

Variation in streamwater chemistry throughout the Hubbard Brook Valley

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Abstract. Streamwater chemistry was measured at 100-m intervals in all streams of the Hubbard Brook Valley, NH during 'spring' (May–July) and during 'fall' (October–December) 2001. Overall, streamwater chemistry was very similar during these two periods, but fall median concentrations were consistently higher than spring values, except for ANC, pH, NO_3^- and PO_4^{3-} , which had lower values in fall. Median concentrations for NH_4^+ were approximately the same in spring and fall. Stream chemistry varied throughout the Hubbard Brook Valley by elevation, channel length, drainage area and type of drainage, but most of the variability in stream chemistry was subtle and relatively small. Overall, there were relatively large (two- to 10-fold) changes in chemistry with longitudinal distance of wetted channel, elevation and/or size of drainage area in some streams and for some elements (e.g., H^+ , Al^{3+} , DOC), but other chemical concentrations changed relatively little (e.g., Cl^- , dissolved Si). The main Hubbard Brook, a fifth-order stream at the mouth of the Valley, was remarkably constant in chemistry throughout its length, except where human disturbance near the mouth changed the chemistry. Differences in vegetation, geologic substrates and wetland areas were related to changes in pattern of streamwater chemistry throughout the Valley.

Introduction

The small watershed-ecosystem approach, pioneered at the Hubbard Brook Experimental Forest (HBEF) in the White Mountains of New Hampshire has shown that streamwater chemistry can be both an important indicator and an integrator of diverse ecosystem processes (Bormann and Likens 1967; Likens and Bormann 1995; Likens 2004b). For example, water quality at the base of a watershed reflects the diverse and complicated ecological, hydrological and biogeochemical functions and inter-relationships within the entire catchment.

During the last 20 years or so, there has been a growing interest in the analysis, interpretation, and extrapolation of spatial patterns in biogeochemistry (e.g., Grimm et al. 1981; Tate 1990; Valett et al. 1996; Cooper et al. 1997; Burke et al. 1998; Likens 1998, 1999, 2004a; Dent and Grimm 1999; Johnson et al. 2000; Dent et al. 2001; Fisher et al. 2001; Lindsey et al. 2001; Caraco et al. 2003). Studies of detailed patterns of streamwater chemistry over larger areas are rare, but are useful ecologically because they can reflect effects of vegetation,

soils, geologic substrate, hydrologic flow paths, precipitation inputs, and biogeochemical interactions throughout a landscape. Landscape features drive temporal trends in streamwater chemistry in numerous ways that relate to spatial variability. As such, large-scale patterns of streamwater chemistry may provide new insights into these complicated landscape features and associated biogeochemical processes. Thus, questions of scale must be addressed carefully or the analysis across ecosystems within a landscape can be misleading relative to overall biogeochemical pattern and process. This point is especially true for stream ecosystems, which are linear and highly dynamic due to their hydrology.

Because most studies are done at local or small scales, there also is a need to understand how the results of these local studies can be extrapolated to regional or even global scales, particularly for management applications. Prediction and forecasting at various scales is an important challenge in ecology and biogeochemistry (Carpenter 1998, 2002; Clark et al. 2001; Canham et al. 2003). Characterizing and understanding patterns at large scales are critical for quantifying and evaluating the impact of human disturbance occurring at large scales, e.g., air and water pollution and regional land-use change. Management issues emanating from such large-scale changes require knowledge about the underlying ecological and biogeochemical patterns and mechanisms.

In a major elaboration of past efforts to measure longitudinal patterns in streamwater chemistry within the Hubbard Brook Experimental Forest (e.g., Johnson et al. 1981; Lawrence et al. 1986; Likens 1999), we have measured the chemistry of stream water at 100-m intervals in all streams of the Hubbard Brook Valley during two different seasons, 'spring' (9 May to 3 July 2001) and 'fall' (17 October to 11 December 2001). These data are reported and discussed here.

Site description

The Hubbard Brook Valley is an elongate, bowl-shaped area in the White Mountain National Forest of central New Hampshire, typical of the terrain in this region. It is ~4000 ha in size, bounded by the Mt. Cushman ridge (977 m above sea level [msl]) on the north and the Mt. Kineo ridge (1015 msl) on the south, and bisected by coordinates of 43°56' N, 71°45' W (Likens and Bormann 1995). The Valley is drained by Hubbard Brook, which flows from west to east for some 14 km, and is joined by 32 tributaries (16 first-order and 16 second-order) before entering the Pemigewasset River (183 msl) (Figure 1a). The 3140-ha Hubbard Brook Experimental Forest (HBEF) occupies most of the Valley, and has been set aside by the USDA Forest Service for hydrologic and ecologic research since the 1950s (Likens and Bormann 1995).

Climate at the HBEF is humid continental with short, cool summers and long, cold winters (Trewartha 1954; Federer et al. 1990; Likens and Bormann 1995; Bailey et al. 2003). Mean annual precipitation within the south-facing,

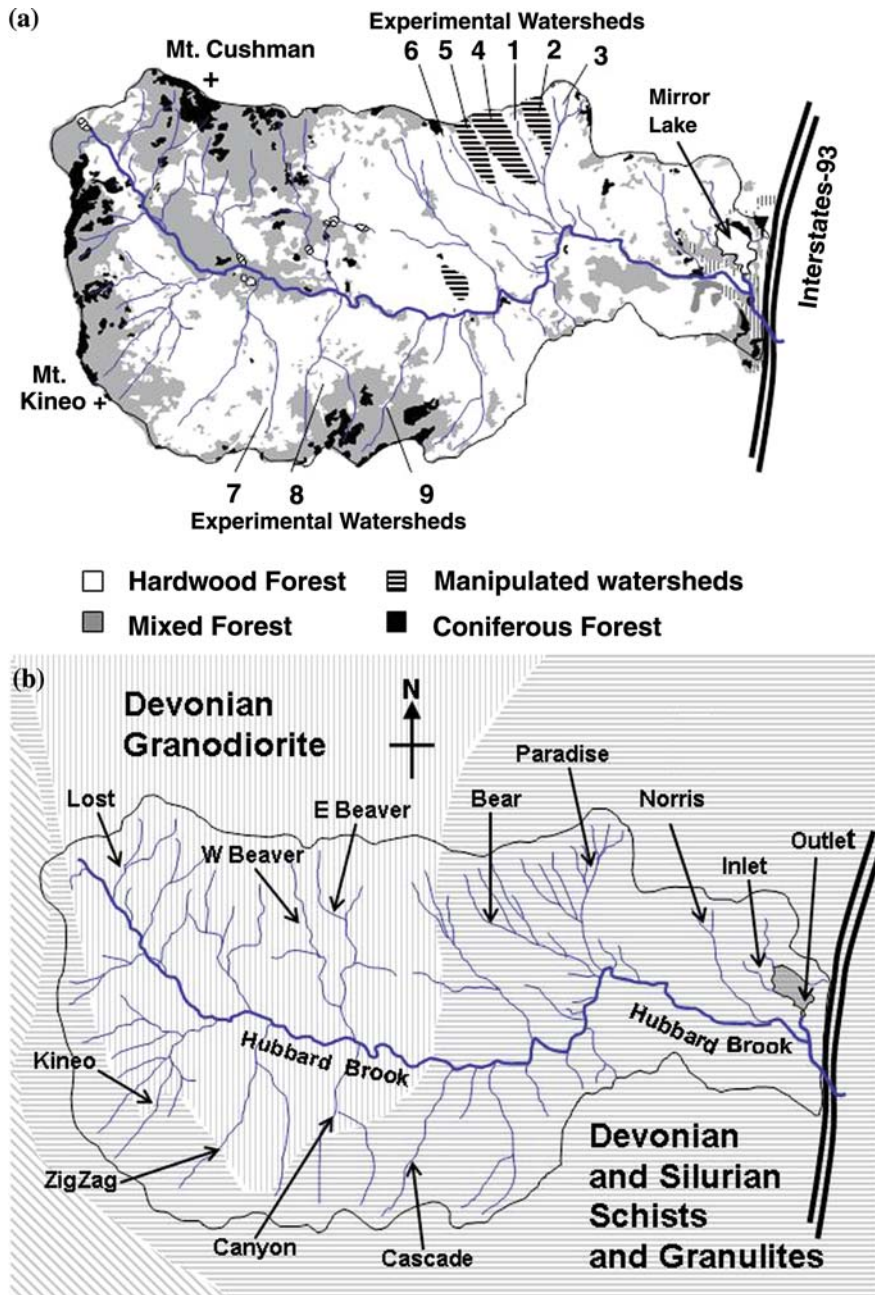


Figure 1. Distribution of (a) vegetation types, experimental watersheds and water bodies; (b) geologic substrates; Vegetation coverage based on J. Berry (unpublished data available on www.hubbardbrook.org), S. Degloria (personal communication) and Schwarz et al. (2003); geologic data based on Barton et al. (1997), Lyons et al. (1997), Burton et al. (2000).

experimental watersheds of the HBEF since 1956 is 1401 mm (SD = 184) with 25–33% of the total as snow. Mean annual streamflow from these watersheds is 905 mm (SD = 216) (Bailey et al. 2003). The vegetation is northern hardwood forest, dominated by American beech (*Fagus grandifolia* Ehrh.), yellow birch (*Betula alleghaniensis* Britt.) and sugar maple (*Acer saccharum* Marsh.) at 500–730 msl. Red spruce (*Picea rubens* Sarg.), balsam fir (*Abies balsamea* (L.) Mill) and white birch (*Betula papyrifera* Marsh.) largely dominate at elevations above 730 msl and on north-facing slopes. Eastern hemlock (*Tsuga canadensis*) is more common at lower elevations, on rocky outcrops and along stream channels (Figure 1a; Likens and Bormann 1995; Schwarz et al. 2003). The Valley was logged intensively between 1909–1917, but there is no evidence of widespread fire in the region (Bormann et al. 1970; Whittaker et al. 1974; Bormann and Likens 1979; Davis 1985; Davis et al. 1985; Likens and Bormann 1995). Some damage occurred from a hurricane in 1938 (Kim 1988; Merrens 1988; Cogbill et al. 2003). Since 1982, forest biomass accumulation has been essentially zero (Likens et al. 1994, 1998, 2002a).

