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Seasonal and spatial patterns of S, Ca, and N dynamics of a Northern Hardwood forest ecosystem

MYRON J. MITCHELL,[1] MARIANNE K. BURKE[2] &
JAMES P. SHEPARD[3]
[1] *State University of New York, College of Environmental Science and Forestry, Syracuse, New York 13210, USA;* [2] *Horn Point Environmental Laboratory, P.O. Box 775, Cambridge, Maryland 21613, USA;* [3] *NCASI, 34134 SW 24th Ave., P.O. Box 14483, Gainesville, Florida 32606, USA*

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Abstract. Seasonal dynamics of S, Ca and N were examined at the Huntington Forest, a northern hardwood ecosystem in the central Adirondacks of New York for a period of 34 months (1985–1988). Solute concentrations and fluxes in bulk precipitation, throughfall (TF) and leachates from the forest floor, E horizon and B horizon were quantified. Both above and below-ground elemental fluxes mediated by vegetation (e.g. uptake, litter inputs, and fine roots production) were also determined. The roles of abiotic and biotic processes were ascertained based on both changes in solute concentrations through the strata of the ecosystem as well as differences between dormant and growing seasons. Concentrations of SO_4^{2-}, NO_3^-, NH_4^+ and Ca^{2+} were greater in TF than precipitation. Forest floor leachates had greater concentrations of SO_4^{2-}, $NO_3^- + NH_4^+$ and Ca^{2+} (9, 6 and 77 μeq L^{-1}, respectively) than TF. There were differences in concentrations of ions in leachates from the forest floor between the dormant and growing seasons presumably due to vegetation uptake and microbial immobilization. Concentrations and fluxes of NO_3^- and NH_4^+ were greatest in early spring followed by a rapid decline which coincided with a demand for N by vegetation in late spring. Vegetation uptake (44.7 kg N ha^{-1} yr^{-1}) could account for the low leaching rates of NO_3^-. Within the mineral soil, changes with soil depth and the absence of seasonal patterns suggest that cation exchange (Ca^{2+}) or anion sorption (SO_4^{2-}) are primarily responsible for regulating solute concentrations. The increase in SO_4^{2-} concentration after leachates passed through the mineral soil may be attributed to desorption of sulfate that was adsorbed during an earlier period when SO_4^{2-} concentrations would have been greater due to elevated S inputs.

Introduction

Over the past decade we have investigated the biogeochemistry of a northern hardwood forest, Huntington Forest (HF), located in the central

Adirondack Mountains of New York. We have recently published annual elemental budgets for this site (Foster et al. 1992; Mitchell et al. 1992b) including comparisons with other forest ecosystems that were part of the Integrated Forest Study (Johnson and Linderg 1992). In this paper, we extend these analyses by assessing how temporal patterns in biogeochemical flux can be used to assess the relative importance of biotic and abiotic processes. Such determinations show how nutrient demands for both above and below-ground production vary during the year, affecting elemental dynamics. Episodic events such as spring snow melt can be particularly important in affecting surface water chemistry (Driscoll and Schafran 1984; Galloway et al. 1987; Wigington et al. 1990). Thus, various factors regulating temporal changes in biogeochemistry need to be ascertained.

We focus on dynamics of three major elements (sulfur, calcium and nitrogen) and their respective ions (SO_4^{2-}, Ca^{2+}, NO_3^-, and NH_4^+). Particularly, we quantify the role of abiotic and biotic processes in regulating the solute chemistry of precipitation, throughfall (TF) and leachates from the forest floor, E horizon and B horizon.

In those areas in North America that have received elevated inputs of acidic deposition, SO_4^{2-} is the dominant anion in precipitation (Mollitor and Raynal 1983; Galloway et al. 1984). Extensive analyses of the role of SO_4^{2-} in forest ecosystems have focused on its effect in altering the flux of cations, including nutrients such as Ca^{2+}, Mg^{2+} and K^+ as well as toxic monomeric Al^{+3} (Mitchell et al. 1992a,c; Johnson et al. 1982). Sulfate is the dominant mineral anion at HF. It contributes 62% of total anionic equivalents in precipitation (collected on an event basis) and 87% in the leachate from B horizon soils (Shepard et al. 1989).

The dynamics of N are of particular importance since it has historically been considered the limiting nutrient for many forest ecosystems (Waring and Schlesinger 1985), but there has recently been increasing concern about N saturation in some forest ecosystems, especially those with elevated inputs of anthropogenic N (Aber et al. 1989, 1991; Malanchuk and Nilsson 1989; Tamm 1991). The characterization of N dynamics at HF is important since NO_3^- and NH_4^+ are important chemical constituents of precipitation (33 and 23%, respectively of anions and cations; Shepard et al. 1989).

At HF, Ca is the dominant base cation (compared to Mg, K and Na) in the vegetation, forest floor and exchangeable pool in the mineral soil (78, 67 and 81% on an equivalent basis, respectively; Foster et al. 1992). The respective contributions of Ca^{2+} to total cationic charge increases from 7% in precipitation to 58% for leachate from the B horizon (Shepard et al. 1989).

In the present paper we will focus on S, Ca and N by addressing three objectives: 1) comparison of seasonal patterns of solute chemistry in precipitation, TF, forest floor and mineral soil; 2) quantification of elemental fluxes in litter inputs and fine root production, focusing on temporal changes in the use of these elements by vegetation; and 3) analysis of the spatial and temporal patterns in solute chemistry at this site to ascertain the relative importances of biotic versus abiotic processes to biogeochemistry.

Site description of Huntington Forest

The Huntington Forest (43°59′N, 74°14′W) is located in western Essex County and eastern Hamilton County within the Adirondack State Park of New York. The regional climate is cool, moist and continental. The mean annual temperature is 4.4 °C, with a January mean of −10.2 °C and a July mean of 17.4 °C; total annual precipitation averages 1010 mm (Shepard et al. 1989).

The mixed northern hardwood site, located at an elevation of 530 m, is typical of much of the Adirondack region. It was heavily cut about 75 years ago and maximum age of overstory trees is about 100 years. There are 643 stems ha^{-1} with a basal area of 27.5 m^{2} ha^{-1} dominated by sugar maple (*Acer saccharum* Marsh.), red maple (*Acer rubrum* L.), American Beech (*Fagus grandifolia* Ehrh.) and yellow birch (*Betula alleghaniensis* Britton) (41, 10, 33 and 13% of total basal area, respectively). Other tree species, including black cherry (*Prunus serotina* Ehrh.) and red spruce (*Picea rubens* Sarg.), constitute the remaining 3% of the basal area. Average DBH was 18.2 cm and the mean height of codominants was 24.2 m.

The soil is a coarse-loamy, mixed frigid, Typic Haplorthod in the Becket-Mundal association. Similar soils are found throughout the Adirondack Region and in other areas of the Northeast United States (Somers 1986). The soil overlies a bedrock of gneiss, is shallow (<1 m depth) and contains a hardpan derived from the parent material of glacial till. There are considerable coarse fragments (5–32%) and high organic concentrations (2.10–20.8 mol C kg^{-1}) in the mineral horizons (Mitchell et al. 1992b).

Methods

Details on experimental design, sampling methodology and chemical analyses have been given previously (Shepard et al. 1989, 1990; Foster et al. 1992; and Mitchell et al. 1992b). Bulk precipitation was collected biweekly with paired funnels during the snow-free season and at least monthly with buckets at other periods. The same sampling schedule and collectors were used for the nine TF collectors. Soil solution was obtained from both tension (ceramic plate and fritted glass maintained at 10 kPa) and plastic zero-tension lysimeters located in six soil pits, the contents of which were also used for characterizing the solid phase chemistry of the forest floor and mineral soil. In each pit, there were two replicate lysimeters for each depth sampled (forest floor, E horizon and B horizon at 0, 8, and 58 cm from the bottom of the forest floor) for a total of 12 lysimeters per depth. Solutions were stored in the dark at 1 °C until analyzed by atomic-absorption spectroscopy (Ca^{2+}), ion chromatograph (SO_4^{2-} and NO_3^-) or Wescan analyzer (NH_4^+).

