SULPHATE, NITROGEN AND BASE CATION BUDGETS AT 21 FORESTED CATCHMENTS IN CANADA, THE UNITED STATES AND EUROPE[†,‡]

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Abstract. To assess the concern over declining base cation levels in forest soils caused by acid deposition, input-output budgets (1990s average) for sulphate (SO_4), inorganic nitrogen (NO_3-N; NH_4-N), calcium (Ca), magnesium (Mg) and potassium (K) were synthesised for 21 forested catchments from 17 regions in Canada, the United States and Europe. Trend analysis was conducted on monthly ion concentrations in deposition and runoff when more than 9 years of data were available (14 regions, 17 sites). Annual average SO_4 deposition during the 1990s ranged between 7.3 and 28.4 kg ha^{-1} per year, and inorganic nitrogen (N) deposition was between 2.8 and 13.8 kg ha^{-1} per year, of which 41–67% was nitrate (NO_3-N). Over the period of record, SO_4 concentration in deposition decreased in 13/14 (13 out of 14 total) regions and SO_4 in runoff decreased at 14/17 catchments. In contrast, NO_3-N concentrations in deposition decreased in only 1/14 regions, while NH_4-N concentration patterns varied; increasing at 3/14 regions and decreasing at 2/14 regions. Nitrate concentrations in runoff decreased at 4/17 catchments and increased at only 1 site, whereas runoff levels of NH_4-N increased at 5/17 catchments. Decreasing trends in deposition were also recorded for Ca, Mg, and K at many of the catchments and on an equivalent basis, accounted for up to 131% (median 22%) of the decrease in acid anion deposition. Base cation concentrations in streams generally declined over time, with significant decreases in Ca, Mg and K occurring at 8, 9 and 7 of 17 sites respectively, which accounted for up to 133% (median 48%) of the decrease in acid anion concentration. Sulphate export exceeded input at 18/21 catchments, likely due to dry deposition and/or internal sources. The majority of N in

deposition (31–100%; median 94%) was retained in the catchments, although there was a tendency for greater NO_3-N leaching at sites receiving higher (>7 kg ha^{-1} per year) bulk inorganic N deposition. Mass balance calculations show that export of Ca and Mg in runoff exceeds input at all 21 catchments, but K export only exceeds input at 16/21 sites. Estimates of base cation weathering were available for 18 sites. When included in the mass balance calculation, Ca, Mg and K exports exceeded inputs at 14, 10 and 2 sites respectively. Annual Ca and Mg losses represent appreciable proportions of the current exchangeable soil Ca and Mg pools, although losses at some of the sites likely occur from weathering reactions beneath the rooting zone and there is considerable uncertainty associated with mineral weathering estimates. Critical loads for sulphur (S) and N, using a critical base cation to aluminium ratio of 10 in soil solution, are currently exceeded at 7 of the 18 sites with base cation weathering estimates. Despite reductions in SO_4 and H^+ deposition, mass balance estimates indicate that acid deposition continues to acidify soils in many regions with losses of Ca and Mg of primary concern.

1. Introduction

Elevated levels of acid deposition and subsequent acid leaching may increase base cation losses from forest soils (Kirchner and Lydersen, 1995; Likens *et al.*, 1996; Watmough and Dillon, 2003a). If the net losses of base cations from soil are not replaced through mineral weathering and deposition, soils will acidify as the exchangeable base cation pool in soil is diminished (Kirchner and Lydersen, 1995; Tomlinson, 2003). Low levels of exchangeable bases in soils have been associated with nutrient deficiencies in trees leading to decreased growth and increased susceptibility to other biotic and abiotic stresses such as drought, freezing and insect defoliation (Bondietti *et al.,* 1989; DeHayes *et al.,* 1999; Duchesne *et al.,* 2002; Horsley *et al.,* 2000; Jiang and Jagels, 1999; Kolb and McCormick, 1993; Shortle and Smith, 1988; Shortle *et al.,* 1995; Watmough, 2002). To evaluate the potential threat that acid deposition poses to forest ecosystems, steady-state critical load models have been developed that estimate the maximum amount of acid deposition that forests can tolerate without causing adverse biological effects (Nilsson and Grennfelt, 1988). Critical load models have been extensively used in Europe as the scientific basis for air pollution policies (Skeffington, 1999). In effect, these models allow soils to acidify but only to a limit determined by a critical chemical criterion, usually a specified base cation-to-aluminium ratio in soil solution (Posch *et al.,* 2001; Skeffington, 1999).

While the concept is straightforward, there is considerable uncertainty regarding the spatial extent and processes responsible for soil acidification. For example, it has been assumed that sulphate (SO_4) acts as a conservative ion, and that stream export of SO_4 should equal inputs in deposition. However, a number of recent studies have reported that SO_4 export from catchments in both Europe and North America exceeds input in deposition (Alewell, 2001; Alewell *et al.,* 1999; Eimers and Dillon, 2002; Houle and Carignan, 1995; Lofgren *et al.,* 2001; Mitchell *et al.,* 1992). The relative importance of nitrogen (N) as a potential acidifying agent is

increasing as sulphur (S) emissions in Europe and eastern North America decrease, yet the behaviour of N in soils is poorly understood (Aber *et al.,* 1989; Henriksen *et al.,* 1997; Stoddard *et al.,* 2001). Generally, forest soils receiving low to moderate levels of N deposition retain the majority of N input (Bringmark and Kvarnas 1995; Campbell *et al.,* 2004; Harriman *et al.,* 2001; Jefts *et al.,* 2004; Mitchell *et al.,* 1996; Park *et al.,* 2003; Watmough and Dillon, 2004), although several workers have expressed concern that gradual accumulation of N in soils may lead to a state of N-saturation (N inputs exceed biotic demand), causing an increase in nitrate (NO_3-N) leaching and undermining the benefits of decreased S emissions (Aber *et al.,* 1989; Bringmark and Kvarnas, 1995).

In many regions, the chemistry of surface waters has not recovered as expected, in part, due to declining base cation concentrations (Stoddard *et al.,* 1999). In some areas the decline in base cation concentration in surface waters has been greater than expected based on declining acid anion concentrations alone (Kirchner and Lydersen, 1995). These decreases have been attributed to lower base cation deposition (Hedin *et al.,* 1994), and/or declining base cation pools in soil (Alewell *et al.,* 2001; Fernandez *et al.,* 2003; Kirchner and Lydersen, 1995; Likens *et al.,* 1996; Watmough and Dillon, 2003a). However, the magnitude of soil acidification has proven difficult to assess, particularly as estimates of base cation weathering are notoriously difficult to obtain (Hodson and Langan, 1999).

The small watershed approach has been particularly useful for the quantitative study of element fluxes because with appropriate hydrological measurements, 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 Europe and many have reported that net losses of base cations from forested watersheds have occurred in recent decades (Alewell *et al.,* 2000a, 2001; Bailey *et al.,* 1996; Evans *et al.,* 2001; Jandl *et al.,* 2004; Likens *et al.,* 1996; Houle *et al.,* 1997; Watmough and Dillon, 2003b,c, 2004). In general, calcium (Ca) appears to be the main base cation of concern (Bailey *et al.,* 1996; Fernandez *et al.,* 2003; Likens *et al.,* 1996; Watmough and Dillon, 2003a,b, 2004). In eastern North America in particular, estimated losses of Ca caused by acid deposition over recent decades are believed to pose a major risk to the health and productivity of forests (Bailey *et al.,* 1996; Likens *et al.,* 1996; Tomlinson, 2003; Watmough and Dillon, 2003b, 2004).

To address the concern over declining base cation levels in soils caused by acid deposition, we have calculated input-output budgets for SO_4, inorganic N (NO_3-N; NH_4-N), Ca, magnesium (Mg), potassium (K) and sodium (Na) at 21 forested catchments from 17 regions in Canada, the United States and Europe (Germany and Norway) using data collected during the 1990s. These sites include a variety of forest types and a wide range of S and N deposition. Estimates of base cation weathering, when available, were also included in the budget calculations. Temporal trends in deposition and runoff chemistry were also examined at sites with more than 9 years of data, using the entire data period available to us. Data were also used

to estimate critical loads of acidity and current exceedances using protocols used by the New England Governors and Eastern Canadian Premiers (NEG/ECP Forest Mapping Group 2001) working group on critical loads at sites where weathering estimates were available.

2. Materials and Methods

Data were provided for 21 catchments from 17 regions (3 catchments are in the Experimental Lakes Area (ELA), and drain into Rawson Lake and 3 are in Muskoka-Haliburton) in Canada, the United States and Europe (Figure 1; Table I). All sites
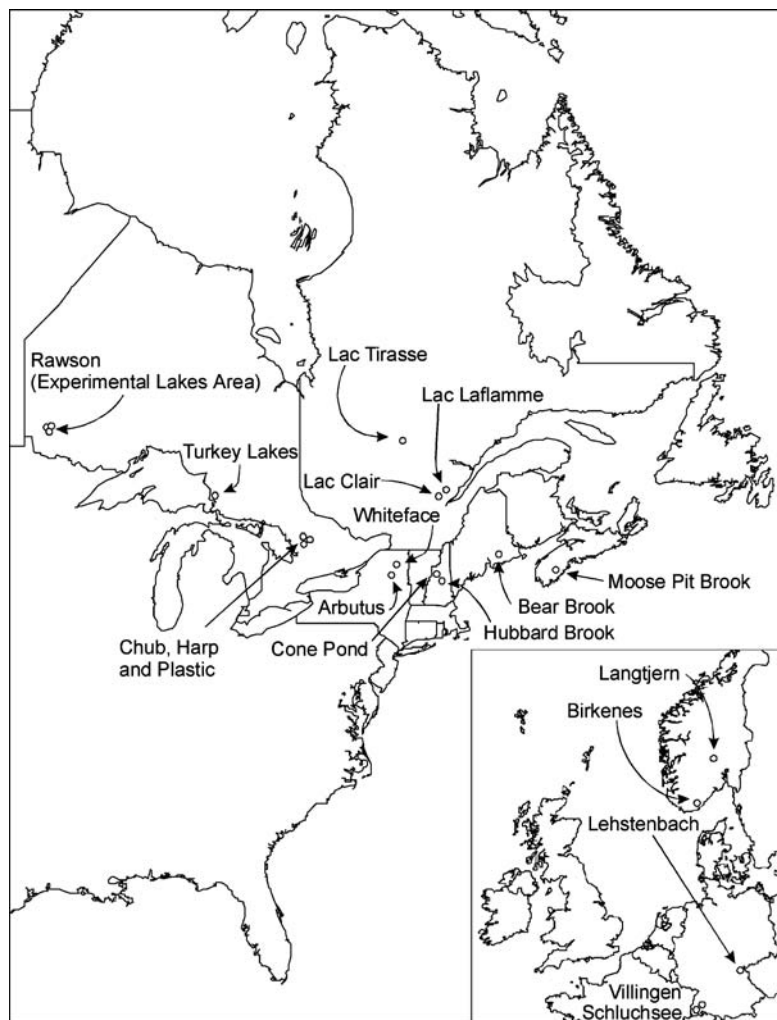

Figure 1. Location of study sites in Canada (11 sites), the United States (5 sites) and Europe (3 sites in Germany and 2 in Norway).

