

TRACE METAL MINERAL EQUILIBRIA
IN LAKE ERIE SEDIMENTS

by

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ABSTRACT

Mineral equilibria were examined for the system $\text{Cd-Pb,Zn-Fe(II)-CO}_3\text{-PO}_4\text{-H}_2\text{O}$ in the interstitial waters of the upper meter of Lake Erie sediments. To closely approximate anoxic sediment conditions, extrusion and squeezing were performed under a nitrogen atmosphere shortly after coring.

Interstitial water concentrations of ferrous iron, zinc, cadmium, lead, and carbonate alkalinity were about a factor of 3-5 greater in the near-shore Ashtabula cores than in the central basin.

Pore waters were supersaturated with respect to vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) and siderite (FeCO_3) which were generally in equilibrium with each other. Cadmium, lead and zinc, however, were undersaturated with respect to carbonate and phosphate minerals phases. Metal concentrations were generally greatest in the 10 cm immediately below the sediment-water interface. Calculations showed 90-98 percent of the lead, 20-60 percent of the zinc, and 5 percent of the cadmium to be inorganically complexed. Organic complexation tied up additional metal and may account for the larger total dissolved metal levels in the upper 10 cm of the sediment pore waters.

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SECTION 1

INTRODUCTION

Zinc, cadmium, and lead can be toxic if their concentrations reach sufficiently high levels in living plants and organisms. It is necessary to understand their behavior and transport to determine the magnitude of their threat to a specific environment. In order to understand chemical behavior, concentrations and reactivities must be determined in the different physical compartments -- overlying waters, sediments, and interstitial waters -- before exchange between the systems can be investigated. In this study, the interstitial waters in Lake Erie sediments were investigated in an effort to identify post depositional mineral equilibria. This work is preliminary to further studies on the overlying waters and sediments and transport between the compartments.

Little work has been done on the interstitial water chemistry of zinc, cadmium, and lead. A large body of data has accumulated describing their distribution in the sediment fraction (Wheeler and Durimig, 1976; Presley, et al., 1972; Semkin and Kramer, 1976; Jenne, 1968) and the surface waters (Chawla and Chau, 1969; Zirino and Healy, 1970; Riley and Taylor, 1972; Bachmann, 1963; Bradford, 1972; O'Connor and Renn, 1964; Hem, 1972) but these studies were not able to elucidate their chemical behavior in the sediment-interstitial water system. Several investigators have attempted to determine the controlling mechanisms responsible for the distribution of zinc, cadmium and lead by analyzing their concentrations in various aqueous and solid fractions in one system (Walters et al., 1974; O'Connor and Renn, 1968; Bachmann, 1963; Cline and Upchurch, 1973; Jurinak and Thorne, 1974; Gardiner, 1974a; Bardiner, 1974b). These studies have made headway towards understanding the relative reactivities of the metals with organics and their adsorption on ferric hydroxides and clay mineral surfaces. Their methods could not identify individual mineral phases and could, therefore, only conclude that the

metals were complexed by other dissolved species or in equilibrium with an unidentified mineral phase (Presley et al., 1972). Analysis of a metal in the sediment fraction alone cannot be used to discern processes controlling its distribution.

More recently, researchers have studied interstitial water chemistry (Muller, 1969; Brooks et al., 1968; Troup, 1974; Duchart et al., 1973) in the hope of understanding the processes controlling the behavior of the metals in the sediments. The interstitial water is the medium connecting the solid phases in the sediments and the soluble species in the overlying water through which ions can diffuse. Because any change in metal behavior will alter the chemical composition of the pore waters, it is a sensitive indicator of chemical reactions and equilibria between solid phases and dissolved species (Berner, 1971). Since the residence time of metals in the interstitial water is longer than that in the overlying water, metals in pore waters are more apt to approach a state of equilibrium with solid phases in the sediments. Consequently, the chemical composition of the interstitial waters can be used to identify and study mineral-water equilibrium reactions in sediments. Once these reactions are determined, then chemical mass transport can be studied.

A thermodynamic equilibria approach has been used successfully to study the behavior of ferrous iron in pore waters (Troup, 1974; Bray, 1973; Nriagu, 1972; Emerson, 1976). Siderite (FeCO_3), vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) and mackinawite (Fe_{1+x}S) were found to be supersaturated in many interstitial waters, and their presence has been confirmed by x-ray diffraction studies. This supports the conclusion that these minerals control the dissolved concentrations of ferrous iron, carbonate, and phosphate, and that thermodynamic studies of the interstitial waters may be used to predict the controlling mineral equilibria. Lu and Chen (1977) examined the overlying seawater for release of trace metals under oxydizing and reducing conditions, and concluded that trace metal sulfides, carbonates, and silicates are controlling their behavior.

Since zinc, cadmium and lead share some chemical properties with ferrous iron, the thermodynamic approach may be applicable to the study of these other trace metals. These metals (like ferrous iron) are relatively insoluble and might, therefore, also form metal carbonates or phosphates

under the conditions found in anoxic sediments. Hence, the thermodynamic approach that has been used in the study of ferrous iron was followed in this study.

SECTION 2

CONCLUSIONS

The trace metals zinc, cadmium, lead and ferrous iron were studied in the interstitial waters of Lake Erie. Total zinc concentrations ranged between 6×10^{-9} and 6×10^{-6} M, lead between 10^{-9} and 1.3×10^{-7} M, and cadmium between 10^{-9} and 1.3×10^{-7} M. Total zinc concentrations were generally two orders of magnitude greater than lead and cadmium. Inorganic complexation significantly decreased the free metal concentrations. Inorganic zinc complexation varied from 20 to 60 percent in the top 60 cm of sediment. Complexation increased with alkalinity and especially pH, due to the formation of ZnOH^+ . Lead was 90 to 98 percent inorganically complexed in the top 60 cm of sediment as PbOH^+ , Pb(OH)_2^0 , PbCO_3^0 , and PbHCO_3^+ . In contrast to zinc and lead, cadmium exists predominantly as the free cation at all depths in the cores studied and does not form hydroxides or soluble carbonate complexes at interstitial pH's.

Interstitial water concentrations were substantially higher at the near-shore Ashtabula dumping grounds than in the central basin. Ferrous iron was about 4 times higher, trace metals were about 5 times higher, and the alkalinity was about 2-3 times higher. The higher values probably reflect a closer proximity to the source of these pollutants.

Solubility equilibria of zinc, cadmium, lead and ferrous iron carbonates and phosphates in Lake Erie interstitial waters showed that zinc, cadmium and lead are undersaturated with respect to their metal carbonates and phosphates. Hydroxypyromorphite does not control phosphate or lead levels as suggested by Nriagu (1974). Lake Erie pore waters are generally supersaturated with respect to vivianite and siderite. These minerals also appear to be in equilibrium with each other. The thermodynamic solubility equilibria can successfully predict chemical controls for interstitial ferrous iron and possibly zinc, if willemite is considered, but not for cadmium and lead. The

metal sulfides are also likely to be supersaturated, but the model could not account for this since dissolved sulfide was below analytical detection.

Organic complexation may bind a significant portion of dissolved zinc, lead, cadmium and ferrous iron in freshwater interstitial water. Zinc and lead exhibit generally high surface concentrations whereas cadmium often did not. Therefore, zinc and lead appeared to be organically complexed to a greater extent than cadmium.

SECTION 3

RECOMMENDATIONS

The interstitial waters and sediments of Lake Erie can provide valuable information about the exchange of nutrients and metals across the sediment-water interface and should continue to be investigated. Detailed studies of the pore waters just beneath the sediment-water interface could provide an estimate of the flux of dissolved materials into the lake water.

Metal sulfides are an important group of minerals that have not been included in this study. They are extremely insoluble, and if forming in the lake sediment, provide the most efficient mechanism available for removal of dissolved metals. The difficulty lies in an inability to a) predict their presence and b) verify their presence in the sediments. Dissolved sulfide is below the detection limit of the sulfide electrode, so that the thermodynamic calculations used in this study cannot be made. An alternate method, such as the polarographic technique described by Davison (1977) should be developed. Verification of all predicted mineral phases is essential. SEM and EDAX studies might provide the required proof.

Once all the mineral phases are verified and all the fluxes and their directions are determined, then mathematical models may be developed to predict the effects of nutrient and metal loadings on the sediments. Eventually, this should be coupled to the biological and hydrodynamic models for the whole lake.

SECTION 4

FIELD METHODS

Study areas

Several factors led us to concentrate our efforts in this study in the central basin of Lake Erie. Interstitial water chemistry is complex and is easier to study if biological and physical processes can be segregated or neglected. McCall and Fisher (personal communication) collected data in the central basin suggesting that bioturbation may be a less important control than chemically-mediated molecular diffusion. During the 1975 sampling season, they estimated the oligochaete population Limnodrilus spp. in Cleveland Harbor to range from 50,000/m² in the fall to up to 200,000/m² in the spring, whereas the estimated population of oligochaetes in the central basin was 10,000/m² and the individuals were smaller in size. Physical mixing processes should be minimal in the central basin compared with the shallower shoreline and western basin areas. Thus, chemical processes are more likely to be dominant in the central basin than elsewhere. Also, this area goes anoxic annually and therefore constitutes a good place for a follow-up study of metal exchanges between pore and lake water. Figure 1 shows the locations of the sampling stations occupied during this study and Table 1 gives the sampling dates for each station.

In addition to the studies in the central and western basins of Lake Erie, a temperal study in the dredge disposal areas off Ashtabula was conducted. Cores were obtained from the dump site prior to disposal and for several months following the dumping. During the study cores were also obtained from two 'control' stations. One of these was the disposal area the previous year; the other was located outside the shipping channels, but in the same area. These stations are hereafter referred to as the dump site, old dump site, and control station, respectively. Some of the long-term chemical effects of dredge disposal are examined.

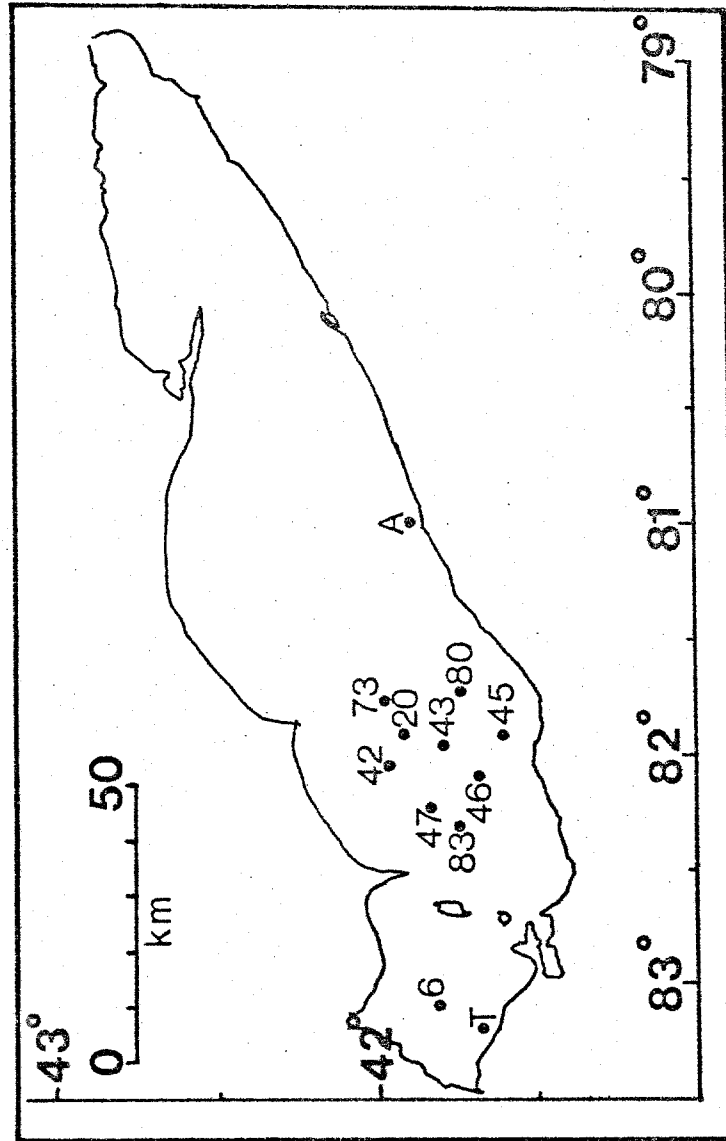


Figure 1. Location of sampling stations in Lake Erie.

TABLE 1
SAMPLING DATES

Sampling Dates	Station Number														
Cruise Name	T*	6	20	42	43	45	46	47	47a	73	80	83	OD*	D*	C*
6/25-6/26/75 GASP II				X	X			X	X	X					
8/12-8/15/75 GASP III				X	X	X	X			X		X			
9/15-9/17/75 GASP IV				X		X	X			X		X			
6/27-6/28/76 GASP X		X	X												
9/28-10/1/76 GASP XI	X	X	X												
4/1-4/277 ADS I														X	X
5/16-5/19/77 ADS II													X	X	X
7/1/77 GASP XX												X			
9/2/77 GASP XXI												X			
9/4/-9/5/77 ADS III													X	X	X

*T is the western basin Tower Station
OD is the old dump site at Ashtabula
D is the present dump site at Ashtabula
C is the control station at Ashtabula

Sampling Procedure

A core was collected in a plastic core liner (cellulose-acetate-butyrate, 7.3 cm O.D., 7.0 cm I.D.) using a Benthos gravity corer with a spring valve. It was then capped and held in a vertical position, measured and described, and 125 milliliters (mls) of overlying water were siphoned directly from above the sediment-water interface. The water sample was capped and filtered. The remaining overlying water was then siphoned off. To minimize oxygen contact with sediment, nitrogen was continuously blown into the core liner during initial sampling. A plastic bag was taped over the end of the core liner to create a small glove bag. A rubber plunger pushed the core up to a point where the first sample could be spooned into a squeezer covered with a N_2 -filled bag.

Once a level was reached where the sediment was cohesive enough to be sampled horizontally, the core was moved into the laboratory. The core liner was inserted into a N_2 -filled glove bag and samples were sliced off as the core was pushed up by a rubber plunger. Ten samples were taken at approximately five consecutive 2 cm intervals in the upper 10 cm, a 3.5 cm layer at about 15 cm and 5-6 cm intervals at about 20, 30, 40 and 50 cm. Samples were spooned into nylon squeezers which were covered and clamped into a squeezing rack. A 50 psi (3.4 atm) pressure of N_2 acting against a rubber diaphragm ("Dental Dam") (Reeburgh, 1967) forced the interstitial water through two circles of nylon mesh supports overlain by two 0.45 μm Whatman filters and one 0.22 μm Millipore filter (76 mm diameter). Since the sample was not exposed to oxygen at any point, the interstitial water closely approximated the natural system.

The interstitial water was apportioned for several analyses:

1. First 8 mls were collected in an electrode cell to measure pH and sulfide.
2. 3 mls of sample were drained into graduated test tubes containing reagents for complexing Fe(II). These samples were later analyzed spectrophotometrically for Fe(II) concentrations. When the ship-board spectrophotometer was not available, total irons were determined.
3. The rest was collected in acid-washed sample bottles to be appor-

tioned as below:

- a. 1 ml for onboard analyses of NH_4^+ , NO_2^- - NO_3^- and soluble reactive phosphate by Ohio State personnel with a Technicon autoanalyzer
- b. 1 ml for an alkalinity titration
- c. 1 ml for a chlorinity titration
- d. The remainder was saved for onshore trace metal or major cation analyses

SECTION 5

ANALYTICAL METHODS

A brief description of the analytical methods used in this study is given below. A more detailed discussion is given in Harris (1977).

Chlorinity

One ml of sample was pipetted into small vials and was titrated with HgNO_3 following the procedure described in Standard Methods (13th Edition) (STM). The pH of the samples was adjusted to 2.5 ± 0.1 when the acidifier-diphenylcarbazone indicator reagent was added. The end point was reached when the solution turned from blue to purple, indicating the presence of excess mercuric ions.

Alkalinity

The Standard Methods (13th Edition) (STM) procedure for total carbonate alkalinity was adapted for titration with 1 ml of sample. The titration was performed on a white stirring plate using a microburette filled with standardized acid (0.02 N HCl) as titrant. At pH 4.7, the solution turned pinkish-violet as the end point was reached. Buffers of pH 4.8 and 4.6 stood on either side of the sample during the titration to facilitate detection of the end point. All the samples taken on one day were analyzed that evening.

pH and Sulfide

Electrode measurements were made on the interstitial water samples under nitrogen atmosphere since (1) oxygen affects the sulfide concentrations in the pore water and (2) equilibration of dissolved CO_2 with CO_2 in the atmosphere affects the pH of the sample. Sample drained from a squeezer directly into the electrode cell as the sample in the cell was stirred. A Fisher miniature glass universal electrode, a calomel or silver/silver chlor-

ide double junction reference electrode and an Orion Ag+/AgS sulfide electrode were used for these measurements. All sulfide values were found to be below the detection limit of the electrode ($\sim 10^{-7}$ M at pH 7) and are not recorded in this report.

Major Cations

Since so little sample was collected, most of which was needed for trace metal analyses, only one set of samples from GASP II-Station 47 was sacrificed for major cation analyses. This was done in order to estimate ionic strength of the interstitial water with depth in the core. It is assumed that the concentrations of calcium, magnesium, sodium and potassium do not vary significantly from station to station, since the major cation concentrations in the overlying water are fairly constant throughout the central basin of Lake Erie (Weiler and Chawla, 1968).

Ca²⁺ and Mg²⁺ concentrations were determined using atomic absorption on undiluted samples with a lanthanum oxide suppressant. Potassium concentrations were determined by flame emission by direct insertion of the undiluted and acidified sample since the original samples had K⁺ concentrations plotting in the linear region of absorbance. Sodium concentrations were also determined by flame emission.

Nutrients

NH₄⁺, NO₂⁻-NO₃⁻ and soluble reactive phosphate (SRP) concentrations for the interstitial, overlying and surface waters were determined with a Technicon Autoanalyzer II. A total of 1 ml of unacidified sample was used for all the analyses. The analyses were run on board ship within six hours of sample collection.

The procedure for each determination was that described by the Procedures Manual - 1973, Center for Lake Erie Research, Ohio State University:

- (1) Orthophosphate: formation of a phosphomolybdenum blue complex by dilution of the sample with one reagent consisting of an acidified solution of ammonium molybdate containing ascorbic acid and a small amount of antimony.
- (2) Nitrate-Nitrite: reduction of nitrate to nitrite by a copper-cadmium reductor column. The nitrite ion then reacts with sulfanilamide under acidic conditions to form a diazo compound. This

compound then couples with N-1-naphthylethylenediamine dichloride to form a reddish purple azo dye.

- (3) Ammonia: determination by the Berthelot reaction whereby ammonium salt and sodium phenoxide form a blue-colored compound. This is followed by the addition of sodium hypochlorite and potassium sodium tartrate and Na citrate to inhibit precipitation of Ca and Mg hydroxides.

Fe(II)

Fe(II) concentrations were determined spectrophotometrically using 1, 10-o-phenanthroline as the colorimetric complexing reagent, as described by Sandell (1959). In the glove box under a nitrogen atmosphere, 3 mls of sample drained into graduated test tubes containing phenanthroline reagent buffered at pH 3.6 (Troup, 1974). Once complexed with the reagent, the Fe(II) complex is stable with respect to oxygen and can be removed from the glove box for onboard colorimetric analysis.

Trace Metals

Zinc, cadmium, and lead were analyzed in this study by differential pulse anodic stripping voltammetry (DPASV) (Matson, 1969; Sinko and Dolezal, 1970; Chou and Chan, 1974) since this analytical method facilitated measurements in the ppb range, the range of concentrations of trace metals in the interstitial water. Also DPASV distinguishes between complexed and total metal concentrations in contrast to flameless atomic absorption which analyzes total metal content only. It analyzes only free metal-and-metal hydroxy complexes, but, by destroying all complexes and reanalyzing the solution for total metal concentrations, the concentrations of metal complexed in the original system would be the difference between the total metal and the free metal-metal hydroxy complexes (Ernst et.al., 1975; Zirino and Healy, 1972). Other advantages of DPASV are its extreme sensitivity, lack of interferences and capability of analyzing four metals with one scan and sample preparation. Three metals, Zn, Cd and Pb were determined; and for samples with low Fe(II), copper could also be analyzed in the same scan.

Anodic stripping voltammetry is a polarographic technique in which metals are reduced for a timed period onto a hanging mercury drop electrode at a potential more negative than that needed to reduce any of the elements to be analyzed. A voltage incrementing in a positive direction is then

applied through the solution which causes the metals to be stripped, i.e., oxidized, at their characteristic potential; the resulting current conducted is proportional to the metal concentration in the solution. A sample scan is shown in Figure 2. The details of the analytical procedures developed in this study for the use of DPASV to determine concentrations of Zn, Cd, Pb and Cu in interstitial waters are given in Appendix A.

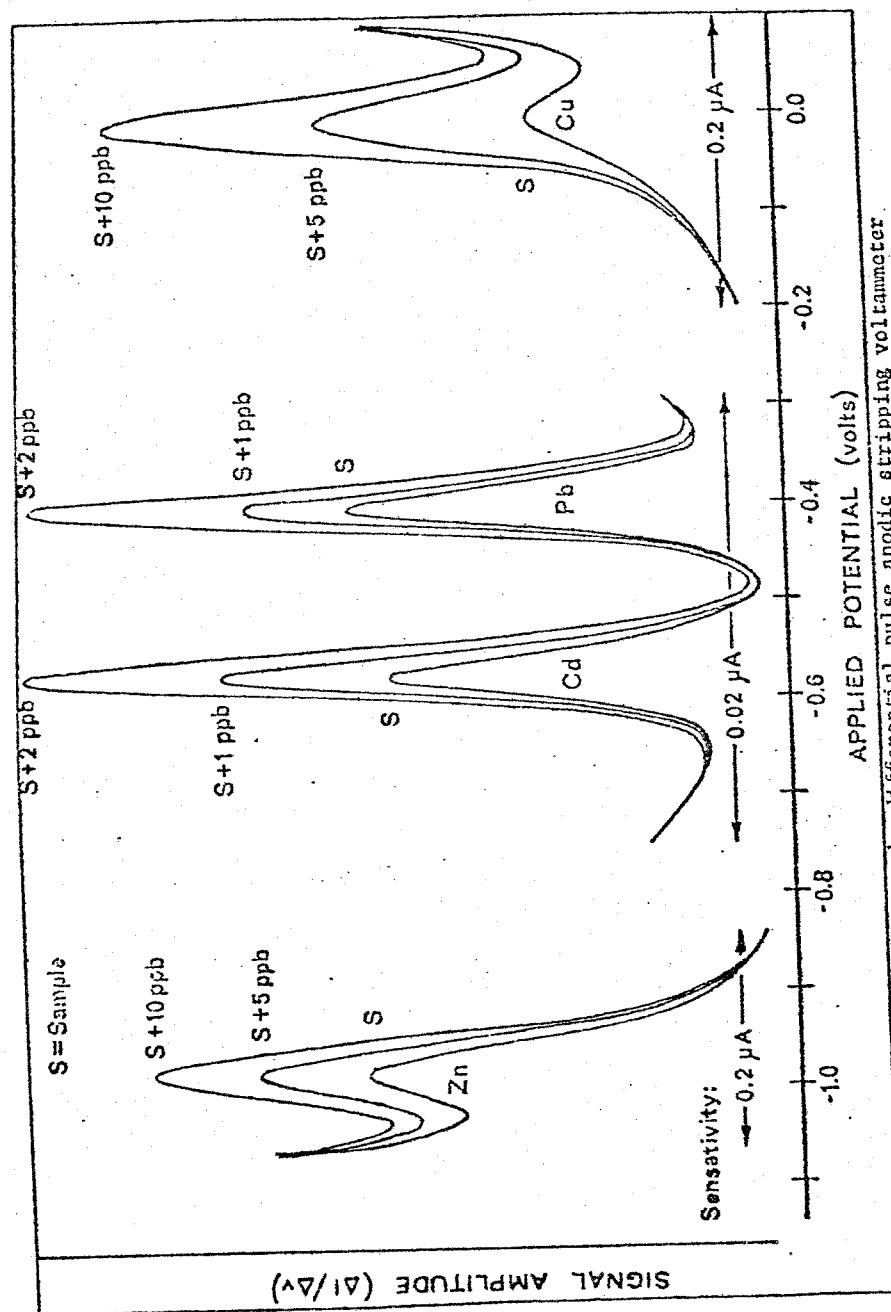


Figure 2. Sample scan by differential pulse anodic stripping voltammeter.

