Base cation and nitrogen budgets for seven forested catchments in central Ontario, 1983–1999

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Abstract

There is widespread concern that the combination of acid (S and N) deposition and tree harvesting may deplete available base cation pools in soils to the extent that forest health and productivity may be impaired. Here we present mass balance budgets for Ca, Mg, K and N for seven forested catchments in Muskoka–Haliburton, Ontario over a 17-year period, during which time SO_4 deposition decreased by $\sim$40%, but N deposition was unchanged. Mass balance budgets were calculated as the difference between inputs from deposition and mineral weathering (base cations only) and export in stream water plus uptake in biomass. There were significant decreases in annual SO_4 export from all catchments, although temporal trends in base cation export were varied. Export of Ca, Mg and SO_4 exceeded inputs in deposition, but concentrations in stream water were highly variable from year-to-year. Temporal patterns in Ca, Mg and SO_4 concentration in stream water were synchronous among all seven catchments and appear related to climate variations over the 17-year period. Most of the N exported from each catchment was organic N, although export of NO_3 varied considerably (10-fold), both between catchments and between years. Differences in NO_3 export appear to be due to differences in catchment characteristics and also climate variations. Nevertheless, net N accumulation at the seven catchments was between 92.6 and 128.1 kg/ha N over the 17-year period. All catchments experienced a net loss of Ca, which varied between 33 and 287 kg/ha over the 17-year period. Net losses of Mg were lower, and in general, mass balance estimates indicate that most catchments are in balance with respect to K. Losses of Ca over this 17-year period, represent up to 60% of the current exchangeable Ca soil pool. If Ca losses, due to acid deposition and harvesting continue at the present rate, forest health and productivity may be impaired within just a few decades.

1. Introduction

Throughout eastern North America and Europe concern has been expressed over the depletion of exchangeable base cation pools in soils due to a combination of acid deposition and tree harvesting (Adams et al., 2000; Federer et al., 1989; Johnson et al., 2000; Sverdrup and Rosen, 1998; Thimonier et al., 2000). If losses of base cations from soils exceed the combined inputs through deposition and mineral weathering, soils will acidify. In areas with low soil base saturation, forest health and productivity may ultimately be impaired (Demchik and Sharpe, 2000; Horsley et al., 2000; McLaughlin et al., 2000; Shortle and Smith, 1988; Sverdrup and Rosen, 1998). In recent years, there has been a significant decrease in SO_4 deposition in

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eastern Canada (Dillon et al., 1988; Environment Canada, 1997), which is expected to lead to a decrease in base cation leaching from forest soils (Kirchner and Lydersen, 1995). In contrast, N deposition has remained unchanged and there is growing concern that some forests in the region are approaching N saturation (Aber et al., 1991). In such instances, NO_3 export is expected to increase, which may counteract the benefits of reduced SO_4 deposition (Aber et al., 1989).

Our knowledge of the impact of acid deposition on biogeochemical cycling in forests in eastern North America is based on a limited number of small-scale watershed studies (Hornbeck et al., 1997; Houle et al., 1997; Johnson et al., 2000; Likens et al., 1996; Watmough and Dillon, 2002a,b), and models are used to extrapolate this information over a wider geographical area (Arp et al., 2001; Ouimet et al., 2001). Recently, Johnson et al. (2000) addressed the issue of scale in these small watershed studies, clearly demonstrating that nutrient budgets at Hubbard Brook were greatly influenced by the part of the watershed under investigation. Similar spatial variability between watersheds within a relatively small region has been reported in other parts of eastern North America (Hornbeck et al., 1997; Lovett et al., 2000). Consequently, information obtained from a single catchment study may not accurately reflect the sensitivity to acid deposition and harvesting exhibited by the majority of forested catchments in a given area. Furthermore, by examining a number of forested catchments within a region, responses acting on a regional scale (climate) may be distinguished from factors such as harvesting that act at a local scale.

In this study, we estimated mass balance budgets for Ca, Mg, K and N over a 17-year period (1983–1999) at seven calibrated catchments in the Muskoka–Haliburton region of central Ontario. The sites were chosen to represent the range of forested catchments (tree species, soil depth, topography, etc.) that are typically found in the region and cover a period during which SO_4 deposition decreased by about 40%, but N deposition was unchanged (Watmough and Dillon, 2002a).

2. Methods

2.1. Study site

All seven catchments (elevation range between 300 and 450 m a.s.l.) are located in the Muskoka–Hali-

burton region of central Ontario on a southern extension of the Precambrian Shield near the southern limit of the Boreal ecozone and are in a region that is considered very sensitive to acid deposition (Fig. 1). The seven catchments were chosen to be representative of upland forests in the region and all are located within a radius of approximately 30 km (Table 1). Four of the catchments drain into Harp Lake (HP3A, HP4, HP6 and HP6A), while the remaining three catchments drain into Plastic Lake (PC1), Red Chalk Lake (RC4) and Chub Lake (CB1), respectively. Streams draining each of the seven catchments are gauged and have been monitored for stream flow and chemistry since the late 1970s. A number of cottage dwellings, both seasonal and permanent, surround Harp Lake and are served by an access road, which is maintained through the winter. This has resulted in road-salt contamination at two of the catchments (HP4 and HP6A) because weirs at these sites are located on the lake-side (downslope) of the road. Road-salt contamination is not a concern at the remaining three lakes, although there are also a small number of cottages on Red Chalk Lake and Chub Lake. Bedrock in the region is mainly granitized biotite and hornblende gneiss, with minor areas of amphibolite and schist. The surface geology in uplands is dominated by basal tills and sand deposits, which are frequently covered by peat in the lowland areas. Upland soils are typically orthic humo-ferric, ferro-humic, sombric humo-ferric podzols and brunisols (Canadian Soil Survey Committee, 1978). Cumulo humisols and humic mesisols are found in low-lying areas and bedrock outcrops or ponds are found in four of the catchments. Parts of some of the catchments were cleared around the turn of the twentieth century (notably at Harp Lake and CB1), but the forests have since been allowed to re-grow when farming was abandoned during the early 1900s. Presently, selective harvesting is practiced at five of the seven catchments (CB1, HP4, HP3A, HP6 and HP6A), but with the exception of HP3A and to a lesser extent HP6 and HP6A, there has been no harvesting during the 17-year study period. Upland forests are dominated by uneven aged sugar maple (*Acer saccharum* Marsh.) and red maple (*A. rubrum* L.), with lesser amounts of American beech (*Fagus grandifolia* Ehrh.), yellow birch (*Betula alleghaniensis* Britt.), red oak (*Quercus rubra* L.), eastern hemlock (*Tsuga canadensis* L.) and white
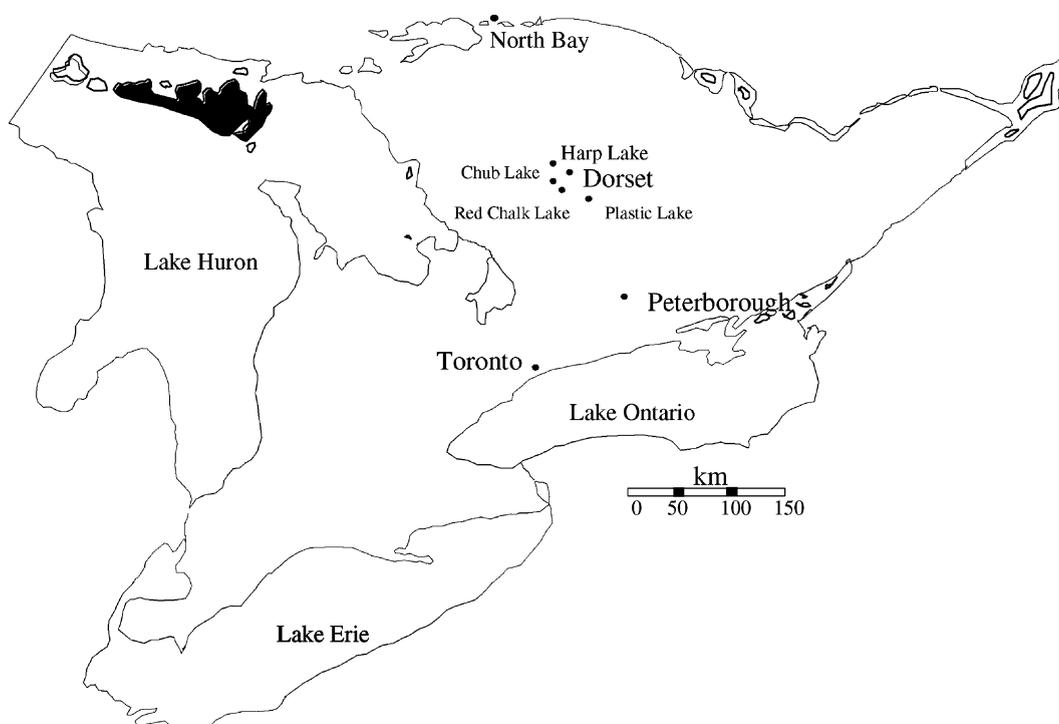
Fig. 1. Location of the study sites in Muskoka–Haliburton, Ontario, Canada.

Table 1
Forest cover and physical characteristics of the seven study catchments

	Catchment						
	PC1	CB1	RC4	HP3A	HP4	HP6	HP6A
Area (ha)	23.34	59.69	45.46	19.95	119.09	9.97	15.28
Slope (%)	5.9	3.0	2.5	8.0	5.0	8.0	10.0
Minor till (>1.0 m, %)	9.6	24.2	76.3	97.1	56.1	45.2	6.6
Thin till, ridges (%)	80.2	72.4	16.0	0.0	32.8	54.8	84.9
Peat (%)	7.0	2.8	2.9	2.9	0.0	0.0	8.5
Pond, bedrock (%)	3.2	0.6	4.8	0.0	0.9	0.0	0.0
BA (m^2/ha)	31.29	26.17	25.98	21.27	23.50	24.04	23.75
Stem density	637	620	592	472	521	452	587
Sugar maple (%)	0.68	14.15	33.52	54.89	41.13	40.78	42.39
Red maple (%)	10.41	19.24	14.84	6.86	12.77	6.52	4.14
Red oak (%)	8.18	17.83	19.48	2.79	1.59	1.14	0.29
White pine (%)	42.45	0.66	0.68	0.00	2.60	0.00	6.50
Hemlock (%)	18.71	0.28	2.60	1.78	4.85	23.0	14.00
Yellow birch (%)	0.50	4.71	6.00	11.31	7.23	12.40	11.23
Beech (%)	1.29	3.3	7.93	4.32	6.89	8.97	1.62
Other (%)	17.78	39.83	14.95	18.05	22.94	7.19	19.83

Tree species cover is given as percentage of basal area (BA).

pine (*Pinus strobus* L.; Table 1). From 1983 to 1998 mean annual precipitation and air temperature were 976 mm and 5.3 °C, respectively.

