EFFECT OF SEDIMENTARY ENVIRONMENT ON TRACE-METAL FIXATION: UPPER LAKE MICHIGAN

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ABSTRACT

EFFECT OF SEDIMENTARY ENVIRONMENT ON TRACE-METAL FIXATION: UPPER LAKE MICHIGAN

By

Richard William Kotsch

Sixty stations were sampled in Lake Michigan from the Mackinac Straits to a line extending from Ludington, Michigan, to Sheboygan, Wisconsin. The data obtained from the bottom water include depth, Cl, temperature, alkalinity, specific conductivity, and dissolved oxygen. Sediment samples were analyzed for: sediment texture, Eh, pH, total carbon, organic carbon, Co, Cr, Cu, Mn, and Zn.

Correlation and R-mode factor analyses show interrelationships between variables and allow understanding of the causes of metal fixation. The variables cluster into 7 groups (accounting for 84% of variability). Three are associated with the occurrence of metals in sediment. The other two groups include temperature, depth, pH, alkalinity, specific conductivity, Cl, phi mean, and phi standard deviation, all of which apparently have little effect on the fixation of the metals. Zinc, Co, Cr, and organic carbon represent one cluster, which supports the concept that these metals are

fixed by complexation with organic compounds. Copper and total carbon represent another somewhat related factor. This factor reflects the distribution of Cu and carbonate-mineral detritus from the drainage basin. Manganese represents the final factor and is relatively independent of other factors, although there are significant correlations between manganese, depth, and cobalt.

Q-mode factor analysis relates sample stations, rather than variables. Seven factors account for 97% of the total variability. One factor consists of samples from the eastern and northern, nearshore environment. These samples are characterized by low, trace-metal and manganese content, shallow depths, and coarse sediments. These samples define areas swept by currents that have not been subject to significant metal loading. The second factor characterized the nearshore zone on the western side of the lake. This area is shallow, sandy, and has somewhat higher, trace-metal loads. Manganese content is variable, but high in some samples. This province is equivalent to the eastern shore, with the exception that there are metals derived from bedrock sources north of the lake. The third factor consists of scattered samples that contain high trace-metal loads from throughout the nearshore of the lake. These samples are generally near known, human sources of metals. The remaining four factors are characterized by high metal content, high organic-carbon content, fine grain sizes, and deep water. These factors are combined to represent the deep lake, where fixation is due to complexation on clays and organic compounds. The high variability in this suite reflects local variation in sediment chemistry and sources of metals.

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By

Richard William Kotsch

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INTRODUCTION

This study examines the relationship between sources and sediment uptake of trace metals in upper Lake Michigan. Trace metals are known to accumulate at the sediment-water interface from different sources, including interstitial and, possibly, ground water, tributary runoff, and the atmosphere. For example, formation of manganese nodules and included trace metals has been attributed to migration of interstitial water toward the sediment-water interface through time (Rossmann and Callender, 1969). In the southern half of Lake Michigan, trace metals have been related to atmospheric sources (Winchester and Nifong, 1971) and to tributary discharge (Kennedy et al., 1971; Shimp et al., 1971). By comparing the distribution of the minor metal Mn and selected trace metals (Co, Cr, Cu, and Zn) to sediment texture, sediment chemistry, and potential sources, the relative importances of source and mechanisms of metal fixation can be evaluated.

Location and Setting

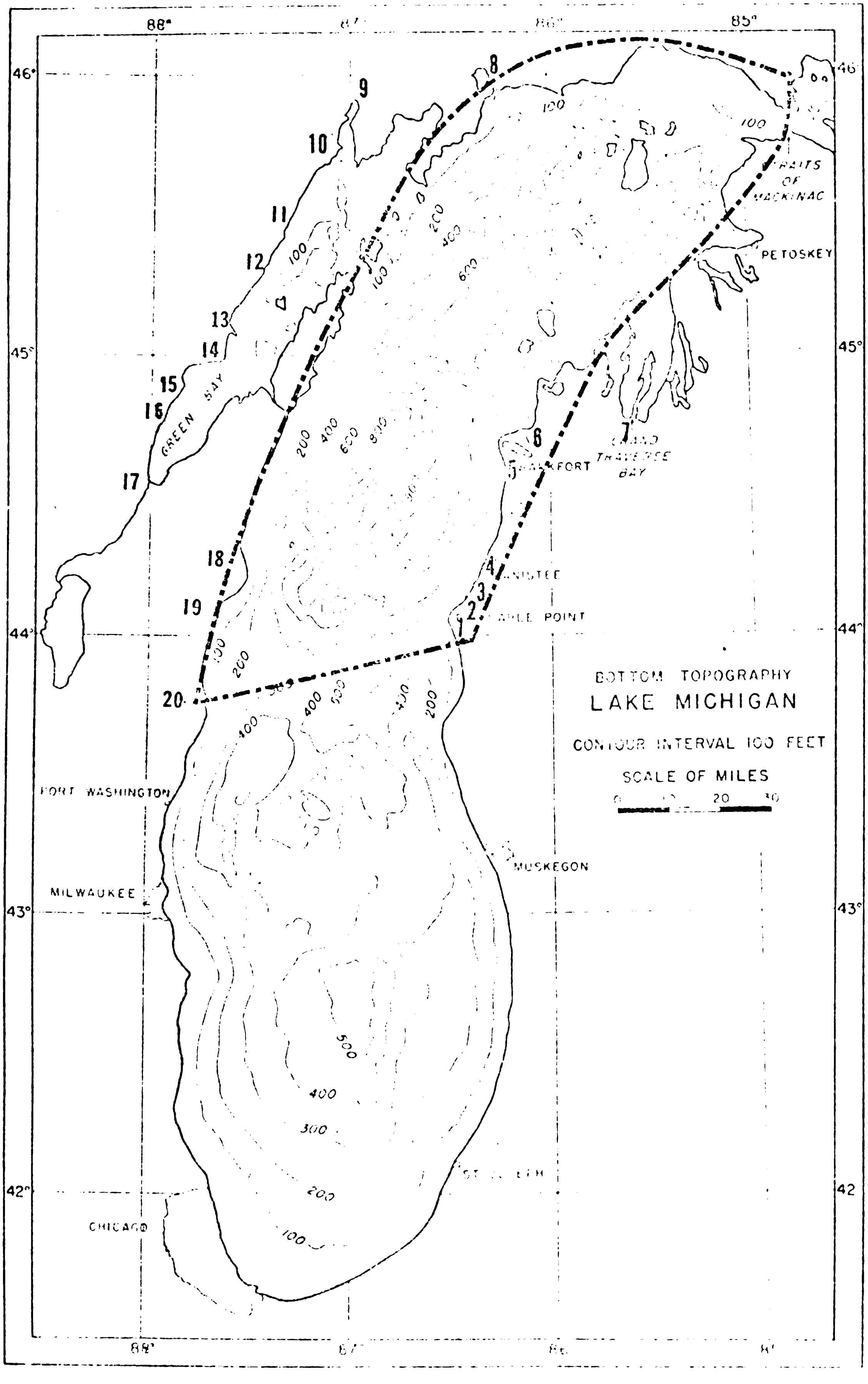
Lake Michigan can be divided into two basins (Hough, 1958) along a morainal ridge that crosses the lake from Sheboygan, Wisconsin, to Ludington, Michigan. This ridge separates the northern basin from the southern basin and is the southern limit of the study area (Figure 1). The northern limit of the study area is the Mackinac Straits. The estuaries, Green Bay and Grand Traverse Bay, are not included in the study area.

According to Hough (1958), the study area lies in the Paleozoic rock province. The sedimentary rocks, mainly shales, limestones, and dolomites, that underlie the lake were eroded by pre-Pleistocene streams and by the Pleistocene glaciers. The result of this complex erosional history is a basin with a maximum depth of 285 m and a mean depth of 85 m. The northern half of Lake Michigan can be characterized by a valley and ridge topography (Figure 1). This topography influences sediment texture and chemistry (Moore, 1961).

Lake Michigan currents and circulation patterns were described by Ayers <u>et al</u>. (1958), who used drift bottles and the dynamic-height method to determine the surface currents, bottom currents, and regions of upwelling and sinking (Figures 2 and 3). The currents are controlled by wind direction. Surface currents in the open lake require about three-fourths of a day lapse with "normal" wind velocities before establishing a new current direction. Under "normal" wind velocities as little as two hours is sufficient for a new current direction to appear in very shallow water along shore. Under "normal" conditions a wind-induced surface current has a velocity about 2% of the causative wind (Ayers, 1962).

Figure 1. Location and bathymetry of study area (Modified from Hough, 1958). Location of tributaries entering upper Lake Michigan (Modified from Robbins *et al.*, 1972).

1. Pere Marquette
2. Lincoln
3. Big Sable
4. Manistee
5. Betsie
6. Platte
7. Boardman
8. Manistique
9. Whitefish
10. Escanaba
11. Ford River
12. Cedar
13. Menominee
14. Peshtigo
15. Oconto
16. Pensaukee
17. Fox River
18. Two Rivers
19. Manitowoc
20. Sheboygan


BOTTOM TOPOGRAPHY
LAKE MICHIGAN
CONTOUR INTERVAL 100 FEET
SCALE OF MILES
0
10
20
30
88°
87°
86°
85°
46°
45°
44°
43°
42°
1
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19
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GREEN BAY
STRAITS OF MACKINAC
PETOSKEY
GRAND TRAVERSE BAY
FRANKFORT
MANISTEE
SABLE POINT
FORT WASHINGTON
MILWAUKEE
MUSKEGON
ST. JOSEPH
CHICAGO
100
200
300
400
500
600
800

Figure 2. Surface currents in Lake Michigan, 23 June 1955 (Modified from Ayers *et al.*, 1958).

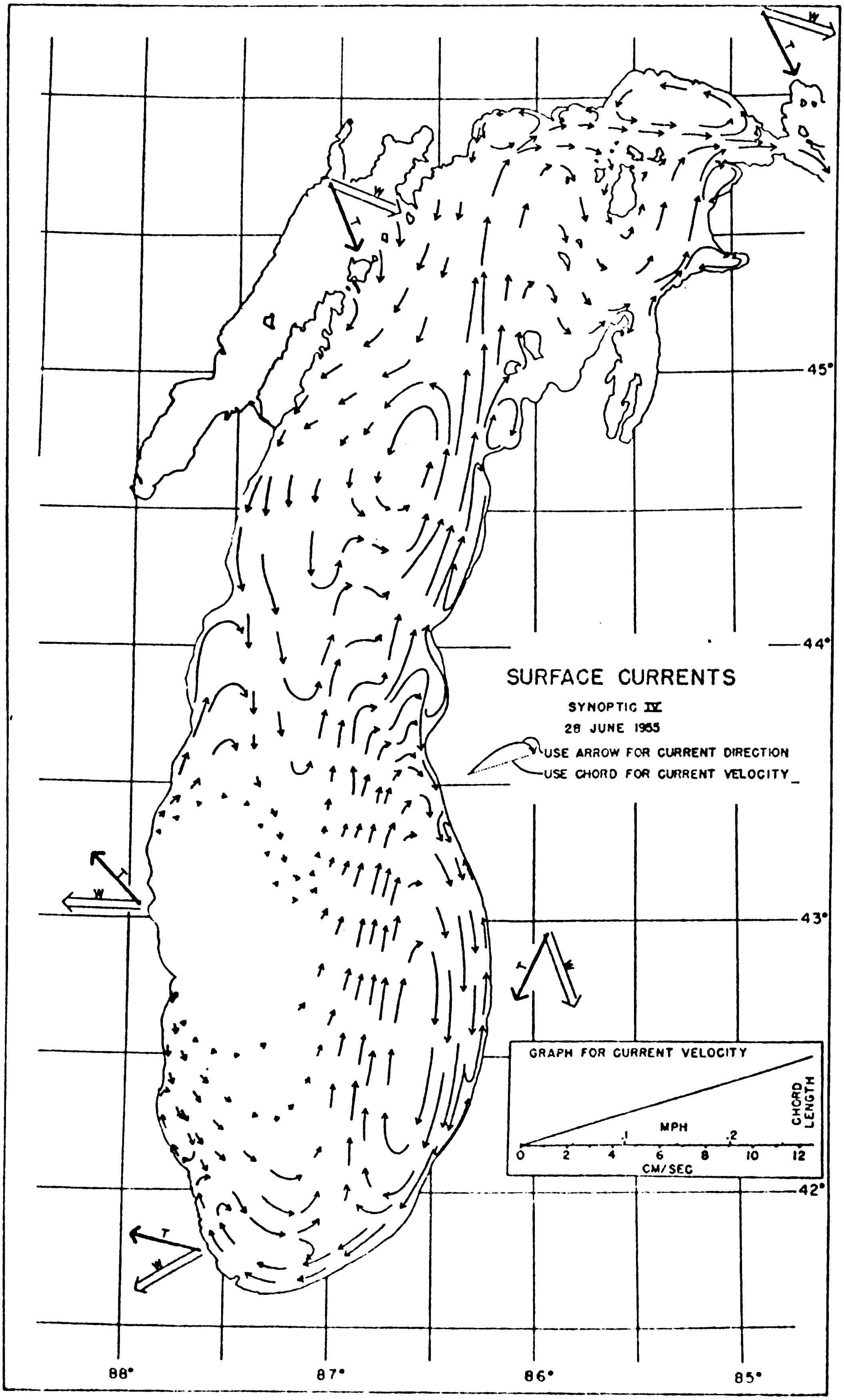
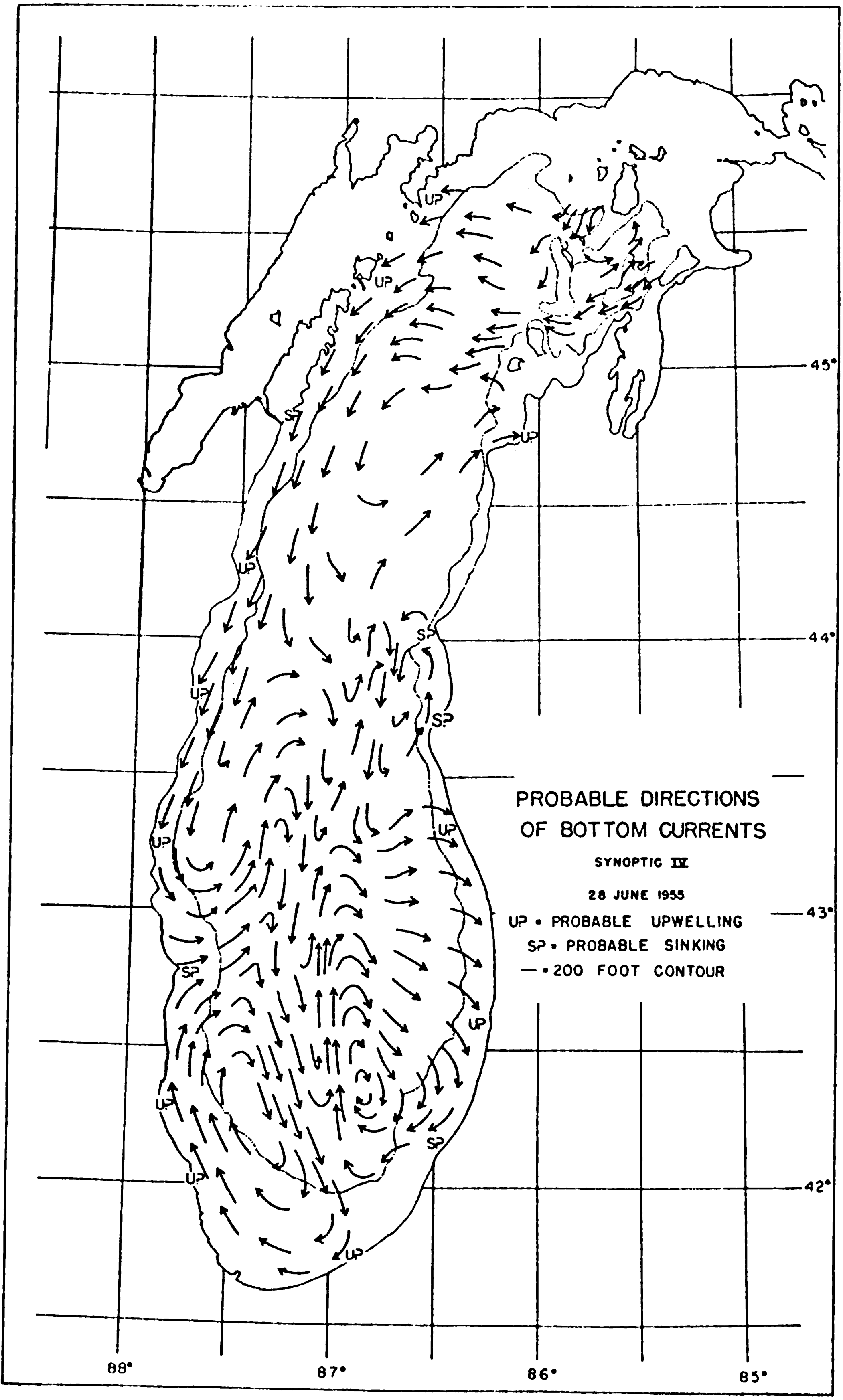

SURFACE CURRENTS
SYNOPTIC IV
28 JUNE 1955
USE ARROW FOR CURRENT DIRECTION
USE CHORD FOR CURRENT VELOCITY
GRAPH FOR CURRENT VELOCITY
CHORD LENGTH
MPH
.1
.2
0
2
4
6
8
10
12
CM/SEC
W
T
45°
44°
43°
42°
88°
87°
86°
85°

Figure 3. Probable directions of bottom currents, 28 June 1955 (Modified from Ayers *et al.*, 1958).



