



Transfers of soluble inorganic elements in a boreal balsam fir forest

Gilles Robitaille and Robert Boutin

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TRANSFERS OF SOLUBLE INORGANIC ELEMENTS IN A BOREAL BALSAM FIR FOREST

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ABSTRACT

The concentrations and fluxes of the major ions were examined for a boreal balsam fir forest located at the Lake Laflamme catchment, Montmorency Forest, 80 km N of Quebec City. The pH of the throughfall (TF) and the incident bulk precipitation (INCB) were equal (4.40) and higher than in the stemflow (SF) (4.18). Below the roots soil solution (BR) and output stream (OS) were less acid with respective pHs of 4.85 and 6.52.

With the exception of NH_4 and NO_3 , the throughfall and stemflow were more concentrated than the INCB. The enrichment factors for K, Mg, Mn, and Ca were 12, 4, 4, and 3 for the throughfall and 83, 14, 21, and 11 for the stemflow. Based on the weighted mean concentrations of seven years for a vegetation period of 5 months, we have estimated that the catchment has accumulated 0.22 kg/ha of H and 4.4 kg/ha of NO_3 and has lost respectively 5.1, 2.0, 1.6, 1.3, and 0.04 kg/ha of Ca, SO_4 , Na, Mg, Cl, and K. The overall canopy process was neutral salt leaching of cations. The use of a lime potential calculation supported the identification of a Ca+Mg front that moves through the forest canopy. Actual proton production in the forest system indicated that soil acidification had several causes.

RÉSUMÉ

Les concentrations et les flux des ions majeurs ont été mesurés pour une forêt de sapin baumier située dans le bassin du lac Laflamme de la forêt Montmorency située à 80 km au nord de Québec. Les eaux d'égouttement (TF) et les précipitations globales incidentes (INCB) avaient des pH identiques (4,40) et étaient moins acides que les eaux d'écoulement le long du fût (SF) (pH 4,18). La solution du sol sous la zone racinaire (BR) et le ruisseau de drainage étaient moins acides ayant des pH respectifs de 4,85 et 6,52. À l'exception de NH_4 et NO_3 , les TF et SF étaient plus concentrés que l'INCB. Les facteurs d'enrichissement pour K, Mg, Mn et Ca étaient de 12, 4, 4 et 3 pour les TF et de 83, 14, 21 et 11 pour les SF. En se basant sur les concentrations moyennes pondérées de sept années pour une période de végétation de cinq mois, on a estimé que le bassin avait accumulé 0,22 kg/ha de H et 4,4 kg/ha de NO_3 et perdu respectivement 5,1; 2,0; 1,6; 1,3 et 0,04 kg/ha de Ca, SO_4 , Na, Mg, Cl et K. Le lessivage de sels neutres est la résultante principale du contact des précipitations avec le couvert forestier. Cela a été confirmé en identifiant, par le calcul du "potentiel en chaux", un front Ca+Mg qui se déplace à travers les strates hydriques. La production de protons a été calculé et indique que les sols du bassin du lac Laflamme s'acidifient par des processus multiples.

INTRODUCTION

As evidenced by the abundant literature on effects from point source emissions, there is no doubt that air pollutants have deleterious effects on the growth of vegetation. The pollutants in question may be gaseous, particulate (Smith 1981), or in solution (Likens and Bormann 1974; Threshow 1984). The effects on vegetation may be direct or indirect. Further, the interactions between a pollutant and other environmental stress factors are extremely complex and depend on its type, duration, and concentration (Fritts 1976; Manion 1981).

In the past, attempts to elucidate pollutant effects on vegetation have concentrated a great deal on the examination of effects due to point source emissions (Robitaille 1977) and on manipulative methods using single pollutants or combinations of pollutants at acute or chronic doses (Last 1984). These approaches have yielded invaluable information on visual and hidden injury effects at the cytological, biochemical, and organism levels of integration.

Studies on the effects of chronic levels of pollutants in the field in combination with other environmental stresses have tended to focus on ambient air exclusion chamber experiments (Heagle et al. 1973; Duchelle et al. 1983) and on the biogeochemical approach (Likens et al. 1977; Ulrich 1983; Richter et al. 1983).

The study of geochemical and biogeochemical transfers is used to elucidate the circulation of elements within an ecosystem (Cronan 1984). These cycles are usually in dynamic equilibrium and therefore can be monitored for a period of time to reach a benchmark or equilibrium "steady state" of the cycles. It is not unreasonable to assume that an acute or chronic stress could cause a shift in the equilibrium of the cycles (Johnson and Richter 1984; Morrison 1984). For example, over several years, a steady input of pH 4.2 incident precipitation could cause a shift in this equilibrium for sensitive forest ecosystems.

Geochemical and biogeochemical transfer studies have shown that basic cations and acid anions are enriched in throughfall and stemflow (Eaton et al. 1973; Mahendrappa 1974; Likens et al. 1977; Feller 1977; Foster et al. 1986). Enrichment is dependent on rain quality (acidity, for example) and on the type of forest canopy (Khanna and Ulrich 1981; Hoffman et al. 1980; Parker 1983; Johannes et al. 1985).

This report establishes in part the geochemical and biogeochemical transfers found in a boreal balsam fir forest and compares the results with those described in the literature on similar ecosystems. An attempt has been made to interpret these results in terms of catchment sensitivity to current levels of acid deposition.

The results of seven years of observations (growing season June to October) on the nutrient solution chemistry found in incident precipitation (INCB), throughfall (TF), stemflow (SF), and soil solution below the roots (BR) are described for a boreal balsam fir forest ecosystem. Data on nutrients leaving the catchment have also been included. The study site, the Lake Laflamme catchment, is the boreal component to the three major biogeochemical studies undertaken by Forestry Canada to establish appropriate baseline characteristics for forests and soils that are affected by long-range transported pollutants.

MATERIALS AND METHODS

Site location and description

The balsam fir forest is located 80 km north of Quebec City in the Montmorency Experimental Forest. The Lake Laflamme catchment is at 47° 19' N latitude and 71° 07' W longitude (Fig. 1). The relief ranges from 777 m at the lake surface to 884 m at the highest summit with a minimum and maximum slope of 0 and 30 percent, respectively. The land and lake surfaces cover 62.3 and 6.1 ha, respectively. The catchment is on the Laurentian Shield and the parent material is composed of charnockitic rock and mangerite. Feldspars, plagioclase, and quartz are the dominant minerals. The glacial till, which may be as deep as 5 m, is mainly sand and gravel enriched with quartz but poor in orthose (Azzaria et al. 1982).

The soil is an orthic ferro-humic podzol of the Laurentide and Des Neiges series (Table 1). It is moderately drained and sandy with a relatively low base saturation. There is a compacted C horizon. Other podzolic soil series may be present depending on the drainage class. Moderately drained soils belong to the Piché and La Foi series and gleyed humic podzols, which are poorly drained, belong to the Colligan series. The humus mor is about 8 cm thick (Martel 1983).

The climate is classed as cool-humid with an average annual temperature of 0.3°C and a maximum (July) and minimum (January) of 34 and -41°C, respectively. On average, there are 232 days with frost and a third of the annual average precipitation (about 145 cm) falls as snow. The Montmorency Forest is located in the Laurentide-Onatchiway forest section (Rowe 1972). The catchment has a very homogeneous forest cover composed of 80 percent balsam fir (*Abies balsamea* (L.) Mill.). White birch (*Betula papyrifera* Marsh.), white spruce (*Picea glauca* (Moench) Voss), and black spruce (*P. mariana* (Mill.) BSP) make up the

