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Longitudinal and seasonal patterns of stream acidity in a headwater catchment on the Appalachian Plateau, West Virginia, U.S.A.

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Abstract. The chemical composition during baseflow was used to elucidate the fundamental processes controlling longitudinal and seasonal patterns of stream acidity in Yellow Creek, a chronically acidic headwater (pH range 3.7–4.2) on the Appalachian Plateau in northeastern West Virginia. Sulfate concentrations controlled the variability of stream acidity within the Yellow Creek catchment. Decreases in stream free H^+ acidity with decreasing elevation likely resulted from SO_4^{2-} retention in riparian wetland areas as well as spatial variation in dominant tree species. Seasonal variations in free H^+ and inorganic monomeric aluminum (Al^{n+}) concentrations appeared related to seasonal fluctuations in baseflow discharge which was controlled by vegetative activity. Baseflow stream discharge, as well as H^+ and Al^{n+} acidity, gradually declined during the growing season (June through October), likely reflecting microbial SO_4^{2-} reduction in saturated anaerobic environments within riparian wetlands. A marked pulse of stream H^+, Al^{n+}, and SO_4^{2-} coincided with an abrupt increase in baseflow discharge resulting from the cessation of transpiration after leaf-fall in November. This seasonal pattern suggests that autumn may be a critical period for eastern brook trout in streams draining wetlands on the Appalachian Plateau.

Introduction

Surface water acidification is a serious environmental problem in industrialized regions of the world (e.g., Steinberg & Wright 1994). Despite reductions in SO_2 emissions and subsequent declines in atmospheric S deposition, little recovery of acidic surface waters is evident in regions of the eastern U.S. (Driscoll & van Dreason 1993; Likens et al. 1996; Burns et al. 1998; Driscoll et al. 1998). The acid-base chemistry of surface waters is of concern because acidity can represent an important stress to aquatic ecosystems with low values of acid neutralizing capacity (ANC; e.g., Baker et al. 1990). The longitudinal and seasonal patterns of stream acidic cation (H^+, inorganic monomeric Al (Al^{n+})) concentrations are potentially critical to aquatic ecology, as spatial variations in these solutes can affect the distribution of fish within catchments (Schofield & Driscoll 1987) while temporal changes may be lethal to aquatic biota (Baker et al. 1996). The ultimate sources of surface water acidity include: (1) atmospheric deposition of strong acids (H_2SO_4, HNO_3), (2) generation of organic acids within the terrestrial environment, (3) microbial oxidation reactions within wetlands, and (4) dissolution of S-bearing minerals (van Breemen et al. 1984).

Hydrological and biogeochemical processes influence patterns of surface water acid-base chemistry within upland forested catchments. Under baseflow conditions, stream water is primarily derived from soil solutions; baseflow acid-base chemistry is therefore strongly related to aqueous H^+ transformations occurring in the subsurface environment. The mechanisms contributing to the production of ANC are: (1) geochemical weathering and exchange reactions replacing aqueous H^+ with dissolved basic cations (C_B: Ca^{2+}, Mg^{2+}, Na^+, K^+), (2) adsorption of dissolved strong acid anions (e.g. SO_4^{2-}) to positively charged soil surfaces, and (3) biological reduction and assimilation of strong acid anions (SO_4^{2-}, NO_3^-; Driscoll & Likens 1982). Dilute acidic surface waters generally drain soils characterized by small pools of readily available C_B (i.e. easily weathered or exchanged) as well as by limited capacity to retain strong acid anions.

Spatial variation in the sources and sinks of aqueous H^+ result in longitudinal patterns of surface water acid-base chemistry. Within watersheds 5 (W5) and 6 (W6) at the Hubbard Brook Experimental Forest (HBEF), upper elevation stream reaches draining coniferous terrain exhibit higher stream SO_4^{2-}, dissolved organic carbon (DOC), and free H^+ acidity concentrations relative to lower elevation reaches where hardwoods are abundant (Lawrence et al. 1986). Spatial patterns in rates of C_B release from soils caused longitudinal gradients in surface water acid-base chemistry within the North Branch of the Adirondack Moose River system (Driscoll et al. 1987a) and within the Falls Brook watershed at the HBEF (Johnson et al. 1981). Wetlands within a watershed can influence longitudinal patterns in stream free H^+ acidity through SO_4^{2-} retention via microbial reduction (Wieder & Lang 1984; Driscoll et al. 1987b).

Temporal changes in biological activity and subsurface hydrological flowpaths can result in seasonal variations in surface water acid-base chemistry. Seasonal variations in surface water H^+ and Al^{n+} acidity within Adirondack catchments are strongly related to seasonal changes in NO_3^- concentrations (Driscoll & Schafran 1984; Schafran & Driscoll 1987; Driscoll & van Dreason 1993). Seasonal patterns in the free H^+ acidity of surface waters draining wetlands can be influenced by temporal water table fluctuations in the soil, with wetlands acting as sinks for aqueous H^+ when the water table is falling during the growing season but acting as sources for surface water H^+ when the water table is rising during autumn (Wieder 1985; Wieder & Lang 1988; Bayley et al. 1986).

The Appalachian Plateau physiographic province, extending from southern West Virginia through Pennsylvania, currently receives among the highest rates of atmospheric S deposition in the eastern U.S. (Church et al. 1992). Although acidic streams are numerous in the Appalachian Plateau (Herlihy et al. 1993), few investigations have been conducted of the processes controlling stream H^+ and Al^{n+} acidity within individual catchments. The primary objective of this study was to use periodic measurements of stream chemistry along an elevational gradient and volumetric rates of stream discharge to elucidate the fundamental processes creating longitudinal and seasonal variations in stream H^+ and Al^{n+} acidity at Yellow Creek, a headwater on the Appalachian Plateau. Study of this chronically acidic stream (pH $\sim$4) may improve understanding of the biogeochemistry of base-poor high elevation Appalachian ecosystems.

Study site and methods

The study area was the unglaciated Yellow Creek (YC) watershed located within the Otter Creek drainage basin in northeastern West Virginia (Figure 1). The Otter Creek watershed was designated a federal Class 1 Wilderness Area in 1975; a liming station is located on Otter Creek above Condon Run (Figure 2). With elevation ranging between 910 and 1190 m, YC is a 4.2 km first-order stream that drains an upland forested catchment with an area of 420 ha (Figure 3). The area was logged between 1910 and 1930 (Webb et al. 1998); vegetation in the YC catchment is second-growth forest composed of mixed northern hardwoods and conifers (American beech (*Fagus grandifolia*), yellow birch (*Betula alleghaniensis*), sugar maple (*Acer saccharum*), eastern hemlock (*Tsuga canadensis*), red spruce (*Picea rubens*)). The underlying bedrock is the Pennsylvanian Pottsville formation; within the YC catchment, the Pottsville consists of base-poor quartz sandstones and clastic conglomerates (Reger 1931). Although a quantitative survey has not been conducted, it is unlikely that fish inhabit YC due to elevated acidity. Brook trout do, however, inhabit the upper reaches of Otter Creek below the liming station and in the area where YC mixes with Otter Creek (Adams et al. 1991). Precipitation measured at the nearby Fernow Experimental Forest (FEF; Figure 2) is distributed evenly throughout the year (mean value for 1951–1990 is 145 cm/yr; Adams et al. 1994). As precipitation tends to increase with elevation at the FEF (Adams et al. 1994), the precipitation rate is likely greater at YC than the FEF (elevation range 533–1112 m) as the result of the higher elevation of YC. Average monthly air temperature at the FEF ranges from −1 °C (January) to 25 °C (July; Adams et al. 1994).

