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Acid-base chemistry and aluminum transport in an acidic watershed and pond in New Hampshire

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Abstract. Cone Pond is one of the few acidic, clear-water ponds in the White Mountains of New Hampshire, a region dominated by high inputs of strong acids from atmospheric deposition and low base content of bedrock. Monitoring was conducted for 13 months to compare and contrast the acid-base chemistry of the terrestrial and aquatic portions of the watershed. Variations in Al concentration and speciation in drainage waters were correlated with changes in the supply of naturally occurring organic ligands. During the study period, the pond retained 28% of Al inputs, including nearly half of the inputs of organically complexed Al. Chemical equilibrium calculations indicated that the entire water-column was oversaturated with respect to the solubility of synthetic gibbsite during summer, as was the hypolimnion during winter. Retention of Al resulted from an increase in pH in the hypolimnion concomitant with SO_4^{2-} reduction, and from loss of organic anions in epilimnetic waters. Acid neutralizing capacity (ANC) generated in the pond primarily through SO_4^{2-} reduction and base cation (C_B) release was balanced by ANC consumed as a result of Al retention.

Key words: Acid neutralizing capacity, acidification, aluminum, dissolved organic carbon, lake, watershed

Introduction

There have been many synoptic surveys of low ionic strength lakes in the eastern U.S (Landers et al. 1988; Baker et al. 1988; Driscoll et al. 1991; Kahl et al. 1991; Stoddard and Kellogg 1993). These surveys have documented numerous clearwater lakes with low values of pH and acid neutralizing capacity (ANC) in the Adirondack region of New York. Despite regionally high inputs of acid deposition and typically low base content of bedrock (Driscoll 1991), few clearwater acidic ponds have been found in other regions of the northeast, including the White Mountain region of New Hampshire (Linthurst et al. 1986; Haines and Akielaszek 1983; Buso et al. 1984).

One hypothesis for the anthropogenic acidification of surface waters is that dilute brown water ponds, which were naturally acidic due to weak organic acids, have become acidic clear water systems through atmospheric inputs of sulfuric and nitric acids since the industrial revolution (Krug and Frink 1983; Davis et al. 1985). Mechanisms may include protonation of organic anions and coagulation of organic solutes by inputs of H^+ and/or Al. Excess loading of strong acid anions (i.e., SO_4^{2-}, NO_3^-) has increased the mobility of Al in forest soils, resulting in enhanced leaching of Al to surface waters, exacerbating acidification (Cronan and Schofield, 1979).

Aluminum plays an important role in the chemistry of acidic drainage waters because it is a strong pH buffer under acidic conditions and is toxic to aquatic and terrestrial biota (Driscoll and Schecher, 1988). Driscoll et al. (1980) found that inorganic monomeric Al (Ali) is the most critical form in determining toxicity to brook trout; concentrations greater than 4 – 8.5 μM are considered toxic.

Studies have further demonstrated that: 1) Al concentrations increase exponentially with decreases in pH; below a pH of about 5.0 the speciation of Al is dominated by Ali (Driscoll and Bisogni 1984); 2) Al is largely released from upland soils and inputs of Al are retained in lake ecosystems (LaZerte 1986; Schafran and Driscoll 1987; Driscoll et al. 1989); and 3) there are marked seasonal variations in the concentration and influx of Al to acidic lakes; these temporal variations closely coincide with changes in NO_3^- concentrations (Schofield et al. 1985; Schafran and Driscoll 1987; Driscoll and Van Dreason 1993).

Our study site, Cone Pond, is one of the few acidic ponds documented in the White Mountains (Buso et al. 1985; Landers et al. 1988). Cone Pond had a viable warm water fishery until the 1950's when native fish were removed by managers in an unsuccessful attempt to establish brook trout. Historical trends in pond chemistry are difficult to quantify due to lack of data and limitations of methodology used in earlier measurements (Buso et al. 1984). Current water chemistry of Cone Pond, characterized by acidic conditions with H^+ and Al as dominant cations and SO_4^{2-} as the dominant anion, would not support a sport fishery (Buso et al. 1985).

The objectives of this investigation were to examine the processes regulating acid/base chemistry of drainage waters and to quantify the transport and fate of Al at CPW. The speciation of Al and its relationships with important ligands were also examined to gain insight into the environmental chemistry of Al in acidic lake ecosystems. The lack of NO_3^- in drainage waters at CPW provided an opportunity to study transport of Al in a system which contrasts with the Adirondack watersheds, providing insight on the roles of Al and dissolved organic carbon (DOC) in lake acidification processes.

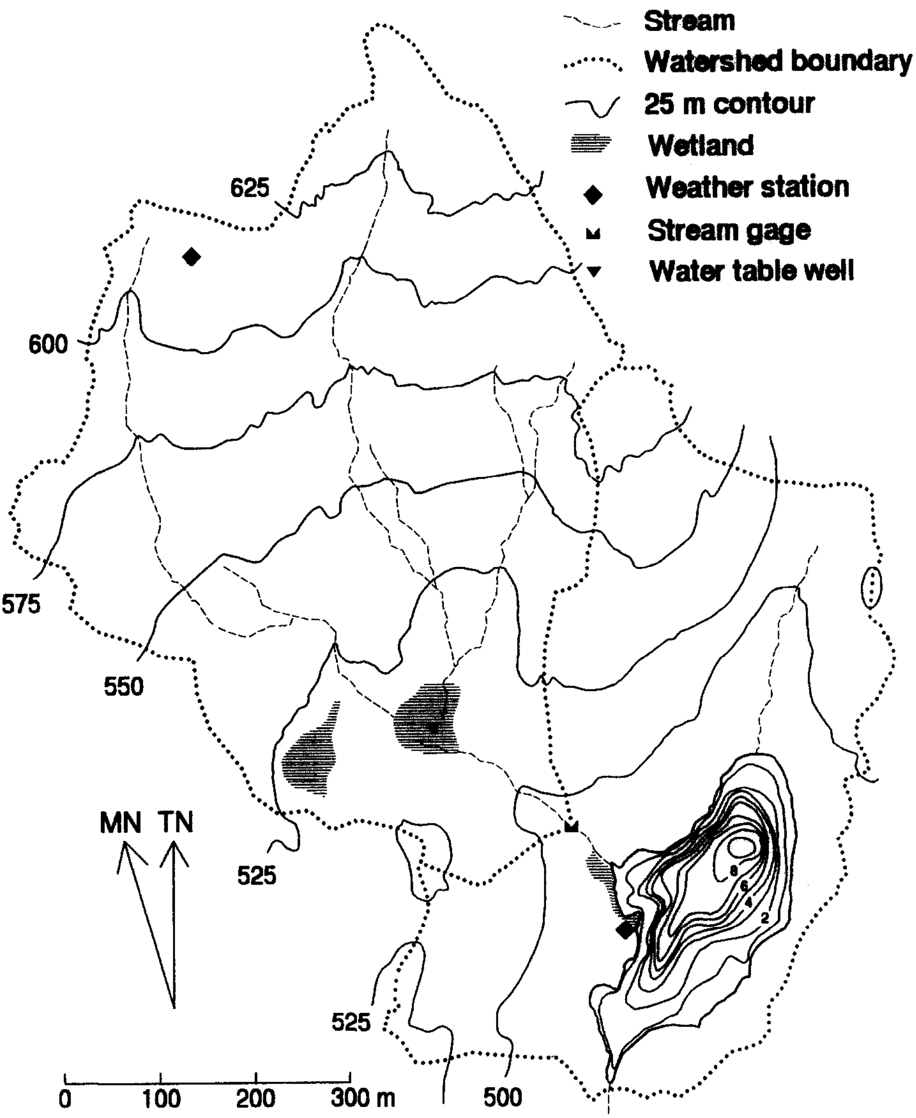


Fig. 1. Cone Pond Watershed showing sample locations. Pond contour interval is 1 m.