SECTION 6

RESULTS

Prior to any temporal or areal interpretation of interstitial water data, it is necessary to evaluate the spatial variations in concentrations of the interstitial waters. Spatial variations define the limits which may be placed upon the instantaneous concentrations of the chemical species as a function of location. Temporal variations interpreted within the framework of the spatial limits may be used to assess the long-term effects of temperature and sediment deposition rates, and enable the more accurate calculation of chemical fluxes. Therefore, several cores were obtained at one station to evaluate the spatial variability; from the same stations at several different times to evaluate the temporal variability; and from several stations in the western and central basins and from the Ashtabula dump site to evaluate the areal variability.

Spatial Study

There are two fundamental sampling patterns which may be used to obtain cores for a spatial study. The first is to obtain cores from precisely marked grid points on the bottom. The second is to collect multiple cores at random while anchored at the station. The latter possibility was chosen because of its similarity to our procedure of finding the station, anchoring, and then collecting a core. One difficulty with this or any other spatial study is the problem of obtaining a sufficient number of cores to generate statistically significant results. Due to time and personnel limitations only three cores were processed, and only the top three or four sections of each were analyzed. The study was conducted at station 20 on September 29, 1976. The data from the spatial study are given in Appendix B, along with the rest of the interstitial water data collected during this study. Figures 3, 4, and 5 graphically display the chlorinity and pH data; the iron, phos-

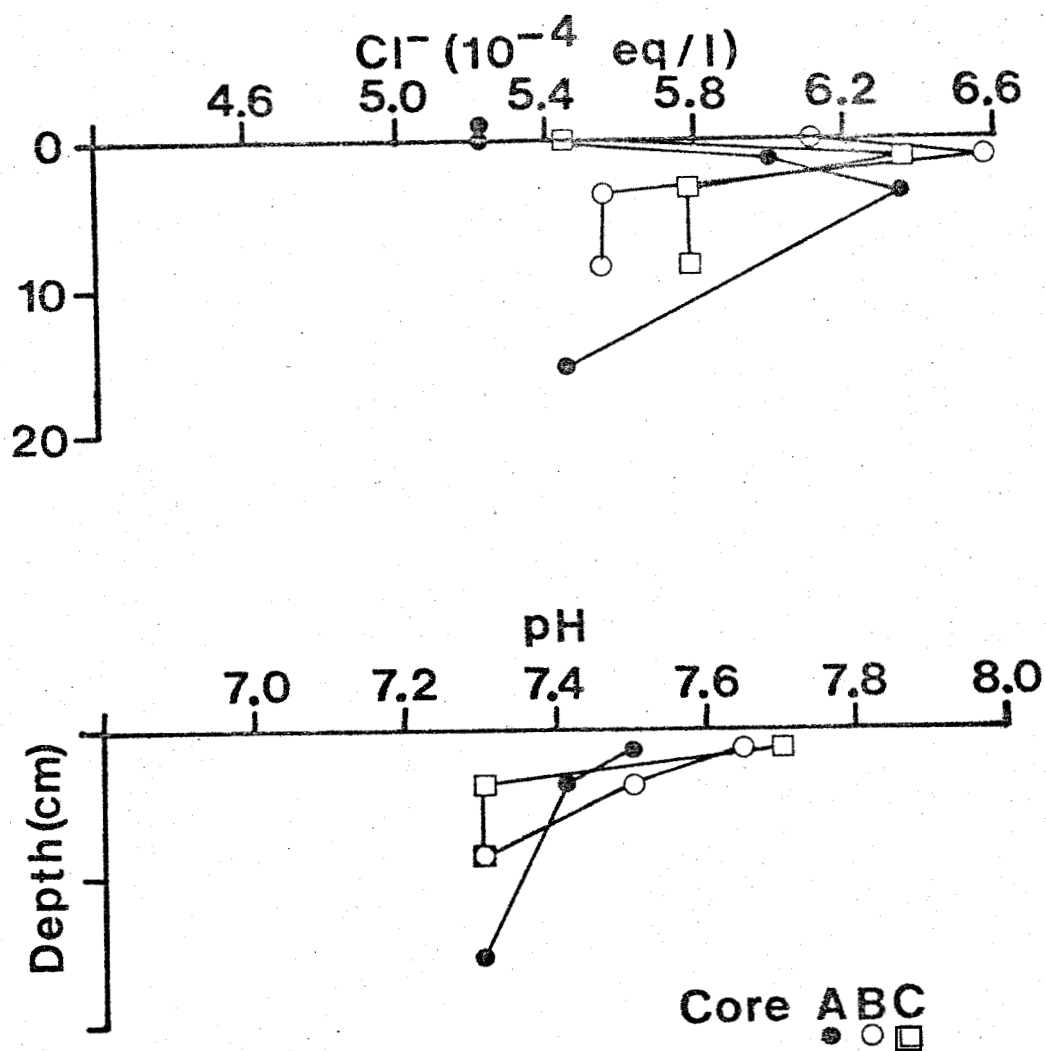


Figure 3. Spatial variation of dissolved chloride and pH from three cores collected at Station 20.

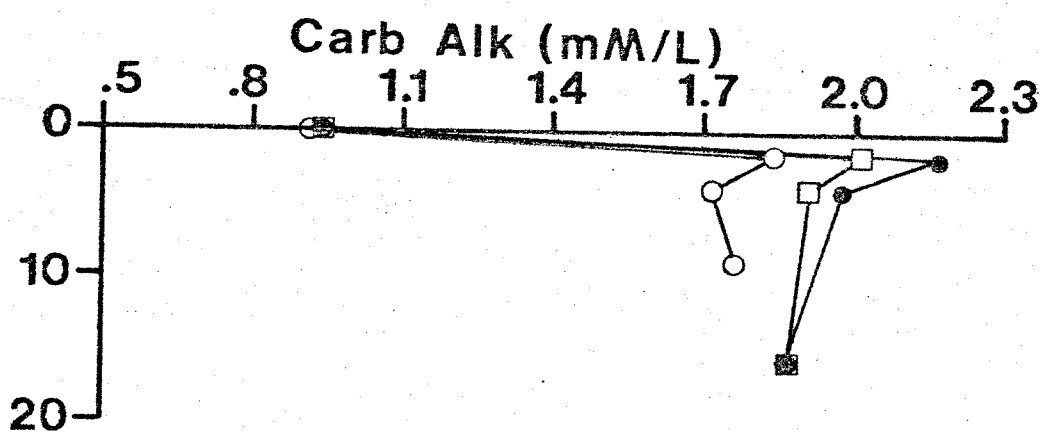
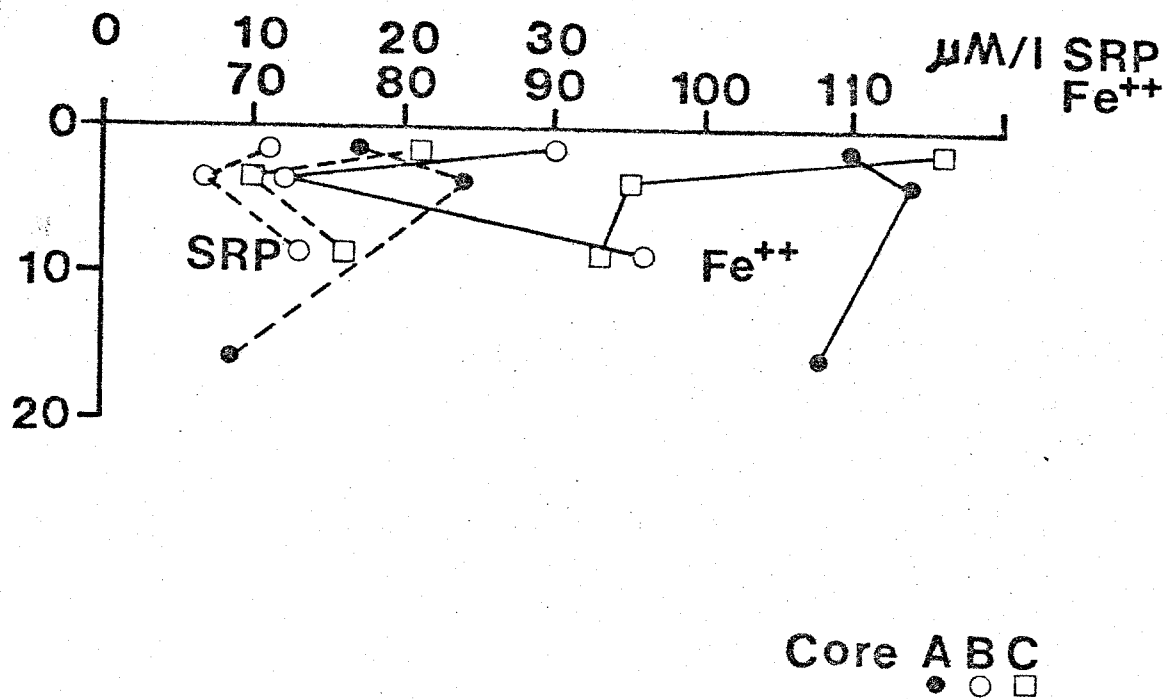


Figure 4. Spatial variation of soluble reactive phosphorous, ferrous iron and carbonate alkalinity from three cores collected at Station 20.

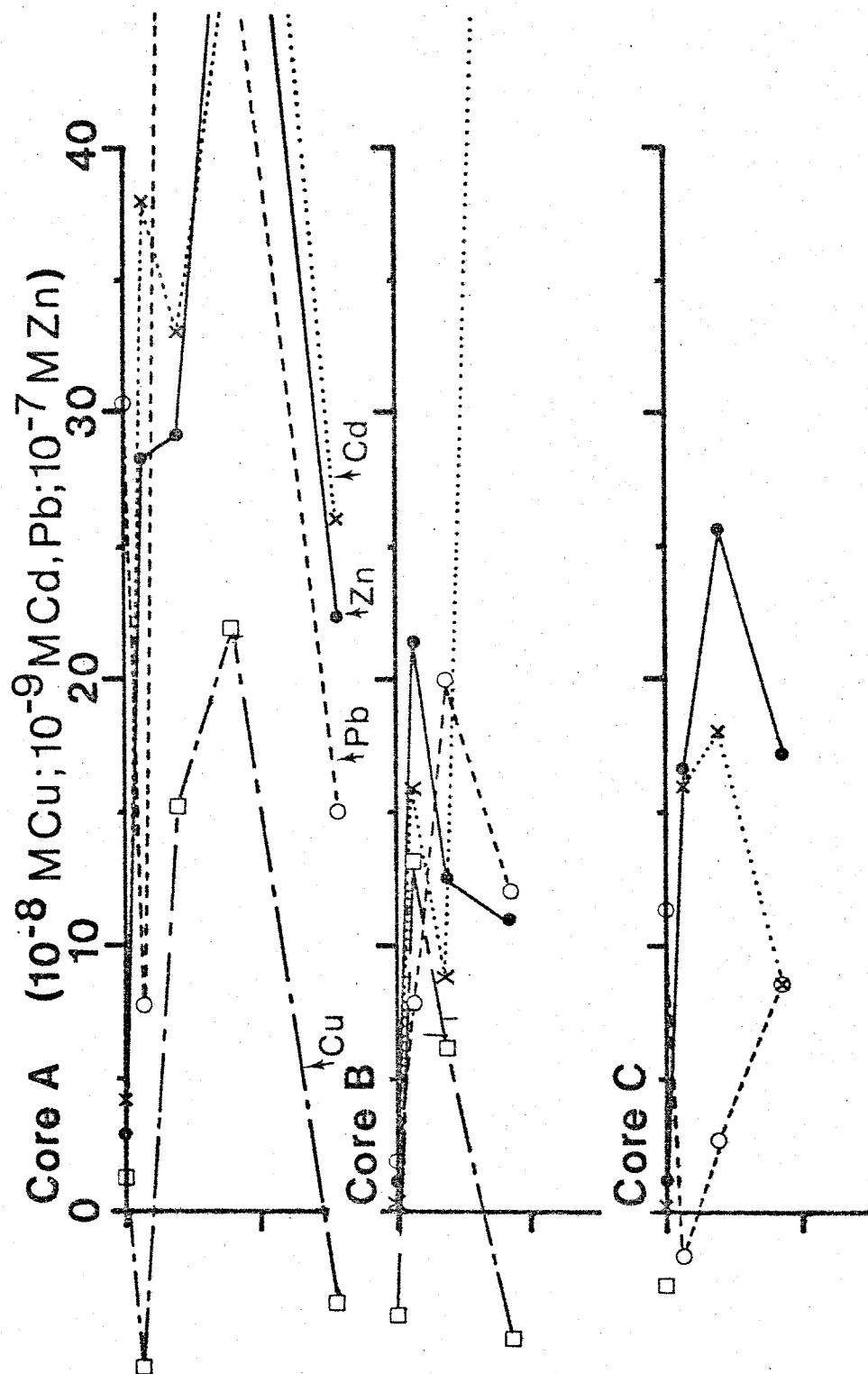


Figure 5. Spatial variation of zinc, cadmium, lead and copper from three cores collected at Station 20.

phate, and carbonate alkalinity data; and the zinc, cadmium, and lead data from the spatial study, respectively. The results indicate that the general profile shapes, i.e., the relative increases and decreases with depth are the same from all the cores, but that there are significant quantitative variations between cores for some parameters. The variations range from about 15% for carbonate alkalinity to a factor of 4 or more for the toxic metals. This large spatial variability is not uncommon. Matisoff et.al. (1975) report similar results for the estuarine sediments of Chesapeake Bay. They found a 1% variation among five cores for chloride (a chemically and biologically conservative element); a 10-15% variation for the nutrients; and a variation of 10%-10X for iron and manganese.

The large spatial variability places severe limitations on the interpretation of temporal and areal data. Therefore, each core will be studied as a separate entity where it is assumed that the interstitial water concentrations are controlled by local mineral equilibria.

Descriptive Chemistry of Interstitial Waters

Even with the large spatial variability in the pore water profiles, a number of general features emerge for each chemical parameter investigated. This section deals with the qualitative shapes of the profiles and several hypotheses are suggested as possible controls.

Chloride

A typical chloride profile from the central basin is given in Figure 6. Interstitial chloride concentrations ranged from 0-1000 $\mu\text{g-at/l}$. With several exceptions, the chloride concentrations were more or less uniform or decreased slightly with depth. Chloride concentrations in the central basin of Lake Erie waters average about 600 $\mu\text{g-at/l}$.

The irregular trend with depth in the interstitial water may reflect changes in the concentration level of chloride in the overlying water at the time of deposition and changes due to subsequent diffusion. A decrease in depth results from an increase in chloride in the overlying water over time, as seen for Lake Ontario (Lerman and Weiler, 1970). Therefore, inconsistent behavior of the chloride may be the result of an anthropogenic influence such as road salt runoff or industrial discharge at the time of deposition. The

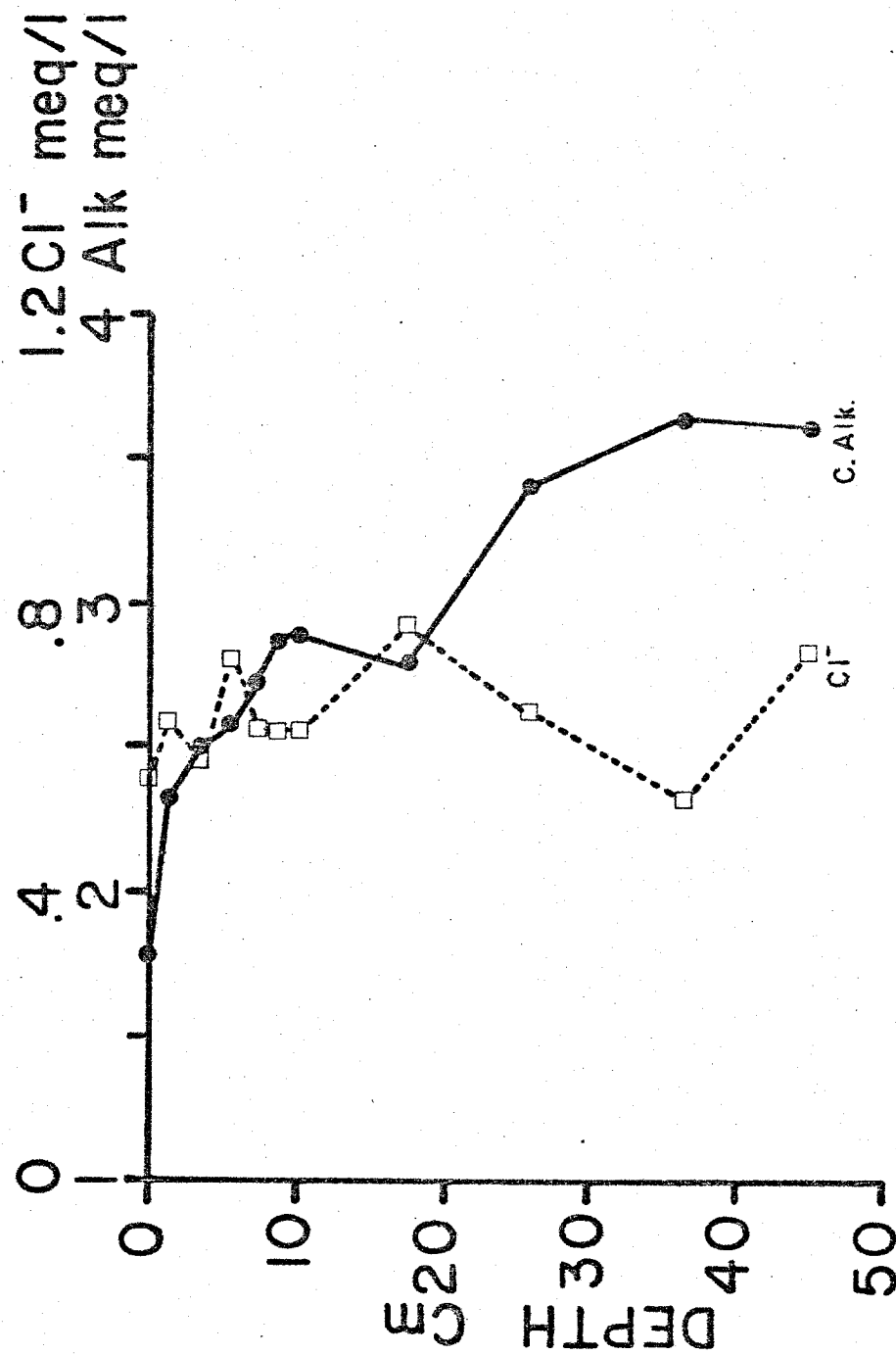


Figure 6. Typical chloride and alkalinity profiles from the central basin. The data are from Station 83 on 1 July, 1977.

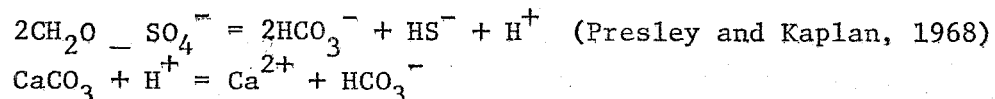
vertical transport of dissolved salt from the salt deposits underlying Lake Erie is a possible mechanism for the observed increase in depth in the several aberrant cores. This may be an important process of chemical mass transfer from the sediments to the overlying water.

Carbonate Alkalinity

The production of bicarbonate ion by intense bacterial respiration results in a significant increase in the alkalinity with depth in the sediments. This can be seen in the typical alkalinity profile in Figure 6. The total carbonate alkalinity values ranged from a minimum of about 1 meq/l at the sediment-water interface to a maximum of about 9 meq/l at 40 cm with the most rapid increase in the top 10 cm. Some samples taken in August and September showed an alkalinity peak in the upper 5 cm. This peak was seen mainly in the August samples and was probably indicative of more intense organic biodegradation at this level than either above or below. In an anoxic environment, bicarbonate ions are produced by both sulfate-reducing bacteria metabolizing organic matter and glycolysis of organic sulfur compounds. These reactions generate acid which can dissolve additional calcite and dolomite, further increasing the alkalinity, and may explain why calcium increased with depth in the interstitial water. Weiler (1973) determined that a ratio of 5 or 10 molecules of bicarbonate are formed per molecule of sulfate reduced but Presley and Kaplan (1968) calculated a 3:1 ratio. Weiler attributes the larger proportion of bicarbonate in Lake Ontario sediments to a fermentation process in which both bicarbonate and methane are produced.

pH and Sulfide

pH of the interstitial water, described in Figure 7, typically increased from as low as pH 6.9 at 0 to 2 cm to as high as 8.0 at about 50 cm. Below the sediment-water interface, increasing sulfide concentrations coincide with increasing pH, which suggest control of the pH by bicarbonate production as a result of sulfate reduction and organic decomposition and calcium carbonate dissolution. The following reactions describe this behavior.



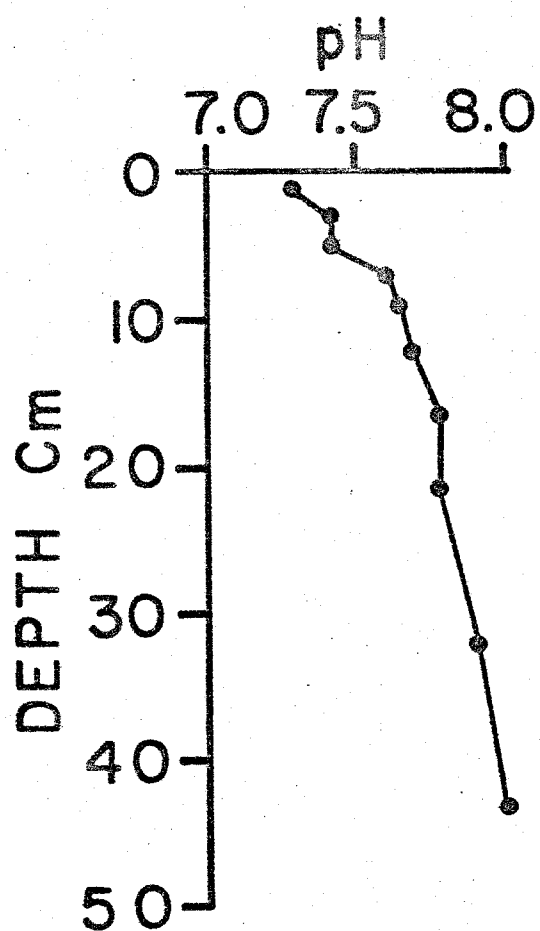


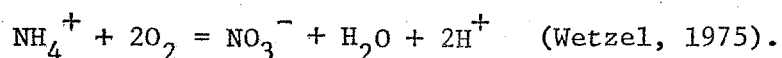
Figure 7. Typical pH profile from the central basin. The data are from Station 83 on 2 September, 1977.

