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Spatial and temporal variations in aluminum chemistry of a dilute, acidic lake

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Abstract. Elevated concentrations of Al have been observed in acidic surface waters. An assessment of the chemistry of aqueous Al is of interest because of its role as a toxicant to aquatic organisms, a pH buffer, and an adsorbent of orthophosphate and organic carbon. In this investigation we evaluated the spatial and temporal fluctuations of Al forms in an acidic drainage lake.

High concentrations of NO_3^- ($51.0 \pm 11\,\mu mol\,l^{-1}$), H^+ ($14.9 \pm 3.5\,\mu mol\,l^{-1}$), and Al ($19.6 \pm 3.5\,\mu mol\,l^{-1}$) were introduced to Dart's Lake through drainage water during the snowmelt period. During low flow periods microbially mediated depletions of nitrate served to neutralize H^+ and aluminum base neutralizing capacity. Thus in Dart's Lake, NO_3^- transformations were extremely important in regulating short-term changes in pH and subsequent changes in the inorganic forms of Al. During stratification periods Al appeared to be non-conservative within the lake system. Although we know very little about the character and transformations of alumino-organic solutes, these substances were correlated with dissolved organic carbon (DOC) concentrations. Alumino-organic substances appear to be introduced to the lake from both drainage water and sediments.

Introduction

Atmospheric deposition of acidic substances appears to influence element cycling in "acid-sensitive" ecosystems (Braekke, 1976; Hutchinson and Havas, 1980). For example, Cronan and Schofield (1979) have hypothesized that acidic deposition alters Spodosol development. Rather than being retained in soils, Al dissolves following strong acid inputs and is transported to the aquatic environment. From synoptic surveys of acidic waters, many investigators have observed the exponential increase in Al concentration with decreasing pH that is characteristic of the theoretical solubility of Al minerals (Hutchinson et al., 1978, Dickson, 1978; Wright and Snekvik, 1978; Hultberg and Johansson, 1981; Vangenechten and Vanderborght, 1980). Johnson et al., (1981) and Driscoll et al., (1984) have investigated the chemistry of Al in acidic surface waters of the Hubbard Brook Experimental Forest (HBEF) in New Hampshire and the Adirondack region of New York, respectively. They observed that organic and fluoride complexes were the most significant forms of aqueous Al and provided evidence to suggest that aquo (free) Al activity in these waters was regulated by the solubility of aluminum trihydroxide ($Al(OH)_3$). These investigators also noted that alumino-organic complexes were strongly correlated with organic carbon concentration.

Elevated concentrations of aqueous Al are significant to aquatic ecosystems for several reasons.

1) Aluminum may be deleterious to fish (Driscoll et al., 1980; Schofield and Trojnar, 1980) and other aquatic organisms (Havas and Hutchinson, 1982; Hall et al., 1985) in low ionic strength waters. Speciation and toxicity are significantly influenced by complexation with inorganic (hydroxide, fluoride, and sulfate) and organic ligands (Driscoll et al., 1980; Baker and Schofield, 1982).
2) Aluminum is a hydrolyzing metal and will, therefore, influence the pH buffering of acidic waters (Dickson, 1978; Johannesson, 1980; Henriksen and Seip, 1980; Driscoll and Bisogni, 1984).
3) Hydrous aluminum oxides, formed by the precipitation of Al, may serve as an adsorbent and scavenge substances from the water column. Through adsorption/precipitation reactions Al may alter the cycling of solutes such as orthophosphate (Dickson, 1978), trace metals (Hohl and Stumm, 1976), and dissolved organic carbon (Dickson, 1978; Davis, 1982) in acidic lake ecosystems.

While considerable information is available through synoptic surveys on total Al concentrations in acidic surface waters, much less information is available on temporal and spatial variations of Al in surface waters. Reported here are results from a study on short-term variations in Al chemistry of an acidic drainage lake in the Adirondack region of New York State.

Material and methods

Study site and field program

The study site, Dart's Lake (43 °47′N, 74 °51′W) is located in the drainage basin that forms the North Branch of the Moose River, in the Adirondack region of New York State. The watershed (107 km^2) is forested except in regions of exposed bedrock. The major vegetation is secondary growth hardwoods. Bedrock geology is characteristically crystalline granitic gneiss and the surficial geology is predominated by thin till (< 3 m) with minor deposits of thick till (> 3 m) (Newton et al., 1987).