A synoptic survey of surface water chemistry (109 sites total) was conducted in the Otter Creek and neighboring Dolly Sods Wilderness Areas (Figure 1) on 23 May 1994 (Webb et al. 1998). YC was selected for further study on the basis of two observations from this survey. First, the chemical characteristics of YC (i.e., low pH, C_B, and ANC, high Al^{n+} and SO_4^{2-}) were similar to other acidic surface waters within these Wilderness Areas (over 50% of survey sites had pH <4.5, ANC <−33 μeq/L). Second, YC showed marked elevational gradients of stream H^+, Al^{n+}, SO_4^{2-}, DOC, and organic monomeric aluminum (Al_o) concentrations on the survey date (Webb et al. 1998).

Six sites along an elevational gradient in YC were selected for detailed study (Figure 3). Stream water was sampled at sites 2, 4, 5, and 6 on 13 occasions between June 1994 and March 1995; sites 1 and 3 were sampled on nine of these occasions (Figure 3). Sites 1 and 3 were not sampled during hunting season because these sites are off-trail. Riparian wetlands occur intermittently along the entire length of YC; the largest expanse (~30 ha) of wetlands is between an elevation of 955 and 960 m (Figure 3). Site 3 was selected to sample stream water entering this wetland while site 4 represents the discharge immediately below the large wetland (Figure 3). The volumetric rate of stream discharge was measured on seven sampling dates by a velocity-area method at site 6 (Figure 3). To estimate continuous discharge at YC, a rating curve was created between these instantaneous measures of stream discharge at YC and the mean daily stream flow on these dates at the hydrological control watershed of the FEF ($Q_{YC} = 1.18 * Q_{FEF}$, $r^2 = 0.43$, $p < 0.05$; M.B. Adams, unpublished data). Soils have not been classified and soil depth has not been measured at YC; soils from pits excavated near sites 2 and 3 were sampled and analyzed for chemical characteristics during this study (Fitzhugh 1996).

Stream samples were collected in 1 L polyethylene bottles which had been previously acid-washed with HCl and thoroughly rinsed with deionized water until the specific conductivity of the rinse was less than 1.2 μS/cm. Three aliquots were prepared from each stream sample: (1) 650 mL with 0.5 mL chloroform added to eliminate microbial activity (Galloway et al. 1982) for

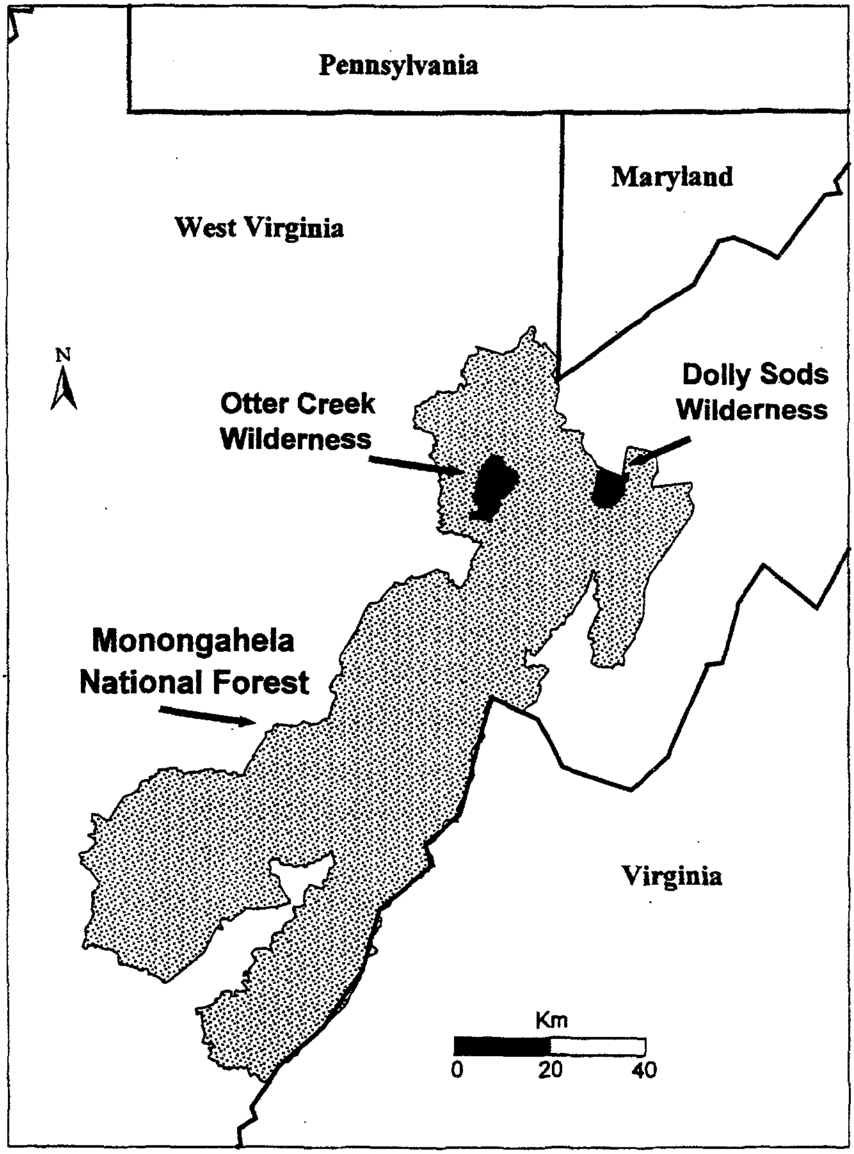

Figure 1. Location of the Otter Creek and Dolly Sods wildernesses.

analyses of pH, C_B, total Fe, and strong acid anions (SO_4^{2-}, NO_3^-, Cl^-), (2) 100 mL passed through a 0.45 μm filter and acidified to approximately pH 2 with H_2SO_4 for DOC analysis, and (3) untreated 250 mL for monomeric Al analyses. Solution pH was determined potentiometrically with a combination electrode. Concentrations of C_B and total Fe were analyzed by atomic