TABLE I

Selected site characteristics (site name, location, forest species, soil type, precipitation (PPT), runoff (Q), temperature (T) and catchment area) and sampling period used in trend analysis for the 21 study catchments

Site name	Location	Main forest species	Main soil type[a]	PPT (m)	Q (m)	T (°C)	Area (ha)	Sampling period
ELA NW (ELA)	49°40′ N, 93°44′ W	*Pinus banksiana*	Podzol, organic	0.69	0.23	2.4	56.4	1970–1996
ELA NE (ELA)	49°40′ N, 93°44′ W	*Pinus banksiana*	Podzol, organic	0.69	0.28	2.4	12.4	1970–1996
ELA E (ELA)	49°40′ N, 93°44′ W	*Pinus banksiana*	Podzol, organic	0.69	0.21	2.4	170.3	1970–1996
Turkey Lakes	47°03′ N, 84°25′ W	*Acer saccharum; Betula alleghaniensis*	Podzol	1.16	0.79	4.0	4.6	1981–2000
Plastic (MUS-HAL)	45°07′ N, 78°50′ W	*Pinus strobus; Tsuga canadensis*	Podzol	0.99	0.50	5.6	23.3	1980–1999
Chub (MUS-HAL)	45°11′ N, 78°55′ W	*Acer rubrum; Quercus rubra*	Podzol, brunisol	0.99	0.41	5.6	59.7	1980–1999
Harp (MUS-HAL)	45°25′ N, 79°10′ W	*Acer saccharum; Acer rubrum*	Podzol, brunisol	0.99	0.50	5.6	119.1	1980–1999
Lac Laflamme	47°19′ N, 71°07′ W	*Abies balsamea; Betula papyrifera*	Podzol	1.29	0.89	0.4	62.3	1981–2001
Lac Clair	46°57′ N, 71°40′ W	*Acer saccharum, Betula alleghaniensis*	Podzol	1.35	0.80	3.4	226.0	1987–2001
Lac Tirasse	49°12′ N, 73°38′ W	*Picea mariana; Pinus banksiana*	Podzol	0.81	0.56	1.2	56.0	1997–2001
Bear Brook	44°52′ N, 68°06′ W	*Fagus grandifolia; Picea rubens*	Podzol	1.40	1.07	4.9	11.4	1988–2000
Moose Pit	44°46′ N, 65°05′ W	*Picea rubens; Abies balsamea*	Podzol	1.40	0.89	6.1	1770.0	1984–1998
Cone Pond	43°54′ N, 71°36′ W	*Picea rubens; Tsuga canadensis*	Podzol	1.28	0.66	5.6	33.4	1989–1999
Arbutus	43°59′ N, 74°14′ W	*Fagus grandifolia; Acer saccharum*	Podzol	1.01	0.75	4.4	352.0	1985–1998
Hubbard Brook	43°56′ N, 71°45′ W	*Acer saccharum; Betula alleghaniensis*	Podzol	1.40	0.80	5.6	13.2	1965–1998
Whiteface	44°22′ N, 73°54′ W	*Abies balsamea; Picea rubens*	Podzol	1.56	0.77	2.0	40.0	1986–1995
Villingen	48°03′ N, 08°22′ E	*Picea abies*	Podzol	1.33	0.55	4.4	11.0	1988–1996
Schluchsee	47°49′ N, 08°06′ E	*Picea abies*	Brunisol	1.87	1.42	6.3	46.3	1988–1995
Lehstenbach	50°09′ N, 11°52′ E	*Picea abies*	Podzol	1.05	0.49	6.0	420.0	1988–2000
Langtjern	60°22′ N, 09°39′ E	*Picea abies; Pinus sylvestris*	Podzol	0.75	0.57	3.0	480.0	1974–2000
Birkenes	58°23′ N, 08°15′ E	*Picea abies; Pinus sylvestris*	Podzol	1.49	1.15	5.4	41.6	1974–2000

[a]Canadian soil classification; ELA (Experimental Lakes Area); MUS-HAL (Muskoka-Haliburton).

are forested catchments and export was determined from stream water samples. Inputs in bulk deposition were considered in the mass balance calculations, except at Whiteface and Moose Pit Brook, where total deposition (wet, dry and fog (Whiteface only)) data were available and at Arbutus and Bear Brook, where wet-only deposition data are collected. As a consequence, deposition inputs will be underestimated at the majority of catchments (Shepard *et al.,* 1989) and the implications of this for the mass balances will be discussed. Most sites are currently free from major disturbance, although some harvesting occurs at Moose Pit Brook and severe fires consumed all or part of the forest cover at the 3 ELA catchments in the mid-1970s and 1980 (Bayley *et al.,* 1992). Prior land-use histories are varied among the sites, with some sites experiencing logging (and farming) and other disturbances (fire, insect outbreaks) in the past. We do not have detailed histories of all the sites and it is possible that some prior land-use history may have a residual impact on nutrient budgets that we observe today.

Sample collection and analysis varied slightly among sites, with runoff sample collection frequency ranging from daily during periods of high-flow at some sites to monthly sampling at other sites. Concentration data are discharge-weighted (mg L^{-1}), and areal fluxes (kg ha^{-1}) were calculated by dividing stream export by catchment area. Further details of the study sites, sampling procedures and chemical analyses conducted at individual sites can be found in earlier publications (e.g., Armbruster, 1998; Duchesne *et al.,* 2002; Foster *et al.,* 1992; Houle *et al.,* 1997; Larssen *et al.,* 2002; Likens *et al.,* 1996; Mitchell *et al.,* 1992; Moritz *et al.,* 1994; Norton and Fernandez 1999; Park *et al.,* 2003; Stainton *et al.,* 1977; Watmough and Dillon, 2003c; Yanni *et al.,* 2000). Input-output budgets were calculated for each water-year used by each site (e.g., June 1–May 31), based on average deposition and export measured during the 1990s, although some sites (ELA, Hubbard Brook) have been continuously monitored since the mid-1960s. Estimates of mineral weathering for each site are based on published results (Bailey *et al.,* 1996) or estimates provided by the principal investigator, or were calculated with the PROFILE model (version 4.0; Warfvinge and Sverdrup, 1992) using site specific data (e.g., mineralogy) collected as part of this study. Weathering estimates were not available for the 3 German sites (Schluchsee, Villingen and Lehstenbach). In order to compare among sites, mass balance estimates were based on the average of all annual deposition and export values available at each site during the 1990s.

The values of the exchangeable base cation pool (Ca, Mg, K) in the soil rooting zone (LFH, A and B horizons) was estimated using salt-extractable Ca, Mg and K concentrations, average depth and bulk density measurements for each horizon. Pools of Ca, Mg, K and N in aboveground forest biomass were approximated using estimates of aboveground biomass and nutrient concentrations in each tree species.

The Seasonal Mann Kendall test (Hirsch and Slack, 1984) was used to detect monotonic trends in monthly volume-weighted concentrations in streams and deposition for sites/regions having more than 9 years of data (using all years; Table I). The trend slopes, which are reported, were estimated according to Sen (1968). Ion

concentrations were not corrected for sea-salt inputs, which are substantial at some of the coastal sites. The changes in base cation (Ca, Mg, K) concentrations were compared with changes in SO_4 and NO_3 concentration in order to assess whether changes in base cations have offset declines in acid anions (Hedin *et al.,* 1994).

Finally, critical loads for S and N (CL(S + N)) were estimated at each site using the Steady-State Mass Balance (SSMB) model (units are in eq ha^{-1} per year):

$$CL(S + N) = BC_{dep} + BC_w - BC_u + N_i + N_u + N_{de} - Alk_{le(crit)} \qquad (1)$$

where BC_{dep} is the base cation (Ca, Mg, K) deposition, BC_w the base cation weathering, BC_U the net base cation uptake, N_i the net nitrogen immobilisation rate in soil, N_u the net nitrogen uptake, N_{de} the net denitrification rate and $Alk_{le(crit)}$ the critical alkalinity leaching rate. For critical load calculations, it was assumed that Na is balanced by Cl and therefore critical load estimates do not include Na (or Cl).

Critical loads for S, for each site were also calculated as:

$$CL(S) = BC_{dep} + BC_w - BC_u - Alk_{le(crit)} \qquad (2)$$

For this study, we followed the approach currently being used by the New England Governors and Eastern Canadian Premiers (NEG/ECP) working group on critical loads, whereby N_i and N_{de} are set to zero, and $Alk_{le(crit)}$ is determined using a BC to Al molar ratio of 10 (NEG/ECP Forest Mapping Group, 2001), a value considerably higher than is used in most European critical load assessments. Critical loads at each site were calculated under 2 scenarios: (a) zero harvesting, in this instance CL(S + N) equals CL(S), and (b) harvesting at the level considered typical for the region in which the site is located. Harvesting removals were based on the nutrient content of stems (wood and bark) or above-ground biomass (depending on which harvesting scenario was considered most likely for the region), divided by the estimated average age of trees at each site. Exceedance (Ex) of the critical load was estimated using bulk deposition values, except at sites where only total (Whiteface, Moose Pit Brook) or wet-only deposition (Arbutus, Bear Brook) data were available.

3. Results and Discussion

3.1. DEPOSITION

3.1.1. *Annual Inputs*
Average annual SO_4 input in deposition during the 1990s varied between 7.3 kg ha^{-1} per year (ELA) and 28.4 kg ha^{-1} per year (Hubbard Brook) excluding Whiteface, which includes a dry/fog component in the estimation (Table II). Surprisingly, average 1990s SO_4 deposition at many of the eastern North American sites is comparable to average SO_4 deposition during the 1990s at the 3 German sites (Table II), although SO_4 deposition at the German sites was much greater during the 1970s and 1980s (Moritz *et al.,* 1994). Inorganic N deposition was between 2.8

TABLE II

Annual average bulk deposition (kg ha^{-1} yr^{-1}) measured during the 1990s at the 17 study regions

Study regions	Ca	Mg	K	Na	SO$_4$	NO$_3$-N	NH$_4$-N
ELA	2.25	0.45	0.43	0.52	7.32	2.13	2.14
Turkey Lakes	3.77	0.41	0.54	0.71	20.65	4.78	3.53
MUS-HAL	2.15	0.40	0.59	0.50	21.67	5.07	3.55
Lac Laflamme	0.78	0.13	0.18	0.39	16.02	1.79	1.93
Lac Clair	1.88	0.28	0.65	0.77	23.89	5.04	3.55
Lac Tirasse	0.71	0.15	0.24	0.26	9.11	1.77	1.06
Bear Brook[b]	0.87	0.53	0.48	5.21	15.84	2.73	1.36
Moose Pit[a]	1.09	1.60	0.73	12.37	18.90	3.75	1.72
Cone Pond	1.03	0.27	0.78	1.35	20.65	4.16	2.28
Arbutus[b]	0.85	0.14	0.13	0.50	17.00	3.72	1.80
Hubbard Brook	1.08	0.33	0.64	1.33	28.41	5.07	2.45
Whiteface[a]	3.27	0.58	1.18	1.13	55.10	10.67	6.51
Villingen	4.21	0.70	2.24	2.90	18.90	4.42	6.18
Schluchsee	3.92	0.73	1.96	3.79	20.94	4.58	5.25
Lehstenbach	4.00	0.50	1.60	4.18	24.13	5.89	7.94
Langtjern	0.86	0.23	0.79	1.33	10.44	2.51	2.69
Birkenes	1.75	2.26	1.36	18.96	26.70	7.16	6.45

[a]Total deposition.

[b]Wet deposition.

(Lac Tirasse) and 13.8 kg ha^{-1} per year (Lehstenbach) (also excluding Whiteface), of which 44–67% was NO$_3$-N (Table II). Inputs of SO$_4$, NO$_3$-N and NH$_4$-N are comparable with previous results published for S and N deposition in eastern North America and Europe (Wright *et al.,* 2001; Forsius *et al.,* 2001; Ito *et al.,* 2002).