Glacially derived soils at HBEF, like those underlying much of New England, are relatively young (ca 14,000 years B.P.; Likens and Davis 1975; Davis et al. 1985), highly acidic (Johnson et al. 1991b) and have low clay content. They are mostly well-drained, coarse-textured Spodosols (Haplorthods) of sandy loam texture, with a well-developed surface organic layer (3–15 cm depth). The mineral soil is characterized by a low (~12%) base saturation (Johnson et al. 1991a). Soil depths are highly variable, ranging from thin accumulations of organic matter on bedrock at ridge tops, to thick (several m), well-developed soil profiles in the Valley bottoms (Lawrence et al. 1986; Likens and Bormann 1995). Most precipitation infiltrates into the soil rapidly and overland flow is uncommon (Pierce 1967).

Bedrock underlying the eastern part of the Valley is Devonian and Silurian schists and granulites, and in the western portion, Devonian granodiorite (Figure 1b; Barton et al. 1997). Till, boulders and coarse soil fragments are primarily a complex mixture of these same lithologies, with minor inclusions of other rocks deposited from glacial transport (Bailey and Hornbeck 1992).

Headwater streams in the Valley are small and perennial during years with average precipitation. Flow in headwater streams ranges from zero during summer droughts to hundreds of thousands of l/ha-day during snow melt and storm events. Hubbard Brook starts as an outlet from a beaver pond, and becomes a fifth-order stream as it leaves the Valley. At base flow during summer, the flow in the lower Hubbard Brook ranges from about 50 to 100 l/s, whereas first- and second-order streams flow at about 1 l/s. In the HBEF, gauged watersheds (Figure 1a), long-term measurements of precipitation and streamflow, and estimates of evapotranspiration indicate that ground water is a negligible contributor to total annual water loss (< 5%) at those elevations (> 490 m msl) (Likens and Bormann 1995). In contrast, monitoring wells and gauging stations in the vicinity of Mirror Lake near the base of the Valley (~200 m msl) indicate that groundwater contributions to annual surface flow

are significant (15–20%), and that base flows in streams are sustained by ground water (Mau and Winter 1997). Some 50% of annual streamflow in headwater streams occurs during March, April and May when the accumulated winter snow pack melts (Likens and Bormann 1995; Bailey et al. 2003).

Bulk precipitation chemistry in the north-facing, gauged watersheds is somewhat more dilute than south-facing, gauged watersheds, but across the Hubbard Brook Valley precipitation chemistry is relatively uniform, particularly as compared to streamwater chemistry (Likens et al. 2002b). Moreover, chemical differences in precipitation concentrations with elevation throughout the HBEF are small (Likens and Bormann 1995; Buso et al. 2000; Martin et al. 2000; Likens et al. 2002b). Annual precipitation amount increases slightly (~6%) from east to west in the south-facing, experimental watersheds (Likens and Bormann 1995; Federer et al. 1990).

Additional information about the hydrology, ecology and biogeochemistry of the HBEF is given in Likens and Bormann (1995).

Methods

Field

Collections of stream water were made immediately upstream of the junction of each major tributary to Hubbard Brook throughout the Hubbard Brook Valley, and along each tributary at 100-m intervals. Samples of Hubbard Brook were taken at the same time as each tributary survey. These samples were collected just upstream of the confluence with each tributary sampled. Water samples were collected from all tributaries that had flow, up to the point of first running water. Where a small waterfall could not be located for sampling, a clean polyethylene ladle was used to scoop up a sample with minimal disturbance. Samples were collected in clean, acid-washed polyethylene bottles and kept refrigerated until analyzed. Intervals along stream channels were measured with a hip-chain, and locations determined using a hand-held GPS receiver (Garmin, Inc.) with an accuracy of up to ± 3 m. Watershed maps were produced using GIS software (Maptech: Terrain Navigator Pro v3.0; and Esri: ArcView v3.1).

Analytical

Except for Ca^{2+} , Mg^{2+} and Al^{n+} , the analytical methods followed the standard protocol for the long-term, streamwater samples at the HBEF (see Table 1) and all chemical and physical data were entered into a database, which included a quality control assessment for each sample (Likens and Bormann 1995; Buso et al. 2000). Most solute concentrations were well above the Method Detection Limit (MDL) for each analysis, but there were many

Table 1. Analytical protocols for streamwater samples.

Analyte	Analysis location	Method	POR (%)	MDL
Calcium	IES	ICP–AES	± 5	0.02 mg/l
Magnesium	IES	ICP–AES	± 5	0.02 mg/l
Sodium	IES	FAAS	± 5	0.01 mg/l
Potassium	IES	FAAS	± 5	0.01 mg/l
pH ^a	RSPEL	potentiometric	± 0.05 units	n/a
Sulfate	IES	IC	± 5	0.02 mg/l
Phosphate	IES	CFA	± 5	1 µg/l
Aluminum ^b	USDA FS Durham, NH	PVC	± 5	0.01 mg/l
Ammonium ^c	IES	CFA	± 10	0.01 mg/l
Nitrate ^d	IES	IC	± 5	0.01 mg/l
Chloride	IES	IC	± 5	0.02 mg/l
Dissolved organic carbon (DOC) ^e	USDA FS Durham, NH	AICDD-HTCEC	± 2	0.05 mg/l
Dissolved inorganic carbon (DIC) ^f	RSPEL	GC	± 5	1 µmol/l
Acid-neutralizing capacity (ANC) ^g	RSPEL	Gran Plot-analysis	± 5	1 µeq/l
Dissolved silica	IES	ICP–AES reported as SiO ₂	± 5	0.1 mg/l

AICDD-HTCED, Analyzed by automated infrared carbon dioxide detection following high-temperature catalyst-enhanced combustion; CFA, continuous flow analysis (automated colorimetry); FAAS, flame atomic absorption spectrometry; GC, gas chromatography; IC, ion chromatography; ICP–AES, inductively-coupled plasma – atomic emission spectroscopy; IES, Institute of Ecosystem Studies, Millbrook, NY; MDL, method detection limit; POR, Precision over range in %; PCV Pyro-chatecol-Violet Chelation; RSPEL, Robert S. Pierce Ecosystem Laboratory, N. Woodstock, NH.

^aMeasured with combination pH/reference glass electrode, air electrode, air equilibrated at lab temperate, and without stirring, within 24 h of collection. Initial surveys (spring 2001) incorporated measurement of pH *in-situ* with a field pH meter, Oakton pH/CON 10 Model); field values agreed with laboratory within ± 0.2 values pH unit (linear regression slope 0.92, $r^2 = 0.98$ over the pH range 4–7). However, frequent re-calibration of the electrodes made the field technique too time-consuming to repeat in the fall 2001 survey.

^bAnalyzed by automated, colorimetric pyro-chatecol-violet (PCV) technique; samples at pH's above 5.5–6.0 were at or below the MDL (47% in spring, 37% in fall). Analytical zeros (< MDL) were assigned a value of 0.005 mg/l in the database. [NOTE: Total and organic monomeric aluminum measured (inorganic monomeric by difference), but only total monomeric aluminum data are presented here.]

^cMost samples (97% in spring, 92% in fall) were at or below MDL. Analytical zeros (< MDL) were assigned a value of 0.005 mg/l in the database.

^dConcentrations often were at or below the MDL (42% in spring, 79% in fall). Analytical zeros (< MDL) were assigned a value of 0.005 mg/l in the database.

^eSamples were not filtered because tests showed no significant difference in DOC between filtered and unfiltered streamwater samples at HBEF (Buso et al. 2000).

^fAnalyzed within 24 hr of collection.

^gAnalyzed by auto-titration using 0.02 N hydrochloric acid.

analytical zeros for ammonium concentrations (97–92% of samples in the first and second surveys, respectively), aluminum (37–47%), nitrate (42–79%), and phosphate (47–63%). All analytical zeroes were assigned a value equal to one-half the MDL to avoid the impact of zeros on statistical tests (Buso et al. 2000).

Periods of collection

The study was designed to provide information on the effects of watershed characteristics on stream chemistry, and to avoid the effects of large streamflow events, from either snowmelt or heavy rain. Thus, the chemical surveys were done after spring snowmelt (May to early July, 2001), prior to summer low-flow conditions, and after fall re-wetting (October to early December, 2001), but before the next winter snowfall. The hydrologic cycle at HBEF is quite predictable over the long-term (Likens and Bormann 1995; Bailey et al. 2003). Based on the stream output from W3 (the hydrologic reference watershed at HBEF), May, October, and November 2001 were significantly drier (mean minus 1 standard deviation [SD]) than the long-term (1963–2000) average. No months were significantly wetter than the long-term mean. Snowmelt occurred entirely during April over the entire valley in 2001, and there were no large, extra-tropical hurricanes in October, as is often the case.

To ensure comparable data throughout a collection period, collections were made as rapidly as possible (total of less than 60 days for each period), and not during heavy precipitation. Thus, we avoided a quickly rising or falling hydrograph, and periods of relatively high flow, which normally are of very short duration (<24 h) in these steep watersheds. High flows are defined as those that exceeded the mean daily flow for the month plus 1 SD of that mean (for reference W3). In May to early July 2001, there were only 3 days in W3 that had such high flows (>5.8 mm/ha-day), and no samples were taken on those days. In October to early December 2001, the mean daily flow plus 1 SD (7.5 mm/ha-day) was exceeded only three times. No samples were taken on those days. All samples from an individual stream were collected on the same day during each sampling period.

Small changes in flow do not impact stream chemistry. From the many decades of study on the nine gauged watersheds at HBEF, it is clear that flow-concentration relationships in these streams are relatively weak for most solutes, even with five orders of magnitude change in flow during an annual cycle (Johnson et al. 1969; Likens and Bormann 1995; Buso et al. 2000).

Results

Stream chemistry was measured throughout the Hubbard Brook Valley at 100-m intervals in all major tributaries during spring and fall of 2001. Samples of Hubbard Brook were taken at the same time as each tributary survey. A total

of 625 streamwater samples were collected in the spring of 2001 and 761 in the fall of 2001.