2.2. Bulk deposition

Deposition data were obtained from collections of bulk deposition (three locations within the region), which we define as that caught in a continuously open, 0.25 m² collector and have been presented elsewhere (Watmough and Dillon, 2002a,b). For mass balance estimations, inputs of base cations in bulk deposition were increased by either 6% (deciduous) or 13% (coniferous) to compensate for additional inputs through dry deposition (Duchesne et al., 2001; Shepard et al., 1989). These estimations were based on Na enrichment in throughfall at PC1 and HP4 that was measured during a 3-year period (1983–1985; Neary and Gizyn, 1994). 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 measured in 1983–1985 was representative of the 17-year period.

2.3. Weathering

Long-term elemental weathering rates at all seven catchments were estimated by examining the bulk and mineralogical composition of soil from between 5 and 10 pits excavated at different locations in the upland parts of each catchment. Mineralogical data were obtained from Law (1991; HP4) and Kirkwood (1990; PC1) and additional soil sampling was conducted during the summer 2000 at the remaining five catchments. The principle of this traditional method for estimating weathering rates was described by Bain et al. (1990). Zirconium (Zr) occurs in soil principally as 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. The amount of Zr is assumed uniform throughout the soil profile at the end of the last glaciation. Over time, the weathering products, including base cations, are progressively removed either by plant uptake or leaching, leaving the upper layer enriched in Zr (Starr et al., 1998). The consistency of the base cation to Zr ratio enables the amount of

base cations lost from the weathered layer to be calculated. Details of the methods are described fully by Kirkwood (1990) and Law (1991). Briefly, soil samples were taken at regular intervals with depth from each soil pit (10–20 samples per pit) extending down to bedrock. Concentrations of elements (CaO, MgO, K_2O, Na_2O, Zr) in the <2 mm fraction were determined by X-ray fluorescence. Elemental concentrations in all samples were corrected for organic matter content using loss on ignition values of each sample. Since bulk compositional analyses are reported as weight percent, the original weight of the till for each catchment must be obtained to calculate useful units for gains and losses. This was achieved using average bulk density values in the lowermost soil sample from each pit and average soil depth. This value permits calculation of total losses/gains of the major oxides since glaciation. Average compositions of the unweathered till and its weathered equivalent, the average soil composition, are required to complete the calculation. For this study, we assumed that the current annual base cation weathering rate was equivalent to the average annual loss of Ca, Mg, K and Na over this long time period (12,000 years).

2.4. Stream export

Water level or stage in each stream was recorded continuously at weirs installed at the catchment outflow, and daily stream discharge (m³ per day) was computed using established stage–discharge relationships. Water samples were generally collected weekly or biweekly, except during periods of high flow during spring melt when samples were collected more frequently (sometimes daily). Samples were filtered through 80 μm Nitex mesh in the field, and transported to the laboratory for chemical analyses in insulated containers. Samples were analysed for Ca, Mg, K and Na by atomic absorption spectrophotometry, SO_4 by ion chromotography and NH_4 and NO_3 were determined colorimetrically (Ontario Ministry of Environment, 1983). In addition, samples were analysed for TKN (total Kjeldahl N) using standard methods. Data are presented as areal fluxes (kg/ha per year) and volume–weighted concentrations (mg/l or μg/l) for each water year (1 June to 31 May) between 1982/1983 and 1998/1999.

2.5. Soil chemistry

Details of the methods for soil analysis are described fully by Lozano (1987). Soil samples (LF, H, Ae, Ah, Bf, Bhf, BC and C) were collected from between 6 and 21 pits dug at sites throughout the upland parts of each catchment. Soils at five of the catchments were sampled in the summer of 2000, while soils at PC1 and HP4 that had previously been sampled in 1983, were sampled again in the summer of 1999 to determine whether changes in soil chemistry had occurred over the 17-year period (Watmough and Dillon, 2002a,b). 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 (Ontario Ministry of Environment, 1983). Each organic layer was ground, 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 standard methods (Ontario Ministry of Environment, 1983).

2.6. Forest biomass and nutrient pool estimates

The forest at HP4 and PC1 were surveyed in 1983 and again in 1999 using a point-sampling technique (Lozano and Parton, 1987; Watmough and Dillon, 2002a,b), while forests at the remaining five catchments were surveyed only in the summer of 2000. Sample point selection was done on a fixed grid system to ensure complete coverage of the entire catchment. At each sample point, a wedge prism with a basal area factor of 2.0 m^2/ha was rotated 360° through the sampling point. All trees with a diameter greater than 12 cm (or 10 cm PC1) 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 each sub-catchment.

Stand biomass and nutrient content were estimated using the equations and nutrient contents established by Lozano and Parton (1987) for use in the region. Tree biomass by species was calculated for each size class (2 cm intervals) from a regression (biomass) 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 (kg/ha). The biomass values for all size classes and all tree species were summed to obtain the total standing live biomass at each catchment. 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 trees were calculated as the product of tree-component biomass and appropriate elemental concentration. Base cation concentrations were measured in trees that were destructively sampled from outside of the catchments (19 white pine, nine red maple, eight sugar maple, six red oak; five hemlock, yellow birch and beech; three balsam fir (*Abies balsamea* L.), black ash (*Fraxinus nigra* Marsh.), white cedar, (*Thuja occidentalis* L.), poplar (*P. grandidentata* Michx.), white birch (*B. papyrifera* Marsh.) and white spruce (*Picea glauca* (Moench) Voss)), and were used to validate biomass equations reported in the literature. Nutrient contents of above and below ground biomass were summed to give the total nutrient content of standing live biomass.

2.7. Major element mass balances

Mass balance budgets (kg/ha per year) for Ca, Mg, K, and N were calculated for each water year between 1982/1983 and 1998/1999. Annual mass balance estimates were computed as the difference between inputs in bulk precipitation (plus additional dry deposition for BC; D) plus weathering (W), and losses in stream export (E) plus uptake by forest biomass (U).

$$\Delta BC, N = \text{inputs}(W + D) - \text{output}(E + U)$$

Annual mass balance budgets at HP4 and PC1 were estimated using measured changes in forest biomass averaged over the 17-year period. In contrast, mass balance estimates for the remaining five catchments were calculated assuming either no net growth (as occurred at PC1) or by dividing the current nutrient content held in biomass by 100 to obtain an annual uptake value (similar to the change measured at HP4 between 1983 and 1999). As we know that some harvesting has occurred during the study period at HP6, HP6A and in particular HP3A, our uptake values

will probably underestimate nutrient uptake by trees at these sites.

Trends in monthly volume–weighted stream concentration were examined using a seasonal Mann Kendall test (treating months as seasons) and trends in annual nutrient export were examined using simple linear regression analysis. Pearson correlation analysis was used to examine relationships among different nutrients in stream water. Annual element concentrations were standardized using Z-scores (annual observation—17-year mean all divided by the standard deviation of the 17-year mean) in order to facilitate comparison of temporal patterns among elements.

3. Results and discussion

3.1. Inputs in atmospheric deposition

Temporal trends in SO_4, N and base cations in bulk deposition in the study area have been discussed in detail previously (Dillon et al., 1988; Watmough and Dillon, 2002b). Briefly, SO_4 deposition decreased from around 33 kg/ha in 1982/1983 to around 18 kg/ha in 1998/1999. Nitrogen deposition has remained relatively constant over the study period, averaging 8.7 kg/ha per year (5.2 kg NO_3; 3.5 kg NH_4). Between 1982/1983 and 1998/1999, there were also small (0.06 kg/ha per year Ca; 0.01 kg/ha per year Na; 0.02 kg/ha per year K) but significant decreases in annual inputs of Ca, K and Na in bulk deposition (Watmough and Dillon, 2002a). Annual bulk deposition of Ca, Mg, K and Na were between 1.63 and 3.48 kg/ha, 0.29 and 0.55 kg/ha, 0.52 and 1.20 kg/ha and 0.43 and 0.76 kg/ha, respectively over the 17-year period.

To compensate for the possible underestimation of base cation deposition in our mass balance calculations, annual bulk deposition at the predominately deciduous sites was increased by 6% (average Na enrichment in throughfall compared with bulk deposition over a 3-year period at HP4; 1983–1985) and by 13% at PC1 (Na enrichment at PC1; 1983–1985). Inclusion of the extra dry deposition estimates however, has very little impact on the total input of base cations in deposition. Between 1982/1983 and 1998/1999, "total" inputs of base cations via deposition at the deciduous sites were estimated to be 44.0 kg/ha

Ca, 7.8 kg/ha Mg and 12.2 kg/ha K. At PC1, base cation inputs were slightly higher and were estimated to be 46.9 kg/ha Ca, 8.2 kg/ha Mg and 13.0 kg/ha K. In this study, no attempt was made to estimate the relative contribution of dry deposition to total N-inputs due to difficulties in interpreting throughfall data (Neary and Gizyn, 1994) and we acknowledge that our measurements of bulk deposition may underestimate total inputs of N to the catchments. Between 1982/1983 and 1998/1999, 147.4 kg/ha N was collected in bulk deposition.

3.2. Weathering inputs

Annual weathering rates for Ca, Mg, K and Na were between 2.66 and 10.0 kg/ha, 0.96 and 4.81 kg/ha, 2.00 and 7.00 kg/ha and 3.04 and 6.8 kg/ha, respectively (Table 2). Differences in weathering rates among sites were largely due to differences in soil depth (Table 2) and are comparable to values reported for acid podzols in Quebec (Houle et al., 1997) and Europe (Langan et al., 1996; Sverdrup et al., 1998; Starr et al., 1998). Notably, some workers have found that weathering rates calculated using the Zr-depletion method are higher than weathering rates estimated using other methods such as PROFILE (Starr et al., 1998). At HP4 and PC1, mineral weathering was also estimated using PROFILE and in general weathering rates were higher using the Zr-depletion method (Watmough and Dillon, 2002a,b). For example, the weathering rates for Ca at HP4 and PC1 estimated using PROFILE were 8.90 and 2.0 kg/ha per year, respectively compared with 10.0 and 2.66 kg/ha per year estimated using the Zr-depletion method (Watmough and Dillon, 2002a,b). A higher weathering rate may be expected from the Zr-depletion method because this method provides a time-averaged value, and it is likely that weathering rates have changed over time as more

Table 2
Weathering rates (kg/ha per year) calculated using the Zr-depletion method at the seven study catchments

	PC1	CB1	RC4	HP3A	HP4	HP6	HP6A
Ca	2.66	4.56	9.15	8.14	10.00	7.20	6.14
Mg	0.96	1.93	4.81	3.36	4.38	3.00	2.47
K	2.81	2.13	3.33	2.71	7.00	2.00	2.41
Na	3.21	3.65	5.12	5.01	6.80	4.20	3.04

easily weathered minerals were 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.

