EFFECTS OF pH ON THE RELEASE OF ALUMINUM, CADMIUM AND LEAD FROM LITTORAL AND PROFUNDAL SEDIMENTS OF LAKES CLARA AND McGRATH, NORTHERN WISCONSIN

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ABSTRACT

The effects of acidification on release of Al, Cd, and Pb from sediments into pore waters was studied in profundal and littoral sediments of two northern Wisconsin lakes. Except for Cd in littoral sediments, pore water concentrations of all three metals and color decreased as pH of the sediments was decreased to approximately 4.5. Cadmium concentrations in littoral pore waters increased as pH of the natural sediment was decreased. Sediment pHs that resulted in the lowest pore water metal concentrations (defined as $\mathrm{pH}_{\mathrm{ads}}$) were variable between lakes, metals, and sediments. The decrease in Al, Cd, and Pb concentrations in the sediment pore waters at $\mathrm{pH}_{\mathrm{ads}}$ appeared to be dependent upon the amount of dissolved organic material, primarily humic and fulvic acids, present. Dissolved organic materials complexed 98% of the dissolved Al and Pb and 63-86% of the dissolved Cd in the profundal natural sediments. In contrast, dissolved organic materials complexed 23-65% and 20-81% of the dissolved Al and Pb, respectively, in the natural littoral sediments. These metal-organic complexes precipitated as sediment pH was decreased to $\mathrm{pH}_{\mathrm{ads}}$, incorporating the metals into the solid phase of the sediment. At pHs less than $\mathrm{pH}_{\mathrm{ads}}$ the complexed metals were subsequently displaced by competing ions, and pore water metal concentrations increased. The sequence of release was Cd > Al $\geq$ Pb for both littoral and profundal sediment. The $\mathrm{pH}_{\mathrm{ads}}$ for Al, Cd, and Pb were similar to the pHs of surface waters containing slightly elevated concentrations of the three metals.

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Finally, I wish to acknowledge those who have been with me from the start. I thank my parents for giving me the confidence and desire to achieve my goals, and hope that I fulfill the role of a parent as well as they have. Lastly, I thank my wife Christie for her assistance in the laboratory and her patience at home. Without her love and understanding this work would not have been completed.

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TABLE OF CONTENTS

PAGE

METHODS AND MATERIALS

RESULTS

TABLE OF CONTENTS - CONTINUED

PAGE

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Lakes and streams susceptible to acidification generally have watersheds consisting of thin soils deficient in acid neutralizing minerals and are underlain by granitic or Precambrian bedrock. Northern Wisconsin is considered to be an area susceptible to acidification because it is situated on acidic bedrock (Likens et al. 1979; Mudry et al. 1982) overlain with sandy acidic soils (Hole 1976). In 1979, Eilers et al. (1983) studied 275 lakes from this region and concluded that 36% were susceptible to acidification, based on the calcite saturation index of Kramer (1976). Evidence indicates that surface waters susceptible to acidification are likely to become acidified if precipitation pH is less than 4.6 (Henriksen 1979, 1980; Wright et al. 1980; Schindler 1980). Precipitation pHs in northern Wisconsin are presently near this threshold (R. W. Becker, Department of Natural Resources, Rhinelander, Wisconsin, pers. comm.).

The occurrence of elevated metal concentrations in surface waters with low pH has been well established (Wright and Gjessing 1976; Almer et al. 1978; Henriksen and Wright 1978; Dickson 1980; Schindler et al. 1980; Schindler and Turner 1982; Schmidt 1985). Wiener (1983) observed enhanced concentrations of Cd and Pb in fish from low pH waters in northern Wisconsin. Laboratory studies indicate that Cd and Pb uptake by fish is enhanced at low pHs (Merlini and Pozzi 1977; Hodson et al. 1978; Kumada et al. 1980). Studies have also demonstrated that waters with low pH have elevated concentrations of Al (Wright and Gjessing 1976; Cronin and Schofield 1979; Driscoll et al. 1980; Schofield and Trojnar 1980;

Schmidt 1985), which can be toxic to fish (Schofield and Trojnar; Baker and Schofield 1982; Brown 1983; Dickson 1983).

Many lakes in northern Wisconsin are susceptible to acidification, hence, continued acid deposition in this area could increase metal concentrations in surface waters and threaten valuable fishery resources. Increased metal concentrations in surface waters possibly result from atmospheric deposition, mobilization from the surrounding watershed by acidic runoff, decreased transport of metals to the sediments, and increased mobilization from the sediments. The relative importance of these possible mechanisms would vary between surface waters depending on parameters such as location, lake type, watershed, etc. However, studies show that metal concentrations are reduced in surficial sediments of acidified systems (Cronan and Schofield 1979; Schindler et al. 1980; Evans et al. 1983), indicating that increased mobilization and/or decreased deposition of metals between surface waters and sediments might be a significant factor controlling surface water metal concentrations.

This study examined mobilization of Al, Cd, and Pb as a response to acidification of sediments collected from two acid-susceptible lakes in northern Wisconsin. Specific objectives were to:

(1) Determine the total acid extractable Al, Cd, and Pb concentrations in surficial littoral and profundal sediments.

(2) Determine the effect of sediment pH on mobilization of Al, Cd, and Pb between the sediments and pore waters.

(3) Determine the pH ranges that result in the release of Al, Cd, and Pb from sediments to pore waters.

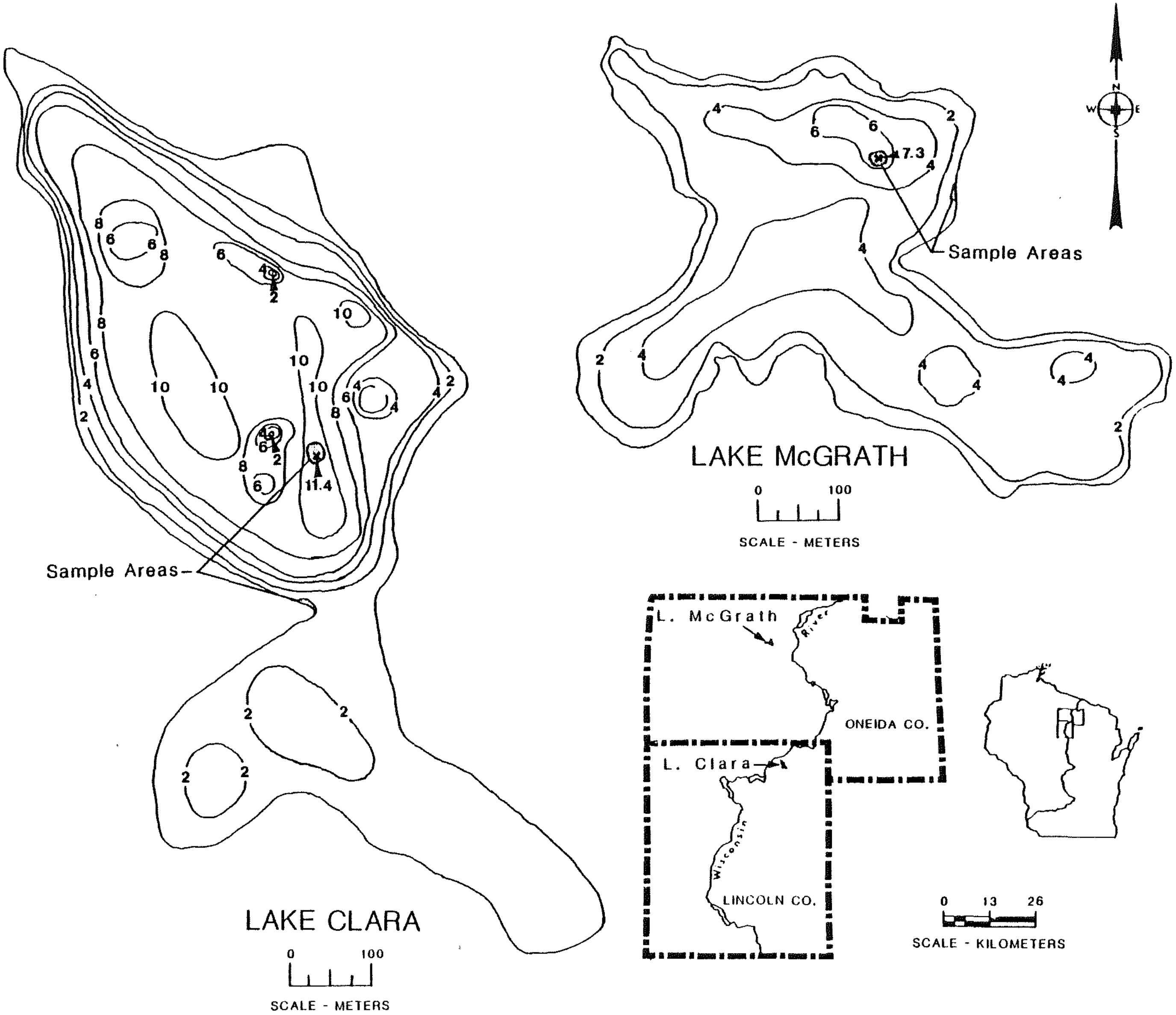
(4) Determine the degree of Al, Cd, and Pb complexation by dissolved organic materials at various pHs.

STUDY AREA

Lakes Clara and McGrath are located on pitted outwash plains in Lincoln and Oneida Counties, respectively, of north central Wisconsin (Fig. 1). Both lakes are situated within the Canadian Precambrian Shield on the partly dissected peneplain that establishes the Northern Highlands Geographical Province of Wisconsin (Martin 1965). During the Wisconsin stage of glaciation, the Chippewa Lobe of the Labrador ice sheet covered all of Oneida County and most of Lincoln County (Andrews and Threinen 1966; Carlson and Andrews 1982). Glacial deposits range from 15 to 90 m in thickness (Mudry et al. 1982) and consist primarily of acidic sands and sandy loams with low cation exchange capacities (Hole 1976). Bedrock is predominately greenschist metamorphic facies of early Proterozoic rock (primarily mafic) and intermediate and felsic metavolcanic rocks with subordinate metasedimentary rocks (Mudry et al. 1982). The numerous lakes in this area are typically small, closely spaced, and irregular in shape. Water covers about 2.5 and 9.5% of the surface areas of Oneida and Lincoln Counties, respectively. Approximately 76% of the study area is forested with mixed hardwoods and conifers (Andrews and Threinen 1966; Carlson and Andrews 1982).

The climate of the study area is cool and humid with an average annual temperature of 4-5 $^{\circ}$C, a frost-free season of approximately 120 d, and an average annual snowfall of about 142 cm (Andrews and Threinen 1966; Carlson and Andrews 1982). Average annual precipitation is approximately 78 cm, of which an estimated 40 cm is lost as evapotranspiration (Hole 1976).

Figure 1. Locations of lakes Clara and McGrath in Lincoln and Oneida Counties, Wisconsin.


LAKE CLARA
Sample Areas
11.4
10
8
6
4
2
0
100
SCALE - METERS
LAKE McGRATH
Sample Areas
7.3
6
4
2
0
100
SCALE - METERS
N
S
W
E
L. McGrath
River
ONEIDA CO.
L. Clara
Wisconsin
LINCOLN CO.
0
13
26
SCALE - KILOMETERS

Lake Clara

Lake Clara (T35N, R7E, S4; Elevation above MSL-462 m) is a highly transparent, clear water, drained lake (no inlet and an intermittent outlet) situated 30 m above bedrock. The watershed consists primarily of moderately acidic (pH 4.5-6.5) silty loams, loams, sandy loams, loamy sands, and sands from the Keweenaw, Vilas, Monico, Pence, and Sayner soil series (United States Department of Agriculture 1982). Small areas of slightly acidic (pH 5.6-7.8) muck and mucky peat from the Carbondale series and strongly acidic (pH 3.6-4.4) fibric, sapric, and humic materials from the Greenwood series are also present. Upland hardwood forest covers 85% of the lake shoreline, with coniferous bog covering the remaining 15%. Sand, muck, and gravel, respectively, cover about 60, 25, and 15% of the littoral zone (Carlson and Andrews 1982). Profundal sediments consist of highly organic, flocculent clays. Physical, chemical, and morphometric characteristics of Lake Clara are presented in Table 1.

Lake McGrath

Lake McGrath (T38N, R7E, S8; Elevation above MSL-484 m) is a highly transparent, clear water, seepage lake (no inlet or outlet) situated 90 m above bedrock. Its watershed consists primarily of moderately acidic (pH 4.5-6.5) loams, sandy loams, loamy sands, sands, and gravel from the Keweenaw, Vilas, Pence, and Padus soil series (United States Department of Agriculture 1976). Areas of strongly acidic (pH 3.6-4.4) muck, mucky peat, peat, and silt from the Dawson and Loxley soil series and strongly acidic fibric, sapric, and humic material from the Greenwood soil series are also present. Upland forest covers 95% of the lake shoreline, with bog and shrub wetlands covering the remaining 5%. Sand, muck, gravel, and boulders, respectively, cover about 55, 20, 15, and 10% of the littoral zone (Andrews and Threinen 1966). Profundal sediments consist of highly organic, flocculent clays. Physical, chemical, and morphometric characteristics of Lake McGrath are presented in Table 1.

Table 1. Physical and chemical characteristics of surface waters (from Schmidt 1985). Water quality data represent averages for the period June 1982 to June 1984

Characteristic	Lake Clara	Lake McGrath
Maximum Depth (m)	11.4	7.3
Mean Depth (m)	5.1	3.0
Lake Surface Area (ha)	34.1	20.2
Drainage Area (ha)	131	24
Watershed to Lake Area Ratio	4.9	2.2
Shoreline Development	1.76	1.76
Secchi Disk Transparency (m)	4.2	6.0
Apparent Color (Pt-Co units)	9	7
Specific Conductance (µS/cm)	35	17
pH	6.0	5.3
Alkalinity (µeq/L)	29	2
SO_4^{2-} (µeq/L)	111	106
Cl^- (µeq/L)	130	11
Ca^{2+} (µeq/L)	99	56
Mg^{2+} (µeq/L)	56	27
Na^+ (µeq/L)	113	14
K^+ (µeq/L)	25	14

METHODS AND MATERIALS

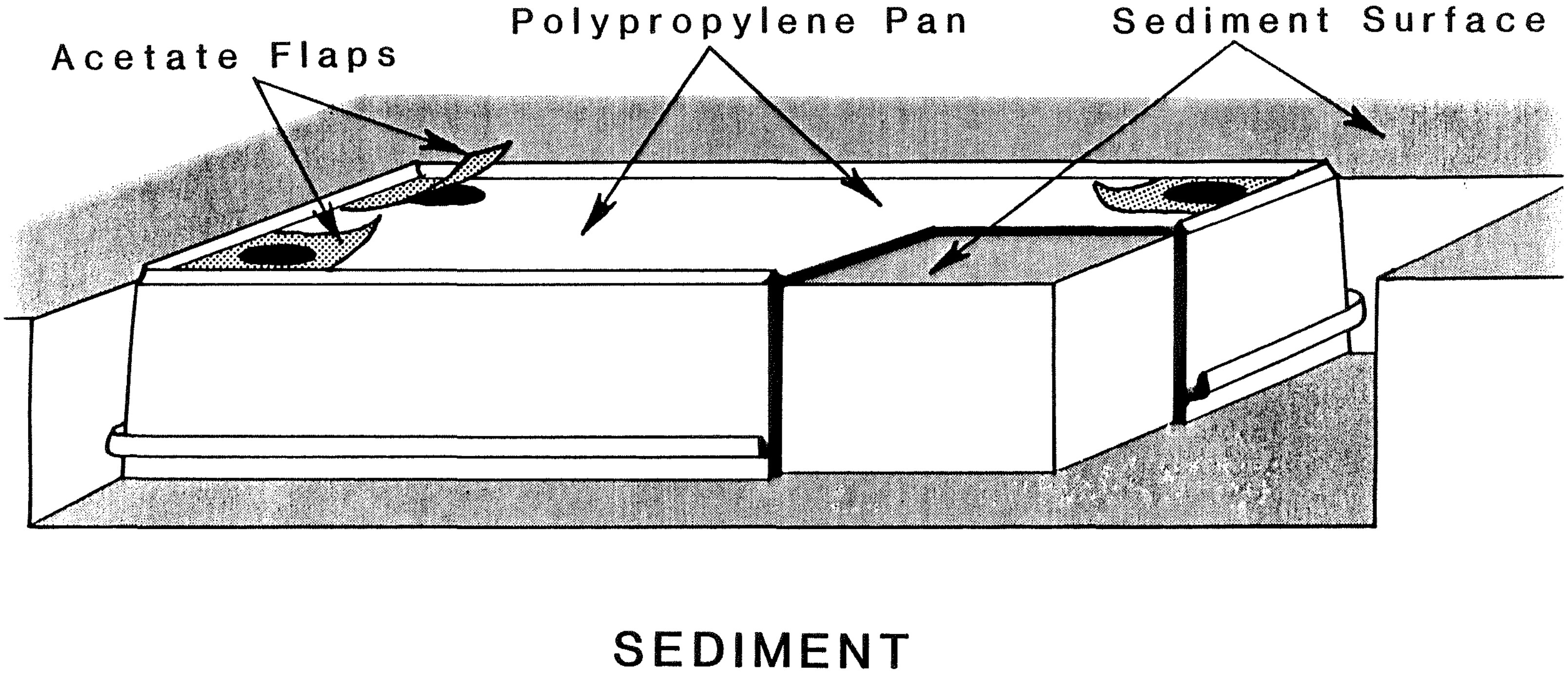
Sediment Collection

Samples were collected from the top six cm of sediment from lakes Clara and McGrath on 13 July 1984. Ten samples were collected from two locations within each lake--four profundal sediment samples from the area of maximum depth and six littoral sediment samples from areas ca 1 m in depth. SCUBA divers collected profundal sediments using polypropylene pans with snap-on lids (Fig. 2). The pans were inverted and gently pushed into the sediments until contact was made between the sediment surface and the pan bottom. Holes in the bottom corners of the pans allowed water to be released during insertion into the sediment. The lid was then carefully placed under the pan and snapped in place. Littoral sediments were collected by carefully removing the upper 6 cm of surficial sediment with a polypropylene scoop. Samples from each specific location within a lake were combined in a 20-L polypropylene container and held on ice during transport to the laboratory where they were stored at 4 °C. Littoral sediment samples were passed through a 2-mm mesh nylon screen (Nitex^{TM}) to remove large particulate material prior to storage. Profundal sediment samples did not require screening.

