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Variation in chemistry of stream water and bulk deposition across the Hubbard Brook Valley, New Hampshire, USA

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Introduction

Chemistry and volume of precipitation and stream water have been measured in south-facing watersheds of the Hubbard Brook Experimental Forest (HBEF), continuously for 37 years. These long-term data have provided important insights into the biogeochemistry of these watershed ecosystems and the region (e.g. LIKENS & BORMANN 1995). They have also been important in identifying or elucidating environmental problems of national or international concern, such as acid rain (LIKENS et al. 1972, COGBILL & LIKENS 1974, LIKENS & BORMANN 1974) and deforestation (LIKENS et al. 1970, HORNBECK et al. 1986, MARTIN et al. 1986), and they have shown that short-term records (e.g. up to 5 years or so) can be misleading relative to long-term trends (LIKENS 1992, LIKENS & BORMANN 1995).

These long-term records of precipitation and streamwater chemistry for the south-facing watersheds at HBEF are the longest known, continuous records of this type in the world. In the present study, 4 years of biogeochemical data for north-facing watersheds, and 26 years for the main Hubbard Brook (HB), which drains the entire Hubbard Brook Valley, are presented, and compared with the long-term data from the south-facing watersheds.

Site description and methods

The 3160-ha HBEF (43° 56' N, 71° 45' W) is located within the White Mountains of central New Hampshire, USA. Bulk precipitation and streamwater chemistry for six south-facing watersheds (12–42 ha) have been measured since 1963, for three north-facing watersheds (59–68 ha) since 1995 and for HB near the mouth of the Valley (ca. 3000 ha) since 1973 (Fig. 1). Watershed 6 (W6) has the longest record at HBEF and, as such, is considered herein as a biogeochemical reference.

Vegetation is characterized by northern hardwood forest with American beech (*Fagus grandifolia* Ehrh.), sugar maple (*Acer saccharum* Marsh.) and yellow birch (*Betula alleghaniensis* Britt) dominating, and with white birch (*B. papyrifera* Marsh.), red spruce (*Picea rubens* Sarg.) and balsam fir (*Abies balsamea* L.) more abundant at higher elevations and on north-facing slopes.

Climate is humid–continental with short, cool summers and long, cold winters. Since 1963, annual precipitation has averaged about 142 cm, with 25–33% falling as snow. Annual streamflow averaged 90 cm with some 50% of the total occurring during March, April and May of each year when the accumulated snowpack melts (FEDERER et al. 1990). Because of the relatively watertight bedrock in the areas of the experimental watersheds, evapotranspiration (ET) can be estimated from the difference between precipitation and streamflow (LIKENS & BORMANN 1995), and averages ca. 52 cm/year.

The bedrock is primarily the Devonian Kinsman Granodiorite (a coarse-grained, porphyritic granodiorite) and Silurian Rangeley (upper and lower) Formations (pelitic schists), with lesser amounts of other Silurian and Devonian schists and granulites (Smalls Falls, Perry Mountain and Littleton Formations) (Fig. 1). Till within the HBEF is a mixture of materials from both the local parent bedrock and lesser amounts of other granitic or schistose formations from areas up to 30 km WNW of the HBEF (BAILEY & HORNBECK 1992). Till depth varies from near zero at ridgetops to 1- to 3-m depth at the base of the experimental watersheds, and up to 15–25 m deep in the lower part of the Hubbard Brook Valley (WINTER 1984). Soils are acidic, mostly well-drained Spodosols (haplorthods) with a thick (3–15 cm) organic layer at the surface. Soils, till and bedrock of the HBEF are relatively base-poor (JOHNSON et al. 1968).