Above-ground biomass was estimated using either published equations or by developing formulations specific for the site. Nutrient concentrations were measured on subsamples of the various vegetation components taken in the late summer for three years. Total S was determined by a Leco-SC 132 analyzer, total N by macro-Kjeldahl with manual analysis and CA by atomic-absorption spectroscopy after acid digestion. Net element requirements (annual elemental increment in bole and branch + current foliage production) were calculated after Morrison (1974). Uptake was defined as annual elemental increment in bole and branch plus the sum of annual loss by litterfall, fine root turnover, and TF minus precipitation inputs. Litter samples were taken monthly from 15 (0.25-m^2) litter traps during the period without snow cover; a single sampling was made after snowmelt. For details on determinations of biomass, vegetation elemental fluxes and ecosystem contents, refer to Foster et al. (1992) and Mitchell et al. (1992b).

Monthly fine root production was calculated using monthly fine root elongation and production estimates of 1.5 t ha^{-1} yr^{-1} from Burke and Raynal (1992). The method of estimating fine root production employed the phenology of fine root elongation to determine the biomass maximum and minimum sampling dates and statistics to identify significant differences in biomass as described in Vogt et al. (1986). This approach generally produces smaller estimates of fine root production than previously used methods because it minimizes random error and potential for overestimation that is inherent in the maximum minus minimum method (Singh et al. 1984, Lauenroth et al. 1986, Kurz and Kimmins 1987). In the present study, monthly rates of fine root production were calculated by assuming each increment of fine root length represented an equal fraction of the annual fine root biomass production. Utilization of N, S and Ca for fine root production was estimated by multiplying monthly fine root production by the mean elemental concentrations of fine roots.

The present study began on December 1, 1985 and terminated on September 31, 1988. Some parameters, such as TF, were measured for the entire period while other data, such as fine root production, were available for only a portion of the study. The growing season was defined from May 1 to September 31, which approximates the period of budbreak to leaf abscission for the overstory vegetation; this designation was also used in other studies at this site (i.e. Shepard et al. 1989).

Water fluxes were calculated using the Hubbard Brook hydrological model BROOK (Feder and Lash 1978). The characteristics of this site are quite similar to those at the lower elevations at Hubbard Brook making this model especially applicable (David et al. 1987). Independent soil water content estimates with a neutron probe (Scott 1987) were very similar to estimates derived from the model (T. J. Scott, unpublished data).

Mean concentrations shown in figures are for all samples collected for each month and are accompanied by standard error bars. The number of samples collected varied among strata due to number of sampling devices and, in the case of lysimeters, sampling effectiveness. For each month the maximum number of collections for precipitation, TF, and leachates from the forest floor, E horizon and B horizon were (8, 36, 22, 20 and 24 respectively). Differences in concentrations among ecosystem strata and between growing and dormant seasons were ascertained by ANOVA, separating means ($\alpha = 0.05$) by Tukey's Honestly Significant Difference (HSD) multiple-comparison procedure (SAS Institute 1985). Concentrations were not volume weighted. Statistical comparisons will focus on concentrations and not fluxes, since error variances were not available for the simulated soil water flux estimates. Monthly fluxes were calculated as the product of mean monthly concentration values and calculated water fluxes.

Results and discussion

Temperature and moisture

Temperature regimes were almost identical during the growing seasons of 1986 and 1987 (mean above-ground temperature of 14.2 and 14.7 °C, respectively), but 1988 was warmer (16.1 °C) (unpublished data). Seasonality was reflected in soil temperature which was highest in mid-summer (15 °C at 10 cm depth) and lowest in winter, but always above freezing due to an extensive snow cover. Soil moisture tension increased during the growing season of 1986–1987, but it was never greater than 25 kPa (Burke 1988). A hydrological study during 1983–1985 also found that soil water tension was never greater than 25 kPa and 60 kPa in the 10–20 cm and 50 cm depths, respectively (Scott 1987). Since the soil water tension was typically less than 100 kPa and hydraulic gradients were near unity, gravitational water dominates the soil moisture at this site. The relatively high moisture contents and low soil water tension indicate that transpiration requirements of vegetation were met during the present study.

Precipitation showed monthly variation, but there was no regular seasonal pattern with inputs being well distributed through-out the year (Fig. 1). These results concur with those of Lin (1991) who found no consistent seasonal variation in precipitation from 1978–1989 at HF. Water flux and moisture contents of the forest floor and mineral soil were greatest during the spring snow melt (e.g. March 1986) and lowest in the summer due to evapotranspiration losses (Fig. 1). The importance of the spring snow melt periods in influencing the chemistry of surface waters in the Adirondack region has been emphasized previously (Rascher et al. 1987; Shepard et al. 1990; Driscoll et al. 1989).

Vegetation dynamics (fine roots production and litter inputs)

The vegetation phenology reflected temperature seasonality of this site. Buds began to swell during the second week of April for both 1986 and 1987, leaves were one-half expanded on May 11 and May 16, and the canopy had full closure by May 21 and May 26 for the two years, respectively. Leaves began to change color by August 31 and August 22, the leaves were half changed by September and 13 and September 23, and leaves had fallen by October 11 and October 16 for the two years, respectively. The latter process resulted in a pulse of litter inputs in the autumn (Sept.–Oct.) (Fig. 2). Fine root production was highest during the summer (June–Aug.) with almost no production occurring during the dormant season (Nov.–April). Thus there was a strong correlation (r = 0.871, $N = 21$, $P < 0.01$) between soil temperature at 10 cm and fine root production.

The estimate of fine root production of 1.5 t ha^{-1} yr^{-1} (Burke and Raynal 1992) was similar to the estimate for another deciduous forest in Missouri (Joslin and Henderson 1987), but lower than estimates given for other deciduous forests (McClaugherty et al. 1982). Although actual differences in fine root production among forests may be expected, variation in published values in often attributed to the methods, which can

