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Processes regulating temporal and longitudinal variations in the chemistry of a low-order woodland stream in the Adirondack region of New York

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Abstract. Watershed processes influence the acid neutralizing capacity of surface waters by mediating changes in concentration of ionic solutes. Acidification of surface waters by atmospheric deposition of mineral acids and the extent to which ecosystem transformations neutralize this acidity are of particular concern. Seasonal variations in flow paths of water through soil and biological processes result in short-term changes in chemistry that may be critical to surface water ecology. In this study, we assessed longitudinal and temporal variations in the chemistry of a low-order stream, Pancake-Hall Creek, located in the west-central Adirondack region of New York. By quantifying changes in ionic solute concentration (e.g. Ca^{2+}, Al^{n+}, SO_4^{2-}, NO_3^-) we were able to evaluate processes responsible for short-term fluctuations in acid/base chemistry.

In the headwater sites, stream water was acidic; changes in pH, acid neutralizing capacity (ANC) and Al were primarily due to seasonal variations in basic cation and NO_3^- concentrations. At the downstream sites, water migrated through a large beaver impoundment and thick till resulting in higher pH, acid neutralizing capacity and basic cation concentrations, and lower concentrations of Al. Neutralization of acidity was particularly evident during the low flow summer period and coincided with retention of SO_4^{2-} in the beaver impoundment. During the high flow non-summer (October to June) period, depressed pH and ANC, and elevated Al concentrations were observed in the downstream sites. Acidic conditions during the non-summer period were not due to the oxidation of reduced sulfur deposits (e.g. SO_4^{2-} events) but rather the resumption of conservative SO_4^{2-} transport through the beaver impoundment (e.g. minimal SO_4^{2-} retention) coupled with increases in NO_3^-.

Introduction

Low ionic strength waters are characterized by weak buffering capacity, and therefore are susceptible to pronounced changes in solute concentrations. Acid neutralizing capacity (ANC) is an important parameter used to quantify acid/base chemistry of solutions; in this paper we define ANC as the ability of a solution to neutralize strong acid inputs. Acid neutralizing capacity is the equivalence of weak acid anions less free H^+ (Eq. 1) and is approximately equivalent to the sum of the basic cation equivalence, Al^{n+} and NH_4^+ less the strong acid anions (Eq. 2)

$$\mathrm{ANC} = [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{OH^-}] + [\mathrm{RCOO_w^-}] - [\mathrm{H^+}] \tag{1}$$

$$= C_B + [NH_4^+] + n[Al^{n+}] - 2[SO_4^{2-}] - [NO_3^-] - [Cl^-] - [F^-] - [RCOO_s^-] \qquad (2)$$

where C_B is the sum of basic cation equivalence ($2[Ca^{2+}] + 2[Mg^{2+}] + [Na^+] + [K^+]$), $[RCOO_w^-]$ is the equivalence of weakly acidic organic anions, and $[RCOO_s^-]$ is the equivalence of strongly acidic organic anions.

Several processes influence the acid/base chemistry of drainage waters (van Breemen et al., 1983). Transformations which alter the concentration of ionic solutes (e.g. Ca^{2+}, SO_4^{2-}) will, because of electroneutrality constraints, result in changes in ANC. Because of recent concern (Altshuller and Linthurst, 1984) and controversy (Krug and Frink, 1983) over the impact of atmospheric deposition of strong acids on the chemistry of low ionic strength waters, an understanding of acid/base transformations in acid-sensitive watersheds is desirable. Johnson (1979) and Johnson et al. (1981) suggested that neutralization of acidic deposition within the Hubbard Brook Experimental Forest in New Hampshire occurred by a two-step process. Strong acid inputs from atmospheric deposition were initially neutralized by dissolution of free Al (non-silicate bound) in shallow acidic soils, resulting in transport of acidic cations (H^+, Al^{n+}) to headwater stream reaches. With increasing drainage area, soil depth increased, causing a greater retention time of water within the mineral soil and subsequent neutralization of acidic cations by the release of C_B. Neutralization of mineral acid inputs can also be accomplished by processes which result in retention of acidic anions (SO_4^{2-}, NO_3^-), such as anion adsorption (Johnson and Todd, 1983), or biologically mediated reduction reactions (Kelly et al., 1982; David et al., 1983).

Seasonal transformations can also cause short-term changes in water chemistry. Several researchers have reported that concentrations of H^+ and Al were highest during winter and spring in surface waters draining acid-sensitive regions (Schofield and Trojnar, 1980; Driscoll and Schafran, 1984; Schofield et al., 1985; Driscoll et al., 1987). In the northeastern U.S., short-term increases in acidic cation concentrations during periods of high discharge have been attributed to dilution of basic cation concentrations and/or increased inputs of NO_3^- (Galloway et al., 1980; Driscoll and Schafran, 1984; Driscoll et al., 1987; Rascher et al., 1987). In systems that strongly retain SO_4^{2-} by reduction (e.g. wetlands) the potential also exists for the subsequent oxidation of this reduced S. The oxidation of reduced S during low flow periods (e.g. summer), followed by an increase in discharge (e.g. autumn rainfall events) could result in short-term release of sulfuric acid to drainage waters. Pulsed inputs of acidic cations may deleteriously affect aquatic organisms (Schofield and Trojnar, 1980; Henriksen et al., 1984; Hall et al., 1985).