Distinct and variable patterns, including ‘hot spots’ (relatively high or low concentrations) of streamwater chemistry were observed across the Hubbard Brook Valley (Figures 2–8). Streamwater concentrations (pH, ANC, Ca^{2+} , Mg^{2+} , K^+ , Na^+ , SO_4^{2-} , NO_3^- , Cl^- , dissolved silica, Al^{n+} , DOC and DIC) are shown for 3 ranges of concentrations on an outline map of the Valley, and as a frequency distribution of median values of all concentrations measured for each solute (Figures 2–8). Also shown are vegetation cover, disturbed areas and water bodies (Figure 1a), geologic substrate (Figure 1b), and specific conductivity (Figure 8b).

Several of the experimental watersheds in the Valley (Figure 1a) have been manipulated since 1965 (W1, 2, 4 and 5). Therefore, these watersheds were not sampled during the streamwater survey (Figures 2–8). Moreover, streamwater chemistry has been changing since 1963 in response to several factors, such as input of acid rain (Likens and Bormann 1995; Likens 2004a). Thus, these surveys represent points in time, separated by about 6 months, along these temporal trends. Long-term changes in streamwater concentrations of Ca^{2+} , Na^+ , SO_4^{2-} , NO_3^- , H^+ and ANC are shown in Figure 9 for W6. All chemical constituents measured have declined significantly since 1963–1964, except ANC, and DOC and DIC (insufficient data) Likens and Bormann 1995; Likens et al. 2002b). Comparing 5-year periods at the beginning (1964–1968) and end (1999–2003) of the long-term record, average streamwater concentrations of Ca^{2+} , Mg^{2+} , H^+ , SO_4^{2-} and NO_3^- declined by 45, 43, 27, 35 and 69%, respectively.

Overall, streamwater chemistry throughout the Hubbard Brook Valley was similar between spring and fall of 2001. Moreover, the pH values for our spring and fall surveys were within the mean ± 1 SD for monthly samples taken for all of these tributaries during June 2002–May 2003. The difference in median streamwater concentrations between the spring and fall surveys is given in Table 2. Fall median concentration values were consistently higher than spring, with the exception of ANC, pH, NO_3^- and PO_4^{3-} (Table 2). In some cases the relative difference was large, e.g., NO_3^- , NH_4^+ , PO_4^{3-} , Cl^- , H^+ and ANC, and in others, e.g., Ca^{2+} , Na^+ , DIC, SO_4^{2-} , dissolved Si, DOC, Mg^{2+} and K^+ , it was small. Concentrations were not normally distributed, but mean Cl^- (1.8 \times), SO_4^{2-} (1.2 \times) and dissolved Si (1.2 \times) concentrations were higher in the fall, and NO_3^- (0.3 \times) concentration was lower. Moreover, cumulative daily stream discharge was $\sim 60\%$ lower, and average streamwater temperature was appreciably colder in the fall (6.7 vs. 10.4 °C).

The patterns of streamwater chemistry with longitudinal distance of channel varied in the different tributary streams. For example, some changed in pH markedly (> 1.5 pH unit) from headwater to mouth (e.g., Kineo, Paradise, Bear, East Beaver); some changed little (e.g., Cascade, Norris) (Figure 10). Higher in the Valley, the pH in many tributaries changed significantly with length (increasing from pH 4.1 at the headwaters to ~ 6.3 at

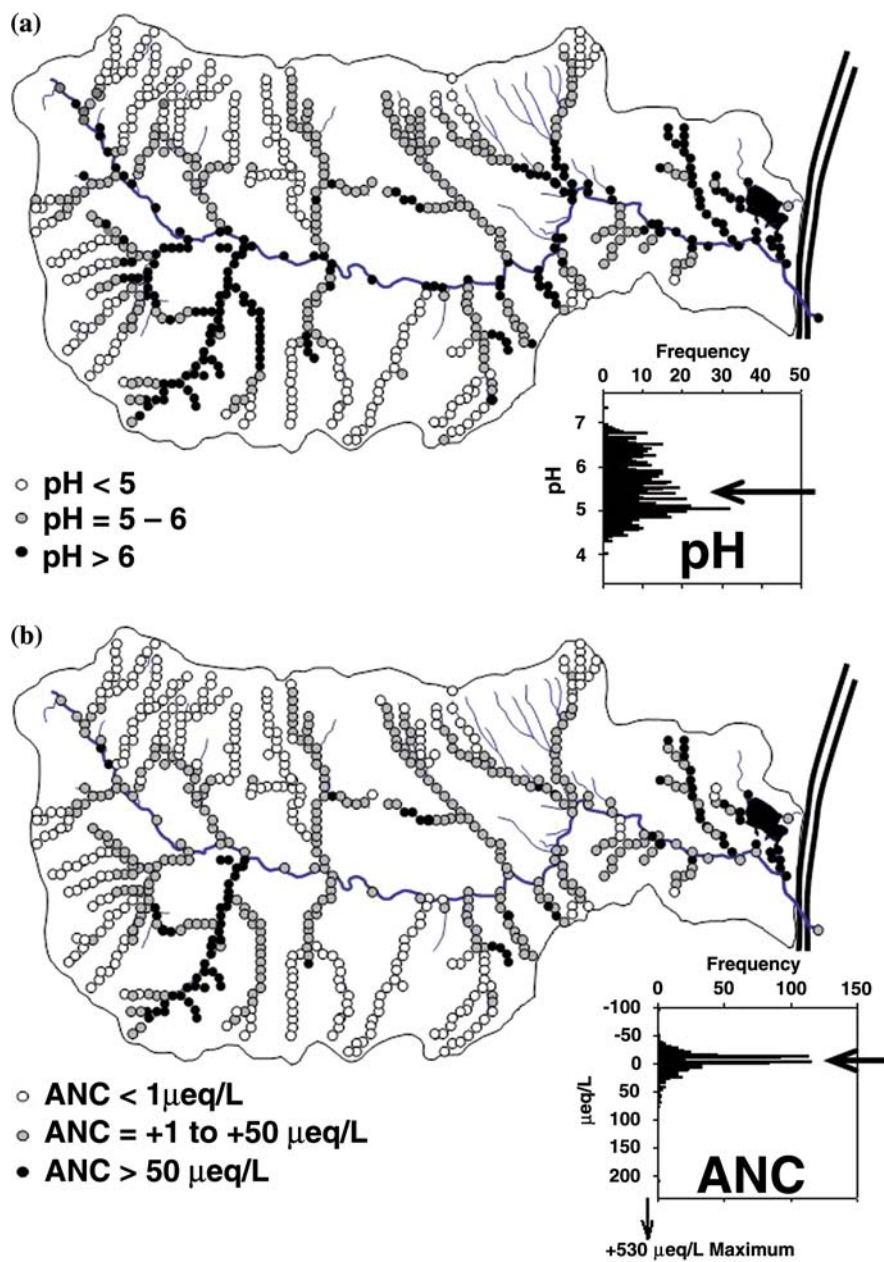


Figure 2. Distribution of (a) streamwater pH; and (b) acid-neutralizing capacity (ANC) throughout the Hubbard Brook Valley, NH during fall 2001. (→ indicates median value).

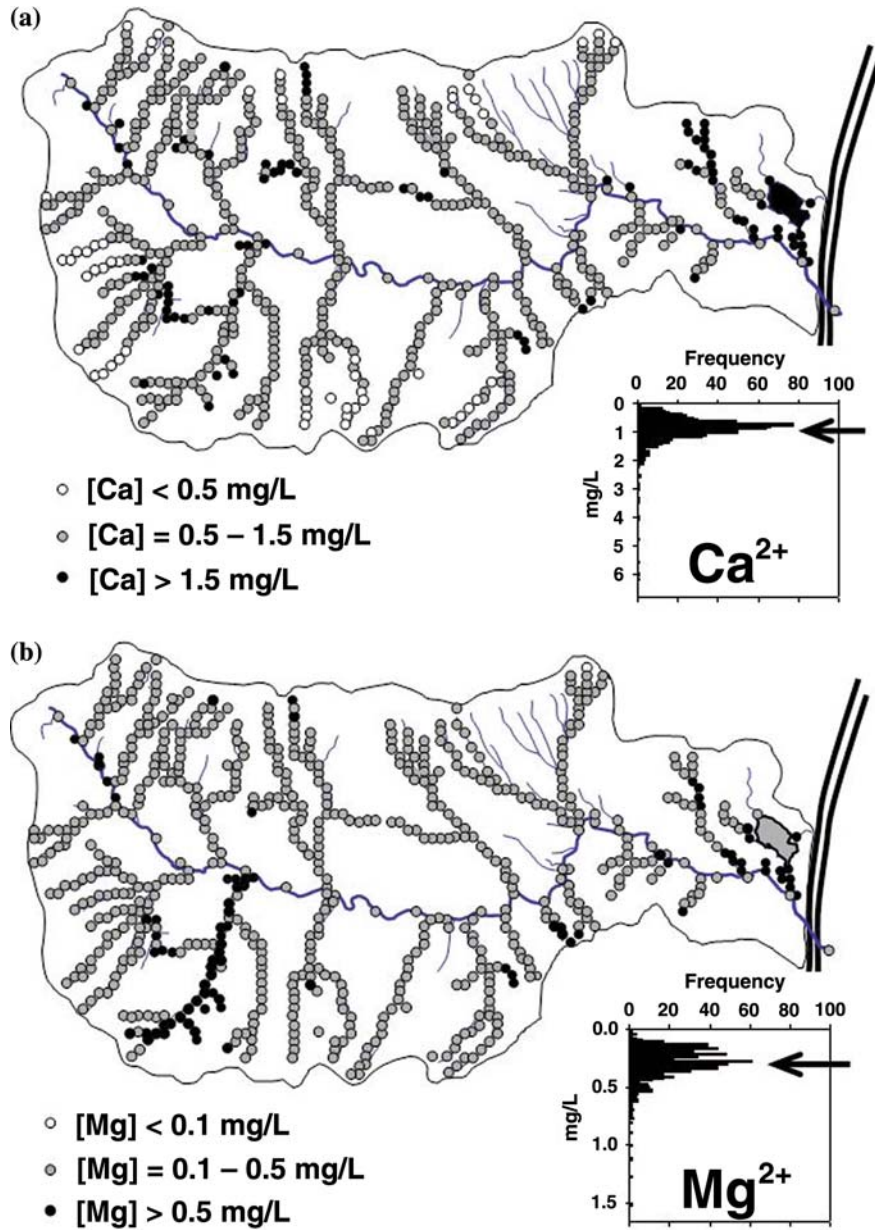


Figure 3. Distribution of streamwater concentrations of (a) calcium; and (b) magnesium throughout the Hubbard Brook Valley, NH during fall 2001. (→ indicates median value).

