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Streamwater chemistry and nutrient budgets for forested watersheds in New England: variability and management implications

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Abstract

Chemistry of precipitation and streamwater and resulting input–output budgets for nutrient ions were determined concurrently for three years on three upland, forested watersheds located within an 80 km radius in central New England. Chemistry of precipitation and inputs of nutrients via wet deposition were similar among the three watersheds and were generally typical of central New England. In contrast, chemistry and nutrient outputs in streamwater varied dramatically between watersheds, with chemistries ranging from acidic to alkaline. Comparisons with data reported for 159 other upland, forested watersheds in central New England show that our study watersheds span the regional range likely to be encountered in stream chemistry. The regional variability stems in part from past natural disturbances such as wildfire, and variations in source of soil parent material. An approach is presented for predicting the important influence of glacial till on stream chemistry, including acid–base relationships, aluminum content, and nutrient outputs. Knowledge of streamwater chemistry and controlling factors can serve as an index of how terrestrial and aquatic ecosystems will respond to forest management activities and atmospheric deposition. © 1997 Elsevier Science B.V.

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1. Introduction

A variety of factors affect biogeochemical cycling in forested watersheds, including mineral weathering, soil and hydrologic characteristics, vegetation, climate, biological processes, and natural and human disturbances. Some knowledge of these factors and their variability is needed when assessing potential impacts of forest disturbances, or when attempting to extrapolate research results to managed forests.

Forested watersheds in central New England are a case in point. Research at the Hubbard Brook Experimental Forest in New Hampshire has documented changes in stream chemistry and nutrient budgets owing to forest harvests (Hornbeck et al., 1987; Lawrence et al., 1987; Lawrence, 1990). However, Martin et al. (1984) showed that baseline stream

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chemistry and responses to harvest are highly variable between forested watersheds at other locations in New England, and may or may not resemble results found at Hubbard Brook. Likewise wide differences have been found across the region in responses of aquatic and terrrestrial nutrient budgets to atmospheric deposition and whole-tree clearcutting (Buso et al., 1984; Federer et al., 1989; Hornbeck et al., 1990). To better apply research results, it is necessary to more fully understand inter-watershed variability in stream chemistry and nutrient budgets and the controlling factors.

In this paper, we present chemical content of precipitation and streamwater and subsequent input–output budgets of nutrients for three gaged, upland, forested watersheds selected to span acidic to alkaline conditions. Cone Pond Research Watershed with a mean annual stream pH of 4.4 represents an acidic end member for central New England. Sleepers River Research Watershed 9 with a mean annual stream pH of 7.6 represents an alkaline end member. Hubbard Brook Experimental Forest Watershed 6 with a mean annual stream pH of 5.0 is an intermediate. Supplementary information collected for these watersheds is used to explain differences in nutrient budgets and streamwater chemistry and show applications for managing and protecting forest ecosystems.

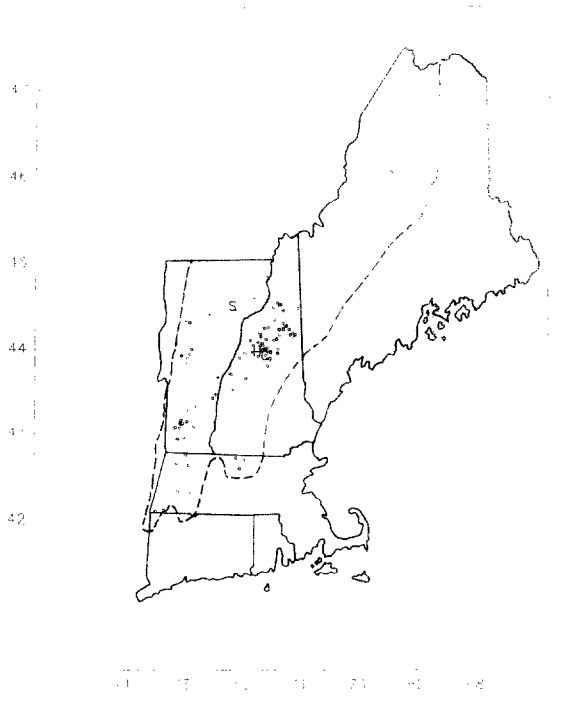

Fig. 1. Location of study watersheds: Sleepers River (S), Hubbard Brook (H) and Cone Pond (C). The dashed line is the boundary for Province M212: New England mixed forest, coniferous forest, alpine meadow. Circles are locations of upland, forested watersheds with one or more stream chemistry records (see text for references). The vertical and horizontal grids are longitude and latitude.

2. Study sites and methods

The three study watersheds are located within an 80 km radius in central New England (Fig. 1). They lie in the heart of the Appalachian–New England Mixed Forest–Coniferous Forest–Alpine Meadow Ecological Province (M212) (Fig. 1), and have characteristics generally representative of ecological sections designated White Mountains (M212-A), New England Piedmont (M212-B), and Green, Taconic, Berkshire Mountains (M212-C) (McNab and Avers, 1994). These three sections comprise 80 000 km^2 of glaciated uplands that are currently 80–90% forested. Dominant land uses are recreation and production of wood for timber and pulp, thus placing importance on quality of forest streams and site productivity.

Specific characteristics of the study sites are summarized in Table 1. The Cone Pond watershed has never been harvested, but the mixed conifer forest was subjected to blowdown during a hurricane in 1815 and a subsequent, severe wildfire around 1820, and to substantial blowdown again during a 1938 hurricane (Buso et al., 1984). The Hubbard Brook watershed was harvested around 1910 (Likens, 1985) and Sleepers River was clearcut in 1929 (Thorne et al., 1988). After the harvests, watersheds at both locations regenerated naturally to northern hardwood species.

Volume of streamflow is measured continuously at all three watersheds with v-notch weirs. At Hubbard Brook the v-notch weir is operated in tandem with a rectangular flume for measuring high flows. Volume of precipitation is sampled with two or more standard gages measured weekly. Data are tabulated on a daily basis with precipitation being prorated, based on time of catch, by a recording gage located

Table 1
Description of study sites

Site (size)	Elevation (m)	Bedrock formations	Principal soil types	Forest type; age
Cone Pond (33 ha)	480–650	Perry Mountain (schists and quartzites)	Coarse, loamy, mixed, frigid, Typic and Lithic Haplorthod	Mixed northern hardwoods and conifers; all ages to 260 years
Hubbard Brook (12 ha)	550–810	Upper Rangeley (schists and quartzites)	Coarse, loamy, mixed, frigid, Typic Haplorthod	Northern hardwoods; even aged 80–90 years
Sleepers River (41 ha)	520–675	Waits River and Gile Mountain (schists)	Coarse, loamy, mixed, mesic, Typic Eutrochrept	Northern hardwoods; even aged 60–70 years

at each site. For chemical determinations, precipitation was sampled with polyethylene, bulk collectors exposed for weekly intervals (Likens et al., 1977). Streams were sampled just upstream of each weir by taking weekly grab samples. All samples were analyzed for pH, Ca^{2+}, Mg^{2+}, Na^{+},K^{+}, Al^{3+}, NH_4^+, SO_4^{2-}, NO_3^-, Cl^- and dissolved organic carbon (DOC) using potentiometry for pH and either automated colorimetric analysis, direct current plasma, or atomic absorption for other constituents (Bailey et al., 1995). Bicarbonate, the dominant anion in streamflow at the Sleepers River watershed, was determined by assuming, based on the range in pH and low DOC, that all acid neutralizing capacity (ANC) equals HCO_3^-. ANC was determined by Gran-plot analysis using an automated, electrometric titration with NBS-traceable 0.02 N HCl to a pH endpoint of approximately 3.5. PO_4^{3-} was determined periodically at all sites, but was always below the detection level of 0.003 mg L^{-1}.

