COPPER, LEAD, ZINC, NICKEL, AND SILVER IN LAKES OF THE CLAM LAKE AND MONICO REGIONS, NORTHERN WISCONSIN

by

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ABSTRACT

The accumulation of copper, lead, zinc, nickel, and silver in lake sediments from the Clam Lake and Monico regions has been studied to provide information on the potential for anomalous mineralization in the underlying Precambrian bedrock. The high organic content of the lakes suggests that the metals in part were fixed within the sediments by absorption onto organic debris.

A positive linear relationship exists between the mean metal contents of Cu, Pb, Zn, and Ni and the mean weight percent organic matter in the lakes, when the data are plotted on semilog paper. The relationship is most clearly demonstrated by lead and nickel. Confidence limits were calculated for the regression of Cu, Pb, Zn, and Ni upon organic matter, and data points falling above the upper limits may represent anomlous metal concentrations within the lake sediments.

The northern part of the Clam Lake region, and the area around Monico in the Monico region, are of greatest interest with regard to possible mineralization in the Precambrian bedrock. In the Clam Lake region, at the 95% level of confidence, Beaver, Tea, Coffee, Mineral, Potter, and Buffalo lakes exhibit anomalous concentrations of one or more of Cu, Pb, Zn, and Ni. The same is true for Ogemago, Sequilla, Kechewaishke, and Tank lakes in the Monico region. At the 99% level, significant metal concentrations in the Clam Lake region occur in Beaver, Tea, Coffee, and Potter lakes; and in the Monico region, in Ogemaga, Kechewaishke, and Tank lakes. Generalizations with respect to silver are difficult because of the low concentrations and the spotty nature of the data. Additional work should be done to more clearly define the potential for anomlous mineralization in the Precambrian rocks of the two regions.

INTRODUCTION

Large areas of the Precambrian bedrock of Canada and the northern United States are covered by glacial deposits. Where the glacial material is local in origin, it may reflect quite well the underlying bedrock composition. However, in regions where it was derived at some distance from the point of deposition, the underlying composition will be poorly represented. Drainage in the shield region generally is characterized by swamps, bogs, and poorly-developed stream patterns. The transported nature of the debris and the poorly-developed drainage present special problems for standard techniques of geochemical exploration such as bedrock sampling, and soil and stream sediment sampling.

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Recently, attention has turned to lake sediment geochemistry as a guide to anomalous mineralization in regions of buried bedrock. The initial efforts in North America have been conducted largely in the shield region of Canada. Little has been published on lake sediment geochemical exploration in the United States. In the present study lake sediment samples were collected from two regions in northern Wisconsin (Figure 1). The purpose was to provide data for copper, lead, zinc, nickel, and silver that may help in determining the potential for anomalous mineralization in the underlying Precambrian bedrock.

The locations of the lakes to be sampled within the two regions shown in Figure 1 were chosen so as to traverse as much of the Precambrian geology as possible. Regional trends in the underlying rocks are shown by Dutton and Bradley (1970). Bedrock information, the locations of the lakes, and the locations of samples within the lakes are shown in Figures 2-5.