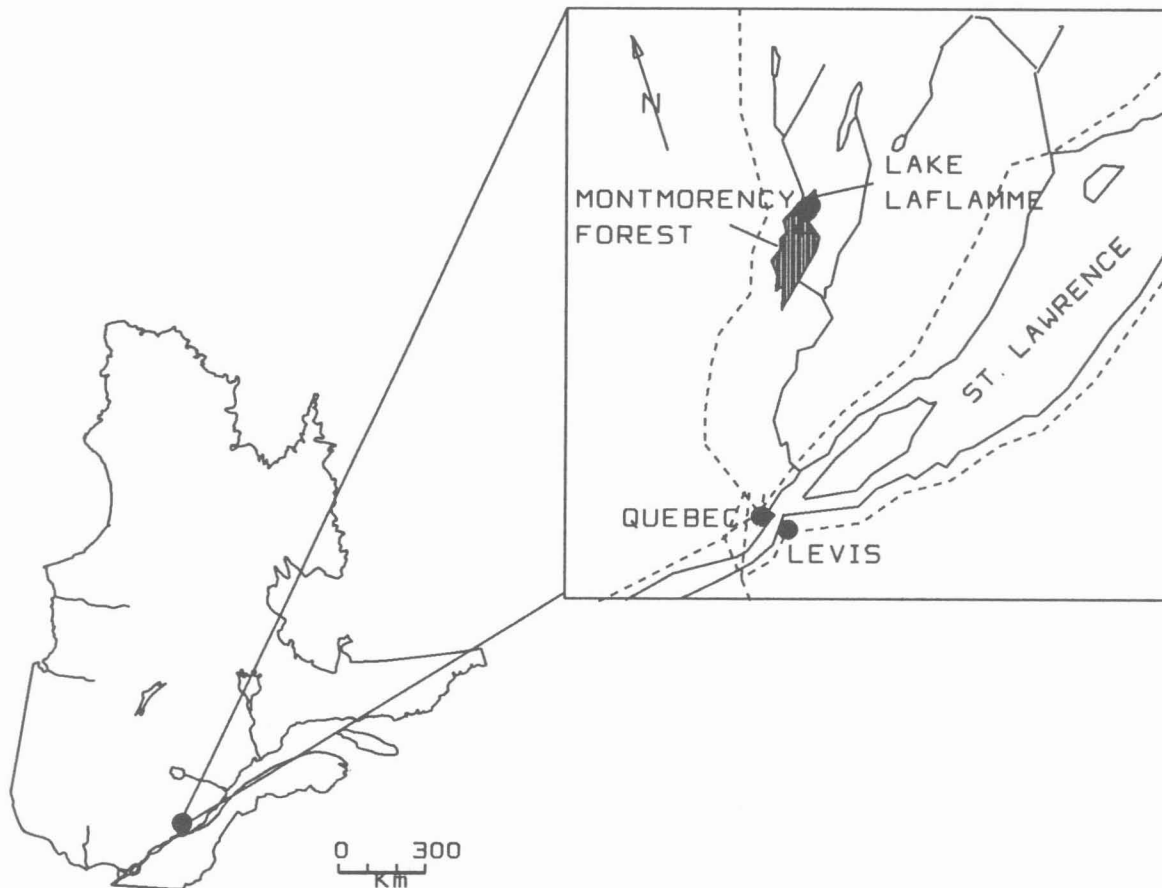


Figure 1. Location of the study site relative to Quebec City.

remaining 20 percent. On the well-drained soil, the spinulose shield-fern (*Dryopteris spinulosa* (O.F. Muell.) Watt) is common along with other acidophilous herbs such as wood-sorrel (*Oxalis montana* Raf.). It is a dense forest with 4800 individuals per hectare (Barry et al. 1988) of average age 50 years originating from a partial cut in 1943.

Spraying with biological and chemical insecticides has given some protection against the spruce budworm. Defoliation was estimated at 40–50 percent in 1982 (Plamondon et al. 1984). Conifer foliage is recovering, presumably as a result of spraying in 1981 and 1982 and a natural decrease in the budworm population. In recent years, windthrow of balsam fir has increasingly become a factor in the evolution of this forest. As a consequence, the canopy has opened up considerably in certain areas of the catchment.

Sampling protocol

Six permanent sample plots of 0.04 ha were established in 1981 and followed to the present. INCB was collected in a clearing at a Canadian Precipitation Monitoring site (CapMon), formerly Air Pollution Network (APN), which is adjacent to the forested catchment. All sampling surfaces were chemically inert. Bulk incident precipitation was collected in clear plastic rain gauges in 1981 and 1982 and, from 1983 to 1987, in semi-opaque nalgene bottle-funnel collectors with filters. Throughfall collectors, installed in the six permanent plots, were identical to the INCB collectors. Lead strip stemflow collars (Mahendrapa 1974), sprayed with an inert plastic material, were placed on the balsam fir. Porcelain cup-PCV tube tension lysimeters of 5 cm id were used to collect BR (negative pressure of 0.3 atm at 20 to 60 cm depth). Water leaving the catchment was collected upstream from a Parshall flume installed in the output stream.

The frequency of sampling varied from event sampling in the early stages to weekly sampling in the later stages. The number of collectors on the six plots varied from 40 to 60 for throughfall, 7 to 60 for stemflow, and 12 to 24 for soil solution over the study period (Table 2).

Chemical analyses

Analytical methods for the parameters studied are shown in Table 3. All samples were filtered at 0.45μ before chemical analysis. Conductivity, pH, SO_4^{2-} , NO_3^- , NH_4^+ , and H_2PO_4^- were measured within 24 hrs of collection and cations within a week, when possible. Long term storage up to six months did occur. These samples were acidified and/or stored at 2°C and refiltered before chemical analysis of cations.

Quality control of the chemical analyses was assured by frequent verification with standard solutions, recalibration, and interlaboratory comparisons.

Calculations

The volume-weighted concentrations ($\mu\text{eq/L}$) of the elements were calculated. To determine the flux in kg/ha/5 months of each element, the following relationship was used:

$$\text{DEPe} = \text{WMCe} * \text{P(INCB,TF,SF,BR)} * \text{Fa}$$

where DEPe is the deposition in kg/ha/5 months ;

WMCe is the weighted mean concentration in $\mu\text{eq/L}$ for selected precipitation periods;

P is the height of the water column (mm) for the five month period for bulk incident rain (INCB), throughfall (TF), stemflow (SF) and below the roots soil solution (BR) (Table 4); and

Fa is a conversion factor used to express the deposition in kg/ha (Table 5).

The flux of water for the stemflow was taken as 2 percent of the INCB (Plamondon et al. 1984). The amount of water passing through the soil profile to the saturated zone was estimated as 60 percent of the INCB precipitation (personal communication Hendershot, McGill Univ.). Both estimates were applied to all years of the study. Using a fixed water flux has certain disadvantages as both under- and overestimates of element fluxes may occur for a given growing season. Flux values may be overestimated in the drier summer months and underestimated during recharge periods in the spring and fall. Water flux may also vary from year to year. For example, throughfall water flux varied between 72 and 84 percent of the incident water flux between 1981 and 1987 (Table 4).

The sampling periods used to calculate the volume-weighted mean concentrations ($\mu\text{eq/L}$) and the fluxes (kg/ha/5 months) were not necessarily the same. The former was usually longer. This occurred because we wanted to use only the sample dates that had sufficient water flux to allow for calculation of element flux in all of the sampled strata (ie. INCB, TF, SF, BR) for any given collection date. This accounts for the apparent discrepancy when one tries to calculate the kg/ha values from the $\mu\text{eq/L}$ in the tables.

The summary statistics were calculated using SAS software (SAS 1985).

RESULTS

Precipitation quantities

Although event sampling was carried out in 1981, only 65 percent of the total precipitation was sampled (Table 4). This was due to major sampling discontinuities in June which were the consequence of spraying for the spruce budworm. Because of this, the five-month flux estimates were underestimated for 1981. The 1982 sampling discontinuity did not affect the quantity of rain collected as no rain fell within this period. We have considered 1981 to 1987 in the discussions on concentration and element fluxes. The amount of water sampled for the 1982 to 1987 period was within 1 percent of the water sampled at the standard rain gauge.

On the average, 20 percent of the INCB precipitation was intercepted by the canopy from 1981 to 1987. The sampling discontinuities in 1981 and 1982 did not seem to alter the ratio of INCB rain to TF (Table 4).

The year-to-year differences in interception due to evaporation had an effect on the concentration and flux of elements in the throughfall and stemflow. If evaporation is high, the concentrations attributed to evaporation alone and those attributed to chemical and biological processes must be separated. The year-to-year variation in interception was small at the Lake Laflamme catchment (Table 4). Therefore, no correction to the concentration was applied to either throughfall or stemflow. Fahey et al. (1988) concluded that canopy evaporation accounted for a 27 percent increase of dissolved solids in throughfall for loblolly pine. Parker (1983) estimated it at between 10 and 20 percent for both conifers and deciduous tree throughfall and at less than 5 percent for stemflow.

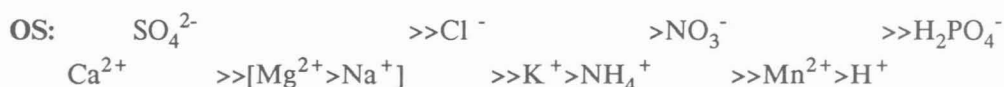
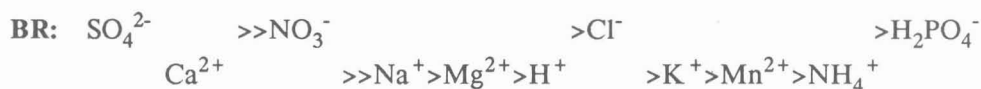
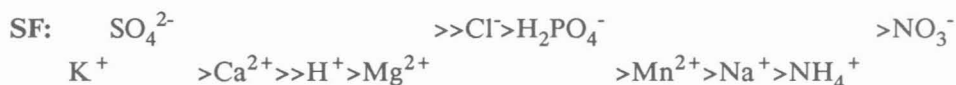
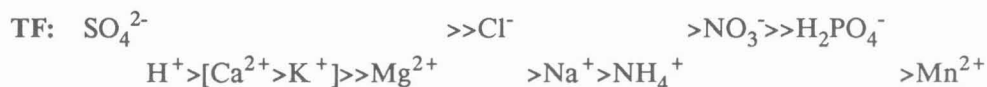
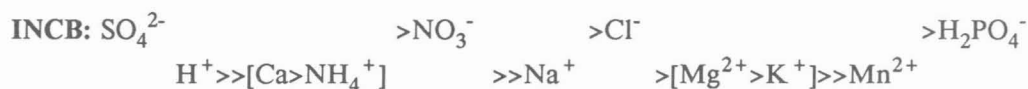
On a five-month basis, the driest years occurred in 1982 and 1984 with deficits of 151 and 196 mm of rain; these figures are based on the 15-year average for the period June to October (data from the Université Laval weather station). The wettest year was 1986 with a surplus of 41 mm. At these extremes, the interception by the canopy was 24, 22, and 18 percent, respectively (Table 4). It would seem that maximum interception occurs in dry years and minimum interception occurs in wet years. Factors that may have contributed to the year-to-year variation in evaporation are the type and intensity of precipitation and the interval between precipitations (Johannes et al. 1986). Needle surface area is also important.