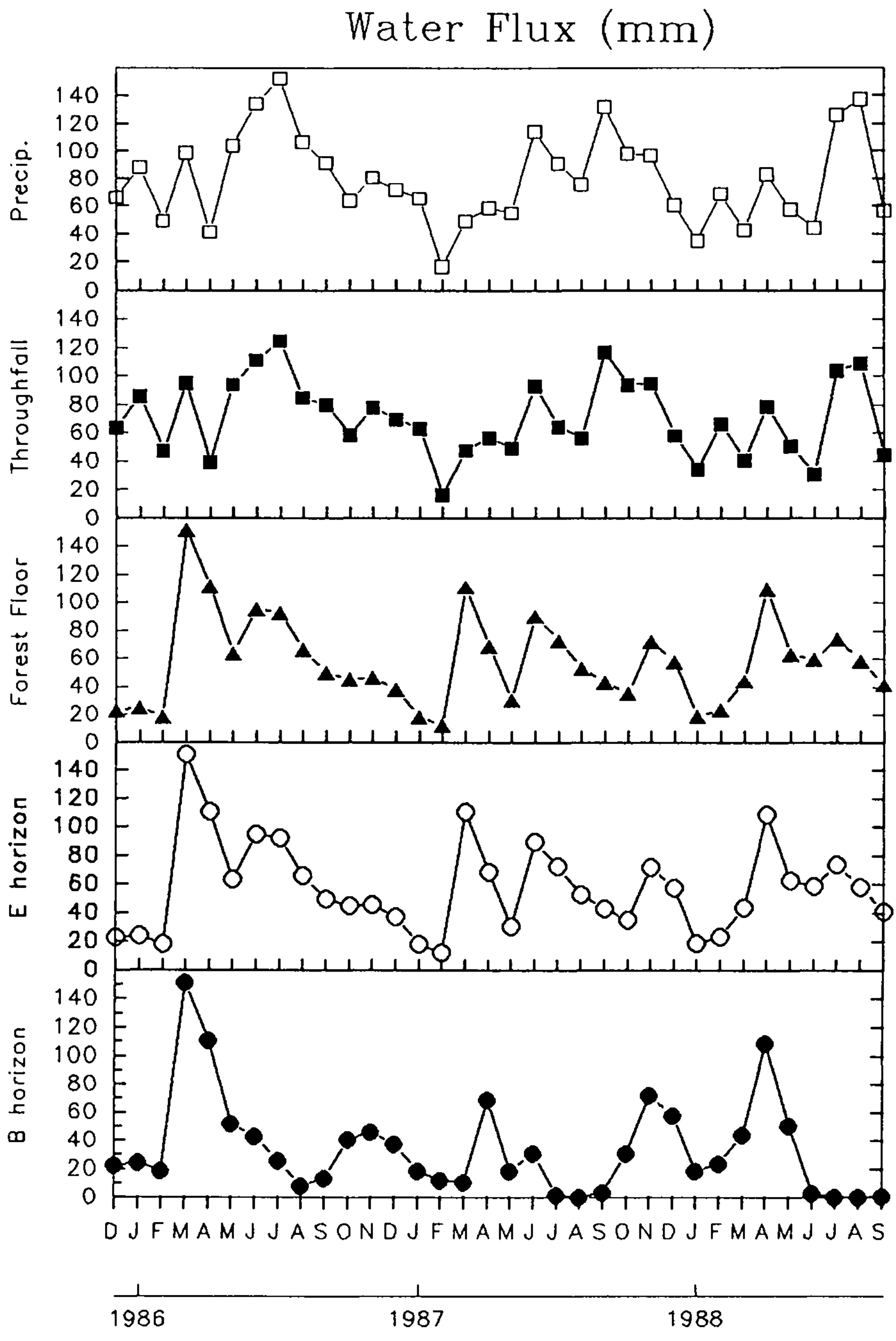


Fig. 1. Hydrology at hardwood site at Huntington Forest in Adirondack Mountains of New York, U.S.A.

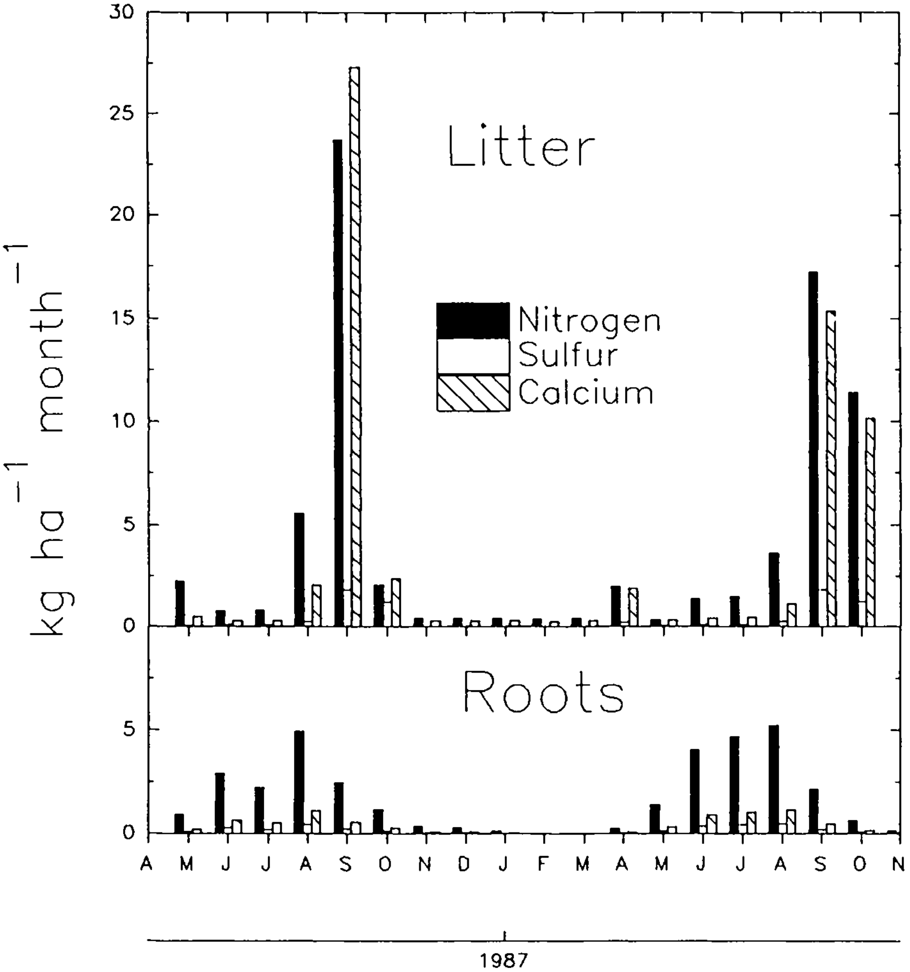


Fig. 2. Inputs from above-ground litter inputs and elemental needs for fine root production for N, S, Ca at Huntington Forest.

result in three fold-differences in estimates at the same site (McClaugherty et al. 1982; Nadelhoffer and Raich 1992).

Sulfur

Sulfate concentration (Table 1, Fig. 3) showed significant increases with passage of solution through all ecosystem strata. The average concentration increase from bulk precipitation to TF was by 20 μeq L^{-1}. This increase was likely due to wash-off of dry deposit S, which constitutes about 26% of the total S deposition at HF (Shepard et al. 1989). At a wide range of sites, there is little leaching of SO_4^{2-} from foliage, and hence SO_4^{2-} inputs from TF are useful predictors of total atmospheric deposition of this element (Lindberg and Garten 1988). There was a further increase in SO_4^{2-} concentration after passage through the O and E horizons (9 and 16 μeq L^{-1}, respectively), which can be attributed to the mineralization of organic S and subsequent release of SO_4^{2-} into solution. Much of this organic S enters the forest floor via litter inputs in the autumn of each year (Fig. 2). It has been previously estimated that mineralization of the organic S in the forest floor (14.2 kg ha^{-1} y^{-1}) exceeds wet atmospheric inputs of S at this site (David et al. 1987). There was a further increase of 37 μeq L^{-1} after the leachate passed through the B horizon. This latter increase could be due to a combination of water loss via evapotranspiration, mineralization and/or desorption. It is unlikely that weathering reactions would contribute to this increase, because no S bearing minerals have been found at this site (April and Newton 1992).

An increase in the concentration of SO_4^{2-} in B horizon leachates may be attributed to desorption of previously stored sulfate since SO_4^{2-} concentrations in precipitation of the northeastern U.S. have been declining (Driscoll and Van Dreason 1992; Likens et al. 1984, 1990). When sulfate concentrations decrease, previously adsorbed sulfate may be released (Harrison et al. 1989).

The concentration of SO_4^{2-} was 22 μeq L^{-1} lower ($P < 0.05$) during the growing season than the dormant season within the E horizon (Table 1) which may be attributed to greater microbial immobilization and plant uptake during the growing season. In contrast, the concentrations of B horizon solutions were almost identical (non-statistical difference of only 1 μeq L^{-1}). Although the flux of water had a major influence on sulfate flux (Fig. 4), it did not have marked affect on SO_4^{2-} concentration in B horizon leachates; the concentration of this ion was remarkably constant (Fig. 3) and showed no correlation ($n = 27$, $r = 0.22$) with water movement (Fig. 1). Sulfate concentrations in Arbutus Lake, which is adjacent to the study site (Mitchell et al. unpublished data), as well as in other lakes in the Adirondack region, show little seasonal variation (Galloway et al. 1980; Driscoll et al. 1989). This lack of variation suggests that sulfate sorption may be regulating the short term seasonal dynamics for solutions exiting the rooting zones.