Amounts of precipitation and streamflow are measured continuously in gauged south-facing and north-facing watersheds (Fig. 1). Flow is estimated in HB from average daily streamflow in W3 and W8, which are the hydrologic reference watersheds used to calibrate missing records for the other gauged watersheds (FEDERER et al. 1990, LIKENS & BORMANN 1995). Samples of precipitation (bulk wet

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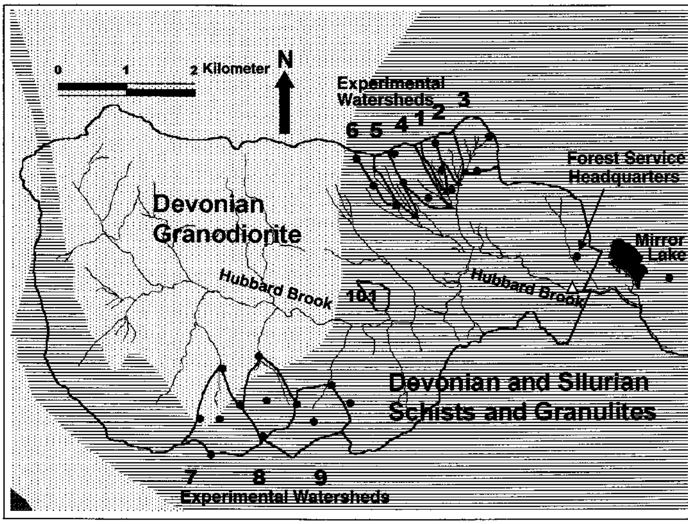

Fig. 1. Map of the Hubbard Brook Valley showing location of watershed ecosystems, gauging stations (closed triangle), ungauged stream sampling stations (open triangle), rain gauges (closed circle) and geologic formations (geologic data based on BARTON et al. 1997, LYONS et al. 1997, BURTON et al. 2000).

deposition) and streamflow are collected and analyzed on a weekly basis for a full suite of chemical constituents, and input–output fluxes are calculated for water-years (1 June–31 May) for the respective watershed ecosystems (LIKENS & BORMANN 1995, BUSO et al. 2000).

Results

Atmospheric bulk deposition

For the purposes of this analysis, the precipitation amount and bulk wet deposition chemistry at Rain Gauge (RG) 11 (at W6) are compared with RG 19 (at W8) during the water-years, 1995–1998. These collectors are located about 2 km apart and at an elevation of 550 and 600 m MSL within the Hubbard Brook Valley (Fig. 1).

Bulk precipitation chemistry in the north-facing watersheds (RG 19) was slightly more dilute than south-facing watersheds (RG11), but overall bulk deposition is relatively uniform throughout the Valley at the elevation of these rain gauges (Table 1). Chemical differences with elevation are small within the HBEF (LIKENS & BORMANN 1995, BUSO et al. 2000, MARTIN et al. 2000). Except for K^+, NH_4^+ and PO_4^{3-}, differences in annual, volume-weighted concentrations of major cations and anions between RG11 and 19 were insignificant (based on paired T-tests and linear regression analyses). Likewise, with the exception of K^+, NH_4^+ and PO_4^{3-}, there were no significant differences in average annual inputs to W6 and W8 during 1995–1998 (Table 1). Analysis of the inputs via dry deposition are beyond the scope of this paper, but it should be pointed out that more scavenging of atmospheric particles probably occurs in north-facing watersheds because of the predominant coniferous vegetation in these watersheds.

Streamwater chemistry

Annual, volume-weighted streamwater concentrations are given in Figs. 2A–2M for Watersheds 6 (south-facing), 7–9 (north-facing) and HB. Some obvious results emerge: (1) streamwater concentrations of Ca^{2+}, Mg^{2+}, K^+, SO_4^{2-}, NO_3^- and Cl^- (Na^+, NH_4^+ and dissolved Si in W6 only) have declined significantly during the study; (2) streamwater concentrations of Ca^{2+}, Mg^{2+}, Na^+, dissolved silica, and pH are significantly higher in HB than in the tributary

Table 1. Average volume-weighted annual concentrations (µmol/L) and average annual inputs (mol/ha-year) and amount of precipitation (mm/year) during June 1995 to May 1999 (n = 4 water years) for Watersheds 6 (W6) and 8 (W8) of the HBEF.