In an attempt to assess how estimated weathering rates compare with current base cation fluxes, Na export from each catchment was compared with the combined annual inputs through weathering and deposition averaged over the 17-year period (Fig. 2). Data from HP6 were excluded from this analysis because of road-salt contamination, and Na fluxes at HP4 were estimated from a small separately gauged sub-catchment (HP4-21) within HP4 for similar reasons. Sodium is generally not retained in vegetation or soil and therefore over time, the Na export in stream water should be approximately equal to the combined Na inputs from weathering and deposition only. As expected, export of Na was greater at sites predicted to have higher Na-weathering rates, although Na-weathering was overestimated by approximately 20–30% at most sites (Fig. 2). This suggests that the current Na-weathering rate is slightly below the range estimated using the Zr-depletion method. This does not necessarily imply that weathering rates of K, Mg and Ca are also underestimated however, because weathering rates for different minerals may change at different rates over time (Kirkwood, 1990).
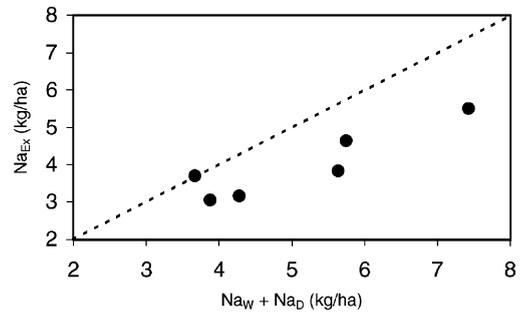

Fig. 2. Relationship between estimated inputs of Na (weathering and deposition) and export in stream water at six of the seven study catchments. Values are the average annual input and export at each catchment between 1983 and 1999. Dashed line represents the 1:1 ratio. See text for further details.

3.3. Forest biomass

Forest biomass at the seven catchments ranged between 170×10^3 kg/ha (HP3A) and 214×10^3 kg/ha (PC1; Table 3). The low biomass value at HP3A is undoubtedly due to some selective cutting that occurred at this site in the late 1990s. The range of biomass estimates in the study area generally falls within the lower range of biomass values typically reported for mature mixed hardwood stands in eastern North America (Adams et al., 2000; Arthur et al., 2001; Martin and Bailey, 1999). Nutrient pools in biomass were fairly consistent among the seven catchments and were typical of values reported for similar forest types in eastern North America (Adams et al., 2000; Arthur et al., 2001; Federer et al., 1989; Table 3). The Ca, Mg, K and N pools in biomass at the seven catchments were between 471 and 705 kg/ha, 42.5 and

Table 3
Biomass and nutrient content of the forests at the seven study catchments

	PC1		CB1		RC4		HP3A		HP4		HP6		HP6A	
	T	A	T	A	T	A	T	A	T	A	T	A	T	A
Biomass[a]	214	164	197	166	213	181	170	145	180	153	185	157	175	146
Ca (kg/ha)	471	394	554	481	705	620	568	500	570	504	589	515	521	456
Mg (kg/ha)	42.6	31.4	42.7	33.4	53.2	41	44.3	36.2	46.9	38.4	49.8	40.7	42.5	34.6
K (kg/ha)	213	170	244	207	245	205	205	177	212	183	231	199	202	173
N (kg/ha)	374	293	399	333	436	352	353	286	367	296	409	331	356	288

T, total tree; A, above ground.
[a] Biomass in 1000 kg/ha.

53.2 kg/ha, 202 and 245 kg/ha; and 353 and 436 kg/ha, respectively.

Nutrient uptake values for PC1 and HP4 over the 17-year period were determined from the change in biomass between 1983 and 1999. At PC1, there was no net growth and nutrient pools in biomass were lower in 1999 than in 1983 because of the relative increase in white pine and hemlock that have lower nutrient concentrations than species such as red oak, red maple and poplar (Watmough and Dillon, 2002a). However, because changes in the standing dead biomass pool were not considered, net nutrient uptake values for the forest at PC1 were set to zero. In contrast, forest biomass at HP4 increased by approximately 20% between 1983 and 1999, representing an uptake of 96.8 kg/ha Ca, 7.6 kg/ha Mg, 31.8 kg/ha K and 61.1 kg/ha N over the 17-year period (Watmough and Dillon, 2002b). For mass balance calculations we assumed that annual net uptake by biomass (removal from soil) at HP4 was equal to the difference in biomass nutrient content between 1983 and 1999, divided by 17. Annual uptake values used in the mass balance calculations for HP4 therefore, were 5.7 kg/ha per year Ca, 0.45 kg/ha per year Mg, 1.87 kg/ha per year K and 3.59 kg/ha per year N.

At the remaining five catchments, we do not have repeated forest measurements and annual nutrient uptake was set to both 0 (similar to PC1) and to a value equal to the current nutrient pool in biomass, divided by 100 (similar to the uptake value obtained at HP4). It is more likely however, that the forests at Harp Lake (HP3A, HP6 and HP6A), CB1 and RC4 have exhibited net nutrient uptake over the 17-year period because these forests are similar (forest type, land use history, basal area, stem density, etc.) to the

forest at HP4 (Table 1). Furthermore, the five catchments currently have basal area values that are between 21.3 and 26.2 m^2/ha, and are lower than the value ($\sim$30 m^2/ha) reported to be typical for climax northern hardwood forests (Martin and Bailey, 1999). Mass balance estimates using an uptake value (but which may differ slightly from the value used in this study) are probably a better indicator of the net nutrient losses/gains from soil at each catchment between 1983 and 1999. Mass balance estimates using zero uptake therefore, represent the minimum possible base cation losses and maximum possible retention in soil over the 17-year period, but are probably unrealistic for 70–100-year-old mixed hardwood forests (Martin and Bailey, 1999).

3.4. Stream export

Annual stream export of Ca, Mg, K and SO_4 were greater than inputs in bulk deposition, although export from all sites in the final 2 years of measure was particularly low because of extremely low discharge in these years (typically 50–60% of the 17-year average; Fig. 3). Mean annual export of Ca, Mg, K and SO_4 from the seven catchments was between 9.94 and 20.71 kg/ha per year, 2.36 and 6.52 kg/ha per year, 0.86 and 4.03 kg/ha per year and 31.9 and 48.2 kg/ha per year, respectively. In contrast, annual NO_3 export from the seven catchments was much lower than N inputs in deposition and was between 0.16 and 1.51 kg/ha per year (Fig. 3).

Annual export of SO_4 from all seven catchments decreased significantly ($P < 0.05$; 0.90–1.48 kg/ha per year) over the 17-year study period (Table 4). In contrast, annual export of base cations and NO_3 in

Table 4
Simple linear regression analysis of annual elemental flux (kg/ha) over the 17-year study period

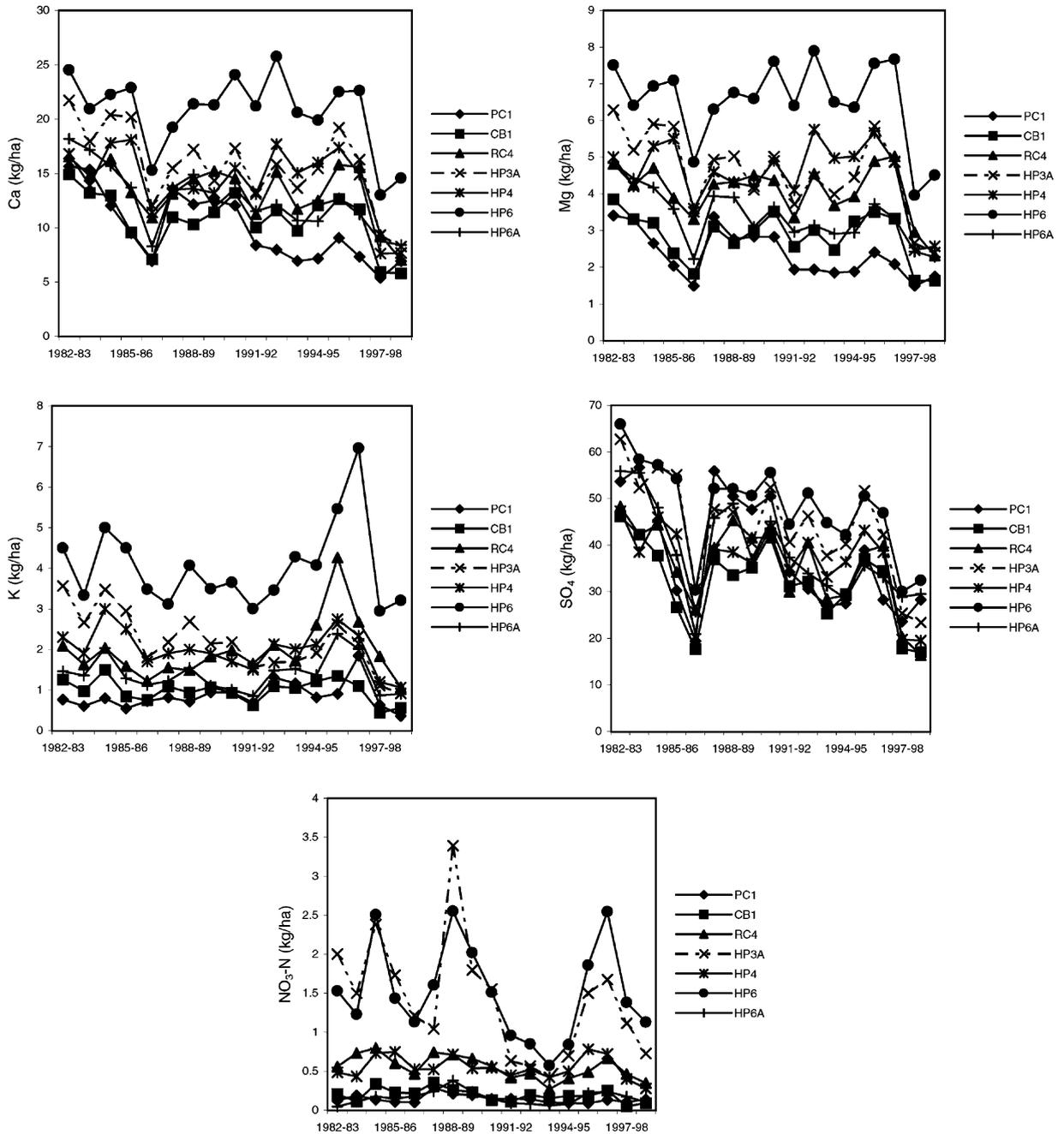|	Ca			Mg			K			SO$_4$			NO$_3$		
	Slope	r^2	P	Slope	r^2	P	Slope	r^2	P	Slope	r^2	P	Slope	r^2	P
PC1	−0.49	0.60	<0.001	−0.08	0.40	0.006	NS	NS	NS	−1.48	0.36	0.011	NS	NS	NS
CB1	NS	NS	NS	NS	NS	NS	NS	NS	NS	−0.90	0.27	0.033	−0.018	0.35	0.012
RC4	−0.26	0.25	0.041	NS	NS	NS	NS	NS	NS	−1.12	0.38	0.008	NS	NS	NS
HP3A	−0.47	0.41	0.005	−0.14	0.38	0.008	−0.11	0.58	<0.001	−1.47	0.47	0.003	NS	NS	NS
HP4	NS	NS	NS	NS	NS	NS	NS	NS	NS	−0.90	0.31	0.021	NS	NS	NS
HP6	NS	NS	NS	NS	NS	NS	NS	NS	NS	−1.30	0.43	0.004	NS	NS	NS
HP6A	−0.43	0.56	<0.001	−0.01	0.46	0.003	NS	NS	NS	−1.33	0.45	0.003	NS	NS	NS

