

“EXCHANGEABLE TRACE IONS IN LAKE ERIE SEDIMENTS”

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Abstract:

Sediment from Lake Erie was leached with distilled water to obtain exchangeable trace elements. Sediment factors considered were organic carbon, pH of leaching and clay composition. Organic carbon decreases with depth in the sediment. The pH remained nearly constant (6.2 - 7.2). Typical concentrations of leached metals are 5 - 150 ppb Zn, 15 - 75 ppb Cd, 6 - 200 ppb Cu, 8 - 34 ppb Cr, and 17 - 100 ppb Ni. The ratio of clay minerals, Kaolinite: Illite: Chlorite = 50:40:10. In all cores exchangeable trace ions highly correlated with organic carbon and both decrease with depth in the sediment.

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Introduction:

Trace metals in the bottom sediments of Lake Erie are fixed by organic matter, clay minerals and $\text{MnO}_2\text{-Fe(OH)}_3$. Lake Erie receives these trace elements from its watershed as natural detritus from the loading of rivers with man's industrial and human waste, and from airborne particles. The organic waste is enriched with nitrogen and phosphorus effluents. The metallic wastes are from industries which release their waste into the waterways and air.

Lake Erie tries to rid itself of this loading. It tries to purify itself by proliferation of its aquatic life which uses the nitrates and phosphates in biological production. Solid detritus settles to the bottom and becomes part of the sediment and/or is acted upon by living matter found near the bottom. The majority of the metallics in solution are assimilated by the biota. Iron, manganese, copper, zinc and vanadium, which have direct functions in the production of chlorophyll and the processes of photosynthesis and respiration, are easily taken up. But the elements such as aluminum, arsenic, cadmium, strontium, beryllium, molybdenum, chromium, nickel, cobalt, tungsten and titanium are also present and must be removed from the water by some means. Usually this is thought to be by the biota. The metals would not be concentrated in bodily fluids as this would lead to supersaturation compared to the outside environment. The metals must be

taken into cellular matter. The primary member of the food chain is then preyed upon by a higher member. This continues up the food chain until we have the highest member concentrated with the metal.

The organisms which die without being predated upon settle to the sediment-water interface where they begin to decay. If the organic matter decays, the ions are either returned to solution or they are fixed by some mechanism in the sediment. The metals may be complexed or chelated by organic matter, absorbed on clays or precipitated; or they may be returned to the water recycle again with the biota.

The aims of this study are to analyze the sediment to see if any relationship exists between the sediment and the exchangeable ions. This study requires total analysis of the sediment; involved are the identification of the clay minerals, determination of organic matter, determination of exchangeable ions present plus such other features which could be incorporated such as Eh-pH potentials and iron content.

Knowing all variables, one can attempt to correlate the various variables such as clay minerals, organic matter and exchangeable trace elements and see if there is any relationship amongst them.

Previous Work:

Grim (7) and Brown (2) have defined the major factors involving clay minerals. Clays defined as being less than 0.002 mm in diameter and are layer-lattice silicates commonly called phyllosilicates. These phyllosilicates are made up of combinations of two structural units, a silicon-oxygen tetrahedron and an aluminum-oxygen-hydroxyl octahedron. They are formed as the result of alteration of primary work forming minerals: feldspars and ferro magnesium minerals. The presence of one clay over another in an environment depends on the primary minerals that were altered.

The major groups of clay minerals are kaolinite, mica, montmorillonite and chlorite. Kaolinite type minerals are hydrated alumino-silicates of general chemical composition $\text{Al}_2\text{O}_3:\text{SiO}_2:\text{H}_2\text{O}=1:2:2$. Micas are layered clays which have the layers held together by potassium ions with water and metallic cations. Montmorillonites have the same structure as the micas but do not have interlayer potassium ions, only water and metallic cations. Chlorites have a general composition of $(\text{Mg}_1\text{Fe}_1\text{Al})_6(\text{Al},\text{Si})_4\text{O}_{10}(\text{OH})_8$. They are similar in structure to the micas but have more iron and magnesium and substitution of silicon by aluminium in the tetrahedral layer.

Preparation of the clay minerals for X-ray diffraction is described by Gibbs(6). Acceptable preparation are:

- (1) smearing of clay on a glass slide and spreading it evenly

- (2) suction of an aqueous solution containing clay thru a ceramic tile depositing the clay on the tile
- (3) powder press techniques.

Unfavourable routing techniques are:

- (1) centrifuge on a glass slide
- (2) centrifuge on a ceramic tile
- (3) evaporation of an aqueous solution containing clay, allowing it to be deposited onto the slide
- (4) dropper of liquid plus clay on a slide and evaporation.