This paper focuses on annual values for both concentrations and nutrient budgets for 1 October through 30 September water years for 1991–1992, 1992–1993, and 1993–1994, the period during which overlapping data were collected at all three sites. An October through September water year was chosen, rather than a calendar year, to minimize impacts of carryover of nutrients in snowpacks and soil solution. Nutrient inputs in precipitation and outputs in streamwater were obtained by multiplying the weekly ionic concentrations (mg L^{-1}) by measured daily water flux (L ha^{-1} per day). Daily mass inputs and outputs were summed over the water year and are reported as kg ha^{-1} per year. In keeping with past convention (Likens et al., 1977), inputs minus streamwater outputs are used to express net gains or losses from the watersheds. Mean annual concentrations for ions in precipitation and streamwater were obtained by dividing the annual mass flux by the annual water flux. The ion concentrations are expressed as μeq L^{-1} to facilitate comparisons of ion balances and strengths.

3. Results

3.1. Hydrologic budgets

As transport media, precipitation and streamflow have significant roles in determining annual nutrient budgets. Data from extremely wet or dry years can be misleading. Long-term records show annual pre-

Table 2
Hydrologic budgets for water years 1991–1992, 1992–1993, and 1993–1994

Category	Cone Pond			Hubbard Brook			Sleepers River		
	91–92	92–93	93–94	91–92	92–93	93–94	91–92	92–93	93–94
Precipitation	1260	1110	1260	1380	1320	1400	1170	1280	1300
Streamflow	690	520	650	890	830	890	640	660	720
ET	570	590	610	490	490	510	530	620	580

All values are millimeter depth for the entire watershed.

Table 3
Ionic composition and balances ($\mu eq\,L^{-1}$) and pH for precipitation, water years 1991–1992, 1992–1993, and 1993–1994

Ion type	Cone Pond			Hubbard Brook			Sleepers River		
	91–92	92–93	93–94	91–92	92–93	93–94	91–92	92–93	93–94
Calcium (Ca^{2+})	3	3	4	3	4	4	5	6	7
Magnesium (Mg^{2+})	1	2	2	2	2	2	2	1	3
Potassium (K^{+})	2	2	2	1	1	1	3	2	3
Sodium (Na^{+})	4	5	5	5	4	5	3	2	3
Aluminum (Al^{3+})	1	1	1	1	1	2	1	1	1
Ammonium (NH_4^{+})	13	15	15	11	13	14	12	9	20
Hydrogen (H^{+})	52	58	47	54	57	49	39	47	37
(pH)	(4.28)	(4.23)	(4.33)	(4.26)	(4.24)	(4.31)	(4.41)	(4.33)	(4.43)
Sulfate (SO_4^{2-})	42	43	36	43	45	41	34	36	39
Nitrate (NO_3^{-})	25	30	23	27	27	28	23	24	22
Chloride (Cl^{-})	6	6	6	6	6	7	4	3	4
Sum cations	76	86	76	77	82	77	65	68	74
Sum anions	73	79	65	76	78	76	61	63	65

cipitation averages of 1100 mm at Sleepers River (Thorne et al., 1988) and 1420 mm at Hubbard Brook (Federer et al., 1990). Thus annual precipitation values for the three years of our study (Table 2) were close to long-term means. Streamflow ranged from 520 to 890 mm, or about 50–60% of precipitation (Table 2). Seepage losses to ground water are thought to be minimal for all three study watersheds so most of the difference between precipitation and streamflow, ranging from 490 to 620 mm, represents moisture returned to the atmosphere through evapotranspiration. These values fall close to the range of 450–600 mm for estimated annual evapotranspiration over a 30-year period at Hubbard Brook (Federer et al., 1990).

3.2. Nutrient concentrations and ion balances

Cone Pond and Hubbard Brook receive precipitation of nearly identical chemical composition,

Table 4
Ion composition and balances ($\mu eq\,L^{-1}$) and pH for streamflow, water years 1991–1992, 1992–1993, and 1993–1994

Ion type	Cone Pond			Hubbard Brook			Sleepers River		
	91-92	92-93	93-94	91-92	92-93	93-94	91-92	92-93	93-94
Calcium (Ca^{2+})	29	29	29	43	39	40	1001	1045	996
Magnesium (Mg^{2+})	13	14	14	20	18	18	83	85	81
Potassium (K^{+})	4	3	3	4	4	4	31	31	29
Sodium (Na^{+})	26	26	30	30	29	31	28	29	27
Aluminum (Al^{3+})	58	60	59	23	24	28	2	3	3
Ammonium (NH_4^{+})	3	2	1	1	2	1	1	1	1
Hydrogen (H^{+})	39	38	39	11	12	10	0	0	0
(pH)	(4.41)	(4.42)	(4.41)	(4.97)	(4.92)	(5.00)	(7.62)	(7.56)	(7.53)
Sulfate (SO_4^{2-})	131	135	139	101	97	100	158	157	163
Nitrate (NO_3^{-})	0	0	0	5	4	3	18	12	11
Chloride (Cl^{-})	22	17	20	11	11	13	9	9	11
Bicarbonate (HCO_3^{-})	0	0	0	0	0	0	936	952	954
Sum cations	172	172	175	132	129	132	1146	1194	1137
Sum anions	153	152	159	117	112	116	1121	1130	1139

whereas precipitation at Sleepers River is slightly more dilute (Table 3). Hydrogen is the dominant cation in precipitation at all sites, giving rise to an average annual pH of 4.2–4.4. Base cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) make up minimal proportions of the ion balance in precipitation, but there is greater than 10 $\mu eq\,L^{-1}$ of NH_4^+, an important source of N for plants. Sulfate and NO_3^- are the dominant anions in precipitation and reflect anthropogenic emissions (Butler and Likens, 1991). The small component of Cl^- reflects the inland locations, away from marine sources.