Annual Ca inputs in deposition were between 0.71 (Lac Tirasse) and 4.21 kg ha^{-1} per year (Villingen), Mg inputs were between 0.13 (Lac Laflamme) and 2.26 kg ha^{-1} per year (Birkenes) and K inputs were between 0.18 (Lac Laflamme) (0.13 kg ha^{-1} y^{-1} wet-only deposition at Arbutus) and 2.24 kg ha^{-1} per year (Villingen). Sodium inputs varied greatly among sites, from 0.26 (Lac Tirasse) to 19.0 kg ha^{-1} per year (Birkenes). Higher deposition of Na and to a lesser extent Mg and SO$_4$ was associated with sea salt inputs as deposition is generally highest at coastal sites (Moose Pit Brook, Bear Brook, Birkenes).

Annual average SO$_4$ deposition during the 1990s was strongly correlated with NO$_3$-N ($r = 0.94$; $p < 0.001$) and to a lesser extent NH$_4$-N ($r = 0.58$; $p < 0.05$) deposition, indicating that regions which receive elevated SO$_4$ deposition also generally receive higher inputs of inorganic N deposition (Table III). In part, the strong correlation between SO$_4$ and N (NO$_3$-N and NH$_4$-N) inputs is due to differences in precipitation levels, although concentrations of SO$_4$ and NO$_3$-N in

TABLE III

Pearson correlation coefficients (r) for average annual inputs and volume-weighted concentrations in deposition measured during the 1990s for the 17 study regions

	SO_4	NO_3-N	NH_4-N	Ca	Mg	K	Na
Deposition							
SO_4	1						
NO_3-N	0.94[c]	1					
NH_4-N	0.58[a]	0.73[c]	1				
Ca	0.36	0.48[a]	0.77[c]	1			
Mg	0.19	0.35	0.33	0.10	1		
K	0.32	0.45	0.78[c]	0.72[c]	0.41	1	
Na	0.10	0.24	0.28	−0.05	0.96[c]	0.32	1
Concentration							
SO_4	1						
NO_3-N	0.57[a]	1					
NH_4-N	0.34	0.70[b]	1				
Ca	0.40	0.43	0.70[c]	1			
Mg	−0.36	0.33	0.27	0.08	1		
K	0.11	0.39	0.76[c]	0.60[b]	0.28	1	
Na	−0.40	0.30	0.28	−0.12	0.92[c]	0.27	1

[a] $p < 0.05$.
[b] $p < 0.01$.
[c] $p < 0.001$.

bulk deposition are significantly correlated (Table III). In contrast, average annual base cation (Ca, Mg, K or Na) deposition measured during the 1990s was not significantly correlated to SO_4 deposition (Table III). Annual deposition of NO_3-N was significantly correlated with NH_4-N deposition ($r = 0.73$; $p < 0.001$) as well as Ca deposition ($r = 0.48$; $p < 0.05$). Annual deposition of both Ca ($r = 0.77$; $p < 0.001$) and K ($r = 0.78$; $p < 0.001$) were also strongly correlated to NH_4-N deposition. Similar, although slightly weaker relationships were observed between NO_3-N, NH_4-N, Ca and K using volume-weighted concentrations in bulk deposition. As expected, Mg and Na deposition were strongly related due to their association in marine aerosols (Table III).

Inconsistent associations between inputs of base cations, SO_4 and inorganic N likely reflect the multiple sources of base cations and inorganic N in deposition (Draaijers *et al.*, 1997a,b; Torseth *et al.*, 1999). Fossil fuel burning is the predominant source of SO_4 and a major source of NO_3-N in deposition; high base cation levels are commonly associated with high SO_4 deposition close to point sources such as fossil fuel power plants (Raper and Lee, 1996). Higher base cation deposition, particularly at the German sites compared with North American sites may reflect their closer proximity to industrial emission sources (Draaijers *et al.*, 1997a,b). The

majority of North American sites are rural, located relatively far from large industrial emission sources, and a greater proportion of base cation inputs may be derived from various sources, including dust/soil particulates, forest fires and marine aerosols, which differ in their base cation composition. For example, soil particles may be expected to have higher Ca concentrations relative to other base cations, whereas marine aerosols will contain elevated Na and Mg relative to Ca (Draaijers *et al.,* 1997a,b; Torseth *et al.,* 1999). Inputs of NH_4-N are generally higher at the European sites and are derived primarily from sources other than fossil fuel burning, namely agricultural livestock emissions and fertiliser application, and wind-blown soil from agricultural areas may account for the strong correlation between NH_4-N deposition and K and Ca deposition (Table III).

3.1.2. *Trends in Deposition*

Sulphate concentrations in deposition decreased significantly at 13 of the 14 study regions with more than 9 years of data (Table IV). Bear Brook was the only exception, where there was no significant change in SO_4 deposition between 1988

TABLE IV

Significant trends (values are in mg L^{-1} yr^{-1}) in bulk deposition and the percentage of acid anion ($SO_4 + NO_3$-N) trend balanced by base cations (Ca + Mg + K) for the 14 study regions with more than 9 years of data (using the entire data period presented in Table I)

Study region	Ca	Mg	K	Na	SO_4	NO_3-N	NH_4-N	%BC
ELA	−0.012[c]	−0.003[c]	−0.002[c]	−0.005[b]	−0.033[b]		0.003[a]	131
Turkey Lakes					−0.080[b]			0
MUS-HAL			−0.001[a]		−0.043[c]			3
Lac Laflamme	−0.002[c]	−0.0003[a]	−0.0004[b]		−0.035[c]			19
Lac Clair					−0.038[a]			0
Bear Brook[d]	0.003[b]						0.004[a]	n.a.
Moose Pit [d]					−0.028[b]			0
Arbutus [d]	−0.002[b]	−0.0084[b]	0.0004[b]	0.0009[a]	−0.039[a]			97
Hubbard Brook	−0.003[c]	−0.0001[c]	−0.0003[a]	−0.00006[a]	−0.038[c]			21
Villingen	−0.016[a]				−0.076[a]			50
Schluchsee	−0.015[b]	−0.003[a]			−0.067[a]		−0.02[a]	72
Lehstenbach	−0.073[a]			−0.049[a]	−0.473[a]			37
Langtjern	−0.003[c]		−0.009[c]		−0.102[c]	−0.005[a]	−0.0008[a]	15
Birkenes	−0.005[c]		−0.009[c]		−0.102[c]		−0.008[c]	23
Median								22

[a] $p < 0.05$.
[b] $p < 0.01$.
[c] $p < 0.001$.
[d] Trend on wet deposition; blank space indicates no significant trend; n.a. (not applicable). Negative value indicates decreasing trend.

and 2000, even though significant decreases in SO_4 have been reported for other regions of eastern North America (Park *et al.,* 2003). Differences at Bear Brook may be due to a strong marine influence, a local point source of S emission or the timing of the collection period used in the analysis (Table I), since reductions in S emissions in the United States were larger in the 1980s relative to the 1990s. Discounting Bear Brook, the decline in annual volume-weighted SO_4 concentration is between 0.028 mg L^{-1} per year (Moose Pit Brook) and 0.473 mg L^{-1} per year (Lehstenbach). In general, decreases in SO_4 deposition are greater at European sites (Table IV), likely due to the historically higher depositions in Europe and the major reductions in S emissions in Europe during the 1990s, compared with the late 1970s and early 1980s in eastern North America (Hedin *et al.,* 1994). The magnitude of decrease in SO_4 deposition estimated in this study is consistent with other studies conducted in Europe and eastern North America (Clair *et al.,* 1995; EMEP, 2001; Erisman *et al.,* 2003; Forsius *et al.,* 2001; Harriman *et al.,* 2001).

In contrast to SO_4, inorganic N concentrations in deposition showed no consistent downward trend (Table IV). A significant decrease in NO_3-N concentration was only observed at one site (Langtjern) whereas NH_4-N concentrations in deposition decreased significantly at 3 sites (Langtjern, Birkenes and Schluchsee) and increased at Bear Brook and the ELA (Table IV), indicating that overall there is no general trend in inorganic N deposition. The lack of a significant general decline in inorganic N deposition is consistent with previous reports (Harriman *et al.,* 2001), and reflects the lower and more varied emission reductions for N compared to S in Europe and North America (Driscoll *et al.,* 2001; Wright *et al.,* 2001).

Base cation concentrations in deposition generally decreased, with significant declines in Ca, Mg, K and Na concentration occurring at 9, 5, 6 and 3 of 14 regions, respectively (Table IV). There were small increases in Ca deposition at Bear Brook, and K and Mg at Arbutus. The increase in Ca at Bear Brook may be due to the same factors (e.g. an unidentified point source, time period considered, etc.) that resulted in no significant decrease in SO_4 deposition. The decline in base cation (Ca + Mg + K) concentrations across all sites accounted for between 0 and 131% of the decline in acid ion (SO_4 + NO_3-N) concentration in deposition; with a median value of 22% (Table IV). In general, the percentage reduction in base cations was greater at the European sites (median 44%), compared with North American sites (median 11%) (Table IV) and suggests a larger contribution of industrial sources to base cation deposition in Europe. In North America, where study sites are generally more remote from industrial emission sources, the influence of declining industrial inputs of base cations may have been partially offset by a greater relative contribution from natural sources of base cation deposition, most of which would have remained relatively unchanged over the study period.

A number of studies have suggested that a decline in base cation deposition has offset the benefits expected from decreased SO_4 deposition (Gimeno *et al.,* 2001; Hedin *et al.,* 1994). Hedin *et al.* (1994) reported that declines in base cation concentration balanced 22–34% of the decline in SO_4 concentration in the Netherlands

and Europe, and 38–110% of the decline in SO_4 concentration in the United States. The reason for the discrepancy in results for the North American sites is partly due to the longer time period (1979–1990) and location of sites considered by Hedin (many were located in the central and southern United States). Declines in base cation concentrations at polluted sites in eastern North America were far more pronounced in the 1960s and 1970s compared with more recent decades (Likens *et al.,* 1996; Hedin *et al.,* 1994), and sites located closer to emission sources will likely receive a greater proportion of industrial base cation emissions.

3.2. RUNOFF

3.2.1. *Annual Export*
Annual export of SO_4, averaged over the 1990s, was lowest at the ELA in northwestern Ontario (5.8–8.5 kg ha^{-1} per year) and highest at Lehstenbach, which exported on average, 105 kg ha^{-1} per year SO_4 during the 1990s, although annual SO_4 export exceeded 25 kg ha^{-1} per year at 14 of the 21 sites (compared with only 3 for deposition). In contrast, annual NO_3-N export ranged from below detection at Moose Pit Brook to a high of 6.8 kg ha^{-1} at Schluchsee, and annual NH_4-N export was low at all sites, ranging from below detection to a high of only 0.25 kg ha^{-1} per year. These findings are consistent with previous studies of forested catchments, which showed that the majority of inorganic N export occurs as NO_3-N and that NH_4-N export is generally low (Bringmark and Kvarnas, 1995; Campbell *et al.,* 2004; Park *et al.,* 2003; Wright *et al.,* 2001).

Annual export of Ca varied between 3.6 kg ha^{-1} per $year^{-1}$ (Cone Pond) and 39.7 kg ha^{-1} per $year^{-1}$ (Turkey Lakes). Annual Mg export was between 0.8 kg ha^{-1} per $year^{-1}$ (Lac Clair) and 4.7 kg ha^{-1} per $year^{-1}$ (Lac Tirasse) and K export was between 0.6 kg ha^{-1} per $year^{-1}$ (Lac Clair) and 7.6 kg ha^{-1} per $year^{-1}$ (Schluchsee). Sodium export was strongly influenced by proximity to the ocean, ranging from lows of 2.1–2.8 at the ELA to a high of 31.9 kg ha^{-1} per $year^{-1}$ at Birkenes.