These four techniques employ particle settling in an aqueous solution. This results in surface segregation of montmorillonite due to its smaller size and lower settling velocity.

The identification of the clay minerals after X-ray diffraction is best described by Carroll (5). She incorporates background information concerning the principal crystallographic features of clay minerals and how this is used in X-ray identification. Included also is a method to apply to X-ray diffractometry to recognize the clay minerals in natural sedimentary materials.

Brunton (4) gives a method for the glycolation of the clay minerals. He proposes uniform heating of ethylene glycol to 60°C thereby having a vapor pressure of 39 mm. In a closed container for one hour leads to expansion of montmorillonite from 14-15 angstroms to 17 angstroms.

Zinc, copper, chromium, cadmium and nickel were studied in water and soil by Lewin (13) and Arnon(1). Lewin notes that copper and zinc exist in the biota. Zinc is related to the formation of chlorophyll and photosynthetic activity. In photosynthesis zinc is found related to carbonic anhydrase, this suggests that it may participate at the level of carbon dioxide fixation. Copper, too, participates in photosynthesis and is also active in respiration.

But these two elements can also be toxic if the concentration is excessive. Moyle (16) states that $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was used extensively to kill algal growth in freshwater lakes. Toxicity levels varied for different algae and type of water. Tolerance of the algae increased due to new strains developing or by increasing tolerance in the existing populations.

Horne (9) notes that cadmium, chromium, and nickel are found in higher animals such as scallops, oysters and mussels. The trace element enrichment factor over the environment ranges from 100,000 to 2,000,000 for cadmium, 60,000 to 300,000 for chromium and 4000-14000 for nickel. Algae were not cited but Arnon explains how these elements might be related to algae. He notes that these elements have a realm in cellular functions. They are not known in the cellular constituents as being intimately related to life processes. The micronutrients have a catalytic function in the cell. All are not required by one organism, but they

may have a relationship in another. In some sources Ni is discredited as functioning in the biota and Cr is questioned. Arnon notes that a systematic investigation of the trace elements in the natural system is required to see how the biota functions and what metals are assimilated.

There are three principle methods by which the trace elements are held in the sediment:

- (1) they are held within molecular lattices of clays or replace H^+ ions on the outer surface of the clays.
- (2) the trace elements are assimilated by the biota and upon death settle to the bottom where they remain attached to the organic layer.
- (3) the trace elements are fixed as minor constituents in or on hydrous Mn-Fe oxides.

Jenne (10) studied the Mn-Fe oxides in oxidizing conditions. Trace elements are either co-precipitated or sorped on the outer surface of the oxides. These oxides form as a film on silicates and take elements from the water-sediment interface. Krauskopf (12) studied seawater in the light of trace elements and finds relationships to organic matter, clay minerals and hydrous Mn-Fe oxides. He notes that in a reducing environment, the hydrous Mn-Fe oxides are destroyed and the organic detritus and clay minerals remove trace elements from water.

Both Jenne and Krauskopf feel that organic matter might be a key component for exchangeable ions. They feel that organic matter upon decay returns the elements to the surrounding environment. Rankama and Sahama (15) see Ni not behaving this way but being concentrated in muds rich in organisms and their remains. This would be under reducing conditions where the nickel is precipitated as a sulfide.

The fixation of trace elements in clay lattices is discounted by Jenne and Bingham (2) but supported by Krauskopf. Krauskopf feels that trace elements in clays are governed by concentration and competition with other elements. Bingham worked with $\text{Cu}(\text{OH})_2$ and $\text{Zn}(\text{OH})_2$ in the presence of H^+ montmorillonite and found no change in the concentration before and after the montmorillonite was added.

Krauskopf finds that Zn and Cu co-precipitating with hydrous Mn-Fe oxides. Zn, Cu and Ni are closely related to the biota. Cr and Cd are not well known. Cr may be reduced to the trivalent ion and precipitated as a hydroxide.

Livingstone (14) cited averages of trace elements in natural fresh water. Cd was only detected once in the Urov River and had an average between 9.66-80.5 ppb. Chromium has a mean between 0.1-10 ppb. Copper has a mean of 10 ppb. Nickel has a mean of 5 ppb and zinc, 10 ppb.

Rankama (15) describes how each element behaves in sediments, Zn and Cd are concentrated where reducing conditions are not too prevalent. They are strongly adsorbed by the

sediment.

Cr is closely associated with ferric iron and Al and little remains in solution. Therefore little reaches the lake to be precipitated. If it does, it is found associated with the clay minerals. Copper is easily removed from natural waters by chemical precipitation as a carbonate and by sorption reactions with suspended material such as clays. In the sediment Cu is found with clays and also as insoluble salts with large organic molecules. Ni is associated with clays and in a reducing environment with rich organic muds.