Solute or category	RG 11 (W6) Annual vol-wt average conc. (µmol/L)	RG 11 (W6) Annual average deposition ± SD (mol/ha-year)	RG 19 (W8) Annual vol-wt average conc. (µmol/L)	RG 19 (W8) Annual average deposition ± SD (mol/ha-year)
Calcium	2.0	31.4 ± 4.6	1.7	27.1 ± 3.3
Magnesium	1.0	15.7 ± 4.1	0.8	13.4 ± 3.7
Potassium	1.1	17.7 ± 2.2	0.9	14.0 ± 2.2
Sodium	5.0	76.9 ± 35.3	4.1	66.9 ± 28.4
Aluminum	0.5	8.3 ± 1.7	na	na
Ammonium	11.1	173 ± 6.8	10.4	167 ± 9.9
Hydrogen ion	42.6	662 ± 108	37.8	611 ± 73.2
Sulfate	16.5	256 ± 28.5	14.7	238 ± 16.9
Nitrate	23.7	369 ± 34.9	20.5	332 ± 14.8
Chloride	6.4	99.7 ± 42.8	5.4	87.2 ± 34.7
Phosphate	0.1	1.2 ± 0.3	0.1	1.1 ± 0.1
Dissolved silica	1.0	15.9 ± 3.7	1.0	15.6 ± 2.5
pH	4.37		4.42	
Water (mm/year)	–	1553 ± 185.9	–	1616 ± 159.7

streams considered herein; (3) streamwater concentrations of Al^{n+}, DOC and DON were the highest and Ca^{2+}, Na^{+} and pH the lowest in W9 – W9 clearly stands apart from the other streams in terms of DOC, Al^{n+} and pH (Fig. 3); (4) streamwater concentrations of dissolved Si are lowest in W6 (Fig. 2M); (5) streamwater concentrations of K^{+}, NH_4^{+}, SO_4^{2-} and Cl^{-} are similar in all streams; and (6) annual, volume-weighted average streamwater NO_3^{-} concentrations are ca. 50% lower in W9 than in W6, W7 or W8.

Seasonal patterns

Concentrations of Na^{+}, Cl^{-} and NO_3^{-} in stream water tended to peak in winter. Stream pH varied more on a monthly basis in W7 and W8 than in W6 or W9, and DOC concentration varied much more and SO_4^{2-} varied somewhat more in W9 than in the other tributaries.

Spatial patterns

Interesting differences were apparent when comparing north- and south-facing watersheds with the entire Valley, with regard to mobile anion relationships in stream water (Fig. 4). Generally, HB has a much higher acid-neutralizing capacity (ANC) than the tributaries because of a higher pH and higher base cation (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}) concentrations. As a result, HB plotted well above the 1:1 line in a relation of sum of base cations vs. sulfate plus nitrate (Fig. 4). In contrast, both north- and south-facing headwater tributaries were near the 1:1 line, with the long-term record for W6 showing a hysteresis pattern in moving toward the 1:1 line since 1970 (LIKENS et al. 1996, 1998, Fig. 4). Of the tributary watersheds considered herein, W7 is most positive and W9 most negative with regard to ANC (Fig. 4). Indeed, stream water in W7 has 30% more base cations than does W9.

In contrast, the gross annual streamwater output of the two dominant, mobile anions, SO_4^{2-} and NO_3^{-}, were essentially the same for streams draining areas of ca. 3–3000 ha within the Valley (LIKENS 1999, JOHNSON et al. 2000). Base cations differed only about 2-fold over this difference of four orders of magnitude in watershed area.

