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Key Points:

- Chemistry of stream and soil water has become less acidic due to decreases in acid deposition
- Snowmelt acidification has recovered at the same rate as the baseline conditions
- Contrary to many sites recovering from acidification, DOC has primarily decreased at Hubbard Brook

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Recovery from chronic and snowmelt acidification: Long-term trends in stream and soil water chemistry at the Hubbard Brook Experimental Forest, New Hampshire, USA

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Abstract Atmospheric acid deposition of sulfate and nitrate has declined markedly in the northeastern United States due to emissions controls. We investigated long-term trends in soil water (1984–2011) and stream water (1982–2011) chemistry along an elevation gradient of a forested watershed to evaluate the progress of recovery of drainage waters from acidic deposition at the Hubbard Brook Experimental Forest in the White Mountains of New Hampshire, USA. We found slowed losses of base cations from soil and decreased mobilization of dissolved inorganic aluminum. Stream water pH at the watershed outlet increased at a rate of 0.01 units yr^{-1}, and the acid neutralizing capacity (ANC) gained 0.88 $\mu eq\ L^{-1}\ yr^{-1}$. Dissolved organic carbon generally decreased in stream water and soil solutions, contrary to trends observed at many North American and European sites. We compared whole-year hydrochemical trends with those during snowmelt, which is the highest-flow and lowest ANC period of the year, indicative of episodic acidification. Stream water during snowmelt had long-term trends of increasing ANC and pH at a rate very similar to the whole-year record, with closely related steady decreases in sulfate. A more rapid decline in stream water nitrate during snowmelt compared with the whole-year trend may be due, in part, to the marked decrease in atmospheric nitrate deposition during the last decade. The similarity between the whole-year trends and those of the snowmelt period is an important finding that demonstrates a consistency between recovery from chronic acidification during base flow and abatement of snowmelt acidification.

1. Introduction

Atmospheric acid deposition resulting from emissions of sulfur and nitrogen oxides has been a widespread environmental problem for many decades in North America, Europe, and Asia [*Rodhe et al.*, 2002]. The impacts include acidification of surface waters [*Driscoll et al.*, 2001], associated toxicity to aquatic biota [*Baker et al.*, 1996], and reduced health and growth of forest trees [*Duchesne et al.*, 2002]. While emission controls have substantially reduced acidic deposition in recent decades [*Lynch et al.*, 2000; *Schöpp et al.*, 2001], and many locations have shown signs of recovery in surface waters [*Wright et al.*, 2005; *Burns et al.*, 2006], the rate of recovery has been slow, especially in acid-sensitive environments [*Akselsson et al.*, 2013; *Sullivan et al.*, 2013; *Borg and Sundbom*, 2014; *Futter et al.*, 2014]. Slow recoveries are generally linked to soils that are depleted in available base cations due to elevated leaching from historical acid deposition [*Lawrence*, 2002; *Sverdrup et al.*, 2005; *Warby et al.*, 2009].

In addition to the chronic effects of acid deposition, episodic acidification is of particular concern in the surface waters of acid-sensitive ecosystems. Episodic acidification occurs when the pH and acid-neutralizing capacity (ANC) are depressed during high-flow events associated with storms or snowmelt. These episodes result from acidification from both natural processes and atmospheric deposition [*Galloway et al.*, 1987; *Laudon et al.*, 2004] and are often driven by changes in hydrologic flow paths as runoff increases. During base flow, groundwater contributions dominate and the flow paths are typically through deeper mineral soil horizons and surficial geologic deposits [*Ohte et al.*, 2004]. During hydrologic events, the flow paths contributing to stream water shift to shallower soil, which tends to be more acidic than deeper soil due to either higher concentrations of naturally occurring organic acids or acidic deposition [*Chen et al.*, 1984; *Potter et al.*, 1988]. The main driver of episodic acidification across the United States has been shown to be the dilution of base cations relative to strong acid anions [*Wigington et al.*, 1990]. Atmospheric deposition of anthropogenically derived acids can cause or exacerbate acidification events in surface waters by (1) providing direct inputs of acids to surface waters; (2) supplying SO_4^{2-}, NO_3^-, NH_4^+, and H^+, which accumulate in the upper soil horizons during relatively dry periods; and (3) lowering the chronic ANC of surface waters, which leads to even lower ANC during episodes [*Galloway et al.*, 1987].

While increases in SO_4^{2-} have been shown to significantly contribute to episodic acidification in mid-Atlantic streams [*O'Brien et al.*, 1993; *DeWalle and Swistock*, 1994], pulses of increased NO_3^- concentrations concurrent with hydrologic events have been especially important contributors to short-term decreases in ANC in catchments of the northeastern U.S. [*Wigington et al.*, 1996; *Sullivan et al.*, 1997; *Driscoll et al.*, 2001]. Acidification from NO_3^- is particularly pronounced during snowmelt when NO_3^- is flushed at high concentrations [*Sebestyen et al.*, 2008]. Following 18 years of experimental acidification through amendments of ammonium sulfate at the Bear Brook Watershed in Maine, however, SO_4^{2-} increased in relative importance during episodic acidification, while NO_3^- did not [*Laudon and Norton*, 2010]. In addition to acidification from NO_3^- or SO_4^{2-}, pulses of organic acids can contribute to episodic acidification in streams with high dissolved organic carbon (DOC) concentrations [*Laudon et al.*, 2001; *Wellington and Driscoll*, 2004].

In higher-elevation forested catchments in the northeastern U.S., DOC has been shown to function in part as a strong acid [*Kramer et al.*, 1990; *Fakhraei and Driscoll*, 2015]. Widespread increases of DOC concentrations in surface waters in recent decades have been observed across many parts of Europe and North America [*Evans et al.*, 2005; *Skjelkvåle et al.*, 2005; *Driscoll et al.*, 2007]. The underlying causes of these increased DOC concentrations are not well understood. A number of studies have suggested decreases in acidic deposition [*Evans et al.*, 2006, 2012; *Monteith et al.*, 2007; *SanClements et al.*, 2012] as the driver of increased DOC concentrations, while others point to climate-related changes [e.g., *Hongve et al.*, 2004; *Worrall and Burt*, 2007; *Lepistö et al.*, 2008] or land management changes [*Yallop and Clutterbuck*, 2009; *Holden et al.*, 2012]. Hubbard Brook, the site of our current study, is an outlier by defying the trends of increasing DOC concentrations in surface waters. During the years 1982–2000, stream water DOC declined at Hubbard Brook, coincident with decreased DOC leaching in soil water [*Palmer et al.*, 2004].

