

Patterns of Streamwater Acidity in Lye Brook Wilderness, Vermont, USA

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ABSTRACT / Under the United States Clean Air Act Amendments of 1977, a class I designation safeguards wilderness areas from the negative effects of new sources of air pollution. We monitored streamwater chemistry in the class I Lye Brook Wilderness in southwestern Vermont from May 1994 through August 1995. Stream samples were collected biweekly at nine

sampling locations throughout the wilderness and were analyzed for major cations and anions, dissolved organic carbon, pH, and acid-neutralizing capacity. Eight of nine sites sampled had mean annual acid neutralizing capacity values below zero. During the study period, decreases in streamwater acid neutralizing capacity values were caused primarily by SO_4^{2-} . At some sites, however, NO_3^- and naturally occurring, weak organic acids were seasonally important. During high discharge, the low pH and high concentrations of inorganic monomeric Al were at levels that are toxic to acid-sensitive aquatic species. Watershed mass balances were calculated to determine annual gains or losses for measured ions. These budgets indicate that S inputs and outputs were nearly equal, there was a net loss of base cations, and a net gain in N. How long these watersheds can continue to assimilate additional N inputs is unknown.

The Lye Brook Wilderness (LBW) is a class I air quality area located in the Green Mountain National Forest in southern Vermont. Under the United States Clean Air Act Amendments of 1977, a class I designation safeguards wilderness areas from the negative effects of new sources of air pollution (Ross 1990). In these areas, only small, incremental increases in new pollution are permitted above baseline levels. Additional pollution is allowed only if national ambient air quality standards are not exceeded and the air quality related values (AQRVs) for the designated class I area are not adversely affected (Adams and others 1991). These values consist of features or properties that contribute to the wilderness characteristic of the area (e.g., visibility, vegetation, wildlife, and water). Prevention of Significant Deterioration (PSD) permits are required for new sources of air pollution and for modifying existing sources that have the potential to impact a class I area. Federal land managers (for LBW, the USDA Forest Service) review these permits to determine possible impacts on AQRVs. If adverse impacts are expected, then the regulatory agency cannot issue a permit. The review period for PSD permits by federal land

managers may be as short as 30 days (Fox and others 1989). Therefore, managers need sufficient information to evaluate permits and render a decision in a timely manner.

Acidic deposition is a concern for managers of the Lye Brook Wilderness because it can have a deleterious impact on soil, vegetation, and streamwater. The LBW is vulnerable because soils throughout most of the wilderness are derived from glacial deposits that are resistant to weathering and are low in base cations (BC) (Adams and others 1991). If acidic deposition increases, these poorly buffered soils may exhibit reductions in soil pH and cation exchange capacity (CEC) and increases in BC leaching and Al mobilization (Cronan and Schofield 1979, 1990, Reuss and Johnson 1985, 1986). Changes in the soil may reduce the health and vigor of vegetation by causing nutrient imbalances and Al toxicity (Shortle and Smith 1988, Schulze 1989, Cronan and Grigal 1995) and may affect surface water quality, resulting in a reduction in the number of species and individuals in streams and lakes (Hall and others 1985, Genter 1995, Baker and others 1996).

In the time since the Clean Air Act was passed in 1970, there has been a reduction in emissions of SO_2 across the northeastern United States (Shannon 1999, Driscoll and others 2001). In 1995, more dramatic decreases in SO_2 emissions were observed following the implementation of more stringent emission regulations

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introduced in the 1990 Clean Air Act Amendments (Lynch and others 2000, Butler and others 2001). In response to reductions in SO_2 emissions, SO_4^{2-} concentrations in precipitation and surface waters have declined over the last 50 years, yet recovery of alkalinity has not been observed because of accompanying declines in BC concentrations in both soils and deposition (Likens and others 1996; Stoddard and others 1999).

During the last decade, acidic deposition research has largely focused on N because emissions of N remain high relative to background levels (NAPAP 1998). In addition to reducing SO_2 emissions, the 1990 Clean Air Act Amendments also limited increases in NO_x emissions. However, emissions of NO_x have not declined in most states, and decreases in N deposition have not been observed (Lynch and others 2000, Butler and others 2001, Driscoll and others 2001). High rates of N deposition have raised concern about the potential for sites to become N saturated, resulting in elevated concentrations of NO_3^- in streamwater (Ågren and Bosatta 1988, Aber and others 1989).

Streamwater chemistry provides an efficient indicator of both forest and aquatic ecosystem status with respect to susceptibility to acidic deposition. Water draining watersheds integrates a suite of terrestrial processes associated with biogeochemical cycling, and its chemistry can be used to make inferences about the nutrient status of upland systems. Thus, streamwater chemistry provides the federal land manager with information that can be used in evaluating PSD permits. Streamwater chemistry data from LBW are also important because the study site is located on an acidic deposition gradient in a region of the northeastern United States where the effects of acidic deposition are not well documented. Additionally, some of the streams in the wilderness contain wetlands in the source area that provide an opportunity to study the contribution of natural, organic acids to streamwater. In this research, we investigated spatial and seasonal variability in stream chemistry as a function of watershed characteristics (i.e., vegetation, soil, geology, wetlands). These data were used to establish factors that contribute to the acidity of streams in the wilderness. Annual mass balances were calculated for three watersheds to establish patterns of gains or losses for major ions.

Site Description

The 6280-ha LBW is located in the Green Mountain National Forest in southwestern Vermont (Figure 1). The elevation of the wilderness ranges from 250 m, near the Battenkill River Valley, to over 800 m in southern and central locations. Forest cover is dominated by

northern hardwood stands composed primarily of American beech (*Fagus grandifolia*), sugar maple (*Acer saccharum*), yellow birch (*Betula alleghaniensis*), and white ash (*Fraxinus americana*), interspersed with successional stands of red maple (*Acer rubrum*) and paper birch (*Betula papyrifera*). Softwood stands consisting of red spruce (*Picea rubens*) and balsam fir (*Abies balsamea*) occur at high elevation, and stands of eastern hemlock (*Tsuga canadensis*) are common on steep slopes adjacent to Lye Brook. Soils in the wilderness are generally acidic and loamy and consist of Typic Humaquepts, Epiaquads, and Haplorthods. These are shallow and poorly drained soils with a well-developed organic horizon that typically overlays a thick E horizon and poorly developed Bh horizon. The geology of LBW consists of formations of the Mount Holly Complex (quartzite, schist, amphibolite, gneiss), Mendon Formation (quartzite, phyllitic conglomeratic quartzite, phyllitic quartzite and quartz-mica-schist), Cheshire Quartzite (recrystallized orthoquartzite), and Dunham Dolomite (Ayuso and Robinson 1984). These formations occur in a west-facing escarpment toward the Battenkill River Valley. A summary of watershed characteristics is listed in Table 1.

