

Base cation cycling in a pristine watershed of the Canadian boreal forest

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Abstract. Base cation cycling was investigated on the Canadian Shield in a pristine catchment of the boreal forest. An input–output budget (atmospheric deposition – stream exports) for the whole watershed indicated that nitrogen (N) was strongly retained, while sulphur (S) and base cations (K, Ca, Mg) were lost. The S losses are attributed to internal sources, such as SO_4 desorption and/or mineralisation of soil organic-S. The base cation losses at the catchment scale, however, might be contributed by weathering of the till below the rooting zone, which has little ecological significance. For this reason, a detailed budget of basic cations, including atmospheric deposition, tree uptake, mineral weathering and leaching losses was constructed for the soil rooting zone of a stand representative of the forest covering the catchment. Different scenarios of tree uptake (whole tree and stem-only harvesting), weathering rates (PROFILE modelled values, PROFILE modelled values corrected for soil Na leaching) and soil leaching losses (depth of 22 and 81 cm) were considered. The element budgets were summed for the 1997–2003 (7 years) period. In every scenario, K was lost (-35.5 to -1.2 kg ha $^{-1}$) from the exchangeable reservoir. Gain or losses of Ca were observable, depending of the scenario considered (28.8 to -20.1 kg ha $^{-1}$) while Mg (-0.8 to 13.3 kg ha $^{-1}$) generally accumulated over the 7-year period. The absolute K losses are very important, given the very small K soil exchangeable reservoir (55.2 kg ha $^{-1}$) at the site. Because the amount of K sequestered in biomass (110 kg ha $^{-1}$) is twice the amount found in the exchangeable soil reservoir, this forest is very sensitive to commercial forestry operations and forest harvesting appears as the main pathway of base cation losses. This raises important questions regarding the sustainability of the boreal forest that lies on K-poor soils of the Canadian Shield.

Introduction

The circumpolar boreal forest is the largest terrestrial ecozone on earth (approximately 14,000,000 km 2) and represents 32% of global forests. In Canada alone the boreal zone occupies 58% and 55% of the terrestrial and aquatic surfaces respectively, and accounts for 60% of the total economic value of forestry, not considering the indirect effect on jobs (Burton et al. 2003). Despite its critical ecological and economic importance, less is known about the biogeochemical processes that govern nutrient cycling (and tree growth) in the boreal forest than for temperate forests. Such information is essential to maintaining forest sustainability for commercial forestry, and understanding

the forest's response to natural and anthropogenic perturbations such as fire, insect defoliation, climate change and atmospheric pollution. Among these disturbances, acid rain has been the topic of numerous studies in the last two decades.

One of the major effects of acid rain is to increase the rate of base cation losses from soils due to accelerated leaching. Numerous reports of decreased availability of soil basic cations have suggested that this phenomenon may be widespread in mixed- or deciduous-forests of northeastern USA and eastern Canada (Kirchner 1995; Likens et al. 1996; Houle et al. 1997; Watmough and Dillon 2003). Other studies have also suggested that tree growth may be affected at certain sites (Ouimet et al. 2001; Duchesne et al. 2002). However, most studies reporting complete base cation budgets were conducted in temperate forested catchments where acidifying deposition of sulphur (S) and nitrogen (N) was relatively high.

Because of the distance from pollution sources, the boreal forest receives relatively small inputs of acidifying substances, which might suggest that such forests are less at risk of showing cation deficiencies induced by acid rain. On the other hand, most of the boreal forest of eastern Canada grows on the base-poor shallow soils derived from granitic rock and typically having low exchangeable bases reservoirs. The productivity of these forests relies on a tight nutrient cycle which is subjected to important losses of nutrients, particularly K, following insect outbreaks (Hunter 2001) and forest fires (Lamontagne et al. 2000). Nutrient losses associated with harvesting and acid rain increase the possibility that even relatively low-level acidic depositions may have an effect on soil fertility, and potentially, forest growth.

Here, we report the results of N, S and base cation (Ca, Mg, K, Na) cycling for a boreal coniferous watershed dominated by a mature black spruce-jack pine forest that is representative of a large part of the Canadian boreal forest. We tested the hypothesis that soil base cation fertility is affected by acidic deposition and forest harvesting.

Methods

Site description

The Tirasse watershed, 56 ha in area, is located in the Ashuapmushuan wildlife reserve (49°12'45" N 73°39'00" W), about 120 km north of Saint-Félicien, Québec, Canada and has been monitored since 1997. The canopy vegetation is composed of even-aged black spruce (*Picea mariana* (Mill.) BSP) and jack pine (*Pinus banksiana* Lamb.). These species occupy 19.1 and 9.9 m² ha⁻¹ in basal area, respectively. This forest type (black spruce-jack pine) is representative of 60% of the Quebec boreal forest. Annual mortality is 3.0% (stem ha⁻¹ year⁻¹), which is within the range observed for diverse types of forests (Manion and Griffin 2001). Based on tree ages, the forest was probably fire-regenerated

between 1921 and 1940, but no historical records on land uses and forest fires are available for this period.

Soils have developed from Precambrian charnockitic gneiss covered by sandy till, and are classified as Spodosols (Haplorthods) (Soil Survey Staff 1998) or Orthic Humo-Ferric Podzol (Canada Soil Survey Committee 1992). Between 1997 and 2003, the average annual mean temperature was 1.1 °C and precipitation was 817 mm with evapotranspiration losses of 223 mm. This watershed contains no lake, but has a first-order stream with a small (2.5 ha) open bog at the stream source.

Sampling and analysis

Precipitation, throughfall, soil solutions and stream solutions

Precipitation, throughfall, soil solutions and stream solutions were sampled weekly between January 1997 and December 2004, except soil solutions which were sampled approximately from May to October, or in the absence of snowpack and frost. Bulk precipitation was sampled using three collectors (2-l plastic bottles fitted with 577 cm² plastic funnels) located in an open site at the border of the watershed. Throughfall was sampled within the study plot (25×50 m²), using 12 collectors (same design as for precipitation) randomly located and installed 1.3 m above the ground. During the winter months (November–April inclusive), collectors were replaced by six 708-cm² pails for snow collection. Soil solutions were sampled at four locations within the study plot using tension ceramic cup lysimeters located at average depths of 22 and 81 cm. Lysimeters were installed in summer 1996. Soil solution sampling began in May 1997. Average soil temperature and volumetric water content were measured using one thermistor (YSI series 400) and one TDR probe installed in the vicinity of each lysimeter cluster. Stream flow was continuously monitored at the watershed's outlet. All the solutions were filtered (0.45 µm, Nucleopore) and analysed for basic cations (K, Ca, Mg, Na) and total S by plasma emission spectrometry, while SO₄ and NO₃ were analysed by ion chromatography. Analyses for NH₄ were done by colourimetry (Technicon AA2). Dissolved organic S (DOS) was calculated as the difference between total dissolved S and SO₄. Total dissolved N was measured after digestion of organic N form to NH₄ with UV in acid conditions. A second UV digestion was performed in alkaline conditions to convert NH₄ to NO₃. NO₃ concentrations were then analysed by colourimetry (Wood et al. 1967). Dissolved organic N (DON) was calculated by subtracting inorganic N (NH₄ and NO₃) from total dissolved N. Oxidation of dissolved organic carbon (DOC) to CO₂ was done by blending samples with a potassium persulphate solution (4% m/v) and irradiating with UV. Samples were then acidified with a sulphuric acid solution (H₂SO₄) in order to transform the dissolved inorganic carbon (DIC) in CO₂. Total CO₂ was then absorbed in a sodium hydroxide solution and total dissolved carbon (TDC) was determined from electrical conductivity. DIC