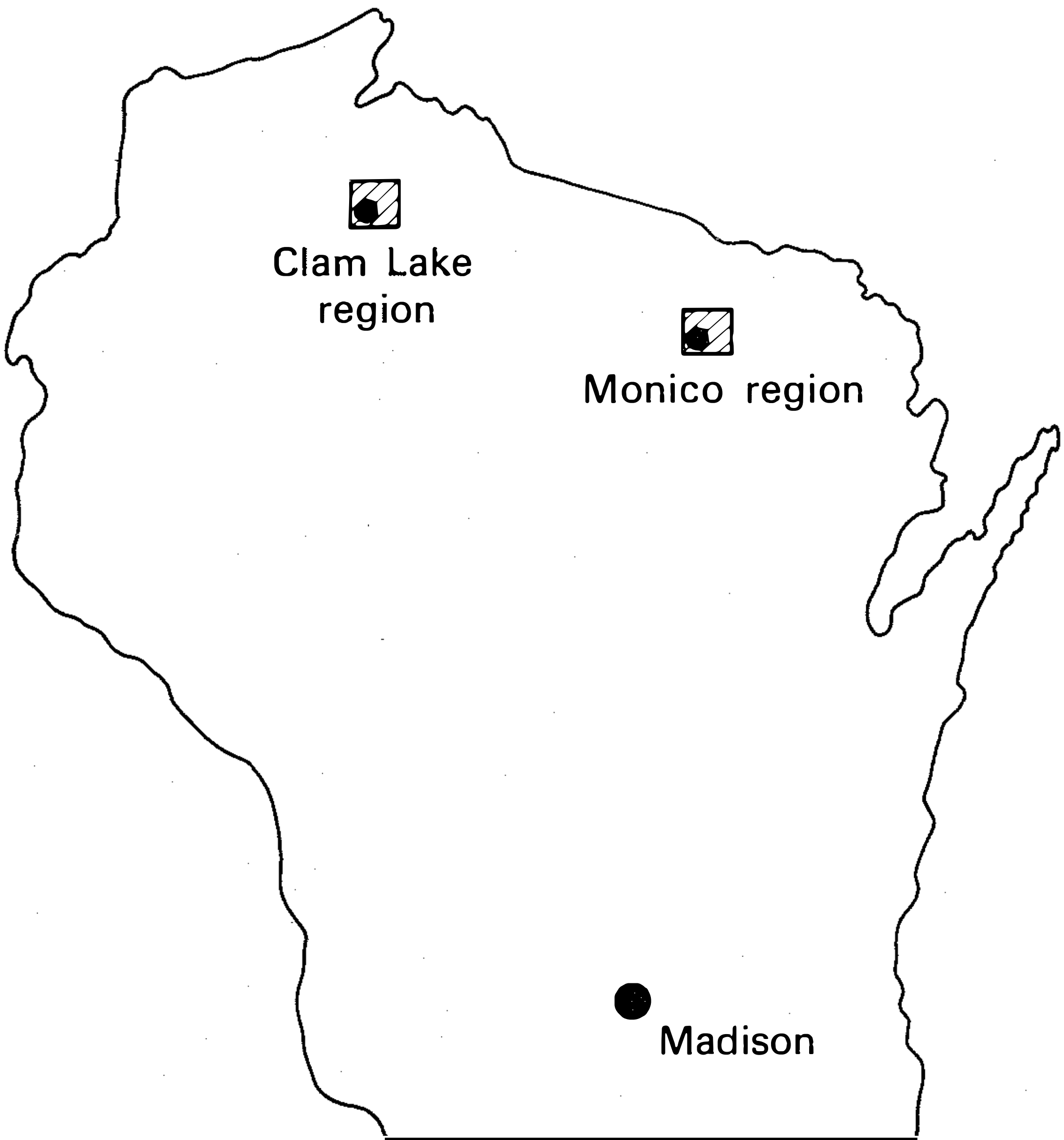

Figure 1. Locations of the Clam Lake and Monico study regions in northern Wisconsin.

Important clues to anomalous mineralization may be transmitted to the lake basins in solution and/or suspended sediment within stream or surface runoff. Groundwater circulating in contact with the underlying bedrock also may transmit important information to the lake sediments. Most of the surface material, even in areas where bedrock outcrops are present, is glacial in origin. Metal anomalies thus become difficult to interpret.

The intent of the present study was to identify potential anomalies resulting (1) from groundwater circulating in contact with the bedrock beneath the lakes, and/or (2) from surface waters draining anomalous rock outcrops. Multiple samples were taken from each lake, the purpose being to separate significant bedrock anomalies from anomalies that might be spawned by metal-rich glacial erratics. The number of samples ranged from 2 to 11, depending on the size of the lake (Figures 4, 5).

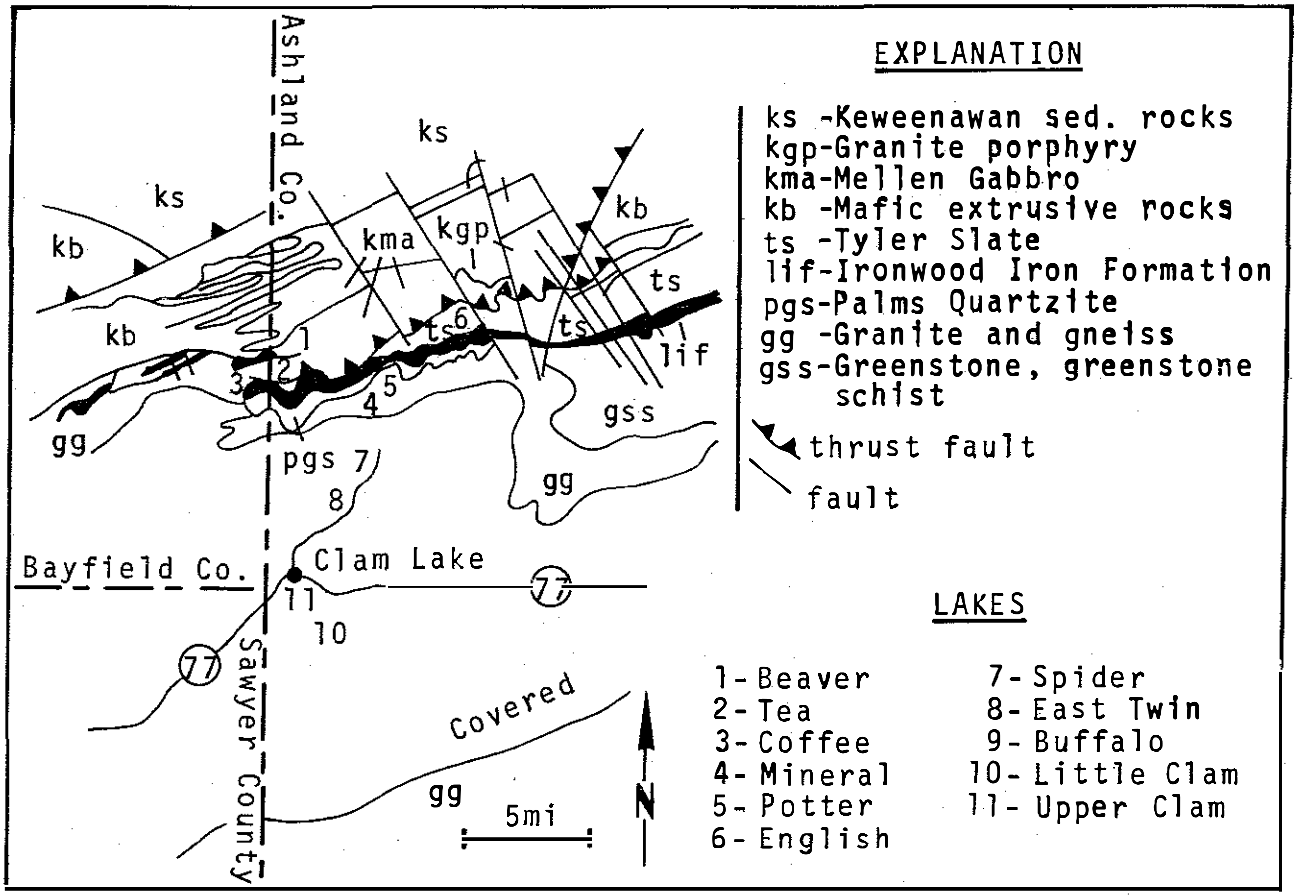

Figure 2. General geology and locations of lakes sampled in the Clam Lake region (geology from Dutton and Bradley, 1970).