Methods

Nine streamwater sampling sites were established throughout the wilderness area by determining the major site characteristics of interest, such as geology, presence of wetlands, and vegetation. Three sites were located on a longitudinal gradient along Lye Brook (sites 5, 7, and 9), two sites were on first-order tributaries to Lye Brook (sites 6 and 8), three sites were in close proximity to wetlands (sites 1, 2, and 3), and the remaining site was on a first-order tributary to the Battenkill River (site 4) (Figure 1).

Technicians hiked to the stream sites and collected samples biweekly from May 1994 through August 1995. Samples were collected in 250-ml high-density polyethylene bottles that were acid washed and rinsed with distilled, deionized water and then sample site streamwater prior to collection. Measurements of pH were made in the field with a portable pH meter. Sample bottles were stored in coolers containing ice and were transported to the laboratory within two days of collection. Upon returning to the laboratory, 50-ml aliquots were stored frozen for NH_4^+ and DOC analyses, which occurred within a maximum of six months, and usually within one month, after collection. The 250-ml bottles were refrigerated for use in all other analyses, which were conducted within one month after collection. Analytical methods are summarized in Table 2.

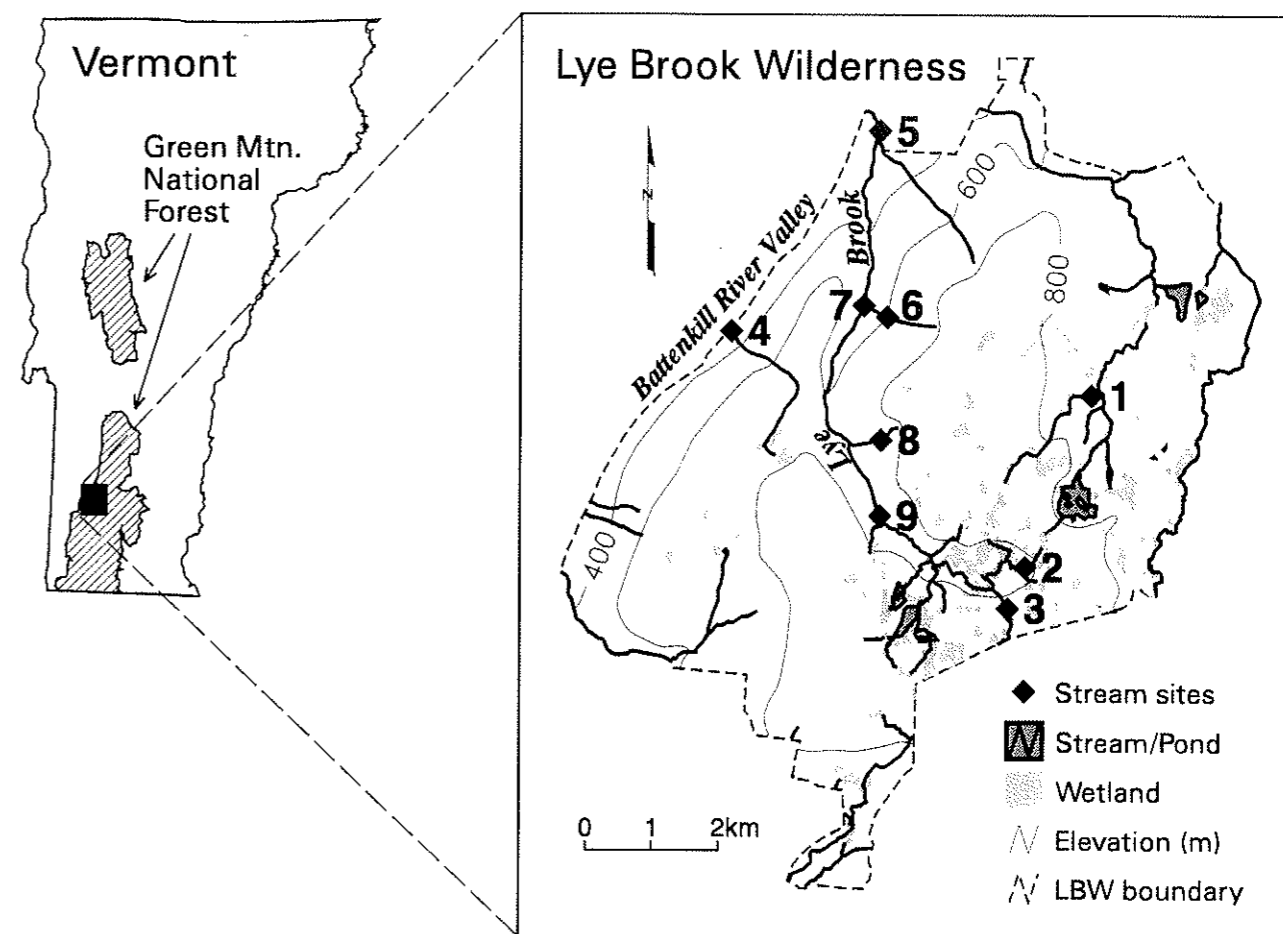


Figure 1. Location and map of the study area.

Inorganic monomeric Al (Al^3) values were converted from milligrams per liter to microequivalents per liter using a charge of 3+. Studies have shown that surface waters with higher pH values, such as those measured at sites 1 and 5, may have a lower Al charge due to complexation with OH and F (Sullivan and others 1989). However, these sites also had the lowest inorganic Al concentrations and would not be greatly affected by the assignment of a lower charge. Dissolved organic carbon was converted from milligrams per liter to microequivalents per liter to make ionic strength comparisons with other anions (Oliver and others 1983). A charge density for DOC was determined by subtracting titrated ANC values from calculated ANC values and dividing by the concentration of DOC. Sites 1 and 5 were omitted from this calculation because, based on pH, both sites were thought to contain appreciable concentrations of HCO_3^- . The calculation yielded a mean charge density of 5.1 $\mu\text{eq}/\text{mg}$ DOC that

is consistent with values in other studies (Kahl and others 1989).