concentration was then determined based on alkalinity, and DOC was determined from the difference between TDC and DIC.

Tree uptake of nutrients

Forest vegetation was inventoried in 1996 and 2001. Every living tree in the study plot having a DBH >1.0 cm (diameter at breast height, i.e., 1.3 m above ground level) was tagged, positioned, and their respective DBHs were measured using either a circumference tape or micrometric compass to the nearest millimetre. In 1999, 17 black spruce and 9 jack pine (DBH range of 3.8–19.4 cm) were harvested for determination of biomass and nutrient concentrations. The data resulted in a set of equations for the estimation of K, Ca and Mg content of foliage, branches and bole as a function of DBH (Tremblay et al., in prep.).

Tree growth was assessed from dendrochronological analysis. In 1996, 30 black spruce and 20 jack pine were sampled at the perimeter of the monitoring plot. For each tree sampled, two increment cores were extracted at breast height from opposite sides of the bole. Cores were dried, mounted in wooden blocks and sanded for dendrochronological measurements. Ring widths of all cores were cross-dated by visual examination of tree-ring sequence before measurement (skeleton plot procedures) (Fritts 1976; Yamaguchi 1991). Ring widths were measured to the nearest 0.01 mm with a WinDendro Image Analysis System for Tree-Ring Measurement (Regent Instruments Inc.). Missing and absent rings were added, when necessary, according to standard procedure (Yamaguchi 1991). Data were verified statistically with the COFECHA program (Holmes 1996). Previous study has shown that basal area increment (BAI) at breast height is a useful representation of tree vigour and whole-stem growth (LeBlanc 1990; Duchesne et al. 2003). Annual ring increment were converted to BAI using the formula:

$$\text{BAI} = \pi(R_n^2 - R_{n-1}^2)$$

where R is the tree radius and n is the year of tree ring formation. An average ring basal area chronology was generated by averaging the BAI of each tree over each year.

Soil basic cations pool and weathering release rate

In the fall of 1996, four 1-m² soil pits were dug to a depth of 1 m within the study plot. All soil horizons with a thickness greater than 4 cm were sampled individually, the maximum depth of the rooting zone was noted and an ocular estimate of percent volume of coarse fragments was made. Core samples for bulk density determination were taken from each main horizon using a stainless steel cylinder (diameter: 53 mm, length: 60 mm). All soil samples were air-dried and sieved to 2 mm. Exchangeable cations (K, Ca, Mg) were extracted with an unbuffered NH₄Cl solution (1 M, 12 h), and measured with inductively coupled plasma emission spectroscopy. Soil depth, bulk density and coarse fragment content were used to convert exchangeable cations concentration to kilograms per hectare for the soil rooting zone (0–50 cm).

Soil mineralogy was reconstructed from total element concentrations by the UPPSALA model (Sverdrup and Warfvinge 1992). The mineralogy was then used as an input in the PROFILE model, version 4.2 (Becker 1999) to estimate the weathering rate of base cations for each of the four soil profiles. Annual precipitation, atmospheric depositions, forest composition and element uptake, soil temperature and density, soil moisture, dissolved organic carbon in soil solution and runoff were measured at the site. Soil surface area was derived from grain size distribution, dry bulk density and coarse fragments (Jönsson et al. 1995). Partial pressure of CO₂ was estimated following Warfvinge and Sverdrup (1995). The negative logarithm of the solution constant of solubility of gibbsite was calculated from H and Al concentrations in soil solution. Mean DOC concentration was calculated from concentrations in soil solution. The PROFILE model is widely used for modelling weathering, and was initially developed for granitic soils with low weathering potential, similar to that of the soil at our site. Previous comparisons of the model's performance with independent estimations of weathering showed that the error associated with weathering rates was below 40% (Jönsson et al. 1995).

Litterfall

Total litterfall was collected monthly with five litter traps randomly distributed in the study plot. The traps consisted of 1 × 1 m boxes with a nylon mesh screen bottom, 30 cm above the ground. Dry mass (60 °C) was determined for all litter samples. Tissue samples from each sample were ground and digested (H₂SO₄ 98%). Potassium, Ca, Mg and Na were measured by plasma emission spectrometry (ICP Jarrel Ash). The annual nutrient transfer by leaf litterfall for each species was calculated by averaging the combination of element concentrations and leaf dry weight at each individual sampling, and by summing these values on an annual basis.

Nutrient budget calculation

The soil rooting zone budget for the 1997–2003 period (seven complete water years, September to October) was evaluated by considering deposition input (*D*), weathering (*W*), net biomass uptake (*U*), and soil leaching (*L*) of basic cations (BC) as follows:

$$\Delta BC = \text{inputs } (W + D) - \text{outputs } (L + U) \quad (1)$$

where ΔBC is the net soil release or retention. Annual bulk deposition was calculated by summing the bulk precipitation on a weekly basis. The Ca, Mg and K depositions were corrected for canopy interaction based on the Na-ratio method proposed by Ulrich (1983), as adapted by Houle et al. (1999b). This method uses the relationship of dry deposition vs. total deposition of Na as an indicator of dry vs. wet deposition of other cations, assuming that Na behaves conservatively in the tree canopy. These estimates yielded higher cation depositions than wet only, and would thus lead to conservative cation losses. Throughfall input of SO₄ was used as surrogate for total SO₄ deposition (e.g.,

Lindberg and Garten 1988; Houle et al. 1999b). The amount of dissolved organic S in atmospheric deposition was added to throughfall SO_4 to yield total S deposition. There are no dry N deposition measurements. Only wet N deposition is considered. Base cation leaching losses under the rooting zone (50 cm) (L) were calculated by combining the monthly average soil solution concentration (average of 22 and 81 cm depths) with the monthly water export under the soil profile evaluated by the FORHYM II hydrological model (Arp and Yin 1992), which was previously calibrated for the site to ensure that the prediction of water exports at the stream output was similar to the observed values on a monthly basis (difference = 1.3%) over the seven-year period studied. There were no significant differences between predicted and observed soil moisture ($p = 0.67$; mean difference 0.7%) on a monthly basis. Although there are no method to directly measure soil water exports at given depths, we assume that the error associated with the predicted soil water fluxes was low, because both stream water exports and soil moisture are well predicted. There is a possibility that the cation fluxes derived from the lysimeter located at a 22 cm depth could be underestimated because of potential losses associated with macropores. However, because of the very shallow rooting in these forest types, it is unlikely that macropores could reach the depth of the deeper lysimeters, 81 cm. Winter soil nutrient fluxes were estimated based on elemental soil/stream export ratios during the collection period. Given the small hydrologic fluxes during the winter months, this estimation of winter fluxes has a weak effect on total annual fluxes. Watershed export of nutrient was calculated by combining concentrations in the stream and the cumulative weekly water export.