The purpose of our study was to evaluate the extent of longitudinal and temporal variations in the water chemistry of a low-order Adirondack stream. By evaluating changes in the concentration of ionic solutes such as C_B, NH_4^+, Al^{n+}, SO_4^{2-} and NO_3^-, we assessed the processes responsible for fluctuations in ANC. Critical to this analysis was an evaluation of the distribution of aqueous Al in stream water.

Study site and methods

The study site, Pancake-Hall Creek, is located in the Adirondack region of New York (Figure 1; 43°50′N, 74°52′W). The stream is first and second order with a watershed drainage area of 74 ha. It drains into Big Moose Lake and is a tributary of the North Branch of the Moose River. Vegetation is primarily deciduous (*Acer saccharum, Fagus grandifolia, Betula alleghaniensis*) with small stands of coniferous species (*Picea rubens, Abies balsamea, Tsuga canadensis*). The surficial geology is primarily thin till (< 3 m depth) although deposits of thick till (> 3 m depth) occur in the lower elevations. Soils are generally acidic with relatively low concentrations of exchangeable basic cations (Newton et al., 1987).

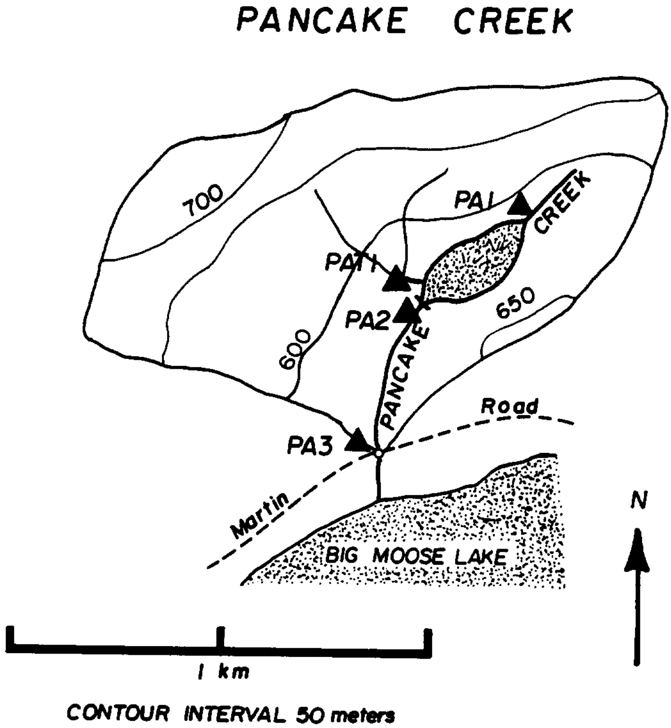

Figure 1. Watershed map of Pancake-Hall Creek. Stream sampling sites are located above (PAT1, PA1) and below (PA2, PA3) a beaver impoundment.

Four sites within the Pancake-Hall catchment were monitored at monthly intervals from January 1984 to January 1985. Site PA1 is first order, while the other sites (PA2, PA3, PAT1) are second order. Sites PA2 and PA3 are located downstream from a large beaver impoundment (Figure 1). Stream solutions were analyzed for all major solutes using methods summarized in Table 1. Monomeric Al extractions and pH measurements were accomplished shortly after collection to minimize chemical transformations due to temperature changes and degassing of CO_2. Samples were refrigerated ($< 4\,^{\circ}C$) and transported to the water chemistry laboratory at Syracuse University. Following filtration (Whatman GF/C), aliquots were measured for dissolved inorganic carbon (DIC) and ampoulated for dissolved organic carbon (DOC) analysis within 48 hours of collection. Samples were stored at 4 °C until all other water chemistry determinations were completed.

We used the fractionation procedure of Driscoll (1984) to evaluate the distribution of aqueous Al. In this procedure, monomeric Al is separated into two fractions: labile monomeric Al, which is thought to include aquo

Table 1. Analytical methods

Parameter	Method	Reference
SO_4^{2-}, NO_3^-, Cl^-	Ion chromatography	Small et al., 1975
NH_4^+	Phenate colorimetry; autoanalyzer	US EPA, 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
Total F	Potentiometrically with ion selective electrode after TISAB addition	Orion, 1976
Total Al	Acid digestion (1 hr, pH 1), 8-hydroxyquinoline extraction into methyl isobutyl ketone (MIBK), analysis by AAS, graphite furnace	Barnes, 1976; Driscoll, 1984
Monomeric Al	Field extraction by 8-hydroxyquinoline into MIBK, analysis by AAS graphite furnace	Barnes, 1976 Driscoll, 1984
Non-labile monomeric Al	Fractionation by ion exchange column, analysis for monomeric Al	Driscoll, 1984
Specific conductance	Conductivity bridge	Standard methods, 1985
Dissolved oxygen	Modified Winkler	US EPA, 1983
Temperature	Thermometer	

Table 2. Forms of inorganic aluminum.