Mass balances were calculated for major anions and cations for the 1994–1995 water year (1 June–31 May) at watersheds 4, 6, and 8. To calculate streamwater fluxes, streamflow was estimated using the Brook90 hydrologic model, which predicts flow rates expressed as millimeters of water per day (Federer 1998, Federer and Lash 1978). Six of the nine watersheds were excluded from this analysis because they contain wetland areas and lack prominent topographical divides and consequently were not suitable for the model. Brook90 was run on a daily time-step using daily precipitation and minimum and maximum temperature inputs in addition to parameters related to physical attributes of the watershed, forest canopy, and soils. For precipitation inputs, wet deposition chemistry was obtained from a NADP/NTN station located in Bennington, Vermont, approximately 50 km south of LBW (NADP

Table 1. Summary of stream sample site characteristics

Site	Watershed elevation (m)	Upstream wetland (m)	Watershed area (ha)	Watershed forest cover type (%)			Dominant watershed bedrock formation(s)
				Hardwood	Softwood	Mixed	
1	725-850	280	241	61	32	7	Mount Holly Complex
2	790-825	55	44	69	31	0	Mount Holly Complex
3	790-805	0	43	21	20	59	Mount Holly Complex
4	305-830	2291	163	53	43	4	Cheshire Quartzite Mendon Formation
5	270-930	7123	2247	68	22	10	Dunham Dolomite Cheshire Quartzite Mendon Formation Mount Holly Complex
6	570-850	—	106	61	23	16	Cheshire Quartzite Mendon Formation Mount Holly Complex
7	400-930	4441	1806	71	22	7	Cheshire Quartzite
8	725-850	—	130	51	29	20	Mendon Formation Mount Holly Complex
9	760-930	749	1062	73	23	5	Mount Holly Complex

Table 2. Summary of streamwater analytical methods

Analyte	Method	Reference
ANC	Potentiometric autotitration	USEPA (1983)
pH	Glass electrode potentiometry	APHA (1992)
Ca ²⁺ , Mg ²⁺ , Na ⁺ , K ⁺	Direct-current plasma atomic emission spectrometry	ASTM (1994)
Al ³⁺ , Al ⁰	Pyrocatechol violet colorimetry; autoanalyzer	McAvoy and others (1992)
NH ₄ ⁺	Flow injection analysis chromatography	USEPA (1983)
SO ₄ ²⁻ , NO ₃ ⁻ , Cl ⁻	High pressure liquid chromatography	ASTM (1994)
DOC	High temperature catalytic oxidation	APHA (1992)

2001). Precipitation volume was based on data from the National Weather Service cooperative observation station at Dorset, Vermont, located approximately 10 km SE of LBW at an elevation of 284 m. Precipitation volume was corrected for elevation using multiple regression equations calculated for the northeastern United States (Ollinger and others 1995).

Chemical fluxes in precipitation and streamwater were calculated by multiplying respective weekly and biweekly chemical concentrations (milligrams per liter) times the daily water flux (liters per hectare per day). Daily inputs and outputs were summed for the 1994-95 water year and are reported as kilograms per hectare per year. Dry deposition inputs of SO₄²⁻, SO₂, NO₃⁻, NH₄⁺, and HNO₃ were measured at a Clean Air Status and Trends Network (CASTNet) site adjacent to the wilderness boundary at an elevation of 730 m (US Environmental Protection Agency, Washington DC). Dry deposition inputs of BC were not measured; therefore atmospheric inputs of BC only include wet deposition values. Nutrient budgets were calculated by subtracting streamwater outputs from atmospheric inputs

to determine gains and losses for measured ions (Likens and Bormann 1995).

Soil samples were collected within the watershed boundaries of sites 6-9 for determination of pH, exchangeable cations, CEC, and percent base saturation (%BS). Three pits were excavated at representative locations in each of the four watersheds. At each pit, soil samples were collected from organic (Oa horizon) and mineral soil horizons (B and C horizons). Samples were air-dried at approximately 25°C for one week and were then sieved through a 0.2-mm screen. Subsamples were oven-dried for 48 hours at 65°C for organic soil and 105°C for mineral soil to calculate dry mass. Soil pH was determined by mixing the soil sample with distilled, deionized water followed by potentiometric measurement (Robarge and Fernandez 1987). Replaceable H⁺ and BC were removed from exchange sites with NH₄Cl, and Al was removed with KCl using a mechanical vacuum extraction procedure (Kalra and Maynard 1991). Base cations and Al were measured using direct current plasma spectroscopy, and exchangeable acidity was measured with an autotitrator.

Table 3. Chemical properties of soil at four Lye Brook watersheds

Horizon	Watershed (n ^a)	Exchangeable cations (cmol/kg)							%BS	pH	
		Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	Al ³⁺	H ⁺	CEC			
Oa	6 (3)	2.8	0.9	0.3	0.0	10.4	18.0	32.4	12.5	3.6	
	7 (3)	2.0	0.6	0.9	0.0	5.3	10.8	19.6	18.0	3.2	
	8 (3)	3.2	1.0	0.8	0.1	14.2	17.7	37.0	14.3	3.2	
	9 (3)	5.7	0.7	0.3	0.0	10.6	14.8	32.2	19.7	3.4	
	Mean		3.4	0.8	0.6	0.0	10.1	15.3	30.3	16.1	3.4
B	6 (3)	0.1	0.1	0.1	0.0	13.0	10.1	23.3	1.1	3.9	
	7 (3)	0.1	0.1	0.1	0.0	9.1	8.7	18.2	1.8	4.0	
	9 (3)	0.2	0.1	0.1	0.0	9.6	9.0	19.0	2.0	4.1	
	Mean		0.1	0.1	0.1	0.0	10.6	9.3	20.2	1.6	4.0
	C	7 (1)	0.2	0.0	0.0	0.0	8.5	6.5	15.2	1.6	4.3
8 (3)		0.1	0.0	0.0	0.0	5.6	5.3	11.2	1.6	4.1	
9 (1)		0.2	0.0	0.0	0.0	8.5	6.9	15.7	1.6	4.7	
Mean			0.2	0.0	0.0	0.0	7.5	6.2	14.0	1.6	4.4

^aNumber of samples.

Table 4. Streamwater chemistry and ion balances for each sampling site (1994-1995 water year)

Item	Site									
	1	2	3	4	5	6	7	8	9	
pH	4.9	4.4	4.2	4.6	5.8	4.4	4.5	4.1	4.6	
ANC	-2	-48	-74	-27	159	-46	-44	-113	-37	
Cations [μeq/liter (%)]										
Ca ²⁺	60 (34)	41 (25)	40 (23)	55 (35)	139 (43)	37 (23)	40 (24)	26 (13)	41 (27)	
Mg ²⁺	48 (27)	28 (17)	22 (12)	34 (22)	127 (39)	20 (13)	24 (15)	17 (9)	26 (17)	
K ⁺	15 (9)	15 (9)	13 (7)	14 (9)	21 (7)	23 (15)	20 (12)	21 (11)	15 (10)	
Na ⁺	36 (20)	35 (21)	33 (19)	20 (13)	29 (9)	21 (13)	24 (15)	28 (14)	35 (23)	
Al ³⁺	4 (2)	6 (4)	7 (4)	10 (6)	2 (1)	21 (13)	22 (13)	14 (7)	6 (4)	
H ⁺	13 (7)	37 (23)	60 (34)	23 (14)	2 (1)	37 (23)	34 (20)	88 (45)	28 (18)	
NH ₄ ⁺	1 (1)	1 (1)	1 (1)	1 (1)	1 (0)	0 (0)	1 (1)	1 (1)	1 (1)	
Anions [μeq/liter (%)]										
SO ₄ ²⁻	80 (48)	75 (45)	88 (47)	116 (66)	96 (59)	105 (60)	104 (58)	102 (49)	69 (45)	
NO ₃ ⁻	10 (6)	6 (3)	6 (3)	11 (6)	14 (9)	20 (12)	21 (12)	7 (3)	8 (5)	
Cl ⁻	18 (11)	18 (11)	17 (9)	20 (11)	15 (9)	17 (10)	20 (11)	20 (9)	16 (11)	
DOC	59 (35)	69 (41)	76 (41)	29 (17)	37 (23)	32 (18)	34 (19)	81 (39)	59 (39)	
ΣCations μeq/liter	177	163	176	157	321	159	165	195	152	
ΣAnions μeq/liter	167	168	187	176	162	174	179	210	152	
Net μeq/liter	10	-5	-11	-19	159	-15	-14	-15	0	