In contrast to precipitation, chemistry of streamwater is much more variable between study watersheds (Table 4). Concentration owing to evapotranspiration could be expected to cause about a two-fold enrichment in base cations in streamwater compared to precipitation. However, actual enrichment in streamwater compared to precipitation is by about four times at Cone Pond, eight times at Hubbard Brook, and 100 times at Sleepers River. Sleepers River also has far greater HCO_3^-, producing a mean annual stream pH of 7.6 compared to 5.0 at Hubbard Brook and 4.4 at Cone Pond. Aluminum concentrations increase almost two orders of magnitude from Sleepers River to Hubbard Brook to Cone Pond reflecting increased solubility of Al at lower pH.

Streamwater concentrations for NH_4^+ decrease by an order of magnitude compared to precipitation

Table 5
Input–output budgets (kg ha^{-1} per year), water years 1991–1992, 1992–1993, and 1993–1994

Water year	In; out; net	Ca^{2+}	Mg^{2+}	K^+	Na^+	Al^{3+}	H^+	NH_4^+-N	NO_3^--N	SO_4^{2-}-S	Cl^-
Cone Pond											
1991–92	In	0.6	0.2	0.8	1.3	0.1	0.7	2.9	4.3	8.5	2.7
	Out	4.0	1.1	1.0	4.2	4.7	0.3	0.3	0.0	14.4	5.4
	Net	−3.4	−0.9	−0.2	−2.9	−4.6	0.4	2.6	4.3	−5.9	−2.7
1992–93	In	0.8	0.2	1.0	1.2	0.1	0.6	2.3	4.6	7.5	2.3
	Out	3.0	0.9	0.7	3.1	3.7	0.2	0.2	0.0	11.3	3.1
	Net	−2.2	−0.7	0.3	−1.9	−3.6	0.4	2.1	4.6	−3.8	−0.8
1993–94	In	1.1	0.3	0.7	1.3	0.1	0.6	2.5	4.1	7.3	2.8
	Out	3.8	1.1	0.7	4.5	4.5	0.3	0.1	0.0	14.4	4.7
	Net	−2.7	−0.8	0.0	−3.2	−4.4	0.3	2.4	4.1	−7.1	−1.9
Hubbard Brook											
1991–92	In	0.9	0.3	0.6	1.4	0.1	0.8	2.2	5.1	9.4	2.8
	Out	7.6	2.2	1.4	6.1	2.4	0.1	0.2	0.6	14.4	3.3
	Net	−6.5	−1.9	−0.8	−4.7	−2.3	0.7	2.0	4.5	−5.0	−0.5
1992–93	In	1.0	0.3	0.6	1.4	0.2	0.8	2.4	5.0	9.4	2.6
	Out	6.5	1.9	1.4	5.5	2.4	0.1	0.2	0.4	12.8	3.1
	Net	−5.5	−1.6	−0.8	−4.1	−2.2	0.7	2.2	4.6	−3.4	−0.5
1993–94	In	1.2	0.4	0.7	1.7	0.2	0.7	2.7	5.5	9.2	3.6
	Out	7.1	2.0	1.4	6.4	3.0	0.1	0.1	0.3	14.1	4.3
	Net	−5.9	−1.6	−0.7	−4.7	−2.8	0.6	2.6	5.2	−4.9	−0.7
Sleepers River											
1991–92	In	1.5	0.2	1.2	0.8	0.1	0.5	1.9	3.7	6.4	1.6
	Out	137.0	6.4	7.6	4.1	0.0	0.0	0.1	1.6	16.1	2.0
	Net	−135.5	−6.2	−6.4	−3.3	0.1	0.5	1.8	2.1	−9.7	−0.4
1992–93	In	1.5	0.2	1.0	0.7	0.1	0.6	1.7	4.2	7.3	1.2
	Out	137.0	6.7	7.9	4.4	0.1	0.0	0.1	1.1	16.4	2.1
	Net	−135.5	−6.5	−6.9	−3.7	0.0	0.6	1.6	3.1	−9.1	−0.9
1993–94	In	1.9	0.4	1.7	0.8	0.1	0.5	3.7	4.0	8.0	1.9
	Out	143.9	7.0	8.2	4.5	0.1	0.0	0.1	1.1	18.9	2.7
	Net	−142.0	−6.6	−6.5	−3.7	0.0	0.5	3.6	2.9	−10.9	−0.8

(Table 4), most likely as a result of plant uptake. Nitrate in streams at all three locations is well below precipitation values, especially at Cone Pond where it seldom reaches detection levels. Sulfate concentrations are highest at Sleepers River, intermediate at Cone Pond, and lowest at Hubbard Brook.

The annual ion balances are reasonably close for all sites (Tables 3 and 4), indicating that no important ions are missing from the analyses. The small anion deficit for Hubbard Brook and Cone Pond streams may reflect unmeasured organic anions. Dissolved organic carbon averaged 4.2 mg L^{-1} at Cone Pond, 2.0 mg L^{-1} at Hubbard Brook, and 1.1 mg L^{-1} at Sleepers River, suggesting a potential for greater organic anion concentrations at Cone Pond and Hubbard Brook. In fact, if dissolved, organic carbon is assigned a negative charge of 6.1 μeq mg^{-1} as suggested by Bailey et al. (1995), the ion balances for Cone Pond and Hubbard Brook fall nearly in line.

3.3. Input–output budgets

Table 5 summarizes mean annual inputs in precipitation, outputs in streamflow, and net gains or losses over the three years of data collection. Annual inputs in bulk precipitation were fairly uniform for all sites, although Sleepers River experienced slightly lower inputs of H, SO_4^{2-}-S, and NO_3^--N owing to lower acid content and volume of precipitation. Annual inputs of SO_4^{2-}-S ranged from 6.4 kg ha^{-1} at Sleepers River to a maximum of 9.4 kg ha^{-1} at Hubbard Brook. Total inorganic N inputs (NO_3^--N plus NH_4^+-N) averaged about 7 kg ha^{-1} per year and were proportioned approximately two-thirds NO_3^--N to one-third NH_4^+-N.

The most striking differences in annual outputs are for base cations, especially Ca^{2+}. Sleepers River had 14 times greater Ca^{2+} outputs in streamflow than Hubbard Brook and 26 times greater outputs than Cone Pond. All three sites experienced substantial outputs of SO_4^{2-}-S, ranging from 11.3 to 18.9 kg ha^{-1} per year (Table 5). Total inorganic outputs for N were small with the maximum being 1.7 kg ha^{-1} per year at Sleepers River.

Over the study period, all sites showed net gains (inputs exceeded outputs) of inorganic N ranging from 3.9 to 7.8 kg ha^{-1} per year. There were also net gains for H^+. Otherwise, all base cations, SO_4^{2-}-S, and Cl^- showed net losses (Table 5).

