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Major element fluxes from a coniferous catchment in central Ontario, 1983–1999

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Abstract. Acid deposition over time scales of decades may deplete essential base cation (BC) reserves in soils to the extent that forest health may be affected. In order to assess the nutrient status of soils in central Ontario, input–output budgets for calcium (Ca), magnesium (Mg), potassium (K) and nitrogen (N) were calculated over a 17-year period (1983–1999) for a coniferous catchment in the Muskoka-Haliburton region. Inputs through deposition and weathering (BCs only), were compared with outputs through stream export and net accumulation in forest biomass. Despite a lack of forest growth at PC1, annual NO_3–N concentrations in the stream were low (<0.1 mg/l) over the 17-year period, and over 80% of the atmospheric N input was retained in the catchment, indicating this catchment has not reached N-saturation. Stream export of Mg, and in particular Ca, exceeded input of these elements through deposition and weathering, indicating a net loss from the catchment over the 17-year period. Mass balance calculations indicated there was no net loss of K from the catchment. Soil re-sampling measurements confirmed large losses of Ca, but not Mg, and there were significant decreases in both NaCl-exchangeable Ca concentrations and soil pH between 1983 and 1999. The measured decline in soil Ca concentration amounted to a loss of approximately 85 kg/ha Ca from the exchangeable pool over the 17-year period. Similarly, input–output budget calculations indicated a net loss of Ca from the catchment in the range of 76 to 88 kg/ha between 1983 and 1999. Although the magnitude of Ca export decreased over the 17-year period, current stream export continues to exceed Ca input through deposition and weathering.

Introduction

There is continuing concern that exchangeable base cation (BC) reserves in forest soils are being depleted over large parts of eastern North America, due to a combination of acid deposition and tree harvesting (Federer et al. 1989; Likens et al. 1996; Houle et al. 1997; Adams et al. 2000). Depletion of BC reserves in soils will lead to a greater fraction of exchange sites occupied by Al (aluminum) and H^+, and ultimately a decline in the BC:Al ratio in soil solution. It has been argued that a decreasing BC:Al (or Ca:Al) ratio in soil solution will diminish forest health and decrease forest productivity. A BC:Al molar ratio of 1.0 in soil solution draining the rooting zone has been adopted as the acidification criteria that is used in critical load models by several European countries (Sverdrup et al. 1992; Sverdrup and Warfvinge 1993; Cronan and Grigal 1995). These steady state models indicate that forests in large parts of central Ontario receive acid deposition (S and N) in excess of the critical load by more than 500 eq/ha/year (Arp et al. 1996).

Exceedance of the critical load implies that soils will continue to acidify to a biologically damaging level at some undefined point in the future. Several studies in

Europe and eastern North America have reported significant decreases in soil pH and/or exchangeable BC pools over periods of just a few decades (Tamm and Hallbacken 1988; Drohan and Sharpe 1997; Lawrence et al. 1997; Thimonier et al. 2000). These re-sampling studies demonstrate that changes in soil chemistry have occurred, but they do not necessarily provide information concerning temporal patterns in BC fluxes, or whether changes in soil chemistry are due to acid deposition and/or internal processes such as BC uptake in biomass.

The small watershed approach has been particularly useful for the quantitative study of element fluxes because with appropriate hydrological control, relatively precise estimates of chemical inputs and outputs can be obtained (Johnson et al. 2000). Several calibrated watersheds are currently being monitored throughout eastern North America and in general, these studies have reported that net losses of BCs from forested watersheds have occurred in recent decades (Likens et al. 1996; Houle et al. 1997). Indeed, depletion of BC reserves in soils has been proposed as a major factor that has prevented the chemical recovery of streams despite substantial reductions in SO_2 emissions in recent years in both Europe and eastern North America (Kirchner and Lydersen 1995; Likens et al. 1998).

Furthermore, high levels of NO_3 measured in streams may indicate that some forests in the region are approaching N-saturation even though N is normally considered to be the growth-limiting nutrient in many forests (Lovett et al. 2000). As N accumulates in forest soils, N supply may approach or exceed biotic demand leading to the release of N (usually as NO_3) in runoff. An increase in NO_3 leaching will also increase the rate of BC leaching from the rooting zone, which may counteract the benefits of reduced SO_4 leaching. Continued losses of BCs from soils may lead to nutrient deficiencies in trees (Bernier and Brazeau 1988; Kolb and McCormick 1993) and ultimately a decrease in growth (Shortle and Smith 1988; Watmough 2001). In addition to reducing tree growth, nutrient deficiencies may also predispose trees to stresses such as drought (Demchik and Sharpe 2000) and insect defoliation (Horsley et al. 2000), leading to an overall decrease in forest health and productivity.

The Muskoka-Haliburton region of south-central Ontario is particularly sensitive to acid deposition, and substantial biological and chemical effects of acidification have been documented in lakes in this area (Dillon et al. 1987; Shaw and Mackie 1989). In order to assess forest vulnerability to acidification effects in this area, we calculated input–output budgets of nutrient BCs (Ca, Mg, K) for a coniferous catchment (Plastic Lake-1; PC1) in Haliburton County over a 17-year period (1982–1999). In addition, input–output budgets of N (as NO_3, NH_4 and TON were calculated over the same time period, in order to assess the current N-status of the catchment.

Methods

Study site

Plastic Lake is located in Haliburton County on a southern extension of the Precambrian Shield in central Ontario, Canada (45°11′N, 78°50′W). This 32 ha headwater lake is drained by seven small streams and is typical of lakes sensitive to acid precipitation (Dillon et al. 1987). The largest of seven sub-catchments (PC1) is 23.3 ha in area and is underlain by biotite gneiss with amphibolite bedrock present in some low-lying areas. The gneiss's are dominant and are composed of quartz, potassium feldspar and plagioclase feldspar with lesser amounts of biotite and minor iron oxides. The amphiboles are dominated by hornblende, with lesser amounts of plagioclase and biotite, and minor pyroxene, olivene and titanite (Kirkwood and Nesbitt 1991). The essential mineralogy of the soils includes quartz, plagioclase feldspar, potassium feldspar, amphibole and vermiculite (Kirkwood and Nesbitt 1991). Upland soils (average depth 0.37 m to bedrock) are orthic humo-ferric and ferro-humic podzols, formed from thin, sandy basal tills (Canadian Soil Survey Committee 1978) . Humic mesisols underlie the 2.2 ha *Sphagnum*-conifer swamp (Figure 1). PC1 is drained by a headwater stream that passes through the swamp before discharging into Plastic Lake. Over the 17-year study period, the average volume-weighted DOC concentration at PC1 was 9.6 mg/l and the mean annual volume weighted pH was 4.4. A small ephemeral stream that drains a small (3.45 ha) sub-catchment (PC1-08) and discharges into the swamp was also monitored for a 9-year period (1986/87–1994/95) during the study (Figure 1). The annual DOC concentration at the upland draining stream (PC-108) was lower (average, 2.2 mg/l), and the annual volume weighted pH was slightly higher than PC1 (average pH, 4.8). The forest experienced some logging in the early 1900s, but has not experienced any major disturbance (logging, fire) for at least 50-years. The uneven-aged forest (average age 87, baseline 2000, with a maximum age of 200) is dominated by white pine (*Pinus strobus* L.), eastern hemlock (*Tsuga canadensis* L. Carriere), red oak (*Quercus rubra* L.), red maple (*Acer rubrum* L.) and large toothed aspen (*Populus grandidentata* Michx.) in the upland areas; white cedar (*Thuja occidentalis* L.) is the dominant tree species in the wetland. From 1983 to 1998 mean annual precipitation and air temperature at PC1 were 976 mm and 5.3 °C, respectively; site elevation ranges from 380 m.a.s.l. at the stream gauging station to approximately 420 m.a.s.l. at the northern ridgeline.

Bulk deposition

Deposition data were obtained from collections of bulk deposition, which we define as that caught in a continuously open, 0.25 m^2 collector. The collectors are fitted with Teflon-coated funnels that are screened (80 µm Nitex mesh) to prevent contamination by insects and debris. Precipitation samples were removed from collectors when there was sufficient volume for chemical analyses, typically weekly. Analytical methods for Ca, Mg, K, Na, SO_4, NO_3 and NH_4 are outlined in detail in Ontario Ministry of Environment (1983). Briefly, BCs were measured by atomic absorption spectrophotometry, SO_4 by ion chromatography and NH_4 and NO_3 were determined colorimetrically. Deposition and volume-weighted concentrations were calculated for each water year (June 1 to May 31) between 1982/83 and 1998/99. In this study, additional inputs of BCs through dry deposition beyond that collected