Net hydrologic flux (input in bulk precipitation minus output in stream water)

The net hydrologic flux (NHF) for water and

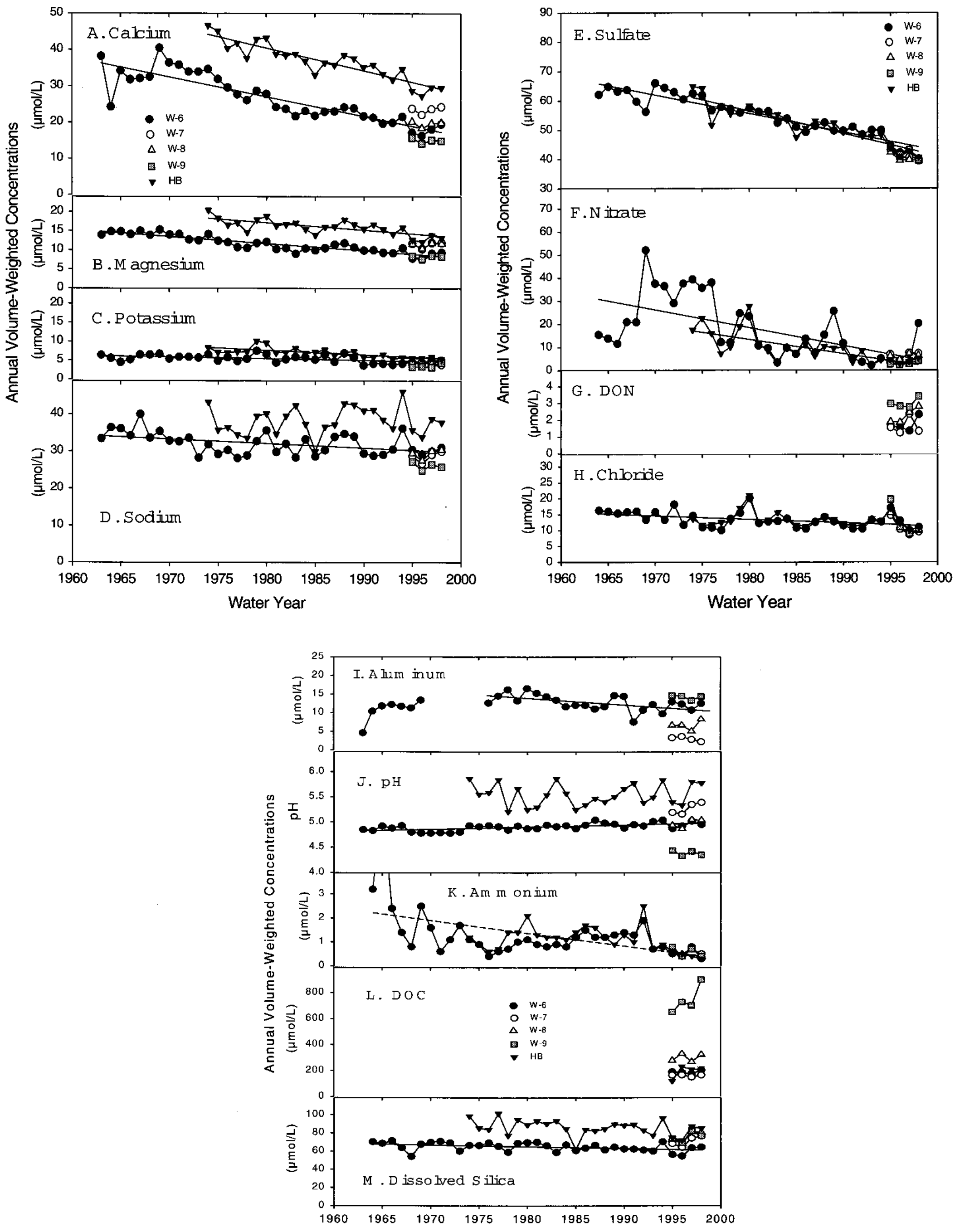

Fig. 2. Annual volume-weighted streamwater concentrations for Watersheds 6, 7, 8, 9 and main Hubbard Brook (HB) within the Hubbard Brook Valley. DOC, dissolved organic carbon; DON, dissolved organic nitrogen. Linear Regression lines are shown if $P < 0.05$.