4. Discussion

4.1. Regional comparisons and representation

The chemistry and bulk inputs for precipitation are fairly uniform among our three study sites. Comparison with maps and tables of wet deposition from the monitoring network operated by the National Atmospheric Deposition Program (1994) shows that values for our study sites are consistent with network sites across interior New England. Stream chemistry was much more variable between our three study sites and additional data were assembled to determine how our sites represent Ecological Province M212. A survey of literature and other sources turned up stream chemistry data for 159 small, upland, predominantly forested watersheds within the Province (Fig. 1) (Johnson and Reynolds, 1977; Martin, 1979; Hornbeck and Kropelin, 1982; Langdon, 1983, 1985; Buso et al., 1984; Martin et al., 1984; Kahl et al., 1993; Kellogg et al., 1994; Ross et al., 1994; and D. Buso, J. Campbell, M. Mattson, J. Kellogg, S. Jones, and USDA Forest Service, personal communication, 1995). These data had been collected for a variety of purposes and range from single to many observations. For sites with multiple observations, we calculated an arithmetic mean to arrive at a single value. Our comparisons used pH and the three most commonly reported ions, Ca^{2+}, NO_3^-, and SO_4^{2-}. The plotted values for Cone Pond, Hubbard Brook, and Sleepers River (designated C, H, and S in Fig. 2) are means for the three-year period of overlapping records.

Cumulative frequency plots (Fig. 2) show that stream pH values within the province are fairly evenly distributed across pH values ranging from 3.5 to 7.8 with a median pH of about 6.0. Most streams have relatively low levels of Ca^{2+}: only 29 of the 159 sampled streams had Ca^{2+} concentrations exceeding 200 μeq L^{-1}, and median Ca^{2+} concentration is about 100 μeq L^{-1}. Cone Pond is among the most acidic and has among the lowest Ca^{2+} concentrations of streams sampled within the province (Fig. 2). Streamflow from our study watershed at Hubbard Brook also has Ca^{2+} concentrations and pH well below the median for all sampled streams. In contrast, only three sampled watersheds in the province had higher Ca^{2+} and pH than Sleepers River (Fig.

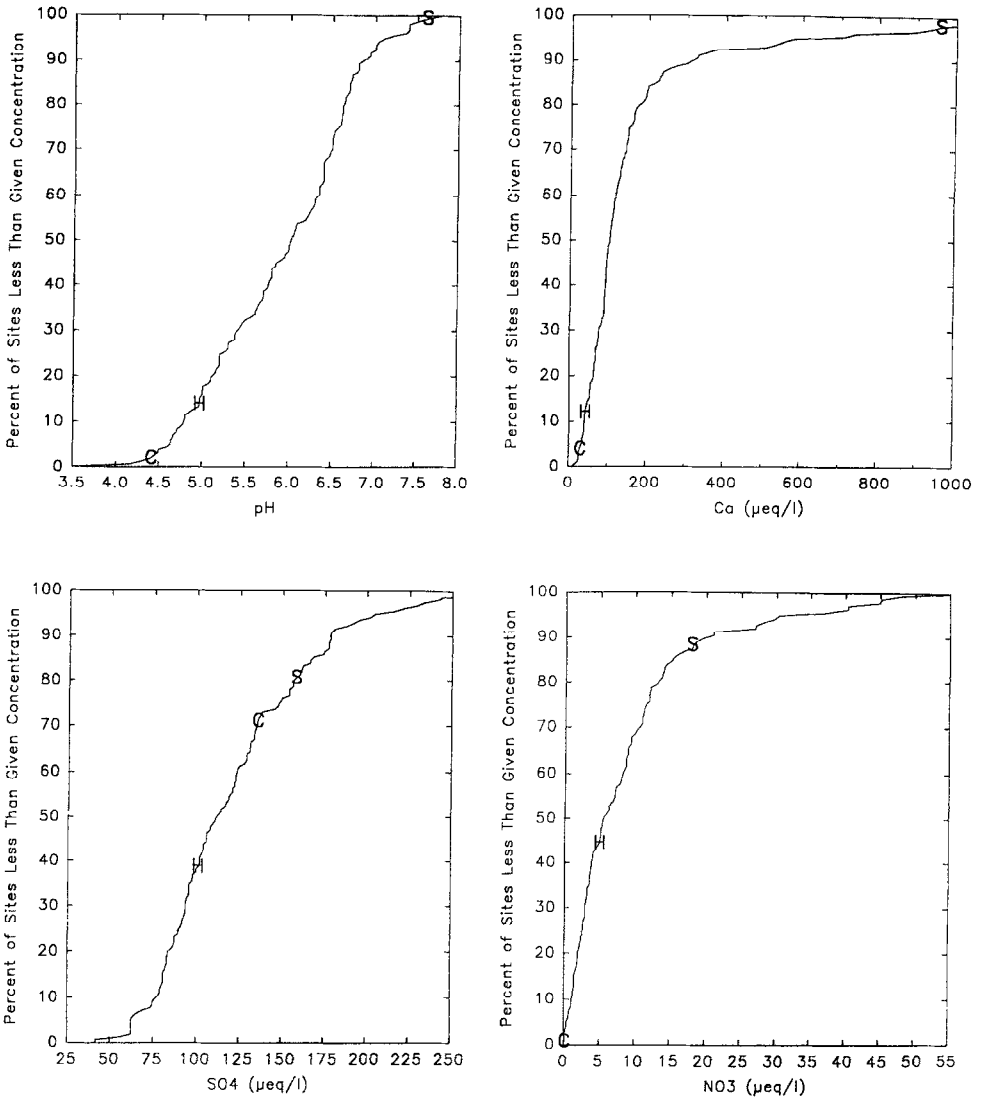

Fig. 2. Cumulative distribution plots for streamwater pH and concentrations of Ca^{2+}, SO_4^{2-} and NO_3^- for 159 small, upland, forested watersheds. Mean values for Cone Pond, Hubbard Brook and Sleepers River are shown by C, H, and S.

2). These three sites have geology characterized by nearly pure carbonate as opposed to Sleepers River where carbonates are included in formations that are predominantly silicate. Stream data for Hubbard Brook and Cone Pond (Table 4) suggest that reduced levels of Ca^{2+} may be countered by increasing levels of Al.

Sulfate concentrations in streams from our study watersheds are more typical of the province, although Hubbard Brook is below the median ($110\,\mu eq\,L^{-1}$) and Cone Pond and Sleepers River are well above (Fig. 2). Sulfate is the dominant anion in most of the sampled streams and as would be expected, SO_4^{2-} and Ca^{2+} mobility are related as reflected by a positive and strong correlation ($r = 0.82$; $P < .001$). The long-term record of 31 years at

Hubbard Brook Experimental Forest shows a similar, strong relationship of streamwater SO_4^{2-} to Ca^{2+} ($r = 0.95$; $P < .001$).