Ionic concentrations and fluxes

INCB, TF, SF, BR

The volume-weighted concentrations ($\mu\text{eq/L}$) for the ions measured in successive years appear in the appendix (Tables 11 to 13). The seven-year average concentrations appear in Table 6.

The volume-weighted concentrations of the major ions for the seven-year period 1981-1987 were in the following rank order for the different strata (similar groups of values in brackets » indicate **much** smaller concentrations, Table 6):



Sulfate was the dominant anion measured in the solutions collected in the balsam fir forest. The proportion of SO_4^{2-} to the total anionic charge was 60, 48, and 32 percent in the INCB, throughfall, and stemflow, respectively (Table 6). We included the anionic deficit in the calculation of the total anionic charge. Soil solution SO_4^{2-} occurred in the same proportion as INCB SO_4^{2-} but the proportion was less in the OS samples. For BR samples, the negative deficit was not included in the calculation and we assumed that organic anions and HCO_3^- were negligible. The highest proportion of NO_3^- to the total anionic charge was in the BR. Phosphate and Cl^- , at 4 and 6 percent of the negative charge, were relatively constant for all of the sample types.

The proportion of protons to the total cationic charge decreased from 50 to 30 to 14 percent in the INCB, throughfall, and stemflow. Ammonium and Na^+ proportions also decreased. The proportions of K^+ , Ca^{2+} , Mg^{2+} , and Mn^{2+} increased progressively in passing from INCB to throughfall to stemflow. In the BR and the OS, calcium and K^+ accounted for the highest proportion of the total cationic charge.

Sulfate plus hydrogen accounted for 55, 39, and 22 percent of the total charge in the INCB, throughfall, and stemflow, respectively. Nitrate and NH_4^+ ions accounted for 16 percent of the charge in the INCB but decreased to 4 and 0.4 percent in the throughfall and stemflow, respectively. Calcium and K^+ took up 20, 48, and 72 percent of the cationic charge in the INCB, throughfall, and stemflow samples. While the proportions of H^+ , SO_4^{2-} , NO_3^- , NH_4^+ , and Na (Group 1) decreased from INCB to throughfall to stemflow as a fraction of the total charge for these strata (Table 6), the proportions of K^+ , Ca^{2+} , Mg^{2+} , Mn^{2+} , and H_2PO_4^- (Group 2) increased.

In group 1, SO_4^{2-} was slightly enriched in the throughfall and the stemflow by factors of 1.3 and 3.3. All elements of group 2 were enriched in the throughfall and stemflow samples by factors of 12 (K^+), 2.6 (Ca^{2+}), 4.4 (Mg^{2+}), 4.4 (Mn^{2+}), and 9.5 (H_2PO_4^-) and by factors of 82.9, 11.2, 14.3, 20.6, and 54.3, respectively, for the stemflow when compared to the INCB. Chloride was also enriched by factors of 1.8 and 4.3 in the throughfall and stemflow.

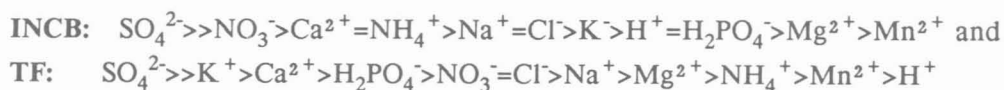
The enrichment of cations in the throughfall was in the order $\text{K}^+ > \text{Mg}^{2+} > \text{Mn}^{2+} > \text{Ca}^{2+}$ and in the stemflow, it was $\text{K}^+ > \text{Mn}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+}$. For the anions, the order was $\text{H}_2\text{PO}_4^- > \text{Cl}^- > \text{SO}_4^{2-}$ in both the throughfall and stemflow. Both NO_3^- and NH_4^+ were taken up by the balsam fir canopy at Lake Laflamme. On average, throughfall acidity was equivalent to the bulk precipitation acidity and less acid than the stemflow. On a year-to-year basis (Table 11), throughfall acidity was higher or lower than INCB acidity. The range of the ratios of throughfall acidity to INCB acidity was 0.7 to 1.3.

It was also evident that the anion deficit (Table 6) increased from INCB to throughfall to stemflow. Output stream solution also had an anion deficit. There was no anion deficit in the BR.

Over the seven-year period (Table 6), and on a yearly basis (Tables 11 to 13), the rank order of the soluble basic cations was $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ in the ratios of 9:3:2:1, respectively, in the BR. The only exception was in 1982 when magnesium tended to be higher than sodium. The rank order of the exchangeable cations of the Lake Laflamme soil was $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ (Boutin and Robitaille 1987; exchangeable Na was not measured).

As expected, the BR was less acid than the solutions impinging upon it. A cation deficit of 20 $\mu\text{eq/L}$ was observed over the seven-year period (Table 6). The cation deficit shown in Table 6 was strongly influenced by the high concentrations of NO_3^- observed in 1981, 1982, and 1983 relative to the sum of the cations for those years (Table 13).

Over the seven years, the average deposition of protons, NH_4^+ and NO_3^- was higher in the INCB than in the bulk throughfall below the canopy by factors of 1.3, 2.6, and 3.2, respectively (Table 7). The rank order of deposition in the INCB and fluxes in the throughfall (Table 7) was as follows:



Sulfate and NO_3^- were the most deposited ions on the catchment at 21 and 5 kg/ha/5 months. The SO_4^{2-} and NO_3^- load for the five-month period represented approximately 55 and 48% of the total annual wet deposition to the catchment, respectively. A $\text{SO}_4:\text{NO}_3$ ratio of 2.7:1 was observed for the INCB as compared to the ratio of 2.2:1 for wet deposition from 1981 to 1986 (Papineau 1987; Vet et al. 1988). Passage through the canopy increased the flux of all elements except protons, Na^+ , NO_3^- , and NH_4^+ and changed the rank order of the elements. Sulfate increased slightly and was the dominant ion in the throughfall. Potassium and calcium fluxes, the next most abundant elements, increased by factors of 9 and 2, respectively. Similar increases have been reported elsewhere (Parker 1983). This ranking reflects the mobility of these elements in the soil-plant environment and is in agreement with Tukey (1970), Yawney (1978), and Yawney et al. (1978).

Concentrations and fluxes in the OS

Sodium, Ca^{2+} , Mg^{2+} , and SO_4^{2-} concentrations were higher at the OS than in the INCB and throughfall by factors of 4.9, 7.4, 13.4, and 1.6 (INCB) and 4.3, 2.8, 3.1, and 1.2 (TF), respectively (Table 6). Potassium concentrations were higher in the OS than in the INCB, but lower than in the throughfall. Hydrogen, NH_4^+ , NO_3^- , H_2PO_4^- , and Mn^{2+} had lower concentrations in the OS than in the INCB. Nitrate, however, behaved differently in 1982 as the output stream had a much higher concentration than in other years which seemed to be correlated to the high NO_3^- in the BR (Table 13). Assuming that the catchment was watertight, a simple input/output balance sheet showed that the catchment tends to accumulate hydrogen and NO_3^- if there is no denitrification or loss of nitrogen as gases. Over the 7 years of five-month growing seasons, this amounted to an accumulation rate of approximately 2 kg/ha of hydrogen and 31 kg/ha of NO_3^- (Table 7). Sulfate and K^+ may or may not be retained on a seasonal basis. The remaining ions, Na^+ , Ca^{2+} , Mg^{2+} , and Cl^- , were always exported from the catchment at a rate of about 11, 36, 9, and 2 kg/ha/5 months over the 7 annual periods of 5 months (Table 7).

