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Long-term trends in soil solution and stream water chemistry at the Hubbard Brook Experimental Forest: relationship with landscape position

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Abstract. In acid-sensitive watersheds of the northeastern US, decreases in SO_2 emissions and atmospheric deposition of sulfur have not been accompanied by marked changes in pH and acid neutralizing capacity (ANC). To better understand this phenomenon, we investigated the long-term trends in soil solution (1984–1998) and stream water (1982–2000) chemistry along a natural soil catena at the Hubbard Brook Experimental Forest, New Hampshire, USA. Significant declines in strong acid anion concentrations were accompanied by declines in base cation concentrations in soil solutions draining the Oa and Bs soil horizons at all elevations. The magnitude of change varied with position in the landscape. Recovery, as indicated by increasing ANC (mean 2.38 $\mu Eq\,L^{-1}\,year^{-1}$) and decreasing concentrations of inorganic monomeric Al (mean 1.03 $\mu mol\,L^{-1}\,year^{-1}$), was confined to solutions draining the Bs horizon at mid-to-higher elevations. However, persistently low Ca^{2+}/Al_i ratios (<1) in Bs soil solutions at these sites may be evidence of continuing Al stress to trees. In Bs soil solution at a lower elevation site and in Oa soil solutions at all sites, declines in base cations (mean 3.71 $\mu Eq\,L^{-1}\,year^{-1}$) were either similar to or exceeded declines in strong acid anions (mean 3.25 $\mu Eq\,L^{-1}\,year^{-1}$) resulting in no change in ANC. Changes in the chemistry of stream water reflected changes in soil solutions, with the greatest improvement in ANC occurring at high elevation and the rate of increase decreasing with decreases in elevation. The pH of soil solutions and stream waters either declined or did not change significantly. Therefore pH-buffering processes, including hydrolysis of Al and possibly the deprotonation of organic acids, have prevented increases in drainage water pH despite considerable reductions in inputs of strong acids.

Introduction

Atmospheric deposition of sulfur (S) has been declining for the past 30 years in response to SO_2 emission controls in many parts of Europe and North America, resulting in decreases in sulfate (SO_4^{2-}) concentrations in surface waters (Likens et al. 1996; Stoddard et al. 1999; Driscoll et al. 2001). However, in acid-sensitive watersheds of the northeastern US, decreases in strong acid anions in stream water have not been accompanied by widespread increases in pH or acid neutralizing capacity (ANC: Stoddard et al. 1999). This pattern is largely because atmospheric inputs of base cations have also declined and exchangeable base cation pools in soil are low, possibly due to depletion by acidic deposition (Likens et al. 1996, 1998; Stoddard et al. 1999; Driscoll et al. 2001; Gbondo-Tugbawa and Driscoll 2003). Atmospheric deposition of base cations have been declining in the northern and eastern US during the last four decades (Hedin et al. 1994; Likens et al. 1996; Stoddard et al. 1999), although rates of decline have slowed in recent years relative to longer-term trends (USEPA 2003). Furthermore, in regions with acid-sensitive soils, elevated inputs of strong acid anions from atmospheric deposition resulted in the mobilization of aluminum (Al) from soil to drainage waters and a shift in the speciation of aqueous Al from organically bound to potentially toxic inorganic forms (Cronan and Schofield 1990).

Typically, acid-sensitive soils are characterized by a base saturation of less than 20%, limited retention of atmospheric SO_4^{2-} and elevated leaching of nitrate (NO_3^-) (Cronan and Schofield 1990). Landscapes that are naturally sensitive to acidic deposition are often characterized by shallow organic soils upslope that are natural producers of acidity, and thicker soils downslope that provide a sink for acidity (Johnson et al. 1981; Krug and Frink 1983; Driscoll et al. 1988b; Lawrence et al. 1999). At higher elevations, shallow soils derived from base-poor parent material offer little opportunity for the neutralization of strong acid inputs by base cations released from mineral weathering, and solutions are often neutralized in part by the release of Al.

Furthermore, shallow soils have little potential to adsorb either strong acid anions derived from atmospheric deposition or organic anions that are naturally leached from forest floor soils. With decreasing elevation, deeper mineral soils provide more opportunity for base cation release, and a greater surface area for adsorption of organic and inorganic anions. This geochemical soil catena is often reflected as a gradient in stream acidity, with stream pH and ANC increasing with decreasing elevation. As a consequence of these spatial patterns in soil parameters, considerable differences in the response of drainage waters to changing acidic inputs are likely over relatively short distances.

Waters draining the Hubbard Brook Experimental Forest (HBEF), NH are naturally acidic and sensitive to acid deposition inputs (Johnson et al. 1981). Since records began in 1963, long-term declines in the concentrations of SO_4^{2-} and base cations in both bulk deposition and stream water have been observed at the HBEF. During the period 1964/65 to 1997/98, annual volume-weighted average concentrations of SO_4^{2-} in bulk deposition decreased by 49.5% (Likens et al. 2002). In stream water, annual volume-weighted concentrations of SO_4^{2-} declined from $124.4\,\mu Eq\,L^{-1}$ in 1964/65 to $86.2\,\mu Eq\,L^{-1}$ in 1997/98 (watershed 6; Likens et al. 2002). During the period 1963–1993, concentrations of C_B in both bulk deposition and stream water declined by $30–40\,\mu Eq\,L^{-1}$ (Likens et al. 1996). By 1993, the pH of stream water had increased slightly to 5.01 from 4.85 in 1963, and ANC remained negative (Likens et al. 1996).

The importance of landscape position to soil solution and stream water recovery from acid deposition has not been addressed at the HBEF, despite considerable spatial variations in soil solution and stream water chemistry within experimental watersheds (e.g., Driscoll et al. 1985; Lawrence et al. 1986, 1988; Johnson et al. 2000). The objective of our study was to evaluate the changes in the chemistry of drainage waters along a natural soil catena in response to recent declines in acidic deposition.

Site description

The HBEF lies within the White Mountain Forest in central New Hampshire and encompasses the upper 3120 ha of the Hubbard Brook watershed. The climate is humid-continental with an average annual precipitation of approximately 1400 mm, of which approximately 30% falls as snow (Federer et al. 1989). This study was conducted in and near experimental watershed 6, which is south-facing, ranges in elevation from 540 to 800 m, and has an area of 13.2 ha. The underlying geology is dominated by the Silurian Rangely formation (sillimanite-grade pelitic schists) and the Kinsman formation (quartz monzonite). Much of the area is covered with glacial till derived primarily from local bedrock, ranging in depth from zero along ridge tops to several meters downslope. Soils are predominantly base-poor Spodosols with an average depth of 60 cm (Johnson et al. 1991). The forest is mainly dominated by northern hardwood species including American beech (*Fagus grandifolia*), sugar maple (*Acer saccahrum* Marsh.) and yellow birch (*Betula alleghaniensis* Britt.), with balsam fir (*Abies balsamea* (L.) Mill), red spruce (*Picea rubens* Sarg.), and white birch (*Betula papyrifera* var. *cordifolia* (Marsh) Regel) prominent at uppermost elevations and along ridges. The primary source of soil Al at this site is weathering of Al-rich minerals in tills and bedrock; inputs of strong acids in atmospheric deposition have resulted in the mobilization of Al in soil solutions and surface waters (Driscoll et al. 1985; Johnson et al. 1981; Lawrence et al. 1986).