Calcium

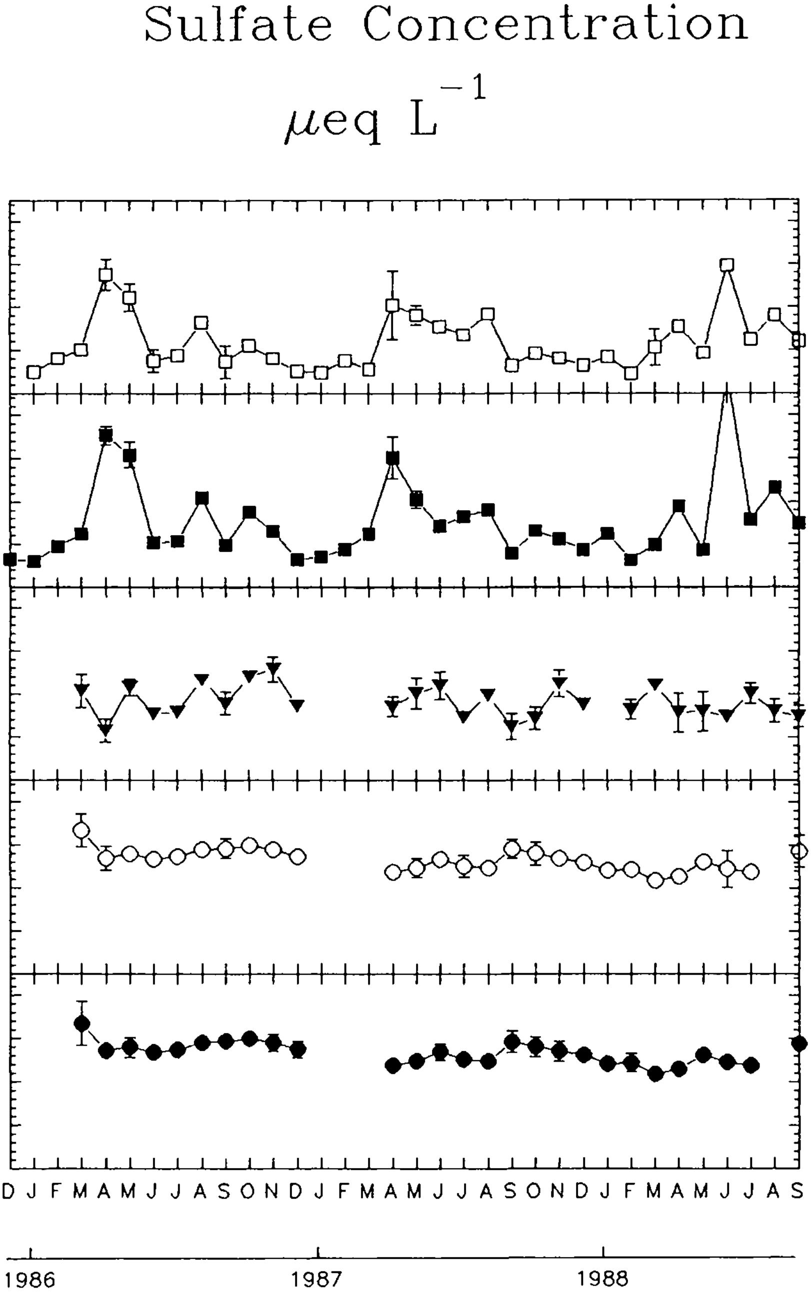
Calcium showed a pattern similar to that of SO_4^{2-} with increasing ($P <$

Table 1. Solute concentrations at Huntington Forest (μeq L^{-1})

Strata		SO_4^{2-}			NO_3^-		
	Dormant	Growing	Annual	Dormant	Growing	Annual	Dormant
Precip	58 ± 7(61)	74 ± 6(32)	63 ± 5bcde	44 ± 3(31)*	25 ± 3(31)*	38 ± 3c	15 ± 2(50)*
TF	81 ± 5(253)	88 ± 5(113)	83 ± 4ade	67 ± 3(254)*	30 ± 2(113)*	55 ± 3cde	16 ± 1(193)*
FF	93 ± 4(101)	90 ± 3(115)	92 ± 3ae	79 ± 9(99)	77 ± 9(114)	78 ± 6abde	8 ± 1(81)
E	111 ± 3(76)*	89 ± 3(93)*	99 ± 2abe	44 ± 9(73)	34 ± 7(81)	39 ± 5bce	3 ± 1(65)
B	136 ± 3(129)	137 ± 3(111)	136 ± 2abcd	22 ± 3(114)*	13 ± 3(106)*	18 ± 2bcd	1 ± 0(108)

Strata		NH_4^+			Ca^{2+}	
	Dormant	Growing	Annual	Dormant	Growing	Annual
Precip	58 ± 7(61)	34 ± 8(27)*	22 ± 3	26 ± 7(56)	36 ± 6(34)	30 ± 5bcde
TF	81 ± 5(253)	46 ± 16(98)*	26 ± 6cde	60 ± 6(227)	73 ± 5(119)	64 ± 4acd
FF	93 ± 4(101)	10 ± 1(81)	9 ± 1b	126 ± 7(87)*	152 ± b(113)*	141 ± 4abde
E	111 ± 3(76)*	4 ± (59)	4 ± 1b	101 ± 8(61)	119 ± 7(90)	112 ± 5abce
B	136 ± 3(129)	1 ± 0(93)	1 ± 0b	73 ± 2(109)	77 ± 2(115)	75 ± 1acd

Mean ± standard error (N) [For annual values *N* is the sum of the dormant and growing season values]. Significant ($p \leqslant 0.05$) differences determined by ANOVA with mean separation by Tukey's Honestly Significant Difference (HSD). Differences between dormant and growing seasons for an ion within an ecosystem strata are designated with "*". Differences in annual concentrations among strata are designated as a, b, c, d and e, as different from precipitation (Precip.) throughfall (TF), forest floor (FF), E horizon (E) and B horizon (B), respectively.



Sulfate Concentration

$\mu eq\ L^{-1}$

Fig. 3. Concentration of SO_4^{2-} in solutes from ecosystem strata at Huntington Forest (vertical bars ar standard errors).

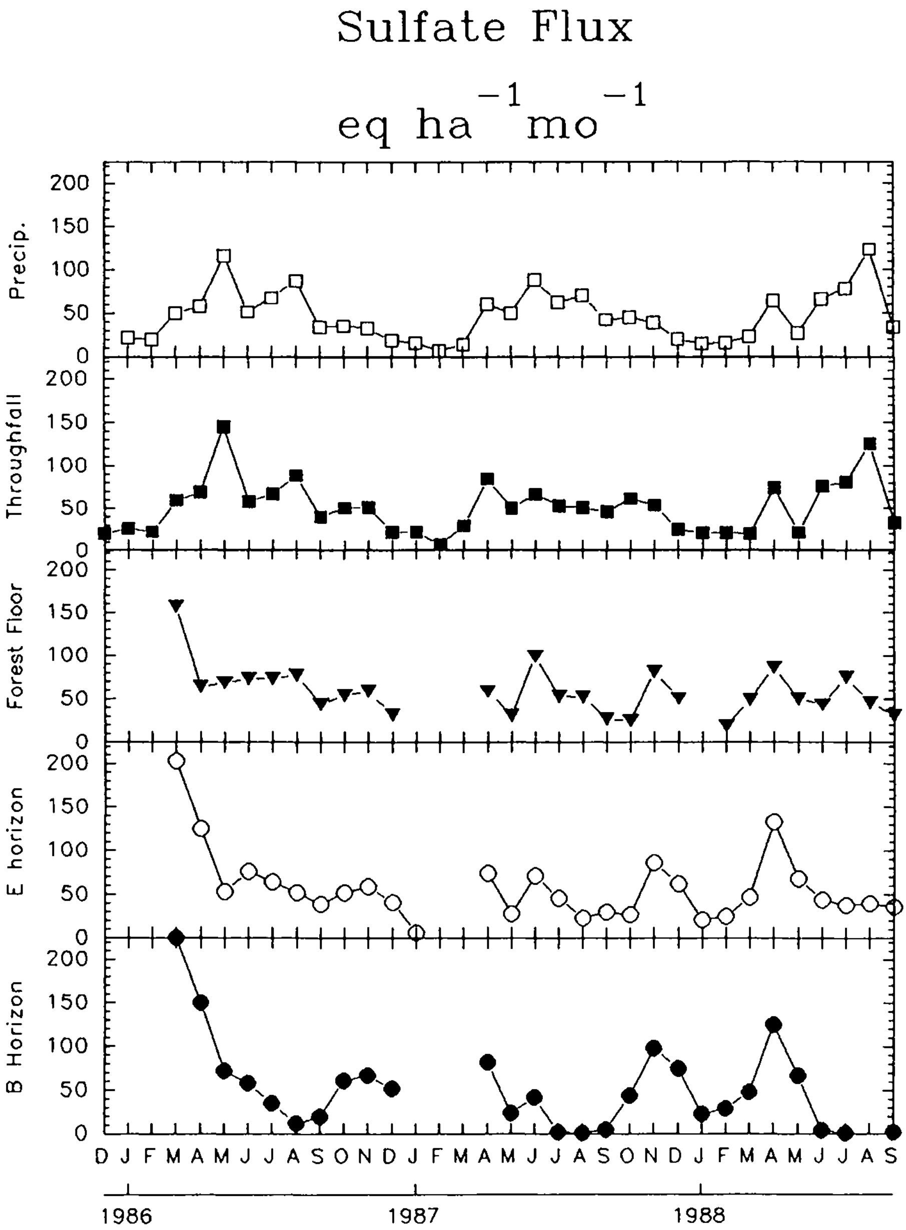


Fig. 4. Flux of SO_4^{2-} through ecosystem strata at Huntington Forest.