DISCUSSION

Ionic concentrations and fluxes for TF and SF

Throughfall acidity is controlled to a large extent by hydrogen ion exchange on the leaf surfaces as well as INCB acidity. Usually the amount of base cation gained in the throughfall is greater than the amount of hydrogen lost from the INCB (Miller 1984). Abrahamsen (1980) also noted that in spruce forests supplied with artificial rain of varying acidity, throughfall was enriched with cations in the sequence $\text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ and this increased as the pH of the artificial rain increased. He also showed that the content of NH_4^+ and NO_3^- was less in the throughfall than in the applied rain, regardless of rain acidity. Mahendrappa (1974) noted that for balsam fir, the rank order of cations in the SF was

$K^+ > Ca^{2+} > Na^+ > Mg^{2+} > Fe^{2+}$. Olson et al. (1981) found that in sub-alpine balsam fir, the order of cation enrichment was $K^+ > Mn^{2+} > Ca^{2+} > Mg^{2+} > H^+$. Ammonium was absorbed. For the major anions, the order of enrichment at their sites was $Cl^- > SO_4^{2-} > NO_3^-$. Potassium, Mn^{2+} , Ca^{2+} , Mg^{2+} , and H^+ in the stemflow were 23, 5, 3.2, 2.8, and 1.2 times greater than the concentrations found in the INCB. The anions were 3.4, 1.5, and 1.2 times as concentrated. The acidification of the throughfall was attributed in part to NH_4^+ uptake, washout of acidic dry deposition, or leaching of plant-derived organic acids (Olson et al. 1981). In radiata pine, Will (1959) noted high values of K^+ and $PO_4^{=}$ in the throughfall, about 5 times more flux for K^+ and three times more for $PO_4^{=}$. Calcium and Na^+ were also enriched. Paster and Bokheim (1984) showed canopy uptake of nitrogen. Usually K^+ and Ca^{2+} are the most readily leached foliar cations (Tukey 1980). Tukey et al. (1958) determined a sequence of leachability from plant leaves using radioisotopes and found a rank order of $Na > Mn \gg Ca, Mg, S, K \gg Cl$. Differences in leachability are primarily related to plant species differences and leaf wettability.

Stemflow was probably enriched at the Lake Laflamme catchment because of the abundant growth of lichens on the tree trunks that can capture large quantities of particles (Robitaille 1977). Absorption of NO_3^- and NH_4^+ may be related to the lichens' cycling of inorganic N. Dead bark tissue may also be a major source of Ca^{2+} in the stemflow (Carlisle et al. 1967). The increase in K^+ and $H_2PO_4^-$ may also be related to lichens and dead bark material. The increase in the anion deficit from INCB to SF could be due to increases in the proportion of organic anions (Carlisle et al. 1966). Organic anions were not measured in our study. Cronan (1980, 1984) used the anion charge deficit to estimate organic anions in throughfall of coniferous forests. We did note, however, that organic peaks occurred on the chromatograms of the anion runs for these three strata. The anion deficit at the OS may be attributed to bicarbonate (Papineau 1987).

The loss of NH_4^+ and NO_3^- to the canopy was also observed for other coniferous canopies (Foster 1974; Päivänen 1974; Abrahamsen et al. 1976; Verry and Timmons 1977; Bringmark 1980; Cronan and Reiners 1983). However, Wells et al. (1972) and Parker (1982) observed an increase in NH_4^+ and NO_3^- flux in throughfall of pine and loblolly pine, and Abrahamsen and Stuanes (1986) noted a decrease in NH_4^+ and an increase in NO_3^- in *Pinus sylvestris*. All of these authors reported increases in SO_4^{2-} , K^+ , Ca^{2+} , Mg^{2+} , Na^+ , and Cl^- . From our observations, it would seem that the absorption of NO_3^- counterbalances the absorption of NH_4^+ . The absorption of NH_4^+ would normally add protons to the throughfall while the uptake of NO_3^- would consume an H^+ . This was found to be one of the possible canopy processes controlling proton flux in this balsam fir forest (Table 6).

Soil solution

The rank order of soluble basic cations in the BR may be explained because feldspars such as albite and anorthite (sodium and calcium aluminosilicates), which are actually plagioclase feldspars, are dominant in the Lake Laflamme catchment (Azzaria et al. 1982). Weathering of these aluminosilicates is in the order $\text{Ca}^{2+} > \text{Na}^+ > \text{K}^+$ (Bohn et al. 1985) so we could expect that BR concentrations of the basic cations would be in the order observed. The Ca:Na:K ratio was 9:3:1 for the BR solution at Lake Laflamme.

The cation deficit in the BR may be related to the charge of the aluminum ions in the BR and to protonated organic amines. Rutherford et al. (1985) noted a 20% cation deficit in BR solutions subjected to simulated acid precipitation on soils taken from Lake Laflamme. We indicated in a related experiment (Boutin and Robitaille 1989) that the cation deficit they measured may also be related to positive organic forms. In their experiment, aluminum was included in the cation charge. As both NO_3^- and SO_4^{2-} decreased (Tables 13 and 16) in the BR solution, a balance in the charge occurred. In 1986 and 1987, the difference in charges was 5 and 4 $\mu\text{eq/L}$ respectively. The anion concentrations in the aqueous phase of non-saline soils is usually less than the cation concentrations and in the BR solution, the anion charge usually equals the cation charge (Bohn et al. 1985).

As expected, Cl and NO_3^- were of similar mobility in the soil solution. Sulfate and H_2PO_4^- were less mobile. Chloride and NO_3^- soil solution concentrations were well correlated over the seven-year period with an R^2 of 89 percent as compared to SO_4^{2-} and Cl ($R^2 = 25\%$) and H_2PO_4^- and Cl^- ($R^2 = 7\%$). Within years, and for the majority of years, Cl^- was significantly correlated with NO_3^- . As shown by analyses of "breakthrough curves" (Bohn et al. 1985), chloride has been used as an indicator of NO_3^- mobility in soils because Cl is not subject to biological reactions as is NO_3^- . The mobility of the anions were found to be in the order $\text{NO}_3^- > \text{SO}_4^{2-} > \text{PO}_4^{=}$ as observed in the literature (Bohn et al. 1985).

When there is an exchange of protons for cations on the soil exchange complex and a mobile anion is present, nutrient leaching of calcium, magnesium, and other cations may occur. These mobile anions are, in general, in increasing order of mobility: HCO_3^- , HPO_4^- , H_2PO_4^- , SO_4^{2-} , NO_3^- , Cl^- (Cook 1983). As for the acidity of the BR (pH 4.8, Table 6) the mole fraction of HCO_3^- and HPO_4^- contributes little to cation leaching (Lindsay 1979). At the Lake Laflamme catchment, the possible carriers of cations in the BR were SO_4^{2-} , NO_3^- , and Cl^- (Table 6). Although NO_3^- and Cl^- are extremely mobile, the data would suggest that SO_4^{2-} was the major carrier anion except in 1982 when the NO_3^- concentration was high (177 $\mu\text{eq/L}$) in the soil solution. Chloride may also have participated in cation leaching to a greater extent in 1982. A soil solution ratio of $\text{SO}_4:\text{NO}_3:\text{Cl}::11:3:1$ (except for 1982) supports this (Table 6). We deduced from laboratory leaching experiments (Boutin and Robitaille

1989) with sulfuric acid on the podzol from the Lake Laflamme catchment, that SO_4^{2-} was the major carrier anion of the major cations in the absence of strong nitrification, in which case NO_3^- would be the major carrier. High and low values of SO_4^{2-} in the soil solution corresponded to high and low values of SO_4^{2-} in the INCB precipitation, suggesting that the SO_4^{2-} in the soil solution may be of atmospheric origin. Cronan et al. (1978) and Richter et al. (1983) suggested that SO_4^{2-} from atmospheric deposition was the major mobile anion in the BR of their sites in New Hampshire and Tennessee.

In 1982, the major carrier anion was probably NO_3^- . Increased mineralization in the forest floor may have accounted for the increased concentration of NO_3^- in the soil solution and to the greater participation of NO_3^- as a carrier anion. Vitousek et al. (1982) noted that NO_3^- was in high concentration ($> 100 \mu\text{eq/L}$) in forest soil solutions perturbed by cutting and trenching. Nitrate concentration and NO_3^- flux in the soil solution peaked in 1982 at $177 \mu\text{eq/L}$ and $30 \text{ kg/ha/5 months}$ and gradually decreased to $6 \mu\text{eq/L}$ and 1 kg/ha/5 months in 1987 (Tables 14 and 17). The NO_3^- peak observed in 1982 corresponded to the lowest NH_4^+ values (Tables 12 and 15) of the seven-year period. Nitrogen is usually leached from soils as NO_3^- and NH_4^+ are retained by cation exchange. Increased mineralization, increased organic matter input from the spruce budworm defoliation, and subsequent root mortality accompanied by higher forest floor temperatures due to canopy opening, may account for the increased concentrations and flux of NO_3^- in the BR in 1982.

Canopy processing of incident bulk precipitation

A comparative analysis of the chemistry of the INCB and of the throughfall bulk precipitation can give us some insight as to how the canopy processes the chemical matrix of the bulk precipitation (Table 8). Six types of canopy processes have been identified (Cronan 1984):

- 1) Neutral salt leaching or washout which results in no net change in proton equivalents in the bulk throughfall;
- 2) Canopy washout or leaching of organic or mineral acids resulting in a potential increase in proton equivalents;
- 3) Uptake of NH_4^+ and release of protons giving a potential increase in protons;
- 4) Ion exchange that removes INCB precipitation protons giving a decrease in proton equivalents and increased cations;
- 5) Canopy leaching or washout of organic or bicarbonate alkalinity resulting in a decrease in protons; and
- 6) Uptake of NO_3^- and release of hydroxyl or bicarbonate by the canopy also causing a decrease in protons.

Several types of canopy processes could be suggested from our results because of the significant enrichment of cations and the loss of NO_3^- and NH_4^+ in the throughfall of the balsam fir forest.