Methods

Soil solutions were collected approximately monthly from tension-free lysimeters installed at three elevations adjacent to watershed 6 (Figure 1); the design and placement of the lysimeters is described in detail in Driscoll et al. (1988a). Near the top of watershed 6, lysimeters were installed in an area dominated by red spruce, balsam fir and white birch (SFB, 750 m); the mid- (HH, 730 m) and lower- (LH, 600 m) elevation lysimeters were installed in areas dominated by hardwood species (Figure 1). Soil solutions were collected from three replicate lysimeters installed below the Oa horizon and in the Bs horizon at the HH and LH sites, and from two replicate lysimeters in the same horizons at the SFB site. Between 1984 and 1986, samples were collected separately from all individual lysimeters and the arithmetic means of solute concentrations for each horizon and elevation were used to evaluate long-term trends. Analysis of those data revealed no significant differences among replicate lysimeters. Thus, since 1986, solutions have been bulked in the field for each set of elevation-horizon replicates.

In conjunction with the soil solution sampling, stream water samples were collected approximately monthly from six sites spaced longitudinally between the stream source and the gauging station in watershed 6 (Figure 1). Stream sites 1 and 2 drain the SFB zone, sites 3 and 4 drain the HH and SFB zones, and sites 5 and 7 (upstream of the weir) drain the combined LH, HH and SFB vegetation zones.

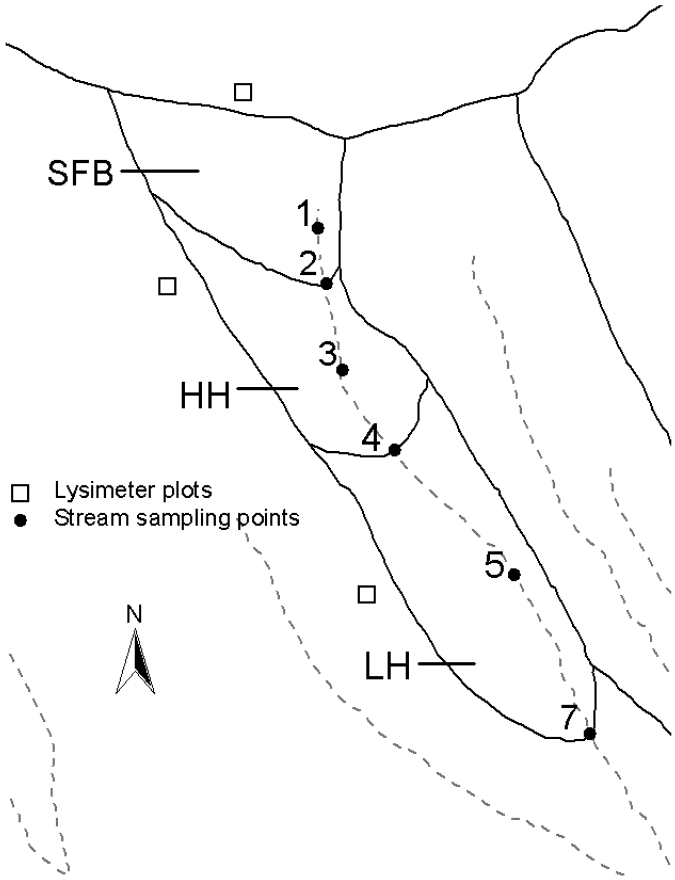

Figure 1. Map of watershed 6 at the HBEF, showing locations of lysimeters, stream sampling points and vegetation zones.

Stream samples have also been collected weekly just above the weir of watershed 6 since 1963 (Likens et al. 1996). However, in this study, we only report data from the monthly samples. This allowed us to compare temporal trends in stream chemistry at the longitudinal sampling sites with changes in soil solution chemistry within the respective subcatchments. Furthermore, the weekly samples were not analyzed for Al fractions, which was an important aspect of this study. Volume weighting of soil solution data was based on stream water run-off between successive samplings, with evapotranspiration corrections based on the distribution of fine root biomass in soil horizons (Fitzhugh 2000). We examined 14 years (1984–1998) of soil solution data collected at the three elevations, and 18 years (1982–2000) of stream water data from the longitudinal stream sites in watershed 6.

For all soil solution and stream water samples, calcium (Ca), magnesium (Mg), sodium (Na) and potassium (K) concentrations were determined by flame atomic spectroscopy (AAS); SO_4^{2-}, NO_3^- and chloride (Cl^-) by ion chromatography; ammonium and dissolved silica by colorimetric autoanalysis; and total fluoride (F) by ion selective electrode. Infrared detection was used to determine dissolved organic (following persulfate oxidation) and inorganic carbon (DOC and DIC, respectively). Prior to 1989, total monomeric Al (Al_m) was determined by field extraction with 8-hydroxy-quinoline in MIBK and graphite furnace AAS; post-1989 Al_m was determined colorimetrically following chelation with pyrocatechol-violet. Non-labile (organic) monomeric aluminum (Al_o) was determined by the same method as Al_m, after passing the sample through an ion exchange column. Inorganic monomeric aluminum (Al_i) was determined from the difference between Al_m and Al_o. Further details of chemical methods can be found in Johnson et al. (2000). Total base cations (C_B; $\mu Eq\,L^{-1}$) are the sum of $2[Ca^{2+}] + 2[Mg^{2+}] + [K^+] + [Na^+]$; total acidic anions ($C_A$; $\mu Eq\,L^{-1}$) are the sum of $2[SO_4^{2-}] + [NO_3^-] + [Cl^-]$. The Ca, Mg, Na and K concentrations measured by AAS were assumed to equal the corresponding free ion concentrations. We define ANC as C_B-C_A. The equivalence of Al^{n+} in solution was modeled from thermodynamic principles considering complexation with inorganic ligands (MINEQL$^+$; Schecher and McAvoy 1992). The concentration of organic acid anions (OA^-, $\mu Eq\,L^{-1}$) was estimated from the anion deficit (Driscoll et al. 1994).

Monotonic trends in soil solution and stream water chemistry were detected using the non-parametric modified seasonal Kendal Tau test (SKT; Hirsch et al. 1982; Hirsch and Slack 1984). The SKT test is suitable for data that exhibit seasonality and autocorrelation. As part of the SKT test, the slopes for long-term trends are calculated as the median of the two-point slopes computed for all possible pairs of samples within the same months of different years (Hirsch et al. 1982).