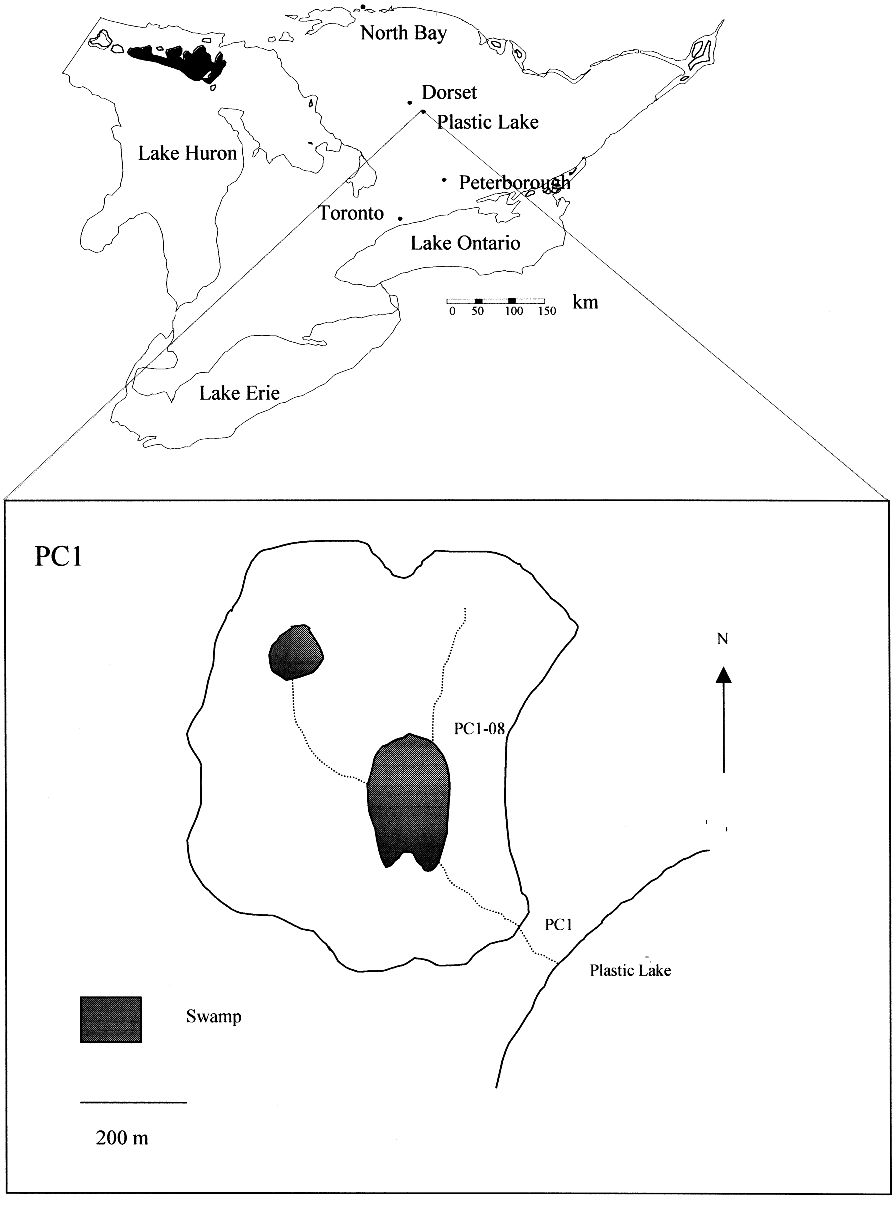

Figure 1. Map of the Plastic Lake-1 (PC1) sub-catchment.

in bulk deposition were included in order to estimate BC mass balances over the 17-year period. This was done because some reports indicate inputs via dry deposition can be substantial and account for up to 20–60% of the total BC input to forests (Shepard et al. 1989), although these high dry deposition values are generally found close to emission sources.

Additional inputs of Ca, Mg and K by dry deposition were estimated using throughfall and bulk deposition measurements collected during a 3-year period (1983–1985) at PC1 (Neary and Gizyn 1994) . This method uses measurements of Na deposition as a model substance for dry deposition of particles:

$$X_{\mathrm{dry}} = \frac{\mathrm{Na}_{\mathrm{tf}} - \mathrm{Na}_{\mathrm{bulk}}}{\mathrm{Na}_{\mathrm{bulk}}} \times X_{\mathrm{bulk}}$$

where X_{dry} is the dry deposition on the canopy surface of element X (kg/ha), $\mathrm{Na}_{\mathrm{tf}}$ is the total throughfall flux of sodium (kg/ha), $\mathrm{Na}_{\mathrm{bulk}}$ is the bulk deposition of sodium (kg/ha) and X_{bulk} is the bulk deposition of element X (kg/ha). These calculations were based on the mean annual deposition measured during the 3-year period and they assume that foliar leaching of Na is negligible. Versions of this equation have been adopted in other studies, although in some cases wet deposition is used rather than bulk deposition (Duchesne et al. 2001). Therefore, in this study we are estimating additional dry deposition that was not measured in bulk deposition rather than the total contribution of dry deposition and we assume that the relative contribution (%) of dry deposition has been constant over the 17-year period. The implications of uncertainties in our estimations are discussed later.

Weathering

In order to complete BC mass balance estimates for PC1 some estimate of inputs due to mineral weathering are required. Estimates of mineral weathering are notoriously difficult to obtain and considerable uncertainty is associated with each method (*see* Kolka et al. 1996; Starr et al. 1998; Sverdrup et al. 1998; Hodson and Langan 1999). In this study, BC inputs from mineral weathering were estimated using three commonly used methods (Zr-depletion, total analysis correlation and PROFILE) that have been reported in the literature and for which data readily exist at PC1. Details of each method are outlined below.

Zr-depletion

Podzols in the Plastic Lake catchment are developed from glacial till deposited 12,000 years ago. Long-term elemental weathering rates were estimated by Kirkwood and Nesbitt (1991), who examined the bulk and mineralogical composition of soil and bedrock in 10 pits excavated at different locations in the upland part of the PC1 catchment, and calculated total weathering at these sites since glaciation. The principle of this traditional method for estimating weathering rates was described by

Bain et al. (1990). Zirconium (Zr) occurs principally in the form of the mineral zircon ($ZrSiO_4$), which is extremely resistant to weathering and can therefore be used as an internal standard by which the depletion of other elements can be judged. At the time of glaciation, the amount of Zr is assumed uniform throughout the profile. With time, the weathering products, including BCs, are progressively removed by plant uptake and leaching, leaving the upper layer enriched in Zr (Starr et al. 1998). The consistency of the BC to Zr ratios enables the amount of BC lost from the weathered layer to be calculated. For this study, we assumed that the current weathering rate was equivalent to the average over this long time period (12,000 years).

Total analysis correlation model

Olsson and Melkerud (1990) derived a series of equations that calculate BC weathering rates (obtained from element-depletion estimates) of soils using the elemental composition of the soil together with soil temperature and depth. The equations were derived using data on elemental composition of seven soils from Sweden developed on granitic tills, together with the weathering rates of those soils calculated on the basis of depletion of elements in soil. This method only applies to granitic soils, and has been evaluated in several studies that compare different methods of estimating weathering rates (Starr et al. 1998; Sverdrup et al. 1998; Hodson and Langan 1999) .

The equations are:

$$\mathrm{WR_{Ca}} = z \times ((10^{-4} \times \mathrm{wt\%CaO} \times (768 + 104T)) - 0.08),$$

$$\mathrm{WR_{Mg}} = z \times ((2.12 \times 10^{-4} \times \mathrm{wt\%MgO} \times (768 + 104T)) - 0.09),$$

$$\mathrm{WR_{Na}} = z \times (0.37 \times 10^{-4} \times \mathrm{wt\%Na_2O} \times (768 + 104T)),$$

$$\mathrm{WR_{K}} = z \times (0.21 \times 10^{-4} \times \mathrm{wt\%K_2O} \times (768 + 104T)),$$

where $\mathrm{WR_{Ca,\ Mg,\ Na,\ K}}$ = weathering rate (kequiv/ha/year) of Ca, Mg, Na and K; T = average temperature (°C); z = soil depth (m); wt%CaO, MgO, Na_2O and K_2O = oxide content of the soil expressed in terms of weight percent. For mass balance estimates weathering rates were converted to kg/ha/year.

The PROFILE model

PROFILE is a steady-state soil chemistry model used to calculate weathering rates for a defined number of soil layers (Sverdrup and Warfvinge 1993). The version of PROFILE we used (4.0) is based on the weathering rates of common minerals that are subsequently modified for field conditions using H^+, CO_2, dissolved organic carbon (DOC), BC and Al concentrations, and corrections for soil moisture content, temperature, soil surface area and bulk density. PROFILE is a steady state model and so only single values for each input parameter can be given even though the property may show considerable seasonal and annual variability. We ran PROFILE with 3 soil layers with average depths of 5, 27 and 5 cm. The mineralogy input data were that of the <2 mm fraction calculated by Kirkwood and Nesbitt (1991) using X-ray diffraction. The majority of input data (i.e. precipitation; throughfall, litterfall, uptake, soil chemistry; bulk density) were obtained from field studies conducted at PC1 during the 1980s (Lozano 1987; Neary and Gizyn 1994). When data were not available (i.e. soil moisture; surface area) we used default values or used values estimated from soil texture or from the pH of the soil solution.

Stream export

Water level or stage was recorded continuously at a V-notched weir installed at the catchment outflow, and daily stream discharge (m^3/day) was computed using established stage–discharge relationships. Between 1986/87 and 1994/95, stream discharge was also monitored at a V-notched weir installed at the inflow to the swamp (Figure 1). This stream drained a small (3.45 ha) sub-catchment (PC1-08). Water samples for chemical analyses were collected at the weir at regular intervals (at least biweekly) when there was flow, although sampling was more frequent during the spring melt period. Water samples were filtered through 80 μm Nitex mesh in the field, and transported to the laboratory for chemical analyses in insulated containers. Filters (Nitex mesh) were rinsed in deionized water in the laboratory and rinsed in stream water immediately prior to sampling. Samples were analyzed for Ca, Mg, K, Na, SO_4, NH_4 and NO_3 as outlined above. In addition, samples were analyzed for Kjeldahl N (TKN) using standard methods (Ontario Ministry of Environment 1983). Total organic nitrogen (TON) is calculated as the difference between Kjeldahl N and NH_4. Data are presented as areal fluxes (kg/ha/year) and volume-weighted concentrations (mg/l) for each water year between 1982/83 and 1998/99.

Soil solutions

Between 1987/88 and 1994/95 water draining beneath the soil profile (B-horizon average lysimeter depth 38 cm) was collected using six zero tension lysimeters within (or just outside) the PC1-08 sub-catchment (Lazerte and Scott 1996) . Lysimeter pits, which housed collection bottles were framed, insulated and heated from October to April in each year of operation. The accumulated sample was usually collected weekly, or when there was sufficient sample for analysis. As accurate estimates of sample volume were not available, an estimate of annual export from the hillslope was calculated using the annual discharge measured at PC1-08 and the mean annual concentration of each element measured in lysimeter leachate. This assumption is valid at PC1-08 because water flux is primarily downward through the sandy soil until bedrock is reached and then laterally toward the stream channel or swamp along the soil–bedrock interface (Peters et al. 1995) . Water collected in the B-horizon is therefore considered representative of water draining the upland soils into the swamp. In addition, BC concentrations in the B-horizon samples exhibited little seasonal variation and Cl concentrations in lysimeters and PC1-08 were very similar with less than 8% difference in each year.

