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Longitudinal and temporal trends in the water chemistry of the North Branch of the Moose River

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Abstract. Surface water acidification is potentially a problem in regions with low ionic strength drainage waters. Atmospheric deposition of sulfuric acid has generally been implicated as the causative agent of this problem, although other sources of acidity may contribute. The Adirondack region of New York State is an area with "acid-sensitive" surface waters and an abundance of acidic lakes. The intent of this study was to evaluate the processes regulating the acid/base chemistry of a series of lakes draining a large heterogeneous watershed in the Adirondack region of New York.

The study site, the North Branch of the Moose River, is heterogeneous in its soil and geological characteristics. This variability was reflected through differences in water chemistry that occurred within the basin. The northern headwaters generally drain subcatchments with shallow, acidic soils. The resulting water chemistry was acidic (equivalence of acidic anions exceeded equivalence of basic cations) with high concentrations of Al and dissolved organic carbon (DOC). As this water migrated through a large lake (Big Moose Lake) with a moderate hydrologic retention time (~ 0.5 yr), considerable loss of DOC was evident.

As acidic water was transported through the drainage area, it mixed with waters that were enriched in concentrations of basic cations from the eastern subbasins. As a result, there was a successive increase in the acid neutralizing capacity (ANC) and a decrease in Al concentrations as water migrated from the northern reaches to the outlet of the watershed.

In addition to these general trends, short-term changes in water chemistry were evident. During low flow summer periods concentrations of basic cations were elevated, while concentrations of SO_4^{2-} and NO_3^- were relatively low. These conditions resulted in less acidic waters (higher ANC) with relatively low concentrations of Al. During high flow winter/spring conditions, elevated concentrations of SO_4^{2-} and NO_3^- were evident, while concentrations of basic cations were reduced resulting in low pH (low ANC) waters with high concentrations of Al.

Variability in the processes regulating the pH buffering of waters was apparent through these short-term changes in water chemistry. In the northern subbasin short-term fluctuations in ANC were minimal because of the buffering of Al under low pH conditions. Seasonal changes in the ANC were more pronounced in the eastern subbasin because of the predominance of inorganic carbon buffering in the circumneutral pH waters.

Lakes in the west-central Adirondacks have characteristically short hydraulic residence times and elevated nitric acid inputs. As a result these waters may be more susceptible to surface water acidification than other "acid-sensitive" lake districts in eastern North America. Given the apparent interregional differences, extrapolation of chemical trends in the Adirondacks to other areas may be tenuous.

Introduction

There is concern over the potential impact of acidic deposition on surface waters. Atmospheric inputs of strong acids may be neutralized by the release of basic cations (C_B; Ca^{2+}, Mg^{2+}, Na^+, K^+) from the terrestrial environment (e.g. weathering of soil minerals or cation exchange; Johnson et al., 1981) or by the retention of acidic anions (SO_4^{2-}, NO_3^-, Cl^-; e.g. by biological reduction reactions, Kelly et al., 1982; or by chemical sorption reactions, Johnson and Todd, 1983). If these transformations only occur to a limited extent, then a region is considered to be sensitive to acidic deposition. "Acid-sensitive" areas generally have acidic soils with small pools of "readily available" basic cations (exchangeable or easily weatherable) and have a relatively short hydraulic retention time within the mineral soil due to shallow soil depth coupled with high hydrologic loading (Goldstein et al., 1984; Chen et al., 1984a). Because of these conditions, the neutralization of acidic inputs to "acid-sensitive" regions may be incomplete. Due to the constraint of electroneutrality if inputs of acidic anions (SO_4^{2-}, NO_3^-, Cl^-) are not neutralized by the release of basic cations or retained by soil/sediment processes, elevated concentrations of acidic cations (H^+, Al^{n+}) will result in drainage water (Driscoll and Newton, 1985).

In addition to these general trends, short-term changes in water chemistry are evident in acid-sensitive regions. During periods of high hydrologic loading (e.g. snowmelt), the ability of mineral soil to transmit water may be exceeded resulting in short-circuiting through organic and upper mineral soil horizons (Chen et al., 1984a, b). This condition may result in episodic acidification of surface waters and short-term increases in H^+ and Al concentrations.

The chemistry of Al is particularly important in understanding the effects of acidic deposition on surface waters. Aqueous Al exists not only as an aquo complex but also coordinated with OH^-, F^-, SO_4^{2-} (Roberson and Hem, 1969) and organic ligands (Lind and Hem, 1975). Driscoll et al., (1984) observed two major fractions of Al in low ionic strength (dilute) waters in the Adirondack region of New York. Labile monomeric Al, which is thought to represent inorganic forms of Al (Driscoll, 1984), increased exponentially with decreases in solution pH. Non-labile monomeric Al, which is an estimate of organically bound Al (Driscoll, 1984), was strongly correlated with organic carbon concentrations. Aluminofluoride complexes were the predominant fraction of labile monomeric Al in Adirondack surface waters. While concentrations of aquo Al and hydroxy Al complexes were also significant, SO_4^{2-} complexed Al was insignificant.

The toxicity of Al to fish (Baker and Schofield, 1982) and other aquatic organisms (Hall et al., 1985) appears to be closely linked to its speciation. In laboratory bioassay experiments using synthetic solutions, Baker and Schofield (1982) observed that the addition of complexing ligands, citrate and to a lesser extent fluoride, mitigated Al toxicity to fish fry. Moreover, Henriksen et al., (1984) reported that fish kills in Norway coincided with high concentrations of labile monomeric (inorganic) Al using the fractionation procedure of Driscoll (1984). Results of these and other studies suggest that aquatic organisms are sensitive to inorganic forms of aqueous Al.

In the Adirondack lake district there are a large number of lakes that are acidic or sensitive to episodic acidification. Colquhoun et al., (1984) reported that of 980 ponded waters sampled in the Adirondacks 231 were acidic (ANC < 0), 204 were extremely sensitive to acidification with ANC values between 0–40 μeq.1^{-1}, and 409 were moderately sensitive with ANC values between 40 and 200 μeq.1^{-1}. Many of these acidic waters are high elevation headwater lakes located in the western portion of the Adirondack Park.

Due to glacial processes, many of the Adirondack lakes are chain-lake systems. Although chain-lake systems are common in the Adirondack region, there has never been a systematic evaluation of the chemical transformations that occur as water migrates through a chain-lake catchment. The intent of our study was to evaluate the processes regulating longitudinal and temporal variations in the acid/base chemistry of a series of lakes, the North Branch of the Moose River, located in the western portion of the Adirondack region of New York. Moreover, this research served to provide information on water chemistry that was used in studies of the geology (Newton et al., 1987), vegetation (Cronan et al., 1987), hydrology (Peters and Driscoll, 1987), fisheries (Schofield and Driscoll, 1987; Johnson et al., 1987), paleolimnology (Charles et al., 1987), and water quality modeling (Davis et al., 1987) of the North Branch of the Moose River.

Study sites and methods

The study sites were located within the North Branch of the Moose River (Figure 1) in the Adirondack region of New York (43°45′ to 43°51′N, 74°50′ to 74°55′W). The watershed occupies a drainage area of 142 km^2, with a maximum elevation of 761 m near Andys Creek north of Big Moose Lake and a minimum elevation of 521 m at the outlet of Lake Rondaxe.

The watershed is forested except for minor areas of exposed bedrock, with deciduous hardwoods predominating. The major vegetation consists of secondary growth hardwoods, American beech (*Fagus grandifolia*, yellow birch (*Betula alleghaniensis*), sugar maple (*Acer saccharum*), and red maple (*Acer rebrum*). In addition, coniferous vegetation (balsam fir; *Abies balsamea*, red spruce; *Picea rubens*) is evident particularly near lakeshores. A more detailed description of the catchment vegetation is available elsewhere (Cronan et al., 1987).