PROBABLE DIRECTIONS
OF BOTTOM CURRENTS

SYNOPTIC IV

28 JUNE 1955

UP = PROBABLE UPWELLING

SP = PROBABLE SINKING

— • 200 FOOT CONTOUR

Therefore, large-scale circulation in the open lake is relatively persistent, while nearshore circulation is ephemeral and dependent on local wind conditions.

Hough (1958) and Ayers et al. (1958) show a general northeastern flow of water along the east shore of Lake Michigan, westward currents along the Upper Peninsula of Michigan, and southward flow past Green Bay, Wisconsin. There are several small eddy currents along the Wisconsin coast, in Traverse Bay and in Green Bay. The major circulation crosses the lake in a northeasterly direction from Sheboygan, Wisconsin, to Ludington, Michigan.

Sediments

Sediment distribution patterns in the northern basin are not well known. Lewis (1972) gave the only description of general sediment types. Lake bottom topography exerts a strong control on the distribution of sediments, especially in the vicinity of the ridges and valleys (Hough, 1958; Moore, 1961). Coarse-grained sediments occur on the ridges and adjacent ridge flanks, while fine-grained sediments are restricted to the depressions. Fine to medium, moderately well-sorted sands cover most of the northern area near the Straits and continue southward in a narrow band, parallel to both shorelines. Brown and reddish-brown clays cover the deeper area (Lewis, 1972).

Moore (1961) made a detailed study of the northeastern Lake Michigan ridge and valley province, from Beaver Island to the Mackinac Straits, south to Petoskey and west to North Fox Island and north again to Beaver Island. Moore's petrographic study of the bottom sediments shows a direct relationship between sediment properties, sources of material, post-glacial history and environment of deposition.

Lauff *et al.* (1961) working on the bottom sediments of the Mackinac Straits region, concluded that the west to east currents in the Straits are reflected in the distribution of silt-sized sediments. Silt is scarce in Lake Michigan and in the Straits, while upper Lake Huron is characterized by an abundance of silt. The eastward increase in silt is a result of a decrease in current velocity in Lake Huron. Sandy sediments predominate over most of the Mackinac Straits area and are the characteristic sediments of depths to 30 m of water. Clays are characteristic of the deepest portion of the Straits. The clays for the most part are sandy, red clays and frequently contain pebbles (Lauff *et al.*, 1961).

A study of sedimentation in the Manitou Passage (45° N Lat., 86° W Long.; Figure 1) was made by French (1964). The wind-controlled currents produce rapid, sediment erosion and transport of the coarse, well-sorted sands in a northeastward direction, causing the Manitou Passage area to be in a state of rapid geological change.

Minor and Trace Metals

Kennedy et al. (1971) and Shimp et al. (1971), among others, studied the trace metals and sediments in southern Lake Michigan. They found a definite increase in concentration in such metals as Cu, Hg, Pb, and Zn in the upper 10 to 20 cm of the sediments. They concluded that the increased concentration is related to recent contributions from coastal sources, such as urban areas and tributary streams. They also noted a strong correlation between metal accumulation and clay and organic-carbon concentration in the sediments.

Robbins et al. (1972) measured the input of soluble trace metals into Lake Michigan from tributary rivers. Table 1 lists the rivers and the amount of trace metals entering the northern portion of the lake. A systematic distribution of the trace metals from origin to sink has not been worked out for the northern basin of Lake Michigan.

Rossmann and Callender (1968, 1969) showed that manganese nodules are forming at the sediment-water interface, possibly from the upward migration of metals in interstitial water. Eh, pH, sediment type and dissolved oxygen are the critical factors for nodule growth. Within the sediment interstitial water, manganese is stable in the Mn^{+2} state (Fricker, 1965), while manganese precipitates as a hydroxide when the metal enters the oxidizing environment in the interstitial water near the sediment interface (Rossmann and Callender, 1969).

Table 1. Trace-metal concentrations in upper Lake Michigan tributaries (Modified from Robbins <u>et al</u>., 1972).

River	Drainage Area (Sq. Mi.)	Mean Discharge (CFS)	Mn (ppb)	Cr (ppb)	Zn (ppb)	Cu (ppb)
Pere Marquette	770	610	17.6	0.1	4.9	1.4
Lincoln	-	-	25.6	0.1	4.9	2.0
Big Sable	127	139	8.7	0.1	1.7	1.6
Manistee	2010	2100	14.7	1.6	1.3	2.2
Betsie	95	76	6.9	0.7	0.9	1.9
Platte	92	72	1.3	0.3	6.0	2.0
Boardman	350	190	10.7	0.8	2.3	1.8
Manistique	1450	1700	21.0	0.4	6.0	2.4
Whitefish	315	-	8.2	0.3	5.5	0.9
Escanaba	920	900	24.5	0.3	21.6	2.1
Ford River	470	320	7.0	0.3	3.9	1.5
Cedar	9	11	13.1	0.8	3.4	1.3
Menominee	1450	1700	10.8	-	2.4	1.1
Peshtigo	1160	830	28.2	1.0	15.3	0.9
Oconto	930	570	36.8	1.6	0.5	2.1
Pensaukee	-	-	14.7	1.2	2.0	2.3
Fox River	6440	4140	17.5	7.5	7.5	2.7
Two Rivers	-	-	2.1	1.1	1.5	1.4
Manitowac	440	-	30.6	0.9	4.2	2.9
Shegoygan	440	230	8.1	1.4	27.6	2.7

The manganese hydroxide occurs as a coating and crust on sand grains, pebbles and as sediment clasts without nuclei (Rossmann and Callender, 1968). The upper 10 cm of several sediment samples were enriched in manganese coating as compared to the lower part of the samples. The manganese content of the interstitial water extracted from the samples shows a pronounced increase with sediment depth (Rossmann and Callender, 1968). The data of Rossmann and Callender fit the model of Cline and Upchurch (1973), who suggested that some trace metals may be concentrated at the surface by resolublization of the metals associated with organic complexes at depth in the sediment and upward migration through dewatering, diffusion and, possibly, transport on bubble surfaces.

Minor and Trace-Metal Fixation Models

There are two possible mechanisms that can lead to the distribution of metals in sediments of upper Lake Michigan. The metals may be introduced to the lake via surface water with direct uptake on clays and organic complexes in the lake sediments. If this is the case, then the metals would be expected to be concentrated close to the point source and in areas of high clay and organic content. The metals present in the sediments reflect both natural and cultural sources. The primary, naturally-occuring metals to be expected in upper Lake Michigan are Cu, which could be derived from the

Cu-bearing strata of the western Upper Peninsula, and Mn, which is an ubiquitous minor element in most rock types. All metals, including Co, Cr, Cu, Mn, and Zn, are cultural contaminants and should be concentrated near ubran areas. If the metals have an atmospheric origin they should be more widely distributed. All of the metals included in this study have been shown to be available to Lake Michigan from the atmosphere (Winchester and Nifong, 1971). Significant atmospheric sources of these trace metals are heavy industry and urban areas. The industrial metropolitan areas around southern Lake Michigan are potential major sources upwind from upper Lake Michigan, so atmospheric contribution is likely.

Rossmann and Callender (1968, 1969) and Cline and Upchurch (1973) have argued that the accumulation of metals at the sediment-water interface may be due to upward migration of the metals in interstitial water with fixation in a chemically suitable environment. If this is the case, then metals may cycle in the lake sediment until fixed.

Manganese is fixed along with Fe and trace metals by precipitation as a hydroxide (Bricker, 1965) and manganese nodules occur in highly oxygenated, low organic-carbon environments (Rossmann and Callender, 1969). Sediments characterized by low organic content appear necessary for manganese-nodule formation because organic sediments will complex Mn^{+2} and prevent nodule formation (Bricker, 1965). The other metals, Co, Cr, Cu, and Zn, form complexes with organic compounds and clays (Walters et al., 1972; Cline, 1974). Thus, manganese and trace-metal fixation is restricted to specific sedimentary environments. By comparing metal content and associations within similar sedimentary environments, the importances of source and uptake mechanism can be evaluated.

Correlation analysis and R-mode factor analysis are used to determine interrelationships of chemical properties and dependence of the metals on sedimentary environments in upper Lake Michigan. By use of correlation and R-mode factor analysis, those metals restricted to specific chemical environment can be identified and their uptake related to the environment. Q-mode factor analysis is used to delineate zones of comparable trace-metal content and sediment character. Q-mode factor analysis allows the correlation of sample distribution, sediment type, and metal content. Integration of the two methods allows identification of sources and sinks of metals.

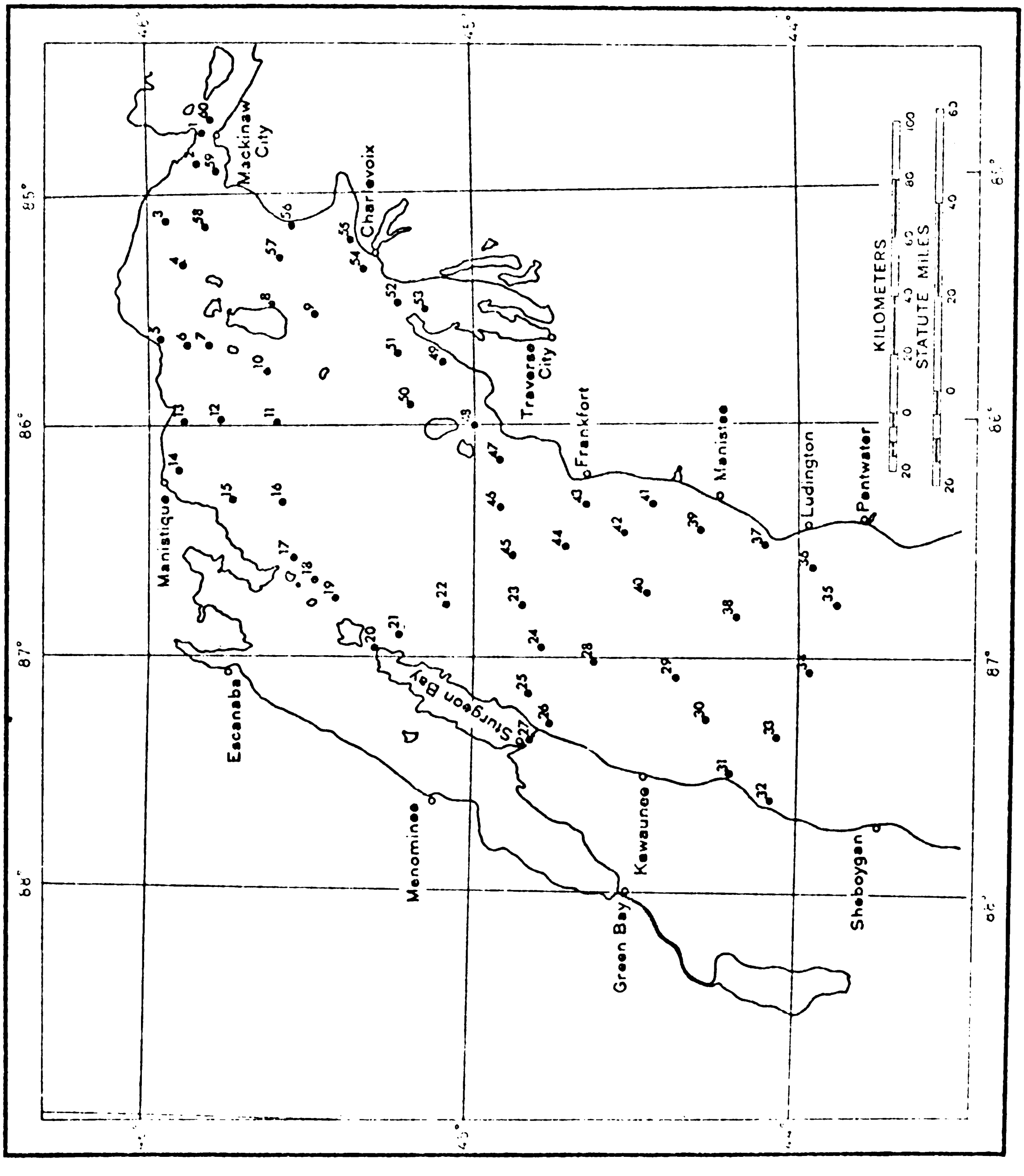
PROCEDURE

Sample Collection

Sixty samples were collected from aboard the R/V Shenehon (NOS - NOAA) on Cruise 01, from May 26, 1970 to June 9, 1970. Sampling stations (Figure 4) were located by two methods. Radar was used to locate the position of stations within 50 km of shore. Stations greater than 50 km from shore were located by radio-direction finder. Latitude and longitude were calculated for each station from these data and are recorded in Appendix A. Depth at each station was measured by two methods. A fathometer was used for primary depth data. The depths were also measured on a meter block on the cable used to collect the bottom samples. The depths were checked by comparing with chart depth at each station location.

The water column was sampled with a string of Fjarlie bottles. Reversible thermometers on the bottles and a continuous bathythermograph measured the temperature profile at each station. Chloride concentration, phenolphthalein alkalinity, total alkalinity, specific conductivity, and dissolved-oxygen concentration were determined according to Standard Methods (American Public Health Association, 1971)

Figure 4. Sample locations in upper Lake Michigan.
Cruise 01, May 25, 1970 to June 3, 1970.



Mackinaw City
Charlevoix
Traverse City
Frankfort
Manistee
Ludington
Pentwater
Manistique
Escanaba
Menominee
Sturgeon Bay
Green Bay
Kewaunee
Sheboygan
85°
86°
87°
88°
46°
45°
44°
KILOMETERS
20 0 20 40 60 80 100
STATUTE MILES
20 0 20 40 60
1
2
3
4
5
6
7
8
9
10
11
12
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aboard ship. Dissolved-oxygen saturation was calculated from the dissolved oxygen and temperature data. Synopic, water-quality data from these measurements are available at the Lake Survey Center (NOS - NOAA), Detroit, Michigan.

The sediment samples were collected with a Shipek dredge. Eh and pH were measured on each sediment sample by inserting probes directly into the sediment while still in the dredge. The samples were put into plastic jars and a few milliliters of 0.1N H_2SO_4 (Chambers, personal communication) were added to preserve the samples from bacterial action.

Laboratory Analysis

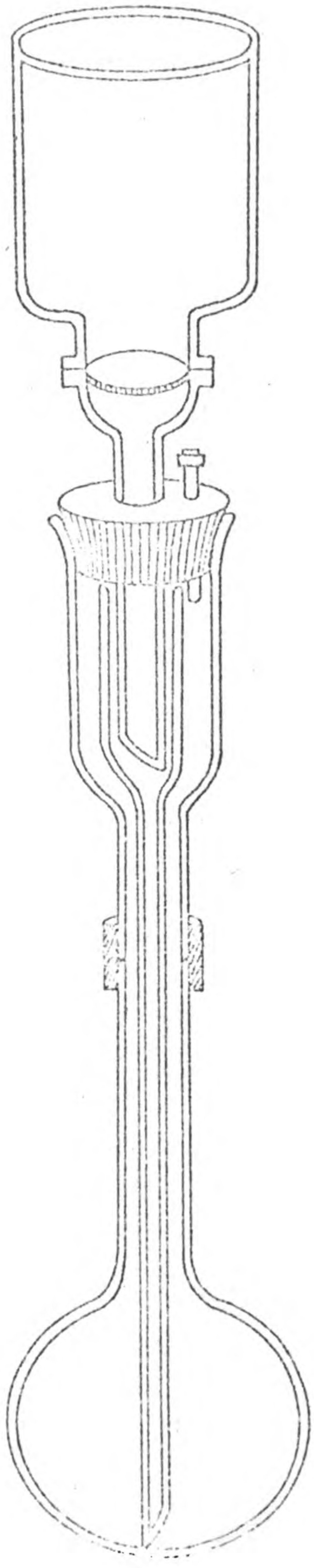
In the laboratory the samples were analyzed for trace metals and carbon content. A set of beakers was washed and rinsed with distilled water and concentrated HNO_3. The beakers were then dried at 110°C overnight. Each beaker was pre-weighed. Then, 10-15 g of wet, homogenized sediments were placed into each beaker. The samples were dried for 72 hours at 85°C and reweighed. All chemical calculations are based on the dry sediment weight. The percent moisture was not calculated, since the value has little meaning in this study.

The sediments were digested to free the various trace metals from organic complexes and minerals (Curtis, [illegible]). Ten ml of reagent grade HNO_3 were added to each beaker to put the trace metals in solution (D'Itri, personal communication). The samples were digested on a hot plate at [illegible]°C until white fumes began to form and the sediments reached incipient dryness. After digestion, the cooled sediments were washed with 5-10 ml distilled water and a second 10 ml portion of concentrated HNO_3 was added to each sample. The samples were allowed to digest overnight on the hot plate.