Analysis Of Bulk Sediments

All analyses were conducted using wet composite sediment samples that were homogenized prior to each subsampling. A dual impeller was used to mix profundal sediment samples. Littoral sediment samples were mixed with a glass spoon.

Figure 2. Polypropylene pan used to collect profundal sediments from lakes Clara and McGrath, Wisconsin.


Acetate Flaps
Polypropylene Pan
Sediment Surface
SEDIMENT

Percent water content of the sediments was measured by weight loss on evaporation when dried at 25 °C and at 103 °C (American Public Health Association 1985). Sediment texture was determined by a sieve-pipet method (United States Geological Survey 1969). Texture was defined using the following size gradations: sand, 2000-62 µm; silt, 62-4 µm; clay, <4-µm. Total organic matter content was estimated by weight loss of volatile residue on ignition at 550 °C (American Public Health Association 1985).

Total acid extractable (TAE) aluminum, cadmium, and lead were measured on aqua regia digested samples (United States Environmental Protection Agency 1981). Wet sediments (20-g aliquants; approximately equal to 1 g dried profundal sediment or 16 g dried littoral sediment) were digested in 5 mL of concentrated Ultrex^{TM} HCl, 0.5 mL concentrated Ultrex^{TM} HNO_3, and deionized water (30 mL for the profundal sediment samples or 50 mL for the littoral sediment samples). Samples were digested with heat (temperatures were maintained just below boiling point) until digestates were reduced to approximately 20 mL. Digestates were clarified by centrifugation at about 1200X g for 10 min. The supernatant was decanted into a 50-mL volumetric flask, and the residue twice resuspended with deionized water and re-centrifuged. Both rinses were added to the initial supernatant, which was then diluted to volume with deionized water and stored at 4 °C in linear polypropylene containers.

Metal concentrations in the diluted digestates were determined by flame atomization using an Instrumentation Laboratory 551 atomic absorption spectrophotometer. Instrument parameters are listed in

Table 2. Potassium chloride (3.8 g/L) was added to all aspirated solutions to suppress flame ionization of aluminum.

Acidification Of Sediments

To determine the effect of sediment pH on metal release, aliquants of each sediment sample were serially acidified with solutions prepared from a stock mixture of Ultrex™ H_2SO_4 and Ultrex™ HNO_3. The stock acid mixture was prepared so that H_2SO_4 contributed two-thirds of the total hydrogen ion activity. Sulfuric acid and nitric acid contribute approximately 65% and 34%, respectively, of the total acidity in precipitation of northeastern United States (Cogbill and Likens 1974; Galloway et al. 1976; Glass et al. 1980; Haines 1981). All sample acidifications were conducted at ca 25 °C in 150-mL polymethylpentene (PMP) screw-cap Erlenmeyer flasks while shaken @ 100 rpm on a Lab-Line 3590 orbital shaker. Experimental conditions for the sediment acidifications were determined from the results of preliminary studies that monitored pH stabilization of sediment samples after addition of an acid solution.

Preliminary Studies - Profundal Sediments. Stabilization of sediment pHs after addition of acid was compared between wet and dry sediments to determine if air-dried sediment could be used in the acidification study. Aliquants of wet profundal sediment (100-g) and reconstituted profundal sediment (5-g dry sediment that was reconstituted with 95 mL deionized H_2O prior to addition of acid) were acidified with 0.032 meq of H^+. At various time intervals, pH was determined on samples that were removed without replacement. All samples were incubated

Table 2. Instrument parameters utilized for flame atomization analyses.

Parameter	Cadmium	Lead	Aluminum
Wavelength (nm)	228.8	217.0	309.3
Band-pass (nm)	1.0	1.0	1.0
Lamp current (mA)	3.0	8.0	10.0
Photomultiplier voltage (V)	620	760	620
Background correction (D_2)	no	yes	no
Integration			
- mode	auto	auto	auto
- time (sec)	1.0	1.2	1.5
A.A. mode	single beam	single beam	single beam
Gases	air/C_2H_2	air/C_2H_2	N_2O/C_2H_2
Flame stoichiometry	oxidizing	oxidizing	reducing
Concentration range (µg/L)[a]	16.5-337	120-3890	0.12-57.4
Detection limit (µg/L)[b]	1.1	30	110

[a] Aluminum concentration range expressed in mg/L.

[b] Two standard deviations of the background signal in a sample with low concentration (Slavin et al. 1972).

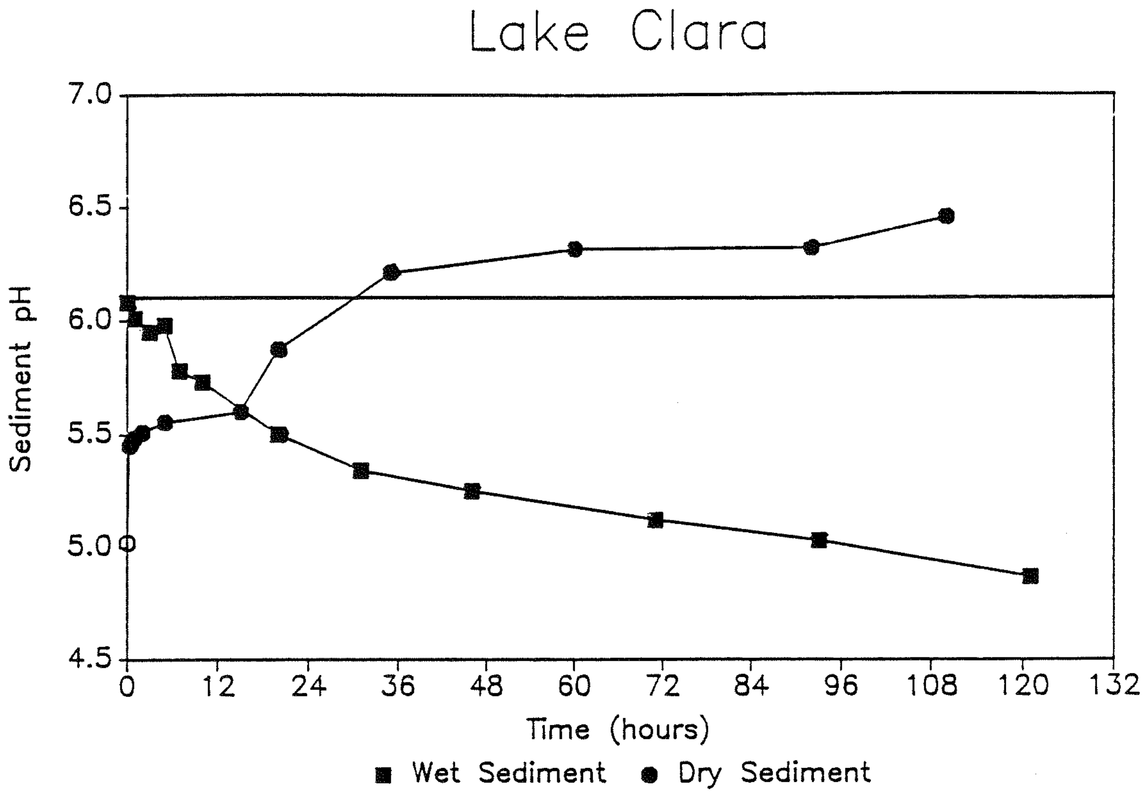
aerobically. Aerobic conditions were maintained by oxygen diffusion through the flask walls.

Approximately 15 h after the acid addition, a large increase in pH was observed for the reconstituted dry profundal sediments from both lakes (Fig. 3). The pH values of reconstituted sediments were greater than those of the wet, natural sediments after 25 h and 17 h for Clara and McGrath, respectively, and continued to increase over the rest of the 120-h study. In contrast, pH values of the wet profundal sediments continually decreased over the entire study.

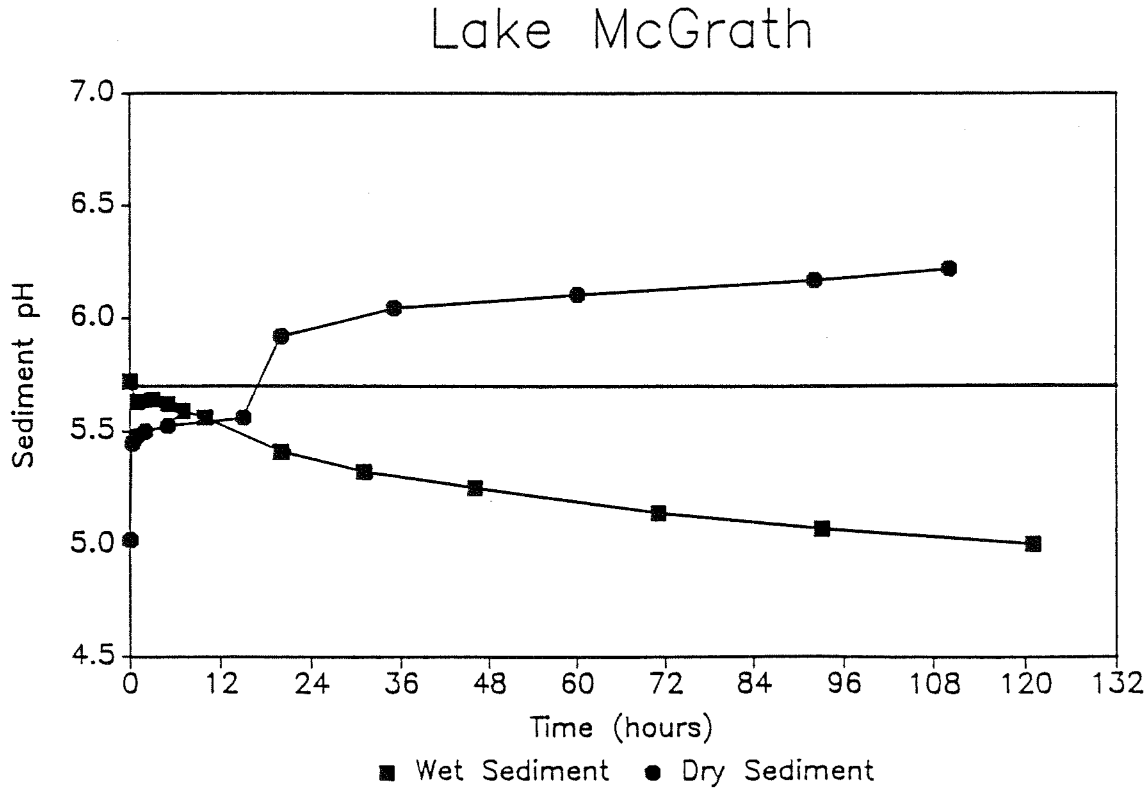
The pH stabilization curves for both the wet and reconstituted dry sediments indicate that sediment pH was significantly influenced by biological activity. The observed pH increase of reconstituted dry sediments may have been caused by increased alkalinities resulting from bacterial reduction of NO_3^- and SO_4^{2-} in anaerobic micro-zones within aggregated sediment particles. Dry profundal sediments that were sterilized prior to reconstitution had lower pHs that stabilized 5 h after addition of H^+ and increased only slightly during the rest of the study (Fig. 4). Because the sediments were dried, native populations of nitrate- and sulfate-reducing bacteria may have become reestablished in anaerobic microcosms after sediment reconstitution and acid addition. The 15-h time period that occurred before the pH increase may reflect the lag phase of a population growth curve. An extended lag phase, as evidenced by the pH stabilization curves of the dry sediments, is indicative of the growth of small density populations (Atlas and Bartha 1981).

The continual decrease in pH observed with wet sediments may have been caused by increased H_2SO_4 resulting from bacterial or chemical

Figure 3. Stabilization of pH in wet and reconstituted dry profundal sediments after addition of 0.032 meq H^+. The solid horizontal line represents the pH of the natural sediment. Sediments were collected from lakes Clara and McGrath, Wisconsin, 13 July 1984.