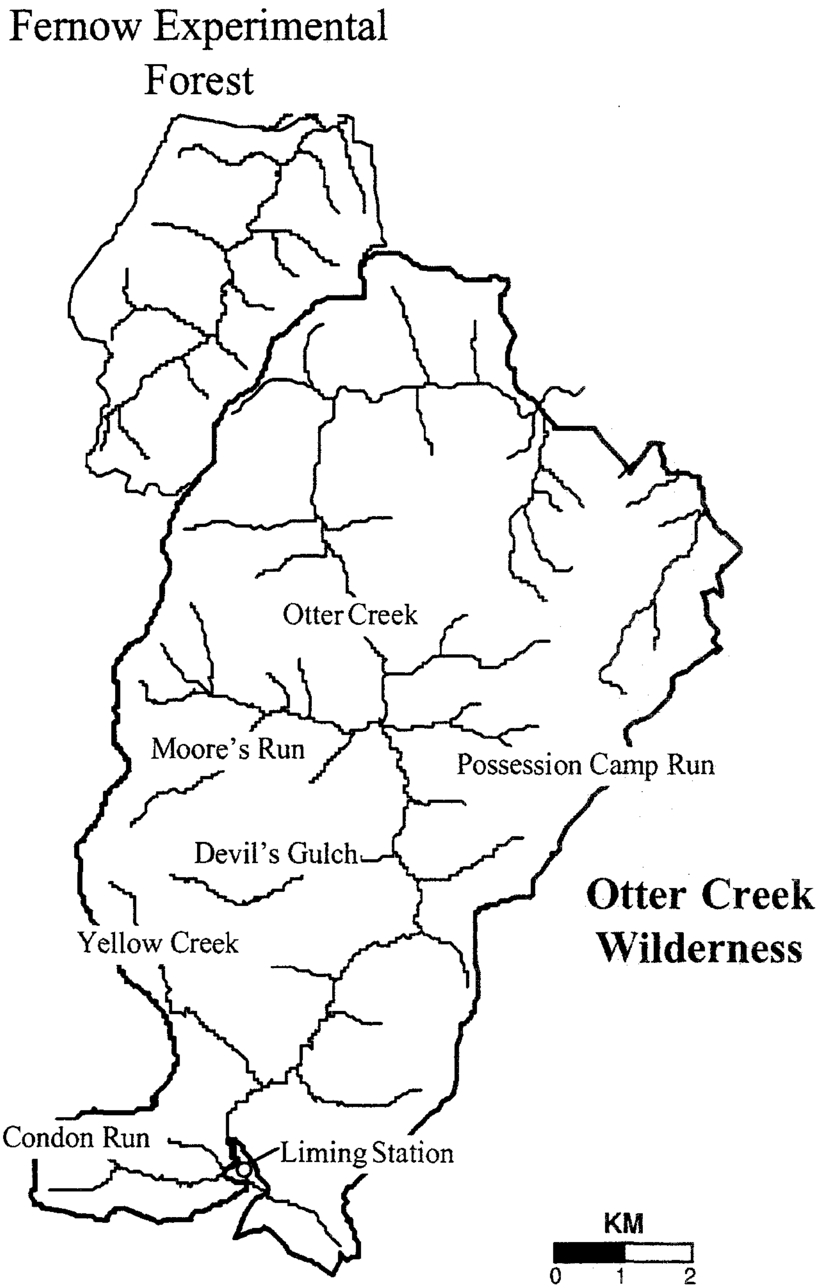

Figure 2. Map of the Otter Creek wilderness area and the Fernow experimental forest.

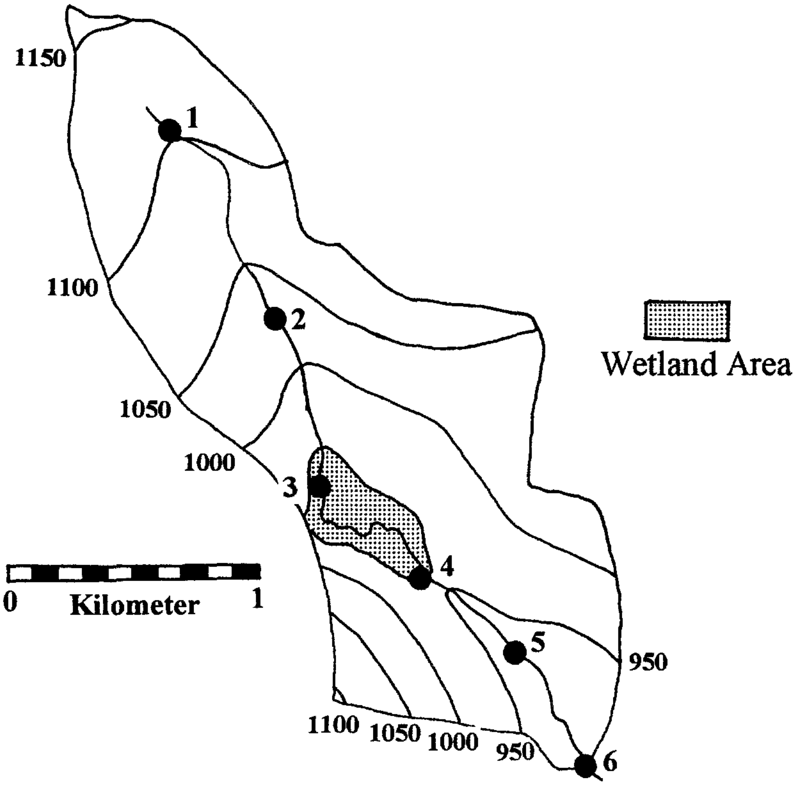

Figure 3. Map of sampling sites within the Yellow Creek watershed. Elevation of site 1 is 1109 m, site 2: 1012 m, site 3: 960 m, site 4: 954 m, site 5: 924 m, and site 6: 914 m. The extensive wetland and contour lines are indicated.

absorption spectrophotometry (Slavin 1968). Strong acid anion concentrations were analyzed by ion chromatography (Small et al. 1975). Monomeric Al was analyzed with a colorimetric technique utilizing pyrocatechol violet (McAvoy et al. 1992). The Al_0 was separated from the Al^{n+} fraction of monomeric Al with a cation exchange chromatography method (Driscoll 1984). DOC concentrations were analyzed by ampulation, persulfate and ultraviolet enhanced oxidation, followed by syringe stripping and gas chromatography (McDowell et al. 1987).

Organic anion (A^{n-}) concentrations were estimated by an electroneutrality approach as the difference in equivalents between the sum of inorganic cations ($Ca^{2+} + Mg^{2+} + Na^{+} + K^{+} + H^{+} + Al^{n+} + Fe^{2+}$) and the sum of inorganic strong acid anions ($SO_4^{2-} + NO_3^{-} + Cl^{-}$; e.g., Eshleman & Hemond 1985; Driscoll et al. 1989, 1994). With this approach it is assumed that all inorganic solutes significantly contributing to charge balance have been measured so that any discrepancy in electroneutrality is attributable to unanalyzed A^{n-}. Although total Fe was not analytically speciated into Fe $^{2+}$ and Fe^{3+}, we assumed total Fe was entirely present as Fe^{2+}; this assumption did not affect our interpretation of the results because Fe^{2+} was only used to calculate the anion deficit. The Al^{n+} fraction of monomeric Al was divided into Al^{3+} and $AlOH^{2+}$ species by utilizing thermodynamic data from the ALCHEMI model (Schecher & Driscoll 1995) in a computational method combining mass balance and chemical equilibrium. $Al(OH)_2^+$ and Al-SO_4^{2-} complexes were insignificant fractions (<5%) of Al^{n+} and were therefore not considered in Al^{n+} speciation. As dissolved F was not measured, Al-F species were also not considered in Al^{n+} speciation.

Results

General hydrochemical characteristics

Stream water in the YC catchment was characterized as a dilute acidic solution dominated by H^+ and SO_4^{2-} (Table 1). All sampled sites shared common chemical characteristics; the following description for site 6 was therefore representative of stream water in the YC catchment. H^+ was 50% of the mean cationic composition, with smaller contributions from Al^{n+} (17%), Ca^{2+} (12%), Mg^{2+} (8.6%), Fe^{2+} (5.7%), Na^+ (3.8%), and K^+ (1.9%). Calculations indicated that Al^{3+} (mean 32 μeq/L) was the predominant Al^{n+} species and that stream water was undersaturated (mean saturation index = −1.14) with respect to the solubility of synthetic gibbsite reported by May et al. (1979). Al_o was a significant (26%) fraction of the total monomeric Al. Stream concentrations of H^+ and Al^{n+} were both above the threshold for potential detrimental effects to aquatic biota (e.g., Baker et al. 1990). The mean anionic equivalence was dominated by SO_4^{2-} (77%), followed by A^{n-} (14%), Cl^- (7.9%), and NO_3^- (1.1%). As the name of the stream suggests, YC exhibited a dark tannish color associated with high DOC levels (mean 633 μmol/L) relative to most Appalachian surface waters. Stream C_B concentrations (mean 53 μeq/L) were among the most dilute concentrations reported for surface waters in the eastern U.S. (e.g., Kaufmann et al. 1988). For comparison, the interquartile ranges of DOC and C_B concentrations for acidic Mid-Appalachian streams sampled by the National Stream Survey were 75–150 μmol/L and 91–187 μeq/L, respectively (Herlihy et al. 1993).

Stream H^+ + Al^{n+} acidity varied nearly stoichiometrically with SO_4^{2-} concentration for all samples (Figure 4). Although stream SO_4^{2-} exhibited better correlation with H^+ than Al^{n+} among all samples (Table 2), a strong

Table 1. Mean chemical composition of sampling sites in the Yellow Creek catchment. Standard deviations are indicated in parentheses. Sites 2, 4, 5, and 6 were sampled thirteen times while sites 1 and 3 were sampled on nine occasions. All units are in μeq/L except Al_o and DOC which are in μmol/L.

