

# LONG TERM TRENDS IN ATMOSPHERIC DEPOSITION AND SEEPAGE OUTPUT IN NORTHWEST GERMAN FOREST ECOSYSTEMS

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**Abstract.** Long term trends of element fluxes in atmospheric deposition and of concentrations in seepage output of seven coniferous and deciduous forest stands in northwestern Germany have been evaluated for the period 1981 - 1994. Decreasing deposition rates of  $\text{SO}_4$  (50 - 70% ) and  $\text{H}^+$  (60 - 80%) occurred at all sites concomitant with the decline of  $\text{SO}_2$  emission rates in the former Federal Republic of Germany. Deposition of Ca, Mg, and K decreased at the Solling and Göttinger Wald stands. During this period no consistent trends in the flux rates of  $\text{NH}_4$  and  $\text{NO}_3$  were apparent. Sulfate concentrations in soil solution decreased at the Solling and Göttinger Wald stands, whereas an increase occurred at Lange Bramke south slope. As a consequence of reduced deposition and mobile anion concentrations a decrease of Ca, Mg, K, Al, and Mn in soil solution has been observed at the Solling stands. At the other stands trends of cations in soil solution are not consistent. Nitrate concentrations in soil solution decreased at the Göttinger Wald. A rising tendency with great fluctuations of  $\text{NO}_3$  concentrations occurred at the Solling spruce stand.

**Key words:** sulphur deposition, nitrogen deposition, soil solution, nitrogen saturation, exchangeable cations

## 1. Introduction

The deposition of atmospheric pollutants significantly altered the geochemical cycles of forest ecosystems specially in heavily polluted areas such as Central Europe. Meanwhile efforts were made to reduce air pollution. In the former Federal Republic of Germany (FRG) sulfur dioxide ( $\text{SO}_2$ ) emissions decreased by 67% between 1981 and 1991. In the former German Democratic Republic (GDR)  $\text{SO}_2$  emissions increased until 1987 and were reduced by 35% since then (Umweltbundesamt, 1994).

If atmospheric deposition to forest ecosystems has changed, altering soil output of solutes has to be expected. But little is known about the time lags between the reduction of input and changes in soil output fluxes. The response of sulfate ( $\text{SO}_4$ ) soil output to reduced  $\text{SO}_4$  input depends on the retention characteristics of the soil, which influences the release of cations from the soil as well. High deposition rates of nitrogen (N) should enhance the N saturation of forest ecosystems (Dise and Wright, 1995).

Trends of major ions in deposition and seepage output of seven forest stands of northwest Germany have been evaluated for the period 1981 - 1994. The purpose of this paper is to evaluate, (i) whether or not changes in deposition rates to forest stands are detectable and if so, (ii) whether or not soil solution output responds to these alterations.

## 2. Sites and Methods

The study sites are located within the State of Lower Saxony (table I). The soils are acid (Al buffer range) and low in exchangeable  $\text{M}_b$ -cations with the exception of Göttinger

Wald, where the soil has developed on limestone. Detailed descriptions are given elsewhere (Bredemeier, 1987, Meiwes and Beese, 1988, Hauhs, 1989, Matzner, 1989).

TABLE I  
Study sites characteristics.

site	stand	latitude longitude	altitude (m a.s.l.)	tree species	stand age (1994)	mean air temp. (°C)	soil type (FAO)	depth of lysimeters (cm)
Sellhorn	oak	N 53°11' E 09°54'	109	<i>Quercus robur</i> L., <i>Q. petraea</i> LIEBL.	113	8.0	podzolic Cambisol	150
	pine	N 53°10' E 09°53'	82	<i>Pinus sylvestris</i> L.	108	8.0	podzolic Cambisol	150
Lange Bramke	north slope	N 51°41' E 10°25'	600	<i>Picea abies</i> KARST.	43	5.8	podzolic Cambisol	80
	south slope	N 51°41' E 10°25'	600	<i>Picea abies</i> KARST.	43	5.8	podzolic Cambisol	80
Solling	beech	N 51°46' E 09°34'	504	<i>Fagus sylvatica</i> L.	145	6.4	dystric Cambisol	90
	spruce	N 51°46' E 09°34'	508	<i>Picea abies</i> KARST.	110	6.4	dystric Cambisol	90
Göttinger Wald	beech	N 51°31' E 10°02'	420	<i>Fagus sylvatica</i> L.	115	7.5	Terra fusca- Rendzina	100

Open field precipitation and throughfall were collected from May to October in 15 funnel type bulk samplers and from November to April in 9 buckets (Mewes *et al.*, 1984). Stemflow was collected with polyurethane collars around the stems. Weekly samples were combined to a monthly sample for subsequent analysis. Stand precipitation is the sum of throughfall and stemflow. Total deposition was estimated according to Ulrich (1994).