Results

Soil Chemistry

Soils at LBW are highly acidic and have low concentrations of exchangeable BC (Table 3). Aluminum and H⁺ dominated soil exchange sites and occupied more than 84% of the sites in the Oa horizon and 98% in the mineral horizons. Compared to mineral horizons, the Oa horizon had a lower pH and higher concentrations of exchangeable H⁺. Exchangeable Al ranged from 5.3 to 14.2 cmol/kg with mean concentrations similar in the Oa and B, and lower in the C horizon. Percent base saturation was low in the Oa and extremely low in the

B and C horizons. Calcium was the dominant BC at all sites.

Stream Chemistry

Average streamwater pH values ranged from 4.1 to 5.8 and ANC values ranged from -113 to 159 μeq/liter for the 1994-1995 water year (Table 4). With the exception of site 5, all sample locations had negative ANC values. Total BC concentrations (ΣBC) were highest at site 5 (316 μeq/liter), followed by site 1 (159 μeq/liter). The range of ΣBC at the remaining seven sites was fairly narrow (92-123 μeq/liter) and the lowest mean concentration occurred at site 8. The mean an-

nual concentration of strong acid anions typically occurred in the following order: $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$. Sulfate was the dominant anion at all sites, and mean SO_4^{2-} concentrations were at least four times greater than Cl^- . The second most abundant strong acid anion was Cl^- except for sites 6 and 7, which had higher concentrations of NO_3^- . Weak organic acids associated with DOC also contributed to the acidity of streamwater. Using the charge density calculation for DOC described previously (1 mg = 5.1 μeq), the average organic acid concentration was less than SO_4^{2-} and greater than NO_3^- and Cl^- . The summed charges of measured cations in streamwater nearly balanced the summed charges of measured anions at all sites with the exception of site 5. The large difference between cations and anions at this site (159 $\mu\text{eq}/\text{liter}$) is thought to be mostly due to the presence of HCO_3^- . The difference between the sum of cations and anions at all other sites was < 11%.

To investigate seasonal trends in stream chemistry, sites were aggregated into three groups: dolomite (site 5), wetland (sites 1, 2, 3, and 9), and nonwetland (sites 4, 6, 7, and 8). At all sites, concentrations of NO_3^- were low from May through November and gradually increased over winter (Figure 2A). The highest NO_3^- concentrations occurred from February through April and generally peaked during snowmelt runoff. Sulfate concentrations at the wetland sites were also lower than other sites throughout the year and differences were greatest from May through September (Figure 2B). Wetland and nonwetland sites had similar ΣBC concentrations and there was little variability throughout the sampling period (Figure 2C). In contrast, site 5 had higher ΣBC concentrations, and there was a seasonal pattern with higher concentrations occurring during the summer compared to winter.

Dissolved organic carbon concentrations were higher at wetland sites, and a seasonal pattern was evident, with highest streamwater DOC concentrations during summer and fall (Figure 2D). At nonwetland sites, DOC concentrations increased sharply during high discharge and seasonal patterns were less evident. Concentrations of Al also peaked during high discharge when the pH was lowest (Figure 2E-G). Inorganic Al concentrations were lower at wetland sites compared to nonwetland sites, and the lowest Al concentrations occurred at the site underlain by dolomite (Figure 2E). At nonwetland sites Al concentrations were greatest from September through May and concentrations were lower and less variable throughout the year at the other sites.

The relationship between discharge and stream chemistry was examined at watersheds 4, 6 and 8, where streamflow was modeled. There was a significant negative relationship between ANC and discharge at the three watersheds ($r^2 = 0.22$ to 0.49 , $P < 0.005$), showing that streams were most acidic during high flow. Discharge was also negatively related to ΣBC ($r^2 = 0.13$ – 0.41 , $P < 0.18$) and positively related to Al ($r^2 = 0.5$ to 0.7 , $P < 0.005$). For strong acid anions, discharge was not significantly related to SO_4^{2-} or Cl^- , but the relationship between discharge and NO_3^- was more complex. Concentrations of NO_3^- at sites 4 and 6 were positively related to discharge, but there was not a significant relationship at site 8. The relationship between DOC and discharge was also inconsistent across sites and was positively related at sites 6 and 8, but not at site 4. We were not able to model streamflow at sites that contained wetlands in the headwaters, so we could not definitively determine the effect of discharge on these sites. However, Figure 2 indicates that the chemistry of streams draining wetlands was less responsive to discharge than nonwetland streams.

To further investigate the influence of wetlands on stream chemistry, we compared the distance upstream from each sampling site and the closest wetland upstream from the site, to the concentration of $\text{SO}_4^{2-} + \text{NO}_3^-$, DOC, and Al (Figure 3). There was a decrease in DOC concentrations and a general increase in concentrations of Al and $\text{SO}_4^{2-} + \text{NO}_3^-$ with increases in the distance between the source wetland and the sample location. Site 5 did not fit this model because it had the lowest Al concentrations despite being relatively far from a wetland source. Site 8 was also an exception because it had the second highest mean DOC concentration (81 $\mu\text{eq}/\text{liter}$ for 1994–1995 water year) and the headwaters do not originate in a wetland. At all sites, there was a significant positive relationship between concentrations of DOC and organic aluminum (Al) ($r^2 = 0.77$, $P < 0.0001$).