	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
H^+	137 (15)	185 (18)	148 (14)	116 (23)	108 (17)	100 (17)
Al^{n+}	41.4 (2.5)	34.2 (9.3)	33.8 (3.3)	37.0 (9.7)	34.3 (11.7)	34.0 (11.7)
Ca^{2+}	17.8 (1.4)	23.0 (5.5)	23.3 (1.5)	24.3 (4.9)	23.0 (4.5)	24.6 (4.3)
Mg^{2+}	10.9 (1.0)	14.3 (4.3)	14.1 (1.2)	16.3 (3.9)	15.8 (3.6)	17.0 (3.8)
Na^+	7.5 (0.9)	8.2 (1.2)	7.6 (0.7)	8.2 (1.2)	7.5 (0.9)	7.5 (0.9)
K^+	2.4 (1.2)	3.0 (1.4)	3.0 (1.0)	3.7 (1.4)	3.2 (1.4)	3.8 (1.7)
C_B	38.7 (3.1)	48.5 (11.5)	48.1 (3.4)	52.5 (10.2)	49.5 (9.5)	52.9 (9.8)
Fe^{2+}	6.97 (1.93)	12.1 (2.22)	13.3 (2.52)	15.5 (4.65)	13.2 (3.21)	11.2 (2.35)
SO_4^{2-}	192 (13.9)	220 (31.5)	191 (16.7)	166 (32.9)	159 (31.1)	153 (31.1)
NO_3^-	1.5 (3.2)	6.3 (9.0)	2.7 (4.9)	2.4 (4.8)	2.8 (4.7)	2.1 (4.8)
Cl^-	13.7 (1.6)	18.2 (4.1)	16.5 (2.0)	17.4 (3.8)	15.9 (3.9)	15.7 (3.9)
DOC	685 (207)	1080 (284)	906 (131)	743 (167)	691 (149)	633 (173)
Al_o	6.26 (1.10)	7.00 (1.27)	6.37 (0.73)	4.41 (0.99)	4.33 (0.98)	3.93 (0.78)
A^{n-}	16.6 (9.6)	35.4 (11.0)	32.8 (8.49)	35.1 (17.2)	28.1 (9.1)	27.1 (8.7)

Table 2. Slope, r^2 value, and significance level (p) of linear regression between H^+ + Al^{n+}, as well as individual H^+ and Al^{n+} concentrations, and selected solutes for all samples (n = 70). All slopes are in μeq/L except DOC and Al_o which are in μmol/L.

Parameter	$H^+ + Al^{n+}$			H^+			Al^{n+}		
	Slope	r^2	p	Slope	r^2	p	Slope	r^2	p
SO_4^{2-}	0.96	0.86	<0.001	0.79	0.69	<0.001	0.16	0.41	<0.001
NO_3^-	1.8	0.07	0.025	na	0.038	0.11	0.60	0.13	0.0018
C_B	na	<0.01	0.78	na	0.012	0.37	0.52	0.30	<0.001
Fe^{2+}	na	<0.01	0.77	na	<0.01	0.58	na	0.011	0.38
DOC	0.091	0.35	<0.001	0.095	0.46	<0.001	na	0.011	0.38
Al_o	17	0.47	<0.001	17	0.58	<0.001	na	<0.01	0.69

'na' denotes not applicable as the result of nonsignificant regression.

coupling between SO_4^{2-} and Al^{n+} was evident at sites 2, 4, 5, and 6 (Figure 5). Of the six dominant chemical constituents (SO_4^{2-}, NO_3^-, C_B, Fe^{2+}, Al_o, DOC), SO_4^{2-} was the best predictor of variations in stream H^+ + Al^{n+} as well as of H^+ and Al^{n+} concentrations (Table 2). There were significant correlations between stream SO_4^{2-} and C_B as well as between DOC and Al_o among all samples (Table 3).

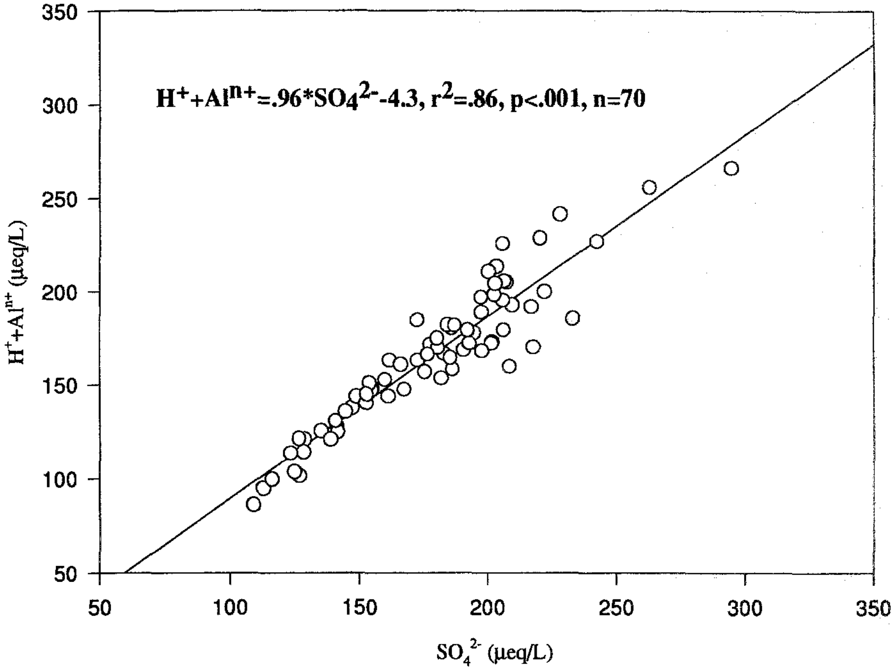

Figure 4. Stream H^+ + Al^{n+} acidity as function of SO_4^{2-} concentration for all samples. All units of linear regression equation are in μeq/L.

Table 3. Slope, r^2 value, and significance level (p) of linear regression between C_B and SO_4^{2-} and between Al_o and DOC for all samples (n = 70) and for individual sites. Sites 2, 4, 5, and 6 were sampled 13 times while sites 1 and 3 were sampled 9 times. Slopes are in μeq/L for the regressions between C_B and SO_4^{2-} and in μmol/L for the regressions between Al_o and DOC.

	C_B:SO_4^{2-}			Al_o:DOC		
	Slope	r^2	p	Slope	r^2	p
All samples	0.065	0.060	0.042	0.0045	0.51	<0.001
Site 1	na	0.013	0.77	na	0.05	0.55
Site 2	0.29	0.65	<0.001	0.0033	0.54	<0.01
Site 3	na	0.011	0.79	0.0044	0.63	0.010
Site 4	0.19	0.40	0.021	0.0035	0.35	0.034
Site 5	0.18	0.33	0.041	na	0.30	0.051
Site 6	na	0.13	0.23	0.0035	0.62	<0.01

'na' denotes not applicable as the result of nonsignificant regression.