Upon completion of digestion, the samples were prepared for filtration by washing each sediment residue with 15-25 ml of 5% $CaCl_2$ solution in order to remove trace cations at exchange sites on the clay minerals (Mortland, personal communication; Orzeck et al., 1972; Cline et al., 1973). The sediment residues were filtered in a specially designed 0.45μ Millipore filter system (Figure 5). The advantage of this system is that the filtrate goes directly into a 100 ml volumetric flask, which reduces the danger of contamination. The volumetric flask used was cleaned and rinsed with 50 ml of concentrated H_2SO_4 and $K_2Cr_2O_7$ solution (Chemical Rubber Publishing Co., 1959-1960); rinsed with distilled water and dried. The pH of the filtrate was measured with a Photovolt-Digicord pH meter using reference and glass electrodes. The samples with a pH $<$ 2.0 were adjusted to this pH with 1.0N NaOH solution in order that the filtrate could be used on the atomic absorption spectrophotometer. Seven samples were adjusted in this manner. All samples were diluted to 100 ml with distilled water.

The trace-metal concentrations were determined on a Perkin-Elmer Atomic Absorption Spectrophotometer, Model 303,

Figure 5. Millipore filter system. This permitted direct sediment filtration into a 100 ml volumetric flask.



using an acetylene-air flame. The concentration of Cu was measured with a single-slot burner. A triple-slot burner was used to measure Co, Cr, Mn, and Zn. Standard solutions for each element were prepared. The standards and samples were analyzed simultaneously. The absorbance of each standard was measured at least five times, while the absorbance of each sample was measured at least three times. The use of multiple measurements of both standard and samples provided a high degree of reliability in the standard curves, reduced random instrument errors, and provided a statistical means of calculating confidence limits on the resulting metal concentrations. For each concentration value in the standard set, standard deviation was calculated about the mean absorbance. Table 2 gives the mean, maximum, and minimum range in standard deviation for each element. Note that the maximum errors are at the extreme limits of analysis, where concentrations are at the lower limits of detection or approaching the upper, nonlinear portion of the standard curve. Most unknowns were in the concentration range of minimum percent error.

Total carbon and organic carbon were measured on a second set of samples. The samples were air dried for a week and ground to a fine powder in a Spex Mixer/Mill. Total carbon was measured on a Leco dry-combustion carbon analyzer. Two standards were used for calibration. One standard had

Table 2. Error estimate for trace-metal analysis.

Metal	Source of Standard	Standard Deviation of Absorption Reading of Standard		Standard Deviation of Absorption Reading of Sample	
		σ	Range	σ	Range
Zn	$ZnCl_2$ (HCl Aqueous)	0.85	0.40-1.30	1.26	0.65-1.87
Mn	$KMnO_4$ (Aqueous)	0.74	0.51-0.97	1.05	0.85-1.25
Cr	$K_2Cr_2O_7$ (Aqueous)	0.57	0.36-0.78	0.94	0.37-1.51
Co	$CoCl_2$ (Aqueous)	1.13	0.43-1.83	1.61	1.40-1.82
Cu	Cu wire (HNO_3 Aqueous)	0.65	0.53-0.77	1.72	1.51-1.93

0.100% carbon by weight and the other contained 0.65% carbon by weight. The analyzer was adjusted to read percent total carbon based on a 0.1 g sample. The Leco Carbon Analyzer gave results that were reproducible within ± 5% (Hammond, personal communication).

The samples for organic carbon were prepared by weighing out 0.3 g of sediment into a 50 ml bottle. To release carbonate that might be present in the sediment, five ml reagent grade 20% HCl were added to each sample. The samples were placed in a sonic agitator for five minutes. The samples were diluted to 30 ml with distilled water and agitated for another five minutes. The agitation was necessary to insure a uniform distribution of sediments throughout the 30 ml of solution before analysis. Reagent grade potassium hydrogen phthalate was used as an organic-carbon standard. A Dohrmann DC-50 analyzer was used to determine organic carbon. The results obtained were reproducible within ± 2% (Cline, personal communication).

The sediment grain-size distribution was calculated from settling-tube and Coulter Counter data. A computer program (Program SEDSTAT, Upchurch, 1969) was used to calculate the size-distribution statistics, including mean phi, standard deviation, skewness and kurtosis, according to the method of moments. All shipboard, physical, and analytical chemistry data are listed in Appendix F.

Data Processing

The variables (Table 3) were correlated using the Pearson product-moment correlation coefficient (Harbaugh and Merriam, 1968). The program Filebuilt of Michigan State University Stat System (Michigan State University Computer Laboratory, 1973), with missing data option, was used to calculate the correlation-coefficient matrix (Table 4). The correlation-coefficient matrix was calculated on all sixty-one sampling stations and twenty-one variables measured at each station. The correlations (Table 4) were tested for significance at both 99% and 95% confidence levels.

R-mode factor analysis (Harbaugh and Merriam, 1968; Nie *et al.*, 1970) was used on the thirty-eight stations with complete data. The variables depth; water temperature; pH; Eh; specific conductivity; phenolphthalein alkalinity; total alkalinity; dissolved-oxygen concentration; dissolved-oxygen saturation; concentrations of Cl, Co, Cr, Cu, Mn, and Zn; total carbon; organic carbon; and sediment mean phi and standard deviation were analyzed using the R-mode method. Nie *et al.* (1970) program Statistical Package for the Social Sciences, version 5.1, July 31, 1973 was used with the following options, PA2 Varimax rotation and Statistics All. Tables 5 and 6 list the eigenvalues and communalities of the factors. Table 7 lists the variables used and the loading of each variable on each factor. In spite of the large number of

Table 3. Variables used in correlation-coefficient matrix.

Name	Number of Samples	Units	Minimum Value	Maximum Value	Mean	Standard Deviation
Depth	61	ft.	26.0	828.0	235.1	227.2
Water temperature	61	C°	3.05	12.47	5.16	1.85
pH	59	-	6.70	8.12	7.22	0.30
Eh	59	Volts	-0.200	0.305	0.213	0.093
Specific conductivity	61	umhos	210.	297.	272.	15.45
Chloride concentration	61	mg/l	4.31	9.20	6.40	0.78
Phenolphthalein alkalinity	61	mg/l	0.00	3.00	0.27	0.74
Total alkalinity	61	mg/l	76.0	110.0	101.5	6.06
Dissolved-oxygen concentration	61	mg/l	10.52	13.17	11.90	0.69
Dissolved-oxygen saturation	61	%	83.0	111.0	96.4	6.04
Copper	51	mg/kg	0.00	214.3	17.1	39.7
Cobalt	57	mg/kg	0.00	0.52	0.13	0.12
Zinc	49	mg/kg	0.00	17.8	1.1	3.57
Manganese	52	mg/kg	0.00	872.1	178.6	220.4
Total carbon	60	%	0.00	9.96	1.64	1.78
Organic carbon	60	%	0.018	2.503	0.339	0.53
Mean grain size	51	Ø	-2.11	7.67	3.79	2.37
Standard deviation of sediment	51	Ø	-2.11	3.30	1.33	0.83
Sediment skewness	51	-	-1.62	1.68	-0.04	0.68
Sediment kurtosis	51	-	0.28	23.10	4.64	4.42
Chromium	54	mg/kg	0.00	27.50	4.09	6.06

Table 4. Correlation-coefficient matrix.

	Depth	Water temperature	pH	Eh	Specific conductivity	Chloride concentration	Phenolphthalein alkalinity	Total alkalinity	Dissolved-oxygen concentration	Dissolved-oxygen saturation	Copper	Cobalt	Zinc	Manganese	Total carbon	Organic carbon	Mean grain size	Standard deviation of sediment	Sediment skewness	Sediment kurtosis	Chromium
Depth																					
Water temperature	-0.716*																				
pH																					
Eh																					
Specific conductivity																					
Chloride concentration					0.606*.																
Phenolphthalein alkalinity		0.696*																			
Total alkalinity					0.892*	0.574*															
Dissolved-oxygen concentration																					
Dissolved-oxygen saturation	-0.554*	0.487**							0.838*												
Copper																					
Cobalt	0.563*										0.434**										
Zinc																					
Manganese	0.447**											0.454**									
Total carbon																					
Organic carbon	0.646*										0.481**	0.478**			0.470**						
Mean grain size	0.624*	-0.503**																			
Standard deviation of sediment	0.448**																0.711*				
Sediment skewness																					
Sediment kurtosis																					
Chromium															0.485**	0.461**					

* significate at 99.0% ≤ 0.549 df=19

** significate at 95.0% ≤ 0.433 df=19

Table 5. Eigenvalues and communalities for R-mode factor analysis of bottom-chemistry variables.

Factor	Eigenvalue	Percent Communality	Cummulative Percent Communality
1	4.47680	23.6	23.6
2	3.33486	17.6	41.1
3	2.45447	12.9	54.0
4	2.04261	10.8	64.8
5	1.47253	7.8	72.5
6	1.17588	6.2	78.7
7	1.04181	5.5	84.2
8	0.67445	3.5	87.8
9	0.52491	2.8	90.5
10	0.36287	1.9	92.4
11	0.35651	1.9	94.3
12	0.30260	1.6	95.9
13	0.23827	1.3	97.2
14	0.19910	1.0	98.2
15	0.15332	0.8	99.0
16	0.08892	0.5	99.5
17	0.05895	0.3	98.8
18	0.03209	0.2	100.0
19	0.00906	0.0	100.0

Table 6. Eigenvalues for R-mode analysis using varimax rotated factor matrix, with Kaiser normalization.

Factor	Eigenvalue	Percent Communality	Cummulative Percent Communality
1	4.26443	29.4	29.4
2	3.15130	21.7	51.1
3	2.23588	15.4	66.5
4	1.92028	13.2	79.7
5	1.23566	8.5	88.2
6	0.85770	5.9	94.1
7	0.85058	5.9	100.0

Table 7. R-mode factor loadings using varimax rotated factor matrix with Kaiser normalization.

	Communality	Rotated Orthogonal Factors						
Variable	h	1	2	3	4	5	6	7
			FACTOR 1					
Water temperature	0.966	0.934	-0.046	-0.048	-0.273	-0.016	-0.002	-0.122
Phenolphthalein alkalinity	0.749	0.829	0.228	0.081	-0.030	0.015	-0.041	-0.032
			FACTOR 2					
Specific conductivity	1.00	-0.037	0.995	0.040	-0.067	0.011	-0.001	0.087
Total alkalinity	0.911	0.071	0.904	0.132	0.011	0.025	-0.259	0.053
Chloride concentration	0.625	0.341	0.656	-0.157	-0.091	0.149	0.110	-0.106
pH	0.296	0.053	-0.448	0.035	-0.059	-0.124	-0.265	-0.050
			FACTOR 3					
Chromium	0.784	0.190	-0.105	0.847	0.062	0.053	0.086	0.076
Organic carbon	0.828	-0.201	0.122	0.701	0.177	0.453	-0.204	-0.044
Zinc	0.471	-0.037	0.047	0.643	-0.157	0.015	-0.168	-0.016
Cobalt	0.659	-0.229	-0.044	0.502	0.124	0.466	0.053	0.343
			FACTOR 4					
Mean grain size	0.897	-0.142	-0.156	-0.017	0.907	0.103	0.021	0.136
Standard deviation of sediment	0.578	-0.086	0.031	-0.025	0.746	0.045	0.085	0.050
Depth	0.797	-0.499	0.178	0.276	0.518	0.253	-0.245	0.218

Table 7 (cont'd.)

Variable	Communality h^2	Rotated Orthogonal Factors 1	2	3	4	5	6	7
			FACTOR 5					
Copper	0.787	-0.057	0.143	0.162	0.129	0.835	-0.030	-0.149
Total carbon	0.819	0.417	0.073	0.392	0.347	0.502	0.063	0.331
			FACTOR 6					
Dissolved-oxygen saturation	1.000	0.403	-0.002	-0.159	-0.079	-0.112	0.891	-0.044
Dissolved-oxygen concentration	0.956	-0.413	0.044	-0.040	0.196	-0.112	0.850	0.093
Eh	0.516	-0.086	-0.083	-0.018	0.009	-0.612	0.143	-0.327
			FACTOR 7					
Manganese	0.865	-0.156	0.079	0.051	0.199	0.093	0.050	0.884

positive eigenvalues, it is clear that the clusters identified in the analysis reflect expected chemical associations. Seven factors were selected as optimal for relating the metals to specific chemical variables. The seven factors accounted for 84% of the total variability.

Q-mode factor analysis (Harbaugh and Merriam, 1968; Nie *et al.*, 1970) was made on the thirty-eight stations with complete data. The program Statistical Package for the Social Sciences (Nie et al., 1970), version 5.1, July 31, 1973 was used with the following options, Factor Type PA2, Varimax rotation and Statistics All. The data, Co, Cr, Cu, Mn, Zn, organic carbon, total carbon and sediment mean phi, and standard deviation was normalized to make the variables dimensionless by dividing by the mean of each variable and the data matrix was inverted before the Q-mode factor analysis was computed. Q-mode factor analysis with the total variable set does not add any new knowledge but increases the error to the random noise in the data. Again seven eigenvalues were selected to account for the data (Tables 8 and 9). These seven clusters accounted for approximately 90% of the variability. Again, seven factors is a large number, but the last four factors (Table 10) can be combined, as they represent the highly variable pattern of metal fixation in the center of the lake.

Table 8. Factors and eigenvalues for Q-mode factor analysis of trace metals in upper Lake Michigan.

Factor	Eigenvalue	Percent Communality of Variables	Cummulative Percent Communality
1	14.01885	36.9	36.9
2	7.04476	18.5	55.4
3	6.76974	17.8	73.2
4	3.55846	9.4	82.6
5	2.39502	6.3	88.9
6	2.06745	5.4	94.4
7	1.22917	3.2	97.6
8	0.91656	2.4	100.0
9	0.00000	0.0	100.0
10	0.00000	0.0	100.0
.	.	.	.
.	.	.	.
.	.	.	.
38	0.00000	0.0	100.0

Table 9. Eigenvalues and communalities for rotated* Q-mode factors using varimax rotation with Kaiser normalization.

Factor	Eigenvalue	Percent Communality	Cummulative Percent Communality
1	13.93584	38.6	38.6
2	6.92176	19.2	57.7
3	6.62904	18.4	76.1
4	3.39942	9.4	85.5
5	2.20260	6.1	91.6
6	1.91927	5.3	96.9
7	1.11052	3.1	100.0

* Factor axes rotated according to varimax algorithm, after Kaiser normalization.

Table 10. Q-mode factor loadings using varimax rotated factor matrix after Kaiser normalization.

	Communality	Rotated Orthogonal Factors						
Sample	h^2	1	2	3	4	5	6	7
				FACTOR 1				
28	1.00	.991	.076	.017	-.025	-.080	.064	-.012
60	1.00	.985	.056	.007	.020	-.079	.132	.051
36	0.97	.972	.032	-.003	.040	-.161	-.056	-.027
33	0.99	.968	.067	.141	-.011	.120	-.061	-.115
7	0.98	.942	-.027	-.037	.066	-.082	.277	.088
13	0.96	.938	.223	.079	-.121	-.004	.001	.120
50	0.96	.928	.084	-.023	.110	-.036	-.120	.251
57	0.99	.912	-.052	-.113	.190	-.203	.168	-.196
37	0.99	.799	.059	.046	-.042	-.039	.095	.576
6	0.98	.762	.128	.102	-.072	-.062	-.168	.581
59	0.93	.746	.482	.008	.022	-.057	-.002	.370
51	0.97	.711	.567	-.047	.104	-.185	-.262	.104
47	0.88	.654	-.027	-.110	-.036	.069	.653	-.109
54	0.92	.327	-.119	-.029	-.809	-.014	-.285	.014
				FACTOR 2				
14	0.97	.022	.971	-.107	.035	.114	.080	.057
32	0.93	.063	.897	-.204	.222	-.118	.024	-.121
15	0.98	.135	.873	.285	.187	-.277	-.099	-.033
11	0.98	.172	.816	.511	-.094	-.098	.062	.077
25	0.93	.277	.765	-.113	.191	.199	-.082	.416
45	0.98	.059	.740	-.389	.419	-.286	.146	.056
22	0.97	-.031	.672	-.360	.555	.185	.158	.134
16	1.00	.581	.642	.333	-.047	-.166	.165	.031
				FACTOR 3				
58	0.98	.189	-.076	.927	-.059	.073	.039	.255
8	0.99	.249	-.217	.892	.065	-.107	.183	.201
31	0.97	-.125	-.359	.857	.259	-.099	-.110	-.033
42	0.97	-.347	.343	.843	.040	.071	.064	.078
39	0.91	.052	.132	.830	.297	.028	.339	-.020
26	0.84	-.060	-.202	.801	.249	.161	-.034	-.262
1	0.96	.007	.562	.759	.053	-.168	-.074	-.183

Table 10 (cont'd.)

