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Effects of air pollutant-temperature interactions on mineral-N dynamics and cation leaching in reciplicate forest soil transplantation experiments

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Abstract. Increased emissions of nitrogen compounds have led to atmospheric deposition to forest soils exceeding critical loads of N over large parts of Europe. To determine whether the chemistry of forest soils responds to changes in throughfall chemistry, intact soil columns were reciprocally transplanted between sites, with different physical conditions, across a gradient of N and S deposition in Europe.

The transfer of a single soil to the various sites affected its net nitrification. This was not simply due to the nitrification of different levels of N deposition but was explained by differences in physical climates which influenced mineralization rates. Variation in the amount of net nitrification between soil types at a specific site were explained largely by soil pH.

Within a site all soil types showed similar trends in net nitrification over time. Seasonal changes in net nitrification corresponds to oscillations in temperature but variable time lags had to be introduced to explain the relationships. With Arrhenius’ law it was possible to approximate gross nitrification as a function of temperature. Gross nitrification equalled net nitrification after adaptation of the microbial community of transplanted soils to the new conditions. Time lags, and underestimates of gross nitrification in autumn, were assumed to be the result of increased NH_4^+ availability due either to changes in the relative rates of gross and net N transformations or to altered soil fauna-microbial interactions combined with improved moisture conditions.

Losses of NO_3^- were associated with Ca^{2+} and Mg^{2+} in non-acidified soil types and with losses of Al^{3+} in the acidified soils. For single soils the ion equilibrium equation of Gaines-Thomas provided a useful approximation of Al^{3+} concentrations in the soil solution as a function of the concentration of Ca^{2+}. The between site deviations from this predicted equilibrium, which existed for single soils, could be explained by differences in throughfall chemistry which affected the total ionic strength of the soil solution.

The approach of reciprocally transferring soil columns highlighted the importance of throughfall chemistry, interacting with the effect of changes in physical climate on forest soil acidification through internal proton production, in determining soil solution chemistry. A framework outlining the etiology of forest die-back induced by nitrogen saturation is proposed.

Introduction

There is an increasing body of evidence that the chemistry of the atmosphere strongly influences throughfall chemistry which, in turn, may influence the chemistry of forest soils (Parker 1983; Bredemeier 1988). Forest canopies trap gaseous and aerosol pollutants from the atmosphere very efficiently, subjecting forest soils, over large areas of Europe, to acidifying pollutants. These changes in throughfall chemistry, on top of internal soil processes, generate acidity in the soil. Additionally, there is increasing awareness of the role played by NH_3 in acidifying forest ecosystems (Nihlgård 1985; Aber et al. 1989; Fangmeier et al. 1994).

Up to the middle of this century, nitrogen was the major limiting factor in the productivity of most forest ecosystems of the Northern hemisphere (Keeney 1980; Tamm 1991). Increased use of internal combustion engines and the intensification of animal husbandry changed this situation drastically. The N load to large areas of forest in Europe now exceeds the annual growth requirement of the trees (Ågren & Bosatta 1988) and has contributed to a destabilization of forest ecosystems (Bredemeier 1988; Skeffington & Wilson 1988). Besides N deposition, other disturbances, such as changed land-use, forest harvesting, and proposed climatic change have been identified as factors increasing N-mineralization in forest soils (Gordon & Van Cleve 1983; Matson & Boone 1984; Kirschbaum 1995).

Recognition of the effects of disturbance on the processes behind the cycling and loss of elements in terrestrial ecosystems has increased over the last few decades and, within the N-cycle, responses of nitrification has been identified as being particularly important. The production of mobile NO_3^- can result in losses of NO_3^- to groundwater and stream water and, in this respect, attention has been given to the potentially high losses of base cations, associated with the NO_3^-, which might affect long-term forest fertility (Fangmeier et al. 1994). In acid forest soils in the Netherlands high atmospheric deposition of NH_4^+, when nitrified, leads to leaching of considerable amounts of Al^{3+} (Van Breemen et al. 1982) which far exceed the toxic limit for plant roots (Runge & Rode 1991). Leaching of NO_3^-, other nutrients and toxic elements can alter the vegetation cover (Steubing & Fangmeier 1991; Rosén et al. 1992) which often results in changed heat and water fluxes and consequently affects mineralization and nitrification rates (Focht & Verstraete 1977; Vitousek et al. 1982; Moore 1986; Berg et al. 1993). In addition, as nitrification is a proton source, significant acidification of forest soils can result (Binkley & Richter 1987; Gundersen & Rasmussen 1990).

Traditionally, biogeochemical research has tended to concentrate on single sites in attempts to understand and describe the development of soil processes under prevailing conditions. The concept behind the current research project was to use the different physical and chemical climates existing across Europe to investigate the developments and changes in forest soil processes when soils are exposed to changing conditions. To achieve this, six coniferous forest sites were selected along a transect of increasing N and S deposition from Ireland to Germany and intact soil columns were reciprocally transferred between them. In addition to the sites representing specific pollution situations, they differed in their climatic conditions. The focus of the research presented in this paper is the hypothesis that changes in climate and throughfall chemistry, manipulated as a result of transplanting soil columns, affect mineral-N cycling and determine the soil solution chemistry of certain ions.

Material and methods

Site characteristics and experimental design

Six coniferous forest sites were selected along a transect of increasing atmospheric deposition of N and S from Ireland to Germany. They were located in Ireland (Kilkenny), UK (Haldon and Grizedale), France (Fontainebleau, Foljuif), the Netherlands (Wekerom), and Germany (Solling) (Figure 1, Table 1).

Intact soil cores were reciprocally transported between sites and each site hosted all soil types. Soil cores were taken using Plexiglas cylinders (15 cm diam; 24 cm deep) fitted onto a metal corer, which was carefully forced into the ground. After checking that the soil cores were undisturbed, the bases were trimmed, a base-cap fitted and sealed with silicone adhesive. A ceramic suction cup (Type P80: Fa. KPM, Berlin) was inserted through the side of the core and sealed with silicone adhesive. The core, with cylinder, sealed bottom and ceramic cup, is referred to as a lysimeter (Figure 2). Construction of the lysimeters was centralised to ensure standard materials and protocols, with the lysimeter sampling and placement being supervised by the same personnel at each site.

Forty-nine lysimeters were collected at each site and 7 extra cores were sampled to determine soil characteristics. Within a few days, 7 lysimeters were transferred to each of the six sites where they were established such that the soil surface within the core was level with the surrounding soil surface

Table 1. Characterization of the CORE sites shown in Figure 1. Measurements are based upon the period 1989–1990. Stand age as in 1990.

Site	Longitude	Latitude	Elevation (m)	Precipitation (mm)	Annual mean temperature (°C)	Species	Age (years)	Soil texture
Kilkenny	52°4′ N	7°2′ W	175	826	9.3	*Picea abies*	20	Silt loam/silty clay loam
Haldon	50°4′ N	3°4′ W	90	1329	11.0	*Picea abies*	45	Clay loam/silty clay loam
Grizedale	54°2′ N	3°0′ W	170	1556	8.6	*Picea abies*	40	Silt loam
Fontainebleau	48°2′ N	2°4′ E	83	559	11.0	*Pinus sylvestris*	30	Loamy sand
Wekerom	52°1′ N	5°4′ E	23	750	10.9	*Pinus sylvestris*	35	Loamy sand
Solling	51°8′ N	9°5′ E	500	968	6.4	*Picea abies*	109	Silt loam/silty clay loam

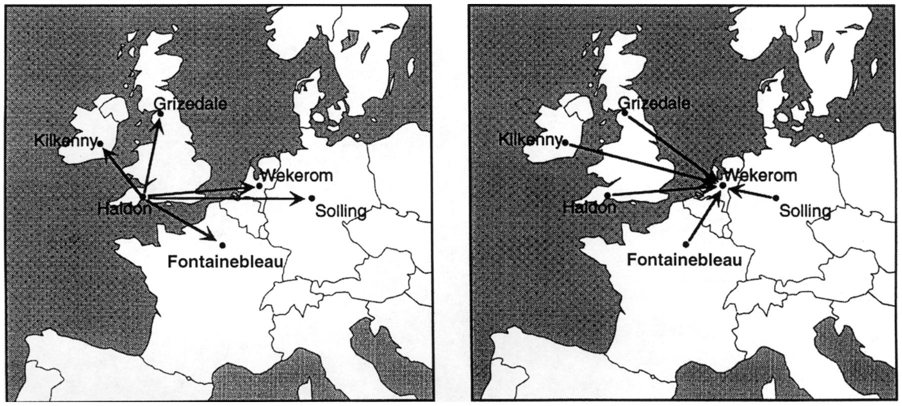

Figure 1. Location of the forest sites. Lysimeters (n = 7) were transplanted from one site to each of the other sites, e.g. soil type Haldon (and the control), and each sites received lysimeters from all the other sites (e.g. host site Wekerom).

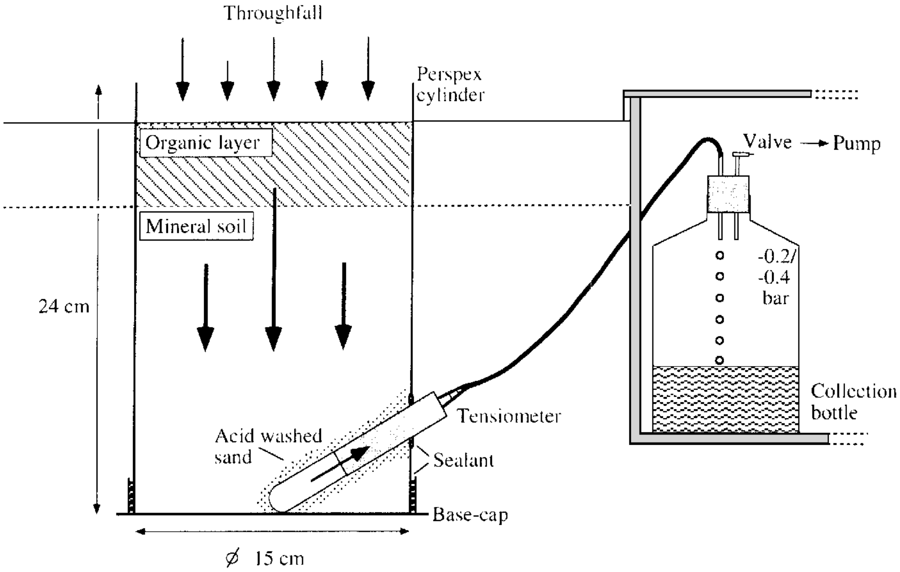

Figure 2. Lysimeter design. Cross-section through an undisturbed soil core in a Perspex cylinder with a ceramic suction cup and sealed base-cap (Lysimeter). Lysimeters are connected to glass bottles which were pumped down to −0.2/0.4 bar.

at the site. The site from which the soil was transferred is referred to as the ‘source’, and the receiving site is referred to as the ‘host’ site (Figure 1).

