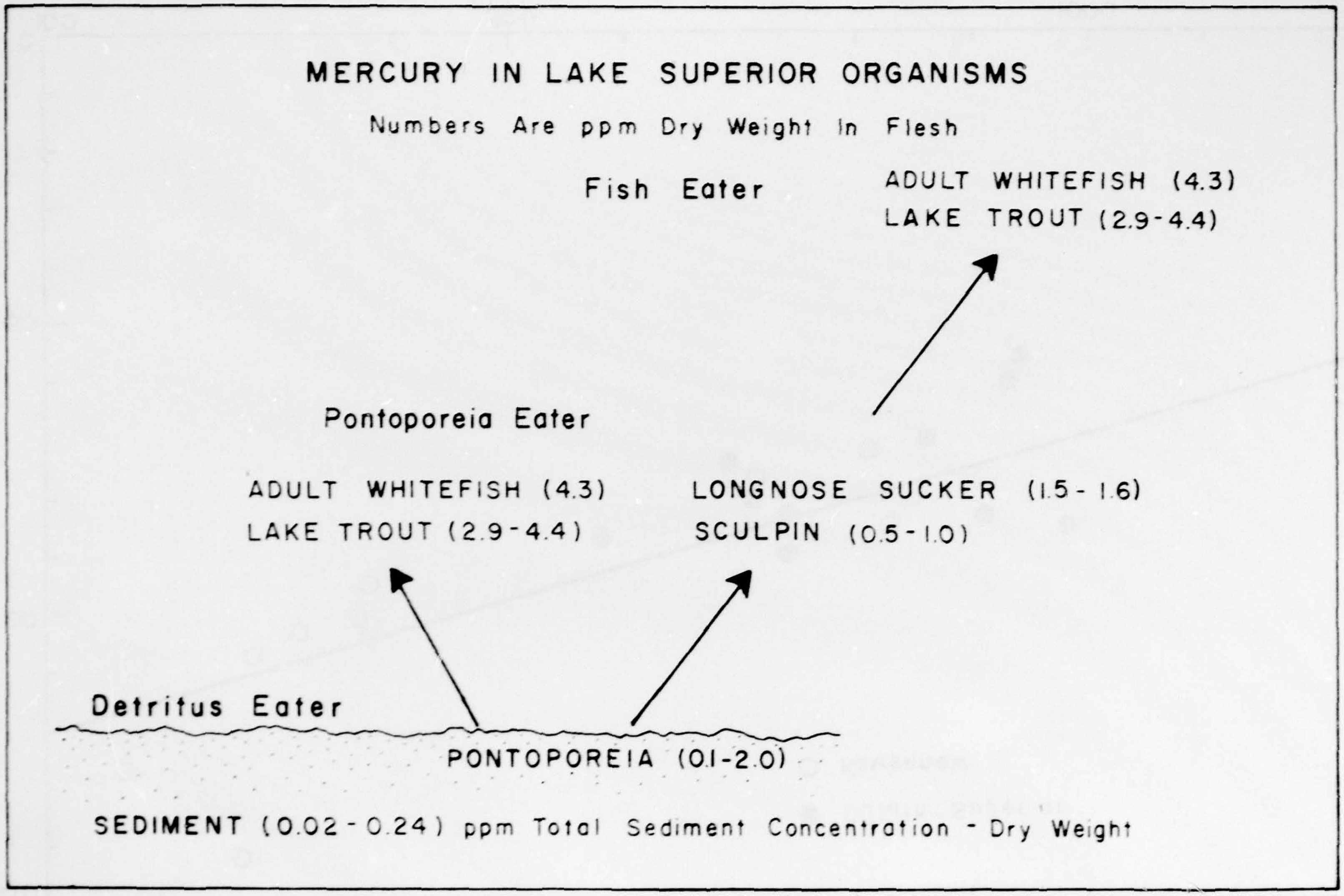
SEDIMENT (30-156) ppm Total Sediment Concentration - Dry Weight



COPPER IN LAKE SUPERIOR ORGANISMS

Numbers Are ppm Dry Weight In Flesh

SEDIMENT (4-101) ppm Total Sediment Concentration - Dry Weight



MERCURY IN LAKE SUPERIOR ORGANISMS

Numbers Are ppm Dry Weight In Flesh

Fish Eater

ADULT WHITEFISH (4.3)
LAKE TROUT (2.9-4.4)

Pontoporeia Eater

ADULT WHITEFISH (4.3)
LAKE TROUT (2.9-4.4)