Results

Forest floor soil solutions

Soil solutions draining the Oa horizon have become significantly more acidic in the period 1984–1998, despite reductions in sulfur emissions and bulk SO_4^{2-} deposition (Driscoll et al. 2001). We observed the largest decline in pH at the LH site (0.047 pH units $year^{-1}$; Table 1), such that soil solution pH was fluctuating around 4.3 by the end of the sampling period. Smaller declines occurred at the HH and SFB sites (0.023 and 0.007 pH units $year^{-1}$, respectively), with solution pH values typically fluctuating around pH 4.0 at both sites in the late 1990s. This pattern emerged despite large declines in concentrations of total strong acid anions, which were due to decreases in SO_4^{2-} (Table 1; Figure 2) and, in the HH zone, NO_3^- concentrations (1.35 $\mu Eq\,L^{-1}\,year^{-1}$). We observed no significant trends in NO_3^- concentrations at the SFB and LH sites. Declines in SO_4^{2-} concentrations were considerably greater at the SFB site (3.47 $\mu Eq\,L^{-1}\,year^{-1}$, Table 1) compared to declines at the HH and LH sites (2.37 and 2.70 $\mu Eq\,L^{-1}\,year^{-1}$ respectively,

Table 1. Long-term trends in soil solution chemistry at three sites adjacent to watershed 6 at the HBEF. Values represent the annual rate of change in pH units year^{-1}, μmol L^{-1} year^{-1} (Al$_i$, Al$_o$ and DOC) or μEq L^{-1} year^{-1} (C$_A$, C$_B$, SO_4^{2-}, Ca^{2+} and ANC) as determined by the SKT test (see text). Values in italic are significant at $p < 0.10$.

		pH	C$_A$	C$_B$	SO_4^{2-}	Ca^{2+}	Al$_i$	Al$_o$	ANC	DOC
Oa soil solution										
SFB	Median slope	*−0.007*	*−3.35*	*−2.16*	*−3.47*	*−1.17*	*−0.07*	−0.23	1.20	−29.4
	Significant level	0.045	0.023	0.035	<0.01	<0.01	0.098	0.123	0.201	0.149
	n	118	111	110	113	111	109	112	107	109
HH	Median slope	*−0.023*	*−4.31*	*−4.85*	*−2.37*	*−2.16*	−0.10	*−0.35*	−0.31	−2.00
	Significant level	0.012	0.011	<0.01	<0.01	<0.01	0.244	0.016	0.478	0.474
	n	122	118	116	118	118	117	117	115	116
LH	Median slope	*−0.047*	−2.88	*−5.2*	*−2.70*	*−2.70*	−0.02	*−0.34*	−1.27	*−40.21*
	Significant level	<0.01	0.123	0.044	0.013	0.020	0.437	0.060	0.296	0.086
	n	108	110	105	110	106	105	105	105	105
Bs soil solution										
SFB	Median slope	−0.007	*−3.35*	*−1.54*	*−2.42*	*−0.31*	*−0.61*	*−0.83*	*2.49*	*−18.17*
	Significant level	0.105	0.010	<0.01	0.015	0.046	<0.01	<0.01	0.011	<0.01
	n	129	126	123	127	125	123	125	121	123
HH	Median slope	*−0.010*	*−3.34*	*−1.36*	*−2.56*	*−0.89*	*−0.42*	*−0.39*	*2.28*	−2.25
	Significant level	0.077	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.012	0.187
	n	123	122	116	122	118	120	120	116	120
LH	Median slope	*−0.031*	*−2.44*	*−2.61*	*−2.08*	*−1.83*	0.15	*−0.14*	−0.31	*−1.90*
	Significant level	0.013	<0.01	<0.01	<0.01	<0.01	0.218	<0.01	0.290	<0.01
	n	92	88	83	88	84	89	89	83	87

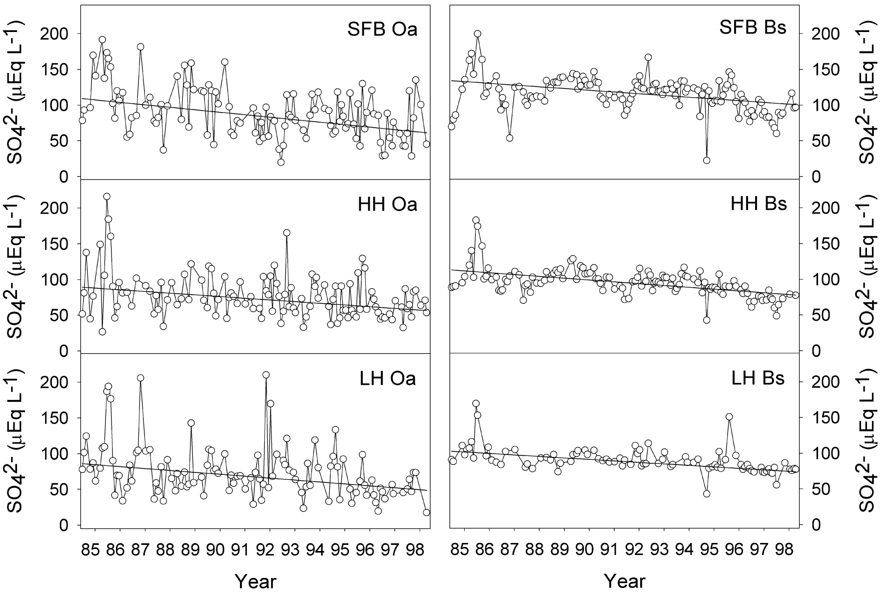

Figure 2. Time series for sulfate (SO_4^{2-}) equivalence in soil solutions draining Oa (left panel) and Bs horizons (right panel) at three sites at the HBEF; spruce–fir–white birch (SFB); mid-elevation hardwoods (HH); low-elevation hardwoods (LH). Slopes for regression lines represent the long-term trends calculated using the SKT test (see text).

Table 1). At all three sites, declines in SO_4^{2-} concentrations (Table 1; Figure 2) were accompanied by declines in C_B concentrations (Table 1). The rates of decline in C_B and individual base cations were small at the highest elevation and increased in magnitude at lower elevations (Table 1; Figure 3). At the LH site the decline in C_B was almost double the decrease in C_A, consistent with the significant decline in pH at that site. Whilst concentrations of the individual cations Ca^{2+}, Mg^{2+} and K^+ all declined, on an equivalence basis the largest rates of concentration decrease were observed for Ca^{2+} at all sites (Table 1; Figure 3).