An additional 42 columns were collected from the Haldon site, and 7 were transported to each of the sites where they were capped, in such a way that gas exchange was not seriously obstructed, to prevent the input of throughfall. These ‘control’ lysimeters received distilled water every two weeks at a rate equivalent to the measured amounts of throughfall which reached the other lysimeters at the host site. The control lysimeters were established in order to differentiate between effects of changes in physical and chemical climate on transplanted soils.

Sampling and chemical analyses

At the field site the suction cups of the lysimeters were connected to glass jars which were stored in isolated, frost-proof boxes. Soil solution was sampled through the ceramic cup which was maintained at a negative pressure of 0.2 to 0.4 bar. All groups commenced monitoring in January 1989 and finished in September 1990. Soil solution chemistry was monitored every two weeks. Throughfall was collected every two weeks (10 replicate gauges) and rainfall was sampled (5 replicate gauges) at a nearby open location. Volumes were noted in the field and pH was measured within 24 hours in the laboratory. Precipitation, throughfall and soil solutions were routinely analysed for Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, NH_4^+-N, Cl^-, NO_3^--N, SO_4^{2-}-S) either directly after each sampling or after storage during a quarter of a year, and combined to proportional samples. To evaluate the chemical analysis performed at each laboratory using common protocols a ‘round-robin’ calibration check was carried out. Differences in analytical results between the laboratories were shown to be less than 5%.

Soil temperature was either measured daily at different depths with data loggers (Delta logger: Fa U&P or DataLog: Fa Earth science VUA) or monitored with Zeolite cells, and the average daily temperatures were simulated using the SOIL-model (Jansson 1991).

Rainfall and throughfall description

Maritime inputs of Na^+ and Cl^- dominated at the sites Haldon and Grizedale, both situated close to the sea (Table 2). Low inputs of sea-derived elements of Kilkenny arise because of the predominantly westerly winds resulting in relatively low rainfall and low sea-salt concentrations. Throughfall deposition of K^+, Ca^{2+} and Mg^{2+} at the Kilkenny and Haldon showed a low proton load but a high sulphate deposition. This sulphate is imported as a dilute neutral salt and, as such, is expected to have a low acidifying effect.

Wekerom and Solling were distinguished by their large throughfall enrichments of inorganic pollutants, with the Solling site receiving high levels of SO_4^{2-} and H^+. At the Wekerom site, with the highest NH_4-N inputs in both rainfall and throughfall, co-deposition of ammonium sulphate was seen as

Table 2. Element input in rainfall and throughfall ($kg \cdot ha^{-1} \cdot a^{-1}$) from March 1989 to March 1990.

Site		Na^+	K^+	Ca^{2+}	Mg^{2+}	Al^{3+}	NH_4-N	H^+	Cl^-	SO_4S	NO_3-N
Kilkenny	Rainfall	31.52	2.44	11.13	3.81	0.39	3.32	0.07	35.13	5.66	1.95
	Throughfall	31.03	26.35	8.88	4.59	0.20	6.05	0.01	51.04	8.88	3.51
Haldon	Rainfall	90.38	12.36	9.37	9.46	0.10	3.57	0.42	149.67	23.66	4.44
	Throughfall	76.96	25.97	11.49	8.98	0.00	10.24	0.05	175.55	46.35	7.05
Grizedale	Rainfall	57.36	2.70	5.21	6.76	0.00	4.44	0.79	105.83	14.48	4.25
	Throughfall	92.22	19.51	13.52	11.97	0.10	7.72	0.91	177.58	34.76	5.60
Fontainebleau	Rainfall	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	Throughfall	26.75	11.78	10.14	3.09	0.19	4.73	0.09	20.66	10.62	5.79
Wekerom	Rainfall	18.12	3.45	3.62	2.83	0.00	15.11	0.20	32.26	14.32	9.37
	Throughfall	30.58	14.58	5.39	6.45	0.09	41.89	0.05	58.42	31.82	10.16
Solling	Rainfall	8.02	2.21	4.61	1.20	0.00	9.22	0.38	15.02	13.18	7.83
	Throughfall	18.90	23.41	20.83	4.15	0.83	17.97	1.08	37.33	43.32	19.17

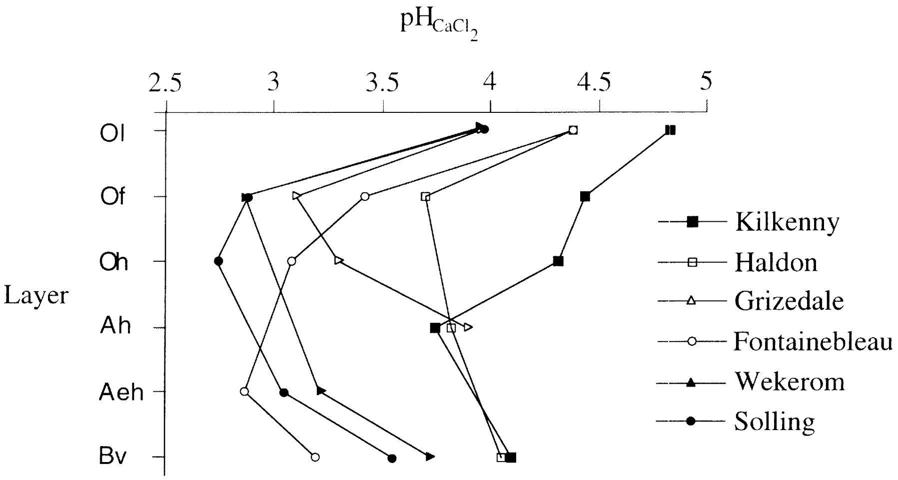

Figure 3. pH_{CaCl_2} profiles for the soil types Kilkenny, Haldon, Grizedale, Fontainebleau, Wekerom, and Solling.

a major acidifying influence. The proton load at Grizedale and Solling was high, but at Grizedale this was largely due to very high precipitation amounts (Table 1).

Soil characteristics

Seven core per site were taken for characterisation of the soils, with the research group from Germany preparing all soil samples for full analysis. The soil samples were separated into horizons and sieved to 2 mm. Dried mineral soil, 10 g, or surface layers, 10 cm^3, were mixed with 25 cm^3 of either distilled water or 0.01 M $CaCl_2$ to determine pH_{H_2O} and pH_{Cl_2}. Exchangeable cations were measured as described by Meiwes et al. (1984), which involved the percolation of 80 cm^3 of 1 M $(NH_4)_2SO_4$ solution through 2.5 g soil.

The pH_{CaCl_2} values for the sites decreased in the order: Kilkenny, Haldon, Grizedale, Wekerom and Solling, and showed a typical decline with depth between the Ol horizon and the mineral soil, with the pH values then increasing with depth below this level (Figure 3). However, the pH profile of the Fontainebleau soil was unusual, showing a strong decline in pH, 1.3 pH units, between the Ol and Oh horizon. The pH in the Ol horizon were as high as those of Haldon soil but, in marked contrast, the mineral soil from Fontainebleau showed the lowest pH values of all soils under study.

For all soils, the sums of exchangeable cations decreased down the soil profile with the sandy soils from Fontainbleau and Wekerom having the lowest exchange capacities due to a low clay and carbon content (Table 3). All of

Table 3. pH_{H_2O} and cation exchange capacity ($mmol_c \cdot kg$ dry weight^{-1}). Ah* mixed horizon Oh/Ah; sd standard deviation.

Site	Horizon	*n*		pH	Al	Ca	K	Mg	Na	Sum
Kilkenny	Ah	6	Mean	4.4	57.9	42.0	2.2	14.1	2.8	119.0
			sd	0.2	4.9	14.6	0.6	2.6	1.1	15.9
	Bv	6	Mean	4.8	50.4	23.0	1.8	7.9	2.3	85.4
			sd	0.2	12.9	9.7	0.8	3.4	0.9	5.6
Haldon	Ah*	3	Mean	4.5	57.4	53.2	5.9	13.5	6.6	136.6
			sd	0.1	6.0	13.6	1.6	3.4	0.9	51.9
	Bv	6	Mean	4.8	43.2	25.0	2.9	9.4	2.9	83.4
			sd	0.2	9.7	10.5	0.6	2.1	0.5	12.8
Grizedale	Ah	5	Mean	4.6	104.0	36.6	0.7	8.7	2.4	152.4
			sd	0.1	33.5	24.0	0.7	2.8	1.3	25.7
Fontainebleau	Aeh	6	Mean	3.8	9.4	6.7	0.3	1.5	0.0	17.9
			sd	0.1	2.4	1.5	0.2	0.2	0.1	3.3
	Bv	7	Mean	4.0	6.3	0.7	0.2	0.4	0.2	7.7
			sd	0.1	2.2	0.7	0.3	0.1	0.3	2.9
Wekerom	Aeh	6	Mean	4.0	13.9	0.9	0.4	0.9	0.5	16.6
			sd	0.1	5.8	0.6	0.4	0.3	0.3	2.6
	Bv	6	Mean	4.5	7.9	0.4	0.1	0.4	0.2	9.0
			sd	0.1	2.0	1.1	0.1	0.1	0.2	3.0
Solling	Ah	10	Mean	3.5	100.9	9.3	3.4	3.8	3.4	120.8
			sd	0.2	12.2	4.5	1.4	0.9	3.9	19.2
	Aeh	10	Mean	3.6	82.2	2.2	1.1	1.7	0.8	88.0
			sd	0.1	11.2	0.9	0.4	0.3	0.2	11.8
	Bv	10	Mean	4.0	75.5	0.4	0.7	1.0	0.5	78.1
			sd	0.1	12.0	0.1	0.5	0.2	0.5	8.8

the soils were located in one of the two buffer ranges: cation exchange buffer range (CEBR: $4.2 < pH < 5.0$) or aluminum buffer range (ABR: $3.0 < pH < 4.2$) (Table 3). Across small differences in soil pH the base saturation can be very different. The pH of the Ah-horizon at Grizedale was high compared to the same horizon at Kilkenny and Haldon but the base saturation was distinctly lower. Additional information on soil characteristics are given in Raubuch (1992).