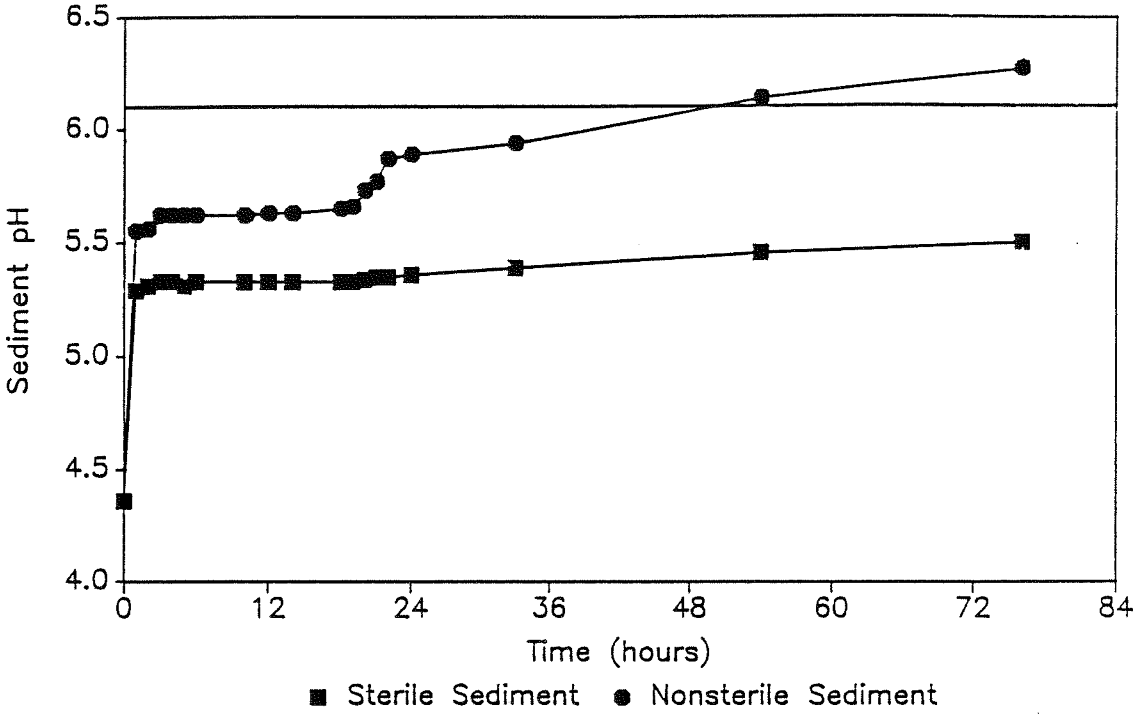


Lake Clara

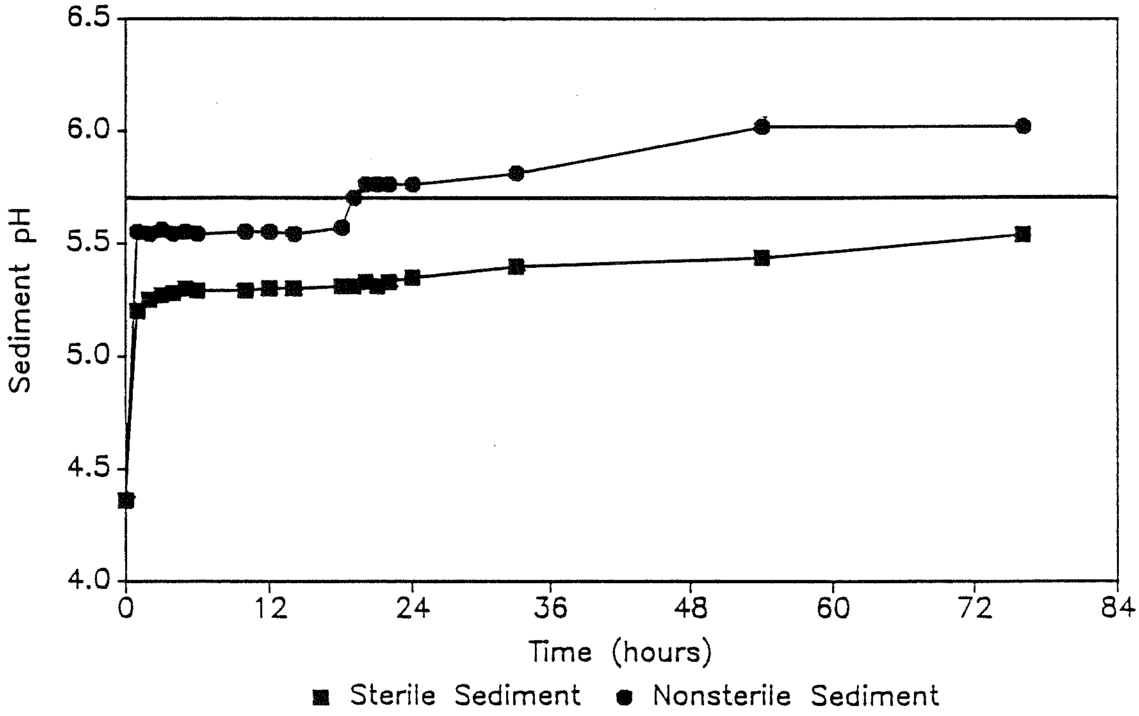


Lake McGrath

Figure 4. Stabilization of pH in sterile and nonsterile reconstituted dry profundal sediments after addition of 0.032 meq H^+. The solid horizontal line represents pH of the natural sediments. Sediments were collected from lakes Clara and McGrath, Wisconsin, 13 July 1984.



Lake Clara



Lake McGrath

oxidation of H_2S, S^o, or FeS_2. Diffusion of O_2 through the flask walls could maintain an aerobic micro-layer at the sediment/flask interface where the oxidations could occur. In contrast to the reconstituted dry sediments, a lag phase was not observed in the pH stabilization curve of the wet sediments. If the decrease in pH was bacterial in origin, natural bacterial populations may have been well established and oxidation of sulfur species may have occurred as soon as samples were placed into the PMP flasks. Chemical oxidations could also occur immediately.

Because of the continual pH decrease observed in aerobically incubated sediments, studies were conducted to compare pH stabilization of wet sediments incubated both anaerobically and aerobically. Aliquants of wet profundal sediments (100-g) were acidified with 0.03-, 0.13-, and 1.27-meq of H^+ and incubated under both aerobic and anaerobic conditions. Aerobic conditions were maintained by oxygen diffusion through the flask walls. Anaerobic conditions were established and maintained by placing sample flasks in glass chambers (Fig. 5) and flushing the atmosphere with oxygen-free nitrogen. Buffered resorufin dye was injected into a holder within each chamber after oxygen evacuation to confirm that the redox potential (E_H) was maintained at less than -110 mV. Resorufin dye buffered to pH 7 remains colorless at E_Hs less than -110 mV (Jacob 1970). At various time intervals, pHs were determined on samples that were removed without replacement.

The effect of aerobic and anaerobic conditions on sediment pH after acidification was similar between the profundal sediments from both lakes (Fig. 6). The pHs of sediments incubated aerobically after acid addition decreased over the entire 210-h experiment, with the exception of samples

Figure 5. Glass chamber used to maintain anaerobic conditions during incubation of profundal sediments.

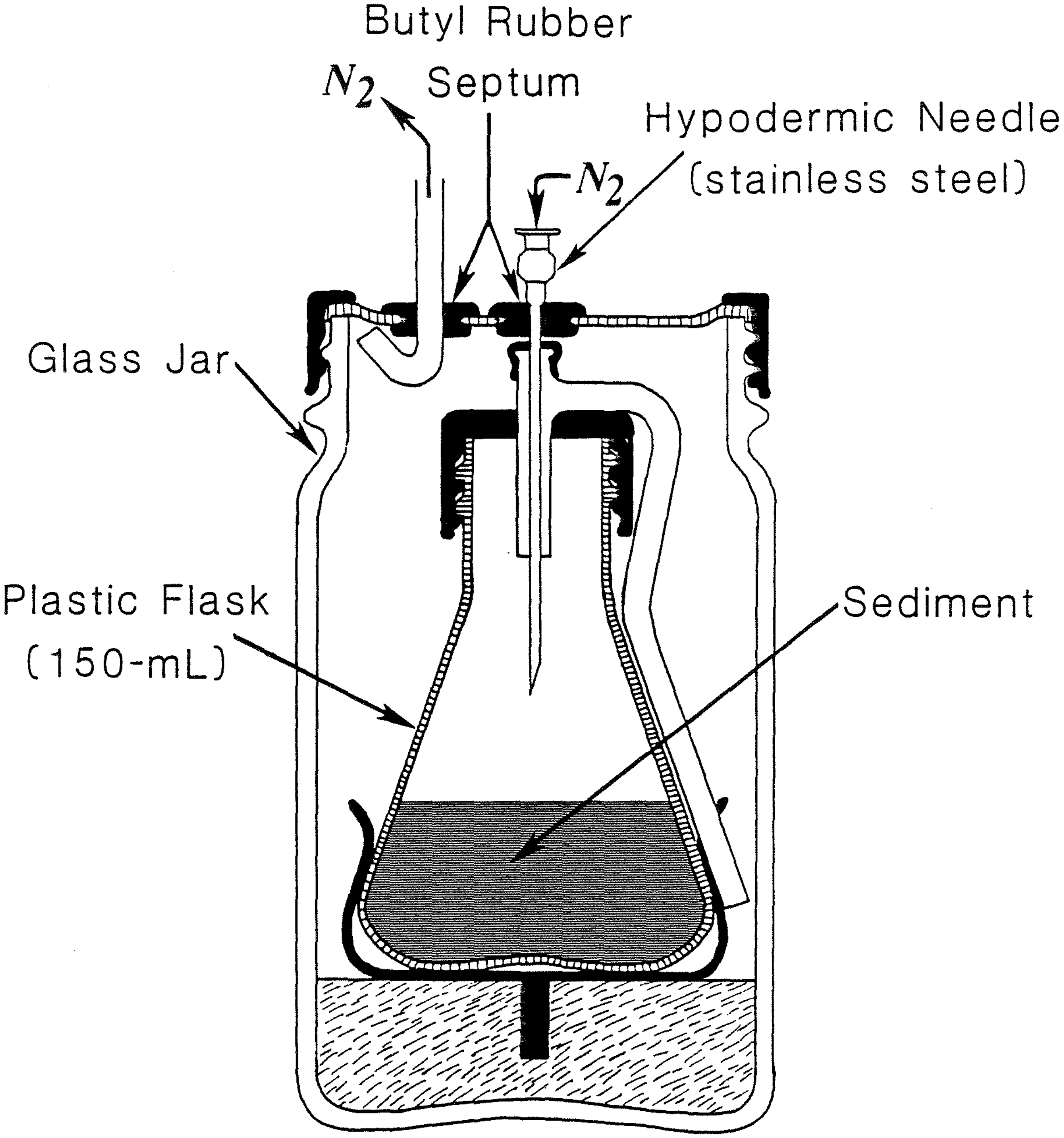
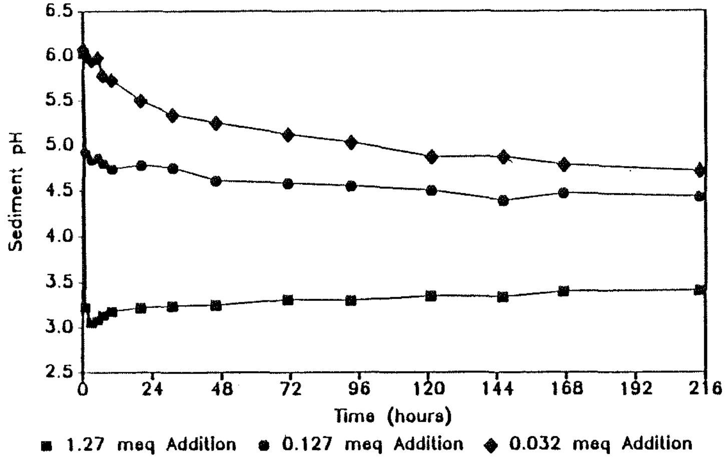
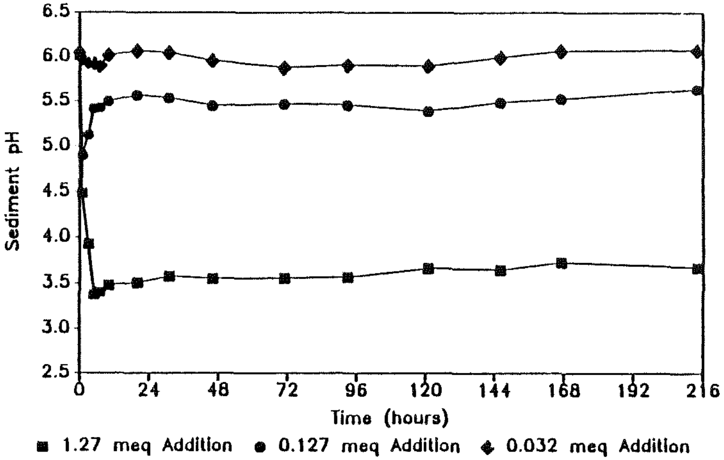
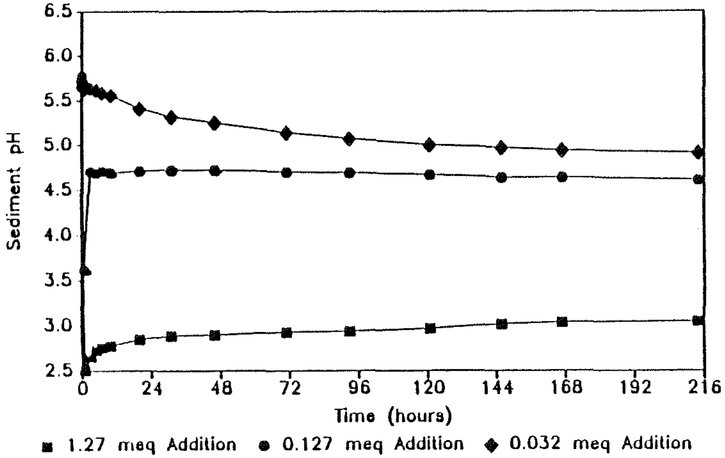
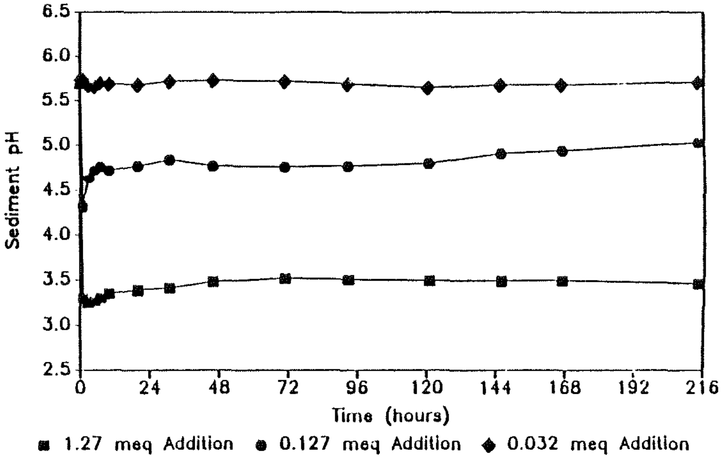

Butyl Rubber
Septum
N_2
Hypodermic Needle
(stainless steel)
N_2
Glass Jar
Plastic Flask
(150-mL)
Sediment

Figure 6. Effects of aerobic and anaerobic incubation on stabilization of pH in wet profundal sediments of lakes Clara and McGrath after addition of 1.27, 0.127, and 0.032 meq H^+.