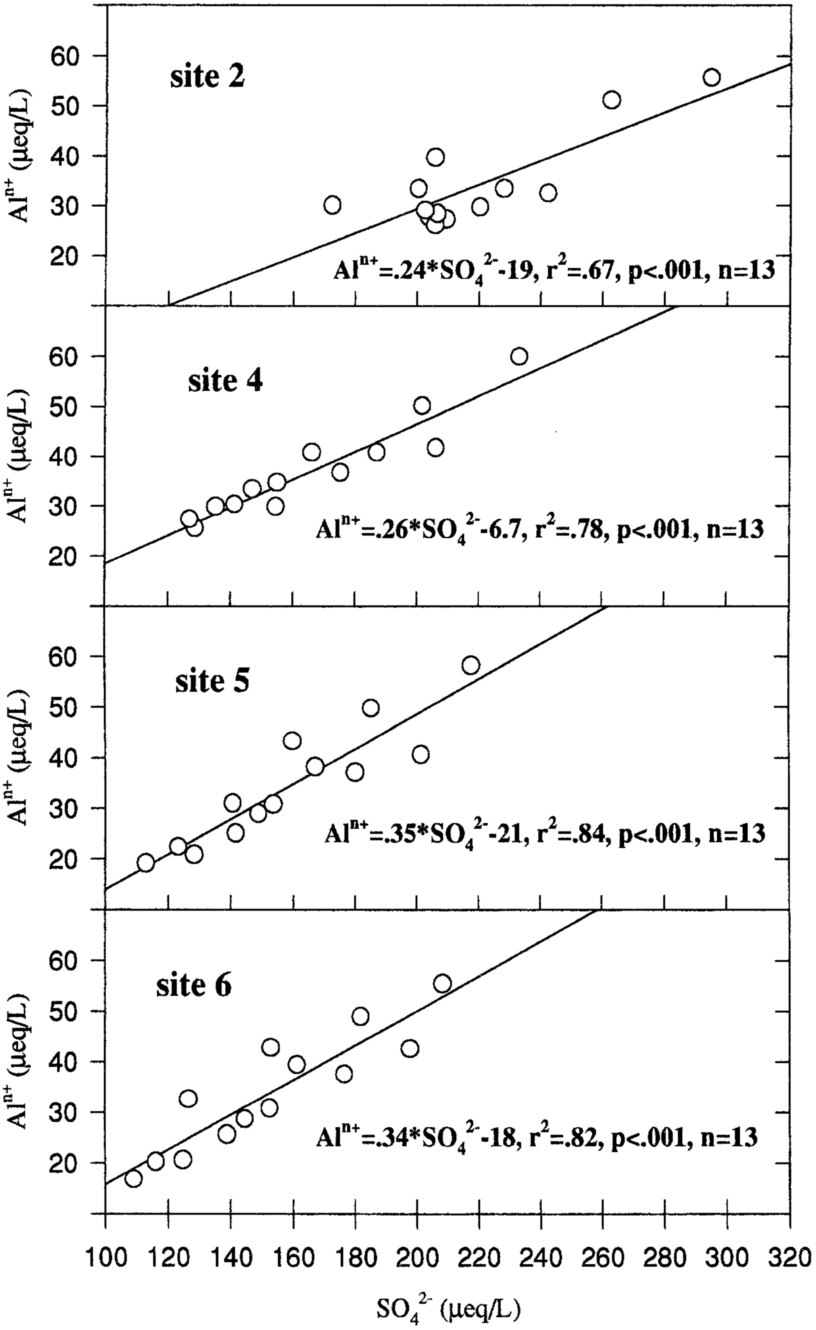

Figure 5. Stream Al^{n+} as function of SO_4^{2-} concentration for sites 2, 4, 5, and 6. All units of linear regression equations are in μeq/L.

Seasonal hydrochemical characteristics

Stormflow was defined by Eshleman et al. (1995) as conditions when stream discharge exceeds the antecedent baseflow by a factor of 4. Applying the criteria of Eshleman et al. (1995) to the estimates of continuous discharge at YC, all sampling dates of YC were considered baseflow conditions except for the first sampling date (30 June 1994; Figure 6). Baseflow stream discharge exhibited strong seasonal patterns. Baseflow on sampling dates fluctuated between July (0.048 cm) and late August (0.183 cm), with values gradually declining from September (0.019 cm) to mid-October (0.002 cm; Figure 6), as water stored within the catchment was depleted by evapotranspiration. As transpiration decreased following leaf-fall in October, 3.68 cm of rain between 1 and 10 November (measured at the FEF; M.B. Adams, unpublished data) replenished soil moisture and resulted in an increased water table, as indicated by the increase in baseflow stream discharge on the November sampling date (0.010 cm; Figure 6). This seasonal pattern of decreasing baseflow during the growing season is characteristic of other streams in the Mid-Appalachian region (Adams et al. 1991; Eshleman et al. 1998).

Stream baseflow chemistry in the YC catchment exhibited distinct seasonal patterns. Stream H^+, SO_4^{2-}, and Al^{n+} concentrations showed similar temporal patterns, with values decreasing during the growing season (June–October) followed by an abrupt increase in late autumn (November), and a gradual decline through the winter (Figure 6). Stream C_B concentrations declined between June and August, then gradually increased to maximum values in late autumn, and decreased during the winter (Figure 6). The temporal variability of C_B was strongly related to SO_4^{2-} at sites 2, 4, and 5 (Table 3). Stream DOC and Al_o exhibited wide fluctuations but generally declined during the growing season, reaching minimal values in the late autumn (Figure 6). Temporal changes in Al_o were significantly correlated with DOC at all sites except site 1 (Table 3). While NO_3^- was below the analytical detection limit (0.8 μeq/L) in 85% of the samples collected during the growing season, stream NO_3^- concentrations increased during the dormant period, peaking in February when snow covered the watershed (Figure 6).

Longitudinal hydrochemical characteristics

In addition to these seasonal patterns, longitudinal patterns in stream chemistry were evident within the YC watershed. Stream H^+, SO_4^{2-}, DOC, and Al_o concentrations exhibited similar longitudinal patterns on every sampling date (Figure 7). A notable decline in concentrations of these solutes occurred between sites 2 and 6, with a difference of 84.8 μeq/L, 66.4 μeq/L, 447 μmol/L, and 3.07 μmol/L for mean stream H^+, SO_4^{2-}, DOC, and Al_o respectively (Table 1). On the nine occasions when all six sites were sampled, the elevational gradient in mean stream SO_4^{2-} concentration was greatest between sites 3 and 4 which bracket the extensive wetland (Figure 7). For these nine dates, longitudinal changes in stream Al_o were strongly related to DOC (Figure 7). Stream H^+, SO_4^{2-}, DOC, and Al_o concentrations at site 1 were not consistent with the elevational pattern observed for these solutes between sites 2 and 6 (Figure 7). C_B and Al^{n+} concentrations did not exhibit regular longitudinal patterns and spatial variation in these solutes did not significantly influence longitudinal patterns of stream acid-base chemistry. Elevational patterns in stream NO_3^- concentration were apparent during the dormant season (November–March), with concentrations decreasing with decreases in elevation (Figure 6). Volumetric stream discharge was only measured at site 6; we therefore could not assess the roles of recharge or discharge along the stream channel on longitudinal patterns of stream acidity.