Over the seven-year period (excluding 1983), we noted an average reduction of 41 eq/ha in the proton flux in the TF+SF (Table 8) relative to the INCB while no pH change was noted (Table 7). The canopy effectively buffers the incoming precipitation. We also noted that the reduction of NO_3^- and NH_4^+ in the TF+SF solution was nearly the same (47 eq/ha and 49 eq/ha respectively). Thus, any addition of H^+ and OH^- due to the absorption of these ions was neutralized. The large increase in basic cations in the TF+SF was not accompanied by an equivalent increase in inorganic anions (Table 8). The basic cation increase was mainly due to the presence of K^+ and Ca^{2+} . These cations accounted for 48 and 33 percent of the total cationic charge, respectively. Although the total anion increase was small (22 eq/ha), SO_4^{2-} accounts for the major part of this increase. There was a large anion deficit which may be equated with the presence of organic anions (Cronan 1984). Since no significant change was observed in the pH between INCB and TF+SF, we suggest a combination of organic and inorganic neutral salt leaching of cations from the canopy. Cronan (1984) also attributed the marked ionic enrichment of cations in the throughfall in both deciduous and balsam fir systems to neutral salt leaching and washout. The carrier ion for K^+ and Ca^{2+} (also Mg^{2+}) was probably SO_4^{2-} in combination with organic anions (Cronan and Reiners 1983). Evidence of neutral salt leaching and washout comes from the observed enrichment of SO_4^{2-} and the cations in the throughfall (Table 6). We considered that the SO_4^{2-} came mostly from wet deposition since dry deposition was small at this site (Barrie and Sirois 1986). A process that may explain the lower values of NH_4^+ and NO_3^- in the throughfall is the uptake of inorganic nitrogen by the lichens in the canopy branches and on the trunk of the balsam fir. Organic nitrogen may be an important exudate from the lichens (Cronan 1984). The two processes of NH_4^+ and NO_3^- uptake with subsequent release of protons and hydroxyls seem to be consistent from year to year but are not necessarily the overriding process.

High SO_4^{2-} values in INCB are associated with low pH precipitation. We would anticipate that this type of precipitation, as compared to less acid precipitation containing low SO_4^{2-} , would cause an increase in the leaching of nutrients from the canopy to the detriment of the nutrient pool in the needles.

Lime potential of solutions

Equilibrium relationships between soluble and exchangeable cations have been expressed by equations such as the sodium-absorption ratio (SAR) for saline soils ($\text{SAR} = \text{pNa} - \frac{1}{2}\text{p}[(\text{Ca}+\text{Mg})/2]$) where Na, Ca, and Mg are the concentrations of the soluble

cations (Schofield 1947). These relationships were derived from laboratory experiments by the leaching of soils with salt solutions to equilibrium. The lime potential ($LP = pH - \frac{1}{2}p(Ca)$) is a similar concept (Schofield and Taylor 1955) wherein pCa is the negative logarithm of the calcium activity. This relationship may be expanded to consider magnesium, in which case $LP = pH - \frac{1}{2}p(Ca+Mg)$ and expresses a balance of protons in solution to the cations calcium and magnesium.

This relationship, which was normally applied to soils and soil solutions, may also be relevant to solutions in contact with other forest strata such as forest canopies, tree trunks, and streams (Reuss and Johnson 1986). By comparing the lime potential (LP) of the solution entering or leaving any strata, we can determine if there is a potential for an increase or decrease in the acidity of that strata. The potential changes in acidity may be related to corresponding decreases and increases in divalent cations such as Ca^{2+} and Mg^{2+} . If the inequality $LP(INCB) < LP(TF)$ was true, then there should be a potential for the acidification of the canopy with a subsequent release of cations (Reuss and Johnson 1986). This would also mean that since the activity of Ca^{2+} and Mg^{2+} , in relation to H , increased in the precipitation during passage through the canopy, the throughfall water entering the soil solution would be less able to acidify the soil than the INCB precipitation. A gain would occur if the reverse inequality was true. An assumption inherent to this relationship is that dry deposition must be low. Our dry deposition estimate for the Lake Laflamme catchment (based on SO_4^{2-}) was about 13 percent. This calculation was based on the difference between INCB and throughfall deposition using the appropriate values in Table 7. Barrie and Sirois (1986) have estimated that for the years 1979 to 1982 the dry deposition at Lake Laflamme was relatively low with a four-year mean of 14 and 16% of the wet deposition for SO_4^{2-} and NO_3^- , respectively.

As shown in Table 9, the lime potential of the INCB precipitation was always less than that of the throughfall. This would suggest that the canopy loses cations such as Ca^{2+} , Mg^{2+} , and K^+ . The higher concentrations of these cations in the throughfall (Tables 6 and 12) and the increased flux of calcium and magnesium (Tables 7 and 15) plus the decrease in protons observed in the throughfall (Tables 6 and 11) due to a neutral salt leaching process (Table 9) would seem to confirm this. The rank order of the sequence shown in Table 9 was:

$$LP(INCB) < LP(TF) < LP(BR) < LP(OS)$$

Following the same reasoning as for the INCB and throughfall lime potential sequence, it is apparent that each strata has the potential to acidify the following one and that a divalent cation front of Ca^{2+} and Mg^{2+} moves within the balsam fir forest at the Lake Laflamme catchment. This front was accompanied by decreasing acidity.

The lime potential calculation (Table 9) may be used as an indicator of forest system sensitivity to acid deposition. It was apparent that the incoming precipitation had a potential to acidify the forest canopy and the soil of the catchment. On average, the more acid precipitations of 1984 had 15 and 17 percent more potential to acidify the forest canopy and soils respectively than the less acid precipitations of 1986. The average pH of the INCB for these years was 4.3 and 4.6, respectively. Hence, small changes in the pH of INCB would have a tendency to acidify the forest system under study.

Actual proton production

The actual proton production for the forest ecosystem was calculated using the relationship:

$$(H^+_{in} - H^+_{out}) + (NH_4^+_{in} - NH_4^+_{out}) - (NO_3^-_{out} - NO_3^-_{in}) - (SO_4^{2-}_{in} - SO_4^{2-}_{out}) > 0$$

(Table 10 and De Vries and Breeuwsma 1987). The input was the kmol/ha/5 month value (calculated from Tables 15 and 17) of INCB (incident bulk precipitation) and the output was the value of BR (below the root soil solution) at the Lake Laflamme catchment. Calculated values greater than zero indicate that there was a net proton production in the forested part of the catchment due to proton input or nitrogen and sulfur transformations and/or that there was a potential for soil acidification (De Vries and Breeuwsma 1987; Berden et al. 1987) due to proton, NO_3^- , and SO_4^{2-} deposition. Plant uptake of NH_4^+ and NO_3^- derived from incident deposition (INCB), and mineralization and nitrification in the soil followed by NO_3^- leaching are two causes of proton fluxes in the forest ecosystem. There was an equivalent release of protons for an uptake of NH_4^+ and an equivalent release of bicarbonate or OH for an uptake of NO_3^- . This release may occur at the canopy level or at the root-soil interface. Two protons are produced when nitrification and NO_3^- leaching occurs. Since the uptake of nitrogen mineralized from organic matter moves from one pool of organic nitrogen to another (i.e., internal nitrogen fluxes), the resulting proton fluxes from organic nitrogen cancel each other. Each equivalent of SO_4^{2-} desorbed (or passing into solution from the dissolution of an aluminum hydroxy-sulfate) produces 1 proton in solution (De Vries and Breeuwsma 1987), thereby contributing to soil acidification.

Table 10 shows that the actual proton production was variable from year to year. The highest proton production occurred in 1982 and 1985 with 0.70 and 0.51 kmol H/ha, respectively. The primary source of proton production varies from year to year. In 1981, there was a strong H component from the atmosphere with no contribution from NO_3^- or SO_4^{2-} . The high proton production for 1982 did not seem to be related to high inputs of atmospheric H^+ or of NH_4^+ , but rather to a very high contribution from soil NO_3^- , possibly due to strong mineralization and nitrification. Soil SO_4^{2-} contributed a small amount to the

actual proton production. In 1983, an input from soil NO_3^- was added to the atmospheric H input to give an actual proton production of 0.23 kmol/ha. From 1984 to 1987, the soil NO_3^- contribution was nonexistent, and it was the atmospheric inputs of H^+ and NH_4^+ transformations that seemed more important. This was especially the case in 1985 with soil sulfur transformation adding little to the proton production. The high actual production for 1982 may be related to the combined effects of spruce budworm defoliation (40–50%) and to a relatively dry, warm summer at the Lake Laflamme catchment (150.7 mm less rain than the previous 15-year average for the period June–October) which would increase the amount of insolation and debris to the forest floor thus augmenting mineralization and nitrification.

By definition, boreal ecosystems of the type described here are sensitive to inputs of acid precipitation. Although effects such as the leaching of nutrients from the canopy, neutralisation of the incident precipitation by the forest canopy, and leaching of nutrients from the soil may be small when compared to the potential leaching of nutrients from more basiphilic ecosystems, the overall impact remains important. The reason for this is that boreal systems are nutrient poor and any additional leaching losses quickly become limiting to forest growth. Deciduous forest growing on brunisols, for example, could lose nutrients to a greater extent and still not be limited in their growth because soil weathering would readily replenish the nutrients lost.