Parameter	
Aluminum hydroxide complexes	$\mathrm{Al{-}OH} = [\mathrm{Al(OH)}^{2+}] + [\mathrm{Al(OH)}_2^+] + [\mathrm{Al(OH)}_4^-]$
Aluminum fluoride complexes	$\mathrm{Al{-}F} = [\mathrm{AlF}^{2+}] + [\mathrm{AlF}_2^+] + [\mathrm{AlF}_3] + [\mathrm{AlF}_4^-] + [\mathrm{AlF}_5^{2-}] + [\mathrm{AlF}_6^{3-}]$
Aluminum sulfate complexes	$\mathrm{Al{-}SO}_4^{2-} = [\mathrm{AlSO}_4^+] + [\mathrm{Al(SO_4)}_2^-]$
Aluminum equivalence	$\mathrm{nAl}^{n+} = 3[\mathrm{Al}^{3+}] + 2[(\mathrm{Al{-}OH})^{2+}] + [\mathrm{Al(OH)}^+] + 2[\mathrm{AlF}^{2+}] + [\mathrm{AlF}_2^+] + [\mathrm{AlSO}_4^+] - [\mathrm{Al(OH)}_4^-] - [\mathrm{AlF}_4^-] - 2[\mathrm{AlF}_5^{2-}] - 3[\mathrm{AlF}_6^{3-}] - [\mathrm{Al(SO_4)}_2^-]$

Al (Al^{3+}) as well as OH^-, F^- and SO_4^{2-} complexes of mononuclear Al (Al–OH, Al–F and Al–SO_4, respectively; Table 2), and non-labile monomeric Al, which is an estimate of Al associated with organic solutes. The distribution of Al (Table 2) was calculated with a chemical equilibrium model. Details of the numerical methods and thermochemical data used in these calculations are found in Driscoll and Schecher (1985) and Ball et al. (1980), respectively.

Temporal and longitudinal trends in water chemistry were evaluated with a two-way analysis of variance. Seasonal differences in water chemistry between sites were assessed with a Duncan's multiple-range test. Linear regression analyses were calculated between ANC and major ionic solutes; the significance of these regressions were evaluated with F statistics.

Results

Water chemistry at sites above (PAT1, PA1) and below (PA2, PA3) the beaver impoundment were similar; therefore, representative data from sites PAT1 and PA3 will be used to illustrate general trends in water chemistry (Figures 2, 3; Table 3). Pancake-Hall Creek was generally acidic, containing elevated concentrations of labile monomeric Al (greater than 5 μmol. l^{-1}). Sulfate was the predominant anion and Ca^{2+} the major cation at all sites on all sampling dates.

In addition to these general characteristics, we observed a variety of short-term fluctuations in water chemistry. Subtle changes in water chemistry occurred above the beaver impoundment. pH and ANC values were lowest during the winter/spring (December–June) period and increased to maximum values during the low flow summer period (July–September) (Table 3). Acidic conditions in winter/spring coincided with low concentrations of basic cations and high concentrations of NO_3^- (Figure 2; Table 3). During the summer period, basic cation concentrations were elevated and NO_3^- concentrations were reduced, resulting in less acidic conditions. Although seasonal fluctuations in SO_4^{2-} concentration occurred (Table 3), they did not coincide with the changes in ANC (Figure 2).

