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Acidifying processes and acid-base reactions in forest soils reciprocally transplanted along a European transect with increasing pollution

M. RAUBUCH[1], F. BEESE[1], T. BOLGER[2], J.M. ANDERSON[3],
M.P. BERG[6], M.-M. COÛTEAUX[4], P. INESON[5], F. MCCARTHY[2],
P. SPLATT[3], H.A. VERHOEF[6] & T. WILLISON[3]
[1]*Institute of Soil Science and Forest Nutrition, University Göttingen, Büsgenweg 2, 37077 Göttingen, Germany;* [2]*Dept. of Zoology, University College Dublin, Belfield, Dublin 4, Ireland;* [3]*Dept. of Biological Sciences, Hatherly Laboratories, University of Exeter, Prince of Wales Road, Exeter EX4 4PS, U.K.;* [4]*CNRS, Route de Mende, BP 5051, F34033 Montpellier Cedex, France;* [5]*Institute of Terrestrial Ecology, Merlewood Research Station, Grange-over-Sands, Cumbria LA11 6JU U.K.;* [6]*Dept. of Ecology and Ecotoxicology, Section Soil Ecology, Vrije Universiteit Amsterdam, De Boelelaan 1087, 1081 HV Amsterdam, The Netherlands*

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Abstract. Forest ecosystems are currently being exposed to changes in chemical inputs and it is suggested that physical climate is also changing. A novel approach has been used to study the effects of ionic inputs and climatic conditions on forest soils by reciprocally exchanging lysimeters containing undisturbed soil columns beween four forest sites in Europe. The soil columns contained no living roots and simulated a clear cut situation. The soils chosen represented different stages of acidification and were taken from sites along a transect of increasing exposure to acidic and nitrogen pollution. The purpose of the study was to quantify the reactions of soils when transferred to different environments. Element balances were used as an aggregated indicator to describe the reaction of the soil. The input of protons in local throughfall increased along the transect from 0.01 kmol ha^{-1} y^{-1} H^{+} at the unpolluted site up to 1.10 kmol ha^{-1} y^{-1} at the most polluted site. Our results show that soil acidification always resulted from a combination of acid deposition and biological transformations of nitrogen through nitrification of imported ammonium, mineralized N, or stored N. The balances indicate that between 54% and 91% of the soil acidification resulted from nitrification processes which were driven by a complex reaction when climatic and pollution conditions were changed simultaneously. The combined changes in atmosphic inputs and climatic conditions, as expected with global change, may have serious consequences for soil acidfication and long term organic matter turnover.

Introduction

Forest soils in Europe have been subject to rapid changes in chemical inputs and it is believed that physical climate is also changing. Over recent decades atmospheric deposition has caused soil acidification, nutrient loss, N eutrophication and destabilization in many central European forest ecosystems (e.g., van Bremen & van Dijk 1988; Ulrich 1994). According to current global climate models, Central Europe will be exposed to increased annual mean temperatures (Kräuchi 1993). These external changes induce internal reactions among the abiotic components of the soils which affect the structure and function of the biotics communities. The responses of soil organisms to changes in temperature and water regimes (physical climate) are well understood and have been documented in a large number of publications (e.g. Insam et al. 1989; Insam 1990; Zak et al. 1993; Lloyd & Taylor 1994). The results of such studies have been used to predict the effects of climate change (summarized by Grinsven 1995). However, changes in the physical climate are often accompanied by changes in input quality (chemical climate), namely the deposition of acids or nitrogen. Under these circumstances the internal reactions will be different and more difficult to predict.

This study was designed to test the hypothesis that acidification of forest soils is not only a function of acidic atmospheric input but is also controlled by biologically mediated dynamics of the soil organic matter and that thus no simple reactions can be expected.

The aim of this study was to investigate the effects of the complex interaction between atmospheric inputs and physical climate on forest soils of different acidity, soil texture and organic matter content. A general difficulty in evaluation the effects of environmental changes on the soil system as a whole is the choice of a sensitive indicator. In this study the balances of the dominant cations and anions were chosen. These not only allow the quantification of changes in single elements but also provide an indication of the internal processes taking place in the soil (Ulrich 1994). A new experimental design was chosen which allowed investigation of the interaction between changes in climatic and atmospheric input in determining element fluxes using reciprocally transplanted undisturbed soil cores as lysimeters.

Methods

Site descriptions

Four sites were selected along a European transect of increasing acid input from Ireland (Kilkenny), to UK (Grizedale), to The Netherlands (Wekerom) and to Germany (Solling). The investigation of these sites were part of the EU funded CORE-project. The locations of these sites and their characteristics are presented in Table 1.

Undisturbed soil columns (20 cm in depth) were collected from each of the sites using Plexiglas cylinders (15 cm diam. × 24 cm deep) (Figure 1a).

Table 1. Characterisation of the CORE sites.