Discussion

Seasonal patterns of stream acidity

The distinct seasonal patterns of stream chemistry and discharge provided insight to the processes influencing stream acidity in the YC watershed. Seasonal variations in stream H^+ and Al^{n+} acidity were predominantly determined by temporal changes in SO_4^{2-}. Although YC stream water was acidic throughout the study, stream H^+, Al^{n+}, and SO_4^{2-} concentrations showed a gradual but significant decline over the course of the growing season (June–October), concurrent with decreasing baseflow discharge (Figure 6). While apparent at all sites along YC, this pattern was most pronounced at sites below the extensive wetland area (sites 4–6, Figure 6). Between June and October, stream SO_4^{2-} and H^+ + Al^{n+} acidity declined 79.0 and 78.6 μeq/L, respectively, at site 4 below the wetland, while these solutes decreased only 39.7 and 28.5 μeq/L at site 2 above the wetland during the same period. Microbially mediated dissimilatory SO_4^{2-} reduction in saturated YC wetlands likely caused the marked decline of stream H^+ and Al^{n+} acidity during the growing season by neutralizing free H^+ acidity and by restricting SO_4^{2-} transport from soils which limited associated Al^{n+} leaching. The relationship between stream discharge and SO_4^{2-} during the growing season may be influenced by three processes: (1) longer hydraulic residence times within the wetland as stream flow decreased, (2) warmer soil temperatures, and (3) a greater proportion of stream water derived from groundwater in riparian wetlands under low flow conditions. All three processes favored the closer association of drainage water with anaerobic conditions occurring within

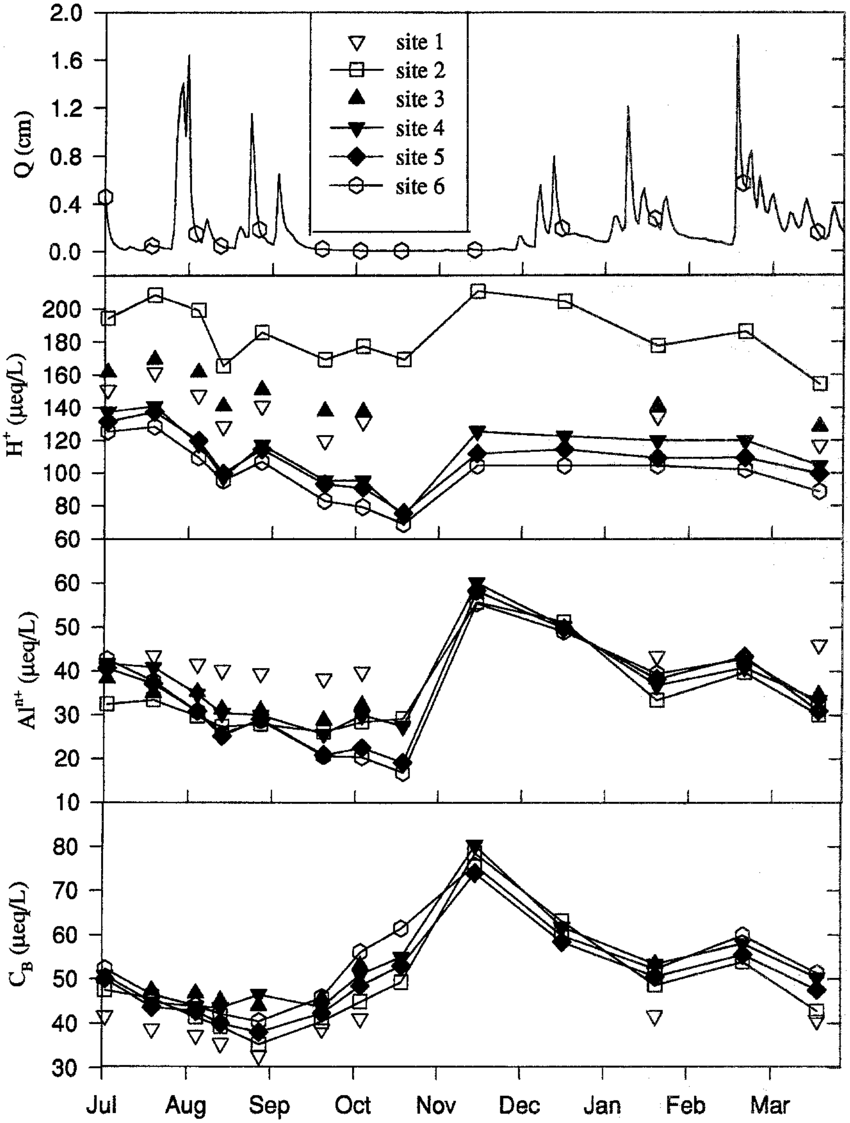

Figure 6. Stream chemical composition and estimated continuous discharge (Q) at site 6 as function of time. Symbols on the plot of Q denote sampling dates.

wetlands or enhanced microbial activity. In contrast, these three processes may be mitigated by the decreasing area of saturated soils which might be expected to cause rising stream SO_4^{2-} concentrations through oxidation reactions. Studies of other streams draining wetlands have also attributed a decrease in SO_4^{2-} concentration during the growing season to microbial SO_4^{2-} reduction (Wieder & Lang 1984; Bayley et al. 1986; Driscoll et al.

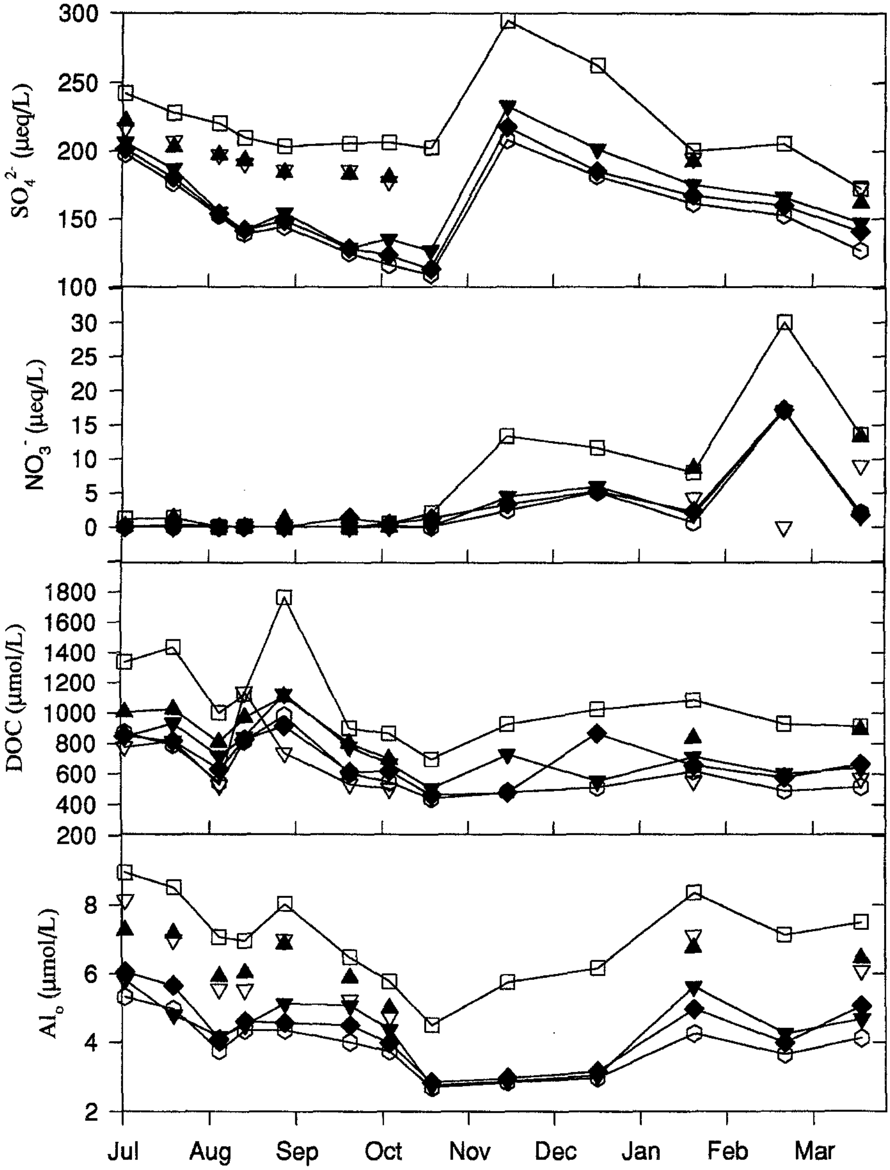

Figure 6. Continued.

1987b; Spratt & Morgan 1990). By contributing to decreases in discharge, transpiration appeared to influence the temporal pattern of declining stream H^+ and Al^{n+} acidity during the growing season in the YC watershed.