Dart's Lake has a surface area of 0.58 km^2, a major inlet, and one outlet. Our hydrologic data indicate that $> 95\%$ of the water leaving the lake outlet enters through the lake inlet. The lake bathymetry is characterized by two significant depressions both reaching a maximum depth of 15 m. The mean depth of the lake is 7.1 m.

In our study, samples were collected for water quality analysis approximately every 2–3 weeks from 25 October 1981 to 21 November 1982.

Sampling sites included the lake inlet, outlet, and a pelagic sampling station. Water column samples were collected at the surface, 2, 4, 6, 9, 12, and 14 m depths with a battery operated submersible pump. Temperature was measured in-situ with a thermistor. We measured pH, ampulated samples for DOC determination and extracted samples for monomeric Al shortly after collection.

While it is reasonably well established that pH and DOC are prone to change after sample collection, we feel that it is important to emphasize that monomeric Al concentration may also significantly change during sample storage. Natural solutions, which are generally oversaturated with respect to the solubility of atmospheric CO_2, will increase in solution pH and decrease in monomeric Al concentrations due to CO_2 degassing. Also, as Al transformations are very temperature sensitive, shifts in monomeric Al speciation may occur from temperature changes following sample collection. We have observed 10–20% changes in monomeric Al concentrations within 6 hours of sample collection. To reduce these potential errors in measurement we extracted samples for monomeric Al as shortly after collection as possible (< 2 hrs).

Analytical methods

Samples were measured for pH potentiometrically by glass electrode. We used a fluoride ion selective electrode to measure free and total fluoride. Free fluoride was determined by direct measurement, while total fluoride was analyzed using a total ionic strength adjustor and buffer (TISAB II; Orion, 1976). Dissolved organic carbon (DOC) was measured using persulfate oxidation (Menzel and Vaccaro, 1964) followed by syringe stripping of CO_2 (Stainton, 1973). A gas partitioner was used to detect the CO_2. Sulfate and NO_3^- were determined colorimetrically using the methylthymol blue (Lazrus et al., 1968) and hydrazine reduction (Kamphke et al., 1967) methods, respectively, on an autoanalyzer.

In our study two separate measurements of Al were made. Monomeric Al was determined by complexation with 8-hydroxyquinoline of an untreated aliquot of sample followed by extraction in methyl isobutyl ketone (Barnes, 1975). Extractions were completed in the field with the extract transferred to a separate vile following extraction. Detection of Al was made colorimetrically at a wavelength of 395 nm.

Monomeric Al was separated into two fractions by passing a subsample through a column of strongly acidic cation exchange resin. We term the Al that passes through the column and is then extracted and detected using the procedure for monomeric Al, non-labile monomeric Al. With these two measurements, two Al fractions were determined. Non-labile monomeric Al was measured directly and is an estimate of monomeric Al that is organically complexed. Labile monomeric Al is the difference between monomeric Al and non-labile monomeric Al. This fraction is thought to

Table 1. Forms of labile monomeric aluminum and base neutralizing capacity.

Aquo aluminum	$Al^{3+} = [Al^{3+}]$
Hydroxide-bound aluminum	$Al\text{–}OH = [Al(OH)^{2+}] + [Al(OH)_2^+] + [Al(OH)_4^-]$
Fluoride-bound aluminum	$Al\text{–}F = [AlF^{2+}] + [AlF_2^+] + [AlF_3] + [AlF_4^-] + [AlF_5^{2-}] + [AlF_6^{3-}]$
Sulfate-bound aluminum	$Al\text{–}SO_4 = [AlSO_4^+] + [Al(SO_4)_2^-]$
Aluminum base neutralizing capacity	$Al\text{–}BNC = 3[Al^{3+}] + 2[Al(OH)^{2+}] + [Al(OH)_2^+] + 3[Al\text{-}F] + 3[Al\text{-}SO_4] - [Al(OH)_4^-]$
Hydrogen ion and aluminum base neutralizing capacity	$H\text{–}Al\text{–}BNC = Al\text{–}BNC + [H^+] - [OH^-]$

be an estimate of inorganic monomeric Al and would include aquo Al as well as OH^-, F^-, and SO_4^{2-} complexes of monomeric Al, Further details on the fractionation procedure used for the determination of aqueous Al are available elsewhere (Driscoll, 1984).

Thermodynamic calculations for this study were made using a modified version of the chemical equilbrium model MINEQL (Westall et al., 1976). Thermochemical data of Al equilibria used in our calculations are summarized elsewhere (Driscoll et al., 1984). Thermodynamic calculations were corrected for temperature. Ionic strength corrections were made using the Davies equation (Stumm and Morgan, 1981).

