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Geochemical controls for Al, Fe, Mn, Cd, Cu, Pb, and Zn during experimental acidification and recovery of Little Rock Lake, WI, USA⋆

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Abstract. Concentrations of Al, Fe, Mn, Cd, Cu, Pb, and Zn were measured in the reference and treatment basins of Little Rock Lake (Vilas County, Wisconsin), a low-alkalinity, seepage system (pH ~6.1, alkalinity 25 μeq/L) during six years of a whole-basin acidification and the first four years of the lake's recovery. The treatment basin was acidified with H_2SO_4 in three two-year steps to pH ~5.6, ~5.1, and ~4.7. By the end of year 4 of recovery, treatment basin pH increased to ~5.3 as a result of internal alkalinity generation. During acidification, dissolved Mn and Fe (0.4 μm pore-size filters) increased at pH ~5.6; dissolved Al, Cd, and Zn became elevated at pH ~5.1; and dissolved Pb at pH ~4.7. Dissolved Cu remained similar in both basins to pH ~4.7. Al, Fe and Mn levels declined significantly during the recovery period, approaching values at pH 5.3 intermediate between the concentrations at pH 5.6 and 5.1 during acidification. Dissolved Al and Fe in the reference basin were near the equilibrium levels for solubility of gibbsite ($Al(OH)_3$) and amorphous $Fe(OH)_3(s)$. The acidified basin was undersaturated relative to gibbsite, and dissolved Al was limited by pH disequilibrium between the water column and sediments and possibly by Al-DOC precipitation. Dissolved Fe apparently was controlled by solubility of amorphous $Fe(OH)_3(s)$ and Fe-DOC precipitation. Dissolved Mn levels in both basins were consistent with manganite [γ-MnOOH(s)] solubility. Elevated levels of Cd, Pb, and Zn in the treatment basin during acidification probably resulted from less efficient scavenging of atmospherically-deposited Cd, Pb, and Zn by settling particles.

Abbreviations: ANC – Acid neutralizing capacity; sum of strong base cations minus the sum of strong acid anions, DOC – Dissolved (natural) organic carbon, ELA – Experimental Lakes Area, LRL – Little Rock Lake

Introduction

It is well known that acidification of lakes results in elevated concentrations of Al, Fe, Mn, Zn, and perhaps Cd and Pb (Schindler et al. 1980a; Campbell et al. 1985;

⋆ Dedicated to the memory of Thomas M. Frost (1950–2000): devoted limnologist, educator, fellow Little Rock scientist, and friend

LaZerte 1986). Potential sources of metal ions include release from sediments, mobilization from soils, and atmospheric deposition. Because Al, Fe, and Mn are abundant in soils and bedrock, elevated concentrations of these metals come primarily from natural sources-sediments and soils. Trace metals (e.g. Cd, Pb, and Zn) also may be leached from sediments and soils, but in most cases, their source likely is anthropogenic (e.g., fossil-fuel combustion, ore smelting). They are supplied to watersheds and lakes by atmospheric deposition (Campbell et al. 1985).

Because of widespread observations of elevated Al levels in acidified waters and the toxicity of Al to fish (Driscoll et al. 1980) and other aquatic organisms (Havas 1985; Gensemer 1991), much has been reported on the mechanisms controlling Al in such waters. At $\mathrm{pH} > \sim 5$, dissolved Al is thought to be controlled by gibbsite solubility (Driscoll et al. 1984; Schafran and Driscoll 1987). Controls at $\mathrm{pH} < \sim 5$ are less certain (e.g., Postek et al. (1995)). Many waters are undersaturated with respect to gibbsite (Cronan et al. 1986), and Al may be controlled by co-precipitation with dissolved organic matter (DOM) (Urban et al. 1990) or the solubility of basic Al-sulfate minerals (Nordstrom 1982) or aluminosilicates (Paces 1978). Undersaturation at low pH also may be caused by slow dissolution kinetics of Al-bearing minerals. Less work has been focused on mechanisms controlling Fe and Mn in low-alkalinity waters. Controls on Fe may parallel those for Al: solubility of amorphous $\mathrm{Fe(OH)_3}$ at $\mathrm{pH} > \sim 5$ and Fe-DOM precipitation at $\mathrm{pH} < 5$ (Urban et al. 1990). Possible controls on dissolved Mn, which is toxic to some fish at concentrations $< 50\,\mu$g/L (Nyberg et al. 1995), include solubility of Mn minerals (White and Driscoll 1987a; LaZerte and Burling 1990), ion exchange with sediments (Santschi et al. 1986; Anderson et al. 1987), or processes that limit Mn inputs to lakes (Urban et al. 1990). In contrast to the minor metals, trace metal concentrations in surface waters are far below those predicted by mineral solubilities. Concentrations of these metals may be controlled by adsorption onto suspended particulate matter (Murray 1987).

Much research has been conducted on the aquatic effects of acid precipitation. Early studies focused on drainage lakes underlain by granitic bedrock-the most common lakes in Scandinavia, where acid rain first was recognized as a major environmental problem of the 20th century. Less attention was focused initially on seepage lakes, although they constitute a large fraction of acid-sensitive lakes in the north-central United States. To address this gap, an acidification experiment (Brezonik et al. (1986, 1993)) was initiated in 1983 at Little Rock Lake (LRL), a low-alkalinity seepage lake in northern Wisconsin. This paper describes changes in water-column concentrations of Al, Fe, Mn, Cd, Cu, Pb, and Zn in the treatment and reference basins of LRL during the lake's acidification and recovery and describes likely controlling geochemical processes.

Environmental setting and experimental design

Little Rock Lake has two basins: north (9.8 ha, z_{max} = 10.3 m, $\bar{z}$ = 3.8 m) and south (8.1 ha, z_{max} = 6.3 m, $\bar{z}$ = 3.0 m) and is located in an uninhabited, forested watershed (Brezonik et al. (1986, 1993)). Typical of low-ANC lakes in the region, LRL is low in color, oligotrophic, and chemically dilute (pH 6.1, ANC 25 μeq/L, TOC 2–3 mg/L, conductivity 11 μS/cm, SO_4^{2-} = 2.5 mg/L). The lake has no inlets or outlets and receives 98–100% of its water from precipitation to its surface. Its fish assemblage is dominated by yellow perch (*Perca flavescens*) followed by rock bass (*Ambloplites rupestris*) and largemouth bass (*Micropterus salmoides*).

Monitoring from summer 1983 to spring 1985 demonstrated that the basins were nearly identical in water chemistry and biota (Brezonik et al. 1986). In August 1984, a vinyl barrier was installed at the narrows dividing the basins. Acidification of the north basin began in May 1985: three two-year treatments with technical-grade H_2SO_4 lowered the pH from ~6.1 to target values of 5.6, 5.1, and 4.7. Acid was added by a small boat as necessary during the ice-free season to maintain the pH near the target level. No acid was added after September 1990, and the treatment basin was left to recover on its own. The south (reference) basin was unmanipulated, and its annual-average pH remained near 6.1 during the study period.

Methods

Sampling and analytical methods

Sampling and analytical procedures were described by Mach (1992) and Sampson (1999). A brief summary is provided here. Water samples for metals analysis were collected quarterly from September 1983 through 1986 and monthly thereafter until 1994. Water was collected from mid-basin stations at depths of 0, 4, 6, 8, and 9 m (treatment basin) and 0, 4, and 6 m (reference basin) using a peristaltic pump and weighted Tygon tubing, filtered in-line (0.4 μm Nuclepore polycarbonate membranes) into acid-cleaned, high-density, polyethylene bottles, and acidified with Ultrex grade HNO_3. Metals were analyzed by graphite-furnace atomic-absorption spectroscopy (acidification phase) or inductively-coupled plasma emission spectroscopy (recovery phase). Major cations (Ca, Mg, Na, K) were measured on the same samples by flame AAS. Sampling and analytical procedures for major anions, inorganic nutrients, pH, alkalinity, and total and dissolved organic carbon (TOC, DOC) were described by Brezonik et al. (1993) and Sampson (1999). Temperature and dissolved O_2 were measured on site with a Yellow Springs Model 58 meter and stirrer-assisted electrode.