	Communality	Rotated Orthogonal Factors						
Sample	h^2	1	2	3	4	5	6	7
				FACTOR 4				
10	0.87	-.434	-.021	.198	.603	.339	-.393	-.124
29	0.95	.527	.352	-.346	.595	-.147	-.219	.038
27	0.81	-.054	.512	-.383	.540	-.051	-.221	.236
				FACTOR 5				
35	0.94	-.220	.009	.087	.154	.915	-.163	.014
43	0.94	-.121	-.249	-.131	.057	.893	.214	-.051
				FACTOR 6				
44	0.86	-.001	.195	.449	.109	.004	.780	-.040
46	0.94	-.352	-.211	-.167	-.850	-.180	.208	-.012
				FACTOR 7				
12	0.97	.518	.435	.368	.093	-.094	-.185	.566
48	0.99	-.301	-.215	-.308	-.853	-.053	-.169	.044

RESULTS

Environment of Deposition

The distribution of sediment, mean grain size in upper Lake Michigan (Figure 6) is related to depth of the lake (Figure 1; Tables 4 and 7). The distribution shows a trend of coarse to medium sand close to the shore and progressively finer sediment toward the deeper, central portion of the lake. The coarsest sands are located along the northern shore of Lake Michigan. The sediments along the western shore show a gradual increase in finer sediments in the silt to clay-size range from Manistique, Michigan, to Sheboygan, Wisconsin. The moraine that extends westward from Ludington is reflected in coarse sediments and the various island areas also show coarse sediments.

The degree of sorting of the sediments is shown in Figure 7. The plot generally shows a similar pattern as the mean size of the sediments. The coarse grained sediments are the best sorted, which shows the importance of current and wave energy along the northern shore. The more poorly sorted sediments are located in the central basin.

Specific conductivity distribution has been used to trace water movement in a lake (Owneck *et al.*, 1972) in order to

Figure 6. Sediment mean phi distribution in upper Lake Michigan. Contours range from 1 to 6 phi and are at 1 phi in intervals. Cruise 21, May 25, 1970 to June 9, 1970.

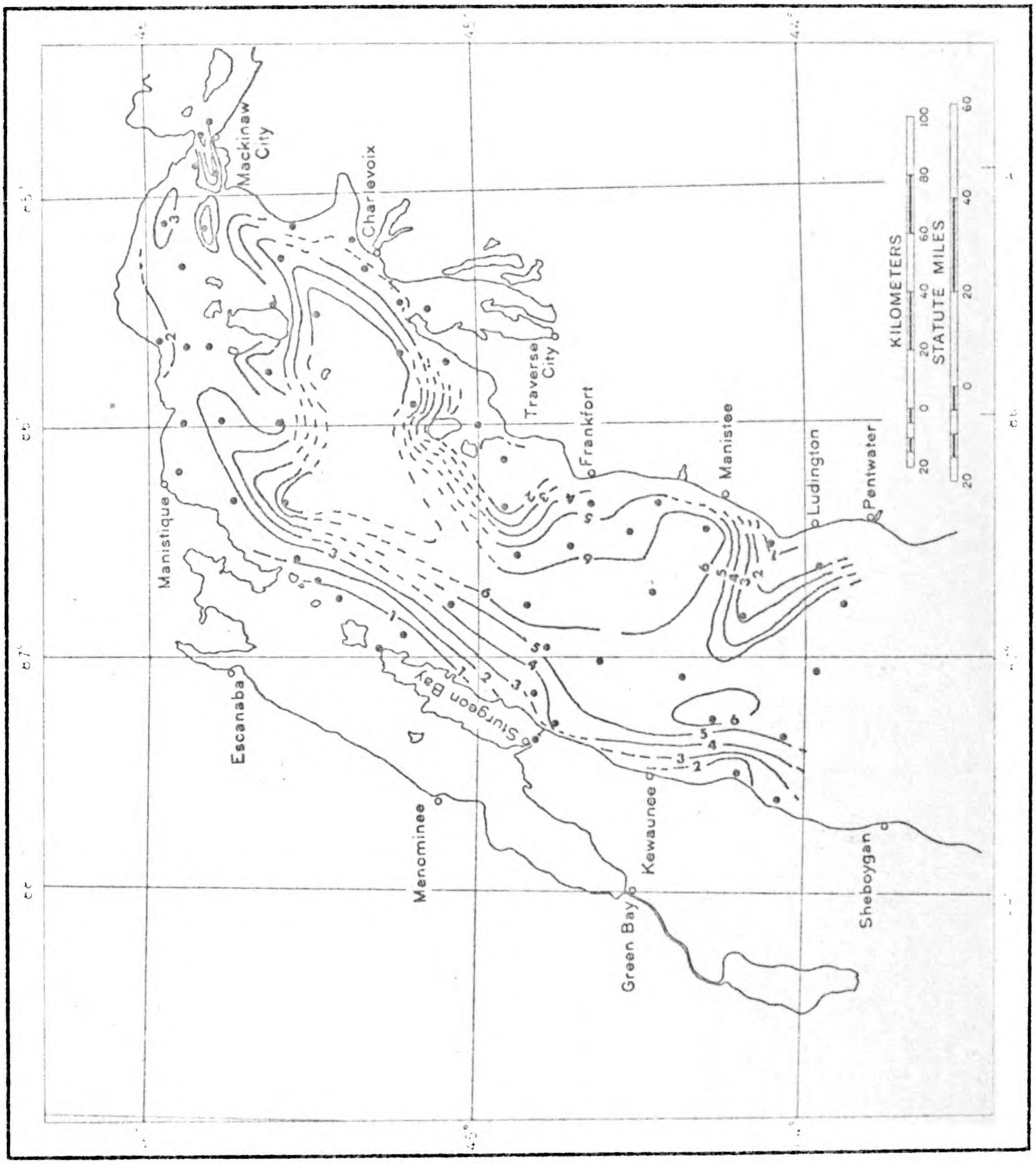
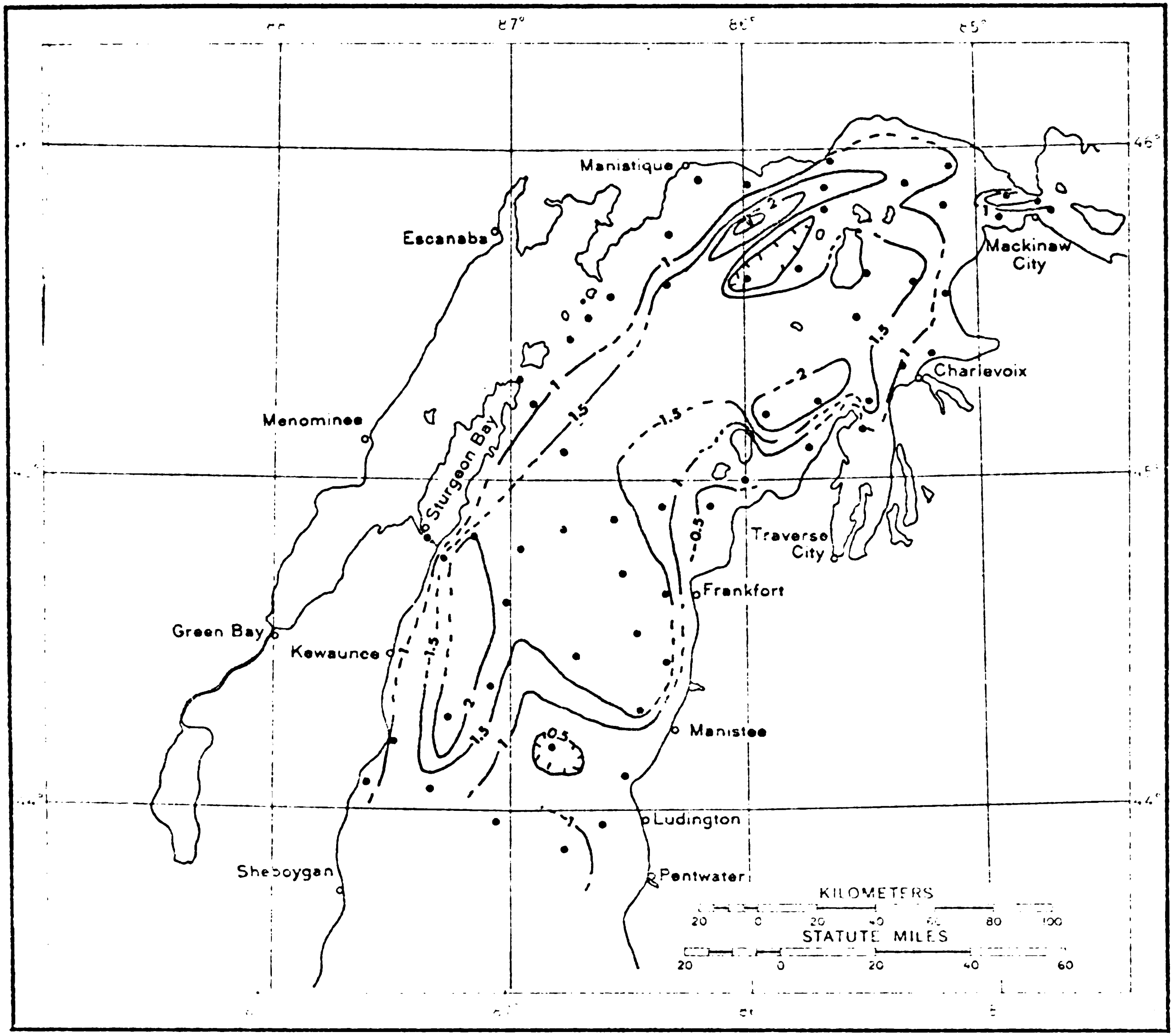

Mackinaw City
Charlevoix
Traverse City
Frankfort
Manistee
Ludington
Pentwater
Manistique
Escanaba
Sturgeon Bay
Menominee
Kewaunee
Green Bay
Sheboygan
KILOMETERS
20 0 20 40 60 80 100
STATUTE MILES
20 0 20 40 60
1
2
3
4
5
6

Figure 7. Sediment standard deviation distribution in upper Lake Michigan. Contours range from 0.5 to 2.0 and are at a 0.5 interval. Cruise 01, May 23, 1970 to June 9, 1970.


88°
87°
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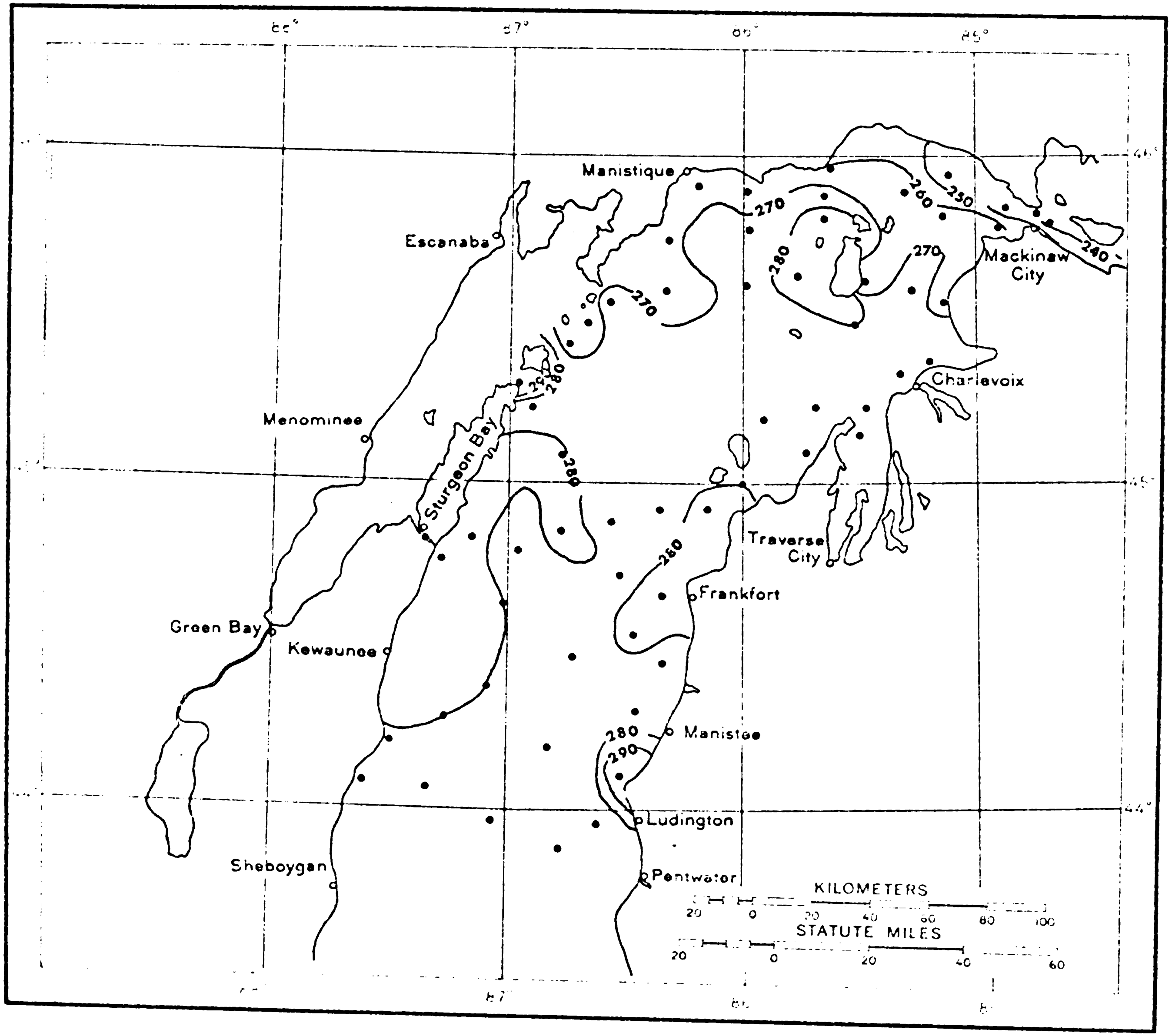
85°
46°
45°
44°
Manistique
Escanaba
Mackinaw City
Charlevoix
Menominee
Sturgeon Bay
Traverse City
Frankfort
Green Bay
Kewaunce
Manistee
Ludington
Sheboygan
Pentwater
0
0.5
1
1.5
2
KILOMETERS
20
0
20
40
60
80
100
STATUTE MILES
20
0
20
40
60

identify potential sources of sediment contamination. Specific conductivity is related to the total concentration of ionized substances in the water (American Public Health Association, 1971). The specific conductivity of water near the bottom in upper Lake Michigan is shown in Figure 8. Bottom water in the northern province, from the Mackinac Straits to Green Bay, has the lowest conductivity, which indicates relatively pure water from the Upper Peninsula. The water entering Lake Michigan from Sturgeon Bay and the water from Green Bay (Figure 8) has a high specific conductivity. The water near shore, north of Ludington, Michigan, has the highest conductivity in the lake, due to high weathering rates in adjacent land areas (Upchurch, 1972) and to cultural loading from the urban areas of the Lower Peninsula of Michigan.

The pH of sediment pore water (Figure 9) varies from a low of 6.70 to a high of 8.12. Near Green Bay there is an extreme variation in pH from 6.75 to 8.12 within a short distance. The pH is uniform in the central basin and over most of the lake. There is a slight trend in the pH pattern. In the northern shore of Lake Michigan, the pH is slightly acidic, which reflects reduced carbonate buffering in this region. Elsewhere, the sediment is partially buffered by interaction with the carbonate minerals. The degree of buffering reflects proximity to source of low pH water and amount of carbonate mineral in the sediments.



88°
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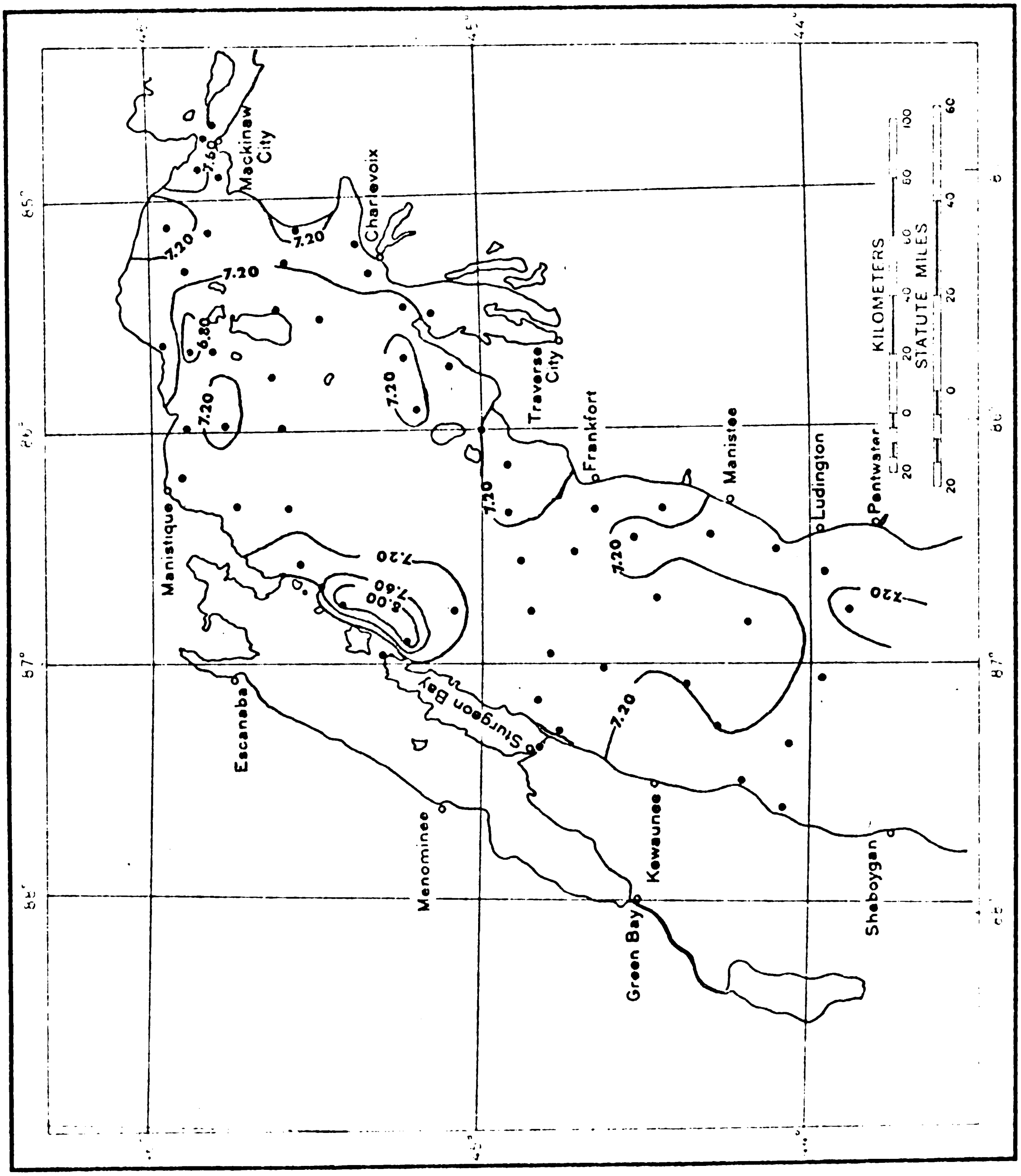
Manistique
Escanaba
Menominee
Sturgeon Bay
Green Bay
Kewaunee
Sheboygan
Mackinaw City
Charlevoix
Traverse City
Frankfort
Manistee
Ludington
Pentwater
240
250
260
270
280
290
KILOMETERS
20 0 20 40 60 80 100
STATUTE MILES
20 0 20 40 60

Figure 9. Distribution of sediment pore water pH. Contours range from 6.00 to 8.00 at 0.40 intervals. Bottom sediments were collected on Cruise 01, May 23, 1970 to June 9, 1970.


