

Thirty-year trends in acid deposition and neutralization in two headwater catchments,
northwestern Massachusetts, USA

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ABSTRACT

Long-term decreases in acidic precursors have changed the chemistry of precipitation and streamflow in two moderately to well-buffered, forested headwater catchments in the Taconic Range of western New England, USA. We report 30-yr geochemical trends from Birch Brook, and annual and seasonal variations from Birch Brook and adjacent Ford Glen, which drain phyllitic and carbonate bedrock. Median pH of precipitation has increased irregularly since 1983, consistent with regional trends. Increases in precipitation pH and decreases in sulfate (SO_4^{2-}) correspond with increasing stream pH and decreasing SO_4^{2-} concentration and flux over at least the past 30 years. Calcium (Ca^{2+}) concentration and acid-neutralizing capacity (ANC) in Birch Brook began to increase about 2005, in contrast to geochemical indicators from some poorly buffered catchments in the NE USA. Point and longitudinal sampling over a range of flows show that Birch Brook chemistry is a mixture of upstream source waters (throughfall, soil water, ground water) with different chemistries. Acidic precipitation and shallow soil water affect stream chemistry directly only in the upper reaches of Birch Brook and during periods of extremely high flow, such as snowmelt. Ford Glen has high ANC and is near saturation with calcite at most flows. Long-term trends measured at Birch Brook and at other streams in western Massachusetts show that stream chemistry reflects changes in acidic deposition in upland catchments, even where ecosystem geochemistry is well buffered by bedrock composition.

KEY WORDS—trends; throughfall; pH; SO_4^{2-} ; well-buffered; acidic deposition; carbonate

1.0 INTRODUCTION

Numerous studies in the northeastern USA and northern Europe have focused on the impacts of acid deposition in poorly buffered, mainly upland ecosystems and surface waters (Driscoll et al., 2003) and, in recent years, gradual recovery of stream and lake chemistry (Strock et al., 2014) and forest health (Kosiba et al., 2018) in some areas. In susceptible catchments, excess acid-anion deposition is linked geochemically to mobilization of aluminum in soils and streams, progressive depletion of calcium from soils, nitrogen fertilization, and decreased acid-neutralizing capacity (ANC) in surface water, all of which impact biota (Likens et al., 1996). For instance, mobilization of soil aluminum is strongly correlated with increased brook trout mortality (Baldigo et al., 2007), and soil calcium depletion may produce increased vulnerability to temperature fluctuations and disease in red spruce (Halman et al., 2014). In the Hopkins Memorial Forest (HMF) study area, sugar maple decline and lack of recruitment after the 1930s had been linked with defoliation events, aluminum mobility from soil acidification, and long-term stand change, but this decline diminished by 2004 (Boonstra, 2004).

Controls on emissions of acid-rain precursors such as SO_2 and NO_x , mandated by amendments to the Clean Air Act, have increased precipitation pH and decreased SO_4^{2-} deposition in the NE USA since about 1990 (McHale et al., 2017). Evidence from upland streams and lakes demonstrates increases of pH and ANC and decreases SO_4^{2-} in some ecosystems in the USA, eastern Canada and northern Europe (Stoddard et al, 1999; Murdoch and Shanley, 2006; Campbell et al., 2007; Strock et al., 2014; Fuss et al., 2015) over the same period. In other areas, minimal or delayed recovery from acidification may result from low soil buffering capacity, long-term soil calcium depletion and slow replacement of exchangeable Ca^{2+} in the soil, mediated by slow rates of silicate weathering, or the influence

of increased dissolved organic carbon (DOC) concentrations (Likens et al., 1996; Burns et al., 1998; Mitchell et al., 2011; McHale et al., 2017). More rapid recovery suggests that rapid release of base cations from easily weathered minerals such as calcite or dolomite in parent material is sufficient to increase soil base saturation values and stream pH, ANC and Ca^{2+} levels.

This study reports geochemical trends over a 30-year period from moderately well buffered headwater streams in the tristate area of Massachusetts, Vermont, and New York. The Birch Brook and Ford Glen catchments drain the eastern flank of the Taconic Range, which extends from central Vermont south along the New York-New England border. Stream chemistry in the study catchments integrates the effects of heterogeneous geologic materials typical of the Taconic Range. Above about 300 m, thin glacial deposits cover slowly weathering bedrock containing veins and isolated lenses of carbonate; at lower elevations, thicker glacial deposits bury carbonate-rich bedrock. Lowland stream pH is circumneutral and ANC values are $> 200 \mu\text{eq L}^{-1}$ in the Taconic Range and other areas of the northern Appalachians where precipitation is buffered by forest canopies, soils, and glacial deposits associated with calcium-rich bedrock (Robinson and Capo, 2003); stream response to acid deposition in these areas has not been studied as thoroughly as in less-well buffered catchments and water bodies.

We hypothesized that upland tributaries may drain calcium-poor materials in moderately buffered areas like the Taconic Range, producing: (1) relatively low ANC values; (2) moderate susceptibility to acidification; and (3) temporal patterns of recovery from decreased acid deposition and longitudinal gradients distinct from those recorded by poorly buffered streams. Longitudinal gradients in upland streams are significant because stream chemistry measured at a site is an aggregated property that integrates the chemistry and surface area of rock and organic materials, mean travel time, reaction rates, and the mixing of

flow from different upstream source areas (Harpold et al., 2010; Harman, 2015), including precipitation. In this paper, we use long-term hydrogeochemical data to test how: (1) acid deposition affects the chemistry of streams that drain upland forested catchments underlain by moderately to well-buffered geologic materials; (2) mixing of water from different source areas affects longitudinal and short-term changes in stream chemistry; and (3) the chemistry of moderately buffered streams has recovered in response to decreased acid deposition during the past two decades. Better understanding of processes that have promoted recovery of these circumneutral streams may help predict conditions necessary for recovery of streams that drain poorly buffered catchments in the northeastern USA and adjacent Canada.

2.0 SETTING

The study site includes two adjacent forested headwater catchments (Fig. 1) and isolated springs in Hopkins Memorial Forest (HMF), an 1100 ha forest reserve managed since 1970 by the

Center for Environmental Studies at Williams College. The Birch Brook catchment (3.88 km²) drains the Taconic Ridge and has a mean elevation of about 475 m whereas Ford Glen (1.35 km²) drains gentler hillslopes with a mean elevation of about 310 m. Long-term research on the hydrology and geochemistry of forested ecosystems began at HMF in the early 1970s; precipitation and stream chemistry on Birch Brook have been monitored since 1983 and streamflow since 1985. In 2007, we expanded monitoring to include the adjacent Ford Glen catchment, which has a similar land-use history but different geology. A northern hardwood forest has grown back to cover the entire Birch Brook catchment and most of the Ford Glen catchment over the past 130 years after a period of late 18th through mid-19th century woodlot clearing, subsistence farming, and grazing. Field comprises ~15 percent of

the Ford Glen catchment and two ponds and adjacent wetlands cover ~ 0.4 %. Forest cover in the two catchments is 70 to 120-year-old mixed hardwood; dominant species are *Acer rubrum* (red maple) and *Quercus rubra* (red oak) in stands younger than about 75 years below 400 m and *Fagus grandifolia* (American beech), *Acer saccharum* (sugar maple), *Betula alleghaniensis* (yellow birch), and *Betula lenta* (black birch) with local groves of *Tsuga* spp. (hemlock) in older stands above 400 m (Art and Dethier, 1986; Ouimet and Dethier, 2002).

2.1 Geology and soils

Local geology is typical of the Taconic Range and tristate area. Lower Paleozoic metamorphic rocks underlie both catchments, covered by 1 to 5 meters of latest Pleistocene till at higher elevations and > 5 m of till and glaciolacustrine deposits in lower areas (Fig. 1). Channels are a meter to a few meters wide; alluvial borders are narrow. Above an elevation of about 400 m in the Birch Brook catchment, bedrock mainly is a grey to greenish phyllite (Nassau Fm) containing quartz lenses, cut locally by thin veins of calcite. The Ordovician Walloomsac Fm, a dark-colored phyllite containing local beds and lenses of carbonate, underlies lower-elevation areas drained by the N. Branch of Birch Brook and the entire Ford Glen catchment (Dahlberg, 1960). Dolomitic marble of the Stockbridge Fm crops out to the east of the Ford Glen sampling site and may underlie the catchment at depth. Soils < 1 m thick in the catchments generally are moderately acidic, moderately-to-poorly drained, and nutrient-poor Inceptisols (Dethier et al., 1988) derived from slow weathering of glacial materials over the past ~15 kyr. Birch Brook soils are mapped as members of the phyllite-derived Taconic-Macomber association whereas soils in Ford Glen are classified mainly as Amenia silt loam and Stockbridge gravelly silt loam; pH and other chemical properties of deeper horizons reflect the influence of carbonate bedrock (Scanu, 1988). The <2-mm

fraction of soils and underlying glacial materials generally includes ~60% silt + clay. Clay-size material is rich in mica, chlorite, quartz, and feldspar, and upper soil horizons contain minor amounts of pedogenic vermiculite (or smectite) and x-ray amorphous material. CEC ranges from ~5 to 60 $\text{cmol}_c \text{ kg}^{-1}$ and base saturation is low, generally <10% in soil horizons; Ca^{2+} dominates exchangeable cations in both organic and mineral-soil horizons (Dethier et al., 1988).

2.2 Climate and hydrology

Climate is humid, continental with cold winters and mild summers. Total annual precipitation at HMF has averaged 1235 mm yr^{-1} since 1983 and is fairly evenly distributed with season; summer months are somewhat wetter. There is no significant difference between total precipitation measured on the Taconic Ridge (el. 670 m) and at ~ 275 m at Station W1 (Fig. 1), but snowfall represents a higher proportion (25%) of total precipitation at higher elevations. Mean annual temperature is ~7.7 °C at Station W1. Mean annual runoff for Birch Brook is $682 \pm 158 \text{ mm}$; calculated evapotranspiration averages about 550 mm yr^{-1} . The annual pattern of median daily runoff at the Birch Brook gage reflects: (1) variable storage of snow from January through mid-March; (2) snowmelt and spring rainfall; and (3) strong effects of evapotranspiration and decreasing water storage from May until October. Birch Brook discharge shows rapid increases and decreases during and after storm events, likely reflecting steep slopes and thin soils; runoff from trails and old roads also may be important.

3.0 MATERIALS AND METHODS

This study summarizes aspects of the field sampling and monitoring program in HMF and laboratory work in the Environmental Analysis Laboratory at Williams College over the period 1983-2016.