0.05) concentrations during passage of precipitation through the canopy and the forest floor (Table 1, Fig. 5). There was also a significant ($P <$ 0.01) correlation between Ca^{2+} and SO_4^{2-} in precipitation ($r = 0.842$, $n =$

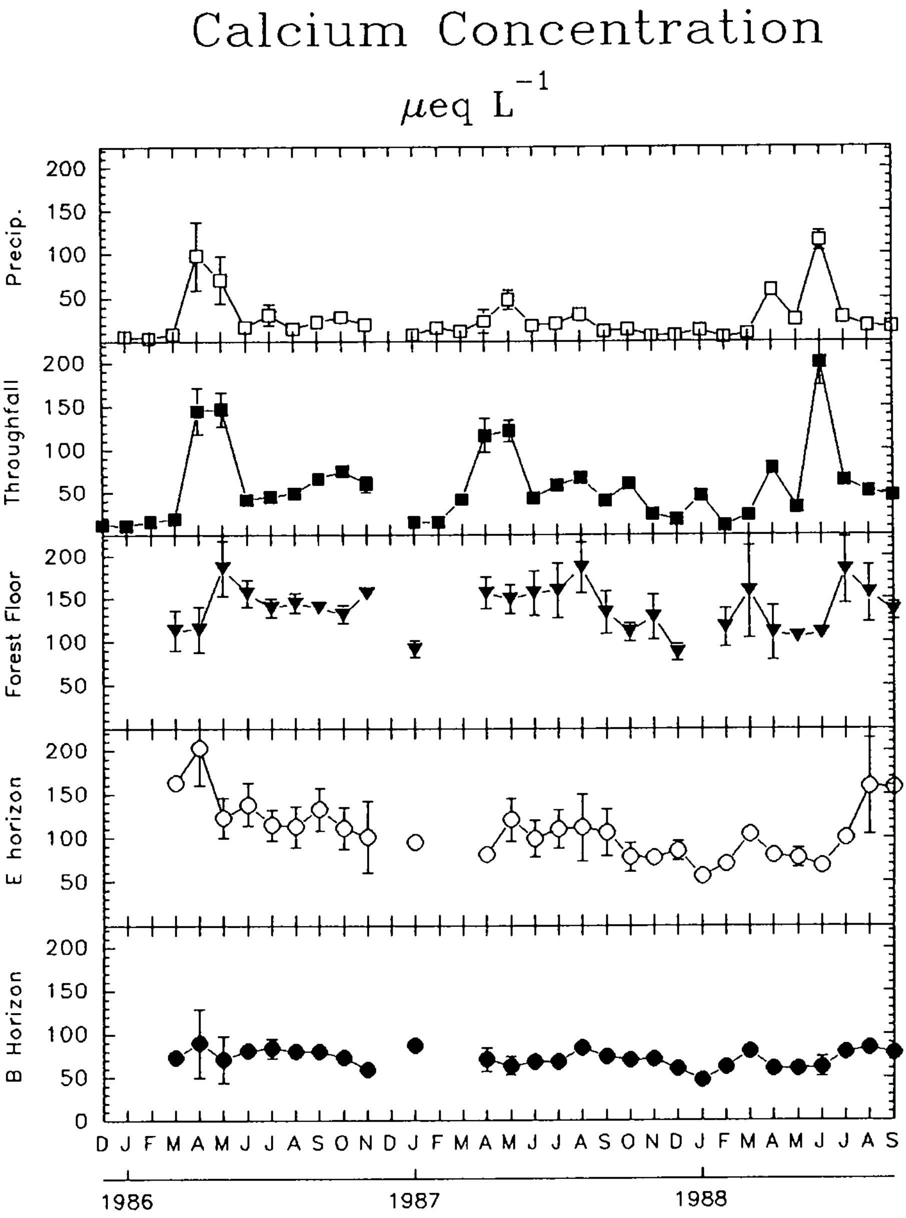


Fig. 5. Concentration of Ca^{2+} in solutes from ecosystem strata at Huntington Forest (vertical bars are standard errors).

31) and TF ($r = 0.930$, $n = 32$). The increase of Ca^{2+} (34 μeq L^{-1}) after precipitation passes through the canopy is attributed to both dry deposition as well as leaching from the canopy (Shepard et al. 1989) with the

former contributing about 58% of the total atmospheric deposition. The importance of the leaf canopy may be reflected in the trend of greater concentration of Ca^{2+} (13 μeq L^{-1}) in TF from the growing versus dormant seasons although this difference was not statistically significant ($P > 0.05$). The most marked change in Ca^{2+} concentration occurs in late spring (May) (Fig. 5), which coincided with the maximum period of leaf development.

There was a large increase in Ca^{2+} ($P \leqslant 0.05$) (77 μeq L^{-1}) as the solution passes through the forest floor (Fig. 5), likely due to the mineralization of Ca from organic matter derived from leaf litter (Fig. 2). The Oi horizon (0–1 cm) is enriched in Ca (11,200 mg/kg) which decreases to 6,861 and 4,609 mg/kg in the Oe (1–4 cm) and Oa (4–5 cm) horizons, respectively (Foster et al. 1992; Johnson and Lindberg 1992). The high Ca values are a reflection of the elevated concentrations of this element in hardwood foliage (Cole and Rapp 1981).

Mean concentration of Ca^{2+} decreases by 29 μeq L^{-1} after passage through E horizon with a further decrease of 37 μeq L^{-1} after passage through the B horizon. The difference in flux from the forest floor to the B horizon equals 9.6 kg ha^{-1} yr^{-1} compared to vegetation uptake of 45.5 (Foster et al. 1992) or 48.8 kg ha^{-1} yr^{-1} (without and with fine roots, respectively). The relatively small contribution of fine roots to Ca^{2+} flux can be explained in part by the turnover rate. The concentration of Ca in fine roots is similar to that of other northern hardwood forests (Safford 1974), but are less than one-half the concentration found for other forests where data on fine root turnover are available (Joslin and Henderson 1987). Nevertheless, most of this decrease in Ca^{2+} was due to uptake by the vegetation and subsequent recycling by canopy leaching and litter inputs. The importance of vegetation and litter inputs with respect to Ca^{2+} has also been noted for hardwood forests at Hubbard Brook in New Hampshire (Likens et al. 1977) and Walker Branch in Tennessee (Johnson and Todd 1990).

The role of forest floor microbes at HF in affecting Ca^{2+} was reflected in the greater ($P \leqslant 0.05$) concentration (26 μeq L^{-1}) during the growing season which suggests that net microbial mineralization was greater during this period. In contrast, the concentrations of Ca^{2+} in the B horizon were almost identical between the growing and dormant seasons (non-significant difference of only 4 μeq L^{-1}). This lack of seasonality is directly linked to the constancy of SO_4^{2-} concentrations in mineral soil leachates, since the leaching of this anion regulates the fluxes of cations at HF (Foster et al. 1992).