While numerous studies have published trends in surface water chemistry in the context of recovery from acidification [e.g., *Stoddard et al.*, 1999; *Driscoll et al.*, 2003; *Skjelkvåle et al.*, 2005; *Warby et al.*, 2005], comparatively few studies have examined long-term trends in soil water chemistry. Fifteen years of soil water chemistry data at Hubbard Brook were examined by *Palmer et al.* [2004]. Trends varied spatially within a small watershed but generally showed slow changes in the chemistry of organic and mineral horizon soil solutions in response to decreased acidic deposition. The changes in soil solution chemistry were taken as signs of early recovery from acidification and included modest increases in ANC and decreased mobilization of dissolved inorganic aluminum (Al_i). As part of the Swedish Throughfall Monitoring Network, *Pihl Karlsson et al.* [2011] analyzed the trends of soil water chemistry across Sweden in relation to decreasing European S and N emissions and found widespread decreases in SO_4^{2-} but irregular recoveries in pH, ANC, and Al_i. In southern Sweden, *Akselsson et al.* [2013] found generally slow recoveries from acidification that were highly sensitive to sea-salt deposition.

The primary objectives of our study were to (1) determine if trends in acid-base chemistry and DOC dynamics of stream and soil waters at Hubbard Brook have continued beyond those reported through the 1990s [*Palmer et al.*, 2004], indicating further recovery of the system, and (2) evaluate if the trends during the snowmelt season, when episodic acidification is of greatest concern, differ from the overall rate of recovery. Our central hypothesis is that while overall recovery has continued with further reductions in acid deposition, recovery from snowmelt seasonal acidification could be diminished relative to the whole-year trends due to (1) an increased relative importance of nitrate to acidification during snowmelt and (2) a long-term cumulative depletion of available base cations from the shallow soils through which preferential flow paths form during snowmelt.

2. Methods

2.1. Site Description

This study was conducted at the Hubbard Brook Experimental Forest (HBEF) in the White Mountain National Forest in central New Hampshire, USA (43°56′N, 71°45′W). Sampling sites were located in and near Watershed 6 (W6), the HBEF biogeochemical reference watershed (13.2 ha, elevation 549–792 m, slope 16°, southeasterly aspect; Figure 1). The HBEF has a cool temperate, humid continental climate, with mean July and January

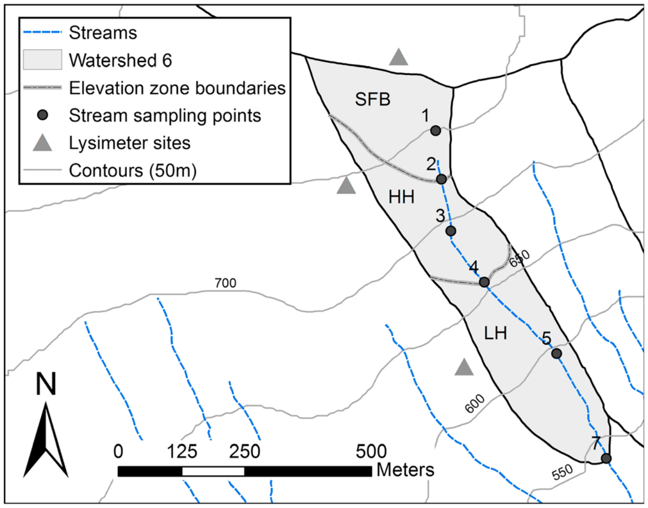

Figure 1. Map of Watershed 6 at the Hubbard Brook Experimental Forest (43°56′N, 71°45′W), showing locations of lysimeter plots and stream sampling points relative to the elevation zones.

temperatures of 18.8 and −8.5°C, respectively (at 450 m elevation). Annual precipitation averages approximately 140 cm and is distributed nearly evenly throughout the year. Approximately 30% of precipitation occurs as snow [*Federer et al*., 1989]. The landscape of the HBEF is generally covered with glacial till derived from local bedrock with a depth ranging from zero along the ridgetops to several meters at the lower elevations [*Palmer et al*., 2004]. The soils are well-drained Spodosols, primarily Haplorthods [*Johnson et al*., 2000], which contain a well-developed organic horizon (3–15 cm [*Likens et al*., 1977]) and are underlain by relatively impervious bedrock (Littleton Formation, schist). Soil depth tends to vary inversely with elevation, with the shallowest soils found along the ridge line at the top of the watershed [*Lawrence et al*., 1986]. The vegetation of W6 is dominated by northern hardwood species, including American beech (*Fagus grandifolia* Ehrh.), sugar maple (*Acer saccharum* Marsh.), and yellow birch (*Betula alleghaniensis* Britt.). At higher elevations, balsam fir (*Abies balsamea* (L.) Mill), red spruce (*Picea rubens* Sarg.), and white birch (*Betula papyrifera* var. *cordifolia* Marsh.) are prominent.

2.2. Sample Collection and Analysis

Soil solutions were collected approximately monthly from tension-free lysimeters since their installation in 1983. Lysimeter sites are located adjacent to W6 at elevations of 600 m (low-elevation hardwood zone, LH), 730 m (high-elevation hardwood zone, HH), and 750 m (spruce-fir-white birch zone, SFB) (Figure 1). Three replicate lysimeters were installed beneath the Oa and Bh horizons and within the Bs horizon at each elevation zone site. Stream samples were collected, concurrent with soil solution sampling, from six longitudinal sites from the headwaters draining the SFB zone to the gauging station at the base of the watershed. Wet deposition is available through the National Atmospheric Deposition Program (site NH02) [*NADP*, 2013].

The pH of all samples was measured potentiometrically with a glass electrode. Calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), and aluminum (Al, graphite furnace) were analyzed using atomic absorption spectroscopy (AAS) for samples prior to 2004 and with inductively coupled plasma mass spectrometry for samples after 2004. Sulfate (SO_4^{2-}), nitrate (NO_3^-), and chloride (Cl^-) were analyzed using ion chromatography. Fluoride (F^-) was analyzed using an ion-selective electrode until 2002 and ion chromatography after 2002. Total base cations (C_B; $\mu Eq\,L^{-1}$) are the sum of $2[Ca^{2+}] + 2[Mg^{2+}] + [K^+] + [Na^+]$; total strong acid anions (C_A; $\mu Eq\,L^{-1}$) are the sum of $2[SO_4^{2-}] + [NO_3^-] + [Cl^-] + [F^-]$. Acid neutralizing capacity (ANC) in this study was calculated as the difference between the sum of base cations and the sum of strong acid anions ($ANC = C_B - C_A$). DOC was measured using infrared detection of CO_2 following UV-persulfate oxidation. Prior to 1989, total monomeric Al (Al_m) was determined by extraction with 8-hydroxy-quinoline in methyl isobutyl ketone in the field and analysis by graphite furnace AAS; since 1989, Al_m was determined colorimetrically following chelation with pyrocatechol violet. Organic monomeric aluminum (Al_o) was determined by the same method as Al_m, after samples passed through a resin ion exchange column. Inorganic monomeric aluminum (Al_i) was calculated as the difference between Al_m and Al_o. We estimate concentrations of organic anions (A^-) as the difference in measured concentrations of solutes with positive charge and negative charge (in $\mu Eq\,L^{-1}$).