As noted previously, precipitation in early November after leaf-fall recharged soil moisture so that baseflow stream discharge increased and the

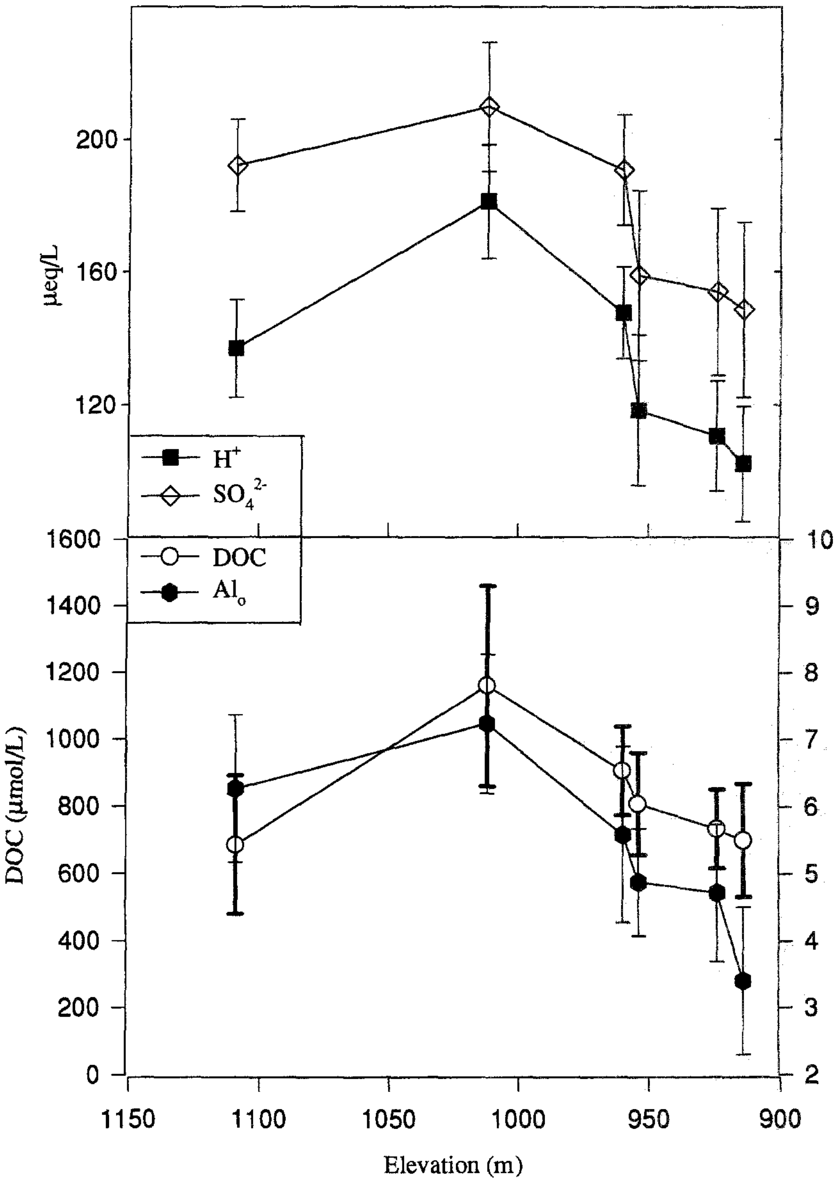

Figure 7. Mean stream SO_4^{2-}, H^+, DOC, and Al_o as function of sampling site elevation for dates when all six sites were sampled ($n = 9$). Error bars indicate the standard deviation resulting from temporal variation. See Figure 1 for sampling site elevations. Results of linear regression between mean values are: (1) $H^+(\mu eq/L) = 1.1*SO_4^{2-}(\mu eq/L) - 62$, $r^2 = 0.92$, $p = 0.0024$, $n = 6$; (2) $H^+(\mu eq/L) = 0.14*DOC(\mu mol/L) + 15$, $r^2 = 0.77$, $p = 0.022$, $n = 6$; (3) $Al_o(\mu mol/L) = 0.0051*DOC(\mu mol/L) + 1.07$, $r^2 = 0.48$, $p = 0.13$, $n = 6$.

water table increased. A marked pulse of all inorganic dissolved constituents occurred in November under baseflow conditions (Figure 6). We hypothesized that this increased water table following approximately two months of low stream flow resulted in an autumnal pulse of stream H^+ and Al^{n+} acidity through two processes: (1) an upward shift in hydrological flowpaths through riparian soils, flushing soil water into the stream and (2) an increase in the hydraulic gradient that caused the re-oxidation of reduced sulfur compounds. Although soil waters and groundwaters were not collected in this study, the data suggest two distinct geochemical environments in the riparian subsurface during the growing season: (1) an unsaturated oxidizing zone overlying (2) a saturated reducing environment through which groundwater travels before discharging to the stream. During the summer, SO_4^{2-} concentration may be enriched in soil water within the unsaturated zone by a combination of evapotranspiration, mineralization of organic S, and re-oxidation of S precipitates. The higher water table likely contributed to increased stream H^+ and Al^{n+} acidity by flushing 'old' summer soil water from soils. We hypothesized that an increased hydraulic gradient may also have caused the re-oxidation of reduced S compounds through transport of these compounds to aerated stream water and/or subsurface mixing of 'new' aerobic precipitation with 'old' anaerobic groundwater. Autumnal pulses of stream SO_4^{2-} have been observed in other upland catchments containing wetlands, most notably associated with an increase in the water table after prolonged drought (Wieder & Lang 1984; Bayley et al. 1986). The link between variations in SO_4^{2-} and stream H^+ and Al^{n+} acidity at YC contrasted with patterns in Adirondack surface waters. Although SO_4^{2-} is the dominant source of acidity, seasonal trends in Adirondack surface water H^+ and Al^{n+} acidity are strongly related to temporal NO_3^- fluctuations (Driscoll & Schafran 1984; Driscoll & Van Dreason 1993). Although the sampling frequency of this study was insufficient to accurately determine the duration and magnitude of the autumnal pulse, stream H^+ and Al^{n+} concentrations generally decreased during the winter after the peak in November (Figure 6).

We hypothesize that this autumnal pulse of acidity at YC also likely occurs in other acidic streams draining wetlands in the Otter Creek Wilderness Area: Condon Run, Devil's Gulch, Moore's Run, and Possession Camp Run. While the chemistry of YC likely does not support fish populations, the autumnal pulse of acidity at YC and the other acidic streams draining wetlands may influence brook trout survival in zones where these acidic tributaries mix with limed water in the main stem of Otter Creek. Mixing zones between acidic and limed streams have been shown to be highly toxic to fish, likely as the result of conditions of oversaturation of Al with respect to mineral phases and subsequent precipitation onto gills (Rosseland et al. 1992).

In the Mid-Appalachian region, spring is generally considered the season of greatest baseflow stream acidity because SO_4^{2-} concentrations are typically highest and C_B lowest during this time (Kaufmann et al. 1988; Herlihy et al. 1993). In contrast, autumn had the greatest stream acidity at YC, indicating that autumn may be the season with chemical conditions most deleterious to aquatic biota over the annual cycle in streams draining wetlands within the Otter Creek and Dolly Sods Wilderness Areas. As early life stages of fish are typically more sensitive to acid than adults (Bulger et al. 1993) and brook trout are fall spawners (Jenkins & Burkhead 1993), fall is a critical period for brook trout in Appalachian Plateau streams. The implications of this seasonal pattern at YC for the Appalachian Plateau region are presently unclear because an inventory of streams draining wetlands within the region has not been conducted. Until additional, more detailed studies of headwater streams in the Appalachian Plateau region are completed, the spatial extent of the influence of wetlands on seasonal patterns of stream chemistry will remain unclear. This seasonal pattern at YC suggests, however, that regional surveys sampling stream ANC in the spring (e.g., National Stream Survey, Kaufmann et al. (1988)) might underestimate the highest acidic stress levels to fish (e.g., Baker et al. 1990) over the annual cycle in streams on the Appalachian Plateau draining wetlands.

