

Impact of decreasing throughfall depositions on soil solution chemistry at coniferous monitoring sites in northern Belgium

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Abstract

Impact of decreasing throughfall depositions on soil solution chemistry at three depths was examined in a Corsican pine (*Pinus nigra* Arn. ssp. *laricio* Poiret) stand in Ravels and a Scots pine (*Pinus sylvestris* L) stand in Brasschaat within a time-span of 6 years (1992-1997). At Ravels depositions of sulphate, ammonium, nitrate, calcium, magnesium and sodium decreased by 463, 468, 169, 121, 63 and 169 mol ha⁻¹ per annum. At Brasschaat deposition reduction rates of sulphate, nitrate, calcium and magnesium were 198, 127, 134 and 46 mol ha⁻¹ per annum. In both stands the substantial reductions in inorganic nitrogen deposition were followed by a decline of nitrate fluxes leaving the forest floor and with the seepage water. The decrease of sulphate deposition since 1992 was only manifested by a decline in sulphate concentrations and fluxes during the first half of the measuring period. The increase at the end of the period could be ascribed to the fact that sulphate adsorption which was important between 1993 and 1995 finally ceased. A significant drop of calcium concentrations was discernible at both plots. Magnesium and potassium levels did not fall significantly at Brasschaat. The concentrations of base cations were largely driven by the concentrations of their counter anions, but were influenced by the base cation throughfall fluxes as well. Although a substantial reduction of throughfall acidity occurred, no improvement of the soil water acidity (acid neutralising capacity (ANC)) was noticed. ANC and molar Ca/Al followed decreasing trends at all depths in both plots. For ANC the decline was significant for the topsoil in Ravels. The decrease of molar cation Ca/Al ratio was significant for two out of three depths at both sites. The decrease was due to the drop in calcium concentrations and the raise of Al³⁺ in some horizons. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

As a consequence of the implementation of air pollution commitments, acid depositions of especially sulphur (S) started to decrease in northwest Europe and North America since the mid 1970s (Driscoll et al.,

1989; Hedin et al., 1994; Matzner and Meiwes, 1994). As a consequence, emphasis was put on the impact of declining deposition of acidifying compounds on soil water chemistry and in general, on the recovery of forest ecosystems which were subject to high acid loads in the past decades.

Responses of soil water chemistry were modelled starting from different emission reduction scenarios (De Vries, 1988; Forsius et al., 1998). Roof experiments were initiated to examine soil solution

responses to sudden and strong declines in acid input and to validate nutrient models (Alveteg et al., 1995; Walse et al., 1995; Alewell et al., 1997). The findings obtained from long-term development of element deposition and soil solutes from monitoring sites, liable to declining trends, are useful as feedback to adjust above-mentioned studies and to study the ecosystem responses to changes in ambient conditions.

Due to the higher canopy filtering efficiency of conifers, declines in throughfall deposition following air pollution abatements are expected to be more manifest in coniferous stands than in hardwood stands (Wesselink et al., 1995). Since the bulk of conifers are growing on soils at low nutrient pools, responses in soil water chemistry are expected to be more apparent at these sites.

The present study aimed to examine the impact of reduced loads to soil solutes and fluxes of two pine stands growing on sandy soils. Both acid-impacted sites were subject to decreasing atmospheric depositions in recent years.

2. Material and methods

2.1. Study area

Both stands are situated on the sandy northern plain of Flanders (northern Campine) and belong to the 'EU/UN/ECE intensive monitoring of the forest ecosystem' in the Flemish region (level II). Both stands are first generation pine stands established on former heathland.

Mean annual temperature is 9.0 °C with January and July means of 1.5 and 16.7 °C, respectively. Mean annual precipitation is 799 mm. Precipitation during the growing season (May-October) averages 430 mm. The frost period extends from the end of October until the end of April. Both stands experience high loads of nitrogen and sulphur. The N turnover (retention of ammonium and net-nitrate leaching) is the main contributor to the actual acid production of both ecosystems, which ranges between 3 and 7 kmolc ha⁻¹ per annum at Ravels and 3 and 5 kmolc ha⁻¹ per annum at Brasschaat during 1992-1997.

2.1.1. Ravels

The stand is a 70-year-old (planted in 1930) first generation plantation of Corsican pine (*Pinus nigra*

Arn. ssp. *laricio* Poiret) located at Ravels in northern Belgium (51°24'N; 5°03'E, elevation: 31 m).

The total stem volume and basal area in 1995 amounted to 623 m³ and 51 m² ha⁻¹, respectively. The crop comprised 408 stems per hectare and attained a mean dbh and height of 39.5 cm and 23 m, respectively. Between 1988 and 1995 annual basal area increment was estimated at 1.6 m² ha⁻¹ per annum. Mean height and girth increment averaged, respectively, 0.21 m and 2.3 cm per annum.