Despite the declines in pH, we did not observe increases in Al concentrations in Oa soil solutions. Indeed, there was a significant, though small, decrease in Al_i concentration at the SFB site (0.07 μmol L^{-1} $year^{-1}$; Table 1). During 1984–1998, Al_i concentrations in Oa soil solutions averaged 3.4, 6.5 and 3.3 μmol L^{-1} at the SFB, HH and LH sites, respectively. There were also significant decreases in Al_o at the HH and LH sites (0.35 and 0.34 μmol L^{-1} $year^{-1}$, respectively). During the late 1990s, Al_o concentrations in Bs soil solutions were commonly in the range 5–15 μmol L^{-1} at both the HH and LH sites, and ranged from 3 to 27 μmol L^{-1} at the SFB site. At all sites there was a trend of decreasing DOC concentration during the period, but only the LH site showed a slope that was statistically significant at $p < 0.10$.

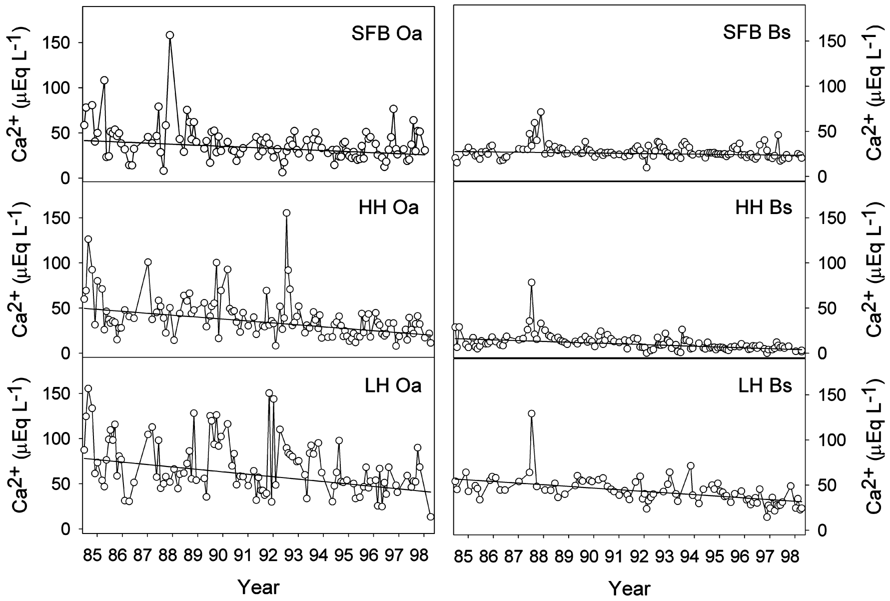

Figure 3. Time series for calcium (Ca^{2+}) equivalence in soil solutions draining Oa (left panel) and Bs horizons (right panel) at three sites at the HBEF spruce–fir–white birch (SFB); mid-elevation hardwoods (HH); low-elevation hardwoods (LH). Slopes for regression lines represent the long-term trends calculated using the SKT test (see text).

We also observed small but statistically significant declines in DIC at the SFB and LH sites (11.3 and 9.7 μmol L^{-1} $year^{-1}$, $p < 0.1$), in F at all sites (0.02–0.04 μmol L^{-1} $year^{-1}$, $p < 0.1$), and in dissolved silica at the SFB and HH sites (1.12 and 1.62 μmol L^{-1} $year^{-1}$ respectively, $p < 0.05$).

Mineral soil solutions

As in the Oa soil solutions, the pH of soil solutions in the Bs horizon declined slightly over the period 1984–1998, although in the SFB zone the decline was not statistically significant (Table 1). During 1984–1998, soil solution pH fluctuated around 4.4 at the SFB and HH sites. At the LH site, soil solution had a mean pH of 5.1 during 1984–1987, falling to 4.7 during 1995–1998. In soil solutions draining Bs horizons, declines in concentrations of strong acid anions and base cations were also accompanied by declines in Al at all sites during 1984–1998 (Table 1). Decreases in C_A were greatest at mid-to-high elevation (SFB and HH) sites, were similar in magnitude to declines observed in Oa soil solutions, and were dominated by SO_4^{2-} (Figure 2). We also observed statistically significant declines in NO_3^- at the SFB and HH sites, though the rates of decline were small (SFB: 0.33 μEq L^{-1} $year^{-1}$, $p = 0.016$; HH: 0.45 μEq L^{-1} $year^{-1}$, $p = 0.027$) relative to declines in SO_4^{2-} at these sites (SFB: 2.42 μEq L^{-1} $year^{-1}$, $p = 0.015$; HH: 2.56 μEq L^{-1} $year^{-1}$, $p < 0.01$). The LH site

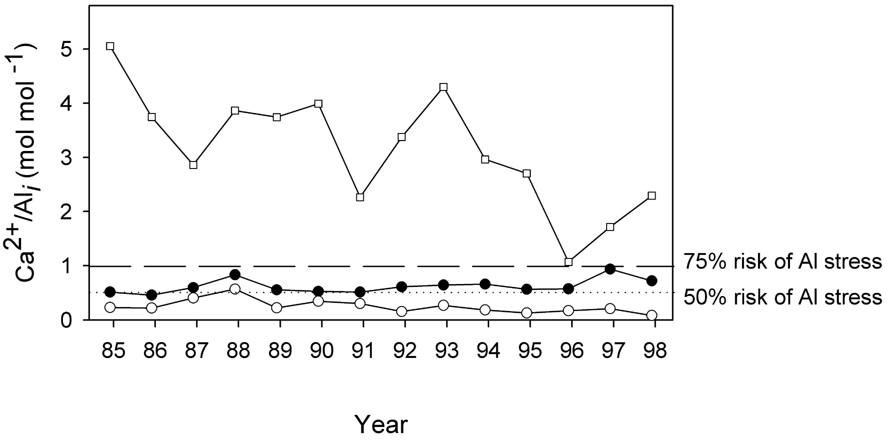

Figure 4. Annual volume-weighted Ca^{2+}/Al_i ratios in Bs soil solutions at three sites at the HBEF; spruce–fir–white birch (●), mid-elevation hardwoods (○), low-elevation hardwoods (☐).

showed the smallest declines in C_A and Al_m concentrations, and the greatest decline in C_B (Table 1). At all sites, rates of C_B and Ca^{2+} concentration declines in Bs horizon soil solutions were considerably smaller than corresponding rates of concentration decline in Oa soil solutions (Table 1, Figure 3). At the HH and LH sites, declines in Ca^{2+} contributed approximately two-thirds to decreases in C_B but were a small component of the C_B decline at the SFB site (Table 1).