Site	Latitude	Longitude	Elevation (m)	Temperature* (°C)	Precipitation* (mm)	Stand	Age (years)	Soil texture	Soil type	Parent material
Kilkenny (Ireland)	52°4′ N	7°2′ W	175	9.3	819	*Picea abies*	20	Silt loam–Silty clay loam	Brown soil	Glacial drift on a cornoniferous shale series
Grizedale (U.K.)	54°2′ N	3°0′ W	170	8.6	1431	*Picea abies*	40	Silt loam	Brown soil	Silurian slates
Wekerom (The Netherlands)	52°1′ N	5°4′ E	23	13.0	693	*Pinus sylvestris*	35	Loamy sand	Podsol soil	Glacial sand
Solling (Germany)	51°8′ N	9°5′ E	500	6.4	1005	*Picea abies*	109	Silt loam–Silty clay loam	Podsolic brown soil	Weathered triassic sandstone covered by loess sediments

* = annual mean

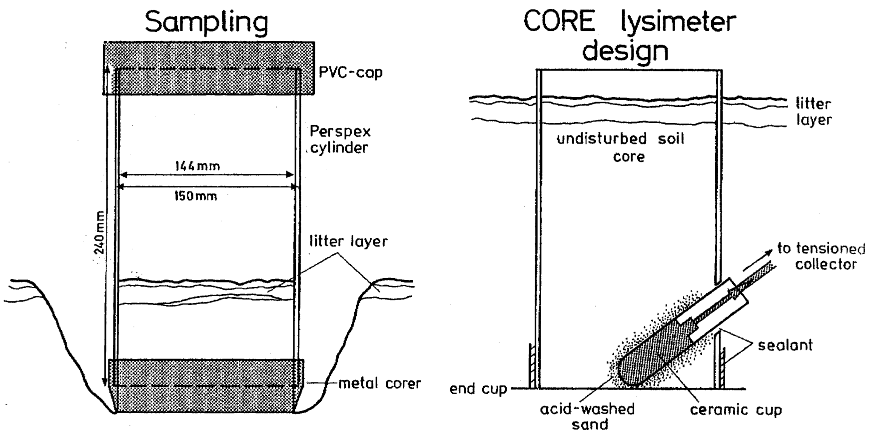

Figure 1. Sampling and lysimeter design (a) Sampling of the transplanted lysimeters, (b) CORE lysimeter design as installed in the field sites.

Soil cores showing signs of disturbance during sampling were discarded. The remainder were trimmed at the base and 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 (Figure 1b). Twenty-eight columns were collected at each site. Seven additional columns were taken from each site to determine soil characteristics. After sampling, seven lysimeters were transferred to each of the four sites and placed into the soil. The site from which the soil was transferred will be referred to as the ‘source’, and the destination site as the ‘host’ site.

Soil characteristics

Soil horizons were separated and sieved to 2 mm Ten g of dried mineral soil or 10 $cm^3$of the surface layers were mixed with 25 cm^3 of either distilled water or 0.01 M $CaCl_2$ to determine pH_{H_2O} and pH_{CaCl_2}. Exchangeable cations were measured as described by Meiwes et al. (1984), by the percolation of 80 cm^3 of 1 M $(NH_4)_2SO_4$ solution through 2.5 g soil. Subsamples were homogenised by milling, and total C and N were measured after dry combustion using a Carlo Erba C/N analyzer.

Sampling and chemical analyses

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 of the lysimeters in January 1989 and continued for 21 months until September of the following year. Volume and chemical parameters of the soil solutions were either measured after each two-week sampling or the solution was collected over a period of three months and combined to provide proportional samples.

The soil cores used in this study had intact soil profiles but, as living roots were excluded from the transplanted soils, the lysimeters represented a clear-fell more closely than an intact forest. Acidification resulting from increased net N mineralisation and nitrification has frequently been observed in clear-felled sites (Lundmann et al. 1978; Wiklander & Nordlander 1991). To prevent such a pulse of mineralization masking the processes of interest, the experiment was started two months after the soil cores were collected and the collection of the data presented began after a further running off phase of four months. Fine roots die within a few days and the output volumes of the leachates from December to May guaranteed a flux of one to two times the total pore volume within the soil-cores. Thus the effects discussed are unlikely to be masked by artifacts resulting from an increased mineralization and nitrification associated with sampling. The experimental design focused on soil processes only and excluded the effect of root uptake.

In addition to the soil solution samples described above, throughfall was collected (10 replicates) at each site and rainfall was collected (5 replicates) at an open location adjacent to each site. Volumes were measured in the field and pH was determined within 24 hours of returning the samples to the laboratory. Open precipitation, throughfall and soil solutions were routinely analysed for Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, NH_4^+, NO_3^-, Cl^-, SO_4^{2-}. Initially, all samples were also analysed for PO_4^{3-}, but the consistently low concentrations in soil solutions (close to analytical detection limits) resulted in this ion being dropped from the suite of analyses. To prove the comparability of the analyses carried out in the different laboratories a calibration check was done. The coefficient of variation was 5.7% between the laboratories for all elements determined in this study.