Fluxes of Ca^{2+} generally reflect water movement at the site. Lowest calcium fluxes (Fig. 6) in the soil coincided with the period of limited water movement in the summer (Fig. 1) compared to the spring and fall period. The high fluxes especially notable in the E horizon of the spring of

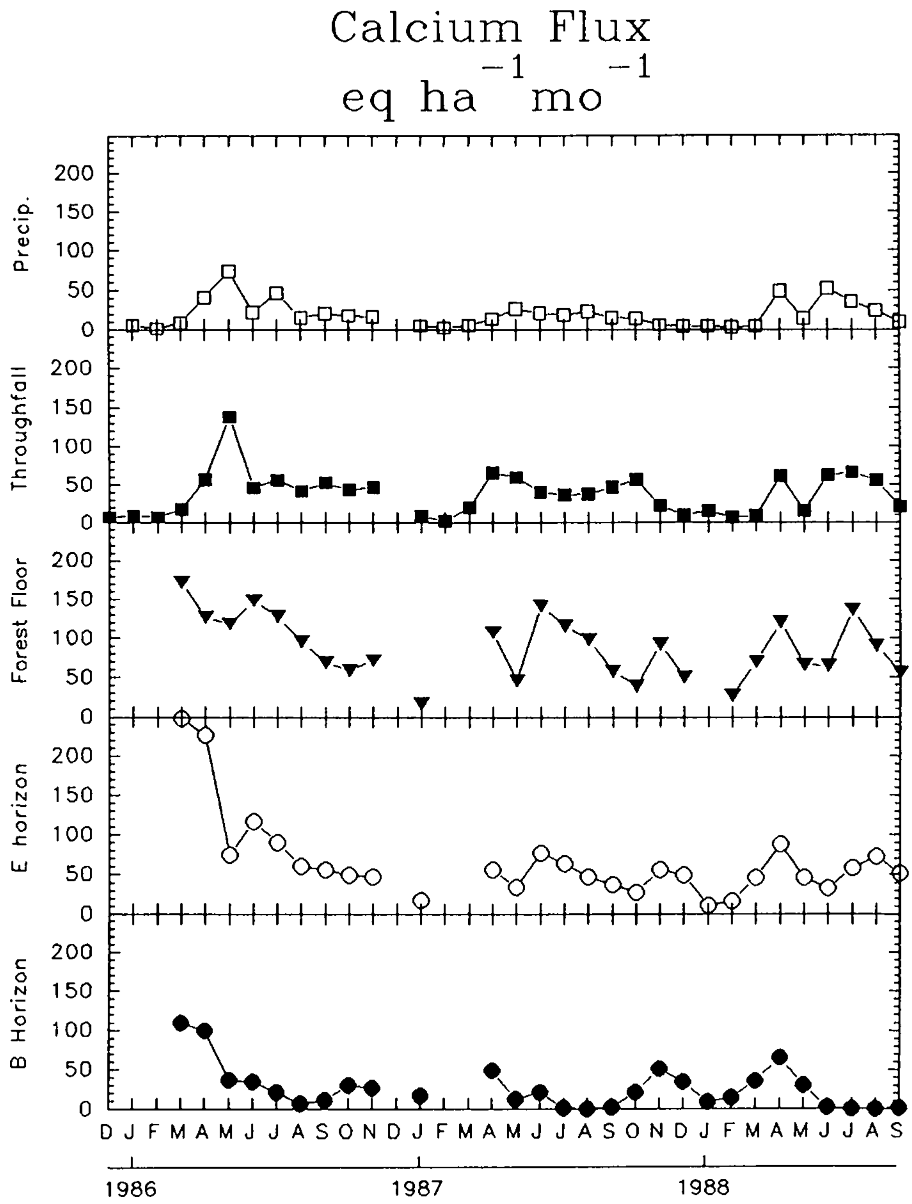


Fig. 6. Flux of Ca^{2+} through ecosystem strata at Huntington Forest.

1986 were mostly attributed to high concentrations of Ca^{2+}, likely caused by soil disturbance associated with lysimeter installation (Shepard et al. 1990).

Nitrogen

Nitrate was the dominant N ion in solutes from all strata (Table 1) although for some months NH_4^+ exceeded NO_3^- in precipitation (Figs. 7 and 8). Seasonal variation of NO_3^- in the bulk precipitation was irregular, due to the combination of changes in the inputs as well as possible alteration of N constituents in samples, especially in warmer months. The latter factor may have contributed to lower ($P < 0.05$) NO_3^- (19 μeq L^{-1}), but higher ($P < 0.05$) NH_4^+ (19 μeq L^{-1}) concentrations in the growing versus dormant season. Such variation has been noted in other studies when bulk precipitation samples were compared with other collection techniques (e.g. Lindberg et al. 1986).

There was a general trend for NO_3^- concentration to increase from precipitation to TF, but the differences were not statistically different, which may be attributed to the high variability of this constituent (e.g. in TF, C.V. = 93%). For NO_3^- and NH_4^+, dry deposition accounts for 55 and 12% respectively of the total deposition of these ions at this site (Shepard et al. 1989).

When TF entered the forest floor there was an increase ($P \leqslant 0.05$) in NO_3^- (23 μeq L^{-1}) and decrease ($P \leqslant 0.05$) in NH_4^+ (17 μeq L^{-1}). The increase in NO_3^- can be attributed to mineralization of organic N to NH_4^+ and its subsequent nitrification. Laboratory incubation studies at 20 °C have found net N mineralization rates of 265 mg N kg^{-1} forest floor $month^{-1}$ at HF (Mitchell et al. 1992b). These values are less than the laboratory mineralization rates (625 mg N kg^{-1} forest floor four $weeks^{-1}$) reported by Vitousek et al. (1982) for a northern hardwood site at Mt. Moosilauke in New Hampshire, which had the highest N mineralization rates of 13 sites across the U.S.A. At HF, a substantial portion of the N in the forest floor is derived from litter inputs which contribute 44.8 kg N ha^{-1} yr^{-1} (Mitchell et al. 1992b) of which the major portion enters the forest floor in the autumn (Fig. 2). The decrease in NH_4^+ concentration is likely attributed to its affinity for exchange complexes and potential fixation in clays since the dominant clay at HF is vermiculite (90% of 2μm fraction, April and Newton 1992) which has a very high affinity for NH_4^+ (Nommik and Vahtras 1982); selective uptake by the biota of this cation (Paul and Clark 1989) and nitrification may also have contributed to the decrease.

There was a decrease ($P < 0.05$) in NO_3^- concentration (39 μeq L^{-1})