Based on equations relating stem wood and bark dry biomass to tree height and diameter, elemental content of tree bole, branches and foliage was evaluated for each tree located in the 0.25 ha study plot based on 1996 and 2001 sampling. Mean net annual K, Ca and Mg sequestration was estimated based on the difference in biomass nutrient content between 1996 and 2001.

Statistical analysis

Monotone trend analyses were performed on pH and on the monthly volume-weighted mean concentration of SO_4 , NH_4 , NO_3 , K, Ca and Mg in wet deposition, soil solution and stream flow by the seasonal Mann–Kendall test (significant p -value ≤ 0.05) (Hirsch et al. 1982). The rate of change was estimated by the seasonal Kendall slope estimator. The error associated with sub-sampling was assessed by evaluating the standard error (SE) of each sub-sampling mean, and then integrating the SE in the budget calculation for each variable for the seven-year period with respect to variance properties (Zar 1974). Budget calculation over the seven-year period reduced the sampling error. Although the SE associated with the weekly fluxes sub-sampling might be quite large for a given element, the SE become much smaller when the fluxes are summed over one month, a season, a year or for a seven-year period (Houle et al. 1999a).

Results

Trend analyses

Volume-weighted mean monthly concentrations and pH of bulk deposition, throughfall, soil solution and the stream output during the 1997–2004 period are shown in Figure 1. There were no significant trends in both deposition and precipitation concentrations of all nutrients studied, with the exception of H, which decreased significantly at an annual rate of 5% (Table 1). In soil solution, NH_4 concentrations increased significantly, while NO_3 and K concentrations fell significantly. In the stream output, SO_4 , NO_3 and NH_4 concentrations decreased significantly at respective rates of 1.6, 6.4 and 6.6% annually, but there was no trend in element stream exports (Table 1) or in water export ($p = 0.88$).

Input–output watershed budget

Annual bulk S- SO_4 deposition averaged $2.9 \text{ kg ha}^{-1} \text{ year}^{-1}$ (Table 2) but increased to $3.8 \text{ kg ha}^{-1} \text{ year}^{-1}$ in throughfall. On average, stream S- SO_4 exports ($4.4 \text{ kg ha}^{-1} \text{ year}^{-1}$) exceeded bulk depositions by $1.5 \text{ kg ha}^{-1} \text{ year}^{-1}$. Deposition of N- NO_3 amounted to $1.7 \text{ kg ha}^{-1} \text{ year}^{-1}$, while $0.25 \text{ kg ha}^{-1} \text{ year}^{-1}$ was exported via stream output, leading to an average retention of $1.5 \text{ kg ha}^{-1} \text{ year}^{-1}$. The difference between N- NH_4 deposition ($1.2 \text{ kg ha}^{-1} \text{ year}^{-1}$) and export ($0.05 \text{ kg ha}^{-1} \text{ year}^{-1}$) indicated a retention of 95% within the watershed. When the total dissolved N fluxes in deposition ($3.1 \text{ kg ha}^{-1} \text{ year}^{-1}$) and stream exports ($0.9 \text{ kg ha}^{-1} \text{ year}^{-1}$) are considered, however, N retention in the whole watershed represents 71% of incoming atmospheric N. Dissolved organic N comprised 67% of total dissolved N in the stream exports (Table 2).

Average annual atmospheric bulk depositions of K, Ca, Mg and Na were 0.23, 0.74, 0.14 and $0.30 \text{ kg ha}^{-1} \text{ year}^{-1}$, respectively. Stream exports were higher for all these elements, reaching 2.2, 15.3, 5.5 and $5.9 \text{ kg ha}^{-1} \text{ year}^{-1}$, in the same order leading to net losses of 2.0, 14.6, 5.4 and $5.6 \text{ kg ha}^{-1} \text{ year}^{-1}$ for K, Ca, Mg and Na, respectively. The high net basic cations exports contributed to an increase in the average pH of the stream to 6.6, as compared to 4.6 for incoming precipitation.

Rooting zone budget

Average throughfall depositions of K, Ca, Mg and Na were 4.4, 3.0, 0.94 and $0.49 \text{ kg ha}^{-1} \text{ year}^{-1}$, with an enrichment factor relative to incident precipitation that varied from 21.0, 3.1, 5.7 and 0.6, respectively (Table 2). When the amount of throughfall is corrected for internal leaching from the canopy using