Statistical analysis

Relationships between the average annual concentrations of NH_4-N, NO_3-N and total mineral-N in throughfall and leachates of individual soils at the various sites were investigated using Pearson correlation coefficients.

Two weeks averages of NO_3^- leaching from the soils of Wekerom, Grizedale and Kilkenny, hosted at the three corresponding sites, were correlated with fluctuations in soil temperature, after the introduction of time lags of various lengths. The data were processed with three point moving averages to suppress the influence of noise.

Pearson correlation coefficients were used to compare the leaching of NO_3^- with the leaching of Ca^{2+}, Mg^{2+} and Al^{3+}. Two weeks averages of NO_3^- and cation leaching were summed per soil type over all hosts as it was assumed that leaching of cations per soil was independent of the site where it was hosted. All correlations were performed with SYSTAT 5.2.

To gain an insight in the process of nitrification attempts were made to predict NO_3^- production in time by modelling the population dynamics of nitrifiers. Under *ad libitum* substrate conditions the rate of nitrate produced by nitrifiers is temperature dependent. The relationship between the rate of physiological process and temperature is described with the equation of Arrhenius, derived from the universal law of van't Hoff (Glasstone et al. 1941). In the Arrhenius equation:

$$k(T) = k(T_1)\exp\left(\frac{T_a}{T_1} - \frac{T_a}{T}\right). \qquad (1)$$

Nitrate production (k) at a given temperature T was related to a reference temperature (T_1) and the Arrhenius temperature (T_a). The Arrhenius temperature is the regression obtained from linear regression of the logarithm of actual NO_3^- leaching against the inverse absolute temperature. The calculated Arrhenius temperature, used to predict NO_3^- production was $T_a = 5500$ for all sites. The Arrhenius temperature has the dimension temperature, but it does not relate to a temperature that exists at a site. The reference temperature (T_1) can be obtained when the observed temperature and the actual NO_3^- leaching against time are plotted together. For T_1 the temperature in the second year, where the curve of actual NO_3^- leaching overlaps with the temperature curve, was used.

A chemical equilibrium equation was used to model effects of changes in throughfall chemistry on the soil solution. To describe short-term effects of changing solution concentrations of aluminum and calcium the equilibrium expression of Gaines-Thomas (1953) was used (after Reuss & Johnson 1986):

$$K_s \cdot \frac{(Al^{3+})^2}{(Ca^{2+})^3} = \frac{E_{Al^2}}{E_{Ca^3}}. \qquad (2)$$

The brackets denote molar activities of aluminum and calcium in the soil solution, K_s is the selectivity coefficient, and E_{Ca} and E_{Al} are the fractions of calcium and aluminum on the exchange complex of the soil solid phase. The E_{Ca} and E_{Al} were obtained from Table 3 by dividing the equivalents of the exchangeable cations, per unit of soil, by the total cation exchange capacity for each soil type. For each soil the K_s was calculated for each host site separately, based on the average (Al^{3+}) and (Ca^{2+}) per site, and averaged over all sites to account for differences in the amounts of data available per site.

In describing the short-term effects of changing solution concentrations, E_{Al} and E_{Ca} were assumed to be constant. The concentration of Al^{3+} in the soil solution is than proportional to the Ca^{2+} activity and is approximated by:

$$(Al^{3+}) = K_t \cdot (Ca^{2+})^{3/2} \tag{3}$$

where K_t was calculated as:

$$K_t = \left\{ \frac{E_{Al^2}}{K_s \cdot E_{Ca^3}} \right\}^{1/2} \tag{4}$$

Results

N balance

The annual nitrogen input in throughfall varied from 9.2 kg ha^{-1} a^{-1} at the Kilkenny site in Ireland to 49.7 kg ha^{-1} a^{-1} at the Wekerom site in the Netherlands (Table 4). The total DIN leached also varied considerably, both between soils within a site, and between the same soil at difference sites (Table 4). Missing values for lysimeters containing soil from Fontainebleau arose at some sites due to blockage of the porous cups by organic materials which were mobilised as pH rose (c.f. Foster et al. 1980).

The control lysimeters from Haldon received only distilled water. As the input of N to these lysimeters at all sites was zero, differences in N dynamics in these lysimeters must have been due solely to climatic factors at the host sites. The amounts of NH_4^+-N leached from the Control lysimeters was low and comparable at all sites. It varied from 0.1 kg N ha^{-1} a^{-1} at the Solling site to 1.4 kg N ha^{-1} a^{-1} at Wekerom. However, the amounts of NO_3^--N leached from these lysimeters were considerably higher and ranged from 101.4 kg N ha^{-1} a^{-1} at Grizedale to 212.3 kg N ha^{-1} a^{-1} at Wekerom. As no plant uptake was allowed the total DIN leached was high and dominated by

Table 4. Annual concentration of NH_4'N, NO_3-N and total mineral-N ($kg{\cdot}ha^{-1}{\cdot}a^{-1}$) in throughfall and leachates of control (Co), Wekerom (We), Solling (So), Haldon (Ha), Grizedale (Gr), Fontainebleau (Fo), and Kilkenny (Ki) soils at the various sites. Balance of NH_4-N, NO_3-N and total mineral-N were calculated based on averages of each sampling time as throughfall minus leaching over the period May 1989 to May 1990.

Host	Soils	Throughfall ($kg{\cdot}ha^{-1}{\cdot}a^{-1}$)			Leaching ($kg{\cdot}ha^{-1}{\cdot}a^{-1}$)			Balance ($kg{\cdot}ha^{-1}{\cdot}a^{-1}$)		
		NH_4-N	NO_3-N	Total mineral N	NH_4-N	NO_3-N	Total mineral N	NH_4-N	NO_3-N	Total mineral N
We	Co	0.0	0.0	0.0	1.4	212.3	213.7	−1.4	−212.3	−213.7
	We	38.0	11.7	49.7	13.4	132.5	145.9	24.6	−120.8	−96.2
	So	38.0	11.7	49.7	4.9	144.9	149.8	33.1	−133.2	−100.1
	Ha	38.0	11.7	49.7	2.3	239.7	242.0	35.7	−228.0	−192.3
	Gr	38.0	11.7	49.7	31.1	110.0	141.1	6.9	−98.3	−91.4
	Fo	38.0	11.7	49.7	28.8	7.6	36.4	9.2	4.1	13.3
	Ki	38.0	11.7	49.7	2.4	173.8	173.8	35.6	−162.1	−126.5
So	Co	0.0	0.0	0.0	0.1	103.5	103.6	−0.1	−103.5	−103.6
	We	19.5	19.5	39.0	5.8	86.1	91.9	13.7	−66.6	−52.9
	So	19.5	19.5	39.0	0.8	81.5	82.3	18.7	−62.0	−43.3
	Ha	19.5	19.5	39.0	0.3	119.1	119.4	19.2	−99.6	−80.4
	Gr	19.5	19.5	39.0	10.6	99.2	109.8	8.9	−79.7	−70.8
	Fo	19.5	19.5	39.0	34.0	8.7	42.7	14.5	10.8	−3.7
	Ki	19.5	19.5	39.0	0.1	46.1	46.2	19.8	−26.6	−7.2
Ha	Co	0.0	0.0	0.0	0.9	133.5	134.4	6.6	−133.5	−134.5
	We	9.3	6.6	15.9	15.8	88.0	103.8	−6.5	−81.4	−87.9
	So	9.3	6.6	15.9	13.8	90.0	103.8	−4.5	−83.4	−87.9
	Ha	9.3	6.6	15.9	2.4	105.6	108.0	6.9	−99.0	−92.1
	Gr	9.3	6.6	15.9	18.9	38.0	56.9	−9.6	−31.4	−41.0
	Fo	9.3	6.6	15.9	–	–	–	–	–	–
	Ki	9.3	6.6	15.9	2.5	61.9	64.4	6.8	−55.3	−48.5
Gr	Co	0.0	0.0	0.0	1.0	101.4	102.4	−1.0	−101.4	−102.4
	We	7.5	6.2	13.7	5.3	24.0	29.3	2.2	−17.8	−15.6
	So	7.5	6.2	13.7	3.1	26.5	29.6	4.4	−2.3	−15.9
	Ha	7.5	6.2	13.7	0.6	121.2	121.8	6.9	−115.0	−108.1
	Gr	7.5	6.2	13.7	14.1	27.3	41.4	−6.6	−21.1	−27.7
	Fo	7.5	6.2	13.7	–	–	–	–	–	–
	Ki	7.5	6.2	13.7	1.3	45.3	46.6	6.2	−39.1	−32.9
Fo	Co	0.0	0.0	0.0	0.8	141.3	142.1	−0.8	−134.3	−142.1
	We	5.0	7.0	12.0	1.0	73.4	74.4	4.0	−66.4	−62.4
	So	5.0	7.0	12.0	0.3	70.9	71.2	4.7	−63.9	−59.2
	Ha	5.0	7.0	12.0	0.1	144.4	144.5	4.9	−137.4	−132.5
	Gr	5.0	7.0	12.0	9.3	63.1	72.4	−4.3	−56.1	−60.4
	Fo	5.0	7.0	12.0	18.3	1.9	20.2	−13.3	5.1	−8.2
	Ki	5.0	7.0	12.0	0.3	73.9	74.2	4.7	−66.9	−62.2
Ki	Co	0.0	0.0	0.0	0.4	111.6	112.0	−0.4	−111.6	−112.0
	We	5.9	3.3	9.2	1.2	61.4	62.6	4.7	−58.1	−53.4
	So	5.9	3.3	9.2	0.7	74.6	75.3	5.2	−71.3	−66.1
	Ha	5.9	3.3	9.2	0.9	131.7	132.7	5.0	−128.4	−123.4
	Gr	5.9	3.3	9.2	13.2	79.4	92.6	−7.3	−76.1	−83.4
	Fo	5.9	3.3	9.2	–	–	–	–	–	–
	Ki	5.9	3.3	9.2	0.7	105.5	106.2	5.2	−102.2	−97.0