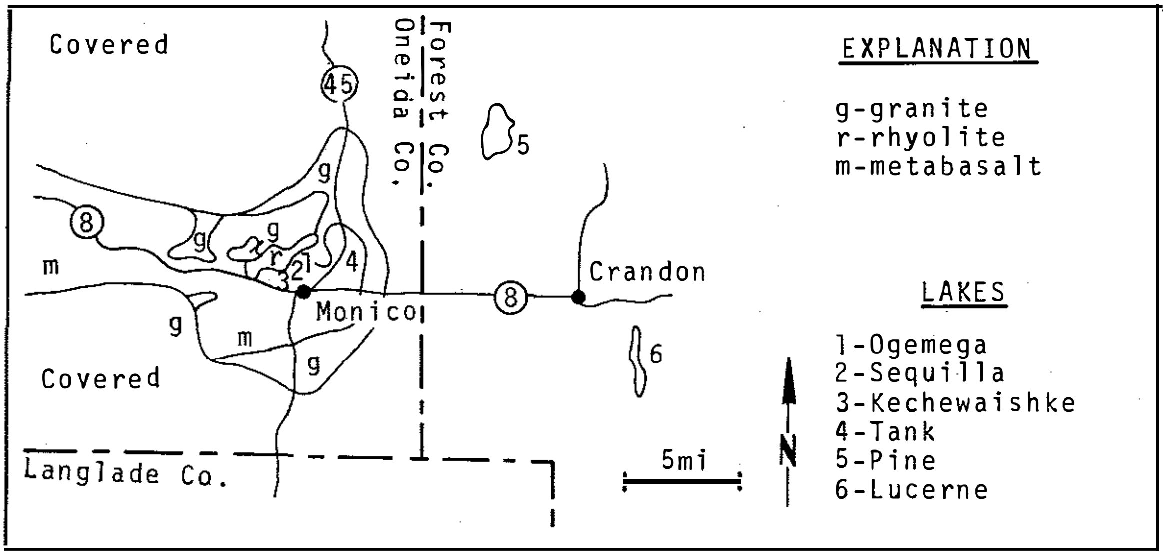

Figure 3. General geology and locations of lakes sampled in the Monico region (geology from Dutton and Bradley, 1970).

FIELD AND LABORATORY STUDY

Sediment samples were collected from a 3.65-meter aluminum boat using a drop-core sample device. The device consists of a heavy stainless steel collar into which is threaded a 30-cm long plastic core barrel. The collar is equipped with a butterfly valve, and samples are taken in such a way that none of the water and sediment remaining in the barrel upon retrieval has touched any metal. The water depth was determined by measuring the length of nylon line needed to take the sample. Following retrieval, the samples were transferred to plastic bags and the sampler was thoroughly rinsed in preparation for the next sample station. The pH of each water-sediment sample was determined upon completion of the sample program for each lake. Indicator paper was used for the pH measurements. Some accuracy thus was sacrificed, but it permitted direct determination of the pH without first having to return the samples to the laboratory. The locations of the sample stations within each of the lakes in the two regions under investigation are shown in Figures 4 and 5.

In the laboratory, two statistically equal portions were selected from each sample: one for elemental analysis, the other for organic determination. The sub-samples selected for chemical analysis were digested in a hot mixture of nitric and perchloric acids, and the residue was heated until dry and leached with 1 M hydrochloric acid. The leachate was diluted with demineralized double distilled water and analyzed for Cu, Pb, Zn, Ni, and Ag with a Perkin-Elmer 303 atomic absorption spectrophotometer. Weight percent organic matter in the samples was determined by measuring the loss in dry weight following digestion in concentrated hydrogen peroxide.

In addition to chemical and organic analyses, one sample from each lake (two from the larger lakes) was subjected to x-ray analysis, to give some measure of the bottom sediment mineralogy. Samples to be x-rayed first were digested in hydrogen peroxide to limit masking effects that the large amounts of organic matter might have on the sample mineralogy.