As with many forest ecosystems, the sensitivity to acid precipitation of the forest system studied here cannot be adequately described without taking into account extraordinary biological and climatic episodes that may occur within a growing season. It was apparent from this study that soil acidification, as indicated by the actual proton production (Table 10), was strongly related to the input of H^+ over all of the years of observation. Acidification, however, pushes (Table 10, for 1982, 1983) that were related to sudden increases in biomass and insolation to the soil which led to increased mineralization and nitrification and NO_3^- production, were also important. The effect of an acid push may be effective over the following year. The cumulative effects of similar acidic pushes with current inputs of acid precipitation may be one of the driving forces for soil acidification and aluminum mobilization observed in certain areas of Germany (Ulrich 1983).

SUMMARY

This study on the inputs and transfers of the major ions in TF, SF, BR, and OS of a boreal balsam fir forest, has given several baseline observations of interest:

1. Interception of the incident precipitation by the forest canopy varied from 15 to 28 percent and was independent of the quantity of the incident precipitation.

2. The throughfall and stemflow were always more concentrated in major ions than the INCB.
3. The concentrations of K^+ , Ca^{2+} , Mg^{2+} , and Mn^{2+} increased in the throughfall and the stemflow with the order of enrichment concentration being $K^+ > Mg^{2+} = Mn^{2+} > Ca^{2+}$ and $K^+ > Mn^{2+} > Mg^{2+} > Ca^{2+}$ in the proportions of 12, 4.4, 4.4, and 2.6 for the throughfall and 82.9, 20.6, 14.3, and 11.2 for the stemflow when compared to the INCB.
4. SO_4^{2-} , $H_2PO_4^-$, and Cl^- concentrations increased in the throughfall and stemflow in the order $H_2PO_4^- > Cl^- > SO_4^{2-}$ in the proportions 9.5, 1.8, and 1.4 (TF) and 54.2, 4.3, and 3.3 (SF).
5. Protons, NH_4^+ , and NO_3^- were absorbed by the forest canopy and an anion deficit was accumulated in the order $INCB < TF < SF$. The anion deficit was probably a function of increased organic anions.
6. Throughfall was less acidic than stemflow.
7. In the BR zone, the order of the soluble basic cations was $Ca^{2+} > Na^+ > Mg^{2+} > K^+ > NH_4^+$.
8. When the seven years were considered collectively, a cation deficit was observed in the BR. This was caused by high NO_3^- values in the BR observed in 1982 or organic protonated species. Al, which is not discussed in this paper, adds to this deficit.
9. Sulfate was the major ion in the BR except for 1982 when NO_3^- was in high concentration.
10. The NO_3^- peak in the BR in 1982 may be attributed to increased mineralization due to an increased amount of biomass falling on the forest floor, as well as an assumed root mortality and an increase in radiation energy to the forest floor because of an infestation of the spruce budworm. The atmospheric input of NO_3^- was low for 1982. The potential proton production was at a maximum in 1982 and the BR tended to be more acidic.
11. The catchment accumulated protons and NO_3^- at a rate of 0.22 and 4.4 kg/ha/5 month period on average for the seven years. Calcium, SO_4^{2-} , Na^+ , Mg^{2+} , Cl^- , and

K^+ were exported from the catchment at a rate of 5.1, 2.0, 1.6, 1.3, 0.3, and 0.04 kg/ha/5 month period.

12. The overall canopy process was neutral salt leaching of cations.
13. A lime potential calculation showed that a calcium-magnesium front moves through the balsam fir forest. The lime potential calculation reinforces the observation of the canopy process mentioned above.

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APPENDIX

Table 1. Characteristics of the Orthic Ferro-Humic Podzol Laurentide series of the Lake Laflamme catchment(a)

HORIZON (depth) cm	SAND %	SILT %	CLAY %	pH (H ₂ O)	CEC (c)	BS (d)	N %	C %
	(b)	(b)	(b)					
LF (10-4)	-	-	-	4.3	123	23.7	2.16	48.0
H (4-0)	-	-	-	3.7	114	11.5	1.67	38.3
Ae (0-6)	96	3	1	4.2	4	10.8	0.06	1.1
Bhf (3-13)	83	2	15	4.2	56	3.0	0.39	8.8
Bf1 (13-24)	86	2	12	4.7	50	1.6	0.25	6.0
Bf2 (24-38)	89	3	9	4.8	25	1.7	0.19	3.0
Bf3 (38+)	90	2	8	5.0	18	2.1	0.12	2.5
BC	96	1	3	4.6	8	13.4	0.05	0.9
C(e)	96	2	2	4.7	5	13.5	0.03	0.5

(a) Based on 17 profiles; (b) Bouyoucos (1962); (c) Cation exchange capacity [cmol(p+)/kg] 1N NH₄OAC pH7 Chapman(1965); (d) Base saturation=(exCa+exMg+exK/CEC)*100 (exNa not determined); (e) C horizon data from Prof. C. Camire Univ. Laval.

Table 2. Sampling protocol for the years 1981 to 1987 at six permanent sample plots on the Lake Laflamme catchment (June to October)

YEAR	FREQUENCY	# COLLECTORS			
		INCB	TF	SF	BR
1981(a)	EVENT	5	30	20	12
1982(a)	EVENT	5	30	60	12
1983(a)	BI-WEEKLY	4	30	12	12
1984(a)	WEEKLY	4	60	12	24
1985(b)	WEEKLY	4	60	12	24
1986(b)	WEEKLY	4	60	12	24
1987(bc)	BI-MONTHLY	4	40	7	15

INCB = bulk incident rain, TF = throughfall, SF = stemflow; BR = soil solution below the roots.

(a) All samples analysed; (b) Samples pooled for analysis of TF(2 per plot for total of 12); (c) 4 plots.

Table 3. Analytical methods for the parameters studied

PARAMETER	METHOD	DETECTION LIMIT*
pH	pH metre	0.01
Conductivity ($\mu\text{S}/\text{cm}$)	cond metre	0.2
SO_4^{2-}	IC	0.1
NO_3^-	IC	0.1
CL	IC	0.01
H_2PO_4^-	IC	0.20
	F.I.A.	0.01
K^+	EMISSION	0.04
Na^+	EMISSION	0.01
NH_4^+	IC	0.01
	F.I.A.	0.01
Ca^{2+}	AA	0.1
Mg^{2+}	AA	0.008
Mn^{2+}	AA	0.05

* Concentrations for anions & cations in mg/L; IC = ion chromatography; F.I.A. = flow injection analysis; AA = atomic absorption.

Table 4. Water flux values (mm) for the various ecosystem processes (June to October)

Year	Period (days)	Strata				
		INCB	TF	SF	BR	Std.
1981*	142-253	341	288	7	205	527
1982*	152-286	468	355	9	281	468
1983	178-284	438**	371	9	263	436
1984	146-283	495	389	10	297	492
1985	149-303	620	482	13	373	627
1986	148-288	814	669	16	489	818
1987	147-294	548	393	11	329	548

INCB = incident bulk precipitation; TF = throughfall; SF = stemflow; BR = water below roots; SF = taken as 2% of INCB (Plamondon et al. 1987); BR = estimated as 60% of INCB; Std = catch in standard rain gauge; * discontinuities in sampling due to spruce budworm spraying; ** value due to a shorter sampling period.

Table 5. Conversion factors ($\text{Fa} \times 10^{-4}$) for calculating kg/ha fluxes for each element or ion

Element	Fa	Element	Fa
H^+	0.1008	Mn^{2+}	2.7470
Na^+	2.2990	Cl^-	3.5453
NH_4^+	1.8039	NO_3^-	6.2005
K^+	3.9102	SO_4^{2-}	4.8031
Ca^{2+}	2.0040	$\text{H}_2\text{PO}_4^{*-}$	9.4975
Mg^{2+}	1.2155		

* in the range of pHs encountered, phosphate is mostly monovalent H_2PO_4^- .