Mackinaw City
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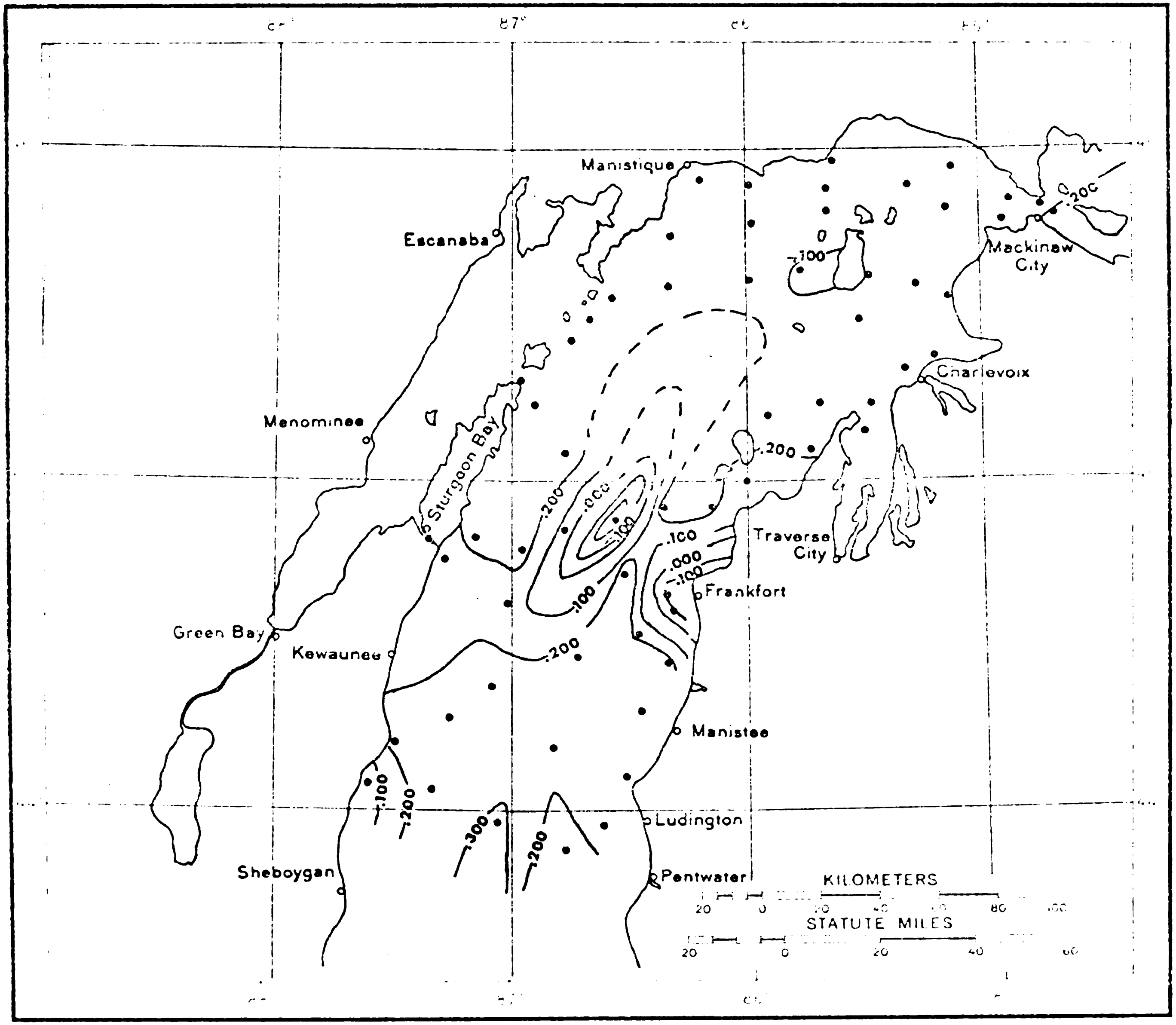
Ludington
Pentwater
Manistique
Escanaba
Menominee
Sturgeon Bay
Kewaunee
Green Bay
Sheboygan
7.60
7.20
6.80
8.00
KILOMETERS
20 0 20 40 60 80 100
STATUTE MILES
20 0 20 40 60
85°
86°
87°
88°
44°
45°

Eh is a measure of the oxidation-reduction potential of the sediments. A negative or low positive Eh means the sediment is in a reducing environment and bacterial activity is anaerobic. The lowest Eh measurements (Figure 10) were at stations 43 and 45 near Frankfort, Michigan. Most of Lake Michigan sediments are in an oxidizing state. The uniformly high value Eh indicates a highly oxygenated bottom sediment near the sediment-water interface.

Carbon in Lake Michigan comes from several sources. Detrital carbon in the form of calcite and dolomite is derived from the lake basin (Upchurch, 1972) and from the tests of a limited number of lake taxa. Organic sources include tissue from plants and animals that are living and have lived in the lake, hydrocarbons (humic substances) from incomplete decomposition and combustion and from tributary biota. Dissolved-inorganic carbon is derived from chemical weathering (Upchurch, 1972) and the atmosphere. Total carbon in the sediments is a measure of both carbonate [$CaCo_3$, $CaMg(CO_3)_2$, $Ca(HCO_3)_2$, H_2CO_3, HCO_3^-, CO_3^{-2}, CO_2] carbon and organic carbon. Of these forms of carbon, organic carbon is most important in metal fixation because humic substances have been shown to quantitatively fix metals (e.g., Curtis, 1964; Cline, 1974). Inorganic carbon, in the form of carbonate minerals, is important as an indicator of glacial and fluvio-lacustrine transport of particulate material derived by erosion on the drainage basin. Since Cu is clustered with total carbon

Figure [illegible]. Distribution of sediment pore water Eh. All contours range from -0.[illegible] volts to +0.[illegible] volts. Contours are at 0.100 volt intervals. The samples were collected on Cruise [illegible], May [illegible], 1970 to June [illegible], 197[illegible].


87°
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Traverse City
Frankfort
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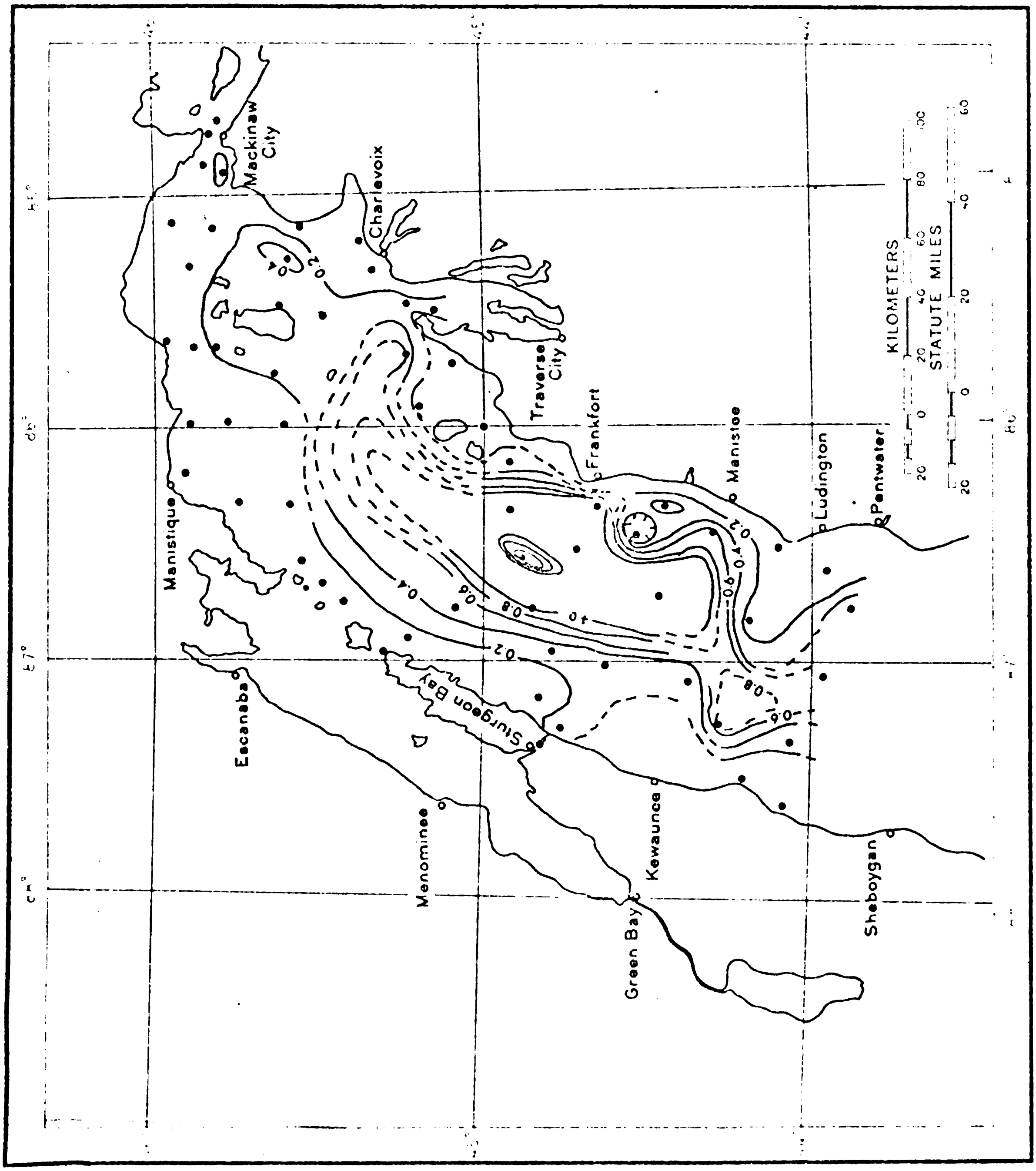
Kewaunee
Manistee
Ludington
Sheboygan
Pentwater
.200
.100
.000
.300
KILOMETERS
20 0 20 40 60 80 100
STATUTE MILES
20 0 20 40 60

(Table 7) and, presumably, carbonate minerals, it appears that the metal is also derived in part from natural weathering. Since the samples were treated with acid to retard bacterial action, the value for carbonate carbon in the sediment should be considered of only limited value. The distribution of organic carbon (Figure 11) closely follows sediment texture and current pattern (Figures 2, 6, and 7) and is, thus, correlated with water depth (Table 4). The highest value for organic carbon in sediment is in the central basin, in deep water, where there is low current activity.

The development of a model for upper Lake Michigan trace metal and sediment distribution is based on correlation and R-mode factor analysis of the variables and a Q-mode factor analysis of data from selected sample stations. Table 3 is a list of the variables; their means, standard deviations, and the number of samples used in the correlation-coefficient matrix (Table 4). The correlation-coefficient matrix (Table 4) shows the significant correlations between variables, based on a 95% confidence limit.

There are significant negative correlations between depth and both water temperature and percent dissolved-oxygen saturation. The former is to be expected during summer stratification. Colder water is usually associated with higher oxygen content (Ruttner, 1972). However, in this case the samples are from the sediment-water interface and

Figure 11. Distribution of organic carbon in sediments. Organic carbon ranges from 0.2% to 1.0% dry weight. Contours are at 0.1% intervals. Collected on Cruise 11, May 2[illegible], 1970 to June [illegible], 1970.


Mackinaw City
Charlevoix
Traverse City
Frankfort
Manistee
Ludington
Pentwater
Manistique
Escanaba
Sturgeon Bay
Menominee
Kewaunee
Green Bay
Sheboygan
0.2
0.4
0.6
0.8
1.0
87°
KILOMETERS
20 0 20 40 60 80 100
STATUTE MILES
20 0 20 40 60

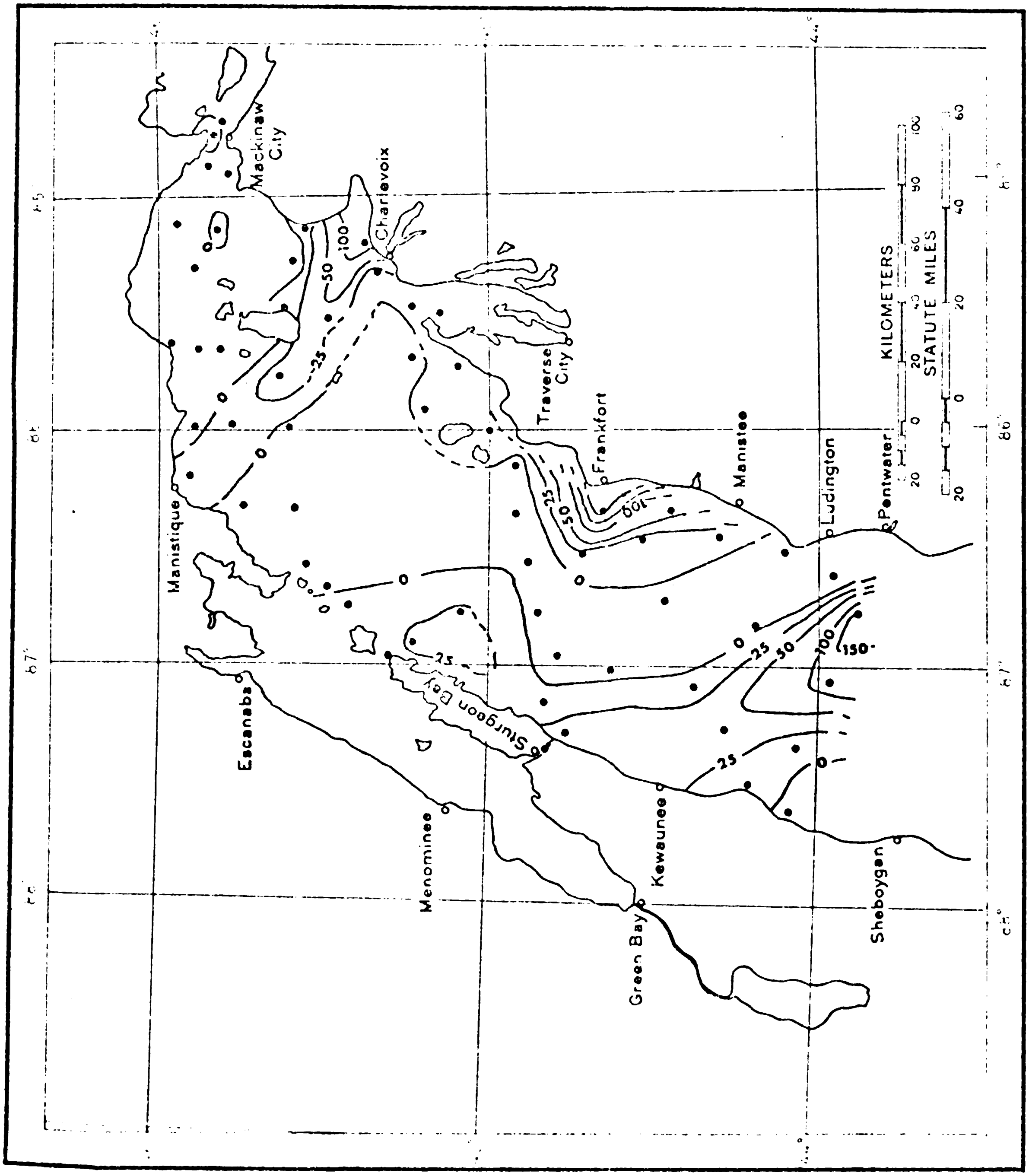
the lower oxygen content is probably due to limited circulation of the bottom water and sediment Biochemical Oxygen Demand (B.O.D.). The R-mode factor analysis (Table 7) clusters the variables into seven different groups. Both the correlation-coefficient matrix and the R-mode factor analysis cluster specific conductivity, total alkalinity and chloride concentration together. Therefore, HCO_3^- and Cl are primary anionic constituents. Depth, sediment mean phi and sediment standard deviation are also directly related. In shallow water the sediments are subjected to current and wave action, causing the sediments to be coarse (sand sized) and well sorted. In deep water there is little or no current and wave action, and the sediments are finer grained and more poorly sorted. Dissolved-oxygen concentration, dissolved-oxygen saturation, and Eh are directly related. Sediment water Eh is positive in a well-oxygenated system. Note that Eh is only weakly clustered with oxygen (Table 7). This is most likely due to interference of Biochemical Oxygen Demand and inadequate sampling of Eh in the sediment system where there is an Eh gradient with depth (Rossmann and Callender, 1969).