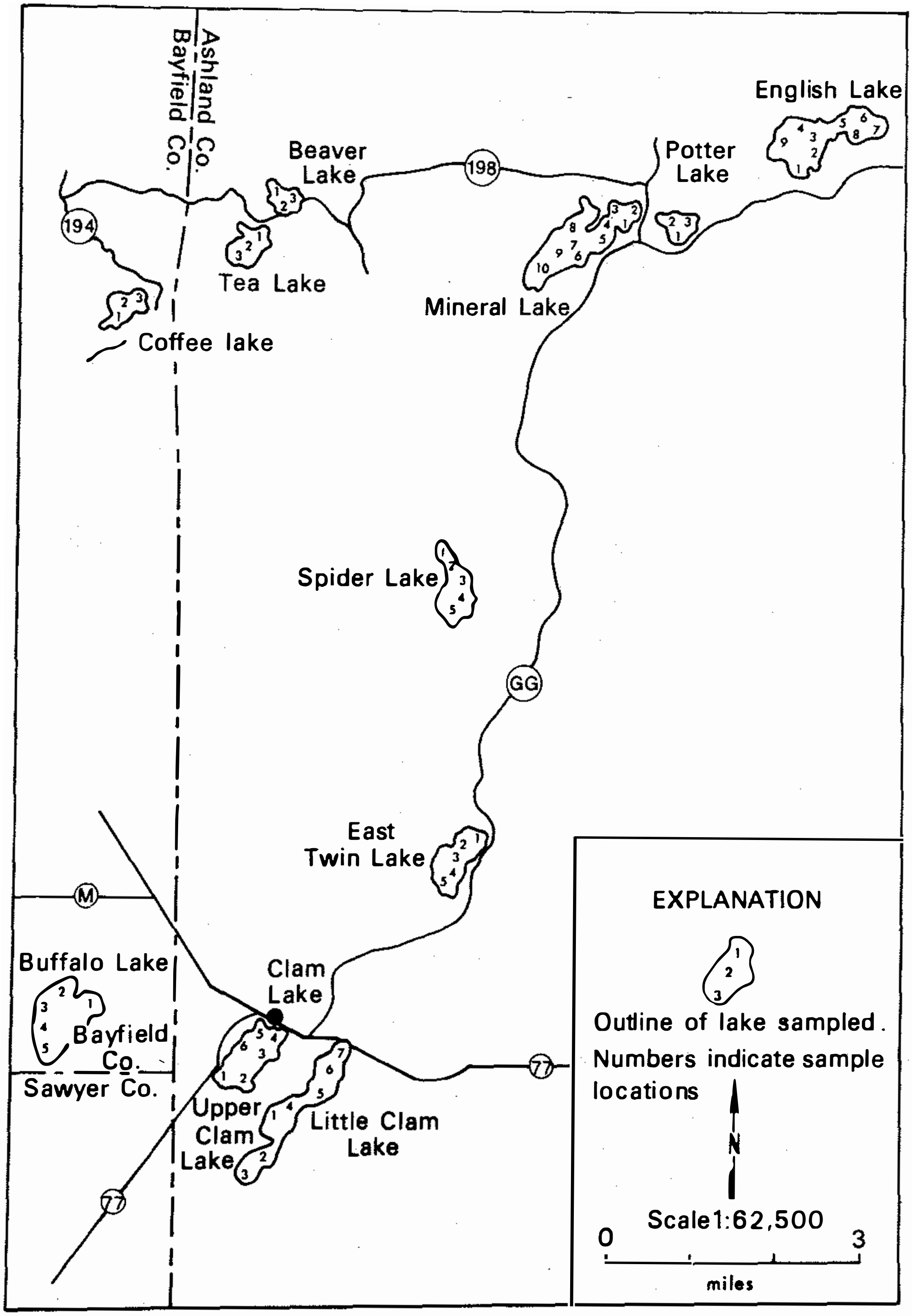

Figure 4. Locations of lakes and sample points within lakes, Clam Lake region.