Annual export of SO_4 was significantly correlated with NO_3-N ($r = 0.70$; $p < 0.01$), NH_4-N ($r = 0.60$; $p < 0.01$) K ($r = 0.48$; $p < 0.05$) and Na ($r = 0.55$; $p < 0.05$) (Table V), although these correlations are strongly influenced by export at Lehstenbach. If Lehstenbach is excluded from the correlation matrix, there are no significant correlations between SO_4 and export or concentration of any single base cation in runoff among sites. Annual NO_3-N export was significantly correlated with Ca export and concentration (with and without Lehstenbach). The relationship between SO_4 and NO_3-N in stream runoff is weaker than in deposition, demonstrating that processes within catchments modify S and N dynamics. Such processes may include differential N-retention and differences in the amount of net SO_4 export among sites. Because NO_3-N concentrations are low it is unlikely that NO_3-N export is driving Ca export. A more likely explanation is that processes favouring NO_3-N export also favour Ca export; in particular nitrification rates may be higher at base-rich sites. Within individual sites, stream concentrations of Ca

TABLE V

Pearson correlation coefficients (r) for average annual stream export and volume-weighted concentration measured during the 1990s at the 21 study sites

	SO$_4$	NO$_3$-N	NH$_4$-N	Ca	Mg	K	Na
Export							
SO$_4$	1						
NO$_3$-N	0.70[b]	1					
NH$_4$-N	0.60[b]	0.30	1				
Ca	0.36	0.61[b]	0.03	1			
Mg	0.28	0.32	0.02	0.59[a]	1		
K	0.48[a]	0.81[c]	0.11	0.24	0.35	1	
Na	0.55[a]	0.52[a]	0.06	0.12	0.48[a]	0.63[b]	1
Concentration							
SO$_4$	1						
NO$_3$-N	0.77[c]	1					
NH$_4$-N	0.60[b]	0.41	1				
Ca	0.35	0.57[a]	0.44	1			
Mg	0.35	0.29	0.67[b]	0.65[b]	1		
K	0.67[b]	0.76[c]	0.58[a]	0.39	0.60[b]	1	
Na	0.69[b]	0.72[c]	0.37	0.20	0.38	0.74[c]	1

[a] $p < 0.05$.
[b] $p < 0.01$.
[c] $p < 0.001$.

and Mg are strongly correlated with the export of SO$_4$ (Houle *et al.,* 1997; Likens *et al.,* 1998; Watmough and Dillon, 2004) or NO$_3$-N (Lovett *et al.,* 2000). However, similar relationships do not occur at sites with substantial surficial deposits (Beall *et al.,* 2001). Furthermore, individual sites considered in this study vary in their ability to buffer a given amount of acid leaching (Kirchner *et al.,* 1992). These variations, along with sea salt influences, likely account for the lack of significant relationship between SO$_4$ and Ca or Mg, although SO$_4$ export and concentration is positively correlated with Na and K among the sites (Table V).

3.2.2. *Trends in Runoff*

In response to declining SO$_4$ concentrations in deposition, there was a significant decrease in stream SO$_4$ concentration at 14 of the 17 sites with more than 9 years of data (Table VI). There was no significant decrease at Moose Pit Brook and at 2 sites (Plastic, Chub) in Muskoka-Haliburton in central Ontario. In central Ontario, this is likely due to the strong influence that climatic variations, and in particular summer droughts have on SO$_4$ export in the region (Eimers and Dillon 2002; Eimers *et al.,* 2004). Sulphate release from Muskoka-Haliburton (MUS-HAL) catchments increases dramatically following

TABLE VI

Significant trends (values are in mg L^{-1} yr^{-1}) in stream chemistry and the percentage of acid anions ($SO_4 + NO_3$-N) trend balanced by base cations ($Ca + Mg + K$) at the 17 study catchments with more than 9 years of data (using the entire data period presented in Table I)

Site name	Ca	Mg	K	Na	SO$_4$	NO$_3$-N	NH$_4$-N	%BC
ELA NW (ELA)	0.014[a]				−0.108 [a]		0.001 [b]	−31
ELA NE (ELA)	0.019[a]		−0.007[c]		−0.230[c]	0.001[c]		−16
ELA E (ELA)	0.034[c]	0.003[c]	−0.014 [a]	−0.012[b]	−0.215[c]		0.001[b]	−36
Turkey Lakes		−0.01[c]	−0.01[b]	−0.007[b]	−0.077[c]			68
Plastic (MUS-HAL)	−0.056[a]		0.008[c]				0.001[c]	n.a.
Chub (MUS-HAL)							0.001[c]	n.a.
Harp (MUS-HAL)				0.039[c]	−0.086[a]			0
Lac Laflamme	−0.019 [c]	−0.002[b]			−0.082[c]	−0.004[c]		56
Lac Clair					−0.073[c]			0
Bear Brook	−0.043[c]	−0.008[c]	−0.004[a]		−0.084[c]	−0.006[b]		134
Moose Pit		−0.004[a]						n.a.
Hubbard Brook	−0.021[c]	−0.004[c]	−0.002[c]	−0.005[c]	−0.064[c]	−0.023[c]	0.001[a]	48
Villingen					−0.173[a]			0
Schluchsee	−0.025[a]	−0.003[a]			−0.054[a]			133
Lehstenbach	−0.050[a]	−0.010[a]		0.123[b]	−0.250[a]			64
Langtjern	−0.015[c]	−0.004[c]	−0.002[b]		−0.104[c]	−0.0003[c]		52
Birkenes	−0.026[c]	−0.008[c]	−0.004[c]		−0.131[c]			76
median								48

Blank space indicates no significant trend; n.a. (not applicable). Negative value indicates decreasing trend.

[a] $p < 0.05$.
[b] $p < 0.01$.
[c] $p < 0.001$.

prolonged summer droughts (Eimers and Dillon, 2002), and a major drought event (peak) occurred in 1998/1999 (Watmough and Dillon, 2004) at the end of the period considered in this study. The reason for the lack of significant change in SO$_4$ concentration at Moose Pit Brook is unknown, but may in part be due to the relatively small decrease in SO$_4$ concentration in wet-only deposition (0.028 mg L^{-1} per year). If dry inputs did not decrease proportionally to wet-only deposition, perhaps due to the contribution of sea salt aerosols, then the change in total deposition might be less than estimated from measured wet-only inputs.

Annual volume-weighted stream NO$_3$-N concentrations significantly increased at only one of the 17 study sites (ELA, NE), and the magnitude of increase was very small (0.001 mg L^{-1} per year) (Table VI). Annual inorganic N deposition in this region is among the lowest of all the study regions (4.3 kg ha^{-1} per year) and the forest at the 3 ELA catchments is young and actively growing, due to a fire in

1980. Because only 1 of the 3 ELA catchments exhibited an increase in NO_3-N concentration, it is unlikely to be an early sign of N-saturation. In fact, annual NO_3-N concentrations significantly decreased at 4 of the 17 sites, by between 0.0003 mg L^{-1} per year (Langtjern) and 0.023 mg L^{-1} per year (Villingen) (Table VI). Similar inconsistent trends in stream NO_3-N concentration were reported by Stoddard *et al.* (2001), who performed trend analysis on 98 ICP-Waters sites in Europe and North America. Annual NO_3-N deposition only declined significantly at Langtjern in Norway; so it is conceivable that the extremely small decrease in stream NO_3-N at this site is related to declining atmospheric NO_3-N input. Covered roof experiments have shown that streams can respond to declining inorganic N deposition very rapidly, within just a few years (Bredmeier *et al.,* 1995; Moldan *et al.,* 2004; Wright and Jenkins, 2001). Similarly, NO_3-N concentrations in runoff decreased in response to large reductions in inorganic N deposition over a period of a decade in the Bohemian Forest and Tatra mountains (Kopacek *et al.,* 2001). At the other sites it appears most likely that stream NO_3-N levels are influenced by biotic and abiotic factors other than deposition, particularly insect attacks and severe winter frost (Mitchell *et al.,* 1996; Park *et al.,* 2003; Watmough *et al.,* 2004).

A small but significant increase in NH_4-N was observed at 5 of the 17 sites (Table VI), which span the range in inorganic N deposition recorded in this study. As with NO_3-N, increases in NH_4-N are unlikely to be an early sign of N saturation, but instead may be related to long-term climatic changes over the study period. Ammonium concentrations in soil water may increase following summer drought due to enhanced mineralisation (LaZerte and Scott, 1996; Lamersdorf *et al.,* 1998). Similarly, Wright and Jenkins (2001) showed that inorganic N export increased at an experimental catchment in southern Norway following a 'climate change' treatment in which air temperature and atmospheric CO_2 were increased over a 4-year period. Increases in stream NH_4-N noted in this study occurred at Ontario sites having notable organic soil or wetland components (e.g. Plastic, Chub, ELA NW, ELA E), and may reflect slightly higher rates of organic matter mineralisation (possibly caused by increasing annual air temperature). In addition, wetland soils in this region tend to have lower rates of nitrification (Devito *et al.,* 1999) and are susceptible to drying during summer droughts (Bayley *et al.,* 1992; Devito and Hill 1999).

Concentrations of Ca, Mg, K and Na significantly decreased at 8, 9, 7 and 3 of 17 sites, respectively (Table VI). In contrast, Ca concentrations significantly increased at all 3 ELA catchments and Mg increased at ELA E. Concentrations of K also increased slightly at Plastic. Increases in stream Ca and Mg at the ELA may be due to a fire that affected all or large parts of the 3 Rawson Lake catchments in 1980 (Bayley *et al.,* 1992). The gradual decomposition of base-rich biomass and the contribution of ash residual could release significant amounts of Ca and Mg to the soil exchangeable pool over time. The release of Ca from burned remnants in particular, could offset any acid-induced Ca leaching losses, and an increase in the soil exchangeable Ca and/or Mg pool will lead to increased Ca and/or Mg

concentrations in steam runoff. The significant increase in K concentration at Plastic is significantly correlated ($r = 0.60$; $p < 0.05$) with NH_4-N and may be due to increased mineralisation of organic matter (particularly in the wetland part of the catchment) and the lack of forest growth observed at this site over the study period (Watmough and Dillon, 2004). Concentrations of Na also significantly increased at 2 sites, likely due to increased road salt usage (Watmough and Dillon, 2003c).

The delay in chemical recovery of surface waters from acidification has been attributed to declining base cation concentrations in surface waters (Alewell *et al.,* 2001; Evans *et al.,* 2001; Stoddard *et al.,* 1999). Decreased base cation (Ca, Mg and K combined) levels in streams accounted for between <0% (base cations increased at ELA) and 133% of the decrease in acid anion concentration, with a median value of 48%. If the ELA catchments are excluded, due to the probable impact of fire, the median value increases to 54%, with similar values for North American (52%) and European (58%) sites. In other words, more than half of the decrease in acid ion leaching at the study sites has been offset by decreased base cation leaching.

3.3. EXCHANGEABLE BASE CATION POOLS IN SOIL AND NUTRIENT CONTENT OF BIOMASS

Exchangeable Ca pools in the rooting zone at the 21 study sites range between 107 kg ha^{-1} at Lac Tirasse to 829 kg ha^{-1} at Harp (Table VII). Exchangeable Mg pools are between 18 kg ha^{-1} (Lac Tirasse) and 438 kg ha^{-1} (Moose Pit Brook), with the largest soil pools generally occurring at coastal sites (Moose Pit Brook and Birkenes). Exchangeable K pools in soil range between 40 kg ha^{-1} (Lac Tirasse) and 530 kg ha^{-1} (Lehstenbach) and are generally higher at the European sites (Table VII). All things being equal (acid leaching, soil depth, flowpaths, etc.), the size of the exchangeable base cation pools should constrain base cation concentrations in runoff (Kirchner *et al.,* 1992). Calcium concentrations in runoff at Turkey Lakes are far higher than any of the other sites reflecting the input of Ca from groundwater. If Turkey Lakes is excluded, despite large differences between sites, there are significant positive relationships between concentration in stream runoff and size of the exchangeable pool for Ca ($r = 0.46$; $p < 0.05$) and K ($r = 0.67$; $p < 0.01$), but not for Mg.