Table 6. Volume weighted 7-year mean concentrations ($\mu\text{eq/L}$) of the major ions for the different processes at the balsam fir forest at the Lake Laflamme catchment (June to October)

Ion	Process				
	INCB	TF	SF	BR	OS
H^+	39.1 (3.7)	39.0 (3.3)	65.6 (11.1)	14.2 (1.3)	0.3 (0.03)
Na^{+*}	7.1 (2.9)	8.2 (2.5)	12.4 (1.8)	24.9 (2.5)	35.4 (1.7)
NH_4^{+*}	12.1 (4.0)	5.8 (1.8)	3.2 (0.7)	2.5 (1.0)	2.7 (1.3)
K^{+*}	2.5 (0.5)	30.0 (4.0)	207.3 (65.0)	8.5 (0.9)	4.6 (0.9)
Ca^{++}	12.8 (2.4)	33.6 (5.2)	143.3 (16.6)	75.6 (11.6)	95.4 (7.5)
Mg^{++}	2.7 (0.4)	11.8 (1.1)	38.7 (5.4)	19.0 (2.2)	36.1 (0.8)
Mn^{++}	0.8 (0.1)	3.5 (0.4)	16.5 (1.7)	3.2 (0.3)	0.7 (0.1)
SO_4^{2-}	45.9 (4.1)	62.7 (5.8)	153.4 (20.9)	100.9 (4.0)	72.7 (2.2)
NO_3^-	11.8 (2.2)	4.5 (1.1)	1.0 (0.2)	55.3 (9.8)	2.1 (1.3)
H_2PO_4^-	0.4 (0.1)	3.8 (1.2)	21.7 (4.1)	0.1 (0.04)	0.2 (0.1)
Cl^-	5.2 (1.6)	9.5 (1.5)	22.4 (2.8)	11.3 (2.1)	8.3 (1.7)
Sum cations(C)	77.0	131.9	487.0	147.8	175.2
Sum basic cations	25.8	87.1	418.2	131.1	172.2
Sum anions(A)	63.3	80.5	198.5	167.6	83.3
A/C	0.8	0.6	0.4	1.1***	0.5
Anion deficit	13.7	51.4	288.5	-19.8	91.8
Lime potential**	2.0	2.2	2.3	2.8	4.6

INCB = incident bulk precipitation; TF = throughfall; SF = stemflow;
BR = water below roots; OS = output stream.

() Values in parentheses are the standard error of the mean and indicate a temporal variation. The anion deficit is an estimate of the organic anions or bicarbonate. * 1983 values missing; ** Lime potential = $\text{pH} - \frac{1}{2}\text{p}(\text{Ca}+\text{Mg})$; *** The cation deficit is related to the charge of the aluminum ions which are not given here.

Table 7. Average flux of ions (kg/ha) for the 1981 to 1987 five-month June to October period at the Lake Laflamme catchment

Ion	Process				
	INCB	TF	SF	BR	OS
H ⁺	0.23	0.18	0.01	0.05	0.003
Na ⁺	0.93	0.89	0.03	1.67	2.50
NH ₄ ⁺	1.34	0.49	0.01	0.15	-
K ⁺	0.57	5.12	0.92	1.10	0.61
Ca ⁺⁺	1.44	3.00	0.34	4.36	6.53
Mg ⁺⁺	0.18	0.63	0.05	0.68	1.47
Mn ⁺⁺	0.12	0.44	0.06	0.32	-
Cl ⁻	0.96	1.47	0.08	1.26	1.27
NO ₃ ²⁻	4.51	1.47	0.01	9.23	0.11
SO ₄ ²⁻	12.35	13.24	0.89	13.44	14.36
H ₂ PO ₄ ⁻	0.22	1.64	0.20	0.03	-

INCB = incident bulk precipitation; TF = throughfall; SF = stemflow;
BR = below the root soil solution; OS = output stream; OS: from Papineau (1983, 1984, 1987); Na⁺, NH₄⁺, K⁺ for 1983 were not tallied.

Table 8. Average flux of ions (eq/ha) for the 1981 to 1987 five-month June to October period at the Lake Laflamme catchment

Ion	Process				
	INCB	(TF+SF)	A-B	BR	OS
	(A)	(B)			
H ⁺	230.0	189.0	-41.0	50.0	3.0
Na ⁺	40.5	40.0	- 0.5	72.7	108.9
NH ₄ ⁺	74.3	27.8	-46.5	8.3	-
K ⁺	14.6	154.7	140.1	28.2	15.6
Ca ⁺⁺	71.9	167.0	95.1	217.7	331.0
Mg ⁺⁺	14.8	55.9	40.7	55.9	120.9
Mn ⁺⁺	4.4	18.2	13.8	11.7	-
Cl ⁻	27.0	43.6	16.6	35.4	35.7
NO ₃ ⁻	72.7	23.9	-48.8	148.8	1.8
SO ₄ ²⁻	257.0	295.0	38.0	280.0	299.0
H ₂ PO ₄ ⁻	2.3	19.4	17.1	0.3	-
Sum cations	450.5	652.6	202.1	444.5	579.4
Sum basic cations	146.2	435.8	289.6	386.2	576.4
Sum anions	359.0	381.9	22.9	464.5	336.5
Cations- Anions	91.5	270.7	179.2	-20.0	242.9

INCB = incident bulk precipitation; TF = throughfall; SF = stemflow;
BR = below the root soil solution; OS = output stream.
OS: from Papineau (1983, 1984, 1987); Na⁺, NH₄⁺, K⁺ for 1983 were not tallied.

Table 9. Lime potential* by year for the different processes of the balsam fir forest at Lake Laflamme ($\mu\text{eq/L}$)

Year	INCB	TF	SF	BR	OS
1981	2.10	2.20	2.20	3.06	-
1982	1.87	2.19	2.29	2.82	4.60
1983	2.04	2.19	2.22	2.84	4.81
1984	1.83	2.27	2.17	2.87	4.55
1985	2.01	2.24	2.13	2.68	4.46
1986	2.11	2.27	2.52	2.83	4.43
1987	2.02	2.28	3.03	2.74	4.74
Average 7 yr	2.00	2.23	2.36	2.83	4.60**

* Lime potential = $\text{pH} - \frac{1}{2}\text{p}(\text{Ca} + \text{Mg})$. Values for the calculations were taken from Tables 10, 12, and 13.

** Six year average.

Table 10. Actual proton production (kmol/ha/5 months) at Lake Laflamme for 1981 to 1987

Ion	Contribution						
	1981	1982	1983	1984	1985	1986	1987
H^+	0.24	0.19	0.18	0.27	0.30	0.22	0.19
NH_4^+	0.06	0.06	-0.11	0.09	0.14	0.10	0.07
NO_3^-	0.01	-0.41	-0.13	-0.01	0.00	0.01	0.07
SO_4^{2-}	0.10	-0.04	-0.03	0.07	-0.07	-0.08	-0.04
H prod.	0.19	0.70	-0.23	0.30	0.51	0.39	0.23

$\text{Hprod} = (\text{H}^+_{\text{in}} - \text{H}^+_{\text{out}}) + (\text{NH}_4^+_{\text{in}} - \text{NH}_4^+_{\text{out}}) - (\text{NO}_3^-_{\text{in}} - \text{NO}_3^-_{\text{out}}) - (\text{SO}_4^{2-}_{\text{in}} - \text{SO}_4^{2-}_{\text{out}})$ (De Vries and Breeuwsma 1987); in = kmol/ha value calculated from Tables 15 and 17 for INCB; out = kmol/ha value calculated from Tables 15 and 17 for BR; wet precipitation values were substituted for INCB 1981-1982 for NH_4^+ and NO_3^- (Barrie et al. 1982, 1984).

Table 11. Volume-weighted mean concentrations ($\mu\text{eq/L}$) of the monovalent cations by year and by process for the balsam fir forest at Lake Laflamme (June to October)

Ion	Year	Process				
		INCB	TF	SF	BR	OS
H^+	1981	33.8	43.3	68.6	9.5	-
	1982	39.6	40.0	70.4	18.7	0.3
	1983	47.7	56.5	81.1	16.0	0.2
	1984	53.1	37.2	99.4	11.1	0.3
	1985	41.8	34.9	87.2	17.7	0.4
	1986	25.9	28.8	36.6	12.5	0.4
	1987	31.6	32.6	15.9	13.7	0.2
Na^+	1981	16.4*	15.3*	17.3	36.1	-
	1982	10.1	12.3	15.4	26.1	39.8
	1983	-	-	-	-	-
	1984	5.5	6.8	8.2	21.6	30.5
	1985	5.6	6.0	7.7	25.1	34.2
	1986	2.7	3.5	9.9	18.1	34.3
	1987	2.4	5.7	15.9	22.2	38.2
NH_4^+	1981	1.7**	0.7**	1.2	3.8	-
	1982	0.3	0.8	4.2	0.2	0.6
	1983	-	-	-	-	-
	1984	18.4	8.1	1.1	0.6	T
	1985	25.4	11.7	4.1	6.6***	6.6
	1986	13.9	5.2	3.9	2.1	2.0
	1987	12.8	8.2	4.8	2.0	1.6
K^+	1981	3.0	39.9	81.1	7.7	-
	1982	0.6	25.6	148.3	6.0	1.9
	1983	-	-	-	-	-
	1984	2.8	43.4	147.6	9.8	3.4
	1985	3.6	25.1	120.5	11.7	4.9
	1986	1.8	19.8	229.6	9.0	5.6
	1987	3.4	23.3	516.9	6.9	7.1

INCB = incident bulk pptn; TF = throughfall; SF = stemflow; BR = below the root soil solution; OS = output stream; T = trace amounts; * Na may be overestimated; ** NH_4 was underestimated because of assimilation by algae, wet only precipitation values were 9.6 and 12.3 $\mu\text{eq/L}$ (Barrie et al. 1982, 1984); *** only four values.