The statistical trend analysis was conducted using the nonparametric seasonal Kendal tau test (SKT) [*Hirsch et al*., 1982; *Hirsch and Slack*, 1984]. This test is a modification of the Mann-Kendall test and is designed to eliminate confounding variation associated with seasonality. One of the advantages of this test is that it is

Table 1. Long-Term Trends in Organic Horizon (Oa) Soil Water Chemistry, 1984–2011[a]

		pH	C_B	C_A	ANC	Ca	SO_4^{2-}	NO_3^-	Al_i	Al_o	DOC
Low hardwood	slope	−0.003	−3.64	−3.20	−0.33	−2.05	−1.18	−1.55	+0.04	−0.20	−25.09
	P	0.58	<0.01	<0.01	0.40	<0.01	<0.01	<0.01	0.07	<0.01	<0.01
High hardwood	slope	+0.000	−2.51	−3.13	+0.80	−1.40	−1.54	−1.22	−0.09	−0.28	−15.81
	P	0.97	<0.01	<0.01	0.16	<0.01	<0.01	<0.01	0.06	<0.01	0.02
Spruce-fir-birch	slope	+0.004	−1.80	−2.71	+0.93	−0.94	−2.25	−0.13	+0.05	−0.37	−23.79
	P	0.05	<0.01	<0.01	0.01	<0.01	<0.01	0.12	0.05	<0.01	<0.01

[a] Slope units for C_B, C_A, ANC, Ca, SO_4^{2-}, and NO_3^- are μEq L^{-1} yr^{-1}. Units for DOC are μmol C L^{-1} yr^{-1}. Positive slope values indicate increasing concentrations over time, and negative values indicate decreasing concentrations.

rank based, making it suitable for nonnormally distributed data, data containing outliers, and nonlinear trends. Trends were analyzed for the entire data set to assess the overall changes in the concentration of each solute. The trend analysis for the spring snowmelt period was performed with a Mann-Kendall test using a single annual value from the sampling that most closely represented the peak snowmelt of each year. The date of stream sampling most closely associated with peak snowmelt was identified from Hubbard Brook's long-term streamflow record. The dates varied between February and May but were most common in March or April. Hubbard Brook's snow water equivalence data set was consulted to identify the lysimeter sampling date that included the greatest input from melting snow during the month preceding sample collection. To evaluate the potential influence of changing hydrology during our sampling period, we tested for trends in the streamflow of our sampling dates by applying the SKT and Mann-Kendall analyses to the whole-year and snowmelt data sets, respectively.

Though not included in statistical trend analyses, we also present data as volume-weighted annual values. For soil and stream solutions, volume-weighted solute concentrations were calculated by multiplying each monthly concentration by the percentage of annual streamflow occurring during a given month. The volume-weighted concentrations in soil water of each elevation zone were subsequently multiplied by the relative area of each elevation zone (LH = 0.5, HH = 0.3, and SFB = 0.2) to calculate area-weighted concentration for the whole watershed.

3. Results

3.1. Soil Solution Chemistry Trends

The pH of soil waters draining the Oa horizon did not change significantly at any of the W6 elevation zones over the course of the sampling period of 1984–2011 (Table 1). Within the Bs horizon, only the soil water of the HH zone has experienced a modest upward trend in pH (Table 2). The ANC of soil water has not changed significantly in the Oa soil water but increased in the Bs soil waters of the HH and SFB zones. In the Bs soil waters that significantly increased in ANC, the C_A concentrations declined at a faster rate than C_B. These C_A declines were driven by rapidly decreasing SO_4^{2-} concentrations. The negative trend in SO_4^{2-} concentration was more pronounced in the Bs soil horizon solutions than the Oa horizon, with more rapid decreases in the higher-elevation zones (Tables 1 and 2). Conversely, the decrease in C_B concentrations followed an opposite pattern with respect to elevation; faster declines were observed at lower-elevation sites. This was especially evident in the Bs solutions, where the C_B concentration decline in the LH zone

Table 2. Long-Term Trends in Mineral Horizon (Bs) Soil Water Chemistry, 1984–2011[a]

		pH	C_B	C_A	ANC	Ca	SO_4^{2-}	NO_3^-	Al_i	Al_o	DOC
Low hardwood	slope	−0.002	−2.13	−2.48	+0.43	−1.56	−1.74	−0.34	+0.01	−0.05	−0.67
	P	0.56	<0.01	<0.01	0.12	<0.01	<0.01	<0.01	0.85	<0.01	0.15
High hardwood	slope	+0.006	−0.70	−2.59	+2.04	−0.34	−2.37	−0.09	−0.48	−0.19	−3.68
	P	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	0.19	<0.01	<0.01	<0.01
Spruce-fir-birch	slope	+0.000	−0.92	−3.25	+2.46	−0.51	−2.97	−0.03	−0.68	−0.18	+3.33
	P	0.99	<0.01	<0.01	<0.01	<0.01	<0.01	0.38	<0.01	<0.01	0.22

[a] Slope units for C_B, C_A, ANC, Ca, SO_4^{2-}, and NO_3^- are μEq L^{-1} yr^{-1}. Units for DOC are μmol C L^{-1} yr^{-1}. Positive slope values indicate increasing concentrations over time, and negative values indicate decreasing concentrations.

Table 3. Long-Term Trends in Stream Water Chemistry, 1982–2011[a]

Site	Elevation (m)		pH	C_B	C_A	ANC	Ca	SO_4^{2-}	NO_3^-	Al_i	Al_o	DOC
W6-1	751	slope	+0.004	−1.30	−2.97	+1.79	−0.50	−2.48	−0.01	−0.10	−0.37	−1.54
		P	0.04	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.14	<0.01	0.79
W6-2	732	slope	+0.005	−1.08	−2.86	+1.94	−0.58	−2.54	0.00	−0.22	−0.18	+1.20
		P	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.68	<0.01	<0.01	0.54
W6-3	701	slope	+0.004	−0.97	−2.54	+1.74	−0.58	−2.14	−0.13	−0.39	−0.10	+1.48
		P	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	0.06	<0.01	<0.01	0.22
W6-4	663	slope	+0.004	−0.92	−2.29	+1.48	−0.53	−1.84	−0.16	−0.40	−0.08	−0.77
		P	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.18
W6-5	602	slope	+0.009	−0.87	−2.18	+1.37	−0.61	−1.76	−0.08	−0.36	−0.06	−0.08
		P	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.88
W6-7	544	slope	+0.010	−1.13	−1.94	+0.88	−0.80	−1.54	−0.04	−0.19	−0.04	−0.53
		P	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.04

[a] Slope units for C_B, C_A, ANC, Ca, SO_4^{2-}, and NO_3^- are μEq L^{-1} yr^{-1}. Units for DOC are μmol C L^{-1} yr^{-1}. Positive slope values indicate increasing concentrations over time, and negative values indicate decreasing concentrations.