Nutrient base cation (Ca, Mg, K) and N pools in aboveground biomass are much lower at the ELA than at the other sites, reflecting the relatively young age of the fire-impacted forest at Rawson Lake (Table VII). Pools of Ca, Mg and K in aboveground biomass at the remaining sites are similar in magnitude to the exchangeable pools in soil. Consequently, harvesting could have a huge potential impact on Ca reserves in similar Ca-poor soils (Alewell *et al.,* 2000b; Jandl *et al.,* 2004) Calcium pools in aboveground biomass are between 103 kg ha^{-1} at Langtjern to 960 kg ha^{-1} at Turkey Lakes, a mature sugar maple forest in central Ontario.

TABLE VII

Exchangeable base cation soil pool (kg ha^{-1}) in rooting zone (A and B-horizons) and base cation and N content of above ground forest biomass (kg ha^{-1}) at the 21 study catchments

Site name	Exchangeable pool			Above ground biomass			
	Ca	Mg	K	Ca	Mg	K	N
ELA NW (ELA)	627	92	184	71	7	14	37
ELA NE (ELA)	818	93	186	75	8	15	36
ELA E (ELA)	349	65	204	64	8	12	32
Turkey Lakes	402	45	89	960	48	335	390
Plastic (MUS-HAL)	114	23	100	394	31	170	293
Chub (MUS-HAL)	569	78	301	481	33	207	333
Harp (MUS-HAL)	829	98	238	504	38	183	296
Lac Laflamme	456	51	176	338	45	118	301
Lac Clair	201	27	135	702	75	292	570
Lac Tirasse	107	18	40	305	35	104	196
Bear Brook	255	58	114	301	35	191	315
Moose Pit	324	438	79	263	29	101	254
Cone Pond	161	22	68	483	45	178	443
Arbutus	600	36	78	711	48	223	225
Hubbard Brook	261	35	111	600	56	221	550
Whiteface	515	46	204	214	34	143	154
Villingen	146	46	516	385	41	191	
Schluchsee	266	42	182	335	38	133	
Lehstenbach	500	82	530	519	54	223	552
Langtjern	230	71	147	103	18	154	102
Birkenes	258	139	185	182	43	367	290

Blank space indicates no data.

Excluding ELA, Mg pools in aboveground biomass range from a low of 18 kg ha^{-1} at Langtjern to a high of 75 kg ha^{-1} at Lac Clair, whereas K pools are between 101 kg ha^{-1} at Moose Pit Brook and 367 kg ha^{-1} at Birkenes. Nitrogen pools in aboveground biomass are between 102 kg ha^{-1} at Langtjern and 570 kg ha^{-1} at Lac Clair.

3.4. MINERAL WEATHERING ESTIMATES

In order to compute mass balance budgets for base cations an estimate of base cation input through mineral weathering is required. Estimates of mineral weathering are notoriously difficult to obtain and no single method has proven to be the most reliable indicator of mineral weathering inputs (see Hodson and Langan, 1999;

TABLE VIII

Annual base cation weathering rates (kg ha^{-1} yr^{-1}) estimated for 18 of the 21 study catchments

Site name	Ca	Mg	K	Na
ELA NW (ELA)[a]	1.3	0.3	2.4	3.6
ELA NE (ELA)[a]	1.3	0.3	2.5	3.7
ELA E (ELA)[a]	1.5	0.3	2.7	4.4
Turkey Lakes[a]	4.2	2.9	5.2	7.9
Plastic (MUS-HAL)[a]	2.0	1.0	1.6	3.2
Chub (MUS-HAL)[a]	5.0	3.3	2.5	3.5
Harp (MUS-HAL)[a]	4.6	1.9	3.7	6.8
Lac Laflamme[a]	13.9	3.6	2.1	7.1
Lac Clair[a]	6.2	1.3	3.1	3.9
Lac Tirasse[a]	5.4	1.6	0.6	2.5
Bear Brook[a]	1.5	0.8	5.8	5.3
Moose Pit[a]	3.3	2.0	1.8	2.1
Cone Pond	1.2	1.1	1.1	3.0
Arbutus[a]	5.6	4.1	6.0	5.5
Hubbard Brook	2.1	2.5	1.2	5.1
Whiteface	8.7	2.3	2.9	1.9
Langtjern	6.0	1.0	5.6	1.3
Birkenes	10.0	0.6	1.6	0.9

[a]Estimated using the PROFILE model (version 4.0; Warfvinge and Sverdrup, 1992).

Kolka *et al.,* 1996; Langan *et al.,* 1996; Starr *et al.,* 1998; Sverdrup *et al.,* 1998). Weathering inputs used in this study were calculated using the PROFILE model (Warfvinge and Sverdrup, 1992), Sr-isotopes (Bailey *et al.,* 1996; Miller *et al.,* 1993) or the MAGIC model (Cosby *et al.,* 1985). As with all mass balance studies that include estimates of mineral weathering, results should be interpreted with caution, particularly as different methods may result in different estimates at the same site.

Annual Ca weathering rates at catchments where estimates are available (18 of 21 sites) ranged from 1.2 kg ha^{-1} per year (Cone Pond) to 13.9 kg ha^{-1} per year respectively (Lac Laflamme) (Table VIII). Calcium weathering rates were generally less than 6 kg ha^{-1} per year, and are therefore similar in magnitude to deposition at 14 of the 18 sites. Likewise, estimates of annual Mg, K and Na weathering are 0.3–4.1 kg ha^{-1} per year, 0.6–6.0 kg ha^{-1} per year and 0.9–7.9 kg ha^{-1} per year (Table VIII); which are generally comparable in magnitude to deposition. Draaijers *et al.* (1997a,b) also reported that inputs of base cations in deposition are similar to inputs through mineral weathering for acid podzols in Europe.
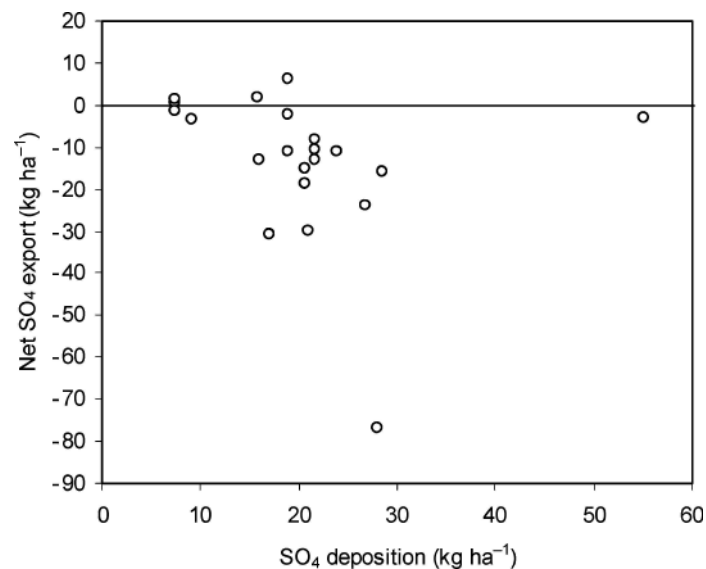
Figure 2. Mean annual SO_4 deposition versus SO_4 export during the 1990s at the 21 study sites. Bulk deposition estimates are used except at Whiteface and Moose Pit Brook where total (wet plus dry) deposition was used and Arbutus and Bear Brook, where wet-only deposition was used.

3.5. MASS BALANCES

3.5.1. *Sulphate*

Export of SO_4 in runoff exceeded inputs in deposition at 18 of the 21 forested catchments (Figure 2). Sulphate mass balances (input in deposition – export in stream water) ranged between an annual net retention of 6.3 kg ha^{-1} per year at Langtjern to an annual net export of 76.9 kg ha^{-1} per year at Lehstenbach in Germany. The high net export of SO_4 from the German sites has been attributed to the large recent reduction in SO_4 deposition (Alewell *et al.,* 1997; Prechtel *et al.,* 2001). Due to the large net release of SO_4, particularly at Lehstenbach, decreases in stream SO_4 concentration are far less than expected from the magnitude of the decrease in SO_4 concentration in deposition (Tables IV and Table VI). At Whiteface and Moose Pit Brook, where estimates of dry deposition are included, there was a small net annual export of 2.8 and 1.9 kg ha^{-1} per year SO_4, respectively. At Arbutus, where wet-only measurements are used, mass balance calculations indicate that there is an annual net export of 30.5 kg ha^{-1} per year SO_4. However, Park *et al.* (2003) conducted similar mass balances at Arbutus (1995–2000) including an estimate of dry deposition and reported that SO_4 export exceeded total inputs by approximately 27 kg ha^{-1} per year. In general, net SO_4 export is greatest at sites that currently receive the highest SO_4 deposition and undoubtedly dry deposition accounts for a portion of the apparent excess export. Several studies have shown that dry deposition can account for up to 50% of total SO_4 input to forested catchments

(Sah and Meiwes, 1993), and the contribution of dry deposition is generally highest close to emission sources (e.g., Edwards *et al.,* 1999).

A number of studies have also suggested that in addition to underestimated dry deposition, there is an internal SO_4 source that may account for the apparent net export (Alewell, 2001; Eimers and Dillon, 2002; Houle and Carignan, 1995; Lofgren *et al.,* 2001; Mitchell *et al.,* 1996). Possible (and not mutually exclusive) internal sources, include release from wetland areas within catchments, desorption in response to declining SO_4 concentrations in deposition, weathering of S minerals and mineralisation of organic S in soil (Bailey *et al.,* 2004; Dillon and LaZerte 1992; Driscoll *et al.,* 1995; Houle and Carignan 1995; Lofgren *et al.,* 2001). The net release of SO_4 from forested catchments may also contribute to the delay in chemical recovery of surface waters, and poses a challenge for scientists who wish to predict the effects of changing SO_4 deposition using dynamic models (Alewell 2001; Lofgren *et al.,* 2001; Prechtel *et al.,* 2001).

3.5.2. *Inorganic Nitrogen*

Export of inorganic N in runoff was less than input at all 21 sites, and the majority of inorganic N in runoff was NO_3-N (Figure 3). Annual inorganic N retention at the study sites was between 2.6 kg ha^{-1} per year at Lac Tirasse and 10.2 kg ha^{-1} per year (Villingen), which can be considered conservative estimates as in general dry deposition values are not included in the mass balance calculations. For example, annual net retention at Whiteface was 15.3 kg ha^{-1} per year, where
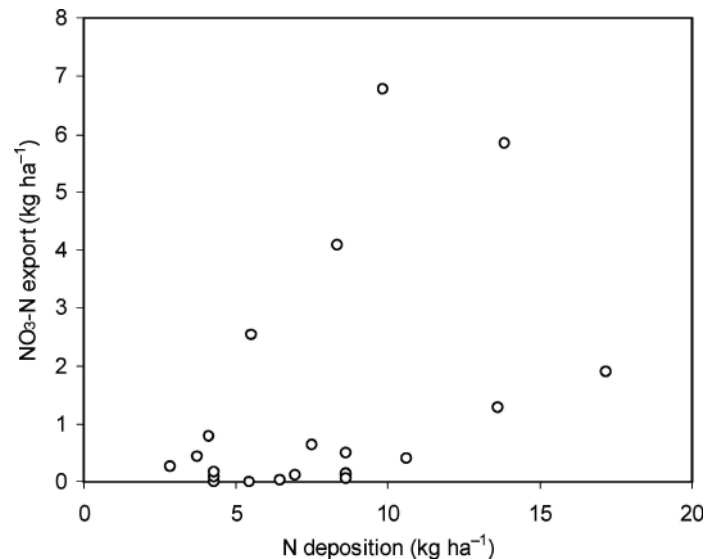

Figure 3. Mean annual inorganic N deposition versus NO_3-N export during the 1990s at the 21 study sites. Bulk deposition estimates are used except at Whiteface and Moose Pit Brook where total (wet plus dry) deposition was used and Arbutus and Bear Brook, where wet-only deposition was used.

inputs of inorganic N also included estimates of dry and fog deposition. However, it should be stressed that organic N losses (or deposition inputs), denitrification or N-fixation estimates are not included in the N mass balance calculation. Between 31 and 100% of inorganic N input in deposition was retained across the study sites, with a median value of 94%. Similar high levels of N retention have been reported for forested catchments throughout Europe and eastern North America (Bringmark and Kvarnas 1995; Campbell *et al.,* 2004; Dise *et al.,* 1998; Fernandez *et al.,* 2003; Harriman *et al.,* 2001; Lawrence *et al.,* 2000; Park *et al.,* 2003; Watmough *et al.,* 2004).