Fig. 3. Annual export (kg/ha) of Ca, Mg, K, SO$_4$ and NO$_3$–N at PC1, CB1, RC4, HP3A, HP4, HP6 and HP6A between 1983 and 1999.

stream water varied among catchments. There were significant ($P < 0.05$) decreases in annual Ca export from PC1, RC4, HP3A and HP6A. Significant decreases ($P < 0.05$) in annual Mg export also occurred at PC1,

HP3A and HP6A, while a significant ($P < 0.05$) decrease in K export was recorded at HP3A. There was a small, but significant ($P < 0.05$) decrease in NO$_3$ export from CB1. Volume weighted nutrient

concentrations in stream water were even more variable among individual catchments and significant ($P < 0.05$) decreases in concentration were only identified for Ca at HP3A and SO_4 at RC4. Mean annual concentrations of Ca, Mg, K, SO_4 and NO_3 in stream water draining the seven catchments were between 1.94 and 3.74 mg/l, 0.46 and 1.17 mg/l, 0.16; and 0.72 mg/l, 6.50 and 8.69 mg/l and 29.3 and 273.9 µg/l, respectively.

Even though SO_4 concentrations differed among catchments, patterns of SO_4 concentration over time were highly synchronous among catchments ($0.96 > r > 0.70$), which is particularly evident when the data are presented as Z-scores (Fig. 4). Within each catchment annual Ca and Mg concentrations were also highly correlated ($0.99 > r > 0.73$) with SO_4 concentrations. Patterns of K concentration in stream water however, differ from those of SO_4, Ca and Mg. Similarities in temporal patterns of SO_4 concentration among catchments in the region have been discussed previously and appear to be largely driven by climate changes, and in particular summer droughts (Dillon et al., 1997; Eimers and Dillon, in press; Watmough and Dillon, 2002a). Peaks in SO_4, Ca and Mg concentration occurred in all streams following summer droughts, particularly in the late 1980s and late 1990s (Fig. 4). These large variations are likely a major reason as to why significant decreases in stream concentration of SO_4, Ca and Mg were generally not observed at the study sites. Furthermore, SO_4 export from the seven catchments exceeds inputs in bulk deposition by up to 100% in some years. The net export of SO_4 from forested catchments appears a common occurrence in eastern North America and may considerably delay the recovery of soils and surface waters from acid deposition (Eimers and Dillon, in press; Friedland and Miller, 1999; Hornbeck et al., 1997; Houle et al., 1997; Mitchell et al., 2001).

There were no significant trends in annual NO_3 concentration in any of the catchments, although annual volume weighted NO_3 concentrations and export differed by more than an order of magnitude among catchments (Fig. 3). At PC1, CB1, RC4, HP4 and HP6A, annual NO_3 export only accounted for between 26.4 (HP4) and 9.4% (PC1) of the total N in stream water. In contrast, over the entire 17-year period, NO_3 accounted for 54.4 and 46.1% of the total N in stream water at HP3A and HP6, respectively and in 1988/1989, NO_3 accounted for 75 and 64% of the

total N at HP3A and HP6, respectively. In general however, the export of organic N from the seven catchments was much greater than annual export of NO_3–N and was between 0.9 (CB1) and 2.1 kg/ha per year N (RC4; data not shown).

Differences in NO_3 export between catchments in the study region have been discussed previously (Devito et al., 1999; Dillon et al., 1991), and appear to be due to a combination of species cover and slope (Dillon et al., 1991). In eastern North America, export of NO_3 is usually greatest in catchments dominated by sugar maple, which have steep slopes with relatively deep till (Foster et al., 1989; Lovett and Rueth, 1999). High rates of nitrification in soil are associated with sugar maple (Lovett and Rueth, 1999), and in soils with steep slopes and deep till, NO_3 export can be high because NO_3 leaches rapidly away from the rooting zone (Creed and Band, 1998). Therefore, even though all catchments receive approximately the same amount of N in deposition, annual volume weighted NO_3 concentrations in stream water at HP3A and HP6 would indicate that these actively growing sugar maple-dominated forests are in stage 2 of N saturation (Aber et al., 1989). In contrast, the lowest NO_3 concentration in stream water was recorded at PC1, which has exhibited no net growth over the 17-year period. It appears therefore, that NO_3 concentrations in stream water alone are not a good indicator of potential N saturation in the study region.

In addition to the considerable variation in NO_3 concentration among the seven catchments, there was also considerable year-to-year variation within each catchment, which is particularly evident when the data are presented as Z-scores (Fig. 5). These differences appear to be mediated by climate variations, but in contrast to SO_4, two distinct groups emerge (Fig. 5). Patterns in annual NO_3 concentration in stream water at PC1, CB1 and RC4 are similar ($0.76 > r > 0.58$), with highest concentrations occurring in 1987/1988 and are primarily due to peaks in NO_3 concentration in the fall (data not shown). At these sites, high NO_3 concentrations appear to be due to release of NO_3 from organic soils following re-wetting after summer drought. As a result, the patterns in NO_3 concentration in these streams are similar to patterns in SO_4 concentration (Watmough and Dillon, 2002a). Patterns of NO_3 concentration in HP3A, HP6, HP6A and HP4 were also similar ($0.92 > r > 0.74$), but the highest
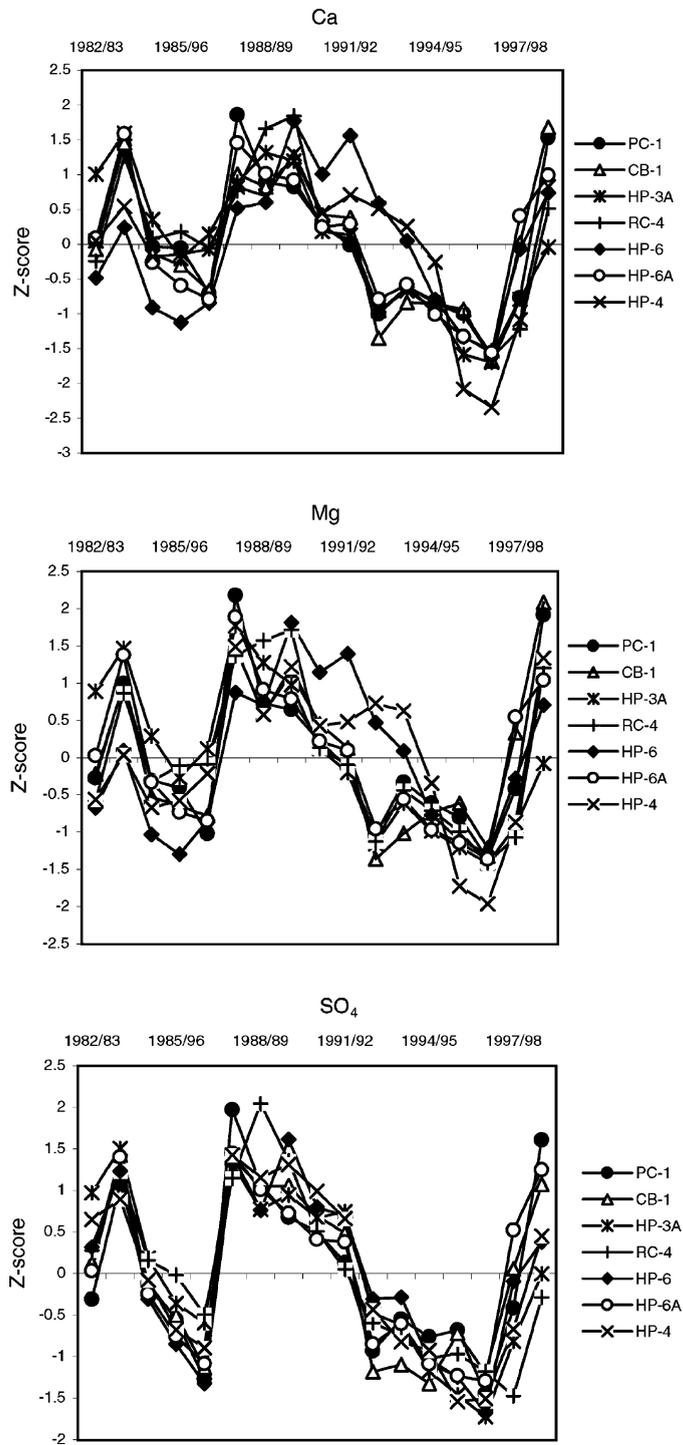
Fig. 4. Temporal patterns in annual stream concentrations of Ca, Mg and SO$_4$ (expressed as Z-scores) at PC1, CB1, RC4, HP3A, HP4, HP6 and HP6A between 1983 and 1999.
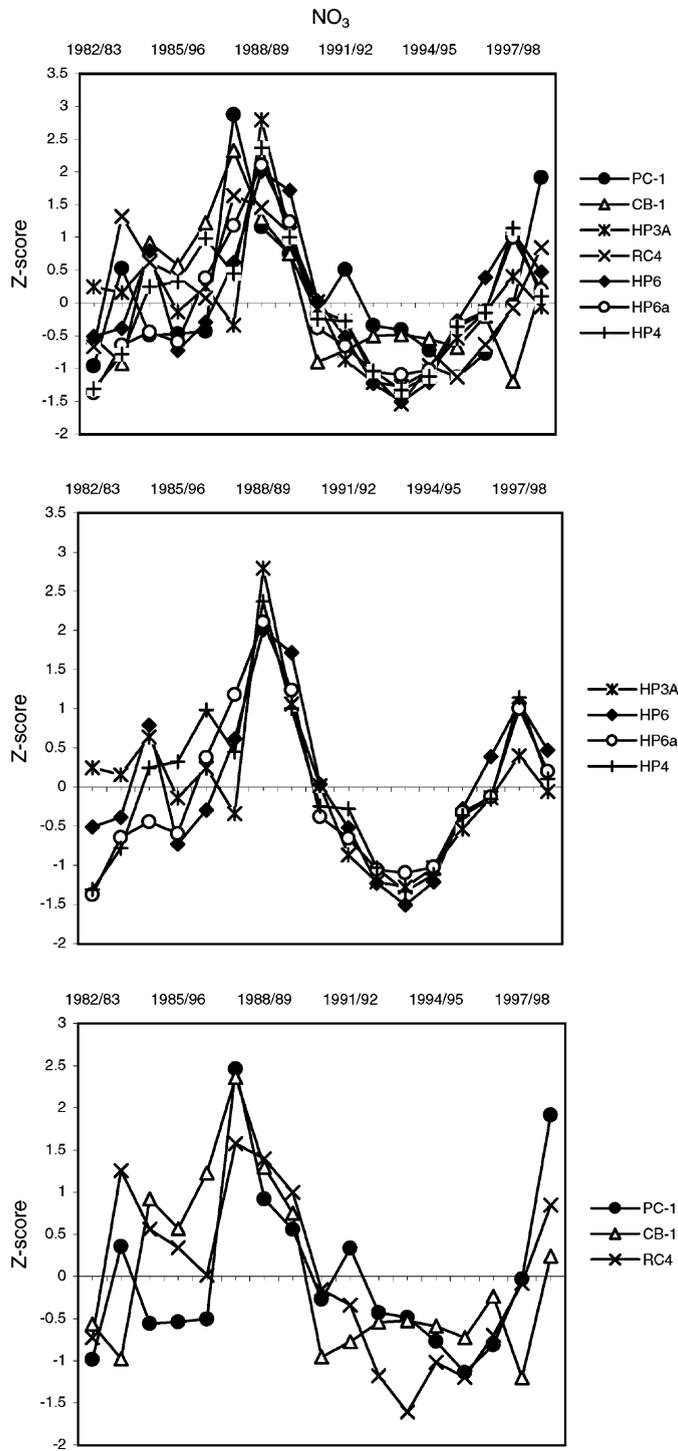
Fig. 5. Temporal patterns in annual stream NO_3–N concentrations (expressed as Z-scores) at PC1, CB1, RC4, HP3A, HP4, HP6 and HP6A between 1983 and 1999.