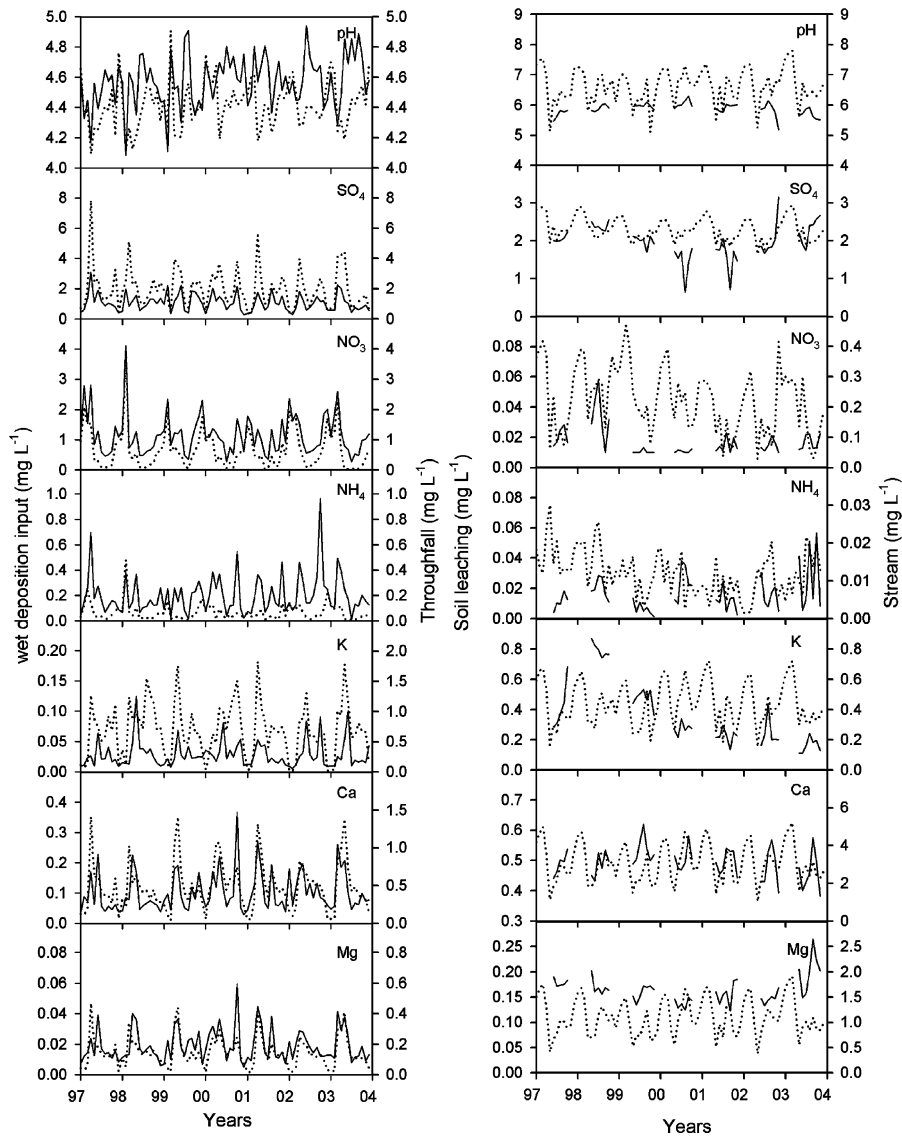


Figure 1. Monthly volume-weighted mean concentration and pH in bulk deposition (solid line), throughfall (dotted line), soil solution (solid line), and stream flow (dotted line).

the element-to-Na-ratio method, the estimated total cation depositions (including the dry component) increased by 63% compared to bulk deposition. Total deposition for the 1997–2003 (7 years) period was estimated at 2.6, 8.3, and 1.6 kg ha⁻¹ for K, Ca and Mg, respectively (Table 3). These latter values were used as input in the soil rooting zone budget calculations.

Table 1. Monotone trend ($\mu\text{g l}^{-1} \text{ year}^{-1}$ or unit for pH) of monthly volume-weighted mean concentration in bulk deposition, soil solution and stream output from year 1997 to 2004.

	Concentrations ($\mu\text{g l}^{-1} \text{ year}^{-1}$)				Fluxes ($\text{g ha}^{-1} \text{ year}^{-1}$)					
	Bulk deposition		Soil solution		Stream output		Bulk deposition		Stream flow	
	Trend	p-value	Trend	p-value	Trend	p-value	Trend	p-value	Trend	p-value
H	-1.7 (-5.0)	0.013	0.1 (8.3)	0.203	-0.1 (-5.8)	0.525	-10.8 (-4.3)	0.175	-0.1 (-1.9)	0.858
SO ₄	-39.4 (-3.2)	0.196	-8.4 (-0.42)	0.809	-38.6 (-1.6)	0.020	-295.0 (-3.1)	0.419	-5.1 (-0.04)	0.994
NO ₃	-32.3 (-2.6)	0.370	-2.0 (8.6)	0.013	-18.4 (-6.4)	0.001	-85.9 (-1.1)	0.715	-61.8 (-4.6)	0.361
NH ₄	8.4 (4.9)	0.317	0.9 (8.4)	0.351	-1.0 (-6.6)	0.001	82.6 (6.9)	0.293	-3.9 (-4.7)	0.344
K	0.3 (0.9)	0.827	-78.3 (11.9)	<0.001	-1.0 (-0.2)	0.902	1.7 (0.7)	0.884	60.7 (3.0)	0.585
Ca	4.2 (4.8)	0.239	-5.4 (-1.0)	0.173	-8.0 (-0.3)	0.886	30.3 (4.8)	0.300	406.7 (2.9)	0.588
Mg	0.02 (1.1)	0.726	1.8 (1.1)	0.407	-0.2 (-0.01)	0.994	-1.2 (-0.9)	0.818	154.0 (3.1)	0.571

Values in parentheses represent annual relative trend (%).

Table 2. Annual fluxes (average \pm inter annual S.E) of total N and inorganic N (N-NH₄ + N-NO₃), total S and S-SO₄, and basic cation for the 1997–2003 period.

Nutrient	Annual fluxes (kg ha ⁻¹ year ⁻¹)		
	Bulk deposition	Throughfall	Stream water exports
N-NO ₃	1.72 \pm 0.12	0.72 \pm 0.07	0.25 \pm 0.02
N-NH ₄	1.12 \pm 0.10	0.25 \pm 0.02	0.05 \pm 0.01
Total N	3.1 \pm 0.27	1.5 \pm 0.09	0.90 \pm 0.11
Inorganic N	2.94 \pm 0.19	0.97 \pm 0.09	0.30 \pm 0.02
S-SO ₄	2.9 \pm 0.22	3.8 \pm 0.24	4.4 \pm 0.24
Total S	3.1 \pm 0.21	4.6 \pm 0.26	4.9 \pm 0.25
K	0.23 \pm 0.01	4.4 \pm 0.14	2.2 \pm 0.07
Ca	0.74 \pm 0.06	3.0 \pm 0.10	15.3 \pm 0.68
Mg	0.14 \pm 0.01	0.94 \pm 0.03	5.5 \pm 0.24
Na	0.30 \pm 0.02	0.49 \pm 0.03	5.9 \pm 0.25

The other source of basic cations available to the soil rooting zone is weathering, whose modelled values over the 1997–2003 period were 7.0, 59.5, 18.9 and 30.1 kg ha⁻¹ for K, Ca, Mg and Na, respectively (Table 3). The cation removal from the rooting zone exchangeable reservoir via tree uptake over the seven-year period were 14.0, 41.3, 4.6 kg ha⁻¹ for K, Ca and Mg, respectively, while base cation leaching under the rooting zone for the same elements was 16.1, 20.2, and 7.0 kg ha⁻¹. When the inputs (deposition + weathering) and the outputs (tree uptake and leaching losses) are summed, the net base cation gains or losses for the rooting zone exchangeable soil reservoir were –20.5, 6.3 and 8.9 kg ha⁻¹ for K, Ca and Mg, respectively for the 1997–2003 period. These values indicated net annual losses of 5.3% for the K soil

Table 3. Nutrient pool and fluxes (kg ha⁻¹) for the 1997–2003 period.