Soil chemistry

Methods of soil analyses are described in detail by Lozano (1987). Unfortunately, archived soil samples were unavailable, although sampling and analytical procedures were identical in 1983 and 1999. In 1983, soil samples (LF, H, Ae, Ah, Bf, Bhf, (BC and C when present) were collected from 15 pits dug at sites throughout the upland part of the catchment, chosen to include soils typical of the catchment according to the Canadian Soil Survey Committee (1978). The sampling was repeated in the summer of 1999, using soil pits adjacent (within ∼5 m) to the original pits. A number of pits were dug close to the original pit until similar soil horizons were identified. Forest floor samples (LFH) were removed from within a 25 cm×25 cm wooden frame. Mineral soil samples were removed by horizon from the four faces of the pit and composite samples were placed in labeled bags. Duplicate cores were taken from the middle of each mineral horizon for bulk density determinations. Soil samples were air-dried for a minimum of 24 h prior to chemical analyses. Soil pH was measured in both distilled water and 0.01 M $CaCl_2$ (soil/solution ratio of 1:2) using a glass electrode pH meter after a 1-h equilibration period (Ontario Ministry of Environment 1983). Each organic layer was ground in a Wiley mill, and individual mineral horizons passed through a 2 mm sieve. Bulk density and exchangeable (2 M NaCl) Ca, Mg and K concentrations were determined for each soil sample using methods outlined in Ontario Ministry of Environment (1983). Briefly, exchangeable BC concentrations were obtained by shaking 5 g soil (<2 mm fraction) in 50 ml 2.0 M NaCl for 2 h. After gravity filtration, samples were analyzed for Ca, Mg and K by flame AAS using standard operating procedures in the same laboratory (Ontario Ministry of the Environment 1983). Calcium concentrations in procedural blanks were low (0.03 ± 0.005 mg/l) although Mg (0.1 ± 0.01) and K (0.22 ± 0.03) were higher. For the estimation of soil exchangeable pools in this study it was assumed that the depth of each soil horizon and the corresponding bulk density were the same in 1983 and 1999, so that changes in exchangeable soil BC pools were due solely to changes in soil chemistry.

Forest biomass and cation pool estimates

The forest at PC1 was surveyed in 1983 and 1999 using a point-sampling technique (Lozano and Parton 1987) . Sample point selection (identical in 1983 and 1999) was done on a fixed grid system to ensure complete coverage of the entire catchment, and to facilitate mapping of forest cover types. Additional sampling was conducted at randomly selected points to improve the accuracy of the basal area estimate. A total of 184 (1983) and 209 (1999) points were surveyed in the PC1 catchment. At each sample point, a wedge prism with a basal area factor of $2.0\,\mathrm{m}^2\,\mathrm{ha}^{-1}$ was rotated 360° through the sampling point. All trees with a diameter greater than 10 cm at breast height, not completely offset when viewed through the prism were tallied by species and diameter class, and basal area (m^2/ha) was calculated for the PC1 sub-catchment.

Tree biomass by species was calculated for each size class (2 cm intervals) from a regression equation, and this calculated value was multiplied by the number of trees per hectare of the corresponding size class to estimate tree biomass per unit land area (Lozano and Parton 1987) . The biomass values for all size classes and all tree species were summed to obtain the total standing live biomass (including roots) at PC1 using survey data collected in 1983 and 1999. Biomass equations were either locally developed or were taken from the literature (Lozano and Parton 1987) . Elemental contents (Ca, Mg, K and N) of standing live trees were calculated as the product of tree-component biomass and appropriate elemental concentration. BC concentrations were measured in trees that were destructively sampled from outside the study area (19 white pine, nine red maple, six red oak; five hemlock, yellow birch (*Betula alleghaniensis* Britt.) and beech (*Fagus grandifolia* Ehrh.); three balsam fir (*Abies balsamea* L. Mill.) and white spruce (*Picea glauca* Moench)). These trees were also used to validate biomass equations reported in the literature. BC and N contents of above and below ground biomass were summed to give the total nutrient content of standing live biomass.

Major element budgets

Budgets for Ca, Mg, K, and N were calculated for each water year between 1982/83 and 1998/99. For Ca, Mg, and K the change in the soil pool for each element was computed as the balance between bulk precipitation (plus additional dry deposition estimated from throughfall measurements) plus weathering, and export from the catchment in the PC1 stream. Sodium is a minor constituent in the forest floor, the soil exchange complex and in secondary minerals, respectively and so the weathering release of Na should be equal to the difference between Na export in PC1 and Na input in deposition.

Differences in mean soil concentrations of Ca, Mg and K (and pH) were tested using a paired *t*-test on log transformed data using pairing both on site and horizon (Zar 1984). A Seasonal Kendall test (treating months as seasons) was used to determine trends in stream water and bulk deposition chemistry (Hirsch and Slack 1984). Simple linear regression analysis and correlation analyses using mean annual stream export was used to identify trends in annual deposition or export. Simple linear correlation analysis using mean annual export or mean annual volume-weighted concentration was used to identify relationships between elements in stream water (Zar 1984).

Results and discussion

Element inputs to PC-1

Atmospheric deposition

Temporal trends in SO_4 and N in bulk deposition at PC1 were similar to trends previously described in eastern North America (Dillon et al. 1988; Clair et al. 1995; Driscoll et al. 1995) and so will not be discussed in detail. Between 1982/83 and 1998/99, SO_4 input in bulk deposition decreased by approximately 45%, from a high of 33 kg/ha in 1982/83 to around 18 kg/ha in 1998/99 (Figure 2). There was also a significant ($p<0.001$; -0.04 mg/l/year) decrease in SO_4 concentration in bulk deposition. In contrast, inputs of N ($NO_3 + NH_4$) were relatively constant over the study period (range 8–11 kg N/ha). There was no significant change in either inputs or concentration of NO_3 or NH_4 in bulk deposition. In this study, no attempt was made to estimate the relative contribution of N dry deposition due to difficulties in interpreting throughfall data (Neary and Gizyn 1994) and we acknowledge that our measurements of bulk deposition will underestimate total inputs of N to PC1. For example, Neary and Gizyn (1994) reported than inputs of NH_4 in throughfall at PC1 were on average 41% lower than inputs in bulk deposition while NO_3 inputs in throughfall were ~21% greater than inputs measured in bulk deposition over a 3-year period in the mid 1980s. However, N retention in the canopy can be considerable (Friedland et al. 1991; Boyce et al. 1996), and as we are uncertain as to the magnitude of N retention by the canopy at PC1 we only report bulk deposition values in this study. Between 1982/83 and 1998/99, a total of 147.4 kg N/ha was collected in bulk deposition, which may be considered a conservative estimate of total N deposition at PC1. Annual inputs of N in bulk deposition at PC1 are similar to values reported in Vermont and New York, where high concentrations of NO_3 (and large seasonal variation) are measured in stream water, and it has been suggested that catchments in this region might be exhibiting the early signs of N-saturation (Campbell et al. 2000; Lovett et al. 2000).

BC inputs in deposition varied considerably from year to year but also declined over the study period (Figure 2) . Between 1982/83 and 1998/99, there were significant decreases in annual inputs of Ca ($r^2 = 0.28$; $p<0.05$), K ($r^2 = 0.38$; $p<0.01$) and Na ($r^2 = 0.41$; $p<0.01$) in bulk deposition; although Mg deposition did not change significantly (Figure 2). The decline in Ca deposition was approximately 20% (~0.06 kg/ha/year), between 1982/83 and 1998/99. There was a small, but significant ($p<0.01$; -0.0008 mg/l/year) decrease in K concentration in bulk deposition (data not shown), although there were no significant decreases in Ca, Mg or Na concentration in bulk deposition. Average annual volume weighted concentrations of BCs in bulk deposition were; 0.25 mg/l Ca; 0.04 mg/l Mg; 0.07 mg/l K and 0.06 mg/l Na. Part of the decrease in BC inputs therefore can be attributed to lower rainfall, particularly during the final 2 years of study. In some regions, high levels of BC deposition, whether from natural or anthropogenic sources, can help to buffer soils from the impacts of acid deposition (Likens et al. 1996; Larssen and Carmichael 2000). A recent decrease in BC deposition has been

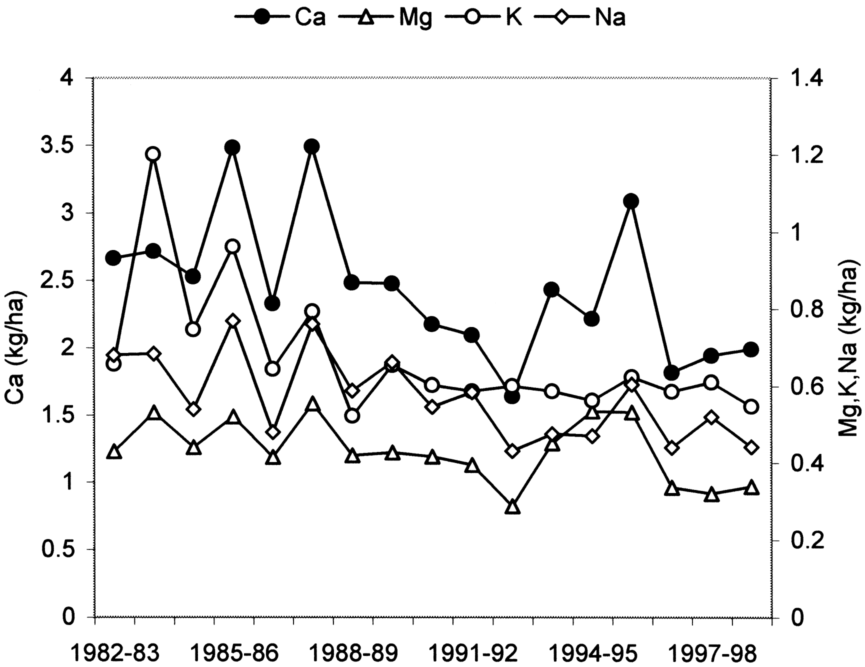

Figure 2. Inputs (kg/ha) of Ca, Mg, K and Na in bulk precipitation (1982/83 – 1998/99). Significant ($p<0.05$) decreases in annual inputs were found for Ca, Na and K using simple linear regression.

proposed as a major reason why the expected chemical recovery in stream water in some regions has not occurred despite large decreases in SO_4 deposition (Hedin et al. 1994). In general however, the largest decline in BC deposition in Europe and eastern North America occurred prior to 1983 and decreases in BC deposition have been minimal after this period (Hedin et al. 1994; Likens et al. 1996). At PC1 therefore, it is unlikely that the small reduction in BC deposition during the study period was large enough to fully account for the observed decrease in BC export.