Table 12. Volume-weighted mean concentrations ($\mu\text{eq/L}$) of divalent cations by year and process for the balsam fir forest at Lake Laflamme (June to October)

Ion	Year	Process				
		INCB	TF	SF	BR	OS
Ca^{2+}	1981	16.0	36.2	98.8	96.8	-
	1982	6.8	26.6	143.3	123.6	104.7
	1983	25.4	63.1	150.5	100.2	126.7
	1984	9.7	33.2	164.3	51.8	74.3
	1985	13.7	26.3	104.8	54.6	94.9
	1986	8.8	21.3	115.5	55.9	85.3
	1987	9.3	28.8	226.1	46.3	86.3
Mg^{2+}	1981	2.0	12.0	24.6	20.8	-
	1982	2.0	11.8	40.9	30.0	37.5
	1983	3.0	15.0	30.1	20.9	37.9
	1984	3.0	15.0	48.5	17.1	36.9
	1985	5.0	11.9	31.9	18.2	36.6
	1986	2.1	7.5	29.7	14.1	32.4
	1987	1.8	9.1	65.3	11.6	35.9
Mn^{2+}	1981	-	-	-	-	-
	1982	T	2.2	13.6	-	-
	1983	0.7	4.0	11.0	3.1	0.5
	1984	0.7	4.7	21.1	3.2	0.8
	1985	1.0	4.0	20.5	4.3	0.8
	1986	1.1	3.2	14.5	3.8	0.9
	1987	0.6	2.9	18.2	2.9	0.4

INCB = incident bulk precipitation; TF = throughfall; SF = stemflow; BR = soil solution below the roots; OS = output stream; T = trace amounts. NOTE: Mn^{2+} not measured in 1981.

Table 13. Volume-weighted mean concentrations ($\mu\text{eq/L}$) of the anions by year and process for the balsam fir forest at Lake Laflamme (June to October)

Ion	Year	Process				
		INCB	TF	SF	BR	OS
SO_4^{2-}	1981	50.6	68.4	111.7	109.0	-
	1982	50.8	69.7	195.5	108.9	769
	1983	58.3	78.6	183.0	102.2	681
	1984	56.6	78.9	243.0	112.1	795
	1985	36.5	49.5	107.5	101.6	746
	1986	29.4	37.9	93.6	86.8	652
	1987	39.4	55.8	139.4	85.9	716
NO_3^-	1981	1.7*	1.3	1.6	61.9	-
	1982	6.4*	0.1	1.5	177.1	87
	1983	14.2	3.2	0.8	74.0	11
	1984	18.0	7.1	0.8	34.5	06
	1985	14.7	6.6	0.9	16.3	11
	1986	12.6	5.3	0.8	16.5	13
	1987	15.3	8.2	0.6	6.2	02
H_2PO_4^-	1981	0.5	12.7	19.0	0.1	-
	1982	0.4	3.1	35.5	T	T
	1983	0.3	3.0	15.6	0.01	04
	1984	0.5	2.9	11.2	0.1	T
	1985	0.5	1.6	7.9	0.1	01
	1986	0.1	0.9	31.3	0.1	01
	1987	0.4	2.2	31.2	0.3	03
Cl^-	1981	5.4	10.5	34.1	15.9	-
	1982	13.7	17.4	23.5	23.7	167
	1983	7.0	10.2	13.4	12.5	76
	1984	2.5	8.3	23.8	8.9	59
	1985	3.3	7.0	15.2	6.4	58
	1986	2.0	6.2	18.5	6.8	68
	1987	2.6	6.7	28.6	9.7	70

INCB = incident bulk pptn; TF = throughfall; SF = stemflow; BR = below the root soil solution; OS = output stream; T = trace amounts; * NO_3^- was underestimated because of assimilation by algae, wet only precipitation values were 12.8 and 13.9 $\mu\text{eq/L}$ (Barrie et al. 1982, 1984).

Table 14. Flux of monovalent cations (kg/ha/five months) in a balsam fir forest (June to October)

Ion	Strata	1981	1982	1983	1984	1985	1986	1987
H^+	INCB	0.23	0.19	0.18	0.27	0.30	0.22	0.19
	TF	0.23	0.12	0.21	0.16	0.19	0.21	0.13
	SF	0.01	0.01	0.01	0.01	0.01	0.01	0.01
	BR	0.01	0.05	0.04	0.03	0.07	0.06	0.06
	OS	0.007	0.001	0.002	0.002	0.001	0.002	na
Na^+	INCB	2.24*	1.09*	ms	0.63	0.83	0.50	0.30
	TF	1.96	1.01	ms	0.61	0.68	0.52	0.55
	SF	0.02	0.03	ms	0.02	0.03	0.05	0.04
	BR	0.63	2.00	ms	1.53	2.12	2.27	1.66
	OS	2.59	2.11	2.47	1.91	2.45	3.46	na
NH_4^+	INCB	0.02**	0.02**	ms	1.65	2.96	2.05	1.34
	TF	0.08	T	ms	0.59	1.00	0.67	0.60
	SF	T	0.01	ms	T	0.01	0.01	0.04
	BR	T	0.02	ms	0.11	0.47	0.18	0.12
	OS	ms	ms	ms	ms	ms	ms	ms
K^+	INCB	0.60	0.12	ms	0.54	0.84	0.63	0.71
	TF	7.40	3.54	ms	6.49	4.60	5.07	3.61
	SF	0.17	0.56	ms	0.57	0.75	1.45	2.02
	BR	0.39	0.78	ms	1.09	1.76	1.73	0.84
	OS	0.45	0.48	1.06	0.07	0.64	0.94	na

OS from Papineau (1984, 1985 and 1987); na = not available; ms = missing; INCB = incident bulk precipitation; TF = throughfall; SF = stemflow; BR = below roots; OS = output stream; T = trace amounts.

* Na^+ may be overestimated

** NH_4^+ was underestimated because of assimilation by algae, wet only precipitation values were 1.12 and 1.08 kg/ha (Barrie et al. 1982, 1984).

Table 15. Flux of divalent cations (kg/ha/five months) in a balsam fir forest (June to October)

Ion	Strata	1981	1982	1983	1984	1985	1986	1987
Ca^{2+}	INCB	1.77	0.64	2.19	1.02	1.86	1.53	1.06
	TF	3.76	1.90	4.84	2.69	2.63	2.87	2.34
	SF	0.14	0.28	0.27	0.34	0.34	0.57	0.44
	BR	2.60	6.90	5.00	3.07	4.48	5.40	3.07
	OS	7.43	5.09	6.43	4.91	6.68	8.62	na
Mg^{2+}	INCB	0.09	0.10	0.16	0.13	0.40	0.22	0.12
	TF	0.79	0.51	0.60	0.72	0.70	0.57	0.45
	SF	0.03	0.05	0.03	0.06	0.06	0.07	0.08
	BR	0.34	0.99	0.68	0.65	0.86	0.82	0.45
	OS	1.61	1.09	1.45	1.09	1.44	2.13	na

OS from Papineau (1984, 1985, and 1987); na = not available; INCB = incident bulk precipitation; TF = throughfall; SF = stemflow; BR = below root soil solution; OS = output stream.

Table 16. Flux of anions (kg/ha/five months) in a balsam fir forest (June to October)

Ion	Strata	1981	1982	1983	1984	1985	1986	1987
SO_4^-	INCB	16.52	11.43	10.69	13.66	11.91	11.61	10.60
	TF	17.91	11.89	12.40	15.21	12.09	12.27	10.90
	SF	0.46	0.94	0.76	1.23	0.96	1.09	0.82
	BR	7.37	15.05	13.04	6.64	18.43	19.40	14.15
	OS	17.03	8.52	13.55	11.14	16.02	19.89	na
NO_3^-	INCB	1.92*	1.87*	3.53	5.78	6.32	6.55	5.59
	TF	0.53	0.03	0.74	1.97	2.35	2.46	2.23
	SF	0.01	0.01	0.01	0.01	0.03	0.01	0.01
	BR	3.46	29.81	11.75	6.28	6.42	5.91	0.99
	OS	0.18	0.09	0.09	0.04	0.18	0.09	na
H_2PO_4^-	INCB	0.17	0.16	0.12	0.21	0.62	0.06	0.20
	TF	6.17	1.04	1.16	1.04	0.69	0.58	0.79
	SF	0.08	0.32	0.12	0.10	0.11	0.47	0.23
	BR	T	0.01	0.02	0.03	0.03	0.03	0.07
	OS	ms	ms	ms	ms	ms	ms	ms
CL^-	INCB	1.04	2.27	1.09	0.48	0.74	0.61	0.51
	TF	1.93	2.19	1.37	1.15	1.18	1.45	1.02
	SF	0.06	0.08	0.04	0.09	0.08	0.13	0.10
	BR	1.13	2.13	1.18	0.92	1.02	1.23	1.21
	OS	1.03	1.21	1.42	0.91	1.22	1.82	na

OS from Papineau (1984, 1985, 1987); na = not available; ms = missing; INCB = incident bulk precipitation; TF = throughfall; T = trace amounts; SF = stemflow; BR = below root soil solution; OS = output stream. * NO_3^- was underestimated because of assimilation by algae, wet only precipitation values were 4.25 and 4.12 kg/ha (Barrie et al. 1982, 1984).