Watershed Budgets

During the 1994–1995 water year, watersheds 4, 6, and 8 had similar trends for nutrient gains and losses (Figure 4). All watersheds showed net gains for N (8.5 to 10.6 kg/ha/yr) and losses for BC (–1.3 to –6.1 kg/ha/yr). Sulfur had the greatest precipitation and streamwater flux, but inputs and outputs were nearly equal. As described in the Methods section, dry deposition was included in mass balances for N and S only (Figure 5). Dry deposition comprised 21%–23% of N inputs and the dominant form was HNO_3 -N with lesser amounts of NH_4^+ -N and NO_3^- -N. Wet deposition of N was dominated by NO_3^- -N (5.3–5.9 kg/ha/yr)

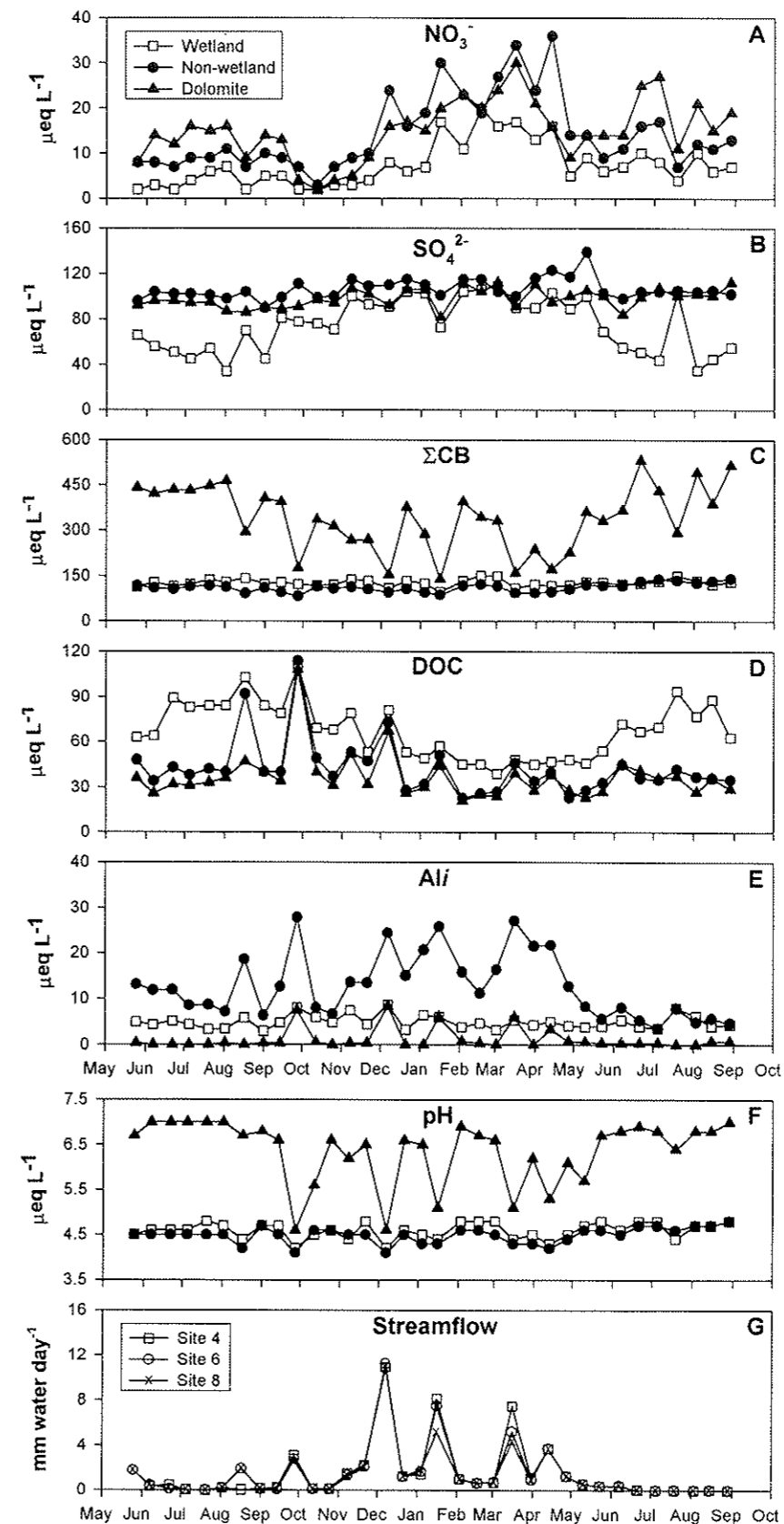


Figure 2. Streamwater chemistry (A-F) and volume (G) from May 1994 through August 1995 at wetland sites (sites 1, 2, 3, and 9), nonwetland sites (sites 4, 6, 7, and 8) and a site containing dolomite in the watershed (site 5).

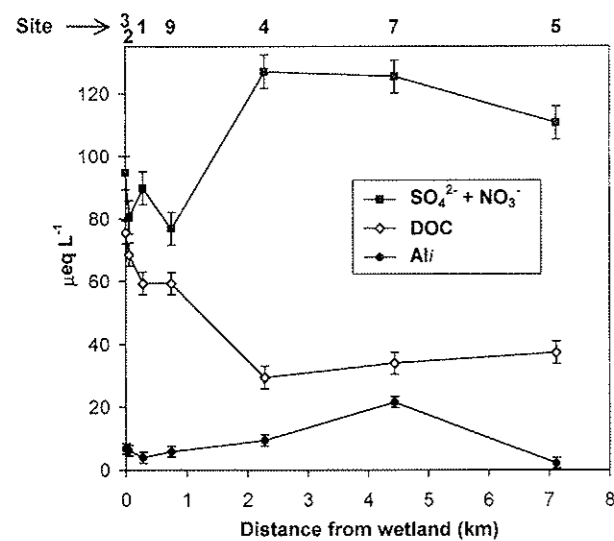


Figure 3. Relationship between the mean annual concentration of ions (1994–1995 water year) at each site and the closest wetland upstream from the site.

with $\text{NH}_4^+\text{-N}$ making up a smaller fraction (2.8–3.1 kg/ha/yr). Streamwater outputs of N consisted almost entirely of $\text{NO}_3^-\text{-N}$, and outputs of $\text{NH}_4^+\text{-N}$ were negligible at all watersheds. Dry deposition comprised 15%–16% of S inputs, primarily as $\text{SO}_2\text{-S}$ (1.4 kg/ha/yr). Most $\text{SO}_4^{2-}\text{-S}$ fell as wet deposition (9.9–11.0 kg/ha/yr) and little was deposited in the dry form (0.5 kg/ha/yr).

Discussion

Increased demand for energy combined with deregulation of electrical utilities in the United States will likely result in the development of new generating capacity in the heavily populated Northeast. This study provides critical data regarding the status of streamwater in LBW, a class I area that has received high levels of acidic deposition for the past 40 years. Federal land managers will be able to use these data in the evaluation of new PSD permits and, with future sampling, monitor trends in streamwater chemistry in response to existing and future changes in air quality.

The data and regulations presented here pertain to a single wilderness area in the northeastern United States; however, the methods used to evaluate its status can be applied to protected lands throughout other regions of the world. The analysis, which relies on a relatively low intensity of field data collection, provides useful data for future comparisons and aids in monitoring air pollution effects in watersheds that receive greater deposition inputs. Since wilderness areas are

relatively pristine and are protected from future increases in atmospheric deposition, they can be used as reference watersheds for comparisons with more highly impacted sites.