To compensate for a possible underestimation of dry deposition in our mass balance calculations, annual bulk deposition was increased by 13% (average Na enrichment in throughfall compared to bulk deposition over a 3 year period). Increasing BC inputs by 13% however, has very little impact on the overall mass balances calculated for Ca, Mg and K at PC1. Between 1982/83 and 1998/99, 'total' inputs of BCs via deposition were estimated to be 46.9 kg Ca/ha; 8.2 kg Mg/ha and 13.0 kg K/ha.

Weathering inputs

BC inputs to PC1 from mineral weathering were calculated using three methods: Zr-depletion, total analysis correlation and PROFILE. Total BC weathering rates at PC1 were generally low (Table 1). The low weathering rates calculated for PC1 are a result of the shallow soils (average depth to bedrock, 0.37 m), and the dominance

Table 1. Estimated weathering inputs for Ca, Mg, K and Na at PC1, calculated using the Zr-depletion, total analysis correlation and PROFILE methods (see text for details).

	Zr-depletion	Correlation	PROFILE
Ca (kg/ha/year)	2.66	2.69	2.02
Mg (kg/ha/year)	0.96	1.66	0.95
K (kg/ha/year)	2.81	1.17	1.60
Na (kg/ha/year)	3.21	1.42	2.13

of slowly weathered minerals including quartz, K-feldspar, plagioclase, vermiculite and amphibole (Kirkwood and Nesbitt 1991). BC weathering inputs at PC1 are similar to those estimated for shallow acidic podzols at Lac Clair watershed in Quebec using PROFILE (Houle et al. 1997) and for podzols at Gardsjon, Sweden that were calculated using a variety of different methods (Sverdrup et al. 1998). Reasonable agreement between methods for estimating BCs weathering has been reported in other studies (Starr et al. 1998; Sverdrup et al. 1998). In both the present study and work by Starr et al. (1998), estimates of weathering inputs calculated using PROFILE were less than estimates from other methods. This may be expected because both the Zr-depletion method and the correlation method are essentially time-averaged values and it is likely that weathering rates have changed over time as the more easily weathered minerals are lost from the soil profile. In contrast, PROFILE is a computer model that estimates current weathering rates based on prevailing soil and environmental conditions (Sverdrup and Warfvinge 1993). However, in a study by Langan et al. (1996) weathering inputs in a number of soil profiles derived from greywackes and shales in the UK were much lower when calculated using the Zr-depletion method compared with PROFILE. In this case, Langan et al. (1996) suggested that current weathering rates are presently higher than the historical rate due to increased acid inputs over the past 200 years.

Even though all three methods gave similar estimates of total BC inputs from weathering, there was considerable variation in weathering rates among individual BCs (Table 1) . Weathering estimates for Ca were the least variable, ranging from 2.02 kg/ha/year to 2.69 kg/ha/year, a difference of only 33%. In contrast, weathering estimates for Mg, K and Na ranged from 0.95 to 1.66 kg/ha/year (75% difference), 1.17 to 2.81 kg/ha/yr (140% difference) and 1.42 kg/ha/year to 3.21 kg/ha/year (126% difference), respectively. For comparison, the average annual net export (average annual stream flux – average annual input in bulk deposition) of Na, which is a minor constituent in the forest floor, vegetation and the soil exchange complex, was 2.55 kg/ha/year. This suggests a current Na-weathering rate that lies within the range of estimates calculated using the three methods. As we cannot determine which of the three weathering methods is most representative of current weathering rates at PC1, mass balance budgets were calculated using each of the three methods. This approach is similar to that suggested by Kolka et al. (1996) who proposed that using multiple approaches to estimate mineral weathering, each with its own specific strengths and weaknesses, would yield the ‘best’ overall estimate.

Table 2. Change in live biomass and nutrient content (dbh <10 cm) between 1983 and 1999 at PC1.

	1983	1999	Δ (1999–1983)	% change
Biomass (kg/ha)	209,000	214,000	5000	2.4
Ca (kg/ha)	509	471	−38	−7.5
Mg (kg/ha)	43.7	42.6	−1.1	−2.5
K (kg/ha)	221	213	−8	−3.6
N (kg/ha)	386	374	−12	−3.1
Basal area (m^2/ha)	31.8	31.3	0.5	−1.6
Stems/ha	838	636	−202	−24.1

Forest biomass

Biomass of the upland forest at PC1 increased slightly (2.4%) between 1983 and 1999 (Table 2). Biomass estimates for the PC1 catchment (~210,000 kg/ha) are similar to biomass estimates reported by Hendrickson et al. (1987) for a mature (~90 years old) mixed conifer and hardwood stand in Ontario. At Hubbard Brook in New Hampshire, Likens et al. (1998) reported biomass at a predominately hardwood forest to be approximately 230,000 kg/ha. Similar to the present study, Likens et al. (1998) found that no substantial increase in biomass occurred at Hubbard Brook after 1982, although they did report an increase in the size of the standing dead pool over the same time period. It has yet to be determined however, whether the negligible forest growth found at PC1 over the 17-year period was due to natural maturation of the forest, or due to Ca-limitation, which could result in lower growth rates and greater tree mortality (Shortle and Smith 1988). However, other recent studies in Ontario have indicated that poor tree health and growth were associated with low base status in soil (McLaughlin et al. 2000; Watmough 2001). There is a growing body of literature linking weak tree health/growth with poor soil nutrition in eastern North America (Demchik and Sharpe 2000; Horsley et al. 2000). In some cases decline symptoms have been alleviated and growth increased by fertilization with Ca and Mg (Moore et al. 2000).

Pools of Ca, Mg, K and N in forest biomass at PC1 are similar to values reported in several studies conducted in eastern North America (*see* Hendrickson et al. 1987; Federer et al. 1989; Likens et al. 1998). Our estimates indicate that despite a small increase in forest biomass, pools of Ca, Mg, K, and N in biomass declined over the 17-year period, with the largest decrease occurring in the Ca pool (Table 2). Over the 17-year period, Ca, Mg, K and N pools in biomass declined by 38, 1.1, 8.0 and 12 kg/ha, respectively (Table 2). This decrease in the biomass nutrient pool between 1983 and 1999 can be attributed to a relative increase in the proportion of white pine and hemlock in the PC1 forest at the expense of hardwood trees such as red oak, red maple and poplar (Table 3). Coniferous tree species generally have lower nutrient contents, compared with hardwood trees, and Ca levels in particular are much lower in coniferous trees (Watmough and Dillon 2001). Differences are most apparent in the bark, which contains approximately 40% of the Ca held in the forest biomass at PC1 and bark accounts for approximately 45% of the Ca in the above ground biomass. For example, Ca concentrations in bark at PC1 are around

Table 3. Percent basal area and stem density of the dominant tree species at PC1 in 1983 and 1999.

	% Basal area		% Stem density	
	1983	1999	1983	1999
White pine	37	42	21	21
Hemlock	17	19	22	23
Red maple	13	10	20	16
Red oak	10	8	5	5
White cedar	7	7	14	14
White birch	7	4	7	3
Poplar	4	3	2	1
Balsam fir	1	2	3	9
Other	4	5	6	8

21,000 mg/kg (maple), 12,000 mg/kg (poplar) and 23,000 mg/kg (red oak) compared with 6000 mg/kg (hemlock) and 3000 mg/kg (white pine). The shift toward less nutrient-demanding species may be a response of the forest community to nutrient-poor soils (Adams et al. 2000) or it may simply be a function of natural forest dynamics. Over the 17-year period, the decrease in the forest nutrient pool may represent a substantial input of BCs to the forest floor, particularly of Ca. However, we do not know how the pool of standing dead trees has changed over the study period and therefore cannot determine the extent of nutrient return to the soil. For this reason, in our mass balance calculations we have assumed that there was no net change in the nutrient pool held in forest biomass between 1983 and 1999.