Means and coefficients of variation for samplings of rainfall, throughfall and leachates at the Solling site are given in Table 2 as an example. Apart from the data on NH_4^+-output most coefficient of variation indicated a fluctuation around the mean of less than 30%, which is surprisingly low for field investigations of element fluxes.

Calculations

Ulrich (1994) distinguished between Mb cations (K^+, Mg^{2+}, Ca^{2+} and Na^+), which react as neutral salts or weak bases, Ma cations (NH_4^+, H^+ and Al^{3+}), potential proton donors, and anions which can react as acids (NO_3^-, SO_4^{2-} and organic acids), as essential parts of elemental budgets. He further described

Table 2. Mean values and coefficients of variation (CV%) of element inputs (kg ha^{-1} y^{-1}) in rainfall and throughfall and of element output (kg ha^{-1} y^{-1}) from soils transplanted to Solling site from May 1989 May 1990 as an example of variation in element fluxes. Means and coefficients are calculated from the input of each individual rainfall and throughfall collector during the experiment.

Table 2a: Variations of element inputs in rainfall and throughfall at Solling site (Mean and (Coefficient of variation).

Input		Na^+	K^+	Ca^{++}	Mg^{++}	Al^{+++}	NO_3^--N	NH_4^+-N	Cl^-	SO_4^{--}-S	H^+
		(kg ha^{-1} y^{-1})									
Rainfall	Mean	8.8	2.4	3.8	1.2	0.1	7.6	9.7	15.9	13.0	0.4
	CV%	*1.1*	*4.9*	*2.8*	*3.3*	*0.0*	*0.6*	*6.0*	*2.7*	*1.2*	*2.5*
Throughfall	Mean	20.2	22.9	20.3	4.2	0.9	19.7	19.5	39.0	43.8	1.1
	CV%	*5.8*	*6.0*	*2.4*	*5.3*	*18.3*	*5.3*	*3.0*	*4.7*	*5.7*	*10.8*

Table 2b: Variations of element ouputs from soils installed at Solling site. Means and coefficients of variation are calculated from the output of each individual lysimeter from May 1989 to May 1990.

Output		Na^+	K^+	Ca^{++}	Mg^{++}	Al^{+++}	NO_3^--N	NH_4^+-N	Cl^-	SO_4^{--}-S	H^+
		(kg ha^{-1} y^{-1})									
Kilkenny	Mean	45.6	2.0	101.1	22.3	1.5	68.9	0.1	36.3	47.9	0.1
	CV%	*12.8*	*52.7*	*39.0*	*52.7*	*34.5*	*45.6*	*170.8*	*15.6*	*23.2*	*65.9*
Grizedale	Mean	33.6	15.0	36.2	23.9	52.5	117.8	11.9	45.4	62.6	1.6
	CV%	*15.6*	*33.8*	*41.8*	*25.3*	*17.7*	*11.3*	*123.5*	*13.9*	*20.4*	*29.7*
Wekerom	Mean	27.7	28.0	24.2	13.1	72.7	99.1	2.5	47.3	74.8	1.0
	CV%	*11.1*	*16.5*	*27.7*	*17.9*	*22.6*	*11.1*	*112.2*	*10.2*	*15.3*	*18.0*
Solling	Mean	21.2	31.4	29.9	9.8	39.2	90.8	0.7	42.3	68.8	2.6
	CV%	*15.6*	*42.4*	*17.4*	*15.6*	*27.5*	*19.9*	*84.6*	*19.1*	*18.2*	*15.1*

CV% = Coefficient of variation

Acid Degree (AD) of rainfall and throughfall as a relative measure of acidity in input and is the percentage of the cations which are Ma-cations:

$$\text{AD } (\%) = (\text{Ma}/(\text{Mb} + \text{Ma})) \times 100$$

It is also possible to calculate the acid base budgets for any compartment if the input and the output of cations and anions is known. For these calculations Ulrich (1994) made the assumption that anion deficits at pH <5 were caused by organic anions and at pH >5 by HCO_3^-. For any ion, the budget is defined as the difference between the input and output $(I - O)$. The acidifying processes and the balancing acid base reactions can be determined depending on whether the compartment is a net source $(I - O < 0)$ or sink $(I - O > 0)$ for the ions mentioned. Changes in the storage of chloride are due to either the accumulation or loss of neutral salts. The accumulation or loss of chloride is not used in the calculations but the budgets for Mb cations are adjusted to take it into account.

Ulrich (1994) defined acidification from the ion input – output budget of the compartment as the sum of the following:

- sink function for acid input $\{I - O > 0\}$ what means that the imported acids (Ma cations) stay in the soil.
- source function for anions $\{I - O < 0\}$ which reflects the dissolution of aluminium sulphates, nitrification and dissociation of dissolved organic acids.
- sink function for Mb cations $\{I - O > 0\}$ (corrected using chloride cf. above). It is presumed that the Mb cations are bound to acidic groups releasing Ma cations.