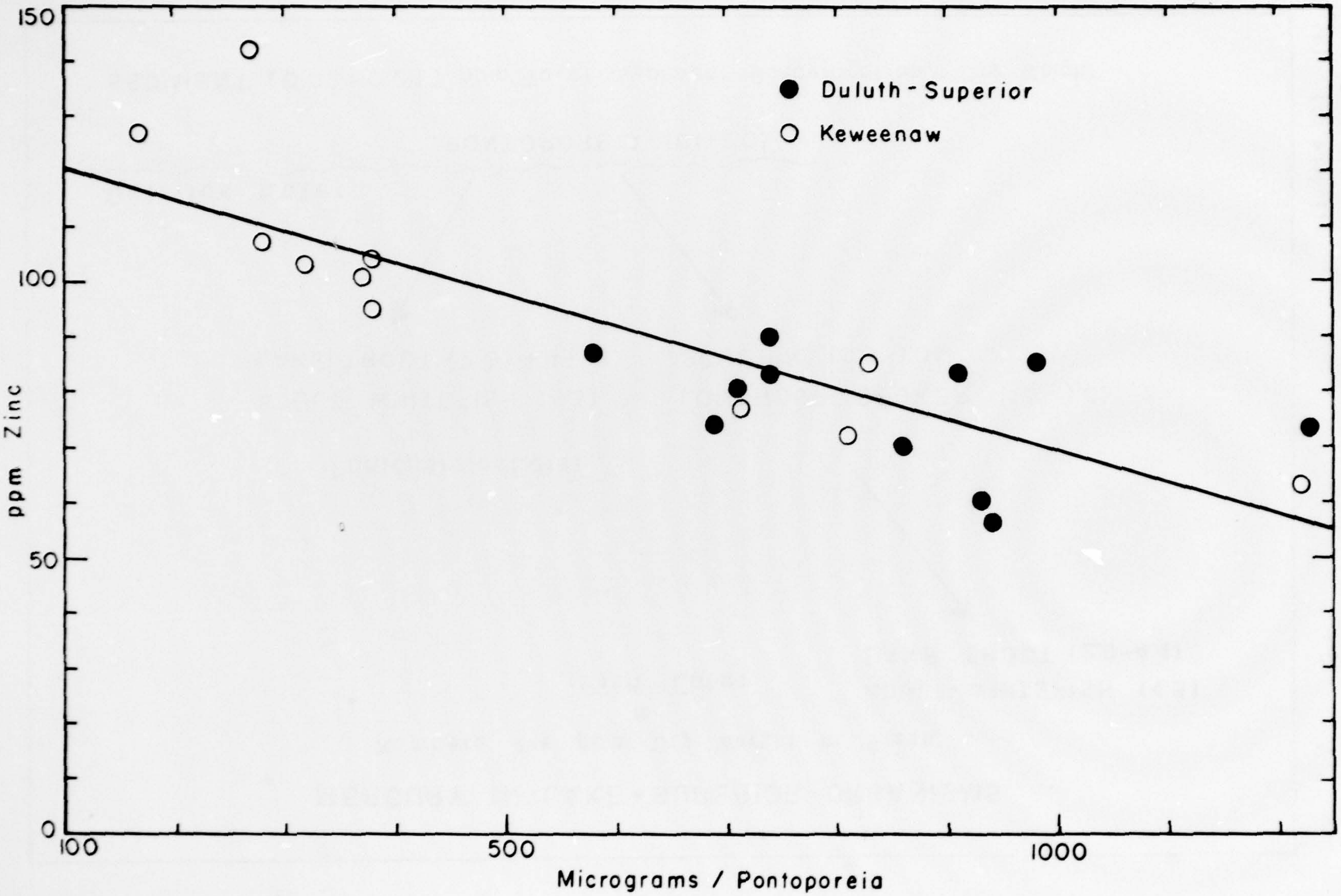
LONGNOSE SUCKER (1.5-1.6)
SCULPIN (0.5-1.0)