Calculations

Aqueous speciation of minor metals, with emphasis on activities of the free metal ions (denoted as {i}, where i = Al^{3+}, Fe^{3+}, Mn^{2+}), was calculated by MINTEQA2 and MINEQL (Westall et al. 1976), as modified by Holm et al. (1987). Epilimnetic temperature, pH, HCO_3^-, and dissolved levels of Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, F^-, SO_4^{2-}, SiO_2, SRP, NH_4^+, Al, Fe, and Mn were used as input; we calculated these for each sampling date by averaging results for the epilimnion. Average concentrations of these parameters for the three treatment periods were reported by Brezonik et al. (1993) and Sampson (1992); average concentrations of all but F^- for the first four recovery years were reported by Sampson (1999). Fluoride in both basins was near the detection limit of 0.01 mg/L. Dissolved organic carbon (DOC) was not distinguishable from TOC by the method used ($p \gg 0.20$, $n = 35$, paired t-test), and so TOC, which was measured during the entire study, was used to estimate DOC, which was measured for only part of the study. Redox potential ($p\epsilon$) was calculated from pH and dissolved O_2 based on the assumption that the O_2–H_2O half-reaction controlled $p\epsilon$ (Stumm 1978). Thermodynamic constants in the MINEQL database were reviewed and updated from lists in Ball et al. (1980) and Nordstrom (1982), Holm et al. (1987), Tipping et al. (1988a, 1988b), Urban et al. (1990).

The fraction of Al, Fe, and Mn bound by dissolved organic matter was estimated using the range of metal-DOC formation constants ($\log K_{MDOC}$) reported in the literature: $\log K_{AlDOC} = 3.8$–7.4, $\log K_{FeDOC} = 8.4$–10.4, and $\log K_{MnDOC} = 3.8$–4.9 (Urban et al. (1990) and references therein). Metal-DOC formation constants vary with pH, ionic strength, and metal to DOC ratio; we assumed that those for Al, Fe, and Mn in LRL fall within these ranges. The resulting uncertainty in calculated speciation of Al, Fe, and Mn is discussed below. A metal-binding capacity for natural organic matter of 1.5 μmol (Al+Fe)/mg DOC was assumed based on literature reviewed by Helmer et al. (1990). Wilcoxon's two-sample non-parametric test was used to identify significant differences in dissolved metal concentrations between basins.

Data reliability

Accuracy, precision, and detection limits for dissolved trace-metal analyses are reported in Table 1. Analytical accuracy was checked by running quality control (QC) samples with each set of standards and samples. QC samples were prepared from concentrated solutions obtained from the U.S. EPA, Quality Control Branch, Cincinnati, Ohio. Results were within 10% of certified values and usually within 5%. Precision was calculated for pairs of field and laboratory replicates as described by Skoog and West (1980). Laboratory precision was better than ±10% for all metals and usually < ± 5%. Field precision was better than ± 10% for Al, Fe, Mn and generally better than ± 20% for Cd, Cu, Pb, Zn). Field precision was poorer for trace metals because water-column concentrations were very low, sometimes near the analytical detection limit. Average metal concentrations in field blanks were (in μg/L); Al 0.3, Fe 1.0, Mn 0.1, Cd 0.025, Cu 0.3, Pb 0.013, and Zn 1.9. All

Table 1. Limit of detection, precision, and accuracy for Al, Fe, Mn, Cd, Cu, Pb, and Zn in filtered lake water samples.[1]

Element	LOD[2]	Relative Precision[3] (no. of pairs)		Accuracy (no. of analyses)
		Field[4]	Lab[5]	% Error[6]
Al	0.2	6% @ <10 (18)	1% @ <10 (28)	7% @ 5 (11)
		5% @ >10 (45)	1% @ >10 (79)	2% @ 12.5 (42)
				9% @ 25 (9)
				–4% @ 50 (4)
Fe	0.8	2% @ <30 (40)	2% @ <30 (74)	1% @ 10 (22)
		7% @ 30–100 (13)	2% @ 30–100 (32)	5% @ 30 (53)
		6% @ >100 (6)	1% @ >100 (7)	
Mn	0.3	2% @ < 20 (37)	1% @ <20 (42)	6% @ 10 (37)
		3% @ > 20 (30)	2% @ >20 (50)	4% @ 30 (19)
Cd	0.01	13% @ < 0.1 (36)	6% @ < 0.1 (50)	2% @ 0.25 (48)
		18% @ > 0.1 (14)	4% @ > 0.1 (34)	1% @ 0.63 (18)
Cu	0.05	12% @ < 1.0 (32)	2% @ < 1 (60)	3% @ 1.0 (33)
Pb	0.02	29% @ < 0.1 (12)	7% @ < 0.3 (16)	4% @ 1.0 (21)
		18% @ 0.1–0.2 (6)	2% @ 0.9–2.5 (25)	4% @ 2.5 (13)
Zn	0.1	11% @ < 10 (39)	4% @ < 10 (46)	2% @ 2.5 (8)
				2% @ 5 (13)
				4% @ 10 (44)

[1] Values in μg/L except (no. of pairs), (no. of analyses), and numbers followed by %

[2] Limit of detection (LOD) defined by International Union of Pure and Applied Chemistry, (IUPAC) (1976)

[3] Median value of relative precision calculated as in Skoog and West (1980) for each pair of laboratory and field replicates.

[4] Field precision for replicate field samples.

[5] Laboratory precision for duplicate subsamples.

[6] Average percent difference between measured and certified value of EPA QC sample

metal data reported below were corrected for field blanks. For minor metals the field blank was a few percent of the measured sample concentration. For trace metals the field blank typically was 20–30% of measured concentrations.

Results

Temporal variations in pH and dissolved O_2

Figure 1A shows near-surface pH for both basins during the baseline period (August 1983–May 1985), six years of acidification, and almost four years of recovery (through fall 1994). Reference-basin pH varied seasonally for the entire study period, with minimum values in late winter, prior to ice-out, caused by a build-up of CO_2 under ice cover (Kratz et al. 1987). After ice-out, reference basin pH increased rapidly as a result of water-column mixing and CO_2 degassing. Starting in May 1985, H_2SO_4 additions during ice-free periods maintained the pH of the acidified basin near the target pH values of 5.6, 5.1, and 4.7 (Figure 1A). Both the natural (under-ice) pH depression in the reference basin and experimental acidification of the treatment basin had effects on the seasonal cycling of metals.

Dissolved O_2 depression occurred under ice cover each winter in both basins, typically reaching ~3 mg/L in near-bottom waters by late March. In March 1986, O_2 approached 0 mg/L in near-bottom waters, causing significant release of Fe and Mn from lake sediments, especially in the shallower reference basin.

Aluminum

Dissolved Al varied seasonally in the reference basin, with higher concentrations under the ice when pH was depressed (Figure 1B). Mean annual near-surface concentrations varied between 5 and 15 μg/L (Figure 2), but long term trends are not obvious. Elevated Al was not observed during ice cover in the reference basin before 1987 because measurements until then were made only quarterly. In the treatment basin, Al increased beginning at pH 5.1 and reached a value of ~60 μg/L during year 2 at pH 4.7. Al remained high in the treatment basin during the first two recovery years (Figure 1B), with the highest near-surface value in the record (85 μg/L) occurring in recovery year 1 (pH 5.0). Mean annual near-surface concentrations of Al in the treatment basin rose steadily during the four years at pH 5.1 and 4.7, declined slightly during the first two years of recovery (Figure 2), and dropped greatly during the last two years of record. Negligible differences in mean annual dissolved Al were observed between basins during baseline sampling and acidification to pH 5.6, but the mean annual dissolved Al at pH 5.1 was higher than reference basin levels by 5–12 μg/L. This difference increased to 24–28 μg/L at pH 4.7 and the first recovery year (pH 5.0) and decreased to < 5 μg/L during the last two years of record.