The acidifying processes were calculated as proportional processes (%). The acidifying processes from the ion input – output budget have to be balanced by acid – base reactions in the compartment. Ulrich (1994) defined the acid – base reactions as:

- the source function for Ma cations $\{I - O < 0\}$, i.e. the consumption of protons through dissolution (export from the soil) of Ma cations in acidic soils.
- the consumption of protons $\{I - O > 0\}$ primarily associated with the formation of uncharged compounds from anions such as the formation of aluminium sulphates, the biogenic transformation of HNO_3 into Norg and the accumulation of organic acids.
- the consumption of protons connected with the release (source function) of Mb cations $\{I - O < 0\}$ (corrected using chloride cf. above). The underlying processes can be the exchange of Ma cations, silicate weathering and mineralization.

Both acidifying and acid-base reactions are expressed as proportions of the total process. In order to show the importance of nitrate fluxes, similar calculations were caried out for nitrate. N-transformations of stored and mineralized N were calculated on the basis of the element fluxes. The source function for N was used to quantify these processes and the source function for nitrate was used to quantify nitrification.

Q_{10} values are used to describe the temperature dependence of biological processes and quantify the increase of activity when temperature increases by 10 °C. In our study we calculated the Q_{10} values of net-N-mineralization based on the N fluxes and the annual mean of temperature.

Table 3. Description of the soil chemical parameters of the soils used in the study.

Site	Horizon		pH_{H_2O}	CEC* $mmol_c$ kg^{-1} (DW)	Al	Ca	K	Mg	Na	C	N
					(molar % CEC)					(% DW)	
Kilkenny	Ah	Mean	4.4	119.0	49.6	34.5	1.9	11.8	2.3	7.73	0.61
		SD	0.2	15.9	9.1	8.0	0.4	0.7	0.6	0.74	0.05
	Bv	Mean	4.8	85.3	59.2	26.9	2.1	9.2	2.6	4.25	0.33
		SD	0.2	5.6	15.0	11.0	0.9	3.9	0.9	0.25	0.05
Grizedale	Ah	Mean	4.6	151.2	67.1	25.1	0.6	5.6	1.4	19.91	1.17
		SD	0.1	25.7	15.2	15.9	0.5	1.0	0.7	4.83	0.26
Wekerom	Aeh	Mean	4.0	13.7	84.9	4.9	1.8	5.7	2.1	2.17	0.50
		SD	0.1	2.6	6.2	3.2	1.4	0.9	2.8	0.73	0.23
	Bv	Mean	4.5	9.1	89.3	3.2	0.5	4.5	2.5	0.50	0.04
		SD	0.1	3.0	9.4	7.8	0.7	1.3	1.6	0.23	0.00
Solling	Ah	Mean	3.5	121.5	82.6	8.3	2.9	3.2	3.0	13.44	0.56
		SD	0.2	19.2	5.2	3.4	0.9	0.7	2.9	3.92	0.14
	Aeh	Mean	3.6	85.0	93.5	2.4	1.3	1.9	0.9	4.18	0.21
		SD	0.1	11.8	1.2	1.0	0.4	0.2	0.2	0.47	0.02
	Bv	Mean	4.0	80.6	96.2	0.5	1.2	1.4	0.8	2.40	0.13
		SD	0.1	8.8	1.5	0.2	0.7	0.2	0.6	0.33	0.02

* = Cation Exchange Capacity

Results

Soil characteristics

For all soils, total exchangeable cations decreased down the soil profile (Table 3) with the sandy soil from Wekerom having the lowest exchange capacities as would be expected from its low clay and carbon contents.

All of the soils were either in the aluminium buffer range (ABR; pH 3.0–4.2 in soil solution) or the cation exchange buffer range (CEBR; pH 4.2–5.0 in soil solution) (Ulrich 1986). The Kilkenny and Grizedale soils were in the CEBR, Solling in the ABR and Wekerom in between the two (Table 2). The molar fractions of exchangeable cations, particularly the values for base saturation and relative aluminium content, are also important in describing the acidification status of the soil and give more information about the state of soil acidification than pH alone (Ulrich 1986). It can be shown that, even across small differences in soil pH, the base saturation of soils can be very different (Table 3) (Ulrich & Malessa 1989). While pH increased with depth, base saturation decreased. The pH of the Ah-horizon at Grizedale was high compared to the same horizon at Kilkenny but the base saturation was