Lake Clara – Aerobic Incubation


Lake Clara – Anaerobic Incubation


Lake McGrath – Aerobic Incubation

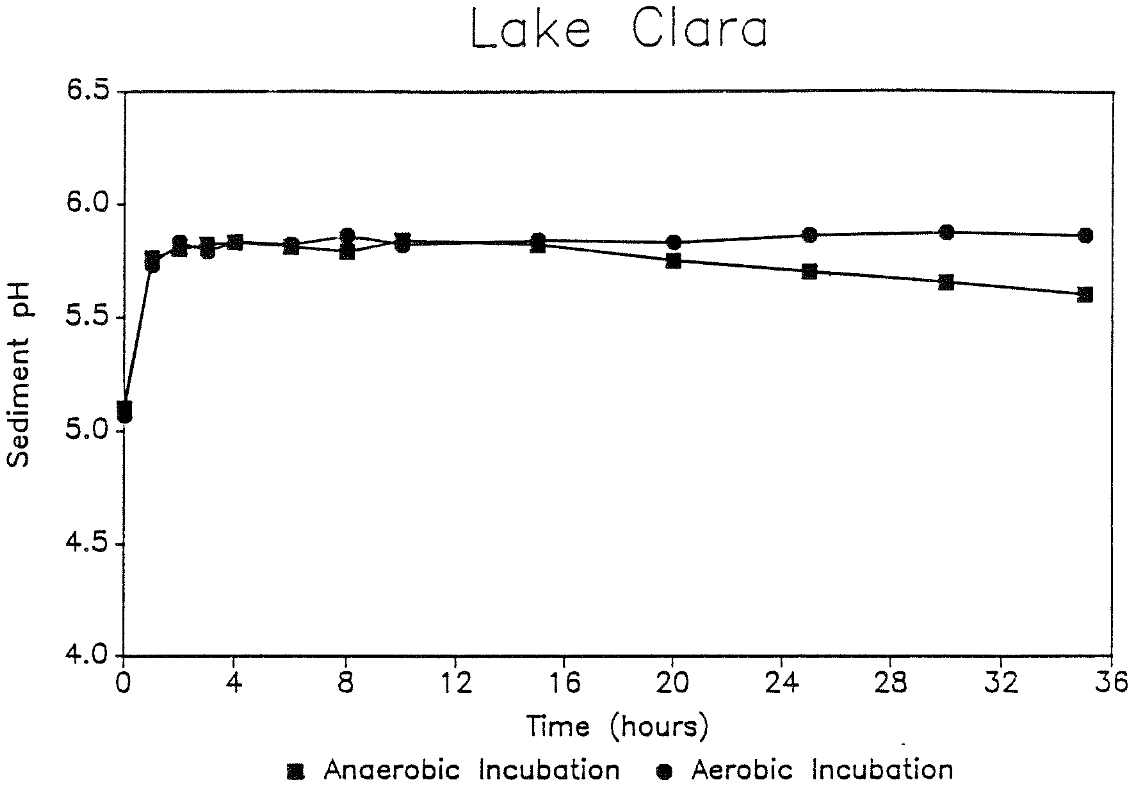

Lake McGrath – Anaerobic Incubation

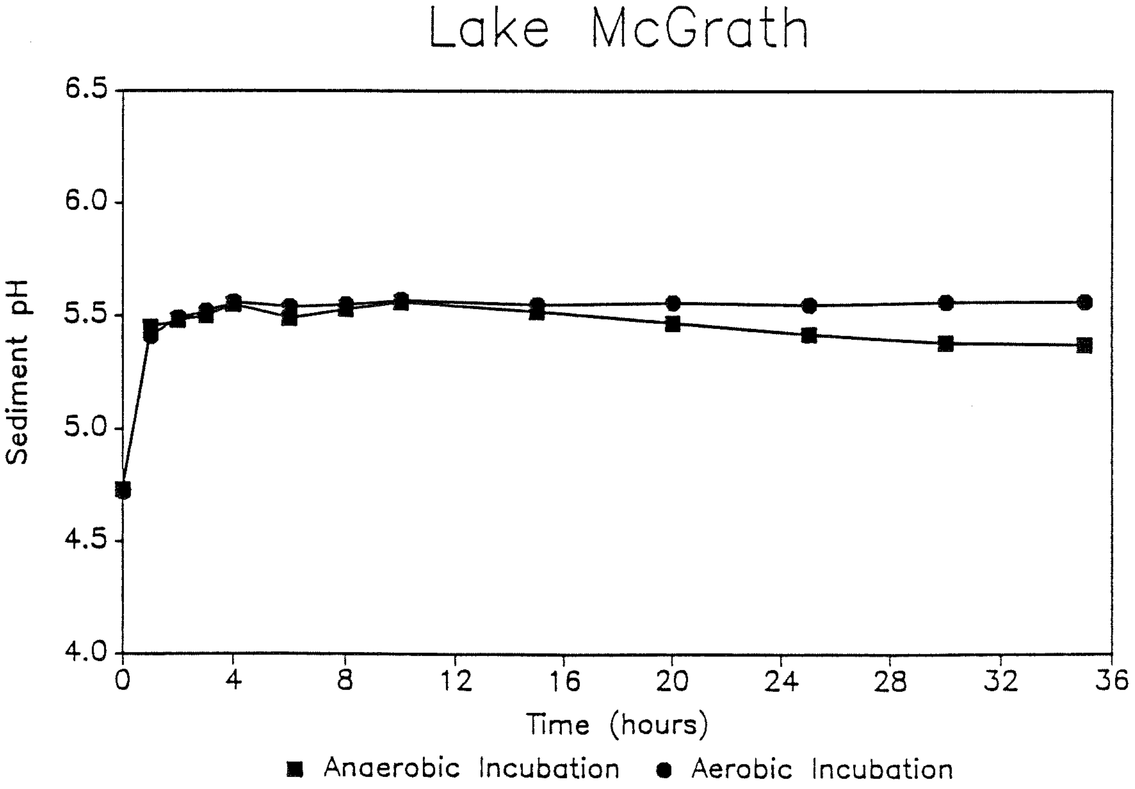
acidified with 1.27 meq of H^+. The sediments acidified with 1.27 meq of H^+ were stable after ca 20 h and increased slightly over the rest of the study. The lowest pH was observed with sediments acidified with 0.032 meq of H^+. In contrast, pHs of sediments incubated anaerobically after addition of acid stabilized after 15 to 50 h (depending on amount of H^+ initially added) with only minor fluctuations over the rest of the study.

Preliminary Studies - Littoral Sediments. Only the effects of aerobic and anaerobic incubation of wet littoral sediments were determined because sediment drying might have affected microbial communities and therefore sediment pH, as evidenced with profundal sediments, . Aliquants of wet littoral sediments (75 g with 100 mL deionized H_2O) were acidified with 0.025 meq of H^+ and incubated under the same conditions described for the profundal sediments.

The effect of oxygen on sediment pH was similar between the littoral sediments from the two lakes (Fig. 7). Stable pHs were observed in both aerobically and anaerobically incubated sediments after ca 8 h. The pHs of anaerobically incubated sediments remained stable for the rest of the 35-h experiment; however, the pHs of aerobically incubated sediments decreased steadily after ca 15 h. The decline of pH may have resulted from bacterially and/or chemically mediated oxidation of sulfur species, as suggested with the profundal sediments. In contrast to the profundal sediments, however, a 15-h lag phase was associated with the decrease in pH. If the hypothesis that the decline in pH was bacterial in origin is correct, the lag phase suggests that the population of sulfur reducing bacteria may have been small and/or that the H_2S and sulfur used in the oxidation were initially limiting and probably resulted from bacterial reduction of SO_4^{2-}.

Figure 7. Effects of aerobic and anaerobic incubation on stabilization of pH in wet littoral sediments of lakes Clara and McGrath after addition of 0.025 meq H^+.


Lake Clara


Lake McGrath

Sediment Acidifications. Wet sediments were used in the acidification experiment because of the results of the above preliminary studies, i.e. the probable influence of bacteria on sediment pH and possible chemical alterations caused by drying (i.e. increased metal binding, changes in oxidation states, etc.). Profundal samples were incubated anaerobically because the sediments were naturally anaerobic when collected and because of the pH decrease observed in samples incubated aerobically. In contrast, littoral samples were incubated aerobically even though preliminary studies indicated that pHs would decrease after 15 h. This protocol was followed because the surficial littoral sediments probably contained a naturally aerobic micro-layer as a result of shallow depth and wave activity. Based on the results from the preliminary studies, aliquants of profundal sediment (100-g) were acidified with 0.03 to 12.7 meq of H^+ and incubated for 55 h. Littoral samples (75-g sediment aliquants and 100 mL of deionized H_2O) were acidified with 0.01 to 2.5 meq of H^+ and incubated for 12 h.

After elapse of respective acidification times, samples were transferred to 50-mL polyallomer screw-cap centrifuge tubes. Final pH was measured on separate portions of each acidified sediment using an Orion Research 701 pH meter and Corning combination electrode. Interstitial water was separated from acidified sediment by centrifugation at about 35 000X g for 20 min on a Beckman J-21 centrifuge with a JA-20 rotor head. Supernatants were decanted into linear polypropylene storage containers, preserved with concentrated Ultrex^{TM} HNO_3 (1 mL/L), and refrigerated at 4 °C. Because dissolved humic substances (as defined by Thurman 1985) precipitated when HNO_3 was added, supernatants with pHs greater than ca 4 were not acid-preserved but were refrigerated at 4 °C and analyzed for Al, Cd, and Pb within 12 h. No differences in metal concentrations ($\underline{P} < 0.05$) were observed between acid preserved and unpreserved samples refrigerated at 4 °C for 36 h.

Concentrations of organically chelated Al, Cd, and Pb were estimated by acidifying sediments to pHs greater than ca 4 and removing the dissolved humic substances (DHS) from supernatants prior to analysis. Removal of DHS was accomplished by serial filtration of supernatants through nested 0.8-µm and 0.4-µm Nucleopore^{TM} polycarbonate membrane filters using a pressure filtration manifold (Fig. 8). Nitrogen (flow rates of 1-5 mL/min and pressures up to 80 psi) was used as the filtration force. Approximately 5 mL of sample was allowed to pass through filters before filtrates were saved. The filtrate was collected in linear polypropylene storage containers, acid preserved, and stored at 4 °C.

Metal concentrations in acidified sediment supernatants were determined using an Instrumentation Laboratory 551 atomic absorption spectrophotometer equipped with a 655 furnace atomizer and 254 FASTAC^{TM} auto-sampler. Both flame and electrothermal atomization were used to analyze aluminum, cadmium, and lead, depending upon concentrations. Flame atomization analyses were as described previously. Instrument parameters for electrothermal atomization analyses are listed in Table 3. Matrix interferences were minimized by modifying the furnace atomizer operation mode and temperature-time programs. Potassium chloride (3.8 g/L) was added to all solutions to minimize matrix interference during Al analysis (both flame and electrothermal).

Figure 8. Pressure filtration manifold used to remove dissolved organic complexes from sediment pore waters.

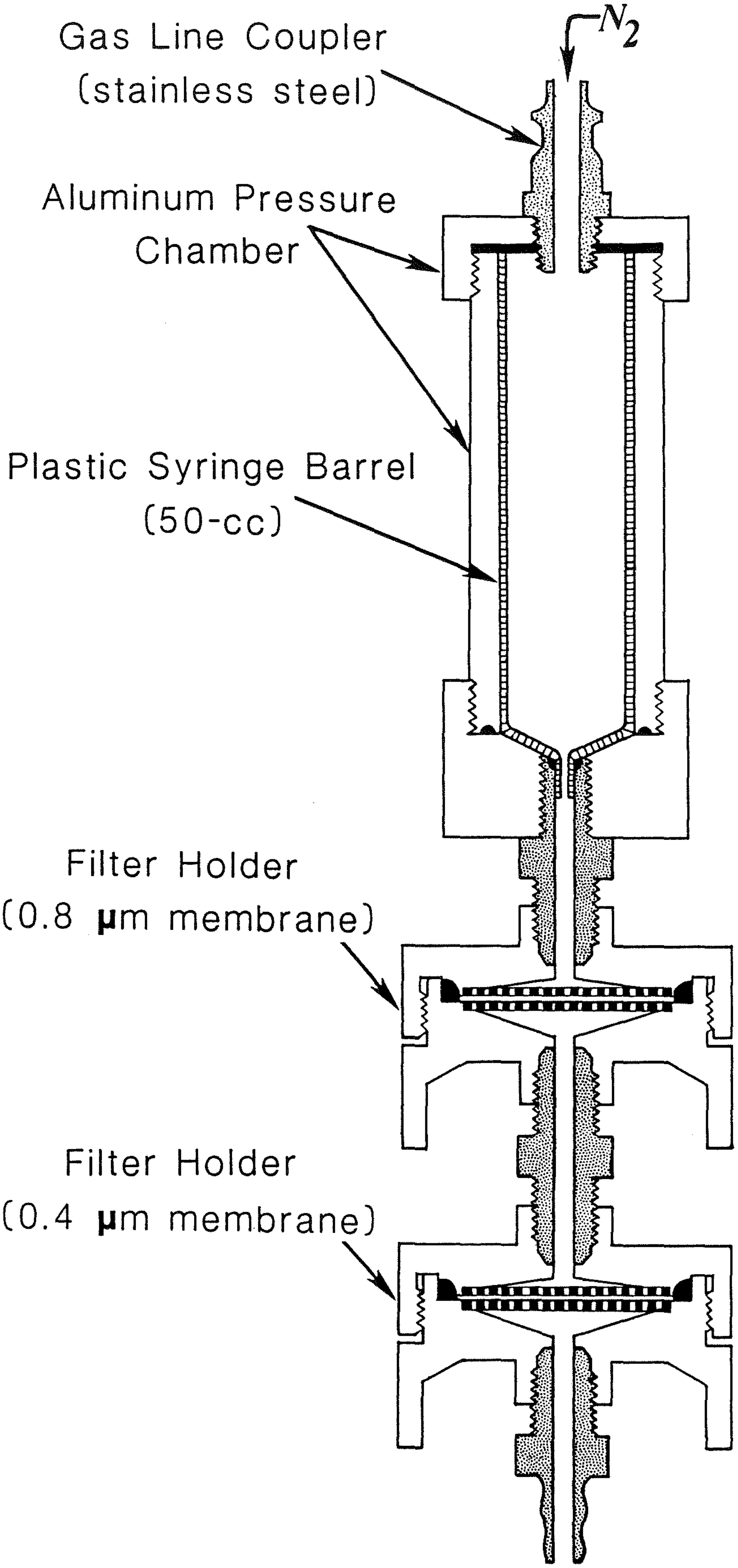

N2
Gas Line Coupler
(stainless steel)
Aluminum Pressure
Chamber
Plastic Syringe Barrel
(50-cc)
Filter Holder
(0.8 µm membrane)
Filter Holder
(0.4 µm membrane)

Table 3. Instrument parameters utilized for electrothermal atomization analyses.

Parameter	Cadmium	Lead	Aluminum
Wavelength (nm)	228.8	283.5	309.3
Band-pass (nm)	1.0	0.5	0.5
Lamp current (mA)	3.0	5.0	10.0
Photomultiplier voltage (V)	620	620	620
Background correction (D_2)	yes	yes	yes
Integration			
- mode	peak height	peak area	peak area
- time (sec)	4.0	3.5	4.0
A.A. mode	single beam	single beam	single beam
Cuvette geometry	round/uncoated	round/uncoated	round/coated
Temperature/time program (°C/sec)			
- step 1	--	--	--
- step 2	130/5	130/5	130/5
- step 3	190/10	400/15	1500/25
- step 4	230/10	650/20	1650/35
- step 5	1700/0	1950/0	2750/0
- step 6	1700/10	1950/10	2750/10
Operation	pressurized (30 psi)	auto	auto
Gases	N_2	N_2	Ar_2
Flush rate (L/min)	0	5	5
FASTAC™ program			
- delay (sec)	10	10	10
- deposit (sec)	15-110	15-95	10-20
Concentration range (µg/L)	0.026-9.59	0.09-35.6	31.2-78.1
Detection limit (µg/L)[a]	0.008	0.07	0.9

[a] Two standard deviations of the background signal in a sample of low concentration (Slavin et al. 1972)

Quality Assurance

All plastic-ware was soaked a minimum of 24 h in a 50% (v/v) solution of HCl, rinsed with deionized water, soaked 5 h in a 2N HNO_3 solution, and rinsed ten times with deionized water to minimize metal contamination. Glassware was soaked a minimum of 24 h in a 50% (v/v) solution of HNO_3 and rinsed with deionized water. Nucleopore^{TM} membrane filters were soaked for 24 h in a 2N HNO_3 solution and rinsed with deionized water before use.

Sediment Digestions. Subsamples from each composite sediment sample were digested and analyzed in two batches. Each batch consisted of ten aliquants of each composite sample (30% of which were spiked prior to digestion), three aliquants of United States National Bureau of Standards (NBS) reference material 1645 (river sediment), procedural blanks, and calibration standards. Calibration standards were prepared from certified 1000 mg/L standard solutions (Curtin-Matheson Chemical Co.).

Samples, calibration standards, and procedural blanks were subjected to the same digestion and storage procedures to evaluate contamination from reagents and storage containers. Analytical accuracy and precision were estimated by metal recovery from NBS river sediments and spiked samples, analysis of replicate digestions, and triplicate analysis of individual digestions. A standard addition technique (four-point) was used to evaluate matrix interferences.

Sediment Acidifications. All acidifications were done in quadruplicate. To minimize errors from electrode fouling and meter drift, calibration procedures were repeated prior to pH measurement of each set of quadruplicate samples. To verify analytical accuracy, supernatants (10% of which were spiked prior to acid preservation) were concurrently analyzed with NBS reference material 1643b (trace elements in water), which had been diluted to approximate the supernatant metal concentrations. Procedural and analytical precision were estimated by analysis of replicate acidifications and triplicate analysis of individual acidifications. Matrix interferences were evaluated by a standard addition technique (four-point) using supernatants from sediments acidified to pHs of ca 2, 4, and 6. During electrothermal atomization, sample deposition times were varied to maintain Al, Cd, and Pb absorbances within the working range of their respective standard curves. Blanks and standards of various pHs were subjected to the same filtration and storage procedures as samples to monitor procedural contamination problems.