(−2.13 μEq L^{-1} yr^{-1}) was relatively rapid compared to the trends in the HH (−0.70 μEq L^{-1} yr^{-1}) and SFB (−0.92 μEq L^{-1} yr^{-1}) zones.

Decreasing concentrations of NO_3^- and DOC occurred to a greater extent in soil waters draining the forest floor relative to the Bs mineral soil. Concentrations of NO_3^- decreased significantly in Oa soil waters in both the LH and HH zones (Table 1). In the Bs solutions a statistically significant decline in NO_3^- concentrations was detected only in the LH zone and at a rate of decline that was lower than Oa soil solutions in the LH zone (−0.34 versus −1.55 μEq L^{-1} yr^{-1}). Concentrations of DOC showed statistically significant declines in the Oa soil solutions of all three elevation zones, ranging from −15.8 μmol C L^{-1} yr^{-1} in the HH zone to −25.1 μmol C L^{-1} yr^{-1} in the LH zone (Tables 1 and 2). For the Bs solutions, only the HH zone soil waters had a significant decrease in DOC (−3.68 μmol C L^{-1} yr^{-1}).

3.2. Overall Stream Chemistry Trends

The stream water of Watershed 6 at Hubbard Brook has become less acidic over the sampling period (1982–2011), changing at a rate of 0.01 pH units yr^{-1} (Table 3 and Figure 2). The pH increased significantly at most longitudinal stream sampling sites and did not decrease at any stream location during the study period (Table 3). The most significant increases in pH occurred in the lower reaches of the watershed. Conversely, the greatest increases in ANC were in the higher-elevation reaches of W6. This resulted from marked declines in C_A concentrations, driven by SO_4^{2-}, relative to C_B trends, which were consistently negative and did not vary appreciably with elevation (Table 3). Concentrations of NO_3^- in stream water declined to a lesser extent than SO_4^{2-}. There was not a clear elevational pattern to the magnitude of NO_3^- trends, but the most significant ($p < 0.05$) declines occurred at lower-elevation sites.

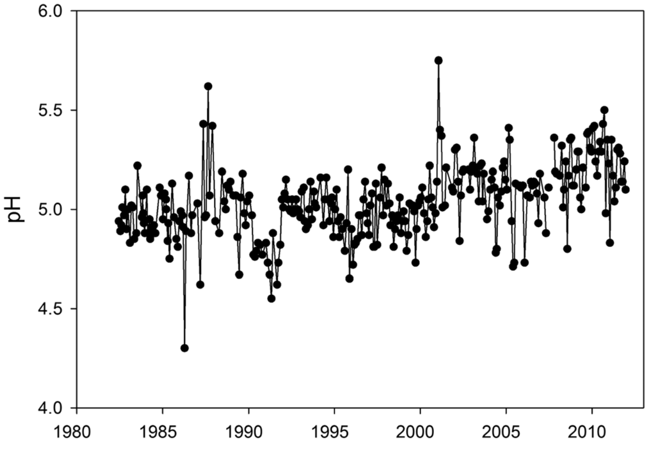

Figure 2. Stream water pH at the W6 gauging station, 1982–2011.

Over the entire record, Al in stream water was distributed among different forms (total Al 8.4 ± 2.8 μmol L^{-1}, Al_m 5.4 ± 3.4 μmol L^{-1}, Al_i 3.6 ± 3.3 μmol L^{-1}, and Al_o 1.9 ± 1.5 μmol L^{-1}). Because Al_m is the dominant and reactive form, and includes the toxic fraction (Al_i), our analysis of trends focused on Al_m, Al_i, and Al_o. Monomeric Al concentrations generally decreased in stream water, although Al_i and Al_o trends differed depending on elevation. At the highest-elevation stream sites, Al_o decreased faster than Al_i, while the reverse was true at the

Table 4. Comparison Between Trends of Whole-Year Stream Chemistry Record and the Trends During the Snowmelt Seasons, 1982–2011[a]

Parameter		Whole-Year Trend	Snowmelt Trend
pH	slope	+0.010	+0.009
	P	<0.01	0.02
C_B	slope	−1.13	−1.21
	P	<0.01	<0.01
C_A	slope	−1.94	−2.00
	P	<0.01	0.01
ANC	slope	+0.88	+0.91
	P	<0.01	<0.01
Ca	slope	−0.80	−0.82
	P	<0.01	<0.01
SO_4^{2-}	slope	−1.54	−1.44
	P	<0.01	<0.01
NO_3^-	slope	−0.03	−0.28
	P	<0.01	0.01
Al_i	slope	−0.19	−0.25
	P	<0.01	<0.01
Al_o	slope	−0.04	−0.04
	P	<0.01	0.04
DOC	slope	−0.53	+0.08
	P	0.04	0.98

[a] Slope units for C_B, C_A, ANC, Ca, SO_4^{2-}, and NO_3^- are $\mu Eq\,L^{-1}\,yr^{-1}$. Units for DOC are $\mu mol\,C\,L^{-1}\,yr^{-1}$.

lower-elevation sites (Table 3). The DOC concentrations decreased slightly at the base of the watershed (W6-7; Figure 1 and Table 3), but no significant trends were observed at the other five longitudinal stream sampling sites. Streamflow on the sampling dates of whole-year record showed no long-term trend over the period of soil solution and stream chemical measurements ($p = 0.25$).

3.3. Snowmelt Stream Water Chemistry Trends

Stream water in W6 during the snowmelt exhibited generally similar trends as the whole-year data record (Table 4). Snowmelt stream water has become slightly less acidic in recent years; the pH increased at a rate of 0.009 unit yr^{-1} ($p = 0.02$), and ANC increased by 0.91 $\mu Eq\,L^{-1}\,yr^{-1}$ ($p < 0.01$). The small increase in ANC results from decreased concentrations of C_A ($-2.00\,\mu Eq\,L^{-1}\,yr^{-1}$; $p < 0.01$) and a slightly slower decline in C_B ($-1.21\,\mu Eq\,L^{-1}\,yr^{-1}$; $p < 0.01$). The decreased C_A trend resulted from a steady SO_4^{2-} decline ($-1.44\,\mu Eq\,L^{-1}\,yr^{-1}$; $p < 0.01$) and some NO_3^- decline ($-0.28\,\mu Eq\,L^{-1}\,yr^{-1}$; $p = 0.01$). Congruent with the decrease in acidity, monomeric Al species declined, with Al_i decreasing 0.25 $\mu mol\,L^{-1}\,yr^{-1}$ ($p < 0.01$) and Al_o decreasing 0.04 $\mu mol\,L^{-1}\,yr^{-1}$ ($p = 0.03$). The DOC concentration in snowmelt stream water did not change over the sampling period ($p = 0.98$). Streamflow on the sampling dates of snowmelt record showed no long-term trend ($p = 0.86$).