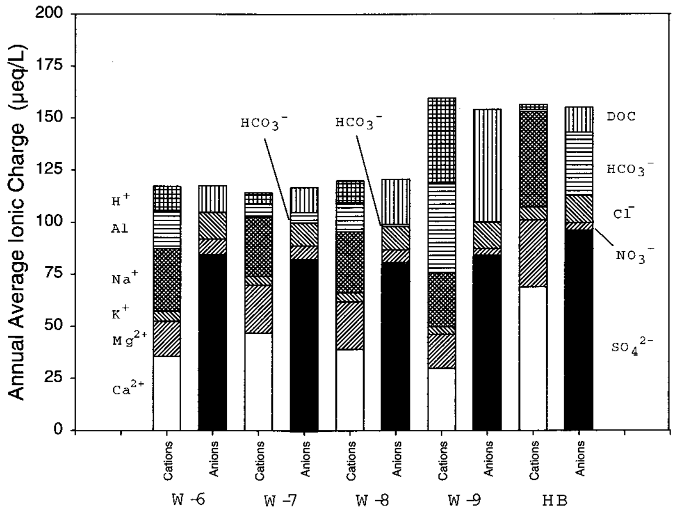

Fig. 3. Comparison of ionic charge distribution for stream water in Watersheds 6, 7, 8, 9 and main Hubbard Brook (HB) during 1995–1998. Differences in average cation/anion balances were <3.6% for annual values during 1995–1998 for all streams. The DOC was assigned a charge of –6 µeq/mg C and Al charge varied from +1 to +3 µeq depending on pH (BUSO et al. 2000). There was no bicarbonate in W6 or W9, and NH_4^+ and PO_4^{3-} concentrations were near analytical detection limit in all streams.

some of the major chemical constituents is shown in Fig. 5. A positive value indicates net gain to the watershed-ecosystem, whereas a negative value indicates a net loss.

Average, annual precipitation was about 5.5% greater for W9 than for W6, yet average annual streamflow was about 2.2% less during 1995–1998. As a result, evapotranspiration (precipitation minus streamflow) was about 24% higher in W9 than in W6 during these 4 years (Fig. 5J). The higher ET on these colder, more coniferous north-facing slopes is intriguing, but data over a longer time will be required to verify these relationships.

Base cation losses from HB were larger than all of the other watershed areas during all years, especially for Ca^{2+}. The NHF for Ca^{2+} from W7 was highest and W9 lowest for the tributary watersheds (Fig. 5A). Hydrogen ion, NH_4^+ and NO_3^- were retained in all of the watersheds (5E, F and G). The significantly smaller NHF for NO_3^- in W6 during 1998–1999 was related to increased streamwater NO_3^- loss as a result of ice-storm damage to vegetation, which

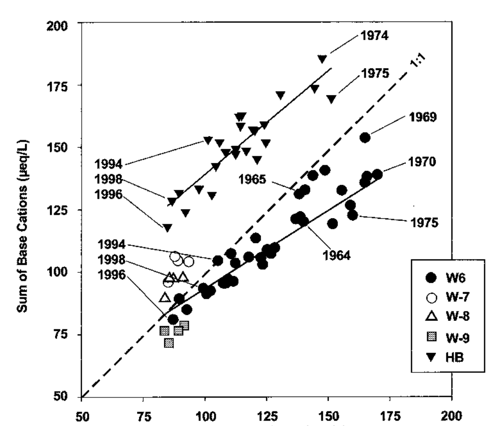

Fig. 4. Sum of base cations vs. sulfate plus nitrate in stream water of Watersheds 6, 7, 8, 9 and the main Hubbard Brook (HB). W6: $P < 0.001$; $r^2 = 0.93$ (1970–1998). HB: $P < 0.001$, $r^2 = 0.80$ (1973–1998).