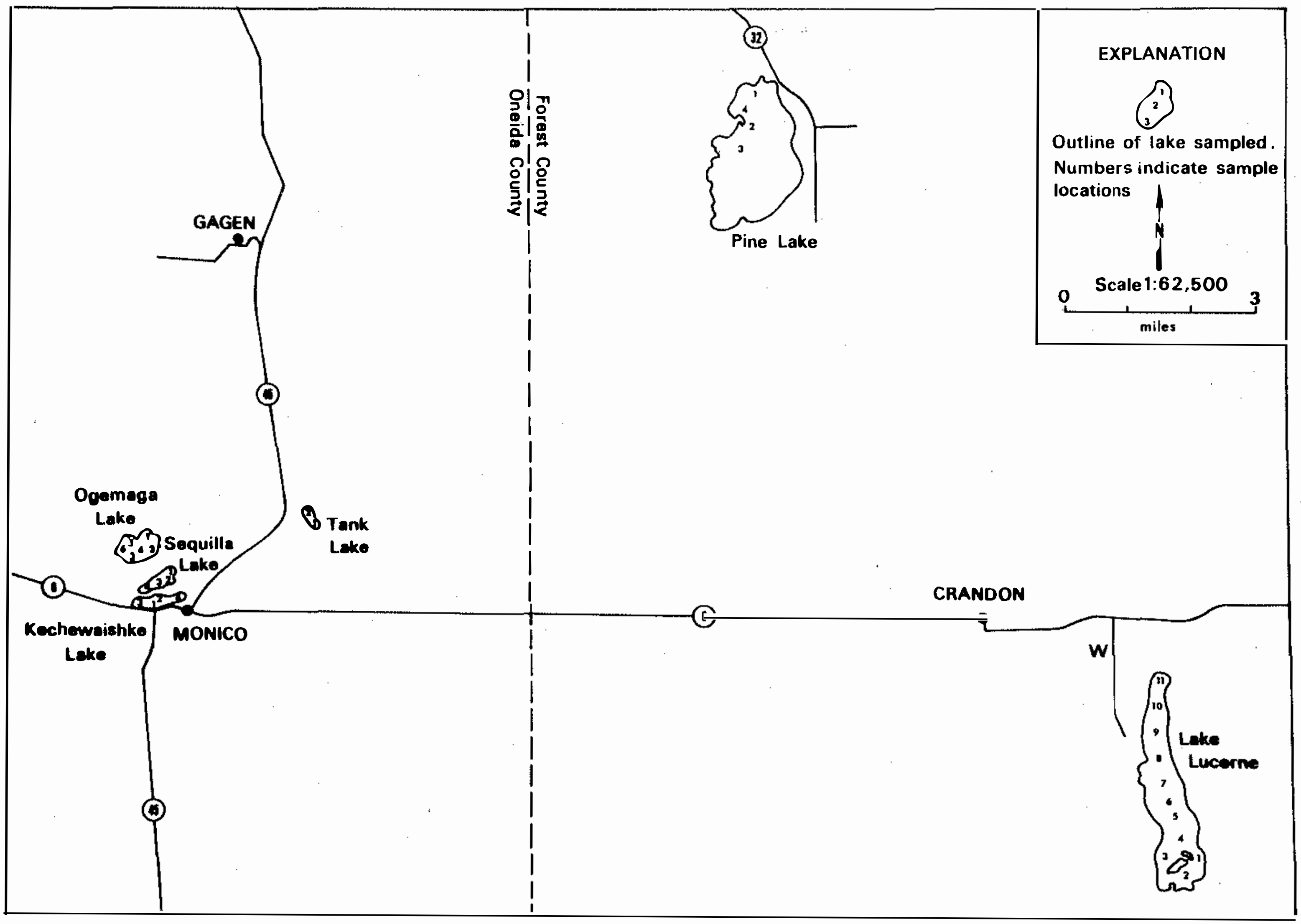

Figure 5. Locations of lakes and sample points within lakes, Monico region.

RESULTS AND DATA EVALUATIONS

Metals accumulate in lake sediments through a variety of complex chemical and biochemical processes. Adsorption of metals onto clay minerals, and onto the hydrous oxides of iron and manganese, as well as accumulations through metal-organic complexing, all may be important in fixing metals within lake sediments.

Specific clay content and the content of the hydrous iron and manganese oxides were not measured. X-ray studies indicate some component of clay minerals in the sediments, in addition to quartz and feldspar. Thus, the potential exists for at least some fixation of metals onto clay minerals. However, the high organic contact (Table 1), dark color, and strong odor of many of the fresh samples suggest that the environment was reducing in nature; and a reducing environment may strongly influence metal accumulations on both clay minerals and the hydrous oxides (Timperly and Allan, 1974). These authors have suggested that in the presence of sulfide ion and organic matter, under reducing conditions, metals accumulate either as metal sulfides or metal-organic complexes, and not by cation exchange onto clays or other silicate minerals. In addition, the hydrous oxides of iron and manganese probably play a minor role in metal accumulations within reducing environments, as they are unstable under reducing conditions (Garrels, 1960; Timperly and Allan, 1974).

Metal sulfides were not noted in the x-ray patterns, and thus metal-organic complexing probably is of greatest importance in concentrating metals within the lake sediments. The relationships of mean concentrations of Cu, Pb, Zn, and Ni to mean weight percent organic content (Table 2) for the 17 lakes from the Clam Lake and Monico regions are shown in Figure 6. The data are plotted on semilog paper, with the metal concentrations measured by the logarithmic scale. The equation for each of the lines is given at the lower right of the graph. The positive relationship between metal concentration and organic matter is most clearly shown by lead and nickel. One-tailed "t" tests were run to determine whether or not the regression coefficients for the equations shown in Figure 6 are significantly greater than zero, that is, whether or not a positive relationship exists between metal concentrations and organic content of the sediments. The coefficients for Pb and Ni were shown to be greater than zero at the 95% level of confidence. The levels were 80% and 50% respectively for Zn and Cu. The influence of organic matter upon Zn and Cu concentrations thus were less than expected, even at the high levels of organic content shown in Table 2. With this qualification, the data for Zn and Cu were subjected to the same manipulations as the data for Pb and Ni.

Because of the influences of organic matter on metal concentrations, the problem was one of determining which of the lakes may contain concentrations in excess of those due to background contributions. It was felt that data points located considerably above the regression lines shown in Figure 6 might reflect anomalous metal concentrations. To this end, the 95% and 99% confidence limits for the regression of the mean contents of Cu, Pb, Zn, and Ni upon the mean organic content were determined, and are shown in Figure 7. Data points falling above the upper confidence limits may be anomalous. Thus, the regression lines are taken to represent background contributions, and the upper confidence limits the threshold values for the various metals.