Iron

No significant difference between basins was observed for dissolved Fe during the baseline period (Figure 1C). Concentrations at pH 5.6 were 5–10 μg/L greater than reference basin values except in early 1986 during the under-ice O_2 depression in the reference basin. Dissolved Fe in the reference basin decreased shortly after ice-out in 1986 and remained below the acidified basin levels for the duration of the acidification and recovery periods (Figure 1C). After acidification to pH 5.1, dissolved Fe increased markedly; the average difference between basins during this period was ~60 μg/L. At pH 4.7, dissolved Fe in the treatment basin was highly variable but still elevated over reference basin levels. However, annual average concentrations for this period (58 and 63 μg/L) were lower than during year 2 at pH 5.1 (72 μg/L) (Figure 2). Near-surface dissolved Fe remained high during the first two years of recovery, with the highest measured values (140 μg/L) occurring in those years (Figure 1C), and the highest annual average (88 μg/L) occurring in

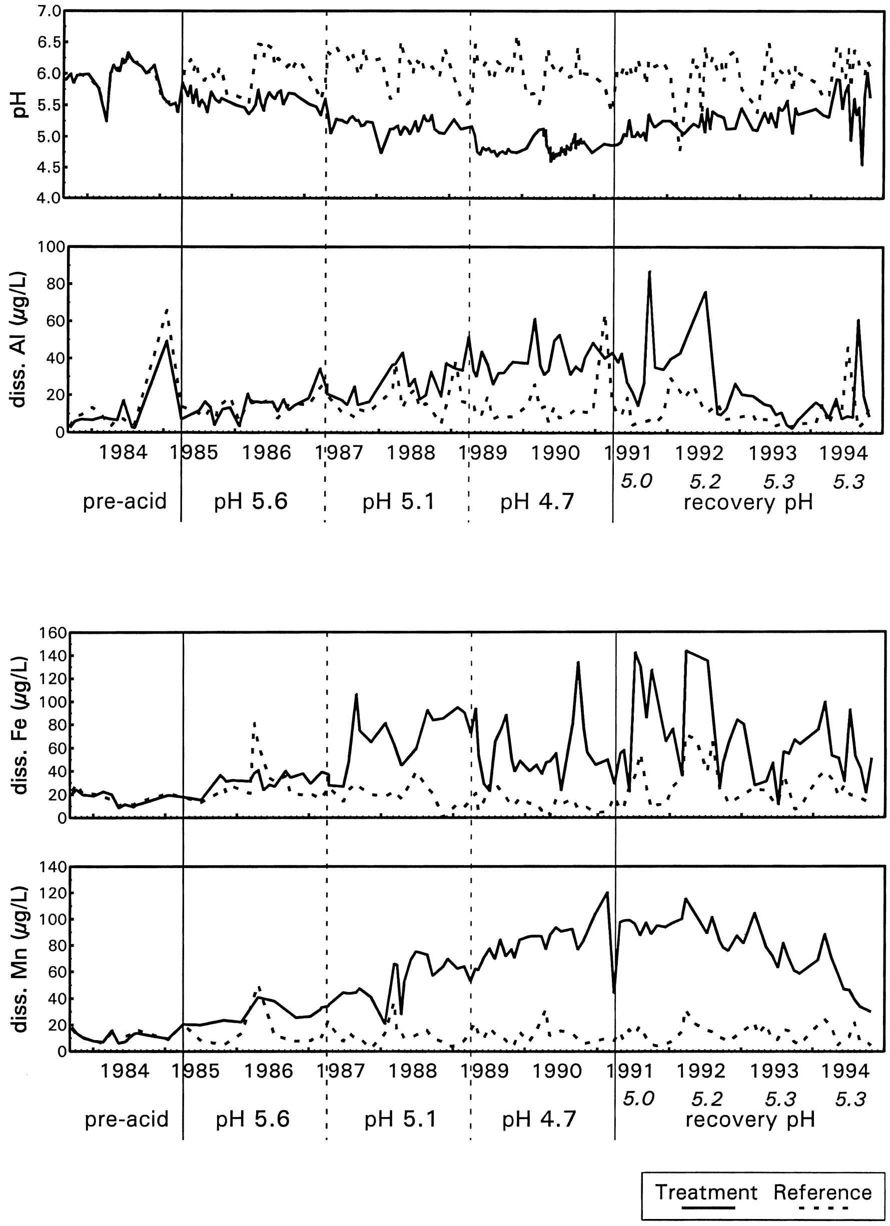

Figure 1. Temporal variations in near-surface (A) pH, (B) dissolved Al, (C) dissolved Fe, and (D) dissolved Mn in acidified and reference basins of LRL over the study period, including acidification to pH targets of 5.6, 5.1, and 4.7 and first four years of recovery.

recovery year 1 (Figure 2). Average annual dissolved Fe concentrations declined during the last two recovery years (pH 5.3) to ~48 μg/L, which is between the

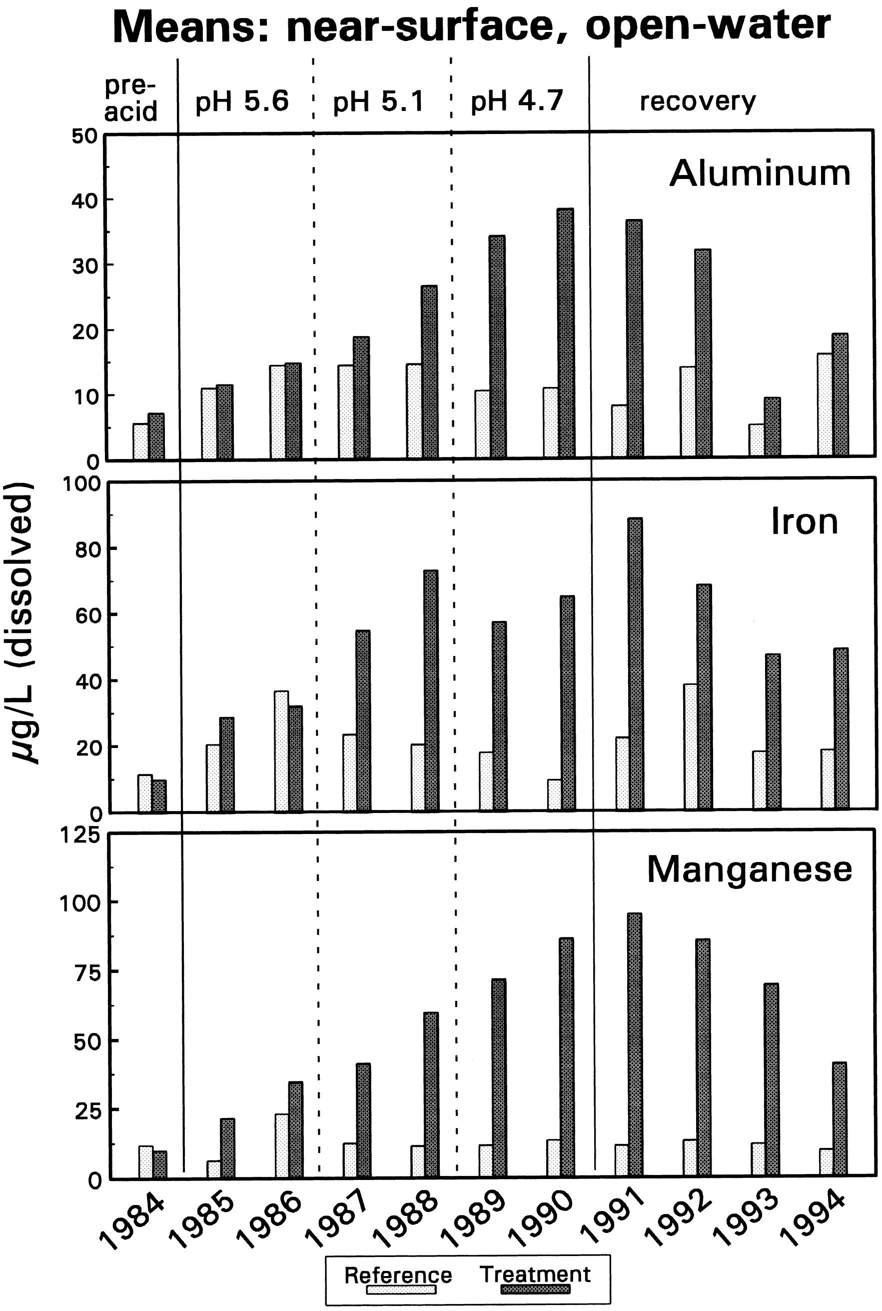

Figure 2. Annual average concentrations of dissolved Al, Fe, and Mn in near surface water of acidified and reference basins of LRL over study period.

average concentrations at pH 5.1 (63 μg/L) and 5.6 (30 μg/L) during the acidification phase.

Manganese

The two basins had nearly identical dissolved Mn levels during the baseline period (Figure 1D), but as soon as acidification began, Mn increased steadily in the treatment basin, reaching a peak of 120 μg/L in February 1991 (year 2 at pH 4.7). Reference basin levels showed some seasonal trends with values increasing under the ice and decreasing during open-water periods (Figure 1D). Peak concentrations typically occurred prior to ice-out in spring. After May 1985, dissolved Mn levels always were higher in the acidified basin (Figure 1D), except in April 1986 when under-ice O_2 depression caused significant release of Mn from reference basin sediments. In terms of annual average concentrations (Figure 2), near-surface Mn peaked at 95 μg/L during the first year of recovery (compared with average values of 87 μg/L during the last year at pH 4.7 and second year of recovery). Both individual and average annual concentrations declined steadily thereafter, reaching an average of 38 μg/L during recovery year 4 (pH 5.3).