If sulfur is conserved, sulfide must be produced as sulfate decreases. But sulfide concentrations in Lake Erie were below the detection limit of the sulfide electrode (total sulfur = 10^{-6} M). This is unexpected and could indicate (1) low total sulfur, (2) redox state of the sulfur system above the sulfide-sulfate boundary, or (3) metal-sulfide interaction. The surface waters in Lake Erie average about 25.7 ppm $\text{SO}_4^{=}$ (Weiler, 1973) which is comparable to four stations sampled on Lake Ontario (Weiler and Chawla, 1969). At these stations, the interstitial waters were analyzed for sulfate and were found to range from 15.3 ppm or lower at the oxic sediment-water interface to 2.1 ppm at 25 to 30 cm of core depth. This indicates that there is reduction of sulfate to sulfide and that the levels of sulfide should be high enough for detection by the sulfide electrode. Thus, the sulfide must be precipitating as very insoluble metal sulfides.

Nitrate, Nitrite, and Ammonia

The interrelationships of nitrogen species in the interstitial water are complex because of several simultaneously occurring processes. Ammonium is an end-product of bacterial organic decomposition and often has a maximum concentration in the upper 10 cm of sediment, where bacterial degradation is most intense. Consequently, ammonia is the source of nitrogen for nitrification which occurs at the anoxic-oxic boundary (Wetzel, 1975). Chen et.al. (1972) found that denitrification in sediments is rapid. They found that within two hours, up to 90 percent of added NO_3^- -N had been reduced, predominantly to $^{15}\text{N}_2$ when $^{15}\text{NO}_3^-$ was used as a tracer. Keeney (1971) observed that in sediments, 37 percent of 2 mg/l NO_3^- -N was incorporated into bacterial organic matter and the remainder was denitrified.

Because nitrification occurs only under aerobic conditions, it is most intense at the sediment-water interface. The overall reaction is



A Project Hypo survey indicated that maximum populations of nitrifying bacteria in Lake Erie occur at the sediment-water interface (Burns and Ross, 1972). According to Quastel (1954), nitrification in the upper sediments is controlled by the adsorption and concentration of nitrifying bacteria and ammonium ions onto clay particles; it is, therefore, more intense in sediments than in the overlying water.

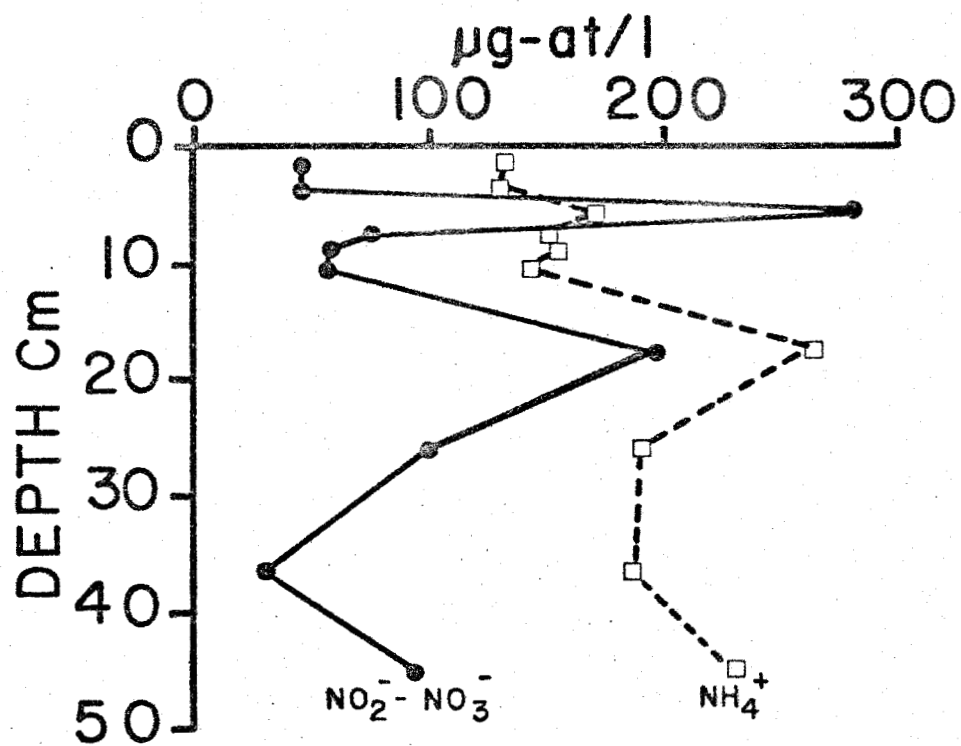


Figure 8. Typical nitrate plus nitrite and ammonium profiles from the central basin. The data are from Station 83 on 1 July, 1977.

The NO_2^- - NO_3^- concentrations in the interstitial water were much higher in June than in August and September (see Appendix II). Generally, levels in June ranged between 0.5 and 5 ppm. Levels in the overlying water were low in June and probably indicate rapid biological uptake. August and September interstitial NO_2^- - NO_3^- concentrations were comparatively lower than those in June but were still higher than the overlying water concentrations. The interstitial water nitrate decrease and the increase in the overlying water in late summer may indicate that nitrates were reduced in the sediments by increased bacterial activity and that NH_4^+ was diffusing out of the sediments and undergoing nitrification. Figure 8 gives typical NO_3^- - NO_2^- and NH_4^+ profiles.

Soluble Reactive Phosphate

Lake Erie pore waters exhibited higher concentrations of soluble reactive phosphate (SRP) than the overlying lake waters. A maximum of 3×10^{-4} M SRP was found at stations 47, 42 and 20 in June. A typical phosphate profile is given in Figure 9. The profiles show higher SRP's at greater depths in the sediment than at the sediment-water interface. This may be due to the adsorption of phosphate on ferric oxyhydroxides in the oxygenated microzone, whereas in the low Eh region, SRP is mobilized due to its release from decomposing organic matter and reduced ferric oxide.

The cores usually exhibited lower SRP concentrations during August and September, ranging between 0 and 50×10^{-6} M SRP. The concentration range was narrower and more constant with depth. Possible explanations of the lowered concentrations include diffusion into the overlying water, increased phosphate in an organic fraction, or some authigenic reaction regulating the phosphate level.

Diffusion is inhibited under aerobic conditions, but under anaerobic conditions phosphate can move up 10 cm to the overlying water (Hynes and Greib, 1970) in 2 to 3 months time. According to Pomeroy et.al. (1965), transport of SRP is diffusion controlled with less than 5 percent of the movement due to microbial activity. Under reducing conditions when the ferric hydroxide boundary is thin, diffusion may explain the observed decrease in SRP concentrations in late summer. Diffusion out of the sediments may be further enhanced by formation of the neutral species, FeHPO_4^0 , which should

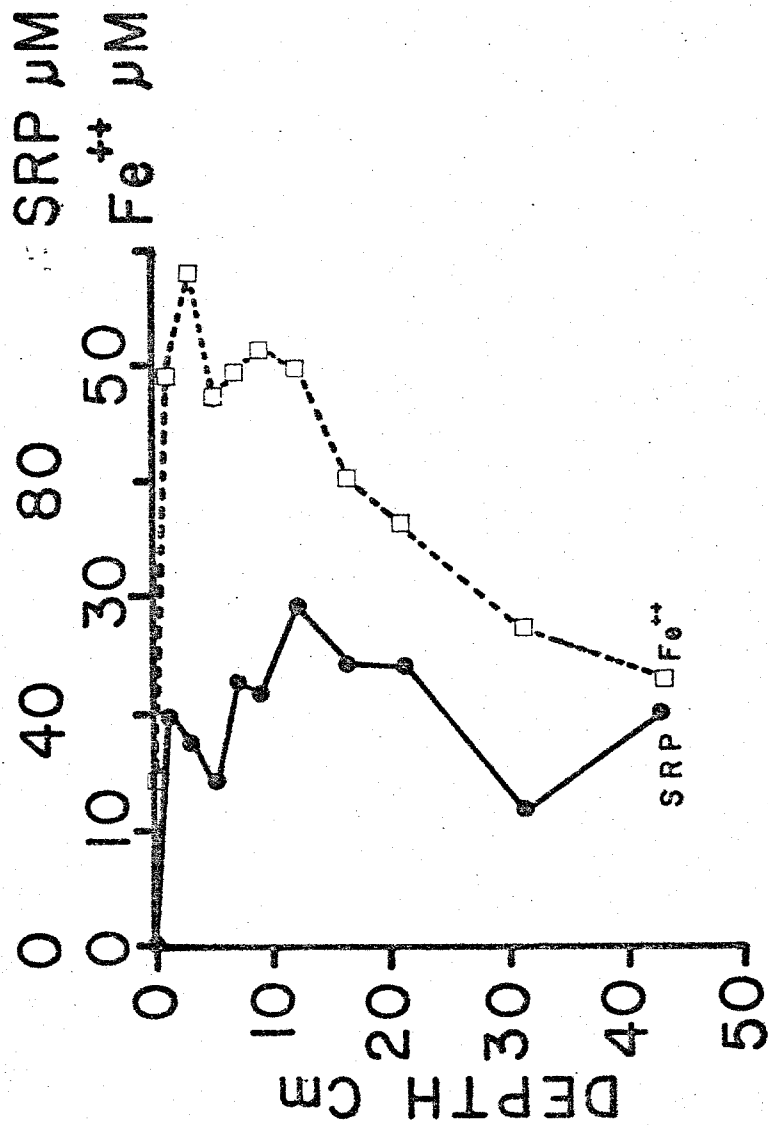


Figure 9. Typical ferrous iron and soluble reactive phosphate profiles from the central basin. The data are from Station 83 on 2 September, 1977.

not adsorb to charged surfaces (Williams and Mayer, 1972) and may, therefore, diffuse through the oxidized microzone. Phosphate release can double if sediments are agitated by turbulence (Zicker et.al., 1965).

Diffusion over a two month period cannot explain completely the change in concentrations at all depths. A change in phosphate speciation may explain the decreased SRP levels in August and September. Christman (1966) claims that 70-80 percent of the phosphate is in a soluble organic phase in late summer which would account for the low orthophosphate levels observed in this study. Authigenesis provides an alternate explanation of the low SRP levels. If a solution-mineral equilibrium regulates the concentration of phosphate and a metal ion in the interstitial water, an increase in the concentration of one species should result in a decrease in the other. Both covariance and inverse variation between phosphate and Fe(II) were observed. This suggests that an iron phosphate is precipitating and that a common source for the dissolved species exists. Most likely, the common source is ferric oxyhydroxide which undergoes reduction upon burial.

Ferrous Iron

The ferrous iron concentrations in the interstitial waters in the central basin ranged from $1.0 \times 10^{-5} \text{ M}$ to a $3.6 \times 10^{-4} \text{ M}$. These values were higher than those reported by Kemp (1969), possibly due to extrusion under nitrogen atmosphere in this study. Ferrous iron concentrations in the pore waters varied from station to station. Interstitial Fe(II) concentrations were high at station 73 and were generally low at station 46. The highest values found were from the Ashtabula cores, where values consistently exceeded $1 \times 10^{-3} \text{ M}$. A typical ferrous iron profile is given in Figure 9.

Ferrous iron concentrations were generally high immediately below the oxidized microzone. When the microzone was thick, i.e., before stratification or after fall overturn, the ferrous iron concentration was low at the sediment-water interface. As ferrous iron diffuses in the oxygenated sediment-water interface, it is oxidized to ferric iron, and little if any reaches the overlying water. When the microzone is thin, diffusion to the overlying water may occur through the ferric hydroxide floc because of turbulence and/or complexation and consequent stabilization of ferrous iron. Low surface Fe(II) concentrations suggest that diffusion was not significant.

Zinc

In the pore waters, the zinc concentrations ranged from 6×10^{-9} M to 6×10^{-6} M. A typical zinc profile is given in Figure 10. Concentration maxima are usually found just beneath or at the sediment-water interface and several centimeters below this in the upper 10 cm. Below 10 cm the profiles are generally uniform. The upper concentration maxima probably is the result of a release of zinc from its source upon burial. The lower concentration maximum might be the result of a secondary source or be caused by an equilibrium with a metal phase.

The actual values were not consistent, especially in the upper 10 cm. Chemical controls may be important but biological (bacterial) controls, bioturbation and adsorption-desorption in response to metal concentrations on the sediment may also be significant.

Cadmium

The cadmium concentrations were lower than either lead or zinc and varied to a lesser extent over the depth studies, ranging from 10^{-9} to 1.3×10^{-7} M. A typical cadmium profile is given in Figure 10. In general, the cadmium profile shapes were the same as those for zinc: concentration maxima just beneath the sediment-water interface and in the upper 10 cm. Many times, however, the secondary maximum was not apparent. The similarity with zinc in the shapes of the profiles suggests common sources and controls of the dissolved metals.

It is important to remember that the observed concentrations are averages over a certain depth. This is particularly important when considering the upper few cm where the concentration gradients are great. A high surface concentration may be indicative of a small oxidized microzone layer with a low metal concentration overlying a reduced zone with a very high metal concentration such that the top layer shows an intermediate concentration.

Lead

In the pore waters, the lead concentrations ranged from 10^{-9} to 1.3×10^{-7} M. These values were almost two orders of magnitude less than the zinc concentrations and on the same order as the cadmium. Generally, the highest concentrations occurred in the upper 10 cm of the cores and decreased with

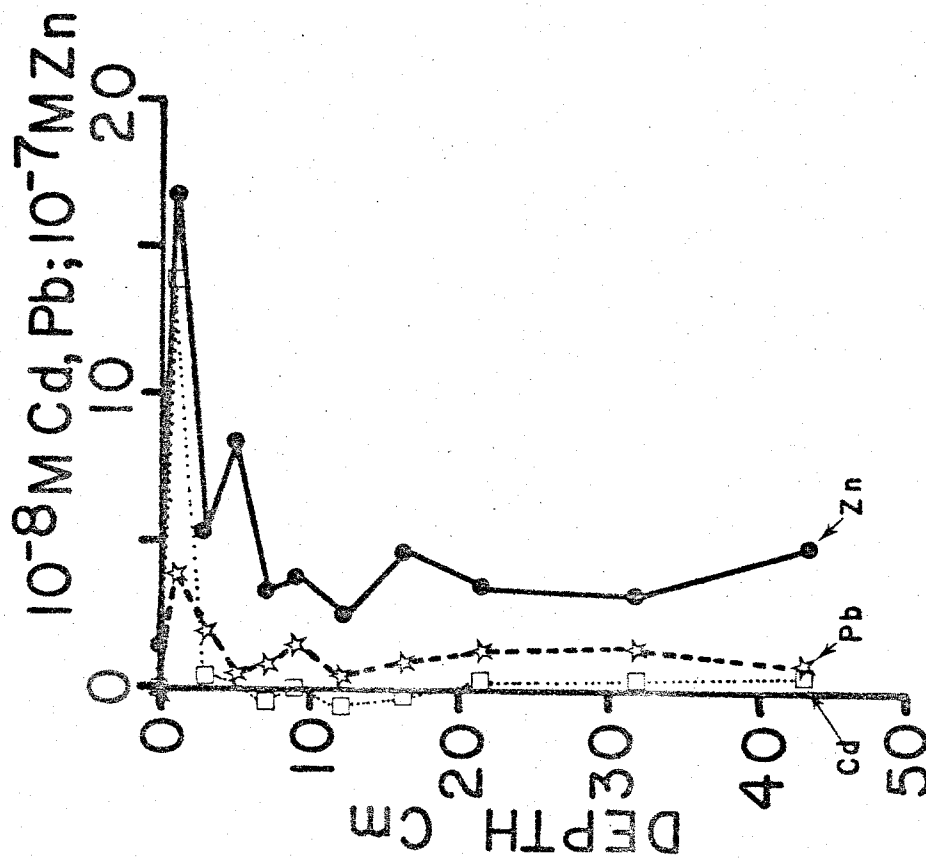


Figure 10. Typical zinc, cadmium, and lead profiles from the central basin. The data are from Station 83 on 2 September, 1977.

depth, with the profile shapes similar to those of zinc and cadmium. The lead profiles also show more scatter in the data than zinc or cadmium and indicate that our sources of lead contamination have not been eradicated. Nevertheless, the data do suggest many similar controls between zinc, cadmium and lead. A typical profile is given with zinc and cadmium in Figure 10.

The remarkable uniformity in the zinc, cadmium and lead profiles below 10 cm suggests some controlling process for all three metals at depth in the sediment. The exact nature of this control is the subject of later sections of this report.

SECTION 7

ASHTABULA STUDY

In August, 1975 and May, 1976 the Army Corps of Engineers dredged Ashtabula Harbor and disposed of the sediment in open water a few miles out into the lake (old dumpsite). In April, 1977, the harbor was again dredged and the material dumped in a second open water disposal area (new dumpsite). This study investigated the old and new dumpsites and a control site prior to the April, 1977 disposal and for several months following the dredging operations. It was hoped that the new dredge spoil would be an easily identifiable blanket of material in terms of its physical and chemical characteristics. Some long-term effects of the dredged material on chemical fluxing could then be evaluated. Station locations are shown in Fig. 11; sampling dates are given in Table 1; and the data from all thirteen cores in Appendix B. The control site showed no visual evidence of dredged material.

There are a number of comparisons between the Ashtabula cores and the central basin cores that are useful. The dissolved trace metal concentrations are about 5 times higher near Ashtabula than in the central basin. The Ashtabula cores also display more noise and greater concentration gradients. The concentration of ferrous iron reaches values typically on the order of 400 μ m near Ashtabula, 2 to 4 times higher than those found in the central basin. The concentration maximum in ferrous iron occurs in the top 10-20 cm in Ashtabula cores, but in the top 5-10 cm in the central basin cores. This may be the result of real differences in the dissolution kinetics of ferric oxyhydroxides and the sedimentation rate at the two areas. Like the metals, the alkalinity is also higher in the Ashtabula cores (about 2-3 times) although the pH's tend to be lower. The higher metal and nutrient concentrations at Ashtabula reflect a closer proximity to the source of these pollutants.

The disposal of the dredged material at the new dump site produced some changes in the pore water chemistry, although not as great as one might

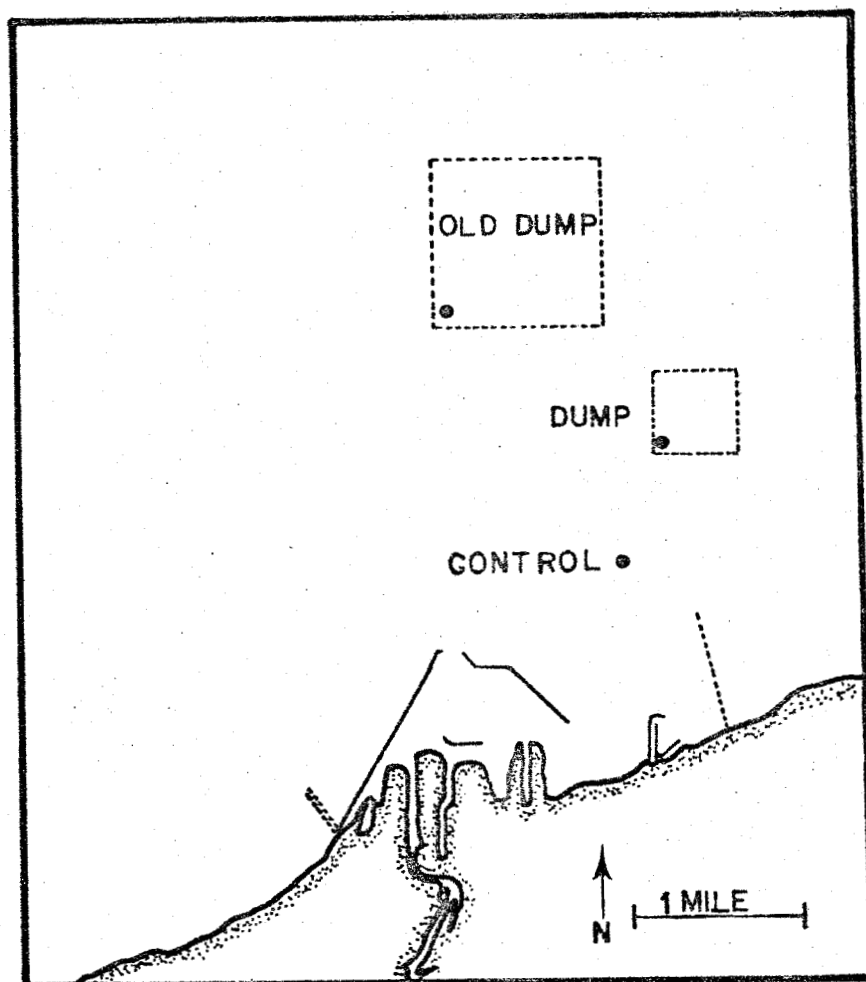


Figure 11. Coring locations at the Ashtabula dump site. The open water disposal areas off Ashtabula harbor are delineated as Old Dump (August, 1975) and Dump (April, 1977).

first suspect. The zinc, cadmium, and lead profiles from before and after the dumping do not reflect the dumping event. In addition, the post dumping profiles from the dump site and the control site are remarkably similar, which implies no evidence for the dumped material. The iron profiles, however, are different after disposal. Fig. 12 shows the April and May iron profiles at the dump site. The concentration maximum is displaced 5-10 cm deeper in the core in the May profile. The concentration gradient at the sediment-water interface is therefore less. This suggests that 5-10 cm of sediment were deposited as a result of the disposal operation. Further evidence is present in the carbonate alkalinity profiles. Fig. 13 shows the April and May profiles at the dump site. The concentration maxima are displaced at least five centimeters deeper, values are lower, and the concentration gradient is less in the May core. Actually, the same can be said for the control station, but the September core from the dump site looks like the May core, while the September core from the control site looks like the April core. The evidence for this identification of 5-10 cm of dredged material is admittedly weak. The rapid response of the pore waters to changing physical and chemical conditions and the large spatial variation in the pore waters makes such an identification difficult. An analysis of the sediment solids for trace metals or some exotic organics might prove to be a more useful indicator of the dredge spoil.

The higher values of the nutrients and metals in the Ashtabula pore water are probably the result of being closer to the sources of these materials. It is possible that a decrease in the concentration could be observed in cores taken along a transect from inshore to offshore.