4. Discussion

4.1. Trends in pH and ANC

The previous analysis of Hubbard Brook soil water chemistry trends over the period of 1984–1998 by *Palmer et al*. [2004] showed that the soil water drainage was generally becoming more acidic. Our current long-term analysis shows that the previous pattern of acidification is no longer evident and has likely reversed in recent years. This change in the pH of soil water is consistent with an increase in stream water pH. While the overall change in the pH of stream water at the W6 gauging station has been 0.01 units yr^{-1} from 1982 to 2011, much of the overall increase has occurred since the late 1990s or early 2000s (Figure 2). *Palmer et al*. [2004] found no significant changes in stream water pH from 1982 to 2000 at Hubbard Brook despite other indicators of recovery from acidification such as increases in the ANC. The authors, however, postulated that the deprotonation of organic acids and the hydrolysis of Al were important factors buffering against increases in pH. These effects could be expected to be temporary as capacity for the extent of dissociation of organic acids is limited and the concentration of Al_i continues to decrease with decreases in strong acid inputs from acidic deposition.

Our results showed very similar trends between the whole-year monthly sampling record and observations for snowmelt. Increases in pH and ANC are remarkably similar between the snowmelt record and the whole-year record. Spring snowmelt runoff is still markedly more acidic than the rest of the year (~10 $\mu Eq\,L^{-1}$; Figure 3) but appears to be recovering from acidification at the same rate as the entire annual cycle. The spring season is prone to episodic acidification as snowmelt waters are often transported via preferential flow paths in the shallow organic soil where base cations are dilute relative to strong acid anions [*Schaefer et al*., 1990; *Wigington et al*., 1990]. The results of our trend comparison suggest that chronic acid deposition may not have depleted base cations in the forest floor to an extent that makes the watershed permanently more

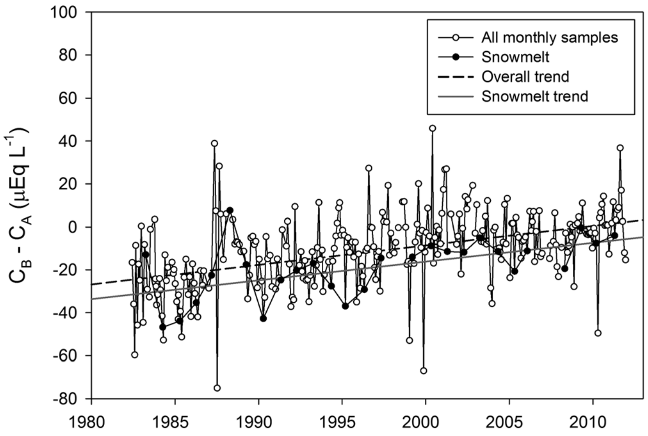

Figure 3. Trends in acid neutralizing capacity, as calculated $C_B - C_A$, from 1982 to 2011. Trend slope for the whole-year data set estimated using SKT. Snowmelt trend is calculated by Mann-Kendall analysis.

susceptible to severe episodic acidification during high-flow events. We note, however, that the snowmelt samplings did not necessarily coincide with the absolute highest discharge events. Rather, our monthly sampling during snowmelt is assumed to be generally representative of the seasonal characteristics.

4.2. Sulfate Trends

We observed consistent significant decreasing trends in the concentration of SO_4^{2-} at all soil water (Tables 1 and 2) and stream sampling sites (Table 3). The declines in stream and soil water SO_4^{2-} appear to be driven primarily by changes in atmospheric deposition during the study period. Sulfate concentration in bulk deposition peaked at Hubbard Brook in the late 1960s and has decreased steadily since [*Likens et al.*, 2001], including the 30 years of our analysis (Figure 4). The negative trend in stream SO_4^{2-} concentration from 1982 to 2011 (-1.54 μEq L^{-1} yr^{-1}) at the base of W6 is a faster decline than what has been observed in wet deposition (-0.98 μEq L^{-1} yr^{-1}) during the same time frame. This discrepancy suggests that there are additional factors influencing SO_4^{2-} dynamics in the watershed. Indeed, previous watershed input-output budgets [*Likens et al.*, 2002], and biogeochemical modeling [*Gbondo-Tugbawa et al.*, 2002], have shown that there is a missing source of S at Hubbard Brook that would explain higher export of SO_4^{2-} relative to atmospheric deposition. *Mitchell et al.* [2011] observed that this imbalance—which indicates an internal source of S—was common in 15 watersheds across the northeastern U.S. and southeastern Canada and attributed it to net mineralization of organic S that had been stored from years of chronic excess SO_4^{2-} deposition. Alternatively, increases in soil pH could drive desorption of previously adsorbed SO_4^{2-} from mineral soil [*Nodvin et al.*, 1986]. *Mitchell and Likens* [2011] showed that the release of internally stored S has become relatively more important to stream water SO_4^{2-} export with time at Hubbard Brook and the overall export of SO_4^{2-} is shifting from control by atmospheric deposition to climatic regulation. We note that changing climatic patterns are likely also to have contributed to decreases in SO_4^{2-} concentrations. Long-term modest increases in precipitation and streamflow [*Campbell et al.*, 2011] have occurred during the time frame of our study and would be expected to dilute SO_4^{2-} during higher flows as flow paths are more likely to shift to shallower soils, where SO_4^{2-} is found in lower concentration.

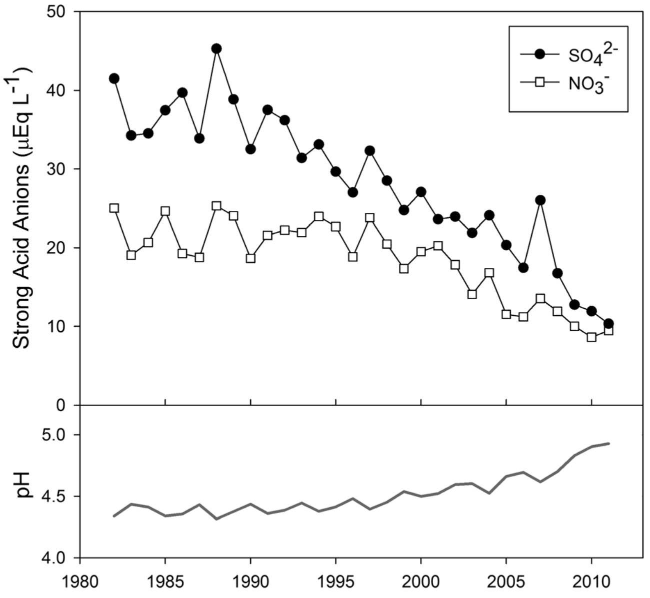

Figure 4. Precipitation-weighted mean annual wet deposition values for (top) SO_4^{2-} and NO_3^- and (bottom) pH from 1982 to 2011. Data were obtained from the National Atmospheric Deposition Program (NH02).