NO_3 concentrations in these streams were measured in the spring of 1989. In these sugar maple-dominated catchments high NO_3 concentrations appear to be related to high levels of precipitation in March, combined with lower than average temperatures (Watmough and Dillon, 2002b). These climatic conditions may have resulted in lower NO_3 immobilization in the spring due to a combination of low biological activity and possibly rapid flushing of NO_3 through the soil during snow melt.

Mitchell et al. (1996) and Murdoch et al. (1998) have previously stated that changes in climate may alter NO_3 concentrations in stream water draining forested catchments in the north-eastern US. Mitchell et al. (1996) attributed high NO_3 concentrations in the spring at four sites located in New York, Maine and New Hampshire to unusually low temperatures in the preceding winter. Murdoch et al. (1998) reported that annual stream NO_3 concentrations were positively related to mean annual air temperature. In our study region, year-to-year variations in NO_3 export can be as great as 2.5 kg NO_3–N/ha (HP3A) or 179 equivalents per ha, which is almost half the current annual SO_4 deposition ($\sim$400 equivalents per ha). Given the potential importance of N cycling and its role in soil acidification, the impact of climate on N cycling from forested catchments clearly requires further investigation. In particular, the effect of climate on NO_3 export in Muskoka–Haliburton appears to be dependent upon catchment characteristics.

A final point is that temporal patterns in stream chemistry (in particular NO_3) were similar at sites that have experienced varying degrees of harvesting (HP6, HP6A, HP3A and HP4) at different times over the study period. This suggests that any effects of the small amount of selective harvesting on stream chemistry measured at the weirs were minimal.

3.5. Base cation mass balance estimates

Mass balance calculations suggest that all seven catchments experienced substantial net losses of Ca over the 17-year study period, even when forest growth was set to zero, which is clearly unrealistic for most catchments (Fig. 6). Net Ca losses were between 32.6 (RC4, no growth) and 287 kg/ha (HP6, growth) over the 17-year study period. At PC1 and HP4, significant decreases in exchangeable

Ca concentrations in soil and soil pH were measured between 1983 and 1999, supporting the estimates from the mass balance calculations (Watmough and Dillon, 2002a,b). Changes in pH and exchangeable Ca were particularly evident in the upper soil horizons, and decreases in the exchangeable Ca soil pool over the 17-year period were comparable to predictions from the mass balance estimates (Watmough and Dillon, 2002a,b). At PC1, the exchangeable Ca pool in soil decreased by approximately 40% between 1983 and 1999 (Watmough and Dillon, 2002a), whereas the exchangeable Ca pool at HP4 decreased by approximately 30% over the same time period (Watmough and Dillon, 2002b). At the remaining five catchments (CB1, RC4, HP3A, HP6 and HP6A), the current exchangeable Ca pools in soil are between 569 kg/ha (CB1) and 1337 kg/ha (HP3A; Table 5). With the exception of PC1 however, differences in the size of the exchangeable Ca pool between sites can be largely attributed to soil depth rather than to differences in Ca concentration within each soil horizon (Table 6).

Mass balance estimates for Mg are more varied than for Ca, and net Mg losses are lower than losses for Ca (Fig. 7). Mass balance estimates range from a net loss of 60.6 kg/ha (HP6-with growth) to a net retention of 17.1 kg/ha (RC4-no growth) over the 17-year study period. These estimates have also been supported by repeated sampling at PC1 and HP4, where there have been no detectable decreases in the exchangeable Mg pools between 1983 and 1999 (Watmough and Dillon, 2002a,b). Similarly, mass balance estimates for K at the seven catchments range from a net loss of 36.3 kg/ha (HP6-with growth) to a net retention of 65.1 kg/ha (HP4), and indicate that there has generally been no net loss of K over the 17-year study period (Figs. 8 and 9). These estimates were also confirmed by repeated soil measurements in 1983 and 1999 at both PC1 and HP4 (Watmough and Dillon, 2002a,b).

If net Ca and Mg losses have occurred from the soil exchange complex, but the magnitude of these losses has decreased over time, a decrease in the Ca (or Mg)/Na ratio in stream water would be expected. Indeed, there were significant linear decreases in the Ca/Na mass ratio at all sites that were unaffected by road salt (Table 7). The largest decrease was observed at PC1, which also experienced the greatest net Ca loss relative to the size of the exchangeable Ca pool over the 17-year study period. In 1982/1983 for example,
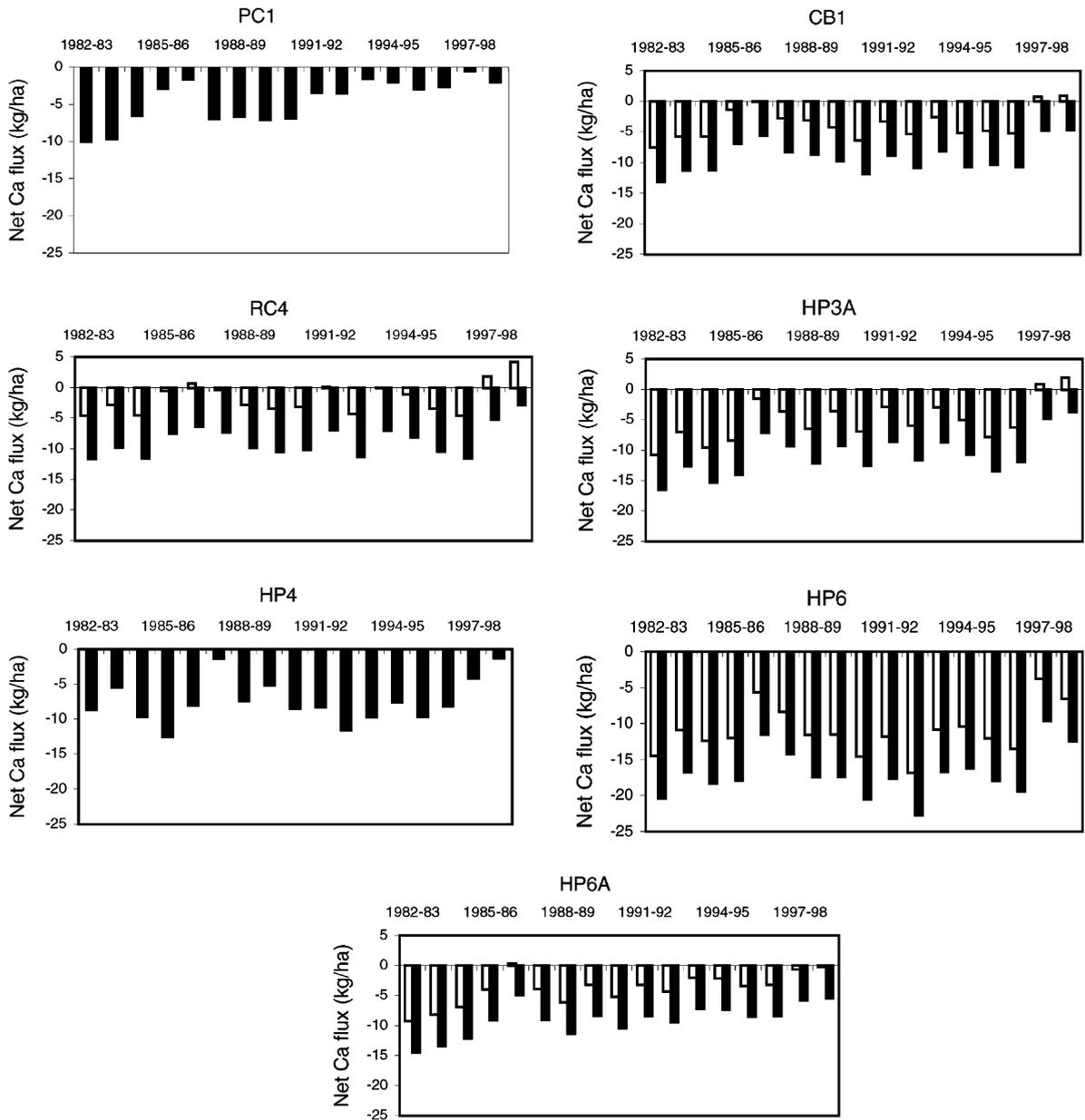
Fig. 6. Annual mass balance budgets for Ca (kg/ha) at PC1, CB1, RC4, HP3A, HP4, HP6 and HP6A between 1983 and 1999. Solid bars represent inclusion of measured (PC1 and HP4) or estimated (CB1, RC4, HP3A, HP6 and HP6A) uptake values. Clear bars assume no annual net uptake between 1983 and 1999.