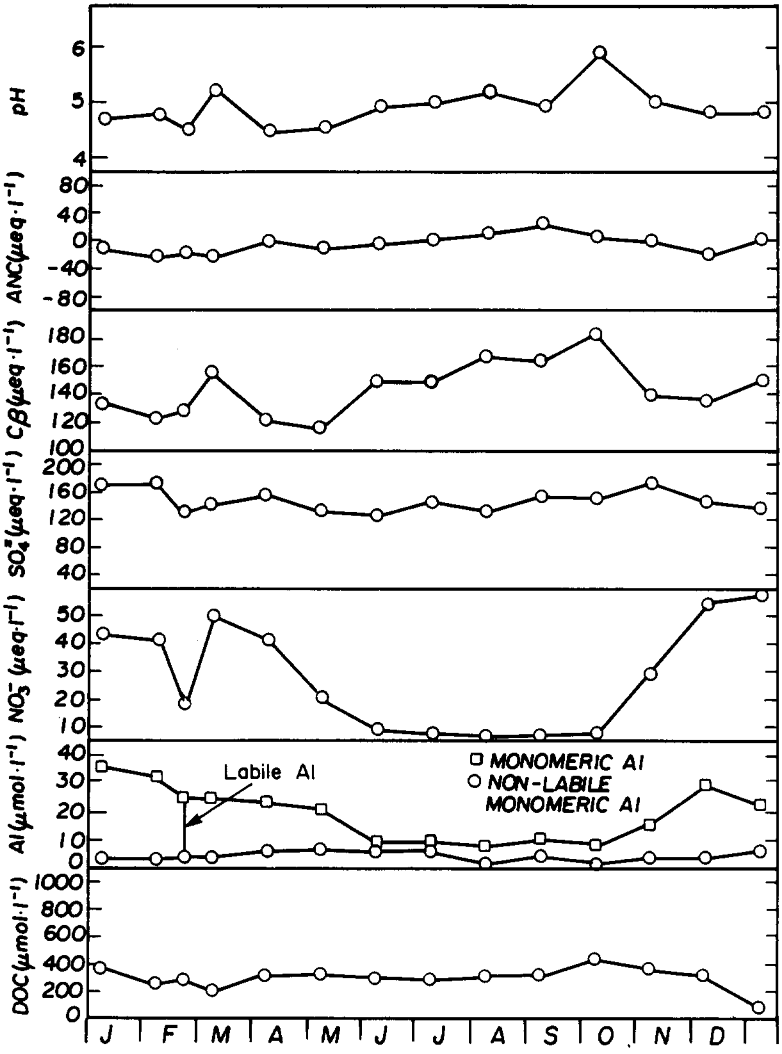

Figure 2. Values of pH, ANC, equivalence of basic cations (C_B; Ca^{2+}, Mg^{2+}, Na^+, K^+), SO_4^{2-}, NO_3^-, monomeric Al fractions and dissolved organic carbon (DOC) at Pancake-Hall Creek tributary (site PAT1) during the study period.

For example, SO_4^{2-} decreased in February (from 174 to 134 $\mu eq.l^{-1}$), a period of low pH and ANC, and increased in August (from 135 to 158 $\mu eq.l^{-1}$), a period of relatively high pH and ANC.

Concentrations of monomeric Al exhibited pronounced seasonal variations; these fluctuations were almost entirely due to changes in the labile

Table 3. Mean values of solute concentrations at sites PAT1 and PA3 for summer (July–September), and nonsummer (October–June) periods. Mean ± SD and ranges for solute concentrations at sites PAT1 and PA3 over the entire study period

Parameter	Site	Annual mean ± standard deviation	Range	Summer mean	Non-summer mean
pH	PAT1	4.9 ± 0.3	4.5 to 5.9	5.3	4.7
	PA3	5.3 ± 0.5	4.7 to 6.1	6.0	5.0
ANC (μeq.l^{-1})	PAT1	−5 ± 13	−22 to 26	11	−11
	PA3	10 ± 25	−24 to 60	44	−4
C_B (μeq.l^{-1})	PAT1	144 ± 17	117 to 175	163	137
	PA3	163 ± 15	133 to 190	164	163
NH_4^+ (μeq.l^{-1})	PAT1	0.9 ± 1.6	0 to 6.4	0.3	1.1
	PA3	4.1 ± 3.3	0 to 12	4.0	4.2
SO_4^{2-} (μeq.l^{-1})	PAT1	152 ± 13	135 to 174	149	153
	PA3	124 ± 33	59 to 155	77	143
NO_3^- (μeq.l^{-1})	PAT1	28 ± 19	5.1 to 58	6.6	37
	PA3	23 ± 16	7.8 to 59	8.6	29
Cl^- (μeq.l^{-1})	PAT1	10 ± 2	7.5 to 15	11	9.6
	PA3	13 ± 5	6.9 to 27	16	12
labile monomeric Al (μeq.l^{-1})	PAT1	35 ± 24	0.6 to 76	7.5	45
	PA3	12 ± 11	0.2 to 36	0.3	17
non-labile monomeric Al (μmol.l^{-1})	PAT1	4.2 ± 1.2	2.6 to 6.1	3.8	4.3
	PA3	3.9 ± 1.0	2.4 to 5.3	3.9	3.9
DOC (μmol C.l^{-1})	PAT1	308 ± 77	99 to 444	348	293
	PA3	474 ± 224	82 to 1010	822	334