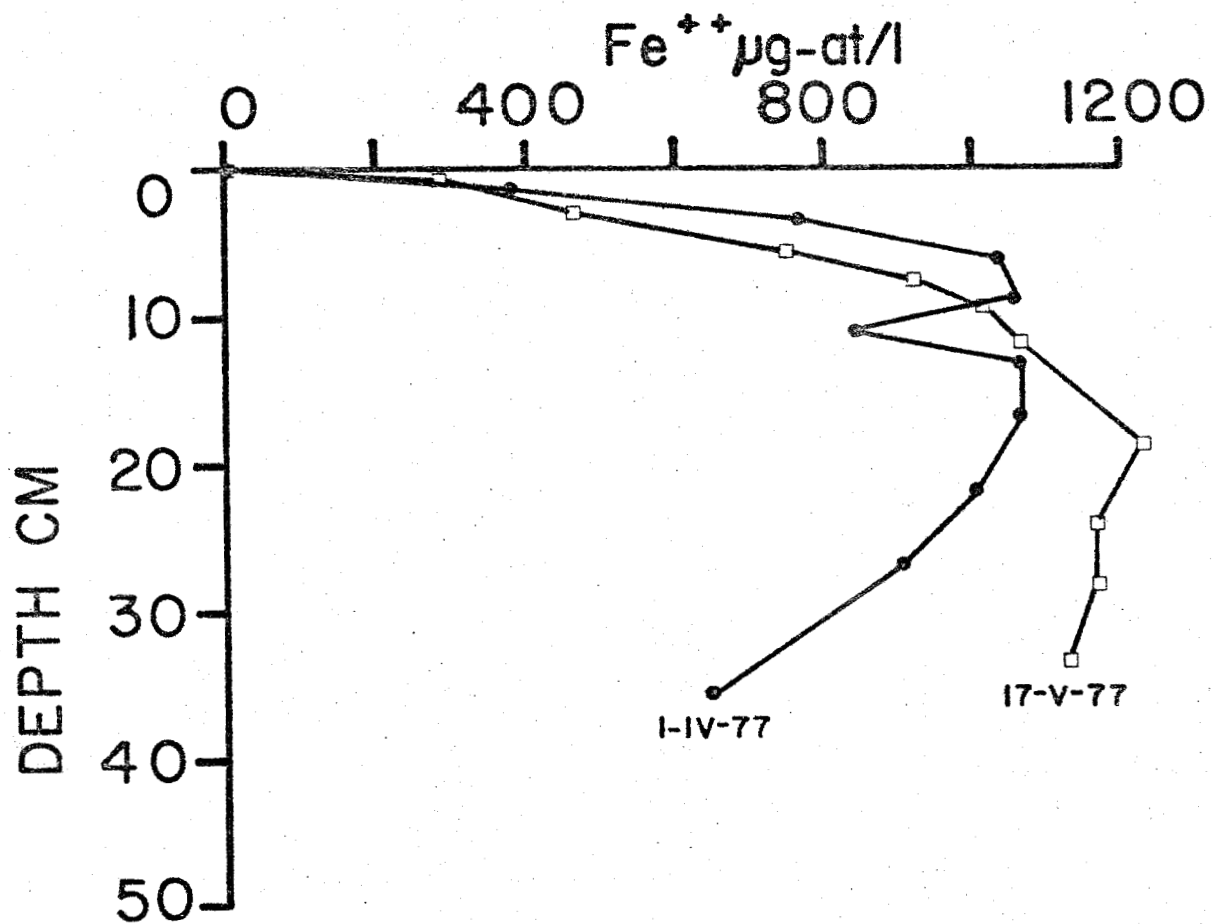


Figure 12. Ferrous iron profiles at the dump site from before (1 April, 1977) and after (17 May, 1977) the disposal operations.

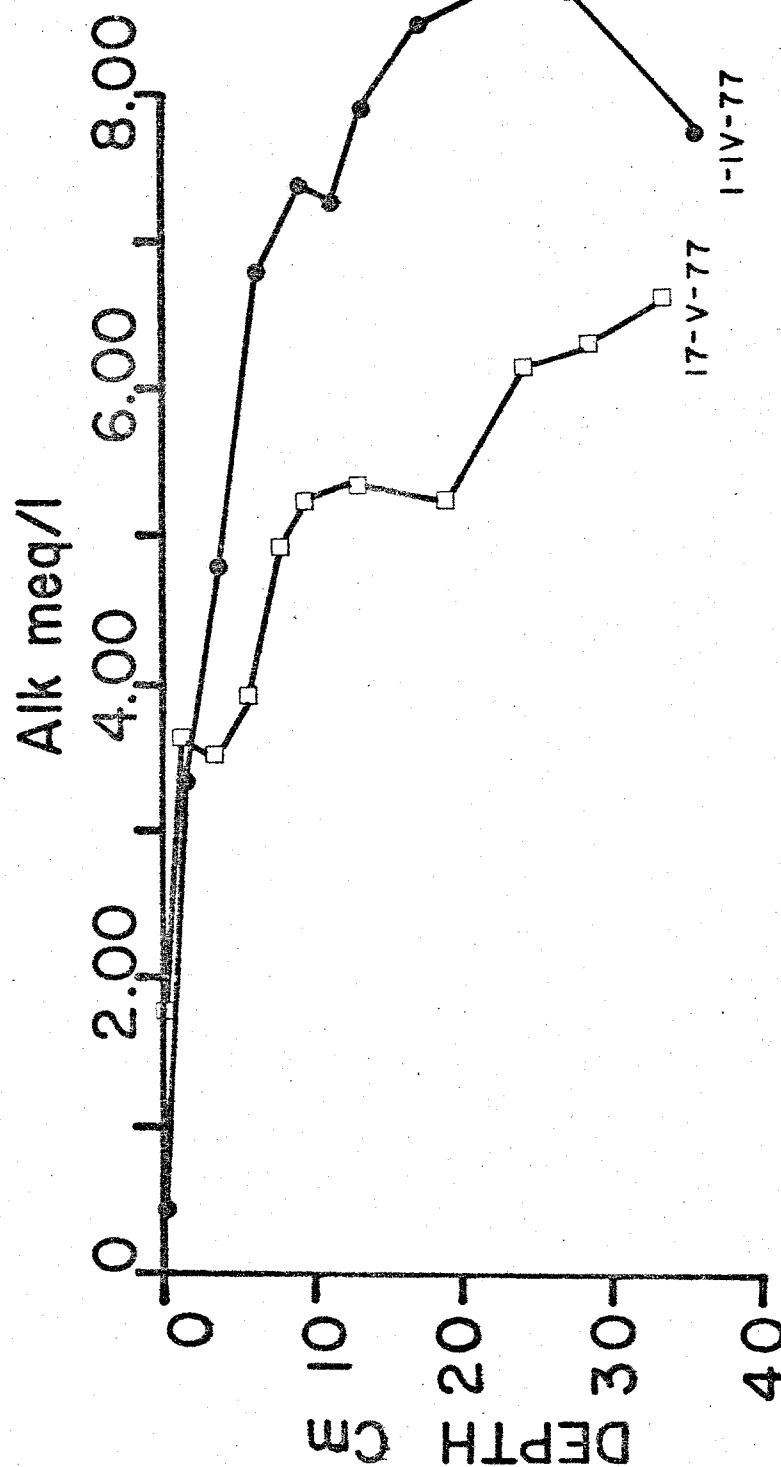


Figure 13. Carbonate alkalinity profiles at the dump site from before (1 April, 1977) and after (17 May, 1977) the disposal operations.

SECTION 8

THERMODYNAMIC MODEL

Calculation of Activities

The ionic strength, activity coefficients and activities of ferrous iron, zinc, cadmium and lead were calculated as part of a computer program to determine the speciation of the metals and the ion activity products of the metal carbonates and phosphates. Ionic strength (I) is defined as $I = 1/2 \sum c_i z_i^2$ where c_i is an analytical concentration and z_i is the charge of a species. In this study the concentrations of the major ions, Na^+ , Ca^{2+} , K^+ , Mg^{2+} , SO_4^{2-} , Cl^- , HCO_3^- , Mn^{2+} and Fe^{2+} were used to calculate ionic strength. For this calculation the total bicarbonate concentration was taken to equal the carbonate alkalinity; for pH's less than 7.8 and ionic strengths less than 0.5, the error introduced is less than 5 percent (Troup, 1974). Concentrations of the major cations, K^+ , Na^+ , Ca^{2+} , and Mg^{2+} , were determined for one sample, GASP II-47, and were used in the calculation of ionic strength for all the samples. Major cations and anions exhibit fairly consistent trends with depth in Lake Erie interstitial waters (Weiler, 1973); therefore, generalization of their concentrations to all cores for purposes of the ionic strength calculation was justified. The measured value for the major cations at GASP II-47 are listed in Table 2. Alongside, in parentheses, are the values used in the calculation of ionic strength. These latter values include changes in the analytical values, based on trends observed in Lake Ontario (Weiler, 1973). Also, based on Weiler's analyses of Lake Ontario interstitial water, concentrations for manganese and sulfate, other significant contributors to the ionic strength, are listed in Table

Activity coefficients were then calculated from the extended Debye-Hückel equation and were used in a computer program to correct trace metal, ferrous iron, bicarbonate and phosphate concentrations for dissolved speciation at varying ionic strengths and pH's. The form used in this study is

TABLE 2
VALUES USED IN THE CALCULATION OF IONIC STRENGTH

<u>Depth</u> <u>cm</u>	<u>Ca</u>	<u>Mg</u>	<u>Na</u>	<u>K</u>	<u>Mn</u>	<u>SO₄</u>
0-2.6	1190 (1190)	334 (400)	520 (520)	93 (93)	nd (58.2)	nd (146)
2.6-5.6	1210 (1200)	362 (400)	488 (499)	89 (89)	nd (58.2)	nd (146)
5.6-6.7	1200 (1210)	455 (400)	478 (478)	83 (83)	nd (58.2)	nd (72.9)
6.7-8.5	1220 (1220)	380 (400)	389 (400)	79 (79)	nd (58.2)	nd (72.9)
8.5-9.9	nd (1245)	nd (400)	nd (435)	nd (78)	nd (58.2)	nd (72.9)
14.6- 17.7	1270 (1270)	461 (400)	478 (479)	77 (77)	nd (89.2)	nd (20)
21.5-25	1200 (1300)	383 (400)	488 (479)	nd (77)	nd (102)	nd (20)
41.5- 44.7	1400 (1400)	545 (525)	484 (479)	78 (77)	nd (102)	nd (20)
44.7-50	1480 (1480)	526 (525)	446 (479)	64 (64)	nd (102)	nd (20)
50-58	1340 (1480)	348 (525)	498 (479)	79 (64)	nd (102)	nd (20)

Table 2. All concentrations in units of $\mu\text{m/L}$. Measured values at GASP II-47 are listed (not in parentheses). Values in parentheses are those used in the calculation of ionic strength, and are based on the measured values of Weiler's (1973) Lake Ontario data. Other parameters used in the calculation of ionic strength include carbonate alkalinity, chloride, iron, SPR, nitrite, and ammonium. Values for these species were measured for each sample.

$$\log \gamma_i = \frac{-Az^2\sqrt{I}}{1 + aB\sqrt{I}}$$

where γ_i is the ion activity coefficient; z , the charge of the ion; I , the ionic strength; a , the effective diameter of the hydrated ion (Keilland, 1937) and A and B are constants for a given solvent at a specified temperature and pressure. In this study, all calculations were made assuming a temperature of 25°C and one atmosphere total pressure; therefore, the constants A and B were equal to 0.33×10^8 and 0.5 respectively.

Although organic sequestering could tie up a significant amount of trace metals in the interstitial water (Gardner, 1974; Hodgson et al., 1966), only inorganic species were considered (for reasons discussed in the analytical section). Species considered in the calculation of the free ion activities are listed in Table 3 with their respective association constants.

The activity of a free ion is calculated by manipulation of a mass balance equation. An example is the determination of free bicarbonate concentration. The total bicarbonate concentration is given by mass balance equation (2),

$$\text{total HCO}_3^- = \text{HCO}_3^-_{\text{free}} + \text{CaHCO}_3^+ + \text{MgHCO}_3^+ + \text{NaHCO}_3^0 \quad (2)$$

The total bicarbonate concentration can be closely approximated by the carbonate alkalinity, which is defined by equation (3),

$$\text{Carbonate alkalinity} = \text{HCO}_3^- + 2\text{CO}_3^{2-} - \text{OH}^- - \text{H}^+ \quad (\text{Stumm and Morgan, 1970}) \quad (3)$$

because the last three terms are at least four orders of magnitude less than the bicarbonate concentration at typical interstitial water pH's.

Equations (4), (5) and (6) are the mass action equilibria for the ion pairs in the bicarbonate mass balance.

$$K_a = \frac{a_{\text{CaHCO}_3^+}}{a_{\text{Ca}^{2+}} a_{\text{HCO}_3^-}} = \frac{\gamma_{\text{CaHCO}_3^+}}{\gamma_{\text{Ca}^{2+}} \gamma_{\text{HCO}_3^-}} \frac{(\text{CaHCO}_3^+)}{(\text{Ca}^{2+})(\text{HCO}_3^-)_{\text{free}}} \quad (4)$$

$$K_b = \frac{a_{\text{MgHCO}_3^+}}{a_{\text{Mg}^{2+}} a_{\text{HCO}_3^-}} = \frac{\gamma_{\text{MgHCO}_3^+}}{\gamma_{\text{Mg}^{2+}} \gamma_{\text{HCO}_3^-}} \frac{(\text{MgHCO}_3^+)}{(\text{Mg}^{2+})(\text{HCO}_3^-)_{\text{free}}} \quad (5)$$

TABLE 3

SOLUBLE SPECIES WITH THEIR RESPECTIVE ASSOCIATION CONSTANTS
INCLUDED IN THE CALCULATION OF FREE METAL ION ACTIVITIES

<u>Species</u>	<u>Log of the Association Constant</u>	<u>Reference</u>
PbOH^+	7.00	Sillen and Martell, 1964
PbCO_3^0	6.40	Zirino & Yamamoto, 1972
PbHCO_3^+	2.9	ibid
Pb(OH)_2^0	10.88	Sillen and Martell, 1964
PbSO_4^0	2.7	Gardner & Nancollas, 1970
CdOH^+	5.0	Zirino & Yamamoto, 1972
Cd(OH)_2^0	10.6	ibid
ZnHCO_3^+	2.1	ibid
ZnCO_3^0	5.3	ibid
ZnHPO_4^0	3.3	Nriagu, 1973
ZnSO_4^0	2.3	Sillen & Martell, 1964
ZnOH^+	5.04	Stumm & Morgan, 1970
FeHPO_4^0	3.6	Nriagu, 1972
$\text{FeH}_2\text{PO}_4^+$	2.7	ibid
FeOH^+	6.1	Sillen & Martell, 1964
FeSO_4^0	2.3	ibid
CaHCO_3^+	1.26	Garrels & Thompson, 1962
MgHCO_3^+	1.07	Baumann, 1974
NaHCO_3^+	-0.25	Garrels & Thompson, 1964
HCO_3^-	6.35	Sillen & Martell, 1964
CO_3^{2-}	10.3	Stumm & Morgan, 1970
H_3PO_4^0	2.2	Butler, 1964
H_2PO_4^-	7.2	ibid
HPO_4^{2-}	12.3	ibid
CaHPO_4^0	2.74	Sillen & Martell, 1964
$\text{CaH}_2\text{PO}_4^+$	1.41	ibid

$$K_a = \frac{a_{\text{CaHCO}_3^+}}{a_{\text{Na}^+} a_{\text{HCO}_3^-}} = \frac{\gamma_{\text{NaHCO}_3^0}}{\gamma_{\text{Na}^+} \gamma_{\text{HCO}_3^-}} \frac{(\text{NaHCO}_3^0)}{(\text{Na}^+)(\text{HCO}_3^-)_{\text{free}}} \quad (6)$$

An activity coefficient of one for uncharged species and, as in Garrels and Thompson's seawater model (1962), an activity coefficient for 1:1 single charged species equal to that of the bicarbonate ion were assumed. The mass action equations (4) through (6) were then substituted into equation (2)... The equation was rearranged and solved for HCO_3^- free according to equation (7).

$$\text{HCO}_3^- \text{ free} = \frac{\text{carbonate alkalinity}}{1 + K_a \gamma_{\text{Ca}^{2+}} (\text{Ca}^{2+}) + K_b \gamma_{\text{Mg}^{2+}} (\text{Mg}^{2+}) + K_c \gamma_{\text{Na}^+} (\text{Na}^+) \cdot \gamma_{\text{HCO}_3^-}} \quad (7)$$

Hence, the free bicarbonate concentration was calculated from the carbonate alkalinity, the stability constants of the ion pairs, and the concentrations of the contributing cations and their estimated activity coefficients.

The ferrous iron and phosphate concentrations were determined from the total analytical concentrations by solving mass balance equations (8) and (9) simultaneously, since soluble FeHPO_4^0 and $\text{FeH}_2\text{PO}_4^+$ complex a considerable proportion of the total ferrous and phosphate ions.

$$\text{Fe(II)}_{\text{total}} = \text{Fe(II)}_{\text{free}} + \text{FeHPO}_4^0 + \text{FeH}_2\text{PO}_4^+ + \text{FeOH}^+ + \text{FeSO}_4^0 \quad (8)$$

$$\text{HPO}_4^{2-} \text{ total} = \text{HPO}_4^{2-} \text{ free} + \text{H}_2\text{PO}_4^- + \text{CaHPO}_4^0 + \text{CaH}_2\text{PO}_4^+ + \text{FeHPO}_4^0 + \text{FeH}_2\text{PO}_4^+ \quad (9)$$

In a manner similar to that used for calculating free bicarbonate concentrations, the $\text{Fe(II)}_{\text{total}}$ and $\text{HPO}_4^{2-} \text{ total}$ equations were manipulated and solved for HPO_4^{2-} and $\text{Fe(II)}_{\text{free}}$ concentrations.

Next, the free zinc, lead and cadmium concentrations were calculated from the total analytical concentrations by solution of mass balance equations (10), (11) and (12) in the same manner as the free bicarbonate values. This approach was used by Elder (1975) and Zirino and Yamamoto (1972) for trace metals. The concentrations of free bicarbonate and phosphate used in equations (10), (11) and (12) were obtained from equations (7) and (9).

$$\text{Zn}_{\text{total}} = \text{Zn}^{2+} \text{ free} + \text{ZnOH}^+ + \text{ZnHPO}_4^0 + \text{ZnCO}_3^0 + \text{ZnHCO}_3^+ \quad (10)$$

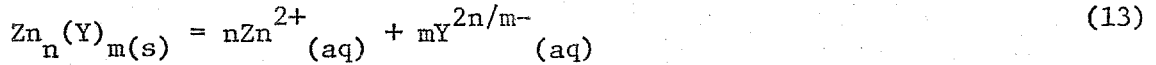
$$\text{Cd}_{\text{total}} = \text{Cd}^{2+} \text{ free} + \text{CdOH}^+ + \text{Cd(OH)}_2^0 \quad (11)$$

$$Pb_{total} = Pb^{2+}_{free} + PbOH^{+} + PbCO_3^0 + PbHCO_3^{+} + Pb(OH)_2^0 \quad (12)$$

Calculation of Ion Activity Products

The precipitation of a mineral phase from a supersaturated solution is a function of (1) reaction kinetics of the precipitation and (2) free energy drive of the reaction. Little is known about the kinetics of precipitation of the trace metal precipitates under consideration and they will not be considered. The free energy drive of heterogeneous reactions involving ferrous iron, zinc, cadmium and lead is discussed to determine the saturation state of any solution with respect to a mineral phase. The minerals considered in this study and their respective solubility products are listed in Table 4. The method of calculating the saturation state follows that used by Troup (1974).

Consider the reaction



The free energy change for this reaction is

$$\Delta G_{Reaction} = \Delta G^0 + 2.3RT \log (a_{Zn}^{2+})^n (a_Y^{2n/m-})^m \quad (14)$$

assuming a value of unity for the activity of the pure solid phase.

The standard free energy change, ΔG^0 , is related to the solubility product according to equation (15).

$$\Delta G^0 = -2.3 RT \log K_{sp} \quad (15)$$

The product of the activities, the ion activity product (IAP) is given by

$$IAP = (a_{Zn}^{2+})^n (a_Y^{2n/m-})^m \quad (16)$$

Substitution of (15) and (16) into equation (14) yields equation (17).

$$\Delta G = 2.3 RT \log IAP/K_{sp} \quad (17)$$

When IAP is greater than the K_{sp} , ΔG is positive, which favors the precipitation reaction. If IAP is less than the K_{sp} , ΔG is negative which favors the dissolution reaction, since, in this case, the solution is undersaturated with respect to the solid. When IAP equals the K_{sp} , ΔG is 0 and the solution is in equilibrium with the solid phase.

Since minerals contain different ratios of metal to anion, the saturation states must be corrected to free energy changes per gram-atom of metal before the log saturations of different solids can be compared directly. The

TABLE 4

SOLUBILITY EQUILIBRIA OF Fe(II), Zn, Cd, AND Pb MINERALS USED IN THE
CALCULATION OF THEIR SATURATION STATE IN INTERSTITIAL WATER

$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}(\text{solid}) = 3\text{Fe}^{2+} + 2\text{PO}_4^{3-} + 8\text{H}_2\text{O}$	-36.0	Nriagu, 1972
$\text{FeCO}_3(\text{solid}) = \text{Fe}^{2+} + \text{CO}_3^{=}$	-10.68	Sillen & Martell 1964
$\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}(\text{solid}) = 3\text{Zn}^{2+} + 2\text{PO}_4^{3-} + 4\text{H}_2\text{O}$	-35.2	Nriagu, 1973
$\text{ZnCO}_3(\text{solid}) = \text{Zn}^{2+} + \text{CO}_3^{=}$	-10.78	Sillen & Martell 1964
$\text{Cd}_3(\text{PO}_4)_2(\text{solid}) = 3\text{Cd}^{2+} + \text{CO}_3^{=}$	-32.6	Sillen & Martell 1964
$\text{CdCO}_3(\text{solid}) = \text{Cd}^{2+} + \text{CO}_3^{=}$	-11.29	Sillen & Martell 1964
$\text{Pb}_5(\text{PO}_4)_3\text{OH}(\text{solid}) + 4\text{H}^+ = 5\text{Pb}^{2+} + 3\text{HPO}_4^{2-} + \text{H}_2\text{O}$	-25.7	Nriagu, 1974
$\text{PbCO}_3(\text{solid}) = \text{Pb}^{2+} + \text{CO}_3^{=}$	-12.83	Stumm & Morgan 1972

equivalent free energy change is determined by dividing the free energy change by the number of moles of metal (n) per gram-atom of solid.

$$\Delta G' = \frac{2.3 RT}{n} \log IAP/K_{sp} \quad (18)$$

Log saturation is then defined as

$$\text{Log saturation} = \frac{1}{n} \log \frac{IAP}{K_{sp}} \quad (19)$$

and is proportional to the free energy normalized to one gram-atom of metal (Troup, 1974). Using this last relationship, the degree of saturation of solutions with respect to a metal and a solid phase can be compared. Log saturation calculations were performed for ferrous iron, zinc, cadmium and lead phosphates and carbonates for the interstitial waters in Lake Erie sediments.

SECTION 9

DISCUSSION

Inorganic Complexes

Alkalinity and pH, which increase with depth in the sediment, alter the inorganic speciation of different metals significantly and to a different extent. The effects of pH changes on the complexation of the metals are demonstrated in Table 5 where alkalinity is held constant, and ionic strength and pH are allowed to vary as they do in core IV-80. Total metal concentrations are held constant and are equal to those in core sample IV-80-5. The effects of alkalinity changes are demonstrated in Table 6, where pH is held constant and ionic strength and alkalinity equal the values for samples IV-80-1 through 9. In both cases the total metal concentration is constant.

The free cadmium ion predominates in fresh water with little change in speciation with changes in alkalinity and pH. CdCO_3^0 becomes important only at pH 9 at which point the cadmium concentration equals the CdCO_3^0 (Ernst et al., 1975). Therefore, according to Table 6 an increase in alkalinity in the system under study does not change the inorganic speciation of cadmium. The pH changes observed in the interstitial water affect the Cd speciation to a greater extent than the alkalinity. As pH increases from 7.02 to 7.95, the inorganically complexed fraction of Cd^{2+} increases from 1 to 11 percent, due to the increased importance of CdOH^+ and $\text{Cd}(\text{OH})_2^0$.

In contrast to cadmium, which exists predominantly as the free cation under most freshwater conditions, Pb is highly complexed. Ninety to one hundred percent of the Pb is complexed as PbOH^+ , PbCO_3^0 , PbHCO_3^+ and $\text{Pb}(\text{OH})_2^0$.

The change in speciation of zinc with respect to increasing pH and alkalinity is greater than for Pb and Cd. With alkalinity constant, a pH increase from 7.02 to 7.95 halves the concentration of free Zn, whereas with pH constant, an alkalinity increase from 2.38 to $3.55 \times 10^{-3}\text{M}$ decreases the free Zn concentration by only 9.3 percent.