To evaluate the distribution of labile monomeric Al we calculated various fractions of Al (Table 1). We define hydrogen ion and aluminum base neutralizing capacity (H-Al-BNC) as the amount of strong base required to increase the pH of an Al solution to 8.3.

To assess the potential for equilibrium with mineral phases we computed mineral saturation indices (SI) for Dart's Lake solutions.

$$SI = \log IAP/K$$

where: SI is the saturation index for a mineral phase of interest,
IAP is the ion activity product of the solution, and
K is the thermodynamic equilibrium constant for the mineral phase of interest

Positive, negative, and zero SI values suggest that a solution is oversaturated, undersaturated, or in equilibrium, respectively, with the mineral phase of interest. While it is possible to use any number of minerals for this analysis, past research by Johnson et al., (1981) and Driscoll et al., (1984) suggest that apparent Al solubility closely follows the theoretical solubility of $Al(OH)_3$. We have chosen to use the relatively soluble phase, microcrystalline gibbsite ($pK_{so} = 9.35$; Hem and Roberson, 1967) as a reference mineral in our SI calculations.

Results and discussion

Processes regulating concentrations of labile monomeric Al in Dart's Lake

Pronounced spatial and temporal variations in labile monomeric Al, pH, and NO_3^- concentrations occurred in Dart's Lake (Figure 1). Elevated concentrations of NO_3^-, H^+, and labile monomeric Al were present in the inlet stream during spring snowmelt (Figure 2) and these inputs strongly influenced lake chemistry during this period. The summer was marked by increases in pH which resulted in decreased Al solubility. Nitrate depletions in the epilimnion were likely the result of biological assimilation which ultimately consumed H-Al-BNC. Decreases in labile monomeric Al in the lower waters during winter and summer stratification were also consistent with increases in pH. Decreases in NO_3^- concentrations suggest sediment microbial processes were responsible for hypolimnetic NO_3^- depletions. The reduction of NO_3^- has been determined to be the major H^+ consuming process in the hypolimnion of Dart's Lake (GC Schafran, unpubl. data), thus processes involving its transformation indirectly influence the solubility of Al. Changes in the H-Al-BNC for the whole lake were strongly correlated to variations in NO_3^- concentration (Driscoll and Schafran, 1984) while no statistically significant relationship was observed between H-Al-BNC and SO_4^{2-}, Cl, basic cations, or DOC. This relationship suggests that microbial processes that utilize NO_3^- strongly influence Al solubility. Further evidence of the importance of microbial NO_3^- utilization in Dart's Lake has been reported by Rudd et al. (in press). In epilimnetic sediment core experiments they attributed sediment H^+ consumption of Dart's Lake water predominately to NO_3^- reduction at the sediment-water interface.

Distribution of inorganic aluminum in Dart's Lake

Within the lake system, labile monomeric Al was distributed among a number of inorganic forms. The mean values of various Al forms as well as the relative distribution of monomeric Al are summarized in Table 2. The concentrations and relative distribution of Al observed for Dart's Lake were similar to values reported by Johnson et al., (1981) for the HBEF and Driscoll et al., (1984) for Adirondack surface waters.