Published material on trace elements in Southern Lake Michigan is given by Shimp et al (17). They studied major, minor and trace constituents in unconsolidated sediments. The values they obtained for trace metals are:

	In natural water *	in Lake Michigan sediments
Zn	10 ppb	40 - 100 ppm
Cd	9.66ppb	5 - 15 ppm
Cu	10 ppb	25 - 40 ppm
Cr	0.1-10 ppb	30 - 60 ppm
Ni	5 ppb	25 - 40 ppm

* figures quoted from Livingstone

Organic carbon in Lake Erie was studied by Kemp (11) he noted that with depth in the sediment, the less organic carbon present. The greatest concentration was found near the surface.

Analytical Procedure:

The sediment for this study was obtained through the courtesy of Dr. N.H. Burns of the Canada Centre of Inland Waters in Burlington. Five cores were studied from the Central Basin of Lake Erie (figure 1). Their locations are:

Core M = 42°08.3' latitude, 81° 26.2' longitude

Core R = 50° and 1.6 miles from latitude 42° 09.9'
longitude 89° 45.1'

Core H = 129° and 4.3 miles from latitude 42° 08.3',
longitude 89° 26.2 '

Core E = 228° and 2.8 miles from latitude 42° 51.2',
longitude 81° 26.0'

Core F = 43° and 1.9 miles from latitude 41° 53.3',
longitude 81° 52.2'.

The cores were obtained in water 72-82 feet deep and contained a vertical section of sediment greater than sixteen inches. The sediment was not exposed to the air but was capped and stored upright in a cool refrigerator. Upon receipt of the cores, several of them were on an angle leading to mixing of the rich organic layer on top and the underlying sediment. This might have introduced errors later on in the data attained.

A flow chart demonstrating the main steps taken in the analysis of the core is given in figure 2. The cores were frozen upright and cut by means of a hacksaw through the vertical. One half was saved and the other half divided into