Nitrate concentrations are generally low. The absence of detectable NO_3^- occurred at Cone Pond and four other sample locations (Fig. 2). Hubbard Brook lies near the middle of the range for NO_3^- in sampled streams while Sleepers River is toward the upper end. There is a weak correlation ($r = 0.28$) between NO_3^- and Ca^{2+} concentrations for sampled streams, but because NO_3^- concentrations are low, Ca^{2+} mobility is tied much more strongly to SO_4^{2-}.

The cumulative frequency plots show that there is wide variability in stream chemistry across the 80 000 km^2 province. Hubbard Brook is the most regionally representative of our three study sites, and Cone Pond and Sleepers River are more representative of regional extremes for important stream parameters such as pH, Ca^{2+}, and NO_3^-.

Supplemental information obtained as part of research programs at our three study watersheds help explain some of the between-watershed and within-region variability in stream chemistry, and point to some implications for forest and aquatic management and protection.

4.2. Base cations

Since factors such as soil physical and hydrologic characteristics and atmospheric deposition are relatively similar between our study watersheds, differences in base cation fluxes to streams are most likely reflecting differences in chemical weathering. However, predicting the role of rock weathering is complex for glaciated terrains of central New England. Most estimates of base cation potential are based on bedrock maps (e.g. Omernik and Powers (1982)). However, surficial till deposits, usually derived from off-site, can be more influential than underlying bedrock as sources of cations for forest streams. Pleistocene glaciation removed essentially all pre-existing soils and surficial deposits from central New England. Present day soils are developed on till, ice contact, and associated outwash deposits left by the last one or two stages of the Wisconsinan Laurentide ice sheet (Koteff and Pessl, 1985). Because soils are developed on transported materials, the chemical and mineralogical composition of the soil parent material reflects a variety of lithologic sources eroded and deposited by the glacier. Resulting spatial variation greatly complicates the assessment of weathering reaction rates and contributions.

Bailey and Hornbeck (1992) devised methods for predicting bedrock sources for soils developed on glacial till parent material, and the potential weathering contributions from rock particles greater than 2 mm in diameter. Although the methods are not yet quantitative, they can provide information about the relative importance of sources for base cations. The methods were developed and tested on the Cone Pond watershed and involve superimposing a source envelope on a bedrock geological map, with the base of the envelope located at the watershed of interest (Fig. 3). The envelope is based on earlier research by Goldthwaite et al. (1951) which showed that 32 km was about the maximum distance rocks were transported by the glacier before being deposited in till, or disintegrating into sand/silt size fractions. Their research also showed that from an initial point, rocks were dispersed in a 60° arc about the mean direction of glacial movement. Thus the envelope devised by Bailey and Hornbeck (1992) extends 32 km "up-glacier" from the watershed in question, and includes all bedrock types within ±30° of the direction of regional glacial movement. For the study region, this direction is an azimuth of 151°.

As a first approximation, Bailey and Hornbeck (1992) hypothesized that each bedrock type contributed to the parent material in proportion to its area in the envelope. The hypothesis was tested by comparing predicted occurrence of bedrock types planimetered from the till source area against observed occurrence of bedrock types in five pits located to represent elevations, soil depths, and forest-cover types at Cone Pond. While there were discrepencies in the predicted versus observed occurrences at Cone Pond (Table 6), the predicted occurrences proved useful for understanding base cation supplies and fluxes at Cone Pond (Bailey and Hornbeck, 1992). Thus we used the same methods to develop bedrock source envelopes for Hubbard Brook and Sleepers River watersheds (Fig. 3) and to determine predicted lithologic composition of soils (Table 6).

Comparison of predicted rock types in till for our study watersheds helps to explain differences in base

Table 6
Predicted till source areas for all study watersheds (%), and observed occurrence at Cone Pond (%) based on sampling of rock fragments in soils

Rock type	Cone Pond		Hubbard Brook	Sleepers River
	Predicted area (%)	Observed area (%)	Predicted area (%)	Predicted area (%)
Diabase	0	1	–	–
Garfield quartz syenite	1	1	–	–
Conway granite	8	4	–	–
Mount Osceola granite	4	1	–	–
Lafayette granite porphry	2	1	–	–
Kinsman quartz monzonite	39	28	18	–
Bethlehem granite gneiss	8	5	13	–
undifferentiated Devonian–Silurian metapelites & quartzites	30	45	41	–
Ammonoosuc Volcanics: amphibolite	6	1	22	–
Oliverian granite	2	5	2	–
Concord granite	–	–	4	–
undifferentiated Devonian granites	–	–	–	5
Gile Mountain Fmm: metapelite	–	–	–	25
Waits River Fmm: metalimestone	–	–	–	53
Missisquoi Fmm: metapelite & quartzite	–	–	–	17
Total	100	100	100	100

cation fluxes, and also demonstrates the value of incorporating till composition in the evaluation. For example, Ca^{2+} concentrations in streams at Hubbard Brook are about 60% higher and net losses of Ca^{2+} are about two times greater than at Cone Pond (Tables 4 and 5). Cone Pond and Hubbard Brook watersheds have different underlying bedrock formations (Table 1), but the formations are relatively similar in lithologic composition (pelite schists and quartzites), suggesting that something more than underlying bedrock is affecting Ca^{2+} fluxes. Comparison of source envelopes shows that Ammonoosuc Volcanics account for 22% of the source area for the Hubbard Brook watershed versus only 6% of the source area for Cone Pond (Fig. 3 and Table 6). Ammonoosuc Volcanics is the only bedrock formation in the vicinity with a large amount of hornblende (Billings, 1956), a relatively unstable mineral in the weathering environment, and a major source of Ca^{2+} weathering. Another major mineral in the Ammonoosuc Volcanics is plagioclase feldspar, also an important source of Ca^{2+}. The presence of Ammonoosuc Volcanics as a source for Hubbard Brook soils may result in higher hornblende and plagioclase content relative to Cone Pond, and increase weathering rates sufficiently to explain the greater net Ca^{2+} loss from Hubbard Brook.

Comparisons of predicted till composition and the underlying bedrock at Sleepers River (Table 6 and Fig. 3) explain the much higher base cation outputs at Sleepers River. Both the bedrock and till are composed of Ca and Mg carbonates which are extremely unstable in the weathering environment. In fact, they weather several orders of magnitude faster than silicates, and thus produce the high base cation and HCO_3^- concentrations in Sleepers River streamwater (Table 3).