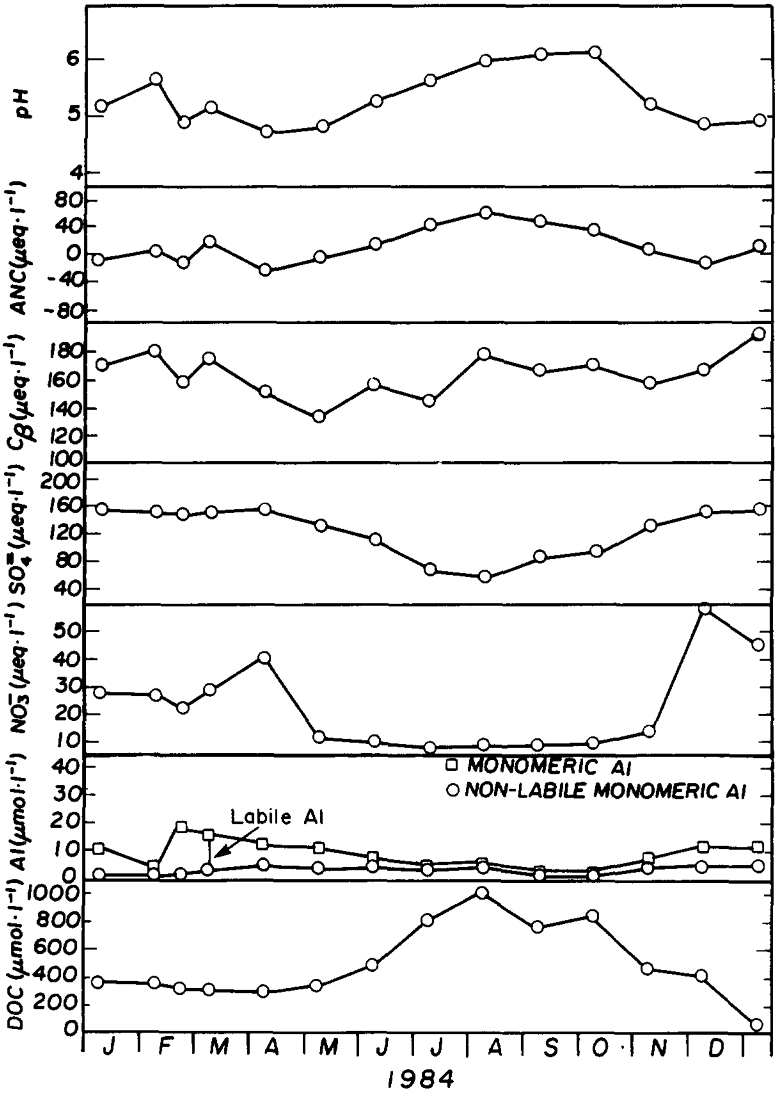

Figure 3. Values of pH, ANC, equivalence of basic cations (C_B; Ca^{2+}, Mg^{2+}, Na^+, K^+) SO_4^{2-}, NO_3^-, monomeric Al fractions and dissolved organic carbon (DOC) below the beaver impoundment at Pancake-Hall Creek (site PA3) during the study period.

(inorganic) fraction of monomeric Al (Figure 2). Concentrations of DOC and non-labile monomeric Al were constant throughout the study period at site PAT1. Changes in the concentration of labile monomeric Al were coincident with pH fluctuations. Concentrations of labile monomeric Al were also strongly correlated with NO_3^- ($Al^{n+} = 7.7 + 0.95 NO_3^-$; in $\mu eq.l^{-1}$, $P < 0.001$, $r^2 = 0.61$) and this relationship was nearly stoich-

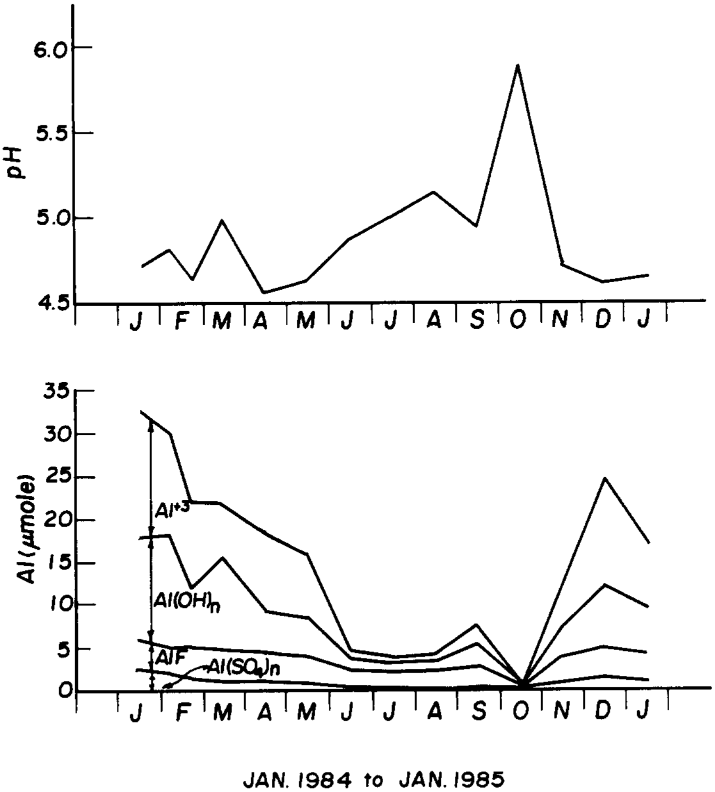

Figure 4. pH and distribution of labile monomeric Al at Pancake-Hall Creek tributary (site PAT1) over the study period. Al^{3+} is aquo aluminum, Al–OH, Al–F, Al–SO_4 represent hydroxide, fluoride and SO_4^{2-} complexes of monomeric Al, respectively.

iometric. Under acidic conditions, aquo Al (Al^{3+}) and Al–OH complexes were the dominant forms of labile monomeric Al (Figure 4), while concentrations of Al–F and Al–SO_4 complexes were low and less significant. During summer, more neutral pH conditions induced a decline in the concentrations of Al^{3+} and Al–OH complexes, resulting in Al–F complexes as the dominant form of labile monomeric Al.