Concern was raised in the late 1980s that high N deposition may result in N-saturation, with increased NO_3-N leaching as one consequence (Aber *et al.,* 1989; Gundersen *et al.,* 1998). Enhanced NO_3-N leaching from forested catchments has been associated with high inputs of N, but losses generally occur above a critical deposition threshold of around $10 \, kg \, N \, ha^{-1}$ per year (Dise and Wright, 1995; Dise *et al.,* 1998; Stoddard *et al.,* 2001; Wright *et al.,* 2001). In this study, NO_3-N export appeared to increase above a threshold of approximately $7 \, kg \, N \, ha^{-1}$ per year, slightly lower than the $10 \, kg \, ha^{-1}$ per year threshold mentioned above. However, dry deposition inputs were generally not considered and would increase total N deposition, particularly at sites close to emission sources.

While elevated inorganic N deposition may be associated with generally higher NO_3-N losses, there is still considerable variation among sites receiving similar levels of N deposition. Site characteristics and forest species composition have been shown to strongly influence NO_3-N leaching losses (Creed and Band, 1998; Dillon and Molot, 1992; Lovett *et al.,* 2002; Schiff *et al.,* 2002). Nevertheless, concern remains that chronic accumulation of N in forest soils may ultimately lead to N-saturation and increased NO_3-N leaching (Bringmark and Kvarnas, 1995; Aber *et al.,* 1989; Wright *et al.,* 2001). In the present study, there is no evidence that NO_3-N leaching losses are increasing even at the highest N deposition sites, despite conservative estimates of net N accumulation of up to $10 \, kg \, ha^{-1}$ per year.

3.5.3. *Calcium and Magnesium*

Mass balance estimations (input-output) for base cations are presented with and without estimates of mineral weathering due to the uncertainty associated with weathering estimates. Negative values indicate that there is a net loss of base cation based on estimates used in this study. Export of Ca in streams exceeds input in deposition at all 21 study sites (Figure 4), and net annual Ca losses amount to between 0.5 and 11.7% of the current exchangeable Ca pool in soil (Table IX). Inclusion of estimates of mineral Ca weathering fail to balance the Ca budget at 14 of the 18 sites that had weathering estimates, although some of the difference between sites may be attributed to the methodology used for assessing mineral weathering (i.e., PROFILE vs. MAGIC). When weathering inputs are considered, annual Ca budgets vary between a net annual retention of $2.4 \, kg \, ha^{-1}$ per year
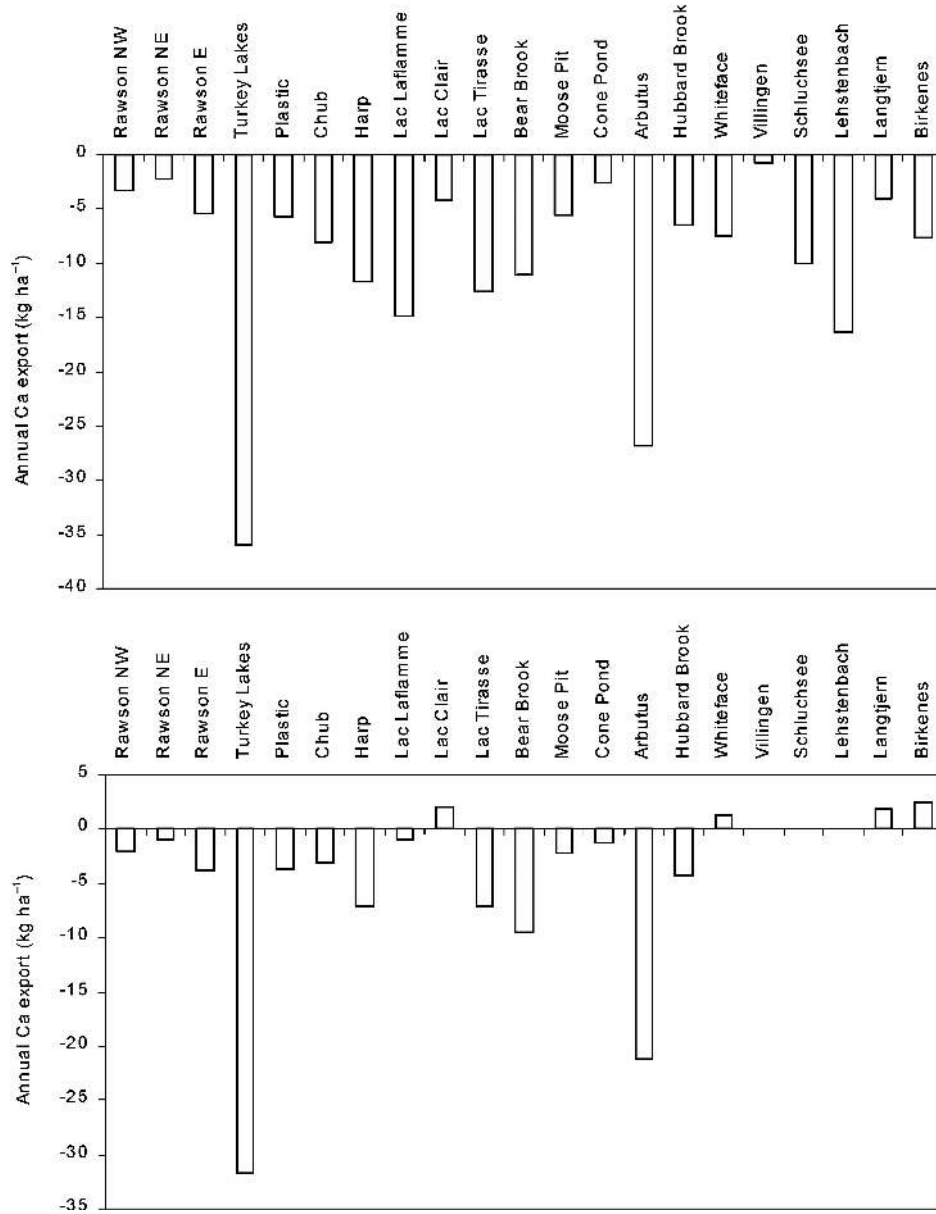
Figure 4. Mean annual Ca input-output budgets during the 1990s, excluding (upper) and including (lower) estimates of Ca weathering.

(Birkenes) to a net loss of 31.8 kg ha^{-1} per year (Turkey Lakes) (Figure 4). At sites where Ca losses are estimated, net losses are up to 7.9% of the exchangeable Ca pool (Table IX). Similarly, export of Mg in streams exceeds input in deposition at all 21 study sites (Figure 5), and net annual Mg losses amount to between 0.6 and

TABLE IX

Net annual base cation loss (1990s average, excluding tree uptake) as a percentage of the current exchangeable pool excluding and including estimates of base cation weathering

Site name	% loss (excluding weathering)			% loss (including weathering)		
	Ca	Mg	K	Ca	Mg	K
ELA NW (ELA)	−0.53	−1.71	−0.26	−0.33	−1.42	1.05
ELA NE (ELA)	−0.28	−0.59	−0.16	−0.12	−0.44	1.18
ELA E (ELA)	−1.55	−2.75	−0.29	−1.11	−2.28	1.06
Turkey Lakes	−8.94	−7.49	−1.39	−7.90	−1.00	4.47
Plastic (MUS-HAL)	−5.05	−7.04	−0.37	−3.30	−2.91	1.23
Chub (MUS-HAL)	−1.43	−3.04	−0.11	−0.55	1.17	0.72
Harp (MUS-HAL)	−1.41	−4.16	−0.54	−0.86	−2.22	1.02
Lac Laflamme	−3.27	−6.49	−0.77	−0.22	0.57	0.43
Lac Clair	−2.07	−2.07	0.02	1.01	2.74	2.32
Lac Tirasse	−11.75	−25.50	−4.13	−6.70	−16.61	−2.63
Bear Brook	−4.37	−3.83	−1.32	−3.76	−2.38	3.77
Moose Pit	−1.69	−0.60	−3.08	−0.68	−0.15	−0.85
Cone Pond	−1.58	−3.14	0.13	−0.84	1.86	1.75
Arbutus	−4.47	−10.42	−1.72	−3.55	0.92	6.03
Hubbard Brook	−2.46	−5.17	−0.88	−1.65	1.97	0.20
Whiteface	−1.45	−2.80	0.05	0.24	2.20	1.48
Villingen	−0.53	−2.46	−0.03			
Schluchsee	−3.78	−3.71	−3.12			
Lehstenbach	−3.12	−5.16	−0.63			
Langtjern	−1.79	−0.83	0.12	0.83	0.54	3.89
Birkenes	−2.95	−0.80	0.02	0.93	−0.36	0.86

Blank space indicates no data.

25.5% of the exchangeable Mg pool in soil (Table IX). Inclusion of estimates of mineral Mg weathering again fail to balance the budget at 10 of the 18 sites with weathering estimates and annual net Mg budgets vary between a retention of 1.0 kg ha^{-1} per year (Whiteface) to a net loss of 3.0 kg ha^{-1} per year (Lac Tirasse). When weathering inputs are considered, net losses of Mg are up to 16.6% of the current exchangeable pool in soil (Table IX).