Methods

The Cone Pond Watershed (N43°54′ W71°36′) consists of 53 ha of all-aged (maximum 260 years) forest in the White Mountain National Forest of New Hampshire (Figure 1; Buso et al. 1984). The forest is dominated by conifers, primarily red spruce, balsam fir and eastern hemlock, with lesser areas of northern hardwoods including American beech, yellow birch, and sugar maple. Soils include Typic, Lithic, and Aquic Haplorthods with lesser areas of Typic and Terric Borohemists in wetlands associated with stream channels (Figure 1). Two-thirds of the watershed (33 ha) are drained by one inlet stream, whereas the remaining 19 ha discharge directly to the pond. The inlet stream consists of three ephemeral branches in the upper watershed, which meet in a wooded wetland and then flow to the pond through a bedrock controlled ravine (Figure 1). Water table in the 2.5 m thick peat soils of the wetland was monitored with a slotted 3.8 cm diameter PVC pipe.

Cone Pond has a surface area of 3.1 ha, maximum depth of 8.6 m, and a volume of 120,000 m^3. Mean hydrologic residence time is 90 days. Hydrologic inputs to the pond include direct precipitation to the pond surface, streamwater runoff, and diffuse runoff and seepage from areas of the watershed not drained by the inlet.

Precipitation was measured with standard and recording rain gauges at the pond shore. Streamwater inputs from the main inlet to the pond were measured continuously with a 120° v-notch weir constructed of wood with a polyester reinforced neoprene liner to avoid stream contamination. Runoff from areas draining directly to the pond was estimated on a proportional area basis from runoff measured at the main inlet. Pond evaporation was estimated by the Thornthwaite method. Change in storage was monitored by comparing readings taken from a staff gauge with a stage-storage chart compiled from a bathymetric survey. Outflow was calculated by difference in hydrologic balance: Total Inflow − Evaporation ± Change in Storage = Outflow. Groundwater inputs and outputs were considered negligible due to the shallow till soils (<2 m) and bedrock outcrops along the pond perimeter.

Bulk precipitation was collected weekly via a polyethylene funnel near the pond shore. Throughfall samples were collected weekly during the growing season at 12 plots located randomly throughout the watershed, stratified by coniferous and deciduous forest cover types. Grab samples for chemical analysis of the inlet were collected at a maximum of weekly intervals for a total of 72 samples; stream water from other points in the watershed was sampled occasionally and demonstrated that the routine site was representative of drainage water chemistry from ungauged areas.

Pond outlet and water-column samples at depths of 0.5, 2, 4, 6, and 8 m were collected on 10 dates at intervals chosen to represent periods of stratification and turnover. Field analyses for dissolved oxygen (DO), dissolved inorganic carbon (DIC) and pH were made within hours of collection. Analyses for other solutes were made at the US Forest Service laboratory in Durham, NH, within one month following collection, using methods summarized in Table 1. Split samples analyzed for SO_4^{2-} by ion chromatography suggest no interference from color in these low DOC waters.

Table 1. Analytical methods used in this study.

Species	Method	Reference
pH	Glass pH electrode potentiometry	APHA 1985
DO	Winkler titration with azide modification	USEPA 1983
Ca, Mg, Na, K, Fe	Flame atomic absorption spectrophotometry	Slavin 1968
Ali	Pyrocatechol violet colorimetry; autoanalyzer	McAvoy et al. 1992
Alo	Pyrocatechol violet with cation exchange	McAvoy et al. 1992
NH_4	Indophenol blue colorimetry; autoanalyzer	USEPA 1983
SO_4	Methylthymol blue colorimetry; autoanalyzer	McSwain et al. 1974
NO_3	Copper-cadmium reduction; autoanalyzer	Willis 1980
Cl	Ferric thiocyanate; autoanalyzer	USEPA 1983
Total F	potentiometrically with F electrode after TISAB addition	Orion 1976
DOC	K-persulfate and UV digestion with phenolphthalein indicator; autoanalyzer	Goulden & Brooksbank 1975
H_4SiO_4	Molybdenum blue colorimetry; autoanalyzer	USEPA 1983

Mass balances were constructed for all major solutes from April 8, 1990 to April 24, 1991. Calculations of lake/watershed mass balance were made from one spring turnover, when the pond water-column was well mixed, to the next in order to minimize year-to-year differences in lake storage. Chemical inputs, outputs and water-column pools were estimated by multiplying measured solute concentrations by appropriate flow rates or pond volumes. Fluxes of Na^+ and Cl^- were used to evaluate the accuracy of the hydrologic balance because these solutes are thought to be conservatively transported within the pond. Estimates of outputs of Na^+ and Cl^- were within 3% of inputs, supporting the accuracy of the hydrologic balance estimated for the study year.

Acid neutralizing capacity (ANC) budgets were constructed by summing net release and storage of ionic solutes which generate and consume ANC. These budgets were calculated for the watershed and the pond in order to characterize terrestrial and aquatic processes important in regulating the acid-base chemistry of drainage water and quantify rates of ANC production.

Speciation of Al was calculated from measured chemical parameters using the chemical equilibrium model ALCHEMI (Schecher and Driscoll 1994). ALCHEMI uses a Newton-Raphson method to calculate species distribution of Al, F, SO_4^{2-}, Si, DIC, and an organic acid analog. Temperature corrections were made with enthalpy values; ionic strength corrections were made with the Davies equation. A triprotic organic acid analog model for organic acid dissociation and formation of organic-Al complexes (Alo) was used to assess the speciation of Al. The binding constants and site density for this model were obtained from empirical calibration of an Adirondack data set (Driscoll et al. 1994; Schecher and Driscoll 1994). These constants are consistent with water chemistry data from the nearby Hubbard Brook Experimental Forest (HBEF) (Santore et al. 1994).

The solubility of monomeric Al in CPW solutions was expressed as a saturation index (SI) with reference to a mineral phase.

$$SI = log(Q_P/K_P) \tag{1}$$

where: Q_P is the ion activity product of the solution, and K_P is the thermodynamic equilibrium constant for a given mineral. Positive, negative, and zero SI values indicate that a solution is oversaturated, undersaturated, or in equilibrium, respectively, relative to the mineral of interest. For the present study, the relatively insoluble mineral, synthetic gibbsite ($Al(OH)_3$), was chosen as the reference ($pK_{so} = 8.1$; May et al. 1979). Dahlgren et al. (1989) showed that solutions in contact with mineral soil at the nearby HBEF exhibit solubilities similar to synthetic gibbsite. They hypothesized that Al was released from hydroxy-interlayer material associated with vermiculite with an Al solubility similar to synthetic gibbsite. Alternatively, solid phase organics with similar solubility to gibbsite might be controlling dissolution of Al (Mulder and Stein 1994).