The bedrock geology of the basin is characteristically granitic gneiss

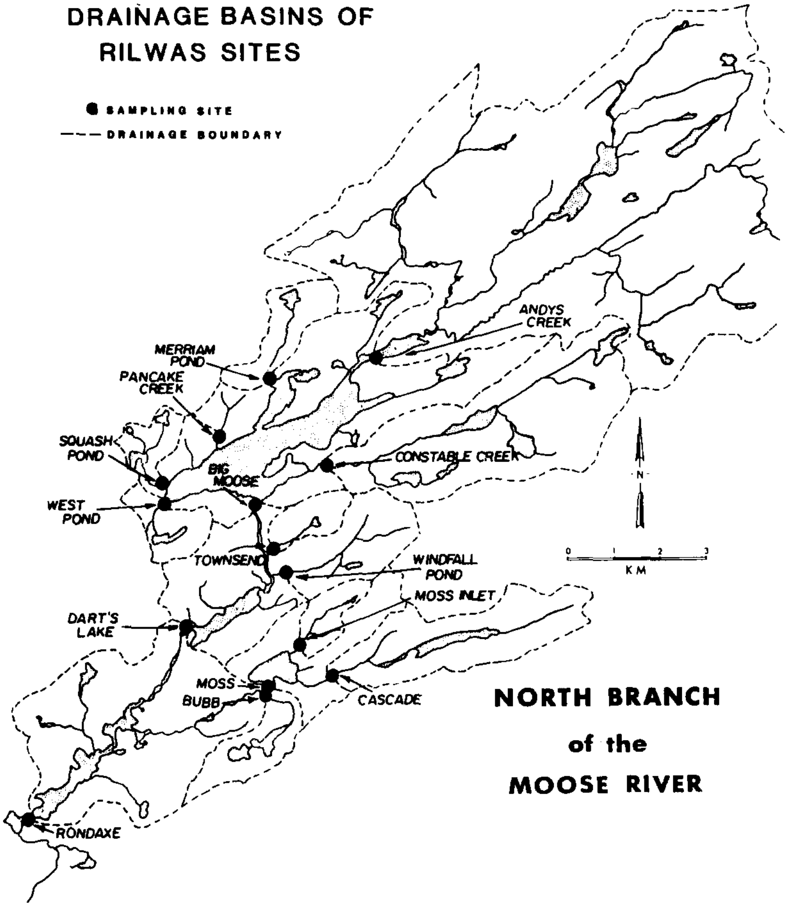

Figure 1. Sampling locations and their respective drainage areas in the North Branch of the Moose River.

interlayered with meta-sedimentary rock (Newton et al., 1987). Specific mineralogy includes biotite, hornblende, quartz and feldspars. The surficial geology is predominantly thin (< 3 m) till, and soils are generally highly acidic (small pools of exchangeable basic cations). However, there is considerable heterogeneity in the soil characteristics within the basin. To facilitate discussion, the catchment can be subdivided into two major subbasins. The major subbasin drains the northern portion of the catchment including Squash Pond, Pancake Creek, Merriam Pond and Constable Creek through Big Moose Lake. This subbasin contains extremely shallow acidic soils. Moreover, wetland areas, particularly Andys Creek and West Pond which contain thick deposits of organic soil, are evident in the northern reaches. Drainage from Townsend and Windfall Ponds

Table 1. Physical characteristics for sites within the North Branch of the Moose River.

Site	Elevation (m)	Lake Area (ha)	Lake Volume ($10^4 m^3$)	Retention Time (years)	Drainage Area (ha)
Andys Creek	552	—	—	—	1562
Big Moose Lake	557	520.5	3600	0.49	9555
Bubb Lake	554	20.5	42	0.21	264
Cascade Lake	554	40	172	0.33	689
Constable Pond	582	22.7	45	0.04	1383
Dart's Lake	536	57.6	415	0.05	10,749
Lake Rondaxe	525	91.7	220	0.02	14,185
Merriam Pond	651	7.8	11.5	0.05	277
Moss Lake	536	45	272	0.29	1,248
Moss Lake Inlet	543	—	—	—	240
Pancake Hall Creek	556	—	—	—	74
Squash Pond	650	3.9	7.2	0.06	170
Townsend Pond	561	1.8	—	—	150
West Pond	579	12.4	—	—	184
Windfall Pond	595	1.55	4.9	0.02	399

Table 2. Chemical parameters analyzed in the North Branch of the Moose River

Parameter	Method	Reference
SO_4^{2-}, NO_3^-, Cl^-	Ion chromatography	Small et al. 1975
NH_4^+	Phenate colorimetry; autoanalyzer	USEPA 1983
Ca^{2+}, Mg^{2+}, Na^+, K^+	Atomic Absorption Spectrophotometry (AAS)	Slavin 1968
pH	Potentiometrically with glass electrode, field measurement	Standard Methods 1985
Acid Neutralizing Capacity (ANC)	Strong acid titration with Gran plot analysis	Gran 1952
Dissolved Inorganic Carbon (DIC)	Syringe stripping of CO_2 and detection by gas chromatography	Stainton 1973
Dissolved Organic Carbon (DOC)	Filtration, ampoulation, persulfate oxidation, syringe stripping of CO_2 and detection by gas chromatography	Menzel and Vaccaro 1964
Dissolved Silica	Heteropoly blue complex colorimetry; autoanalyzer	Standard Methods 1985
Free F	Potentiometrically with ion selective electrode	Orion 1986
Total F	Potentiometrically with ion selective electrode after TISAB addition	Orion 1976
Monomeric Al	Field extraction by 8-hydroxyquinoline into MIBK, analysis by AAS, graphite furnace	Barnes 1976 Driscoll 1984
Non-labile monomeric Al (Al_0)	Fractionation by ion exchange column, analysis for monomeric Al	Driscoll 1984
Specific Conductance	Conductivity bridge	Standard Methods 1985
Temperature	Thermometer	

mix with water from the outlet of Big Moose Lake prior to inflow to Dart's Lake. The eastern subbasin drains Cascade, Sis, Bubb and Moss Lakes. While the soils near Windfall Pond and the eastern subbasin are generally shallow and acidic, they do contain deposits of weatherable minerals and thick till. Waters draining the northern and eastern subbasins mix at Lake Rondaxe and exit the watershed at the outlet. A detailed description of the soil chemistry and surficial geology within the North Branch of the Moose River is available elsewhere (Newton et al., 1987).

To evaluate trends in the water chemistry of the North Branch of the Moose River we sampled 15 sites throughout the watershed at approximately monthly intervals for a period of 31 months (32 suites of samples). The location of the sampling sites with their respective drainage areas are indicated in Figure 1, and additional physical data are summarized in Table 1. The 30 year average precipitation input and runoff for the watershed area are 127 cm and 76.2 cm respectively (Pfeiffer and Festa, 1980; Colquhoun et al., 1984). Note that 50 to 60 percent of the runoff to the region occurs during the months of March, April and May (Troutman and Peters, 1982). As a result of the elevated runoff coupled with the relatively large drainage area, the hydraulic retention time of the study lakes is very short < 0.5 yr; Table 1). Additional information on hydrology of the watershed is available elsewhere (Peters and Driscoll, 1987).

The analytical methods used in this study are summarized in Table 2. Samples were measured for temperature and pH and extracted for monomeric Al in the field to minimize transformations (e.g. changes in temperature and degassing of CO_2) that might alter measured values. Samples were kept cool following collection and transported to the laboratory at Syracuse University where they were analyzed for dissolved inorganic carbon (DIC) and nitrogen forms (NH_4^+, NO_3^-), ampoulated for the determination of dissolved organic carbon (DOC), and processed for the determination of non-labile monomeric Al as shortly after collection as possible (generally less than 72 hours after collection). Samples were stored at 4 °C until the remainder of the analytical determinations were made.

To assess the distribution of Al, samples were fractionated using the procedure described by Driscoll (1984). Labile monomeric Al is thought to represent inorganic forms of mononuclear Al, while non-labile monomeric Al is considered to be an estimate of Al that is associated with organic solutes.

The distribution of labile (inorganic) monomeric Al in solutions was calculated using a chemical equilibrium model. Equilibrium constants and enthalpy values used for this analysis are summarized elsewhere (Ball et al., 1980). Calculations were corrected for the effects of ionic strength, using the Debye-Huckel approximation for individual ion activity coefficients (Stumm and Morgan, 1981) and temperature.