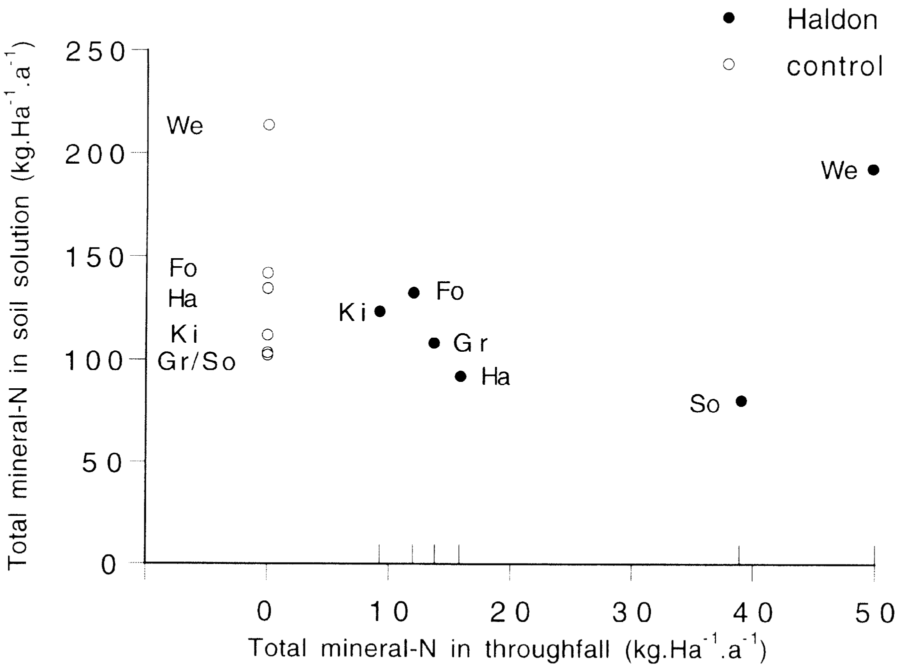

Figure 4. Total mineral-N in throughfall (kg·ha^{-1}·a^{-1}) at the various sites (x-axis) versus total mineral-N in the soil solution (kg·ha^{-1}·a^{-1}) of soil type Haldon (dark circles) and the control soils from Haldon (light circles) at the different sites (y-axis). The sites are indicated with symbols: Ki = Kilkenny; Fo = Fontainebleau; Gr = Grizedale; Ha = Haldon; So = Solling; We = Wekerom.

NO_3^--N. However, no data were available on the loss of organically bound N.

The amounts of total DIN leached from the Haldon lysimeters, which contained the same soil as the Control but which received local throughfall, were comparable to those of the control lysimeters (Figure 4). As there was no input of N to the control lysimeters, the catalyst can only be a high internal NH_4^+ production followed by nitrification if a low C supply inhibits immobilisation of N in the biomass of heterotrophs. No effect of N deposition on total DIN leaching from Haldon lysimeters was found (Figure 4). The amount of total DIN in the soil solution of the control lysimeters corresponded with the annual mean temperature at the various sites. Annual mean temperature at the Wekerom, Fontainebleau and Haldon sites were high in comparison to those at Kilkenny, Grizedale and Solling (Table 1) and subsequent leaching of total DIN was higher at the warmer sites than at the colder sites. High total DIN leaching at Wekerom may be related to the significantly higher summer temperatures compared to those at the Fontainebleau and Haldon sites.

At the individual sites, leaching of NH_4^+-N and NO_3^--N appeared to be related to pH and the buffer range of the soil types. Soils from Haldon and Kilkenny, which were within the 'cation exchange' buffer range and had a higher pH than the other soil, showed comparatively low NH_4^+-N and high NO_3^--N leaching (up to 120 $mg \cdot l^{-1}$). Soils from Wekerom and Soling, in the 'aluminum' buffer range with low pH, showed less NO_3^--N leaching (up to 55 $mg \cdot l^{-1}$). However, larger amounts of NH_4^+-N were leached from the Grizedale soil and virtually no nitrate was lost from the Fontainebleau soil, even when this soil was transported to sites with high N deposition. There was a significant inverse correlation between NH_4^+-N and NO_3^--N leaching when all sites were considered (Pearson: $r = -0.377$; $p < 0.05$).

No relationship was found between throughfall inputs of N at the various sites and NH_4^+-N, NO_3^--N or total DIN leaching. However, NO_3^- leaching was positively correlated with NH_4^+-N content in throughfall for the Haldon and Solling soils (Pearson: $r = 0.816$ and $r = 0.828$; $p < 0.05$, respectively).

Temperature dynamics and NO_3^- leaching

The relationship between temperature dynamics and NO_3^- leaching was analysed for three of the six sites: Wekerom, Kilkenny and Grizedale. These sites share a significant NO_3^- production and have high resolution (bi-weekly) nitrate concentration data. In the first year of the study, differences existed among sites for summer temperature (from May to October), maximum temperature, and time at maximum temperature (Figure 5). Summer temperatures decreased from Wekerom to Kilkenny and Grizedale. Maximum temperature was recorded in July at both Wekerom and Kilkenny, which differed from Grizedale where the maximum temperature was recorded in September. In the second year of the study no clear differences between sites were recorded.

Leaching of NO_3^--N during the year showed a strong seasonal pattern (Figure 6). At the Wekerom and Kilkenny sites NO_3^--N leaching occurred primarily in late autumn/early winter, whereas at Grizedale maximal losses occurred in late spring/early summer. At the Grizedale host site a significant positive correlation, between temperature and NO_3^--N leaching, was found for the Wekerom, Grizedale and Kilkenny soils. At the other two sites significant correlations between temperature and NO_3^--N leaching were found only when lag periods, ranging from 4 to 14 weeks, were introduced (Table 5).

NO_3^- leaching and nitrification rates

For the Grizedale, Kilkenny and Wekerom soils, gross NO_3^--N production was predicted based on the Arrhenius equation and compared with the output in

Figure 5. Soil temperature (°C at −4.0 cm at the sites Wekerom, Kilkenny, and Grizedale. Data were processed using three point moving average.

Table 5. Pearson correlation coefficients, and time lags used to establish the best correlation, of the relationship between soil temperature, at −40.0 cm, and NO_3^--N concentration in soil leachates. We = Wekerom, Ki = Kilkenny, Gr = Grizedale, and no = not significant.

Host site	Soil type	*r*	Time lag (week)	
We	We	0.894	12	$p \leq 0.001$
	Gr	0.753	8	$p \leq 0.001$
	Ki	0.711	14	$p \leq 0.001$
Gr	We	0.720	0	$p \leq 0.001$
	Gr	0.801	0	$p \leq 0.001$
	Ki	0.493	0	$p \leq 0.05$
Ki	We	0.272	4	ns
	Gr	0.382	12	ns
	Ki	0.733	14	$p \leq 0.001$

the leachates. Differences between measured NO_3^--N leaching and predicted NO_3^--N production were expressed as the ratio of measured NO_3^--N leaching to predicted NO_3^--N production (Figure 7a, b, c). When the measured and predicted values are equal, the measured/predicted ratio is one, indicating that leaching of NO_3^-1-N was directly dependent on temperature-related activity of the nitrifier population. When the predicted NO_3^--N production exceeds NO_3^--N leaching the ratio is <1.

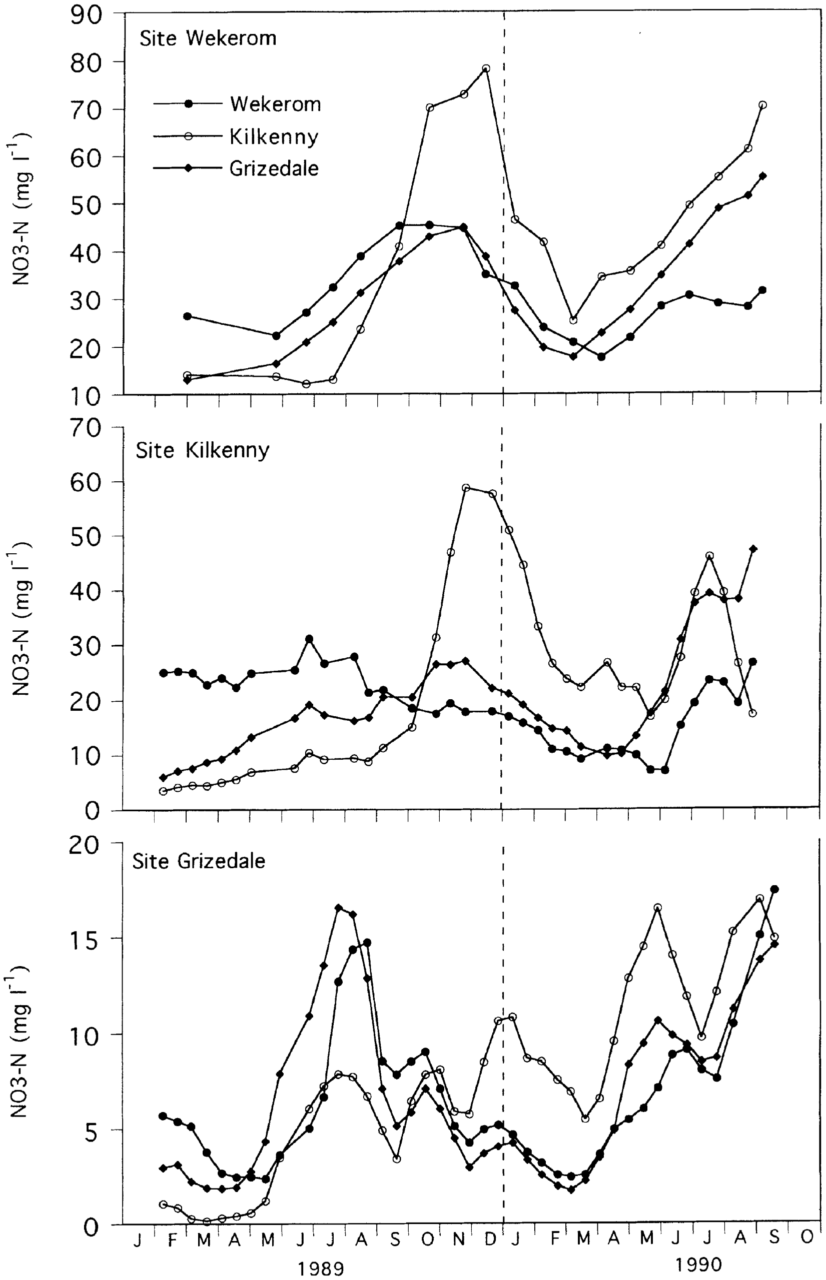

Figure 6. NO_3^--N ($mg{\cdot}l^{-1}$) in the soil solutions of Wekerom, Kilkenny, and Grizedale for the period February 1989 till September 1990 at three sites, Wekerom, Kilkenny, and Grizedale, respectively. Data were processed using three point moving average.