Results and discussion

Temporal and spacial patterns in water chemistry

Ionic composition of CPW solutions was characterized as a dilute acidic solution in which atmospheric deposition of strong acids was partially neutralized by biogeochemical reactions occurring in the lake/watershed ecosystem. Total monomeric Al comprised 44% (volume weighted mean = 84 μeq/l) of the total cationic charge of inlet water, whereas the sum of basic cations (C_B = $Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}$) comprised about 34% (65 μeq/l) and 20% was

H^+ (39 μeq/l). Concentrations of NH_4^+ were very low (2 μeq/l) in drainage water. In comparison, the pond surface water had similar mean C_B concentrations of 69 μeq/l. However, C_B made up 45% of the cations in the pond due to lower concentrations of Al (56 μeq/l; 36%) and H^+ (25 μeq/l; 16%).

The mean SO_4^{2-} concentration was 71% of the total anionic equivalence of the inlet (134 μeq/l) versus 74% in the pond (111 μeq/l). Chloride comprised 10% in both the inlet and pond (17 μeq/l inlet; 14 μeq/l pond). Concentrations of NO_3^- were unusually low (<2 μeq/l) in both the inlet and pond. A mean anion deficit of 36 μeq/l (19%) in the inlet and 23 μeq/l (15%) in the pond surface waters was likely due to organic anions. The small anion deficit is consistent with the low pH values (i.e., protonation of organic anions) and low DOC concentrations (380 μM C inlet; 180 μM C pond surface).

Regression analysis between many solute concentrations and flow rate in the inlet and water table in the wetland were significant ($p < 0.05$), however there was much scatter in the data ($r \leq 0.54$) indicating that other biogeochemical processes were also important in regulating stream chemistry. Seasonal patterns in stream water included increases in H^+, Ali, Alo, and DOC, and a decrease in SO_4^{2-} during the summer. The June through October period outlined by these variations (Figure 2) coincides closely with the growing season in the forest. This pattern suggests a biologic rather than hydrologic component to the control of drainage water chemistry. Seasonal hydrologic patterns were less well defined. Within each season, there was great variation in both streamflow and water table (Figure 2b, c).

Charge (anion) deficit showed seasonal variation which closely coincided with changes in both Ali and Alo, as well as DOC concentration. During the period from June through October, the mean charge deficit of the inlet was 67 μeq/l compared to a mean charge deficit of 19 μeq/l during the rest of the study year. Variation in the supply of organic anions was likely responsible for the seasonality of charge deficit. Concentrations of DOC were correlated with H^+ ($r = 0.86$) suggesting that variations in organic solutes were an important factor controlling changes of the acid-base chemistry of drainage waters in the CPW over the annual cycle. Seasonal variation in Alo and DOC at CPW contrasts with the Adirondacks where no seasonal trend was evident (Driscoll and Van Dreason 1993).

Temporal variations in C_B concentrations in the inlet (Figure 2e) appear to be closely coupled with hydrologic processes. During major runoff periods (e.g., mid August, late December; Figure 2b) C_B decreased to low concentrations. In contrast, during dry periods (e.g., July, mid August through September) C_B gradually increased with the duration of the low flow period. This pattern suggests a change in flow paths, with shallow flow paths during

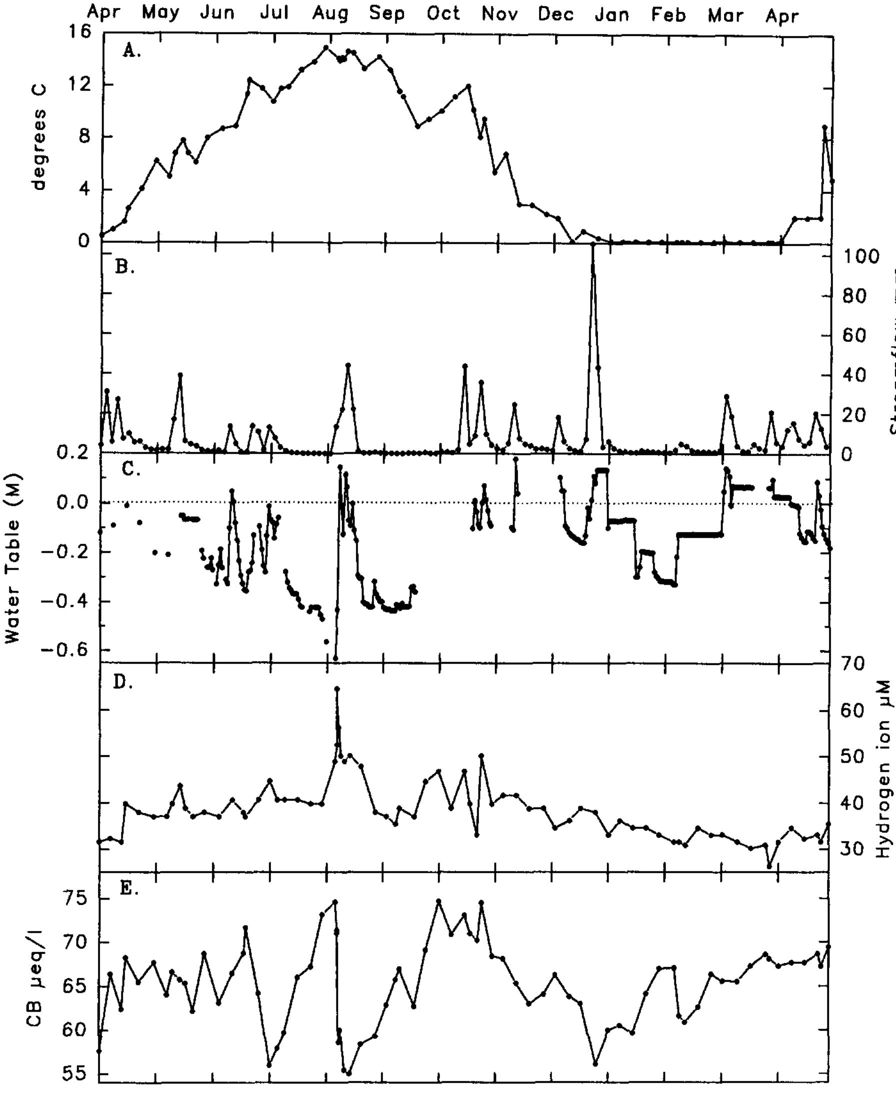
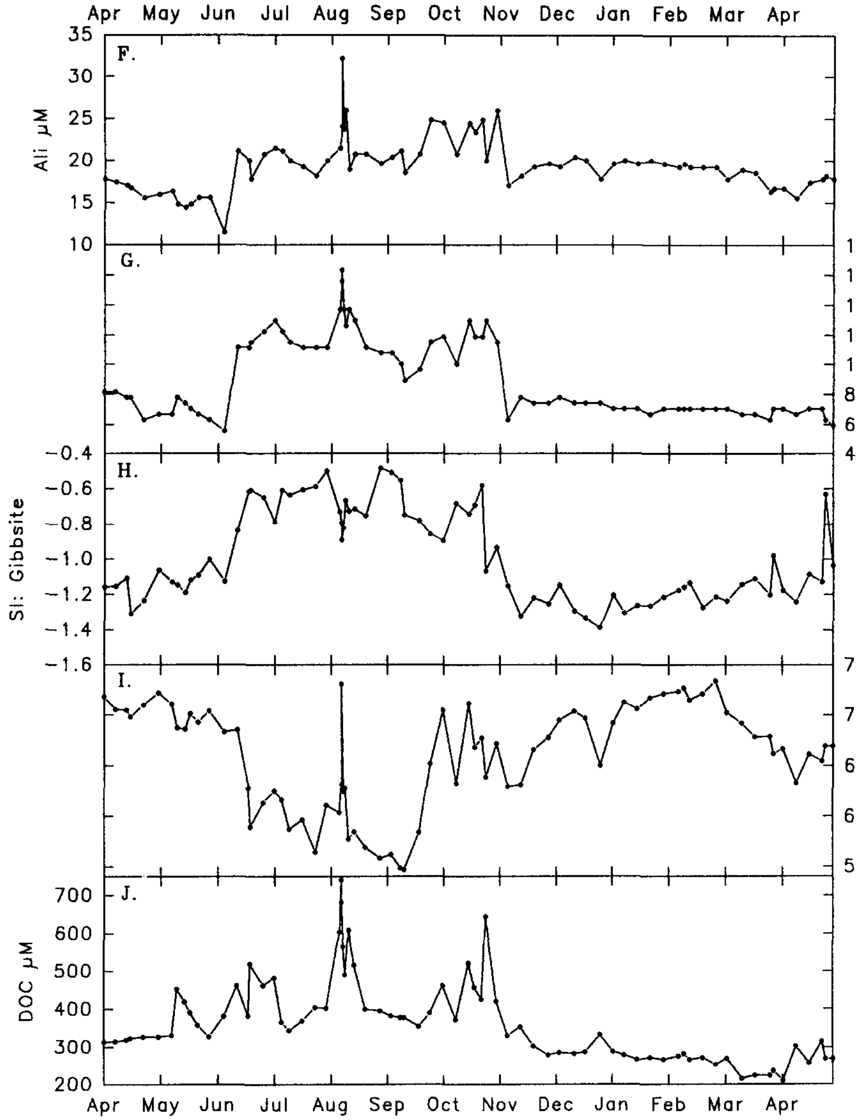