Trace metals (Cu, Cd, Pb, Zn)

Statistically significant differences between basins for dissolved Cd, Pb, and Zn occurred primarily during the last period of acidification (Table 2). No consistent difference in dissolved Cu was observed between basins during the baseline and acidification phases, and concentrations averaged ~0.2 μg/L in both basins over this period.

Only two measurements of dissolved Cd were made during the baseline period, but no difference between lake basins is suggested based on these observations (Table 2). Likewise, no consistent difference in dissolved Cd was observed between basins at pH 5.6. Dissolved Cd became elevated in the acidified basin during year 2 (1988) at pH 5.1; levels increased to ~300 ng/L during September and October and then abruptly decreased to reference basin levels (~30 ng/L) in November. A similar peak occurred in July and August during the year 1 (1989) at pH 4.7. In year 2 at pH 4.7, the average dissolved Cd concentration in the acidified basin was ~20 ng/L higher than in the reference basin, but no short-term peak was observed.

No consistent difference was observed in dissolved Pb between basins during the baseline period or at pH 5.6 and 5.1 (Table 2). Levels at pH 4.7 averaged ~80 ng/L higher than reference-basin values, but the difference resulted from a decrease in the reference basin rather than an increase in the acidified basin (Table 2). No consistent between-basin difference was observed in dissolved Zn during the baseline period and at pH 5.6 (Table 2). Levels at pH 5.1 were higher than reference basin values on 11 of 13 sampling dates. The average difference between basins was small (~2 μg/L; Table 2) but significant ($p < 0.05$). Dissolved Zn levels at pH 4.7 were higher than reference basin values on all sampling dates, and the difference (~3 μg/L, Table 2) was highly significant.

Table 2. Epilimnetic concentrations of dissolved[a] Cd, Cu, Pb, Zn, and Ca[b] in both LRL basins for baseline period and three periods of acidification.

		Reference Basin				Acidified Basin			
Metal	Period[c]	pH[d]	Mean[e]	S.E.[f]	N[g]	pH[d]	Mean[e]	S.E.[f]	N[g]
Cd	1	5.90[h]	0.063	0.039	2	5.87[h]	0.046	0.025	2
	2	6.03	0.098	0.031	9	5.55	0.088	0.014	10
	3	6.01	0.053	0.009	19	5.20	0.076	0.017	19
	4	6.01	0.029	0.004	20	4.89	0.067**	0.013	20
Cu	1	5.90	0.22	0.14	13	5.87	0.26	0.12	13
	2	6.03	0.16	0.11	14	5.55	0.13	0.13	13
	3	6.01	0.22	0.09	9	5.20	0.22	0.07	9
	4	6.01	0.18	0.05	7	4.89	0.13	0.09	7
Pb	1	5.90	0.12	0.08	2	5.87	0.15	0.10	2
	2	6.03	0.11	0.02	18	5.55	0.13	0.03	19
	3	6.01	0.09	0.02	11	5.20	0.13	0.03	11
	4	6.01	0.05	0.01	22	4.89	0.14**	0.01	22
Zn	1	5.90	3.1	0.61	11	5.87	3.6	0.76	11
	2	6.03	4.0	0.70	22	5.55	5.4	0.92	22
	3	6.01	4.5	0.54	16	5.20	6.5*	0.56	16
	4	6.01	3.2	0.36	20	4.89	5.9**	0.39	20
Ca	1	5.90	0.89	0.03	12	5.87	0.88	0.03	12
	2	6.03	0.93	0.02	9	5.55	0.95**	0.05	8
	3	6.01	0.91	0.04	20	5.20	1.3**	0.05	20
	4	6.01	1.0	0.01	19	4.89	1.6**	0.04	19

[a] 0.4 μm pore-size filtered samples

[b] Calcium included because of its ability to ameliorate trace-metal toxicity to aquatic biota

[c] Period: 1 = baseline, Sept. 1983–May 1985; 2 = May 1985–April 1987, target pH of 5.6; 3 = April 1987–April 1989, target pH = 5.1; 4 = April 1989–April 1991, target pH = 4.7.

[d] Time-averaged epilimnetic pH for each period

[e] Cd, Cu, Pb, and Zn in μg/L; Ca in mg/L

[f] S.E. = standard error of mean; same units as mean

[g] Number of dates on which measurements were made

[h] Average pH < 6 because period included two under-ice periods with pH depression, but only one open-water period

* $p<0.05$ based on Wilcoxon's two-sample test.

** $p<0.0005$ based on Wilcoxon's two-sample test.

Because acidification to pH 4.7 produced only small changes in dissolved trace metals, monitoring of these metals was not continued during the recovery phase.

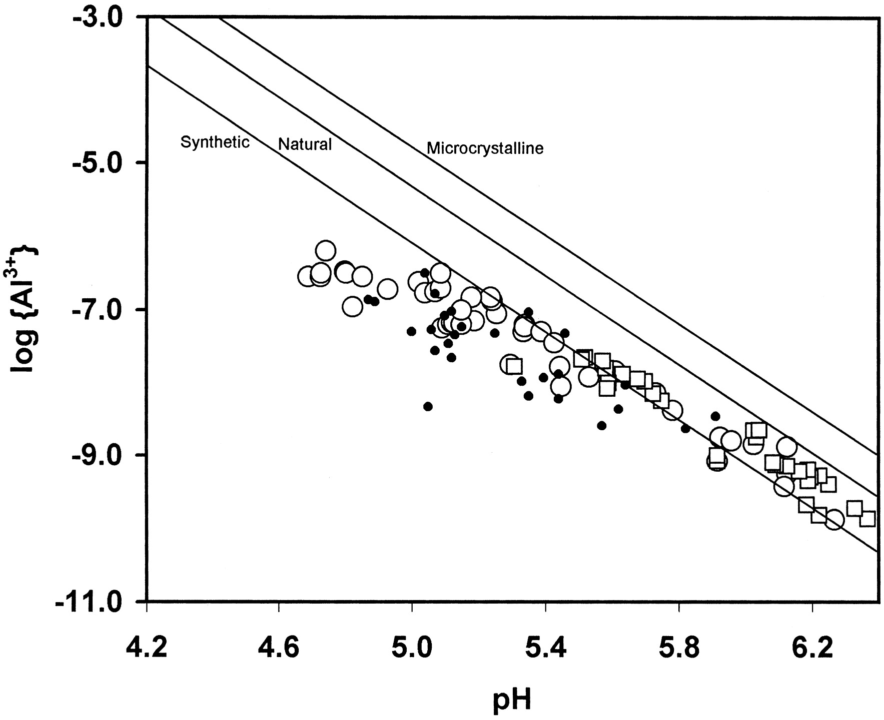

Figure 3. Calculated Al^{3+} activity versus pH in LRL superimposed on gibbsite solubility diagram. Open circles: treatment basin, baseline and acidification phase; closed circles: treatment basin, recovery phase; squares: reference basin, whole study period. Gibbsite lines drawn using K_{s0} values for 10 °C and $I = 1.55\times 10^{-4}$ M, annual averages for reference basin. Points show results for $\log K_{AlDOC} = 6.2$.

Discussion

Aluminum

Thermodynamic calculations suggest that Al in the reference basin was in equilibrium with gibbsite ($Al(OH)_3$). Values of $\log\{Al^{3+}\}$ calculated from measured values of dissolved [Al] and pH fit closest to the equilibrium line for $\log\{Al^{3+}\}$ versus pH calculated for synthetic gibbsite (Figure 3). In addition, the slope of $\log\{Al^{3+}\}$ (calculated from measured dissolved [Al]) versus pH for this basin (−2.53) is close to the value (−3.0) for equilibrium with $Al(OH)_3$. The difference between the observed and theoretical slopes reflects a tendency for supersaturation at pH > ~6.0. This may represent disequilibrium conditions in the lake but also could reflect the fact that the gibbsite solubility lines in Figure 3 are for the annual average temperature of the lake (10 °C), whereas the equilibrium $\{Al^{3+}\}$ values were calculated for the lake temperature on the sampling date. Values for pH > 6.0 are from dates at temperatures mostly > 10 °C, when the solubility of gibbsite is slightly higher than that indicated by the lines in Figure 3.

Table 3. Average values of saturation indices for Al-containing minerals in acidified basin during baseline and three treatment periods.