In summary, pH and alkalinity changes observed in the interstitial water in this study affect the metal speciation. Cadmium is insensitive to alkalinity changes while Pb and Zn are relatively sensitive to such changes. The changes in pH in the interstitial water are, however, more significant. The combined effect of increases in pH and alkalinity with depth in the sediments is to decrease the free metal ion available for reaction with other ligands.

Thermodynamic Tendency for the Precipitation of Ferrous Iron Minerals

Iron sulfides are very insoluble and have been found to regulate Fe(II) behavior in Chesapeake Bay (Troup, 1974) but are not thought to be important in Lake Erie sediments (Nriagu, 1974). Sulfide concentrations were below detection (less than 10^{-13} M). Any sulfide in the interstitial water would result from the reduction of sulfate in the overlying water, and if sulfur is conserved, total sulfide in the interstitial waters would equal 3×10^{-4} M, the value of sulfate in the lake water. This is compared to a total sulfur concentration of 3×10^{-2} M in ocean water. In the oceans, most sulfide is the result of sulfate reduction by bacteria. In freshwater systems, however, organic breakdown of organic sulfur with the subsequent formation of hydrogen sulfide may be more important, based on data from Lake Mendota (Nriagu, 1968). Acid volatile sulfides (approximately FeS) in these sediments are as high as those reported by Aller (1977) for Long Island Sound. Clearly there is ferrous iron-sulfide interaction. The high Fe(II) concentrations may keep sulfide below detection by precipitation of ferrous sulfide. If this is occurring, sulfide should not significantly affect the concentration of Fe(II). No reports were found indicating that sulfide is important in regulating Fe(II) concentrations in Lake Erie sediments.

Log saturation calculations for vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) indicate that the pore waters in Lake Erie sediments are always saturated by one order of magnitude with Fe(II) and PO_4^{3-} , except in the oxidized microzone. This suggests that vivianite may be precipitating. The log saturation of vivianite ranges from -2.3 to 1.7. Nriagu (1972) shows that in sulfide-generating anoxic environments, sulfide activities ($a_{\text{HS}^-} \geq 10^{-6}$ M) stabilize pyrite over a wide range of Eh and phosphate concentrations. Troup (1974) found mackinawite (Fe_{1+X}S), siderite (FeCO_3) and vivianite forming in high-

sulfide waters in lower Chesapeake Bay; therefore, all three are thought to control the behavior of phosphate, sulfide and ferrous iron. In low sulfide waters, as in Lake Erie, vivianite has an increased stability field (Nriagu, 1972). The ferrous iron and phosphate concentrations in Lake Erie fall within the stability field of vivianite diagramed by Nriagu (1972). In low sulfide waters, vivianite is a possible control of phosphate and ferrous iron concentrations when phosphate concentrations are high and Eh is low. This conclusion is supported by Dell's (1973) finding of vivianite nodules in Lake Erie, if they are authigenic in origin.

The pore waters appeared to be supersaturated with respect to hydroxylapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) but according to Nriagu and Dell (1974), Emerson (1976) and Bray et al. (1973), this mineral does not seem to be controlling the ferrous iron and phosphate levels in interstitial waters. No clear explanation has been suggested but it appears that kinetic hindrance prevents the precipitation of hydroxylapatite (Rootare et al., 1962). Stumm and Leckie (1971) showed that its precipitation is accelerated in the presence of calcium carbonate. In Lake Erie, where calcium carbonate is low due to the noncalcareous nature of the sediments, the pore waters appear to remain supersaturated with respect to hydroxylapatite and not in equilibrium with the mineral phase.

The pore waters were also supersaturated, especially deeper in the cores, with respect to siderite. Emerson (1976) observed a ten-fold supersaturation of iron with respect to this mineral below 10 cm in the sediment in the Greifensee, Switzerland. The formation of the iron bicarbonate complex, FeHCO_3^+ , was suggested to explain the supersaturation (Larson, 1967), but Singer and Stumm (1970) found this complex to be unimportant. They suggested a larger equilibrium constant but this does not sufficiently explain the degree of supersaturation. Complexation by simple organics may contribute to increasing the degree of ferrous iron supersaturation, but a much stronger complexing agent that it Fe(II)-specific must be identified if organic complexation is to be significant (Emerson, 1976; Cardiner, 1974). A high level of humic and fulvic acids was found in the superficial sediments of Lake Erie (Kemp, 1972); these acids may be the strong Fe(II)-specific complexing agents.

Throughout the central basin of Lake Erie, pore waters were generally

supersaturated with respect to vivianite and siderite. This relationship was studied by Troup (1974) in Chesapeake Bay and the following replicates his approach.

If two mineral species are in equilibrium their equivalent free energies of formation should be equal, i.e.:

$$\Delta G'_{\text{siderite}} = \Delta G'_{\text{vivianite}} \quad (20)$$

The definitions of $\Delta G'$ and IAP given in equations (16) and (18) respectively, substituted into equation (20), yield

$$\frac{1/3 \log a_{\text{Fe(II)}} a_{\text{PO}_4}^{3-2}}{K_{\text{SP (VIV)}}} = \frac{\log a_{\text{Fe(II)}} a_{\text{CO}_3}^{2-}}{K_{\text{SP (SID)}}} \quad (21)$$

Simplification and rearrangement gives

$$\frac{a_{\text{PO}_4}^{3-2}}{a_{\text{CO}_3}^{2-3}} = \frac{K_{\text{SP (VIV)}}}{K_{\text{SP (SID)}}} = K \quad (22)$$

A linear relationship between carbonate and phosphate results by taking the logarithm of and rearranging equation (22)

$$\log a_{\text{CO}_3}^{2-} = 0.67 \log a_{\text{PO}_4}^{3-} - 0.33 \log K \quad (23)$$

$$\log a_{\text{CO}_3}^{2-} = 0.67 \log a_{\text{PO}_4}^{3-} + 1.35 \quad (24)$$

Graphically, the line described by equation (24) represents the equilibrium between siderite and vivianite stability fields.

Siderite is thermodynamically more stable at high activities of CO_3^{2-} and low activities of PO_4^{3-} , and vice versa for vivianite. Figure 14 shows equation (24) and the activities of carbonate and phosphate from the interstitial waters of Lake Erie. Since a majority of the points parallel the theoretical boundary, siderite equilibrium with vivianite in Lake Erie pore waters is implied.

Thermodynamic Tendency for the Precipitation of Zinc, Cadmium and Lead Minerals

The zinc concentrations in the interstitial waters are a couple of orders of magnitude greater than those of either cadmium or lead and may therefore be controlled by some inorganic precipitate. The ion activity

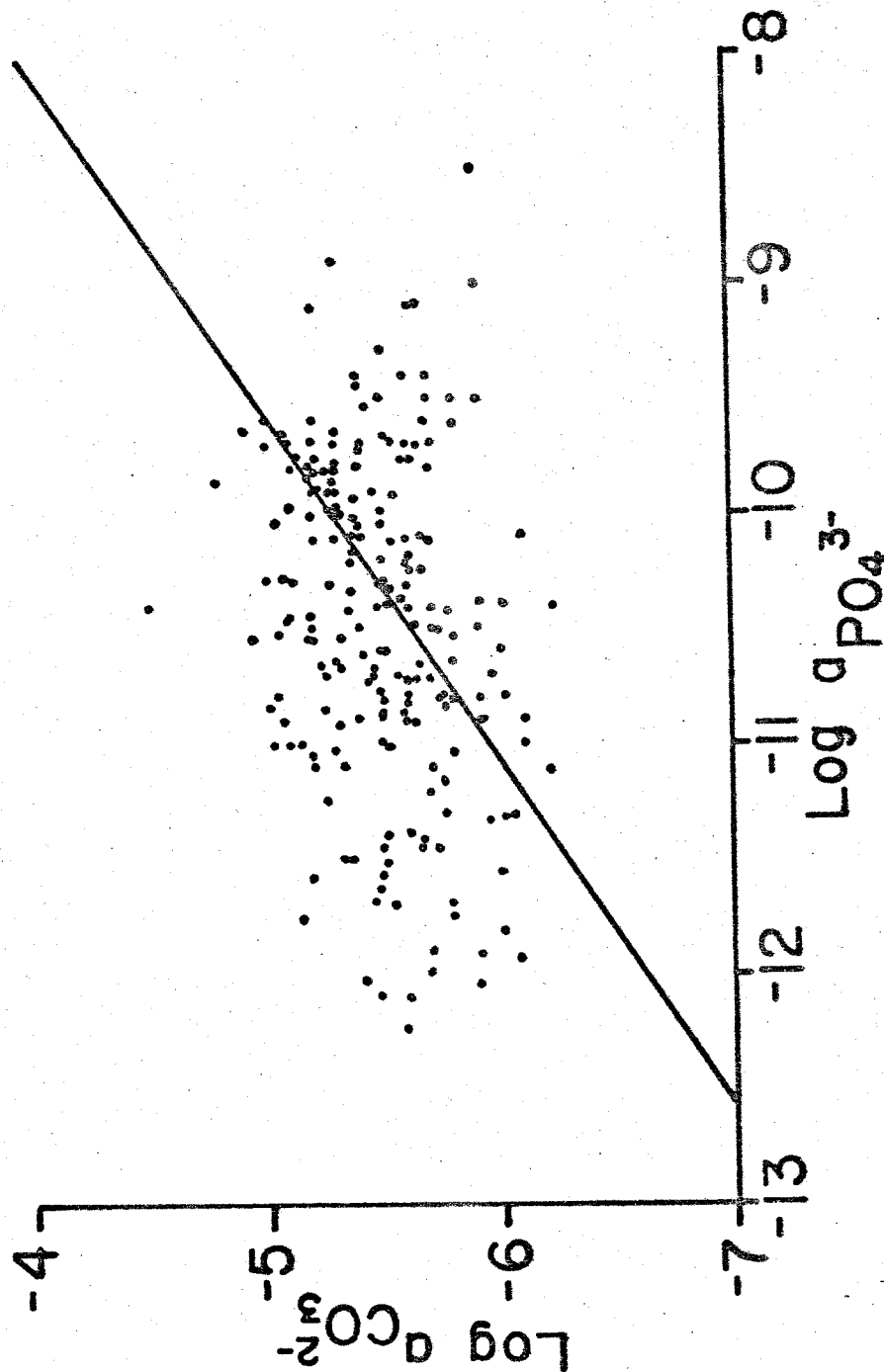
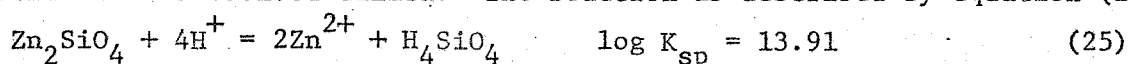


Figure 14. CO_3^{2-} and PO_4^{3-} activities in all the interstitial waters of this study. The line represents the theoretical equilibrium between siderite and vivianite. Note that some of the scatter is due to the inclusion of all the data, and not just from the deeper portions of the cores.

product of ZnS cannot be calculated since sulfide is undetectable. Hem (1972) considered solution mineral equilibria of $\text{Zn}(\text{OH})_2$ (s), ZnCO_3 (s), and willemite, Zn_2SiO_4 , and suggested willemite equilibria as a possible control of zinc concentrations in low sulfide waters. Nriagu (1973) suggested control of zinc levels of α hopeite, $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. Table 4 provides the pertinent thermodynamic data for the considered mineral species.

Pore waters were generally undersaturated with respect to zinc and carbonate by orders of magnitude and did not approach equilibrium with α hopeite, $\text{Zn}(\text{OH})_2$ (s) or ZnCO_3 (s). Lake Erie interstitial waters are, however, only slightly undersaturated with respect to willemite. The precipitation of willemite is very responsive to the pH of the pore waters and less so to the concentration of dissolved silica. The reaction is described by equation (25).



With the substitution of a large zinc concentration and high pH, the pore waters are undersaturated by only one order of magnitude with respect to willemite. Only the presence of authigenic willemite in the sediments could confirm its precipitation from the interstitial water, and it is unlikely that it could be detected due to the low interstitial zinc concentrations and probable poor crystallinity.

Cadmium concentrations in the interstitial waters of Lake Erie are very low, ranging from $10^{-7.7}$ to $10^{-9.0}$ M. Since Cd does not form inorganic complexes in pore waters in Lake Erie, the free Cd is approximately equal to the total concentration. Even with the small amount of complexation, log saturation values from this study indicate that pore waters are undersaturated by 2-3 orders of magnitude with respect to CdCO_3 (s) and $\text{Cd}_3(\text{PO}_4)_2$ (s), despite the fact that the solubility of CdCO_3 (s) is one-twentieth that of ZnCO_3 (Hem, 1972).

The concentration of free lead in Lake Erie pore waters is very low due to lead's tendency to form soluble complexes under the conditions prevalent in pore waters. Greater than 90 percent of the soluble Pb is complexed, resulting in activities of free Pb less than 10^{-10} M. With such a low activity, the Lake Erie pore waters were undersaturated by an order of magnitude or more with respect to hydroxypyromorphite, $\text{Pb}_5(\text{PO}_4)_3\text{OH}$, PbCO_3 , $\text{Pb}(\text{OH})_2$ and PbO .

Hem and Durum (1973) concluded after collecting nationwide values for lead concentrations that surface waters are near saturation with respect to the precipitation of cerussite, PbCO_3 . This is most likely an erroneous conclusion since they did not consider soluble inorganic complexes, particularly PbCO_3 , which Ernst et al. (1961) suggested could be partially formed from PbO_2 as a result of increased anaerobic fermentation of plant material.

From free energy of formation values, Nriagu (1974) suggested that hydroxypyromorphite and diagenetic calcium apatites may be important in controlling phosphate in freshwater systems. However, he used an activity for lead equal to 10^{-6} M. This is larger than the lead activities determined in this study by 3-4 orders of magnitude. The log saturation of hydroxypyromorphite was about -1 and, therefore, this precipitate is not a likely control of lead and phosphate concentrations in Lake Erie.

TABLE 5

EFFECT OF CHANGES IN pH ON SOLUBLE COMPLEXATION OF TRACE METALS (ALKALINITY=CONSTANT)*

Sample Number	pH	Alkalinity	Fe	Zn	Cd	Pb
Total Metal Concentration (moles/l)			1.44×10^{-4}	1.95×10^{-7}	2.94×10^{-10}	1.11×10^{-8}
1	7.02	$2.57 \times 10^{-3}M$	17.4	Percent complexed metal 38.9	1.0	92.3
2	7.26	"	26.4	43.6	2.0	95.2
3	7.31	"	28.5	45.1	2.4	95.7
4	7.33	"	29.2	46.2	2.4	95.8
5	7.35	"	29.9	26.7	2.4	96.0
6	7.47	"	35.4	51.3	3.4	96.9
7	7.62	"	43.8	57.4	4.8	97.8
8	7.82	"	54.2	68.2	8.2	98.6
9	7.95	"	61.8	71.3	11.2	98.9

*Example used alkalinity values of sample IV-80-5 and pH values for IV-80-1 through 9.

TABLE 6

EFFECT OF CHANGES IN ALKALINITY ON SOLUBLE COMPLEXATION OF TRACE METALS (pH = CONSTANT)**

<u>Sample Number</u>	<u>pH</u>	<u>Alkalinity</u>	<u>Fe</u>	<u>Zn</u>	<u>Cd</u>	<u>Pb</u>
Total Metal Concentration (moles/l)			1.44×10^{-4}	1.95×10^{-7}	2.94×10^{-10}	1.11×10^{-8}
1	7.35	2.38	29.9	Percent complexed metal		
2	"	2.61	"	45.1	2.4	95.9
3	"	2.55	"	47.2	"	96.0
4	"	2.63	"	46.7	"	"
5	"	2.57	"	47.2	"	"
6	"	3.20	"	46.7	"	"
7	"	3.39	"	51.2	"	96.3
8	"	3.36	"	53.3	"	96.4
9	"	3.55	"	53.3	"	"

**Example used pH values of sample VI-80-5 and alkalinity values for IV-80-1 through 9.

SECTION 10

OTHER POSSIBLE CONTROLS FOR ZINC, CADMIUM AND LEAD

Sulfides

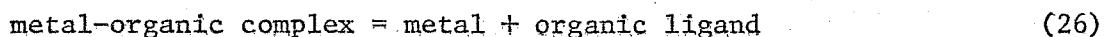
In contrast to the behavior of iron, metal carbonates and phosphates do not explain the concentrations of cadmium, zinc and lead. However, sulfide may be important in regulating their concentrations since zinc, cadmium and lead sulfides are less soluble than mackinawite, Fe_{1+x}S . The free sulfide level is below the detection limit of the sulfide electrode, i.e., less than 10^{-14} sulfide at pH 7. Total sulfur concentration, therefore, is less than 10^{-6} M. Because the overlying water contains 3×10^{-4} M sulfate and total sulfide is less than 10^{-6} M, dissolved sulfur is not conserved, providing the pore waters have an oxidation-reduction potential below the sulfate-sulfide stability boundary. Sulfide may precipitate as metal sulfides. Mackinawite is thought to be important in controlling the ferrous iron and sulfide levels in some Chesapeake Bay sediment pore waters (Troup, 1974) but does not seem to control ferrous iron concentrations in sediment pore waters in Lake Erie. Since sulfide activities could not be measured directly, they were calculated indirectly from the metal-sulfide solubility equilibria expressions and metal activities. All the sulfide activities fell between $10^{-18.6}$ and $10^{-16.1}$ M but were not equal or consistently covariant with depth. Thus, control of metal concentrations by sulfide is not obvious. By substituting a sulfide activity of 10^{-17} M into the cadmium sulfide equilibrium expression, cadmium equals $10^{-8.9}$ M, a realistic value based on data from this study. Further investigation of the levels of sulfide in the interstitial water is warranted. Possibly, the varying amounts of organic complexation not identified in this study can account for the inconsistent sulfide concentrations.

Organic complexation

Neither inorganic complexation nor mineral-solution equilibria with carbonate and phosphate adequately explain the trends exhibited by zinc, cad-

mium or lead concentrations, as they do in the case of ferrous iron. Possibly organic complexation is important in solubilizing the trace metals (Rashid and Leonard, 1973). After analyzing the top centimeter of Lake Erie sediments Kemp (1969) found that humic and fulvic matter comprised 30 percent of the total organic carbon and humin comprised about 60 percent. Nissenbaum et al. (1971) reported that polymerized organic matter accounts for about half of the total dissolved organic matter in the interstitial water in Saanich Inlet sediments, and this matter was found to be high in trace metals, especially iron, copper and zinc. Fulvic and humic acids complex metals at carboxyl and phenolic hydroxyl sites and, when present, are probably responsible for the increased solubilities of trace metals (Gamble and Schnitzer, 1973; Rashid and Leonard, 1973).

Simple organics, i.e., amino acids and hydroxycarboxylic acids, do not significantly complex trace metals relative to inorganic complexation in sulfidic marine waters (Gardner, 1974) but may be important in a low sulfide system. Gardner examined sulfidic waters where bisulfide is believed to tie up essentially 100 percent of the soluble metals. A percentage of the free cations is complexed with simple organics, which is small compared to the total metal complexed. In low sulfide systems, where the bisulfide complex is comparatively small, a significant portion of the metal is complexed with simple organics if the same ratio for organic complexation in sulfidic waters is used in the low sulfide system. Formation of a metal-organic complex follows the reaction



which is defined by the equilibrium expression (27)

$$K = \frac{(\text{metal})(\text{organic ligand})}{(\text{metal-organic complex})} \quad (27)$$

Thus, the ratio of free metal to metal-organic complex is independent of sulfide activity. Gardner's reasoning is shown in Table 7 in addition to calculations for complexation in the present study, a low sulfide system.

For the sample Zn calculation, 20 percent of the zinc is organically complexed $\frac{10^{-6.1}}{10^{-5.4}}$ (100). The amount totally complexed is there increased from 50 percent $\frac{10^{-5.7}}{10^{-5.4}}$ (100) to 71 percent $\frac{10^{-5.55}}{10^{-5.4}}$ (100).

Gardner (1974) concluded that simple organics do not complex significant amounts of metals due mainly to the presence of metal bisulfides in high sulfide waters. However, the calculations in Table 7 indicate that if simple organics are present in low sulfide waters in similar concentrations, they may contribute to the solubilities of the trace metals, especially in the zone of intense biodegradation. Complexation with simple organics is insignificant for Pb, which is highly complexed with inorganic ligands and for Cd, which still exists predominantly in the free state, but is significant for Zn, increasing the amount of total complexation by up to 40 percent.

The metals in the surface pore waters may result from (1) release of adsorbed cations from unstable hydrous oxides under reducing conditions, (2) release of the cation from a mineral surface due to a change in adsorbing capacity under low pH and low alkalinity conditions, (3) organic complexation of released metals from hydrous oxides, and (4) release of metals from organic material.

For interstitial water in marine sediments, Brooks, et al. (1968) believe that it is not improbable that the increased content of the three metals (Cd, Zn and Cu) in the interstitial water can be supplied completely from the marine biosphere. They determined that the cadmium and copper concentrations could be accounted for by decomposing biological matter. Since allochthonous organisms are the source of 90 percent of the organic matter in Lake Erie (Harlow, 1966), biological matter could supply the pore waters with the high levels of metals at the top of the sediment column. Zinc is concentrated in the biota, both on surfaces of and within algae and other organisms, and is released during biodegradation (O'Connor, 1968). Since up to 66 percent of the total zinc complexed with proteins is loosely bound, it may be leached, transported and become available for mineral deposition (Zajic, 1969).

The ferrous iron concentrations in the Lake Erie pore waters are 2000 times greater than those found in Santa Cruz pore waters; it is not unreasonable to suspect that the release of adsorbed ions from ferric hydroxides under reducing conditions is also an important source of trace metals (Duchard et al., 1973). Lead and zinc often showed surface maxima in the cores studies, which may be due to their release from hydrous oxides under reducing conditions (O'Connor, 1969). Decaying organic matter, most concentrated in the surficial sediments, may then complex the metal ions. Upon reduction of

hydrous oxides with the addition of plant material, Kee and Bloomfield (1961) found that the metals were present mostly as soluble organic complexes which could not be removed from the fermented extracts by cation exchange resins.

Many of the cores show maximum metal concentrations at the surface and from 5-10 cm below the surface. Walters and Wolery (1974) report a surface minimum of trace metals in the sediments and a maximum at 7-10 cm in the sediments. The interstitial maximum at 7-10 cm may be caused by solution-mineral equilibria and the surface interstitial maxima may be the result of intense biodegradation and ferric hydroxide reduction, which both release metals to the pore waters. Humic by-products, generated by biodegradation, can complex trace metals and hold them in solution. Cline and Upchurch (1973) explain the surface maxima by the upward transport of metals on bubble surfaces which have been found to concentrate trace metals. They suggest that the gases released by bacteria to form bubbles in sediments could act as a transport mechanism for heavy metals released by the same bacteria from chelation sites on the organics. Upon reaching the biologically active surface sediments, the metals are immobilized as they form new complexes or inorganic precipitates. In Lake Erie most organics, such as lipids, proteins and carbohydrates, disappear in an exponential manner with depth in the first centimeter of sediment as chemi-specific bacteria metabolize functional groups capable of complexing cations (Cline and Upchurch, 1973). Contact of the adsorbed metals with the complexing organic matter may cause the metals to become immobilized in the sediment rather than passing out of the sediments on the bubble surfaces. Since many of the cores collected contain pockets of gas, the upward movement of gas bubbles (e.g., CO_2 , NH_3 , CH_4) carrying adsorbed metals may be a significant mechanism of upward metal transport.