Fig. 2. Temporal variations in (a) water temperature, (b) streamflow, (c) water table in the wetland relative to the ground surface, (d) H^+, (e) C_B, (f) Ali, (g) Alo, (h) SI for synthetic gibbsite, (i) SO_4^{2-}, (j) DOC for the Cone Pond inlet.

wet periods resulting in drainage water characterized by low C_B concentrations (Chen et al. 1984). The wetland along the main inlet (Figure 1) may act as a reservoir for inflowing waters, gradually draining during dry periods (Figure 2c). When the water table in the wetland was substantially below the



ground surface, C_B concentrations increased (Figure 2c, 2e), perhaps reflecting a higher proportion of deeper flow path inputs to the stream channel.

Seasonal patterns in pond chemistry reflected conditions of thermal stratification from mid-June through mid-October and during ice-cover from December through the end of March (Figure 3). Anoxic conditions in the hypolimnion were accompanied by decreases in concentrations of H^+, SO_4^{2-},

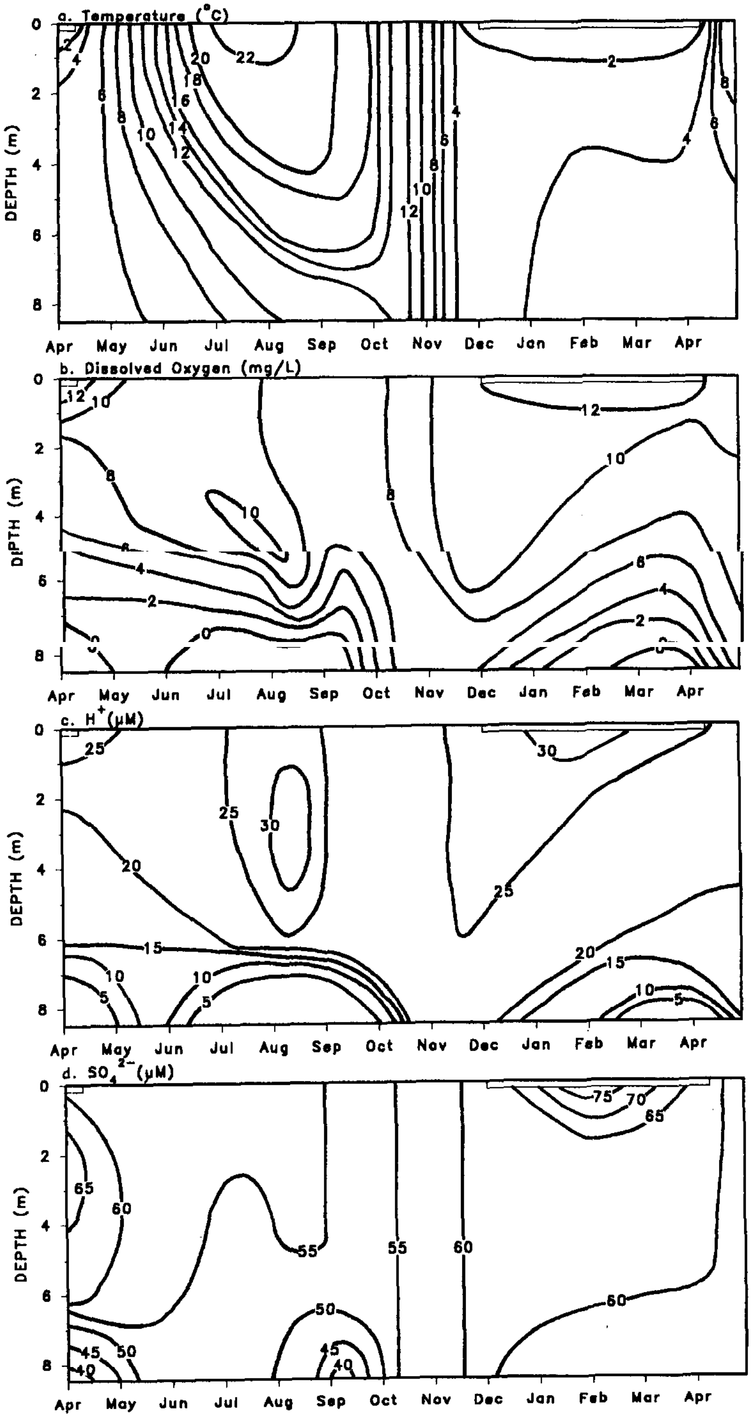
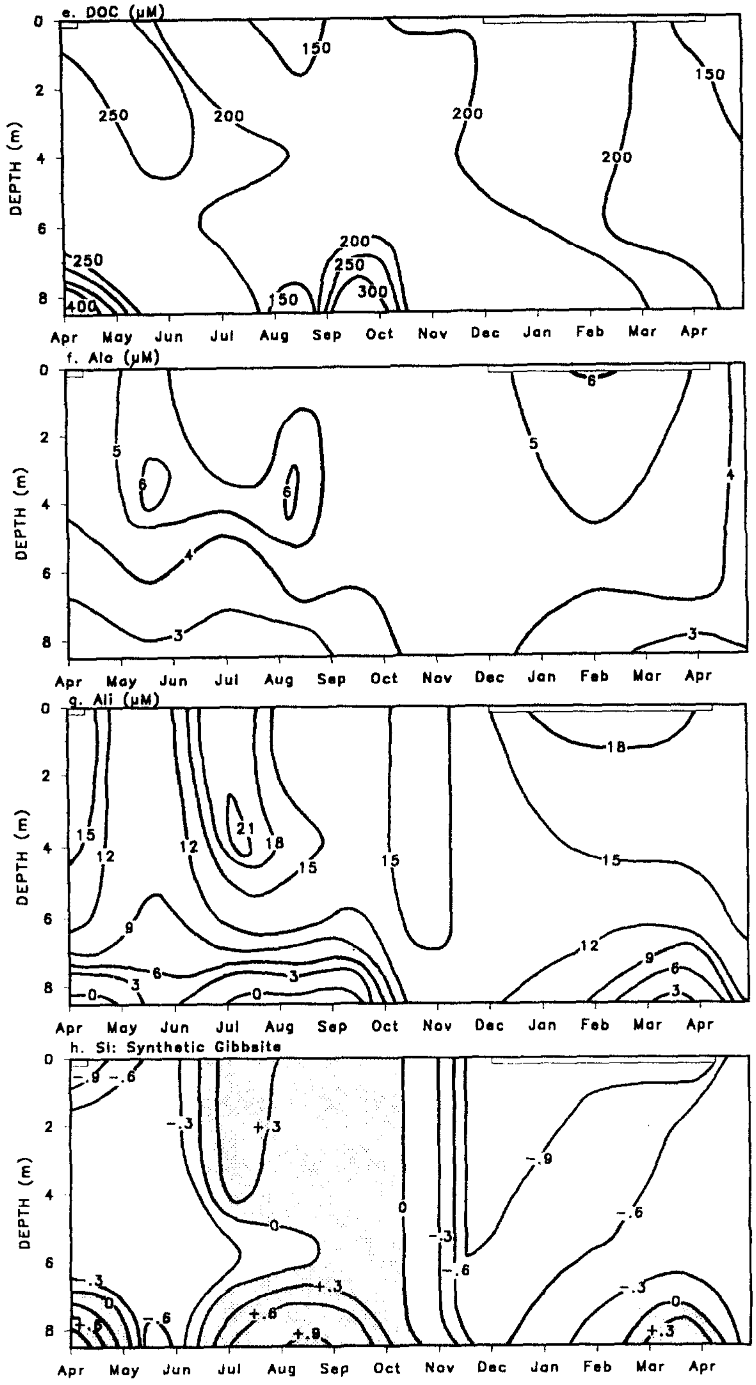