Water chemistry of downstream sites (PA2, PA3) was influenced by the beaver impoundment (Figure 3; Table 3). Generally, pH, ANC and basic cation values were elevated following transport of water through the beaver impoundment and the thicker till located within the lower reaches (Table 3, 4). These increases were most pronounced during the summer (Table 3, 4). In addition, depletion of SO_4^{2-}, and release of NH_4^+ and DOC within the beaver impoundment were evident during the low-flow summer period (Table 3, 4). Although these trends might suggest low dissolved oxygen concentrations at downstream sites, values from the water column

Table 4. Comparison of solute concentrations between sites PAT1 and PA3 for summer (July–September), non-summer (October–June) and annual periods using Duncan's multiple-range test.

Parameter	Annual	Summer	Non-summer
pH	**	**	*
ANC	**	**	NS
C_B	*	NS	**
NH_4^+	**	*	NS
SO_4^{2-}	**	**	NS
NO_3^-	NS	NS	NS
Cl^-	*	NS	NS
Al^{n+}	**	NS	**
non-labile monomeric Al	NS	NS	NS
DOC	**	**	NS

*P < 0.05, **P < 0.01, NS = not significant.

at site PA2 ranged from 290 to 360 μmol $O_2.l^{-1}$ (68 to 88% saturation).

Like site PAT1, concentrations of NO_3^- and labile monomeric Al were elevated during the non-summer period and low during the summer period at sites below the beaver impoundment (Table 3). These values, again, were correlated (e.g. at site PA3, $Al^{n+} = 0.8 + 0.47NO_3^-$; in μeq.l^{-1}; $P < 0.001$, $r^2 = 0.46$); however correlations at downstream sites were weaker than upstream sites and substoichiometric. Nitrate concentrations were not significantly different above and below the beaver impoundment and differences in Al^{n+} concentrations were only evident during the non-summer period (Table 3, 4). We were not able to discern statistically significant differences in concentrations of non-labile monomeric Al above and below the beaver impoundment.

To quantitatively assess the contribution of watershed processes to the short-term generation/consumption of ANC, linear regression analyses were performed on ionic solutes with respect to ANC (Table 5). Above the beaver impoundment ANC was positively correlated with basic cation

Table 5. Slope, r^2 value and significance level of linear regression analyses between acid neutralizing capacity and major ionic solutes at sites PAT1 and PA3 in Pancake-Hall Creek. All values are expressed in μeq.l^{-1}, except for DOC which is expressed as μmol C.l^{-1}

Parameter	PAT1		PA3	
	Slope	r^2	Slope	r^2
C_B	0.43	0.32*	0.8	0.12
NH_4^+	−0.46	0.003	1.29	0.35**
Al^{n+}	−0.41	0.54**	−2.16	0.53**
SO_4^{2-}	−0.11	0.01	−0.85	0.76**
NO_3^-	−0.43	0.41*	−1.57	0.60**
Cl^-	2.35	0.15	2.59	0.16
DOC	0.031	0.03	0.11	0.65**

*P < 0.05; **P < 0.01.

concentrations and negatively correlated with NO_3^- and Al^{n+}, while below the beaver impoundment, ANC was positively correlated with NH_4^+ and DOC, and negatively correlated with Al^{n+}, SO_4^{2-} and NO_3^- (Table 5).

Discussion

Stream chemistry unimpacted by beaver activity

A variety of processes affect the ANC of Pancake-Hall Creek. Trends in the water chemistry of the upstream site (PAT1), unlike the downstream sites (PA2, PA3) were uninfluenced by the beaver impoundment. Regression analyses suggest that short-term changes in ANC at this upstream site were influenced by changes in basic cation, Al^{n+} and NO_3^- concentrations (Table 5). The slope of significant regressions between ANC and other solutes is important because it represents the extent to which a change in the concentration of an ionic solute alters ANC. Our observations were consistent with trends reported by other investigators for surface waters in the west-central Adirondacks (Galloway et al., 1980; Schofield et al., 1985; Driscoll et al., 1987).

Chen et al. (1984) reported that during low flow periods, groundwater, which is enriched in basic cation and ANC from contact with the lower mineral soil, comprises the bulk of total stream discharge. During high flow periods (e.g. spring snowmelt), the rate of infiltration exceeds the hydraulic conductivity of the soil, therefore, water migrates through organic horizons and upper mineral soil prior to surface waters discharge. During this time, water apparently by-passes the lower mineral soil resulting in acidification of surface waters by dilution of groundwater inputs. In addition, Rascher et al. (1987) reported that mineralization of organic N in the organic soil horizons and subsequent nitrification was responsible for nitric acid inputs to surface waters in the west-central Adirondacks.

Observations from the upper reaches (sites PAT1, PA1) of Pancake-Hall Creek suggest that during high flow periods in winter/spring, nitric acid inputs derived from water movement through the organic rich upper soil and dilution of groundwater by meltwater runoff were primarily responsible for short-term reductions in ANC. Furthermore, seasonal variations in NO_3^- coincided with variations in biological activity. During summer, low concentrations of stream NO_3^- were undoubtedly due to assimilation by vegetation. As biological activity decreased in the autumn, NO_3^- concentrations increased. Biological activity also presumably altered stream water chemistry by mediating water movement through the catchment. Transpiration during summer reduced discharge and increased the pathlength of water within the mineral soil resulting in a greater contribtuion of basic cations and ANC enriched groundwater to total stream flow.