the Ca/Na mass ratio at PC1 was approximately 5, but by the late 1990s the Ca/Na ratio in stream water had decreased to around 2 - a decrease of approximately 60%. Based on weathering estimates for PC1 and

deposition values (corrected for dry deposition) a Ca/Na ratio around 1.4 would be expected in stream water at PC1 if there was no loss (or retention) of Ca from the catchment. Similarly, the lowest Ca/Na ratios

Table 5
NaCl-Exchangeable base cation pools (kg/ha) at the seven study catchments

	PC1[a]	CB1	RC4	HP3A	HP4[a]	HP6	HP6A
Ca	114	569	753	1337	829	616	807
Mg	28	78	110	142	98	92	104
K	100	301	307	415	238	390	243
Mean depth (cm)	38	75	110	130	130	110	70

[a] Base cation pools estimated using 2000 soil chemistry except PC1 and HP4 which were calculated using 1999 data.

measured in streamwater at CB1, RC4, HP3A and HP6A (2.8–3.8) are greater than Ca/Na ratios expected under steady state conditions (1.7–2.4), supporting our mass balance calculations that indicate continuing net Ca losses from the exchangeable soil pool in the study region. It is unlikely that the decrease in the Ca/Na ratio is due to changes in Ca weathering relative to Na weathering, or due to decreases in Ca deposition relative to Na deposition (Watmough and Dillon, 2002a).

Significant decreases in the Mg/Na ratio were also measured in stream water at RC4, HP3A and HP6A (Table 8), although there was no significant decrease in the Mg/Na mass ratio at PC1 or CB1. Furthermore, the lowest Mg/Na ratios measured in the late 1990s in stream water at the five catchments (0.5–0.9)

Table 6
Soil pH and base cation concentrations (mg/kg) in soil at the seven study sites

	PC1[a]	CB1	RC4	HP3A	HP4[a]	HP6	HP6A
LFH							
Soil pH[b]	3.78 (0.23)	4.39 (0.31)	4.42 (0.15)	4.88 (0.31)	4.11 (0.42)	4.32 (0.31)	4.35 (0.29)
Soil pH[c]	3.12 (0.24)	4.03 (0.19)	4.03 (0.19)	4.68 (0.32)	3.49 (0.50)	3.90 (0.23)	3.96 (0.33)
Ca	2341 (1434)	4943 (1510)	6503 (1260)	6436 (1962)	2754 (1680)	4893 (938)	5770 (1935)
Mg	236 (107)	542 (167)	693 (78.2)	653 (141)	316 (188)	553 (99.1)	474 (239)
K	609 (222)	1236 (308)	1307 (185)	965 (629)	492 (293)	1256 (294)	978 (294)
A-horizon							
Soil pH[b]	3.76 (0.16)	4.15 (0.35)	4.34 (0.39)	4.68 (0.27)	4.13 (0.38)	4.12 (0.18)	4.22 (0.35)
Soil pH[c]	3.08 (0.11)	3.39 (0.38)	3.53 (0.35)	4.07 (0.38)	3.45 (0.39)	3.52 (0.11)	3.55 (0.41)
Ca	70 (37.0)	365 (172)	413 (310)	851 (505)	423 (742)	560 (340)	455 (339)
Mg	17.5 (6.2)	43.9 (26.1)	130 (36.0)	68.6 (46.4)	51.2 (45.2)	65.8 (32.5)	69.5 (62.1)
K	57.5 (18.0)	128 (45.3)	94.0 (31.2)	52.1 (27.8)	85.0 (48.8)	137 (82.5)	90.0 (45.4)
B-horizon							
Soil pH[b]	4.42 (0.30)	4.93 (0.20)	5.15 (0.25)	5.08 (0.17)	4.80 (0.18)	4.95 (0.19)	4.90 (0.22)
Soil pH[c]	4.05 (0.28)	4.42 (0.30)	4.42 (0.27)	4.43 (0.13)	4.26 (0.20)	4.28 (0.13)	4.23 (0.17)
Ca	29.3 (30.0)	134 (130)	141 (102)	166 (82.1)	97.9 (90.6)	106 (50.3)	168 (105)
Mg	8.7 (4.5)	29.5 (29.1)	18 (16.9)	17.3 (7.8)	10.7 (7.9)	14.7 (4.6)	18.6 (12.8)
K	37.1 (17.3)	55.2 (26.3)	38.2 (11.3)	58.2 (40.4)	31.9 (14.6)	61.4 (30.1)	39.6 (12.1)
C-horizon							
Soil pH[b]	4.63 (0.15)	5.18 (0.28)	5.45 (0.22)	5.18 (0.06)	5.05 (0.16)	5.30 (0.31)	5.17 (0.18)
Soil pH[c]	4.40 (0.08)	4.59 (0.30)	4.80 (0.13)	4.53 (0.04)	4.49 (0.08)	4.56 (0.10)	4.45 (0.05)
Ca	9.3 (2.0)	13.3 (15.2)	24.4 (7.8)	64.5 (38.5)	40.3 (67.0)	28.0 (7.1)	51.0 (10.2)
Mg	4.2 (0.3)	4.75 (2.3)	7.5 (4.2)	7.7 (1.8)	5.7 (1.7)	6.2 (0.9)	8.3 (2.6)
K	18.5 (4.4)	31.5 (2.9)	40 (11.9)	34.0 (3.6)	31.0 (10.3)	44.5 (13.4)	43.0 (5.6)

Standard deviations are given in parenthesis.
[a] Samples collected and analyzed in 1999.
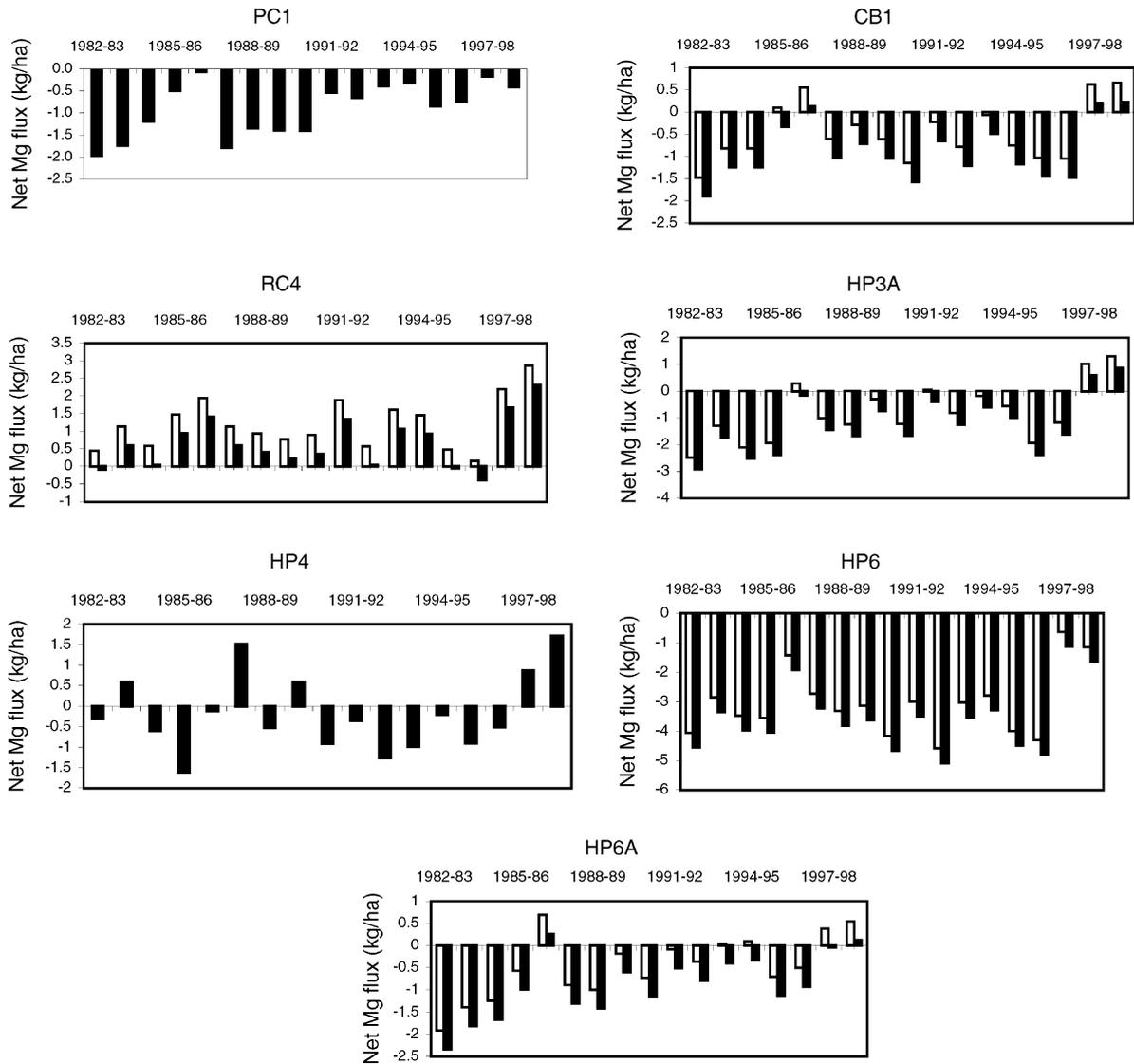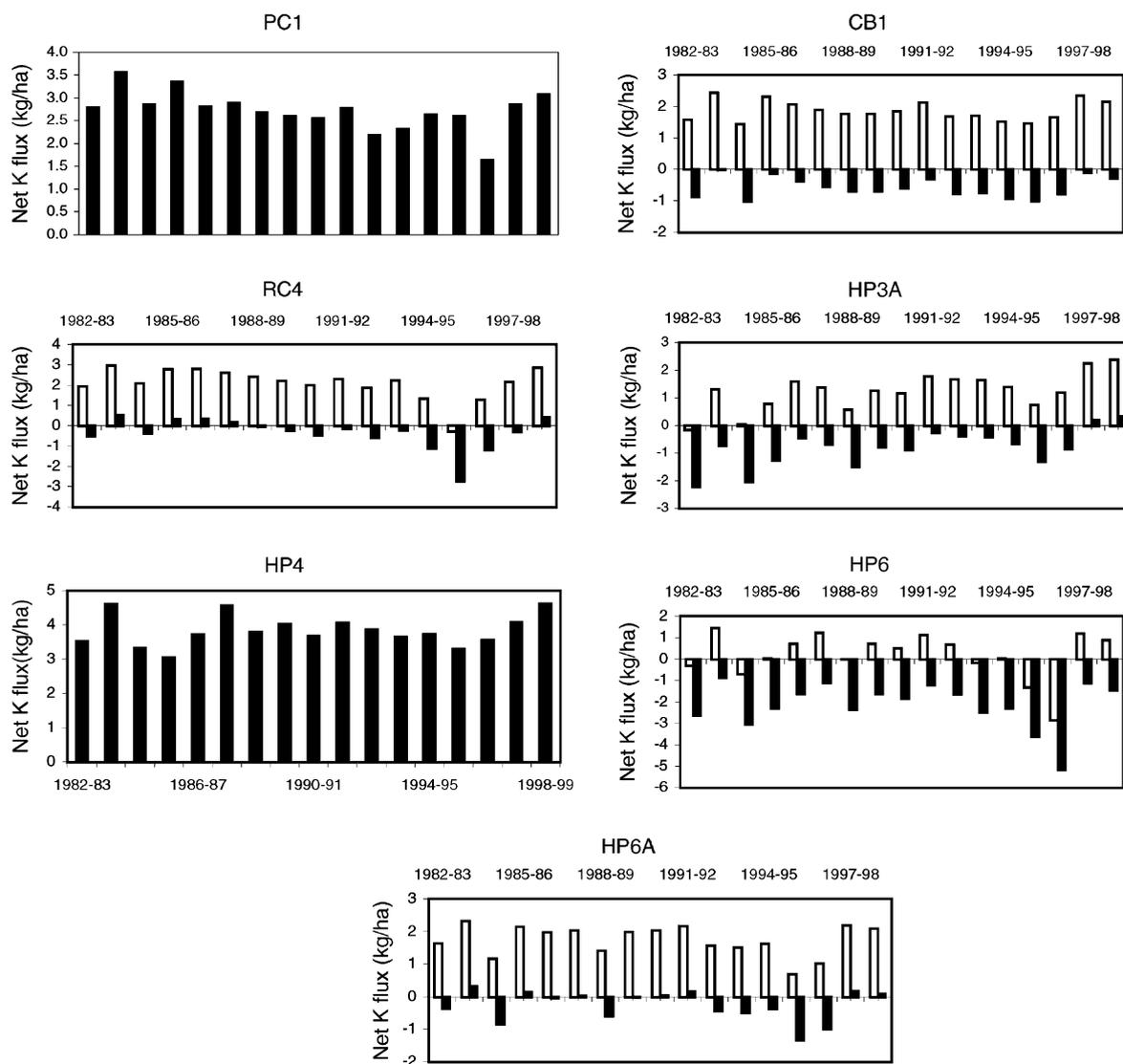[b] pH in H_2O.
[c] pH in 0.01 M $CaCl_2$.