Fig. 3. Temporal and spatial variations in (a) temperature, (b) DO, (c) H^+, (d) SO_4^{2-}, (e) DOC, (f) Alo, (g) Ali, (h) SI for synthetic gibbsite for the Cone Pond water-column.


e. DOC (μM)
DEPTH (m)
0
2
4
6
8
150
150
250
200
200
200
250
400
200
250
300
150
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Jan
Feb
Mar
Apr
f. Ala (μM)
DEPTH (m)
6
5
6
6
5
4
4
3
3
g. Ali (μM)
DEPTH (m)
18
15
12
12
21
18
15
15
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9
12
9
6
6
3
3
0
0
3
h. SI: Synthetic Gibbsite
DEPTH (m)
−.9 −.6
−.3
+.3
−.9
0
0
−.6
−.3
−.3
−.6
−.3
+.3
−.3
0
+.6
−.6
+.6
+.9
0
+.3

Ali, and Alo. Whereas mean pH at the pond surface was 4.6, the average at 8 m depth was 5.0, with a maximum of 6.1 occurring during winter stratification. Peak SO_4^{2-} concentration of 76 μM occurred just under the ice during snowmelt runoff, while minimum concentrations (41 μM) were evident in the hypolimnion during winter and summer stratification.

Concentrations of DOC in the water-column were highest during ice cover (Figure 3e) with high concentrations immediately under ice, decreasing to a minimum value at mid-depth, and increasing toward the sediment-water interface. Variations of both Ali and Alo closely coincided with changes in H^+ (Figure 3). Water-column concentrations were highest during the winter and spring, and low during the summer. During both winter and summer stratification, concentrations of Al decreased with pond depth (Figure 3f, 3g).

Aluminum chemistry

In as much as Al was an important solute in CPW waters, information on Al transport gained through speciation modeling is important for understanding acid/base chemistry in this system. Chemical equilibrium calculations revealed that Al^{3+} was the dominant species of Al (~40%) in the inlet stream (Table 2). About 25% of the Al was bound by organic ligands whereas 20% was complexed with F and 10% was complexed with Si. The remaining 5% was complexed with SO_4^{2-} or OH^- ligands. Variation in the proportions of Al species was much less than the variation in total monomeric Al concentrations over the study period. Concentrations of fluoride complexed Al (F-Al) were fairly constant because of invariant concentrations of total F, at about 5 μM; F^- is one of the strongest complexing ligands for Al. As concentrations of DOC were elevated during the growing season, the proportion of Alo to total monomeric Al was also greater. The pond did not show one dominant species of Al, instead Al^{3+}, F-Al and Alo abundance varied with depth and time of year.

Comparison of modeled and measured Alo using a triprotic organic analog model calibrated for the Adirondack region showed that the model underpredicted values of Alo (Figure 4a). This discrepancy suggests that the site density of organic solutes at CPW is greater than values reported in the literature, which have been largely DOC originating from deciduous forests (0.043 mol sites/mol C; Schecher and Driscoll, 1994). The coniferous forest at CPW may generate DOC with a different site density than reported for deciduous regions. By increasing the site density from 0.043 mol sites/mol C to 0.073 mol sites/mol C, good agreement between modeled and measured values of Alo was obtained (Figure 4b).

Table 2. Mean measured and modeled concentrations of aluminum species. Standard deviation is shown in parentheses.

Species	Inlet			Pond surface		
	μM		%	μM		%
Measured						
Total Al	28.6	(5.5)	100	18.5	(5.2)	100
Alo	9.1	(2.7)	32	4.3	(1.1)	23
Ali*	19.4	(3.2)	68	14.2	(4.3)	77
Modeled						
Al^{3+}	11.8	(2.7)	41	6.7	(2.4)	36
$AlOH^{2+}$	0.8	(0.3)	3	1.1	(0.8)	6
F-Al	5.1	(0.0)	18	5.0	(0.2)	27
Si-Al	3.5	(1.0)	12	1.8	(1.0)	10
S-Al	0.5	(0.2)	2	0.3	(0.1)	2
Alo	6.7	(1.9)	23	3.4	(1.4)	18
Total	28.4		99	18.3		99

*Computed by difference

In the Adirondack region, concentrations of Al peak during spring snowmelt; seasonal variations in Al concentration are closely coupled with changes in NO_3^- (Schafran and Driscoll, 1987; Driscoll and Van Dreason 1993). In contrast, at CPW highest concentrations of both Ali and Alo occurred during summer. Seasonal changes in Al concentration were not linked to NO_3^- as NO_3^- concentrations were below the analytical detection limit. Changes in concentrations of SO_4^{2-} also did not appear to control seasonal variations in Al chemistry as there was actually an inverse correlation between SO_4^{2-} and Alo ($p < 0.05$; $r = -0.50$). However during a midsummer runoff event, both SO_4^{2-} and Al showed marked increases (Figure 2) when the water table in the wetland increased from its lowest levels.