LOCATION of SAMPLES

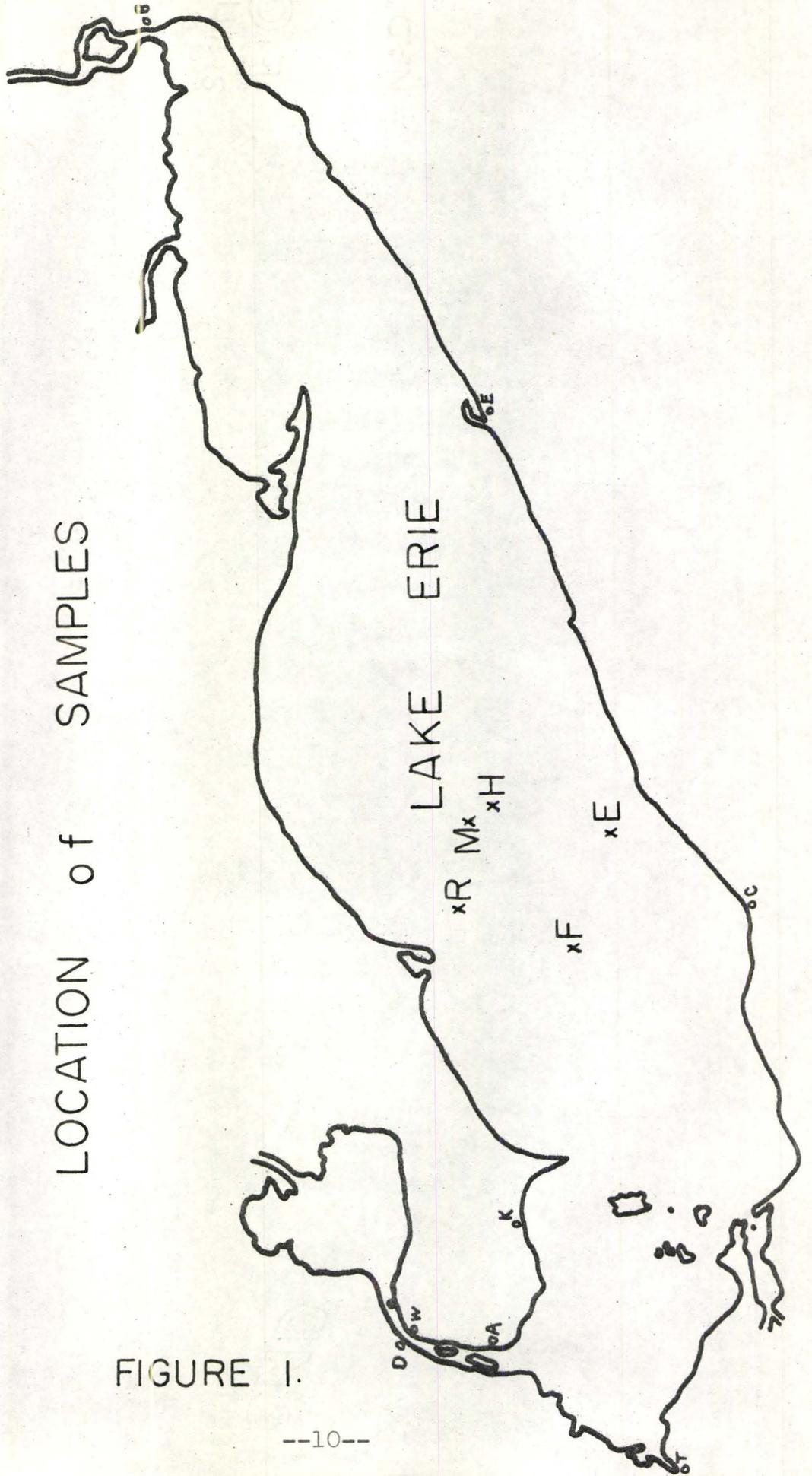


FIGURE 1.

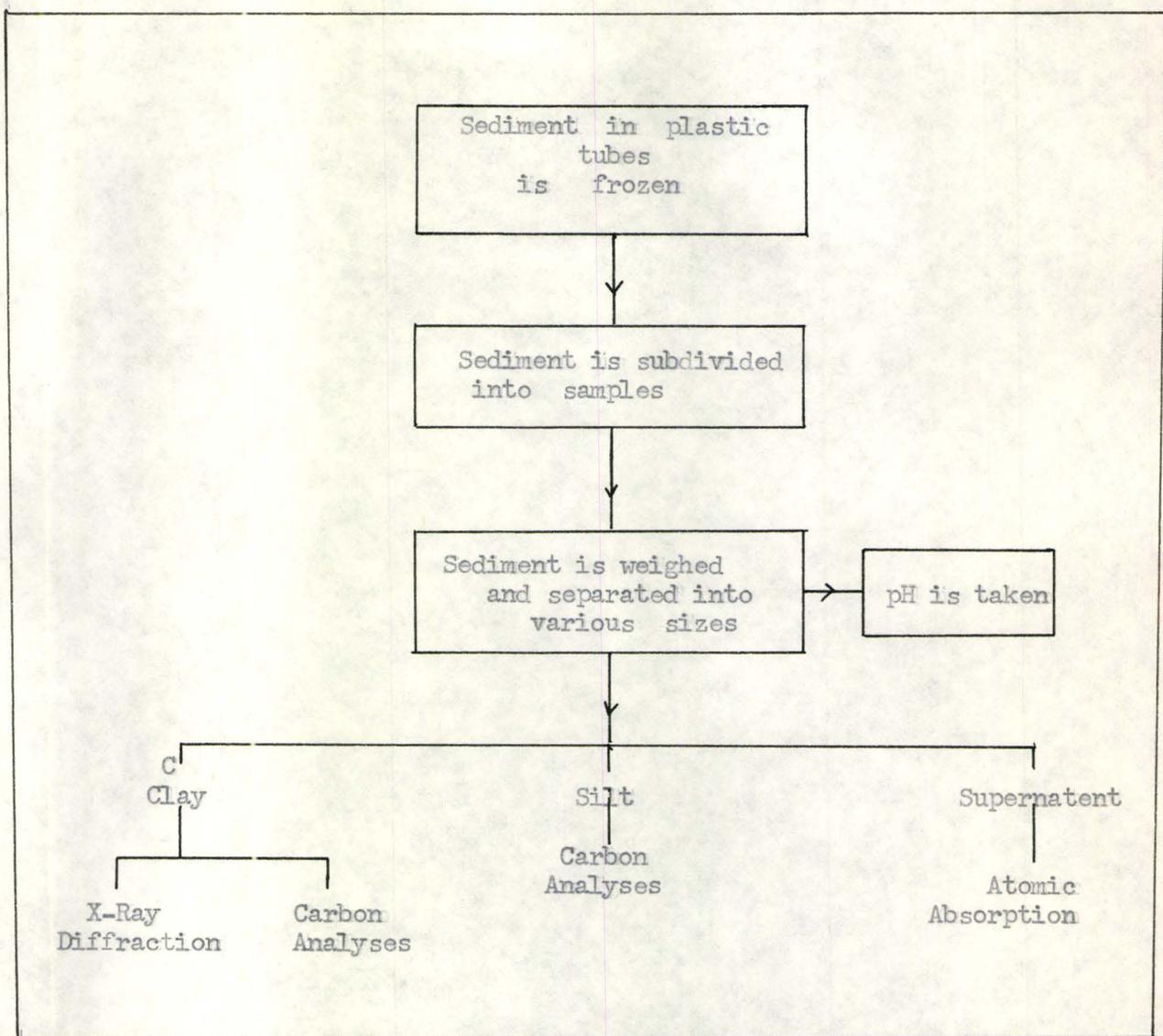


Figure 2. Flow chart demonstrating the main steps taken on the sediment.

sections. A one inch section was cut off the top to get the rich organic layer on top; next a two inch section was cut. The following two sections were each four inches long and the fifth section was what remained of the core.