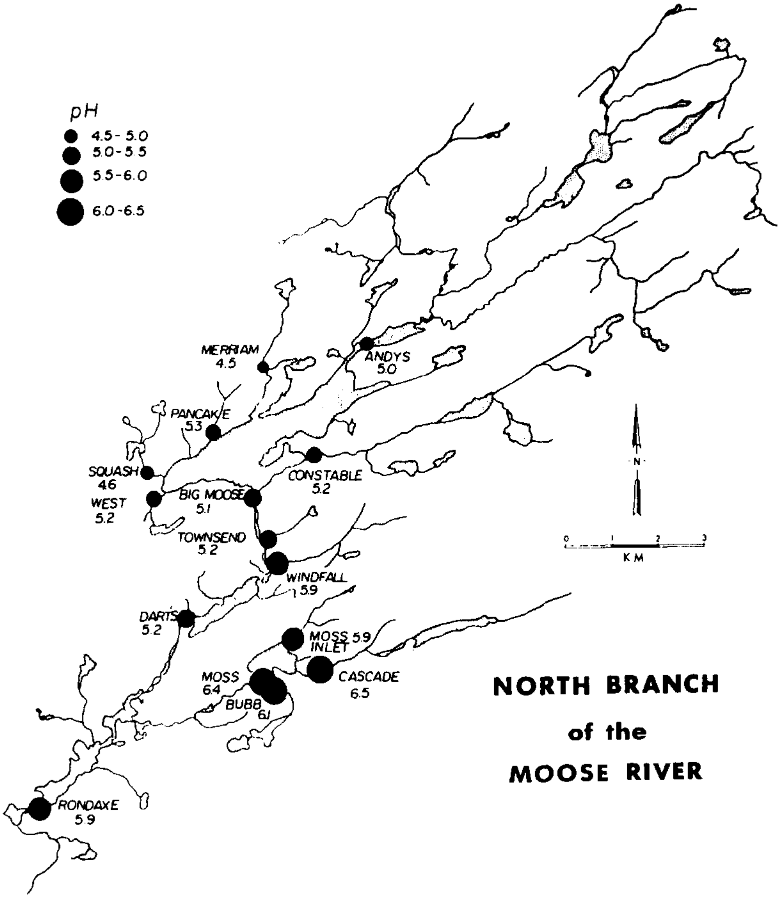

Figure 2a. Trends in the pH of waters draining the North Branch of the Moose River. Values represent the mean of 32 samples collected over a 31 month period.

To evaluate the potential for the formation of solid phase Al, we calculated saturation indicies (SI) of waters with respect to the solubility of a readily forming Al mineral phase.

$$SI = \log Qp/Kp$$

Where: Qp is the ion activity product of the mineral phase of interest, and Kp is the thermodynamic solubility of the mineral phase of interest.

A positive SI value indicates that the solution is oversaturated with respect to the solubility of the mineral phase of interest, while zero and negative values suggest equilibrium and conditions of undersaturation, respectively. For this study, we chose natural gibbsite ($p^{*}Kso = 8.77$;

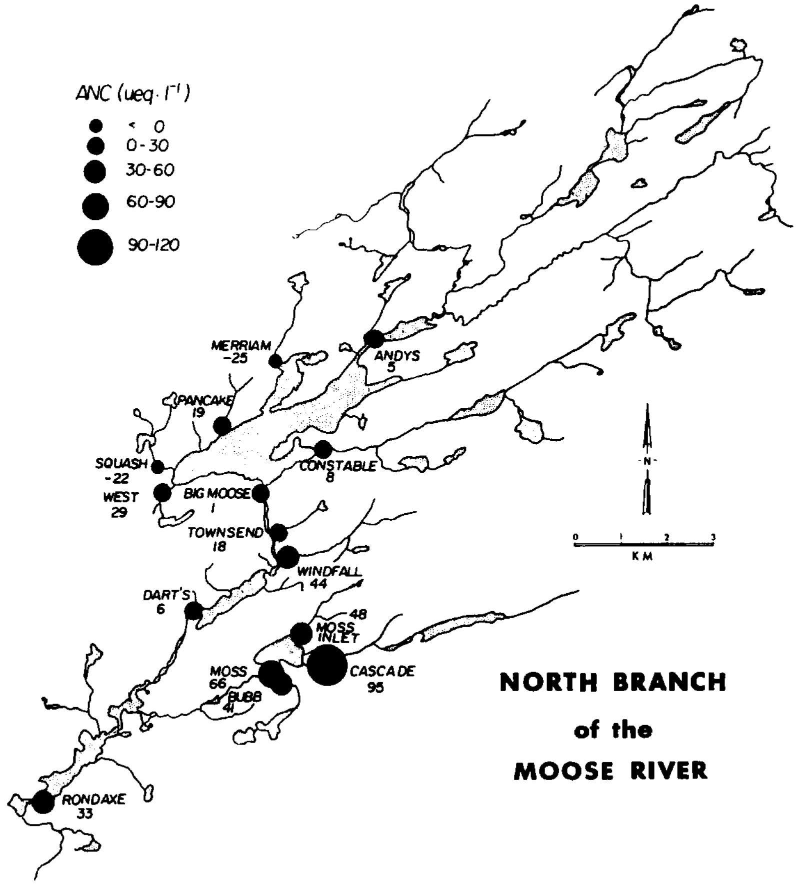

Figure 2b. Trends in the acid neutralizing capacity (ANC) of waters draining the North Branch of the Moose River.

May et al., 1979) as a reference mineral phase. Johnson et al., (1981) reported that stream solutions at the Hubbard Brook Experimental Forest were near saturation with respect to the solubility of natural gibbsite.

Results

There were marked spatial variations in the water chemistry within the North Branch of the Moose River (Figures 2a–2g). The distinction between the chemical characteristics of the northern and eastern subbasins was particularly evident. The northern subbasin generally contained sites with highly acidic water chemistry (Figures 2a, b; ANC $< 30\,\mu\text{eq.l}^{-1}$). In particular Squash Pond, Merriam Pond and Andys Creek exhibited extremely low pH values (< 5.0). In the western subwatershed (Moss Inlet,

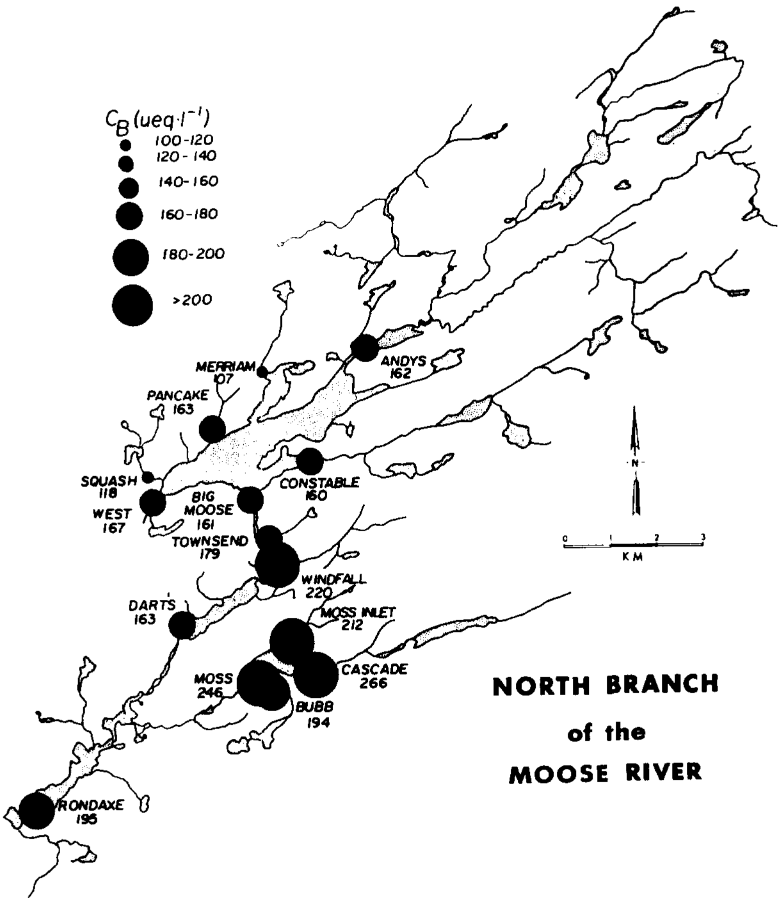

Figure 2c. Trends in the equivalence of basic cations (C_B; Ca^{2+}, Mg^{2+}, Na^+, K^+) of waters draining the North Branch of the Moose River.