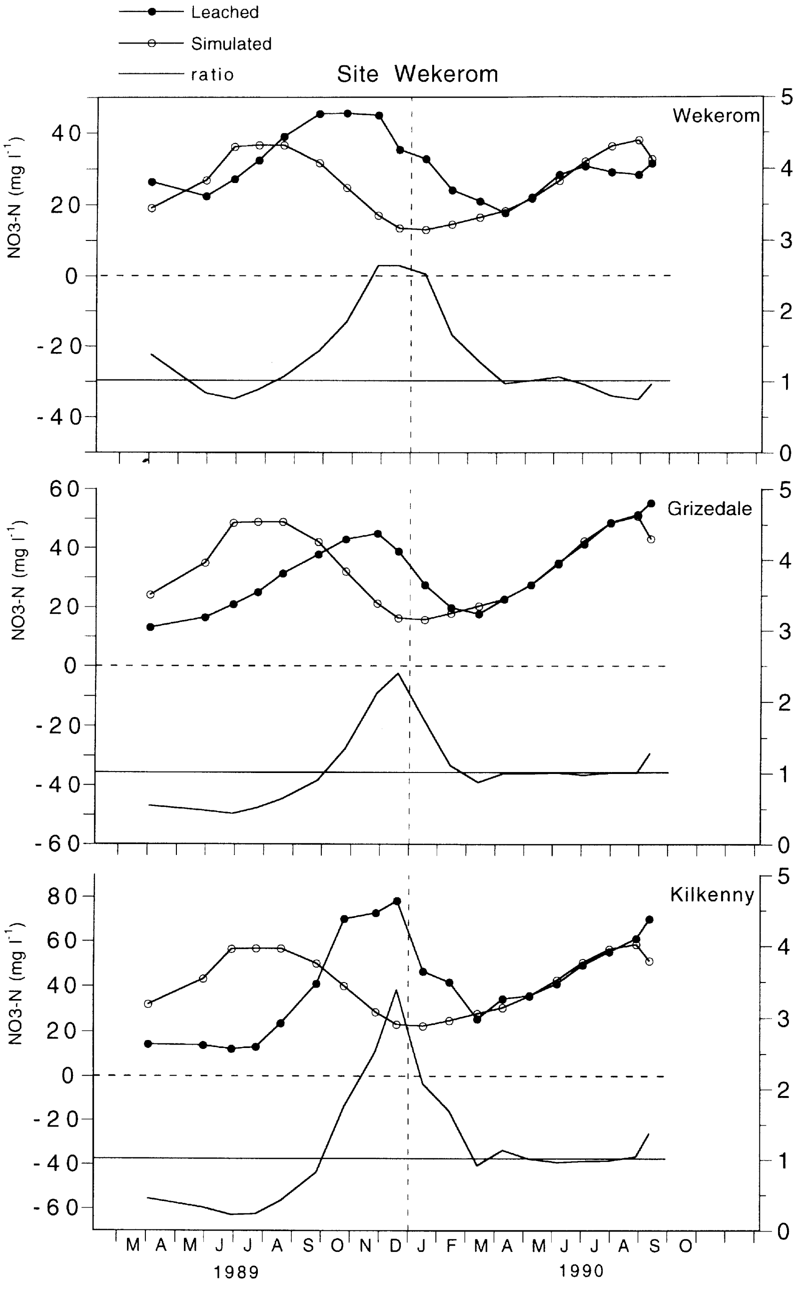

Figure 7a. NO_3^--N ($mg \cdot l^{-1}$) in the soil solution and simulated NO_3^--N ($mg \cdot l^{-1}$) production for the soil types Wekerom, Kilkenny, and Grizedale at site Wekerom (y_1-axis) for the period February 1989 till September 1990. Given is the ratio: actual NO_3^--N leaching/simulated NO_3^--N production (Y_2-axis). Data were processed using three point moving average.

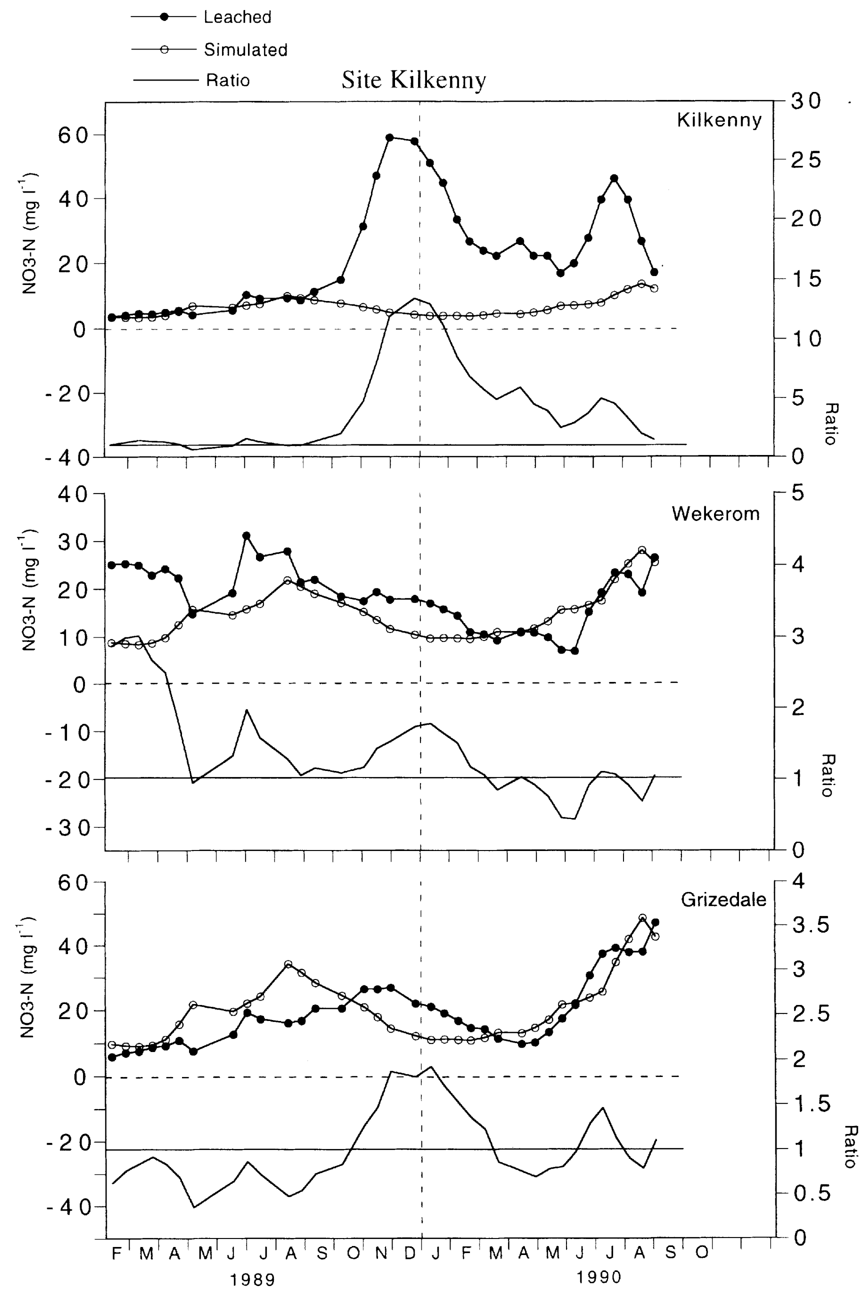

Figure 7b. NO_3^--N ($mg \cdot l^{-1}$) in the soil solution and simulated NO_3^--N ($mg \cdot l^{-1}$) production for the soil types Wekerom, Kilkenny, and Grizedale at site Kilkenny (y_1-axis) for the period February 1989 till September 1990. Given is the ratio: actual NO_3^--N leaching/simulated NO_3^--N production (Y_2-axis). Data were processed using three point moving average.