Stream export

In the absence of harvesting, stream export is the major route by which nutrients are lost from the catchment. Stream export of Ca and Mg was extremely variable over time, and large peaks in Ca and Mg concentrations and export in the PC1 stream occurred at several times during the study period (Figures 3 and 4). Even though there was considerable inter-annual variation in stream chemistry, significant decreases in stream water SO_4 ($p<0.01$; -0.107 mg/l/year), Ca ($p<0.001$; -0.047 mg/l/year) and Mg ($p<0.01$; -0.005 mg/l/year) over the 17-year period were identified (Figure 3). In contrast, there were small, but significant increases in K ($p<0.01$; 0.008 mg/l/year) and Na ($p<0.05$; 0.006 mg/l/year) concentration in stream water (Figure 3). There were also significant ($p<0.05$) decreases in annual export of SO_4, Ca and Mg (Figure 4), although part of the decrease in Ca and Mg export can be attributed to extremely low flow ($\sim$50% of 17-year average) during the final 2 years of study. Stream concentration and export of Ca ($r = 0.96$) and Mg ($r = 0.98$) were strongly correlated with SO_4, and peaks tended to occur in the autumn of years that had prolonged summer droughts. High SO_4 concentrations in stream water following dry periods have previously been attributed to the influence of a conifer *Sphagnum* swamp directly upstream of the PC1 catchment outlet (Figure 1) (Dillon et al. 1997; Devito et al. 1999; Eimers and Dillon 2002). During

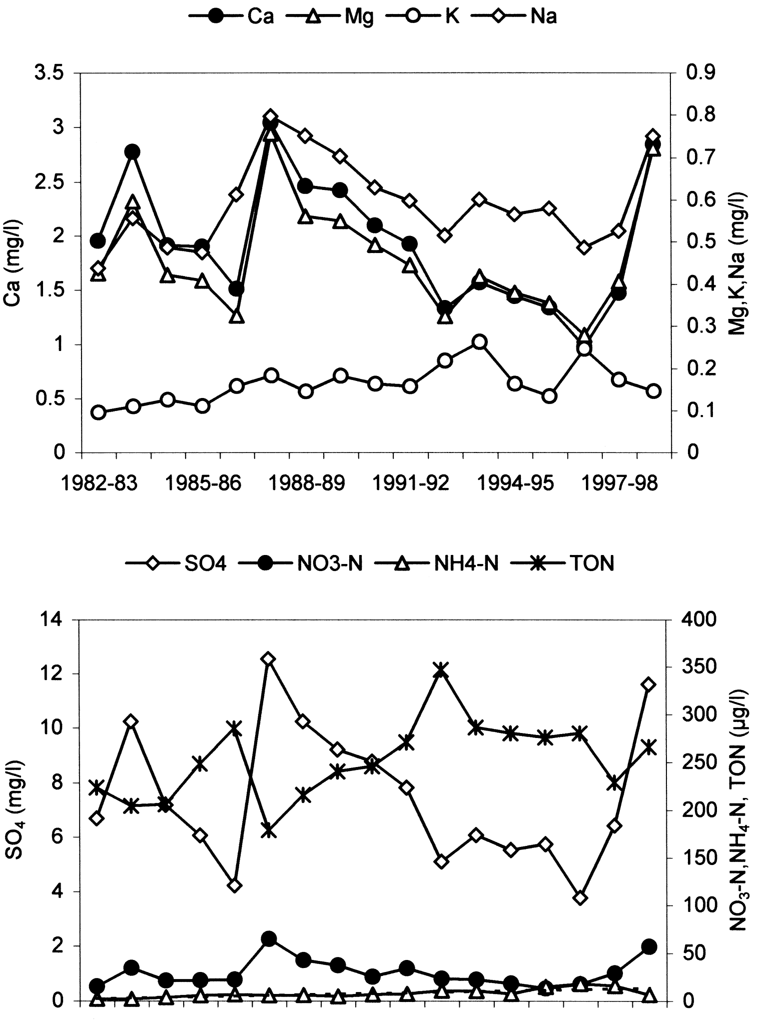

Figure 3. Volume weighted annual concentrations (mg/l) of Ca, Mg, K, Na, SO_4, NO_3–N, NH_4–N and TON in stream water draining PC1 (1982/83 – 1998/99). Significant decreases in Ca ($p<0.001$; −0.047 mg/l/year), Mg ($p<0.05$; −0.005 mg/l/year) and SO_4 ($p<0.01$; −0.107 mg/l/year) concentration were found. Significant increases in K ($p<0.001$; 0.008 mg/l/year), Na ($p<0.05$; 0.006 mg/l/year), NH_4 ($p<0.001$; 0.0007 mg/l/year) and TON ($p<0.001$; 0.005 mg/l/year) concentration were found using the seasonal Kendall test.

dry periods, water table draw-down in the swamp allows the re-oxidation of S stored in organic soils, which is subsequently exported as SO_4 when normal hydrologic conditions resume. Increases in Ca and Mg concentrations, and to a lesser extent NO_3, accompanied post-drought sulfate peaks in PC1. Conversely, during years in which the water table was maintained near the surface of the swamp, SO_4

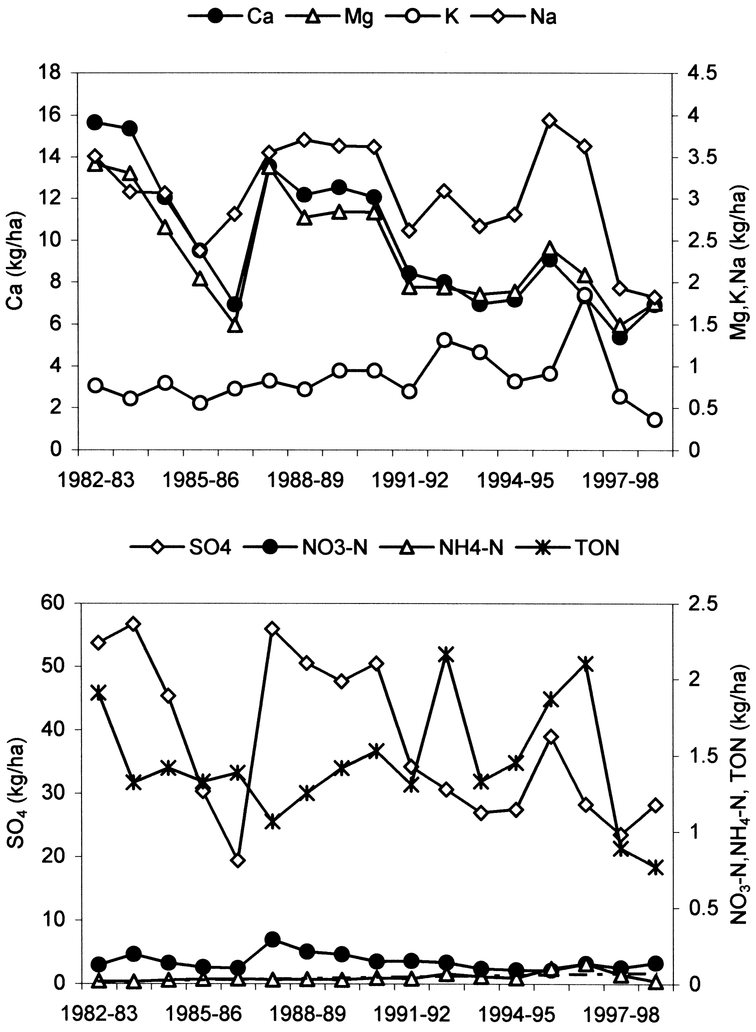

Figure 4. Annual export of Ca, Mg, K, Na, SO_4, NO_3–N, NH_4–N and TON in stream water draining PC1 (1982/83 – 1998/99). Significant ($p<0.05$) decreases in annual inputs were found for Ca, Mg and SO_4 using simple linear regression.

concentrations and export were lower than average in PC1, and accordingly Ca and Mg concentrations and export were also less (LaZerte 1993).

Within-swamp processes can therefore explain much of the inter-annual variation in Ca and Mg concentrations and export measured in the PC1 stream (LaZerte 1993). However, this raises the question as to whether the export of cations and N as measured in PC1 are indicative of changes in the upland forest soil. In order to address this concern, we examined BC export in the upland-draining PC1-08 stream (Figure 1) between 1987/88 and 1994/95. The total areal flux (kg/ha) of Ca and

Table 4. Annual Ca, Mg, K and Na flux (kg/ha/year) from B-horizon lysimeters (HS), PC1-08 and PC1 between 1987/88 and 1994/95.

	kg/ha/year											
	Ca			Mg			K			Na		
	HS	PC-108	PC-1	HS	PC-108	PC-1	HS	PC-108	PC-1	HS	PC-108	PC-1
87/88	11.49	9.28	13.85	2.72	2.51	3.37	0.94	1.16	0.82	3.85	3.73	3.55
88/89	11.21	9.12	12.14	2.34	2.29	2.77	1.07	1.19	0.71	3.47	3.65	3.70
89/90	9.23	9.26	12.52	2.11	2.34	2.84	1.05	1.06	0.94	2.85	3.43	3.63
90/91	11.79	10.31	12.03	2.79	2.65	2.83	1.49	1.46	0.94	3.99	3.84	3.62
91/92	9.16	7.81	8.41	1.92	1.91	1.94	0.48	0.64	0.69	2.95	2.78	2.61
92/93	11.58	9.68	7.98	2.49	2.32	1.94	0.31	0.51	1.31	3.23	3.44	3.08
93/94	6.12	6.06	6.96	1.60	1.59	1.85	0.35	0.35	1.16	3.58	2.21	2.66
94/95	8.17	8.53	7.16	2.18	2.09	1.88	0.23	0.60	0.81	3.39	2.91	2.81
Sum	78.94	70.05	80.76	18.14	17.69	19.41	5.93	6.97	7.38	27.31	26.01	25.65

Mg in PC1-08 over this 8-year period was similar (within $\sim 15\%$) to the flux measurement at PC1, as well as to that measured in soil leachate (Table 4). For example, between 1987/88 and 1994/95, 80.8 kg/ha Ca was the export measured at PC1 compared with 70.1 kg/ha Ca at PC1-08 and 78.9 kg/ha Ca estimated from lysimeter leachate collected at the base of the soil profile. Between 1987/88 and 1990/91, the annual flux of Ca and Mg in PC1 was greater than in PC1-08 or from the upland soils. This time period was also characterized by dry summers, low wetland water tables and consequently greater SO_4 export from the swamp (Eimers and Dillon 2002). However, between 1991/92 and 1994/95, fluxes of Ca and Mg measured at PC1 were generally lower than at PC1-08 or from the upland soils (Table 4). Therefore, even though chemical processes occurring in the swamp can have a profound effect on stream water chemistry resulting in large year-to-year variations, over a long period of time the export of BCs measured in PC1 appears to reflect losses from the catchment as a whole. A final point to note is that export of Ca and Mg in stream water was much greater than inputs measured in deposition (even with additional dry deposition) and SO_4 export was also about 40% greater than inputs measured in bulk deposition in most years. The source of this 'excess' SO_4 at PC1 is currently under investigation (Eimers and Dillon 2002), and has serious implications for continued net BC losses.