Cascade, Bubb, Moss) and at Windfall outlet pH values were generally above 6.0., and ANC values were above 30 μeq.l^{-1}.

The reason for these spatial variations in pH and ANC becomes evident upon examination of the concentration of basic cations (C_B; Figure 2c) relative to the concentration of SO_4^{2-}, on an equivalence basis (Figure 2d). Sulfate was clearly the predominant anion in waters draining the North Branch of the Moose River. Although the watershed is a large drainage area with heterogenous soil characteristics, the SO_4^{2-} concentration was remarkably uniform (Figure 2d). The only deviation from this pattern was observed in West Pond, which generally contained lower SO_4^{2-} concentrations. This discrepancy might be attributed to SO_4^{2-} reduction occurring within the West Pond bog. Unlike SO_4^{2-}, we observed substantial varia-

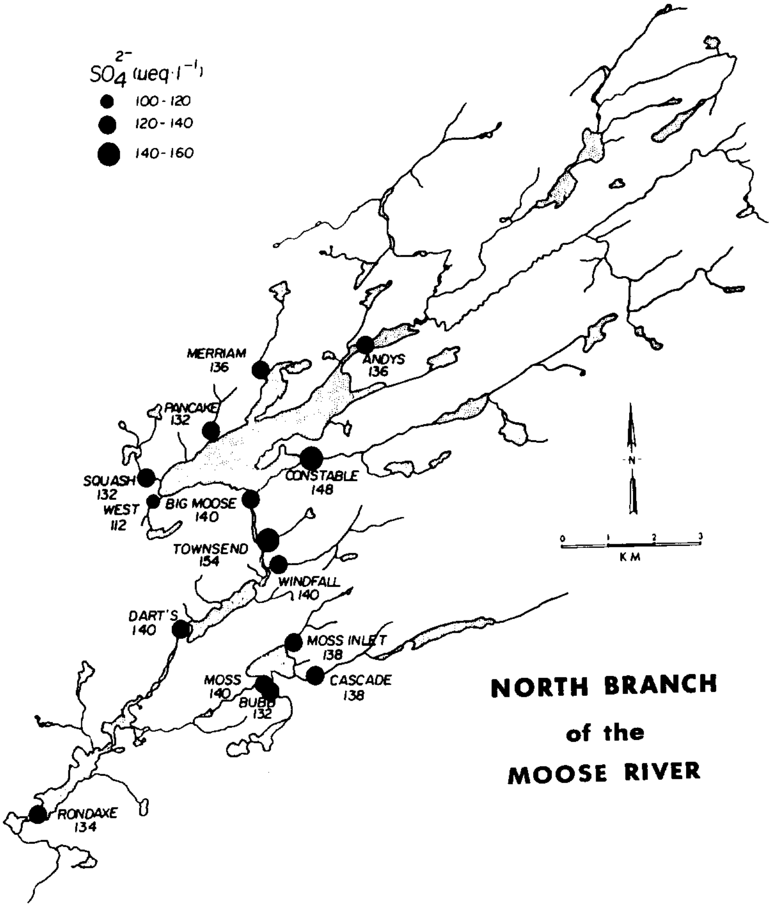

Figure 2d. Trends in the SO_4^{2-} equivalence of waters draining the North Branch of the Moose River.

tions in the concentration of basic cations within the North Branch of the Moose River (Figure 2c). The acidic sites in the northern reaches of the watershed generally contained low concentrations of basic cations. This pattern was consistent with the thin acidic soils in the northern subbasin (Newton et al., 1987). Low ANC water draining the northern subbasin was somewhat neutralized by inputs of water containing higher basic cation concentrations and ANC at Windfall Pond and ultimately by the drainage water from the eastern subbasin at Lake Rondaxe. Variations in the ANC within the watershed were highly correlated with basic cation concentrations ($ANC = -110 + 0.73C_B$; where ANC and C_B are in $\mu eq.l^{-1}$; $r^2 = 0.71$, $p < 0.01$).

We also detected substantial variations in the concentration and chemistry of Al in the North Branch of the Moose River (Figure 2e). Con-

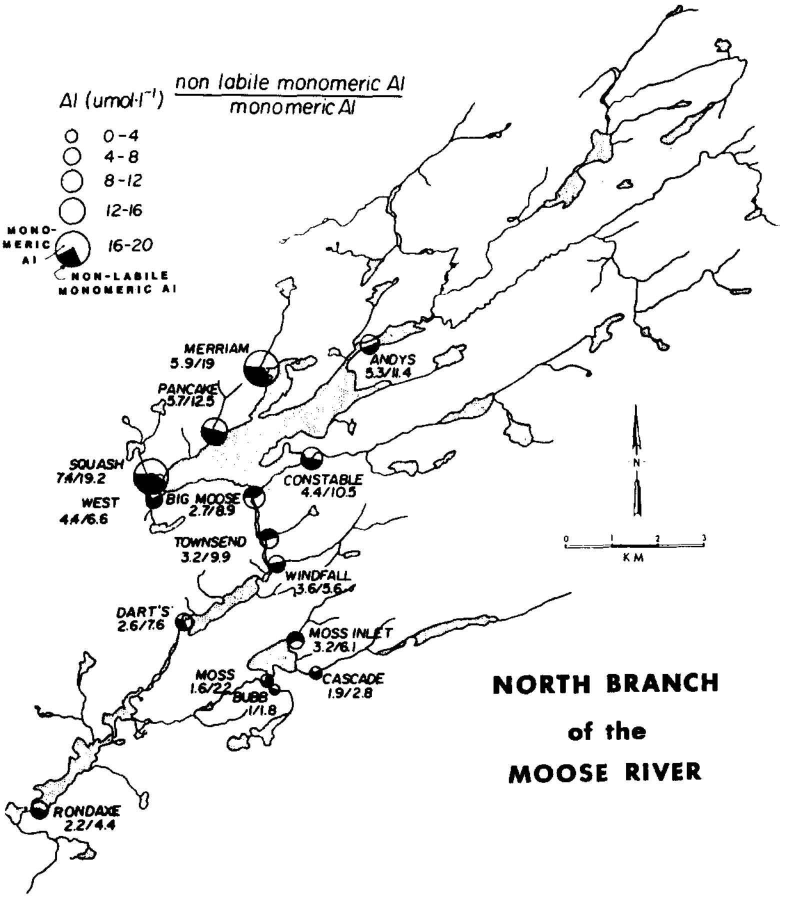

Figure 2e. Trends in the concentration of monomeric and non-labile monomeric Al in waters draining the North Branch of the Moose River.

centrations of monomeric Al were elevated in waters draining the northeastern subcatchment. In particular Squash Pond and Merriam Pond, with very low pH values, contained extremely high concentrations of monomeric Al. Aluminum concentrations were considerably lower in the southern and eastern reaches of the watershed. In general, concentrations of labile (inorganic) monomeric Al increased exponentially with decreases in solution pH (Figure 3), while concentrations of non-labile (organic) monomeric Al were strongly correlated with DOC ($Al_0 = 0.084 + 0.0086.DOC$; where Al_0 is the concentration of non-labile monomeric Al in $\mu mol.l^{-1}$ and DOC is in $\mu mol C.l^{-1}$; $r^2 = 0.43$, $p < 0.01$).