Since fluoride is a significant Al complexing ligand in Adirondack

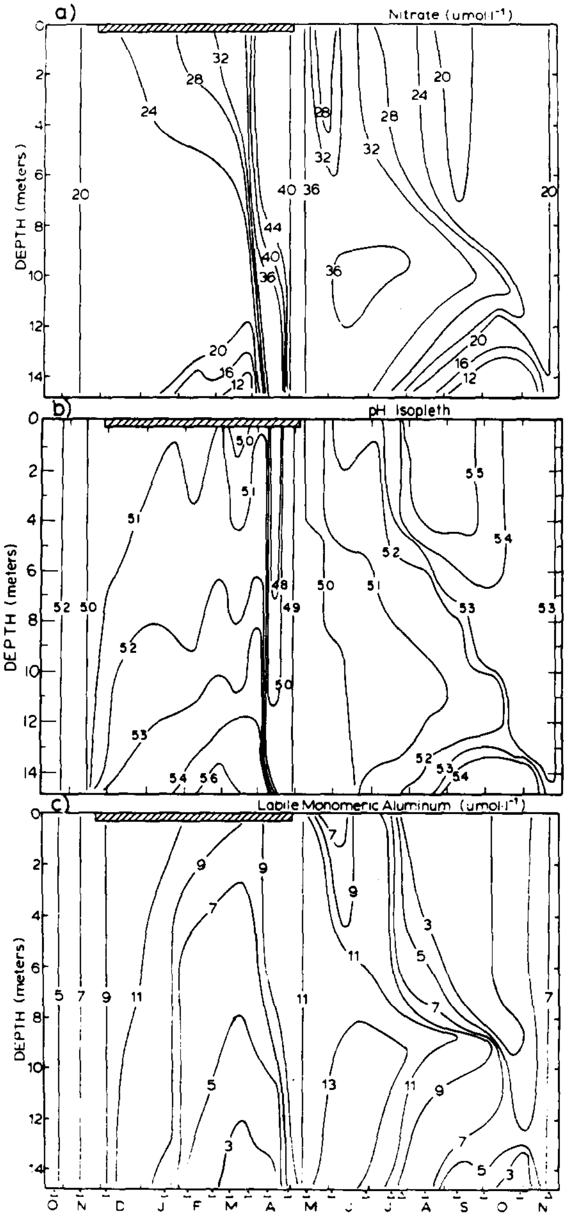

Figure 1. Temporal and spatial variations in (a) nitrate, (b) pH values, and (c) labile monomeric aluminum within the Dart's Lake water column.

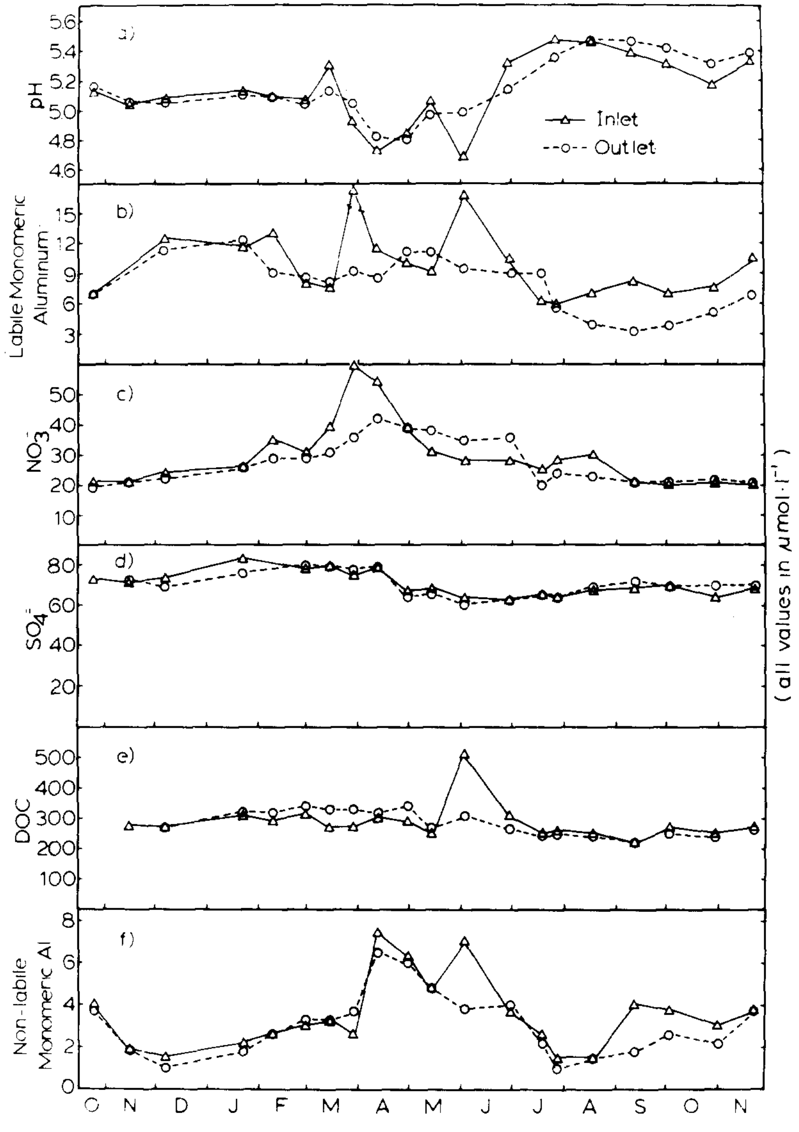

Figure 2. Temporal variations in (a) pH values, (b) labile monomeric aluminum, (c) nitrate, (d) sulfate, (e) dissolved organic carbon, and (f) non-labile monomeric aluminum within the Dart's Lake water column.

surface waters and may potentially mitigate the toxicity of Al to aquatic organisms (Baker and Schofield, 1982), it is important to understand spatial and temporal variations. Although some seasonal variation was apparent, total fluoride (F_t) concentrations within the lake were relatively stable throughout the study (Figure 3). This trend implies that Dart's Lake

Table 2. Distribution of Monomeric Aluminum in Dart's Lake.