The soil is classified as a Haplic Podzol (FAO, 1988) developed in aeolian sand deposits overlying terrace-crossing deposits from the Meuse and Rhine streams. The sandy soil (sand fraction between 89 and 97%) is moderately dry with a distinct humus and/or iron B-horizon and a loamy substrate starting at 115 cm of depth. The soil is excessively drained, never saturated, with a ground water table at 2.25 m of depth. The pH_{CaCl2} averages 3.2 in the organic layers and topsoil while it exceeds 4 in the subsoil (Table 1). Base saturation of the mineral soil (extracted with unbuffered BaCl₂ 0.1N) ranges between 5 and 10%. C/N ratio of forest floor (consisting of L-, F- and H-layer) and upper soil layers is about 36, whereas it ranges between 21 and 29 in the subsoil. The amount of nitrogen sequestered in the organic layers (95.6 t DW ha⁻¹) amounted to 1039 N kg ha⁻¹. The amount of nitrogen returned in litter was estimated at 41 kg ha⁻¹ (foliage: 25 kg) in 1988. Nitrogen levels of current year needles varied between 1.8 and 2.0%.

The ground vegetation is composed mainly of ferns (*Dryopteris dilatata* (Hoffm.) A. Gray and *Dryopteris carthusiana* (Vill.) H.P. Fuchs) and *Molinia caerulea* (L.) Moench. A shrub layer is not present.

2.1.2. Brasschaat

The stand is a 71-year-old (planted in 1929) first generation plantation of Scots pine (*Pinus sylvestris* L.) located at Brasschaat, near Antwerpen (51°18'N; 04°31'E) at an altitude of 15 m. The standing crop and basal area amounted to 324 m³ and 36 m² ha⁻¹, respectively in 1995, comprised 650 stems and attained a mean dbh and height of 26.2 cm and 20.5 m, respectively. Annual basal area increment between 1988 and 1995 was estimated at 0.5 m² ha⁻¹ per annum. Mean height and girth increment averaged, respectively, 0.12 m and 1.1 cm per annum.

Table 1
Soil characteristics of study sites

Depth	pH _{CaCl2}	CEC (cmol _c kg ⁻¹)	Base saturation (%)	C (g kg ⁻¹)	N (g kg ⁻¹)	C/N	Sand (%)	Silt (%)	Clay (%)
Ravels									
6-0	3.2	16.7	65.2	398	10.873	36.6			
0-12	3.1	4.0	9.1	33	0.921	35.8	89	9	2

12-25	3.4	3.3	5.5	23	0.614	37.5	91	8	1
30-60	4.0	1.8	9.9	12	0.417	28.8	95	5	
60-100	4.4	1.1	8.3	3	0.144	20.8	97	3	
Brasschaat									
6-0	3.3	17.9	66.8	454	13.001	34.9			
0-5	3.0	2.7	17.7	30	1.021	29.4	81	13	6
5-30	3.3	1.6	9.8	8	0.457	17.5	89	7	4
40-65	3.7	1.8	6.9	3	0.164	18.3	89	9	2
65-105	3.8	3.3	5.8	3	0.167	18.0	98	0	0

The soil is classified as an Umbric Regosol (FAO, 1988) developed in sand deposits covering a 0.5 m thick loamy clay layer at 1.75 m of depth. The sandy soil (sand fraction between 80 and 98%) is moderately wet with a distinct humus or iron B-horizon. The soil is poorly drained but rarely saturated with a ground water table at 2.7 m. The pH_{CaCl2} averages 3.2 in the organic layers while it reaches 3.7 in the subsoil (Table 1). The base saturation (extracted with unbuffered BaCl₂ 0.1 N) is 18% in the topsoil but is below 10% deeper in the soil. C/N ratio is 35 in the forest floor and 29 in the topsoil. It drops below 20 just under the topsoil. The amount of nitrogen incorporated in the organic layers (140.8 t DW ha⁻¹) amounts to 1831 N kg ha⁻¹. The amount of nitrogen returned in litter was estimated at 46 kg ha⁻¹ (foliage: 27 kg) in 1988. Nitrogen levels of current year needles averaged 2.1%.

An obvious shrub and herb layer is lacking. A moss layer mainly consisting of species of *Polytrichum* and *Hypnum cupressiforme* is well developed.

2.2. Sampling

Throughfall was measured from 1992 onwards and was sampled with 10 systematically distributed bulk collectors in a 0.25 ha large plot. They consisted of a polyethylene funnel (14 cm Ø) placed at a standard height of 1 m which was connected to a subterranean 2 l polyethylene bottle. A nylon mesh was placed in the funnel to avoid contamination by large particles.

The throughfall was monthly sampled in 1992, but fortnightly from 1993 and onwards. Samples from all collectors were bulked together at every sampling event. Bulk precipitation was sampled from 1993 onwards.

Soil water from three horizons (Ravels: Ah/E/Bh (10 cm), Bh (30 cm) and Cgl (75 cm); Brasschaat: Ap (10 cm), A/E/Cg (45 cm) and Cg (70 cm)) was sampled at three locations using suction lysimeter candles with ceramic cups. Sampling was conducted on a monthly to fortnightly basis. Samples from every depth were bulked to one composite sample. Humus water (forest floor percolates) was sampled using zero tension percolation meters. They consisted of a 5 cm thick inox box provided by a mesh and were installed just below the forest floor. The biweekly sampling of the humus water started from mid 1993.

2.3. Chemical analysis

Base cations and total Al were analysed by atomic absorption spectrophotometry. All strong anions and ammonium were analysed by ion chromatography, pH was measured with an ion electrode. Bicarbonates were determined by titration with 0.1N HCl to pH 4.2.