TABLE 7
COMPARISON OF THE EXTENT OF ORGANIC COMPLEXATION
IN FRESHWATER AND MARINE SYSTEMS

	log a in moles/l		
	<u>Pb</u>	<u>Cd</u>	<u>Zn</u>
<u>Gardner's Study (marine--high sulfide)</u>			
Total cation	-9.0	-7.6	-6.0
Total inorganically complexed in sulfide system	-9.0	-7.6	-6.0
Free cation	-15.7	-15.6	-13.8
Total organically complexed	-16.1	-16.9	-14.2
Free/organically complexed	+0.4	+1.3	+0.4
<u>This Study (fresh water--low sulfide)</u>			
Total cation	-9.0	-8.0	-6.0
Total inorganically complexed	-9.0	-9.3	-6.7 to -6.2
Free cation	-10.7 to -10.0	-8.02	-6.4 to -6.1
Total organically complexed	-11.1 to -10.4	-9.32	-6.8 to -6.5
Total complexed	-9.04 to -9.0	-9.0	-6.3 to -6.1
<u>Samples values calculated for Zn, II-43-6</u>			
	log a _{Zn}		
Total cation	-5.4		
Free cation	-5.7		
Total inorganically complexed	-5.7		
Total organically complexed	-6.1	$= \frac{10^{-5.7}}{10^{0.4}} = \frac{\text{free}}{\text{free/org. complex from Gardner (1974)}}$	
Total complexed	-5.55		

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APPENDIX A

ANALYTICAL PROCEDURES FOR THE DPASV DETERMINATION OF TRACE METALS

Preparation of the Sample for Trace Metal Analyses

One of the problems with much of the previous work on trace metals is that the data are not all that reliable because of the difficulties encountered in the sampling and analytical procedures. Therefore, it is necessary that the procedures which are used be carefully checked and evaluated. Included in this section is a summary of our methods for the trace metal analyses.

1) Preheating

Once the samples were collected, they were capped and refrigerated at 3°C until the time of analysis at which time they were acidified with Aristar nitric acid to pH 1. Samples which were collected at a later date (1976 on) were acidified immediately after collection onboard ship. The following preheating step could then be omitted. To dissolve any particulate matter that had formed, the sample bottles were heated in a water bath at 50°C for 24 hours. Heating at 60°C softened the plastic and resulted in a decrease in trace metal concentrations. Probably the chemical structure of the plastic expands at higher temperature and traps metals. The results of an adsorption-desorption experiment whereby the sample and containers were heated for 24 hours at 30, 40, 50 and 60°C are given in Table A-1.

TABLE A-1

ADSORPTION-DESORPTION EFFECTS, RESULTING FROM HEATING SPIKED BLANKS
AND CONTAINERS FOR 24 HOURS AT 20, 40, 50 and 60°C

	<u>M</u>	<u>Cd</u>	<u>Pb</u>
20°C (t = 0)	19.4	20.7	10.4
20°C (t = 24 hrs.)	20.2	19.7	11.6
40°C " "	23.4	21.6±2%	10.2±3.4%
50°C " "	24.1±2%	19.8	11.9
60°C " "	17.4±2.2%	18.9	10.8

2) Digestion

Because the earlier samples sat unacidified for as long as eight months before analysis, it was necessary to digest the samples. At times, a surface scum formed in the samples, so a representative aliquot could not be pipetted from the bottle. Since the bottles had not been opened, the scum was formed from the sample, and did not represent contamination. Digestion of the samples also breaks down metal complexes and aids in complete solubilization of the metals. Hence, in order to obtain a total concentration by DPASV, digestion was also found to be necessary for the acidified samples.

Sodium hypochlorite and hydrogen peroxide, separately, were also tried as possible digestants since their probable low metal content would introduce a minimal amount of contamination. Bleach proved unsatisfactory since sample peak heights increased with successive scans on the DPASV. Possibly the excess bleach oxidized the metal off the Hg electrode and interfered with the analysis.

Complete digestion with 1 ml of Aristar nitric acid per 10 ml sample followed by evaporation to dryness was chosen. Evaporation decomposed the nitric acid without appreciably changing the sample composition and pH. Also, the samples could be stored dried until the time of analysis.

A test was performed by DPASV to compare the sensitivities of the trace metals of diluted digested versus undigested spiked blanks. The results of this test, shown on Table A-2, show that digestion enhanced the sensitivities of the trace metals in DPASV.

TABLE A-2
SENSITIVITIES OF METALS IN DIGESTED AND UNDIGESTED BLANKS WITH SPIKES

Metal	Sensitivity = $\Delta i / \Delta v$ / ppb	
	Digested Sample	Undigested Sample
Zn	1.25	1.14
Cd	1.53	1.17
Pb	1.03	0.86
Cu	2.04	1.65

3) Dissolution and dilution

At the time of analysis, the dried sample was dissolved in 10 ml 0.1 N HNO_3 and 100 μl hydroxylamine hydrochloride ($\text{HN}_2\text{OH}\cdot\text{HCl}$) for 20 minutes at 80°C in an acid-washed glass beaker. This heating of the solution at pH 1 dissolved the Fe(III) before it was reduced to Fe(II) by the reducing agent, since higher pH's kinetically favor the oxidation and precipitation of Fe(III) . Once the Fe(II) was reduced and complexed, the pH of the sample could be raised without the oxidation of Fe(II) .

An experiment was run to determine whether to add the hydroxylamine hydrochloride before or after heating. When the solution was not heated, a hump in the DPASV scan appeared between the Pb and Cu peaks, but heating with hydroxylamine hydrochloride flattened the baseline. Therefore 100 μl hydroxylamine hydrochloride was added to 10 ml of the acid-prepared sample solution before heating.

Once heated, the 10 ml of acid and sample was diluted with 15 ml of 0.2 N ammonium citrate according to the suggested procedure of Princeton Applied Research (1975). Ten ml of sample plus 15 ml 0.2 N ammonium citrate buffer (pH 3.6) yielded a solution pH of 3.00 ± 0.02 . The pH was further adjusted with purified ammonium hydroxide using the glass membrane part only of a standard combination electrode. The pH electrode was standardized against the reference electrode in the reaction cell and was connected, only during a reading, to a Fisher Accumet Digital pH/mv meter. During the operation of the instrument, the pH electrode was disconnected to lessen the chance of electrical interference with the reaction cell.

4) The reagent

The original intent of the project was to study complexation of trace metals in the interstitial water. Therefore, a method of sample preparation which closely duplicated the original natural water system was sought. But significant time passed between sampling and analysis so that the sample no longer resembled the natural system. The entire sample was digested and analyzed for total metal concentration only. Since speciation was no longer to be investigated, the need for a chemical system approximating the natural system was no longer necessary, i.e., a system with pH and alkalinity of natural waters. At the pH of natural waters, Fe(II) oxidizes to Fe(III)

instantaneously and, in the interstitial water where Fe(II) concentration is high, Fe(III) interferes with electrolytic behavior of the cell.

Fresh water samples cannot be analyzed directly since the ionic strength is not high enough for current conductance in the electrolytic cell of the ASV instrument. Thus, the sample must be prepared in an ionic medium. A sodium acetate buffer looked promising since its maximum buffering capacity was at pH 5-6 which is close to that of natural waters. Background noise was minimal and sensitivities were high. But this pH was too high for samples high in iron. The interference from the ferric iron was insurmountable even with the addition of the reducing agent, hydroxylamine hydrochloride, to the acid-sample solution.

Alternatively, ammonium citrate was tested since it has a maximum buffering capacity at pH 3.03, a pH at which Fe(II) is more stable when reacted with hydroxylamine hydrochloride. Taylor (personal communication) said that ammonium citrate buffer is preferred for high iron samples for the following additional reasons:

- 1) better reproductibility than sodium acetate
- 2) complexes Cu and Fe better (also Lerman and Childs, 1973)
- 3) less interference from chloride (more important in marine than fresh water).

Also, unpurified sodium citrate contained less than 1.5 ppb Zn and Pb and less than 0.25 ppb Cd, so that purification was unnecessary. Sodium acetate on the other hand was very contaminated with trace metals, particularly Cu, and even after electrolytic purification was not of acceptable purity.

One problem with ammonium citrate is that the Fe-citrate peak (form of complex undetermined) overlaps the copper peak. The Fe(II)-Fe(III) peak normally lies to the positive side of the mercury peak but in citrate it lies between the Hg and Cu peaks. With iron concentrations in the ppm range, the small Cu concentration of 2-10 ppb is seen as a shoulder off the Fe peak or is completely covered. Consequently, Cu was not determined for most samples.

5) Choice of pH of the reaction

The best operation conditions for ammonium citrate is at a pH of about 3-3.6 since ammonium citrate has a maximum buffering capacity at pH 3.03. The peak corresponding to the hydrogen potential moves in a positive direction and begins to interfere with the Zn peak at pH's less than 3. At pH's

greater than 3.0 the Fe-citrate and Hg peaks interfere with the Cu peak. A pH of 3.00 minimized interferences and therefore was chosen.

6) Instrumental conditions for ASV scan

The best instrumental conditions for the concentrations observed in the interstitial water are described below. A new Hg drop was dialed for each scan even though it was possible to reuse a drop. If a drop were reused, it would be conditioned whereby a potential less positive than that of Hg was applied to the solution resulting in the oxidation of all metals with lower potentials than Hg. Since a new drop was used each time, no conditioning was necessary. Next, metals were deposited on the Hg electrode at -1.2 volts for 120 seconds. When metal concentrations were high, a 60 or 90 second deposition time was sufficient to give a measurable peak. The solution was stirred at a constant rate throughout the deposition step since metal deposition is a function of liquid surface area exposed to the electrode. Following this step, the solution was equilibrated for 15 seconds during which stirring was terminated and the solution allowed to settle. Modulation amplitude was set at 25 mv. A higher amplitude (50) enhanced the sensitivity, but the lower setting was preferred since peaks were narrower. This allowed better resolution between Pb and Cd whose oxidation potentials differ only slightly. The sensitivity setting varied depending on the metal and its concentration in the sample. Zinc was generally analyzed at a less sensitive setting of 1 or 2 μ A where Cd and Pb were analyzed at 0.5 or 0.2 μ A. The setting was changed during a scan without interrupting the stripping or oxidation process as long as approximately 10 seconds was allotted for equilibration of the electrical circuitry at the new setting. With a scan rate of 5 mv/sec, one scan was completed within 11 minutes. Oxygen which would interfere with the stripping and reduction process was purged from the system with nitrogen for 10 minutes initially and one minute between spikes. Also, nitrogen constantly blanketed the solution to further reduce oxygen penetration.

7) Precision and accuracy

One difficulty with using ASV in this study is the lack of standards with which to compare the samples. Rock standards cannot be used since a preparation procedure would involve dissolution of the rock, a procedure which is drastically different from the one used for interstitial water and

would introduce too great a contamination risk. Instead, sample solutions were internally standardized by repeated spikings with diluted standards. Standards were prepared daily from 50 ppm stock solutions according to the PAR methods (1975). Each ASV run was repeated until a consistent reading was obtained (less than 10% variability) and each solution was spiked three times. The average peak height of the spikes minus sample were plotted versus concentration to make a calibration curve from which the sample concentration could be read directly. Each sample was diluted to 25 ml, enough for two 10 ml aliquots which were run to insure no contamination resulted from pipetting. One of the aliquots was then standardized. Two blanks were prepared according to the sample digestion procedure for each batch of ten samples and run before the samples.

Another reason for internal standardization of the samples was the possibility of matrix effects in the interstitial water. Iron and probably organics decreased the sensitivity of metal concentration readings. Organics, which are greater in surficial interstitial waters (Weiler and Chawla, 1968), probably interfered with the reproducibility of the scans. Possibly, some organics were not decomposed by the digestion procedure.

Several tests were performed to evaluate the precision and accuracy of the entire procedure. The concentrations of the sample blanks over a period of several months were compiled and the results are given in Table A-3.

TABLE A-3
CONCENTRATIONS OF METALS IN BLANKS
n = 37

<u>Metal</u>	<u>Mean (ppb)</u>	<u>Standard Deviation (ppb)</u>
Zn	1.27	.57
Cd	.03	.06
Pb	.59	.22
Cu	.94	.36

A similar study on a synthetic sample was conducted. A sample consisting of (approximately) 30 ppb Zn, 3 ppb Cd, 4 ppb Pb, and 20 ppb Cu was made and aliquots withdrawn over a period of about 7 months and analyzed. The results are given in Table A-4.

TABLE A-4
CONCENTRATIONS OF METALS IN SYNTHETIC SAMPLE
n = 12

<u>Metal</u>	<u>Mean (ppb)</u>	<u>Standard Deviation (ppb)</u>
Zn	24.64	2.95
Cd	3.93	2.39
Pb	4.33	2.80
Cu	13.97	4.13

This test gives a realistic estimate of the accuracy and precision of the entire procedure. The precision is good, considering the concentration levels of these particular metals. It may be improved somewhat by using a higher purity nitric acid in the digestion procedure and even stricter controls against contamination (using a laminar flow hood, for example). The accuracy is difficult to evaluate. The differences between the measured concentrations and the 'true' concentrations in the sample could have resulted from 1) the 'true' concentrations successive dilutions involved in making the standards, 2) loss (or gain) of metal by adsorption (or desorption) on the sides of the volumetric and storage bottles during the sample preparation and storage, and/or 3) a statistically significant inaccuracy in the analytical procedure and method. Irregardless, the data are reliable enough to permit their interpretation and use in a thermodynamic model of the system.

Sample Number	Sampling Interval (cm)	pH	Carb. Alk. meq/L	Chloride meq/L	Fe(tot). µg-at/L	SRP µg-at/L	NO ₂ ⁻ - NO ₃ ⁻ µg-at/L	NH ₄ ⁺ µg-at/L	Zn ²⁺ ng-at/L	Cd ²⁺ ng-at/L	Pb ²⁺ ng-at/L
Station II-42											
0	O.W.		1.60	0.623		0.032	1.8ng-at/L	0.067	nd	nd	nd
1	0-2.5		2.55	0.638		53.3	65.2	143	137	7.47	82.4
2	2.5-4.5		2.60	0.638		214	83.7	262	279	3.29	42.1
3	4.5-6.0		2.60	0.653		222	152	269	322	54.4	51.7
4	6.0-8.5		2.70	0.653		254	43.5	350	nd	nd	nd
5	8.5-11.0		2.78	0.653		247	51.1	338	220	28.1	42.0
6	11-17.5		2.86	0.653		299	46.7	395	nd	nd	nd
7	25-30		3.15	0.608		298	50.0	451	nd	nd	nd
8	35-40.5		3.25	0.638		291	48.0	388	nd	nd	nd
9	48-53		nd	nd		291	50.0	368	360	21.8	9.27
10	53-58		nd	nd		298	44.6	524	nd	nd	nd
Station II-43											
0	O.W.		1.79	0.653		DL	23.8	2.28	nd	nd	nd
1	0-1.5		1.77	0.608		80.7	60.7	171	139	25.4	19.2
2	1.5-4.25		2.06	0.653		209	60.7	298	332	3.47	17.3
3	4.25-6.5		2.51	0.653		205	60.7	291	171	2.22	3.57
4	6.5-8		2.76	0.683		172	60.7	275	56.0	2.76	25.6
5	8-11		2.78	0.668		171	71.4	253	187	4.72	15.0
6	15-18		2.95	0.668		221	71.4	340	397	9.70	6.90
7	25-28.8		3.19	0.623		190	64.3	353	582	3.56	8.45
8	35-41		3.46	0.579		207	71.4	386	nd	nd	nd
9	47-51.5		3.61	nd		253	64.3	439	nd	nd	nd
10	56.5-61.5		3.40	0.964		256	100	453	nd	nd	nd
Station II-47A											
0	O.W.		1.73	0.593		DL	0.0016	2.86	806	1.51	2.61
1	0-2.5		2.97	0.623		64.6	214	161	129	1.51	8.01
2	2.5-4		3.11	0.623		102	42.8	231	96.2	4.72	10.8
3	4-6.25		3.05	0.608		113	286	248	242	1.78	15.3
4	6.25-7.75		2.97	0.653		157	35.7	283	nd	nd	nd
5	7.75-10		nd	nd		nd	nd	nd	nd	nd	nd
6	15-18.3		3.25	0.534		135	286	289	nd	nd	nd
7	23-27.5		3.44	0.415		154	393	318	DL	3.83	13.0
8	32.8-37.5		3.63	0.430		136	393	301	nd	nd	nd
9	43-49		3.83	0.386		169	428	358	168	1.69	11.0
10	55-64		nd	nd		270	107	nd	nd	nd	nd

Key: SRP = Soluble Reactive Phosphate

nd = not determined

DL = Detection Limit

Sample Number	Sampling Interval (cm)	pH	Carb. Alk. meq/L	Chloride meq/L	Fe(II) µg-at/L	SRP µg-at/L	NO ₂ ⁻ - NO ₃ ⁻ µg-at/L	NH ₃ µg-at/L	Na µg-at/L	Mg µg-at/L	Ca µg-at/L	K µg-at/L	Mn µg-at/L
Station II-47	0 W.		1.72	0.593		DL	0.001	0.857	217	128	998		
Lat. 41°50'18"N	0-2.6		1.93	0.608		81.3	53.5	348	520	384	1190	93	58.2
Long. 82°12'48"W	2.6-5.6		2.35	0.638		250	71.4	328	488	362	1210	89	58.2
	5.6-6.7		2.29	0.638		239	104	353	478	455	1200	83	58.2
Depth: 19m	6.7-8.5		2.31	0.653		276	85.7	371	389	380	1220	79	58.2
Date: 25/VI/75	8.5-9.9		2.41	0.623		279	107	394					58.2
	14.6-17.7		2.70	0.600		282	86.7	437	478	461	1270	77	89.2
	21.2-25								488	383	1200		102
	41.5-44.7		2.74	0.608		282	96.4	436	484	545	1400	78	102
	44.7-50.0		3.28	0.504			50.0	161	446	526	1480	64	102
	50-58		3.07	0.504		281	100	460	498 ²⁺	348 ²⁺	1340 ²⁺	79	102
									Zn ng-at/L	Cd ng-at/L	Pb ng-at/L		
Station II-73	0 W.		1.83	0.638		DL	DL	1.5	nd	nd	nd		
Lat. 41°58'40"N	0-2.5		1.63	0.668		21.8	682	79	140	10.6	57.0		
Long. 81°45'25"W	2.5-4.75		2.14	0.668		118	571	393	225	14.9	53.6		
	4.75-6.75		2.37	0.638		236	446	521	20.9	12.4	41.9		
Depth: 23m	6.75-8.5		2.72	0.638		43.3	428	246	296	DL	9.12		
Date: 25/VI/75	8.5-11.0		2.70	0.593		156	732	407	824	12.4	20.1		
	15-17.8		3.17	0.564		50.4	971	264	847	49.6	22.3		
	25-30		3.40	0.356		52.0	1000	394	605*	20.1	26.2		
	35.5-41		3.67	0.356		54.2	946	318	nd	nd	nd		
	46-50.5		3.85	0.356		49.1	946	257	nd	nd	nd		
	50-61		4.06	0.356		53.3	1040	338	450	DL	12.5		
Station III-43	0 W.		1.78	0.550		DL	38.2	4.7	119	14.8	6.08		
Lat. 41°47'18"N	0-2	6.85	2.50	0.592	132	38.1	132	350	516	3.20	23.8		
Long. 81°56'42"W	2-4	7.30	2.54	0.536	171**	31.6	14.3	146	377	2.14	5.84		
	4-6	7.22	2.56	0.578	159	30.2	35.7	203	286	54.4	20.9		
Depth: 21m	6-8	7.10	2.41	0.522	127	36.5	114	191	1340	4.18	17.4		
Date: 12/VIII/75	8-9.5	7.06	2.70	0.592	128	29.5	114	204	331	96.1	7.72		
	12.5-16	7.02	2.67	0.468	115	30.7	42.8	186	325	3.02	13.0		
	20.5-26	7.21	3.07	0.509	117	58.1	114	385	nd	nd	nd		
	35-40.5	7.05	3.31	0.399	117	30.7	28.6	214	61.2	DL	0.24		
	45-49	7.35	3.20	0.330	117	26.8	42.8	241	nd	nd	nd		
	54-59.5	7.68	3.27	0.330	100	39.3	39.3	234	449	32.4	33.9		

Key: DL = Detection Limit
nd = not determined

SRP = Soluble Reactive Phosphate

Sample Number	Sampling Interval (cm)	pH	Carb. Alk. meq/L	Chloride meq/L	Fe(II) $\mu\text{g-at/L}$	SRP $\mu\text{g-at/L}$	$\text{NO}_2^- - \text{NO}_3^-$ $\mu\text{g-at/L}$	NH_3 $\mu\text{g-at/L}$	Zn^{2+} ng-at/L	Cd^{2+} ng-at/L	Pb^{2+} ng-at/L
Station III-46 Lat. 41°41'54"N Long. 82°05'12"W Depth: 19.5 m Date: 14/VIII/75											
0	O.W.	nd	2.00	0.564	DL	.258	35.9	1.21	nd	nd	nd
1	0-2	7.38	2.29	0.564	136	27.9	28.6	196	402	4.63	4.44
2	2-4	7.48	2.31	0.524	85	18.9	14.3	131	532	12.6	DL
3	4-6	7.46	2.56	0.551	102	21.6	14.3	140	1030	8.81	4.25
4	6-8.5	7.64	2.66	0.511	85	21.6	21.4	178	399	20.1	2.65
5	8.5-10	7.66	2.81	0.564	99	22.3	25.0	203	1.5	7.92	2.94
6	13-15.4	7.80	3.20	0.416	80	29.4	25.0	161	nd	nd	nd
7	20-24	8.00	3.33	0.483	67	23.6	21.4	130	444	6.41	DL
8	30-34.5	7.80	3.54	0.390	59	21.8	14.3	139	nd	nd	nd
9	40-44.5	8.22	3.68	nd	37	27.4	25.0	207	881	7.21	1.40
10	50-54.5	8.04	3.93	0.201	28	26.6	25.0	163	nd	nd	nd
Station III-80 Lat. 41°45'N Long. 81°43'W Depth: 22m Date: 15/VIII/75											
0	O.W.	nd	nd	nd	nd	0.28	47.4	2.8	139	11.8	6.03
1	0-2	7.13	2.32	0.578	nd	26.3	17.8	137	nd	nd	nd
2	2-4.75	7.15	2.36	0.536	nd	21.8	14.0	282	653	2.58	31.2
3	4.75-7	7.39	2.67	0.592	nd	37.9	53.5	250	169	2.22	7.09
4	7-9	7.46	2.78	0.550	nd	35.5	71.3	203	241	DL	2.41
5	9-10	7.57	2.84	0.578	nd	32.6	107	209	430	3.47	9.46
6	13-15	7.62	3.03	0.523	nd	29.4	60.7	188	nd	nd	nd
7	20-23.8	7.68	3.12	0.536	nd	26.3	92.8	190	347	7.56	22.1
8	30-34.3	7.75	3.18	0.454	nd	35.3	57.1	203	nd	nd	nd
9	40.5-44	7.75	3.22	0.454	nd	37.8	50.0	223	300	12.9	7.05
10	50-54	7.82	3.37	0.399	nd	nd	75.0	250	nd	nd	nd
Station III-73 Lat. 41°58'40"N Long. 81°45'25"W Depth: 24m Date: 13/VIII/75											
0	O.W.	nd	nd	0.499	DL	.030	nd	5.0	nd	nd	nd
1	0-2	7.06	3.40	0.550	119	21.0	35.7	131	1090	12.6	24.2
2	2-4	7.18	3.44	0.550	73	16.9	17.8	137	742	4.45	14.0
3	4-6	7.30	3.57	0.629	96	10.7	50.0	203	887	4.36	8.59
4	6-8.5	7.22	3.71	0.539	225	21.0	67.8	263	683	28.6	9.60
5	8.5-10	7.27	3.99	0.488	301	18.1	278	284	1640	37.3	10.9
6	13-15.5	7.32	4.74	0.488	285	20.0	53.5	300	nd	nd	nd
7	20-24.5	7.35	3.61	0.398	387	19.4	4.6	334	767	2.05	15.9
8	30-34.5	7.50	3.82	0.304	303	29.7	4.6	381	nd	nd	nd
9	40-44.5	7.52	4.01	0.322	364	16.6	4.3	403	928	20.8	11.1
10	50-54.5	7.40	4.19	nd	365	16.1	4.6	423	nd	nd	nd