Four major analytical techniques were employed. These were

- (1) size separation of the sediment
- (2) X-ray Diffraction of the clay minerals
- (3) Atomic absorption of the supernatant
- (4) Carbon analyses of clay and silt

The separation of the sediment into size fractions was undertaken following a method outlined by Hathaway (8). This method makes use of Stokes Law

$$T = \frac{n \log_{10} \frac{R_2}{R_1}}{3.81r^2N^2(\rho - \rho^o)} - \frac{2(ta + td)}{3}$$

where R_1 = initial distance of particle from axis of rotation (top of liquid) This was 12.5 cm.

R_2 = final distance of particle from axis of rotation (level of accumulated sediment in centrifuge bottle) This was 19 cm.

Using this equation we get a value for $T=48.6$ allowing 20 seconds for ta and td which are the time for acceleration to 600 rpms and the time for deceleration to 0 rpm.

This removes all particles greater than 2μ from the supernatant leaving only clay in suspension. The clay is flocculated by adding 8 ml. of $1/2$ N $MgSO_4$ per litre of supernatant. The solution was then centrifuged at maximum speed for ten minutes and forced to settle to the bottom of the centrifuge jars.

Another step to remove sand by decanting after settling was not required as sand was not present in the sediment.

The X-ray identification of the clay minerals was done modifying a scheme laid out by Carroll. The steps taken are:

- (1) taking a small amount of clay, smear it evenly on a glass slide so as to get a consistent thin surface
- (2) allow the clay to dry at room temperature
- (3) an X-ray diffractogram is made from $2\theta=2-40^\circ$
- (4) place the mounted sample in a dessicator, add ethylene glycol; heat to $60^\circ C$ and allow the vessel to become saturated with ethylene glycol vapour. Leave the sample in for one to two hours allowing time for montmorillonite to spread to $17\overset{\circ}{\text{A}}$.
- (5) make a diffractogram of glycolated sample from $2\theta=2-17^\circ$
- (6) heat the sample to a specified temperature to

test for a specific clay and make another diffractogram.

After all these steps have been followed, the clays can quantitatively be identified and crude percentages of each clay present can be made. This is done by integrating over the area of each major peak of each clay present.

The analysis of the trace elements present in the supernatant was carried out on a Perkins-Elmer 290 Atomic Absorption Spectrophotometer. Concentrations of exchangeable ions being very low, care had to be taken so as not to contaminate the samples.

The supernatant could not be used directly but had to be filtered thru a millipore filter; all material greater than $.45\mu$ was removed. The filter was thoroughly washed with deionized water to rid it of any free ions that might be present. The supernatant was then filtered and was ready to be tested. Concentrations of trace elements present was very low so organic solvents were used to extract the trace elements. The metals were chelated with APDC (ammonium pyrrolidone dithiocarbamate) and extracted with MIBK (methyisobutyl ketone).

The following steps were taken:

- (1) to 100 ml of supernatant add 5 ml buffer solution and 5 ml APDC, shaking inbetween the addition of each
- (2) add 10 ml of MIBK and shake for 5-10 minutes:

the entire mixture is then put in a separatory funnel and allowed to settle

- (3) after separating and saving the MIBK layer, centrifuging was done on the MIBK so as to drive all H₂O present to the bottom of the vessel.

The buffer solution consisting of sodium acetate and acetic acid was used to bring the pH of the system to 4.5-5.5.

Carbon analyses on clays and silts was done on a Thomas Micro Carbon-Hydrogen Analyzer. The samples were dried for 24 hours and then placed in small aluminum capsules. These capsules were burned at 900°C and the CO₂ was collected in tube consisting of 1/3 Dehydrite and 2/3 Ascante. Knowing the weight of sample and CO₂, the organic carbon was calculated as a per cent.

Results:

Five cores were analysed, called M,R,H,E and F (See figure 1 for location). Each core was divided into five samples. Sample 1 being the top one inch, sample 2, the next 2 inches, samples 3 and 4 respectively 4 inches each and sample 5 being what was left over. Table 1 gives the complete experimental results.

The sediment was wet weight and dilution of the sample was according to this weight. The effect of this would be to depress the value of exchangeable ions present in the sediment if a great deal of interstitial water was present.