2.4. Calculation of deposition and output fluxes

Throughfall fluxes were obtained by multiplying precipitation volume with concentrations. Drainage fluxes from forest floor or soil were calculated

assuming conservative behaviour of chloride (no root uptake, no changes due to mineralisation). Throughfall fluxes of chloride were divided by the annual average chloride concentration of humus and soil water in order to obtain yearly drainage fluxes from forest floor (from 1993 till 1997) and below the deepest lysimeter (from 1992 to 1997), respectively. Input-output budgets were made assuming that litterfall equalled mineralisation fluxes. Also the occurrence of soil emission of nitrogen oxides was disregarded.

Acid neutralising capacity (ANC) was obtained by subtracting the equivalent sum of strong acid anions (SO_4 , NO_3 and Cl; strong acid anions (SAA)) from the equivalent sum of base cations (SBC). The equivalent sum of SAA is used as index for ionic strength. Throughfall acidity was calculated as the equivalent sum of acid ion deposition (NH_4 , SO_4 , NO_3 and Cl) minus the base cation deposition (BC deposition).

2.5. Statistics

Throughfall trends were calculated using linear regressions of the annual deposition flux. For the soil solutes monthly averages were used to assess linear trends. The relative change was calculated using the start value and end value of the prediction estimates. Trends in the soil solution were reassessed when a time trend in the chloride concentration due to changes in soil moisture was discernible. In this case the ion levels were expressed as ratio to chloride. The statistical analyses were performed with the statistical package Statgraphics plus (Manugistics Group Inc., 1997). Levels of statistical significance are * $P < 0.05$, ** $P < 0.01$ and *** $P < 0.001$.

3. Results

3.1. Throughfall deposition

At Ravels and Brasschaat throughfall water flux decreased during the measuring period by 46 and 32%, respectively (Table 2). Depositions of most elements were significantly correlated with the water flux ($P < 0.05$) except for K and HCO_3 at Ravels and inorganic N, HCO_3 and Cl at Brasschaat.

Although pH values of throughfall were already high (pH range: 4.5-6.5), all sites experienced a decrease in deposition of hydrogen ions ($P < 0.05$). Depositions of sulphate decreased by 463 and 198 molc ha^{-1} per annum at Ravels and Brasschaat, respectively ($P < 0.01$ and $P < 0.05$). This led to a 69% decrease in sulphate deposition at Ravels and a 39% decrease at Brasschaat. Calcium and magnesium deposition dropped at both sites by about 120-130 and 50-60 molc ha^{-1} per annum ($P < 0.05$). At Ravels this implied a reduction in deposition of about 75% for both elements whereas at Brasschaat reduction rates resulted in a 60% reduction for calcium and a 46% reduction for magnesium. Other base cations (K and Na) also followed declining trends but this was found to be only significant for sodium at Ravels (62% reduction). Nitrate fluxes decreased by 169 and 127 molc ha^{-1} per annum at Ravels and Brasschaat, respectively ($P < 0.05$). At Ravels also a significant decreasing trend in the deposition of NH_4 was observed ($P < 0.05$). The decreasing deposition rate (-468 molc ha^{-1} per annum) resulted in a 58% reduction and was concomitant with the decrease in sulphate (-463 molc ha^{-1} per annum). At Brasschaat no decline in deposition of NH_4 occurred which resulted in a change of the $\text{NH}_4\text{-N}$ to $\text{NO}_3\text{-N}$ ratio from 1.5 to 3.2. Fluxes of inorganic nitrogen at both plots approached similar levels at the end of the measuring period (1996-1997).

The changes in deposition rates resulted in a substantial reduction of the acid input precipitation at Ravels. The throughfall acidity decreased by 60% ($P < 0.01$) which reflected the steeper decline of acidifying compounds in the throughfall (NH_4 , SO_4 and NO_3) compared to base cations. At Brasschaat only a slight insignificant decrease in throughfall acidity (-18%) occurred.

3.2. Soil solutes and fluxes

3.2.1. Inorganic nitrogen

A significant change in nitrate concentrations was only noticed in the soil water of the Bh- and Cg1-horizon at Ravels. Nitrate decreased by 44% from 0.79 to 0.44 mmolc l^{-1} in the Bh-horizon and by 37% from 1.00 to 0.63 mmolc l^{-1} in the Cg1-horizon ($P < 0.05$) (Table 3). Nitrate levels also showed a decreasing trend in the soil water at Brasschaat, however, this was

Table 2

Water (mm per annum) and element fluxes (kmol³ ha⁻¹ per annum) and linear regression coefficients of trend analysis of throughfall deposition during 1992 and 1997 in Ravels and Brasschaat