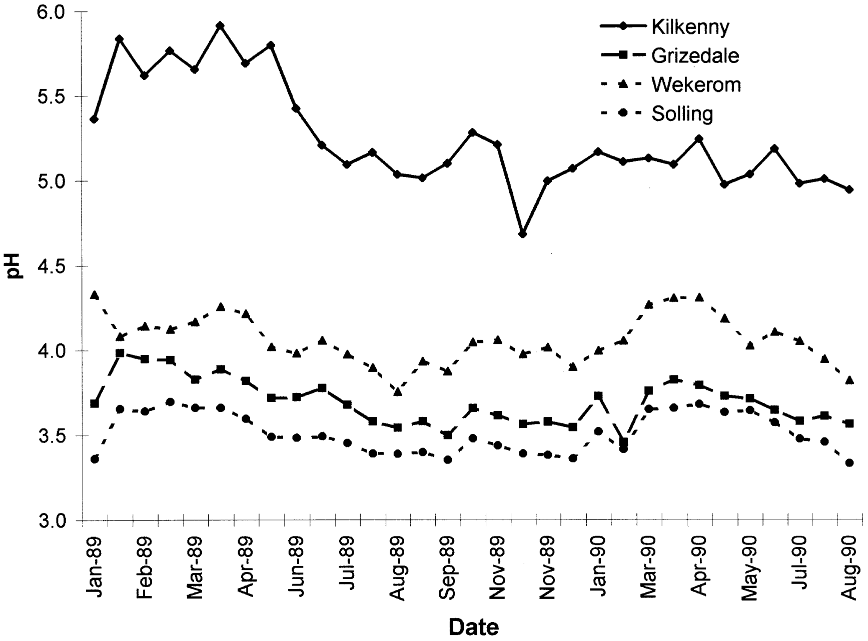

Figure 2. pH in the soil solution of the transplanted soils from Haldon, Grizedale, Wekerom and Solling at Solling host site.

distinctly lower. Further down the pH of the Bv-horizon at Wekerom indicated CEBR but the base saturation was low (Table 3). The pH of leachates from the soils housed at the Solling site indicated very clearly that the Kilkenny soil was less acidified than the other three soils (Figure 2).

In general, the C and N contents of the soils decreased down the profile (Table 3), with the sandy soil from Wekerom having the lowest C and N contents.

Rainfall and throughfall

As anticipated, very clear differences were observed in the chemistry of the rainfall and throughfall between the different sites (Table 4). Maritime inputs of Na^+ and Cl^- dominated at the site close to the sea, with Grizedale having very high inputs of these ions (Table 4). The surprisingly low inputs at Kilkenny arise because of the predominantly westerly winds resulting in relatively low rainfall and low sea-salt concentrations in this part of Ireland.

Along the transect the Acid Degree of throughfall input increased. Acidification due to throughfall inputs is not simply a matter of the wet deposition by rainfall, but also of bulk deposition, interception deposition and leaching

Table 4. Volume and element input in rainfall (Rain) and throughfall (Thr) (kmol ha^{-1} y^{-1}) and Acid Degree (AD%) as a mass for canopy buffering reactions in the period May to May at the CORE sites. Values are calculated as the sum of the averages of rainfall and throughfall of each sampling period.

Site	Input	Element input at the CORE sites											AD$^!$	Volume
		Na^+	K^+	Ca^{++}	Mg^{++}	Al^{+++}	NO_3^--N	NH_4^+-N	Cl^-	SO_4^--^{--}S	H^+	Org. ani.*		
		(kmol$_c$ ha^{-1} y^{-1})											(%)	mm
Kilkenny	Rain$^\$$	1.24	0.07	0.58	0.34	0.07	0.14	0.31	0.94	0.35	0.07	1.24	16.4	819
	Thr§	1.25	0.63	0.42	0.37	0.04	0.23	0.40	1.30	0.54	0.01	1.03	14.2	400
Grizedale	Rain$^\$$	2.47	0.08	0.26	0.55	0.00	0.28	0.28	3.01	0.85	1.13	0.62	29.6	1431
	Thr§	4.22$^\$$	0.49	0.65	1.03	0.05	0.40	0.56	5.37	2.03	0.87	0.07	18.8	1001
Wekerom	Rain$^\$$	0.90	0.10	0.19	0.29	0.05	0.68	1.02	1.03	0.92	0.24	0.15	47.0	693
	Thr§	1.49	0.42	0.26	0.69	0.06	0.75	3.04	1.81	1.89	0.08	1.58	52.6	490
Solling	Rain$^\$$	0.38	0.06	0.19	0.10	0.01	0.55	0.69	0.45	0.81	0.37	0.01	70.7	1005
	Thr§	0.88	0.59	1.01	0.34	0.10	1.41	1.39	1.10	2.73	1.10	0.16	58.5	734

* = organic anions (calculated cations − anions)
$^!$ = AD(%) = (Ma/(Mb + Ma)) $*$ 100
$^\$$ = Rainfall
§ = Throughfall

Table 5. Elements balances of the four transplanted soils at the four host sites derived from May to May. Values are calculated as the sum of the average input in throughfall over each sampling period minus the sum of average output in the soil solution over each sampling period (kmol ha^{-1} y^{-1}).