TABLE 1. TABULATION OF EXPERIMENTAL RESULTS

Sample	pH	Sample weight in grams	Per Cent		Exchangeable ions in ppb*				
			Organic in clay	Carbon in silt	Zn	Cd	Cu	Cr	Ni
M-1	6.8	97.8	3.50	2.43	124.5	30	150	- ¹	100.5
M-2	6.6	94.8	1.05	1.99	150	75	75	-	75
M-3	6.4	203.3	1.90	1.77	118.5	-	37	-	75
M-4	6.8	220.7	1.10	1.39	75	15	206	-	-
M-5	6.9	220.9	1.11	1.27	68.7	150	87.5	-	25
R-1	7.4	15.9	- ["]	2.56	-	-	9.4	-	-
R-2	6.7	107.0	1.85	2.02	-	-	6.3	34.5	-
R-3	6.9	168.6	1.65	1.27	-	-	68.8	34.5	-
R-4	7.0	176.2	0.53	1.56	-	-	75	-	-
R-5	6.8	292.5	0.38	0.78	65	-	84.4	-	-
H-1	6.5	144.4	2.75	2.63	2.5	-	-	-	68.9
H-2	6.3	69.1	2.55	0.88	-	-	-	-	68.9
H-3	6.3	228.2	0.35	0.93	-	-	-	-	34.5
H-4	6.3	280.4	1.95	1.19	-	-	-	-	51.7
E-1	6.2	119.0	-	3.04	36.3	-	12.5	-	51.7
E-2	6.3	113.7	1.90	1.93	-	-	6.2	-	103.4
E-3	6.2	201.6	1.88	2.06	-	-	12.5	-	51.7
E-4	6.8	229.6	0.45	0.93	-	-	6.2	-	-
E-5	6.9	200.9	1.25	0.43	-	-	6.2	18	17.5
F-1	6.1	91.8	2.08	2.85	-	-	6.2	-	51.7
F-2	6.3	73.0	2.16	3.26	50	-	6.2	-	-
F-3	6.5	191.1	1.13	1.23	35	-	-	-	68.9
F-4	6.6	224.3	1.02	0.96	5	-	-	8	17.2
F-5	6.6	267.3	0.40	0.55	-	-	12.5	-	-

ppb* Parts per billion in the sediment

-["] Sample not available-¹ Exchangeable ions not detectable

This effect is very prevalent in sample 1 of cores M and F where there was water above the sediment. If it were considered that the average top 1 inch of sediment weighed 45 grams, then the exchangeable ions in M-1 and F-1 could be doubled. An improvement could be made here by drying the sediment before weighing and dilution.

General observations can be made that organic carbon decreases with depth in the sediment in both size fractions. Figure 3 shows this relationship of organic carbon in clay versus sample. There is a negative slope in all cases. This same trend would hold for the silt fraction as organic carbon closely parallels that in the clay.

The exchangeable ions are given in parts per billion. This refers to the ions in the sediment, not to detectable ions in the supernatant. Each sample was leached with deionized water of amount equal to five times the wet-weight of the sample.

In the exchangeable ions, only Zn and Ni decrease with depth in the sediment. This parallels the organic carbon content in the sediment. Results for Cd, Cr and Cu are erratic and show no trends. Cd was only detected in sample M and Cr was detected only occasionally throughout the various samples.

Exchangeable ions in core M was plotted in figure 4. It can be seen that a linear relationship exists between the exchangeable ions Zn and Ni and depth in the sediment. This can be related to organic carbon content in the samples. Cd