	1992	1993	1994	1995	1996	1997	1997-1992/ 1992 (%)	Slope (kmolc ha ⁻¹ per annum
Ravels								
Water (mm)	729	829	668	581	473	439	-46	-74
H	0.016	0.020	0.020	0.015	0.005	0.003	-77	-0.003
HCO ₃	0.85	1.40	1.08	0.66	0.67	1.11	-18	-0.037
SO ₄ -S	3.74	2.69	2.29	1.71	1.48	1.35	-69	-0.463
NO ₃ -N	1.07	1.50	0.96	0.62	0.49	0.53	-66	-0.169'
NH ₄ -N	3.84	4.06	3.21	2.07	1.89	2.09	-58	-0.468
Ninorg	4.91	5.56	4.17	2.69	2.38	2.64	-60	-0.637'
Cl	1.24	1.48	0.99	0.97	0.73	0.97	-39	-0.103
Ca	0.80	0.96	0.44	0.25	0.39	0.33	-73	-0.121
Mg	0.43	0.38	0.29	0.21	0.15	0.14	-75	-0.063'
K	0.49	0.48	0.49	0.38	0.37	0.45	-19	-0.019
Na	1.37	1.29	0.95	0.85	0.63	0.60	-62	-0.169
BC deposition"	3.09	3.11	2.17	1.69	1.54	1.52	-60	-0.373''
Throughfall acidity"	6.80	6.62	5.28	3.68	3.05	3.44	-60	-0.831
Brasschaat								
R (mm)	817	760	764	749	544	578	-32	-53
H	0.196	0.136	0.225	0.169	0.038	0.038	-76	-0.031
HCO ₃	0.13	0.82	0.33	0.15	0.36	0.88	+50	+0.05
SO ₄ -S	2.94	2.04	2.02	1.85	1.71	1.79	-39	-0.198'
NO ₃ -N	1.16	0.91	1.16	0.71	0.57	0.57	-55	-0.127'
NH ₄ -N	1.80	1.77	2.16	1.76	1.60	1.89	-4	-0.013
Ninorg	2.96	2.62	3.32	2.47	2.17	2.46	-23	-0.140
Cl	1.16	1.08	1.46	1.58	1.02	1.02	-9	-0.022
Ca	1.06	1.24	0.79	0.49	0.63	0.55	-60	-0.134
Mg	0.50	0.40	0.47	0.38	0.29	0.26	-46	-0.046'
K	0.51	0.46	0.49	0.50	0.39	0.43	-17	-0.018
Na	1.30	1.00	1.25	1.13	0.91	1.11	-16	-0.038
BC deposition"	3.38	3.11	3.00	2.50	2.22	2.36	35	-0.234''''
Throughfall acidity"	3.69	2.70	3.80	3.40	2.68	2.91	-18	-0.125

" BC deposition: deposition of all base cations.

" Throughfall acidity: equivalent sum of acid ion deposition (NH₄, SO₄, NO₃ and Cl) minus BC deposition.

'p < 0.05.

''p < 0.01.

''''p < 0.001.

not significant. In the A/E/Cg-horizon nitrate levels even increased again at the end of the measuring period. Ammonium concentrations decreased below the detection limit in the solution of the subsoil at Ravels. In the topsoil an increase was noticed. At Brasschaat NH₄ disappeared completely only in the soil water of the deepest horizon.

To obtain a better insight in the nitrogen dynamics, incoming fluxes of inorganic nitrogen and its losses from the forest floor and in seepage water were calculated (Fig. 1).

At Ravels the substantial decline in input of inorganic nitrogen from 5.5 to 2.5 kmolc ha⁻¹ per annum was concurrent with losses of nitrate in the seepage water which declined from 3.6 to 0.9 kmolc ha⁻¹ per annum. Nitrate fluxes through the forest floor declined from 2.1 to 0.5 kmolc ha⁻¹ per annum and closely matched the development of nitrate fluxes in the throughfall. The cumulative amount of nitrate leaving the forest floor over the period 1993-1997 (4.7 kmolc N ha⁻¹) nearly equalled the cumulative amount of nitrate reaching the forest floor by throughfall (4.1 kmolc N ha⁻¹). In

Table 3
Trends in soil solution chemistry during 1992-1997, analysed by linear regression analysis"

	Period 1992	Period 1997	Change (%)	Slope (mmolc l ⁻¹ month ⁻¹)	St. err.
Ravels					
pH					
Ah/E/Bh	3.96	3.28	-17.2	-0.0095 [']	0.0044
Bh	3.45	3.86	+11.9	0.0057 ^{""'}	0.0015
Cg!	3.73	4.14	+11.0	0.0058 ^{*"}	0.0016
Al (mmolc l ⁻¹)					
Ah/E/Bh	0.22	0.38	+69.5	0.0022	0.0018
Bh	0.54	1.12	+107.0	0.0081 ^{""'}	0.0028
Cg!	1.68	1.83	+8.9	0.0021	0.0054
Ca (mmolc l ⁻¹)					
Ah/E/Bh	0.99	0.29	-70.7	-0.0098 ^{*"}	0.0034
Bh	0.62	0.55	-11.3	-0.0010	0.0014
Cg!	0.41	0.24	-41.5	-0.0025 [']	0.0012
Mg (mmo!, l ⁻¹)					
Ah/E/Bh	0.13	0.12	-8.0	-0.0002	0.0006
Bh	0.11	0.11	-0.0	-0.0001	0.0003
Cg!	0.13	0.11	-15.4	-0.0003	0.0004
K (mmolc l ⁻¹)					
Ah/E/Bh	0.083	0.094	+13.6	0.0002	0.0005
Bh	0.031	0.016	-48.3	-0.0002	0.0001
Cg!	0.024	0.018	-25.0	-0.0001	0.0001
Na (mmo!, l ⁻¹)					
Ah/E/Bh	0.36	0.31	-12.6	-0.0006	0.0009
Bh	0.29	0.35	+20.7	0.0008	0.0007
Cg!	0.34	0.51	+50.0	0.0024 ^{*'}	0.0010
NH ⁺ (mmolc l ⁻¹)					
Ah/E/Bh	0.016	0.209	+1325	0.0027 ^{""'}	0.0009
Bh	0.009	0.003	- 64.9	-0.0014	0.0014
Cg!	0.000	0.000		0.000	
NO ₃ (mmolc l ⁻¹)					
Ah/E/Bh	0.64	0.96	+49.4	0.0044	0.0043
Bh	0.79	0.44	-44.3	-0.0050 ^{''}	0.0023
Cg!	1.00	0.63	-37.0	-0.0052 [']	0.0023
SO ₄ (mmot l ⁻¹)					
Ah/E/Bh	1.02	0.54	-46.8	-0.0066	0.0038
Bh	0.62	0.51	-17.7	-0.0016	0.0021
Cg!	0.82	0.97	+18.3	0.0022	0.0029
Cl (mmolc l ⁻¹)					
Ah/E/Bh	0.59	0.37	-38.0	-0.0032	0.0021
Bh	0.43	0.48	+11.6	0.0007	0.0011
Cg!	0.26	0.67	+257.7	0.0068 ^{""*"}	0.0013
ANC (mmolc l ⁻¹)					
Ah/E/Bh	-0.10	-1.27	-1170	-0.0200 ^{*""}	0.0037
Bh	-0.98	-1.01	-3.1	-0.0004	0.0040
Cg!	-1.36	-1.46	-7.4	-0.0014	0.0050