Soil water samples were obtained using ceramic tension lysimeters and analyzed on a monthly basis. The lysimeters were installed with 5 to 9 replicates in depths of 80 to 150 cm depending on site characteristics (table I).

Analysis of pH was carried out using a glass electrode. Sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), and manganese (Mn) were determined by atomic absorption spectrometry (AAS) until 1989, since 1990 by inductively coupled plasma - atomic emission spectrometry (ICP-AES). Aluminium (Al) was determined colorimetrically until 1982, by AAS until 1990, and by ICP-AES afterwards. All Al in soil solution was assumed to be  $Al^{3+}$ .  $NH_4$ ,  $NO_3$  and Cl were analysed colorimetrically with a continuous flow system. Sulfate was measured by precipitation with Ba and by potentiometric titration of excess Ba with EDTA until 1982, from 1983 to 1992 by the methyl-thymol-blue method, since 1993 by ICP-AES.

Temporal trends of element fluxes with atmospheric deposition for the period 1981-94 have been evaluated using linear regression. Regression coefficients indicate mean annual

change of element fluxes (table II). Trends in monthly averaged soil solution concentrations have been evaluated for the same period using the non-parametric seasonal Kendall (SK) test (Hirsch *et al.*, 1982, table III).

### 3. Results and Discussion

#### 3.1. ATMOSPHERIC DEPOSITION

Flux rates of sulfur (S) and N in open field precipitation and total deposition of forest stands in northern Germany are on a high level compared to other European stands (Hauhs *et al.*, 1989, table II). The coniferous stands at the Sellhorn and Solling sites have higher total deposition rates for all elements than the adjacent deciduous stands.

TABLE II

Water ( $\text{H}_2\text{O}$  [ $\text{mm}\cdot\text{yr}^{-1}$ ]) and element fluxes [ $\text{mmol}_c\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ ] in open field and total deposition (upper row) and linear regression coefficients of trend analysis (lower row) for the period 1981-94 (total deposition was estimated according to Ulrich, 1994; \* denotes significant  $p \leq 0.05$ , \*\* denotes significant  $p \leq 0.01$ ; Sellhorn total deposition pine without 1994, Lange Bramke without 1988).

site	flux	$\text{H}_2\text{O}$	Na	K	Mg	Ca	$\text{H}^+$	$\text{NH}_4$	$\text{NO}_3$	$\text{SO}_4$	Cl
Sellhorn	open field	766	59	11	15	22	22	89	51	84	66
		6	-1	0.0	-0	-0	-3**	2	-0	-4*	-3
	total dep. oak	656	75	13	19	28	66	114	65	138	92
		4	-2	-0.0	-1	-1	-6**	2	-0	-8**	-3
total dep. pine	589	95	18	25	37	76	144	84	166	111	
	2	-3	0.3	-1	-0	-8**	3	0	-13**	-4	
Lange Bramke	open field	1331	40	7	12	27	47	79	60	106	40
		9	1	-0.2	-0	-1	-5**	-2	-0	-7**	-1
	total dep. spruce north slope	1126	56	9	16	38	160	112	86	230	66
		21	2*	-0.1	-0	-1	-12**	-1	1	-13**	-0
total dep. spruce south slope	1030	55	9	16	38	179	109	89	241	66	
	5	2*	-0.1	-0	-1	-10*	-1	1	-12**	-1	
Solling	open field	1142	41	8	11	31	54	80	63	104	44
		-1	1	-0.4*	-0	-2**	-8**	-2	-2*	-7**	-1
	total dep. beech	890	64	13	17	51	154	129	102	241	81
		-0	0	-0.9**	-1*	-5**	-16**	-5*	-5**	-17**	-3*
total dep. spruce	830	81	17	22	64	295	170	137	375	103	
	-0	1	-1.1**	-1*	-6**	-22**	-4	-3**	-24**	-3*	
Göttinger Wald	open field	711	29	7	11	46	31	59	58	93	30
		-16	0	-0.8**	-0	-4**	-2*	-1	-0	-5**	-1
	total dep. beech	617	39	9	15	63	100	87	80	173	54
		-8	-0	-1.4**	-1**	-7**	-10**	-2	-2*	-15**	-3**

Significant decreasing trends in deposition rates can be observed for  $\text{SO}_4$  and hydrogen ions ( $\text{H}^+$ ) (table II). Other ions did not follow consistent trends for the entire sites.