Soil solutions draining Bs horizon soils at SFB and HH sites showed significant declines in both Al_i and Al_o concentrations. During 1984–1987, Al_i concentrations at the SFB and HH sites averaged 24.1 and 22.4 μmol L^{-1} respectively, falling to 18.7 μmol L^{-1} (SFB) and 18.3 μmol L^{-1} (HH) during 1995–1998. The strong decline in Al_o at the SFB site, from a mean of 17.3 μmol L^{-1} during 1984–1987 to a mean of 6.8 μmol L^{-1} during 1995–1998, was accompanied by a significant decline in DOC (Table 1). We observed much smaller declines in Al_o and DOC at the LH site, and no statistically significant decline in Al_i concentration. The low and declining Ca^{2+} concentrations have contributed to persistently low (SFB and HH) and declining (HH and LH, $p < 0.01$) Ca^{2+}/Al_i ratios in mineral soil solutions, despite significant decreases in Al_i concentrations (Figure 4). As with Oa soil solutions, we observed declines in DIC in Bs soil solutions at all sites (6.7–10.3 μmol L^{-1} year^{-1}, $p < 0.05$). There were also small but statistically significant declines in dissolved silica (HH: 0.59 μmol L^{-1} year^{-1}, $p = 0.07$; LH: 1.42 μmol L^{-1}, $p < 0.01$) and F (all sites: 0.04 μmol L^{-1} year^{-1}, $p < 0.05$).

Stream water

Changes in stream water pH between 1982 and 2000 were either statistically insignificant or very small (Table 2). Average pH values ranged from 3.99 (site 1) to

Table 2. Long-term trends in stream water chemistry at 6 sites in watershed six at the HBEF. Sites are ordered from highest (site 1) to lowest (site 7) elevations. Values represent the annual rate of change in pH units yr^{-1}, $\mu mol\,L^{-1}\,yr^{-1}$ (Al_i, Al_o and DOC) or $\mu Eq\,L^{-1}\,yr^{-1}$ (C_A, C_B, SO_4^{2-}, Ca^{2+} and ANC) as determined by the SKT test (see text). Values in italic are significant at $p < 0.10$.

		pH	C_A	C_B	SO_4^{2-}	Ca^{2+}	Al_i	Al_o	ANC	DOC
Site 1	Median slope	0.002	*−3.79*	*−1.48*	*−3.65*	−0.15	−0.058	*−0.36*	*2.47*	*−27.80*
	Significant level	0.159	<0.01	0.019	<0.01	0.165	0.168	0.020	<0.01	0.090
	n	43	43	43	44	43	44	44	41	42
Site 2	Median slope	0.000	*−2.85*	*−0.81*	*−2.60*	*−0.44*	*−0.11*	*−0.23*	*1.95*	−3.51
	Significant level	0.438	<0.01	0.012	<0.01	<0.01	0.066	<0.01	<0.01	0.213
	n	112	112	108	112	110	107	107	108	110
Site 3	Median slope	*−0.005*	*−2.11*	*−0.74*	*−2.12*	*−0.53*	*−0.41*	*−0.18*	*1.36*	−0.45
	Significant level	0.029	<0.01	0.067	<0.01	<0.01	<0.01	<0.01	<0.01	0.360
	n	135	134	132	134	133	129	129	131	133
Site 4	Median slope	*−0.006*	*−1.90*	*−0.50*	*−1.91*	*−0.41*	*−0.45*	*−0.13*	*1.25*	*−2.62*
	Significant level	<0.01	<0.01	0.088	<0.01	<0.01	<0.01	<0.01	<0.01	0.011
	n	149	149	142	149	145	142	142	142	146
Site 5	Median slope	−0.002	*−1.89*	−0.182	*−1.80*	*−0.31*	*−0.41*	*−0.08*	*1.38*	−1.30
	Significant level	0.191	<0.01	0.324	<0.01	0.056	<0.01	0.026	<0.01	0.107
	n	166	166	159	166	161	156	157	159	162
Site 7	Median slope	−0.001	*−1.70*	*−0.59*	*−1.52*	*−0.49*	*−0.26*	*−0.03*	*1.21*	*−1.40*
	Significant level	0.391	<0.01	0.046	<0.01	<0.01	<0.01	0.047	<0.01	0.016
	n	180	178	173	180	174	164	167	171	171

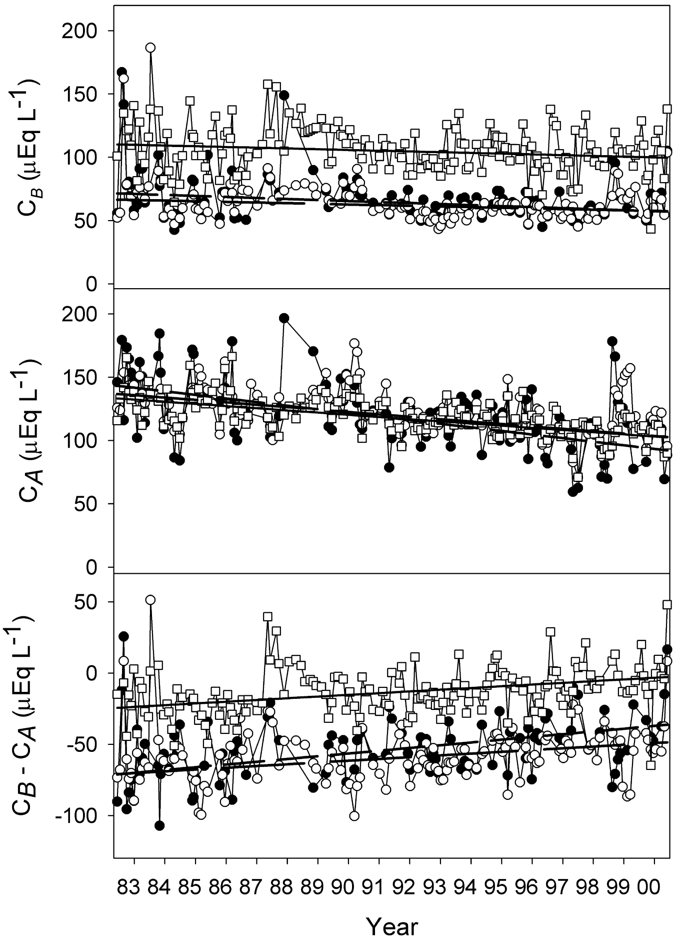

Figure 5. Time series for total base cations (C_B), total acidic anions (C_A) and ANC (C_B-C_A) in stream water at three longitudinal sites in watershed 6 at the HBEF. Site 2 (●) drains the spruce–fir–white birch zone (SFB); site 4 (○) drains the mid-elevation hardwood (HH) and SFB zones; site 7 (□) drains the combined low-elevation hardwood (LH), HH and SFB zones. Slopes for regression lines represent the long-term trends calculated using the SKT test (see text); site 2 (short dash); site 4 (long dash) and site 7 (line).