Aluminum Form	Concentration	Relative Distribution as Monomeric Aluminum
Monomeric Aluminum	11.5 ± 3.7	—
Labile Monomeric Aluminum	8.1 ± 3.2	0.70
Al^{3+}	1.9 ± 1.7	0.17
Al-OH	2.5 ± 1.3	0.22
Al-F	3.6 ± 0.7	0.31
$Al\text{-}SO_4$	0.1 ± 0.1	0.01
Non-labile Monomeric Aluminum	3.5 ± 1.8	0.30

water has a relatively constant capacity for Al complexation by F and that further increases in Al concentration to the lake would likely be distributed among the other Al fractions.

Fluctuations in free fluoride (F_f) were much more dramatic than F_t (Figure 4). Very low F_f concentrations ($< 0.5\,\mu mol\,l^{-1}$) coincided with very acidic conditions (Figure 1) and indicate substantial F complexation by Al. Increasing F_f values indicate that decomplexation of Al occurred as a consequence of decreasing Al concentrations. The substantial variations which occurred both spatially and temporally indicate the dynamic nature of alumino-fluoride complexation in Dart's Lake.

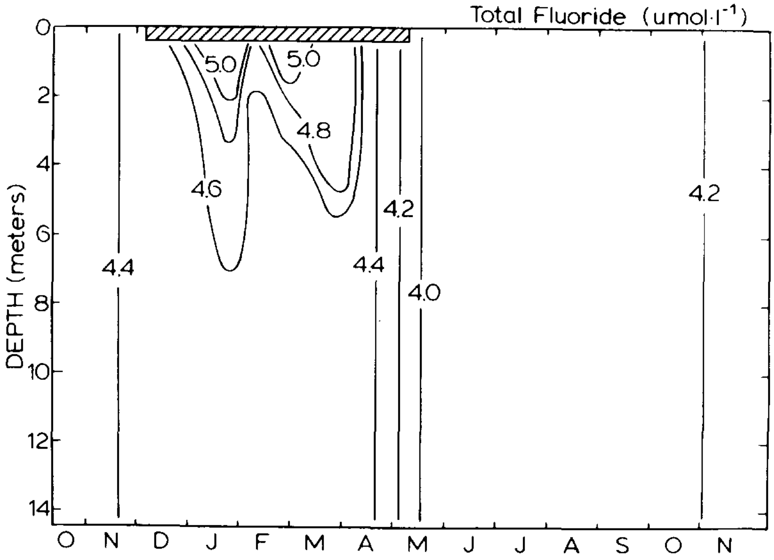

Figure 3. Temporal and spatial variations in total fluroide within the Dart's Lake water column.