In contrast to Ca and Mg, N tended to be retained in the catchment (Figure 5). Most of the N measured in the PC1 stream was organic N; the average annual volume weighted concentrations of NO_3–N and NH_4–N were 29.9 µg/l and 6.4 µg/l compared with 266 µg/l for TON (Figure 3). There was no significant trend in NO_3–N export or concentration over the 17-year period. Annual volume weighted NO_3–N concentrations measured at PC1 are comparable to the lowest concentrations recorded in a survey of 39 streams (range 29.4–505 µg/l) in New York (Lovett et al. 2000). Using the 5-stage classification system adopted by Lovett et al. (2000) that is based on NO_3 levels in stream water, PC1 would be placed in stage 1, which is the lowest stage of N-saturation.

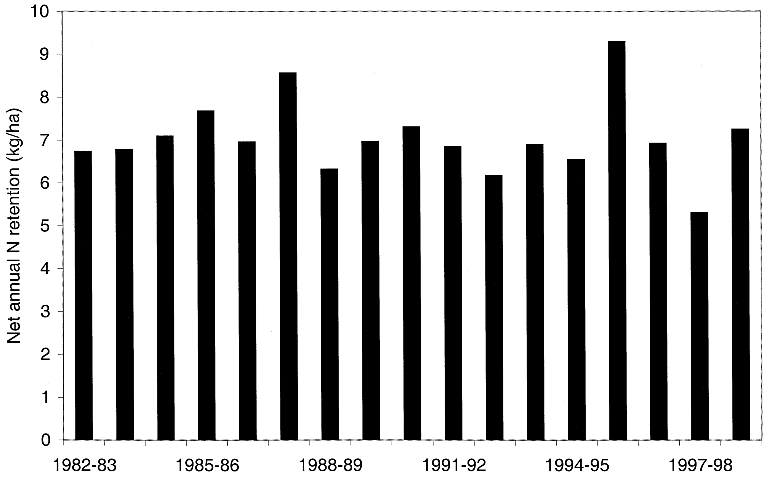

Figure 5. Net annual N retention (kg/ha) in the PC1 sub-catchment (1982/83 – 1998/99).

There were small, but significant increases in concentrations of NH_4 ($p<0.001$; 0.0007 mg/l/year) and TON ($p<0.001$; 0.005 mg/l/year) measured at PC1 during the study period (Figure 4). An increase in NH_4 and K (see earlier) may be due to an increase in mineralization at PC1 during the study period and/or a decrease in biological demand. The increase in NH_4 and K concentration at PC1 may be due to processes occurring in the swamp, the upland soils or both. Unfortunately, we do not have sufficient measurements at PC1-08 or in lysimeter leachate to compare temporal trends in stream water entering the swamp with trends recorded at PC1. The 1990s were characterized by several unusual climatic events in Ontario (Dillon et al. 1997), which may have resulted in an increase in mineralization because of higher than average temperatures or by the alteration of hydrological pathways. Lamersdorf et al. (1998) for instance reported that peaks in DOC, TKN, NH_4 and K were observed in soil leachate at several Norway spruce (*Picea abies* (L.) Karst.) dominated sites following periods of artificially induced drought as well as natural droughts. Similar peaks in NO_3, NH_4 and K have been recorded in the forest floor at PC1 following summer droughts (Lazerte and Scott 1996). Clearly, the influence of climate changes on mineral export warrants further investigation.

Mass balance estimates

Nitrogen

On average, 81% of the N measured in bulk deposition was retained in PC1, which represents a net input to the catchment of approximately 120 kg N/ha over the 17-year study period discounting any additional inputs from dry deposition (Figure 5). Despite the high net accumulation of N, there was no increase in NO_3 levels in stream water suggesting that N inputs have not exceeded the assimilation capacity

Table 5. Mean annual concentrations (μg/l) (1989/90–1993/94) of TKN, NO_3–N and NH_4–N collected in B-horizon lysimeters, PC1-08 and PC1.

	Lysimeter	PC1-08	PC1
T–KN	114.7 (22.9)	88.8 (7.2)	306 (39.0)
NH_4–N	15.4 (4.1)	5.5 (1.4)	8.0 (2.5)
NO_3–N	6.1 (4.1)	3.9 (1.3)	28.4 (6.7)

Values are annual means ± standard deviations.

for N at PC1. High levels of N retention have been reported for many catchments in eastern North America, although considerable variation in NO_3 export can occur within the same region (Dillon and Molot 1990; Lovett et al. 2000) . In some areas, such as the Turkey Lakes region in Ontario, export of N as NO_3 from soil beneath the rooting zone of sugar maple can be greater than total N deposition (Foster et al. 1989). The general lack of agreement between N deposition and NO_3 export has led to the conclusion that N (NO_3) export in parts of eastern North America is influenced by catchment characteristics rather than the level of N deposition (Lovett et al. 2000).

The high rate of N-retention at PC1 has occurred despite a lack of forest growth, indicating that the excess N is immobilized in the soil, denitrified or that concentrations of N in biomass have increased. Identifying the fate of the retained N is critical if we are to understand the long-term impact of chronic N-inputs at PC1. Denitrification is generally considered to be minimal in well-drained upland soils, although in the *Sphagnum*-conifer swamp or the riparian stream bed, waterlogged conditions may favor denitrification, and processes occurring in the swamp may be responsible for the low N export from PC1 (Burns 1998). However, average TKN and NO_3 concentrations measured in PC1-08 and in B-horizon leachate are much lower than values measured at PC1 (Table 5), suggesting that denitrification in the swamp or stream bed is not responsible for the excess N retained in PC1.

A number of factors can affect the N-retention capacity of upland soils, including prior land use, tree species composition, climate and physical factors such as slope and till depth (Dillon and Molot 1990; Lovett et al. 2000). The low NO_3 export at PC1 is likely due to a combination of the topography and species composition, although the impact of previous fires in the catchment cannot be excluded. Lovett et al. (2000) suggested that NO_3 export is low in watersheds that have red oak and hemlock as the dominant tree species because of the poor-quality litter with high lignin:N ratio and low nitrification rates. Furthermore, the shallow slopes and thin soils at PC1 may also contribute to the low NO_3 export. The highest levels of NO_3 export generally occur in the spring during snowmelt when biological activity is low or after prolonged summer droughts. At sites with deep till and steep slopes, NO_3 can be transported beneath the rooting zone in the deeper till or possibly *via* shallow subsurface flow and subsequently exported in stream-water. At PC1, overland flow accounts for only a small proportion of the water export and the shallow soils and generally moderate slope (5.9%) at PC1 indicate that NO_3 is available to plants and microorganisms throughout the soil profile.

BCs
Our mass balance estimates indicate that there has been a net loss of Ca and Mg, and a net retention of K in the PC1 catchment during the 17-year period regardless of the weathering method used in the calculations (Figure 6). Between 1982/83 and 1998/99, estimated losses of Ca were between 76.3 and 87.7 kg/ha; losses of Mg were between 3.5 and 15.4 kg/ha, and the net retention of K was between 18.3 and 46.2 kg/ha. Despite large annual variations, annual net losses of Ca and Mg decreased over the study period.

Because Na is not strongly retained in the soil or vegetation (Johnson et al. 2000), over time the Na flux at PC1 approximates the input of Na through mineral weathering and deposition. If Ca and Mg losses were occurring from the soil exchange complex, but the magnitude of these losses have decreased over time, a decrease in the Ca (or Mg): Na ratio in stream water would be expected. There has been a significant decrease (r^2=0.53; $p<0.001$) in the Ca:Na mass ratio at PC1 over the study period and including 1999–2000 (Figure 7). In 1982/83 the Ca:Na mass ratio was approximately 5, but by the mid-1990s the Ca:Na ratio in stream water approached 2, a decrease of approximately 60%. The higher Ca:Na ratios measured during the late 1990s are probably due to increased Ca export accompanying the drought-induced increases in SO_4 export, because these years were characterized by long summer droughts resulting in increased export of SO_4 in the autumn (Figure 3). In 1999/00 the Ca:Na ratio was again around 2. Based on weathering estimates for PC1 and deposition values (corrected for dry deposition) a Ca:Na ratio between 1.4 and 1.8 would be expected in stream water at PC1 if there was no loss (or retention) of Ca from the catchment. These expected values do not include estimates from the total correlation analysis because weathering rates for Na using this method were less than half the measured values at PC1. It is unlikely that the decrease in the annual Ca:Na ratio is due to changes in Ca weathering relative to Na weathering, or decreases in Ca deposition relative to Na deposition. As there has been no net forest uptake of Ca over the study period, it is more likely that the change in annual Ca:Na ratio in stream water is due to the release of Ca from the soil exchange complex, which has decreased over time. This decrease in the Ca:Na ratio further supports the suggestion that there has been a net loss of Ca from soils at PC1 over the 17-year period, although the magnitude of annual net loss has decreased over time.