4.94 (site 7) during the period. For other solutes, there were distinct longitudinal patterns in the long-term trends in stream water chemistry that generally reflected the temporal changes observed in soil solution chemistry in the subcatchments. Rates of C_B and C_A declines were greatest at the high elevation stream site, although comparison between this site and sites at lower elevations is difficult because of the relative paucity of data due to ephemeral stream flow at site 1. Decreases in C_A were greater than decreases in C_B, and exhibited somewhat stronger elevational trends, although between-site differences in slope were small

(Table 2; Figure 5). Consequently recovery in terms of ANC was greatest in stream sites draining the SFB zone (sites 1 and 2) and decreased with elevation (Table 2; Figure 5). Decreases in SO_4^{2-} dominated the declines in C_A (Table 2); we observed no significant trends in NO_3^- concentrations except for a very small decline at the lowest elevation site (site 7: 0.005 μEq L^{-1} $year^{-1}$, $p = 0.06$). At the gauging station (site 7), the slope for SO_4^{2-} decline (1.52 μEq L^{-1} $year^{-1}$) was considerably smaller than the slope observed in LH soil solutions (Oa: 2.70 μEq L^{-1} $year^{-1}$; Bs: 2.08 μEq L^{-1} $year^{-1}$), and almost 40% less than the decline observed at stream site 2 (2.6 μEq L^{-1} $year^{-1}$).

Aluminum concentrations declined significantly at all sites, except for Al_i at site 1 (Table 2). The greatest declines in Al_o concentrations occurred at the ephemeral high elevation site, whereas the greatest declines in Al_i concentrations occurred at mid-to-low elevation sites (Table 2). At site 1, the strong decline in Al_o was accompanied by a corresponding decline in DOC, with somewhat smaller, but statistically significant DOC decreases also occurring at sites 4 and 7 (Table 2).

We observed small declines in F at all sites (0.01–0.04 μmol L^{-1} $year^{-1}$; $p < 0.01$). There were also significant declines in dissolved silica at sites 1 and 4 (1.19 and 0.28 μmol L^{-1} $year^{-1}$ respectively, $p < 0.05$), and in DIC at site 1 (16.1 μmol L^{-1} $year^{-1}$; $p = 0.03$), site 4 (0.68 μmol L^{-1} $year^{-1}$; $p = 0.09$) and site 5 (0.50 μmol L^{-1} $year^{-1}$; $p = 0.06$).

Discussion

There has been considerable speculation in recent years that in areas where soils are derived from base-poor glaciated tills, forest productivity will become limited by base cation supply, particularly Ca^{2+} (Federer et al. 1989; Likens et al. 1996). Soil stores of base cations have been depleted by: (i) forest harvesting (Federer et al. 1989); (ii) leaching as a consequence of acidic deposition (Likens et al. 1996; Lawrence et al. 1999); and (iii) declines in atmospheric base cation deposition (Hedin et al. 1994; Likens et al. 1996), an important source of base cations to vegetation (Miller et al. 1993).

Since 1975, inputs of Ca^{2+} and C_B in bulk precipitation at the HBEF have decreased (Likens et al. 1996, 1998). However, although this decline has influenced the base status of soil and soil waters, it would appear that the large declines in C_B in forest floor soil solutions during 1984–1998 (Figure 3) have occurred primarily in response to decreasing concentrations of strong acid anions in solution (Gbondo-Tugbawa and Driscoll 2003). Furthermore, the declines in C_B in Oa horizon solutions are of similar magnitude to the declines in C_A, with little overall change in ANC ($C_B - C_A$) during the sampling period (Table 1). In contrast, the C_B response to declining C_A in mineral soil solutions has been small, resulting in an improvement in ANC, particularly at higher elevations. This is not surprising since cation exchange capacity and base saturation are low in HBEF mineral soils compared to Oa horizons (Johnson et al. 1991). In an environment of either increasing or decreasing C_A, HBEF mineral soils have little potential for buffering. Furthermore, fluxes of C_B are considerably greater in soil solutions draining Oa horizons at the HBEF than in solutions draining Bs horizons (Johnson et al. 2000). Thus, much of the Ca^{2+} and C_B released from HBEF soils appear to be derived from the forest floor. Our data suggest that the large net losses of base cations from the HBEF soil system observed by Likens et al. (1996, 1998) may be explained by the persistent loss of C_B from the forest floor as a direct consequence of historically elevated atmospheric inputs of SO_4^{2-}. Other researchers have attempted to measure changes in exchangeable or extractable Ca in Hubbard Brook soils (Lawrence et al. 1995; Yanai et al. 1999). Lawrence et al. (1995) reported significantly lower exchangeable Ca^{2+} concentrations in Oa horizon soils under spruce–fir stands for samples collected in 1987 and 1992, compared to samples collected in 1969 and 1970. They proposed that the loss of Ca^{2+} from coniferous forest floor soils was a consequence of the mobilization of Al in mineral soils and subsequent redistribution into the forest floor, where the high affinity of Al for organic matter binding sites causes Al to be retained more effectively than Ca^{2+}. However, neither Lawrence et al. (1995) nor Yanai et al. (1999) detected statistically significant changes in extractable or exchangeable Ca concentrations throughout the watershed.

Sulfur dynamics in forest watersheds are not completely understood. Evidence from watershed mass balance calculations (Mitchell et al. 1996; Johnson et al. 2000; Likens et al. 2002) and biogeochemical modeling (Driscoll et al. 1998; Gbondo-Tugbawa et al. 2002) suggest that there is a missing, or poorly quantified, source of S to forest ecosystems. Net ecosystem outputs of S typically exceed inputs at HBEF, with net mineralization from organic soils and net desorption in mineral soils being the most likely sources of the imbalance. Mineral weathering inputs or underestimated dry deposition of S may also be contributing sources (Likens et al. 2002). Sulfate concentrations in soil solutions at the HBEF exhibit small increases with depth, and decrease with decreasing elevation, although the differences are not statistically significant. Stream SO_4^{2-} concentrations do not differ significantly from one site to another (Figure 5; Johnson et al. 2000; Likens et al. 2002). In this respect, the spatial variation we observed in the long-term rates of decline in stream water SO_4^{2-} is surprising. Furthermore, the rates of decline in SO_4^{2-} in soil solutions and at most stream sites were greater than the average change in annual volume-weighted SO_4^{2-} concentrations in bulk precipitation at HBEF ($1.2\,\mu Eq\,L^{-1}\,year^{-1}$ in 1984/85 to 1997/98; Likens et al. 2002). Long-term changes in dry deposited S (the portion not captured in bulk precipitation) may also be occurring but are difficult to evaluate because of (i) the lack of suitable methods to compare air concentrations with concentrations in wet-only or bulk precipitation and (ii) the relatively short record of dry deposition data that is available for trend analysis. A large decline in dry S deposition would be consistent with the large decreases in SO_4^{2-} concentrations observed in Oa soil solutions (Figure 1) during 1984–1998. However, there is a lack of dry S deposition data for the entire period. Dry deposition data have been collected at Hubbard Brook (WST109) since 1989 through the US Environmental Protection Agency's Clean Air Status and Trends Network (www.epa.gov/CASTNet). Since measurements were initiated, atmospheric concentrations of both SO_2 and particulate SO_4 have been declining (www.epa.gov/CASTNet), such that the dry to bulk S deposition ratio has decreased in recent years.