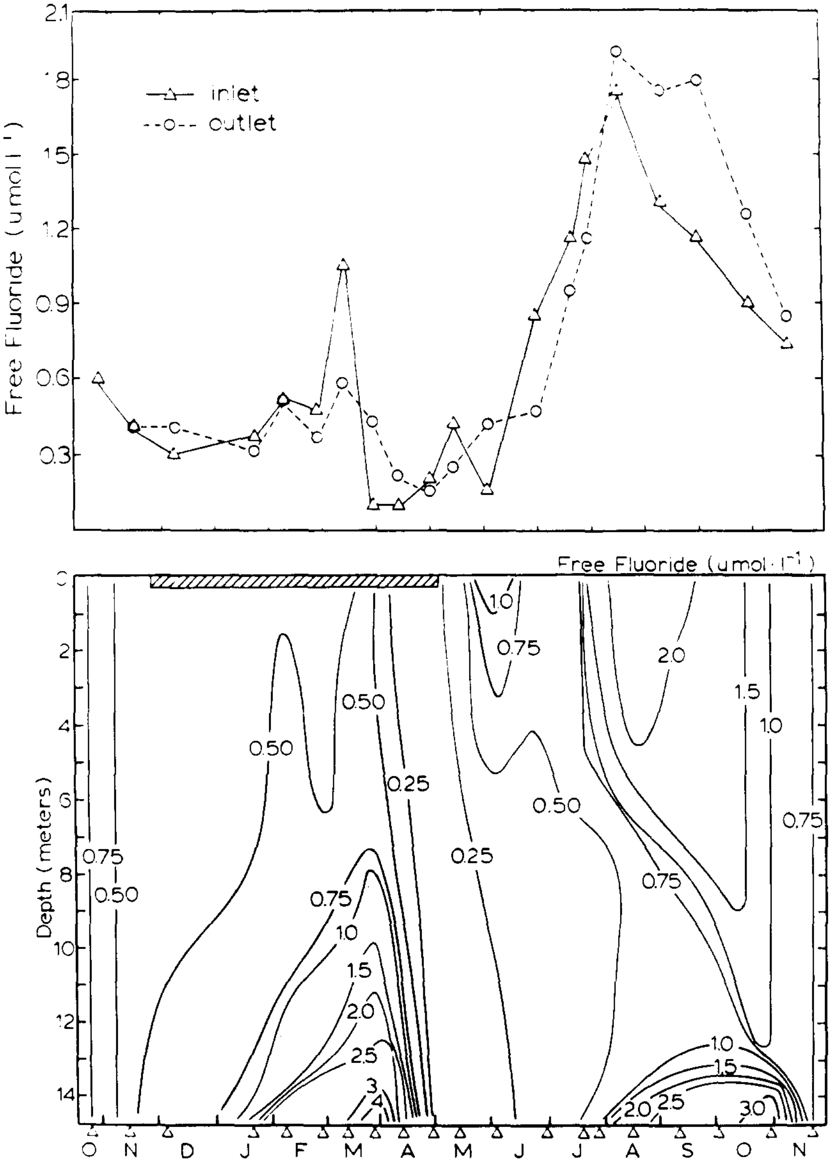

Figure 4. Free fluoride variation within the (a) inlet and outlet and (b) water column within Dart's Lake.

Trends in DOC and alumino-organic substances

In Dart's Lake a substantial portion of monomeric Al appeared to be complexed with natural organic ligands. We observed a weak but statistically significant empirical relationship between non-labile monomeric Al (OMAl) and DOC (OMAl) = $-1.84 + 0.018\,\mathrm{DOC}$; in $\mu\mathrm{eq}\,\mathrm{l}^{-1}$, $r^2 = 0.14$, $p < 0.0001$, $n = 172$).

Similar empirical relationships have been reported for Adirondack lakes and streams and for HBEF streams (Driscoll et al., 1984; Driscoll, 1984). The correlation between non-labile monomeric Al and DOC was considerably weaker for Dart's Lake than these other systems. This relatively poor correlation may be attributed in part to the limited range of DOC concentration measured in the lake. Also, DOC is a relatively crude parameter because it encompasses a great diversity of organic solutes. Individual organic compounds may be of allochtonous or autochtonous origin and vary greatly in their capacity to complex Al.

Dissolved organic carbon concentrations were relatively consistent in the inlet and outlet streams while concentrations of non-labile monomeric Al were more variable (Figure 2e, f). Within the water column there were significant spatial and temporal trends in DOC and non-labile monomeric Al (Figure 5). Minimum DOC values were observed in the epilimnion during summer while highest concentrations occurred directly under the ice in winter. Following similar trends to DOC, non-labile monomeric Al was elevated during the early stages of snowmelt and within the hypolimnion during summer stratification while low concentrations were observed in the epilimnion in the summer. Within the lower waters during summer stratification the apparent increase in non-labile monomeric Al was accompanied by only a slight increase in DOC. The ratio of DOC to non-labile monomeric Al for all samples ($n = 172$) was 87 while for the period 16 August to 1 October the ratio for the samples ($n = 6$) below 12 m was 44. This observation indicates that during this period, DOC of the hypolimnion was characteristically different than that of the rest of the lake and an increased complexation capacity of the DOC is suggested. However, it is also possible that non-labile monomeric Al was solubilized from the sediment, rather than the result of complexation of inorganic Al by sediment derived DOC. Due to microbial activity within the lake sediments a decrease in the organic carbon to Al ratio of these materials may occur. The elevated concentrations in the hypolimnion had little effect on whole lake concentrations at overturn due to the small volume this region of the lake occupies (16% below 9 m). Variations within the lake were both the result of temporal variation in inputs as well as in-lake processes. Trends of immobilization in the epilimnion and mobilization from hypolimnetic sediments suggest that cycling of non-labile monomeric Al was occurring within the lake.