A similar, though much less pronounced decrease ($r^2 = 0.29$; $p<0.05$) in the annual Mg:Na ratio was recorded at PC1 (Figure 7). In 1982/83 the Mg:Na ratio was around 1, but by the late 1990s the Mg:Na ratio was around 0.6. When calculated in an identical method for Ca:Na, the expected Mg:Na ratio in stream water at PC1 is between 0.4 and 0.57. The smaller decrease in the Mg:Na ratio indicates that there has been a smaller net loss of Mg from the exchange complex on the soil compared with Ca. Furthermore, a greater decrease in the exchangeable Ca pool relative to Mg should lead to a decrease in the Ca:Mg ratio in stream water. Over the 17-year period the Ca:Mg mass ratio at PC1 decreased significantly ($r^2 = 0.76$; $p<0.001$) from around 4.6 to around 3.6 (Figure 7). In contrast to Ca and Mg, there was no trend in the K:Na ratio in stream water. Clearly, export of K at PC1 is governed by factors that differ from those controlling export of Ca and Mg (SO_4)

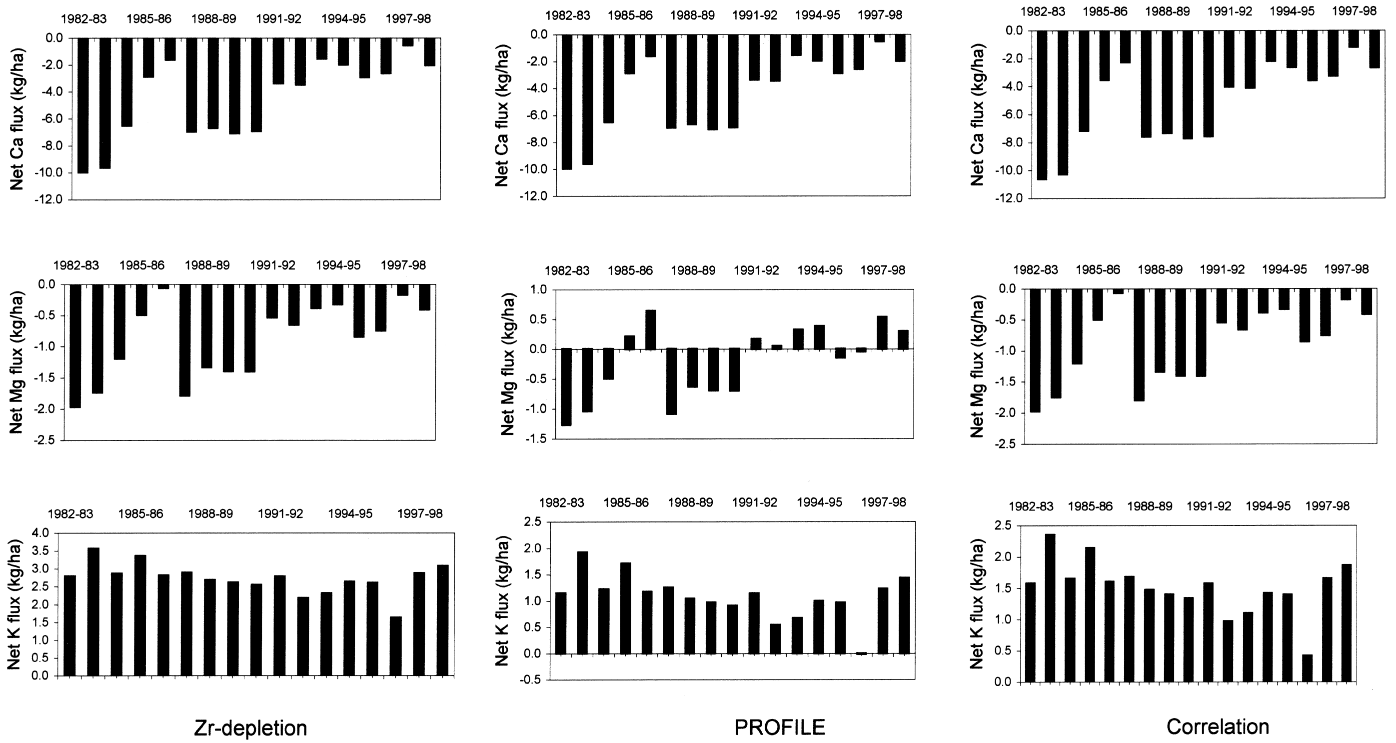

Figure 6. Annual mass balance estimates (kg/ha) for Ca, Mg and K using three estimates (Zr-depletion, PROFILE and correlation methods) of mineral weathering (1982/83 – 1998/99).

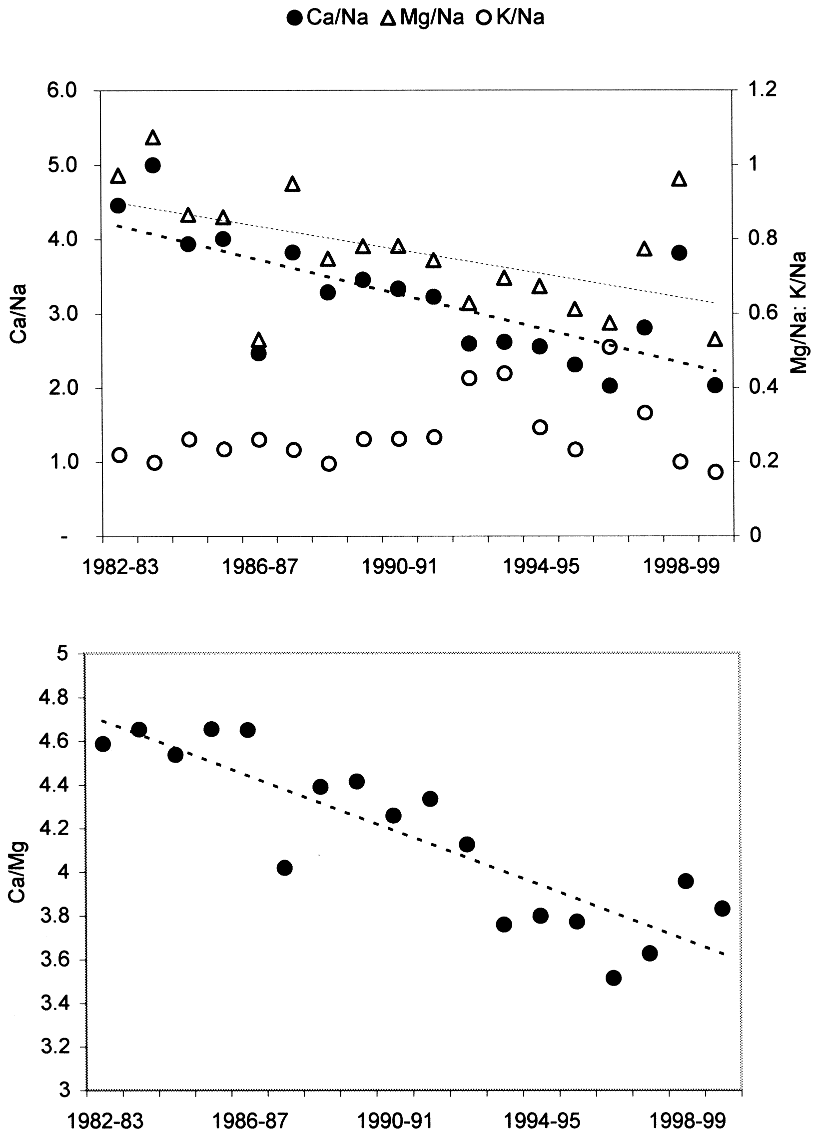

Figure 7. Mass ratios (Ca/Na; Mg/Na and K/Na (upper) and Ca/Mg (lower)) in the PC1 stream (1982/83 – 1999/2000). Dashed lines indicate significant linear trends ($p<0.05$).

and should be taken into account during studies that investigate the impact of acid deposition on the base status of soils (i.e. critical load models).

Measured changes in soil BC concentrations

Despite the large variation in soil chemistry within each horizon, significant changes in some soil chemical parameters were found (Table 6; Figure 8). Soils at

Table 6. Exchangeable (2 M NaCl) Ca, Mg and K concentrations in LFH, A, and B soil horizons in 1983 and 1999 at PC1.

		mg/kg		*p*
		1983	1999	
LFH	Ca	2630 (898)	2340 (1434)	0.07
	Mg	281 (98)	236 (107)	0.08
	K	956 (430)	609 (222)	0.002
A-horizon	Ca	189 (157)	70 (37)	<0.001
	Mg	22.4 (20.2)	17.5 (6.2)	0.37
	K	81.2 (65.8)	57.5 (18)	0.11
B-horizon	Ca	58.3 (77.4)	29.3 (30)	0.05
	Mg	5.6 (4.2)	8.7 (4.5)	<0.001
	K	28.3 (17.4)	37.1 (17.3)	0.006

Standard deviation given in parenthesis.

PC1 are acidic, and between 1983 and 1999 there were significant decreases in mean pH (H_2O and $CaCl_2$) values in the LFH, A- and B-soil horizons. Decreases in mean pH ($CaCl_2$) values were similar in all three horizons (0.3 – 0.4 pH units), although decreases in pH (water) were greater in the A- and B-horizons (0.3 – 0.5 pH units) compared with the LFH horizon (0.2 pH units). Only three of the soil pits had a BC or C-horizon, and although soil pH in this horizon was lower in 1999 compared with 1983, the limited sample size precludes a meaningful interpretation of changes over time. Several studies in Europe have reported significant decreases in soil pH during the latter half of the 20th century, which are believed to be due to acid deposition. In many cases however, the influence of vegetation dynamics is substantial (*see* Nilsson and Tyler 1995; Tamm and Hallbacken 1988). Long-term changes in soil pH in eastern North America are not as well documented although a few studies have reported that soil pH in forests has decreased in recent decades (Johnson et al. 1994; Drohan and Sharpe 1997). In the present study, the significant decrease in soil pH is most likely due to acid deposition because there has been no net uptake of BCs during the 17-year study period.