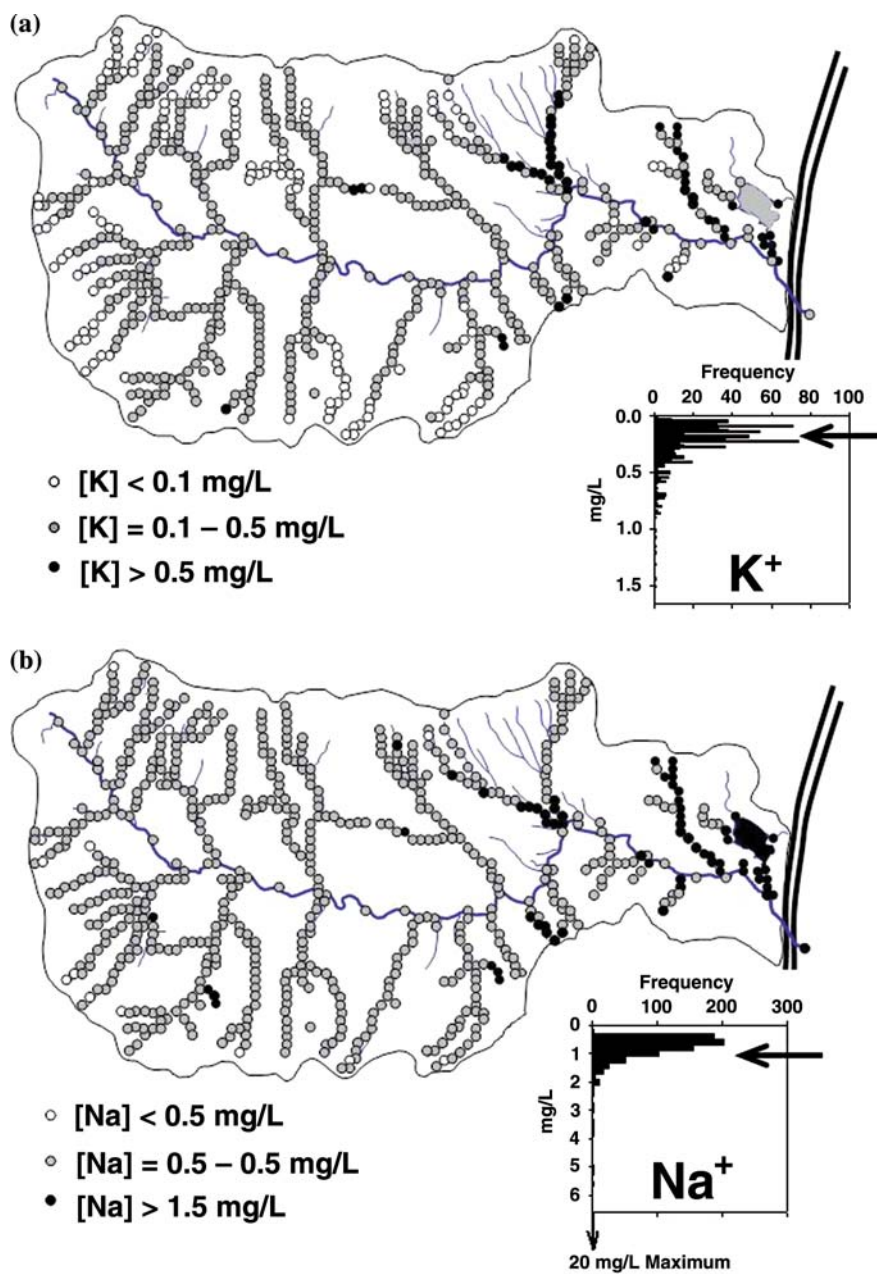


Figure 4. Distribution of streamwater concentrations of (a) potassium; and (b) sodium throughout the Hubbard Brook Valley, NH during fall 2001 (→ indicates median value).

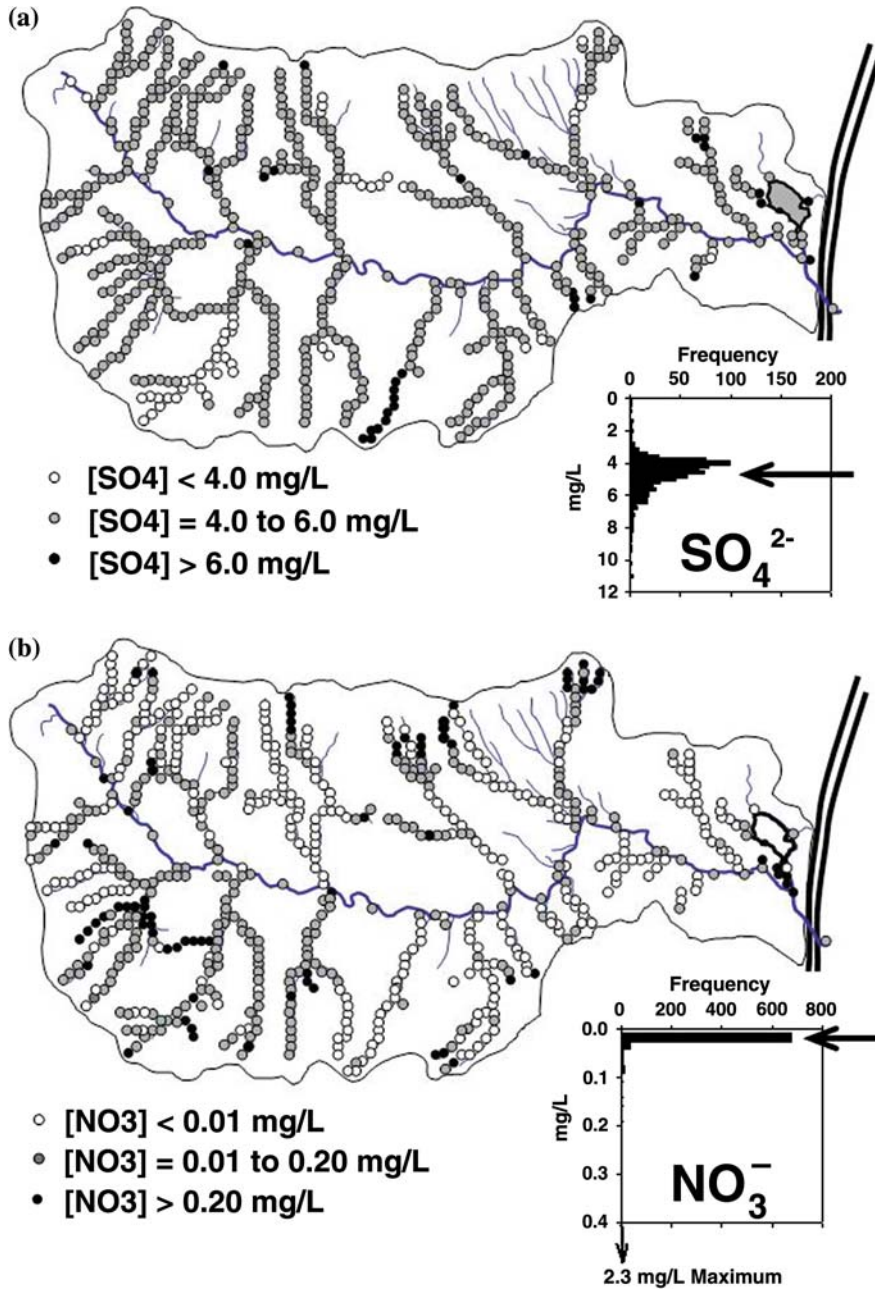


Figure 5. Distribution of streamwater concentrations of (a) sulfate; and (b) nitrate throughout the Hubbard Brook Valley, NH during fall 2001 (→ indicates median value).

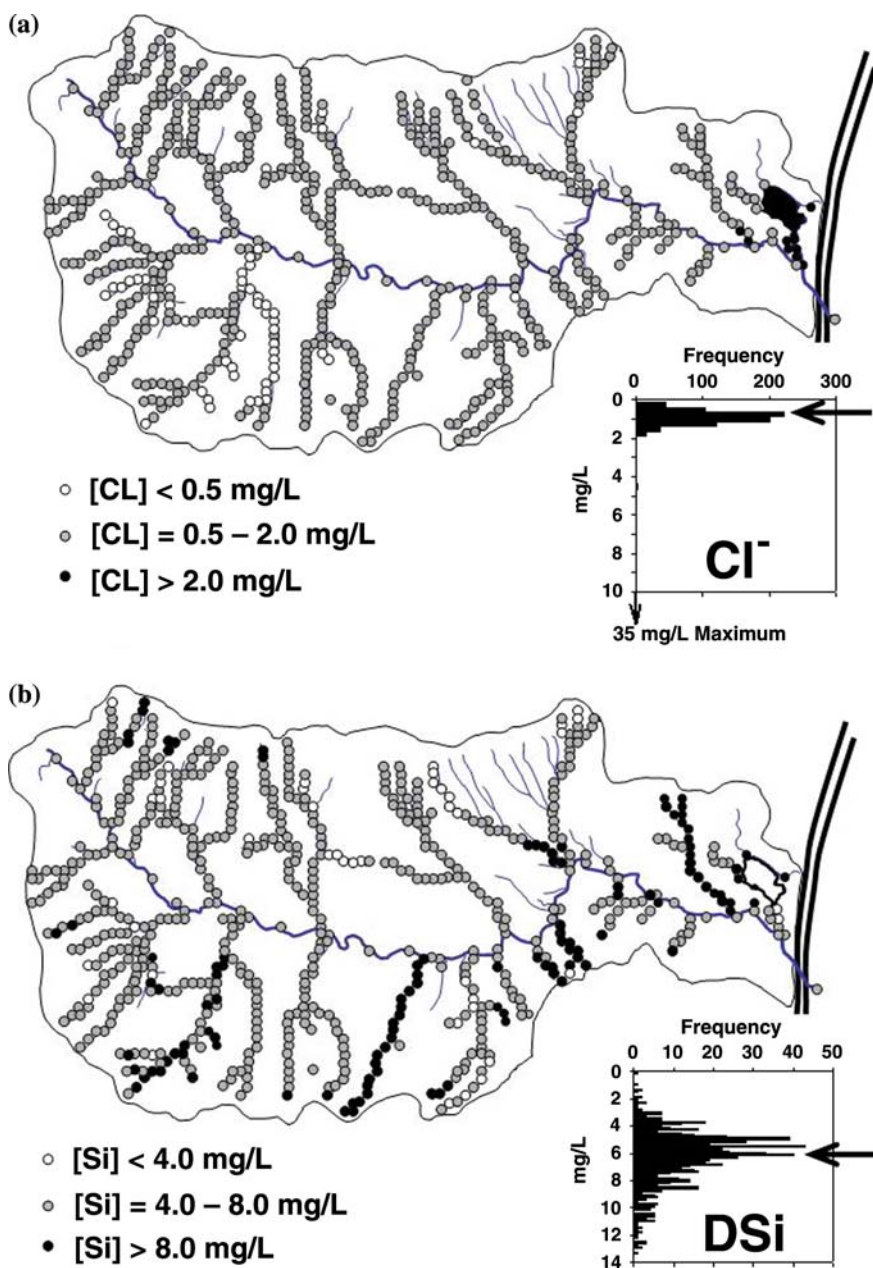


Figure 6. Distribution of streamwater concentrations of (a) chloride; and (b) dissolved Si (DSi) throughout the Hubbard Brook Valley, NH during fall 2001 (→ indicates median value).