Clearly, mass balances using weathering inputs from the soil rooting zone at sites that show large annual net losses of Ca and Mg (e.g. Turkey Lakes and Arbutus) must be underestimating inputs of Ca and Mg. As with SO_4 and inorganic N, mass balances in this study are generally based on bulk deposition, and therefore will underestimate total inputs to forest systems, possibly by up to 50% (Shepard *et al.,* 1989; Tordeth *et al.,* 1999). However deposition inputs are usually small relative to net losses and even increasing Ca and Mg inputs by 50% is unlikely
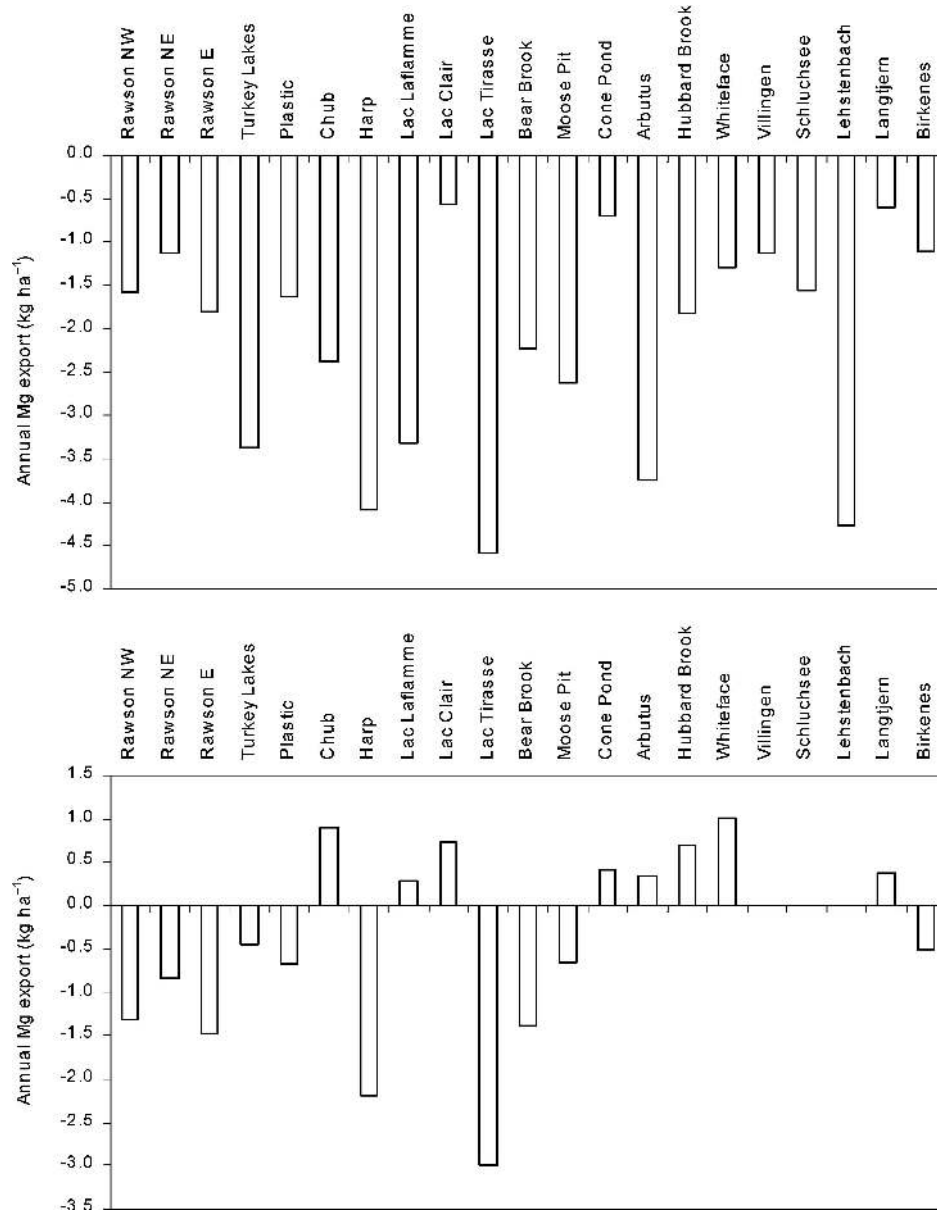
Figure 5. Mean annual Mg input-output budgets during the 1990s, excluding (upper) and including (lower) estimates of Mg weathering.

to fully account for the discrepancy in the budget. Sites such as Turkey Lakes and Arbutus are characterised by areas of deep surficial till deposits that provide an additional source of base cations to stream water (Beall *et al.,* 2001; Mitchell *et al.,* 1992). In this study, weathering estimates were calculated for the rooting

zone and do not take into account weathering reactions in deeper till. Much lower estimates of Ca and Mg export have been reported at Turkey Lakes and Arbutus based on lysimeters placed at 65 cm depth (Foster *et al.,* 1992). Similarly, Houle *et al.* (1997) reported that export of base cations measured in lysimeter samples collected at 60 cm depth were only 39% of the export recorded in stream water. Release of Ca and Mg from base-rich minerals in till beneath the rooting zone likely explains much of the discrepancy in the mass budget at sites showing large net losses of Ca and Mg (Arbutus and Turkey Lakes). There is also considerable uncertainty associated with estimates of mineral weathering (average soil depth, surface area, etc.) and mineral weathering inputs may also be underestimated at sites lacking appreciable till deposits if base rich minerals are present in the fine soil fraction, since coarse soil mineralogy was used to estimate base cation weathering. On the other hand, it is equally possible that the methods used in this study underestimated weathering inputs to the rooting zone (Hodson and Langan, 1999).

With these uncertainties in mind, mass balance calculations show that Ca and Mg losses are occurring from the rooting zone at the majority of sites considered in this study. Net Ca depletion from forest soils due to acid leaching is a major concern, particularly in eastern North America (Bailey *et al.,* 1996; Lawrence *et al.,* 1997; Likens *et al.,* 1996; Tomlinson, 2003; Watmough and Dillon, 2003b,c, 2004). Declining Ca levels have been associated with a number of adverse effects on trees, including reduced growth, increased susceptibility to biotic and abiotic stress including insect defoliation, drought and extreme cold events (Bondietti *et al.,* 1989; DeHayes *et al.,* 1999; Duchesne *et al.,* 2002; Horsley *et al.,* 2000; Jiang and Jagels, 1999; Kolb and McCormick 1993; Shortle and Smith, 1988; Shortle *et al.,* 1995; Watmough, 2002). Furthermore, declining Ca levels in soil will lead to declining Ca concentrations in surface waters, a feature that has been reported throughout eastern North America (Driscoll *et al.,* 1995; Keller *et al.,* 2001; Watmough *et al.,* 2003), and is partly responsible for the lack of chemical recovery in lakes and streams.

3.5.4. *Potassium*

Export of K in streams exceeded input at 16 of the 21 sites (Figure 6). In contrast to Ca and Mg, inclusion of estimates of mineral K weathering more than balanced the K budget at 16 of the 18 sites where weathering estimates were available. At sites where net K losses are reported, these losses are up to 2.6% of the exchangeable K pool in soil (Table IX). The net retention of K observed at most sites is most likely due to accumulation in biomass as cycling of K in forest soils is strongly influenced by biological cycling. It is also possible that K may accumulate in soils through secondary mineral formation. In contrast to Ca and Mg, increased inputs of K through dry deposition or increased losses of K from weathering below the rooting zone are generally not needed to balance the K budget. The fact that weathering estimates of K approximately balance the K budget provides some
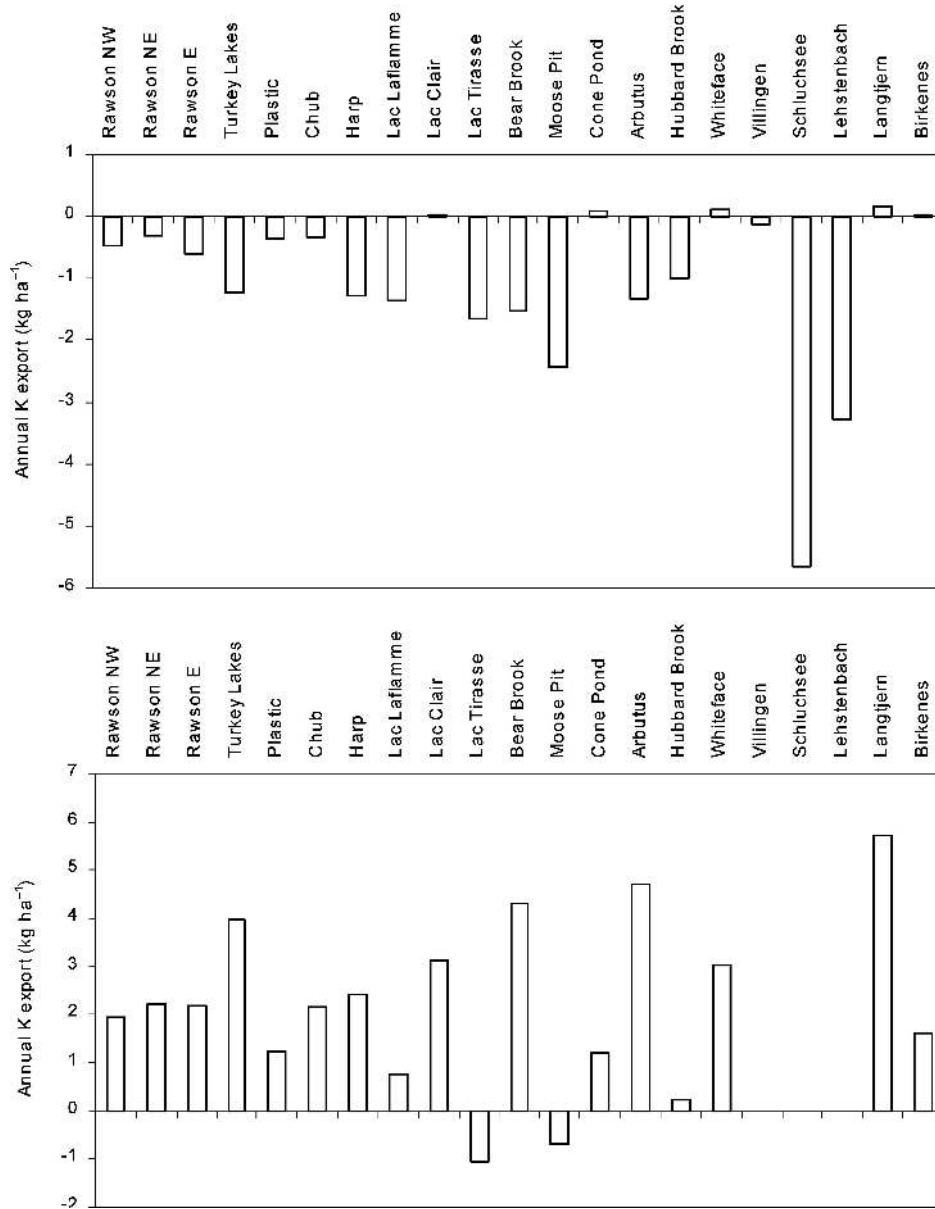
Figure 6. Mean annual K input-output budgets during the 1990s, excluding (upper) and including (lower) estimates of K weathering.

degree of confidence in our estimates of base cation weathering. These results suggest that forests considered in this study are not at risk of K deficiency, a condition that appears more prevalent in base-rich sites with high Mg levels (Bernier and Brazeau, 1988).

3.5.5. *Sodium*

Sodium is not an essential plant nutrient and is only a minor component of the soil exchangeable pool. Therefore, inputs of Na from deposition and mineral weathering should balance losses in stream water and may be used to further assess the accuracy of mineral weathering inputs. As expected, export of Na in streamwater exceeded inputs in deposition at all 21 sites (Figure 7). When estimates of Na weathering are incorporated in mass balance calculations, net Na losses occur at 8 sites and net retention is observed at 10 of 18 sites (Figure 7). At the majority of sites (13 of 18), net retention or net export is usually under 2 kg ha^{-1} per year, indicating that mineral Na weathering estimates used in this study are reasonable. The most notable exceptions occur at the coastal catchments of Bear Brook, Moose Pit Brook and Birkenes, where net export is between 5.0 and 12.0 kg ha^{-1} per year; this is likely due to unmeasured dry deposition of marine aerosols. Since the majority of sites retain Na, even without considering dry deposition, it appears that weathering rates may be slightly overestimated, at least for Na. This does not necessarily mean that weathering rates of Ca and Mg are similarly overestimated, and at some sites there are Ca and Mg deposits in deep till that are not accounted for in mass budget calculations.

3.6. CRITICAL LOADS AND CURRENT EXCEEDANCES

Critical loads were developed with the assumption that high levels of acid deposition cause excess base cation leaching, and that some base cation depletion in soils was acceptable provided soils did not exceed a critical chemical threshold. There is considerable debate over the choice of critical limit, and how N dynamics should be treated in the SSMB model (Lokke *et al.*, 1996; Posch *et al.*, 2001). In this study we use a relatively conservative critical chemical criterion of a molar BC:Al molar ratio of 10 in soil solution, assume the aluminium solubility is controlled by gibbsite (pK$_{gibb}$ = 9.0), and that N immobilisation and denitrification rates are effectively zero.