While the SO_4^{2-} concentration declines observed in stream and soil waters are undoubtedly contributing to an overall modest recovery from acidification, the mineralization of legacy S pools in the soil and release as SO_4^{2-} appear to be keeping SO_4^{2-}

concentrations in drainage waters higher than would be expected based on deposition changes alone. This is further demonstrated in our analysis of SO_4^{2-} trends longitudinally in stream water, which shows that the higher-elevation portion of W6 has experienced nearly double the rate of SO_4^{2-} decline as the base of the watershed (Figure 5 and Table 3). The soil depth of W6 is inversely related to elevation [*Johnson et al.*, 2000], so it would reason that the deeper soils in the lower portion of the watershed would have greater pools of S available for mineralization to SO_4^{2-}. We would expect that as this S pool decreases with time, the rate of recovery from acidification would increase, leading to faster gains in pH and ANC.

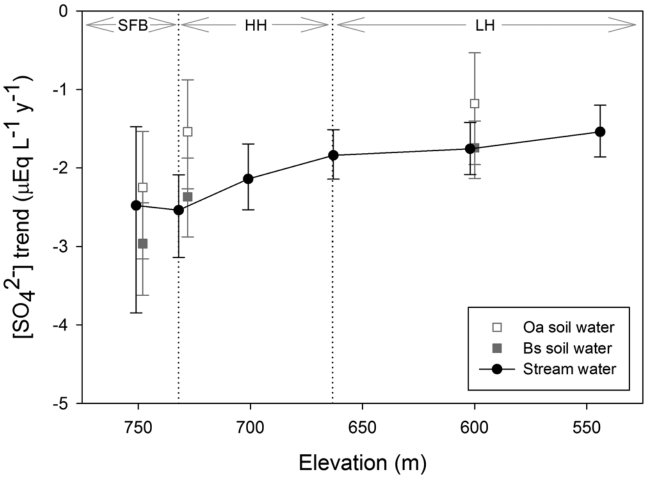

Figure 5. Sulfate concentration trends (1984–2011) versus elevation for W6 soil water and stream water. Median trends are estimated by SKT analysis. Vertical bars represent 95% confidence intervals. Transitions between elevation zones are marked with vertical dotted lines.

4.3. Base Cation and Aluminum Mobilization

In soils with low base saturation, the deposited strong acid anions are typically neutralized in drainage waters by a combination of base cations and Al (Figure 6) [*Cronan and Schofield*, 1990]. As would be expected, the leaching of C_B has declined steadily throughout the course of our soil water chemistry record, especially in relation to decreasing SO_4^{2-} deposition. Monomeric Al concentrations have also generally declined in stream and soil waters. As the solutions draining the Oa horizon are typically rich in DOC, it is not surprising that the decrease in monomeric Al has predominantly been in the organically complexed Al_o fraction. Studies of Al dynamics in acidic soils have suggested that formation of organic matter-Al complexes can be more important to overall Al solubility than pH-dependent mineral phase solubility [*Berggren and Mulder*, 1995; *Skyllberg*, 1999]. *Palmer et al.* [2004] hypothesized that changes in organic-Al complex formation could explain the moderate decreases in Al_i concentrations of soil waters despite their unchanged or even decreasing pH.

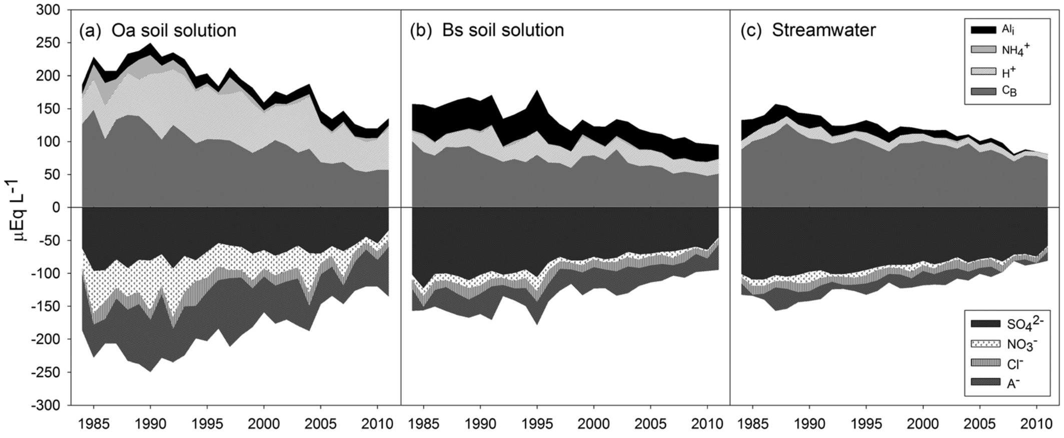

Figure 6. Soil solution and stream water charge balances represented by annual volume-weighted concentrations of major ions in (a) Oa horizon, (b) Bs horizon, and (c) stream water. Cation charge is expressed by positive values of μEq L^{-1}, while anion charge is negative. Organic anion concentrations (A^-) were calculated from the charge discrepancy of measured positive and negative species [*Driscoll et al.*, 1989]. Soil solution values are weighted by elevation zone to represent the entire watershed; stream water values are from the gauging station at the base of the watershed.

The concentration Al_i in stream water has declined from an average of 7.6 μmol L^{-1} during the first 5 years of monitoring (1982–1985) to 2.0 μmol L^{-1} during the most recent 5 years of our data analysis (2007–2011). The concentration of mobilized Al_i is an important measure of surface water quality as Al_i has been shown to be a primary factor affecting fish in acid-impacted waters [*Baker and Schofield*, 1982], whereas organically complexed Al (Al_o) is considered to be nontoxic to fish in comparison to Al_i. Our results show that while Al_o concentrations in stream water have decreased, the portion of total monomeric Al as Al_o has increased from an average 26% during the first 5 years of the study (1982–1986) to 69% during the most recent 5 years (2007–2011). The current low concentrations of Al_i would suggest that hydrolysis of Al is not contributing nearly as much acidity to stream water as in past years.