occurred primarily on south-facing watersheds during January 1998. The NHF of SO_4^{2-} and Cl^- were lowest during 1997–1998 (Fig. 5H

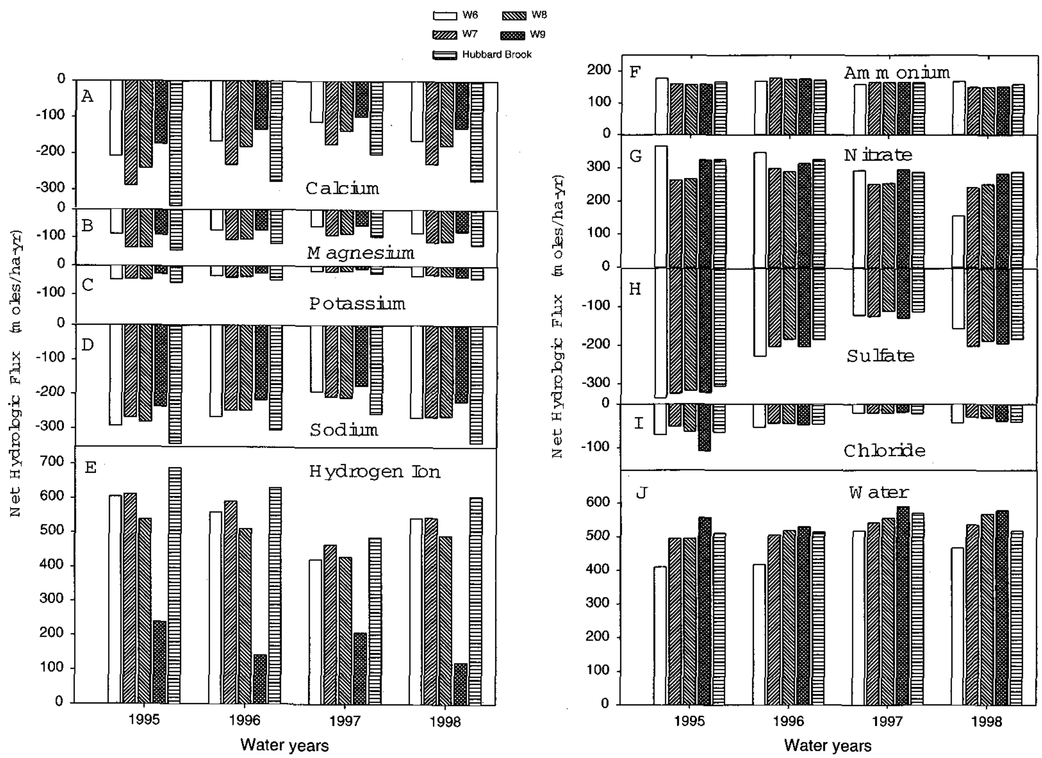

Fig. 5. Net hydrologic flux (input in bulk precipitation minus output in stream water) for W6, 7, 8, 9 and HB during 1995–1998.

and I) due to markedly lower streamwater output.

General discussion

In addition to differences in vegetation, hydrology and geology, which depend on slope, aspect and location within the Hubbard Brook Valley, many disturbances such as weather, air pollution and forest damage, have impacted on the vegetation and biogeochemistry of the Valley since 1963. For example, the water-years of 1973–1974 and 1995–1996 were the wettest on record; about two times more precipitation occurred during those years than during the drought year of 1964–1965, and chemical budgets reflect these extremes in hydrology (Likens & Bormann 1995). In addition, acidic deposition has been impacting the area since the mid-1950s (Likens et al. 1972, Cogbill & Likens 1974) and a major ice storm damaged vegetation on south-facing slopes in January 1998.