In the northern subbasin labile monomeric Al was generally the predominant fraction of monomeric Al, although concentrations of non-labile

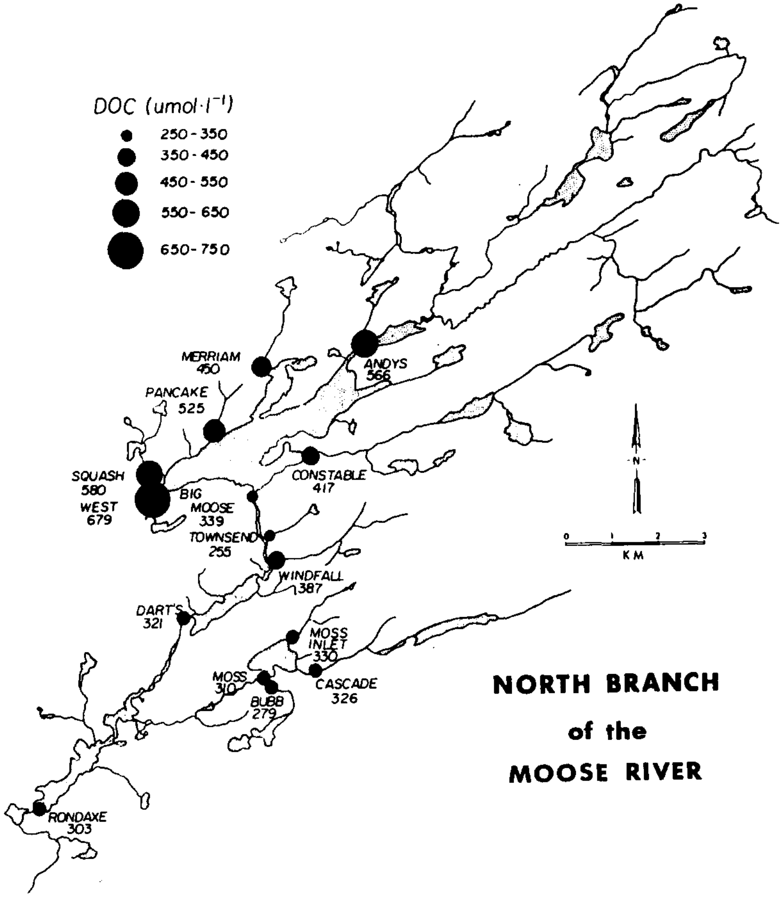

Figure 2f. Trends in the dissolved organic carbon (DOC) concentration in waters draining the North Branch of the Moose River.

monomeric Al were certainly significant. The only exception to this trend occurred in the wetland area, West Pond, which contained a large fraction of non-labile monomeric Al. The elevated concentrations of non-labile monomeric Al in the northern subbasin were consistent with high concentrations of DOC (Figure 2f). High concentrations of DOC were particularly evident in the wetland areas of West Pond and Andys Creek. In the southern and eastern reaches of the watershed concentrations of both fractions of monomeric Al and DOC were considerably lower than in the acidic northern reaches. Although concentrations of non-labile monomeric Al were lower in these circumneutral waters, this fraction was the predominant form of mononuclear Al.

Trends in the distribution of F were consistent with the observed chemistry of Al (Figure 2g). Johnson et al., (1981) indicated that in dilute

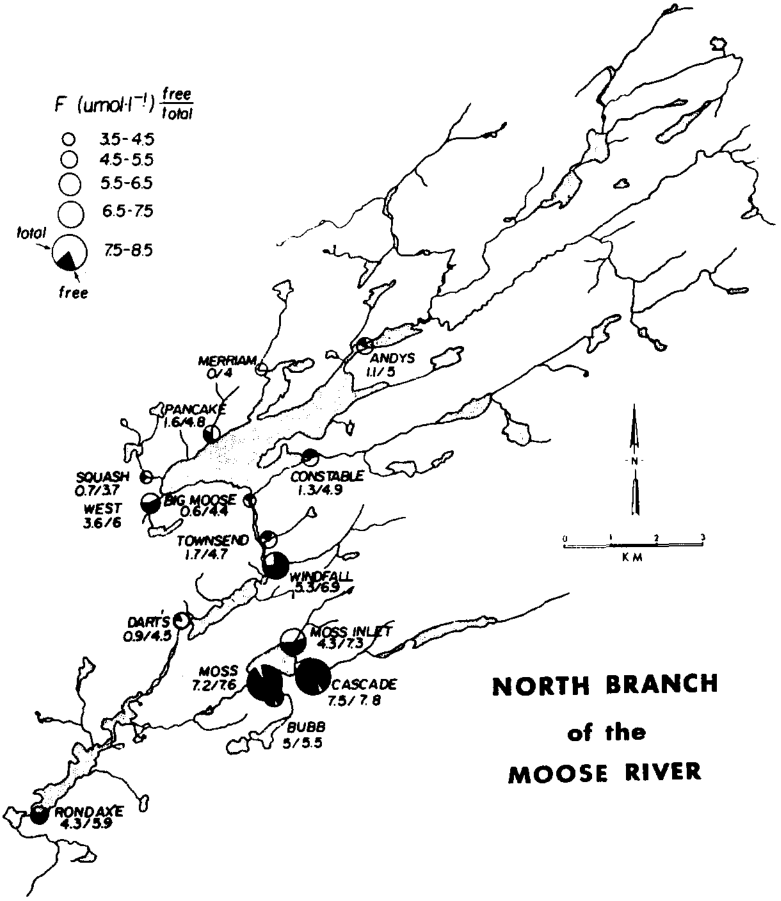

Figure 2g. Trends in the concentration of free and total F in waters draining the North Branch of the Moose River.

acidic waters, Al was the only cation capable of complexing significant quantities of F. Therefore, the F ion selective electrode, which can be used to detect both free and total F, is an important tool to independently evaluate the chemistry of Al. Free F values, calculated with pH, labile monomeric Al, total F and SO_4^{2-} measurements using the chemical equilibrium model (Driscoll, 1984) can be compared with measured concentrations (activity) obtained from the F ion selective electrode (Figure 4). For our study there was generally good agreement between the two approaches, which provides an independent verification of the validity of the Al fractionation procedure and thermochemical calculations used to evaluate the distribution of Al.

In the acidic sites of the northern subcatchment, concentrations of total F were low, and free F was generally a minor fraction of this total F. This

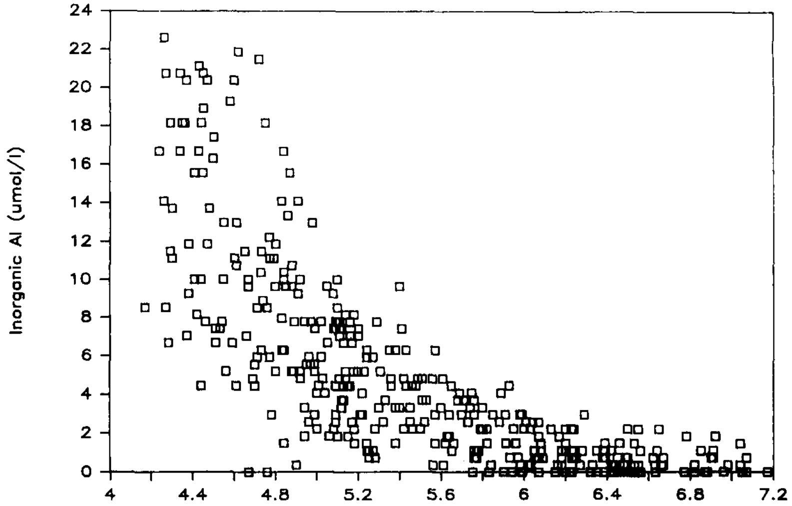

Figure 3. Concentrations of labile monomeric Al as a function of pH in solutions collected from the North Branch of the Moose River.

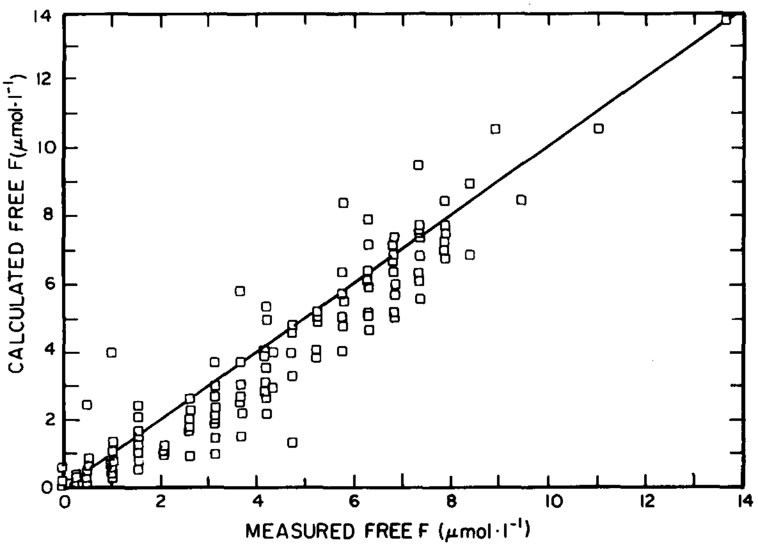

Figure 4. Values of free F calculated from the distribution of Al using a chemical equilibrium model as a function of measured values of free fluoride. One-to-one line is indicated.

observation suggests that F at these acidic sites was largely bound with complexing cations and was consistent with the high concentrations of labile monomeric Al. In the eastern subbasin and at circumneutral Windfall outlet, total F concentrations were considerably higher than the acidic northern reaches, and this F was predominantly in a free form reflecting the relatively low concentrations of labile monomeric Al.