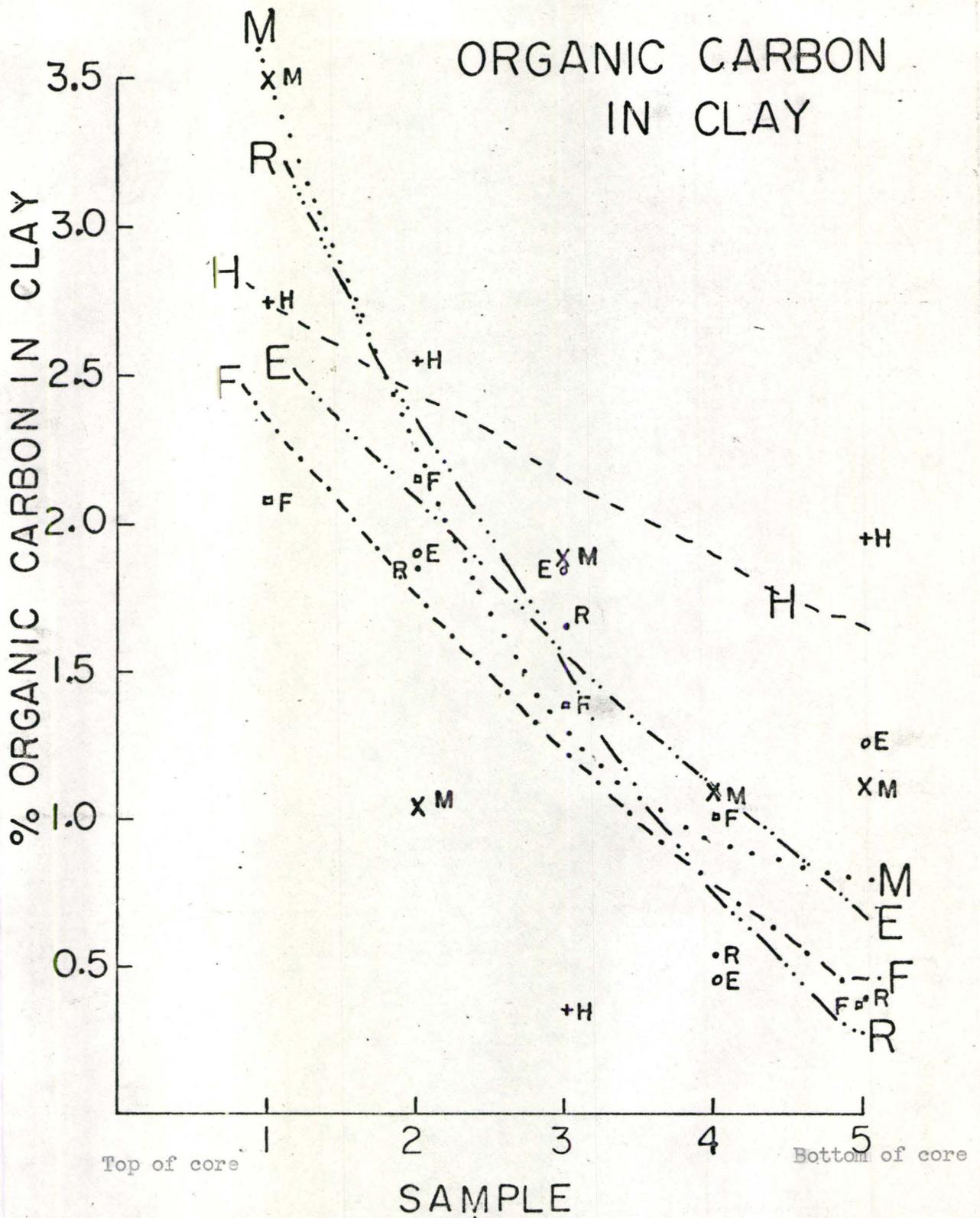


Figure 3.