Source site	Host site	Na^{++}	K^{++}	Ca^{++}	Mg^{++}	Al^{+++}	NO_3^--N	NH_4^+-N	Cl^-	SO_4^--$^{--}$S	H^+	Org. ani.*
							($kmol_c$ ha^{-1} y^{-1})					
Kilkenny	Kilkenny	−2.03	0.52	−5.12	−1.95	−0.12	−7.85	0.33	−0.69	−0.58	−0.04	0.72
	Grizedale	0.71	0.40	−3.81	−1.28	−0.43	−3.09	0.46	1.62	−0.03	0.81	−1.65
	Wekerom	−2.16	0.24	−7.82	−2.97	−0.71	−12.35	2.85	−0.22	−0.98	−0.04	2.94
	Solling	−1.11	0.53	−4.03	−1.50	−0.08	−3.51	1.39	0.07	−0.26	1.03	−0.06
Grizedale	Kilkenny	−0.80	0.37	−0.69	−0.55	−2.98	−5.59	−0.61	−1.18	−0.59	−1.51	0.61
	Grizedale	2.36	0.28	0.29	0.48	−2.25	−2.07	−0.60	2.91	0.58	0.42	−0.44
	Wekerom	0.04	0.18	−0.32	−0.03	−6.48	−7.81	0.63	0.21	−1.09	−1.45	1.26
	Solling	−0.58	0.20	−0.79	−1.63	−5.74	−7.00	0.54	−0.18	−1.17	−0.47	−0.11
Wekerom	Kilkenny	−0.53	0.13	−0.65	−0.33	−3.79	−4.29	0.29	−0.58	−0.46	−0.78	−0.31
	Grizedale	2.39	0.16	0.27	0.61	−2.32	−1.87	0.23	2.73	0.83	0.62	0.28
	Wekerom	0.14	−0.13	−0.40	0.30	−9.12	−9.38	2.04	0.01	−0.47	−1.06	1.59
	Solling	−0.27	−0.08	−0.11	−0.61	−7.04	−4.69	0.95	−0.22	−1.74	0.12	−0.38
Solling	Kilkenny	−0.25	0.44	−0.90	−0.68	−5.06	−5.38	0.33	−0.80	−0.83	−1.14	−0.23
	Grizedale	2.15	0.28	0.12	0.64	−1.88	−1.87	0.33	2.27	−0.03	0.27	1.52
	Wekerom	0.31	0.15	−0.96	0.20	−9.29	−10.46	2.65	0.06	−0.86	−1.44	2.86
	Solling	0.01	−0.17	−0.34	−0.38	−3.82	−4.17	1.26	−0.07	−1.44	−1.19	1.05

* = organic anions (calculated cations − anions)

or buffering in canopy. Lowest concentrations of acidifying input and AD was found at the Kilkenny site. The high proton input at Grizedale was due to high throughfall volumes. The high throughfall volume and buffering reactions in the canopy also led to high amounts of Mb-cations and resulted in low AD of throughfall. The Wekerom site, in the Netherlands, and the Solling site, in Germany, were distinguished by their large throughfall enrichments of inorganic pollutants, with the Solling site receiving high levels of SO_4^{2-} and H^+. Wekerom had the highest NH_4^+-N inputs in both rainfall and throughfall. The increase of AD and the decrease of H^+ in throughfall at the Wekerom site is explained by the interception of gaseous NH_3 by the canopy and wet transformation to NH_4^+. This process buffers in the canopy but increases the acidic load to soil. At the Solling site the AD decreased but proton load increased. This indicates that the canopy buffered a high proton load. However, since SO_2 and NO_x are acid precursors, their emission results in the formation of equivalent amounts of acidity which results in high proton loads (Ulrich 1994).

Ionic balances

Al was the dominant cation in the leachates from the Grizedale, Wekerom and Solling soils at all host sites (Table 5). On the other hand, Mb cations were dominant in the leachates from the Kilkenny soil. However, there was a similar trend, in Kilkenny source soils, to that observed for the acidified soils in that the concentrations of Al in leachate were highest at the Wekerom host-site, where external acid load and acidifying processes were always highest. In turn all soils showed a clear sink function for the Mb cations sodium and potassium at Grizedale where the sum of the acidfying processes ($kmol_c\ ha^{-1}\ y^{-1}$) was in general lowest (Tables 5 and 6). This was also the case for the Mb-cations Ca and Mg in the leachates from the acidic soils originating at Grizedale, Wekerom and Solling (Table 5).

There was a general trend for acid deposition (sink function for Ma cations) to become more important under polluted conditions (Table 6). The relative contribution of acidic input to all soil acidification was lowest at the unpolluted Kilkenny site and and highest at the heavily polluted sites at Wekerom and Solling. This was particularly obvious for the CEBR soil from Kilkenny where acidic input contribiuted up to 36% of total acidification at the Solling site. However, the trend was not absolutely consistent as the positive balances of Ma-cations were most important for the Grizedale soil at the Grizedale site (Table 6).

In turn the high load with Mb-cations for the acidic soils from Grizedale, Wekerom and Solling at Grizedale was an important factor for soil acidfication while for the CEBR soil from Kilkenny it was not (Table 6). This is in

Table 6. Sum of soil acidification (kmol$_c$ ha^{-1} y^{-1}) and the proportion of the single processes of soil acidfication and the proportion of nitrate fluxes for soil acidfication, and the proportion of the single processes of acid base reactions.