Despite this mosaic of differences and disturbances within the Valley, the chemical characteristics of stream water, with the major exception of pH, are essentially established in headwater tributaries. Relatively little change occurs as the drainage water moves toward the mouth of the Valley, in the fifth-order HB (Figs. 1 and 3). The stream draining Watershed 9 is an anomaly in this regard, being much more acidic and with much higher concentrations of DOC and Al^{n+}. Yet, such differences are almost fully reduced and integrated by the time the main HB exits the Valley. Watershed 9 has some two to eight times more coniferous vegetation cover and 5–10 times more wetland areas, yet the NHF of S in W9 is similar to the other watershed-ecosystems (Figs. 2E, 5H).

Because of U.S. Federal legislation to reduce emissions of SO_2 and because of the strong relationship between SO_2 emissions and SO_4^{2-} concentrations in bulk deposition and stream water (LIKENS et al. 2002), SO_4^{2-} concentrations have been declining at the same rate since 1964–1965 in W6, and since our record began in 1973–1974 in HB (Fig. 2E). Data from W7, W8 and W9 are from too short a period, however, to evaluate these trends.

The January-1998 ice storm severely damaged vegetation on the south-facing watersheds, and throughout the New England/south-eastern Canada region on similar aspects and elevations. Little vegetation damage occurred in W7, W8 and W9. As a result of the ice-storm damage, NO_3^- export increased and NHF decreased for W6 (Figs. 2F and 5G). The long-term chemical records for these watersheds allow a quantitative assessment of this disturbance.

Our chemical data for HBEF streams can be placed in a regional context by comparing them with a summary of chemistry for 159 streams draining small, upland, predominantly forest watersheds in central New England (HORNBECK et al. 1997). For the regional sample, pH of stream water ranged from 3.5 to 7.8 with a median of 6.0, and Ca^{2+} ranged from <5 to >500 µmol/L with a median of about 50 µmol/L. The HBEF streams, with pH values averaging between 4.5 and 5.5 and Ca^{2+} concentrations <25 µmol/L (Fig. 2), thus fall at the lower end of the regional range in terms of acidity and Ca^{2+} buffering. Only 15% of the regional stream sample had pH values below those for HBEF streams and only 12% had lower Ca^{2+} concentrations. The HBEF streams were more representative in terms of NO_3^- and SO_4^{2-}; 40% of streams in the regional sample had lower SO_4^{2-} values and 45% had lower NO_3^- values.

This comparison places all sampled streams at HBEF among the more dilute, acidic, and poorly buffered streams in the north-eastern U.S. and south-eastern Canada. The research at HBEF thus has important regional implications regarding how and why streams reach this sensitive chemical state, and how they respond to disturbances such as harvesting and atmospheric pollution. The addition of more streams to the sampling network within HBEF, while not showing vastly different streamwater chemistries in comparison to south-facing watersheds, does provide a wider variety of conditions for study in terms of forest cover types, soil and geologic characteristics, and biogeochemical processes. The added sampling also helped demonstrate that anomalies can occur. The best example was north-facing W9 where processes controlling streamwater acidity appear different than those on other watersheds sampled at HBEF.

Implications

The comparisons herein have some important implications for studies at HBEF and elsewhere. The relatively small differences in streamwater chemistry and fluxes between first- or second-order headwater watersheds and the fifth-order HB are fortuitous. Smaller watersheds are easier to gauge and experimentally manipulate than larger watersheds, and the valley-wide similarities in chemistry suggest that results can be readily compared, scaled-up or extrapolated.

Users of the present research include watershed and aquatic managers in New England and elsewhere. The studies at HBEF focus on one of their most difficult problems: management of dilute, acidic streams. Knowledge of chemical variability and change (e.g. a rise in pH), as such streams increase in order, can help managers optimize the use of streams for fisheries, recreation, and drinking water. Also, such information is critical in designing monitoring networks.

Disparities in regional streamwater chemistry, such as occurred for W9, should be watched for and even sought out for study. Knowing and understanding stream chemical balances for as many different streams as possible aids in the better understanding and predicting of chemistry of higher order streams, which are usually the primary sites of human habitation and use.

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