RESULTS

Quality Assurance

Sediment Digestions. Results of quality assurance procedures are summarized in Table 4. Results for metal concentrations in NBS sediment, except for Al, were well within the certified concentration ranges. The low recovery of Al from NBS river sediment was expected because certified concentrations were determined from sediments digested with hydrofluoric acid (T. Gills, National Bureau of Standards, pers. comm.). Hydrofluoric acid digestion is much more vigorous and dissolves aluminum silicates, unlike the aqua regia digestion used in this study. Precision (percent relative standard deviation, RSD) between analyses of NBS sediment were 8.8, 8.3, and 1.5% for Al, Cd, and Pb, respectively. Slopes of four-point standard addition curves for all three metals were within 5% of slopes for aqueous standard curves. Mean recoveries of Al, Cd, and Pb from sediment samples spiked prior to digestion ranged from 98 to 105%. Mean RSDs between metal concentrations in replicate digestions were 6.7, 4.5, and 4.9% for Al, Cd, and Pb, respectively. Mean RSDs between triplicate analyses of individual digestions ranged from 0.8 to 2.8%. Concentrations in procedural blanks were less than the calculated detection limits.

Sediment Acidifications. Results of quality assurance procedures are summarized in Table 5. Analyzed Cd and Pb concentrations in NBS water were well within the certified concentration ranges (Al is not certified in NBS water). RSDs for analyses of NBS water were 5.2 and 4.8% for Cd and Pb, respectively. Slopes of four-point standard addition curves for all three metals from littoral sediment supernatants were

Table 4. Quality assurance results for metal analyses of digested sediments.

Procedure	Aluminum	Cadmium	Lead
Analysis of NBS river sediment			
Study results			
- Mean concentration (µg/g)	4,420	10.5	700
- RSD (%)[a]	8.8	8.3	1.5
- 95% confidence limits (µg/g)	±390	±0.4	±4
- n	24	24	24
Certified concentrations			
- Mean concentration (µg/g)	22,600	10.2	714
- 95% confidence limits (µg/g)	±400	±1.5	±28
Recovery from spiked samples			
- Mean recovery (%)	105.4	98.0	100.7
- RSD (%)	9.7	5.0	3.5
- n	32	32	32
Precision between analysis of replicate digestions			
- Mean RSD (%)	6.7	4.5	4.9
- n	70	70	70
Precision between triplicate analyses of individual digestions			
- Mean RSD (%)	1.3	2.8	0.8
- Range (%)	0.1-6.7	0.0-9.5	0.0-1.4
- n	27	27	27

[a] RSD = relative standard deviation

Table 5. Quality assurance results for metal analyses of acidified sediments.

Procedure	Aluminum	Cadmium	Lead
Analysis of NBS water			
Study results			
- Mean concentration (μg/L)	--	19.6	23.6
- RSD (%)[a]	--	5.2	4.8
- 95% confidence limits (μg/L)	--	±0.3	±0.4
- n	--	45	41
Certified concentrations[b]			
- Mean concentration (μg/L)	--	20.0	23.7
- 95% confidence limits (μg/L)	--	±1.0	±0.7
Recovery from spiked samples			
- Mean recovery (%)	103.7	99.3	96.2
- RSD (%)	3.1	5.3	8.5
- n	30	30	30
Precision between analyses of replicate acidifications			
- Mean RSD (%)	10.2	9.6	12.9
- Range (%)	0.5-55.0	1.1-31.1	1.0-58.8
- n	300	297	299
Precision between triplicate analyses of individual acidifications			
- Mean RSD (%)	5.2	2.8	7.3
- Range (%)	0.2-17.2	0.2-8.2	1.5-22.5
- n	43	43	43

[a] RSD = relative standard deviation

[b] NBS water is not certified for aluminum

within 10% of slopes for aqueous standard curves at the test pHs of 2, 4, and 6. Except for Al at pH 4, slopes of standard addition curves for all three metals from profundal sediment supernatants were within 10% of slopes for aqueous standard curves at the test pHs of 2, 4, and 6. The slope of the standard addition curve for Al at pH 4 was within 15% of the aqueous standard curve. RSDs for pH between replicate acidifications ranged from 0.1 to 4.2% and had a mean of 0.8%. Mean recoveries of Al, Cd, and Pb from supernatants spiked prior to acid preservation ranged from 96.2 to 103.7%. Mean RSDs for metal concentrations between replicate acidifications were 10.2, 9.6, and 12.9% for Al, Cd, and Pb, respectively. The high RSDs between acidifications were caused by samples acidified to pHs near the inflection point of the acidification curve where small changes in pH resulted in relatively large changes in metal concentration. Mean RSDs between triplicate analyses of individual acidifications were 5.2, 2.8, and 7.3% for Al, Cd, and Pb, respectively. The large range in RSDs between triplicate analyses for Al and Pb (17.2 and 22.5%, respectively) were associated with analyses at low concentrations. Concentrations in procedural blanks (including filtered blanks) were less than or equal to calculated detection limits.

Texture, Organic Content, And Metal Concentrations In Bulk Sediments

Physical characteristics of sediment samples were similar between lakes Clara and McGrath (Table 6). Profundal sediments from both lakes were about 95% water and were texturally indicative of clays. Surface sediments were not consolidated when observed by divers during sample collection but were very flocculent in nature. About 50% of the profundal sediment residues were comprised of organic materials. In

Table 6. Physical and chemical characteristics of bottom sediments collected from lakes Clara and McGrath, Wisconsin, 13 July 1984.

Characteristic	Lake Clara		Lake McGrath	
	Profundal	Littoral	Profundal	Littoral
Water Content (%)[a]	95.0	19.3	95.2	19.4
Sediment residue (%)[a]	5.0	80.7	4.8	80.6
Volatile solids (%)[b]	49.9	0.5	52.7	0.5
Sediment texture (%)[b]				
- sand	0.5	98.7	1.0	98.1
- silt	17.8	<1.0	21.3	<1.0
- clay	31.8	<1.0	25.1	<1.0
pH[a]	6.1	6.0	5.7	5.3
Acid neutralizing capacity (μeq/g)[a]				
- pH 5.5	14	1.0	8	----
- pH 5.0	57	1.6	41	0.2
- pH 4.5	114	2.1	78	0.8
- pH 4.0	185	3.2	130	1.7
- pH 3.5	288	4.9	208	3.2
- pH 3.0	438	8.0	346	6.8
- pH 2.5	676	15.1	561	15.0
- pH 2.0	1000	41.6	866	----
- pH 1.5	1638	----	1431	----
Total Acid Extractable Metal[a]				
- Aluminum (mg/g)	0.698	0.863	0.612	1.202
- Cadmium (μg/g)	0.151	0.027	0.375	0.047
- Lead (μg/g)	4.88	2.34	4.69	3.50
Pore Water Metal Concentrations[a] (nonfiltered samples)				
- Aluminum (mg/L)	4.24	0.47	10.49	0.18
- Cadmium (μg/L)	0.236	0.036	1.106	0.035
- Lead (μg/L)	11.37	2.21	30.66	0.56

[a] Values based on wet sediment

[b] Values based on dry sediment

contrast, the littoral sediments were ca 20% water with ca 98% of the residue comprised of sand. Less than 1% of the littoral sediment residue was organic matter.

The pHs of Lake Clara sediments were greater than those in sediments from Lake McGrath, which parallels pHs of their respective surface waters. Littoral sediment pHs of both lakes were the same as their respective surface water pHs (i.e., 6.0 for Clara and 5.3 for McGrath). Acid neutralizing capacities (ANC, as defined by Baker et al. 1985) of McGrath sediments were less than those of the corresponding Clara sediments, which is apparent from their respective sediment pHs (Table 6). The ANCs of profundal sediments were considerably greater than littoral sediments.

Total acid extractable (TAE) Al, Cd, and Pb concentrations were different between sediment types within the lakes and between sediments of the two lakes (Table 6). The greatest concentrations of Cd and Pb occurred in the profundal sediments of both lakes. In contrast, Al concentrations were greatest in the littoral sediments. Concentrations of Al and Pb were similar between the profundal sediments from the two lakes, although slightly greater concentrations of both metals were observed in Lake Clara profundal sediments. In contrast, the Cd concentration in profundal sediments of Lake McGrath was 2.5 times greater than in profundal sediments of Clara. Similarly, littoral sediments from McGrath contained 1.4, 1.5, and 1.7 times more Al, Cd, and Pb, respectively, than littoral sediments from Clara.

The largest difference in metal concentration between the two sediment types was observed with Cd. Profundal sediments contained 5.6 and 8.0 times more Cd than littoral sediments for Clara and McGrath, respectively. A similar trend was observed for Pb except to a lesser extent, with concentrations being 2.1 and 1.3 times greater in profundal sediments than littoral sediments for Clara and McGrath, respectively. In contrast, littoral sediments had 1.2 and 2.0 times more Al than the profundal sediments in Clara and McGrath, respectively.

Effects Of Acidification On Metals In Profundal Sediments

Responses of Al, Cd, and Pb to acidification of the profundal sediments were similar between the two lakes. The lowest concentrations of all three metals in nonfiltered pore waters of sediments from both lakes were observed at pHs (defined here as the adsorption pH or pH_{ads}) less than the pH of the nonacidified, natural sediment (pH_{nat}). The acidified sediment pH that produced pore water with metal concentrations the same as the nonacidified sediment pore water was defined as the release pH (pH_{rel}). Both pH_{ads} and pH_{rel} were different between sediments of the lakes (Table 7). Maximum concentrations of Al, Cd, and Pb in pore waters were observed at the minimum study pHs of 1.4 and 1.3 for Clara and McGrath profundal sediments, respectively.

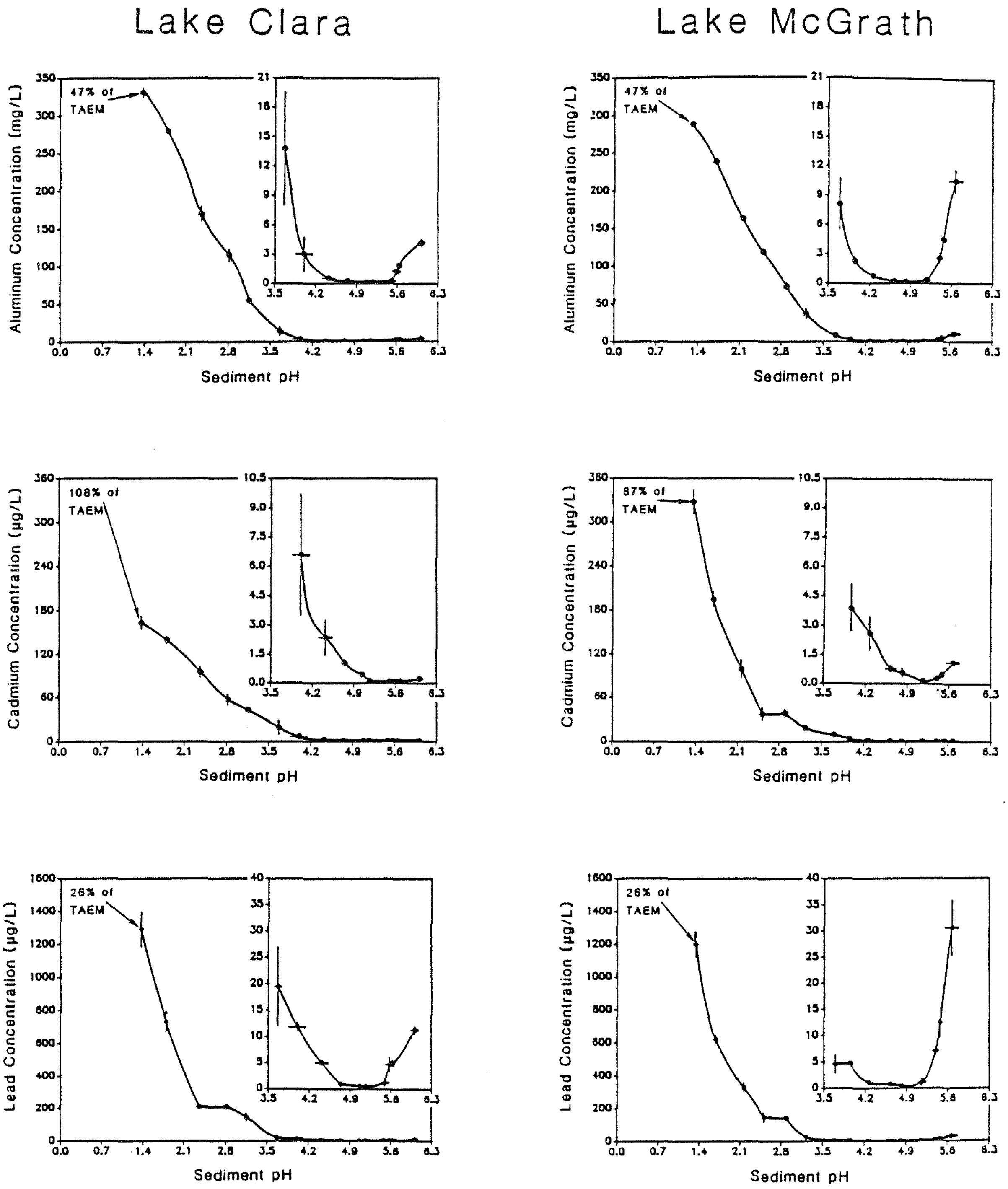
Aluminum. Aluminum concentrations in pore waters from profundal sediments of both lakes initially decreased as pH was lowered from pH_{nat} to pH_{ads} (Fig. 9 - insert graph). The diminution was greatest in McGrath sediments, with pore water Al decreasing from 10.5 to 0.18 mg/L. Aluminum in pore waters from Clara sediments similarly decreased from 4.24 to 0.14 mg/L. The pH_{ads} for Al in sediments from Clara and McGrath were 5.2 and 4.8, respectively. As acidification continued, Al was released from the sediments. The pH_{rel} for Al was ca 4.0 for Clara and 3.5 for McGrath.

Table 7. Natural, adsorption, and release pHs for bottom sediments collected from Lakes Clara and McGrath, Wisconsin, 13 July 1984.

Metal	Lake Clara		Lake McGrath	
	Profundal	Littoral	Profundal	Littoral
Aluminum				
- pH_{nat}[a]	6.1	6.0	5.7	5.3
- pH_{ads}[b]	5.2	4.4	4.8	4.3
- pH_{rel}[c]	4.0	4.0	3.5	4.2
Cadmium				
- pH_{nat}	6.1	6.0	5.7	5.3
- pH_{ads}	5.5	6.0	5.2	5.3
- pH_{rel}	5.1	6.0	4.6	5.3
Lead				
- pH_{nat}	6.1	6.0	5.7	5.3
- pH_{ads}	5.2	4.4	4.8	4.3
- pH_{rel}	4.0	2.9	3.2	4.1

[a] pH_{nat} = natural sediment pH
[b] pH_{ads} = adsorption pH
[c] pH_{rel} = release pH

Figure 9. Concentrations of Al, Cd, and Pb in pore waters of acidified profundal sediments collected from lakes Clara and McGrath, Wisconsin, 13 July 1984. Inset graphs represent enlarged portion of respective main graphs. Horizontal and vertical bars represent 95% confidence intervals for pH and concentration, respectively.


Lake Clara
Lake McGrath
Aluminum Concentration (mg/L)
47% of TAEM
47% of TAEM
Cadmium Concentration (µg/L)
108% of TAEM
87% of TAEM
Lead Concentration (µg/L)
26% of TAEM
26% of TAEM
Sediment pH
0.0
0.7
1.4
2.1
2.8
3.5
4.2
4.9
5.6
6.3
0
50
100
150
200
250
300
350
0
3
6
9
12
15
18
21
0
60
120
180
240
300
360
0.0
1.5
3.0
4.5
6.0
7.5
9.0
10.5
0
200
400
600
800
1000
1200
1400
1600
0
5
10
15
20
25
30
35
40

Pore water Al concentrations were greater in Clara than McGrath when sediment pHs were less than ca 4.8, which follows TAE Al concentrations in their respective sediments. In contrast, pore water Al was greater in McGrath than Clara at equivalent pHs above ca 4.8. Aluminum concentrations in pore waters from both lakes were approximately 0.20 mg/L at pH 4.8. Pore water Al concentrations at the minimum study pHs were 331 and 288 mg/L for Clara and McGrath, respectively.