Minor and Trace-Metal Distribution

The metals measured, Co, Cr, Cu, Ni, and Zn, are both naturally-occuring and culturally-important metals. Robbins et al. (1972) measured the tributary input of these metals into Lake Michigan (Table 1). The rivers draining the Precambrian metamorphic rock areas of Michigan and Wisconsin have high concentrations of naturally-occuring metals. Rivers entering Green Bay, such as the Ford, Menominee, and Fox Rivers, are located in industrial areas and have industrial waste in their discharge. This also occurs in Michigan rivers, such as the Pere Marquette and Manistee Rivers, which receive industrial discharge.

Copper (Figure 12) is clustered (Table 7) with total carbon, but not clustered with Co, Cr, Zn, and organic carbon in the R-mode factor analysis. Cu clustering with total carbon in the R-mode factor analysis is probably due to naturally-occuring Cu from the Precambrian igneous and metamorphic rock areas in northern Michigan and Wisconsin. Correlation analysis (Table 4) shows that Cu is weakly, but significantly, correlated with organic carbon and Co. This correlation indicates that Cu can be complexed on organic molecules in the sediment in much the same fashion as the other metals. Copper is concentrated close to industrial sites in the shallow water, nearshore areas around the lake basin. There are plumes of Cu near Frankfort and Charlevoix, Michigan. Along the Wisconsin shore line, a plume of Cu enters the lake from Green Bay at Sturgeon Bay and trends in a southerly direction which coincides with prevailing currents. The high Cu across the northern portion of Lake Michigan may be related to naturally-occuring Cu in the glacial drift. The inputs of

Figure 12. Distribution of copper in sediments. Copper in the sediments range from 0 mg/kg to 150 mg/kg dry weight. Contours are at 25 mg/kg intervals. Collected on Cruise 01, May 23, 1970 to June 9, 1970.


Mackinaw City
Charlevoix
Traverse City
Frankfort
Manistee
Ludington
Pentwater
Manistique
Escanaba
Sturgeon Bay
Menominee
Kewaunee
Green Bay
Sheboygan
KILOMETERS
STATUTE MILES
0
20
40
60
80
100
0
25
50
100
150
45°
86°
87°
88°

Cu from streams in the upper Lake Michigan drainage basin are all about the same (Table 1) (Robbins *et al.*, 1972) with the exception that the Manistique and the Escanaba show somewhat higher Cu concentrations, which may reflect either cultural or natural loads.

Cobalt (Figure 13) is concentrated in the central basin and with the finer sediments of the lake. Cobalt, like Cu, also occurs in plumes near cities, such as near Charlevoix and Manistique, Michigan. Highest concentrations are located in the deeper portion of the lake basin. The trace metals, Co, Cr, and Zn, are clustered with organic carbon (Table 7). High correlation and clustering of these trace metals with organic carbon is due to the ability of trace metals to form complexes with the organic carbon (Cline and Upchurch, 1973; Cline, 1974). Since organic accumulations are greatest in deep water, cobalt is positively correlated (Table 4) with depth and sediment mean phi. Robbins *et al.* (1972) did not measure the amount of Co entering Lake Michigan. Winchester and Nifong (1971) showed that aerosol fallout of Co is a source of the metal in Lake Michigan, although Co is present in the atmosphere in the lowest quantities of all metals studied.

Chromium (Figure 14) is similar to cobalt in distribution, with maximum loading on the high organic carbon and finer sediments of the central basin. Chromium is also correlated (Table 4) with total carbon. There is a plume of

Figure [illegible]. Distribution of cobalt in sediments. Cobalt in the sediment ranges from [illegible] mg/kg to 0.[illegible]0 mg/kg dry weight. Contours are of 0.1 mg/kg interval. Collected on Cruise 31, May 2[illegible], [illegible] to June [illegible], [illegible].

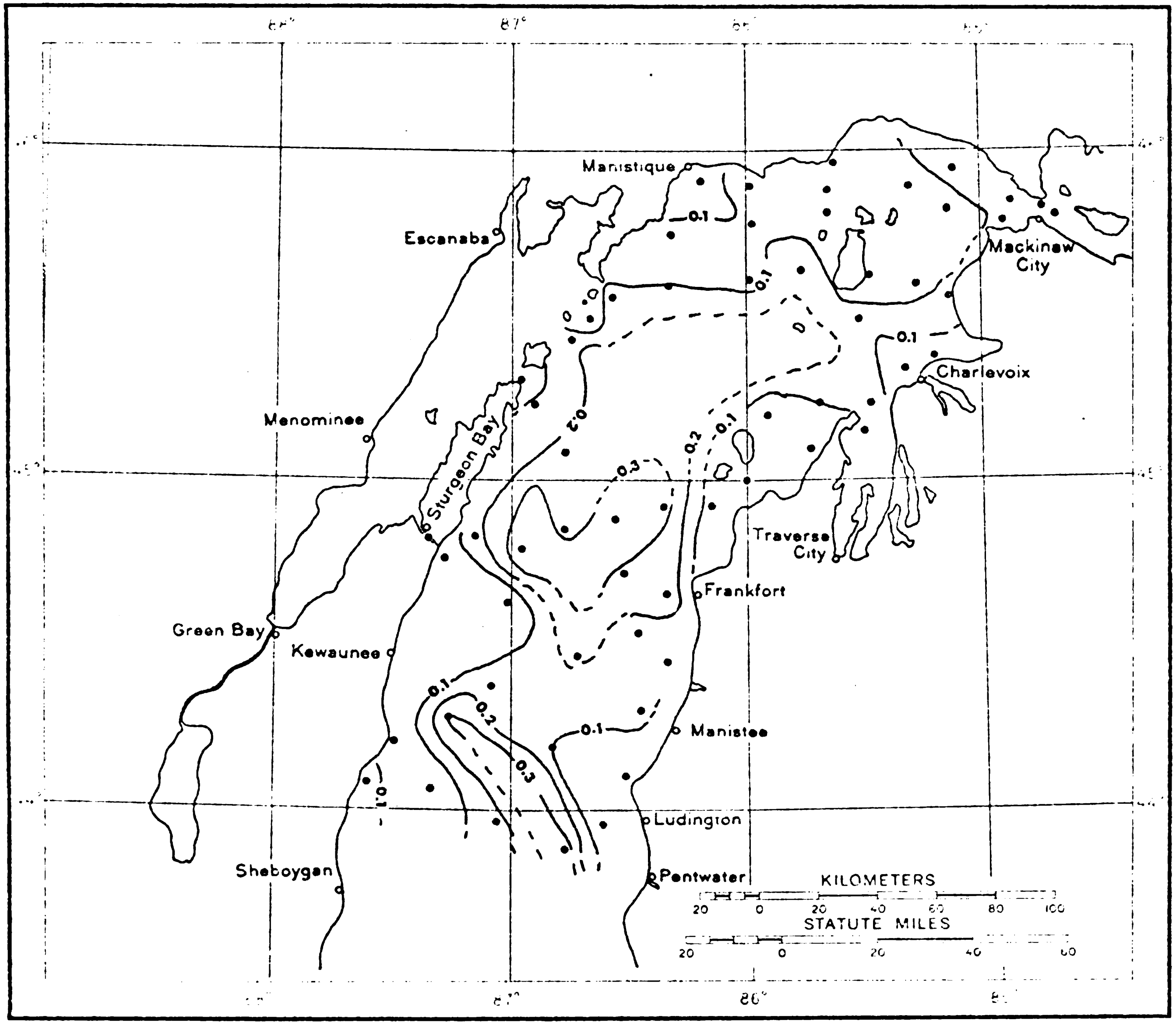
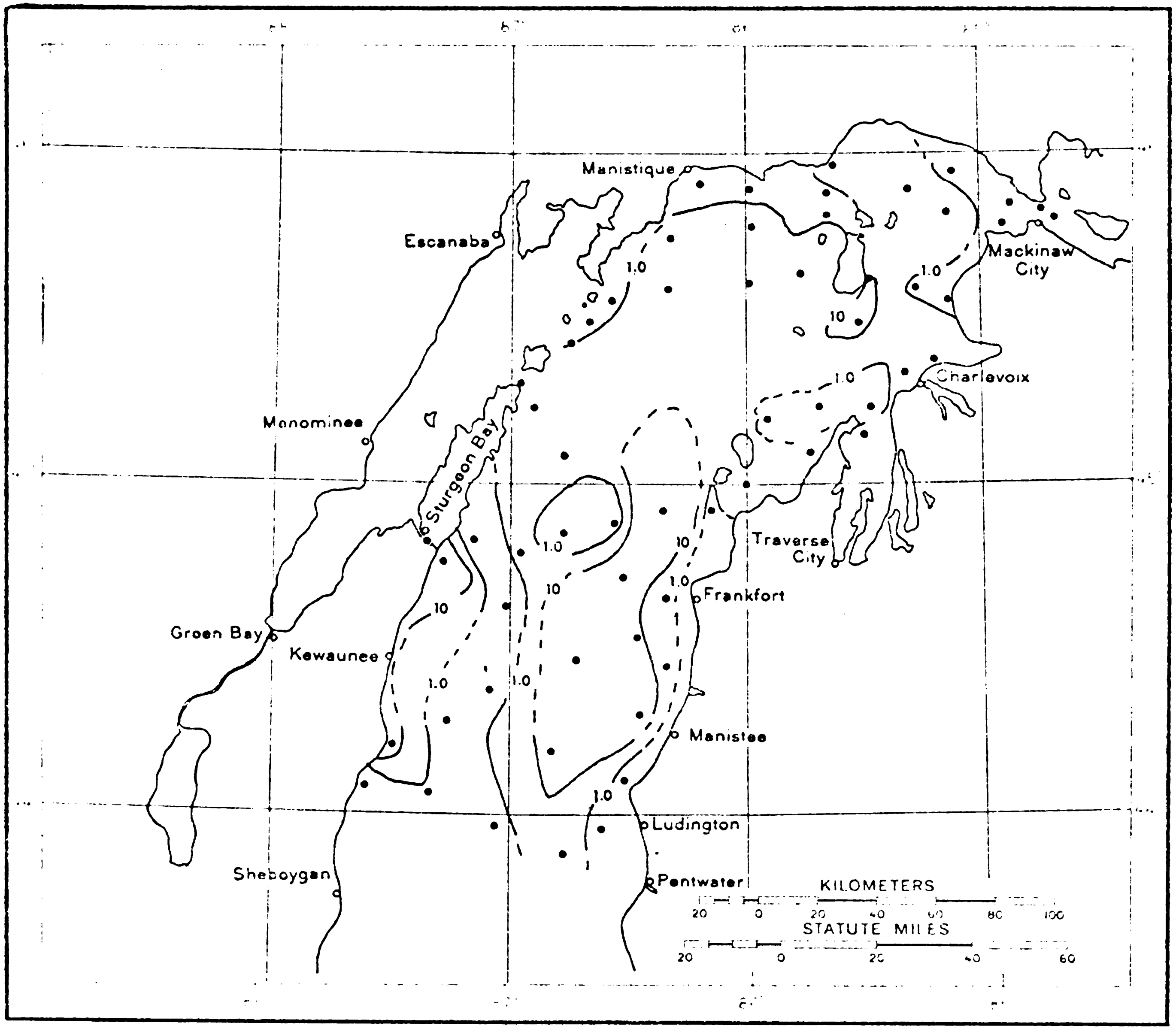

87°
86°
Manistique
Escanaba
Mackinaw City
Charlevoix
Menominee
Sturgeon Bay
Traverse City
Frankfort
Green Bay
Kewaunee
Manistee
Ludington
Pentwater
Sheboygan
0.1
0.2
0.3
KILOMETERS
20 0 20 40 60 80 100
STATUTE MILES
20 0 20 40 60

Figure 14. Distribution of chromium in sediments. Chromium in the sediments range from 0 mg/kg to 27.5 mg/kg dry weight. Contours are at 1.0 mg/kg and 10 mg/kg intervals. Collected on Cruise 07, May 27, 1970 to June 9, 1970.


Manistique
Escanaba
Mackinaw City
Charlevoix
Menominee
Sturgeon Bay
Traverse City
Frankfort
Green Bay
Kewaunee
Manistee
Ludington
Sheboygan
Pentwater
1.0
10
KILOMETERS
20 0 20 40 60 80 100
STATUTE MILES
20 0 20 40 60

Cr in the sediment from Sturgeon Bay south along the Wisconsin coast. In the northern portion of the lake, along the ridges near the shore, are high concentrations of Cr. These high concentrations in the coarse sands may be due to aerosol fallout of Cr (Winchester and Nifong, 1971) from industries located in the Green Bay industrial complex or to natural weathering. Robbins _et al_. (1972) show that streams from the Wisconsin side of the lake contribute more Cr in solution than do Michigan streams. This increase in concentration of Cr may be related to the industrial areas in Wisconsin and is reflected in the distribution of Cr in the sediments.

The distribution of Zn (Figure 15) is similar to Cu, with maximum concentrations located near cities around the upper Lake Michigan basin. Along the eastern shore of Lake Michigan there is a plume of Zn from north of Ludington to Charlevoix and a smaller plume near Manistique, Michigan. Winchester and Nifong (1971) have shown that atmospheric Zn in their inventory exceeds calculated natural water input by a factor of 60. This is a strong indication of airborn Zn pollution. Robbins _et al_. (1972) have shown that the Escanaba, Peshtigo, and Sheboygan Rivers contribute the most Zn in upper Lake Michigan. These rivers have industry in their watershed area.

Manganese (Figure 16) has the greatest variation in concentration of the metals measured. Manganese ranges in concentration from 0 to 872 mg/kg. The method used in