Table 3 (Continued)

	Period 1992	Period 1997	Change (%)	Slope (mmolc1 ⁻¹ month ⁻¹)	St. err.
SAA (mmol ⁻¹ l ⁻¹)					
Ah/E/Bh	1.79	1.99	+11.1	0.0029	0.0057
Bh	1.89	1.68	-11.1	-0.0030	0.0049
Cgl	2.40	2.36	-1.7	-0.0005	0.0058
SBC (mmol ⁻¹ l ⁻¹)					
Ah/E/Bh	1.57	0.78	--50.3	-0.0112	0.0046
Bh	1.07	1.02	-4.7	-0.0007	0.0026
Cgl	0.86	0.93	+8.1	0.0009	0.0019
Ca/Al (mol mol ⁻¹)					
Ah/E/Bh	5.17	1.22	-76.4	-0.0556'	0.0162
Bh	1.42	0.73	-48.6	-0.0097''	0.0027
Cgl	0.26	0.20	-23.1	-0.0009	0.0009
Brasschaat					
pH					
Ap	4.54	3.93	-13.4	-0.0086	(1.0117
A/E/Cg	3.87	3.41	-10.4	-0.0064'	-0.0063
Cg	3.57	3.55	-2.0	-0.0003	0.0009
Al (mmolc l ⁻¹)					
Ap	0.12	0.14	+16.8	0.0003	0.0012
A/E/Cg	0.83	0.78	-6.0	-0.0064	0.0024
Cg	0.87	1.31	+50.6	0.0063'	0.0027
Ca (mmol ⁻¹ l ⁻¹)					
Ap	0.63	0.22	-65.8	-0.0058	0.0036
A/E/Cg	0.63	0.40	-36.5	-0.0032'	0.0014
Cg	0.41	0.28	-31.7	-0.0018	0.0008
Mg (mmolc l ⁻¹)					
Ap	0.24	0.10	-60.2	-0.0021'	0.0015
A/E/Cg	0.19	0.13	-31.6	-0.0008'	0.0004
Cg	0.19	0.15	-21.1	-0.0006	0.0003
K (mmolc l ⁻¹)					
Ap	0.122	0.035	-71.1	0.0012	0.0004
A/E/Cg	0.092	0.091	-1.1	-0.0000	0.0002
Cg	0.129	0.085	-34.1	-0.0006	0.0001
Na (mmol ⁻¹ l ⁻¹)					
Ap	0.32	0.38	+20.2	0.0009	0.0013
A/E/Cg	0.43	0.51	+18.6	0.0042	0.0005
Cg	0.45	0.53	+17.8	0.0012	0.0008
NH ₄ (mmolc l ⁻¹)					
Ap	0.152	0.076	-50.4	-0.0006	0.0011
NE/Cg	0.126	0.161	+28.3	0.0052	0.0087
Cg	0.016	0.003	-83.4	-0.002	0.0017
NO ₃ (mmolc l ⁻¹)					
Ap	0.35	0.25	-29.0	-0.0014	0.0014
A/E/Cg	0.95	0.92	-3.2	-0.0004	0.0032
Cg	1.16	1.03	--11.2	-0.0018	0.0016

Table 3 (Continued)