A significant ( $p \leq 0.05$ ) decrease of  $\text{SO}_4$  input fluxes occurred during the study period at all sites. Highest reduction rates were found for sites with highest average fluxes. At the Solling site  $\text{SO}_4$  fluxes decreased by  $7 \text{ mmol}_c \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$  in open field precipitation and by  $24 \text{ mmol}_c \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$  under spruce. Within 14 years this means a reduction of about 60%. Less polluted sites such as Sellhorn experienced a decrease of  $4 \text{ mmol}_c \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$  in open field precipitation resulting in a 50% reduction. Decreasing  $\text{SO}_4$  deposition rates at all studied forest sites reflect a decrease in  $\text{SO}_2$  emissions in the former FRG.

Nitrate fluxes in open field precipitation were high at all study sites (table II). A slight decrease of  $\text{NO}_3$  total deposition was observed only at the Solling and Göttinger Wald stands. Ammonium fluxes were generally higher as  $\text{NO}_3$  fluxes. At the Solling beech stand  $\text{NH}_4$  showed a decreasing trend. Total N deposition increased at the Solling stands from 1970 to 1980 (Matzner, 1989) and were slightly reduced since then.

Calcium, Mg, and K deposition decreased at the Solling and Göttinger Wald sites. Total deposition of Ca changed by about  $2\text{-}7 \text{ mmol}_c \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$  leading to a reduction of 60 to 85% within 14 years. This trend can be explained by decreasing dust emissions in the former FRG (1980:  $0.70 \text{ Mt} \cdot \text{yr}^{-1}$ ; 1991:  $0.45 \text{ Mt} \cdot \text{yr}^{-1}$ , Umweltbundesamt, 1994).

Changes in deposition rates of  $\text{SO}_4$ ,  $\text{NO}_3$ ,  $\text{NH}_4$ , and Ca have an influence on  $\text{H}^+$  flux rates. At all sites a substantial reduction of  $\text{H}^+$  fluxes occurred between 1981 and 1994. The highest  $\text{H}^+$  reduction ( $22 \text{ mmol}_c \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ ) was found at the Solling spruce site. The change in  $\text{H}^+$  flux is generally positively related to the absolute level of  $\text{H}^+$  fluxes.

### 3.2. SOIL SOLUTION

A reduced input of  $\text{SO}_4$  into soils should reduce the output of  $\text{SO}_4$  with seepage water in the long term. In shorter periods the response of  $\text{SO}_4$  concentrations in soil solution may be delayed by the release of retained S from the soil. Sulfate concentrations in soil solution only decreased significantly at the Solling and Göttinger Wald sites between 1981 and 1994 (table III). At the Solling stands  $\text{SO}_4$  soil solution concentrations increased until 1978 and decreased since then. This behaviour was attributed to the formation and dissolution of  $\text{AlOH}_2\text{SO}_4$  (Prenzel 1984). At Lange Bramke south slope  $\text{SO}_4$  concentrations increased until 1984 and remained at the same level since then. At Lange Bramke this pattern may be explained by the high adsorption capacity of the soil for  $\text{SO}_4$  and/or by the precipitation of Al-hydroxysulfates (Lükewille and Prenzel, 1993).

Nitrate concentrations at the Sellhorn stands, at Solling beech, and at the south slope of Lange Bramke were always very low or below detection limit. At Lange Bramke north slope high  $\text{NO}_3$  concentrations have been observed between 1988 and 1992.  $\text{NO}_3$  showed a decreasing trend at the Göttinger Wald. At the Solling spruce stand fluctuations of  $\text{NO}_3$  in soil solution with a period of 3 - 4 years have been observed. At all investigated stands throughfall fluxes of N are above the minimum threshold of  $65 \text{ mmol}_c \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$  yielding enhanced N output at some European forest ecosystems (Dise and Wright, 1995). At the Solling stands N input is above the maximum threshold of  $180 \text{ mmol}_c \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$  as well, where high N leaching can be observed generally at European forests. N saturation seems to be approached only at the Solling spruce stand. If we define any ecosystem with significant nitrogen loss as N saturated, also Lange Bramke north slope is N saturated.