3.1 Sample collection

Bulk precipitation has been sampled biweekly from 1983 to present in the open field that surrounds Station W1 (Fig. 1); throughfall has been sampled since 1986 in an adjacent forest stand where sugar maple comprises ~ 50% of the basal area. We collect bulk precipitation and throughfall in open polyethylene funnels that drain through water traps to polyethylene bottles in the summer and in plastic-bag lined buckets in the winter. During some seasons, windblown leaves and pollen land in the funnels and buckets. We measure precipitation amount and intensity at 4 recording rain gages and have sampled stream chemistry monthly since fall 1983 (Birch Brook), 2007 (Ford Glen), and 2014 (Birch Brook subcatchments). Flows sampled for stream chemistry have the same mean and standard deviation ($2.93 \text{ ft}^3\text{s}^{-1} \pm 3.56$, $n = 383$ vs $2.94 \text{ ft}^3\text{s}^{-1} \pm 3.71$, $n = 11312$) as the entire 30-year daily discharge record and stream chemistry includes 8 to 10 samples from both the lowest and highest 2% of the flow distribution. We sampled three springs (“Bear”, “Tepid”, and “Tristate”; see Dethier and Harman, 1998) on an irregular basis. Strings of 6 to 10 longitudinal samples were collected downstream on Birch Brook in 1989-90, 1996, 2008-09, and 2016, and along Ford Glen in 2009 to help characterize downstream gradients. Our sampling employed a 50 to 100 m spacing during low and high flow periods in the fall and wider, irregular intervals during winter low flow when snow and ice limited access to the stream (Fig. 1). We have monitored water discharge in the Birch Brook catchment at V-notch weirs continuously at two sites since 1985. Ford Glen is unaged, but we estimate annual discharge using catchment area and assuming that specific discharge is 0.85 times that measured at Birch Brook (see Fig. 3 of Simcox, 1992). Thirty-year records from the two HMF gages and the two nearby U.S. Geological Survey gages show that annual discharge decreases slightly with mean basin elevation (<https://waterdata.usgs.gov/ma/nwis/rt>).

3.2 Laboratory

We measured the pH and ANC of unfiltered stream and precipitation samples within 24 hr of collection using a single-endpoint technique, a Corning Model 12 Research pH meter and Hach digital titrator and, from 2012 to 2016, a Radiometer-analytical TIM840 auto-titrator (see Appendix A). Alkalinity values (as HCO_3^-) for selected samples of bulk precipitation were measured using single endpoint titration (1983-2014) or double endpoint Gran titration (2014-16). After sample filtration through a 0.45-micron filter (Millipore nitrocellulose membrane) and storage in the dark at 4°C, we measured cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) using atomic absorption spectroscopy (Perkin-Elmer 403 through Analyst 300 from 1983-2017). Anions (Cl^- , PO_4^{3-} , HCO_3^- , SO_4^{2-} , NO_3^-) were measured using a Technicon Autoanalyzer (1983-1987), a Dionex DX-4000i Ion Chromatograph (1987-2000), a Dionex DX-600 Ion Chromatograph (1983-2014) and a Metrohm 883/863 Ion Chromatograph (2015-16). We used a Technicon Autoanalyzer II to measure NH_4^+ and SiO_2 on all samples and DOC on selected precipitation and stream samples during 1988-1993. Cations and anions generally were analyzed from 2 to 4 times within 3 weeks to 3 months after sample collection. Average analytical uncertainty during 2015 was 0.5 to 5% (2 sigma) for cations, < 1% for anions and ~5 to 10% for Autoanalyzer measurements (Appendix A). Before 2000 analytical uncertainty generally was 5 to 10% for precipitation samples and ~5% for Birch Brook stream samples.

3.3 Data analysis

Hydrogeochemical data have been collected over a ~33-year period in HMF. For precipitation samples, long-term summaries mainly are based on median values and ionic flux is calculated as the sum over time of the total ionic input per biweekly sampling period. Significant year-to-year variation in streamflow and our monthly sampling protocol

complicate analysis of long-term trends (see Section 4.4) for the flux of ions such as Ca^{2+} and SO_4^{2-} . Error for precipitation and stream chemistry is calculated and reported as standard error ($1\sigma/n^{0.5}$).

For stream chemistry, we use: (1) median concentration based on monthly sampling and yearly streamflow for long-term analysis; (2) sample chemistry and daily discharge for the sample date for regression analysis; and (3) the Seasonal Kendall test (Helsel and Hirsch, 2002), used in similar watersheds to test temporal trends (e.g. McHale et al., 2017), dividing the year into four 3-month seasons (DJF, MAM, JJA, and SON). To plot long-term trends for concentration we use the weighted-curve fit and the locally weighted least squares error (Lowess) method of Chambers et al. (1983) and we chose the weighted regression on time, discharge and season (WRTDS) technique of Hirsch and DeCicco (2015) to plot flow-normalized pH, SO_4^{2-} concentration and SO_4^{2-} flux. Hirsch and DeCicco suggest that the WRTDS technique may not work well for small catchments with rapid discharge changes, so we coupled average daily discharge values with measured chemistry, allowing us to compare Birch Brook trends with those from three regional catchments. We excluded stream Ca^{2+} and ANC values for 1993 from the analysis because of missing samples and contamination of three sample bottles with CaCO_3 dust. Median DOC concentration in Birch Brook was 1.07 mg L^{-1} during 1988-1993, although these results are not discussed further here.

In this paper, we define source-area waters informally using field observations and the chemistry of end members (Johnson et al., 1969; Hooper, 2003) defined by samples collected at the lowest and highest discharge at the Birch Brook gage and by throughfall. End members are “groundwater” (Birch Brook low flow, 0.12 mmd^{-1} on 8.12.97); “soil water” (Birch Brook high flow, 8.16 mmd^{-1} on 10.10.05); and throughfall (median values). Geologic influences, from northwest to southeast (Fig. 1), include: (1) phyllite bedrock and thin till; (2)

phyllite bedrock/carbonate lenses and thick till; and (3) dolomitic marble bedrock and thin till.

4.0 RESULTS

To portray and analyze changes in surface-water chemistry, we characterize bulk precipitation and throughfall chemistry, including its seasonal and long-term variation and estimated deposition that reached the forest floor. Then we report seasonal, long term and spatial differences in stream and spring chemistry, focusing on Birch Brook and using data from Ford Glen mainly to illustrate the substantial local differences in water chemistry.

4.1 Seasonal and long-term changes in precipitation chemistry

Precipitation in northwestern Massachusetts and adjacent areas is acidic (Fig. 2). Ion concentrations in bulk samples from HMF generally were 10 to 40% higher than wet-only samples of precipitation collected weekly at Bennington, Vermont, ~20 km north of the study area (with the exception of NO_3^- , which was ~ 2.75 times higher in Bennington. The annual median concentration of NO_3^- in wet precipitation at the Bennington NADP site (<http://nadp.sws.uiuc.edu/data/animaps.aspx>; National Atmospheric Deposition Program, 2018) has decreased since 1990, but we have not observed a significant NO_3^- decrease in bulk precipitation or throughfall at Hopkins Forest. Our biweekly sampling schedule likely affects measured NO_3^- concentrations and the forest adjacent to our bulk collectors is different than the open fields that surround the Bennington site. Values for pH were similar at both sites.

Over the period 1983-2015, bulk precipitation pH at HMF increased from about 4.3 to 4.9 (Fig. 3a); the long-term median value is 4.6. Bulk pH was slightly lower during July and August; Ca^{2+}

values decreased during the late summer and fall months. Throughfall showed strong seasonal patterns during the leaves-on season: median pH and Ca^{2+} were significantly higher ($p < 0.001$) from May through November, particularly during the leaf-fall period of mid- to late October. Yearly median throughfall pH was ~ 5.3 and averaged about 6.0 during May through November. Throughfall pH increased significantly from 1983-2015, but interannual variability was high and seasonal effects persisted over the 30-yr period. Reconnaissance monitoring of throughfall beneath adjacent stands dominated by other species demonstrated buffering of precipitation pH and alkalinity, but effects were not as pronounced as they were for sugar maple stands (Art and Dethier, 1986). Bulk precipitation SO_4^{2-} concentrations decreased sharply after 1988, only slightly between 1990 and 2006, and then sharply until 2015 (Fig. 3b).

4.2 Surface water and spring chemistry

4.2.1 Stream and spring chemistry: influence of bedrock composition

After precipitation passes through the forest canopy, soils and glacial deposits derived from bedrock, as well as underlying, locally fractured bedrock help to control the chemistry of streams and groundwater springs draining the Taconic Range. In contrast to bulk precipitation, which is dominated by H^+ , SO_4^{2-} and NO_3^- , streamflow had a dilute (Birch Brook) to saturated (Ford Glen) calcium bicarbonate and SO_4^{2-} chemistry (Table 1). During

most of the year, stream chemistry was well buffered ($\text{ANC} > 150 \mu\text{eq L}^{-1}$) in Birch Brook, its branches and the two springs (Bear and Tristate) that drain Nassau Fm phyllite. Streamwater was near saturation with calcite and relatively enriched in SiO_2 in Ford Glen and Tepid Spring. Shallow groundwater from the Nassau Fm (see also Dethier and Harman, 1998) and low flows on the South Branch (S. Br.) Birch Brook had Ca/Mg ratios of 1.7-2.1 and neutral pH (~ 7.0). Two of the waters sampled were mildly alkaline with Ca/Mg ratios of 1.8 for Tepid Spring and ~ 3.9 for Ford Glen (Fig. 1); pH is ~ 8.05 and ANC is $>2000 \mu\text{eq L}^{-1}$ at both sites. Tepid Spring emerges from dolomitic marble of the Stockbridge Fm; Ford Glen drains Walloomsac Fm phyllite. Both Tepid Spring and Ford Glen samples contained high concentrations of Ca^{2+} and Mg^{2+} and relatively high concentrations of SiO_2 , but the high Ca/Mg ratio in Ford Glen reflects weathering of more calcitic carbonate than the rock materials drained by Tepid Spring.

4.22. Seasonal and longitudinal changes in stream chemistry

Streamwater chemistry sampled monthly at the Birch Brook sample site displayed consistent seasonal trends for several constituents such as Ca^{2+} , likely mediated by mixing of different source waters. Stream pH ranged from ~ 7.0 during spring high flow periods to 7.8 during the lowest flows in late summer. ANC was relatively high in Birch Brook (median of $275 \mu\text{eq L}^{-1}$) and was lowest at high flow, particularly during spring snowmelt, and highest in late summer/early fall low flow. Median monthly concentrations of Ca^{2+} generally were high ($>375 \mu\text{eq L}^{-1}$), exceeded $580 \mu\text{eq L}^{-1}$ during the late summer/early fall low-flow period, and decreased to $<200 \mu\text{eq L}^{-1}$ during high flow periods. In Birch Brook, monthly changes in dissolved SiO_2 mimicked SO_4^{2-} values except during July-October low flow, when increases in SO_4^{2-} were much smaller than those in SiO_2 (Fig. 4). Seasonal trends were less apparent in the shorter record from Ford Glen, but ANC was $>1000 \mu\text{eq L}^{-1}$ in most samples and

concentrations of Ca^{2+} exceeded $1700 \mu\text{eq L}^{-1}$ (Table 1) and were higher during late summer and fall.