In an attempt to further quantify the above ideas, rock types from Table 6 were grouped into four general categories. Average Ca contents of each group were calculated from published analyses (Hall, 1959; Billings and Wilson, 1964) (Table 7). The published Ca contents were multiplied by percentages of till source areas to predict Ca content of soil parent material (Table 7). The predicted values are in good agreement with measured values for total Ca obtained by acid digestion of three soil samples from C horizons on each watershed (Table 7). The agree-

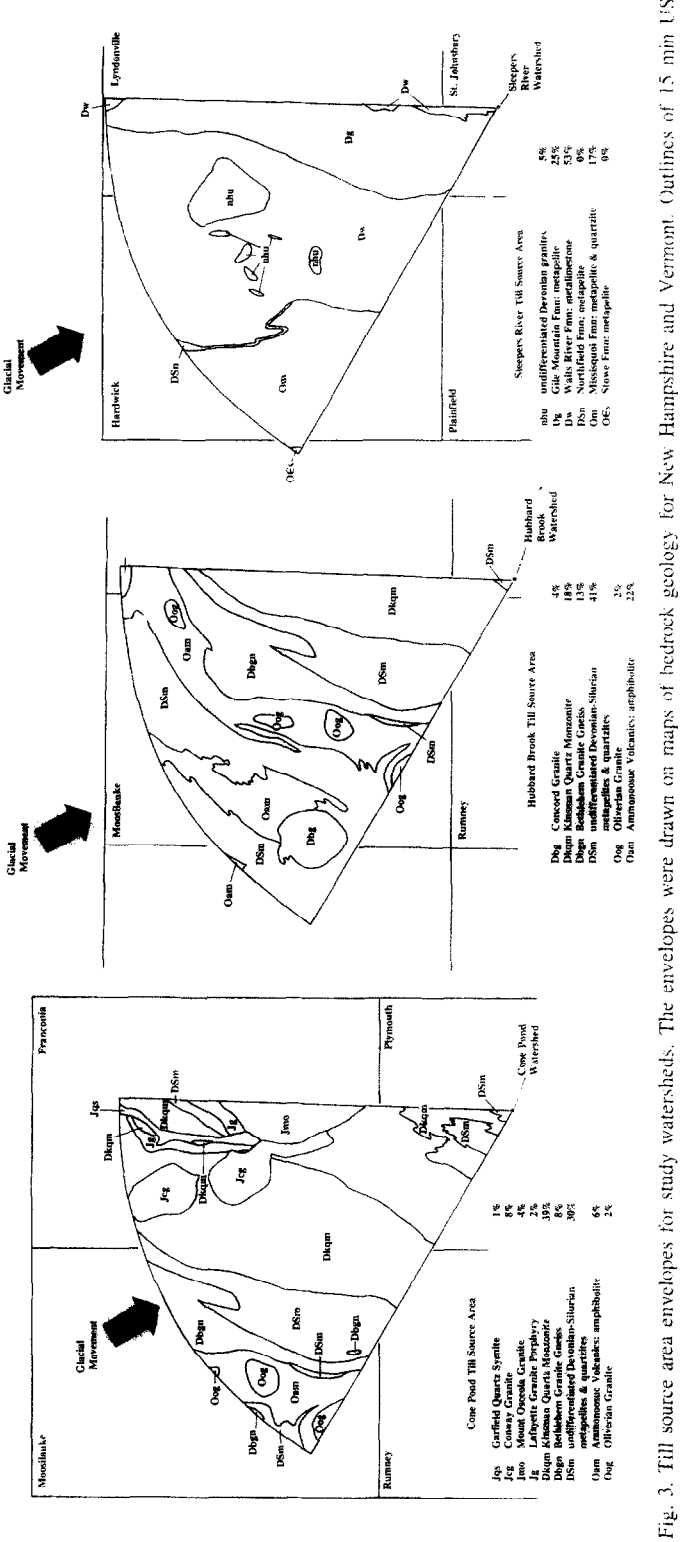

Fig. 3. Till source area envelopes for study watersheds. The envelopes were drawn on maps of bedrock geology for New Hampshire and Vermont. Outlines of 15 min US Geological Survey quadrangles show location.

Table 7
Predicted and measured Ca as % of soil parent material

General rock type	Ca content of rocks	Till source area:		
		Cone Pond	Hubbard Brook	Sleepers River
Granite & granite gneiss	1.43	64	37	5
Metapelites & metasandstones	0.71	30	38	42
Metalimestone	12.20	0	3	53
Metavolcanic	2.14	6	22	0
Ca in C horizon				
Predicted		1.3	1.6	6.8
Measured		1.8 ± 0.1	1.4 ± 0.1	6.1 ± 0.2

Predicted values are obtained by multiplying individual till source areas by Ca content of rocks, then summing for all till source areas.

ment is further evidence that glacial till materials strongly influence base cations levels in soils and streams, and also suggests the possibility of using till source area envelopes as an index of base cation budgets and streamwater concentrations.

4.3. Nitrogen budgets

Lovett and Lindberg (1993) found that for lower elevation forests like those on our study watersheds, dry deposition of N averaged 85% of values for wet deposition. Thus an estimate for sum of wet plus dry deposition for our sites would be about 13 kg of N per hectare per year (7 kg wet (Table 5) and 6 kg dry). Outputs of inorganic N in streams are small, averaging < 1 kg of N per hectare per year. We have only recently begun to determine dissolved organic N at our study sites using a new high-temperature, catalytic oxidation technique (Merriam et al., 1996). Preliminary data show dissolved organic N is in the range of 0.1–0.2 mg L^{-1}, which places outputs of dissolved organic N at around 1 kg of N per hectare per year or similar to inorganic N outputs. The relatively small outputs of N in streamwater coupled with estimated gaseous losses of less than 1 kg of N per hectare per year for temperate forests (Bowden, 1986) suggest that all three sites are accumulating N at a substantial rate. This is despite estimates that forests at Cone Pond and Hubbard Brook are at near steady state regarding tree biomass (Bailey et al., 1996; Likens et al., 1996).

The rate of accumulation is least at Sleepers River owing to slightly lower deposition and greater outputs in streamflow (Table 5). Sleepers River had over two times greater outputs of NO_3^--N than Hubbard Brook, compared to no detectable outputs of NO_3^--N from Cone Pond. More of the NO_3^- in precipitation may escape uptake or other forms of immobilization at Sleepers River, possibly owing to deeper soil water pathways. Also, Thorne (1985) showed that conditions for nitrification such as soil pH, total N capital, available NH_4^+, and C:N ratios are more favorable at Sleepers River than at Hubbard Brook and Cone Pond.

The near-absence of NO_3^- in streams at Cone Pond is puzzling. Vitousek and Reiners (1975) suggested that mature forests like those at Cone Pond are inefficient at cycling N and would thus have higher NO_3^- concentrations in streamflow. This relationship was in fact documented using six watersheds in New Hampshire (Leak and Martin, 1975).

Studies of canopy throughfall at Cone Pond show that concentrations of NO_3^- in precipitation are only slightly diluted during passage through the canopy (Fox, 1995). However, soil solution collected with tension lysimeters located at the base of O horizons and in upper B horizons seldom has detectable NO_3^- (Fox, 1995), suggesting that immobilization takes place almost immediately upon contact of throughfall with the forest floor, and that nitrification is minimal. We are currently exploring the possibility that the intense fire on the Cone Pond watershed around 1820 (Buso et al., 1984) altered N and C dynamics at Cone Pond to the extent that conditions are still unfavorable for nitrification.