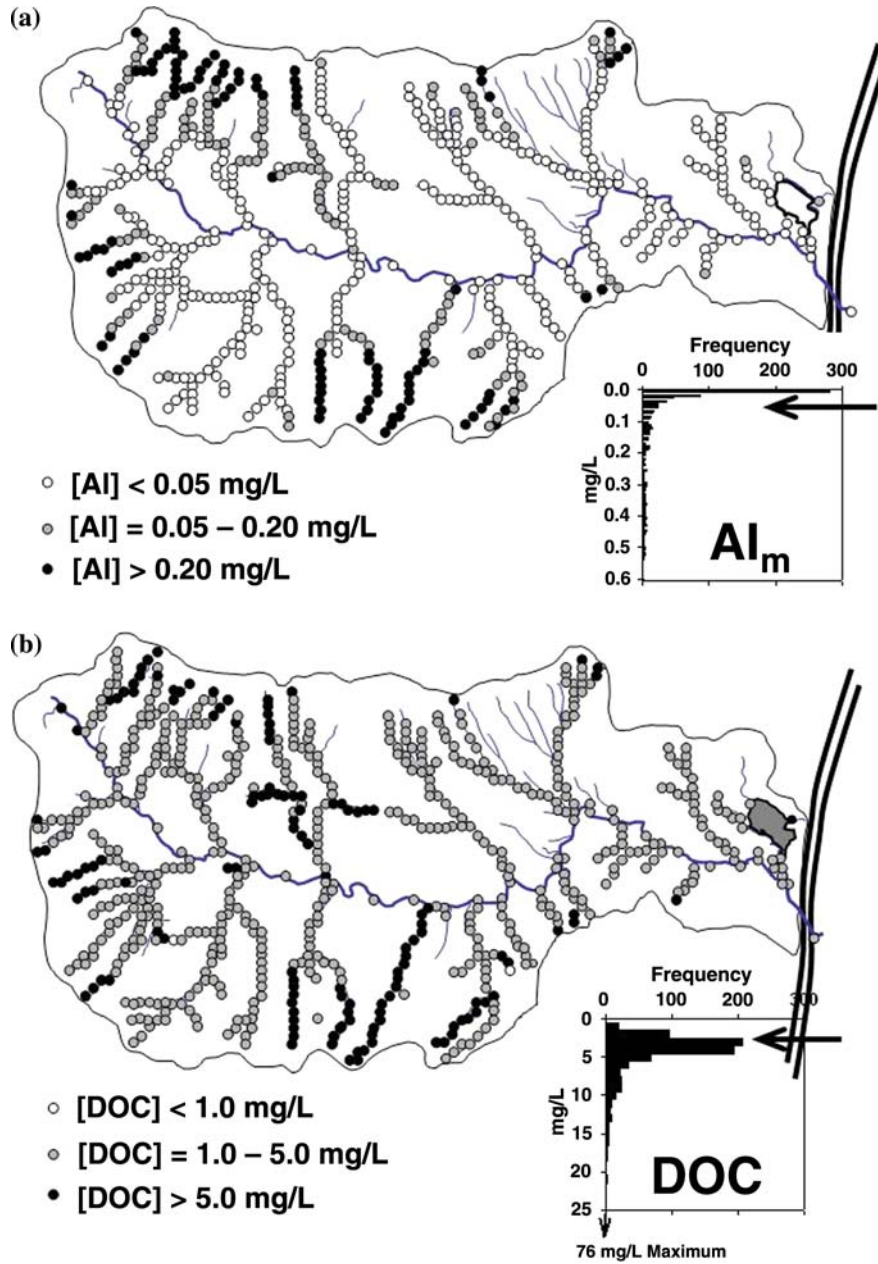


Figure 7. Distribution of streamwater concentrations of (a) monomeric aluminum (Al_m); and (b) dissolved organic carbon (DOC) throughout the Hubbard Brook Valley, NH during fall 2001 (→ indicates median value).

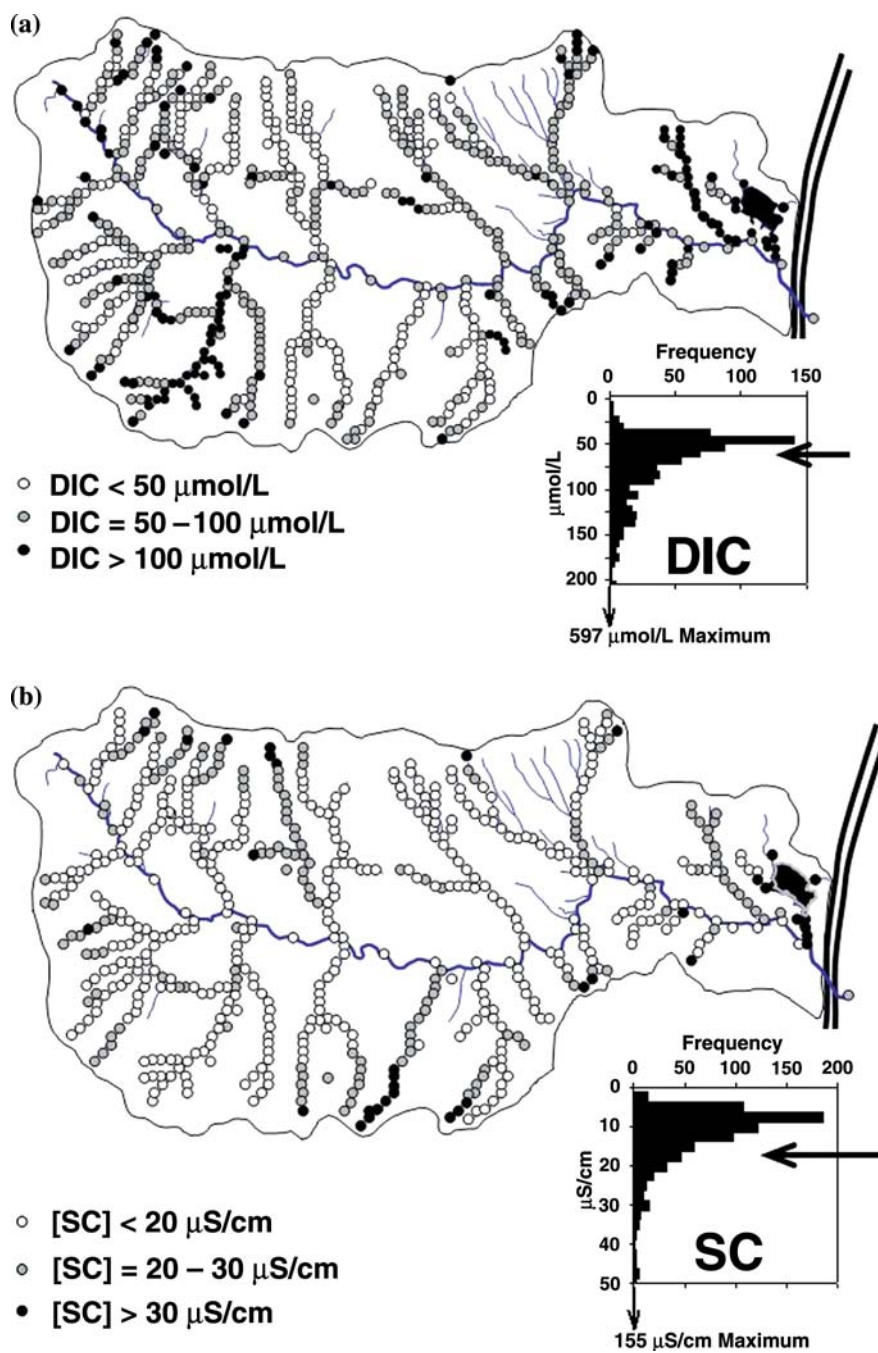


Figure 8. Distribution of streamwater concentrations of (a) dissolved inorganic carbon (DIC); and (b) specific conductance (SC) values throughout the Hubbard Brook Valley, NH during fall 2001 (→ indicates median value).