Cadmium. Cadmium concentrations in pore waters from profundal sediments of both lakes initially decreased as pH was lowered to pH_{ads} (Fig. 9 - insert graph). This was observed over the largest concentration gradient in McGrath sediments, with pore water Cd decreasing from 1.106 to 0.153 µg/L. Cadmium in pore water from Clara sediments likewise decreased from 0.236 to 0.087 µg/L. The pH_{ads} for Cd in sediments was 5.5 for Clara and 5.2 for McGrath. As acidification continued, Cd increased in pore waters. The pH_{rel} for Cd was ca 5.1 for Clara and 4.6 for McGrath.

Similar to Al, pore water Cd was greater in sediments from Clara than McGrath along most of the acidification profiles (Fig. 9), although sediments from Lake McGrath contained more TAE Cd than sediments from Lake Clara. Cadmium in pore waters from both Clara and McGrath were approximately 0.17 and 120 µg/L at pHs 5.2 and 2.1, respectively. Pore water Cd was 163 µg/L for Clara and 328 µg/L for McGrath at their respective minimum study pHs.

Lead. Similar to Al and Cd, Pb concentrations in pore waters from profundal sediments of both lakes initially decreased as pH was lowered (Fig. 9 - insert graph). The decrease was greatest in McGrath sediments, with pore water Pb decreasing from 30.7 to 0.46 µg/L. Likewise Pb in pore waters from Clara sediments decreased from 11.4 to 0.50 µg/L. The pH_{ads} in sediments from Clara and McGrath were 5.2 and 4.8, respectively. The pH_{rel} was ca 4.1 for Clara and 3.2 for McGrath.

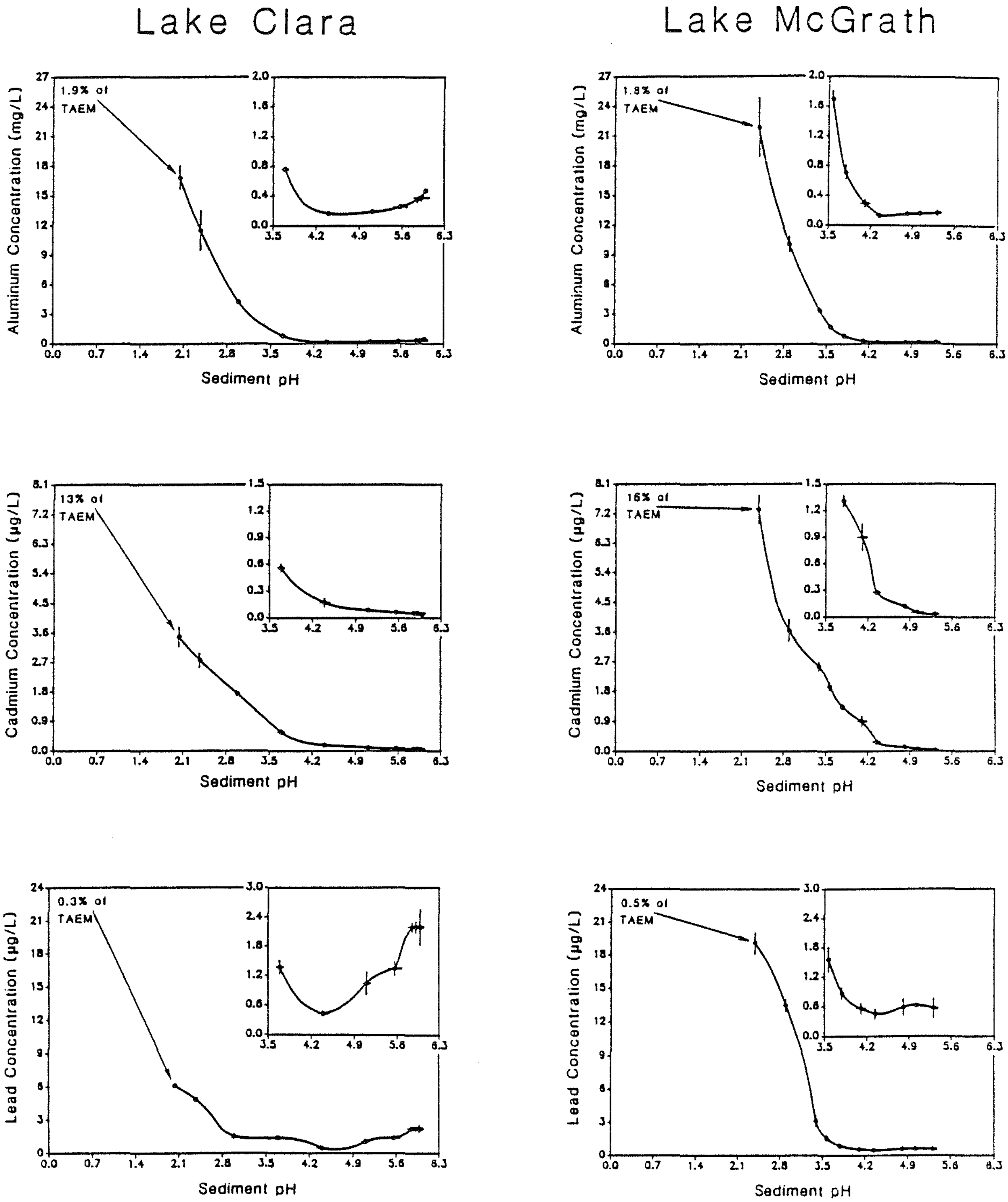
Like the trend observed for Al and Cd, pore water Pb concentrations were greater in Clara sediments than McGrath at pHs less than ca 4.9 (Fig. 9), which also parallels the TAE Pb concentrations of each respective sediment. Pore water Pb was, however, greater in McGrath than Clara at equivalent pHs above ca 4.9. Lead concentrations in pore waters from both lakes were approximately 0.70 µg/L at pH 4.9. Pore water Pb was 1289 ug/L for Clara and 1202 µg/L for McGrath at the minimum study pHs.

Effects Of Acidification On Metals In Littoral Sediments

Effects of acidification on Al, Cd, and Pb concentrations in pore waters of littoral sediments were similar between the two lakes. The pH_{ads} for Al and Pb in nonfiltered pore waters was observed at pHs less than pH_{nat} for sediments of both lakes (Table 7). In contrast, pore water Cd concentrations increased with decreasing pH. Hence pH_{nat}, pH_{ads}, and pH_{rel} for Cd were the same within each lake. Maximum concentrations of Al, Cd, and Pb in pore waters were observed at the minimum study pHs of 2.0 and 2.4 for Clara and McGrath littoral sediments, respectively.

Aluminum. Aluminum concentrations in pore waters from littoral sediments of both lakes initially decreased as pH was lowered to pH_{ads} (Fig. 10 - insert graph). The diminution was greatest in Clara sediment, with pore water Al decreasing from 0.473 to 0.166 mg/L. Aluminum in pore waters from McGrath sediments decreased from 0.176 to 0.136 mg/L. The

Figure 10. Concentrations of Al, Cd, and Pb in pore waters of acidified littoral sediments collected from lakes Clara and McGrath, Wisconsin, 13 July 1984. Inset graphs represent enlarged portion of respective main graphs. Horizontal and vertical bars represent 95% confidence intervals for pH and concentration, respectively.


Lake Clara
Lake McGrath
1.9% of TAEM
1.8% of TAEM
Aluminum Concentration (mg/L)
0 3 6 9 12 15 18 21 24 27
0.0 0.4 0.8 1.2 1.6 2.0
13% of TAEM
16% of TAEM
Cadmium Concentration (µg/L)
0.0 0.9 1.8 2.7 3.6 4.5 5.4 6.3 7.2 8.1
0.0 0.3 0.6 0.9 1.2 1.5
0.3% of TAEM
0.5% of TAEM
Lead Concentration (µg/L)
0 3 6 9 12 15 18 21 24
0.0 0.6 1.2 1.8 2.4 3.0
3.5 4.2 4.9 5.6 6.3
0.0 0.7 1.4 2.1 2.8 3.5 4.2 4.9 5.6 6.3
Sediment pH

pH_{ads} for Al in sediments from Clara and McGrath were 4.4 and 4.3, respectively. The pH_{rel} for Al was ca 4.0 for Clara and ca 4.2 for McGrath.

Aluminum concentrations in pore waters from sediments of both lakes were similar at pHs greater than ca 3.8. At pHs less than 3.8, however, Al concentrations were greater in McGrath pore waters. This is contrary to the trend observed in profundal sediments. Pore water Al concentrations at the minimum study pHs were 16.8 and 21.8 mg/L for Clara and McGrath, respectively. These Al concentrations are more than an order of magnitude lower than the concentrations observed at the minimum study pHs of the profundal sediments.

Cadmium. Unlike Al, Cd concentrations in pore waters of littoral sediments from both lakes increased as pH was lowered (Fig. 10 - insert graph). In both lakes, pH_{ads} and pH_{rel} for Cd were equal to pH_{nat} of the respective littoral sediment.

Pore water Cd concentrations in sediments were greater in McGrath than Clara along most of the acidification profile, with concentrations being very similar at pHs above ca 4.4. This is opposite of the trend observed with profundal sediments. Although McGrath sediments had nearly twice the TAE Cd, pore water Cd was greater in Clara than McGrath at equivalent pHs above ca 4.8. Cadmium in pore waters from both Clara and McGrath were approximately 0.13 µg/L at pH 4.8. Pore water Cd was 3.7 µg/L for Clara sediment and 7.3 µg/L for McGrath sediment, at their respective minimum study pHs. These values are much lower than Cd concentrations at the minimum study pHs of the profundal sediments.

Lead. Similar to Al, Pb concentrations in pore waters from littoral sediments of both lakes initially decreased as pH was lowered from pH_{nat}

to pH_{ads} (Fig. 10 - insert graph). The diminution was greatest in Clara sediments with pore water Pb decreasing from 2.21 to 0.43 µg/L. Lead in pore waters from McGrath sediments decreased from 0.56 to 0.45 µg/L. The pH_{ads} for Pb in sediments from Clara and McGrath was 4.4 and 4.3, respectively. The pH_{rel} for Pb was 2.9 for Clara and 4.1 for McGrath.

Lead concentrations in pore waters from McGrath sediments were considerably greater than Clara at pHs less than 3.6, which parallels trends of Al and Cd. Concentrations were similar between the two lakes at pHs above 3.6, with slightly greater concentrations observed in Clara. Pore water Pb was, however, greater in Clara than McGrath sediments at pHs above 3.6. Pore water Pb was 6.1 µg/L for Clara and 19 µg/L for McGrath sediments at the minimum study pHs. This contrasts with >1200 µg/L in profundal sediments at minimum study pHs.

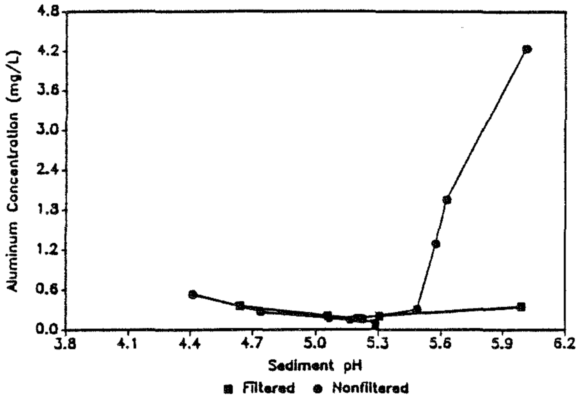
Effects Of Filtration On Metals In Pore Waters From Profundal Sediments

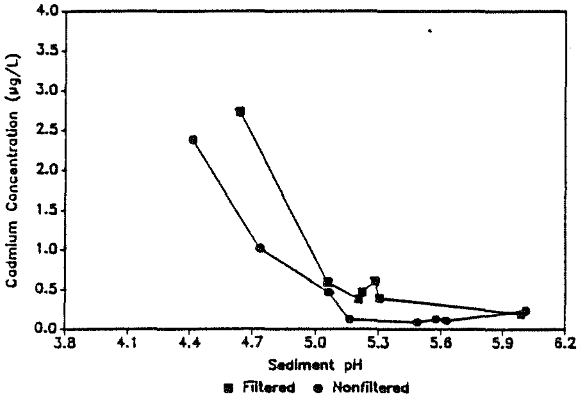
Removal of dissolved humic substances (DHS) from profundal pore waters by filtration decreased pore water concentrations of each metal in sediments from both lakes (Fig. 11). The largest difference in Al, Cd, and Pb concentrations between nonfiltered and filtered pore waters was observed in McGrath sediments. Results for Cd in filtered pore water are doubtful as filtration procedures may have contaminated the samples. Nonfiltered pore waters from nonacidified McGrath profundal sediments was 2.5, 4.7, and 2.7 times more concentrated in Al, Cd, and Pb, respectively, than nonfiltered pore water from nonacidified Clara profundal sediment (Table 6).

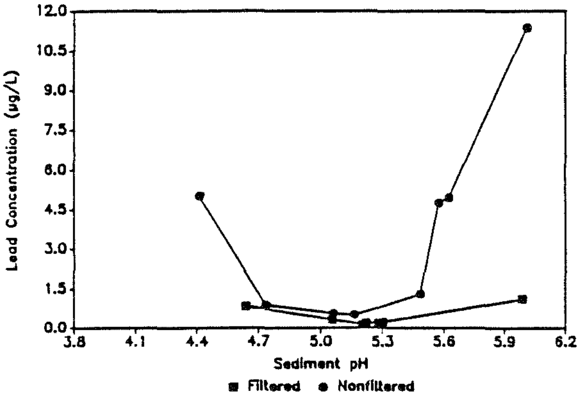
Aluminum. Filtered pore waters from profundal sediments with pHs greater than 5.3 for Clara and 4.8 for McGrath contained significantly

Figure 11. Concentrations of Al, Cd, and Pb, in filtered and nonfiltered pore waters of acidified profundal sediments collected from lakes Clara and McGrath, Wisconsin, 13 July 1984.

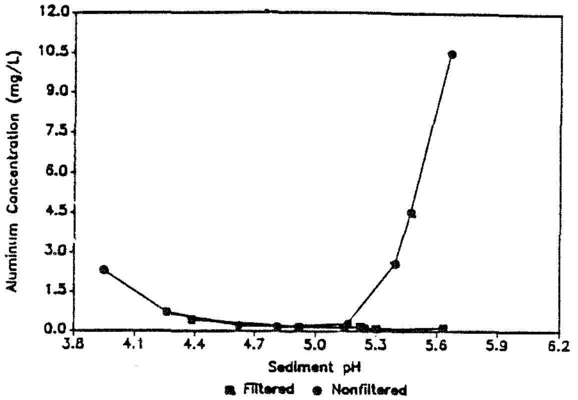
Lake Clara

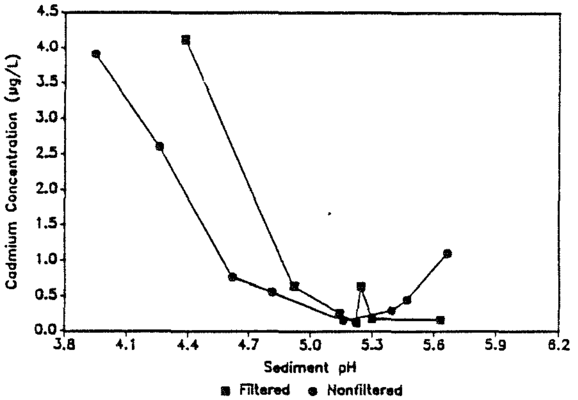


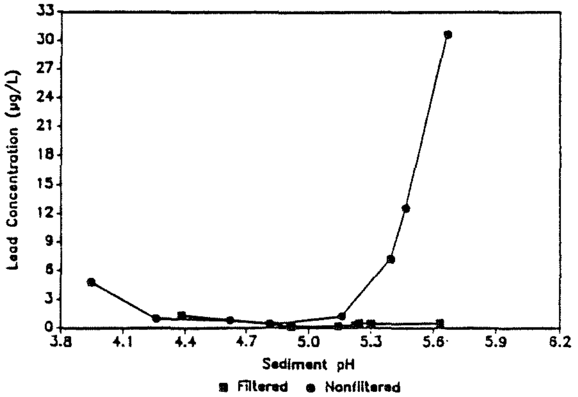




Lake McGrath







less Al than nonfiltered pore waters (Student's T-test, $\underline{P} \leq 0.0005$). Significant differences were not observed, however, between Al concentrations in filtered and nonfiltered pore waters from sediments with pHs less than 5.3 and 4.8 for Clara and McGrath, respectively. Aluminum concentrations in respective nonfiltered and filtered pore waters from sediments at pH_{nat} were 4.24 and 0.35 mg/L for Clara sediment and 10.5 and 0.14 mg/L for McGrath sediment.