Mineral	Saturation Index[a]			
	Baseline	Treatment-pH periods		
	pH 6.1	5.6	5.1	4.7
Basic Al-Sulfate Minerals				
Alunite $KAl_3(SO_4)_2(OH)_6$	–5.2	–4.4	–3.7	–3.8
Jurbanite $Al(SO_4)(OH)$	–3.7	–2.9	–2.4	–2.1
Basaluminite $Al_4(SO_4)(OH)_{10}$	–3.2	–2.6	–3.3	–3.9
Aluminum Silicates				
Kaolinite $Al_2Si_2O_5$	–1.3	–1.5	–2.7	–3.1
Halloysite $Al_2Si_2O_5$	–6.8	–7.1	–8.2	–8.7
Amorphous Ideal[b]	–0.4	–1.7	–2.6	–2.8
Reversible Non-ideal[b]	0.3	–1.0	–1.9	–2.1
Aluminum Trihydroxides				
Synthethic Gibbsite	0.05	–0.2	–0.4	–0.8
Natural Gibbsite	–0.7	–0.9	–1.1	–1.5
Microcrystalline Gibbsite	–1.2	–1.5	–1.6	–2.0

[a] Saturation index (SI) = $\log_{10}$(IAP/K), where IAP = ion activity product; K = mineral thermodynamic solubility product. Negative SI = under-saturation; positive SI = oversaturation.

[b] Variable composition aluminosilicates of form: $[Al(OH)_3]_{1-x}[SiO_2]_x + (3-3x)H^+ = (1-x)Al^{3+} + xH_4SiO_4 + (3-5x)H_2O$, where x = 1.24 – 0.135 pH (Paces 1978).

It should be noted that plots like Figure 3 have the potential for spurious self-correlation because the axes are not totally independent (Neal 1988). (The $\log\{Al^{3+}\}$ values are computed from an equilibrium relationship based on measured $[Al]_{dis}$, pH, temperature, and other water chemistry information.) Spurious self-correlation becomes a problem in such plots when the common variable (pH, in this case) has a much wider range than the unique variable (here, $\log[Al]_{dis}$) (Kenney 1982). However, both variables had similar ranges in the LRL data set. In any case, we do not need to use the data in Figure 3 to define a $\log\{Al^{3+}\}$-pH equilibrium line but simply can compare calculated $\{Al^{3+}\}$ values at a given pH to the established relationship.

In the acidified basin, calculated Al^{3+} levels were close to equilibrium values for synthetic gibbsite during the baseline period (Figure 3), but became progressively undersaturated with respect to known forms of gibbsite as pH decreased (Table 3). Above pH 5.8, uncertainty in the value of K_{AlDOC} caused little uncertainty in calculated $\{Al^{3+}\}$ because OH^- outcompeted DOC for Al. Uncertainties in $\log K_{AlDOC}$ (assumed range = 3.8–7.2) at lower pH produced a range of calculated $\{Al^{3+}\}$ of ~ 0.4 log units.

Several mechanisms may account for gibbsite undersaturation at low pH, and each was examined as a possible explanation. The acidified basin was undersaturated with respect to alunite, jurbanite, and basaluminite (Table 3), and thus it is unlikely that basic Al-sulfate minerals formed *in situ*, thereby controlling Al levels. The acidified basin also was undersaturated with respect to kaolinite, halloysite, and variable-composition aluminosilicates described by Paces (1978). Thus it is unlikely that they controlled Al levels. Aluminosilicates in the sediments of the acidified basin could control Al levels in the water column by slowly dissolving at low pH, but this would cause a concurrent increase in SiO_2, which was not observed (Sampson 1992). SiO_2 levels in the acidified basin were not consistently elevated over reference basin levels until the second year at pH 4.7 (and then only slightly). We conclude that basic Al-sulfate or aluminosilicates minerals did not control dissolved Al in the acidified basin.

Metal-DOC precipitation could regulate dissolved Al and Fe concentrations in low-pH surface waters if the (Al+Fe):DOC ratio exceeds the metal-binding capacity of dissolved organic matter. Under such conditions, some of the DOC may undergo charge destabilization, flocculate, and settle from the water column. Acidification caused an increase in the (Al+Fe):DOC ratio (Figure 4), initially because of elevated Al and Fe (Figure 1B, C), but also because of subsequent lower DOC levels in the two years at pH 4.7 and recovery year 1 (pH 5.0) (Figure 4). The (Al + Fe):DOC ratios in these three years were greater than the effective metal-binding capacities of dissolved organic matter reported by Helmer et al. (1990) and Urban et al. (1990) (Figure 4). Our data thus suggest that Al-precipitation could have controlled dissolved Al at $pH < \sim 5.0$.

Because Al levels were near equilibrium with respect to gibbsite ($Al(OH)_3$) solubility during the baseline period, an increase in dissolved Al consistent with gibbsite solubility seemed likely at pH 5.6 and 5.1. However, the slope of calculated $\{Al^{3+}\}$ versus pH was only 1.9 for data from the pH 5.6 period, and 0.4 for the pH 5.1 period, in contrast to 2.52 for the pre-acidification period (pH 5.9–6.3). As discussed above, it is unlikely that Al at pH 5.6 and 5.1 was controlled by the solubility of other Al-containing minerals or Al-DOC precipitation. Moreover, because gibbsite dissolution is rapid (Hsu 1977) relative to the two-year treatment periods, slow kinetics of gibbsite dissolution does not provide an explanation. A more likely explanation is disequilibrium in pH between the water column and sediments of the basin. For example, during the pH 5.6 period, water at the sediment surface and sediment porewater was at pH 6.1 (Sherman et al. 1994). Gibbsite undersaturation in the water column at pH 5.6 may have resulted from this difference in pH. During recovery, dissolved Al at a given pH was somewhat more undersaturated than during the acidification phase. This relationship is unexplained.

Iron

Equilibrium calculations suggest that the solubility of amorphous ferric hydroxide controlled dissolved Fe in the reference basin and acidified basin to pH 5.1 (Figure 5). Above pH 5.4, the uncertainty in K_{FeDOC} caused little uncertainty in calcu-

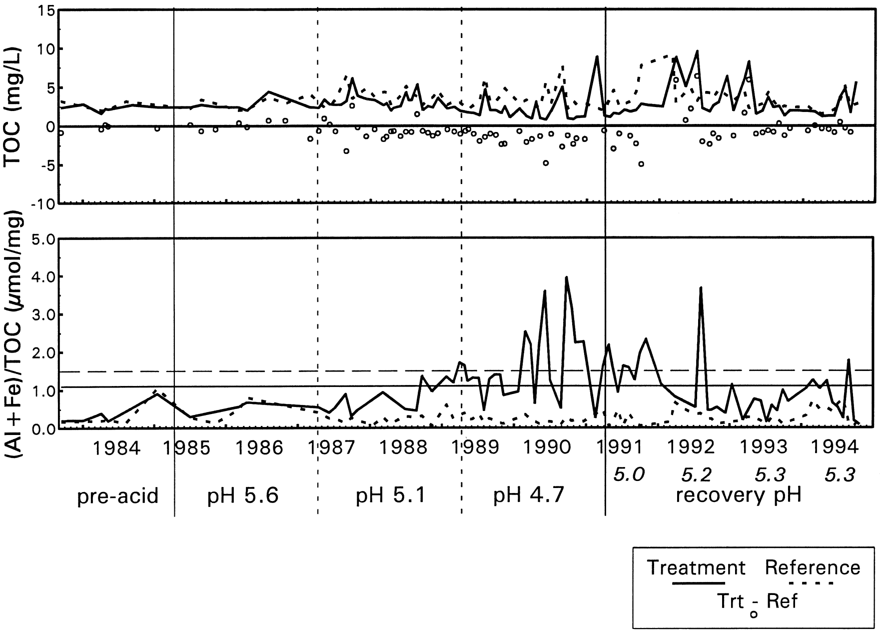

Figure 4. Temporal trends in (A) total organic carbon (TOC) and (B) the ratio (Al+Fe):TOC (µmol/mg) in acidified and reference basins over the three acidification periods. Horizontal lines in (B): effective metal-binding capacity of dissolved organic matter (1 to 1.5 µmol(Al+Fe)/[mg DOC]) Helmer et al. (1990) and from 37 Nova Scotian Lakes (Urban et al. 1990).