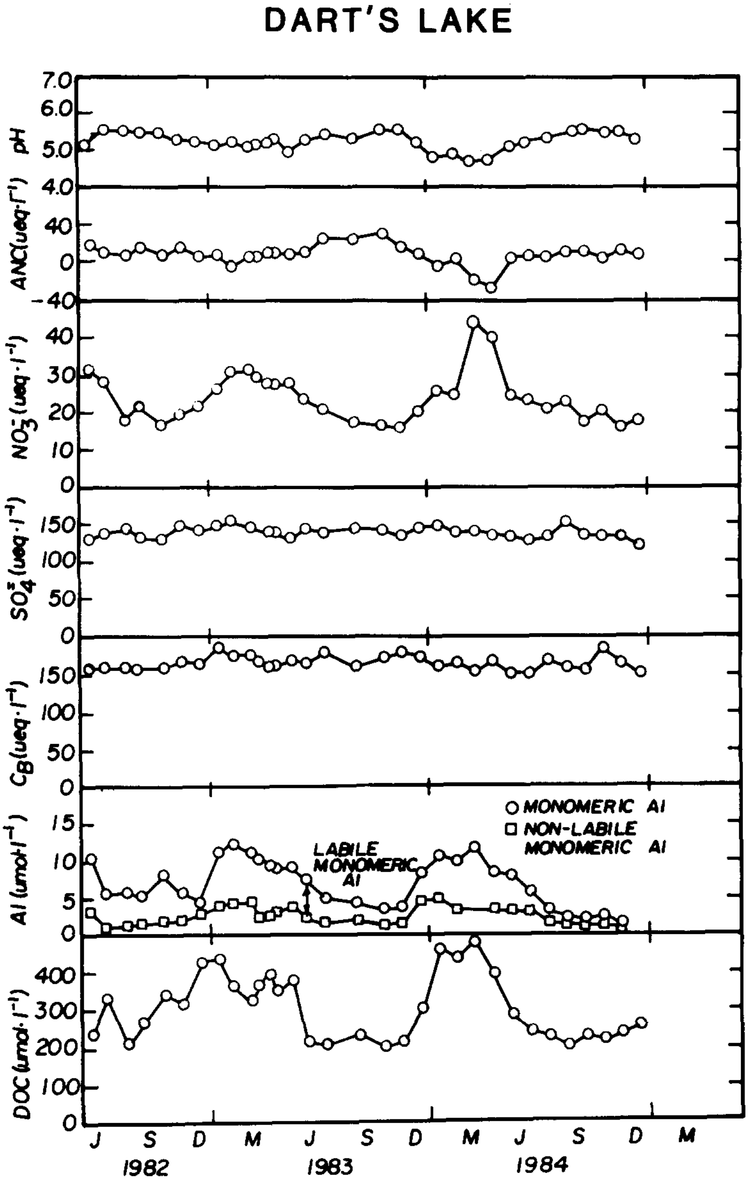

Figure 5. Temporal variations in pH, acid neutralizing capacity (ANC), NO_3^-, SO_4^{2-}, equivalence of basic cations (C_B; Ca^{2+}, Mg^{2+}, Na^+, K^+), total and non-labile monomeric Al, and dissolved organic carbon (DOC) of Dart's Lake outlet over the study period.

In addition to spatial trends in water chemistry, there were distinct temporal variations within the North Branch of the Moose River. To illustrate the nature and extent of these temporal variations, we present

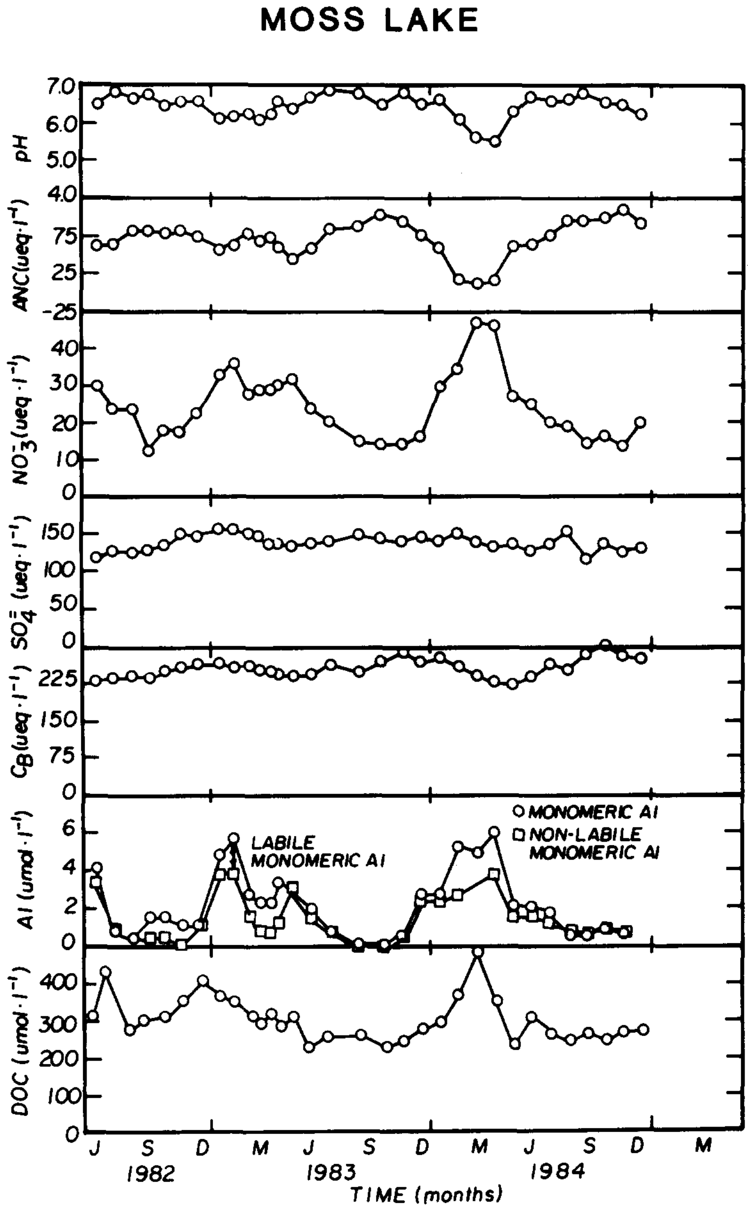

Figure 6. Temporal variations in pH, acid neutralizing capacity (ANC), NO_3^-, SO_4^{2-}, equivalence of basic cations (C_B; Ca^{2+}, Mg^{2+}, Na^+, K^+), total and non-labile monomeric Al, and dissolved organic carbon (DOC) of Moss Lake outlet over the study period.

water chemistry data from the acidic northern subbasin (Dart's Lake outlet; Figure 5), the circumneutral eastern subcatchment (Moss Lake outlet; Figure 6) and the confluence of these two subcatchments (lake