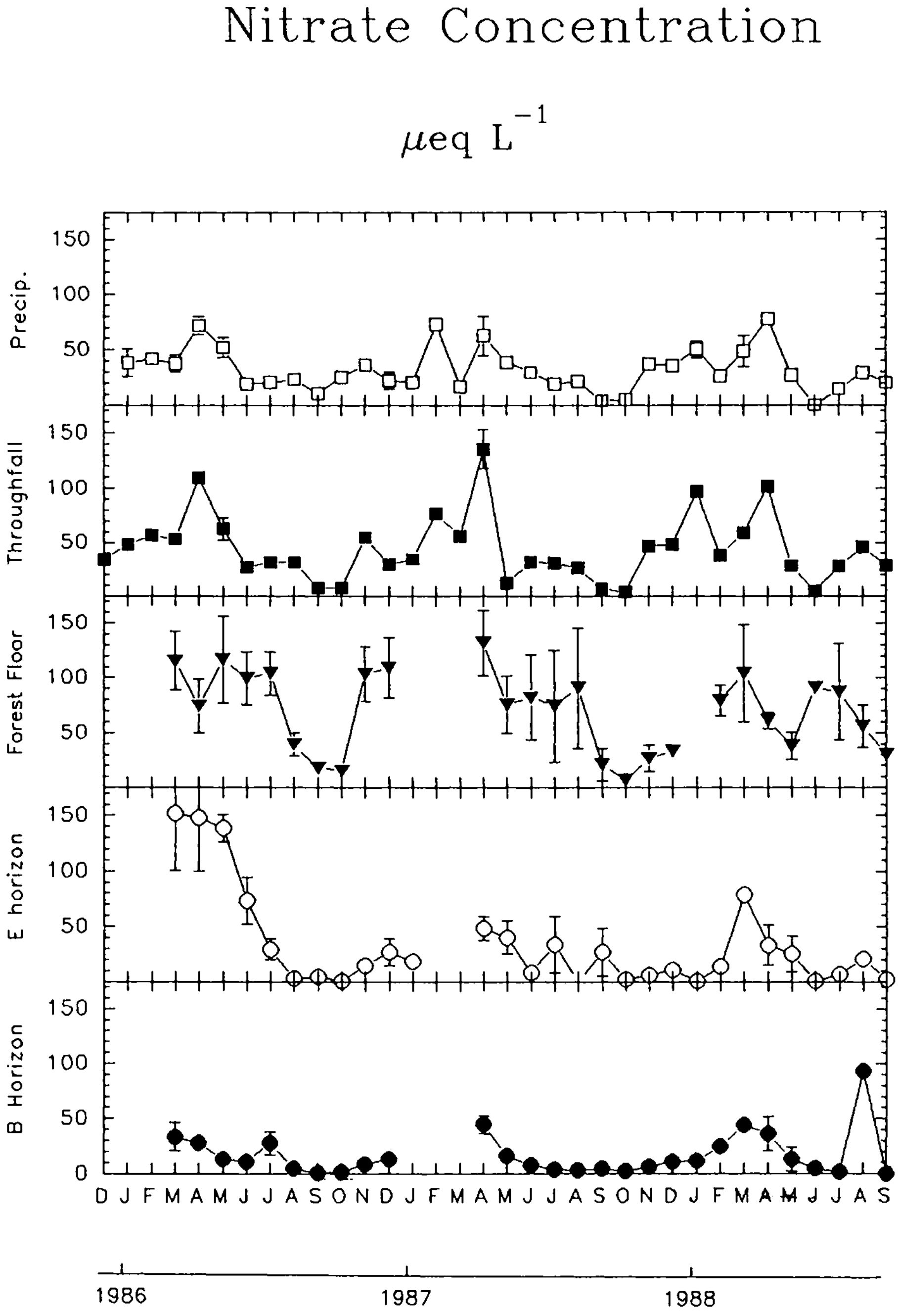


Fig. 7. Concentration of NO_3^- in solutes from ecosystem strata at Huntington Forest (vertical bars are standard errors).

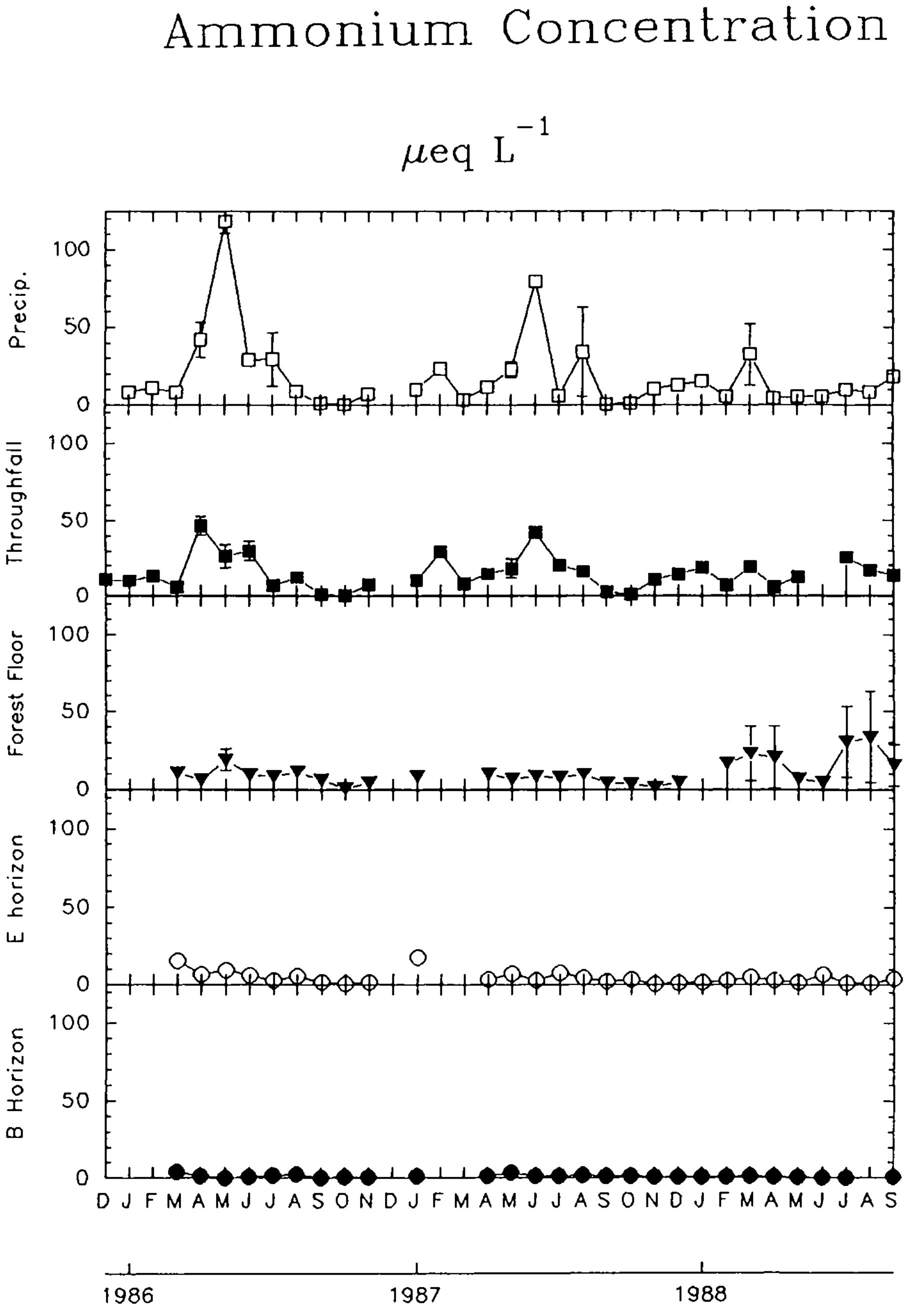


Fig. 8. Concentration of NH_4^+ in solutes from ecosystem strata at Huntington Forest (vertical bars are standard errors).

after leachate passed through the E horizon with an additional decrease of 21 μeq L^{-1} after passage through the B horizon (Table 1). The high concentration of NO_3^- in the spring of 1986 (Fig. 7) was likely associated with lysimeter installation (Shepard et al. 1990), as was previously mentioned with respect to Ca^{2+}. Concentration of NO_3^- in the B horizon was 8 μeq L^{-1} lower ($P < 0.05$) in the growing compared to the dormant season. An experimental study adjacent to the present site, in which NH_4NO_3 was added at 100 kg N ha^{-1} yr^{-1} for two years, found that little of the N was leached from the system during the growing season (Porter 1990). The ability of the HF to utilize N may be attributed to the strong sink for this element due to vegetation demand (uptake of 44.7 or 59.5 kg ha^{-1} yr^{-1}, without and with fine roots, respectively). This lack of nitrogen leaching can be contrasted to a deciduous forest site at Turkey Lakes (Ontario, Canada) in which N requirements are substantially lower (uptake of 32.2 kg ha^{-1} yr^{-1}), contributing to higher levels of nitrate leaching (Mitchell et al. 1992b). In the forest floor and mineral soil, highest nitrate concentrations were generally found in early spring (April–May) with lowest concentrations in the summer and autumn (July–October). These low concentrations coincided with the growing season and specifically the production of fine roots and subsequent demand for N (Fig. 2). Models of temperate forest ecosystems, including northern hardwoods, show that fine root production is closely coupled with nitrogen uptake on an annual basis (Aber et al. 1991).