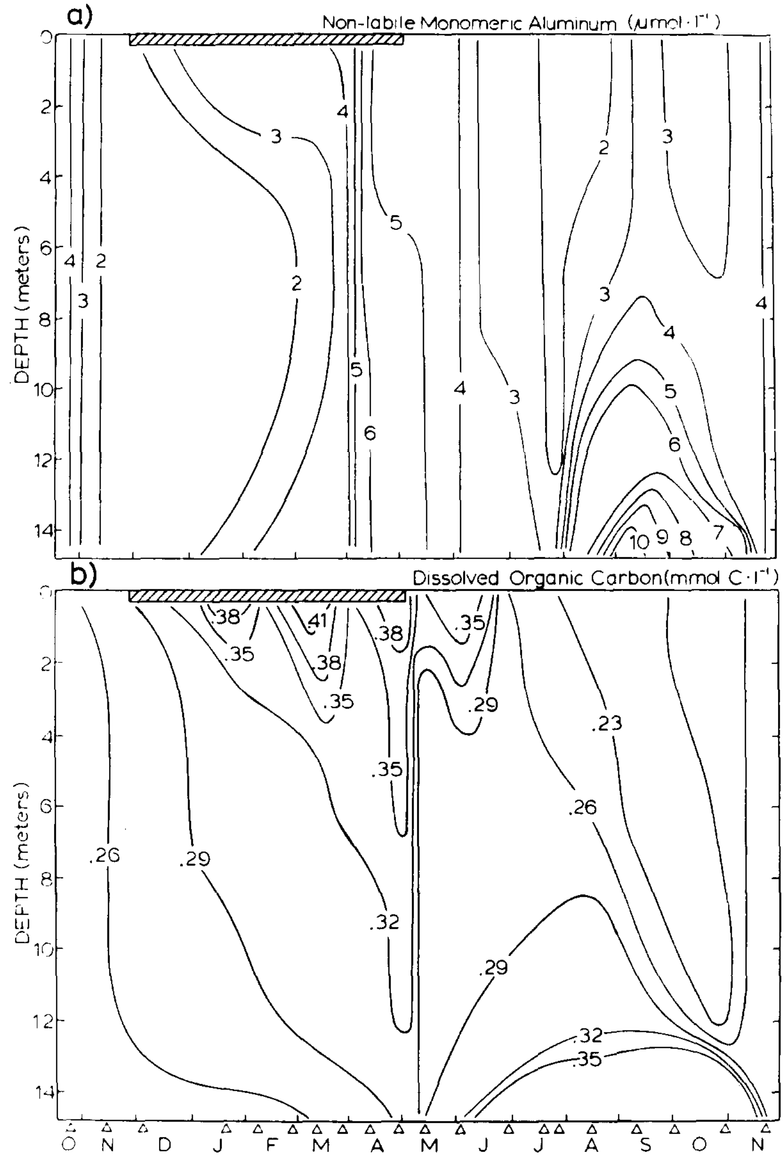

Figure 5. Temporal and spatial variations of (a) non-labile monomeric aluminum and (b) dissolved organic carbon.

Al transformations in the water column

Like other studies of acidic surface waters (Johnson et al., 1981; Driscoll et al., 1984) we observed that inorganic Al chemistry was reasonably well described by $Al(OH)_3$ mineral solubility. The ion activity products of inlet,

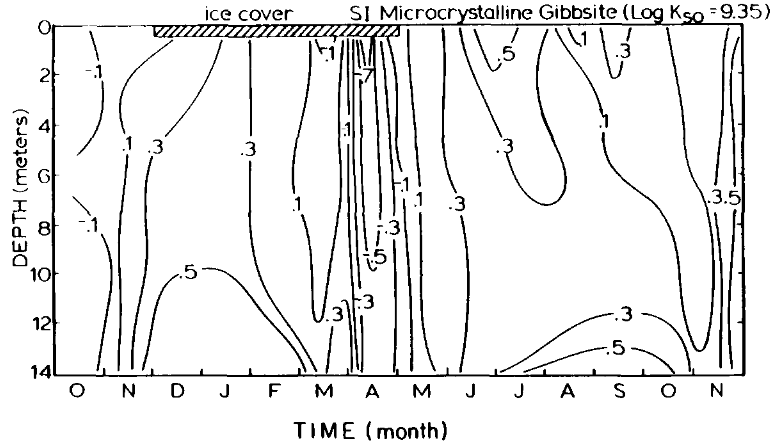

Figure 6. Temporal and spatial variations in the saturation index (SI) with respect to microcrystalline gibbsite within the Dart's Lake water column.