lated log$\{Fe^{3+}\}$ because FeDOC complexes were of minor importance in Fe^{III} speciation. The uncertainty increased at lower pH, reaching almost one log unit at pH 4.6 (see vertical line for datum at pH ~4.7 in Figure 5). The solubility lines in Figure 5 are for molar OH:Fe ratios of 3.0 and 2.35. Generally, the molar OH:Fe ratio of ferric hydroxide is assumed to be 3 to balance ionic charges, but Fox (1988) reported a range of 2.0 to 2.7 for the ratio in amorphous "ferric hydroxide." Ratios < 3 may result from inclusion of other anions or mixed Fe oxidation states in precipitating iron hydroxides. Fox proposed the following expression for solubility of colloidal amorphous "ferric hydroxide:" $\{Fe^{3+}\}\{OH^{-}\}^{2.35} = 10^{-31.7}$. Regression of calculated log$\{Fe^{3+}\}$ versus pH (Figure 5) for all data at pH > 5 (both basins) gave a slope of −2.43, close to that for Fox's relationship. Below pH 5, the slope was −1.49. Coupled with the decrease in dissolved Fe at pH 4.7 compared with pH 5.1 (Figure 2), and high (Al + Fe):DOC ratio at pH 4.7 (Figure 4), this suggests that dissolved Fe was limited by Fe-DOC precipitation at pH 4.7. The increase in dissolved Fe in recovery year 1 (pH 5.0) (Figure 2), while TOC remained low (Figure 4), suggests that the link between Fe and TOC levels is not so simple, however. An alternative explanation for the decrease in dissolved Fe and DOC at pH 4.7 is enhanced photodegradation of natural organic matter at lower pH (Molot and Dillon 1997). The decline in dissolved Fe at pH 4.7 could be explained by the lower concentration of Fe-complexing DOC in the treatment basin, but this does not ex-

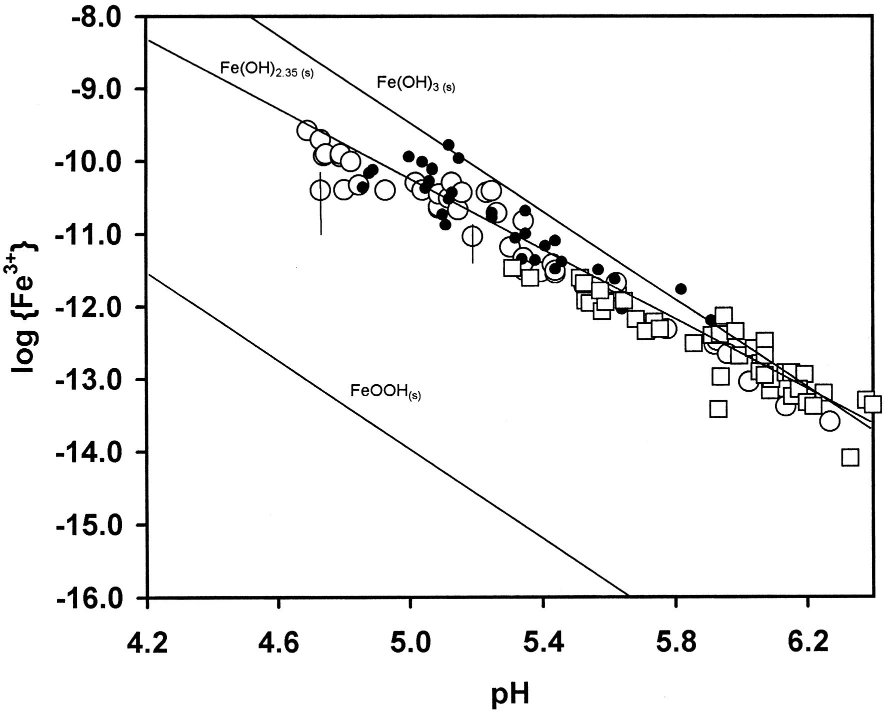

Figure 5. Calculated Fe^{3+} activity versus pH for LRL superimposed on amorphous ferric hydroxide solubility diagram. Open circles: treatment basin, baseline and acidification phase; closed circles: treatment basin, recovery phase; squares: reference basin, whole study period. Lines for selected Fe minerals drawn using K_{s0} corrected to 10 °C and $I = 1.55\times10^{-4}$ M, annual averages for reference basin. Points show results for $\log K_{FeDOC} = 9.4$; lines through data points at pH 4.7 and 5.2 show range in $\log\{Fe^{3+}\}$ for range of $\log K_{FeDOC}$ (8.4–10.4).

plain how the Fe released from natural organic matter as a result of photodegradation was lost from the water column and also does not explain the increase in dissolved Fe and constant (still low) TOC during recovery year 1.

Calculated equilibrium $\{Fe^{3+}\}$values during recovery generally fell within the envelope of calculated equilibrium $\{Fe^{3+}\}$ for the acidification period (Figure 5), indicating that there were no hysteresis effects. Although we can explain dissolved Fe concentrations in the acidified basin in terms of Fe(III) (i.e., concentrations were below the solubility of ferric hydroxide), we cannot rule out the occurrence of meta-stable Fe^{2+} in the water column. The half-life of Fe^{2+} with respect to oxidation by O_2 is ~115 days at pH 5.0 (based on kinetic studies summarized by Brezonik (1994)), and consequently Fe^{2+} released from the anoxic hypolimnion at fall overturn or possibly diffusing from anoxic sediments would persist in the water column for several months.

Manganese

Figure 6 compares $\{Mn^{2+}\}$calculated from LRL water chemistry to $\{Mn^{2+}\}$ in equilibrium with manganite [γ-$MnOOH_{(s)}$], feitknechtite [μ-$MnOOH_{(s)}$], and hausmannite [$Mn_3O_{4(s)}$]. These metastable minerals form readily in laboratory solution (Hem and Lind 1983) and possibly in surface waters (Hem et al. 1982; LaZerte and Burling 1990), but with time they age to more thermodynamically stable solids such as MnO_2 (pyrolusite). Activities of Mn^{2+} in both basins were much less than the equilibrium values for hausmannite and feitknechtite, but they fall on both sides of the line for $\{Mn^{2+}\}$ equilibrium with manganite (Figure 6). Uncertainty in $K_{Mn\text{-}DOC}$ had no effect on calculated Mn speciation because Mn-DOC binding constants are small. Regression of $\{Mn^{2+}\}$ in the basins versus pH gave a slope of 0.67, far less than the theoretical slope of 2.0 for control by manganite. Values of $\{Mn^{2+}\}$ in the acidified basin are below the solubility line, which implies that the basin was undersaturated relative to manganite. This is consistent with the steady increase in dissolved Mn during acidification (Figure 1D). Values of $\{Mn^{2+}\}$ in the reference basin are above the manganite solubility line for open-water periods but below or near it for ice-covered periods.

Values of $\{Mn^{2+}\}$ in the reference basin approached equilibrium with γ-MnOOH(s) from oversaturation during open water and from undersaturation during ice cover. Seasonal shifts between over- and undersaturation in the reference basin can be explained by under-ice pH depression (Figure 1D), which averaged 0.7 pH units, and the pH-dependent solubility of manganite. The reaction for manganite solubility is: $Mn^{2+} + 3/2H_2O + 1/4O_{2(aq)} = \gamma\text{-}MnOOH_{(s)} + 2H^+$, log K = –4.50, and its ion-activity product is $\{H^+\}^2/\{O_2\}^{1/4}\{Mn^{2+}\}$. Acidic and reducing conditions thus promote manganite dissolution. The $\{H^+\}^2$ term in the numerator implies that manganite solubility was strongly affected by seasonal pH changes in the reference basin. The pH depression under ice caused γ-$MnOOH_{(s)}$ undersaturation, and dissolved Mn increased (Figure 1D). The rapid pH increase after ice-out produced manganite oversaturation, and dissolved Mn decreased during open-water. This sequence explains the scatter in $\{Mn^{2+}\}$ and the slope (< 2) in $\{Mn^{2+}\}$ versus pH for the reference basin (Figure 6). The temporal changes in $\{Mn^{2+}\}$ thus suggest that manganite equilibria “controlled” dissolved Mn in the reference basin on a long term basis, but reaction kinetics controlled concentrations on a given date. During open-water periods, the decrease in dissolved Mn^{2+} was determined by its rate of oxidation to γ-MnOOH, which is a microbially or particle-mediated process (Diem and Stumm 1984; Richardson et al. 1988). Homogeneous chemical oxidation of Mn^{2+} is an extremely slow reaction (Morgan 2000).

Trace metals (Cu, Cd, Pb, Zn)

Possible explanations for elevated Cd, Pb, and Zn levels in the acidified basin include: (i) input with the technical-grade H_2SO_4 used to acidify the basin; (ii) release from sediments at low pH; and (iii) reduced scavenging of atmospherically-deposited Cd, Pb, and Zn from the water column by settling particles at low pH.