Detritus Eater

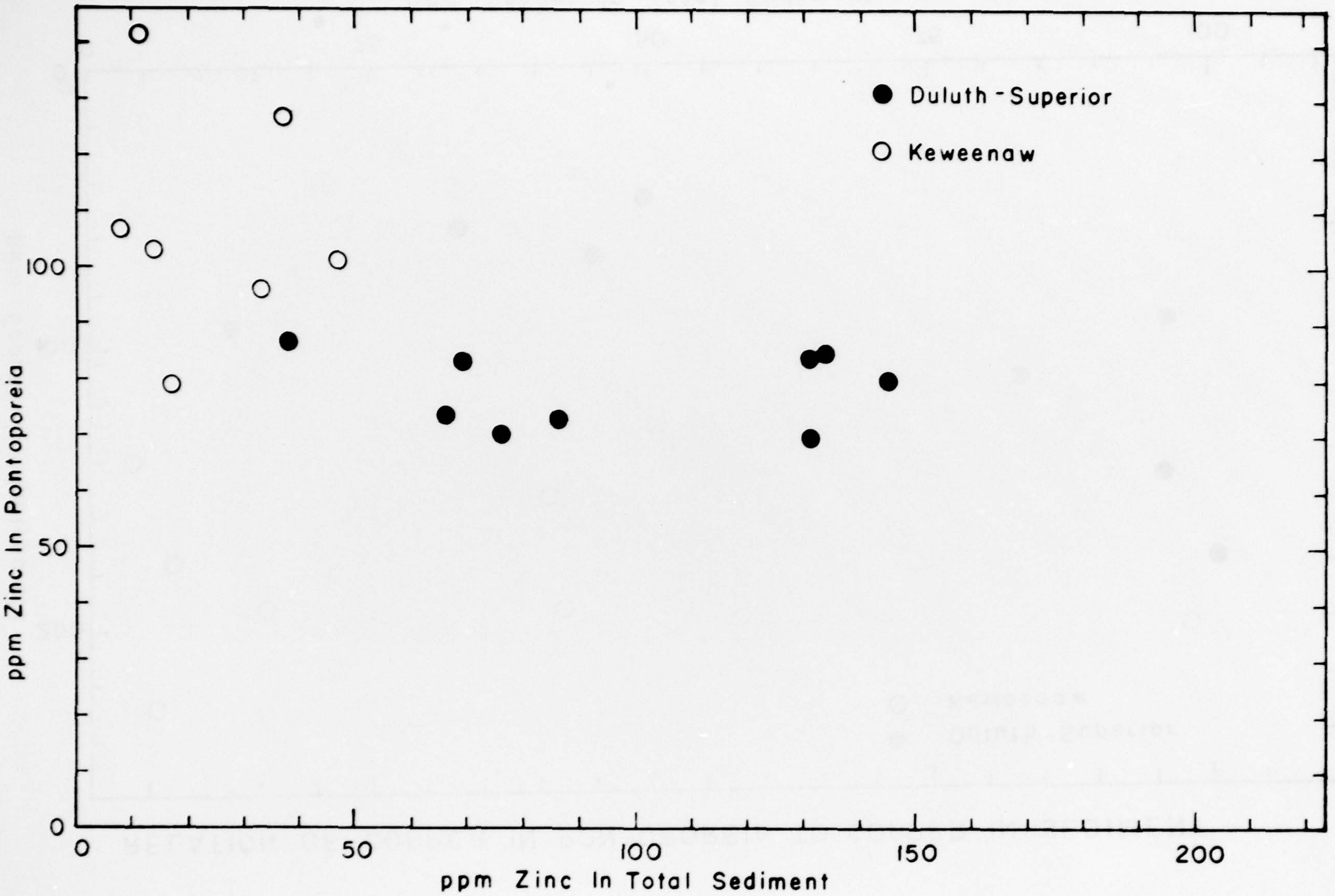
PONTOPOREIA (0.1-2.0)