Several longitudinal sample sequences collected since 2008 along the S. Br. Birch Brook downstream to the Birch Brook sampling site (Fig. 1) indicated that at low (10/16) and high (11/08) discharge, ANC levels (Fig. 5), pH, and Ca^{2+} (not shown) increased as an irregular function of catchment area. Lowest synoptic ANC values were approximately $40 \mu\text{eq L}^{-1}$ in the

cold season at drainage areas of $< 0.1 \text{ km}^2$, rising to values $>100 \mu\text{eq L}^{-1}$ downstream where drainage area $>1 \text{ km}^2$, coincident with changes in the underlying bedrock (Fig. 1). Low-flow, mid-fall ANC decreased slightly downstream along the S. Br. Birch Brook in 2016, then increased at the lithologic boundary and downstream along Birch Brook. ANC in Ford Glen also increased downstream with increasing drainage area; concentrations are more than an order of magnitude greater than those in Birch Brook.

4.2.3 Source-area waters

Using discharge/concentration relations, longitudinal changes in stream chemistry and field observations for guidance, we plotted informal end members for source-area waters (Fig. 6) whose mixing contributed to temporal and downstream changes in Birch Brook chemistry. Compared to precipitation, streamflow had near neutral pH and was significantly more concentrated with respect to ions such as Ca^{2+} . During the early spring and late fall, water tables tend to be high and near-channel areas are moist. Because channel area is small (~6%) and little surface flow occurs on catchment slopes during intense rainstorms, low Ca^{2+} and SiO_2 concentrations in the highest Birch Brook flows (point HF, Fig. 6) likely represented soil water and saturation overland flow, including throughfall, from near-channel

wet areas. We hypothesize that deeper soil water and groundwater, including small springs and channel seeps, provided SiO₂-rich streamwater in the lowest 10% of sampled flows (LF point, Fig. 6). At low flow, stream samples from both Birch Brook and N. Br. Birch Brook contained significantly more Ca²⁺ and Mg²⁺ than upstream sample sites and upland phyllite springs and were relatively enriched in SO₄²⁻ and SiO₂, (Table 1). Stream samples collected from 2013-15, during a range of flows, fell mainly within the boundaries defined by the soil water, groundwater and throughfall end members.

4.3. Relationships between water yield and stream chemistry, Birch Brook gage

Birch Brook water yield explains ~40% of the variance in dissolved concentrations of Ca²⁺ and ANC (not plotted), 15 to 20% of the variance in SO₄²⁻ and dissolved SiO₂ (Fig. 7), and relatively small amounts of the variance in Cl⁻ and biologically mediated ions such as NO₃⁻ (not plotted). Concentrations of Ca²⁺, SiO₂, and SO₄²⁻ are not significantly related to yield for the lowest 10% of daily flows; concentrations decrease with increasing discharge at high flows, suggesting source dilution.

4.4. Long-term changes in stream chemistry and flux

The long-term record from Birch Brook displays comparable changes in Ca²⁺ and ANC concentrations (Fig. 8), a slight increase in pH, and decreases in SO₄²⁻. Since about 2005, concentrations of Ca²⁺, ANC, and SO₄²⁻ in Birch Brook have changed substantially; Ca²⁺ (and ANC) have increased by >60% and SO₄²⁻ has continued a long-term downward trend. Assuming that years are independent, trends for ANC and Ca²⁺ from 2005 to 2015 are highly significant ($t= 5.07$ and 4.57 , respectively; $p=0.001$). The significant upward trends in

Ca²⁺ and ANC highlight the recovery in Birch Brook's buffering capacity and distinguish its chemistry from that reported for most poorly buffered catchments in the NE USA, where neither median Ca²⁺ nor ANC have increased significantly (compare to Fuss et al., 2015). Median SO₄²⁻ concentration in Birch Brook decreased from 170 ± 10 µeq L⁻¹ to 110 ± 6 µeq L⁻¹, a long-term decrease of ~2 µeq L⁻¹ yr⁻¹ since 1983. With the exception of Mg²⁺, which is highly correlated with Ca²⁺ concentrations, long-term changes for other base cations and anions, including NO₃⁻, are less significant.

Stream SO₄²⁻ concentrations in Birch Brook were ~5 times greater than those measured in bulk precipitation and annual catchment export was ~2 times the deposition rate in 2015. Flow-normalized SO₄²⁻ flux decreased significantly after about 1985 and was ~ 30 kg ha⁻¹ in 2015. In 2015 the normalized flux was 10-12 kg ha⁻¹ higher than values measured at Hubbard Brook Watershed 3 (HB) in New Hampshire, at Biscuit Brook, in the Catskill Mountains of eastern New York (Fig. 9) and at Sleepers River W9 (SR) in northern Vermont. Precipitation is ~35% greater at the HB and Biscuit Brook sites than at Birch Brook, and SR precipitation and runoff are lower.

4.5. Long-term net annual flux from Birch Brook and Ford Glen catchments

We calculated long-term, net annual flux from the adjacent Birch Brook and Ford Glen basins and compiled comparable data from a range of other Appalachian catchments (Table 2).

Despite similar soils, bedrock, land-use history and climate, the long-term flux of Ca²⁺ and Mg²⁺ from Ford Glen is about 4 times that of Birch Brook and SiO₂ export from Ford Glen is about 1.7 times that of Birch Brook. Over the past three decades, net streamflow flux of K⁺ and Cl⁻ has been minimal in the Birch Brook catchment; NO₃⁻ shows net accumulation.

5.0 DISCUSSION

Precipitation in HMF is acidic, but Birch Brook surface waters are moderately buffered and ANC fell below $200 \mu\text{eq L}^{-1}$ only during rare spring high-flow periods and on the upper reaches of first-order tributaries. Long-term trends in the flux of Ca^{2+} , SO_4^{2-} , and SiO_2 reflect changes in acid-deposition patterns and the influence of relatively soluble rock materials in the upland, mainly old-growth forested catchments of the tristate area. Increasing Ca^{2+} and ANC concentrations in Birch Brook and decreasing export of hydronium and SO_4^{2-} since about 2005 record stream recovery coincident with long-term decreases in acid SO_4^{2-} deposition. Long-term trends suggest that effects of acid deposition also are decreasing in some streams and lakes in poorly buffered northern Appalachians catchments (Stoddard et al., 1999; Strock et al., 2014; Fuss et al., 2015; McHale et al., 2017). Local biogeochemical buffering and flow pathways likely control the differential response in stream chemistry and timing in different NE USA catchments.

5.1 Changes in the chemical composition of precipitation and streamflow from 1983-2015

Over a 30-year time period marked by decreasing acidic emissions, the pH of both bulk precipitation and throughfall in a sugar maple stand increased irregularly in HMF at rates of 0.02 and 0.03 pH units yr^{-1} , respectively. Median SO_4^{2-} concentration in bulk precipitation decreased by $1.3 \mu\text{eq L}^{-1} \text{yr}^{-1}$ during the period 1983-2015, comparable to values reported elsewhere in the region (McHale et al., 2017).

Long-term changes in the chemistry of Birch Brook, notably increases in Ca^{2+} , ANC, and pH since about 2005 (Fig. 8a) and decreases in SO_4^{2-} , are associated with decreased SO_4^{2-} in precipitation in NW Massachusetts. Steep decreases in stream Ca^{2+} concentrations in many NE USA catchments before ~1980 and more recent gradual decreases in some areas may be

linked to acid-deposition mediated changes in Ca^{2+} on soil exchange sites (Likens et al., 1996; Fernandez et al., 2003; Lawrence et al., 2011). Relatively high concentrations of Ca^{2+} throughout the measurement period (lowest value $> 150 \mu\text{eq L}^{-1}$) in Birch Brook, an upland stream, did not suggest control by low base-saturation values, but the decade-long increase in Ca^{2+} must reflect changing soil or shallow-groundwater chemistry, or flow pathways. Field observations and hydrologic response to storm events do not indicate contemporary changes in flow pathways in HMF; we did not monitor shallow-groundwater chemistry. Systematic data about historic changes in soil base saturation in HMF are not available, but there was no significant difference between exchangeable Ca^{2+} concentrations measured in 62 soil mineral horizons in 1985 (Art and Dethier, 1986) and reconnaissance measurements of 16 mineral horizons resampled in 2017 (J. Racela, unpublished data, 2017). These measurements suggest that any changes in soil exchangeable Ca^{2+} at HMF likely were confined to the O and A horizons.

At the Birch Brook sampling site, Ca^{2+} , ANC and pH (not shown) have increased significantly since about 2004 (Fig. 10) whereas at HB, stream ANC has increased slightly, the frequency of snowmelt acidification episodes has decreased, and net export of Ca^{2+} and changes in soil-exchange Ca^{2+} both have stabilized since about 1984 (Fuss et al., 2015). The sharp increases measured in Birch Brook are consistent with increases in available Ca^{2+} in HMF soils following a period when acid sulfate deposition had decreased base saturation. Exchange calcium (and magnesium) likely reflect the high solubility and relatively fast kinetics of carbonate weathering. In the decade after 2004, HB streamwater Ca^{2+} concentrations decreased by $<1\%$ per year. Concentrations of Ca^{2+} and ANC at Biscuit Brook are low and similar to those measured in HB (Fig. 10). In contrast, the high Ca^{2+} concentrations at SR have decreased about 1% per year and ANC values have increased by about 1% per year since 2004. Trends at SR suggest that

SO_4^{2-} decreases in precipitation directly affect the annual flux of Ca^{2+} in streamflow at that site.

Since about 2010, SO_4^{2-} flux from the Birch Brook catchment has been somewhat higher than values measured at Biscuit Brook and at HB (Fig. 9). Annual flux is variable, driven mainly by fluctuations in precipitation that are likely to enhance geochemical processes mediated by soil moisture. Export of SO_4^{2-} from HMF and other regional catchments such as HB continues to exceed input, suggesting an additional source of catchment SO_4^{2-} such as the weathering of pyrite (cf. Bailey et al., 2004), which is present as an accessory mineral in Taconic bedrock. Mineralization of organic S represents an additional potential source of SO_4^{2-} , as noted by McHale et al. (2017) for Biscuit Brook. Recent SO_4^{2-} export values from SR are lower than other values plotted in Figure 9 and correspond with a decrease in the high Ca^{2+} concentrations at that site. The contrast between post-2004 solute changes in Birch Brook and at SL, both well-buffered systems at low flow, is puzzling and may reflect differences in soil chemistry and flow pathways at the sites.