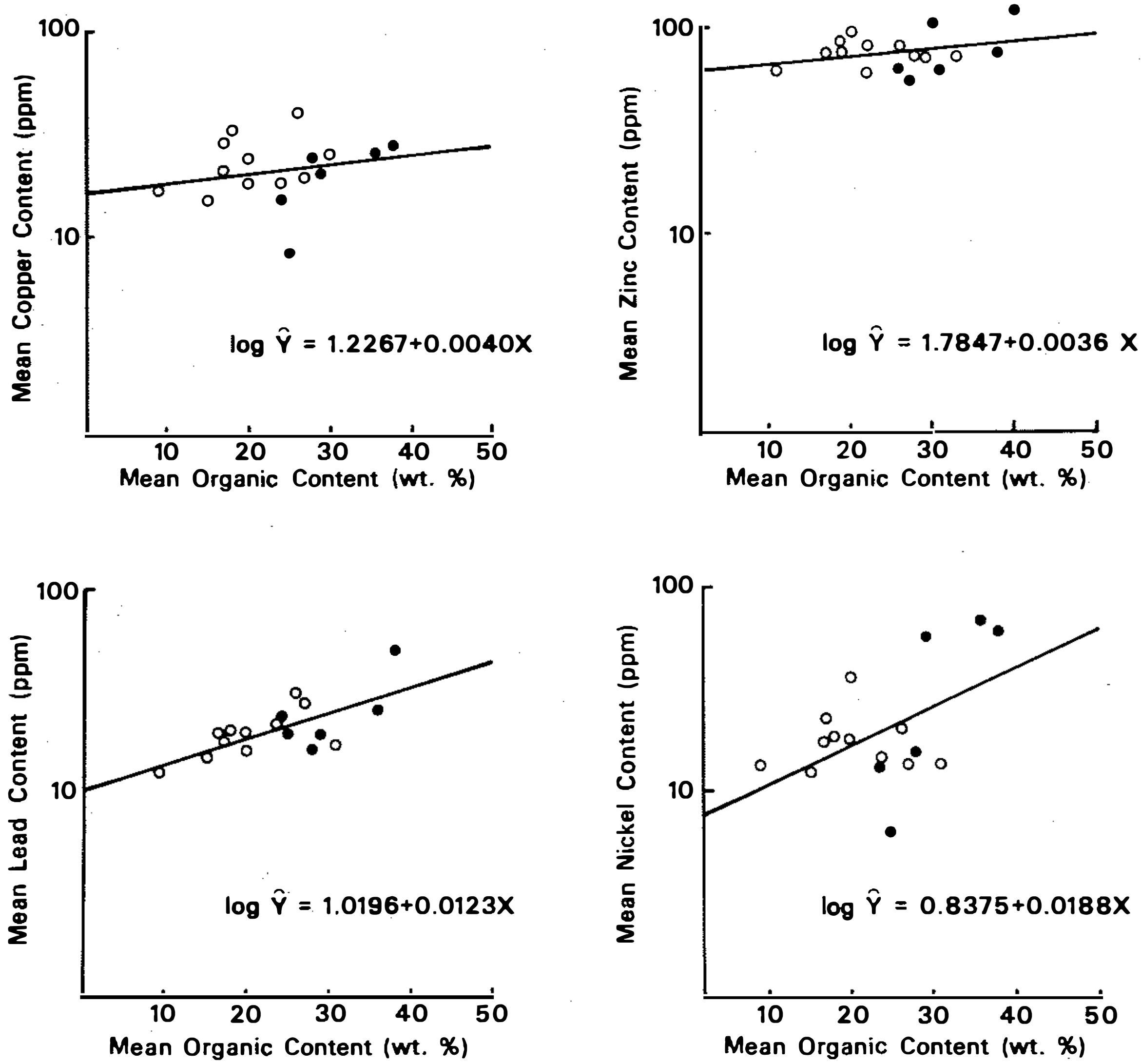

Figure 6. Mean contents of Cu, Pb, Zn and Ni versus mean organic contents in lakes from the Clam Lake and Monico regions, northern Wisconsin (0 = Clam Lake region, ● = Monico region). The equation for the line is given at the lower right for each graph.

CONCLUSIONS AND COMMENTS

Several of the lakes from both the Clam Lake and Monico regions exhibit potentially anomalous metal concentrations at the 95% and 99% levels of confidence (Tables 3, 4). The northern part of the Clam Lake region and the area near Monico appear most promising. Multiple element anomalies exist at the 95% level (Table 3) in Beaver, Tea, Coffee, Mineral, and Potter lakes from the northern Clam Lake region, and in Kechewaishke Lake in the Monico region. Cu-Pb and Cu-Zn anomalies persist at the 99% level (Table 4) in Beaver and Coffee lakes, and Kechewaishke Lake exhibits a Pb-Zn anomaly also at the 99% level (Table 4).

Rock outcrops are evident in both the northern Clam Lake and Monico regions (Dutton and Bradley, 1970), and the trace element chemistry thus may accurately reflect the characteristics of the underlying bedrock. The problem becomes one of differentiating between mineralized versus unmineralized bedrock. For example, high average nickel contents in Ogemaga, Sequilla, and Kechewaishke lakes (Table 2) near Monico may reflect the composition of the basalts that outcrop nearby (Fig. 3, Table 1). However, Cu values in these lakes are not correspondingly high, and the high nickel values plus the elevated contents of lead and zinc in Kechewaishke Lake (Table 2) may indicate abnormal mineralization in the underlying bedrock. The geology of the northern Clam Lake region is complex (Figure 2), and the metal anomalies noted in Tables 3 and 4 also may reflect contributions from unmineralized bedrock. However, the persistence of the multiple metal anomalies at the 99% level of confidence suggests that anomalous mineralization may be present in the area.

Silver concentrations are low throughout the two study regions, with concentrations ranging only to 13 ppm and rarely exceeding 5 ppm (Table 1). Notably, samples containing more than 5 ppm contain at least 25 weight percent organic matter. Samples from Sequilla and Kechawaishke lakes contain some silver, but these concentrations also may reflect the composition of the nearby basalts.

It should be noted that lead contamination from gasoline for motor boats is a possibility in all but the very small lakes. This may be particularly true for Buffalo Lake in the Clam Lake region (Table 3), as it is subjected to considerable motorized boat traffic. Lead anomalies probably are of greater significance in lakes exhibiting anomalous concentrations of one or more of the other trace metals.

The lake sediment sampling program provides intriguing clues to the possible existence of anomalous mineralization in rocks of the northern Clam Lake region and in the vicinity of Monico in the Monico region. Additional sampling of lakes and available outcrops should be undertaken to further define the potential for significant bedrock mineralization.