Dissolved organic carbon was the only solute related to streamwater Al concentration ($r = 0.87$ for Alo; $r = 0.52$ for Ali, $p < 0.05$). Despite relatively low DOC concentrations (volume-weighted mean 380 μM C), this pattern suggests that availability of organic solutes could be regulating concentrations of Al at CPW. McAvoy (1988) also reported a relationship between DOC and Al at a stream draining a wetland area at Bickford Reservoir watershed in

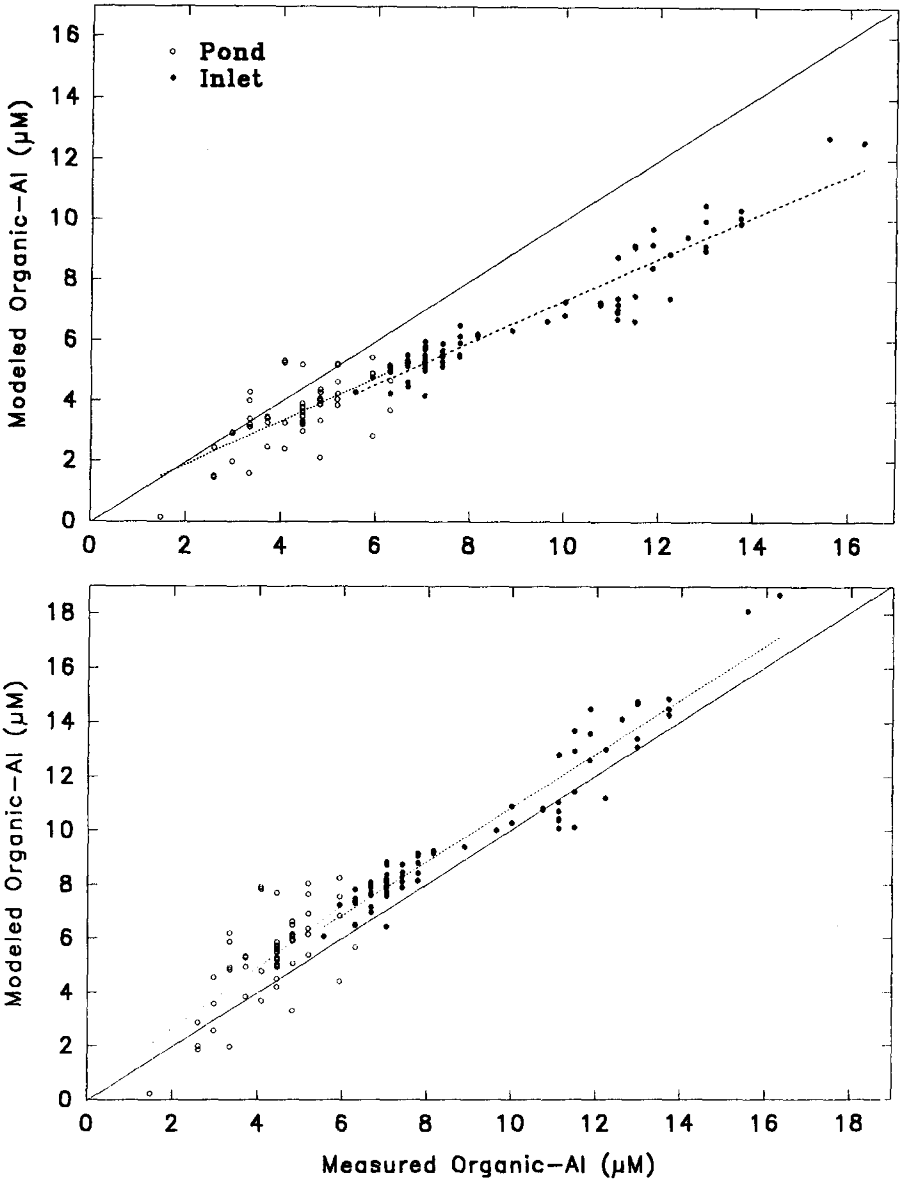

Fig. 4. Comparison of modeled and measured Alo for (a) calibration to the Adirondack data set (DOC site density = 0.043 mol sites/mol C), and (b) best fit for the Cone Pond data (DOC site density = 0.073 mol sites/mol C).

Massachusetts. Mulder and Stein (1994) show that solubility of Al in strongly acidified forest soils may be controlled by complexation with solid phase organics.

The SI of solutions with respect to the solubility of synthetic gibbsite in CPW drainage waters showed a distinct seasonal trend, approaching zero (saturation) during June through October (Figure 2). Dahlgren et al. (1989) found that Al in leachates from mineral horizons in northeastern Spodosols approached equilibrium with respect to synthetic gibbsite. Undersaturation was typical when a significant portion of stream drainage was derived from organic soil horizons. Activity of Al^{3+} was possibly controlled by humic adsorption/exchange, suggesting the importance of flow paths dominated by soil organic horizons during the dormant season.

In Cone Pond, the SI with respect to the solubility of synthetic gibbsite was positive in the hypolimnion in early spring and throughout the water-column in June through October, indicating conditions of oversaturation (Figure 3h). The increase in pH due to reduction of SO_4^{2-} in the hypolimnion, resulted in sharp decreases in the solubility of Al. This pattern explains the positive SI values noted in the hypolimnion during stratification, and provides a mechanism for Al retention in Cone Pond. Through a comparison of trends in SI and Al retention (below), other possible mechanisms are suggested.

Mass balances

Comparison of element inputs and outputs from both the watershed and the pond revealed pronounced chemical changes during transport of drainage waters through each of these systems (Table 3). Bulk precipitation inputs to the watershed were dominated by H^+ (68% of cation inputs), whereas SO_4^{2-} was 60% of the anions on an equivalent basis. Cationic output from the watershed was dominated by Al, with lesser amounts of H^+ and C_B. Release of Al from the watershed was accompanied by the consumption of 46% of incoming H^+. Essentially all NO_3^- and 89% of NH_4^+ atmospheric inputs were retained in the watershed.

Streamwater outputs of Cl^- and SO_4^{2-} were nearly twice inputs in bulk precipitation. This apparent source of Cl^- and SO_4^{2-} is partially due to unmeasured atmospheric inputs via dry deposition. Although direct measurement of dry inputs is difficult, throughfall fluxes can be used as an approximation of total atmospheric inputs of Cl^- and SO_4^{2-}, if one assumes no canopy exchange. Considering throughfall fluxes of Cl^- and SO_4^{2-} as a measure of total atmospheric inputs during the summer period, the annual Cl^- output from the watershed was within 1% of the input. In contrast, the output of SO_4^{2-} was 60% greater than the input. This discrepancy in SO_4^{2-} flux may indicate desorption of soil-bound SO_4^{2-} that was deposited during a period of higher atmospheric inputs. Atmospheric SO_4^{2-} deposition in the CPW region follows a decreasing trend (Likens et al 1990). Dahlgren et al. (1990)

Table 3. Cone Pond chemical fluxes (keq), April 8, 1990–April 24, 1991. Calculated retention coefficients for the watershed (Rw) and the pond (Rp) are *R* = In-Out/In.

Parameter	Watershed input	Watershed output	Rw	Pond input	Pond output	Rp
C_B	7.43	30.2	−3.1	30.6	34.2	−0.12
H^+	34.0	18.2	0.46	20.3	12.2	0.40
Total Al	0	39.1	∞	39.1	28.2	0.28
Ali	0	26.5	∞	26.5	21.5	0.19
Alo	0	12.6	∞	12.6	6.7	0.47
NH_4^+	8.63	0.94	0.89	1.45	0.93	0.36
Fe	0	1.33	∞	1.33	1.17	0.12
SO_4^{2-}	38.3	62.6	−0.63	64.3	57.7	0.10
NO_3^-	16.8	0	1.0	1.00	0.30	0.70
Cl^-	7.97	7.88	0.01	8.00	8.20	−0.02
Σ Cation	50.1	89.8	−0.79	92.8	76.7	0.17
Σ Anion	63.1	70.5	−0.12	73.3	66.2	0.10
DOC*	43.8	177	−3.0	180	86.4	0.52
H_4SiO_4*	0	33.0	∞	33.0	24.1	0.27

*DOC and H_4SiO_4 in kmol

found that following reduction in SO_4^{2-} loading there was a net release of SO_4^{2-} from soil adsorption sites.