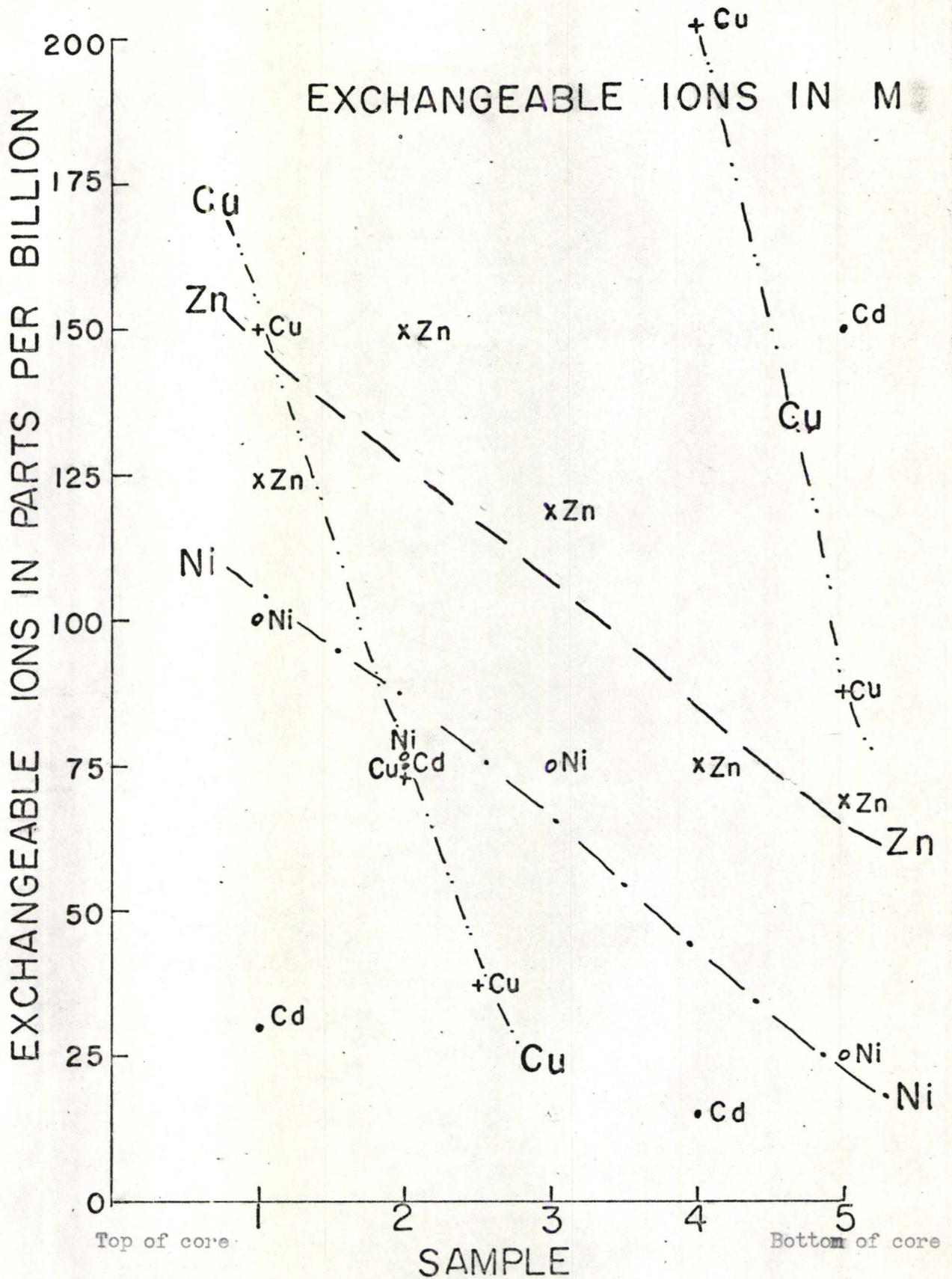


Figure 4.

and Cu do not show this relationship. The same holds true for the other cores.

An error that could account for Cu values is that the supernatant was stored in glass bottles and Cu has a tendency to be absorbed by the silica. As the supernatant was stored for a period of time in the bottles, this could have had an effect on Cu content.

The pH shows no great dissimilarities which could explain the exchangeable ions. The maximum spread in pH is from 7.4 to 6.7 and within each individual core it was on the average 0.5.

Analysis of the clay minerals did not bring out any relationships. Composition of each core was quite uniform being made up of three types of clay, Kaolinite, illite and chlorite. The average percent of each clay was:

Kaolinite	40-55%
illite	40-50%
Chlorite	5-15%

The results obtained for organic carbon in the sediment parallels Kemp's findings, that organic carbon decreases as you go into the sediment. The exchangeable metal ions follow the same trend as the organic carbon; they also decrease with depth in the sediment. This may indicate that the metal ions may attach onto the surface of the organic carbon present in the sediment.

Interpretation:

Lake Erie during the summer is stratified; photosynthesis in the hypolimnion is reduced due to light penetration of the water. Respiration of organisms, settling from the epilimnion, continues at the same pace as previously. There is also the added factor of respiration of bacteria that are engaged in breaking down the organic material settling from above. Oxygen is used up and CO_2 is produced; the thermocline does not allow rapid gas exchange with the atmosphere resulting in the accumulation of CO_2 and a change from an oxidizing to a reducing environment. Reducing conditions are verified by Kemp's findings which show reducing conditions near the top of the sediment and proceeding toward oxidizing conditions with depth into the sediment. Therefore Jenne's hydrous Mn-Fe oxide model is unfeasible as reducing conditions would result in the dissociation of the oxides. The clays being of uniform ratios throughout the sediment pile could not produce the distribution of exchangeable ions. Therefore by a method of elimination and a close relationship, it can be said that the organic carbon present in the sediment controls exchangeable trace ions.

This relationship shows both a decrease in organic carbon and exchangeable ions with depth in the sediment. Ni and Zn show correlating results with organic carbon and it is thought that these two elements are

essentials to biological production. Lewin states that Cu is also used in photosynthesis and respiration but exchangeable Cu ions do not parallel organic carbon. Rankama partially explains Cu distribution by the fact that Cu has an affinity for silicon dioxide and would be easily sorped onto the glass bottles. The supernatant was stored in glass bottles prior to testing. Rankama has found Ni to be closely associated with rich organic muds when in a reducing environment.

Ni may then be related to the organic carbon by reason of the environment or through biological processes. Cd and Cr cannot be explained and further research would be required to understand the controlling factors.

In summary, the exchangeable trace elements found in the sediments of Lake Erie are directly related to the organic carbon present.

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