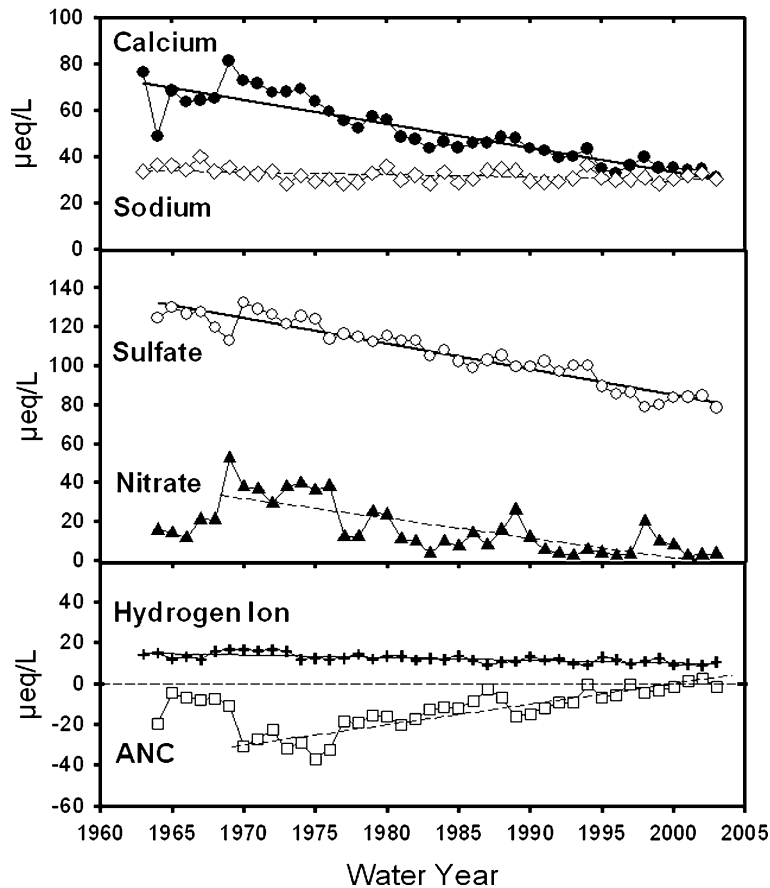


Figure 9. Long-term trends in streamwater concentration of Ca^{2+} , Na^+ , SO_4^{2-} , NO_3^- , H^+ and ANC in Watershed 6 of the Hubbard Brook Experimental Forest. Linear trend lines are statistically significant ($p = <0.05$).

the confluence with Hubbard Brook (e.g., Canyon Brook). Lower in the Valley, pH changes in many tributaries were less marked, particularly relative to H^+ concentration. Flow from the outlet of Mirror Lake appears to affect the pH of Hubbard Brook downstream of the confluence (Figure 10a). For the 16 major tributaries to Hubbard Brook (i.e., other than first-order streams), the relationships between pH and distance were: 31% matched the pH of Hubbard Brook within ± 0.1 pH units when entering Hubbard Brook; 19% of tributaries were higher by at least $+0.1$ pH units when they entered Hubbard Brook; and 50% were lower by at least -0.1 pH units when they flowed into Hubbard Brook. Despite tributaries entering at lower (e.g., Lost, Cushman, Crazy Brooks) or higher (e.g., Bear, Mirror Lake Outlet) pH values than Hubbard Brook, Hubbard Brook stream water had a remarkably constant pH value at about 6.4 throughout its length (Figure 10a). The

Table 2. Streamwater concentration values for all sites measured during spring or fall 2001.

Solute (units)	Spring 2001 (N = 625 samples)		Fall 2001 (N = 761 samples)		Maximum	Minimum
	Average (%CV)	Median	Average (%CV)	Median		
Calcium (mg/l)	0.95 (56)	0.89	1.05 (51)	0.98	8.47	0.16
Magnesium (mg/l)	0.29 (45)	0.27	0.36 (39)	0.34	2.31	0.05
Potassium (mg/l)	0.15 (87)	0.13	0.21 (86)	0.17	1.86	0.01
Sodium (mg/l)	0.92 (212)	0.78	1.03 (93)	0.88	46.20	0.11
Aluminum (mg/l)	0.09 (156)	0.02	0.10 (140)	0.03	0.71	0.01
Ammonium (mg/l)	0.01 (400)	0.005	0.01 (200)	0.005	1.00	0.01
pH	5.48 (13)	5.57	5.39 (13)	5.35	7.47	3.73
Sulfate (mg/l)	4.01 (14)	4.05	4.72 (17)	4.57	6.85	0.45
Nitrate (mg/l)	0.10 (160)	0.04	0.03 (467)	0.005	2.32	0.01
Chloride (mg/l)	0.45 (233)	0.33	0.81 (199)	0.67	35.40	0.04
Phosphate (mg/l)	0.003 (596)	0.0020	0.003 (337)	0.0005	0.411	0.0005
Dissolved silica (mg/l)	5.1 (30)	5.0	6.3 (28)	6.1	14.1	0.3
DOC (mg/l)	3.6 (68)	2.5	3.9 (94)	3.0	75.8	0.4
DIC (μ mol/l)	79 (100)	52	74 (63)	57	750	13
ANC (μ eq/l)	+6.4 (734)	+7.5	+6.0 (735)	+3.2	+821.9	-224.9
Conductance (μ S/cm)	17.3 (74)	15.2	19.7 (45)	17.4	286.0	10.1
Temperature ($^{\circ}$ C)	10.4 (27)	10.4	6.7 (31)	6.5	18.6	1.0

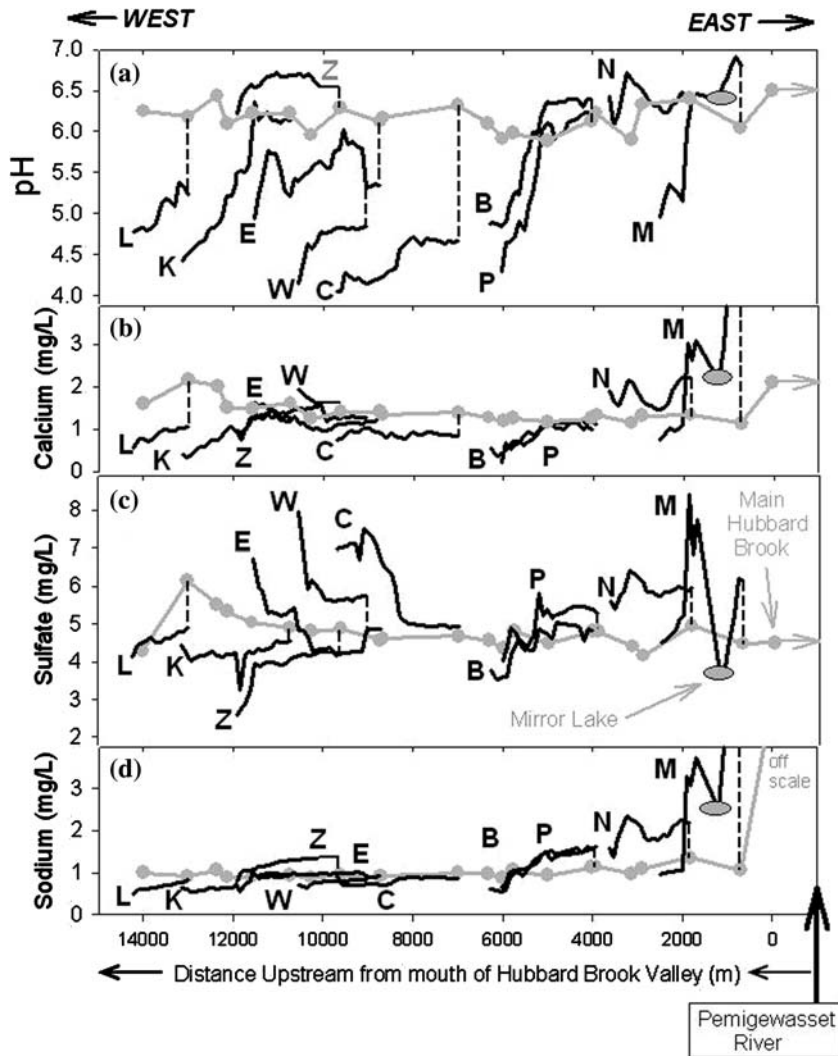


Figure 10. Changes in pH (a), and concentration of Ca^{2+} (b), SO_4^{2-} (c) and Na^+ (d) with length of wetted channel in selected tributary streams and Hubbard Brook within the Hubbard Brook Valley. The dashed lines indicate disparity in chemistry at the mouth of a tributary and the chemistry of Hubbard Brook at the point of confluence (see Figure 1b for locations). L = Lost Brook; K = Kineo Brook; Z = West Zig Zig Brook; E = East Beaver Brook; W = West Beaver Brook; C = Cascade Brook; B = Bear Brook; P = Paradise Brook; N = Norris Brook; M = West Inlet to Mirror Lake and Mirror Lake Outlet.

pattern of ANC in tributaries and Hubbard Brook was similar to that of pH because the solute strength of stream water throughout the entire Valley did not change greatly (average total dissolved solids in mg/l was 15.8 ± 6.9 SD in spring and 18.6 ± 6.0 in fall).

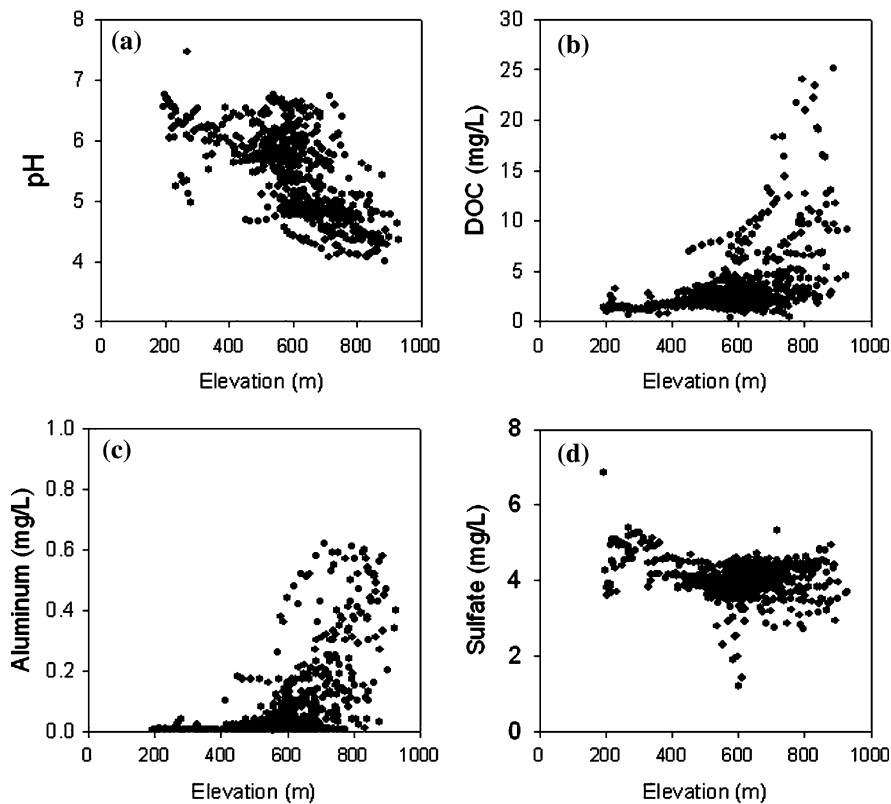


Figure 11. Distribution of pH (a), DOC (b), total monomeric aluminum (c) and sulfate (d) values in stream water by elevation throughout the Hubbard Brook Valley during spring 2001.