There was a significant decrease in mean exchangeable Ca concentrations in the A- and B-horizons between 1983 and 1999 (Table 6). There was also a significant decrease in K concentration in the LFH horizon, although exchangeable concentrations of Mg and K in the B-horizon were significantly greater in 1999 compared with 1983 (Table 5). Base cation concentrations measured in the BC and C horizon were used to estimate the BC pools, but as with soil pH measurements, the limited sample size precludes a comparison of changes over time. Even though BC concentrations were greatest in the LFH horizon, the B-horizon contains the largest pool of BCs (Table 7). Using bulk density estimates of each soil horizon (and assuming no change in bulk density or depth of each horizon), the exchangeable soil Ca pool decreased from about 199 kg/ha in 1983 to 114 kg/ha in 1999, a decrease of about 85 kg/ha. In contrast, the exchangeable soil Mg pool

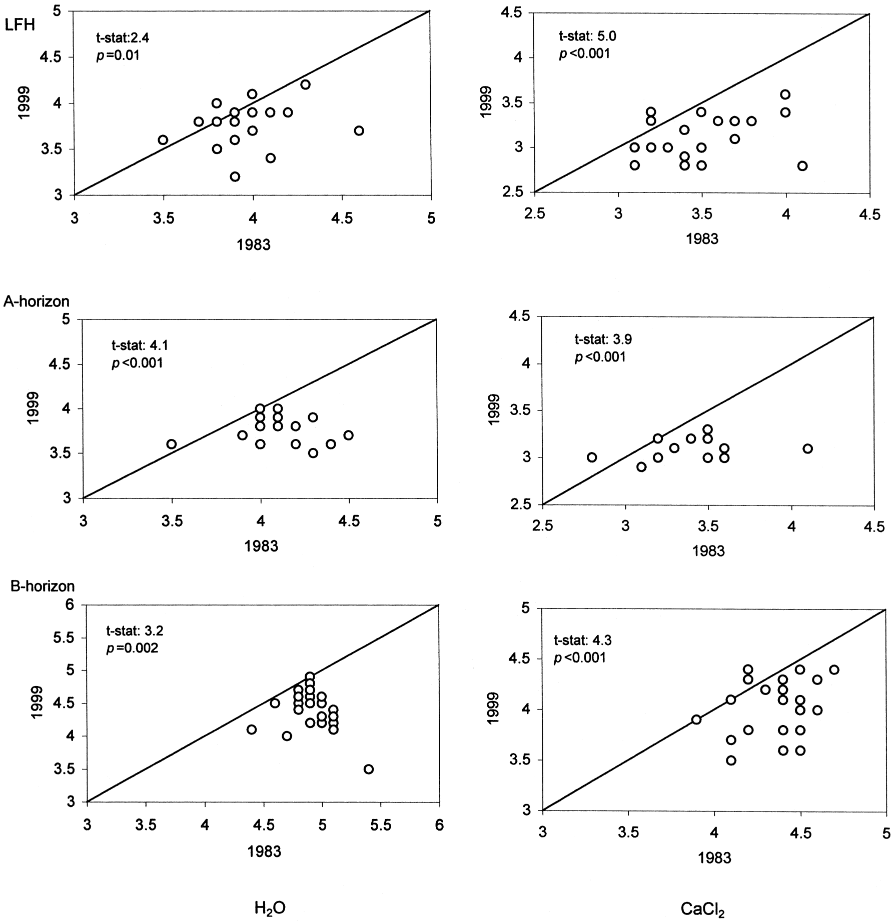

Figure 8. Relationship between pH (H_2O and $CaCl_2$) measured in 1983 compared with 1999, in LFH, A- and B-horizon soil at PC1.

increased from 22.9 kg/ha in 1983 to 27.7 kg/ha in 1999, and the exchangeable K pool in soil was unchanged.

Numerous studies in Europe and eastern North America have expressed concern over BC losses from soil due to acid deposition and harvesting (Daldoum and Ranger 1993; Houle et al. 1997; Likens et al. 1998; Adams et al. 2000; Thimonier et al. 2000). In eastern North America, losses of Ca are generally of the greatest concern (Federer et al. 1989; Lawrence et al. 1997; Adams et al. 2000). Some watershed mass balance studies have indicated that Ca losses through tree uptake and stream flux exceed inputs through mineral weathering and deposition (Houle et al. 1997; Likens et al. 1998). Lawrence et al. (1997) re-sampled soils from red spruce (*Picea rubens* Sarg.) forests in several north-eastern states in the U.S. and reported that significant decreases in exchangeable Ca pools occurred in the second

Table 7. Estimated exchangeable (2 M NaCl) Ca, Mg and K pools (kg/ha) at PC1 in 1983 and 1999.

Horizon	1983			1999		
	Ca	Mg	K	Ca	Mg	K
LFH	23.9	2.4	8.4	25.3	2.3	7.7
A	42.6	4.7	18.9	15.5	3.9	14.4
B	126.2	14.7	67.1	66.3	20	70.3
BC	6.5	1.1	3.9	6.4	1.5	7.1
Sum	199	22.9	98.3	114	27.7	99.5

BC pools were calculated assuming that there was no change in bulk density or depth of each soil horizon, and differences in pools were solely due to changes in exchangeable Ca, Mg and K concentration between 1983 and 1999.

half of the 20th century and acid deposition was attributed as the probable cause. A similar long-term decrease in exchangeable Ca and Mg was found in Pennsylvania (Drohan and Sharpe 1997). In the present study, measured losses of Ca (~ 85 kg/ha) were very similar to mass balance estimates (76–88 kg/ha). Because there was negligible forest growth over the 17-year period, these losses can be solely attributed to acid deposition and the loss of Ca represents a 40% decrease in the exchangeable Ca pool. In 1999, the exchangeable Ca pool was approximately 114 kg/ha, which is only one quarter of the Ca pool held in biomass (~ 471 kg/ha). Mass balance estimates indicate that small net losses of Ca from PC1 continue (1–3 kg/ha/year), which may threaten the health of the upland forest at PC1 if SO_4 export (and therefore Ca export) does not decrease. This is particularly true if decreases in Ca lead to an increase in Al mobilization in soil solution, which may further damage trees either directly by toxicity or indirectly by competition with the limited Ca available to trees (Thornton et al. 1986; Shortle and Smith 1988) .

In contrast to Ca, there was no measurable decrease in the exchangeable Mg and K pools in soil at PC1 between 1983 and 1999 (Table 7). Our mass balance estimates indicated that losses of Mg ranging from 3.5 to 15.4 kg/ha occurred over the 17-year period. The slight decrease in the Mg:Na ratio measured at PC1 also suggests that there was a net loss of Mg from the catchment, which was not found in the soil re-sampling study. This may simply be because losses of exchangeable Mg from the upland soils were so small that differences could not be detected, even with our sampling strategy, because of the large variation in soil Mg concentrations. Other possible reasons for the discrepancy include an underestimate of Mg weathering inputs – however this does not explain the decrease in Mg:Na, and the release of Mg into the exchangeable pool from decomposing organic matter. At present, it appears that the loss of Mg from soil at PC1 is approximately balanced by inputs through mineral weathering and deposition. Other studies in eastern North America have suggested that losses of Mg have occurred in recent years (Houle et al. 1997; Friedland and Miller 1999), although in most cases these studies were performed in actively growing forests that also deplete soil Mg reserves. There was very little change in the exchangeable K pool over the 17-year period, even though our mass balance estimates indicated that there was a net retention of K in PC1 of between 18.3 and 46.2 kg/ha. Overall, it appears that there has been no net loss of K from soils at PC1 over the 17-year study period.

Uncertainties in the mass balance calculations

Each component of the mass balance calculations is of course subject to some uncertainties that should be considered. In this study we increased BC inputs in bulk deposition by 13% to account for the underestimation of dry deposition beneath the canopy. We also assume that the ratio of Na to each BC in bulk deposition is the same as in dry deposition. It is more likely that the proportion of dry deposition was greater in dry years and that the Na:BC ratio is slightly different in dry deposition compared with bulk deposition. However, these uncertainties will have little impact on our mass balance calculations because inputs of BCs in deposition are small relative to other fluxes such as stream export. Our N mass balance calculations were not corrected for dry deposition and are based on PC1 measurements where organic N is derived primarily from the swamp. As a result, our mass balances may represent a conservative estimate of N accumulation in upland soils at PC1, although the importance of denitrification or N-fixation on N budgets at PC1 remains to be quantified.

Export in stream water represents a larger flux for BCs than deposition at PC1. In this study, stream flow was continuously monitored and our calculations were based on the chemical analysis of over 1100 separate samples collected over 6200 days. Samples were often collected daily during periods of high flow in spring and fall and we feel that the error associated with stream flux measurements is small and insignificant in our calculations. Based on forest surveys in 1983 and 1999, we set uptake values to 0, although there is obviously error associated with this estimation. It is quite possible that there was some net release of nutrients from the dead trees over the study period, or continued accumulation in dead biomass or in trees <12 cm (dbh) that we are unable to quantify.

The greatest uncertainty in our mass balance estimates concerns mineral weathering estimates. Several reports in the literature have discussed the uncertainties associated with mineral weathering estimates and the implications of such uncertainty (Hodson and Langan 1999). All our weathering estimates are based on the mineralogy or bulk composition of the < 2 mm soil fraction, and the potential for weathering inputs from larger soil fractions is not considered. Similarly, we use an ‘average’ soil depth, where in reality soil depth varies from a few cm to almost 1 m. Obviously, mass balances conducted on individual plots throughout PC1 would reveal large variations in BC mass balance budgets due to the heterogeneity in soil depth, forest growth, flow paths, etc. However, assuming Na retention in PC1 to be negligible, our mineral weathering estimates for Na using the three methods appear to lie within the true Na weathering at PC1. Of course, this does not necessarily imply that weathering estimates of Ca, Mg and K are equally reliable. At present, our mass balance calculations must be considered to be the current best available estimates given the available data, the heterogeneous nature of PC1 and the uncertainties associated with the methodology in estimating mineral weathering. Nevertheless, weathering estimates included in our mass balance calculations are consistent with observed changes in soil and stream water chemistry at PC1 over the 17-year period.

Summary

Our mass balance estimates at PC1 indicate that there has been a net loss of Ca and Mg from the catchment over a 17-year period. Significant decreases in exchangeable soil Ca concentrations and soil pH were found, supporting our mass balance estimates. Losses of Mg were not detected by our soil analyses, possibly because losses of Mg were smaller than for Ca. Our mass balance estimates indicate that despite a large reduction in SO_4 deposition, annual net losses of Ca continue. There was no trend in NO_3 export from PC1 and the low levels of NO_3 in stream water suggest the catchment has not reached N-saturation, despite small peaks in NO_3 concentration and export in years with prolonged summer droughts. Losses of Ca represent a $\sim 40\%$ reduction in the soil exchangeable pool, which is currently about 114 kg/ha and is only a quarter the magnitude of the Ca pool in biomass. Continued net losses of Ca due to acid deposition and soil acidification therefore, may threaten the future health of the upland forest at PC1.

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