5.2 Annual, seasonal, and short-term controls on stream chemistry

Annual and shorter-term changes in Birch Brook stream chemistry result from mixing of waters from source areas that have different transit times, chemistries, and hydrologic flow paths. Our monitoring data do not include event-based sampling of storm hydrographs or spring snowmelt, nor the detailed sampling of source areas over time required for forward modeling of stream chemistry. Long term and longitudinal sampling suggests, however, that simple, qualitative mixing describes seasonal variability, downstream changes, and the low slopes of C_i/Q relations in Birch Brook (Fig. 7). Streamflow at the sampling site mainly is a mixture of soil water and shallow groundwater except at the highest flows (Fig. 6), mainly in the spring, when rainfall and snowmelt inputs are larger. During the highest-flow periods,

Ca^{2+} and SiO_2 concentrations are variable and chemically similar to soil water mixed with throughfall and to streamflow sampled at upstream locations where soils are thin and transit times are short. Soil and sediment thicknesses are greater at lower elevations, bedrock is richer in calcium (Fig. 1), and transit times are longer, increasing ANC and base cations downstream. Calcium and SiO_2 concentrations in the lowest flows plot between the soil-water and groundwater end members (Fig. 6) and are higher than concentrations measured in the upper slope springs that drain fractures in the phyllite. Small water yields ($< 0.2 \text{ mm d}^{-1}$) in Birch Brook at low flow (Fig. 7) suggest that contributions from deep groundwater are small and that slow weathering rates (e.g. Yuretich et al., 1996) result in moderate streamwater concentrations of Ca^{2+} and SiO_2 . At the highest flows most water arrives in the channel buffered by travel through soil. The overall effect of flow pathways and mixing is that variation in ionic concentrations in Birch Brook are not fully explained by discharge and that concentrations remain relatively high, even at high flow, compared to less well-buffered streams,

In the adjacent Ford Glen catchment, concentrations of Ca^{2+} and SiO_2 are much higher (Table 1) than those measured in Birch Brook, consistent with longer subsurface pathways through materials richer in carbonate. Stream concentrations of SiO_2 in Ford Glen are somewhat lower and more variable at high flow (Dethier and Racela, unpublished data, 2018). Specific flow pathways and the slow kinetics of silicate dissolution reactions probably control concentrations, as April and Newton (1985) proposed for a pair of catchments in the southern Adirondacks of New York and Yuretich et al. (1996) demonstrated for catchments in central Massachusetts.

5.3 Bedrock controls on stream water chemistry in the tristate area

Stream chemistry in Birch Brook and Ford Glen records buffering imposed by locally reactive rock materials in the tristate area and long-term trends for Ca^{2+} and ANC illustrate how Birch Brook chemistry has recovered over time. Significant increases in stream Ca^{2+} concentrations in Birch Brook during the past decade probably reflect the relative abundance of calcium carbonate in near-surface materials. Reconnaissance sampling of numerous streams in northwestern Massachusetts in 1983-85 (Fig. 11) showed low values and sharp spatial gradients of ANC and pH (Godfrey et al., 1985) mediated by geochemically resistant rocks in upland areas like the Taconic and Hoosac Ranges and reactive rocks such as marble and dolomite in adjacent valleys. Resampling of many sensitive surface-water bodies in Massachusetts in 2016, including a population of streams in northwestern Massachusetts (Hatte and Drury, 2016) showed that most ANC and pH values have increased since the mid-1980s, similar to regional trends of recovery reported by Strock et al. (2014).

5.4 Chemical flux from Hopkins Forest and other Appalachian catchments

In the broader context of the Appalachians, Birch Brook and Ford Glen show substantial export of calcium, low to moderate losses of other base cations, and relatively low SiO_2 export (Table 2) compared to Sleepers River (Vermont) and the deeply weathered upland catchments of the southeastern USA. If we use SiO_2 flux as a proxy for the rate of silicate weathering, the phyllitic Birch Brook catchment is weathering slowly. Ford Glen chemistry implies that longer flow pathways, greater mineral surface area in thick glacial deposits, and more abundant carbonate minerals may account for higher export of Ca^{2+} , Mg^{2+} , and SiO_2 (April and Newton, 1985). High SiO_2 flux from the Coweeta and Panola Mountain catchments in the southern Appalachians is a function of higher specific runoff, a high proportion of groundwater flow, and warm temperatures (White and Buss, 2013). High

values at Sleepers River, however, must reflect an unusual combination of silicate and carbonate weathering of generally resistant, schist-derived materials (Peters et al., 2006). Soil water has low pH and is rich in SiO₂, whereas groundwater is relatively rich in calcium. Chemical weathering of these materials results in export of ~26 T km⁻² yr⁻¹ of dissolved solids at Sleepers River compared to ~9 T km⁻² yr⁻¹ from Birch Brook.

6.0 Conclusions

Long-term trends of precipitation and streamflow chemistry in NW Massachusetts and elsewhere in New England and adjacent New York show that deposition and streamflow flux of SO₄²⁻ have decreased and that pH has increased in the past 30 years. Trends measured at Birch Brook and other streams in western New England show that stream chemistry mirrors decreases in acidic deposition in upland catchments, even where ecosystem chemistry is buffered by bedrock composition, and that stream chemistry is improving. Stream Ca²⁺ concentrations and ANC in Birch Brook were relatively high in the 1980s and 1990s and increased after about 2005, in contrast to many sites in the region where geochemical buffering is less pronounced. Sharp differences in the geochemistry of adjacent drainages (Birch Brook and Ford Glen) demonstrate that flow pathways and the composition of bedrock and soil derived from glacial materials provide important controls on stream chemistry.

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Table 1. Summary of water chemistry, Hopkins Memorial Forest.

	Ca (SE) ¹	Mg (SE)	Na (SE)	K (SE)	NH ₄ (SE)	ANC (SE)	SO ₄ (SE)	Cl (SE)	NO ₃ (SE)	SiO ₂ (SE)	pH (SE)
Bulk precipitation ²	22 (2.9)	4.9 (1.2)	7.7 (3.2)	2.3 (1.6)	11.5 (6.1)	8.2 (4.7)	36.3 (3.5)	10.5 (2.1)	14.6 (2.6)	0 (0.0)	4.61 (0.06)
Throughfall	64.8 (11.4)	18.6 (5.2)	7.0 (20.9)	42.2 (12.3)	15.9 (5.9)	60.5 (14.2)	53.0 (8.4)	19.4 (5.5)	18.7 (7.6)	0 (0.0)	5.62 (0.14)
Birch Brook (all)	303 (9.0)	104.2 (2.9)	22.6 (0.8)	3.6 (0.1)	3.9 (0.9)	275 (10.3)	141 (1.8)	18.9 (0.5)	4.0 (0.5)	41.4 (0.5)	7.5 (0.01)
Ford Glen ³	1718 (142.8)	475 (62.7)	120 (14.9)	11.2 (1.1)	0.0 (1.0)	2073 (149)	146.8 (13.0)	108 (16.1)	10.1 (3.0)	81.0 (5.4)	8.13 (0.06)
Birch Brook (high ⁴ flow)	197.5 (19.0)	75 (3.6)	17.2 (3.4)	3.5 (0.5)	5 (1.9)	160 (21.6)	130.5 (4.4)	18.1 (2.1)	5.5 (2.6)	32.5 (2.3)	7.06 (0.04)
Birch Brook (low ⁴ flow)	584 (23.3)	208.3 (8.2)	32.6 (1.5)	5.4 (0.5)	5 (1.9)	636.0 (33.4)	170.2 (7.2)	19.5 (1.2)	12.3 (1.3)	46.4 (0.7)	7.65 (0.06)
S. Br. Birch Br.	142.8 (11.1)	69.8 (5.5)	12.4 (1.3)	1.3 (0.4)	0.3 (0.4)	124.4 (9.0)	87.3 (3.3)	26 (2.1)	6.9 (1.2)	33.9 (1.4)	7.01 (0.10)
M. Br. Birch Br.	171.4 (13.7)	78.8 (6.1)	15.8 (1.4)	1.3 (0.2)	3.1 (1.3)	167.9 (14.3)	88.1 (3.5)	25 (1.9)	4 (1.2)	35.6 (1.2)	7.11 (0.10)
N. Br. Birch Br.	300.8 (30.4)	90.3 (13.9)	18.9 (2.0)	1.5 (1.4)	0.9 (0.4)	267 (43.5)	101.8 (5.2)	23.2 (2.1)	3 (1.1)	44.1 (2.2)	7.33 (0.10)
Bear Spring	274 (28.0)	145 (11.0)	18.5 (5.8)	4.9 (3.2)	6.1 (1.2)	245.4 (36.2)	146.9 (10.4)	42.9 (5.8)	35.8 (33.1)	38 (2.3)	6.72 (0.10)
Tristate Spring	344.7 (21.7)	209.9 (7.1)	10.8 (10.5)	3.3 (1.7)	2 (1.6)	411.1 (34.7)	185.9 (8.8)	31.8 (6.4)	19.8 (1.0)	39.3 (3.2)	7.31 (0.24)
Tepid Spring ⁵	1752 (31.5)	962 (23.2)	75.2 (1.8)	17.6 (0.3)	3.3 (1.4)	2334 (71.7)	244.0 (9.4)	69.3 (2.9)	19.1 (1.1)	133 (6.2)	8.06 (0.02)

1. Concentrations are median values and standard error (SE), in μeqL^{-1} except for SiO₂ ($\mu\text{mol L}^{-1}$) and pH.

2. Bulk precipitation collected biweekly from 1983-2015; throughfall from 1986-2015; Birch Brook samples are monthly from 1983-2015; Birch Brook tributary samples are monthly in 2015-16.

3. For median values calcite saturation indices =0.16 (Ford Glen at 15°C) and 0.96 (Tepid Spring at 20°C) (<http://www.aqion.de/site/86>)

4. High ($>4.6 \text{ mmd}^{-1}$) and low flow ($<0.13 \text{ mmd}^{-1}$) samples collected from daily flows with $p < 0.1$ in the 31 year record on Birch Brook.

5. Tepid Spring sampled monthly from 7/04 to 5/07; other springs irregularly from 1988 to present (n=6-9).

Table 2. Calculated net flux of dissolved constituents from Birch Brook, Ford Glen and selected forested, upland catchments in the Appalachian Mountains, USA.