Likewise, Ca^{2+} concentrations in Hubbard Brook were relatively constant except for the most upper and lower parts of the Valley (Figure 10b). Inputs from the outlet of Mirror Lake and the drainage from I-93 highway appeared to alter concentrations in Hubbard Brook downstream of this confluence. Concentrations of SO_4^{2-} in Hubbard Brook also were quite constant at ~ 4.5 mg/l, except for the uppermost reaches (Figure 10c). Relative to changes in SO_4^{2-} concentrations, Ca^{2+} , and especially Na^+ , in major tributaries changed much less with length of channel (Figure 10b, c, d). In contrast, the H^+ concentration in tributaries changed over almost 3 orders of magnitude from headwaters to Hubbard Brook (Figure 10a). Terrestrial net retention and instream uptake and processing of NH_4^+ and PO_4^{3-} dominated throughout the Valley and, as a result, only trace amounts were present in streams (see, Meyer 1978; Bernhardt et al. 2003).

Each tributary to Hubbard Brook can have a unique pattern of streamwater chemistry. Nevertheless, overall patterns of streamwater concentration vs. elevation are apparent for the Valley as a whole (Figure 11). For example,

pH decreases with increasing elevation (Figure 11a), and DOC and total monomeric Al concentrations increase with increasing elevation (Figure 11b, c). Overall, SO_4^{2-} concentration is relatively constant with elevation (Figure 11d), although embedded in that aggregated relationship are distinct longitudinal elevation patterns for individual streams (Figure 10c).

The streamwater concentrations of Mg^{2+} , K^+ , NO_3^- and Cl^- changed relatively little (mostly < 2 mg/l, or a change of $\leq 20\%$ of the full range of concentrations measured in the Valley above the input to Mirror Lake) with increasing size of area drained by the 16 major tributaries to Hubbard Brook. The size of these tributary drainage areas ranged from < 1 to 304 ha throughout the Hubbard Brook Valley.

Discussion

Subtle and not-so-subtle patterns in streamwater chemistry exist throughout the Hubbard Brook Valley (Figures 1–8). Vegetation, soils and hydrologic flowpaths commonly change with elevation in the Valley. Moreover, dissolved and particulate matter entering a stream can be transformed, stored or transported within a stream ecosystem. The chemistry of water at any point in a stream reflects the combined effects of these various factors (see, Likens 1992). Knowledge about these patterns is important for evaluating long-term changes, experimental manipulations, biological distributions of aquatic and amphibious organisms, providing ground ‘truth’ for remote sensing of patterns, and for establishing monitoring networks. For example, ‘unusual’ streamwater chemistry in ‘isolated’ locations in the Valley may provide refugia for organisms during periods of environmental change, such as from the effects of acid rain, or may represent ‘hot spots’ (McClain et al. 2003) for biogeochemical processes (e.g., denitrification). Changes in the overall chemical pattern may reflect differences in geology or hydrologic flowpaths (e.g., SO_4^{2-} or dissolved Si) (Figures 1–8).

Calcium, K^+ , pH and ANC all declined strongly in an upstream direction (not necessarily with shorter pathways in an absolute sense [m], but in a relative sense [% of total wetted channel]). Magnesium, Na^+ and dissolved Si concentrations declined less in an upstream direction. Elevated K^+ concentrations were often associated with poorly drained areas (wetlands), whether at high or low elevation. Concentrations of DOC and total monomeric Al were highest at highest elevations (Figure 11b, c). Abrupt increases in DOC concentration were typically associated with transition into the more coniferous forest zone. Inorganic, monomeric aluminum concentrations peaked between 600 and 800 msl (at about 50% of total monomeric), with most of the increase in aluminum above that elevation existing as the organically bound species (up to 70% of total monomeric). Sulfate and Cl^- concentrations were relatively uniform throughout the entire Valley (see Figure 11d). Non-point source pollution, such as atmospheric SO_4^{2-} deposition, appears to have saturated the

entire ecosystem at every site, despite the varied terrain and the variety of other solutes present in stream water. Interestingly, the streamwater export per unit area of catchment of both SO_4^{2-} and NO_3^- , which are derived largely from atmospheric deposition in the Hubbard Brook Valley, varied relatively little as the drainage area increased by 4 orders of magnitude from the upper headwaters to mouth of the Valley (Likens 1999). Higher SO_4^{2-} concentrations in the Mirror Lake area (Norris Brook and West Inlet; (Figure 10c) may be related to human disturbance or to a transition of the local till and bedrock from west to east in the Valley. During the last decade, active beaver ponds in the upper part of the Valley tended to have lower SO_4^{2-} values (< 3 mg/l), while small, ‘pocket’ wetlands and poorly drained areas in upper elevation conifer stands had much higher concentrations (> 6 mg/l). Localized eutrophication in the beaver ponds from animal activity and organic sediments likely led to anoxic conditions and SO_4^{2-} reduction, whereas increased organic sediments and higher dry deposition of S in the ridge-top, pocket wetlands could have contributed to SO_4^{2-} absorption/ desorption during seasonal wet/dry cycles. Overall, these results argue for the value of protected headwater areas (Lowe and Likens 2005) and long-term data.

Large changes over distance in fifth-order, ‘pristine’ watersheds would not be expected, unless solute concentrations were dominated by point-source inputs as from human disturbances, such as NaCl. Other than from the influence of road salt in the lower drainages of the Valley, only a few remote sites had elevated Cl^- concentrations, and these were associated with wet areas frequented by moose.

While NO_3^- was typically below detection limits, detectable concentrations generally increased upslope, reaching modest concentrations (0.1–0.2 mg/l) around 600–800 msl, and then declined in streams that extended higher to the ridgeline (and usually into the more coniferous forest). Nitrate concentrations were often much higher (> 0.5 mg/l) in seeps or springs, regardless of the elevation of the site so that longitudinal trends for individual streams were idiosyncratic. In conjunction with higher NO_3^- concentrations, these wet sites were also ‘hot-spots’ for base cations, and elevated pH, ANC and dissolved Si. A good example of a watershed with many active seeps and springs is Zig Zag Brook, which stands out as a stream with unusually high pH and ANC, extending upslope nearly to the ridgeline (Figure 2a, b). Recent electro-surveys of native brook trout (*Salvelinus fontinalis*) populations revealed that Zig Zag Brook had among the highest numbers in the Valley (D. Warren, personal communication).

The DIC concentration and electrical conductance in streams throughout the Valley exhibited bimodal patterns: high concentration at low elevation, decreasing with mid-slope position, and increasing again upstream. The conductance follows the parabolic distribution of ionic strength as would be expected, with base cation and bicarbonate concentrations dominating low in the Valley, and strong acid anion, H^+ and monomeric aluminum concentrations contributing more at upper sites. Mid-slope sites have the lowest total ionic strength, and also the most variation in chemistry because they are not

strongly buffered by either acidic or alkaline solutes. Thus, these sites represent a good place in the Valley to look for chemical changes because the streams are least well buffered. Similarly, the pattern for DIC may reflect undiluted CO_2 from soil microbial respiration at higher elevation, but increasing bicarbonate (+ ANC) from deep seepage and longer flow paths at lower elevation sites (Johnson et al. 1981). The combination of vigorous degassing and short, soilwater flowpaths at mid-elevation sites may result in the observed lower values for DIC.

'Hot spots', such as seeps and springs with higher pHs, base cations and even elevated NO_3^- concentrations were definitely a facet of the hard, crystalline rock landscape in the Hubbard Brook Valley and were detectable from the 100 m intervals of our survey (Figures 2–8). These survey data suggest that groundwater discharge areas (based on higher pH and base cation concentrations) are much more common on lower slopes than at the elevations typical of the streamgauging stations in the HBEF.

The heart of the small-watershed approach for studying forest ecosystems at HBEF has been the routine collection of streamwater samples for chemical analysis from fixed sites above gauged watersheds (Bormann and Likens 1967; Likens and Bormann 1995). This approach assumes that streamwater chemistry at the weir integrates, and is the result of, the diverse biogeochemical processes throughout the watershed. The small watershed-ecosystem approach has proven to be an extremely useful scientific tool because it reduces an almost impossibly complicated system to one that can be defined and compared with other watersheds, simply and elegantly in time and space. When the HBEF was formed in 1955, there was no pre-conceived idea about what to expect or what was important regarding streamwater chemistry. In fact, hydrology, not biogeochemistry, was the impetus to locate and instrument the HBEF (J. W. Hornbeck, personal communication). With the initiation of the Hubbard Brook Ecosystem Study in 1963, the sites for the initial stream chemistry samples were chosen on the basis of the location of the stream gauging stations at the base of relatively small (tens of hectares), headwater watershed-ecosystems. The location of those instruments had been determined primarily by the presence of exposed bedrock necessary for a watertight seal to prevent significant leakages of water at the weir. Thus, the chemistry used to characterize and compare nearby watersheds, and to monitor them over time, was not a random selection, but one based on an important physical and hydrologic characteristic within the landscape, and shared by all the sites.