Key: SRP = Soluble Reactive Phosphate
nd = not determined
DL = Detection Limit

Sample Number	Sampling Interval (cm)	pH	Carb. Alk. meq/L	Chloride meq/L	Fe(II) µg-at/L	SRP µg-at/L	NO ₂ ⁻ - NO ₃ ⁻ µg-at/L	NH ₃ µg-at/L	Zn ng-at/L	Cd ng-at/L	Pb ng-at/L
Station III-42											
0	0.W.	nd	1.61	nd	DL	0.15	38.4	45.8	nd	nd	nd
1	0-2	7.09	1.67	0.685	170	60.4	28.6	134	361	12.2	17.1
2	2-4	7.08	2.10	0.645	158	19.4	25.0	143	375	33.1	9.42
3	4-5.5	7.37	1.96	0.658	160	33.1	42.8	278	nd	nd	nd
4	5.5-7.5	7.48	2.54	0.672	149	37.9	21.4	166	nd	nd	nd
5	7.7-9.5	7.48	2.43	0.698	143	32.6	14.3	232	458	25.0	25.8
6	13-17	7.60	2.60	0.752	157	31.8	17.8	242	nd	nd	nd
7	20-23.4	7.65	2.73	0.752	161	34.4	14.3	318	292	6.05	29.6
8	30-34.5	7.62	2.89	0.887	178	33.9	17.8	202	nd	nd	nd
9	40-44.5	7.68	3.02	0.954	209	34.4	21.4	268	394	27.2	14.9
10	50-54.5	7.67	3.13	0.994	184	38.9	25.0	252	nd	nd	nd
Station III-45											
0	0.W.	nd	1.93	0.604	DL	0.28	36.8	11.6	903	1.87	4.25
1	0-2	7.25	2.29	0.551	77	32.8	28.6	137	406	17.8	8.79
2	2-4	7.36	2.31	0.604	71	25.8	25.0	152	38.2	1.42	DL
3	4-5.5	7.45	2.56	0.524	78	21.0	17.8	142	582	9.88	1.64
4	5.5-6.8	7.53	2.66	0.591	93	23.2	25.0	224	539	9.79	15.0
5	6.8-8.5	7.60	2.81	0.470	109	19.7	28.6	225	766	8.63	22.3
6	8.5-11.3	7.68	3.20	0.564	105	25.0	32.1	195	806	8.27	17.2
7	15.2-19.8	7.70	3.33	0.483	78	24.7	25.0	242	nd	nd	nd
8	25.3-30	7.78	3.54	nd	81	28.6	35.7	281	281	11.7	6.08
9	35-39.8	7.83	3.68	0.403	73	35.5	50.0	332	nd	nd	nd
10	45-49.8	7.90	3.93	nd	61	25.5	42.8	138	881	26.7	30.2
Station IV-45											
0	0.W.		1.79	0.530	DL	0.13	45.0	3.43	nd	nd	nd
1	0-2	7.31	2.81	0.731	292	32.3	60.7	155	542	3.91	8.21
2	2-4	7.32	3.05	0.590	229	28.7	17.8	130	351	5.16	12.4
3	4-6.5	7.29	nd	0.604	78.6	24.2	14.3	98.9	863	1.96	10.7
4	6.5-8.7	7.40	2.96	0.618	77.9	22.3	21.4	98.2	516	0.98	2.27
5	8.7-10.3	7.57	2.96	0.660	63.2	31.0	50.0	111	206	1.96	10.5
6	15-19	7.70	3.11	0.660	66.1	26.3	28.6	163	172	2.40	5.79
7	25-29	7.63	3.46	0.832	75.9	33.9	21.4	148	122	2.84	10.1
8	35-40	7.73	3.24	0.747	72.7	35.5	57.1	142	501	5.34	8.30
9	45-50	7.74	3.72	0.905	68.6	39.4	25.0	153	295	18.9	8.01
10	55-60	7.83	3.74	0.962	76.8	37.1	35.7	178	248	26.5	25.2

Key: SRP = Soluble Reactive Phosphate

nd = not determined

DL = Detection Limit

Sample Number	Sampling Interval (cm)	pH	Carb. Alk meq/L	Chloride meq/L	Fe(II) µg-at/L	SRP µg-at/L	NO ₂ ⁻ - NO ₃ ⁻ µg-at/L	NH ₃ µg-at/L	Zn ²⁺ ng-at/L	Cd ²⁺ ng-at/L	Pb ²⁺ ng-at/L
Station IV-80											
0	O.W.	nd	1.80	0.685	DL	0.08	17.5	2.89	nd	nd	nd
1	0-2	7.02	2.38	0.657	87.2	24.2	129	162	454	8.19	DL
2	2-4	7.26	2.61	0.643	35.6	10.8	114	157	1240	7.30	23.0
3	4-6.25	7.31	2.55	0.657	98.5	18.3	67.8	152	DL	6.32	9.70
4	6.25-8.5	7.33	2.63	0.671	128	21.8	146	172	408	8.63	21.9
5	8.5-9.8	7.35	2.57	0.657	144	21.1	143	186	195	0.294	11.1
6	15-17.5	7.47	3.20	0.700	108	19.4	71.4	193	335	11.7	8.74
7	25-30.8	7.62	3.39	0.685	118	26.2	57.1	161	833	6.76	1.34
8	35.5-39.8	7.82	3.36	0.731	98.8	17.5	85.7	187	929	51.1	3.26
9	39.8-8-44	7.95	3.55	0.731	109	21.6	78.5	195	889	16.3	18.2
Station IV-73											
0	O.W.	nd	1.92	0.544	DL	0.16	29.1	3.28	nd	nd	nd
1	0-2	7.44	3.03	0.615	183	22.2	214	302	nd	nd	nd
2	1-4	7.50	3.30	0.643	201	15.8	125	284	nd	nd	nd
3	4-6	7.37	3.28	0.573	250	21.2	60.7	309	nd	nd	nd
4	6-8	7.48	3.41	0.615	308	17.9	39.3	302	nd	nd	nd
5	8-10.3	7.45	3.51	0.671	299	19.4	57.1	301	nd	nd	nd
6	13-18	7.52	3.95	0.544	265	19.4	28.6	314	nd	nd	nd
7	20-25	7.47	4.16	0.471	338	17.3	82.1	370	nd	nd	nd
8	30-35.3	7.43	4.60	0.344	325	6.62	35.7	389	nd	nd	nd
9	40-43.5	7.37	4.91	0.344	257	9.46	89.2	232	nd	nd	nd
Station IV-46											
0	O.W.	nd	1.88	DL	DL	0.13	7.0	5.9	60.6	0.267	3.19
1	0-2	6.95	2.26	24.0	24.0	15.8	125	143	868	16.5	6.13
2	2-4	7.15	2.30	22.5	22.5	16.7	71.4	155	679	2.67	3.91
3	4-5.25	7.35	2.49	18.0	18.0	19.9	50.0	195	258	6.05	5.07
4	5.25-7	7.47	2.53	19.4	19.4	19.4	57.1	162	385	5.16	9.51
5	7-8.5	7.45	2.61	22.3	22.3	19.4	50.0	111	354	6.58	1.60
6	13-16	7.63	2.95	19.1	19.1	19.5	35.7	143	nd	nd	nd
7	20-25	7.56	3.22	18.5	18.5	20.8	53.5	148	nd	nd	nd
8	30-35	7.62	3.47	15.9	15.9	16.9	46.4	141	nd	nd	nd
9	40-44.5	7.81	3.64	15.2	15.2	19.8	64.3	159	nd	nd	nd
10	50-54.5	7.83	3.70	14.6	14.6	18.2	82.1	193	230	10.9	3.14

Key: SRP = Soluble Reactive Phosphate
nd = not determined
DL = Detection Limit

Sample Number	Sampling Interval (cm)	pH	Carb. Alk. meq/L	Chloride meq/L	Fe(II) $\mu\text{g-at/L}$	SRP $\mu\text{g-at/L}$	$\text{NO}_2^- - \text{NO}_3^-$ $\mu\text{g-at/L}$	NH_3 $\mu\text{g-at/L}$	Zn^{2+} ng-at/L	Cd^{2+} ng-at/L	Pb^{2+} ng-at/L
0	O.W.	nd	1.88	0.612	DL	0.077	26.6	1.14	nd	nd	nd
1	0-2	7.3	2.01	0.598	50.5	3.2	46.4	82.8	6.45	8.03	7.04
2*	0-2	7.5	1.99	0.666	nd	4.7	75.0	100	6.39	8.04	7.92
3	2-4	7.4	1.99	0.558	74.9	9.4	35.7	171	6.58	DL	8.07
4*	2-4	7.3	1.84	0.652	51	3.2	71.4	73.2	6.00	8.17	7.55
5	4-6	7.43	1.92	0.558	113	3.7	32.1	42.8	6.78	8.08	8.05
6	4-6	7.41	2.70	0.612	82.3	8.5	32.1	91.0	6.65	8.19	8.04
7	6-10.8	7.51	2.70	0.558	137	12.4	32.1	170	6.68	7.66	7.85
8	13-18	7.59	3.11	0.530	129	20.3	35.7	182	6.59	8.19	7.93
9	20-25.5	7.69	3.34	0.477	141	22.2	28.6	207	6.73	7.62	7.80
10	30-35.5	7.70	3.59	0.381	143	28.7	32.1	237	6.46	7.80	8.14
*	O.W. divers	nd	1.86	0.570	DL	nd	75.0	nd	nd	nd	nd

Key: SRP = Soluble Reactive Phosphate

DL = Detection Limit

* = Duplicate core taken by divers

Station	Sample Number	Sampling Interval (cm)	Carb. Alk. meq/L	Chloride meq/L	Fe(tot.) µg-at/L	SRP µg-at/L	NO ₂ ⁻ -NO ₃ ⁻ µg-at/L	NH ₄ ⁺ µg-at/L	Zn ²⁺ ng-at/L	Cd ²⁺ ng-at/L	Pb ²⁺ ng-at/L	Cu ²⁺ ng-at/L
Control-A	0	0.W.	DL	0.808	3.92	4.4	n.d.	-33	119998	17	13	64
Lat. 41° 55.9'N	1	0-2	3.98	0.723	189	1.6	132	361	419	1.1	2.9	
Long. 80° 46.9'W	2	2-3.5	5.96	0.695	449	2.3	139	753	378	2.7	3.6	
	3	3.5-4.7	8.46	0.851	685	3.2	453	982	163	-1.6	-0.1	
	4	4.7-6	7.22	0.539	808	3.7	100	1017	284	2.4	4.7	
Depth: 17m	5	6-8	9.05	1.09	883	5.6	171	982	198	2.7	-2.5	
Date: 2-IV-77	6	8-11.7	9.52	0.822	925	9.7	114	971	381	1.0	5.5	
	7	18.22	8.97	0.865	818	6.6	54	910	151	-2.1	2.2	
	8	22-27	7.23	0.666	385	4.8	111	436	207	1.4	25	
	9	29.5-33.5	5.12	0.921	599	9.2	109	637	626	7.3	4.0	
	10	33.5-39	6.81	0.907	561	7.8	61	667	118	2.2	4.6	
			7.45									
		1m	1.85	0.737	D.L.	0.05	11	1.5	5.5	0.4	-3.8	-2.4
		8m	1.80	0.765	D.L.	0.05	13	1.8	65	0.7	3.1	47
		16m	1.76	0.737	D.L.	0.06	12	2.5	45	-2.3	-5.3	-26
Station Control-B	0	0.W.	1.69	0.723	D.L.	3.2	482	30	984	11	89	187
Lat. 41° 55.9'N	1	0-2.5	3.23	0.680	193	3.7	75	328	15	2.9	-1.2	
Long. 80° 46.9'W	2	2.5-4.5	4.02	0.794	284	6.6	154	473	811	10	26	
	3	4.5-6	5.45	0.680	463	5.8	64	605	235	2.0	4.6	
Depth: 17m	4	6-8	5.89	1.08	525	6.1	71	638	394	7.6	13	
Date: 2-IV-77	5	8-9.5	5.96	0.851	564	11.3	57	607	371*	9.6*	17*	
	6	9.5-12.5	6.37	0.822	612	14.8	107	671	120	3.9	7.1	
	7	12.5-16.5	6.75	0.879	559	9.7	75	655	308	4.4	6.3	
	8	16.5-21.5	6.81	0.765	450.	12.9	43	530	203	2.2	4.1	
	9	21.5-26	6.81	0.992	291	4.4	61	517	73	3.8	20	
	10	none										

*Low boundary

Station	Sample Number	Sampling Interval (cm)	pH	Carb. Alk. meq/L	Chloride meq/L	Fe(tot.) µg-at/L	SRP µg-at/L	NO ₂ ⁻ O ₃ ⁻ µg-at/L	NH ₄ ⁺ µg-at/L	Zn ²⁺ ng-at/L	Cd ²⁺ ng-at/L	Pb ²⁺ ng-at/L	Cu ²⁺ ng-at/L
DUMP-A	0	O.W.	n.d.	0.46	0.723	1.78	0.09	n.d.	n.d.	1429	81	5.9	150
Lat. 41° 56.3'N	1	0-2.5	6.89	3.34	0.907	386	3.4	114	301	384	8.6	28	
Long. 80° 46.1'W	2	2.5-4.5	7.14	4.77	0.964	767	1.9	71	725	461	2.9	19	
Depth: 11m	3	4.5-7.5	7.10	6.81	0.907	1035	1.9	204	934	3030	14	26	
Date: 1-IV-77	4	7.5-10	7.10	7.36	0.765	1056	1.4	64	1078	5839	46	21	
	5	10-12	7.20	7.27	0.652	842	1.4	93	1058	273*	8.6*	26*	
	6	12-14	7.45	7.91	0.780	1066	2.4	164	1206	847*	11*	41*	
	7	14-19.5	7.11	8.48	0.765	1066	8.1	46	1167	731	5.9	16	
	8	19.5-24	7.25	8.75	0.879	1006	5.5	54	1388	550	2.9	13	
	9	24-29.5	7.29	8.73	0.482	905	4.7	161	1057	1213	12	33	
	10	33-38	7.50	7.74	0.156	648	1.1	111	888	1219	6.1	30	
*Low boundary													
Station													
DUMP-B													
Lat. 41° 56.3'N	0	O.W.	n.d.	0.53	0.780	12.5	0.1	20	5.5	80	1.4	2.5	23
Long. 80° 46.1'W	1	0-1.5	7.26	1.12	0.836	301	5.3	218	238	392	4.3	7.6	
Depth: 11m	2	1.5-3.5	7.05	7.03	0.808	759	3.4	54	665	490	4.0	8.3	
Date: 1-IV-77	3	3.5-6	7.26	4.00	0.822	888	3.9	57	931	381	2.8	4.8	
	4	6-8.5	7.12	6.77	0.865	1032	5.2	32	1011	477	7.4	5.4	
	5	8.5-11	7.18	7.54	0.780	866	3.2	29	1100	78	5.5	3.2	
	6	11-13.5	7.24	7.65	0.794	978	5.0	54	1077	326	4.4	3.8	
	7	13.5-19	7.24	8.42	0.822	1015	12.8	43	1030	280	5.3	0	
	8	19-23.5	7.12	8.37	0.822	806	2.6	36	977	252	2.1	2.7	
	9	23.5-28.5	7.28	8.48	0.907	752	4.5	32	890	88	1.9	3.3	
	10	28.5-33	7.37	8.20	0.794	624	5.3	43	734	274	7.2	2.8	

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Station	Sample Number	Sampling Interval (cm)	pH	Carb. Alk. meq/L	Chloride meq/L	Fe(tot.) $\mu\text{g-at/L}$	SRP $\mu\text{g-at/L}$	$\text{NO}_2^- - \text{NO}_3^-$ $\mu\text{g-at/L}$	Ni^{+4} $\mu\text{g-at/L}$	Zn ng-at/L	Cd ng-at/L	Pb ng-at/L	Cu ng-at/L
OLD DUMP-A	0	0-W.	n.d.	1.80	0.599	9.66				668	6.2	46	0.5
Lat. $41^\circ 57' \text{N}$	1	0-2	7.19	3.20	0.790	98	18.6	89	257	738	7.3	2.7	
Long. $80^\circ 47.8' \text{W}$	2	2-4	6.96	3.53	0.894	365	6.6	118	375	815	9.0	0.3	
	3	4-6	6.98	4.15	1.07	508	2.3	154	600	777	8.6	6.9	
	4	6-8	6.97	4.46	1.07	574	3.4	132	660	909	7.6	4.3	
Depth: 17 m	5	8-10	6.95	3.13	1.03	786	15.3	104	792	665	4.3	4.8	
Date: 19-V-77	6	10-13	6.97	3.86	0.998	739	14.0	86	814	388	6.8	5.9	
	7	15.8-20.5	6.98	5.77	0.911	769	6.5	139	907	621	6.6	5.8	
	8	25.5-30.2	7.08	5.24	0.061	531	15.6	121	800	520	5.3	2.0	
	9	32-37	7.38	7.02	D.L.	413	16.3	93	678	515	0.4	8.4	
	10	39-45	7.47	6.97	0.859	314	4.4	228	657	1232	15	14	

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Station	Sample Number	Sampling Interval (cm)	pH	Carb. Alk. meq/L	Chloride meq/L	Fe(tot.) $\mu\text{g-at/L}$	SRP $\mu\text{g-at/L}$	$\text{NO}_2^- - \text{NO}_3^-$ $\mu\text{g-at/L}$	Ni^{+4} $\mu\text{g-at/L}$	Zn ng-at/L	Cd ng-at/L	Pb ng-at/L	Cu ng-at/L
OLD DUMP-B	0	0-W.	n.d.	1.78	0.581	D.L.				118	2.7	6.1	17
Lat. $41^\circ 57' \text{N}$	1	0-2.5	6.95	2.49	0.807	57.3	3.7	250	225	366	2.8	5.7	
Long. $80^\circ 47.8' \text{W}$	2	2.5-4.5	6.92	3.48	0.790	258	4.0	100	428	563	6.5	16	
	3	4.5-6	6.93	4.26	0.842	464	4.0	104	506	339	0.8	4.9	
Depth: 17 m	4	6-7.5	6.95	3.44	0.894	572	6.6	118	616	704	0.1	5.8	
Date: 19-V-77	5	7.5-9.5	6.97	5.42	0.911	588	8.6	136	714	401	2.7	6.8	
	6	9.5-12.3	6.95	5.73	0.894	647	6.5	154	721	285	1.3	3.7	
	7	12.3-17.3	6.95	6.33	0.894	480	9.0	100	800	190	4.8	3.7	
	8	22.8-27.5	7.00	6.82	1.07	801	10.3	250	878	390	2.5	6.0	
	9	34-39	7.00	7.30	1.10	457	10.5	96	685	286	5.1	5.9	
	10	44-49	7.10	6.33	1.15	292	8.6	68	560	133	1.2	1.3	
		1m		D.L.	0.581		0.12	11	1.9	135	0.8	2.3	92
		8m		1.62	0.373		0.07	13	1.3	585	2.1	7.5	45
		16m		1.73	0.616		0.07	14	2.1	86	0.5	3.7	30

Station	Sample Number	Sampling Interval (cm)	pH	Carb. Alk. meq/L	Chloride meq/L	Fe(tot.) µg-at/L	SRP µg-at/L	NO ₂ ⁻ , NO ₃ ⁻ µg-at/L	NH ₄ ⁺ µg-at/L	Zn ²⁺ ng-at/L	Cd ²⁺ ng-at/L	Pb ²⁺ ng-at/L	Cu ²⁺ ng-at/L
Station Control Lat. 41° 55.9'N Long. 80° 46.9'W Depth: 11m Date: 16-V-77	0	O.W.	n.d.	1.73	0.616	3.16				489	4.1	21	66
	1	0-2.3	7.57	2.71	0.703	17.3	4.4	393	96	1055	42	4.6	
	2	3.5-6	7.18	3.42	0.998	251	2.1	196	*	760	n.d.	-9.0	
	3	6-8.5	7.30	4.97	0.911	545	3.7	211	*	526	9.3	3.9	
	4	8.5-11.3	7.31	5.08	0.946	477	2.9	150	*	1914	7.6	4.6	
	5	11.3-13	7.70	5.64	1.08	n.d.	2.7	232	*	421	7.8	8.8	
	6	13-15	7.60	6.46	0.009	749	4.4	189	*	260	1.1	-1.3	
	7	15-19.5	7.20	6.72	D.L.	720	4.2	157	*	217	2.2	6.0	
	8	22-27	7.61	7.33	0.009	n.d.	9.2	143	*	82	1.5	3.7	
	9	29-33.5	8.15	6.79	0.234	657	4.2	271	*	152	5.1	4.4	
Station Lat. 41° 55.9'N Long. 80° 46.9'W Depth: 11m Date: 16-V-77	10	36.5-41.5	7.26	7.37	D.L.	480	1.1	343	*	769	4.2	9.7	
	1m			1.69	0.686	2.63	0.05		n.d.	87	2.2	1.9	n.d.
	5m			1.69	0.582	2.28	0.03		n.d.	4300	2.1	2.2	3.5
Station Lat. 41° 55.9'N Long. 80° 46.9'W Depth: 11m Date: 16-V-77	10m			1.82	0.599	3.34	0.04		n.d.	95	3.4	4.5	9.1

*All too high. (>1428)

Station	Sample Number	Sampling Interval (cm)	pH	Carb. Alk. meq/L	Chloride meq/L	Fe(tot.) µg-at/L	SRP µg-at/L	NO ₂ ⁻ , NO ₃ ⁻ µg-at/L	NH ₄ ⁺ µg-at/L	Zn ²⁺ ng-at/L	Cd ²⁺ ng-at/L	Pb ²⁺ ng-at/L	Cu ²⁺ ng-at/L
Station DUMP-A Lat. 41° 56.3'N Long. 80° 46.1'W Depth: 15m Date: 17-V-77	0	O.W.	n.d.	1.80	0.651	3.90				272	5.7	20	55
	1	0-2	7.36	3.64	0.842	325	15.7	204	300	556	3.1	22	
	2	2-4	7.36	3.53	0.998	466	12.4	178	3000	219	7.2	23	
	3	4-6.5	7.27	3.91	1.03	755	7.7	189	5150	624	-2.7	14	
	4	6.5-8.3	7.45	4.93	0.998	924	7.6	102	27800	1254	-14	9.5	
	5	8.3-10.2	7.35	5.24	0.911	1018	7.7	68	7320	827	8.5	5.7	
	6	10.2-13.5	7.40	5.35	0.929	1071	9.2	68	9100	464	-11	2.7	
	7	16-21.4	7.32	5.24	0.824	1231	11.8	50	29100	292	-9.2	2.9	
	8	21.4-26.5	7.21	6.15	0.894	1168	10.0	107	29500	599	4.5	4.7	
	9	26.5-31	7.21	6.31	0.026	1168	15.2	54	18600	329	-3.6	4.0	
Station Lat. 41° 56.3'N Long. 80° 46.1'W Depth: 15m Date: 17-V-77	10	31-35.5	7.20	6.62	0.182	1130	11.8	89	18200	298	7.2	0.6	
	1m			1.64	0.703	4.04	0.10	22	1.7	846	3.2	-0.4	22
	7m			1.75	0.686	2.45	0.10	26	1.5	61	5.5	-1.4	18.4
Station Lat. 41° 56.3'N Long. 80° 46.1'W Depth: 15m Date: 17-V-77	14m			1.86	0.564	2.45	0.22	13	3.6	260	2.2	6.1	177