Catchment	Rock Type	Years	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	SO ₄ ²⁻	Cl ⁻	SiO ₂
			kg ha ⁻¹ yr ⁻¹						
Birch Brook ^a	Phyllite; glacial	1983-2015	35.2	7.8	1.8	0.6	24.5	0.5	19.9
Ford Glen ^b	Phyllite and marble; thick glacial	2007-2015	152	32.6	nd	nd	51.9	nd	35
Sleepers River, VT ^c	Calcareous schist; glacial	1991-1994; 1999-2009	137	6.4	3.4	6.6	52.6	0.7	44.8
Hubbard Brook, NH ^d	High-grade metamorphic; thin glacial	1972-2013	9	2.1	6.9	0.68	17.7	1.1	45.6
Biscuit Brook, NY ^e	Sedimentary	1992-2014	21.3	4.6	3.1	2.2	41.4	nd	19.9
Coweeta, NC ^f	High-grade metamorphic	<1988	1.8	2.3	8.3	2.9	-8.3	1.1	76.7
Panola Mountain, GA ^g	Granodiorite	2000-2009	4.8	2	7.4	0.7	7.2	nd	46.1

a This study; corrected for bulk precipitation flux. Input of NO₃⁻ is nearly 6.5 times the amount exported.

b This study; comparison of samples from the west and east branches shows that Na⁺, K⁺, and Cl⁻ chemistry at sample site is altered by effluent from a single house in the catchment.

c Values from Hornbeck et al. (1997) except SO₄²⁻ and SiO₂, which are calculated from Aulenbach et al. (2016, Table 4).

d Watershed 3 from Likens, G.E. 2016. Chemistry of Streamwater at the Hubbard Brook Experimental Forest, Watershed 3, 1963-present. Hubbard Brook Data Archive w3_stream_chem. <http://hubbardbrook.org/data/dataset.php?id=81> (accessed 13 May 2017)

e Values from Burns, D.A., unpublished data, 2017.

f Values from Swank and Waide (1988, Table 4.1.1; Watershed 2); see also Velbel and Price (2007)

g Values from White et al. (2002) except SO₄²⁻ and SiO₂, which are calculated from Aulenbach et al. (2016, Table 4); White et al. report a value of 41.1 for SiO₂

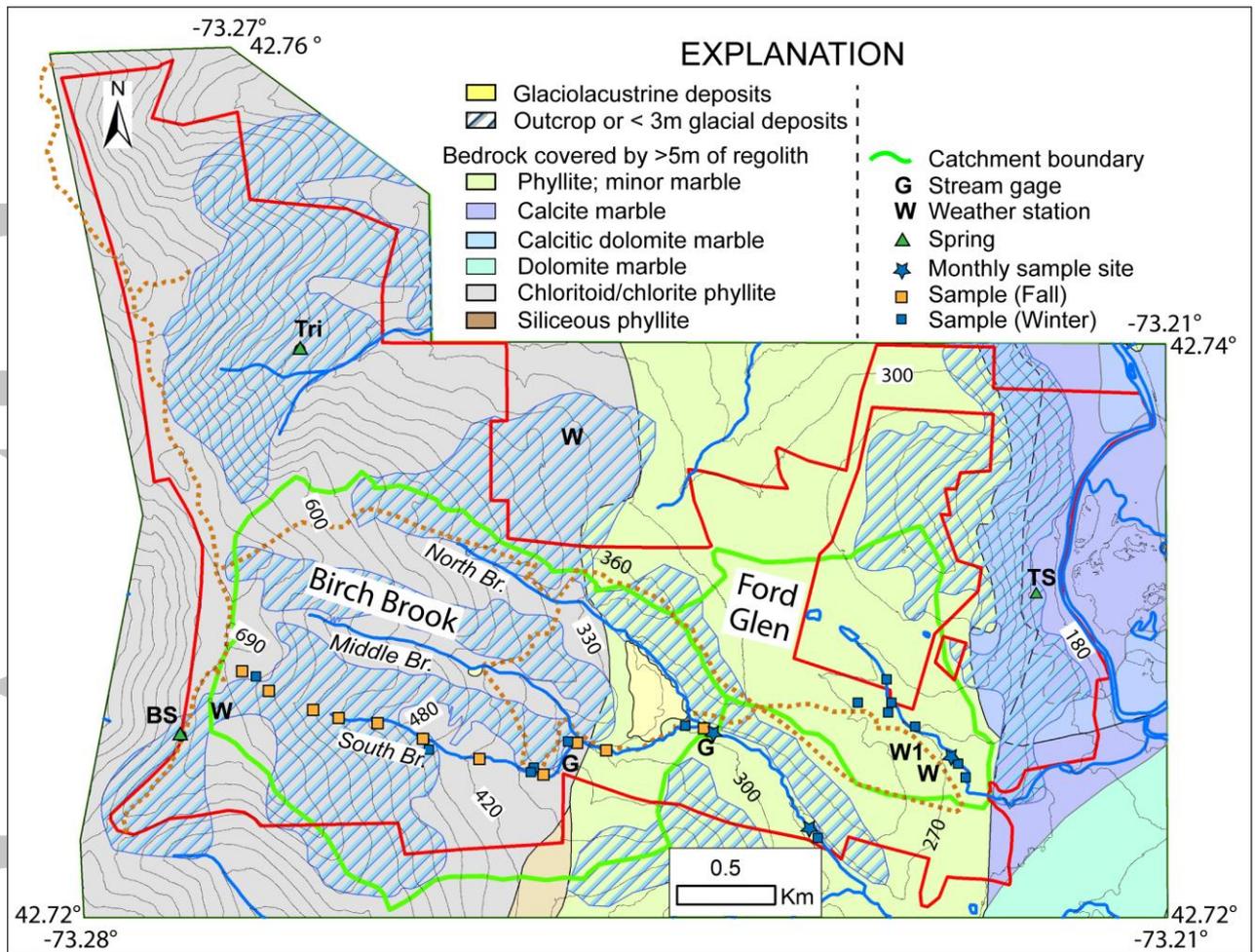


Figure 1. Map of Hopkins Memorial Forest and adjacent areas showing surficial deposits and underlying bedrock (modified from Robinson and Capo, 2003), Birch Brook and Ford Glen catchments (green lines), stream channels, and monitoring sites. Contours in meters; interval is 30 m. Dashed brown lines are trails. Red lines outline boundaries of Hopkins Memorial Forest.

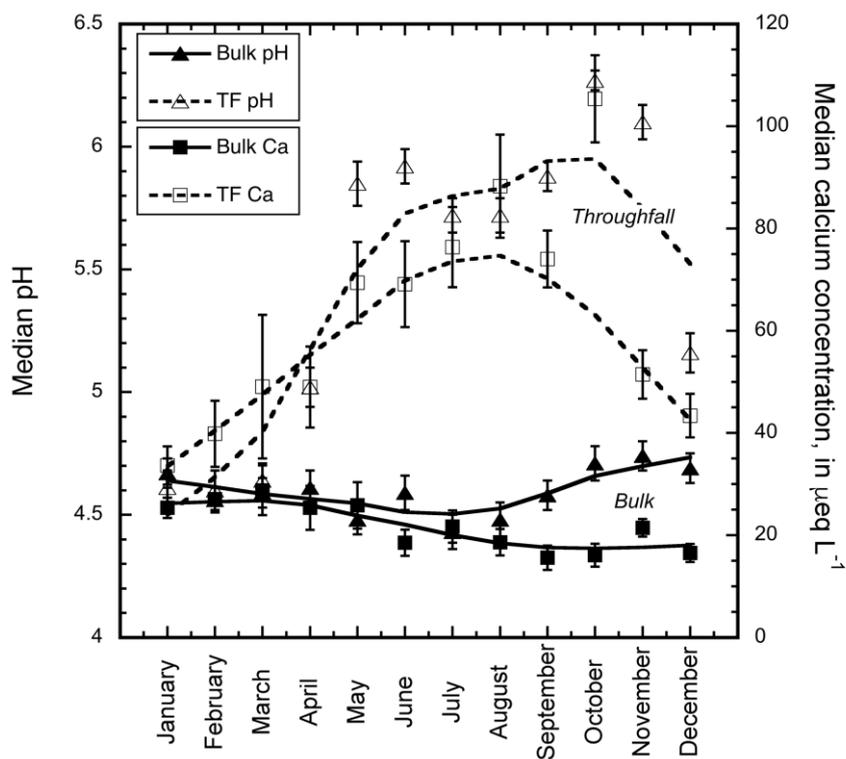


Figure 2. Median monthly pH and calcium concentration in bulk precipitation and throughfall (TF), 1983-2015. Trends smoothed using the locally weighted least squares error (Lowess) method with 0.4 smoothing parameter. Bars show standard error.

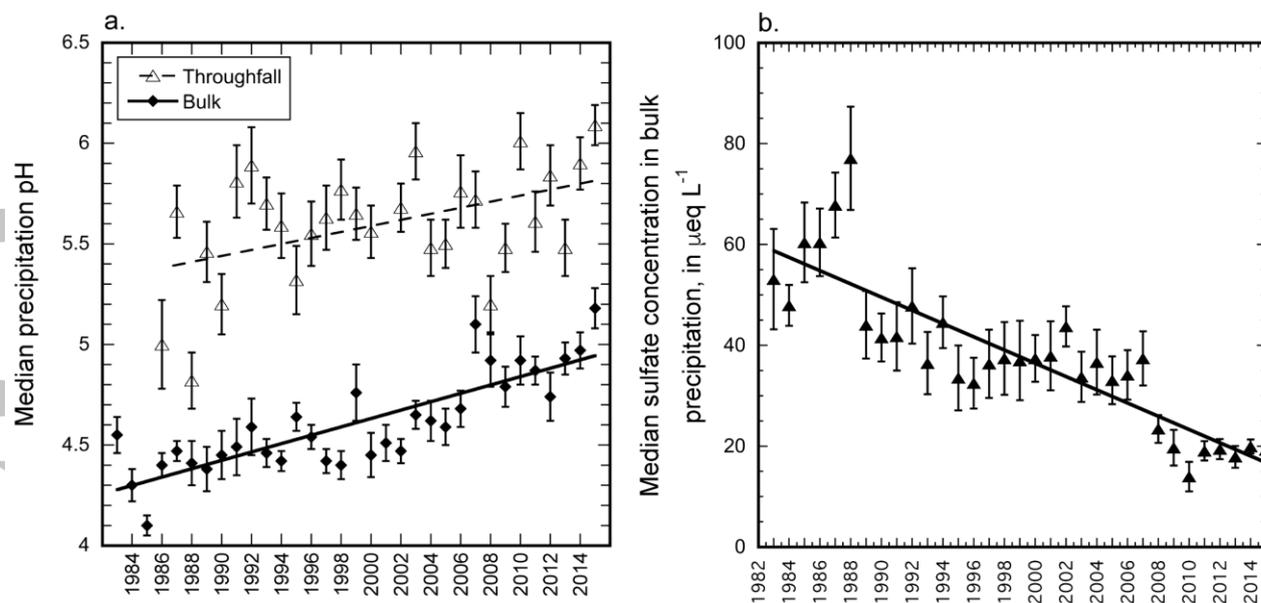


Figure 3. Trends and linear fits for yearly precipitation chemistry, 1983-2015, Hopkins Memorial Forest. Bars show standard error. a. Bulk precipitation $\text{pH} = 4.3 + 0.021x$, $r^2 = 0.68$, $p < 0.001$; throughfall $\text{pH} = 5.4 + 0.015x$, $r^2 = 0.21$, $p < 0.01$, where x = years after 1982 and 1985, respectively. b. Trend and linear fit for yearly median SO_4^{2-} concentration in bulk precipitation, $\text{SO}_4 = 60 - 1.3x$, $r^2 = 0.74$, $p < 0.001$, where x = years after 1982.