4.4. Sulfur flux

All three study watersheds show sizable net losses of SO_4^{2-}-S (Table 5). These net losses may reflect additional inputs from unmeasured dry deposition. Likens et al. (1990) estimate that dry deposition calculated as SO_4^{2-}-S makes up an average of 37% of total S deposition at Hubbard Brook watersheds. This proportion represents an addition of about 3 kg of S per hectare per year to our wet deposition values and brings the annual input-output budgets

into closer balance. However, net losses range from 3.8 to 10.9 kg of S per hectare per year (Table 5), suggesting that other sources of S are also involved. Iron sulfides are constituents of several rock types at all three study sites, occuring at trace to 5% of rocks. Thus rock weathering is an additional possibility for some of the net loss of S. At the Cone Pond watershed, Bailey and Hornbeck (1992) found interior pitting of rocks caused by preferential dissolution of minerals that are more easily weathered than the overall rock mass. They suggested that sulfides are likely candidates for preferential dissolution. Dissolution pits were found in rocks as large as 209 g, showing the potential for large, seemingly impermeable rocks to contribute to the S cycle. Another possible source suggested by Houle and Carignan (1995) is release of SO_4^{2-}-S from soil organic S reservoirs. They suggest that such releases could account for net SO_4^{2-}-S losses averaging 5 kg ha^{-1} per year from the Lake LaFlamme watershed on the Canadian Shield.

Over the past decade, considerable effort has been devoted to developing critical loads for S deposition that will protect aquatic and terrestrial ecosystems (Holdren et al., 1993). In an analysis appropriate to our study region, Schindler (1988) proposes a limit to SO_4^{2+} deposition of 3–5 kg of S per hectare per year to protect sensitive aquatic ecosystems. The average wet deposition and estimated dry deposition (37% of wet deposition) for our sites total 11 kg of S per hectare per year, even in the face of gradually declining inputs of S (Driscoll et al., 1989). This rate is more than two times Schindler's proposed limit (Schindler, 1988), and seemingly places Cone Pond and Hubbard Brook in jeopardy in terms of cation depletion and Al mobilization.

4.5. pH and aluminum relationships

Inorganic aluminum is mobilized under acidic conditions at Hubbard Brook and Cone Pond but not under the alkaline conditions at Sleepers River (Tables 4 and 5). The differences in aluminum mobility between sites are somewhat more pronounced and thus more biologically important during snowmelt run-off events (Fig. 4). At Hubbard Brook and Cone Pond, when compared to annual means, slightly increased concentrations of mineral acids, specifically sulfuric at Cone Pond and sulfuric and nitric at Hubbard Brook, are released from the snowpack or flushed from soils (Hornbeck and Likens, 1974), causing increases in the proportion of H + and aluminum, and decreases in base cations. This results in what is commonly termed "acid shock" and places stream biota at risk from toxic, inorganic aluminum (Cronan and Schofield, 1979, 1990). Sleepers River, with higher concentrations of base cations and high acid neutralizing capacity in the

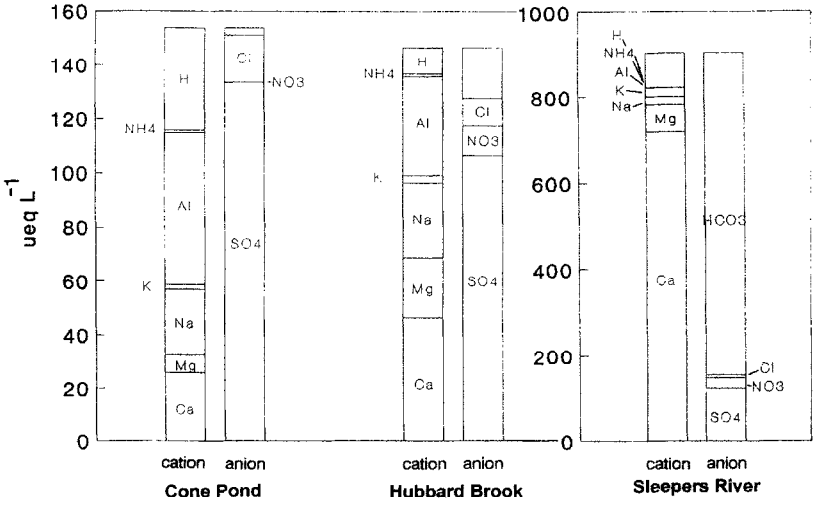

Fig. 4. Ion balances for a weekly sample collected at peak of snowmelt runoff. Note scale change for Sleepers River.

form of HCO_3^-, has a far greater ability to buffer snowmelt run-off and protect stream biota.

There are growing concerns over impacts of aluminum mobilization on cation depletion and tree health (Shortle and Smith, 1988; Lawrence et al., 1996). Cronan and Grigal (1995), in a literature review, point out that the molar ratio of Ca to Al in soil solution can serve as one of four measurement endpoints that, when taken successively, can serve as an indicator of Al stress. They estimate that the endpoint for soil solution that would contribute to a 50% risk of adverse impacts on tree growth or nutrition is a Ca:Al molar ratio in soil water of less than or equal to 1.0. For our study watersheds, the Ca:Al molar ratios for stream water are 0.8 for Cone Pond, 2.6 for Hubbard Brook, and 1740 for Sleepers River. To the extent that stream water represents an integration of soil water, the potential risk to tree health owing to nutrient imbalances is much greater under the more acidic conditions at Cone Pond and Hubbard Brook.

4.6. Implications for forest and aquatic managers

Understanding causes of different stream chemistries and the resulting net gains or losses in input–output budgets can help forest and aquatic managers evaluate how forest nutrient cycles and streams will respond to human disturbances. Major concerns regarding forest harvesting in New England include depletion of nutrients, especially base cations (Federer et al., 1989), and acidification and increased inorganic ion concentrations of soils and streams (Hornbeck et al., 1987; Lawrence, 1990). Nutrient depletion accompanying harvest is due, primarily, to removal of nutrients incorporated in harvested biomass, and to relatively smaller losses from increased leaching during the first few years of stand regeneration (Hornbeck et al., 1987, 1990). As discussed earlier, these concerns are exacerbated in central New England by acid deposition which is also reducing cation pools and acidifying soils and streams (Federer et al., 1989) and creating nutrient imbalances.

Based on these concerns, dilute and acidic stream chemistry like that occurring at Cone Pond should convey caution to forest managers regarding harvest activities. The low concentrations of base cations, especially Ca^{2+}, suggest that capitals and weathering rates are already low. In fact, Bailey et al. (1996) have used Sr isotopes to show that weathering rates are well below what is needed to sustain annual net losses from the Ca^{2+} cycle.