Proportion of the soil processes calculated from the balances

Source site	Host site	Soil acidification* (kmol$_c$ ha^{-1} y^{-1})	Proportion of all acificying processes			Acid load by nitrate only	Proportion acid base reactions		
			Retention of deposited Ma-cations	Retention of deposited Mb-cations	Release of all anions	Release nitrate	Rentention of deposited anions	Release of Mb-cations	Release of Ma-cations
			%			%	%		
Kilkenny	Kilkenny	9.29	3.5	5.6	90.8	84.6	7.7	90.5	1.8
	Grizedale	6.05	21.0	0.0	79.0	51.1	8.6	84.3	7.1
	Wekerom	16.42	17.3	1.5	81.2	75.2	17.9	78.9	3.2
	Solling	6.71	36.0	6.9	57.1	52.4	0.0	98.9	1.1
Grizedale	Kilkenny	6.55	0.0	5.6	94.4	85.3	9.3	13.0	77.8
	Grizedale	3.43	12.3	14.5	73.2	60.4	16.9	0.08	3.1
	Wekerom	9.54	6.6	0.1	93.4	81.9	13.2	3.7	83.1
	Solling	9.03	6.0	2.2	91.8	77.6	0.0	31.2	68.8
Wekerom	Kilkenny	5.50	5.3	2.4	92.2	78.1	0.0	16.9	83.1
	Grizedale	3.43	6.6	20.8	54.4	54.4	32.5	0.0	67.5
	Wekerom	12.31	16.6	3.4	80.0	76.2	12.9	4.3	82.8
	Solling	7.88	13.6	0.0	86.4	59.5	0.0	10.6	89.4
Solling	Kilkenny	7.22	4.6	6.1	89.3	74.6	0.0	14.1	85.9
	Grizedale	3.40	17.5	26.8	55.7	54.8	44.7	0.0	55.3
	Wekerom	14.56	18.2	4.1	77.7	71.9	19.7	6.6	73.7
	Solling	6.88	18.4	0.1	81.5	60.5	15.3	11.9	72.9

* = calculated sum of all acidfying processes

agreement with the interpretation of Ulrich (1994) that the Mb cations replace Ma cations in acidified soils.

The negative balances for nitrate showed that the nitrate loss from soils clearly exceeded the input of both forms of nitrogen. This indicates a biological turnover of stored or mineralized N (Table 5). On the basis of the N-balances for the transplanted soils at the Kilkenny and Wekerom sites, where throughfall volume was similar we calculated the Q_{10} values. The Q_{10}values ranged above a Q_{10} of 5 (Kilkenny = 5.3, Grizedale = 5.9, Wekerom 9.0, Solling 7.5).

In the present study the main acidifying process in the soils resulted from them acting as sources for anions (Table 6) since the negative balances for anions ranged between 54.4% and 94.4% of the acidifying processes. Thus the release of anions was dominated by nitrate loss and show that soil acidification was dominated by nitrification (Table 6). The highest relative values due to this process were at the Kilkenny site where they ranged from 74.6% to 85.3%. The proportion decreased from Kilkenny through Wekerom and Solling to Grizedale. At Grizedale, all soils showed lowest levels of nitrate flux (Table 5). This indicates very low biological activity resulting in an increase in the importance of the other processes such as the sink fuction (storing) of Ma- and Mb-cations for soil acidification (Table 6).

The acid-base balance was due mainly to loss of Mb-cations for the Kilkenny soil and of Ma cations from the Grizedale, Wekerom and Solling soils (Table 6). It was only driven to some extend by a sink function for anions. At Grizedale it was mainly due to a sink function for chloride caused by an extremly high chloride input during the period of investigation (Table 6). Secondly, positive balances for organic anions were included in buffering processes whilst there were no, or small, sink functions for sulphate.

Discussion

The rainfall and throughfall data indicate very clearly that the term AD of Ulrich (1994) is a more useful indicator of the acidification potential of deposition that the absolute amount of acidifying components input. For example, proton input in throughfall was high at Grizedale (0.87 kmol ha^{-1} y^{-1}) but this was due to high rainfall and throughfall volume and was balanced by high inputs of Mb-cations. The data allow us to conclude that the proton input was buffered in the canopy at Kilkenny, Grizedale and Wekerom. At Wekerom this may have been due partially to interception deposition, especially the absorption of gaseous NH_3 from intensive animal production systems leading to increases in pH through the consumption of protons in the production of NH_4^+ on wet surfaces in the canopy. Nevertheless this process increased

AD of the throughfall input as NH_4^+ has a high acidifying potential. This interpretation agrees with earlier studies in the Netherlands (van Bremen et al. 1982; van Bremen & van Dijk 1988). Buffering reactions due to the leaching of Mb-cations can be observed in the canopy at the Solling site. But the increased proton load in throughfall (1.10 kmol ha^{-1} y^{-1}) compared to rainfall (0.37 kmol ha^{-1} y^{-1}) indicates that interception deposition, due to the absorption of gaseous compounds of NO_x and SO_2, results in the production of strong acids and that the buffering capacity for protons was exceeded. This observation agrees with earlier investigations of this spruce site (Bredemeier 1988).