Sulfur adsorption/desorption processes are unlikely to contribute to decreases in SO_4^{2-} concentrations in solutions draining the forest floor, due to the limited number of positively charged adsorption sites. However, the release of previously adsorbed S in mineral soils could account for the elevated concentrations and slight attenuation of the SO_4^{2-} decline in Bs solutions relative to Oa solutions, particularly at the LH site, where the mineral soil is deeper. This mechanism is also consistent with patterns in stream SO_4^{2-} declines. The rate of decline in SO_4^{2-} concentration decreased downstream; as the stream drains watershed areas that are increasingly dominated by deeper mineral soils, it appears that desorption of previously sorbed SO_4^{2-} may be limiting the recovery in stream SO_4^{2-} concentrations. This is consistent with the conceptual model proposed by Cosby et al. (1985), wherein stream water response to declining inputs of SO_4^{2-} is delayed as a consequence of non-linear sulfur adsorption processes.

In many forest ecosystems underlain by soils with low base saturation, inputs of C_A in drainage waters are neutralized in part by a mixture of base cations and Al (Cronan and Schofield 1990). Consequently, as concentrations of C_A in drainage waters decline in response to changing acidic deposition, a decline in C_B and Al is also to be expected.

Declines in C_A in Oa soil solutions have not been accompanied by substantial declines in Al_i concentrations. Total monomeric Al concentrations have declined, but the change has been primarily in the Al_o fraction – the predominant form of Al in DOC-rich solutions draining the forest floor. The strong positive relationship between Al_o concentration and DOC in soil solutions draining both the Oa and Bs horizons at the HBEF (Figure 6) is a clear indicator of the affinity of Al for OA^-. At some sites, but not all, declines in Al_o in Oa and Bs soil solutions and in stream water were accompanied by significant declines in DOC (Table 1). At the HBEF, we observed the greatest declines in Al_i concentrations in mineral soil solutions at the SFB and HH sites (Table 1). Soil solutions at these sites historically had the highest concentrations of Al_i and low C_B concentrations. Furthermore, they exhibited the slowest rate of C_B recovery relative to mineral soil solutions at the LH site or to solutions draining the forest floor (Table 1).

The decline in Al_i concentrations with decreasing pH is puzzling. The solubility of Al is strongly pH dependent, with increasing solubility at lower pH. Thus we would expect to have observed increasing Al_i in HBEF soil solutions and stream waters in which pH had declined. Several studies have suggested that Al concentrations in solutions of acid forest soils are controlled by reactions with Al-organic matter complexes rather than pH-dependent solubility of mineral phases such as $Al(OH)_3$ (Berggren and Mulder 1995; Skyllberg 1999). Therefore, lower Al_i concentrations may be related to changes in organically bound Al in soils and/or soil solutions.

The implication of decreasing soil solution Al_i (the potentially more toxic form of Al) and Ca^{2+} concentrations for the health of terrestrial ecosystems is difficult to evaluate but is a critical issue for assessment of the effects of acidic deposition.

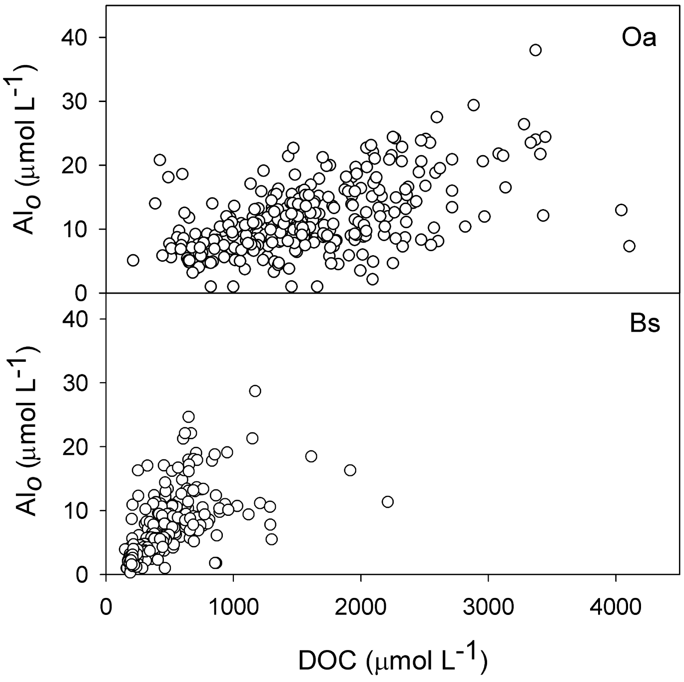

Figure 6. Organic monomeric aluminum (Al_o) as a function of DOC in Oa soil solutions and Bs soil solutions at the HBEF.

Based on a comprehensive examination of the literature, Cronan and Grigal (1995) concluded that there is a 50% risk of Al stress to trees if the soil solution Ca/Al molar ratio is less than 1, increasing to 75% risk of damage if the Ca/Al ratio is <0.5 (Figure 4). An examination of the Ca^{2+}/Al_i molar ratios in mineral soil solutions at the HBEF suggests that there may indeed be evidence for past and continuing ecosystem stress, particularly at the SFB and HH sites (Figure 4). This pattern may pose the greatest risk to red spruce growing at high elevations. In a number of studies, red spruce have exhibited a stress response at Ca/Al ratios greater than those observed at the HBEF (e.g., Thornton et al. 1987). Sugar maple, which is prominent throughout the HBEF, may also be susceptible to Al stress (Thornton et al. 1986) at the very low Ca^{2+}/Al_i ratios (<0.5 mol mol^{-1}) observed at the HH site. The LH site, where the Bs soil solution typically is base-rich, has a higher pH and lower concentration of Al_i relative to solutions draining mid-to-higher elevations, and large declines in Ca^{2+} have occurred with no change in Al_i concentrations. Consequently, Ca^{2+}/Al_i ratios in mineral soil solutions at the LH site are declining, and could fall to values <1.0 within 5 years if the current rate of decline (0.19 mol mol^{-1} year^{-1}; $p < 0.01$) continues. However, the usefulness of soil solution Ca/Al_i ratios as an indicator of forest stress will ultimately depend on the species-specific threshold concentration for Al toxicity to plants. A further indication of susceptibility to Al stress at the HBEF comes from the very low effective base saturation (9%) in the mineral soil (Johnson et al. 1991). This is well below the threshold of 15% suggested as one of the multiple assessment tools for determining the probability of ecosystem stress from elevated Al concentrations (Cronan and Grigal 1995; Cronan and Schofield 1990).

Despite significant declines over the period 1984–1998, Al_i concentrations in stream water draining the HH subcatchment (stream site 4) are still typically in excess of $10\,\mu mol\,L^{-1}$, greatly in excess of concentrations that are harmful to fish (1–$3\,\mu mol\,L^{-1}$; Bulger et al. 1993). This is due to the low base cation supply and relatively low DOC concentrations in stream waters at this site, where elevated concentrations of SO_4^{2-} have historically been accompanied by elevated concentrations of potentially toxic Al_i (Lawrence et al. 1986, 1988). In contrast, stream water concentrations at site 7 are much lower (mean $3.3\,\mu mol\,L^{-1}$ during 1997–2000) and are predicted to fall below $1\,\mu mol\,L^{-1}$ within 10 years if current rates of decline are maintained (Palmer and Driscoll 2002).