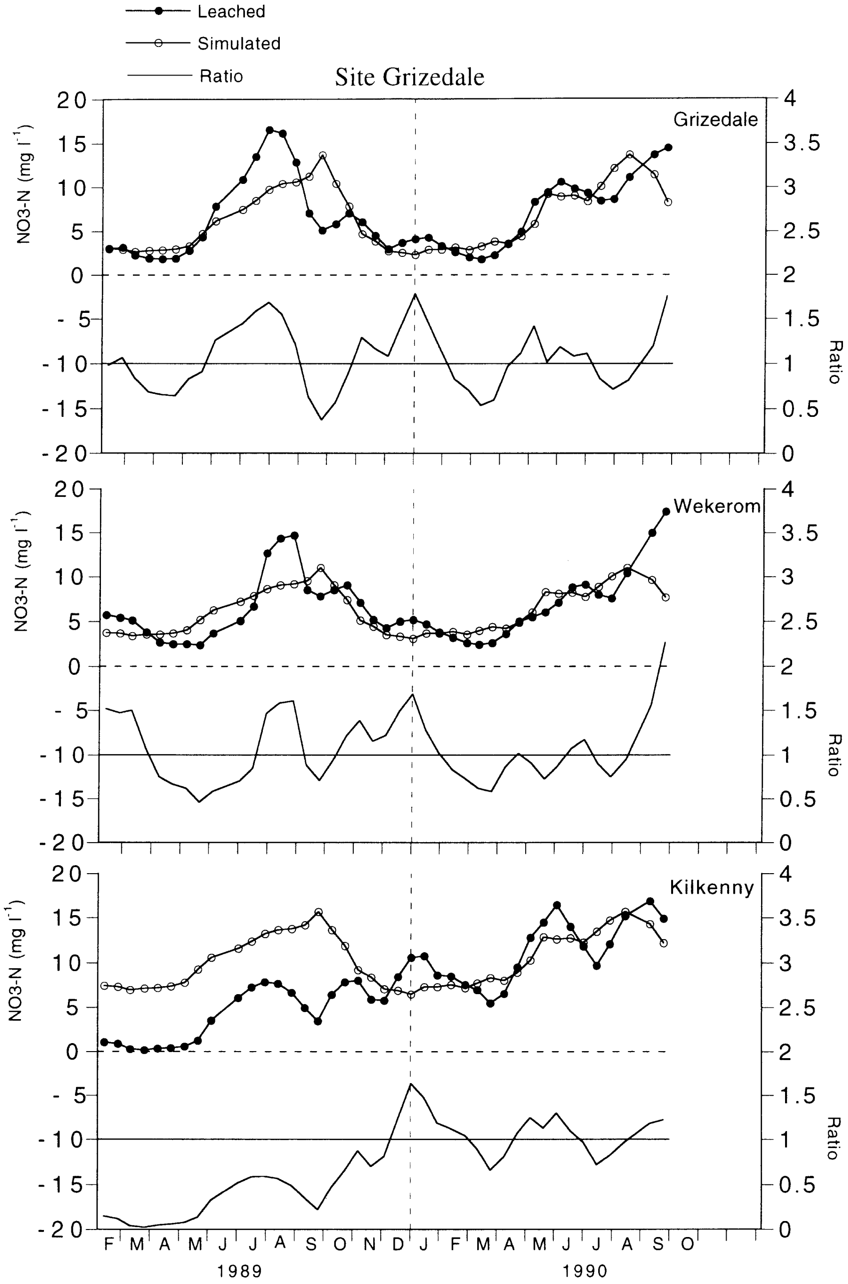

Figure 7c. NO_3^--N ($mg \cdot l^{-1}$) in the soil solution and simulated NO_3^--N ($mg \cdot l^{-1}$) production for the soil types Wekerom, Kilkenny, and Grizedale at site Grizedale (y_1-axis) for the period February 1989 till September 1990. Given is the ratio: actual NO_3^--N leaching/simulated NO_3^--N production (Y_2-axis). Data were processed using three point moving average.

Table 6. Pearson correlation coefficient between Ca^{2+}, Mg^{2+} and Al^{3+} and NO_3^--N in the soil solution for the ‘cation exchange’ buffer range group Haldon (Ha), Control (Co), and Kilkenny (Ki) and the ‘aluminium’ buffer range group Solling (So), Grizedale (Gr), and Wekerom (We). The level of significance is indicated. ns = not significant.

Soil type	NO_3^- × Ca^{2+}	Mg^{2+}	NO_3^- × Al^{3+}		NO_3^- ×	
Ha	0.676	$P < 0.001$	0.593	$P < 0.001$	0.139	ns
Co	0.701	$P < 0.001$	0.596	$P < 0.001$	0.109	ns
Ki	0.601	$P < 0.001$	0.631	$P < 0.001$	0.283	$P < 0.001$
So	0.233	$P \leq 0.01$	0.230	$P < 0.01$	0.659	$P < 0.001$
Gr	0.130	ns	0.344	$P < 0.001$	0.703	$P < 0.001$
We	0.159	ns	0.116	ns	0.734	$P < 0.001$

At the Wekerom site, the Wekerom soil had a measured/predicted ratio of 1 for the period February to September in both the first and second year (Figure 7a). For the other two soils the ratio during February to September of the first year was smaller than for the same period in the second year. The soils from Wekerom, Grizedale and Kilkenny at the Wekerom site showed a high measured/predicted ratio in winter which can only be explained by high NH_4^+ concentrations, either internally produced or stored, becoming available to the nitrifiers. All available NH_4^+ in this period is converted to NO_3^-, irrespective of lower temperatures.

High values of the measured/produced ratio were also found at the Kilkenny site during winter for the Kilkenny and Grizedale soils, i.e. from August to May and October to March, respectively. Lysimeters from Wekerom were transplanted from a location of high temperature and enhanced N deposition to one of low temperature and decreased N deposition. Initially the measured/produced ratio was greater than 1, but subsequently leaching of accumulated NO_3^- occurred. During the period February to October of the first year, the measured/produced ratio for the Grizedale soil had a value of less than 1. However, a measured/produced ratio of 1 was found in the second year.

At Grizedale, the measured/produced ratio for the Grizedale and Wekerom soils was 1. Throughfall volume was high at Grizedale, and stored NO_3^- in the Wekerom soil was efficiently transported out of the lysimeters. The soil from Kilkenny had a lower measured/produced ratio in the first year. In the second year the average value for all soils was 1.

Soil solution interactions

Aluminum and calcium were the dominant cations in terms of the total charge of the exchange complex (Table 3). The importance of Ca^{2+} on the exchange complex declined from the soils of Haldon, Kilkenny and Grizedale to those of Wekerom and Solling. The dominant cation in the leachate from the Haldon, Control, and Kilkenny, soils was Ca^{2+}, while Al^{3+} dominated the leachates from the Grizedale, Solling and Wekerom soils (Figure 8). The dominance of Al^{3+} in the leachate in the latter three soils increased with a decline in the percentage of Ca^{2+} saturation of the exchange complex.

For each soil type the relationship between the concentration of Al^{3+} and Ca^{2+} in the soil solution could be described by the Gaines & Thomas equation: the concentration of Al^{3+} is assumed to increase to the $-3/2$ power of Ca^{2+} (Figure 8). The scatter of data points shows that the host site has a significant effect on the Al/Ca ratio measured in the leachates of a soil type, compared to what is expected from the composition of the source soil, using the equation of Gaines & Thomas (1953). All soils leached higher concentrations of Al^{3+} leaching when housed at the Wekerom and Grizedale sites, and higher concentration of Ca^{2+} when housed at Kilkenny. At the Haldon site the Al^{3+} and Ca^{2+} concentrations in the leachates were more or less equal to or lower than the predicated Ca/Al ratio.

With the exception of the soil from Fontainebleau, where no nitrification was observed, the negative total N balance of the remaining soils could be explained by losses of NO_3^-. Nitrification results in additional internal proton production and exchange with cations on the exchange complex. For soils such as those from Kilkenny and Haldon, with a pH > 4.2, i.e. within the cation exchange buffering zone, losses of NO_3^- were accompanied by losses of Ca^{2+} and Mg^{2+} with little loss of Al^{3+} (Figure 9). In nitrifying soils with a pH < 4.2, within the aluminum buffer range, such as the soils from Solling, Wekerom and Grizedale, the loss of NO_3^- was accompanied by leaching of Al^{3+}. For the Kilkenny and Haldon soils, clear and significant correlations, summed over all sites, were observed between the amounts of NO_3^- leached and the amounts of Ca^{2+} ($r = 0.676$; $r = 0.601$, respectively) and Mg^{2+} in soil solutions ($r = 0.593$; 0.63, respectively). In the acidified soils a significant correlation existed between NO_3^- and Al^{3+} (Solling, $r = 0.659$; Grizedale, $r = 0.703$; Wekerom, $r = 0.734$) but in a few cases there was also a smaller but significant correlation between NO_3^- and Ca^{2+} or Mg^{2+}.

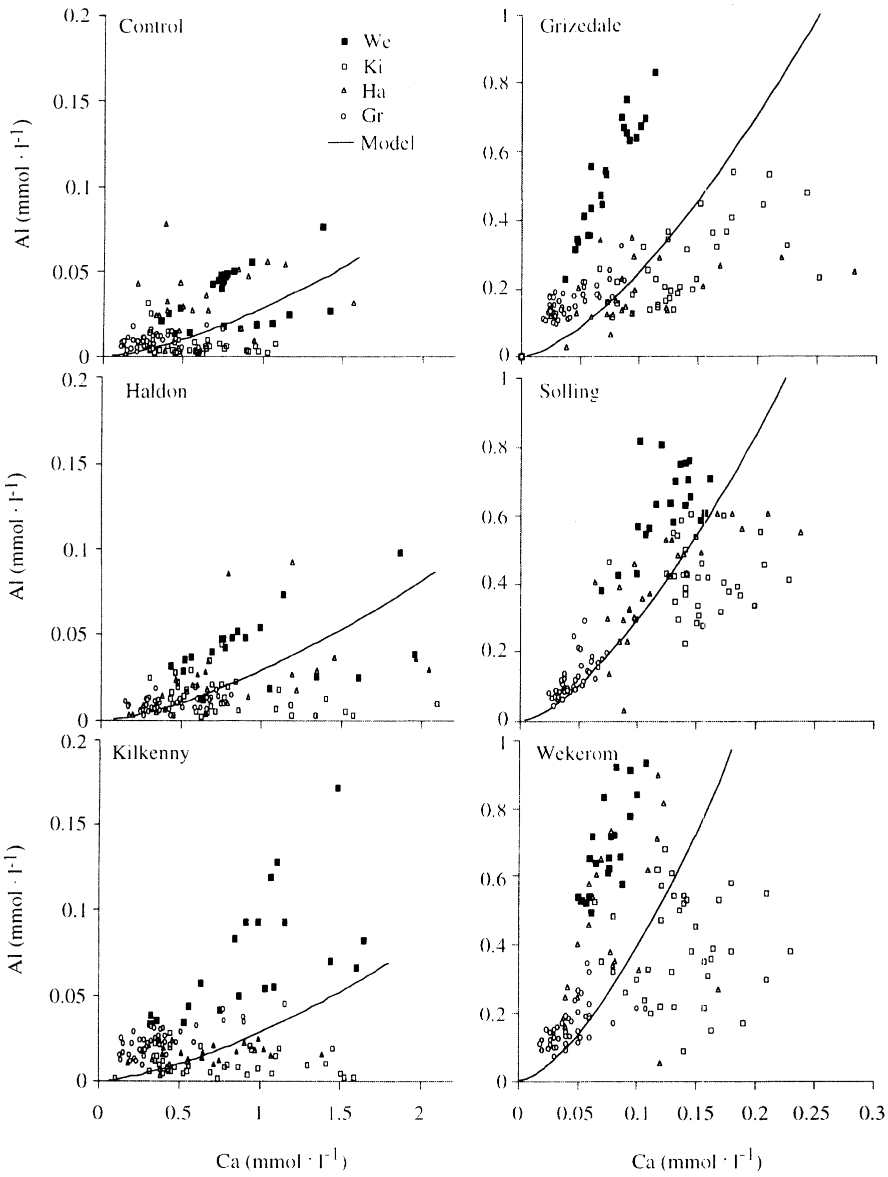

Figure 8. Concentration of Al^{3+} versus Ca^{2+} ($mmol{\cdot}l^{1-}$) in the soil solutions of six soil types, Haldon, Control, Kilkenny, Grizedale, Solling, and Wekerom, hosted at the sites Wekerom (We), Kilkenny (Ki), Haldon (Ha) and Grizedale (Gr). The lines indicates the average $Ca^{2+} - Al^{3+}$ ion exchange equilibrium for the given soil types based on the Gaines & Thomas equation.