Sample Number	Sampling Interval (cm)	pH	Carb. Alk. meq/L	Chloride meq/L	Fe(cot.) $\mu\text{g-at/L}$	SRP $\mu\text{g-at/L}$	$\text{NO}_2^- \text{NO}_3^-$ $\mu\text{g-at/L}$	NH_4^+ $\mu\text{g-at/L}$	Zn^{2+} ng-at/L	Cd^{2+} ng-at/L	Pb^{2+} ng-at/L	Cu^{2+} ng-at/L
Station	0 W.	n.d.	1.78	0.703	3.30		71	200	219	9.1	16	86
DUMP-B	0-2.3	7.34	3.77	0.772	87.6	10.8			213	2.4	7.6	
Lat. 41° 56.3'N	2.3-3.7	7.58	3.60	0.963	126	11.0	146	289	370	9.7	11	
Long. 80° 46.1'W	3.7-5.5	7.80	3.93	0.981	177	5.8	143	403	546	10	8.1	
Date: 18-V-77	5.5-7	7.88	4.42	0.963	250	7.7	161	471	288	2.7	3.1	
Depth: 14m	7-8.5	7.10	4.44	0.842	163	9.2	132	457	474	4.7	6.2	
	8.5-12	7.40	4.88	0.807	271	13.7	132	460	309	4.0	9.4	
	12-17	7.30	5.00	0.807	339	12.6	57	410	334	3.6	4.6	
	17-20.5	7.60	4.53	9.738	177	1.9	18	357	1365	45	18	
	none											
	none											

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Sample Number	Sampling Interval (cm)	pH	Carb. Alk. meq/L	Chloride meq/L	Fe(cot.) $\mu\text{g-at/L}$	SRP $\mu\text{g-at/L}$	$\text{NO}_2^- \text{NO}_3^-$ $\mu\text{g-at/L}$	NH_4^+ $\mu\text{g-at/L}$	Zn^{2+} ng-at/L	Cd^{2+} ng-at/L	Pb^{2+} ng-at/L	Cu^{2+} ng-at/L
Station	0 W.	7.70	1.85	0.600	0.52		7.1	126	38	4.4	4.0	28
DUMP-B	0-1.5	7.34	2.20	0.708	161	30.7			714	4.2	15.0	56
Lat. 41° 56.3'N	1.5-3	7.49	2.91	0.760	173	35.0	7.1	143	659	34	14.5	
Long. 80° 46.1'W	3-5.2	7.48	3.09	0.699	167	25.7	14	208	376	9.3	3.4	
Date: 4-IX-77	5.2-7.2	7.47	3.43	0.755	220	31.1	21	270	545	7.3	9.8	
Depth: 14m	7.2-9.3	7.45	3.70	0.735	247	51.8	43	415	265	4.9	-10.9	
	9.3-12.2	7.43	3.96	0.721	384	56.8	D.L.	396	156	0.4	5.7	
	12.2-17	7.38	4.24	0.775	424	65.7	D.L.	451	214	18.5	-14.8	
	17-22	7.37	4.76	0.785	414	105	18	532	537	1.3	2.8	
	22-27.5	7.43	5.26	0.769	435	86.4	14	546	346	2.0	2.1	
	27.5-32.5	7.52	5.35	0.721	355	47.5	21	515	321	4.0	2.2	

Station	Sample Number	Sampling Interval (cm)	pH	Carb. Alk. meq/L	Chloride meq/L	Fe (II) $\mu\text{g-at/L}$	SRP $\mu\text{g-at/L}$	$\text{NO}_2^- - \text{NO}_3^-$ $\mu\text{g-at/L}$	NH_4^+ $\mu\text{g-at/L}$	Zn $^{2+}$ ng-at/L	Cd $^{2+}$ ng-at/L	Pb $^{2+}$ ng-at/L	Cu $^{2+}$ mg-at/L
OLD-DUMP	0	0.W.	7.70	2.02	0.608	1.92				34	-0.2	8.0	26
Lat. 41° 57'N	1	0-1.5	7.28	3.72	0.622	281	148	43	286	817	26	52	
Long. 80° 47.8'W	2	1.5-3	7.37	4.05	0.660	334	26.6	D.L.	438	141	7.3	-2.7	
Depth: 16m	3	3-5.8	7.40	4.63	0.737	485	12.4	D.L.	546	196	14.2	-2.7	
Date: 5-IX-77	4	5.8-8.5	7.43	5.05	0.762	578	14.4	14	632	138	7.8	-1.0	
	5	8.5-10.5	7.47	5.21	0.889	606	18.2	D.L.	693	none	none	none	
	6	10.5-13.2	7.55	6.14	0.864	671	18.9	18	711	none	none	none	
	7	13.2-18	7.52	6.51	0.852	714	19.7	14	711	242	6.9	36	
	8	20-25	7.49	7.05	0.890	551	17.3	11	693	339	4.4	9.8	
	9	25-30	7.59	6.95	0.882	527	24.0	7	628	184	5.6	6.9	
	10	36.5-41.5	7.90	7.05	0.987	336	24.2	29	490	215	11.1	16.4	

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1m	0.08	2.6	0.08	0.63	72	0.9	-0.1	6.1
8m	0.08	2.3	0.08	0.61	145	3.9	2.0	63
15m	0.12	8.3	0.12	7.1	113	3.1	-3.0	24

Station	Sample Number	Sampling Interval (cm)	pH	Carb. Alk. meq/L	Chloride meq/L	Fe (II) $\mu\text{g-at/L}$	SRP $\mu\text{g-at/L}$	$\text{NO}_2^- - \text{NO}_3^-$ $\mu\text{g-at/L}$	NH_4^+ $\mu\text{g-at/L}$	Zn $^{2+}$ ng-at/L	Cd $^{2+}$ ng-at/L	Pb $^{2+}$ ng-at/L	Cu $^{2+}$ mg-at/L
Control	0	0.W.	7.87	2.05	0.621	D.L.				15.9	1.3	1.0	15.6
Lat. 41° 55.9'N	1	0-1.5	n.d.	4.93	0.687	387	14.2	14	615	793	11.1	1.8	
Long. 80° 46.9'W	2	1.5-3.3	n.d.	6.33	0.917	677	14.0	64	1094	426	10.0	-10.3	
Depth: 13m	3	3.3-5.8	n.d.	7.47	0.748	870	6.9	39	1449	267	11.6	-7.6	
Date: 5-IX-77	4	5.8-7.5	n.d.	9.23	0.155	1127	9.4	68	2298	364	22.6	-4.4	
	5	7.5-9.5	n.d.	10.74	0.127	1241	9.4	36	2844	207	21.1	5.2	
	6	9.5-12	n.d.	12.12	0.762	1013	21.2	50	*	612	14.0	-4.2	
	7	12-16.5	7.31	11.88	0.183	1164	19.5	14	*	7.6	4.9	9.7	
	8	16.5-22	7.36	11.26	0.028	1108	15.3	14	2734	70.4	8.2	-0.1	
	9	22-26.5	7.48	10.44	0.254	1013	13.7	18	1598	129	3.1	-11.5	
	10	26.5-31	7.17	9.77	0.762	1043	14.4	25	1415	166	5.8	-0.8	

1m	1.95	0.667	0.17	0.54	305	2.0	4.4	15.4
6m	1.74	0.660	0.10	0.52	18.7	-0.2	3.6	30
12m	2.05	0.590	0.10	3.6	72	-0.6	0	15

*Minimum value is 2856

Station	Sample Number	Sampling Interval (cm)	pH	Carb. Alk. meq/L	Chloride meq/L	Fe (II) $\mu\text{g-at/L}$	SRP $\mu\text{g-at/L}$	$\text{NO}_2^- - \text{NO}_3^- \mu\text{g-at/L}$	$\text{NH}_4^+ \mu\text{g-at/L}$	$\text{Zn}^{2+} \text{ng-at/L}$	$\text{Cd}^{2+} \text{ng-at/L}$	$\text{Pb}^{2+} \text{ng-at/L}$	$\text{Cu}^{2+} \text{ng-at/L}$
Station DUMP-A Lat. 41° 56.3'N Long. 80° 46.1'W Depth: 14m Date: 4-IX-77	0	0.W.	7.81	1.87	0.598	1.03				11	1.8	3.5	8.5
	1	0-1.5	7.58	3.61	0.760	278	52.6	8.9	268	2204	20.2	103	-78
	2	1.5-3.5	7.63	3.98	0.736	206	42.1	11	387	1347	11.3	34.9	-1.6
	3	3.5-5.7	7.67	4.13	0.792	340	45.7	32	436	940	6.0	26.2	-75
	4	5.7-7.5	n.d.	4.26	0.884	259	43.2	18	500	1667	33.4	116	12.4
	5	7.5-9.0	7.69	4.70	0.880	360	48.2	3.6	460	1308	10.5	29.1	-348
	6	9-11.5	7.59	4.78	0.875	527	51.8	D.L.	504	771	8.2	19.2	
	7	11.5-17.5	7.52	4.89	0.861	525	51.7	20	472	347	2.0	10.6	
	8	17.5-23	7.41	5.35	0.908	552	51.0	25	523	379	-2.2	11.2	
	9	23-28	7.49	5.43	0.844	565	46.4	25	525	547	2.4	9.4	
	10	28-33	7.40	5.78	0.888	563	50.0	32	556	745	4.7	43	
Station GASP-XX-83 Lat. 41° 43'N Long. 82° 18.8'W Depth: 20m Date: 1-VII-77	0	0.W.	n.d.	1.82	0.564	2.3				58	1.5	2.7	10
	1	0-2.5	n.d.	2.32	0.636	67.6	5.2	46	134	3896	30	53	
	2	2.5-4.5	n.d.	2.50	0.593	42.1	1.6	46	129	663	4.3	10	
	3	4.5-6.5	n.d.	2.58	0.721	66.7	1.7	282	172	3288	6.5	1.7	
	4	6.5-8	n.d.	2.72	0.636	60.1	4.4	75	151	1256	-7.4	5.2	
	5	8-9.5	n.d.	2.87	0.636	52.2	4.2	57	154	2135	n.d.	-0.2	
	6	9.5-11	n.d.	2.89	0.636	49.0	3.1	57	143	663	2.2	3.0	
	7	15-20	n.d.	2.80	0.750	37.0	3.0	196	263	2402	353	-3.0	
	8	24-28	n.d.	3.42	0.650	36.7	2.7	100	189	1630	-0.4	-7.7	
	9	34-39	n.d.	3.64	0.536	31.2	2.1	29	186	1150	10	2.8	
	10	43-47	n.d.	3.61	0.736	29.4	1.7	93	228	870	4.4	4.0	
Station GASP-XX-83 Lat. 41° 43'N Long. 82° 18.8'W Depth: 20m Date: 1-VII-77	1m					0.08		15	2.5				
	13m					0.05		14	2.6				
	16m					0.04		13	2.4				
	19m					0.09		14	3.2				

Station	Sample Number	Sampling Interval (cm)	pH	Carb. Alk. meq/L	Chloride meq/L	Fe (II) $\mu\text{g-at/L}$	SRP $\mu\text{g-at/L}$	$\text{NO}_2^- - \text{NO}_3^-$ $\mu\text{g-at/L}$	NH_4^+ $\mu\text{g-at/L}$	Zn^{2+} ng-at/L	Cd^{2+} ng-at/L	Pb^{2+} ng-at/L	Cu^{2+} ng-at/L
GASP-XXI-83-A Lat. 41° 43'N Long. 82° 18.8'W Depth: 20m Date: 2-IX-77	0	O.W.	n.d.	1.99	0.596	7.32	20.5	21	180	146	-1.1	-2.6	0.5
	1	0-2	7.28	2.97	0.574	98.2	17.6	D.L.	157	1671	138	38	432
	2	2-4	7.42	2.90	0.644	116	14.2	D.L.	165	625	4.4	20	331
	3	4-6	7.42	2.81	0.617	94.7	22.6	D.L.	113	839	2.4	4.6	-55
	4	6-8	7.61	2.97	0.612	99.4	22.0	D.L.	112	336	-4.4	8.6	3.1
	5	8-10	7.65	2.85	0.617	103	29.1	D.L.	112	379	-0.4	15	188
	6	10-14	7.68	3.31	0.628	99.0	23.9	D.L.	151	245	-5.8	4.1	-50
	7	14-18.5	7.77	3.26	0.617	80.5	21.5	46	154	463	-2.4	8.8	-15
	8	18.5-24	7.77	3.40	0.596	73.0	11.5	29	124	354	1.6	13	3.5
	9	29-34.5	7.90	3.60	0.631	55.0	21.6	36	122	318	3.3	14	7.5
	10	39-47	8.00	3.76	0.547	45.6	0.13	0.8	0.5	478	5.3	9.7	-4.3
GASP-XXI-83-B Lat. 41° 43'N Long. 82° 18.8'W Depth: 20m Date: 2-IX-77	0	O.W.	7.77	2.22	0.629	13.1	31.8	D.L.	151	62	2.7	-2.9	2.2
	1	0-2	7.61	3.01	0.659	179	27.1	193	224	480	5.8	0.8	n.d.
	2	2-4	7.40	2.97	0.628	111	32.0	D.L.	158	407	6.5	0.6	70
	3	4-6	7.34	2.94	0.702	118	40.4	D.L.	146	423	4.9	1.4	181
	4	6-9	7.49	2.97	0.626	158	29.5	14	165	279	8.2	25	n.d.
	5	9-11.2	7.47	2.99	0.702	136	32.0	21	151	570	6.4	19	78
	6	14.5-17.5	7.41	2.99	0.674	122	30.4	211	241	108	3.6	2.2	119
	7	25.5-31	7.53	3.03	0.689	108	26.8	14	161	234	0.9	0.6	n.d.
	8	40.5-46.5	7.67	3.19	0.614	88.6	28.2	393	341	141	2.4	1.7	31
	9	60.5-66	7.89	3.83	0.735	69.5	27.4	178	219	615	6.2	11	78
	10	79-84	7.85	3.49	0.689	66.1				90	2.0	1.2	-85

Station	Sample Number	Sampling Interval (cm)	pH	Carb. Alk. meq/L	Chloride meq/L	Fe(II) $\mu\text{g-at/L}$	SRP $\mu\text{g-at/L}$
GASP-X-20 Lat. 41° 52'N Long. 81° 55'W Depth: 25m Date: 27-VI-76	0			1.87	0.608	0	
	1	0-2.5	7.24	2.87	0.633	607	258
	2	2.5-5	7.57	3.56	0.645	941	228
	3	5-7.5	7.57	3.52	0.608	863	244
	4	7.5-10	7.43	3.65	0.596	732	244
	5	10-12.5	7.23	3.48	0.620	972	304
	6	17-20	7.31	3.52	0.608	1080	334
	7	25-30	7.25	3.48	0.608	1200	304
	8	35-41	7.21	3.70	0.620	1120	319
	9	45-50	7.10	2.87	0.547	1030	330
	10	55-60	7.21	3.96	0.487	1170	326
CO CO		2m		2.09	0.572	1.25	
		10m		1.91	0.633	0	
		20m		1.96	0.633	0	
		24m		1.91	0.547	0	

Station	Sample Number	Sampling Interval (cm)	pH	Carb. Alk. meq/L	Chloride meq/L	Fe(II) $\mu\text{g-at/L}$	SRP $\mu\text{g-at/L}$
GASP-X-6 Lat. 41° 46.4'N Long. 82° 59.2'W Depth: 9m Date: 28-VI-76	0			1.78	0.474	1.25	46
	1	0-2.5	7.55	1.96	0.523	70	25
	2	2.5-5	n.d.	1.96	0.535	100	61
	3	5-7.5	7.50	2.39	0.547	220	50
	4	7.5-10	n.d.	2.65	0.487	199	78
	5	10-12.5	7.50	2.74	0.523	218	100
	6	17-20	n.d.	3.09	0.511	261	68
	7	25-30	7.63	3.52	0.511	270	132
	8	35-41	n.d.	3.39	0.620	315	61
	9	45-50	7.48	3.65	0.620	317	18
	10	55-60	n.d.	3.56	0.560	267	
		2m		1.70	0.426	0.72	
		8m		1.78	0.450	0	

Station	Sample Number	Sampling Interval (cm)	pH	Carb. Alk. meq/L	Chloride meq/L	Fe(tot.) µg-at/L	SRP µg-at/L	NO ₂ -NO ₃ µg-at/L	NH ₄ ⁺ µg-at/L
GASP-XI-20 Lat. 41° 52'N Long. 81° 55'W Depth: 25m Date: 28-IX-76	0			1.87	0.556		0.97	n.d.	14
	1	0-2	7.22	3.17	0.612	72	11	n.d.	238
	2	2-4	7.22	3.35	0.623	127	13	n.d.	335
	3	4-6	7.20	3.65	0.657	85	13	n.d.	350
	4	6-8	7.41	3.65	0.556	99	12	n.d.	343
	5	8-10	7.41	3.74	0.567	94	11	n.d.	358
	6	15-20	7.41	4.15	0.464	105	10	n.d.	413
	7	25-30	7.20	4.43	0.385	105	3.2	n.d.	501
	8	35-40	7.67	5.13	0.408	105	13	n.d.	450
	9	45-50	7.50	4.56	0.352	100	2.9	39	552
	10	55-60	7.40	4.48	0.352	99	1.1	121	625
89		1m		1.78	0.578		0.13	1.7	1.8
		12m		1.78	0.533		0.16	1.5	2.2
		22m		1.87	0.544		0.22	1.5	2.1
		23m		1.83	0.567		0.21	1.4	2.4

Station	Sample Number	Sampling Interval (cm)	pH	Carb. Alk. meq/L	Chloride meq/L	Fe(tot.) µg-at/L	SRP µg-at/L	NO ₂ -NO ₃ µg-at/L	NH ₄ ⁺ µg-at/L
GASP-XI-6 Lat. 41° 46.4'N Long. 82° 59.2'W Depth: 9m Date: 1-X-76	0			1.67	0.476		0.37	16	3.0
	1	0-2.5	7.55	2.72	0.488	50	37	n.d.	78
	2	2.5-4.5	7.51	2.57	0.544	39	12	n.d.	108
	3	4.5-6.5	7.54	2.83	0.533	105	27	n.d.	171
	4	6.5-8.5	7.55	3.06	0.522	102	16	n.d.	166
	5	8.5-10.5	7.60	3.30	0.567	74	29	n.d.	176
	6	16-19	7.58	3.48	0.692	86	16	n.d.	203
	7	23-29	7.74	3.54	0.760	95	16	n.d.	231
	8	33-39	7.60	3.72	0.930	80	9.5	n.d.	299
	9	39-44	7.55	3.80	1.021	122	7.3	n.d.	343
	10	44-47	7.71	3.80	1.043	114	2.7	n.d.	358
		1m		1.65	0.431		0.34	13	1.4
		4m		1.65	0.499		1.62	13	2.8
		7m		1.61	0.454		0.25	13	0.9
		8m		1.76	0.476		0.64	14	2.0

Station
GASP-XI-20-SS
Lat. 41° 52'N
Long. 81° 55'W
Depth: 24 m
Date: 29-IX-76

Sample Number	Sampling Interval (cm)	pH	Carb. Alk. meq/L	Chloride meq/L	Fe(tot.) µg-at/L	SRP µg-at/L	NO ₂ -NO ₃ ⁻ µg-at/L	NH ₄ ⁺ µg-at/L	Zn ²⁺ ng-at/L	Cd ²⁺ ng-at/L	Pb ²⁺ ng-at/L	Cu ²⁺ ng-at/L
1A	0-2.5	7.50	4.35	0.601	110	17	50	469	2829	38	7.7	~666
2A	2.5-5	7.41	3.89	0.635	114	24	32	371	2913	33	94	152
3B	0-2.5	7.65	3.70	0.657	90	11	43	286	2142	16	7.8	132
4B	2.5-5	7.50	3.43	0.556	72	6.6	50	275	1261	8.9	20	62
5C	0-2.5	7.70	4.04	0.635	116	21	50	359	1668	16	-1.7	n.d.
6C	2.5-5	7.30	3.83	0.578	95	9.8	29	257	2565	18	2.7	n.d.
7A	5-12	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	9182	72	49	219
8A	12-19	7.30	3.74	0.544	108	8.6	46	309	2234	26	15	~35
9B	5-12	7.30	3.52	0.556	96	13	50	278	1104	135	12	47
10C	5-12	7.30	3.52	0.578	93	16	46	287	1728	8.5	8.6	n.d.
	1m		1.90	0.522		0.27	1.9	3.7				
	11m		1.90	0.612		0.24	2.1	4.1				
	21m		1.87	0.510		0.37	2.3	5.2				
	22m		1.90	0.590		0.36	2.3	5.6				
OA			1.84	0.522		0.35	3.5	5.4	290	4.2	30.2	12.7
OB			1.83	0.612					111	0.5	1.9	-39.5
OC			1.87	0.544					119	0.5	11.4	-27.2

90

Station
GASP-XI-Tower
Lat. 41° 42.8'N
Long. 83° 10.3'W
Depth: 7m
Date: 1-X-76

Sample Number	Sampling Interval (cm)	pH	Carb. Alk. meq/L	Chloride meq/L	Fe(tot.) µg-at/L	SRP µg-at/L	NO ₂ -NO ₃ ⁻ µg-at/L	NH ₄ ⁺ µg-at/L	Zn ²⁺ ng-at/L	Cd ²⁺ ng-at/L	Pb ²⁺ ng-at/L	Cu ²⁺ ng-at/L
0	0-2	7.25	1.61	0.386	108	24	n.d.	470				
1	2-5	7.33	3.59	0.476	72	16	n.d.	448				
2	5-7	7.52	4.04	0.522	71	13	n.d.	386				
3	7-9	7.70	4.30	0.510	65	16	n.d.	326				
4	9-12	7.77	3.93	0.488	27	8.1	n.d.	229				
5	17-19	8.06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.				
6												
	1m		1.61	0.340		0.15	16	0.6				
	3m		1.72	0.386		0.39	16	1.0				
	5m		1.61	0.363		0.25	16	0.8				
	6m		1.61	0.374		0.26	16	0.9				

Station	Sample Number	Sampling Interval (cm)	pH	Carb. Alk. meq/L	Chloride meq/L	Fe (tot.) $\mu\text{g-at/L}$	SRP $\mu\text{g-at/L}$	$\text{NO}_2\text{-NO}_3$ $\mu\text{g-at/L}$	NH_4^+ $\mu\text{g-at/L}$
GASP-XI-20 Lat. 41° 52'N Long. 81° 55'W Depth: 24m Date: 30-IX-76	0			1.87	0.590		0.21	38	7.5
	1	0-2.5	7.32	3.65	0.601	129	16	n.d.	388
	2	2.5-4.5	7.35	3.52	0.612	102	17	n.d.	357
	3	4.5-6.5	7.30	3.57	0.612	125	12	n.d.	344
	4	6.5-8	7.19	3.61	0.567	113	7.4	n.d.	328
	5	8-10	7.33	3.67	9.567	95	16	n.d.	328
	6	11.5-15	7.39	3.83	0.544	155	12	n.d.	333
	7	23-27	7.32	3.76	0.454	141	5.3	n.d.	343
	8	35-40	7.49	4.22	0.669	102	12	n.d.	358
	9	44-50	7.39	4.22	0.363	90	4.4	n.d.	392
	10	53-59	7.59	4.33	0.386	47	3.4	n.d.	398
		1m		1.96	0.578		0.33	2.5	3.4
		12m		1.87	0.544		0.48	2.7	3.1
		22m		1.90	0.590		0.16	3.1	3.2
		23m		1.87	0.567		0.19	2.8	3.5