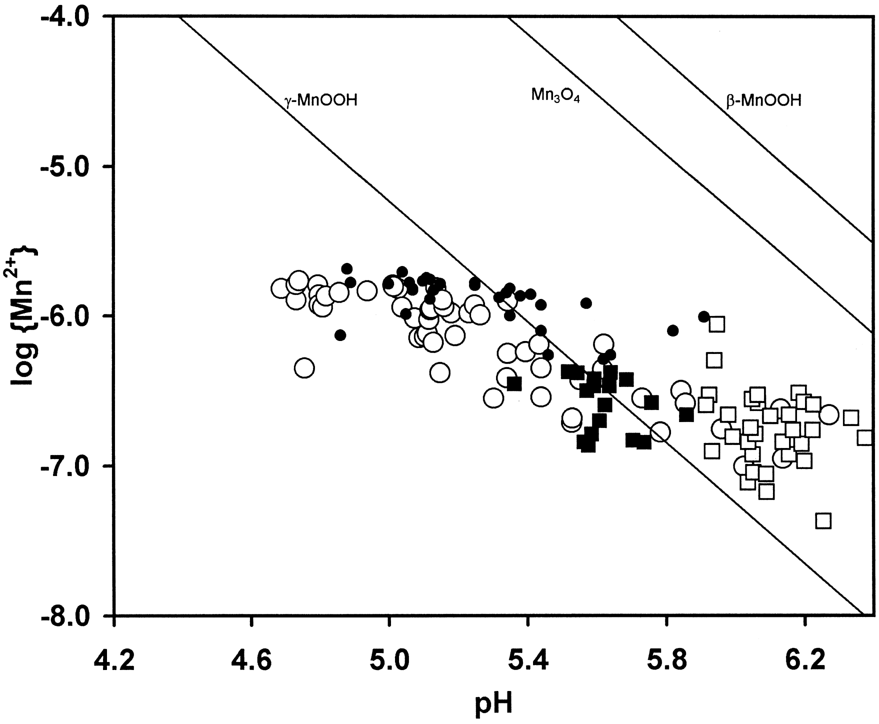

Figure 6. Calculated Mn^{2+} activity versus pH for LRL superimposed on Mn (hydr)oxide solubility diagram. Open circles: treatment basin, baseline and acidification phase; closed circles: treatment basin, recovery phase; open squares: reference basin, study period except during ice cover 1983–1990 (solid squares). Lines for manganite [γ-MnOOH(s)], feitknechtite [β-MnOOH(s)], and hausmannite [Mn_3O_4(s)] derived from Hem (1981) and Hem and Lind (1983), assuming O_2(aq) = $10^{-3.5}$ M.

The technical-grade H_2SO_4 used to acidify the lake was analyzed for trace-metals by graphite-furnace AAS, and metal contamination was several orders of magnitude below that needed to account for the concentrations of Cd, Pb, and Zn in the treatment basin. For example, in 1989 (first year at pH 4.7), 454 l of technical-grade H_2SO_4 were added to the treatment basin; this is the largest volume of acid added in any year. The trace-metal content of the acid was: Cd 1.2 μg/L, Pb 91 μg/L, and Zn 8.3 mg/L. Trace-metal contaminants added with the acid increased the concentration of Cd in the treatment basin by 0.002 ng/L, Pb by 0.12 ng/L, and Zn by 0.01 μg/L. These increases are 10^{-2} to 10^{-4} of the measured concentration differences between treatment and reference basins in 1989: 73 ng/L for Cd, 100 ng/L for Pb, and 3.5 μg/L for Zn. Elevated levels of Cd, Pb, and Zn in the treatment basin were not caused by the H_2SO_4 used to acidify the basin.

Release of trace metals from sediments at low pH is a second possible explanation of higher levels in the acidified basin. Laboratory desorption experiments with sediments from this basin (Downing 1986) showed that the pH of first release was 4.5 for Cd, <4 for Pb, and 5.0 for Zn. The low pH required to release Cd and Pb in

Table 4. Comparison between dissolved Cd, Cu, Pb, and Zn in water column of Little Rock Lake (μg/L) and wet precipitation at rural locations in Lake Superior region of North America (μg/L).

Location	Precipitation-Weighted Mean Concentration			
	Cd	Cu	Pb	Zn
Quetico Center, Ontario[a]	0.073	1.2	3.3	3.1
Lac la Croix, Ontario[a]	0.13	1.8	2.7	6.6
Hovland, Minnesota[b]	0.15	3.5	7.1	93
Northern Wisconsin[c]	0.25	–	3	–
Marcell, Minnesota[d]	–	1.4	1.8	14.3
I. Median[e] of above sites	0.14	1.6	3	10.5
II. Reference basin mean[e]	0.052	0.19	0.083	3.7
Ratio (I/II)	2.7	8.4	36	2.8
III. Acidified basin mean[f]	0.067	0.13	0.14	5.9
Ratio (I/III)	2.1	12	21	1.8

[a] Chan et al. (1986)
[b] Thornton et al. (1981)
[c] Estimated from figures presented by Gatz et al. (1989)
[d] Rain samples for 1981–83 (Metzer 1986)
[e] Time-averaged dissolved metal concentrations for 1983–90
[f] Time-averaged epilimnetic dissolved metal concentrations for pH ~ 4.7

the laboratory suggests that sediment release was not a major source of these metals to the acidified basin. The pH of first increase for Zn in the treatment basin (5.1) agrees reasonably with the pH of first release of Zn in the laboratory. Sediments thus were a possible source of Zn to the acidified basin.

A third possible explanation for the elevated levels of trace metals assumes that atmospheric deposition is their source to the lake and that metal scavenging by suspended particulates was lower at low pH. Atmospheric deposition is a major source of trace metals to many environments (Campbell et al. 1985). This is particularly true for seepage lakes like LRL, which receives nearly all its water directly from precipitation to its surface. The importance of atmospheric deposition as a source of Cd, Cu, Pb, and Zn to the lake can be examined by comparing levels in wet deposition with average dissolved concentrations in LRL. The metals exist predominantly in dissolved form in wet deposition (Campbell et al. 1985), and concentrations at rural sites in the Lake Superior region are much higher than dissolved concentrations in both basins (Table 4). Moreover, metals also are deposited to lakes in dry deposition, some of which can dissolve (Lindberg and Harriss 1983). If Cd, Cu, Pb, and Zn behaved conservatively in LRL, their water-column concentrations would exceed concentrations in wet deposition, because solutes in the lake are concentrated approximately two-fold by evaporation.

The non-conservative behavior of Cd, Cu, Pb, and Zn was quantified by comparing residence times of the metals in LRL basins (t_M, yr) to the lake's residence time for conservative chemicals ($t_{cc} = \sim 10$ yr). t_M values were calculated from

Table 5. Total (wet+dry) atmospheric deposition of Cd, Cu, Pb, and Zn to the Lake Superior region of North America.

Site	Sampling Period	Atmospheric Deposition (mg/m^2 yr^{-1})			
		Cd	Cu	Pb	Zn
Lake Superior[a]	–	0.10	–	2.9	–
Lake Superior[a]	–	0.67	–	7.9	–
Lake Superior[b]	1970s	0.9	10	17	130
Quetico Center, Ontario[c]	1982	0.07	1.32	4.1	3.0
Lac la Croix, Ontario[c]	1982	0.12	1.62	2.9	5.6
Northeast Minnesota[d]	1978–79	0.28	2.91	7.1	–
Median		0.2	2.3	5.6	5.6

[a] From Gatz et al. (1989)

[b] Averages of 3–5 values from Schmidt and Andren (1984)

[c] Chan et al. (1986)

[d] Wet-deposition estimated from Thornton et al. (1981). Dry-deposition calculated from trace-metal content of northeast-Minnesota aerosol (Mach, unpublished) and deposition velocities from Chan et al. (1986).

total metal concentrations (dissolved + particulate) in the water column, mean depths of the basins, and total (wet + dry) atmospheric deposition:

$$\tau_M(\mathrm{yr}) = \frac{(\mathrm{dissolved} + \mathrm{particulate\ metal}(\mathrm{mg/m^3}))\cdot(\mathrm{mean\ depth\ (m)})}{(\mathrm{annual\ loading}(\mathrm{mg}/m^2\cdot\mathrm{yr}))} \qquad (1)$$

Atmospheric deposition was assumed to be the only significant source of trace metals to the lake. Dissolved concentrations were from Table 2; particulate concentrations were from Mach (1992); deposition was from Table 5. Particulate concentrations were not available for Cd and Zn, and they were estimated from particulate/dissolved ratios for Cu and Pb, for which ~70% of total metal was in dissolved form. t_M values for the treatment basin are for pH ~5.1, the only period for which particulate metal concentrations in the water-column are available.