Subtracting inorganic N leached from the B horizon from that leached from the forest floor gives a value of only 3.8 kg ha^{-1} yr^{-1} compared to a net vegetation requirement of 78.1 kg ha^{-1} yr^{-1} (Mitchell et al. 1992b), suggesting that most of the decrease in inorganic N can be accounted for by the uptake of N by vegetation and subsequent recycling by canopy leaching and litter inputs. In other sites in the northeast U.S. with substantial amounts of roots in the forest floor, experimental trenching and hence disruption of vegetation uptake increases NH_4^+ and NO_3^- concentrations in the soil (Vitousek et al. 1982). Due to the demand for N at the HF, fluxes of inorganic N were rapidly attenuated in this ecosystem (Fig. 9). However, for the E and B horizon there were greater fluxes in the spring which coincided with higher concentrations, high water flux associated with the melting of the snow pack and low biotic demand. These enhanced fluxes result in high spring NO_3^- concentrations in the surface waters of Arbutus Lake which is adjacent to this site (Shepard et al. 1990) as is typical for Adirondack Region (Rascher et al. 1987; Driscoll et al. 1989). Moreover, from 1984–1991 the average concentration of NO_3^- in Arbutus Lake significantly increased 1.1 μeq L^{-1} yr^{-1} (Driscoll and Van

Dreason 1992) which suggests that the capacity for this ecosystem to retain N may be decreasing (Mitchell et al. 1992b).

Biotic and abiotic regulations of S, Ca and N

The role of abiotic and biotic processes varies both among strata and with season for S, Ca and N. Within the forest canopy both abiotic and biotic processes are important. For example, the increase in SO_4^{2-} concentration when precipitation passes through the canopy is mostly attributed to the contribution of dry deposited S to TF. The contribution of dry deposition is dependent on both the concentrations of gases and particles as well as the deposition velocities. Since the deposition velocity is a function of both leaf area as well as the physiological condition of the leaves (Hicks et al. 1987), seasonal differences of Ca^{2+} in TF reflect interactions of the lead surface with dry deposited materials and exchanges within the leaf canopy (Parker 1983) which is only present during the growing season.

The forest floor is the location of intense biotic activity due to the co-occurrence of labile organic matter, nutrients (Gosz et al. 1976) and fine roots (Burke 1988). The increase of Ca^{2+} in the floor leachates compared to TF is likely due to mineralization which would be highest during the growing season due to favorable temperature and moisture conditions. Similarly, the increase of SO_4^{2-} in the forest floor leachates reflects the importance of organic S mineralization (David et al. 1987). The increase could also be due to direct sorption of gaseous S by the forest floor which may contribute about 20% of the total S deposition at the HF (T. Myers, personal communication). As for SO_4^{2-} and Ca^{2+}, there is an increase in NO_3^- in the forest floor, but the availability of this ion is rapidly attenuated as leachates pass through the mineral soil, especially during the growing season. The strong coupling of solute N dynamics and vegetation is shown by the coincidence of rapid loss of N during the period of the greatest demand by vegetation for this element (Figs. 2 and 9). The importance of biological processes is reflected in the high spatial and temporal variability of solute NO_3^- chemistry in the forest floor at HF (David and Gertner 1987; Shepard et al. 1990). The importance of this variability with respect to N has also been shown for hardwood forests in Michigan (Zak and Pregitzer 1990). Such variation may contribute to the seasonal variation of surface water chemistry especially during spring snow melt periods where water movement from the forest floor may be especially important (Wigington et al. 1990).

In contrast to the forest floor, changes in SO_4^{2-} and Ca^{2+} leaching in the mineral soil appear to be regulated primarily by abiotic processes. For

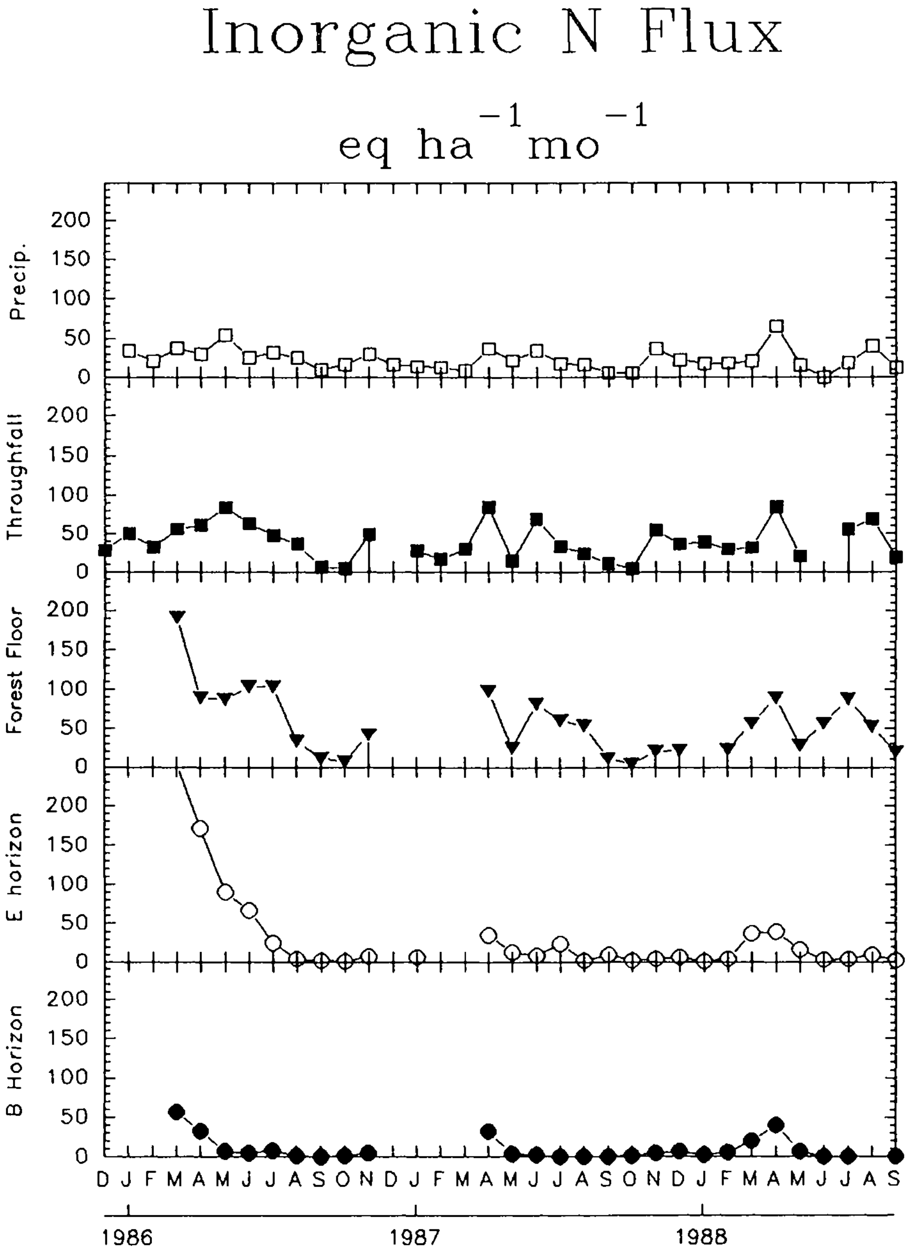


Fig. 9. Flux of inorganic N (NO_3^- + NH_4^+) through ecosystem strata at Huntington Forest.

example, the increase in SO_4^{2-} as well as the lack of temporal variation of this constituent both suggest that sulfate adsorption-desorption processes play a dominant role in regulating SO_4^{2-} in the mineral soil at this site.

Similarly, the changes in Ca^{2+} indicate that exchange reactions in the mineral soil are controlling the concentration of this element. The role of these abiotic processes has been a major feature of models, such as ILWAS and Trickle-Down (Schnoor 1984), which predict changes in surface water chemistry associated with acidic deposition.

The mineral soil has the largest pools of most elements in the forest system including N, S and Ca. Notwithstanding the importance of weathering reactions in affecting Ca availability (Likens et al. 1977), it is also critical to quantify long term changes in the pools of N (Huntington et al. 1989) and S (Mitchell et al. 1989) since over 90% of these latter two elements is contained in the organic matter of the mineral soil; small relative changes in these organic pools may have a marked impact on the elemental cycles of S and N. Although such changes cannot be easily detected over short periods, it is nevertheless important to quantify alterations of these large pools since these changes have important implications in predicting elemental dynamics especially over extended periods such as those relevant to pedogenesis and global change. Understanding the relationships between such long term transformations and those changes over shorter periods, such as within a year, constitutes a major challenge in the study of the biogeochemistry of forested ecosystems.

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