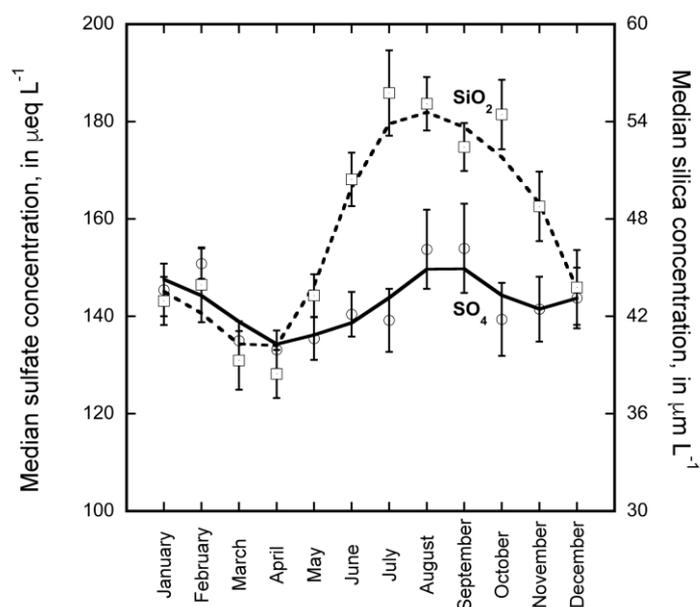


Figure 4. Monthly variation in median SO₄ and SiO₂ stream concentration measured at Birch Brook sampling site, 1985-2015. Trends smoothed using the locally weighted least squares error (Lowess) method with 0.4 smoothing parameter. Bars show standard error.

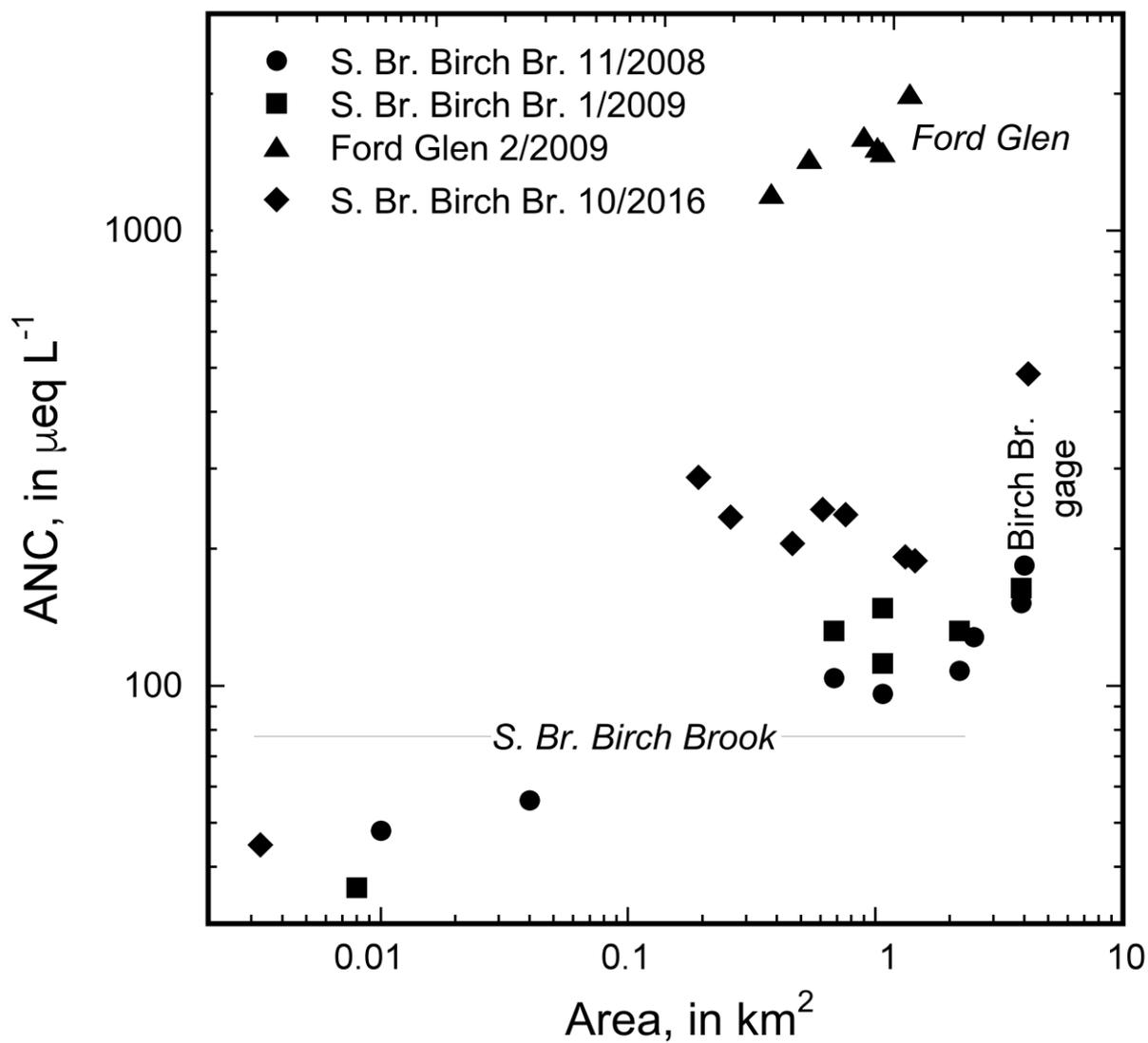


Figure 5. Relationship of ANC to upstream drainage area for longitudinal samples from Birch Brook and Ford Glen. Upper reaches of S. Br. Birch Brook were dry in October 2016.

Accp

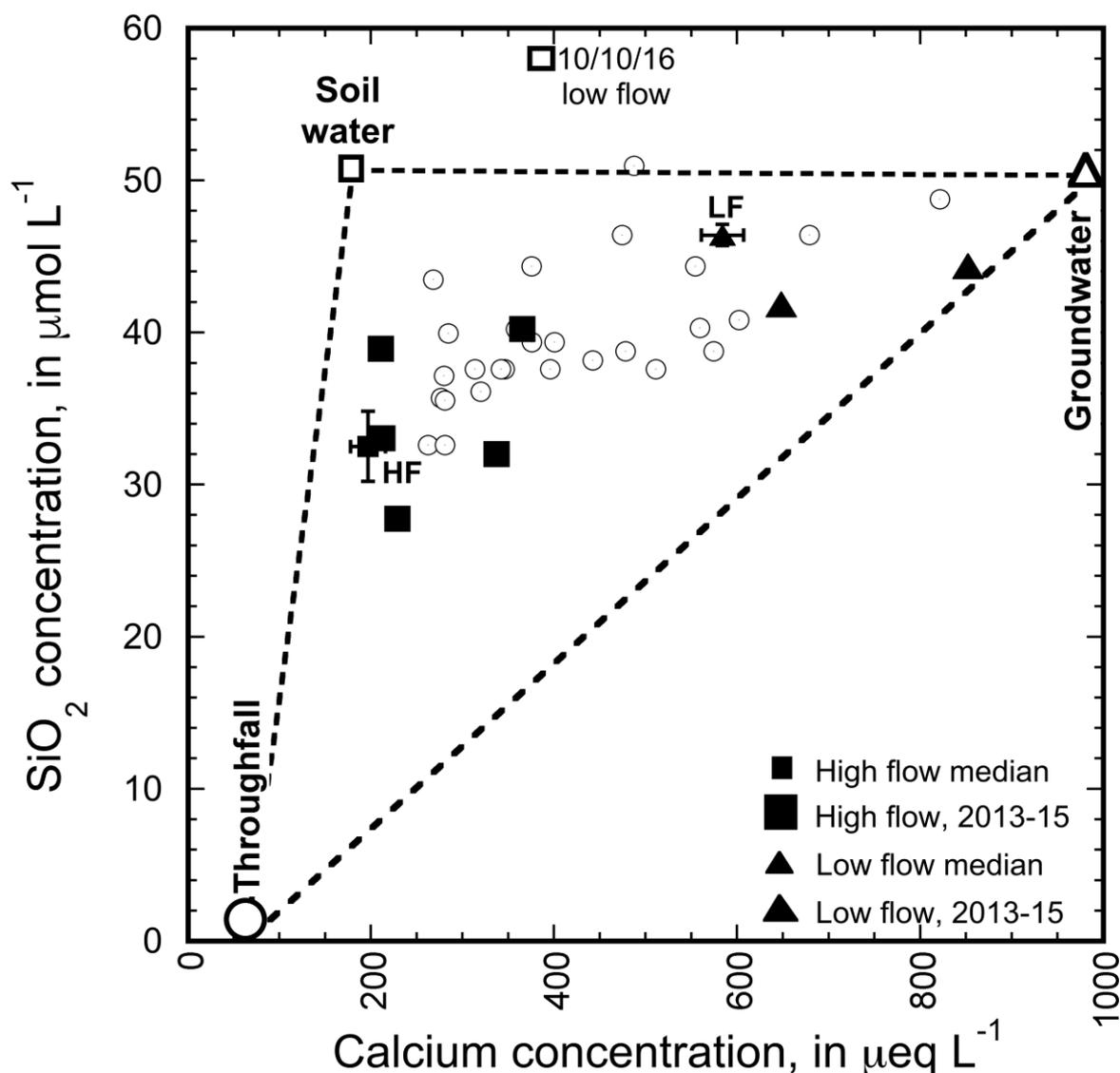


Figure 6. End-member concentration plot of Ca and SiO₂ showing source-area waters that contribute to chemistry measured at the Birch Brook sampling site. “HF” is the median value (\pm SE; n=34) for the highest 10% of daily discharge in Birch Brook from 1985-2015; “LF” is the median value (\pm SE; n=34) for the lowest 10% of discharge. For monthly samples collected in 2013-2015, open circles represent intermediate discharges, large squares fall in the highest 20% of daily discharge (1985-2015) and large triangles fall in the lowest 20%. Yield on 10/10/16 was 0.11 mm d⁻¹, in the “LF” category.