	Period 1992	Period 1997	Change (%)	Slope (mmolc l ⁻¹ month ⁻¹)	St. err.
S₀₄ (mmol., l⁻¹)					
Ap	0.74	0.44	-40.5	-0.0042	0.0039
A/E/Cg	0.96	0.81	-15.6	-0.0021	0.0019
Cg	0.90	0.73	-18.9	-0.0023	0.0020
Cl (mmolc l⁻¹)					
Ap	0.53	0.46	-12.7	-0.0009	0.0021
A/E/Cg	0.53	0.52	-1.9	-0.0001	0.0008
Cg	0.57	0.57	-0.0	-0.0000	0.0013
ANC (mmolc l⁻¹)					
Ap	-0.32	-0.44	-37.5	-0.0016	0.0058
-A/E/Cg	-0.29	-0.33	-13.8	-0.0006	0.0026
-Cg	-1.23	-1.70	-38.2	-0.0066	0.0035
SAA (mmolc l⁻¹)					
Ap	1.62	1.15	-29.0	-0.0066	0.0056
A/E/Cg	2.45	2.25	-8.1	-0.0027	0.0039
Cg	2.29	2.41	+5.2	0.0048	0.0048
SBC (mmol., l⁻¹)					
Ap	1.31	0.73	-44.3	-0.0082	0.0060
A/E/Cg	1.32	1.15	-12.9	-0.0023	0.0021
Cg	1.16	1.03	-11.2	-0.0018	0.0016
Ca/Al (mol mol⁻¹)					
Ap	4.90	2.35	-52.0	-0.0360	0.0311
A/E/Cg	1.05	0.46	-56.1	-0.0084"	0.0040
Cg	0.60	0.32	-46.7	-0.0038	-0.0038

"Number of replicates (11) for Ah/E/Bh, Bh and Cg horizon in Ravels are 19, 44 and 31. In Brasschaat number of replicates for Ap, A/E/Cg and Cg-horizon are 35, 59 and 62.

"*p* < 0.05.

***p* < 0.01.

****p* < 0.001.

1993, 68% of the input of NH₄ was retained in the forest floor. The remainder amounted to 1.3 kmolc ha⁻¹ and nitrified in the topsoil. From 1994 onwards ammonium was almost fully retained in the forest floor with annual output never exceeding 0.8 kmolc ha⁻¹. The cumulated output of inorganic nitrogen in the seepage water (10.7 kmolc N ha⁻¹) over 6 years was 48% of the cumulated input (22.4 kmolc N ha⁻¹). The 5-year cumulated amount of inorganic N leaving the forest floor was estimated at 90% of the total soil output of nitrogen.

At Brasschaat the significant reduction in nitrate deposition (55%) resulted in a slight but pronounced decrease in nitrate leachates of forest floor and soil (Fig. 1). The course of nitrate leaching losses through

the forest floor (cumulated amount: 3.8 kmolc N ha⁻¹) coincided with the fall in nitrate input over the 5-year period (cumulated amount: 3.9 kmolc N ha⁻¹). **IN** fluxes leaving the forest floor remained at the same level which lead to a higher contribution of reduced N in the inorganic N flux leaving the organic layers during the study period. The remaining ammonium, which was about 31% of the amount in throughfall, disappeared in the subsoil. The 6-year cumulated amount of N soil output (13.5 kmolc N ha⁻¹) was estimated at 84% of the total cumulated N input (16.0 kmolc N ha⁻¹) which indicated a lower N ecosystem demand compared to Ravels. In 1995 nitrogen output exceeded its input. The 5-year cumulated amount of inorganic N leaving the forest floor was estimated at 72% of total soil output

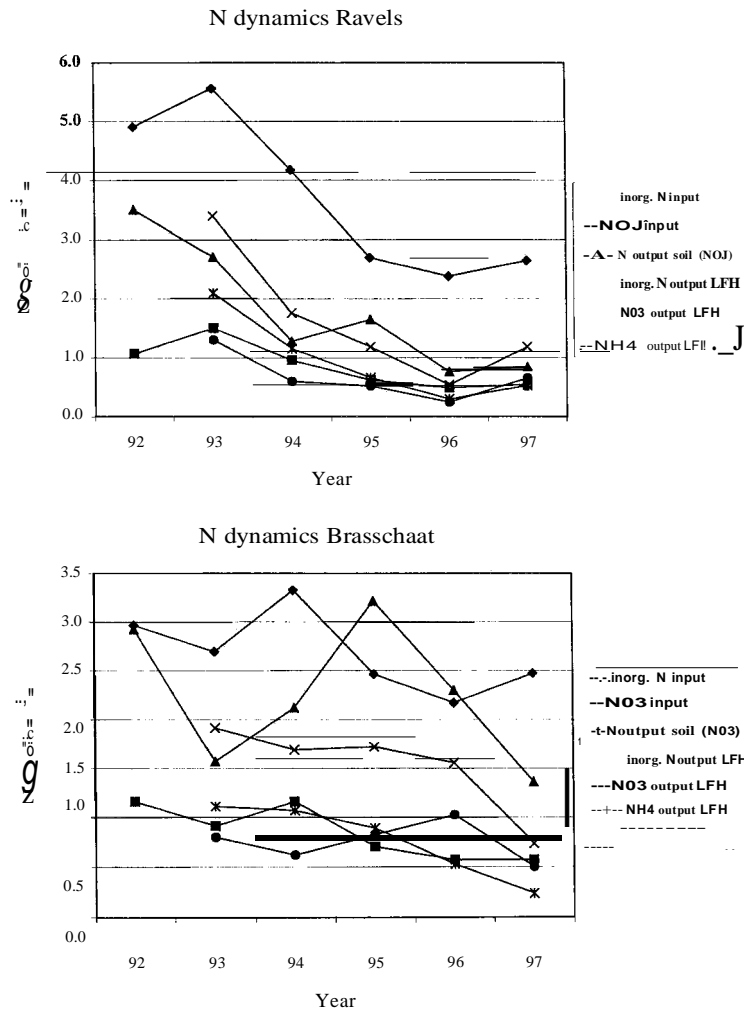


Fig. 1. Nitrogen dynamics at Ravels (upper) and Brasschaat (lower) between 1992 and 1997. Fluxes of inorganic nitrogen in throughfall vs. fluxes in seepage water and forest floor (LFH).

of nitrogen which may indicate an additional N release from the soil.