	Nutrient			
	K	Ca	Mg	Na
Forest floor exchangeable pool	20.7 \pm 2.25	72.9 \pm 25.1	11.7 \pm 3.7	n.e.
Soil exchangeable pool	34.5 \pm 8.8	56.8 \pm 10.6	9.3 \pm 1.2	n.e.
Annual fluxes (kg ha ⁻¹)				
Weathering	7.0 \pm 0.8	59.5 \pm 16.9	18.9 \pm 1.5	30.1 \pm 4.1
Total deposition ^a	2.6 \pm 0.1	8.3 \pm 0.1	1.6 \pm 0.01	3.3 \pm 0.04
Soil water exports (22 cm)	28.0 \pm 8.1	20.3 \pm 1.3	8.4 \pm 0.4	16.1 \pm 1.6
Soil water exports (Average, 50 cm)	16.1 \pm 3.8	20.2 \pm 1.0	7.0 \pm 0.4	21.0 \pm 1.3
Soil water exports (81 cm)	6.3 \pm 0.5	21.0 \pm 0.8	5.6 \pm 0.3	25.2 \pm 1.5
Biomass immobilisation	14.0	41.3	4.6	n.e.
Soil depletion or retention ^b	–20.5 \pm 3.9	6.3 \pm 16.9	8.9 \pm 1.5	n.e.

^aBulk deposition*dry deposition enrichment.

^b(Deposition + weathering)–(soil leaching exports at 50 cm + biomass immobilisation).

n.e. = not estimated.

exchangeable reservoirs ($55.2 \pm 9.1 \text{ kg ha}^{-1}$). Inversely, the exchangeable Ca ($129.7 \pm 27.2 \text{ kg ha}^{-1}$) and Mg reservoirs ($21 \pm 3.9 \text{ kg ha}^{-1}$) were increasing at an annual rate of 0.7 and 6.0%, respectively.

Discussion

Precipitation: composition and trends

The SO_4 , NO_3 , NH_4 and basic cations bulk depositions at the Tirasse site are among the lowest reported for northeastern North America and Europe being typically half to one third than for other calibrated catchments (Johnson and Lindberg 1992; Watmough et al. 2005). This was expected given the site's northern location which is distant from pollution sources. The absence of a decrease in deposition and precipitation concentration for SO_4 contrasts with many other sites in the northeastern USA (Butler et al. 2000; Likens et al. 2001) and eastern Canada (Clair et al. 1995; Houle et al. 1997). This could be due to the relatively short data period (8 years) and also to the different periods of time that are compared. The absence of a trend at the Tirasse watershed (1997–2004) fits well with reports of stabilizing SO_4 concentrations in wet precipitation since 1995 in both the USA and Canada (Butler et al. 2000; Likens et al. 2001; Houle et al. 2004). The absence of decreasing trends in base cation depositions and precipitation concentrations, as compared to previous reports of general declines in North America and Europe (Hedin et al. 1994), also may be explained by the different periods of time considered. The absence of trends for both NO_3 , NH_4 and total inorganic N depositions (Table 1) corresponds with the overall situation prevailing in northeastern North America, with reports of stable or increasing N deposition (NADP 2000).

Watershed budgets

The difference between precipitation S- SO_4 ($2.9 \text{ kg ha}^{-1} \text{ year}^{-1}$) and stream SO_4 exports ($4.4 \text{ kg ha}^{-1} \text{ year}^{-1}$) yielded a net S export of $1.5 \text{ kg ha}^{-1} \text{ year}^{-1}$, 52% of the incoming bulk atmospheric S (Table 2). However, to obtain a more accurate budget, the dry S deposition component, as well as DOS inputs and outputs must be taken into account. Although dry deposition of S was not measured at our site, throughfall S fluxes ($3.8 \text{ kg ha}^{-1} \text{ year}^{-1}$) may be used as a surrogate for total S deposition (e.g., Lindberg and Garten 1988; Houle et al. 1999b). We therefore used the throughfall S deposition, plus the contribution of DOS in incoming precipitation ($0.2 \text{ kg ha}^{-1} \text{ year}^{-1}$) as total S deposition ($4.0 \text{ kg ha}^{-1} \text{ year}^{-1}$), minus the total dissolved S exported at the stream output ($4.9 \text{ kg ha}^{-1} \text{ year}^{-1}$), which still indicates a net S loss of $0.9 \text{ kg ha}^{-1} \text{ year}^{-1}$.

The observed excess S export corresponds well with numerous studies in northeastern North America (Norton et al. 1988; Mitchell et al. 1992, 1996; Driscoll et al. 1995; Houle and Carignan 1995; Houle et al. 1997; Eimers and Dillon 2002). Houle and Carignan (1995) concluded that mineralisation of soil organic S was the likely candidate for the excess S source after accounting for dry deposition, SO_4 desorption, and weathering of S bearing minerals as potential S sources at the Lake Laflamme watershed.

Most (90%) of the atmospherically deposited inorganic N (N-NO_3 and N-NH_4) accumulated within the catchment. Because the contribution of dry N deposition is unknown for this site, the accumulation rate is a minimum. A high retention of available N forms was expected given the low N inputs in deposition and the well-known N limitation in the boreal forest (Tamm 1991). In fact, about 67% of the total dissolved N stream exports occurred as DON (Table 2). This observation is typical of pristine sites and was observed in remote areas of South America (Perakis and Hedin 2002). When the amount of DON is summed with the inorganic N stream export, the watershed N retention drops from 90 to 71% of total N deposition, indicating the importance of considering the contribution of DON, particularly at unpolluted sites. N saturation is not a potential threat for this forest. NO_3 and NH_4 concentrations in streamflow declined significantly at 6.4 and 6.6% annually but these decreases are not linked to changes in deposition.

The stream base cation exports greatly exceeded atmospheric deposition (Table 2). However, unlike S and N, an important part of the catchment losses may come from weathering of soil minerals located below the rooting zone which might be different and not representative of soil rooting zone exports. It is the soil rooting zone that is of real ecological significance for forest growth.

Soil rooting zone basic cations budget

Throughfall fluxes

The interactions of incoming rain with the forest canopy led to important increases in throughfall basic cation concentrations (Figure 1; Table 2). The Na-ratio method permitted estimation of the contribution of the throughfall enrichment, which was derived from canopy leaching. Canopy leaching of K was particularly high in relative terms, contributing 91% of the total K throughfall, while lower values occurred for Ca (75%) and Mg (60%). This corresponds with the high internal recycling rate of K compared to Ca and Mg for forested ecosystems. Such a high contribution of K canopy leaching to total throughfall has also been observed under other forest covers (Lovett and Schaefer 1992; Lawrence and Fernandez 1993; Houle et al. 1999b). Canopy leaching of K ($4.0 \text{ kg ha}^{-1} \text{ year}^{-1}$) exceeded litterfall fluxes ($2.3 \text{ kg ha}^{-1} \text{ year}^{-1}$), while the opposite was true for Ca and Mg.