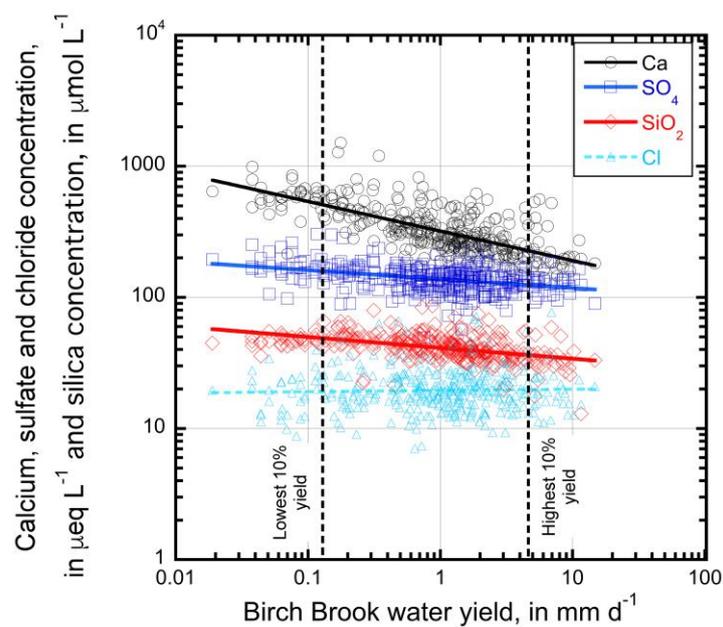


Figure 7. Relationship of Birch Brook daily water yield and dissolved stream chemistry, 1985-2015. $\text{Ca} = 320 * Q^{-0.23}$, $r^2 = 0.43$; $\text{SO}_4 = 140 * Q^{-0.068}$, $r^2 = 0.17$; $\text{SiO}_2 = 41 * Q^{-0.083}$, $r^2 = 0.18$; $\text{Cl} = 20 * Q^{0.009}$, $r^2 = 0.00$.

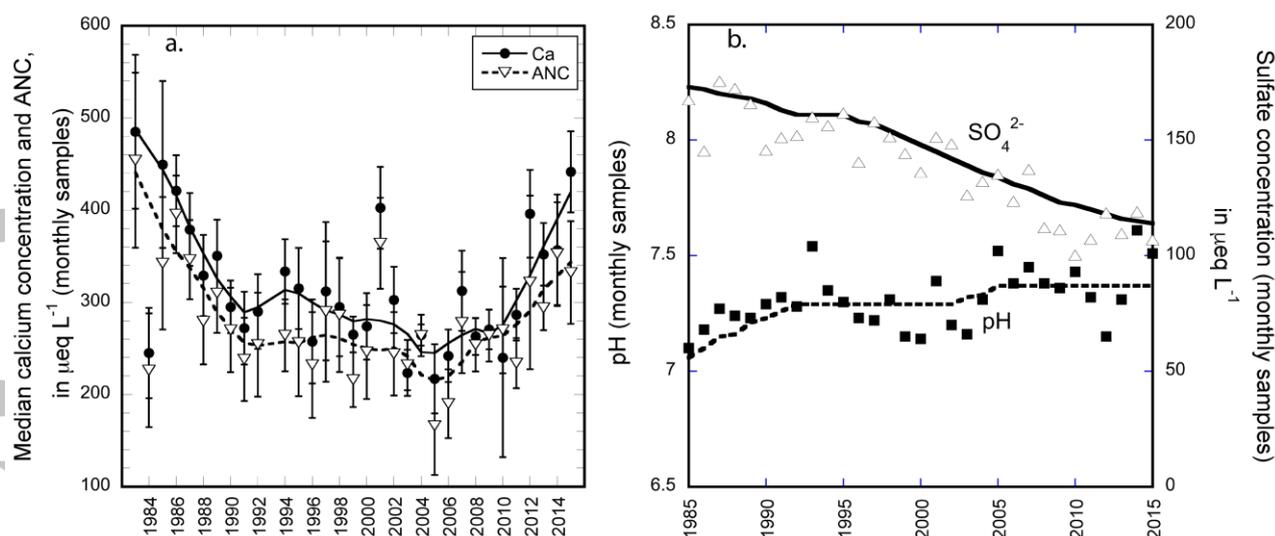


Figure 8. Long-term changes in Birch Brook chemistry. a. Calcium and acid neutralizing capacity trends from 1983-2015, smoothed using the locally weighted least squares error (Lowess) method with 0.2 smoothing parameter; b. pH and SO_4^{2-} trends from 1985-2015, both plotted as flow-normalized concentrations.

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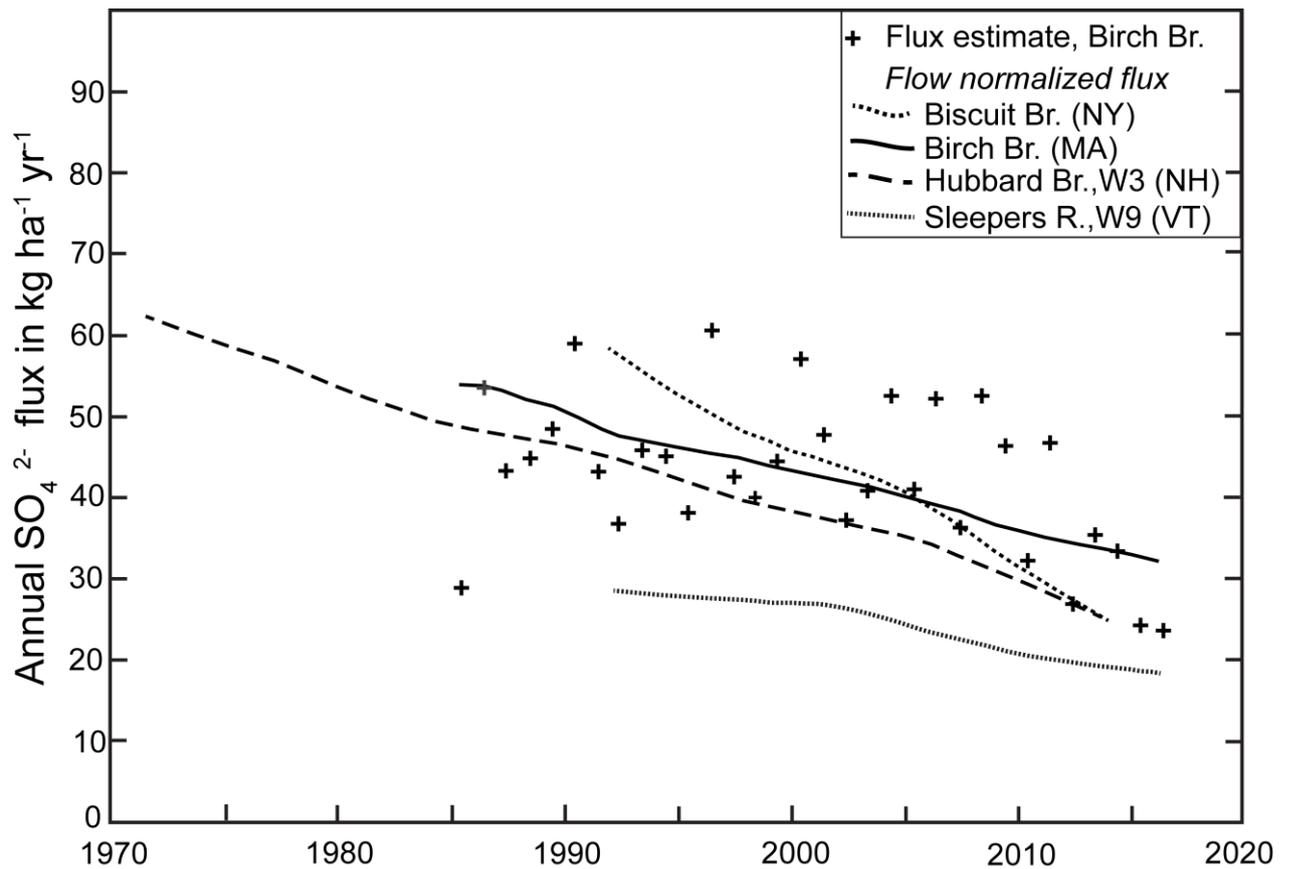


Figure 9. Long-term trends in flow-normalized SO_4^{2-} flux from four NE USA catchments. Flux-estimated values plotted only for Birch Brook. Biscuit Br. values from McHale et al., 2017; Hubbard Br. Watershed 3 (W3) SO_4^{2-} flux data from Likens, 2016; Sleepers River Watershed 9 (W9) data from J. Shanley (U.S. Geological Survey, unpublished data, 2018)

Accepted

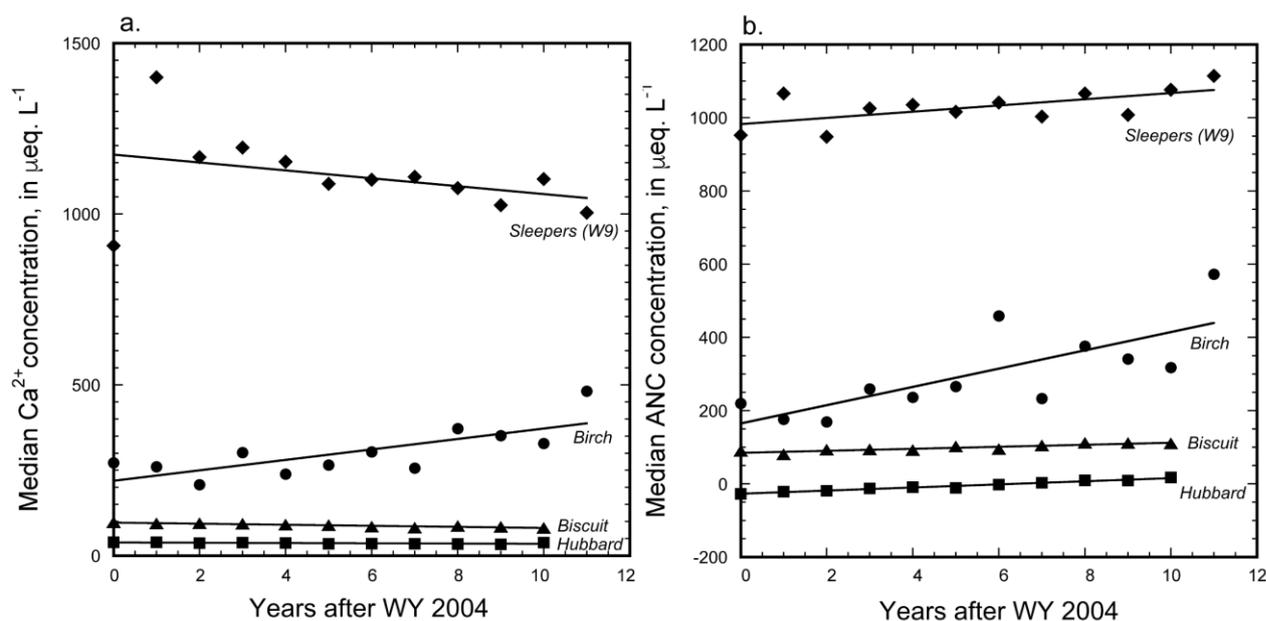


Figure 10. Concentration trends for Water Year 2004 to Water Year 2015, where x refers to years after WY 2004. a. Median Ca^{2+} concentration ($p < 0.001$ for all relationships) in Hubbard Brook-W3 ($\text{Ca}^{2+} = 39 - 0.44x$; $r^2 = 0.44$), Biscuit Brook ($\text{Ca}^{2+} = 97 - 1.6x$; $r^2 = 0.87$), Birch Brook ($\text{Ca}^{2+} = 220 + 15x$; $r^2 = 0.56$), and Sleepers River--W9 ($\text{Ca}^{2+} = 1200 - 12x$; $r^2 = 0.12$). b. Median ANC concentration ($p < 0.001$ for all relationships) in Hubbard Brook-W3 ($\text{ANC} = -27 + 4.2x$; $r^2 = 0.97$), Biscuit Brook ($\text{ANC} = 85 + 2.8x$; $r^2 = 0.82$), Birch Brook ($\text{ANC} = 170 + 25x$; $r^2 = 0.56$), and Sleepers River--W9 ($\text{ANC} = 980 + 8.5x$; $r^2 = 0.39$).