We show in Figure 12, the pH of stream water for five streams from first running water at ridge top to confluence with Hubbard Brook. These streams have quite different pH distributions, with Cascade being consistently more acid and West Inlet having the broadest range in pH. These data for each stream are best fit by a third-order polynomial regression line ($r^2 \geq 0.93$ for all streams). Each of these streams has a gauging weir and its location is shown on the graph by an arrow. Considering these pH distributions as a 'titration curve' for water moving downstream, some important points can be made:

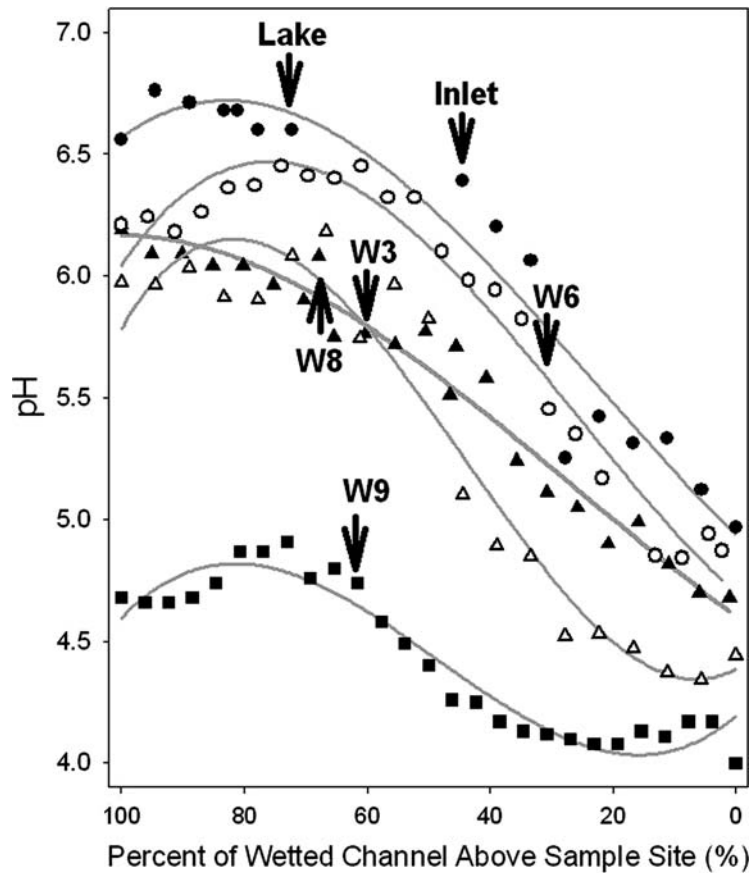


Figure 12. pH values from first running water to the confluence with Hubbard Brook for West Inlet to Mirror Lake (●), Bear Brook (○), Canyon Brook (△), Paradise Brook (▲), and Cascade Brook (■). The arrows mark the location of gauging weirs on these streams. The 3rd-order polynomial lines for these distributions have r^2 of 0.94 for West Inlet, 0.97 for Bear Brook, 0.97 for Paradise Brook, 0.94 for Canyon Brook and 0.93 for Cascade Brook.

- (1) Because maximum data on change can be obtained at the inflection point on such a distribution, the locations of the weir for sampling hydrology and chemistry are close to optimal, especially for Bear Brook (Watershed 6 of the HBEF). This is a fortuitous situation, as the location of the weirs was determined entirely on hydrologic considerations at the time of formation of the HBEF;
- (2) The optimum location for the sampling point for stream chemistry in all of these rather diverse streams is between about 30 and 60% of wetted channel below first running water.
- (3) Of the 16 major tributaries we sampled in the Valley, only 2 (13%) did not demonstrate a similar pH relationship. These two watersheds contained

more atypical, upper slope hydrologic features, such as seeps, springs or wetlands.

Researchers at HBEF have long recognized that biogeochemical characteristics within the watersheds are not uniform and that ecosystem processes driven by these differences must be addressed with other tactics, such as detailed sampling and analyses ‘inside’ the watershed. Thus, collecting samples from the lower reaches of a stream up to the first running water is not a new idea at HBEF. Using this approach, divergent hydrochemical models, such as the ‘graded-change’ paradigm (Johnson et al. 1981) and the ‘source-area’ concept (Lawrence et al. 1986), have been tested.

For example in 1967, water samples were collected from W2 at numerous sites above the weir to determine the location of possible nitrification ‘hot-spots’ after that watershed had been experimentally deforested (Likens et al. 1970). During the 1970s, John S. Eaton and Gene E. Likens and a group of graduate students sampled streamwater chemistry from the headwaters of Hubbard Brook to the Atlantic Ocean. Sloane (1979) began surveys of nitrate and ammonium concentrations in several headwater streams across the HBEF Valley, by sampling at 3, evenly spaced nodes within streams from low to high elevation. Over the period 1974–1978, Noye M. Johnson and colleagues sampled Falls Brook longitudinally and seasonally (4× per year at 8 fixed sites) to develop a hydrogeochemical model for streamwater neutralization of acid rain (Johnson et al. 1981). McDowell (1982) and McDowell and Likens (1988) described changes in the processing of dissolved organic carbon (DOC) by collecting from sites along increasing stream order throughout the Hubbard Brook Valley. Subsequent work on longitudinal aluminum transformations built on this developing understanding (Lawrence et al. 1986). The most recent efforts in using longitudinal sampling to understand internal ecosystem processes involved the exchange of base cations in stream sediments (Hall et al. 2001; Likens et al. 2004), stream uptake of nitrogen after forest disturbance (Bernhardt et al. 2003), and aluminum–DOC–organic nitrogen relationships (Palmer 2004). In these ways and others, the understanding of spatial and temporal variation in stream chemistry within small watersheds at HBEF has grown considerably.

This current study has set the stage to move our watershed-ecosystem research to the next level of understanding, at an increased spatial scale. The Hubbard Brook Valley is a relatively pristine system, with drainage streams having dilute chemical characteristics (average total ionic charge < 300 $\mu\text{eq/l}$), and very low concentrations of biologically critical nutrients, such as NH_4^+ , NO_3^- and PO_4^{3-} (median values of 0.005, ≤ 0.04 and ≤ 0.02 mg/l, respectively; Table 2). The gravel access roads within the HBEF are not maintained for travel by vehicles during winter and thus there is no input of road salt. However, the Valley does have increased inputs of SO_4^{2-} and NO_3^- from its airshed through rain, snow and dry deposition.

The lower watersheds in the Hubbard Brook Valley, comprising the three Mirror Lake inlets and Norris Brook are not completely protected by the HBEF and are not pristine, having paved roads, several houses and associated septic systems that contribute to the higher levels of most of the solutes we measured. In fact, the increase in some compounds, such as NaCl, is on the order of 10- to 100-fold. Nevertheless, in the forested, upper reaches of even these lower Valley streams, the solute concentrations and patterns are similar to that found higher in the HBEF. This result clearly demonstrates the potentially fragile nature of these upland watersheds, as well as the strong degree of biogeochemical control exercised by these natural systems when protected.

The soils, till and bedrock of the Valley have various influences on stream-water chemistry as the chemical composition of the rusty-weathering schists on the eastern side of the HBEF can be very different from the feldspar-rich Granodiorite in the western part (Barton et al. 1997). The combination of longer flowpaths from deeper till deposits and the till composition itself in the western upper Valley, may explain why calcium concentrations increase slightly in Hubbard Brook from east to west (beyond the impact of human disturbance near the mouth of the Valley) (Figure 10b).

Nearly every tributary we surveyed had marked longitudinal pH trends until it reached fourth- to fifth-order status. Although the streamwater concentrations of Ca^{2+} and SO_4^{2-} currently are lower than in 1975–1978, the longitudinal pattern has not changed and the H^+ neutralization paradigm proposed by Johnson et al. (1981) still stands as the model by which we can study change over space and time in most watersheds in the HBEF. A stream without a pH gradient is a poor choice for long-term chemical studies in our area.

The pH of Hubbard Brook did not characterize the pH of stream water in the majority of stream channels in the Valley (Figure 10a). Specifically, Hubbard Brook does not represent the pH of headwater streams, including W6, the long-term, biogeochemical reference for the HBES (e.g., Likens and Bormann 1995). Surprisingly, unchanneled inputs seem to dominate the chemistry of Hubbard Brook throughout the entire reach, at least under the relatively low flow conditions during which the surveys were done. Thus, a long-term study focused on Hubbard Brook would not have been as informative or as interesting biogeochemically as that done on W6.

Streams with large, complex watersheds rarely have one or a few physical characteristics or processes that can dominate the watershed-ecosystem over such large areas, so the streamwater chemistry tends to be homogenous. Thus, the best place to compare the impact of particular characteristics or processes is within a smaller watershed. How small? The fact that the routine stream sampling sites on the experimental watershed-ecosystems at HBEF are also places with bedrock exposure (Likens and Bormann 1995) means that the watershed characteristics can be constrained to the area above that point, and the inflection point on the longitudinal pH pattern provides a sharp gradient (Figure 12).

From knowledge gained after four decades using the small watershed-ecosystem approach with well-matched and intensively studied watersheds, we are

now asking the question: Do these concepts work elsewhere, in watersheds of different fundamental characteristics, such as those of larger size? Is there a Fundamental Landscape Biogeochemical Unit analogous to (and obviously linked with) the Fundamental Landscape Hydrologic Unit proposed by Winter (2001)? More specific questions include: How spatially variable are larger watersheds? Are ecosystem controls simply area-weighted? Do obvious changes in stream chemistry relate to measurable ecosystem boundaries or thresholds? How does dispersal of animals, such as salamanders, trout and stoneflies, reflect and relate to these spatial patterns? Where is the best place to monitor change or experimentally manipulate a watershed ecosystem, and how can spatial and temporal sampling scales be coordinated? Can space be substituted for time across streamwater gradients and does this substitution increase predictive value? These are topics of our ongoing research in the HBEF, and data from our valleywide surveys provide an important tool for addressing these questions.

Conclusions

Tributary stream chemistry varies throughout the Hubbard Brook Valley by elevation, channel length, drainage area and type of drainage. Much of this variation is subtle and relatively small for concentrations of Na^+ , Ca^{2+} , Mg^{2+} , dissolved Si and Cl^- , and occurs primarily in the upper reaches of each watershed throughout the Hubbard Brook Valley. The chemistry of Hubbard Brook, under low flow conditions, is relatively constant for all solutes throughout its length, and above the effects of human disturbance near its mouth.

Patterns in streamwater chemistry in different watersheds are remarkably repeatable, especially pH. There are small areas, e.g., seeps and springs, that are chemically anomalous and may represent 'hot spots' for refugia and biogeochemical 'surprises' within the larger landscape. These areas do not appear to have a significant impact on nutrient export on an areal basis.

Given the cost of establishing and maintaining long-term, biogeochemical studies of forest watershed-ecosystems, it would be appropriate to measure a fundamental parameter, like longitudinal stream chemistry, first, and establish its spatial context before assigning a fixed sampling site to answer a specific question.

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