Tree uptake of nutrients

Figure 2 shows the evolution of radial growth for both of the main species since 1927. The abundance of jack pine in the stand (34% of basal area) suggests that fire was the most recent stand-replacing disturbance. Species transition previously occurred in the stand: whereas pine is declining since approximately 1940, BAI of spruce increased and stayed relatively constant between 1940 and 1970 (Figure 2). Between-year variations in tree growth were mainly due to climatic conditions, systematic changes in tree ages and inter-individual competition (Fritts 1976). For unknown reasons, BAI of spruce trees decreased since the late 70s (Figure 2). A negative trend in BAI is a strong indicator of a true growth decline (Leblanc 1990). Inter-individual competition, a reaction to spruce budworm defoliation or changes in environmental conditions such as soil fertility may be proposed to explain the observed decline in spruce growth. All these variations in the history of stand growth have probably resulted in a great variability in cation sequestration rates. To calculate a budget that is representative of present conditions, biomass immobilisation of cations was first estimated from the difference in above-ground biomass as assessed from inventory data gathered in 1996 and 2001. The basic cations sequestration in biomass (2.0 , 5.9 and $0.65 \text{ kg ha}^{-1} \text{ year}^{-1}$ for K, Ca, and Mg, respectively) based on the difference between the two forest inventories, is slightly higher than the average biomass sequestration over an entire forest rotation (1.4 , 4.0 and $0.46 \text{ kg ha}^{-1} \text{ year}^{-1}$ for K, Ca, and Mg, respectively), as estimated by the amount of a given element currently immobilised in biomass divided by the stand age (~ 80 year). Both estimations, however, lie within the range of element removal reported for whole-tree harvesting of mixed black spruce/jack pine forests (Paré et al. 2002). Whole-tree harvesting is the most common ($\sim 60\%$) harvesting method used in the Québec's boreal forest (MRNFP 2003). Stem only harvesting, where foliage and branches are left on the ground, is also a common practice. Stem-only harvesting would reduce base cation export by 57%, 47% and 56% for K, Ca and Mg, respectively.

Soil leaching and weathering

The base cation fluxes below the rooting zone were considerably higher than total depositions. The increases range from 2.4- to 6.4-fold for Ca and Na, respectively. The leaching losses were constant during the study period, except for K, which exhibited a decreasing trend mainly from the high soil solution concentrations observed in 1998, presumably associated with a severe drought (data not shown). Average concentrations in lysimeters located at depths of 22 cm and 81 cm were used to estimate leaching below the rooting zone (50 cm). The bias of this estimation over the seven-year period is of small importance for Ca and Mg fluxes which change slightly between the two depths, increasing from 20.3 to 21.0 kg ha^{-1} and decreasing from 8.4 to 5.6 kg ha^{-1} , respectively (Table 3). Inversely, K fluxes decrease greatly from 28.0 to 6.3 kg ha^{-1} between 22 and 81 cm of soil depth. This may be explained by a high K tree uptake at depths between 22 cm and the end of the 50-cm

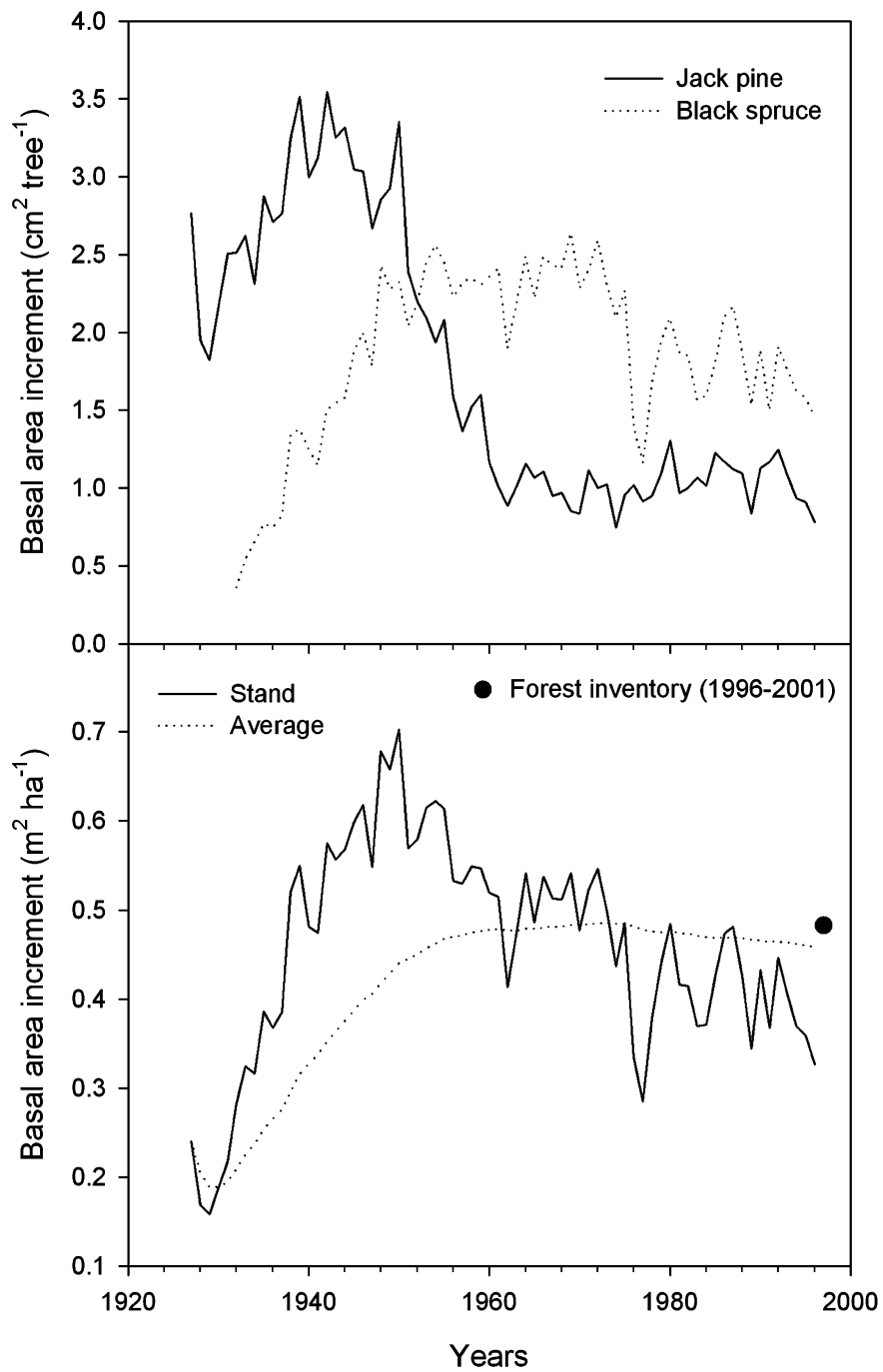


Figure 2. Average basal area increment of black spruce and jack pine trees and average basal area increment of the entire stand at the Lake Tirassee watershed.

rooting zone. Given the differences in the K exports, different scenarios will be considered in the budget calculations (see below).