Acidification that results from removal of base cations in harvested biomass and sequestering in regeneration (Hornbeck, 1992) could further stimulate aluminum mobilization, adding to concerns over forest health and productivity and stream biota. It is unknown whether harvesting at Cone Pond would stimulate nitrification and subsequent stream acidification and mobilization of cations and aluminum such as that which occurs after harvesting at Hubbard Brook (Lawrence and Driscoll, 1988; Lawrence, 1990). If this response were to occur, negative impacts of harvest would be further magnified. The above possibilities, coupled with the low potentials for base cation replenishment (Bailey and Hornbeck, 1992; Bailey et al., 1996), suggests a conservative approach to forest management. Possibilities include exclusion of harvest or infrequent, low-volume, selection cuttings.

At the other extreme, the higher pH and levels of base cations and HCO_3^- for the stream at Sleepers River suggest that harvesting would have considerably less impact on soil and stream chemistries. Base cations are plentiful and the till source envelope (Fig. 3 and Table 6) suggests high potential for replenishing harvest removals. Thus long-term acidification that would be expected to accompany regrowth at Cone Pond should not be a problem at Sleepers River. If nitrification is stimulated at the time of harvest, the HCO_3^- dominated system should readily buffer acidification and aluminum mobilization, just as during snowmelt run-off (Fig. 4). Management recommendations could include intensive harvests such as clearcutting, a desired form of harvest for regenerating northern hardwood species, provided recommended rotations of 100-plus years are followed (Leak et al., 1969; Solomon and Leak, 1969).

Sites such as Hubbard Brook, which are intermediate in terms of stream chemistry and input–output budgets, present more of a challenge to forest managers. The stream chemistry and till source envelope (Fig. 3 and Table 6) indicate that base cation supplies and potential for replenishment are significantly less than at Sleepers River. Calcium weathering rates

of about 2 kg ha^{-1} per year reported for Hubbard Brook (Likens et al., 1996) indicate a situation more like that at Cone Pond. The weathering rates are well below annual net losses, despite the greater abundance of Ca-bearing minerals in till at Hubbard Brook. Repeated sequences of harvest removals of base cations and uptake by the regenerating forest could lead to long-term acidification of both soils and streams. Also, several studies have shown that intensive harvesting at Hubbard Brook stimulates increased nitrification for three–five years after harvest, in turn acidifying streams and mobilizing base cations and aluminum (Hornbeck et al., 1987; Lawrence and Driscoll, 1988). When harvest impacts are coupled with those of acid deposition, nutrient capitals at Hubbard Brook could be severely depleted over the next two or three harvest rotations (Federer et al., 1989). To limit nutrient depletion, management recommendations for sites like Hubbard Brook might include less intensive harvests such as shelterwood or group selection cuts practiced over fairly long rotations (Hornbeck and Leak, 1992).

As mentioned earlier, the stream chemistry and input–output budgets for Hubbard Brook are thought to represent far more of the central New England landscape than do Cone Pond or Sleepers River (Fig. 2). This is important to forest managers in the region as research at the Hubbard Brook Experimental Forest is a primary source of information for biogeochemical cycling (Likens, 1985). As demonstrated above, results of detailed nutrient cycling studies at Hubbard Brook, and also from less intensive studies at Cone Pond and Sleepers River, can and should serve as one guide for forest managers when deciding upon the wisest use of forest and stream ecosystems in central New England. To make optimum use of available information, the manager might consider obtaining chemical analyses for one or more stream samples collected seasonally from sites in question and determining where they fit in the Cone Pond–Hubbard Brook–Sleepers River continuum. Further insights can also be obtained by the relatively simple process of constructing and using a till-source envelope (Bailey and Hornbeck, 1992) as an index to potential replacement of base cations removed during harvest. Geological maps at the state level, usually available on geographic information systems, are satisfactory for constructing till-source envelopes.

4.7. Impacts of atmospheric deposition

While all three study sites receive relatively similar levels of acidic deposition, the Sleepers River watershed is much less prone to harmful impacts. On an equivalency basis, mobilization of cations by SO_4^{2-} and NO_3^-, the dominant components of acid deposition, are greatest at Sleepers River (Table 4). However, these anions represent only 16% of the streamwater total, the remainder being largely HCO_3^-. Thus the bulk of the cation output at Sleepers River is not mediated by anthropogenic acid deposition or natural soil acidification, and does not include mobilized aluminum. Weathering of calcareous till and underlying bedrock appears adequate to sustain base cation capitals and buffer against soil and stream acidification at current levels of acid deposition. Cone Pond and Hubbard Brook are the antithesis of Sleepers River. Net losses of base cations are linked closely with SO_4^{2-} (Table 4), and the relatively slow release of base cations by weathering in these watersheds raises serious concerns over depletion by acid deposition. For example, net losses of Ca^{2+} at Hubbard Brook averaged 6.0 kg ha^{-1} per year for the three years of our study (Table 5), and 9.7 kg ha^{-1} per year from 1963 through 1980 (Likens, 1985). At these rates, and with estimated weathering inputs of only 2.1 kg of Ca per hectare per year (Likens et al., 1996), the total soil capital at Hubbard Brook of about 9600 kg of Ca per hectare (Federer et al., 1989) could be depleted in less than 2000 years. The same applies for Cone Pond where the net losses are less, averaging 2.8 kg of Ca per hectare per year (Table 5), but the estimated total soil of 3100 kg of Ca per hectare (Bailey et al., 1996) is also much smaller. The net losses of base cations accompanying acid deposition and their impact on site capitals should be a consideration when determining harvest recommendations.

The net loss of Ca^{2+} from the Cone Pond and Hubbard Brook watersheds suggests that acid deposition is a fairly recent phenomenon. Unlike Sleepers River, these watersheds do not have significant weathering sources for replenishing Ca^{2+} lost in streamflow. If the Cone Pond and Hubbard Brook watersheds had been losing Ca^{2+} at these same rates over recent millennia, total soil Ca^{2+} capitals would have been depleted long ago.

There is concern in central New England over N saturation resulting from chronic inputs of wet and dry deposition of N (Aber et al., 1991). Aber et al. (1989) suggest that one of the ecosystem responses to N saturation would be a measurable increase in leaching of NO_3^- to the point of reaching N deposition input levels. Based on net losses from input–output budgets (Table 5), none of our study watersheds indicate excessive leaching of NO_3^-, and Cone Pond shows no detectable leaching losses of NO_3^-. Also, the long-term record at Hubbard Brook shows no significant trend in annual leaching losses of NO_3^- since 1963 (Likens et al., 1996). Thus all three watersheds are accumulating N at a fairly significant rate (Table 5), but are not yet meeting one of the primary criteria indicating N saturation. However, other symptoms must be watched for including increased emissions of nitrous oxide, reduced fine root biomass in the forest floor, and changes in species of mycorrhizae (Aber et al., 1989; Arnolds, 1991).

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