To evaluate the current status of LBW streams, we compared our data to cumulative distribution plots of streamwater chemistry data from 159 low-order streams compiled by Hornbeck and others (1997). This comparison indicated that LBW streams are some of the most acidic in New England. The pH of the streamwater at LBW (mean = 4.5, excluding site 5) was lower than 95% of the streams included in this regional data set. Calcium concentrations were lower than all but 12%. Nitrate concentrations were high relative to most other streams in New England, especially for streams included in our study that did not originate in wetlands. Sulfate was the dominant anion at LBW; however, concentrations were lower than about 70% of the streams that were sampled in New England.

Geologic and Pedologic Controls on Inorganic Elements

At LBW, watershed geology and soils strongly affected concentrations of ions in streamwater. Base cation weathering was the dominant factor contributing to increases in stream ANC and pH at site 5, which contains dolomite in the streambed and watershed. The high concentration of soil exchangeable Ca^{2+} at one of the soil pits at site 9 may also be the result of a geologic or pedologic source of Ca^{2+} . However, this is probably a minor source of Ca^{2+} within the watershed because the streamwater at site 9 was relatively acidic. Dolomite is not a major feature of the wilderness and is limited to a small area near the northwest boundary where Lye Brook flows out of the wilderness area. Therefore, site 5 is unique and is not representative of the stream chemistry throughout the wilderness. Most areas of LBW have mineralogical substrates that are highly resistant to chemical weathering and that contain low amounts of BC.

LBW soils sampled in this study had low pH, CEC, and %BS and consequently are not well buffered against incoming acids (Table 3). Reuss and Johnson (1986) found that for soils with pH values greater than 4.5 and %BS greater than 20%, the charge balance of mobile anions such as SO_4^{2-} and NO_3^- is provided by BC and HCO_3^- . For soils with pH values less than 4.5 and BS less than 20%, Al is mobilized and can provide much of the charge balance to mobile acid anions. The pH of soil was below 4.5 for all but one sample and the %BS was between 12% and 20% for the Oa horizon and below 2% for the B and C horizons. Aluminum was the dominant cation

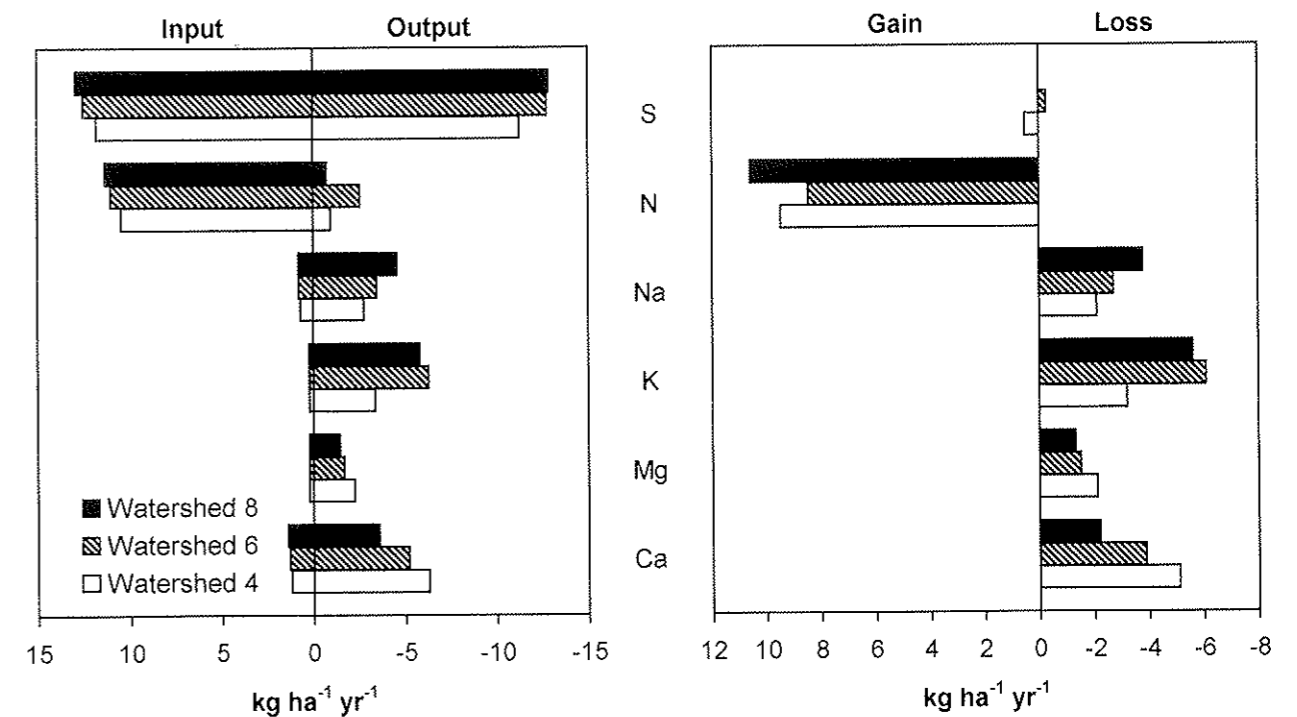


Figure 4. Budgets for major ions (1994–1995 water year) showing inputs in precipitation and outputs in streamflow, and watershed gains or losses. N and S budgets include wet and dry deposition. Budgets for other elements include wet deposition only.

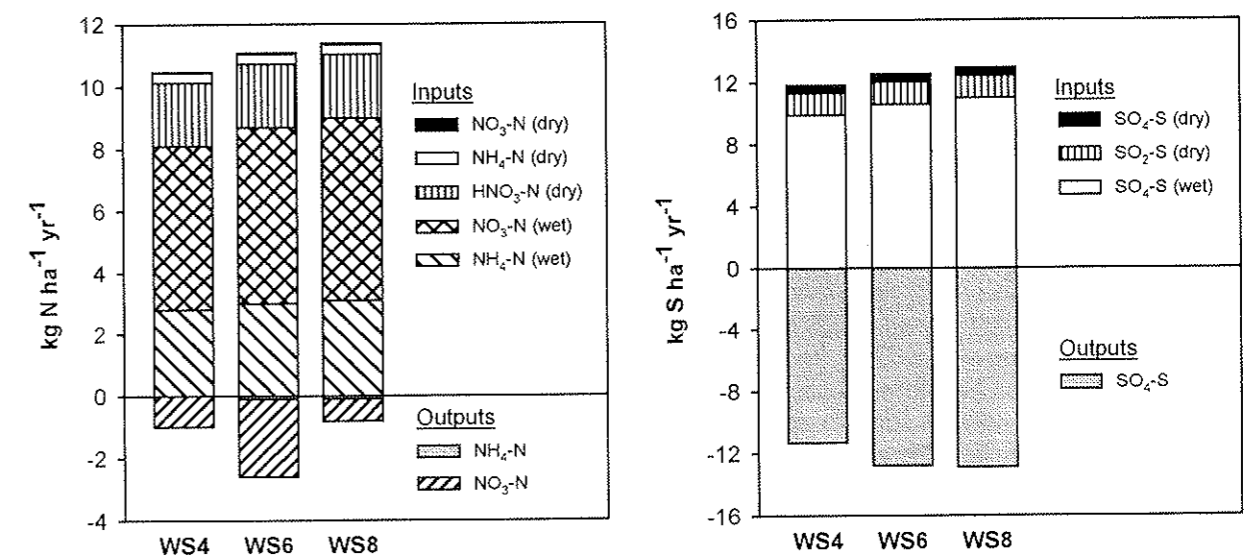


Figure 5. Watershed N and S budgets (1994–1995 water year) indicating wet and dry deposition inputs and streamwater outputs.