The increase between base cation atmospheric input and soil rooting zone exports may be provided in part by the weathering of soil minerals. The annual weathering rates obtained with the PROFILE model for Ca ($8.5 \text{ kg ha}^{-1} \text{ year}^{-1}$), Mg ($2.7 \text{ kg ha}^{-1} \text{ year}^{-1}$), K ($1.0 \text{ kg ha}^{-1} \text{ year}^{-1}$) and Na ($4.3 \text{ kg ha}^{-1} \text{ year}^{-1}$) are within the range previously reported for other soils that have developed on acidic substrates (Adams and Boyle 1979). Weathering rates, however, are notoriously difficult to estimate. A partial validation of the weathering rates may be obtained assuming that Na behaves conservatively within the forest ecosystem (i.e., no accumulation in biomass or in the exchangeable soil reservoir). In such conditions, the net Na exports (atmospheric input minus soil export) should be equal to the Na weathering rate (Bailey et al. 2002). The conservative behaviour of Na at our site is supported by the near absence of recycling through the biota, as shown by the insignificant litterfall fluxes ($0.06 \text{ kg ha}^{-1} \text{ year}^{-1}$) which are between one (Mg, $1.2 \text{ kg ha}^{-1} \text{ year}^{-1}$) and two (Ca, $11.9 \text{ kg ha}^{-1} \text{ year}^{-1}$) orders of magnitude lower than the other cations (Figure 3). The difference between atmospheric input minus soil export ($2.4 \text{ kg ha}^{-1} \text{ year}^{-1}$) is lower than the modelled Na weathering rate for the rooting zone ($4.3 \text{ kg ha}^{-1} \text{ year}^{-1}$), suggesting that Na weathering rates may be overestimated by a factor of 1.8. If we reduced the annual weathering rates in the same proportion for Ca, Mg and K, the new values would become 4.7, 1.5 and $0.6 \text{ kg ha}^{-1} \text{ year}^{-1}$, respectively.

Net base cation budgets

Because many elements considered in the inputs (deposition + weathering) and the outputs (tree uptake + leaching losses), the rooting zone budget may vary depending upon the scenario considered, different calculations were made. First, three scenarios of tree uptake (current period, whole rotation and whole rotation stem-only harvesting) and two scenarios of weathering (PROFILE values, PROFILE values corrected for Na weathering) were considered. In addition, given the variability of soil K exports with depth, additional scenarios were calculated with soil exports observed at 22 and 81 cm depths. The different scenarios are listed in Table 4. Different levels of error are considered. The error associated with deposition and soil leaching measurements is a sampling error which, when summed over the seven-year period by carefully taking into account the variance properties (Zar 1974), is small for every cation (Table 3). The error associated with the forest plot biomass is also small, because each single tree with a diameter greater than 1.0 cm ($n = 1421$) in the forest plot (consisting of the whole population) was taken into account in the calculation. The error associated with the prediction of elements sequestered in the aboveground biomass from the allometric equations developed for black spruce and jack pine is nearly insignificant (Tremblay et al., in prep.), as typically observed when using this type of equation (Bond-Lamberty et al. 2002). The weathering values take into account the variability found in the four soil

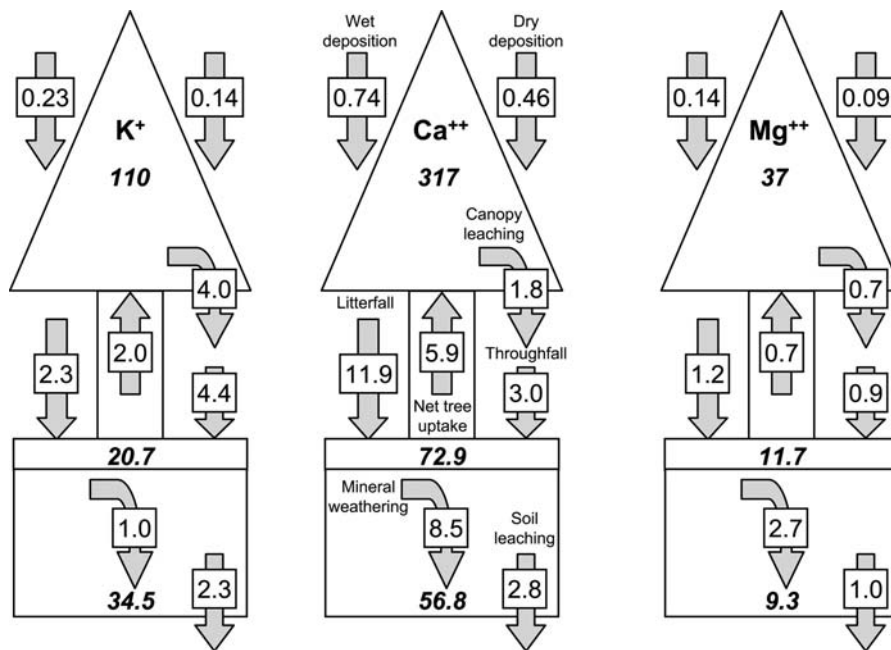


Figure 3. Illustration of base cation cycling at the Lake Tirassee watershed.

profiles. Finally, the use of many scenarios (three scenarios for tree uptake, two scenarios for weathering, two scenarios for soil leaching exports), for a total of 12 different scenarios, is a robust approach that takes into account the potential range of variability that is expected to exist in the different fluxes.

Clearly, in every scenario Mg accumulated in the soil rooting zone exchangeable reservoirs, while K was lost. Calcium was lost in four of the 12 scenarios (1,2,7 and 8).

Implications of K losses for forest sustainability

Although the absolute K losses resulting from the different scenarios are relatively low, they are large with respect to the very small exchangeable K reservoir comprised within the soil rooting zone. For instance, what might be considered a very conservative situation over an entire rotation (scenario 11), including whole-tree uptake, the lowest soil exports value (6.3 kg ha^{-1}) and the higher soil weathering rate would represent a cumulative 6.5 kg ha^{-1} K loss over the 1997–2003 period (or $0.93 \text{ kg ha}^{-1} \text{ year}^{-1}$), which would virtually lead to a depletion of the K exchangeable ($55.2 \text{ kg ha}^{-1} \text{ year}^{-1}$) reservoir in 59 years if we assume a linear decrease of the soil reservoir. A comparison with many northeastern North American sites showed that the Tirassee site has the lowest K, Ca and Mg reservoirs. For instance, average values of exchangeable

Table 4. Base cation budgets for the 1997–2003 period considering different scenarios of tree harvest (whole-tree or stem only), soil leaching (depths of 22 and 81 cm), and weathering rates.