The magnitude of slopes from the linear regression analyses for site

PAT1 between both basic cation and NO_3^- concentrations with ANC indicate that short-term concentration changes in these parameters resulted in ANC changes (Table 5). Inputs of strong acid (e.g. NO_3^-) or strong base (e.g. C_B) do not result in an equivalent change of ANC in acidic solutions (pH < 5.5) because of pH buffering by the dissolution/hydrolysis of Al (Driscoll and Bisogni, 1984; Driscoll et al. 1987). Concentrations of Al increased with decreasing pH and ANC (Figure 2; Table 5) at Pancake-Hall Creek; therefore, the release of Al from soil reduced the extent of ANC decrease during acidification (e.g. negative slope from regression analysis with ANC). Slopes of regression analyses between basic cation, NO_3^- and Al^{n+} concentrations with ANC at site PAT1 were all less than one indicating that a given change in the concentration of any of these solutes resulted in less than an equivalent change in ANC (Table 5). These substoichiometric reactions reflect the comparable magnitude of short-term changes in basic cation, NO_3^- and Al^{n+} concentrations at site PAT1 (Figure 2; Table 3) and indicate that all these transformations contributed to observed variations in ANC. For example, a comparison of summer and non-summer mean values of ANC suggest that there is a difference of 22 μeq.l^{-1} between the two periods (Table 3). The reduction in ANC during the non-summer period relative to the summer can be largely explained by a decrease in basic cation concentrations ($\Delta C_B = -26\,\mu eq.l^{-1}$) and increase in NO_3^- ($\Delta NO_3^- = 30\,\mu eq.l^{-1}$), coupled with an increase in Al ($\Delta Al^{n+} = 37\,\mu eq.l^{-1}$) ($\Delta ANC = -22\,\mu eq.l^{-1} \simeq \Delta C_B + \Delta Al^{n+} - \Delta NO_3^- = -19\,\mu eq.l^{-1}$).

The strong correlations between Al^{n+} and NO_3^- at Pancake-Hall Creek and other sites in the northeastern U.S. (Johnson et al., 1969; Driscoll and Schafran, 1984; Driscoll et al., 1987) is somewhat perplexing. Rascher et al. (1987) suggested that NO_3^- loss to surface waters during winter/spring was largely due to mineralization/nitrification in the forest floor; however, Al concentrations in forest floor leachates were low. Other studies (David and Driscoll, 1984; Driscoll et al., 1985) have indicated that Al exported from the forest floor is largely associated with organic solutes (non-labile). Given the current thinking of water flow paths through soil during high discharge periods (Chen et al., 1984), the source of labile monomeric Al is unclear. Nitric acid release of labile monomeric Al may possibly occur in the upper mineral soil (e.g. E horizon) or directly in the stream bed (Hall et al., 1980; Norton and Henriksen, 1984). In view of the apparent significance of episodic inputs of acidic cations to surface waters (e.g. Leivestad and Muniz, 1976; Henriksen et al., 1984), additional research on the source of this mobile Al is warranted.

Driscoll (1984) reported that concentrations of labile monomeric Al increased exponentially with decreases in pH, while non-labile monomeric Al was strongly correlated with concentrations of dissolved organic carbon (DOC) in acidic waters in the northeastern U.S. The Al chemistry in

Pancake-Hall Creek was consistent with these patterns. Also, the distribution of inorganic forms of Al were similar to previous observations of Adirondack surface waters (Driscoll et al., 1984; Schafran and Driscoll, 1987). The speciation of aqueous Al is pH dependent (Figure 4). At low pH values, aquo Al and Al–OH were the most significant forms of labile monomeric Al, while Al–F predominated at more neutral pH values. Although concentrations of total F were low (3.2–4.0 μmol. l^{-1}) in Pancake-Hall Creek, F forms extremely strong complexes with Al (Roberson and Hem, 1969). Therefore, the concentration of Al–F was apparently limited by the concentration of total F available. Concentrations of nonlabile monomeric Al were low and little seasonal fluctuation was evident. Note that this pattern is similar to trends in DOC (Figure 2).