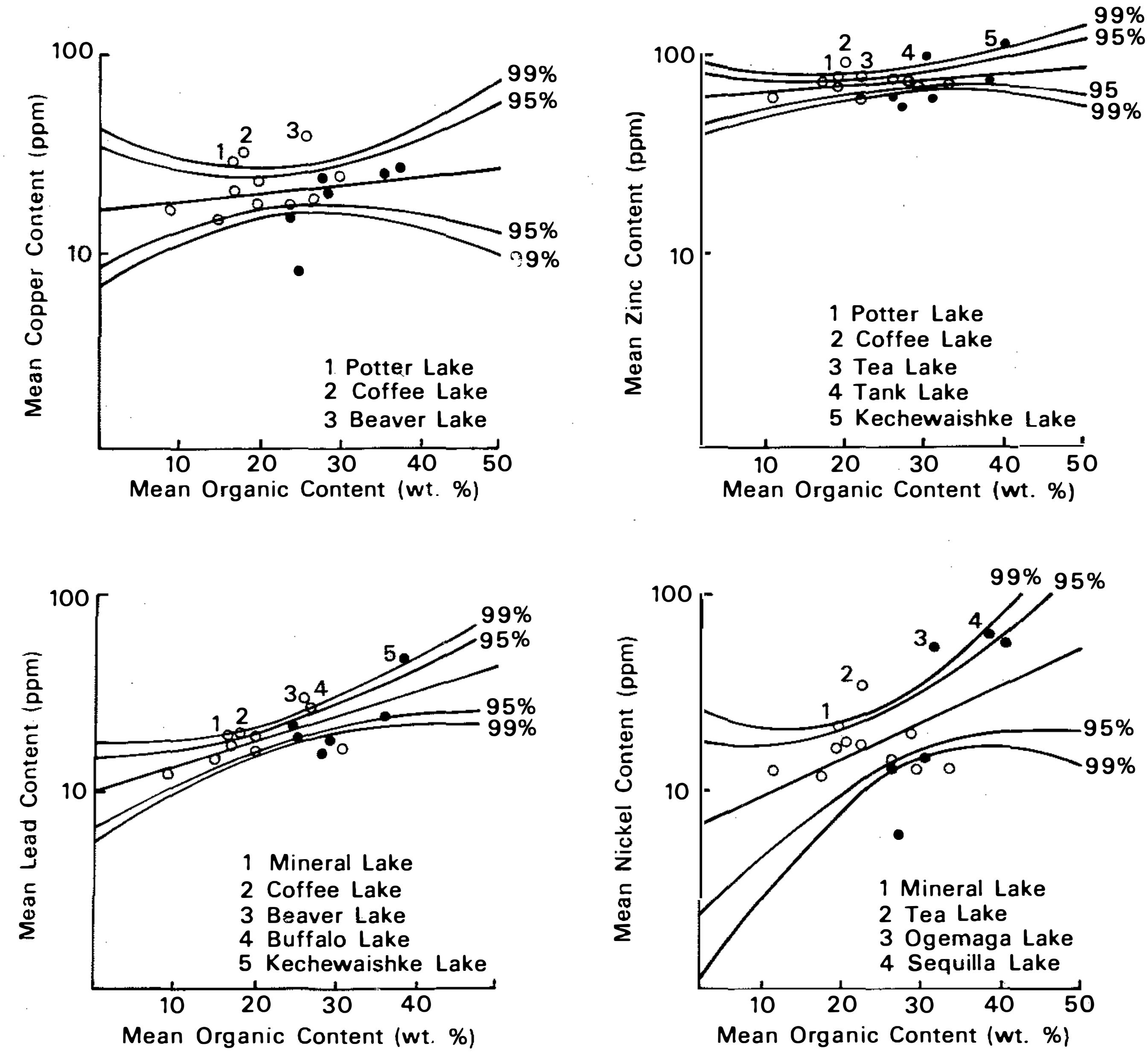

Figure 7. 95 percent and 99 percent confidence limits for mean contents of Cu, Pb, Zn and Ni about the least squares lines shown in Figure 6. Numbers indicate lakes from which the mean metal content falls above the 95 percent and 99 percent confidence limits.

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Table 1. Analytical data on lake geochemistry

Lake		Cu (ppm)	Pb (ppm)	Zn (ppm)	Ni (ppm)	Ag* (ppm)	Organic content (wt.%)	pH+	water depth (feet)	nearby bedrock
Clam Lake Area										
Beaver	1	47	39	83	21	3	28	4.5-5.0	11	
	2	36	29	83	20		26	4.5-.50	15	
	3	37	22	55	18		21	4.0-4.5	7	
Tea	1	29	23	91	16		24	4.0-4.5	29	
	2	28	26	101	21	3	20	4.5-5.0	46	
	3	14	9	48	69		17	4.5-5.0	21	
Coffee	1	28	16	104	21		17	4.5-5.0	9	
	2	45	28	115	20	5	23	4.5-5.0	14	
	3	25	15	60	14		14	4.5-5.0	10	
Mineral	1	27	23	81	16		25	4.5-5.0	9	
	2	32	24	87	16		24	4.5-5.0	10	
	3	31	8	70	23		20	4.5-5.0	8	
	4	6	12	35	6		4	4.5	4	granite
	5	25	24	81	34		22	4.5-5.0	17	granite
	6	9	15	74	15		9	4.5-5.0	12	
	7	21	26	95	17		21	4.5	18	
	8	19	15	78	20		14	4.5-5.0	12	
	9	20	26	87	53		21	4.5-5.0	20	
	10	19	15	65	16		14	4.5-5.0	15	
Potter	1	26	19	78	16		14	4.0-4.5	8	
	2	30	10	80	20		14	4.0-4.5	9	
	3	30	25	77	14		23	4.0-4.5	8	
English	1	11	3	31	7		7	4.5-5.0	10	
	2	23	20	53	17		22	4.5-5.0	12	
	3	13	--	59	34		23	4.5-5.0	15	
	4	4	4	28	5		2	4.5	15	
	5	19	16	67	19	9	26	4.5	10	granite
	6	14	13	71	21		24	4.5-5.0	14	
	7	36	38	86	22	4	28	4.5-5.0	34	
	8	26	22	69	17		26	4.5-5.0	14	
	9	19	28	71	13		21	4.5-5.0	14	