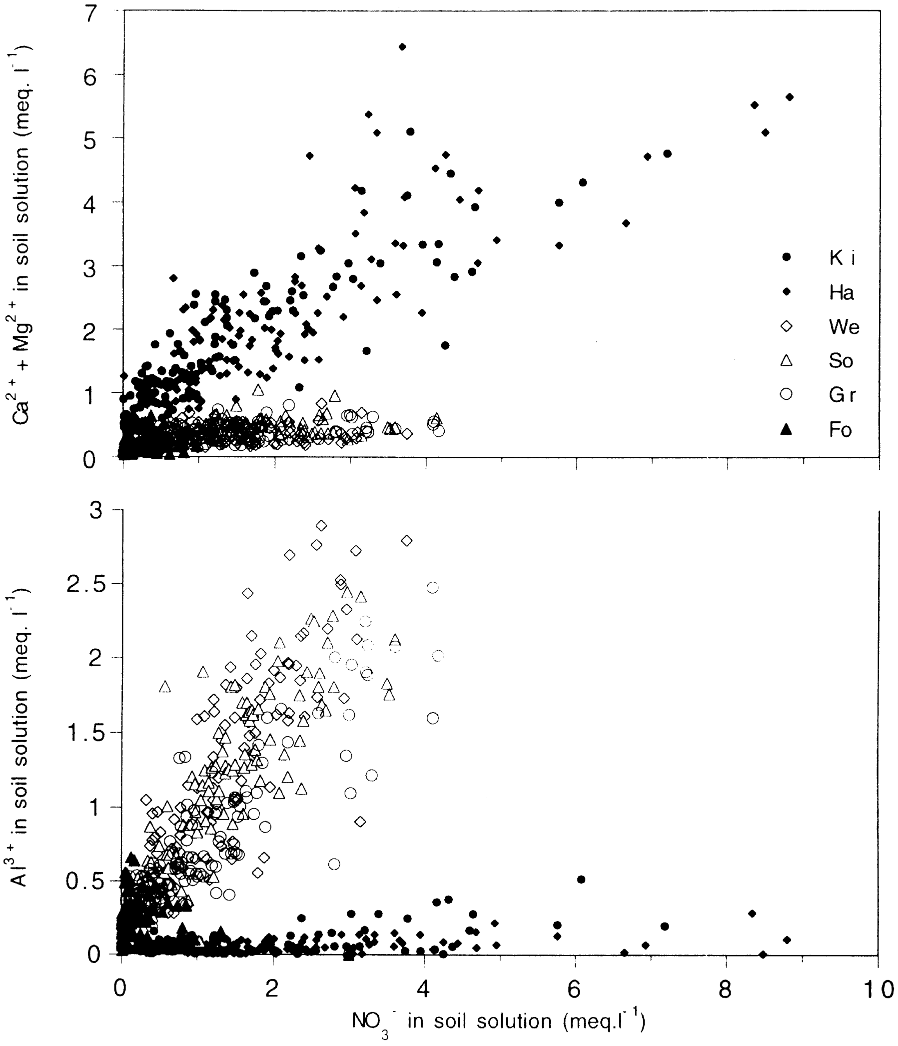

Figure 9. Two weekly averages ($n = 7$) of Ca^{2+}, Mg^{2+} and Al^{3+} (meq·l^{-1}) in the soil solution versus NO_3^--N in the soil solution (meq·l^{-1}) for Control (Co), Kilkenny (Ki), Haldon (Ha), Solling (So), Grizedale (Gr), Wekerom (We), and Fontainebleau (Fo) soils at all sites.

Discussion

Influence of physical and chemical environment on N-dynamics

The concentration of NO_3^-, the dominant form of N in the soil solution, was affected by the transfer of intact soil columns to the various sites. Soils moved to the site with the highest N deposition showed large increases in net nitrification whereas nitrification declined in the soil from this high N site when it was moved to lower N sites. This was not due simply to nitrification to the high levels of ammonium deposition at the polluted site, but was also related to differences in the physical climate at the site, since the covered series of lysimeters also exhibited high net nitrification. The effect appears to be caused by the higher temperatures experienced by the soils under the canopy at the site receiving the highest N deposition. Soil surface temperatures of up to 35 °C were recorded beneath the canopy, due to the low leaf area index. The canopy at this site was very thin, due to poor retention of older needles, and it is suspected that this is the result of pollution damage caused by excess N deposition (Fangmeier et al. 1994).

The majority of the soil types showed no correlation between deposition of N and the leaching of NH_4^+, NO_3^- or total DIN. The amounts of NO_3^- leached from the soils exceeded the deposition of N significantly, reflecting the degradation of the soils i the lysimeters. In spite of the differences in N deposition, one silty clay loam soil, with or without ambient N deposition, leached high and comparable amounts of NO_3^-, suggesting that NO_3^- leaching was not directly influenced by NH_4^+ deposition. This is in contrast to the results of other studies which show a strong relationship between deposition and leaching of N (Dise & Wright 1992; Emmett et al. 1995; Gundersen 1995).

For each site a relationship was noted between bulk soil pH and the amounts of NO_3^- leached annually. The soils with $\text{pH} \geq 4.2$ showed much higher net nitrification (up to 120 mg/l NO_3^--N) than the soil types with $\text{pH} \leq 4.2$ (up to 55 mg/l NO_3^--N). Regression of pH against nitrification for a wide variety of forest soils suggests that while pH may potentially be an important local regulator of nitrification (Persson & Wirén 1995), in general, it is not a good predictor of regional differences (Robertson 1982). This may be related to shifts, at different pHs, in the relative significance of different types of nitrifiers, acid-tolerant versus acid-sensitive nitrifiers (De Boer et al. 1990) or heterotrophic versus autotrophic nitrifiers (Proser 1989; Stams et al. 1990; Barracclough & Purig 1995).

One forest site at which there was a large amount of precipitation showed relatively low levels of NO_3^- leaching. The relationship between gross nitrification rates and soil moisture has been assumed to be linear, but conditions of relative high water contents can result in oxygen limitation, due to reduced O_2 diffusion, which inhibits aerobic microbial activity (Skopp et al. 1990; Grundmann et al. 1995). Water content may interact with soil temperature and influence the diffusion of O_2 and CO_2 in soil water, and thus O_2 distribution, depending on the soil structure (Grundmann et al. 1995). For the soils transferred to this site a synchrony between temperature and NO_3^- leaching was observed.

When different soil types were transferred to sites with moderate precipitation, correlations between temperature fluctuations and net nitrification over time were found, however, time lags of varying length, ranging from 2 to 14 weeks, had to be introduced. Variable time lags could be associated with different retention times in soils which have different textures. In an additional experiment, to investigate the importance of hydrology on leaching of nutrients, leaching volumes could not be clearly related to Cl^- or NO_3^- leaching. Increases in net nitrification after a long period of low NO_3^- leaching have been reported previously (e.g. Johnson et al. 1980; Vitousek & Matson 1985; White 1986; Hart et al. 1994) and have often been interpreted as resulting from growth of initially low populations of nitrifiers or decreased inhibition of nitrification by allelochemical suppression (Sabey et al. 1959; Johnson et al. 1980; Vitousek & Matson 1985; White 1986; Van Miegroet et al. 1990), but these factors are unlikely to be responsible for the observed variable time lags for the same soil under different environmental conditions.

From previous attempts to relate temperature fluctuations to nitrification rates it appears that this relationship follows Arrhenius' law (Macduff & White 1985; Grundmann et al. 1995). For soils hosted at their site of origin, the estimated gross nitrification, using the equation of Arrhenius, equalled the measured net nitrification except for the autumn period during the first year of study. A possible explanation of the problem of variable time lags or overestimation of gross nitrification in autumn for soils located at their sites of origin or transplanted to other sites is given by Davidson et al. (1992) and Hart et al. (1994). These authors argue that high net nitrification rates could result from changes in the relative rates of gross nitrification and NO_3^- immobilisation by microorganisms as NH_4^+ availability increases. Their results suggest that the availability of NH_4^+ increases over time as a response to the utilisation of lower quality C substrates by the heterotrophs when the input of fresh C is prevented. Under these conditions the population of heterotrophs is stationary or declining and the nitrifiers are successful competitors. Moreover, the dominant soil microbial populations apparently prefer NH_4^+ to NO_3^- as a N source (Jones & Richards 1977), and an increase in NH_4^+ availability will result in a reduction of NO_3^- immobilisation. Neither labile C pools, nor gross nitrification rates or dynamics of nitrifier populations have been quantified to substantiate this argument.

At the Wekerom site, rates of mass loss and fungal biomass were greatest in autumn which coincided with the observed NO_3^- peak in the leachate (MP Berg, pers. comm.). A release of the grazing pressure, due to low populations of soil fauna, and improvement in moisture conditions may explain the strong increment in the fungal biomass. This suggests that, at the moment of increased net nitrification, C is not in short supply and heterotrophic populations are very active. High N deposition, in combination with high decomposition rates and changes in soil fauna-microbial interactions, may also indicate high NH_4^+ availability (Verhoef et al. 1989) and could be an alternative explanation for increased net nitrification rates. For the transferred soil types housed under equivalent conditions these factors may also have played a role. As microorganisms adapt to the environmental conditions of their soil habitat (Schmidt 1982; Hunt et al. 1988; Grundmann et al. 1995), this may account for the overestimation of gross nitrification in transplanted soil columns during the first year while in the second year predicted gross nitrification equalled measured net nitrification when the population of nitrifiers were adapted to their new site conditions.