TABLE III

Mean concentrations (upper row;  $\mu\text{mol}_c\cdot\text{l}^{-1}$ ) and Z' values of trend analysis with SK test (lower row) for ions in soil solution for the period 1981-94 (negative Z' values indicate decreasing trends; \* denotes significant  $p \leq 0.05$ , \*\* denotes significant  $p \leq 0.01$  for two sided tests; Sellhorn pine without 1993 and 94; n.d. = not detectable).

site	stand	K	Mg	Ca	Al	H <sup>+</sup>	Mn	NO <sub>3</sub>	SO <sub>4</sub>	Cl
Sellhorn	oak	14	126	240	95	30	9	n.d.	451	261
		-4.22**	-0.02	-2.73**	0.47	0.67	0.97	n.d.	1.36	0.67
	pine	41	91	136	464	55	6	n.d.	720	358
		2.14**	-1.24	-1.63	-2.08*	-0.03	-2.63**	n.d.	-0.63	2.96**
Lange Bramke	spruce	10	21	33	331	40	9	163	243	63
	north	2.98**	3.38**	3.19**	2.20*	-0.99	0.11	1.50	0.51	0.49
	spruce	13	50	63	395	53	22	n.d.	535	133
	south	-4.49**	0.45	-1.60	6.89**	-1.58	3.11**	n.d.	4.32**	1.62
Solling	beech	11	35	37	322	44	20	14	405	107
		-10.51**	-0.19	-4.21**	-7.09**	-4.26**	-9.85**	-1.50	-8.13**	-0.98
	spruce	19	93	101	1392	65	58	258	1337	268
		-6.10**	-6.60**	-10.10**	-7.52**	-3.11**	-9.76**	2.29*	-10.70**	-1.52
Göttinger Wald	beech	19	119	5010	n.d.	0	n.d.	182	646	194
		-6.92**	-6.94**	-0.89	n.d.	-2.26*	n.d.	-9.55**	-4.76**	-5.25**

Ca soil solution concentrations decreased at the Solling stands and at the Sellhorn oak stand. The reduction can be explained either by decreasing Ca deposition, by a reduced concentration of mobile anions, or by depletion of Ca from the exchange sites. At the Solling stands all of the three processes have been observed. Exchangeable Ca decreased by 65% between 1968 and 1990 at Solling spruce and by 55% between 1968 and 1986 at the beech stand (Wesselink *et al.*, 1995). With the exception of Göttinger Wald, Ca and Mg from deposition contributes to a large extent to the nutrition of the stands, where pools of exchangeable M<sub>b</sub>-cations are small and weathering rates are low.

Mg concentrations in soil solution declined at Göttinger Wald and Solling spruce stand, whereas an increase occurred at Lange Bramke north slope. The concentrations of K in soil solution decreased at all investigated stands except at Sellhorn pine and Lange Bramke north slope, where an increase occurred.

Al exhibit also decreasing concentrations as a result of reduced SO<sub>4</sub> concentrations at the Solling stands. A reduction of Al in soil solution also occurred at the Sellhorn pine stand. At Lange Bramke north slope, Al showed high concentrations between 1988 and 1992 simultaneously to the peak in NO<sub>3</sub> content. At Lange Bramke south slope an increase of Al concomitant with SO<sub>4</sub> concentrations has been observed.

Mn showed the same pattern as Al at all study sites except at Lange Bramke north slope, where no Mn peak between 1988 and 1992 occurred. Decreasing trends of Mn contents in soil solution at the Solling sites and at Sellhorn pine stand may be attributed to a depletion of Mn from exchange sites and to the reduced dissolution of Mn-oxides and -hydroxides.

Concentrations of H<sup>+</sup> in seepage output decreased at the Solling stands as a consequence of reduced contents of mobile anions.

#### 4. Conclusions

The deposition of  $\text{SO}_4$  declined between 1981 and 1994 at all study sites by about 50-70%, which is in the order of the reduction of  $\text{SO}_2$  emissions. As a consequence of the  $\text{SO}_4$  decline, a simultaneous decrease of the  $\text{H}^+$  deposition occurred. A decline in Ca, Mg, and K deposition occurred at the Solling and Göttinger Wald stands. For the Solling stands, this may have negative effects on buffering of acidity in precipitation and on forest nutrition. High N deposition did not increase  $\text{NO}_3$  concentrations in soil solution of the forest stands. This is unexpected, because the deposition of N to northwest German forest stands exceeds by far the demand for wood increment of about  $50\text{-}100 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$  for more than two decades. Nevertheless these ecosystems are at risk of increasing N saturation leading to nutrient imbalances and an enhanced output of  $\text{NO}_3$  from the soils. An exception might be the Solling spruce stand, where fluctuations of  $\text{NO}_3$  with a rising tendency occurred. Reduced  $\text{SO}_4$  input led to a decreased  $\text{SO}_4$  concentration in seepage output only at the Solling and Göttinger Wald stands. At the Lange Bramke and Sellhorn stands, S retention delays the response of soil solution to reduced input of  $\text{SO}_4$ . Declining concentrations of  $\text{M}_b$ -cations in soil solution at the Solling stands may be explained by reduced deposition rates, declining concentrations of mobile anions and a depletion of exchangeable  $\text{M}_b$ -cations.

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