Spider	1	5	6	51	10		8	4.5-5.0	10	
	2	3	16	47	15		5	4.5-5.0	10	
	3	34	18	83	14		21	4.5-5.0	20	
	4	17	12	102	11		18	4.5-5.0	20	
	5	16	22	86	12		21	4.5-5.0	20	
East-Twin	1	47	11	50	8		25	5.0	5	
	2	15	25	55	11		38	5.0	10	
	3	25	28	100	17		25	5.0	10	
	4	13	5	12	12		31	4.5-5.0	5	
	5	25	16	80	15	13	38	4.5-5.0	5	
Buffalo	1	22	39	81	11	3	32	4.5	18	
	2	25	24	104	19		30	4.5	18	
	3	14	18	35	12		26	4.5	8	
	4	22	35	104	15		32	4.5	17	
	5	11	17	31	8		15	4.5	10	
Little Clam	1	15	21	90	14		27	4.0-4.5	9	
	2	18	17	82	17		25	4.0-4.5	9	
	3	12	10	75	12		29	4.0-4.5	10	
	4	19	51	56	16		15	4.0-4.5	5	
	5	21	--	68	12		27	4.0-4.5	5	
	6	25	31	87	15		23	4.0-4.5	8	
Upper Clam	1	31	17	74	18			5.0-5.5	16	
	2	20	21	53	17			5.0-5.5	11	
	3	12	7	37	10			5.0-5.5	7	
	4	6	8	82	5			5.0-5.5	10	
Monico Area										
Ogemaga	1	19	15	46	94		29	4.0-4.5	3	
	2	14	24	68	192		33	4.0-4.5	2	
	3	13	30	60	26		26	4.0-4.5	4	
	4	28	20	65	--		29	4.0-4.5	5	
	5	24	16	70	7		--	4.0	4	basalt
	6	19	11	56	8		--	4.0	4	
Sequilla	1	21	15	82	164		44	5.0-5.5	10	
	2	23	16	65	12		30	5.0-5.5	11	
	3	31	33	83	76	12	39	5.0-5.5	15	
	4	26	36	68	10		30	5.0-5.5	20	

Kechewaishke	1	17	65	124	48	7	41	5.5	20	basalt
	2	29	25	93	16		33	5.5	17	
	3	22	50	141	149		44	5.5	15	
	4	38	54	112	18	4	32	5.5	16	basalt
Tank	1	23	17	101	15		28	4.5-5.0	10	
	2	25	14	101	15		27	4.5-5.0	12	
Pine	1	4	23	53	4		34	4.5	5	
	2	20	27	78	12		--	4.0-4.5	12	
	3	6	23	59	--		33	4.0-4.5	20	
	4	3	1	31	6		1	4.0-4.5	5	
Lucerne	1	4	7	49	4		4	4.0-4.5	10	
	2	19	12	50	11		--	4.0-4.5	10	
	3	4	4	22	10		4	4.0-4.5	15	
	4	17	39	73	14		29	4.0-4.5	42	
	5	21	16	64	11	3	29	4.0-4.5	56	
	6	8	21	64	24		27	4.0-4.5	65	
	7	22	32	82	15		34	4.0-4.5	70	
	8	17	21	51	11		13	4.0-4.5	55	
	9	17	42	76	13		29	4.0-4.5	52	
	10	20	34	76	21		29	4.0-4.5	45	
	11	12	28	73	13		23	4.0-4.5	20	

* because of machine fluctuations, Ag contents recorded only when exceed 2 ppm

\+ pH measurements made with indicator paper

Table 2. Summary of analytical data on lake geochemistry

Lake	Mean Cu (ppm)	Mean Pb (ppm)	Mean Zn (ppm)	Mean Ni (ppm)	Mean Organic Content (wt. %)	pH range
Clam Lake Area						
Beaver	40	30	74	20	26	4.0-5.0
Tea	24	19	80	35	20	4.0-5.0
Coffee	33	20	92	18	18	4.5-5.0
Mineral	21	19	75	22	17	4.5-5.0
Potter	29	18	78	17	17	4.0-4.5
English	18	16	59	17	20	4.5-5.0
Spider	15	15	74	12	15	4.5-5.0
East Twin	25	17	71	13	31	4.5-5.0
Buffalo	19	27	71	13	27	4.5
Little Clam	18	22	76	14	24	4.0-4.5
Upper Clam	17	13	62	13	9	5.0-5.5
Monico Area						
Ogemaga	20	19	61	55	29	4.0-4.5
Sequilla	25	25	75	66	36	5.0-5.5
Kechewaishke	27	49	118	58	38	5.5
Tank	24	16	101	15	28	4.5-5.0
Pine	8	19	55	6	25	4.0-4.5
Lucerne	15	23	62	13	24	4.5-5.0

Table 3. Significant metal concentration at 95 percent level of confidence

Lake \ Metal	Cu	Pb	Zn	Ni
Beaver	X	X		
Tea			X	X
Coffee	X	X	X	
Mineral		X		X
Potter	X		X	
Buffalo		X		
Ogemaga				X
Sequilla				X
Kechewaishke		X	X	
Tank			X	

Table 4. Significant metal concentration at 99 percent level of confidence

Lake \ Metal	Cu	Pb	Zn	Ni
Beaver	X	X		
Tea				X
Coffee	X		X	
Potter	X			
Ogemaga				X
Kechewaishke		X	X	
Tank			X	

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