At the end of the measuring period when differences in deposition of reduced and oxidised N between the two sites were levelled out, retention of reduced nitrogen in the forest floor was found to be lower at Brasschaat ($0.9 \text{ kmolc N ha}^{-1}$) compared to Ravels ($1.5 \text{ kmolc N ha}^{-1}$) (Table 4). The remainder of the deposited NH_4 at Brasschaat disappeared in the deeper soil layers. Soil output of inorganic nitrogen (nitrate) amounted to $1.8 \text{ kmolc ha}^{-1}$ per annum in 1996–1997, which was twice as high compared to Ravels.

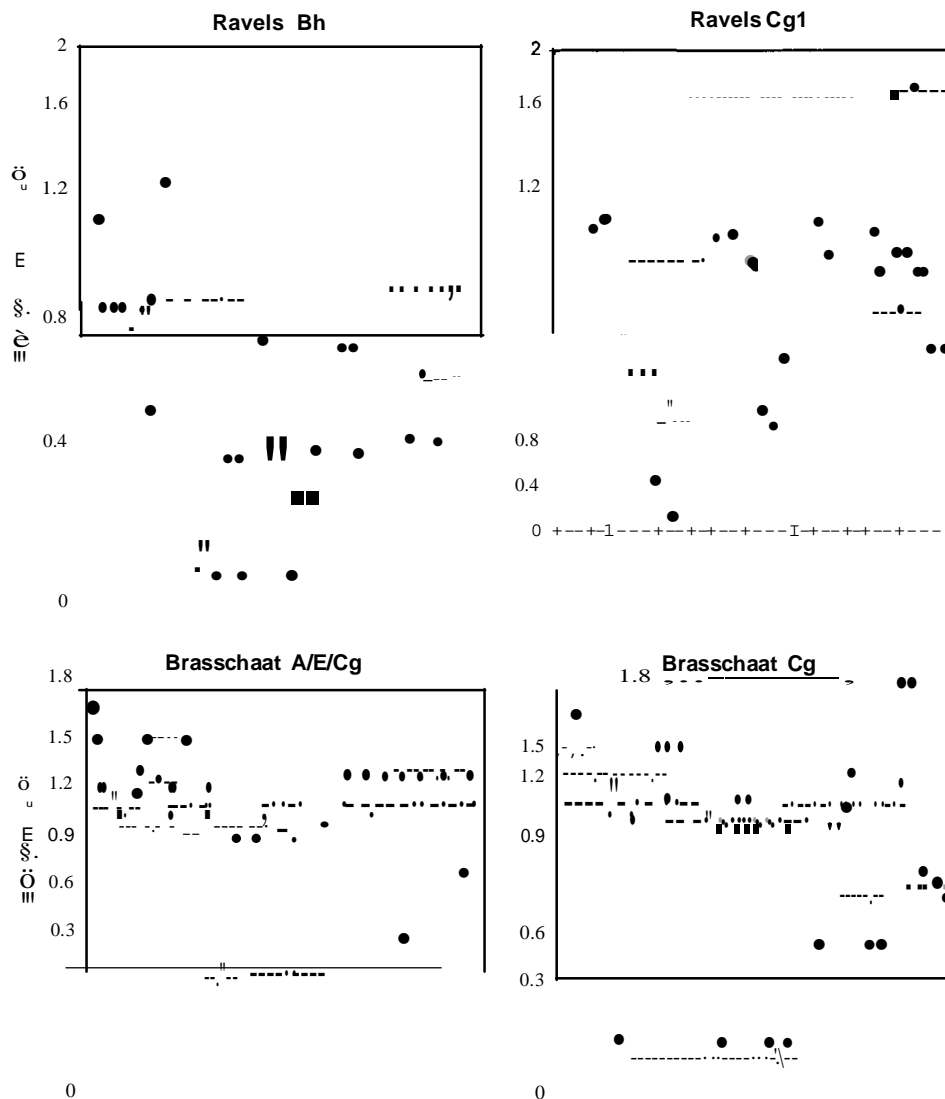
3.2.2. Sulphates

No significant trend in sulphate levels was found at both sites. Decreases by 40% in the topsoil water could not be substantiated by statistics due to large variation and probably low number of replicates. In the soil water of the Bh-horizon at Ravels and the A/E/Cg and Cg-horizon at Brasschaat a substantial decline was observed from 1992 till 1995 but this was offset by a recovery at the end of the measuring period (Fig. 2, Table 3). Net fluxes of sulphate were predominantly positive but became slightly negative at the end of the measuring period indicating a shift from adsorption to

Table 4

Annual input, output and accumulation of water (mm) and nitrogen (kmoIc ha⁻¹ per annum) at Ravels and Brasschaat in forest floor (LFH) and soil for the period 1996-1997