Fig. 7. Annual mass balance budgets for Mg (kg/ha) at PC1, CB1, RC4, HP3A, HP4, HP6 and HP6A between 1983 and 1999. Solid bars represent inclusion of measured (PC1 and HP4) or estimated (CB1, RC4, HP3A, HP6 and HP6A) uptake values. Clear bars assume no annual net uptake between 1983 and 1999.

were similar to Mg/Na ratios predicted under steady state conditions (0.4–0.9), suggesting that the catchments appear to be approaching balance with respect to Mg.

Our mass balance estimates therefore, suggest that there has been a decrease in the exchangeable Ca pool in soil relative to the exchangeable Mg pool and if a generalized formulation of the Gaines–Thomas equa-

tion is considered, this change should be reflected in stream water chemistry.

$$\frac{[\text{Ca}^{2+}]}{[\text{Mg}^{2+}]} = K_{\text{gt}} \frac{(\text{Ca}^{2+})}{(\text{Mg}^{2+})}$$

where parentheses denote exchange phases; square brackets denote solution phase and K_{gt} is the Gaines–Thomas selectivity coefficient, a constant. Over the

Fig. 8. Annual mass balance budgets for K (kg/ha) at PC1, CB1, RC4, HP3A, HP4, HP6 and HP6A between 1983 and 1999. Solid bars represent inclusion of measured (PC1 and HP4) or estimated (CB1, RC4, HP3A, HP6 and HP6A) uptake values. Clear bars assume no annual net uptake between 1983 and 1999.

17-year period the Ca/Mg mass ratio decreased significantly at five of the seven catchments (Table 7). This decrease was much greater at PC1 compared with the other six catchments. Only at HP3A and HP6, both of which were calculated to have experienced the greatest net loss of Mg between 1983 and 1999, was the change in the Ca/Mg ratio insignificant.

If we assume that the exchangeable Mg pool at the seven catchments was unchanged between 1982/1983

and 1998/1999 (and that K_{gt} has remained constant), the change in the exchangeable Ca pool between 1982 and 1999 can be estimated using the change in the [Ca]/[Mg] ratio in stream water and current exchangeable pools (Table 8). These calculations suggest that the exchangeable Ca pool at the seven catchments has decreased by between 0 and 123 kg/ha. Small losses in the exchangeable Mg pool between 1982 and 1999 however, can have a great effect on these calculations.
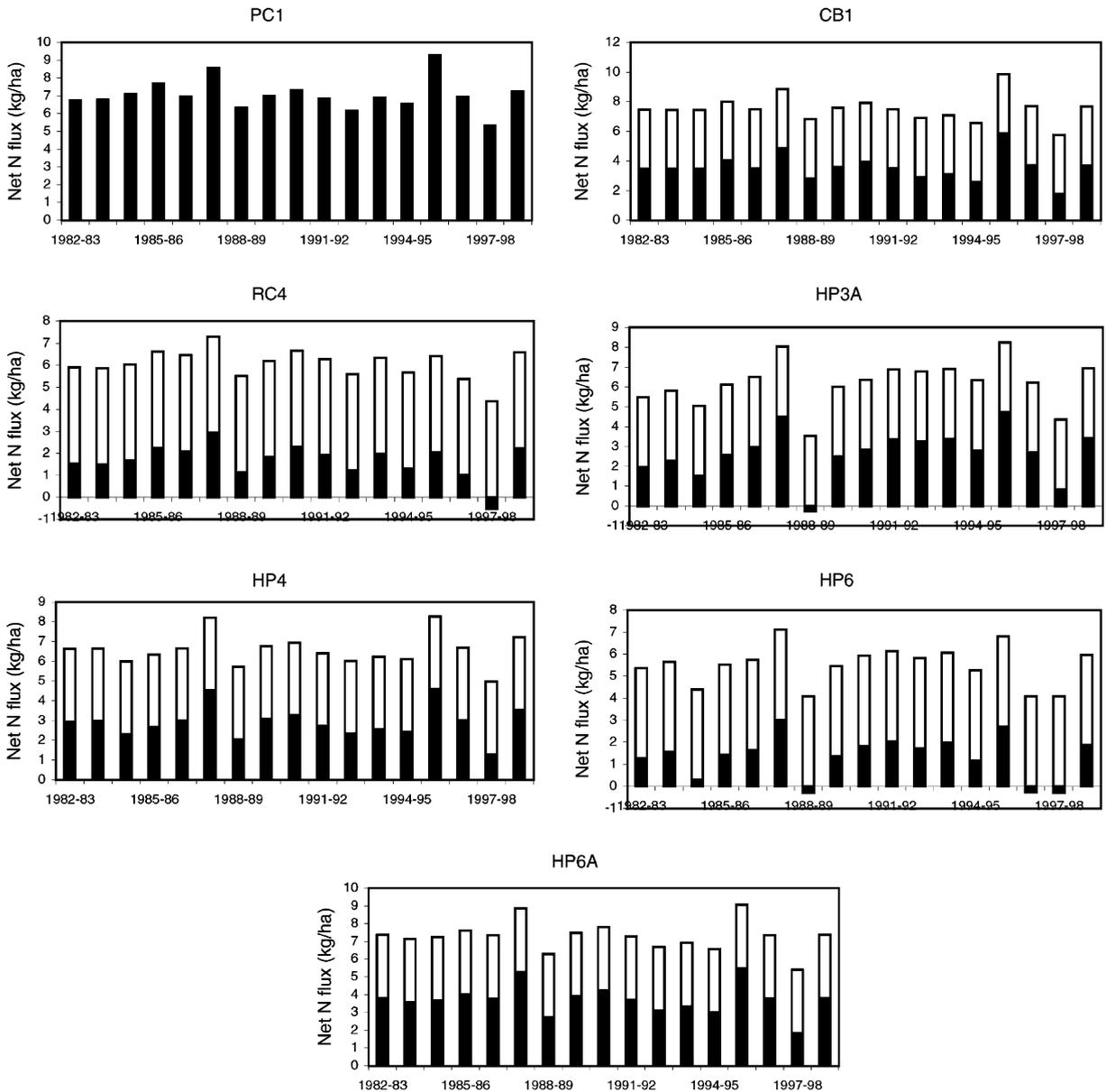
Fig. 9. Annual mass balance budgets for N (kg/ha; including TON export) at PC1, CB1, RC4, HP3A, HP4, HP6 and HP6A between 1983 and 1999. Open bars represent amount of N accumulated in biomass using measured (PC1 and HP4) or estimated (CB1, RC4, HP3A, HP6 and HP6A) uptake values.

For example, if the exchangeable Mg pool at PC1 in 1982/1983 was 35 kg/ha (as suggested by mass balance estimates and the slight decrease in the Mg/Na ratio in stream water), the exchangeable Ca pool decreased by 73 kg/ha rather than 36 kg/ha between 1982 and 1999. This value is consistent with our mass balance estimates for PC1 (Watmough and Dillon, 2002a). These calculations therefore, represent the minimum Ca losses from the exchangeable pool at the seven sites. In particular, our mass balance estimates suggest that the greatest net losses of Mg occurred at HP3A and HP6, Ca losses calculated using

Table 7

Simple linear regression analysis of annual Ca/Na, Mg/Na and Ca/Mg mass ratios in stream water at seven forested catchments in Muskoka–Haliburton, 1982/1983 to 1998/1999

	Ca/Na			Mg/Na			Ca/Mg		
	Slope	r^2	P	Slope	r^2	P	Slope	r^2	P
PC1	−0.11	0.47	0.002	NS	NS	NS	−0.07	0.77	<0.001
CB1	−0.06	0.43	0.004	NS	NS	NS	−0.02	0.48	0.002
RC4	−0.05	0.68	<0.001	−0.009	0.53	<0.001	−0.02	0.61	<0.001
HP3A	−0.08	0.54	<0.001	−0.022	0.53	<0.001	NS	NS	NS
HP4	ND	ND	ND	ND	ND	ND	−0.02	0.50	0.001
HP6	ND	ND	ND	ND	ND	ND	NS	NS	NS
HP6A	−0.11	0.43	0.004	−0.026	0.39	0.01	−0.02	0.26	0.019

NS, not significant; ND, not determined because of road-salt (NaCl) contamination.

differences in the Ca/Mg ratio in stream water greatly underestimate Ca losses from the exchangeable pool at these catchments.