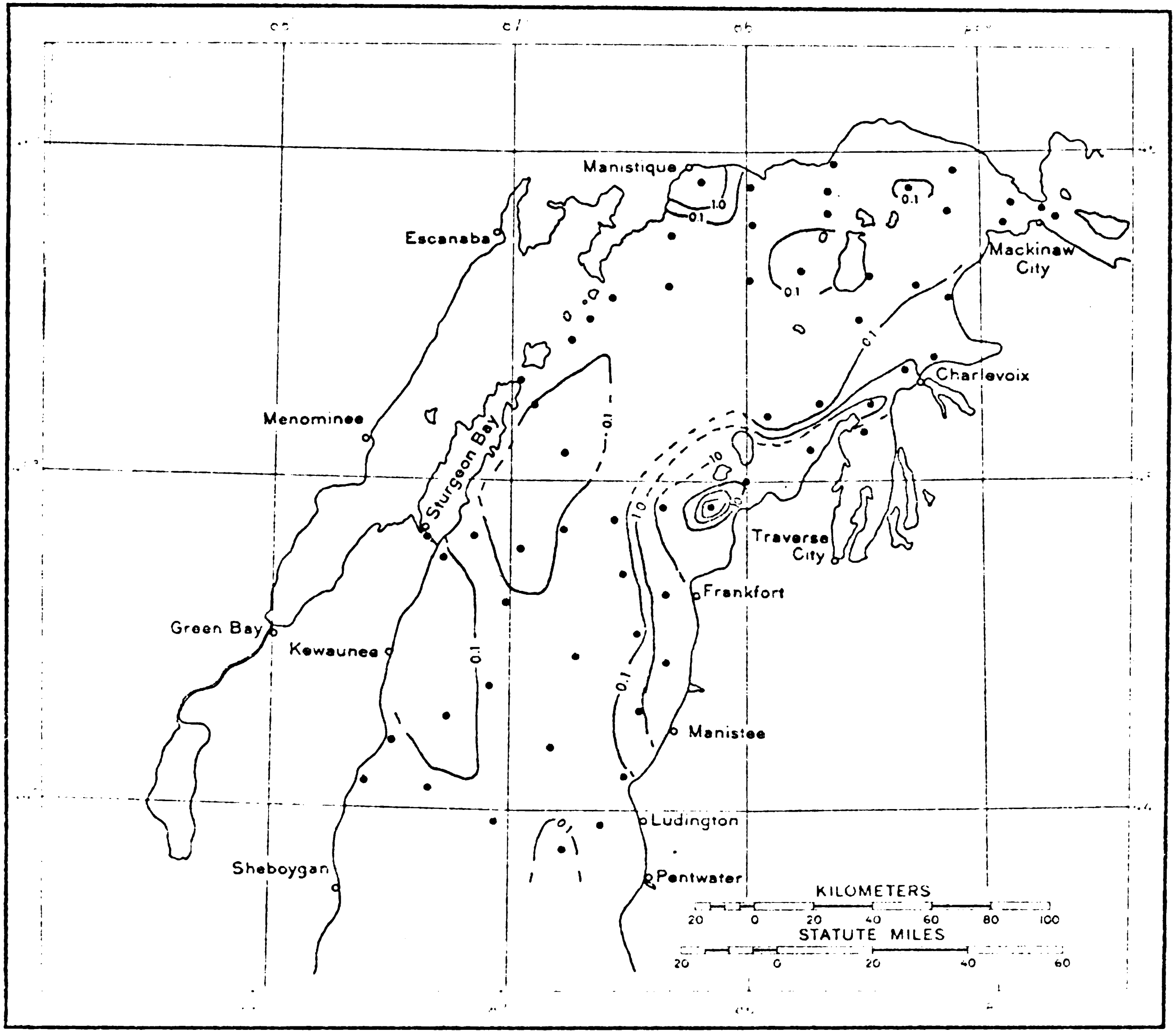
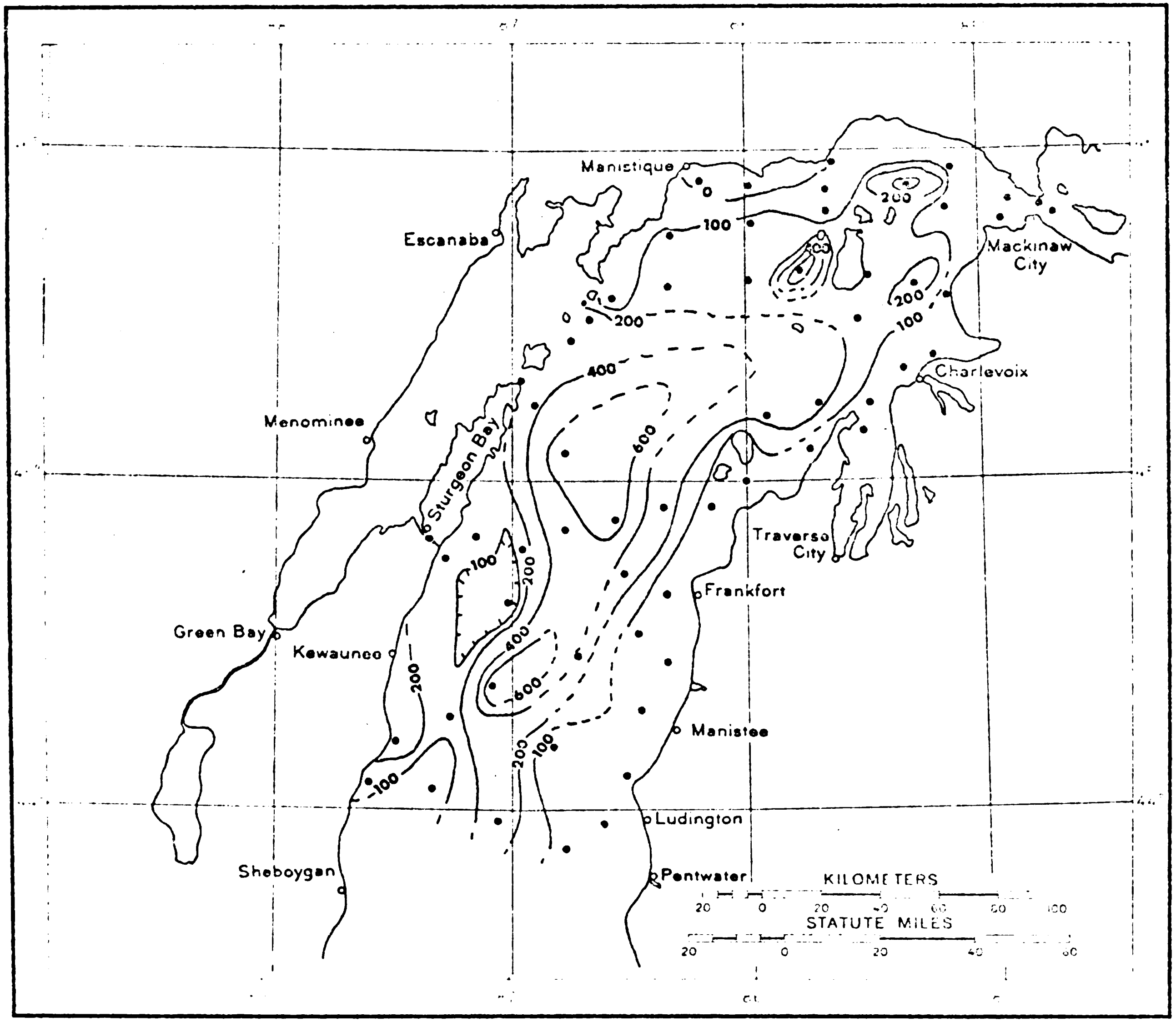

Manistique
Escanaba
Mackinaw City
Charlevoix
Menominee
Sturgeon Bay
Traverse City
Frankfort
Green Bay
Kewaunee
Manistee
Ludington
Pentwater
Sheboygan
1.0
0.1
10
KILOMETERS
20 0 20 40 60 80 100
STATUTE MILES
20 0 20 40 60

Figure 16. Distribution of manganese in sediments. Manganese distribution ranges from 0 mg/kg to 600 mg/kg. Contours are at 200 mg/kg with a 100 mg/kg interval. Collected on Cruise 01, May 25, 1970 to June 9, 1970.


Manistique
Escanaba
Mackinaw City
Charlevoix
Menominee
Sturgeon Bay
Traverse City
Frankfort
Green Bay
Kewaunee
Manistee
Ludington
Sheboygan
Pentwater
0
100
200
400
600
KILOMETERS
20 0 20 40 60 80 100
STATUTE MILES
20 0 20 40 60

preparation of the sediment samples specifically put Mn^{+2} in solution (Chemical Rubber Publishing Company, 1959-1960), so the values recorded are for Mn^{+2}. The digestion using only concentrated HNO_3 did not effect the Mn present in manganese nodules, which exists in the higher oxidation state as Mn^{+4}. A physical and qualitative chemical analysis (D'Itri, personal communication) of those sediments that showed zero concentration of Mn in this study indicates the presence of manganese nodules and gave a positive manganese chemical test, which indicates that the technique used in this study is not suitable for determination of total manganese. Bricker (1965) stated that manganese oxides are sensitive to the intensity of oxidation conditions in the environment and may be a sort of oxygen barometer. Manganese is related to Eh, pH, dissolved-oxygen concentration and dissolved-oxygen saturation (Bricker, 1965). The highest concentration of Mn^{+2} measured is in areas of low or negative Eh values (Figure 9).

The various sources of Mn entering upper Lake Michigan are from aerosol fallout (Winchester and Nifong, 1971), tributary input (Robbins _et al_., 1972) and "ground-water" influx (Rossmann and Callender, 1968). Winchester and Nifong (1971) point out the present input of Mn into Lake Michigan from aerosol fallout from the Chicago industrial areas would require only 1.1 years to raise the water concentration by 0.1 g/l. The input of Mn from the tributaries entering upper Lake Michigan is the highest of the trace metals measured

(Robbins et al., 1972). Rossmann and Callender (1968) have suggested that large concentrations of Mn may be entering the lake by means of "ground-water" influx.

Models for Minor and Trace-Metal Origin and Uptake

From the preceding discussion it is apparent that the uptake of trace metals in the sediments of upper Lake Michigan is dependent upon both the source of the metals and the sedimentary environment. The atmospheric distribution of metals to the system is copious. There are high concentrations of metals in the deeper portions of the lake, which may be due to atmospheric contributions, but may also be due to the presence of organic compounds and clays in the profundal environment. The natural and cultural contributions of metals from point sources can be identified by the local occurrence of plumes of trace metals in the sediments near the respective sources. It now remains to determine the relationship of the metals and sedimentary-environment parameters to the sources and sinks and to relate the concentration of the metals that have a point-source origin to either natural or cultural causes.

The Q-mode factor analysis (Tables 8, 9, and 10) makes it possible to identify those samples in the lake system that are genetically and arealy related. Seven factors were identified in the Q-mode factor analysis (Table 11). The first three

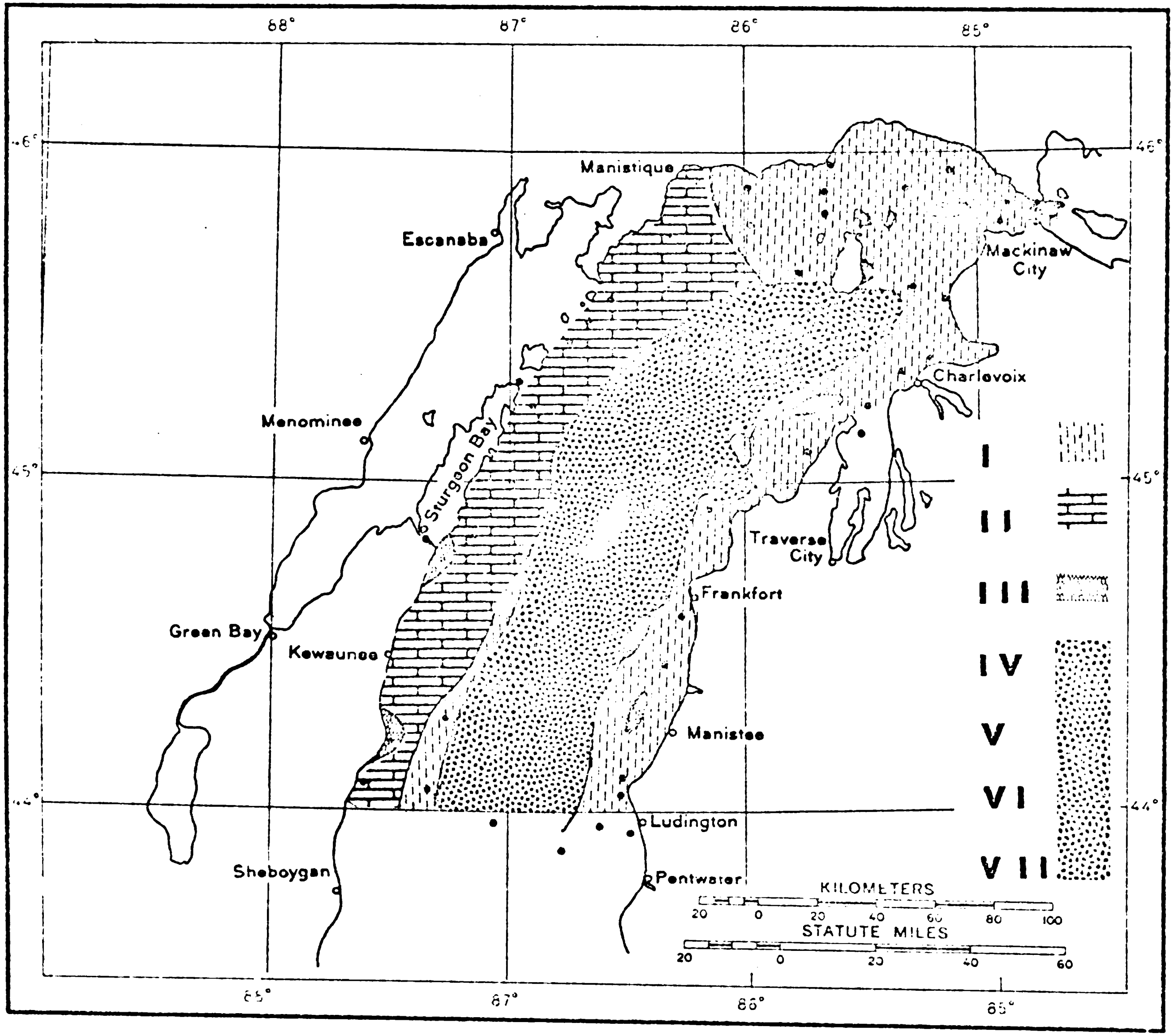
Table 11. Sediment texture and chemistry of upper Lake Michigan samples, analyzed according to Q-mode factor analysis.

Factor	Sample	h	Cu mg/kg	Co mg/kg	Zn mg/kg	Mn mg/kg	Total Carbon %	Organic Carbon %	Mean Ø	Standard Deviation	Cr mg/kg
I	28	1.00	0.0	0.0	0.064	12.2	2.20	0.310	5.78	1.99	0.0
	60	1.00	0.0	0.0	0.0	10.6	0.64	0.108	1.69	0.65	0.0
	36	0.97	0.0	0.0	0.033	23.5	1.03	0.086	1.89	0.70	0.0
	33	0.99	6.6	0.0	0.047	20.0	1.65	0.220	5.33	1.37	0.8
	7	0.98	0.0	0.0	0.0	21.6	1.15	0.216	2.24	1.06	0.0
	13	0.96	0.0	0.0	0.0	0.0	0.02	0.091	2.63	0.78	0.0
	50	0.95	6.4	0.0	0.0	284.4	1.03	0.261	6.80	2.60	0.0
	57	0.99	0.0	0.0	0.0	200.9	3.30	0.416	5.54	1.54	0.0
	37	0.99	0.0	0.0	0.011	6.3	0.00	0.069	0.87	0.86	0.0
	6	0.98	0.0	0.0	0.035	3.8	0.00	0.020	2.12	1.92	0.0
	59	0.93	0.0	0.12	0.0	19.2	1.45	0.213	5.47	3.30	0.0
	51	0.97	0.0	0.099	0.0	281.9	1.02	0.058	6.98	2.10	0.0
	47	0.88	0.0	0.0	0.0	3.7	0.12	0.314	1.89	0.39	0.0
	54	0.92	6.7	0.0	1.46	29.2	0.49	0.077	4.35	0.93	1.9
II	14	0.97	1.9	0.16	0.0	0.0	0.00	0.057	2.30	0.55	0.0
	32	0.93	0.0	0.15	0.0053	111.2	1.58	0.079	2.43	0.54	0.0
	15	0.98	0.0	0.09	0.0	104.8	0.90	0.079	2.19	0.56	2.1
	11	0.98	0.0	0.072	0.0	0.0	0.00	0.032	2.16	0.52	2.4
	25	0.93	10.7	0.18	0.0044	132.0	0.58	0.094	3.04	2.00	0.0
	45	0.98	0.0	0.33	0.066	798.9	3.24	0.420	5.17	1.73	0.0
	22	0.97	25.6	0.29	0.257	741.1	2.81	0.521	4.97	1.80	2.0
	16	1.00	0.0	0.10	0.0041	141.8	0.36	0.059	7.23	1.52	3.4
III	58	0.98	6.6	0.00	0.0	11.9	0.12	0.043	-1.67	0.83	4.8
	8	0.99	9.7	0.00	0.0118	146.0	1.71	0.286	3.09	1.83	10.0

Table 11 (cont'd.)

Factor	Sample	h^2	Cu mg/kg	Co mg/kg	Zn mg/kg	Mn mg/kg	Total Carbon %	Organic Carbon %	Mean Ø	Standard Deviation	Cr mg/kg
	31	0.97	16.4	0.00	0.016	288.5	3.64	0.106	1.85	1.04	10.7
	42	0.97	15.1	0.16	0.0052	39.6	0.34	0.058	-2.11	0.87	11.9
	39	0.91	15.0	0.13	0.964	78.7	1.08	0.610	7.67	1.76	17.1
	26	0.84	42.1	0.11	0.127	101.0	9.98	0.397	4.92	1.92	17.7
	1	0.96	7.3	0.22	0.0067	113.1	3.67	0.061	7.52	1.31	12.6
IV	10	0.87	48.4	0.19	0.703	872.1	6.04	0.272	4.99	1.34	8.5
	29	0.95	11.7	0.12	0.0147	626.1	3.55	0.253	5.58	1.82	0.0
	27	0.81	7.2	0.086	0.0066	406.8	0.27	0.057	1.85	0.55	0.0
V	35	0.94	159.5	0.35	0.964	22.5	4.10	0.541	5.51	1.87	7.9
	43	0.94	214.3	0.27	2.69	39.6	5.03	2.503	4.81	1.56	4.8
VI	44	0.86	15.3	0.29	0.022	335.3	2.45	1.583	5.77	1.95	18.0
	46	0.94	0.0	0.34	17.8	242.7	4.51	2.157	1.61	1.10	27.5
VII	12	0.97	5.2	0.079	0.0130	176.7	0.36	0.042	3.52	2.29	3.3
	48	0.99	19.9	0.077	11.5	18.0	0.83	0.075	0.88	0.64	3.8

Figure 17. Distribution of Q-mode factor areas in upper Lake Michigan.


88°
87°
86°
85°
46°
45°
44°
Manistique
Escanaba
Mackinaw City
Charlevoix
Menominee
Sturgeon Bay
Traverse City
Frankfort
Green Bay
Kewaunee
Manistee
Ludington
Sheboygan
Pentwater
I
II
III
IV
V
VI
VII
KILOMETERS
20
0
20
40
60
80
100
STATUTE MILES
20
0
20
40
60

factors account for 75% of the total variability (Table 9) in the sample set and include 29 of the 58 samples in the analysis. The remainder of the factors, Factors IV, V, VI, and VII, are individually relatively unimportant in the extent of the lake area that they represent. Figure 17 shows the areas represented by each factor, assuming that Factors IV, V, VI, and VII can be combined. Table 11 indicates the metal content, grain-size distribution and carbon content of the samples in each factor. Comparison with Table 11 indicates that these last four factors represent highly variable metal uptake in the deeper-water environments. Therefore, they are combined into one factor in Figure 17.