Cadmium. Although filtration procedures to remove DHS appeared to have contaminated the samples (i.e. several of the filtered samples contained greater Cd concentrations than nonfiltered samples), filtered pore waters from McGrath profundal sediments with pHs greater than 5.3, contained significantly less Cd ($\underline{P} < 0.05$) than nonfiltered pore waters. Filtered pore waters from Clara sediments contained significantly less Cd ($\underline{P} = 0.005$) than nonfiltered pore waters only at pH 6.0 (pH_{nat}). Cadmium concentrations of filtered pore waters from sediments with pHs less than 6.0 and 5.3 for Clara and McGrath, respectively, were not significantly different or were greater than Cd concentrations in nonfiltered pore water. Cadmium concentrations in respective nonfiltered and filtered pore waters from sediments at pH_{nat} were 0.236 and 0.189 µg/L for Clara sediments and 1.106 and 0.165 µg/L for McGrath sediments.

Lead. At pHs greater than 4.7, Pb concentrations were significantly lower ($\underline{P} \leq 0.005$) in filtered than nonfiltered pore waters of profundal sediments from both lakes. Significant differences were not observed for Pb between nonfiltered and filtered pore waters from sediments with pHs less than 4.7. Lead concentrations in respective nonfiltered and filtered pore waters from sediments at pH_{nat} were 11.4 and 1.1 µg/L for Clara and 30.7 and 0.54 µg/L for McGrath.

Effect Of Filtration On Metals In Pore Waters From Littoral Sediments

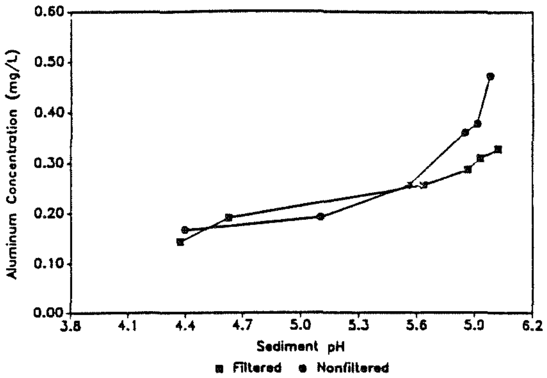
Removal of DHS by filtration decreased concentrations of all three metals in pore waters from littoral sediments of both lakes (Fig. 12). The largest differences in Al and Pb concentrations between nonfiltered and filtered pore waters were observed in Lake Clara sediments. Results for Cd concentrations in filtered pore water are doubtful as filtration procedures are believed to have contaminated the samples. Similar Cd concentrations were observed in nonfiltered pore waters from nonacidified littoral sediments of both lakes (Table 6). Aluminum and lead were 2.6 and 3.9 times more concentrated, respectively, in nonfiltered pore waters from nonacidified Clara littoral sediments than McGrath.

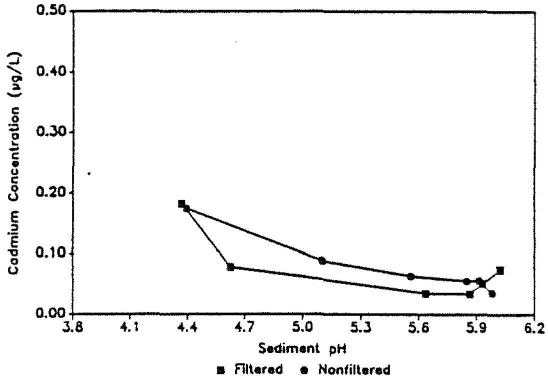
Aluminum. Filtered pore waters from littoral sediments with pHs greater than 5.6 for Clara and 4.5 for McGrath contained significantly less Al than nonfiltered pore waters ($\underline{P} \leq 0.05$). No significant differences were observed in Al concentrations between nonfiltered and filtered pore waters from sediments with pHs less than 5.6 and 4.5. Aluminum concentrations in respective nonfiltered and filtered pore waters from sediments at pH_{nat} were 0.473 and 0.329 mg/L for Clara sediments and 0.176 and 0.088 mg/L for McGrath sediments.

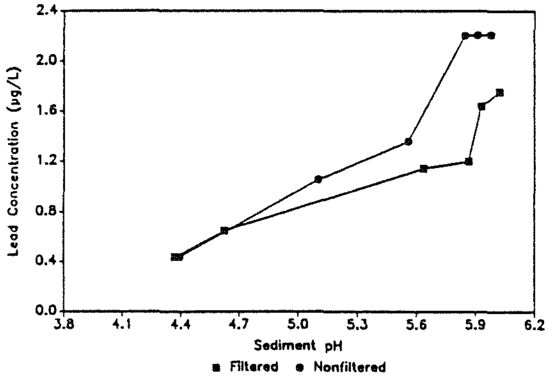
Cadmium. Significantly less Cd was observed in filtered than nonfiltered pore waters from Clara littoral sediments with pHs between 4.4 and 5.9 ($\underline{P} < 0.005$). At pHs outside of this range, Cd concentrations were not significantly different or were greater in the filtered pore waters. Cadmium concentrations in filtered pore waters from McGrath sediments were significantly less than nonfiltered pore water at pHs greater than 4.8 ($\underline{P} < 0.025$). At pHs less than 4.8, concentrations were not significantly different or were greater in filtered pore waters.

Figure 12. Concentrations of Al, Cd, and Pb, in filtered and nonfiltered pore waters of acidified littoral sediments collected from lakes Clara and McGrath, Wisconsin, 13 July 1984.

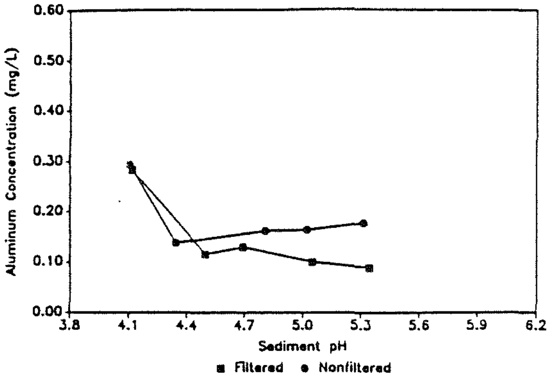
Lake Clara

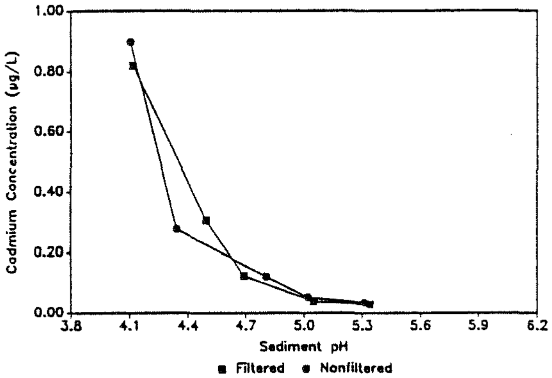


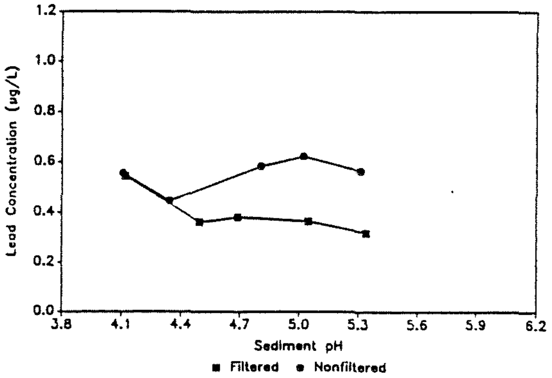




Lake McGrath







Cadmium concentrations in respective nonfiltered and filtered pore waters from sediments at pH_{nat} were 0.036 and 0.074 µg/L for Clara and 0.034 and 0.029 µg/L for McGrath.

Lead. Significantly less Pb was found in filtered than nonfiltered pore waters from littoral sediments with pHs greater than 4.6 and 4.3 for Clara and McGrath respectively ($\underline{P} \leq 0.05$). Filtered pore waters from sediments with lower pHs were not significantly different from nonfiltered pore waters. Lead concentrations in respective nonfiltered and filtered pore waters from sediments at pH_{nat} were 2.21 and 1.75 µg/L for Clara and 0.56 and 0.32 µg/L for McGrath.

DISCUSSION - NATURAL SEDIMENTS (Nonacidified)

Bulk Sediments

Organic Content, Texture, and Acid Neutralizing Capacity. The organic content and texture of nonacidified sediments from lakes Clara and McGrath were similar to sediments from other northern Wisconsin lakes (Table 8). Profundal sediments from both lakes consisted mainly of flocculent organic material, clays, and silts. In contrast, littoral sediments were well consolidated sands that contained relatively little organic material. The pH of sediments from lake Clara was greater than that corresponding to McGrath sediments, which parallels pHs of their respective surface waters.

Acid neutralizing capacities (ANC) of profundal sediments were greater than those of littoral sediments, probably because of the greater amounts of organic material present in the profundal sediments. The ability of a sediment to neutralize acid appears to be related to binding of H^+ by functional groups associated with organic material (Baker et al. 1985). The ANCs of McGrath sediments were less than those of corresponding Clara sediments, which was expected because of the sediment pHs. Baker and coworkers (1985), however, calculated that ANCs of profundal sediments from McGrath were considerably greater than those for Clara. Their results for Clara were almost identical to the results observed in this study. The difference observed between studies for McGrath sediments is probably a function of comparing results based on two different sediment types, i.e. their results for volatile solids and dry weight were 37% and 3.2%, respectively, as compared to 53% and 4.8% for this study.

Table 8. Average metal content of surficial sediments in northern Wisconsin Lakes. Concentrations are based on dry weights.

Lake	Volatile Solids (%)	Total Metal Concentrations (µg/g)[a]		
		Al	Cd	Pb
<u>This Study</u>:				
Clara				
- profundal sediments	49.9	12.6	2.73	88.3
- littoral sediments	0.5	1.1	0.03	2.9
McGrath				
- profundal sediment	52.7	11.6	7.14	89.2
- littoral sediment	0.5	1.5	0.06	4.3
<u>River Studies Center Study</u>:[b]				
Big Carr				
- profundal sediment	42.6	12.2	3.31	122.6
Clara				
- profundal sediment	52.8	11.5	2.26	87.0
Crystal				
- profundal sediment	39.1	14.1	2.35	85.5
Dorothy Dunn				
- profundal sediment	41.4	7.3	3.22	95.5
Garth				
- profundal sediment	48.7	3.5	4.25	40.1
Hilderbrand				
- profundal sediment	54.4	7.0	2.14	42.3
Little Rock (north basin)				
- profundal sediment	57.7	11.7	3.37	78.8
- littoral sediment	2.6	3.1	0.25	7.8
Little Rock (south basin)				
- profundal sediment	50.6	12.1	2.81	88.0
- littoral sediment	2.5	3.8	0.28	7.1
McGrath				
- profundal sediment	48.8	10.23	7.44	92.4
Nelson				
- profundal sediment	25.3	6.0	4.56	80.7

Table 8. Continued.

Lake	Volatile Solids (%)	Total Metal Concentrations (ug/g)[a]		
		Al	Cd	Pb
Sand				
- profundal sediment	47.6	13.4	2.37	69.8
Vandercook				
- profundal sediment	34.9	11.8	2.34	57.0
Zottle				
- profundal sediment	40.4	10.4	1.57	46.8

[a] Aluminum concentrations in mg/g.

[b] Values from R. G. Rada, River Studies Center, University of Wisconsin, LaCrosse, Wisconsin, pers. comm.

Total Acid Extractable Metals. Total acid extractable (TAE) Al, Cd, and Pb concentrations in surficial sediments from Clara and McGrath were similar to concentrations in surficial sediments from other northern Wisconsin lakes (Table 8). An exception was that the Cd concentrations were 2 to 5 times greater in profundal sediments from McGrath than the other lakes. Results from this study are, however, similar to those of Rada (River Studies Center, University of Wisconsin, LaCrosse, Wisconsin, pers. comm.) for McGrath (Table 8). Profundal sediments from Clara contained more TAE Al and Pb than McGrath, whereas McGrath contained considerably more Cd than Clara. Concentrations for all three metals were greater in littoral sediments from McGrath than Clara.

More TAE Cd and Pb was found in profundal than littoral sediments. This was probably due to the high content of organic material, clay, and silt in the sediments. Several studies have demonstrated positive correlations between metal content, particle size, and organic content (Helmke et al. 1977; Forstner and Whitmann 1981; Tada and Suzuki 1982; Bailey and Rada 1984). In contrast to Cd and Pb, the greatest concentrations of TAE Al were observed in the littoral sediments (Table 6). This was probably a result of the high mineral content of these sediments. Sand, silt, and clay fractions comprised approximately 99% of the littoral sediment residues in contrast to only 50% for the profundal sediments. Hydrolysis of aluminum silicates, which are major constituents of sand, silt, and clay particles, releases dissolved Al (Krauskopf 1979). The hydrolysis becomes more efficient under acidic conditions.

Metals In Pore Waters From Sediments At Natural pH

Comparisons of Littoral and Profundal Sediments Within Lakes. Pore waters from profundal sediments contained less than 2.0% of the TAE Al, Cd, and Pb observed in the bulk sediments. Similarly, pore waters from littoral sediments generally contained less than 0.1% of the TAE metal concentrations in bulk sediments. Metal concentrations were considerably greater in pore waters from profundal sediments than littoral sediments (Table 6). The greatest differences in metal concentrations were observed between profundal and littoral sediments of McGrath. Profundal pore waters from McGrath contained 58, 32, and 54 times more Al, Cd, and Pb, respectively, than pore waters from littoral sediments. Pore waters from Clara profundal sediments contained 9, 7, and 5 times more Al, Cd, and Pb, respectively, than littoral sediment pore waters. Profundal sediment pore waters were also highly colored (yellow-brown) in comparison to pore waters from littoral sediments, indicating greater concentrations of dissolved organic matter (DOM). Dissolved organic matter can complex large amounts of dissolved metals and significantly alter solubilities of certain metal species (Rashid and Leonard 1973; Gardiner 1974; Nissenbaum and Swain 1976; Singer and Navrot 1976; Jackson et al. 1980).

Comparisons of Littoral and Profundal Sediments Between Lakes. Pore waters from McGrath profundal sediments contained more Al, Cd, and Pb than those of Clara, even though TAE Al and Pb concentrations were greater in bulk sediments of Clara (Table 6). Pore water from McGrath profundal sediments was also more colored than that from Clara--a trend similar to the one observed for volatile solids of the sediments. The differences in pore water concentrations of these metals from profundal sediments of McGrath and Clara were probably related to the greater DOM and lower pH of McGrath sediments. In contrast to profundal sediments, concentrations of Al and Pb in littoral pore waters were greater in Clara than McGrath. This may have been due to the greater color (DOM) of littoral pore waters and greater TAE metal concentrations in littoral sediments of Clara as compared to McGrath.

The greatest difference in pore water metal concentrations between lakes was observed for Cd in profundal sediment. Profundal pore waters of McGrath contained nearly 5 times more Cd than those from Clara, which parallels the trend observed with TAE Cd. Littoral pore waters of both lakes had similar Cd concentrations. Pore water from McGrath profundal sediments contained almost 3 times more Al and Pb than that of Clara. However, pore waters from littoral sediments of Clara had 3 times more Al and 4 times more Pb than those of McGrath.

Comparison of Sediment Pore Waters to Surface Waters. Concentrations of Al, Cd, and Pb were considerably greater in sediment pore waters than surface waters of the lakes (Table 9). The greatest differences between pore and surface water concentrations (Table 9 - bottom samples) were observed for Lake McGrath. Aluminum, Cd, and Pb in McGrath pore waters was 260, 9, and 61 times more, respectively, than surface waters. Similarly, Clara pore waters contained 85, 8, and 33 times more Al, Cd, and Pb than surface waters. Pore waters are commonly enriched with trace metals (Presley et al. 1972; Hart and Davies 1977; Thurman 1985), which is likely related to their greater amounts of DOM.