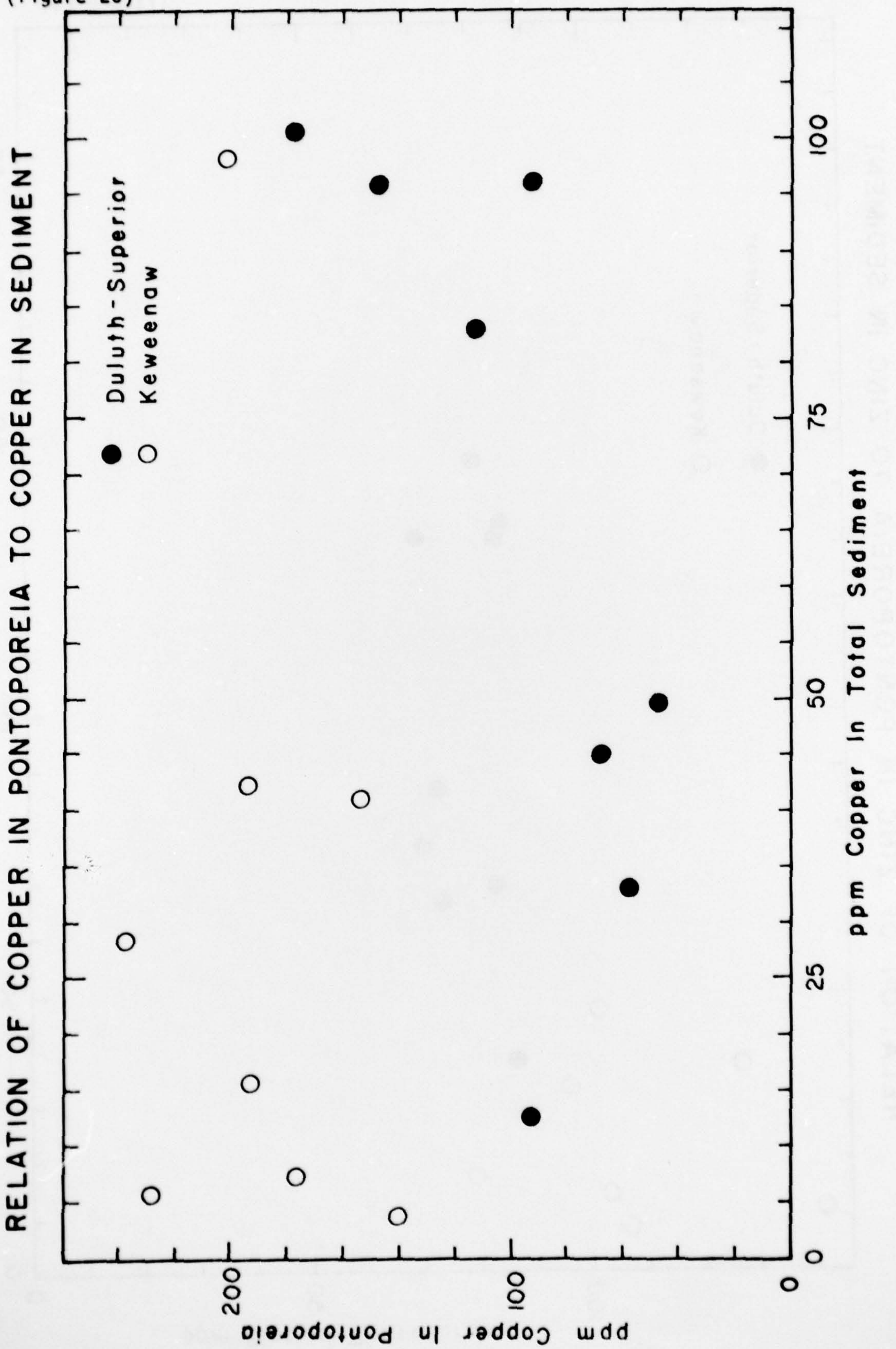
SEDIMENT (0.02-0.24) ppm Total Sediment Concentration - Dry Weight

RELATION OF ZINC CONCENTRATION IN PONTOPOREIA TO BODY WEIGHT



RELATION OF ZINC IN PONTOPOREIA TO ZINC IN SEDIMENT





RELATION OF COPPER IN PONTOPOREIA TO COPPER IN SEDIMENT

F. Conclusions Based on Trace Elements in Organisms

The lack of any simple correlation between the concentrations of copper and zinc in Pontoporeia and sediment indicates that complex mechanisms must be involved in the transfer of elements from sediments to organisms. The association of high concentrations of mercury in Pontoporeia with high mercury concentrations in sediment when combined with the known biomagnification and toxicity of this element shows that potential problems of mercury toxicity can be easily created, if polluted sediments are dumped into the lake. In fact, two of the samples of Pontoporeia (MP and 45) have concentrations of mercury (1, 2 ppm) lower but near the concentrations of 5 ppm measured in Pontoporeia from the bioassay experiments where changes in behavior were observed. All of the samples of Pontoporeia from the lake, when corrected for differences in the size of the organisms, have concentrations of zinc near those found for the control animals in the bioassay experiment. We have found no evidence to indicate that in - lake disposal of dredged materials with concentrations of copper and zinc similar to those found for the sediments in the lake, especially in the clay-size fractions, will change the concentrations of these elements in the biota.

The results of this section indicate that the values of 180 ppm zinc, 75 ppm copper and 0.2 ppm mercury in the clay-size fraction selected on the basis of the sediment studies (Section II, G) are reasonable approximations of the ranges of 160 to 250 ppm zinc, 65 to 88 ppm copper and 0.1 to 0.4 ppm mercury. That is, disposal of dredged material containing these or lower concentrations of the above elements will not affect the concentrations of these elements in organisms. All available evidence suggests that the discharge of mercury needs to be monitored carefully. The value of 0.2 ppm in the clay-size fraction is near the background concentration of mercury in the Duluth-Superior area. We have insufficient evidence to indicate what the upper limit for this element should be.