Several authors have emphasised that deposition of atmospheric acidity is a major source of proton load to forest ecosystems (Ulrich 1981; Bredemeier 1988). It can be seen that there was a trend of increasing importance of acidic input when AD of throughfall increased. But this trend was not as consistent as expected. A probable explanation for this is that the data show the importance of biologically moderated nitrogen transformation, mineralization from organic matter (ammonification – proton consuming process), nitrification (proton producing proccess) and denitrification (proton consuming process).

The data from the soils transplanted to Kilkenny indicate clearly that the underlying processes of soil acidification were driven mainly by the source function for nitrate. As there was a low input of both forms of mineral N at Kilkenny most of exported nitrate must have resulted from the mineralization of organic nitrogen sources. In turn, there was a low acidifying potential in the inputs. In a healthy forest stand, uptake by vegetation will balance the production of mineralized N but seasonal uncoupling of root uptake from mineralization may induce internal proton production (Ulrich 1986).

It has been observed that in cool, wet years the activity of decomposers may be reduced (Ulrich 1987) and this can be seen at the Grizedale site where mineralization processes were generally depressed under the conditions of low temperature and high input volume. The effect may also have resulted from increased denitrification, which is a proton consuming process, as it is well known that water saturated conditions increases gaseous N-losses (Sextone 1988; Aber et al. 1989; Flessa & Beese 1995). The underlying processes of soil acidification indicate that at Grizedale the low rates of nitrification of mineralized and stored N increased the relative importance of the sink function for Ma and Mb cations as acidifying processes. But the data show clearly that the sum of the acidfying processes was very low.

The Wekerom site represented an extreme situation with highest ammonium input and highest rate of N losses. In general, the sum of soil acidifying processes was highest when soils were transferred to this site. These conditions led to increased Al-leaching from all the soils as would be expected from earlier investigations (van Bremen & van Dijk 1988; Verstraeten et al. 1990). The extremely high source function for nitrate may be explained by a combined effect of elevated ammonium input in throughfall and the stimulation of biological transformations of stored N by high temperature. The high levels of nitrate leached and the sink of ammonium in the soils from Kilkenny, Wekerom and Solling indicate that nitrification was increased for imported mineral N and mineralized N. But the response of the Grizedale soil transplanted to Wekerom suggests that nitrification was stimulated less than mineralization. A probable explanation is that acidification may directly reduce the activity of autotrophic nitrifiers (Bramley & White 1989). However, this explanation may not be appropriate as this effect was not observed for the more acidified Solling soil. Nevertheless our data show very clearly that the sum of acidifying processes in all soils transplanted to Wekerom was increased to as much as twice the level seen at the unpolluted Kilkennny site and up to four times the level reported for the Grizedale host site. This and the mobilization of Al-cations, which was also observed, to some extend, in the transplanted Kilkenny soil, suggests that the atmospheric input of acidifying compounds may override the silicate weathering capacity of all the soils investigated and may result in long term acidification.

The Solling site represented a highly polluted situation, although the high levels of acidic input were buffered in the canopy by Mb cations decreasing the AD in throughfall. While low temperature decreased the biological moderated processes in most of the soils it can be concluded that high ammonium and proton load affected the mobilization of Al and Mb-cations (Ulrich 1986). The input of anthropogenically derived sulphur and nitrogen to forests may produce a wide spectrum of effects depending on the length of the exposure and the nutrient status of the forests at the time at which input first significantly intensified (Bondietti & McLaughlin 1992). The reaction of the transplanted Kilkenny soil to the heavily polluted sites at Wekerom and Solling may be interpreted as initial responses as noted by Abrahamsen (1980). The initial response of many forest soils would likely be positive as nutrient cations were mobilized and nitrogen would act as fertilizer (Abrahamsen 1980). Negative impacts on forest health would be seen as a long term consequence of continued nutrient mobilization and loss from the system (Bondietti & McLaughlin 1992). This is known for the Solling soil (Matzner 1988). High AD of throughfall at Solling, resulting from high proton and ammonium inputs, would affect base saturation and pH in all the soils in the long term.

The decomposer communities reacted in an unpredictable way to the changes induced by transplantation. The negative balances of N, especially nitrate fluxes, as well as their contribution to the acidifying processes suggests that nitrogen turnover, an indicator for microbial generated decomposition processes, was not simply a function of the temperature and moisture regime. Calculating Q_{10} values from the nitrogen balances and the annual mean temperatures it can be stated that, for each soil, Q_{10} differed markedly from values reported in the literature for microbial activity (between 1.4 and 3) and net N-mineralization (between 1.64 and 2.40) (Anderson & Domsch 1986; Ross & Tate 1993; Stenger et al. 1995). This indicates that changes occurred in the composition of the microbial decomposer communities during the experiment and that both the physical climate and the quality of atmospheric input influenced, to some extent, the soil organic matter turnover. This results in complex reactions if climatic or pollution conditions are changed simultaneously. However, the results demonstrate that changes in climatic conditions, as expected with global warming, in combination with atmospheric element inputs will have serious consequences in the long term for organic matter dynamics in forest ecosystems and may induce changes which cannot be balanced by internal buffering reactions of terrestial ecosystems.

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