Substance	Throughfall input (kmoIc ha ⁻¹ per annum)	Output LFH (kmoIc ha ⁻¹ per annum)	Accumulation LFH (kmoIc ha ⁻¹ per annum)	Accumulation LFH (% of input)	Output seepage water (kmoIc ha ⁻¹ per annum)	Accumulation LFH + soil (kmoIc ha ⁻¹ per annum)	Accumulation LFH + soil (% of input)
Ravels							
NH ₄ -N	2.00	0.47	1.52	76	0.0	2.00	100
NO ₃ -N	0.52	0.29	0.23	43	0.91	-0.39	-74
Nin	2.52	0.76	1.75	70	0.91	1.61	64
Water (mm)	420.5	297.7	122.8	29.2	136.9	283.6	67
Brasschaat							
NH ₄ -N	1.75	0.86	0.88	50	0	1.75	100
NO ₃ -N	0.57	0.44	0.14	23	1.75	-1.18	-206
Nin	2.32	1.31	1.01	44	1.75	0.57	25
Water (mm)	559.5	268.5	291	52	176.0	383.5	69



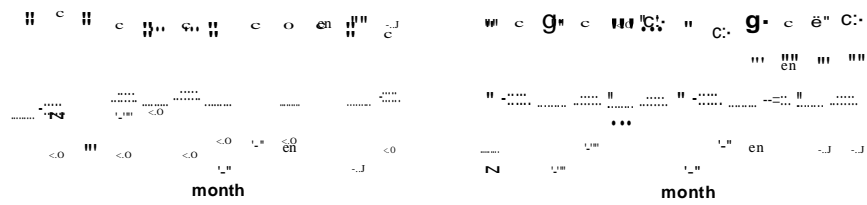


Fig. 2. Time course of monthly concentrations of sulphate in soil water of deep horizons between 1992 and 1997.

Input-output budget S

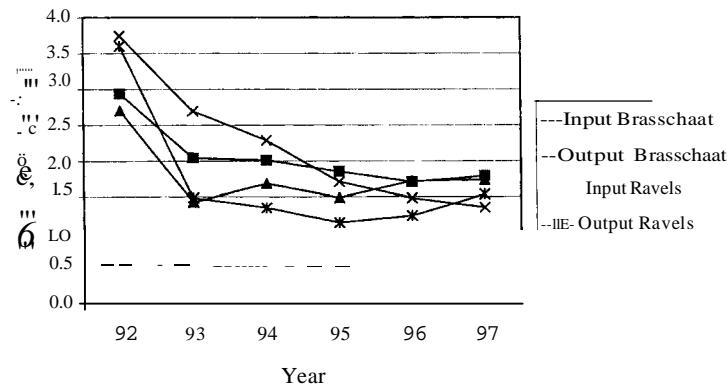


Fig. 3. Sulphur dynamics at Ravels and Brasschaat between 1992 and 1997. Sulphur in throughfall vs. sulphur fluxes in seepage water.

desorption (Fig. 3). Between 1993 and 1995 sulphur adsorption rates amounted to 30-40% and 20-30% of the sulphur input at Ravels and Brasschaat, respectively.

3.2.3. Base cations

At Ravels only a significant reduction in calcium concentration in the topsoil (71%) and the deepest horizon (42%) was detected (Table 3). A more pronounced fall of other base cation concentrations within the latter horizon could have been hidden by a concentration effect due to a decrease in soil moisture. Chloride concentrations doubled since the beginning of the measuring period (Table 3). Including base cations expressed as ratio to chloride in the regression analysis, a significant time trend was assessed for both Ca, Mg and K ($P < 0.05$, $P < 0.05$ and $P < 0.01$, respectively) (not in table).

At Brasschaat, on the contrary, concentrations of Ca, Mg and K dropped by 60-70% in the topsoil water. Also in the soil water of the deeper horizons a significant decline was observed but the reduction was confined to 20-40% of initial concentrations.

The sum of basic cations followed decreasing trends but this was only significant in the topsoil water in Ravels. Raised sodium concentrations, especially in the deepest horizon at Ravels might have mitigated the decrease in SBC at those plots.

3.2.4. pH, Al, Ca/Al, ANC

At Ravels pH dropped with 0.7 units in the topsoil ($P < 0.05$) but increased in the soil water of the deeper

horizons with 0.4 units ($P < 0.01$) (Table 3). The fall in topsoil pH was accompanied by an increase in total Al and a decrease of Ca/Al ratio ($P < 0.01$) and ANC ($P < 0.001$). The significant increase of pH in the deeper soil water was however, not consistent with the course of Al, Ca/Al and ANC. Total Al increased in the Bh-horizon by 107% ($P < 0.01$) which lead to a decrease of the molar Ca/Al ratio from 1.4 to 0.7 ($P < 0.001$).

At Brasschaat pH was lowered in the middle horizon where the pH approached values around 3.4 ($P < 0.01$) at the end of the measuring period. A significant increase of total Al was found in the soil water of the deepest horizon ($P < 0.05$). ANC and molar cation Ca/Al ratios tended to decrease at all depths. This decrease was, however, only significant for the molar Ca/Al ratio in the A/E/Cg and Cg-horizon where a drop was noticed from 1.05 to 0.46 and from 0.60 to 0.32, respectively ($P < 0.05$ and $P < 0.001$).

4. Discussion

4.1. Throughfall fluxes

Reductions in sulphur depositions followed by reductions in hydrogen ions or calcium are often reported in several parts of Europe as a consequence of air pollution abatements (Matzner and Murach, 1995; Puxbaum et al., 1998; Ukonmaanaho et al., 1998). The

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