V. APPENDIX

A. Laboratory Methods Used for Analysis Sediments

Samples of sediments from the harbor area and the old dump sites in the lake were collected in October, 1973, with a 9x9 inch Ponar dredge. This sampler collects a mixture of the top three to six inches of sediment -- the depth depending on the grain size and degree of compaction the sediment. In-lake samples were collected in the summer of 1974 by the same method. Additional scow samples were collected by hand directly from the scows during a Corps of Engineers dredging operation in June, 1975. One core of in-lake sediment was obtained using a plastic corer. Four samples of red clay were collected from the cliffs along the Wisconsin shoreline by cutting the samples out by hand from a location below the zone of weathering. The surface of the sample, where the cliff face was exposed, was discarded. A sample of quartz was obtained by hand picking the quartz grains from a sample of sand from Wisconsin Point Beach under a microscope. To prevent contamination of the samples, they were immediately transferred from the sampler and sealed into double plastic bags on shipboard and sent to the laboratory in Madison for analysis. The samples were mixed thoroughly in the plastic bags and a portion transferred to glass bottles, labelled, and stored until they could be analyzed in a specially designed room where the possibilities of contamination are minimized. The cores were sectioned at 2-cm intervals to a depth of 10-cm and 5-cm intervals below that point. All sample handling was done using stainless steel spatulas to minimize the possibility of contamination. The samples were kept wet until immediately prior to preparation for analysis.

For total sediment analysis, the samples were taken from the bottles, air-dried at 60°C, ground, mixed, and finally subsampled. The clay fraction was collected by shaking approximately 30 grams dry weight basis of wet sediment with 900 ml of deionized water in a clean polyethylene bottle for one hour and then allowing it to stand undisturbed for eight hours. After this time, a sample was withdrawn slowly by pipet, so as to prevent agitation, from a point 10-cm below the water surface. This corresponds to the point to which (according to Stokes' Law) a particle having an equivalent spherical diameter of two microns would fall, if it started at the surface of the water at the beginning of the eight hours. The equivalent spherical diameter is a number equal to the diameter of a sphere of density 2.5 which falls at the given rate. Note that, in this definition, the number refers to the settling rate rather than some physical measure of the particles collected. The water-sediment mixture collected was then filtered through a 0.45 micron Millipore filter and the sediment collected; it was air-dried at 60°C; and weighed in preparation for elemental analysis. A silt plus clay fraction of the sediment was collected similarly except that the settling time was only a few seconds and the sample was collected at a point two cm below the surface of the water. The method used to collect the two size fractions which is biased toward the larger end of each fraction does not collect all of each fraction, but rather only a portion of them. To obtain the total clay fraction, for instance, the sample would have to be shaken and allowed to settle as described previously. However, in drawing off the water and sediment, one would start from the surface and slowly withdraw the mixture down to the 10-cm mark. Deionized water would be added back to the plastic bottle and the procedure repeated as many times as necessary to withdraw almost all of the clay fraction. This procedure was not used in this study because large sample sizes were not needed and the large volume of water that would be collected by this method would take a prohibitively long time to filter. The filters used tended to clog after filtering 50 to 75 ml of water-sediment mixture.

The multielement analyses were by instrumental and radiochemical neutron activation analysis using modifications of the procedures of Allen et al. (1970) and Denechaud et al. (1970). All of the elements measured in the sediment samples were determined by instrumental neutron activation analysis with the exception of copper and mercury. These two elements were determined by neutron activation followed by radiochemical separation and gamma-ray spectrometry. The elements, arsenic, antimony and zinc were determined by both methods. The uncertainties listed represent one standard deviation based on counting statistics. A total uncertainty in the analysis for any element is approximately two percent for those elements with the lowest counting statistics when uncertainties associated with sample handling are taken into account.

Three sediments from the open lake, one sediment from the Superior harbor, a sample taken from the red clay of the Wisconsin shore, and a prehistoric sediment from a core sample were examined by x-ray diffraction. X-ray diffractograms were obtained for both the $<2\mu$ fraction and the total sediment. The sample preparation used is described by Jackson (1973). A quantitative mineralogical examination was not attempted but only the identification of the minerals within each size fraction.

The clay minerals found in both size fractions are illite, a mixed layer 10 Å to 14 Å clay mineral, expandable clay minerals, mainly montmorillonite, chlorite and akolinite. The non-clay minerals present in both size fractions are quartz, plagioclase feldspar and potash feldspar. Additionally, some of the sediments contain small amounts of vermiculite.

VI. Bibliography

VI. Bibliography

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