Under the no harvesting scenario, which is most appropriate for the majority of study sites, CL values are between 0.522 keq ha^{-1} per year (Cone Pond) and 1.997 keq ha^{-1} per year (Lac Laflamme) (Table X). Based on average 1990s deposition, which as previously stated likely underestimates total S and N deposition at many of the sites, 7 of the 18 sites receive acid deposition (S + N) in excess of the critical load (see Ex(S + N) Table X). None of the 18 sites receive S deposition in excess of the critical load (see Ex(S) Table X). This suggests that for sites that exceed the critical load, reductions in S and/or N are required to prevent base cation losses from forest soils exceeding the critical chemical criterion. However, as inorganic N deposition is now greater than SO$_4$ deposition, it may well be more cost-effective to reduce N emissions as opposed to S emissions.

Critical loads were also estimated for each site assuming a typical harvest scenario for the region (whole tree or stem only). As expected, critical loads are lower
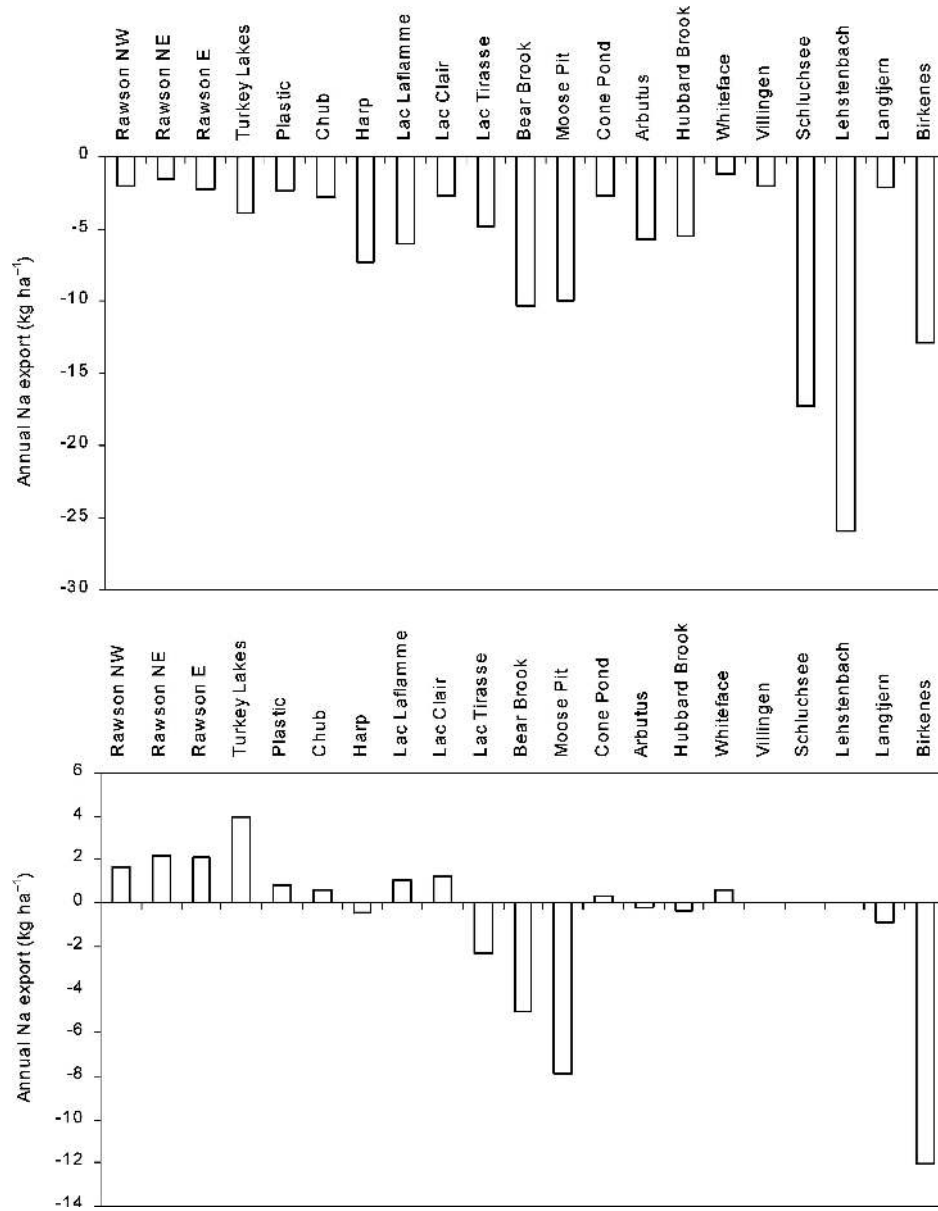
Figure 7. Mean annual Na input-output budgets during the 1990s, excluding (upper) and including (lower) estimates of Na weathering.

under the harvesting scenario with CL(S + N) values ranging between 0.375 and 1.839 keq ha^{-1} per year, although the relative sensitivity of forests was not very different from the no-harvesting scenario. If harvesting occurs, 11 of the 18 sites receive acid deposition in excess of the critical load. Critical load values for S under

TABLE X

Critical loads and exceedances (based on 1990s deposition, Table II) for S and S + N (keq ha^{-1} yr^{-1}) under conditions that assume either no harvesting or harvesting removals typical of the study region[a], and the percent contribution of N to acid (SO$_4$ + N) deposition and acid (SO$_4$ + NO$_3$-N) leaching at the study sites

| Site name | No harvesting | | | Harvesting | | | | N$_{dep}$ % | N$_{leach}$ % |
	CL	Ex(S + N)	Ex(S)	CL(S + N)	Ex(S + N)	CL(S)	Ex(S)		
ELA NW (ELA)	0.585	−0.127	−0.432	0.482	−0.024	0.349	−0.197	66.7	5.2
ELA NE (ELA)	0.607	−0.149	−0.454	0.490	−0.033	0.363	−0.210	66.7	0.2
ELA E (ELA)	0.654	−0.197	−0.502	0.557	−0.100	0.441	−0.289	66.7	9.9
Turkey Lakes	1.514	−0.491	−1.084	1.264	−0.240	0.985	−0.555	58.0	25.7
Plastic (MUS-HAL)	0.644	0.423	−0.192	0.375	0.692	0.232	0.219	57.7	1.4
Chub (MUS-HAL)	1.104	−0.037	−0.652	0.748	0.319	0.582	−0.130 [b]	57.7	1.6
Harp (MUS-HAL)	1.167	−0.100	−0.715	0.684	0.383	0.541	−0.090 [b]	57.7	4.8
Lac Laflamme	1.997	−1.398	−1.664	1.839	−1.240	1.696	−1.362	44.3	7.5
Lac Clair	1.033	0.078	−0.536	0.894	0.296	0.772	0.011	55.2	5.8
Lac Tirasse	0.817	−0.425	−0.628	0.623	−0.231	0.559	−0.369	51.6	6.0
Bear Brook	0.882	−0.260	−0.552	0.610	0.012	0.353	−0.023	47.0	15.8
Moose Pit	0.899	−0.115	−0.505	0.771	0.014	0.551	−0.157	49.8	0.0
Cone Pond	0.522	0.466	−0.091	0.424	0.466	0.107	0.323	51.7	0.5
Arbutus	1.429	−0.681	−1.075	0.869	−0.120	0.654	−0.300 [b]	52.7	21.5
Hubbard Brook	0.855	0.274	−0.263	0.744	0.385	0.351	0.240	47.6	3.5
Whiteface	1.221	1.154	−0.073	1.137	1.238	1.027	0.121	51.7	5.1
Villingen								65.8	4.6
Schluchsee								61.7	31.7
Lehstenbach								66.2	16.1
Langtjern	0.881	0.010	−0.488	0.678	0.213	0.528	−0.135	55.9	2.9
Birkenes	1.220	0.308	−0.664	1.300	0.228	0.890	−0.334 [b]	63.6	8.0

[a]Harvesting estimates based on nutrient content in biomass and typical harvest practice (stem or whole tree).
[b]SO$_4$ export exceeds critical load; positive values indicate current exceedance of the critical load; blank space indicates no data.

the harvesting scenario are between 0.107 and 1.696 keq ha^{-1} per year, and 5/18 sites receive S deposition in excess of the critical load. At these 5 sites (representative of similar sites in the area), further reductions in S deposition are necessary to prevent soils from exceeding the critical load, but at the remaining 6/18 sites reductions in S and/or N are required. However, SO$_4$ export exceeds input at the majority of study sites and if this difference is entirely due to unmeasured dry deposition, then the number of sites that exceed the CL(S) increases from 5 to 9 (Table X).

It is clear that exceedance of the CL(S + N) is much greater than CL(S) at all study sites under both management scenarios. This was expected, since the SSMB model used in this study assumed zero N immobilisation or denitrification and therefore considers that any N not taken up by biomass will ultimately be leached

as NO_3-N. However at present, even though N accounts for between 44 and 67% of the acid deposition (SO_4 and inorganic N) at each site, NO_3-N leaching accounts for only 0–32% of the acid (NO_3-N + SO_4) leaching. Although there is a tendency for NO_3-N leaching to be higher at the high N deposition sites, there is no evidence that NO_3-N losses have increased at any site and a major unknown is whether low-level chronic N accumulation will ultimately lead to the release of NO_3-N; a feature currently assumed in critical load models.

4. Summary

Input-output budgets (1990s) for SO_4, inorganic N (NO_3-N; NH_4-N), Ca, Mg and K were calculated for 21 forested catchments in 17 regions of Canada, the United States and Europe that spanned a range of SO_4 (7.3 to 28.4 kg ha^{-1} per year) and N (2.8 and 13.8 kg ha^{-1} per year) bulk deposition. In response to emission regulations, SO_4 concentration in deposition decreased in 13/14 regions, whereas NO_3-N concentrations decreased in only 1/14 and trends in NH_4-N concentration were varied; increasing at 3/14 regions and decreasing at 2/14 regions. Decreasing trends in deposition were also recorded for Ca (9/14), Mg (5/14), and K (6/14), and on an equivalent basis, accounted for up to 131% (median 22%) of the decrease in acid ion deposition, partly offsetting the benefits of decreased SO_4 deposition. Sulphate concentrations in runoff decreased at the majority (14/17) of catchments and NO_3-N concentrations in runoff decreased at 4/17 catchments and increased at only 1 site. Ammonium concentrations increased at 5/17 catchments. Differences in SO_4, NO_3-N and NH_4-N concentrations and temporal patterns appear to be influenced by deposition, although climate variations and possibly land-use history likely account for some of the variation among sites. Decreases in Ca, Mg and K concentrations in runoff occurred at 8, 9 and 7 of 17 sites, respectively, which accounted for up to 133% (median 48%) of the decrease in acid anion concentration. Mass balance estimates show that SO_4 export exceeded input at 18/21 catchments, likely due to a combination of unmeasured dry deposition and release from internal sources. The majority of N in deposition (31–100%; median 94%) was retained within catchments, although there was a tendency for greater NO_3-N leaching at sites receiving higher (>7 kg N ha^{-1}) deposition. There was no evidence that NO_3-N concentrations in runoff were increasing over time, despite the high level of N-retention. Mass balance calculations show that for Ca and Mg, export in runoff exceeds input at all 21 sites, but K export only exceeds input at 16/21 sites. When estimates of base cation weathering were available and included in the mass balance (18 sites), Ca, Mg and K export exceeded inputs at 14, 10 and 2 sites respectively. Annual Ca losses represent between 0.17 and 7.9% of the current exchangeable Ca pool in soil although at some sites, part of this loss occurs from beneath the rooting zone and there is always uncertainty associated with mineral weathering estimates. Despite reductions in S emissions, acid deposition appears to still be

causing acidification of forest soils at many of the study sites, with Ca and Mg losses of primary concern.

Acknowledgments

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