outlet, and lake solutions were generally similar to the theoretical solubility of microcrystalline gibbsite (SI microcrystalline gibbsite = 0.17 ± 0.28). Johnson et al., (1981) and Driscoll et al., (1984) reported that HBEF and Adirondack waters were somewhat undersaturated with respect to the solubility of microcrystalline gibbsite (SI = −0.69 ± 0.36 and −0.86 ± 0.45, respectively). The higher SI values for the Dart's Lake system may be due to real differences in solution composition or the fact that we extracted samples for monomeric Al in the field.

While the removal of Al was nearly stoichiometric with H^+ there were well defined patterns of disequilibrium in Dart's Lake (Figure 6). High inlet flows which occurred in October (1981) and during spring snowmelt resulted in apparent undersaturation (negative SI values). This was particularly evident at snowmelt when the highest flow rates of the year were observed. The short retention time of water in the soil during these periods and slow rates of mineral dissolution likely contributed to these low SI values. During high flow periods little retention of Al occurred within the lake (Driscoll and Schafran, 1985).

During low flow periods waters were oversaturated with respect to $Al(OH)_3$ solubility throughout the lake. Epilimnetic patterns of SI were distinctly different from those in the lower waters. The SI peak persisted for only a few weeks in the epilimnion and was followed by a rapid decline. As the thermocline migrated down the water column, low SI water encompassed an increasing lake volume. Conversely, in the hypolimnion, during both winter and summer stratification, high SI values persisted for several months. We suggest that the rather rapid depletion of Al in the upper waters was due to algae and other particulate matter which could serve as nucleation sites and facilitate the removal of Al from solution. Moreover, turbulence and the elevated temperatures in the upper waters would promote coagulation and removal of Al. These factors would be less significant in the hypolimnion and therefore rates of Al removal were correspondingly slower.

These periods of apparent oversaturation with respect to $Al(OH)_3$ solubility, suggest active hydrolysis of Al which may be ecologically significant. Baker and Schofield (1982) have reported that hydroxide complexes were the most toxic form of Al to fish. From our results it appears that periods of oversaturation can occur for extended periods of time within different regions of the lake.

Interactions between DOC and labile monomeric Al may also occur within the epilimnion. For the 13 May–10 September period for the 2–6 m sites, DOC was positively correlated to labile monomeric Al (IMAl) ($\mathrm{DOC} = 224 + 5.72\,\mathrm{IMAl}$; $r^2 = 0.47$; $p < 0.0002$; IMAl and DOC in $\mu\mathrm{mol\,l^{-1}}$). We have also observed that DOC was correlated to the vertical absorption coefficient, Kd, (Cole, 1979) for this period (Effler et al., 1985; $\mathrm{Kd} = -1.13 + 0.0062\,\mathrm{DOC}$; $r^2 = 0.83$; Kd in $\mathrm{m^{-1}}$ and DOC in $\mu\mathrm{mol\,C\,l^{-1}}$). Dissolved organic carbon may be removed from solution by coagulation reactions with Al, thus, effectively influencing lake water transparency. If Al alters lake water transparency as suggested by these results, then this represents a significant alteration to both the physical and chemical characteristics of the lake.

Conclusions

Soluble Al concentrations in acidic surface waters can be highly variable both spatially and temporally. As a result of short-term pH changes, significant variation in the concentration of inorganic forms of Al as well as distribution of Al species occurred. During high flow periods (e.g. snowmelt) substantial Al was introduced to Dart's Lake. During stratification, in-lake reduction processes enhanced the removal of Al.

Transformation of DOC and organic forms of Al were also evident in this study. Considerable influx of these solutes occurred during snowmelt and hypolimnetic enrichment due to sediment release was observed during summer stratification. We also observed an epilimnetic depletion of DOC and alumino-organic solutes during summer stratification which may be due to coagulation reactions with Al.

Short-term variations in the chemistry of Al have obvious implications for lake ecosystems. Seasonal changes in the distribution of Al may influence the toxicity of this element. Moreover, the removal of DOC from the upper waters during summer stratification appears to have enhanced the transparency of light. This transformation facilitates hypolimnetic heating and the decreased thermal stability of lakes.

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