on exchange sites in the B and C horizons, occupying 52% and 54%, respectively. Johnson and others (1981) determined that in first- and second-order streams above 700 m in northern New England, acidic deposition inputs are neutralized by Al disso-

lution from the reactive soil matrix, resulting in elevated concentrations of Al³⁺ in streamwater.

In LBW, Al³⁺ poses the greatest threat to aquatic organisms, particularly during high discharge when pH levels are lowest (Figure 2E–G). Three of the sites (sites

6, 7, and 8) had median Al_i concentrations above 100 $\mu\text{g/liter}$, which is a level that is frequently cited as being toxic to fish (Baker and others 1996; Driscoll and others 2001). Fish and macroinvertebrate populations were sampled at sites 5 and 7 during 1993–1995 by the Vermont Department of Environmental Conservation (Kellogg and others 1996). During the three-year period no fish were observed at site 7 (1994–1995 water year median $Al_i = 190 \mu\text{g/liter}$) and three species (brook trout, slimy sculpin, and brown trout) were found each year at site 5 (1994–1995 water year median $Al_i = 10 \mu\text{g/liter}$). Macroinvertebrate sampling indicated a similar trend, with lower densities and taxa richness at site 7 compared to site 5.

The low Ca^{2+} concentrations in streamwater at LBW increases the likelihood of Al_i toxicity to sensitive species, since streams with Ca^{2+} concentrations greater than 100–150 $\mu\text{eq/liter}$ provide better protection against effects of Al_i on aquatic biota (Baker and others 1990). Low BC concentrations in the soils at LBW and low concentrations of Ca^{2+} in streamwater raise concerns about the depletion of Ca^{2+} and other base cations from soils. Likens and others (1996) suggest that depletion of BC from the soil pool can slow the recovery of surface waters affected by acidic deposition. Similarly, BC depletion may also cause streams to be more sensitive to future increases in acidic deposition resulting from local emission sources.

Trends Related to Discharge and Season

The effect of discharge on stream chemistry was examined at the three sites where streamflow was modeled (watersheds 4, 6, and 8). At high discharge, one of the most prominent trends that caused acidity in streamwater was dilution of ΣBC (Figure 2C). During rainstorms, hydrologic flow paths shift from deeper groundwater to shallow soil, which reduces ion exchange between the soil complex and soil water (Mullholland 1993, Ross and others 1994). Concentrations of ΣBC were high during base flow because water moving through the watershed had more contact with the soil, which increased the amount of cation exchange between soil water and the soil exchanger.

At watersheds 4, 6, and 8 there was no significant relationship between SO_4^{2-} and discharge. In some studies, SO_4^{2-} has been shown to accumulate in watershed soils over dry periods followed by subsequent flushing during high discharge (Lynch and Corbett 1989, DeWalle and Swistock 1994). This did not occur in our study, perhaps because there was not adequate time for SO_4^{2-} accumulation between high discharge events. At nonwetland sites, SO_4^{2-} increased during snowmelt runoff, which suggests that SO_4^{2-} that accu-

mulated in the snowpack was released during spring melt (Hornbeck 1986). Wetland sites did not exhibit increases in SO_4^{2-} during snowmelt runoff, presumably because of the initiation of SO_4^{2-} reduction described later.

Nitrate levels did not respond consistently to discharge among the three watersheds, indicating that other factors were important. Since NO_3^- is highly affected by plant uptake and microbially mediated reactions such as N mineralization, nitrification, and denitrification, these processes may have confounded the effect of discharge on NO_3^- concentrations. In LBW streams, N flux was heavily influenced by vegetation during the growing season, which led to a reduction in streamwater NO_3^- . In the northeastern United States, concentrations of NO_3^- generally peak in early spring when soil temperatures increase, and mineralization and subsequent nitrification of N begin before vegetation initiates nutrient uptake (Galloway and others 1987, Rascher and others 1987). At LBW, concentrations of NO_3^- in streamwater increased during the spring, which reduced the pH of streamwater; however SO_4^{2-} remained the dominant strong acid throughout the year.

Effect of Wetlands on Streamwater Nitrate and Sulfate

Sites that drain wetlands appeared to be affected by denitrification and SO_4^{2-} reduction, which are enhanced in semisaturated, anaerobic areas such as these. Johnston and others (1990) found that concentrations of NO_3^- in streamwater were lower at sites in close proximity to wetlands, which was attributed to a combination of plant uptake and denitrification. Since the productivity of wetlands generally exceeds the productivity of terrestrial systems, it can result in greater uptake of NO_3^- . When this factor is coupled with NO_3^- loss through denitrification in wetlands, outlet streams typically have substantially lower NO_3^- concentrations than nonwetland streams.

At LBW, the effect of plant uptake and denitrification on NO_3^- in streams draining wetlands was not as obvious as the effect of SO_4^{2-} reduction on SO_4^{2-} . Wetland sites did appear to have lower concentrations of NO_3^- throughout the year; however, unlike SO_4^{2-} , there were no clear differences in the seasonal pattern of NO_3^- between wetland and nonwetland sites (Figure 2A). During the summer, low NO_3^- concentrations occurred at both wetland and nonwetland sites as a result of uptake by vegetation. This may have depressed NO_3^- levels to a point where denitrification was insignificant. Burford and Bremner (1975) found that denitrification was most rapid in areas where NO_3^- is

readily available; therefore, during the summer when NO_3^- levels are low, denitrification may not play a major role in N dynamics.

A comparison of SO_4^{2-} concentrations among sampling sites revealed that nonwetland sites had higher and relatively stable concentrations throughout the year, whereas wetland sites had lower concentrations, particularly during the summer (Figure 2B). Average SO_4^{2-} concentrations in streams draining wetlands were highest during winter and spring, presumably because of microbial SO_4^{2-} reduction during summer. Several studies have found similar seasonal reductions in SO_4^{2-} concentrations in water passing through wetlands, which decreases the acidity of streams (Bayley and others 1986, Fitzhugh and others 1999).