The total input of solutes to the pond was nearly identical to watershed output (Table 3), as the large watershed-to-pond area ratio of 16.8 diminished the importance of direct atmospheric input to the pond. However, due to nearly complete retention of NO_3^- by the watershed, the only inputs of this solute to the pond were supplied from direct precipitation. In contrast to the watershed, the pond strongly retained Al, SO_4^{2-} and DOC.

Of the 39 keq Al released from the watershed during the study period, 28% was subsequently retained by the pond (Figure 5). This pattern has been reported by LaZerte (1986) for lake/watershed systems in Ontario. Surprisingly, inputs of Ali to the pond were considerably more conservative (19% retention) than inputs of Alo (47% retention; Table 3). The high retention of Alo coincided with a retention of 52% of DOC inputs to the pond. This removal was especially pronounced during the summer, when the entire water-column was oversaturated with respect to the solubility of synthetic gibbsite. During spring in 1990 and 1991 there were brief periods of net release of total monomeric Al from the pond due to large decreases in pond storage, as stage fell from high spring to low summer levels (Figure 5).

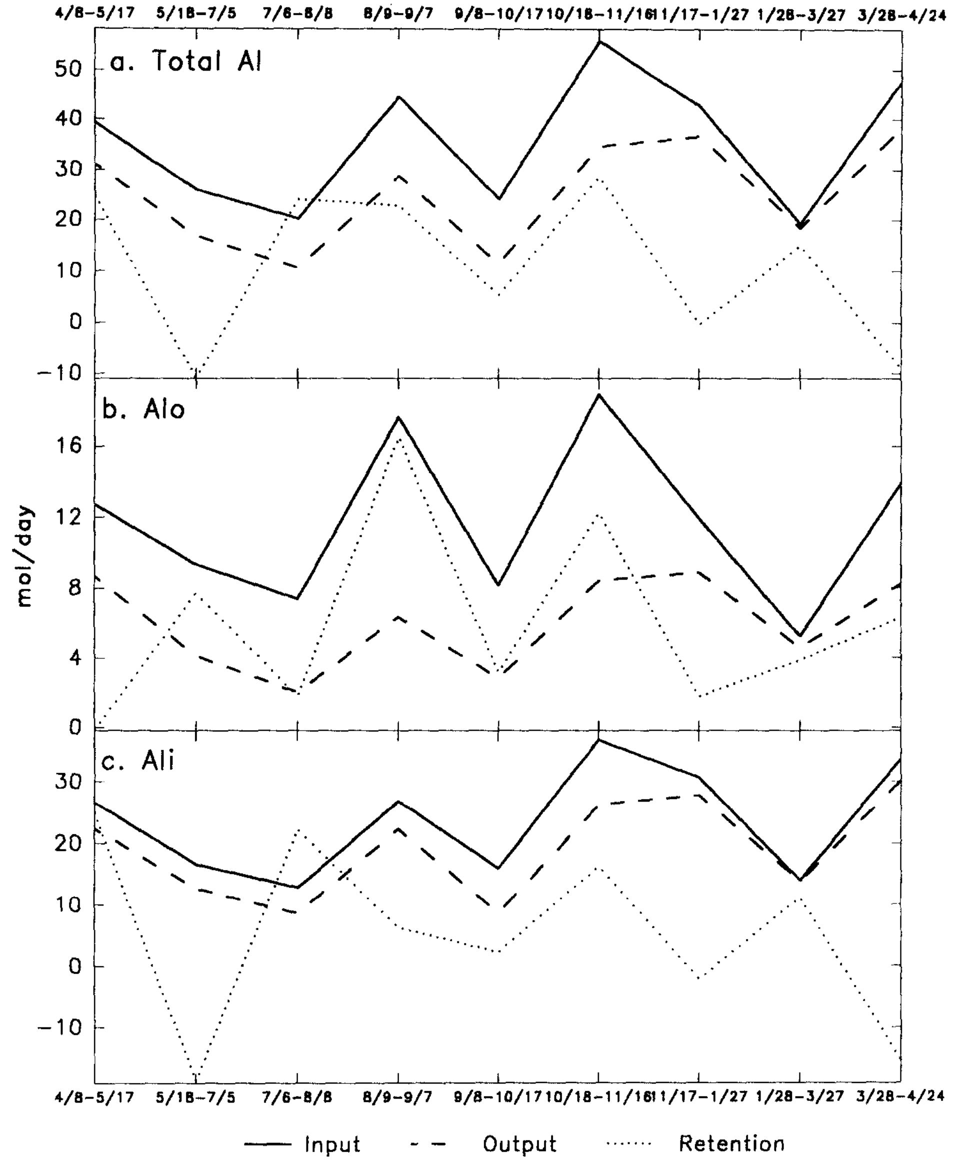

Fig. 5. Input, output, and retention of (a) total monomeric Al, (b) Alo, (c) Ali in Cone Pond.

There are several potential mechanisms of Al loss in lake ecosystems. Organic monomeric Al can be removed from the water-column in association with deposition of DOC, possibly through coagulation. Alternatively, DOC may be oxidized releasing Al in an inorganic form. Loss of Ali from the lake may occur following hydrolysis and/or adsorption to particle surfaces. The molar ratios of DOC:Alo in the inlet and outlet of Cone Pond were similar (42 and 39, respectively) suggesting stoichiometric coprecipitation of DOC and Alo.

By comparison, at Dart's Lake, conditions of oversaturation with respect to the solubility of gibbsite were evident during low flow periods. In contrast to Cone Pond, an increase in water-column pH was attributed to depletion of NO_3^- in the epilimnion by biological assimilation (Driscoll and Schafran 1987).

ANC budgets

Net effects of biogeochemical processes on the acid-base status of the lake/watershed system were integrated and synthesized by developing ANC budgets, both as total values (eq/yr) and values normalized to landscape surface area (eq/ha-yr; Figure 6). Because of its larger size, the watershed showed greater total equivalents consumed and released than the pond. However, the aerial rate of ANC production was considerably larger for the pond (3.5 keq/ha-yr) than the watershed (1.5 keq/ha-yr). Processes generating ANC in the watershed were 2.5 times greater than those consuming ANC, resulting in net production of 45 keq/yr ANC. Aluminum release from soil accounted for 50% of the ANC generated by the watershed. Release of SO_4^{2-}, presumably associated with desorption of SO_4^{2-} from soil, accounted for 76% of the ANC consumed by the watershed.

In contrast, the pond showed a near balance between ANC production and consumption, with a slight net consumption of 180 eq/ha-yr ANC. The close balance of the Cone Pond ANC budget contrasts with other low ionic strength lakes in the Adirondacks and Canada which are large sources of ANC. Schindler et al. (1986) found that a low ANC lake in the Canadian shield, receiving low inputs of acidic deposition, generated an average 1880 eq/ha-yr ANC. Despite the in-lake difference, the rate of ANC generated in the terrestrial portion of CPW of 830 eq/ha-yr was greater than the rate reported by Schindler et al. (1986) for the terrestrial portion of the shield watershed (420 eq/ha-yr).