Numerous reports in Europe and eastern North America have expressed concern over base cation losses from soil due to acid deposition and harvesting (Adams, 1999; Daldoum and Ranger, 1994; Likens et al., 1998; Houle et al., 1997; Sverdrup and Rosen, 1998; Thimonier et al., 2000). In eastern North America, Ca losses are generally of the greatest concern to forest health and productivity (Bailey et al., 1996; Federer et al., 1989; Lawrence et al., 1997). Net Ca losses have been reported at several long-term catchment study sites in eastern North America (Hornbeck et al., 1997; Houle et al., 1997; Johnson et al., 2000; Likens et al., 1998; Watmough and Dillon, 2002a,b).

Furthermore, a decrease in exchangeable Ca levels in forest soils has been observed in several parts of eastern North America. Lawrence et al. (1997) for example, re-sampled soils from red spruce (*P. rubens*) forests in several north-eastern states in the US and reported that significant decreases in exchangeable Ca pools occurred in the second half of the 20th century and acid deposition was attributed as the probable cause. A similar long-term decrease in exchangeable Ca and Mg in soil was found in Pennsylvania (Drohan and Sharpe, 1997). Johnson et al. (1994) reported a 15% decrease in dilute HCl-extractable Ca from the organic soil horizon over a 54-year period at a high elevation spruce-fir forest in the Adirondacks.

At the Lac Clair forest in Quebec, poor growth and die-back were reported in sugar maple trees growing

Table 8

Ca losses from seven catchments in central Ontario, estimated from changes in Ca/Mg mass ratios in stream water between 1983 and 1999 and exchangeable Ca and Mg pools measured in 1999 (or 2000, PC1 and HP4)

	Late 1990s Ca/Mg	Early 1980s Ca/Mg	1999 Ca kg/ha	1999 Mg kg/ha	K_{gt}	1983 Ca kg/ha[a]	1982–1999 Ca kg/ha
PC1	3.5	4.6	114	28	0.86	150	−36
CB1	3.6	4.0	569	78	0.49	636	−67
RC4	3.0	3.5	753	110	0.44	875	−122
HP3A[b]	3.5	3.5	1337	142	0.37	1343	0
HP4	3.0	3.4	829	98	0.35	952	−123
HP6[b]	3.0	3.3	616	92	0.45	674	−58
HP6A	3.4	3.9	807	104	0.44	921	−114

[a] Exchangeable Ca pool in 1983 was estimated assuming that the exchangeable Mg pool and K_{gt} was unchanged.

[b] Mass balance estimates suggest that Mg losses at these sites between 1982/1983 and 1998/1999 were substantial and therefore, Ca losses estimated using this method will greatly underestimate actual Ca losses.

on soils containing approximately 200 kg/ha Ca in the exchangeable pool (Houle et al., 1997). Poor sugar maple growth and high rates of die back were also reported at Hubbard Brook, with similar low exchangeable Ca levels in soil (Likens et al., 1998). In the present study, current exchangeable Ca pools at the maple-dominated sites are between 569 and 1337 kg/ha, although Ca pools in the upper (LFH, A and B) soil horizons are slightly lower (500–1149 kg/ha). At present, our mass balance calculations (assuming growth, which is consistent with continued selective harvesting) suggest that between 5 and 10 kg/ha Ca is lost annually from the exchangeable soil pool (through uptake and leaching) at the maple-dominated catchments. Net Ca losses from the upper soil horizons in these catchments are likely even greater because Ca uptake and the majority of Ca leaching losses and plant uptake occur from the upper soil horizons (Markewitz et al., 1998; Watmough and Dillon, 2002b). If the current exchangeable Ca pool is equivalent to the plant available pool, and Ca losses continue at the current rate, soil Ca reserves in the biologically important upper soil horizons may become depleted to the point that tree growth (and health) is affected within just a few decades. At PC1 for example, where the soil Ca pool is only 114 kg/ha, there has been no net growth over the 17-year study period. Furthermore, our estimates are based on a single (integrated) value for each catchment, but given the high spatial variability within these catchments (Watmough and Dillon, 2002a,b), Ca limitation may occur even sooner in parts of the catchments that are characterized by shallow soils.

In Europe, Mg deficiencies have also commonly been linked with forest decline (Nellemann and Esser, 1998). In eastern North America, some long-term forested catchment or plot studies have indicated that net losses of Mg from soil have occurred in recent years (Friedland and Miller, 1999; Houle et al., 1997; Johnson et al., 1985). Significant decreases in exchangeable Mg in recent decades have also been measured in soil re-sampling studies conducted at a number of forested sites in Pennsylvania (Drohan and Sharpe, 1997) and some studies have suggested that Mg limitation may be affecting tree health in parts of eastern North America (Ke and Skelly, 1994). In this study, mass balance estimates (and Mg/Na ratios) suggest that net Mg losses have occurred from some

of the catchments, but these losses were generally smaller relative to Ca and most catchments appear to be currently in balance with respect to Mg. However, exchangeable Mg pools at the seven sites are much lower than Ca pools, ranging between 28 (PC1) and 142 kg/ha (HP3A; Table 5). Furthermore, net Mg losses from two of the catchments over the 17-year period (HP6 and HP3A) were considerable (13.5 and 52.1 kg/ha), even when Mg uptake was set to zero, but which is clearly unrealistic. Unlike the remaining five catchments, there was no significant decrease in the Ca/Mg ratio in stream water at HP6 and HP3A. Therefore, although net Ca losses are generally much greater than losses of Mg, and annual weathering rates for Mg (0.96– 4.81 kg/ha) are greater than annual uptake values (0–0.53 kg/ha), potentially limiting levels of Mg may arise in soils at some of the catchments. Low Mg levels have been reported in sugar maple foliage in the region (Watmough et al., 1999), and Mg deficiencies have been linked with sugar maple dieback in both Quebec and Pennsylvania (Bernier and Brazeau, 1988a; Horsley et al., 2000). Potassium deficiencies have also been linked with sugar maple decline in Quebec, although K-deficiencies appear to be related to Mg (or Ca) antagonism, rather than due to enhanced leaching losses (Bernier and Brazeau, 1988b; Moore et al., 2000). The seven catchments considered in this study appear to be in balance with respect to K.

3.6. Nitrogen mass balance

Over the 17-year period, between 92.6 (HP6) and 128.1 kg/ha N ((CB1), or 64–87% of N in deposition) was retained in the seven catchments (Fig. 9). Similar findings were reported for Harp Lake and Plastic Lake catchments by Dillon and Molot (1990), using data collected between 1976/1977 and 1982/1983. High rates of N retention have been reported in many forests through eastern North America and have been attributed to both plant uptake and immobilization in soil (Hornbeck et al., 1997; Houle et al., 1997). In forests that were actively growing (or growth was assumed), the majority (49–75%) of the N retained was accumulated in forest biomass, most of which (above ground component) could potentially be removed during harvest (Fig. 9). Accumulation of N in soils over the 17-year period therefore, varied

between 23.1 (HP6) and 119.7 kg/ha (PC1). If we assume that net forest growth occurred at six of the seven catchments (excluding PC1), the annual net retention of N in soil was <3.8 kg/ha per year. At the two sites that exhibit the greatest NO_3 export (HP3A and HP6), net release of N from soil was estimated in some years assuming that these forests are actively growing. Current critical load models generally use a value of 2–5 kg/ha per year as a default or ''safe'' net N accumulation in forest soils (Posch et al., 1995). Therefore, as long as selective harvesting continues in the study region, N saturation in these forests appears unlikely.

At PC1 however, there has been no net forest growth, and so almost 120 kg/ha N ($\sim$7 kg/ha per year) has potentially accumulated in upland soils over the 17-year period. Nitrogen losses resulting from denitrification were not measured, but are assumed to be small in well-drained upland forest soils. Furthermore, our mass balance estimates for Ca and the small exchangeable Ca pool suggest that continued net forest growth is unlikely and that harvesting is not sustainable. As a result, it is likely that N will continue to accumulate in soil at PC1 for the foreseeable future. Atmospheric inputs of N in the study region ($\sim$9.0 kg/ha per year) are much lower than in parts of Europe or at high elevation sites in eastern North America, where N deposition can be between 15 to over 40 kg/ha per year (Dise and Wright, 1995; Friedland and Miller, 1999). Nevertheless, inputs of N in bulk deposition are similar to values reported in Vermont and New York where concerns over early stages of N saturation have been expressed due to high levels of NO_3 (and seasonal variation) measured in stream water (Campbell et al., 2000; Lovett et al., 2000). At PC1 therefore, (or other catchments where harvesting does not occur), N saturation is a potential concern, even though NO_3–N concentrations in stream water at PC1 are currently only around 30 µg/l and are the lowest among the seven study catchments. Such differences between geographically proximal sites clearly demonstrate how catchment characteristics and management practices can affect the long-term sensitivity to moderate inputs of N. Sensible management practices are therefore, necessary to balance the potential negative impacts of base cation losses through harvesting and the concern over N accumulation (and N saturation) in forest soils.

4. Summary

Our mass balance estimates for seven forested catchments in Muskoka–Haliburton indicate that there have been substantial net losses of Ca from all catchments between 1983 and 1999. These losses, which occurred over a 17-year period, represent 10–60% of the current exchangeable Ca pool at the seven study sites. Current exchangeable Ca pools in forest soils are large enough to sustain healthy tree growth at six of the seven catchments. Continued losses of Ca due to leaching and harvesting however, may deplete plant available Ca reserves to the point that forest productivity and health may be affected at all seven catchments within just a few decades. Net losses of Mg were generally smaller than losses of Ca, but net Mg losses from two of the seven catchments are large enough that Mg deficiencies in trees could develop in the near future. All sites appear to be in balance with respect to K. At the regional level, annual export and concentrations of SO_4 and NO_3 in stream water appears to be affected by climate variations (temperature, hydrology), which also affect the annual export of Ca and Mg. Export of NO_3 also varies dramatically among catchments, which is probably due to characteristics such as slope and forest cover. In general however, NO_3 concentrations in stream water are low and the majority of the N in deposition is retained within the seven catchments. At the current level of acid deposition and if selective cutting practices persist, the long-term sustainability of upland forests in the region due to Ca (and Mg) depletion is questionable. A combination of reduced S-inputs and sensible forest management is necessary to ensure the long-term health and productivity of forests in the study region.

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