Longitudinal patterns of stream acidity

Results of this study indicated consistent longitudinal patterns in the chemical composition of YC. Stream H^+, SO_4^{2-}, DOC, and Al_o concentrations exhibited marked elevational gradients (Figure 7). We attributed longitudinal patterns in these solutes between sites 2 and 6 to a combination of spatial variation of dominant tree species and SO_4^{2-} retention in riparian wetlands. Concentrations of these solutes at site 1 may have been inconsistent with the elevational pattern between sites 2 and 6 as the result of a small, unmapped wetland at site 1. While conifers are found along the entire length of YC, these species (eastern hemlock, red spruce) are most abundant within the YC catchment above site 3 (R.D. Fitzhugh, personal observation). Unfortunately, there has not been a detailed vegetation survey for the YC catchment. As the result of greater leaf area index, rates of dry atmospheric S deposition are generally higher to coniferous than deciduous canopies within individual catchments, enhancing SO_4^{2-} concentrations in both throughfall and soil solutions under conifers (Mollitor & Raynal 1983; David & Driscoll 1984; Hultberg et al. 1994). Soil solutions under conifers also often have higher DOC concentrations than those found under hardwoods within individual watersheds (Cronan & Aiken 1985; DeWalle et al. 1985), reflecting the more complete oxidation of hardwood litter (Gosz et al. 1973). The elevational pattern in Al_o

along YC was likely due to the longitudinal pattern of stream DOC (Figure 7). Spatial variation in dominant tree species produced longitudinal patterns of stream H^+, SO_4^{2-}, DOC, and Al_o at W5 and W6 in the HBEF, with higher concentrations of these solutes evident in upper reaches draining coniferous terrain (Lawrence et al. 1986). The elevational trend in dominant tree species also likely influenced the coincident decline of stream H^+, SO_4^{2-}, DOC, and Al_o concentrations along YC.

Sulfate retention via microbial reduction in riparian wetlands may also contribute to longitudinal changes in stream H^+ and SO_4^{2-} concentrations, most notably between sites 3 and 4 bracketing the extensive wetland (Figure 3). The magnitude of SO_4^{2-} retention within the riparian wetland between sites 3 and 4 at any time over the annual cycle appeared related to current hydrological flux. The difference in stream SO_4^{2-} between sites 3 and 4 across the wetland was greatest during the lowest discharge (August–October) and least during the highest discharge (June and January–March, Figure 6). The difference in SO_4^{2-} concentration between sites 3 and 4 increased from June (15.8 μeq/L) to October (45.3 μeq/L); similarly, the difference in H^+ between sites 3 and 4 increased between June (24.1 μeq/L) to October (42.4 μeq/L, Figure 6). In contrast, the difference in DOC between these sites decreased during the growing season, decreasing from June (163 μmol/L) to October (42.4 μmol/L; Figure 6). On the dates when all six sites were sampled, longitudinal variation in mean stream H^+ was better correlated with SO_4^{2-} than DOC (Figure 7). Along the stream length, the highest Fe concentrations (Table 1) and the highest total Fe:SO_4^{2-} molar ratio (mean 0.09) occurred at site 4, consistent with the role of the wetland as a reducing environment because Fe mobility is enhanced under reducing conditions. The noticeable decline of stream NO_3^- across the wetland during the dormant season further suggests that this area acts as a sink for strong acid anions originating from upper elevations within the catchment; denitrification is a potential mechanism removing NO_3^- (Firestone 1982). Stream free H^+ decreased as the result of SO_4^{2-} retention when water migrated through a beaver impoundment at the Adirondack Pancake-Hall catchment (Driscoll et al. 1987). Stream free H^+ acidity decreased due to SO_4^{2-} retention in a riparian wetland at Tub Run on the Appalachian Plateau in West Virginia (Wieder & Lang 1984). The lack of a geological influence on longitudinal patterns of stream acidity at YC, as reflected in the relatively invariant C_B concentrations, contrasted with previous studies of Mid-Appalachian catchments (e.g., Bricker & Rice 1989).

Implications

The acid-base chemistry of stream water in the YC catchment is presently determined by: (1) the rate of SO_4^{2-} transport from soils to stream water and (2) biogeochemical processes which limit the availability of C_B. The current rate of SO_4^{2-} export in stream water greatly exceeds the rate of C_B release, resulting in chronic stream acidification. The sandstones and clastic conglomerates underlying the YC catchment are predominantly composed of quartz; the soils sampled during this study were extremely acidic (pH <4) and base-poor (base saturation <2%; Fitzhugh 1996). As a result, stream C_B (~50 μeq/L) were among the most dilute concentrations reported for surface waters in the eastern U.S. (e.g., Kaufmann et al. 1988). Rates of geochemical weathering and exchange reactions releasing C_B to stream water, an important mechanism for neutralizing solution acidity in most other watersheds, were very low at the YC catchment. In this respect, YC and similarly acidic waters in the Otter Creek and Dolly Sods Wilderness Areas characterized by dilute C_B concentrations represent an endmember of the current effects of acidic deposition on stream acid-base chemistry within the Mid-Appalachian region. Streams draining watersheds underlain by the extremely base-poor Pottsville formation may be the most sensitive waters to acidification in the Mid-Appalachian region.

Results of this study provide a comparison of the relative influence of inorganic strong acids (H_2SO_4) and naturally occurring organic solutes on stream acidity. Despite relatively high stream DOC (Table 1), the mean A^{n-} concentration for all samples (30 μeq/L) was only 13% of the mean total anionic equivalence. Variations of H^+ and Al^{n+} acidity were more strongly related to SO_4^{2-} than DOC concentrations (Table 2). The influence of organic solutes on stream acid-base chemistry in the YC catchment was apparently limited by the protonation of weak organic acids ($pK_a > 5$, Driscoll et al. 1994) as the result of low stream pH (range 3.69–4.23). Dissociation of strong organic acids ($pK_a < 4$, Driscoll et al. 1994) was the source for approximately 20% of the mean stream free H^+ acidity for all samples in the YC catchment. H_2SO_4 was therefore both the dominant source of stream acidity as well as a strong influence on variations of stream acidity.

Conclusions

Biological processes appeared to strongly influence longitudinal and seasonal patterns of stream acidity in the YC watershed. We hypothesized that these influences included: (1) the role of transpiration in seasonal trends of stream discharge, (2) microbial SO_4^{2-} reduction in riparian wetlands, and (3) spatial distribution of dominant tree species. Processes 1 and 2 were of particular interest because there are no prior studies in the Appalachian Plateau region of either seasonal fluctuations in stream Al^{n+} or possible linkages between SO_4^{2-} and Al^{n+} export in streams draining wetlands.

In contrast with other mid-Appalachian (Herlihy et al. 1993) and Adirondack (Driscoll & Van Dreason 1993) catchments, the season of peak stream acidity at YC was autumn. This pattern at YC suggests that regional surveys attempting to sample minimal baseflow stream ANC in the spring might underestimate the highest acidic stress levels to fish (e.g., Baker et al. 1990) over the annual cycle in Appalachian Plateau streams draining wetlands.

Stream acid-base chemistry in the YC watershed is ultimately determined by differences in the cycling of S and C_B. The current rate of SO_4^{2-} transport from soils to stream water significantly exceeds the rate of C_B release, resulting in chronic stream acidification. While H_2SO_4 was the dominant source of acidity, SO_4^{2-} concentrations at YC were comparable to other acidic mid-Appalachian streams (Herlihy et al. 1993). Rather than unusually high SO_4^{2-} concentrations, the extreme acidity at YC compared to other Mid-Appalachian waters was the result of dilute C_B concentrations.

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