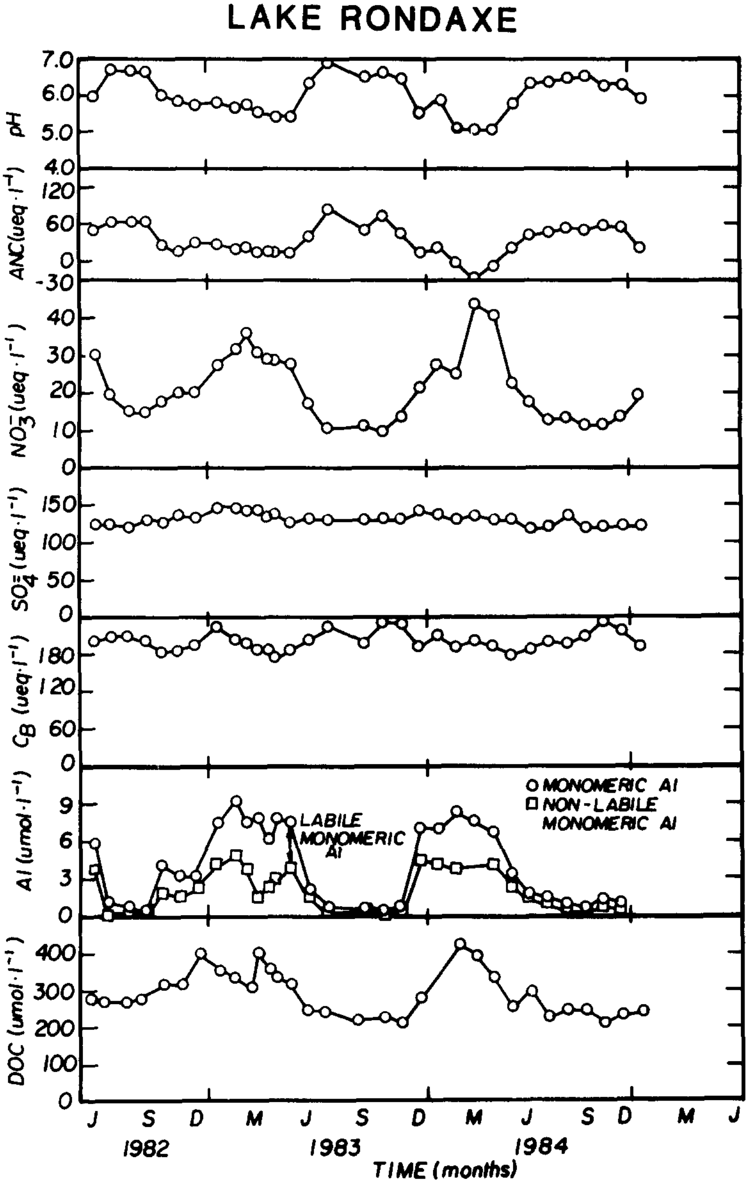

Figure 7. Temporal variations in pH, acid neutralizing capacity (ANC), NO_3^-, SO_4^{2-}, equivalence of basic cations (C_B; Ca^{2+}, Mg^{2+}, Na^+, K^+), total and non-labile monomeric Al, and dissolved organic carbon (DOC) of Lake Rondaxe outlet over the study period.

Rondaxe outlet; Figure 7). Although there were differences in the concentrations of water chemistry parameters at all three sites, temporal patterns were similar. In all three lakes, pH and ANC values were highest during summer low flow conditions and decreased to minimum values during spring snowmelt. We observed very subtle changes in the basic cation and SO_4^{2-} concentrations; values of both parameters were slightly elevated during summer and autumn and were slightly lower during spring high flow conditions. Unlike basic cation and SO_4^{2-} concentrations, all sites exhibited marked fluctuations in the concentrations of NO_3^-, Al and DOC. Concentrations of all parameters were highest during winter and spring and declined to minimum values in the summer and autumn.

Discussion

Temporal and spatial patterns in the water chemistry of the North Branch of the Moose River provide insight as to the nature of acid/base transformations that occur over a drainage area. In the acidic headwater reaches of the northern subbasin, equivalence of basic cations were low relative to equivalence of acidic anions (SO_4^{2-}, NO_3^-, Cl^-). This condition resulted in the dissolution of soil Al and the transport of significant concentrations of labile (inorganic) monomeric Al^{n+} and H^+ from soil to surface water. Coincident with this process was the export of relatively high concentrations of DOC and non-labile (organic) monomeric Al at these sites. Dissolved organic carbon is generally thought to be released from mineralization processes in the forest floor and organic soil horizons. As organic solutes migrate through the soil profile they complex Fe and Al and/or are microbially oxidized (Ugolini et al., 1977). These processes decrease the DOC to Al ratio and solubility of these solutes, resulting in direct precipitation or adsorption on free Fe and Al in the lower (B horizon) mineral soil (Schnitzer and Skinner, 1963a, b). Concentrations of DOC from freely draining Spodosols is usually low (McDowell and Wood, 1984).

The elevated concentrations of DOC and non-labile monomeric Al at sites draining the northern headwater reaches suggest that the acidic soils in this region of the catchment are experiencing intense soil development. It would appear that organic and alumino-organic solutes were not effectively retained in these shallow soils and were transported out of the profile with drainage water.

All waters draining into Big Moose Lake were greatly enriched with respect to DOC and non-labile monomeric Al relative to the outlet (Figures 2e, f). While uncertainties in seepage chemistry and water flux through Big Moose Lake make a quantitative evaluation difficult, differences in the concentrations of inflowing and outflowing water clearly indicate that the lake serves as a sink for DOC and alumino-organic solutes.

Longitudinal changes in the ANC of waters within the North Branch of the Moose River apparently were largely due to intrabasin variations in the release of basic cations from the soil. Alternatively, these variations could be attributed to in-lake retention of SO_4^{2-} and NO_3^-. For example, Schafran and Driscoll (1987) noted that the hypolimnetic depletion of NO_3^- in Dart's Lake coincided with neutralization of acidity. Rudd et al., (1986) reported that rates of SO_4^{2-} and NO_3^- reduction within Big Moose and Dart's Lake were comparable to values reported for other oxygenated waters. However, only minor longitudinal or temporal variations in SO_4^{2-} were evident for the North Branch of the Moose River (Figures 2d, 5, 6, 7). Apparently, the hydraulic retention time of these lakes is so short (< 0.5 yr; Table 1) that in-lake retention of SO_4^{2-} and NO_3^- was not a significant source of ANC generation within the basin (Kelly et al., 1987).

Coincident with increases in ANC were reductions in the concentration of labile monomeric Al as water migrated from the northern subbasin to Lake Rondaxe. Because of difficulty in making mass balance calculations, it is unclear whether this decrease in the concentration of labile monomeric Al was achieved by dilution with water containing relatively low concentrations of Al or by the conversion of aqueous to particulate Al within surface waters. To assess the potential for in-situ formation of particulate Al within the North Branch of the Moose River, we calculated saturation indicies (SI) with respect to the solubility of natural gibbsite (Figure 8). Headwater sites in the northern subbasin were generally highly undersaturated with respect to the solubility of natural gibbsite. These values suggest that labile monomeric Al was probably relatively conservative in these highly acidic waters. As water migrated through the northern subbasin SI values increased, approaching and at times exceeding the solubility of the $Al(OH)_3$ mineral phase. These calculations suggest that as acidic water was neutralized by higher ANC water there was potential for authigenic formation of particulate Al. In a more process-level study, Schafran and Driscoll (1987) reported that in-lake formation of particulate Al occurred in Dart's Lake. In-lake formation of particulate Al is significant because this process may influence the cycling of P (Dickson, 1978), DOC (Dickson, 1978; Effler et al., 1985) and trace metals (White and Driscoll, 1985) through coagulation and/or adsorption reactions.

In addition to these general trends, short-term changes in the water chemistry of the North Branch of the Moose River were noted. Seasonal fluctuations in pH, ANC and Al chemistry of sites within the watershed could largely be attributed to changes in the concentration of NO_3^- and DOC. Following the biologically active summer period, increases in the concentration of NO_3^- and DOC were generally noted in surface water starting in September (Figures 5, 6, 7). These concentrations increased during the winter season and generally peaked during snowmelt. Increased inputs of NO_3^- and DOC resulted in decreased pH and ANC and increased concentrations of both labile monomeric Al and non-labile monomeric Al. Note that elevated acidity during the winter/spring was generally restric-