4.4. Dissolved Organic Carbon

We report highly significant decreases in DOC concentrations in the Oa soil solutions of all elevation zones during the period of 1984–2011 (Table 1), as well as for the Bs soil solution in the HH zone (Table 2). The DOC concentration has also decreased significantly in the stream water measured at the base of the watershed (site W6-7; Table 3), although we observed nonsignificant declines at the upstream longitudinal stream sampling sites. Our results are surprising, considering the widespread phenomenon of increasing DOC in surface waters across Europe and eastern North America [*Stoddard et al.*, 1999; *Worrall et al.*, 2004; *Skjelkvåle et al.*, 2005; *Driscoll et al.*, 2007]. Although fewer studies have long-term measurements of soil water DOC concentrations, the DOC in surface water is generally derived from soils so it would be expected that increased concentrations in soil water should be concurrent with surface water trends. Indeed, increases in stream water DOC concentrations were linked to increasing concentrations in soil waters in two forested catchments in the western Czech Republic [*Hruška et al.*, 2009]. In contrast, several Scandinavian studies have reported trends of decreasing soil water DOC concentrations. *Löfgren and Zetterberg* [2011] analyzed DOC trends at sites across southern Sweden during the period of 1987–2008. Using records from 68 sites with at least 10 years of data, the authors found that DOC concentrations were decreasing at 31 sites, while increasing at only five sites. *Wu et al.* [2010] also found largely negative trends in soil water DOC in conifer plots across Norway during the period of 1996–2006. Hubbard Brook has characteristics—such as soil type, climate, and historical acid deposition—similar to the Scandinavian sites, so it may not be surprising that we found comparable DOC trends in Hubbard Brook soil waters. *Löfgren et al.* [2010] modeled DOC solubility in soil water and concluded that DOC trends could vary between positive and negative depending on changes in pH, ionic strength, and soil Al pools. They concluded that decreasing ionic strength was driving trends of decreasing DOC in soil water. The long-term charge balance at Hubbard Brook (Figure 6) clearly shows substantial declines in major anions and cations in soil water over the past three decades. *Hruška et al.* [2009], on the other hand, suggested that decreasing ionic strength led to DOC increases in soil water at the Czech sites. *Löfgren and Zetterberg* [2011] indicated that differences in soil sampling depth could influence the DOC concentrations and trends, as the increasing DOC reported at the Czech sites by *Hruška et al.* [2009] were for samples collected just beneath the forest floor, while the decreasing DOC reported for Swedish sites by *Löfgren et al.* [2010] were for samples collected at 50 cm depth. Our results, however, indicate that DOC in the soil water draining the forest floor has decreased at a more rapid rate than in the mineral soil solutions. It is not clear why DOC trends in forest floor soil solutions at Hubbard Brook would differ so markedly from those measured by *Hruška et al.* [2009]. One potential explanation is the elevated dissolved Al concentrations at Czech sites—as reported for stream water—relative to values observed at Hubbard Brook. As the model results from *Löfgren et al.* [2010] suggest, higher concentrations of dissolved Al oxyhydroxides should promote higher DOC solubility. Laboratory studies of organic soils show higher solubility of DOC at higher pH [*Tipping and Hurley*, 1988; *Kennedy et al.*, 1996]. Our data set showed invariant pH until the last 10–15 years, after which it has increased significantly (see above). This time frame appears to coincide with a tapering off of declines in DOC concentrations. We also have not observed increases in soil water concentrations of organic anions, but the marked decreases in concentrations of $SO_4{}^{2-}$ and $NO_3{}^{-}$ have increased the relative importance of organic anions in soil solutions (Figure 6).

Similar to the soil waters, DOC concentrations in stream water at Hubbard Brook W6 had previously been reported by *Palmer et al.* [2004] to decrease during the period of 1982–2000 (−1.40 μmol C L^{-1} yr^{-1}; $p = 0.02$). Our updated analysis of the period of 1982–2011 shows that the DOC concentrations have continued to decline but at a much slower overall rate (−0.53 μmol C L^{-1} yr^{-1}; $p = 0.04$). Over the most recent

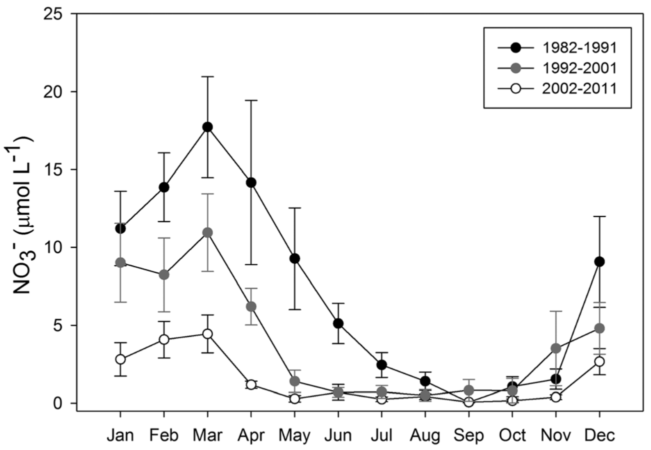

Figure 7. Mean monthly NO_3^- concentrations of stream water draining W6 for 10 year intervals between 1982 and 2011. Vertical bars indicate standard errors.

15 years of our data set, 1997–2011, the DOC concentration of stream water did not change (+0.55 μmol C L^{-1} yr^{-1}; $p = 0.41$). This trend in stream water mirrors soil water observations (see above). Although DOC concentrations have leveled in recent years, our results still contrast with many other sites that show increases in DOC concentration in streams. *Burns et al.* [2006] observed significant increases in DOC concentrations in 80% of the streams they analyzed in the Catskill Mountains of New York. Similar increases have been reported in upland streams in Finland, where eight forested catchments were monitored for 15–29 years [*Sarkkola et al.*, 2009]. While stream DOC increases are common, decreases have been reported at a notable number of sites in southwestern England [*Worrall and Burt*, 2007], as well as in two forested catchments in Nova Scotia [*Clair et al.*, 2008].

It is difficult to determine the underlying cause of the decline of DOC concentration of W6 stream water during the 1980s and 1990s, as Hubbard Brook has many characteristics in common with other surface water sites that primarily are experiencing increasing DOC concentrations. The DOC decline in W6 stream water appears to be driven by the declines in soil solution DOC described above. It is not clear whether the diminishing rate of DOC concentration decline we have noted for approximately the past 15 years indicates a long-term steady state or potentially the beginning of a reversal toward the increasing DOC trends experienced at many other sites. Changes in hydrology at the site in recent years may be contributing to the changes in DOC trends. *Campbell et al.* [2011] reported long-term increases in streamflow in W6 over the entire period of record, which suggests that it would be increasingly likely that DOC sources, such as surficial soils [*Sebestyen et al.*, 2008] and higher-elevation E podzols [*Bailey et al.*, 2014], would be hydrologically connected to the streams.