Factor I represents samples that are distributed around the eastern and northern shores of the lake. These samples contain relatively low trace-metal loads, high Mn^{+2} content, generally coarse sediments, and low organic carbon (Table 11). It is concluded that these samples reflect shallow water, nearshore deposition, with natural metal sources predominating. Therefore, the trace metals are of limited occurrence and manganese is abundant. This interpretation agrees with the data of Robbins et al. (1972). In their study, those tributaries in the eastern and northern shores that do not drain through industrial areas are low in trace-metal content and high in Mn content.

Factor II reflects the nearshore, shallow-water zone on the western side of the lake. The samples in Factor II are low in Cu content, generally coarse grained, and low in organic carbon. The Co, Cr, and Zn content suggests that the samples from the western shore are subject to loading either from cultural sources in the vicinity of Green Bay or from natural weathering of the Precambrian strata exposed in the Upper Peninsula. In comparison with the data of Robbins et al. (1972) and the samples clustered into Factor III, it appears that the source of the samples of Factor II may be natural.

Factor III represents scattered samples that occur near known sources of cultural contamination (i.e., Sturgeon Bay, Manitowoc, and Two Rivers, Wisconsin, and Manistee and St. Ignace, Michigan) are near the island area of the lake (Figure 17). These samples contain high concentrations of Cr and Cu, are low in Co, Mn, and Zn content, and are relatively high in organic-carbon content. With the exception of the samples in the open lake, the samples in Factor III can be attributed to regions of cultural contamination. The samples from the open lake may reflect either cultural contamination or Cu derived from glaciation of the Upper Peninsula.

Factors IV, V, VI, and VII represent samples that are highly variable, but all occur in the deeper, open lake. These samples contain high organic carbon (Table 1). It is assumed that the distribution of metals in the deep lake is due to organic complexing and adsorption on clay minerals in

the sediments. The variability reflects variation in sediment properties, rather than in source.

CONCLUSIONS

It is apparent that the trace-metal concentrations in upper Lake Michigan have been derived from both natural and cultural sources. The uptake of the metals in the lake is not uniform, but corresponds to proximity to source and, more important, to sedimentary environment. The trace metals, Co, Cr, Cu, and Zn, are preferentially fixed by organic compounds and clays, which is reflected by correlations of the metals with depth, sediment texture, and organic-carbon content. The modern sources of the metals can be identified by metal fixation in nearby sediments. However, the distribution of metals in the sediments shows much more variability than would be expected from the data of Robbins _et al_. (1972). This may be due to the fact that the Robbins _et al_. (1972) data reflect current loading patterns, while the distribution of metals in the lake sediments reflects averaging over longer periods of time.

Manganese occurs throughout the lake sediments. The form that the metal takes is dependent upon the Eh and dissolved-oxygen content of the sediment and bottom water. The technique used in this study was sensitive to Mn^{+2}, rather than total Mn, so those areas that can be characterized by manganese nodule formation were not identified. Since Mn is ubiquitous, it can be concluded that the metal has a natural origin for the most part. The manganese nodules occur in coarse, well-oxygenated sediments, while Mn^{+2} occurs in the fine, organic-rich sediments. This may be due to the low Eh and oxygen content of the sediments and to organic complexing of Mn^{+2}.

Factor analysis is a powerful tool for the interpretation of chemical and sedimentary processes in the lake. R-mode factor analysis allows separation of the data into groups of interdependent variables, which reflect physical or chemical interactions. The significant interactions identified include: (1) the association of trace metals, except Cu, with organic carbon, which reflects complexation of metals by organic molecules; (2) the association of Cu and total carbon, which reflects possible detrital deposition from sources in the Upper Peninsula, as well as complexing in organic-rich sediments; and (3) the independence of Mn, which suggests a different origin of the metal and reflects the different stability requirements for the forms of Mn. Q-mode factor analysis allows identification of areas where several sources and fixation processes occur. One cannot absolutely differentiate source and fixation mechanisms, but general trends can be identified.

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Appendices

Appendix A. Sample Locations.

SAMPLE NO.	LOCATION	
1	LAT.45.93N	LON.84.72W
2	45.85N	84.86W
3	45.94N	85.11W
4	45.89N	85.30W
5	45.96N	85.62W
6	45.89N	85.65W
7	45.92N	85.65W
8	45.62N	85.47W
9	45.49N	85.52W
10	45.59N	85.69W
11	45.62N	85.98W
12	45.78N	85.97W
13	45.90N	85.98W
14	45.91N	86.19W
15	45.74N	86.31W
16	45.59N	86.32W
17	45.55N	86.57W
18	45.49N	86.67W
19	45.43N	86.74W
20	45.30N	86.96W
21	45.23N	86.90W
22	45.09N	86.76W
23	44.85N	86.77W
24	44.79N	86.95W
25	44.83N	87.15W
26	44.82N	87.36W
27	44.77N	87.28W
28	44.64N	87.02W
29	44.38N	87.08W
30	44.29N	87.26W
31	44.21N	87.49W
32	44.08N	87.60W
33	44.07N	87.33W
34	43.96N	87.06W
35	43.88N	86.77W
36	43.96N	86.61W
37	43.94N	86.48W
38	44.05N	86.53W
39	44.21N	86.76W
40	44.47N	86.72W
41	44.54N	86.46W
42	44.59N	86.26W
43	44.65N	86.33W
44	44.72N	86.52W
45	44.88N	86.56W
46	44.92N	86.35W
47	44.92N	86.14W
48	45.00N	86.00W
49	45.09N	85.73W
50	45.19N	85.90W
51	45.23N	85.68W
52	45.23N	85.46W
53	45.15N	85.50W
54	45.24N	85.33W
55	45.27N	85.20W
56	45.55N	85.13W
57	45.60N	85.27W
58	45.83N	85.13W
59	45.78N	84.90W
60	45.80N	84.67W

Appendix D. Physical and chemical data collected at each sampling station.

SAMPLE NO.	DEPTH	WATER TEMP.	PH	EH	SPEC. COND.	CLORIDE PPM	PHTH. ALKAL.	TOTAL ALKAL.	DO PPM	DO SAT.
1	47	6.40	7.94	.229	212	4.31	0.0	76	12.00	100
2	28	6.00	7.89	.210	247	5.87	0.0	89	12.17	101
3	72	6.00	7.01	.242	241	6.17	0.0	97	11.16	93
4	95	6.09	7.38	.121	265	6.66	0.0	99	11.91	99
5	39	7.21	7.40	.249	260	5.97	0.0	95	11.75	100
6	82	4.69	6.70	.252	271	6.07	0.0	99	12.83	103
7	65	3.97	6.97	.253	285	6.36	0.0	99	13.05	103
8	50	6.10	7.05	.102	264	5.87	0.0	99	12.45	104
9	306	3.55	7.12	.243	280	6.17	0.0	100	12.26	95
10	185	3.64	6.97	-.050	282	6.75	0.0	100	13.09	102
11	63	4.41	6.90	.250	273	6.17	0.0	99	12.87	102
12	204	3.40	7.32	.261	274	6.75	0.0	100	13.17	102
13	69	6.79	7.10	.262	264	6.56	0.0	98	12.04	102
14	69	6.53	6.90	.278	269	6.75	0.0	99	11.63	98
15	154	5.46	6.90	.275	269	6.36	0.0	99	12.31	101
16	311	3.26	7.18	.272	262	6.56	0.0	99	13.16	102
17	147	4.72	7.48	.255	273	6.21	0.0	99	12.62	101
18	106	6.09	7.20	.264	269	6.26	0.0	99	12.19	101
19	76	6.08	8.12	.232	268	6.60	0.0	99	11.95	99
20	116	6.67	6.75	.270	296	6.56	0.0	104	11.84	100
21	61	7.58	8.12	.250	273	6.17	0.0	104	12.26	106
22	468	3.27	7.38	.288	285	6.26	0.0	104	13.12	101
23	660	3.09			281	6.17	0.0	103	12.71	98
24	425	3.10	7.12	.271	274	5.87	0.0	103	13.03	100
25	223	3.86	7.00	.270	282	7.34	0.0	104	13.11	103
26	26	12.47	6.82	.119	287	8.91	3.0	110	11.45	111
27	50	6.51	6.78	.254	285	6.26	0.0	104	11.03	93
28	674	3.05	7.00	.122	280	7.34	0.0	104	11.63	89
29	735	3.22	7.20	.262	280	6.56	0.0	104	11.93	92
30	415	3.19	7.20	.261	280	6.66	0.0	104	11.59	89
31	35	7.65	7.4	.245	273	6.95	1.0	104	10.95	95
32	52	6.40	7.35	.062	274	7.14	0.5	105	10.82	91
33	276	3.85	7.32	.261	279	7.00	0.0	104	12.50	98
34	369	3.67	7.25	.305	274	6.85	0.0	104	12.33	96
35	570	3.35	6.91	.152	276	6.95	0.0	105	12.08	94
36	138	4.86	7.40	.230	279	7.05	0.0	105	11.65	94
37	44	5.42	7.42	.230	297	9.20	0.0	107	11.70	96
38	59	4.75	7.18	.250	279	8.12	0.0	106	11.66	94
39	500	3.18	7.40	.253	274	5.77	0.0	105	12.15	94
40	828	3.13	7.12	.252	275	5.77	0.0	104	11.35	87
41	628	3.69	7.12	.248	279	5.48	0.0	104	11.07	86
42	47	5.49	7.40	.191	281	6.46	0.0	105	11.95	98
43	600	3.80	7.18	-.103	281	6.75	0.0	106	11.15	87
44	715	3.33	6.98	.233	279	5.87	0.0	105	12.30	87
45	654	3.26	7.05	-.200	274	5.97	0.0	105	11.83	91
46	494	3.49	7.22	.248	276	5.58	0.0	105	11.49	89
47	41	8.19	7.41	.202	287	6.56	2.5	107	11.32	99
48	40	7.40	7.26	.108	280	7.14	1.0	106	11.22	96
49	50	7.10	7.10	.230	278	6.90	2.5	105	12.54	110
50	430	3.85	7.20	.242	277	5.87	0.0	106	12.24	96
51	290	4.01	7.22	.240	274	5.87	0.0	104	11.49	90
52	165	4.99	7.15	.251	274	6.07	0.0	104	11.30	91
53	193	4.30	7.21	.260	272	6.26	0.0	104	10.52	83
54	385	3.89	7.33	.262	272	5.77	0.0	105	11.02	87
55	48	8.77			274	6.17	2.5	105	11.50	102
56	49	7.65	6.78	.242	268	6.56	2.5	104	11.43	99
57	169	4.03	7.20	.248	272	5.87	0.0	104	11.34	89
58	50	7.50	7.40	.200	264	6.07	1.0	105	10.95	94
59	86	5.88	7.32	.240	264	5.77	0.0	97	11.56	96
60	158	5.73	7.55	.188	235	5.48	0.0	86	11.43	94

SAMPLE NO.	CU	CO	ZN	MN	TOTAL C	ORGANIC C	MEAN PHI
1	7.3	0.22	0.0067	113.1	3.67	0.061	7.52
2							
3	0.0	0.17		15.5	0.12	0.067	3.00
4	0.0	0.08	0.114	409.0	1.65	0.165	
5		0.0			0.0	0.078	1.95
6	0.0	0.0	0.035	3.8	0.0	0.020	2.12
7	0.0	0.0	0.0	21.6	1.15	0.216	2.24
8	9.7	0.0	0.0118	146.0	1.71	0.286	3.09
9	30.0	0.17		116.0	1.03	0.263	7.58
10	48.4	0.19	0.703	872.1	6.04	0.272	4.99
11	0.0	0.072	0.0	0.0	0.0	0.032	2.16
12	5.2	0.079	0.0130	176.7	0.36	0.042	3.52
13	0.0	0.0	0.0	0.0	0.02	0.091	2.63
14	1.9	0.16	0.0	0.0	0.0	0.057	2.30
15	0.0	0.09	0.0	104.8	0.90	0.079	2.19
16	0.0	0.10	0.0041	141.8	0.36	0.059	7.23
17	0.0	0.12		49.2	0.17	0.045	2.28
18	0.0	0.0	0.0028	250.9	0.64	0.293	
19		0.19			0.46	0.107	0.85
20	11.5	0.07	0.027	230.9	1.98	0.240	
21	25.6	0.11			2.38	0.095	0.85
22	25.6	0.29	0.257	741.1	2.81	0.521	4.97
23	0.0	0.28	0.069	535.5	3.84	1.028	6.95
24		0.40	0.512	575.0	1.39	0.252	5.36
25	10.7	0.18	0.0044	132.0	0.58	0.094	3.04
26	42.1	0.11	0.127	101.0	9.96	0.397	4.92
27	7.2	0.086	0.0066	406.8	0.27	0.057	1.85
28	0.0	0.0	0.064	12.2	2.20	0.310	5.78
29	11.7	0.12	0.0147	626.1	3.55	0.253	5.58
30		0.30	0.354	157.0	1.92	0.854	6.34
31	16.4	0.0	0.016	288.5	3.64	0.106	1.85
32	0.0	0.15	0.0053	111.2	1.58	0.079	2.43
33	6.6	0.0	0.047	29.0	1.65	0.220	5.33
34	116.0	0.19	0.019	223.3	0.93	0.060	
35	159.5	0.35	0.964	22.5	4.10	0.541	5.51
36	0.0	0.0	0.033	23.5	1.03	0.086	1.89
37	0.0	0.0	0.011	6.3	0.00	0.069	0.87
38	0.0	0.10		10.9	0.49	0.171	2.83
39	15.0	0.13	0.964	78.7	1.08	0.610	7.67
40					3.03	2.227	6.42
41		0.52			1.53	0.480	5.54
42	15.1	0.16	0.0052	39.6	0.94	0.058	-2.11
43	214.3	0.27	2.69	39.6	5.03	2.503	4.81
44	15.3	0.29	0.022	335.3	2.45	1.583	5.77
45	0.0	0.33	0.066	798.9	3.24	0.420	5.17
46	0.0	0.34	17.8	242.7	4.51	2.157	1.61
47	0.0	0.0	0.0	3.7	0.12	0.314	1.89
48	19.9	0.077	11.5	18.0	0.83	0.075	0.88
49					0.48	0.228	
50	6.4	0.0	0.0	284.4	1.03	0.261	6.80
51	0.0	0.099	0.0	281.9	1.02	0.058	6.98
52		0.17	14.5	58.5	1.11	0.211	4.28
53	14.0	0.21	0.53	175.0	0.69	0.331	
54	6.7	0.0	1.46	29.2	0.49	0.077	4.35
55	12.0	0.07	0.356	16.4	1.32	0.144	
56	12.0	0.19	0.605		0.84	0.018	
57	0.0	0.0	0.0	200.9	3.30	0.416	5.54
58	6.6	0.0	0.0	11.9	0.12	0.043	-1.67
59	0.0	0.12	0.0	19.2	1.45	0.213	5.47
60	0.0	0.0	0.0	10.6	0.64	0.108	1.69

SAMPLE NO.	STD. DEV.	SKEWNESS	KURTOSIS	CR
1	1.31	-.51	4.65	12.6
2				
3	2.28	.75	4.60	0.0
4				4.7
5	1.08	1.41	12.6	3.7
6	1.92	1.00	9.60	0.0
7	1.06	1.68	23.1	0.0
8	1.83	1.41	11.3	10.0
9	1.77	-.43	2.78	11.1
10	1.34	.25	2.13	8.5
11	.52	-.08	2.69	2.4
12	2.29	.77	4.18	3.3
13	.78	-1.48	12.3	0.0
14	.55	-.56	5.50	0.0
15	.56	-.30	3.15	2.1
16	1.52	-.20	2.35	3.4
17	.47	-.19	2.92	0.0
18				0.0
19	.55	-.35	4.51	
20				9.7
21	.96	-.33	2.44	
22	1.80	.48	.30	2.0
23	1.93	-.32	2.25	0.0
24	1.69	.06	2.14	2.2
25	2.00	.81	4.97	0.0
26	1.92	.19	1.94	17.7
27	.55	-.61	6.78	0.0
28	1.99	.09	1.98	0.0
29	1.82	.10	2.31	0.0
30	2.18	-.010	1.93	0.0
31	1.04	-.71	4.55	10.7
32	.54	-1.28	12.7	0.0
33	1.37	-.05	1.72	0.8
34				0.0
35	1.87	.06	1.90	7.9
36	.70	-.95	8.09	0.0
37	.86	-.73	5.02	0.0
38	.39	-1.62	15.5	10.8
39	1.76	-.65	4.22	17.1
40	1.92	-.12	2.00	
41	1.70	.12	2.07	
42	-2.11	.86	.28	11.9
43	1.56	.11	2.06	4.8
44	1.95	.08	1.93	18.0
45	1.73	.33	2.63	0.0
46	1.10	.56	9.90	27.5
47	.39	-.09	2.56	0.0
48	.64	-.75	6.43	3.8
49				
50	2.60	-.10	1.45	0.0
51	2.10	-.32	2.18	0.0
52	1.62	.27	1.88	0.0
53				1.3
54	.93	.17	1.97	1.9
55				6.1
56				0.0
57	1.54	-.17	1.78	0.0
58	.83	-.36	1.83	4.8
59	3.30	.054	1.45	0.0
60	.65	-.55	4.20	0.0