The influence of a beaver impoundment on stream chemistry

The same processes that modified the ANC at site PAT1 were generally relevant downstream from the beaver impoundment (sites PA2, PA3; Table 5), although changes in ANC were not significantly correlated with basic cation concentrations at any other sites. In addition to NO_3^- and Al^{n+}, changes in NH_4^+, SO_4^{2-} and DOC were correlated to changes in ANC at downstream sites (Table 5). Differences in ANC above and below the beaver impoundment were only evident during summer low flow conditions and coincided with statistically significant changes in NH_4^+, SO_4^{2-} and DOC concentrations (Table 4). The magnitude of change in these ionic solute concentrations is noteworthy. The difference between summer and non-summer mean concentrations (or range) of SO_4^{2-} (66 μeq. l^{-1}) was much greater than other ionic solutes (NH_4^+, 0.2 μeq. l^{-1}; Al^{n+}, 17 μeq. l^{-1}; NO_3^-, 20 μeq. l^{-1}) that were strongly correlated with ANC at site PA3 (Table 4). The magnitude of these latter concentration changes were consistent with the slopes obtained from the ANC regression analyses. The slope of SO_4^{2-} regression with ANC was slightly greater than negative one (Table 5) suggesting that a given change in SO_4^{2-} could account for much of the corresponding change in ANC. Slopes of regression analyses with NH_4^+, Al^{n+} and NO_3^- were all greater than one or less than negative one, which would apparently indicate that a given change in concentration of these solutes produces greater than a stoichiometric change in ANC. Since greater than stoichiometric changes are not possible, variations in NH_4^+, Al^{n+} and NO_3^- concentration merely coincided with variations in ANC. Therefore, SO_4^{2-} transformations were principally responsible for short-term changes in ANC at site PA3.

Changes in DOC may be used to indicate inputs of organic acids to the stream water. One might anticipate that the large release of DOC and organic acids from the beaver impoundment during the summer season would result in the acidification of downstream waters. However, we observed that DOC was positively correlated with ANC below the beaver impoundment. Naturally occurring organic solutes have a range of proton dissociation constants (pKa values from 1 to 13; Thurman, 1985). If these dissociation constants are below the equivalence point of ANC (ANC = 0 at approximately pH 5.1) they act as strong acids ($RCOO_s^-$) and serve to depress the ANC (Eq. 2). However, if dissociation constants are generally above the ANC equivalence point, they act as weak acids ($RCOO_w^-$) and do not influence ANC (Eq. 1). The positive correlation between ANC and DOC indicates that organic acid inputs were not exerting a predominant influence on the acid/base chemistry of streamwater below the beaver impoundment. Rather, the increase in ANC due to reduction process (e.g. SO_4^{2-} retention) appeared to more than offset any acidification due to organic acid inputs.

Although large seasonal changes in DOC were apparent below the beaver impoundment there was little variation in the concentration of non-labile monomeric Al (Driscoll, 1984). This trend was somewhat surprising given that DOC is generally correlated with this fraction of Al (Driscoll, 1984). Apparently the Al content of organic solutes released from the beaver impoundment was considerably lower than that derived from terrigenous inputs.

During winter/spring, decreases in pH and increases in NO_3^- and Al^{n+} occurred in the lower reaches of Pancake-Hall Creek (Figure 3). However, the magnitude of this short-term acidification was not as extreme as observed in first order reaches despite comparable concentrations of NO_3^-. Downstream sites generally contained higher basic cation concentrations during the winter season (Table 3, 4) resulting in the attenuation of these acidification events. Higher basic cation concentrations may have been the result of thicker glacial till in the lower reaches of the watershed (Newton et al., 1987).

Although changes in ANC induced by SO_4^{2-} retention in the beaver impoundment were pronounced, they were only evident in the summer (Table 4). During the non-summer period, SO_4^{2-} concentrations were relatively constant and similar to upstream values. The exact location of S retention within the beaver impoundment is unclear; however, the reservoir is shallow (less than 1 m mean depth) and contains large deposits of organic matter immediately behind the dam and within the impoundment. The impoundment increases the hydraulic retention time within these organic deposits undoubtedly enhancing S reduction. During the summer period, reduced flow exposes organic deposits previously saturated with water. However, the absence of pulsed increases in SO_4^{2-} associated with autumn discharge indicates that oxidation of reduced S was not extensive during the low flow summer period. Apparently the beaver impoundment served as a SO_4^{2-} sink during the low flow summer period and was not a significant source of SO_4^{2-} at any time during the annual cycle. Because the study period was limited (1 year) it is conceivable that extreme drought conditions followed by high discharge could induce short-term acidification from the release of H_2SO_4. Numerous studies indicate that seasonal variations in SO_4^{2-} are generally subtle in the northeastern U.S. (Likens et al., 1977; Galloway et al., 1980; Driscoll et al., 1987); therefore autumn SO_4^{2-} events would not appear to be a widespread phenomenon in these regions.

Conclusions

We observed temporal and longitudinal variations in the pH, ANC and Al of Pancake-Hall Creek. Processes responsible for these transformations were generally consistent with observations reported by other investigators for watersheds in the northeastern U.S. At sites above the beaver impoundment, the equivalence of SO_4^{2-} and NO_3^- exceeded basic cation concentrations resulting in elevated concentrations of H^+ and Al^{n+}. Seasonal changes in pH, ANC and Al^{n+} at these sites were primarily due to changes in the concentrations of NO_3^- and basic cations. Neutralization of H^+ and Al^{n+} acidity at the downstream sites was accomplished by increased concentrations of basic cations as a result of thicker glacial till deposits and during the summer season by retention of SO_4^{2-} as water migrated through a beaver impoundment. Although short-term changes in the ANC of downstream reaches were largely accomplished by seasonal variations in SO_4^{2-}, pulsed inputs of sulfuric acid due to oxidation of reduced S in the beaver impoundment were not evident.

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