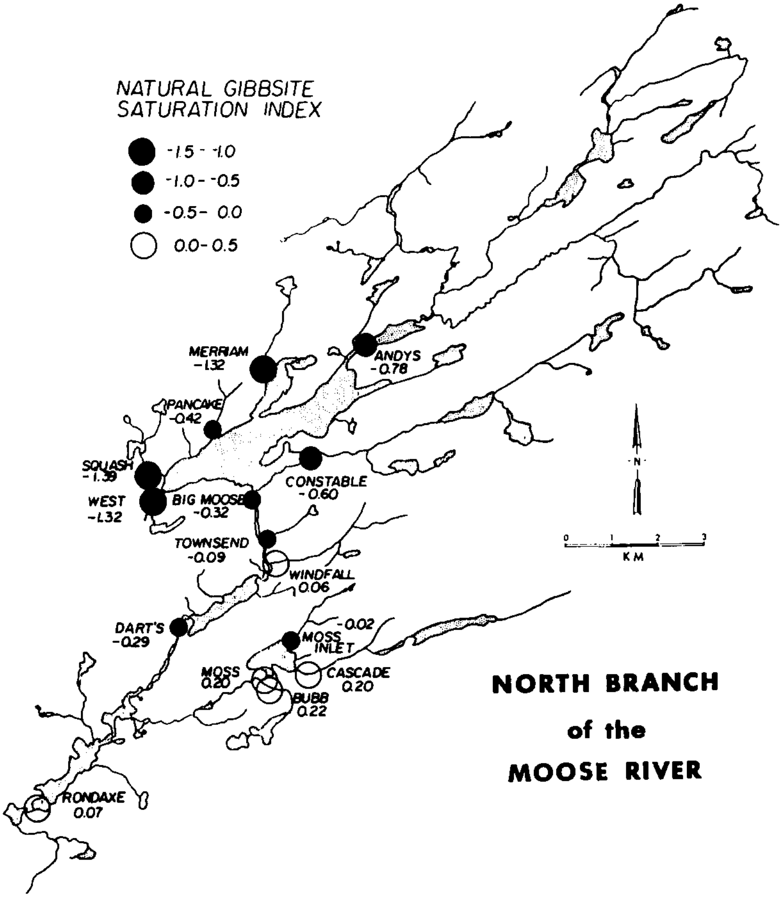

Figure 8. Trends in the saturation index (SI) with respect to the solubility of natural gibbsite of waters draining the North Branch of the Moose River.

ted to stream water and the ice water interface of lakes. Thermal stratification during ice-cover restricted mixing of acidic meltwater with deeper lake water.

Several investigators have reported that short-term increases in NO_3^- during snowmelt coincide with essentially stoichiometric increases in H^+ and labile monomeric Al in chronically acidic lakes in the west-central Adirondacks (Driscoll and Schafran, 1984; Schofield et al., 1985). While the source of this NO_3^- input is not evident, it may be due to some combination of 1) NO_3^- storage from snowpack (Galloway et al., 1980), 2) snowpack oxidation of NH_4^+, 3) reduced biological assimilation of N during winter, or 4) mineralization and oxidation of organic N within the soil (Rascher et al., 1987).

Differences in the magnitude of short-term changes in the water chemistry between the acidic (Dart's Lake; Figure 5) and circumneutral sites (Moss Lake; Figure 6) illustrate the role of Al and inorganic carbon in the pH buffering of two systems. In circumneutral Moss Lake, seasonal fluctuations in concentrations of NO_3^-, SO_4^{2-} and basic cations resulted in ANC fluctuations of 40 to 100 $\mu eq.l^{-1}$ between summer low flow and spring high flow conditions. Comparable variations in the concentration of NO_3^-, SO_4^{2-} and basic cations of acidic Dart's Lake produced seasonal ANC ranges of only 20 to 50 $\mu eq.l^{-1}$. This discrepancy in ANC fluctuation may be attributed to differences in the mechanisms of pH buffering at the two sites. Seasonal fluctuations in the equivalence of basic cations and acidic anions of acidic Dart's Lake resulted in pronounced changes in the concentration of labile monomeric Al (7 to 8 $\mu mol.l^{-1}$) and modest fluctuations in ANC. In Moss Lake these temporal variations in basic cation, SO_4^{2-} and NO_3^- concentrations resulted in considerably less dissolution of labile monomeric Al (1 to 2 $\mu mol.l^{-1}$) and translated directly into ANC fluctuations. These observations are consistent with the pH buffering model proposed by Driscoll and Bisogni (1984) for Adirondack drainage waters. These researchers indicated that in waters with pH values above 5.5 inorganic carbon buffering dominated, while at lower pH values the dissolution/hydrolysis of Al was the predominant mechanism controlling the pH buffering of dilute waters.

Because Lake Rondaxe is a mixture of waters draining the acidic northern subbasin and circumneutral eastern subbasin, the pH buffering reflects this mixture. During high flow winter/spring conditions inputs of HNO_3 and DOC, and to a lesser extent dilution of basic cations, resulted in acidification. During this season Al buffering was evident in Lake Rondaxe water. Under low flow conditions pH and ANC values increased, and pH buffering by dissolved inorganic carbon (DIC) predominated. Although Lake Rondaxe is a mixture of waters buffered by Al hydrolysis/dissolution (Dart's Lake) and DIC (the eastern subbasin), dilution reduced the effectiveness of both pH buffering systems. As a result, radical fluctuations in pH, ANC and Al were apparent over the annual cycle (Figure 7).

It is useful to place the magnitude of these short-term changes in perspective of surface waters at risk with respect to episodic acidification. As discussed previously, Colquhoun et al., (1984) reported that a large number of Adirondack lakes exhibited positive but low values of ANC. It is reasonable to assume that ANC values obtained from synoptic surveys conducted during summer low-flow periods are the highest values drainage lakes experience over the annual cycle. Based on results of temporal data from the North Branch of the Moose River, it is not unreasonable to anticipate that drainage waters with circumneutral summer pH values and ANC of 100 to 250 μeq.l^{-1} would experience snowmelt acidification by dilution of basic cations and inputs of NO_3^-, resulting in pH values near or below 5 and concentrations of labile monomeric Al of 1 to 5 μmol.l^{-1} (Figures 6, 7). Therefore, it would appear that a significant number of Adirondack waters are at a risk with respect to episodic acidification.

In some respects surface waters of the west-central Adirondacks are different than other acid-sensitive lake districts. An important characteristic is the extremely short hydraulic residence time of these lakes (Table 1). Kelly et al. (1987) have demonstrated that as the hydraulic retention time of lakes decreases the importance of in-lake production of ANC also decreases. Because of the short retention time of Adirondack lakes, in-lake generation of ANC is not as significant as reported for other regions (Rudd et al., 1986).

The chemical characteristics of Adirondack surface waters may also be somewhat unique. Nitrate concentrations appear to be elevated in the Adirondacks relative to other lake districts in eastern North America (Driscoll and Schafran, 1984). In the west-central Adirondacks, snowmelt acidification appears to be largely the result of nitric acid inputs coupled with dilution of basic cations. In other acid-sensitive regions episodic acidification has been attributed to basic cations and/or inputs of SO_4^{2-} (e.g. Johannessen et al., 1980; Cadle et al., 1984).

The short hydraulic retention times and elevated nitric acid inputs both serve to enhance the susceptibility of west-central Adirondack lakes to acidification. These characteristics undoubtedly contribute to the large number of acidic lakes in the Adirondack region (Colquhoun et al., 1984) relative to other lake districts in eastern North America and make interregional comparisons tenuous.

Conclusions

Significant spatial and temporal fluctuations in water chemistry were evident in the North Branch of the Moose River. Headwaters draining shallow acidic soils in the northern reaches of the watershed contained low concentrations of basic cations relative to the concentrations of acidic anions. These conditions resulted in low pH solutions with relatively high concentrations of labile monomeric Al. These acidic solutions contained relatively high concentrations of DOC and non-labile monomeric Al. As these headwaters migrated through Big Moose Lake, considerable loss of solution DOC and non-labile monomeric Al was evident. With increasing drainage area, solution acidity was largely neutralized by dilution with waters containing higher concentrations of ANC due to intrabasin variations in the release of basic cations from the soil.

Superimposed on these general trends were seasonal variations in the acid/base chemistry of these waters. Short-term changes in water chemistry were largely due to seasonal changes in NO_3^-, DOC and basic cation concentrations. Seasonal fluctuations in the ANC of circumneutral waters may be attributed to the predominance of inorganic carbon buffering, while similar changes produced moderate changes in the ANC of acidic sites due to the pH buffering of Al.

Lakes of the west-central Adirondacks are somewhat unique due to their short hydraulic residence times and elevated inputs of nitric acid during the winter/spring period, in comparison to other lake districts of eastern North America. These characteristics enhance surface water acidification and may contribute to the relatively large number of acidic lakes in this region.

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