Hubbard Brook W3 data from Likens, 2016; Biscuit Brook data from McHale et al. (2017); Sleepers River W9 data from J. Shanley (U.S. Geological Survey, unpublished data, 2018).

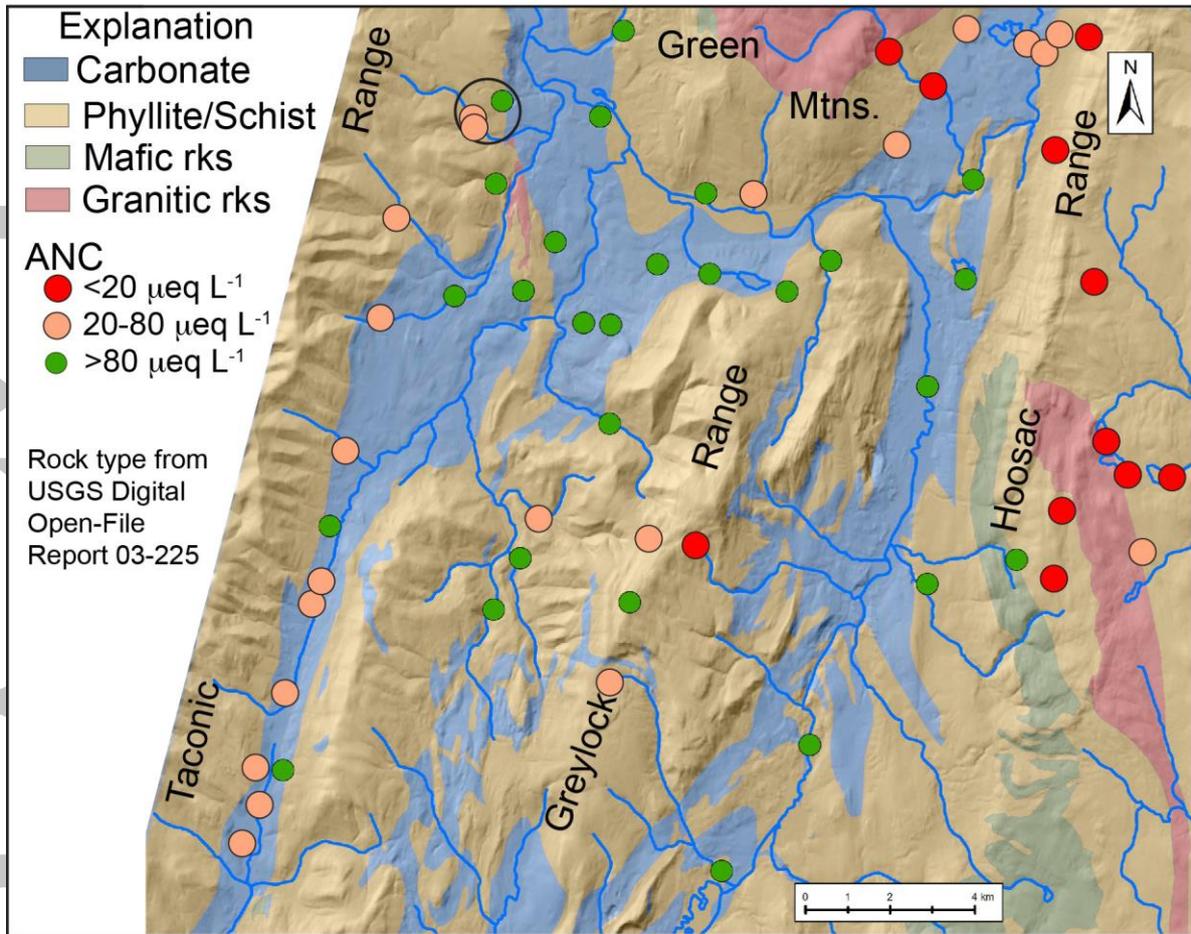


Figure 11. High flow surface-water ANC values measured in NW Massachusetts during 1983-85 (data from Godfrey et al., 1985). Circle encloses two sites on Birch Brook and one on Ford Glen.

Accepted

Appendix A. Summary information for water analysis techniques in the Environmental Analysis Laboratory, Williams College, from 1983-2017

1.0 Analyses

After field collection, precipitation and stream samples are filtered through 0.45 μm Millipore nitrocellulose membrane filters, stored in the dark at 4°C until analysis, but are not acidified. Unfiltered splits of precipitation and stream samples are analyzed for pH and ANC within 24 hours of collection. From 1983-2011, pH was measured and ANC titrated to an endpoint of 4.5 using a laboratory Corning Model 12 Research pH meter, a Hach digital titrator, and 0.16 M H_2SO_4 . Beginning in 2012, samples have been titrated with 0.016N H_2SO_4 to 4.5, then 3.5 with a Radiometer Analytical TIM840 Autotitrator.

Base cations and common anions are analyzed on filtered samples, generally 3 weeks to 3 months after sample collection. For cation analysis, a small amount of either 5% lanthanum chloride (Ca^{2+} , Mg^{2+}) or 0.5% cesium chloride (Na^+ , K^+) is added to each aliquot of sample. Ca^{2+} , Mg^{2+} , Na^+ , K^+ have been measured by atomic absorption and emission spectroscopy on the following instruments:

- Perkin-Elmer 403 (1983-1989)
- Perkin-Elmer 1100B (1989-2000)
- Perkin-Elmer Aanalyst 300 (2000-2017)
- Perkin-Elmer PinAAcle 900H (2017-present)

The anions Cl^- , NO_3^- , PO_4^{3-} , and SO_4^{2-} have been measured on the following instruments:

- Technicon Auto-Analyzer II (1983-1987)
- Dionex 4000i Ion Chromatograph (1987-2000)
- Dionex DX600 Ion Chromatograph (2000-2015)
- Metrohm 883/863 Ion Chromatograph (2015-present)

NH_4^+ was measured on filtered samples with a Technicon Auto-Analyzer using the Berthelot Reaction, a colorimetric analysis in which alkaline phenol and sodium hypochlorite react with ammonium to form indophenol blue. SiO_2 was analyzed on filtered samples with a Technicon Auto-Analyzer utilizing the reduction of silicomolybdate to “molybdenum blue” with ascorbic acid.

2.0 Quality assurance and control

Most samples have been analyzed 2 to 4 times. Sample charge balance is used as the initial screen. For individual ions, quality control (QC) and quality assurance (QA) uses both commercial reference standards and intralaboratory comparison samples. The standard reference materials are used as a single-blind setup

until after results were obtained. Using archived samples for intralaboratory tests permits us to evaluate reanalysis statistics over time. Analytical precision and accuracy at the lowest levels have improved slightly since 1987, but we have not observed significant trends in measured values for QA or QC samples over time. However, there may still be data anomalies for individual analyses or samples that should be carefully evaluated by users.

Current analyses:

Analysis	Instrument	Detection limit (2015-2017)	Run Precision (2015-2017)
Calcium (Ca ⁺²)	Perkin-Elmer PinAAcle 900H	0.49 µeq/L	0.90 %RSD
Magnesium (Mg ⁺²)	Perkin-Elmer PinAAcle 900H	0.41 µeq/L	0.53 %RSD
Sodium (Na ⁺)	Perkin-Elmer PinAAcle 900H	0.43 µeq/L	0.55 %RSD
Potassium (K ⁺)	Perkin-Elmer PinAAcle 900H	0.26 µeq/L	0.78 %RSD
Ammonium (NH ₄ ⁺)	Technicon Auto-analyzer II	0.56 µeq/L	2.64 %RSD
Silica (SiO ₂)	Technicon Auto-analyzer II	0.33 µeq/L	1.46 %RSD
Chloride (Cl ⁻)	Metrohm 883/863 IC	0.57 µeq/L	0.28 %RSD
Nitrate (NO ₃ ⁻)	Metrohm 883/863 IC	0.16 µeq/L	0.10 %RSD
Phosphate (PO ₄ ⁻²)	Metrohm 883/863 IC	0.21 µeq/L	0.16 %RSD
Sulfate (SO ₄ ⁻²)	Metrohm 883/863 IC	0.21 µeq/L	0.18 %RSD
pH	Radiometer Analytical TIM840	pH 2 to 12	pH 2 ± 0.02 to 12 ± 0.12
Alkalinity by auto-titrator	Radiometer Analytical TIM840	0.16 µeq/L	0.45 %RSD

Historical analyses:

Analysis	Precision estimated from reruns of standards (1983-2000)	Accuracy estimated from running standards as unknowns (1983-2000)
Cations by Flame Atomic Absorption ¹	0.1 to 30 mg/L (±5 to 10%)	± 10% at 0.3 mg/L; ± 5% at higher values
Anions by Auto-Analyzer ²	0.1 to 25mg/L (±10%)	±10% for NH ₄ ⁺ and SiO ₂
Alkalinity by manual titration ³	0.2 to 200 mg/L (±7 to 10%)	±5 to 10%

¹ from 1989-2000, ² 1983-1987, ³ 1984-2012

Additional information, including data files, is available at

<https://geosciences.williams.edu/weather/files/2018/06/ChemnotesV10.pdf>

Missing Data--missing sample values mainly reflect field conditions such as no or low precipitation, storms that overturned all precipitation collectors, or pervasive contamination from bird fecal matter. They are indicated as a blank field in the data sheet.

“Incorrect” analyses—Analyses are highlighted when sample charge balances fall outside a range of 0.80 to 1.20; analyses may include one or more incorrect values, most often for Ca^{+2} or HCO_3^- .

Substitute data—missing pH values for bulk precipitation collection 38 and 79 were filled using pH = 4.55, the median value for 30+ years of samples

3.0 Miscellaneous notes

These data provided by the Center for Environmental Studies, Williams College -- including HMF precipitation and Birch Brook chemistries--are preliminary and subject to revision. Inaccuracies in the data may be present because of instrument malfunctions or database issues. Subsequent review may result in significant revisions to the data. Data users are cautioned to consider carefully the provisional nature of the information before using for decision-making. Information concerning the accuracy and appropriate uses of these and other chemical data from Hopkins Memorial Forest can be obtained from the Lab supervisor, Jay Racela, or from Williams College Geosciences Prof. David Dethier.

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