Organic Matter Exports

The concentration of organic matter in lotic systems varies considerably according to production, consumption, and discharge. Organic fluxes are affected by biotic uptake and subsequent release through decomposition. During periods of high discharge, decomposed organic matter in the watershed may be washed into streams, resulting in an increase in organic matter concentrations (Hruška and others 2001). At LBW, DOC concentrations were higher at sites draining wetlands compared to nonwetland sites, indicating that wetland systems are a source of organic C (Figure 3). Wetlands produce a large amount of biomass and also trap organic matter that washes down from the surrounding uplands. In addition, decomposition is slow in saturated areas, resulting in the accumulation of relatively large quantities of organic matter and subsequently high DOC concentrations in outlet streams (Mullholland and Kuenzler 1979, Dalva and Moore 1991, Mann and Wetzel 1995).

The concentrations of DOC at sites in close proximity to wetlands varied seasonally with highest concentrations occurring during the summer and early fall (Figure 2D). This increase in DOC is likely the result of greater turnover of organic matter due to a combination of primary productivity and microbial decomposition, both of which are enhanced during warmer periods (Dalva and Moore 1991). In addition, during stream base flow conditions, groundwater inputs, which have low concentrations of DOC, are greatly reduced and much of the streamwater is composed of wetland drainage, which is high in DOC relative to groundwater. For nonwetland sites, DOC concentrations were typically low and appeared to be influenced by discharge-related events rather than by biotic activity or seasonal cycles. Storm-related increases in DOC are likely due to a shift to shallower flow paths through

organic soil horizons and leaching of organic compounds from litter (Meyer and others 1988).

Site 8 is unique with respect to DOC because it is a nonwetland site that had DOC concentrations that rivaled concentrations at wetland sites. In other studies, high concentrations of organic C have been linked to watersheds dominated by conifers (Lawrence and others 1986) due to slower litter decay rates of softwood species (Gosz and others 1973, Melillo and others 1982). Soil leachates become enriched with DOC in organic horizons; therefore, higher DOC concentrations are found at sites with thick organic layers. Although the watershed of site 8 is dominated by deciduous species (Table 1), red spruce and balsam fir are prevalent adjacent to the stream channel, which most likely resulted in high concentrations of DOC in streamwater.

Factors regulating organic C concentrations are important because organic C may influence mineral weathering, cation leaching, and trace metal speciation. In this study, streams with high concentrations of DOC typically had a low pH because of the contribution of organic acidity. Organic acids can also cause a reduction in the concentration of Al_i by binding Al_i in less toxic, organic forms (Driscoll and others 1980). In this study, the strong relationship between DOC and Al_i at all sites indicates that Al chelation appeared to be a factor. The LBW wetland sites had low Al_i concentrations, whereas nonwetland sites had high Al_i , particularly those with low pH values. Inorganic Al concentrations were high enough in some of the nonwetland streams to cause damage to acid-sensitive species (Baker and others 1990, 1996, Kellogg and others 1996) (Table 4).

Nutrient Mass Balances

Mass balances at the three study watersheds showed similar trends for gains and losses of ions included in the analysis (Figure 4). Nutrient inputs increased slightly with watershed elevation due to greater precipitation associated with orographic effects. In contrast, outputs of nutrients were generally more variable due to watershed processes discussed previously. There was a net loss of all base cations, indicating the importance of mineral weathering and cation exchange relative to meteorological inputs. Dry deposition of BC was not included in the data presented. Miller and others (1993) indicate that dry deposition comprises a relatively small percentage of total BC inputs for sites at a similar elevation at Whiteface Mountain, New York. Therefore, the inclusion of dry deposition in mass balance calculations for LBW would only slightly increase BC inputs and would not be nearly enough to offset

losses. Over the last two decades there has been a marked decline in the concentration of BC in precipitation (Hedin and others 1994, Lynch and others 1995). Future declines in BC inputs may further reduce the buffering capacity of streamwater and may slow recovery from acidic deposition.

Sulfur inputs and outputs, which include dry deposition, were balanced, indicating that mineral weathering of S is not a major factor in these watersheds. In similar ecosystems SO_4^{2-} outputs are highly related to inputs, which suggests that SO_4^{2-} is sensitive to future changes in atmospheric deposition of S (Friedland and Miller 1999). If the decreasing trend in SO_4^{2-} inputs continues, further reductions in SO_4^{2-} exports would be expected. Decreases in SO_4^{2-} exports may also affect BC exports because of charge balance requirements.

Outputs of NH_4^+ and NO_3^- are less sensitive to atmospheric inputs of inorganic N and ecosystems can retain large amounts of N in vegetation and forest soils (Johnson 1992). At LBW, there was a net gain in total N (8.5–10.6 kg/ha/yr), indicating that more N was added in precipitation than was lost in streamwater. Similar studies show that gaseous loss of N is relatively small (Bowden 1986, Davidson and Swank 1990) and that fixation of gaseous N may increase inputs of N (Bormann and others 1993, Hurd and others 2001). Dissolved organic N (DON) data were not included in the watershed N budgets in this study. However, Campbell and others (2000) show that DON inputs are similar to outputs and do not have a large impact on the overall N budget. Based on the data presented here, the study watersheds are accumulating N; however, it is difficult to estimate this ecosystem's capacity to retain future N inputs.

Conclusion

This research showed that most of the streams at LBW are acidic and have a low ANC, except near the northwest boundary of the wilderness where dolomite is present. Sites that are not underlain by dolomite have a low buffering capacity and are consequently susceptible to acidic deposition. Our research highlights the importance of assessing spatial variability when addressing the effectiveness of the Clean Air Act in protecting air quality related values in class I wilderness areas. Sampling Lye Brook only at its outlet from LBW would mask the sensitivity of the great majority of LBW to increased acidic deposition. Future increases in air pollution in the vicinity of LBW would likely increase streamwater concentrations of SO_4^{2-} , and possibly NO_3^- , causing further reductions in pH and additional mobilization of Al. Increases in streamwater acidity

and Al would be most pronounced in the upper reaches of the LBW watershed and would not be apparent at the base of the watershed due to the dolomitic intrusion at the boundary of LBW.

In this study, decreases in pH were most pronounced during rainstorms and snowmelt runoff. When these episodes occurred, Al concentrations in streams without a wetland influence reached levels that can be toxic to aquatic biota. Wetlands regulate discharge; therefore, episodic acidification was less of a factor at sites with a wetland influence. In addition, wetlands are a source of organic C, which can form complexes with Al. Consequently, concentrations of the more toxic, inorganic forms of Al were low at wetland sites because Al complexed with C, creating less toxic, organic forms of Al. Watershed mass balances showed that S inputs and outputs were balanced and that there was a net loss of BC and a net gain in N. Future changes in atmospheric deposition will likely affect patterns of gains and losses, but the extent of change and time frame of responses are not known.

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