The loamy sand soil from Fontainebleau showed no nitrification notwithstanding the great changes in soil climate and throughfall chemistry due to transplantation to the various sites. It suggests that one or more soil characteristics, such as pH or clay content, within the tolerance range of some heterotrophs but outside the range of nitrifiers, were responsible for the lack of nitrification (Alexander 1977; Macura & Stotzky 1980; Persson & Wirén 1995). Moreover, low N availability at the site of origin could cause plants to produce and eventually release polyphenols and other allelochemicals which might function as inhibitors of nitrification (Rice & Pancholy 1972; Koeppe et al. 1976; Killham 1990) even, if they are persistent in the soil, under altered environmental conditions.

Cation leaching

As predicted by the ion equilibrium model of Reuss & Johnsson (1986), describing soil-solution interactions between Ca and Al, Ca^{2+} (and to a lesser extent Mg^{2+}) dominates the soil solution when Ca occupies more than about 20% of the exchange complex. Below a Ca saturation of 20%, Al dominates the leachates and, as the model predicts, aluminium displacement increases rapidly as the Ca saturation at the exchange sites declines.

The transplantation of intact soil columns highlighted the importance of throughfall chemistry and nitrification in determining acidification and cation leaching in the soils. For a single soil, summed over all sites, the application of the chemical equilibrium equation of Gaines-Thomas (1953) (see Reuss & Johnson 1986; Binkley et al. 1988) provided a useful approximation of expected concentrations of Al^{3+} in the soil solution. Between sites, for single soils, the ratio of Al to Ca in the soil solution is influenced by differences in throughfall chemistry. When transferred to a site with higher input of ions, either large loads of NH_4^+ which are absorbed or nitrified or enhanced anion input (e.g. Cl^- or SO_4^{2-}, the Al/Ca ratio increases as the total ionic strength of the soil solution increases. This forces aluminium, more than divalent and monovalent cations, into solution by displacing them on cation exchange sites (Reuss & Johnson 1986; Binkley et al. 1988; Egli & Fitze 1995; Nissinen 1995). A reduced input of ions at a site results in a fairly rapid decrease of the Al/Ca ratio and is in agreement with other studies in which the input of N and S were reduced (Emmett et al. 1995; Bredemeier et al. 1995).

Aluminium and calcium accompany anions in the soil solution to maintain ionic equilibrium. According to calculations of the balances for cations and anions, SO_4^{2-} behaved as a conservative anion (Raubuch 1992). Output of SO_4^{2-} in the leachate was in equilibrium with the input as throughfall. In the non-nitrifying soil, SO_4^{-2} leached together with Al^{3+}. In all nitrifying soils, NO_3^- was the most important anion in the soil solution. Associated with solution losses of NO_3^- are losses of Ca^{2+} and Mg^{2+} in the non-acidified calcareous soil types, which eventually can contribute to nutrient deficiencies (Van Dijk & Roelofs 1988; Skeffington & Wilson 1988), and losses of Al^{3+} in the acidified soil types, with possible toxicological aspects on trees (Van Breemen et al. 1987; Mulder et al. 1987; Van Breemen & van Dijk 1988; Boxman et al. 1991; Runge & Rode 1991).

An explanation of the etiology of forest die-back

A framework which may describe one of the major underlying mechanisms causing forest die-back has been constructed based upon the results presented in this paper (Figure 10). This framework outlines the feedback mechanisms which may lead to forest decline on certain soil types and under certain conditions of N saturation. If canopy cover decreases through whatever stress factor(s), the heat and water flux to the soil increases, and the frequency and intensity of wetting and drying cycles in the forest floor increases. Both have important consequences for soil organic matter turnover and result in an increase in organic matter decomposition and enhanced mineralisation of N in response to canopy thinning. Additionally, N-deposition may influence positively the early stages of decomposition.

If the soil is N limited, soil warming leads to increased soil concentrations of NH_4^+ and low concentrations of NO_3^-. The roots will compete effectively with the nitrifiers, resulting in increased root uptake, mainly of NH_4^+, and tree growth. Given appropriate pH and concentrations of aluminium this process will result in recovery of canopy structure.

High deposition of atmospheric N, over extended time periods, causes increases in N flux densities (deposition plus mineralization) in excess of vegetation demands (often referred to as N saturation). If soils are N saturated, which is equivalent to the conditions in the lysimeters, the impact on soil

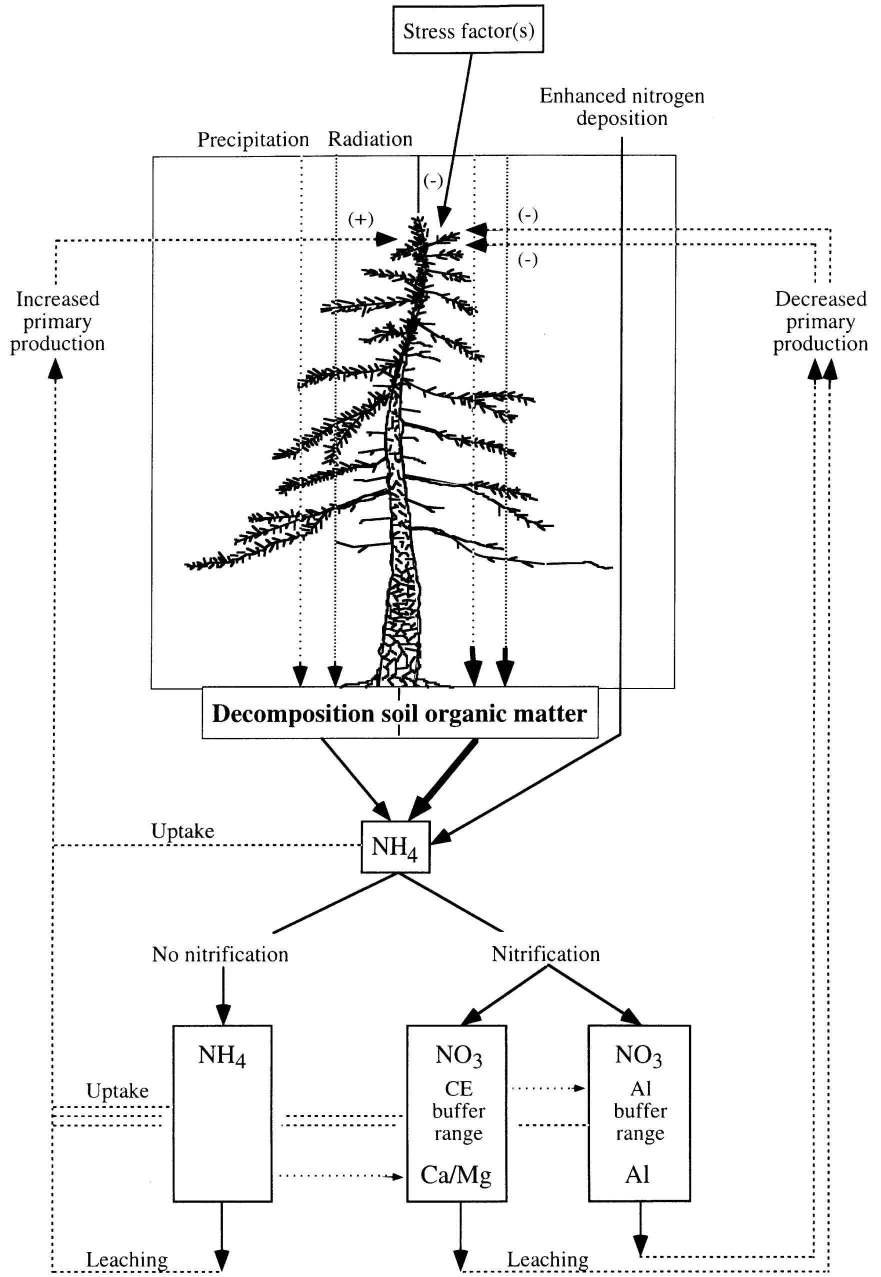

Figure 10. Hypothetical scheme which summarise the obtained experimental results (solid lines) and possible consequences for forest ecosystems (dashed lines). The numbers refer to specific situations. 1) soil N-limited and non-nitrifying (Fontainebleau); 2) soils N-limited or N-saturated and nitrifying; 3) soils N-saturated, nitrifying an din 'cation-exchange' buffer range (Haldon, Kilkenny); 4) soils N-saturated, nitrifying and in 'aluminium' buffer range (Wekerom, Grizedale and Solling). Nitrifying route in bold lines, non-nitrifying route in plain lines (+ increase; − decrease).

chemistry depends on whether the soil is nitrifying or non-nitrifying. If the soil does not nitrify there is a low impact of enhanced NH_4^+ on Ca/Mg leaching. In nitrifying soils, depending on the pH and buffer range of the soil, there is either enhanced leaching of Ca/Mg or release of Al. A key question is the amount of acidity that can be buffered by a soil as this will determine the time that a soil will take to shift from the cation exchange buffer range into the aluminium buffer zone.

Increased leaching of Ca/Mg may lead to nutrient deficiency of the trees. It is expected that high Al^{3+} concentrations in the soil solution will damage roots through aluminium toxicity. Since damaged roots lead to decreased water and nutrient uptake, this will result in a reduction in canopy cover, an acceleration of this positive feedback occurs, and the forest has little chance of recovery. When this is the case, the results suggest that recovery can only be achieved either through addition of Ca/Mg, inhibition of nitrification, cooling of the soil, or removing the source of N saturation (Figure 10).

Reciprocally transplanting intact soil cores across a pollution gradient in Europe, using different forest soils, appears to be applicable to the study of the impact of site specific features, such as physical and chemical characteristics, on soil specific nutrient dynamics. The results emphasise the importance of throughfall chemistry, interacting with the effect of changes in physical climate on soil acidification through internal proton production, in determining the soil solution chemistry of certain ions.

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