In contrast to profundal pore waters, differences in metal concentrations were not as great between littoral pore waters and surface waters (Table 9 - surface samples). The greatest differences were

Table 9. Average metal content in pore waters from Clara and McGrath sediments relative to annual mean of surface and bottom waters.

Lake Name and Water Type	Al (mg/L)	Cd (µg/L)	Pb (µg/L)
Clara Profundal Pore Water			
- pH_{nat}	4.24	0.24	11.37
- pH_{ads}	0.14	0.09	0.50
Clara Littoral Pore Water			
- pH_{nat}	0.47	0.04	2.21
- pH_{ads}	0.17	0.04	0.43
Clara Surface Waters[a]			
- surface samples	0.03	0.03	0.28
- bottom samples	0.05	0.03	0.35
McGrath Profundal Pore Water			
- pH_{nat}	10.49	1.11	30.66
- pH_{ads}	0.18	0.15	0.46
McGrath Littoral Pore Water			
- pH_{nat}	0.18	0.04	0.56
- pH_{ads}	0.14	0.04	0.45
McGrath Surface Waters[a]			
- surface samples	0.04	0.06	0.38
- bottom samples	0.04	0.13	0.50

[a] Values for surface waters taken from Schmidt (1985).

observed between pore and surface waters in Clara. Pore water from Clara littoral sediment contained 16, 1.3, and 7.9 times more Al, Cd, and Pb, respectively, than surface waters. McGrath littoral pore water, however, contained less Cd and only 4.5 and 1.5 times more Al and Pb, respectively, than surface waters.

DISSCUSSION - ACIDIFIED SEDIMENTS

Comparison Of Pore Waters From Sediments At Natural And Adsorption pH

Profundal Sediments. Concentrations of Al, Cd, and Pb in pore waters from profundal sediments of both lakes significantly ($P \leq 0.05$) decreased as pH was lowered from pH_{nat} to pH_{ads}. Concentrations of Al, Cd, and Pb in pore waters from Clara were 30, 3, and 23 times greater, respectively, at pH_{nat} than pH_{ads}. Similarly, McGrath pore waters contained 58, 7.3, 67 times more Al, Cd, and Pb, respectively, at pH_{nat} than pH_{ads}.

Littoral Sediments. Although metal concentrations in littoral sediment pore waters also appeared to decrease as pH was lowered, the decrease was statistically significant ($P = 0.05$) only for Al and Pb in Clara. Pore waters from Clara littoral sediments at pH_{nat} contained 3 times more Al and 5 times more Pb than pore waters from sediments at pH_{ads}. In contrast, however, Cd concentrations increased as pH was reduced below pH_{nat} (i.e. $pH_{nat} = pH_{ads}$).

Comparison of Profundal and Littoral Sediments. Pore water Al and Pb concentrations in sediments at pH_{ads} were not significantly different between sediment types within lakes. This is opposite the trend observed at pH_{nat}. Concentrations of Cd at pH_{ads} were, however, greater in pore waters from profundal than littoral sediments of each lake.

Comparison Between Lakes. Aluminum and Pb concentrations in pore waters from sediments at pH_{ads} were similar in both profundal and littoral sediments of both lakes (i.e. ca 160 µg/L for Al and 0.46 µg/L for Pb). Cadmium concentrations at pH_{ads} were not significantly different between profundal sediments or between littoral sediments of the two lakes. Concentrations in both lakes were ca 0.12 µg/L for profundal sediments and 0.04 µg/L for littoral sediments.

Effects of Filtration of Pore Waters. Although serial filtration of pore waters from natural littoral sediments through 0.8 and 0.4 µm filters appeared to decrease Al and Pb concentrations, the decreases were not statistically significant ($\underline{P} > 0.5$). Cadmium concentrations showed the same trend for McGrath but were greater in filtered pore waters from Clara, indicating contamination problems. In contrast, however, serial filtration of pore waters from natural profundal sediments decreased concentrations of all three metals and also removed color -- a trend similar to the effect of acidification. Except for Cd and Pb in Clara, metal concentrations in filtered pore water from sediments at pH_{nat} were not significantly different from those in nonfiltered pore waters at pH_{ads}, indicating that metals in pore waters at pH_{nat} were largely complexed by DOM. Concentrations of Cd and Pb in filtered pore waters from Clara profundal sediments at pH_{nat} were significantly greater than those in pore waters from sediments at pH_{ads}.

Comparisons of metal concentrations in nonfiltered pore waters from Clara profundal sediments at pH_{nat} and pH_{ads} indicated that 97, 63, and 96% of the pore water Al, Cd, and Pb, respectively, was removed as pH decreased (Fig. 9 - inset graph). Similarly, 98, 86, and 99% of McGrath pore water Al, Cd, and Pb was removed as pH decreased (Fig. 9 - inset graph). Except for Cd in Clara, comparisons of metals in filtered and nonfiltered pore waters from profundal sediments at pH_{nat} indicated that almost identical percentages of Al, Cd, and Pb were removed from pore water by filtration (Fig. 11 - inset graphs), as was removed by reducing pH from pH_{nat} to pH_{ads}. Only 20% of the natural pore water Cd in Clara sediments was removed by filtration.

Pore water color decreased with pH and was also removed by filtration, indicating that Al, Cd, and Pb present in the sediment pore waters were complexed with humate ligands. Humic substances (humate) comprise the majority of the DOM in surface waters (Rashid and Leonard 1972; Thurman 1985) and possibly pore waters. Because the filterable fraction of Al-organic complexes can be significantly underestimated if 0.45-μm filters are used (Kennedy et al. 1974; Wagemann and Brunskill 1975; Diamadopoulos and Woods 1984), it is likely that nearly all of the Al and Pb and the majority of Cd in pore waters was organically complexed.

The observation that filtration removed only 20% of the pore water Cd indicates that Cd (1) was not as strongly complexed to the DOM as Al and Pb, (2) was complexed to smaller weight organics that were not retained by the 0.4-μm filter, or (3) was displaced by competing ions. Alberts and Giesy (1983) have demonstrated that Al can effectively prevent binding sites of dissolved organic matter from reacting with Cd and Pb. Because Clara profundal sediments contained less organic material, it is possible that reactive binding sites of the dissolved organic material was saturated with Al and other major metal constituents, thus preventing Cd complexation. Furthermore, Cd binding appears to be caused by inorganic rather than organic compounds (Giesy et al. 1978).

The decrease in pore water concentrations of Al, Cd, and Pb that occurred in profundal sediments as pH_{nat} was lowered to pH_{ads} may have resulted from the formation of colloidal and/or insoluble metal-humate complexes. Dissolved humic substances are commonly differentiated into two subclassifications based on solubilities in acidic solutions. Dissolved humic substances that precipitate at pH 2.0 or higher comprise the humic acid fraction and those that stay in solution comprise the fulvic acid fraction. Fulvic acid and humic acid are structurally similar; however, the humic acid fraction has fewer oxygen-containing functional groups (e.g., -COO-, -C=O, $-RO^-$, $-ROCH_2^-$), has higher molecular weights, and becomes less soluble as acidity and/or molecular weight increases (Schnitzer and Khan 1972). The greater number of carboxyl groups associated with the fulvic acid fraction cause it to be more hydrophilic (MacCarthy and O'Cinneide 1974; Stumm and Morgan 1981) and remain in solution even at low pH.

Because the apparent metal-humate complex in this study was colloidal in nature (i.e. the complex could be removed by filtration but not by centrifugation), the humate ligand was probably comprised mainly of humic acid. Humic acid is colloidal in size and constitutes a major fraction of colloidal organic matter in water (Thurman et al. 1982; Thurman 1985). Davis and Gloor (1981) demonstrated that high molecular weight dissolved organic carbon had greater adsorption affinities than smaller molecular weight fractions for Al_2O_3 and that the adsorption affinities were greatest in the pH range of about 5 to 6. Furthermore, the affinity decreased when pH was lowered or raised out of this range. This pH range is almost identical to the pH_{nat} - pH_{ads} ranges observed for Al, Cd, and Pb in this study. Concentrations of pore water Al, Cd, and Pb probably decreased as pH was lowered because metal-humic acid complexes precipitated and consequently were removed by settling and/or centrifugation. Because they generally contain about 20% fewer carboxyl groups than the fulvic acid fractions, humic acid fractions become less soluble and form precipitates as pH is decreased (Thurman 1985).

Another possible explanation for the loss of pore water Al, Cd, and Pb with acidification to pH_{ads} is the formation of insoluble metal-fulvic acid complexes. Formation of these complexes is dependent upon pH, concentration of metals and fulvic acid, and molecular weight of the fulvic acid. Depending upon pH, the fulvic acid functional groups, particularly carboxyl and phenolic hydroxyl groups, can be protonated or deprotonated (Saar and Weber 1982) and interact in complexation of metals. Because of the large TAE Al concentrations, the possible formation of metal-fulvic acid complexes probably involves Al, as well as other metals such as Fe. Fulvic acid complexes involving Al and Fe become increasingly water-insoluble as the molar ratio of metal to fulvic acid in the complex increases above a 1:1 threshold (Schnitzer 1971). As more metal ions react with the fulvic acid, it becomes less soluble until it precipitates. Studies using fulvic acids extracted from soils and/or sediments (Davis and Gloor 1981; Diamadopoulos and Woods 1984) revealed that solubility of Al-fulvic acid complexes (determined by amount of fulvic acid removed from solution by filtration through 0.45-um filters) decreased as pH was lowered. Without the addition of Al, however, fulvic acid was not removed by filtration and acted like a soluble substance. Diamadopoulos and Wood (1984) demonstrated that precipitation (and subsequent removal by filtration through a 0.45-um filter) of fulvic acid complexed with Al increased as pH decreased from 8 to 6 and that nearly 100% of the fulvic acid could be removed by filtration at pH 6. Intermediate pHs of 5 to 6 favors the complexation between fulvic acid and metal ions (Saar and Weber 1982; Davis and Gloor 1981; Diamadopoulos and Wood 1984).

Comparison of Sediment Pore Waters to Surface Waters. In contrast to pore waters of sediments at pH_{nat}, pore waters from profundal and littoral sediments at pH_{ads} had Al, Cd, and Pb concentrations that were very similar to surface water concentrations (Table 9). This was especially apparent with Cd in littoral pore waters. Considering that pH_{nat} and pH_{ads} for littoral Cd were equal to the surface water pH within each lake, the close similarities between Cd concentrations in surface waters and littoral pore waters indicates that Cd release is dependent on pH and not organic content. Studies that regressed surface water metal concentrations with selected lake parameters (Giesy et al. 1978, Schmidt 1985), suggest that surface water Cd is negatively correlated with pH but not with dissolved organic material (DOM), supporting this hypothesis.

Pore Water Metal Concentrations In Sediments With pHs Less Than Adsorption pH

As pHs decreased below pH_{ads}, Al, Cd, and Pb were released and pore water concentrations of the three metals increased. Their concentrations were greater in pore waters than surface waters at all pHs less than pH_{ads}. However, they did not exceed natural sediment pore water concentrations until relatively low pHs were established (Table 7 - pH_{rel}). The estimated pH_{rel} for Cd and Pb in sediments used for this study were similar to pHs that resulted in release of Cd and Pb from sediments in other studies (Lagerwerff et al 1976; Davis et al. 1982; Trefry and Metz 1984); however, they were considerably lower than pHs observed in surface waters that had elevated Al, Cd, and Pb concentrations (Schmidt 1985). In contrast, the pH_{ads} for the three metals were similar to the surface water pHs that result in mobilization of Al from sediments to surface waters (Schindler et al. 1980; Schindler and Turner 1982) and in elevated concentrations of Cd and Pb in surface waters (Schmidt 1985). This indicates the possibility of metal release from sediments to surface waters at pHs less than or equal to pH_{ads}. Maximum release of Al, Cd, and Pb from sediments into pore waters was observed at the lowest study pHs (Figs. 9 and 10).

The possible release of Al, Cd, and Pb into sediment pore waters as pH decreased below pH_{ads} probably resulted from the displacement of metal ions from humic and fulvic acid complexes by H^+. As pH decreases, H^+ competes with metal ions for anionic binding sites, rendering the humate ligand less available for complexation (Saar and Weber 1982). The degree of displacement or ion exchange is dependent upon the stability of the metal-humate complex (Guy and Chakrabarti 1976). Based on the observed pH_{ads} or pH_{rel} for each of the three metals in pore waters, the following order of release was observed within both lakes; littoral Cd, profundal Cd, profundal Al and Pb, littoral Al and Pb. The stability of a metal-humate complex is dependent upon several factors including concentration of both metal and humate, ionic strength of the solution, pH, and temperature (Thurman 1985). Conditional stability constants (i.e. stability constants determined under controlled experimental conditions) determined at pHs of 3 and 5 indicate the order of metal-humate complex stabilities as Al > Pb >> Cd (Schnitzer 1969; Schnitzer and Hansen 1970; Guy and Chakrabarti 1976; Stevenson 1976; Figura and McDuffie 1980), which follows the trend observed in this study for the release of Al, Cd, and Pb into sediment pore waters. The conditional stability constants for Al were determined only at a pH of 3 (Schnitzer 1969; Schnitzer and Hansen 1970); however, complex stabilities of Al generally increase as pH increases.

SUMMARY

Analysis of sediments from lakes Clara and McGrath indicated that littoral sediments and profundal sediments were physically and chemically similar between the two lakes. Profundal sediments were approximately 95% water, 2.5% organic material, and 2.5% inorganic material (i.e. sands, silts, and clays). Silts and clays comprised 99% of the inorganic fractions. In contrast, littoral sediments were 19% water and 79% sand. Individually, organic material, silt, and clay comprised less than 1% of the littoral sediment.

Profundal sediments from Clara contained more total acid extractable (TAE) Al and Pb than those from McGrath but littoral sediments from McGrath contained more TAE Al and Pb than those from Clara. Concentrations of TAE Cd in both sediment types were greatest in McGrath. Except for Al, TAE metal concentrations were greater in profundal than littoral sediments. Because the TAE metal concentrations closely followed the trend observed for organic content of the sediments, metal concentrations in the bulk sediments were likely more dependent on organic content than texture size.

In contrast to the TAE metal concentrations, the greatest concentrations of Al, Cd, and Pb in pore waters occurred in McGrath profundal sediments and Clara littoral sediments. The amount of dissolved organic material present in the pore waters (as estimated by the amount of color) followed the same trend as the metal concentrations, again indicating a relationship between the metals and organic matter.

The lowest concentrations of all three metals in pore waters from acidified sediments were observed at pHs less than the pH of the natural sediment (pH_{nat}). These pHs (pH_{ads}) ranged from 6.0 to 5.0; however they varied among metals and between sediments within a lake and were generally lower in sediments from McGrath. Color also decreased over the same pH range, indicating possible metal complexation and precipitation by dissolved organic material.

As pH decreased from pH_{nat} to pH_{ads}, pore water Al and Pb concentrations decreased by 98% and Cd concentrations decreased by 60 to 80%. Filtration of pore waters from sediments at pH_{nat} removed almost identical percentages of the three metals as well as color. Thus it is apparent that nearly all of the dissolved Al and Pb and the majority of Cd was organically complexed in the sediment pore waters at natural pH. Precipitation of these complexes occurred with decreasing pH and resulted in removal of the three metals from the pore waters.

As sediment pHs decreased below pH_{ads}, pore water concentrations of all three metals increased, indicating that metal ions in the precipitated organic complexes were displaced by competing ions such as H^+. Because the chelation capacity of the sediments is apparently exceeded at pHs less than or equal to pH_{ads}, displaced metal ions may be released from the sediment pore waters to the surface waters. Hence, equilibrium would favor the release because pore water concentrations were greater than surface water concentrations. The release of metals would be more efficient in the profundal sediments due to their flocculent, hydrous nature. Based on the magnitude of the respective pH_{ads}, Cd would be released at higher pH than Al or Pb, both of which are released at similar pHs.

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