We observed decreasing or unchanged DOC concentrations in soil solutions and stream water during 1984–1998. Unfortunately, there is a dearth of published data on long-term trends in DOC concentrations in freshwaters at other sites. Krug and Frink (1983) postulated that in organic-rich soils, acidic deposition would result in an increase in SO_4^{2-} and a decrease in organic acid leaching with little change in pH and base cation leaching. This would imply that decreases in SO_4^{2-} leaching such as those observed at the HBEF should be accompanied by an increase in DOC and organic acids. Significant increases in DOC concentrations and somewhat inconsistent trends for pH and SO_4^{2-} concentrations were reported at 19 out of 22 upland freshwater sites across the UK, and were attributed to local climatic influences rather than declines in atmospheric S deposition (Monteith et al. 2001). Other studies at forested sites in Scotland and the Adirondack region of New York have reported significant increases in DOC with declines in SO_4^{2-} in lake waters (Harriman et al. 2001; Driscoll et al. 2003). The only statistically significant trends in DOC in our data were decreases. In contrast, we found small but statistically significant increases in OA^- in Oa soil solutions (SFB: $1.61\,\mu Eq\,L^{-1}\,year^{-1}$, $p = 0.1$; HH: $1.89\,\mu Eq\,L^{-1}\,year^{-1}$, $p = 0.07$) and Bs soil solutions (SFB: $2.35\,\mu Eq\,L^{-1}\,year^{-1}$; HH: $1.97\,\mu Eq\,L^{-1}\,year^{-1}$, $p = 0.07$ both sites). These changes in DOC and OA^- concentrations have important implications for acid-base chemistry in HBEF drainage waters. Increasing OA^- in the presence of unchanged or decreasing DOC indicates that reductions in acidic deposition have resulted in a higher degree of dissociation of organic acids at the HBEF. Thus it appears that the release of H^+ from naturally occurring organic solutes (i.e., DOC) during the recovery period is an important factor in the continued declines in pH we have observed (Tables 1 and 2). However, as the degree of dissociation increases, the buffer capacity remaining declines, suggesting that continued declines in acid deposition will eventually produce increases in pH.

By the end of our sampling period (1982–2000), ANC at stream site 7 was fluctuating around $0\,\mu Eq\,L^{-1}$ (Figure 5). This result supports the prediction of Likens et al. (1996) that ANC in stream water at the HBEF would become positive again around autumn 1999. At stream sites draining mid-to-high elevation subcatchments, ANC remains low (Figure 5). If current rates of decline in SO_4^{2-} and C_B continue, ANC will approach $0\,\mu Eq\,L^{-1}$ around the year 2030 at site 2 (SFB subctachment) but not until 2050 at site 4 (HH subcatchment). The projected changes in stream chemistry will alter the existing longitudinal pattern in stream water chemistry of increasing ANC with decreasing elevation. Our data indicate a stronger decline in C_A relative to C_B in waters draining the SFB subcatchment, probably a reflection of the contribution of shallow flow paths through relatively base-rich organic soils to stream run-off at this site (Johnson et al. 2000). In the steep HH zone, the slow recovery in ANC is a consequence of rapid flow paths through mineral soils where drainage waters are depleted in C_B but continue to leach SO_4^{2-} (Figures 2–3; Johnson et al. 2000).

At the HBEF, depletion of soil base cation pools has clearly limited the rate of recovery from acidic deposition. However, other mechanisms may also have contributed to the slow recovery in stream pH and ANC. As with soil solutions, we observed increases in OA^- concentrations in stream waters ($0.84\,\mu Eq\,L^{-1}\,year^{-1}$ at site 7, $p = 0.03$). This may be evidence of an increasing role for deprotonation of organic acids in buffering against increases in pH and ANC. There is also evidence that past and continuing hydrolysis of Al is an important control on pH buffering and ANC. The net charge on Al species (Al^{n+}/Al_i) is small and has changed little during the sampling period (5-year means of 1.2 and $1.3\,Eq\,mol^{-1}$ during 1986–1990 and 1996–2000, respectively). The species that contribute to this charge are predominantly Al-OH and Al-F complexes, and Al^{3+}. However, if Al_i concentrations continue to decline, we anticipate that the relative importance of Al hydrolysis in buffering waters against increases in pH and ANC will diminish in the future.

Summary and conclusions

Our data show that there are clear spatial differences in the response of soil solutions and stream waters draining an acid-sensitive forest ecosystem to declines in atmospheric deposition of SO_4^{2-}. In summary, our main findings are:

1. In Oa soil solutions, C_B concentrations have declined approximately in line with C_A. This response has resulted in little impact on the ANC of drainage waters.
2. In mineral soil solutions at mid-to higher elevations, declines in C_A were accompanied by smaller declines in C_B, and significant declines in Al_i. The inability of the shallow soils to neutralize inputs of strong acid anions through C_B release has resulted in persistently low and declining concentrations of Ca^{2+} in soil solution while Al_i concentrations have remained high ($15–20\,\mu mol\,L^{-1}$). This presents a continued risk of Al stress to the forest ecosystem in areas dominated by shallow soils and steep slopes. At lower elevation, soils continue to leach SO_4^{2-} despite long-term declines in atmospheric deposition. At this site, where soils are deeper and solutions more base-rich relative to mid-to-higher elevations, there has been no change in Al_i concentrations, and base cation concentrations in mineral soil solutions have declined at a similar rate to C_A.

3. Changes in the chemistry of stream water at longitudinal sampling points reflect changes observed in the chemistry of soil solutions at corresponding elevations and the contribution of flow generated in different soil horizons to stream runoff. Consequently, the most beneficial effect on the aquatic environment occurred at the highest elevation sites, where recovery in terms of an increase in ANC and potential for alleviation of Al stress were greatest. Nevertheless, at mid elevation stream sites, concentrations of $\mathrm{Al_i}$ remain high (typically $>10\,\mu\mathrm{mol\,L^{-1}}$) and ANC low ($-50$ to $-75\,\mu\mathrm{Eq\,L^{-1}}$), contributing to a chemical environment that may continue to be stressful to aquatic biota. At lower elevations, where flow paths through deeper mineral soils contribute more to stream flow, recovery in ANC has been limited by the persistent release of accumulated $\mathrm{SO_4^{2-}}$. Nevertheless, by the end of the sampling period, ANC values were fluctuating around $0\,\mu\mathrm{Eq\,L^{-1}}$ and $\mathrm{Al_i}$ concentrations were around $3\,\mu\mathrm{mol\,L^{-1}}$ at the lowest elevation stream sampling site.

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