4.5. Nitrate

The concentrations of NO_3^- in stream water have declined in the lower portion of the watershed (Table 3), apparently driven by the particularly pronounced decreasing NO_3^- trends in the soil solutions of the LH zone (Tables 1 and 2). Atmospheric N deposition has decreased, although we do not directly attribute the decreased NO_3^- leaching in soil solutions and stream water to decreased atmospheric deposition. The decline of NO_3^- export in stream water began in the late 1970s, relatively early in Hubbard Brook's record, after having initially increased from the early 1960s to the mid-1970s [*Bernhardt et al.*, 2005; *Yanai et al.*, 2013]. The trend of declining stream NO_3^- is evident throughout the entire annual cycle (Figure 7). While concentration decreases have been most marked in the winter and spring, there also has been a distinct lengthening of low NO_3^- during the summer-fall period. The NO_3^- concentration in bulk deposition was relatively constant from approximately 1970 to 2003, after which it has declined [*Likens and Buso*, 2012]. The decline in watershed losses of NO_3^- is puzzling, as it runs counter to the long-standing theories of forest development and nutrient cycling, which suggest that as biomass accumulation slows, N losses should increase if N inputs remain unchanged [*Vitousek and Reiners*, 1975]. In fact, predictions have been made that continuous excess N deposition on previously N-limited northern forest systems would lead to a state of "nitrogen saturation" which should be accompanied by marked increases in stream NO_3^- losses [*Aber et al.*, 1989]. Biogeochemical models employed at Hubbard Brook have consistently overpredicted stream NO_3^- compared to measured data since the early 1980s [e.g., *Aber and Driscoll*, 1997; *Gbondo-Tugbawa et al.*, 2001; *Pourmokhtarian et al.*, 2012]. *Yanai et al.* [2013] found that the recent low stream water export of N at Hubbard Brook—relative to inputs—could not be explained by measured accumulation of N in the forest floor or vegetation, and the watershed mass balance indicated a missing sink for N. The authors suggested the N budget imbalance could be explained by either increased gaseous loss through denitrification or increased storage in the mineral soil, for which a statistically significant change is difficult to detect. Indeed, measurements of soil water N species do support the suggestion that NO_3^- is being immobilized in the mineral soil, as fluxes draining the Oa horizon are significantly greater than what drains the Bs horizon [*Dittman et al.*, 2007; *Yanai et al.*, 2013]. Moreover, *Bernal et al.* [2012] used isotopic evidence to suggest that denitrification was an unlikely explanation of decreases in stream NO_3^-, although soil drainage patterns could promote hot spots of N cycling [*Bailey et al.*, 2014] including important points of denitrification in hydrologically disconnected shallow groundwater [*Wexler et al.*, 2014].

Nitrate concentrations in stream water have been decreasing more rapidly during the snowmelt period ($-0.28\ \mu mol\ L^{-1}\ yr^{-1}$) than for the whole-year record ($-0.03\ \mu mol\ L^{-1}\ yr^{-1}$). The relatively rapid long-term decline in stream NO_3^- concentrations observed during snowmelt was likely driven by decreased atmospheric deposition of NO_3^-. *Sebestyen et al.* [2008] used isotopic evidence at Sleepers River, Vermont, to show that during base flow conditions, stream NO_3^- is almost exclusively derived from nitrification in the soil, while during early pulses and the beginning of peak snowmelt, atmospheric sources account for approximately half of NO_3^- in stream water. During snowmelt, NO_3^- derived from atmospheric deposition that had accumulated in the snowpack can be transported directly to the streams via overland or shallow subsurface flow paths with little transformation. The decreased NO_3^- deposition that has occurred over approximately the past 10 years would be expected to disproportionately affect the trend during the snowmelt seasons, as this is the period of the annual cycle when stream NO_3^- is most likely to be sourced most directly from deposition.

4.6. Future of Recovery and Ecosystem Health

While our results suggest that base cations have not been depleted from the forest floor to such a degree as to inhibit recovery from acidification during the higher-flow (and relatively acidic) snowmelt period, it is likely that a depletion of exchangeable base cations from the soil is slowing the overall recovery and affecting forest health. In acid-sensitive soils, deposition of strong acid anions displaces soil-available base cations faster than they can be replaced through mineral weathering processes or atmospheric cation deposition. This alteration of the soil base status has prevented faster recovery in surface water ANC at Hubbard Brook and across the northeastern U.S., despite marked reductions in acidic deposition [*Likens et al.*, 1996; *Lawrence et al.*, 1999; *Palmer et al.*, 2004]. A watershed-scale calcium silicate addition was conducted at Watershed 1 (W1) at Hubbard Brook in 1999 as an experiment to test the effects of replacing Ca lost due to acidic deposition. Indeed, this Ca manipulation at W1 has resulted in mitigation of acidification and is supplying ANC to drainage waters [*Cho et al.*, 2012].

Acidic deposition can permanently affect the composition and health of forest ecosystems [*Halman et al.*, 2014]. Red spruce has been severely impacted by acidic deposition across the northeastern U.S., including growth declines and mortality. Acidic deposition affects red spruce directly by leaching Ca from the needles [*DeHayes et al.*, 1999] and indirectly by changing underlying soil chemistry [*Cronan and Grigal*, 1995]. Acid-impacted soils were found to be a factor explaining impaired growth of sugar maple [*Duchesne et al.*, 2002]. The highest incidences of sugar maple dieback in Pennsylvania were found to be at sites with low supplies of Ca and Mg, which increases sensitivity to stresses such as drought and insect defoliation [*Horsley et al.*, 2000]. Studies of sugar maple health and seedling survivorship at Hubbard Brook have shown that the species has fared significantly better since the Ca amendment in W1 relative the reference W6 [*Juice et al.*, 2006; *Battles et al.*, 2014].

5. Summary and Conclusions

Our data show that the drainage waters at Hubbard Brook are slowly recovering from acidic deposition, including small increases in pH and ANC, as well as decreased leaching of base cations and mobilization of Al_i. We also observed a pattern of long-term decreases in snowmelt acidification that were largely similar to the whole-year trends. These results suggest that the susceptibility to high-flow-driven seasonal acidification during snowmelt is slowly improving.

The recovery we observed has been driven in part by declines in the atmospheric deposition of strong acids. Deposition of SO_4^{2-} has declined steadily throughout the 30 years of our data set due to regulations on emissions through the Clean Air Act, and the deposition of NO_3^- has declined over the past decade due to emission controls put in place through the NO_x Budget Trading Program. While SO_4^{2-} deposition has declined markedly, the overall recovery of stream and soil waters from acidification is slowed by SO_4^{2-} exports that exceed imports due to mobilization of legacy SO_4^{2-} from the soil. The recent decrease in NO_3^- deposition has contributed to the decreased acidity of precipitation and likely has further reduced leaching of base cations. We also observed overall decreasing trends in DOC concentrations, contrary to patterns observed in many similar systems, although these decreases appear to have diminished approximately over the past 15 years. These shifts are changing the character of soil and stream solutions at Hubbard Brook, from waters previously dominated by strong acid anions (i.e., SO_4^{2-} and NO_3^-) to solutions increasingly dominated by naturally occurring dissolved organic matter. Continued monitoring should provide insight into the future of DOC and NO_3^- dynamics, both of which directly and indirectly influence acid-base conditions. We also anticipate that sustained monitoring will resolve the rate at and the extent to which all recovery trends continue. Recovery from acidification in drainage water could accelerate if the deposition of acidic compounds continues to decline and the legacy SO_4^{2-} stored in soil is gradually depleted.

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