τ_M values for Cu in the reference and treatment basins are 0.3 and 0.4 yr, respectively; corresponding values for Pb are 0.10 yr and 0.11 yr. These values are much shorter than t_{cc}. t_M values for Cd were estimated to be 1.1 and 1.9 yr for reference and treatment basin, respectively; corresponding values for Zn are 2.9 and 5.6 yr. These values are larger than those for Cu and Pb (the former metals generally are less reactive than the latter) but still far lower than t_{cc}. All four metals thus are removed from the water column by process(es) besides groundwater outflow. Possible mechanisms are mineral precipitation and sorption onto settling particles. Saturation indices of Cd-, Cu-, Pb-, and Zn-containing carbonate, hydroxide, and silicate minerals in both basins were highly negative–between -5 and -28 for $CdCO_3$, amorphous $Cd(OH)_2$, $CdSiO_3$, $Cu_3(OH)_2(CO_3)_2$, $Cu(OH)_2$,

$Cu_2(OH)_2CO_3$, $PbCO_3$, $Pb(OH)_2$, $PbSiO_{3(s)}$, $ZnCO_3$, amorphous $Zn(OH)_2$, and $ZnSiO_3$, strongly suggesting that mineral precipitation was not responsible.

To evaluate the role of removal by sorption-particle settling, we compared sedimentation rates of Cu and Pb measured by sediment traps in the reference basin in 1987 (Mach 1992) with median atmospheric inputs of the metals (Table 5). For Cu, sedimentation was estimated to be 2.0 ± 1.5 mg m^{-2} yr^{-1}, and the median total atmospheric deposition is 2.3 mg m^{-2} yr^{-1}. Corresponding values for Pb are 10.7 + 7.7 and 5.6 mg m^{-2} yr^{-1}. The similar magnitudes for sedimentation and atmospheric deposition suggests that sorption-particle settling is important in removing Cu and Pb from LRL. This also may be true for Cd and Zn, but sediment-trap blanks for these metals were too high to calculate sedimentation rates.

In summary, atmospheric deposition appears to be the major source of Cd, Cu, Pb, and Zn to LRL, and particle settling removes the metals from the water column. The most likely explanation for elevated dissolved Cd and Pb levels in the acidified basin is reduced scavenging by settling particles. Increased competition by H^+ for surface-binding sites and lower formation rates of fresh Fe (hydr)oxide surfaces at low pH (due to lower rates of Fe^{II} oxidation at low pH) could explain the reduced scavenging. This could explain elevated Zn levels in the acidified basin as well, but desorption from sediments also may have played a role.

Comparison with other studies

It is well known that surface-water acidification results in elevated Al levels; values up to several hundred μg/L have been reported for lakes in Europe and North America (e.g. Wright et al. (1980)). High Al levels in acidified drainage lakes result from transport by runoff from surrounding uplands (e.g. Johnson et al. (1981) and Schafran and Driscoll (1987)). However, LRL is hydrologically isolated: the lake has no surface inlets, overland runoff into the lake is virtually nil, and groundwater inflow is minor–at most about 2% of the total water inflow and often entirely absent. As a result dissolved Al levels were much lower in acidified LRL than in low-pH drainage lakes. The small increases in Al nonetheless are biologically relevant; McCormick and Jensen (1992) found reduced survival of young-of-the-year largemouth bass in laboratory bioassays with simulated LRL water at pH 5 and 4.5 and dissolved Al = 30 μg/L.Control of dissolved Al in the reference basin by gibbsite agrees with published studies on controls at pH > 5 (Driscoll et al. 1984). Postek et al. (1995) also concluded that gibbsite controlled dissolved Al at least to pH $\sim$5.0 in surface waters of Maine. In contrast, Neal and Christophersen (1989) concluded that variations in dissolved Al levels in three streams draining acidified catchments in Norway and Wales could not be explained by solubility control of a single mineral phase. Instead, they concluded that Al levels in the streams were controlled by both conservative and non-conservative two-component mixing of upper soil and ground waters.

Control of dissolved Al in LRL at pH 4.7 by Al-DOC precipitation agrees with results of Urban et al. (1990) for Nova Scotian lakes at pH < 5. Gibbsite undersaturation in LRL at pH 5.6 and 5.1 probably resulted from pH disequilibrium between the sediments and water-column.

Few previous studies have focused on Fe in surface waters of acidic lakes. Studies have been reported on Fe in sediments (White et al. 1989) or anoxic hypolimnia (Cook 1984), where its ability to form stable solids with reduced sulfur species is important for internal alkalinity generation. Dissolved Fe increased after acidification of in-lake enclosures at the Experimental Lakes Area (ELA) in Ontario (Schindler et al. 1980a; Anderson et al. 1987), but Fe levels in ELA Lake 223 decreased by ~60% during five years of acidification from pH 6.6 to 5.4 (Schindler and Turner 1982). In a survey of 37 Nova Scotian lakes ranging from pH 4.0 to 6.1, Urban et al. (1990) found that Fe levels increased as pH decreased to pH ~5, in accordance with amorphous $Fe(OH)_3$ solubility. Below pH ~5, Fe levels did not increase further and apparently were limited by Fe-DOC precipitation, or possibly by low rates of watershed/atmospheric inputs of Fe, to values well below those predicted by amorphous $Fe(OH)_3$ solubility. It appears that dissolved Fe in LRL was controlled by the same processes.

Trends for Mn in LRL agree with results from regional surveys (Almer et al. 1978; Borg 1987), other lake acidification studies (Schindler and Turner 1982), and enclosure experiments (Schindler et al. 1980a), which reported elevated Mn levels at lower pH. Few have examined the processes controlling Mn levels in low-pH waters, however. White and Driscoll (1987a) suggested that manganite [γ-MnOOH] controlled dissolved Mn in Darts Lake (Adirondacks, New York), but Urban et al. (1990) found no evidence for control of dissolved Mn by mineral solubility in Nova Scotian lakes. They concluded that levels were controlled by rates of Mn inputs. Dissolved Mn generally has been considered not to be toxic to aquatic organisms at the concentrations found in surface waters, but Nyberg et al. (1995) reported evidence that Mn^{2+} is toxic to some fish at concentrations well below the values found at $pH < 5.1$ in LRL.

Dissolved Cu was not affected by acidification in LRL in agreement with results at the ELA (Schindler et al. (1980a, 1980b)). Literature reviews by Campbell et al. (1985) and LaZerte (1986) also concluded that Cu is not mobilized by soil and lake acidification. Previous acidification experiments (Hall et al. 1980; Schindler et al. (1980a, 1980b)) did not find elevated Cd at reduced pH, in contrast to our findings, but some regional surveys (e.g. Borg (1983) and Schmidt (1985)) have reported negative correlations between lake-water Cd levels and pH. The pH gradient in large-scale lake surveys is thought to be caused primarily by a gradient in atmospheric deposition, and the basis for the correlation thus is confounded because trace metal and acid deposition may co-vary. However, Schmidt (1985) found an inverse pH-Cd trend in 14 north-central Wisconsin lakes, in an area small enough for uniform atmospheric deposition to the lakes.

Elevated levels of dissolved Pb in LRL at pH 4.7 agree with lake surveys that found inverse relationships between Pb and lakewater pH (Schmidt 1985; Borg 1983). Atmospheric metal and acid deposition were not confounded in either of these studies, and the inverse relationship may have resulted from reduced particle scavenging at low pH. Elevated Pb levels were not found in the acidification of

ELA Lake 223 (Schindler et al. 1980b) or acidified enclosures in that lake (Schindler et al. 1980a), but pH values as low as 4.7 were not reached in these studies and atmospheric deposition of labile Pb probably is very low at the ELA.

Finally, the increase in dissolved Zn observed at pH 5.1 and 4.7 in LRL agrees qualitatively with other acidification experiments and lake surveys, but levels in LRL were much lower than those in other low-pH lakes. White and Driscoll (1987b) reported dissolved Zn levels of 10–78 μg/L (annual-average 26 μg/L) in Darts Lake, New York (average pH 5.1), and Borg (1983) reported dissolved Zn levels of ~ 25 μg/L in lakes at pH ~ 5. Most of the lakes in these studies are drainage systems. Zinc and cadmium are readily mobilized from soil by acid precipitation, and acidic runoff is an important cause of elevated Zn and Cd levels in streams (Johansson et al. 1995) and Zn levels in drainage lakes (Campbell et al. 1985). In contrast, levels in LRL averaged only 6 μg/L at pH 5.1, reflecting the lake's hydrologic isolation.

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