Under acidic conditions, dissolution/hydrolysis of Al is a strong pH buffer (Driscoll and Bisogni 1984). The acid/base status of Cone Pond is closely regulated by the dissolution of Al in the watershed and retention of Al in the pond. The potential net production of ANC in the pond through SO_4^{2-} reduction and C_B exchange was balanced by Al hydrolysis, resulting in no net production of positive ANC.

At Cone Pond, 61% of ANC generated was by SO_4 reduction, 33% was from exchange of base cations from the sediments, and only 6% was from reduction of NO_3. Aluminum retention accounted for 95% of the ANC con-

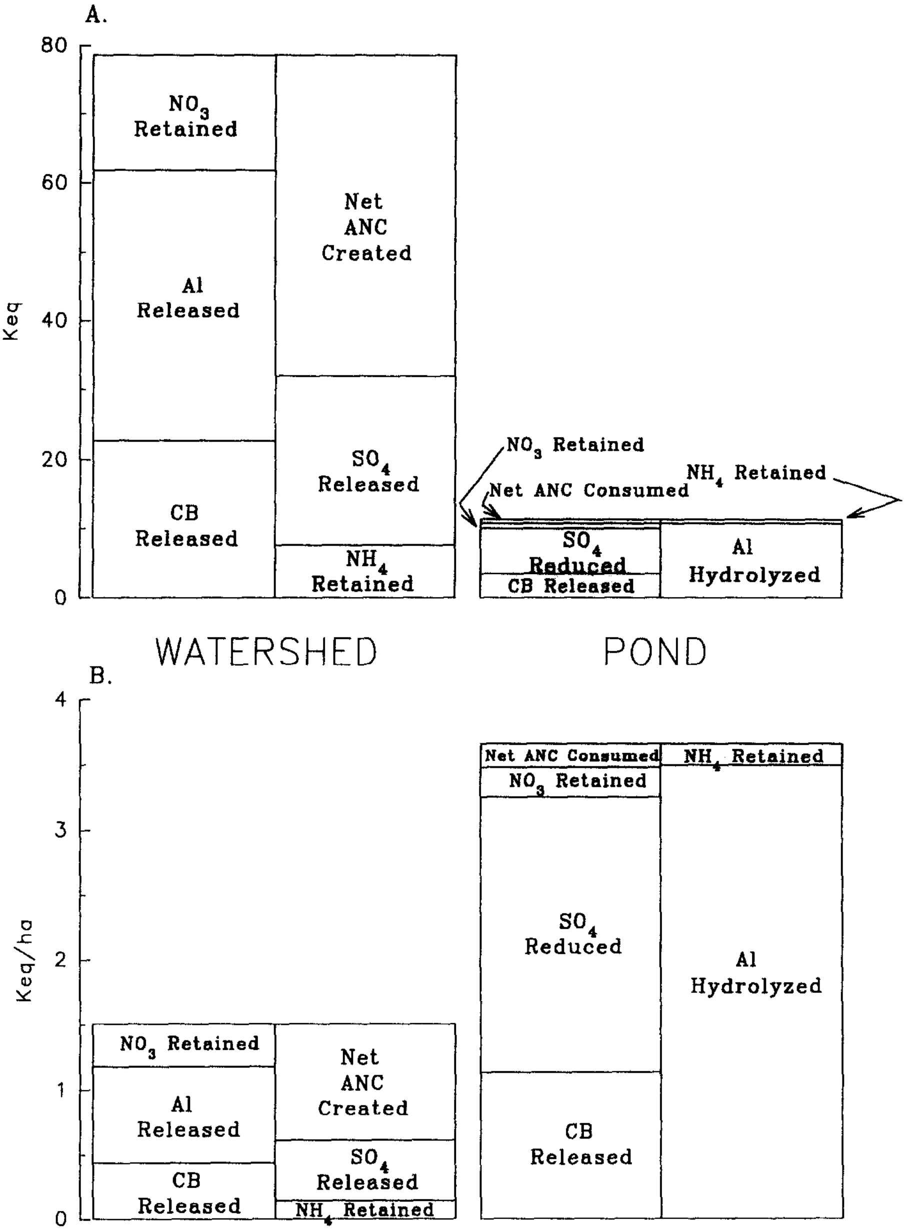

Fig. 6. Comparison of net generation and consumption of ANC for the Cone Pond Watershed and Cone Pond on (a) a total basis and (b) a unit area basis. Rates measured for the 381 day study period were pro-rated to a per-year basis.

sumed. Major processes generating ANC in the shield lake were reduction of SO_4^{2-} (53%), exchange of H^+ for Ca^{2+} in sediments (39%) and reduction of NO_3^- (26%; Schindler et al. 1986). In an experimentally acidified lake, Cook et al. (1986) found that 66 to 81% of sulfuric acid added was neutralized by ANC production in the lake. Nearly 85% of the ANC generated was through SO_4^{2-} reduced by bacterial activity coupled with iron sulfide formation.

At Dart's Lake, reduction of NO_3^- in the hypolimnion during stratification was a major process consuming H^+, and was accompanied by a decrease in Ali (Schafran and Driscoll 1987). Changes in base neutralizing capacity (BNC) were correlated with NO_3, but not SO_4^{2-}, Cl^-, C_B, or DOC. Generation of ANC in the terrestrial portion of Dart's Lake (1204 eq/ha-yr) was similar to CPW, however the in-lake ANC generation was much greater (2990 eq/ha-yr) than reported here.

Summary

High loading of H^+ and SO_4^{2-} coupled with elevated leaching of SO_4^{2-} and low rates of C_B supply from CPW resulted in acidic conditions and elevated concentrations of Al in drainage waters. Despite relatively low concentrations of DOC, naturally occurring organic anions were important in regulating seasonal variability in pH, and Al concentration and speciation in surface waters.

Much of the Al released by the watershed was subsequently retained by the pond. Retention largely occurred through two mechanisms. First, SO_4^{2-} reduction in the hypolimnion during stratification resulted in increases in pH and hydrolysis of Al. Retention of DOC by the pond through coagulation or metabolism resulted in decreased ligand availability and loss of Al throughout the water-column, particularly during the warmer months.

Biogeochemical processes within CPW, largely through release of C_B and Al, resulted in net production of ANC. Unlike many low-ionic strength lakes, Cone Pond did not show net production of ANC. Potential production of ANC through SO_4^{2-} retention and C_B exchange was completely offset by acidity produced through hydrolysis of Al. The contrast between the chemistry of Cone Pond and its inlet waters suggests an ongoing mechanism of clarification as DOC and Al exported from the watershed are retained in the pond. This may be an expression of long-term historical changes that the pond underwent as Al export from the watershed was enhanced by increased inputs of atmospheric acids.

If reduced air pollution emissions result in a decrease in Al transport from the watershed, Cone Pond may begin to generate ANC at rates comparable to other northeastern lakes. Reductions in SO_4^{2-} deposition and streamwater output, and slight increases in streamwater ANC have been reported for some surface waters in the northeast with higher C_B and lower Al concentrations than CPW (Stoddard and Kellogg 1993; Kahl et al. 1993). Longer-term monitoring of CPW is needed to reveal any temporal changes in surface water chemistry which may result from changes in the atmospheric environment.

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