Input-output scenario	Soil depletion or retention between 1997 and 2003 (kg ha ⁻¹)				Annual soil depletion or retention (% of exchangeable reservoir)			
	K	Ca	Mg		K	Ca	Mg	
1. Actual uptake, Na corrected PROFILE weathering, Leaching (22 cm)	-35.5 ± 8.1	-20.1 ± 9.5	-0.8 ± 0.94		-9.2	-2.2	-0.5	
2. Whole rotation uptake, Na corrected PROFILE weathering, Leaching (22 cm)	-31.3 ± 8.1	-6.8 ± 9.5	0.3 ± 0.94		-8.1	-0.7	0.2	
3. Whole rotation stem-only uptake, Na corrected PROFILE weathering, Leaching (22 cm)	-26.0 ± 8.1	2.6 ± 9.5	2.1 ± 0.94		-6.7	0.3	1.5	
4. Actual uptake, PROFILE weathering, Leaching (22 cm)	-32.4 ± 08.1	6.2 ± 17.0	7.6 ± 1.56		-8.4	0.7	5.1	
5. Whole rotation uptake, PROFILE weathering, Leaching (22 cm)	-28.2 ± 8.1	19.5 ± 17.0	8.6 ± 1.56		-7.3	2.1	5.9	
6. Whole rotation stem-only uptake, PROFILE weathering, Leaching (22 cm)	-22.9 ± 8.1	28.8 ± 17.0	10.5 ± 1.56		-5.9	3.2	7.1	
7. Actual uptake, Na corrected PROFILE weathering, Leaching (81 cm)	-13.8 ± 0.69	-20.8 ± 9.5	2.0 ± 0.88		-3.6	-2.3	1.4	
8. Whole rotation uptake, Na corrected PROFILE weathering, Leaching (81 cm)	-9.6 ± 0.69	-7.5 ± 9.5	3.1 ± 0.88		-2.5	-0.8	2.1	
9. Whole rotation stem-only uptake, Na corrected PROFILE weathering, Leaching (81 cm)	-4.3 ± 0.69	1.9 ± 9.5	4.9 ± 0.88		-1.1	0.2	3.4	
10. Actual uptake, PROFILE weathering, Leaching (81 cm)	-10.7 ± 0.98	5.5 ± 16.9	10.4 ± 1.53		-2.8	0.6	7.0	
11. Whole rotation uptake, PROFILE weathering, Leaching (81 cm)	-6.5 ± 0.98	18.8 ± 16.9	11.4 ± 1.53		-1.7	2.1	7.8	
12. Whole rotation stem-only uptake, PROFILE weathering, Leaching (81 cm)	-1.2 ± 0.98	28.1 ± 16.9	13.3 ± 1.53		-0.3	3.1	9.0	

reservoirs for the IFS sites are 1119, 334 and 518 kg ha⁻¹ (Johnson and Lindberg 1992), compared to 130, 21 and 55 kg ha⁻¹ for the Tirasse site for Ca, Mg and K, respectively.

Most published data for forested ecosystems reports Ca and Mg losses (Likens et al. 1996; Houle et al. 1997; Wathmough et al. 2005) but most data originate from temperate forests, for which the natural perturbation regime is different from the boreal forest. Dynamics of the Canadian Shield boreal forest are mainly controlled by forest fires and spruce budworm outbreaks (Bergeron 2000). Interestingly, K leaching losses are increased in the boreal forest following perturbations such as forest harvesting and forest fires. Lamontagne et al. (2000) reported that stream K losses from burnt or harvested catchments were 3–8 times higher than for neighbouring undisturbed catchments. However, there are no available data for the leaching losses associated with spruce budworm outbreaks in black spruce stands, although rooting zone leaching of K was increased by nearly ten-fold during an outbreak in a boreal balsam fir forest in Québec (Houle et al., in prep). Such a response at the Tirasse site would likely be less important because spruce budworm outbreaks are less severe in black spruce stands, and also because black spruce account for 60% of stand basal area at our site, the remaining being jack pine which is not affected by the spruce budworm. The importance of leaching losses associated with perturbations must, however, be weighted by taking into account its persistence and the recurrence pattern of the perturbations. For example, if fires and harvesting in the black spruce/jack pine forest increase exports due to K leaching (2.3 kg⁻¹ ha⁻¹ year⁻¹) by five times, that the effect persists for three years (Carignan et al. 2000) and that the recurrence of the perturbations is 100 years, we would end with leaching losses of 34.5 kg ha⁻¹ ($2.3 \times 5 \times 3$) over a 100-year period. Contrary to fires, harvesting removes the biomass, and losses due to net immobilisation (2.0 kg ha⁻¹ year⁻¹) must be added (200 kg ha⁻¹ for a 100 year rotation). When the export due to biomass removal is summed with the associated leaching losses, the total K losses caused by harvest are 234.5 kg ha⁻¹ over 100 years. The direct contribution of acid rain to the leaching losses over a 100-year period is not possible to establish with our data set. However, because estimates of annual leaching losses (2.3 kg ha⁻¹) and total net annual losses due to harvest (2.34 kg ha⁻¹) are fairly close, and because it is unlikely that acid rain is responsible for 100% of the leaching losses, it suggests that harvesting is the main cause of K losses at the Tirasse site.

Conclusion

Although the boreal forest likely was sustainable for thousands of years in terms of its K nutrition under its regime of natural disturbances, it is possible that the combined effect of harvesting and acid rain may have increased the K leaching losses beyond the threshold of natural rates of replenishment from atmospheric deposition and weathering. Because of the very high amount of

basic cations found in biomass, as compared to the amount found in the exchangeable soil reservoir, one-time harvesting would represent a 66% loss in the total base cation pool. Although Ca and Mg exchangeable reservoirs may potentially rebuild over an 80-year rotation, K weathering and atmospheric deposition will not be sufficient to palliate the cumulative losses due to leaching and tree harvesting. These data suggest that the boreal forest growing on poor sites of the Canadian Shield may not be sustainably harvested over the long term, and that important K limitations may occur after two or three rotations. For this reason, stem-only harvesting is recommended for sensitive boreal forest stands.

In this context, a better understanding of the processes that govern element dynamics, namely K in these forests, is particularly relevant. Acquisition of soil chemistry data is particularly important in order to develop simple indicators of site sensitivity that may be useful for forest management.

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