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Correlations between nitrate and sulfate in the soil solution of disturbed forest ecosystems

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Abstract. Based on data from three German forest ecosystems severely disturbed by windthrow events, correlation patterns between NO_3^- and SO_4^{2-} dynamics in the soil solution are described. Each of the correlation types was related to site-specific SO_4^{2-} retention processes. The relative importance of SO_4^{2-} adsorption/desorption and precipitation/dissolution was found to be different for the studied soils depending on their contents of SO_4^{2-}-adsorbing sesquioxides and of Al hydroxy sulfate minerals. Enhanced NO_3^- concentrations in the soil solution resulting from excess nitrification promoted either SO_4^{2-} adsorption or the dissolution of Al hydroxy sulfates. Both processes result in different ecological consequences: Whereas the former reaction reduces anion concentration peaks in the soil solution, the latter increases them. Thus, a prediction of cation export from soil ecosystems subjected to excess nitrification has to regard site-specific interrelationships between NO_3^- and SO_4^{2-}. As a third type of correlation the independence of NO_3^- and SO_4^{2-} concentrations in the soil solution is presented. This type is suggested to be typical for soils with low SO_4^{2-} adsorption capacity and absence of Al hydroxy sulfates.

Key words: disturbance, excess nitrification, forest ecosystem, nitrate, sulfate

Introduction

In most cases the ionic compounds of soil solutions show specific patterns of intercorrelation. The total equivalent sum of cations equals the total equivalent sum of anions due to the law of electroneutrality. Thus, for a system consisting only of one anion and one cation species, the correlation between the two ions is perfect. For systems with one anion species, but more than one cation species, the concentrations of all ions are positively correlated, if the cations originate from the same source, as e.g. the exchange complex, a congruently weathering mineral or congruently decaying organic matter. A congruent uptake of nutrient cations by plants might be another mechanism leading to positive correlation. On the other hand, ion concentrations in the soil solution may exhibit a distinct independence, if the cations in question are related to different sources and sinks in the ecosystem.

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The anions SO_4^{2-} and NO_3^- enter the soil solution by atmospheric deposition and by various processes taking place within the forest ecosystem. For NO_3^-, the microbial oxidation of NH_4^+ is the only ecosystem-internal source of relevance (Bredemeier et al. 1990); concerning SO_4^{2-}, besides oxidation of reduced inorganic S and mineralization of organic S compounds, geochemical processes as desorption or the dissolution of sulfate-containing minerals may be of importance (Johnson 1984).

Forest ecosystems affected by strong disturbance such as windthrow or clearcutting with a sudden decrease of vegetative coverage are in many cases characterized by excess nitrification (Bormann et al. 1967, Likens et al. 1970), leading to a strong increase in the ionic strength of the soil solution (Kölling 1993) and a characteristic change in its cation composition. Compared to N_{org} mineralization and subsequent NH_4^+ nitrification, the mineralization of organically bound sulfur only results in minor changes in the ionic strength of the soil solution, since under conditions of congruent humus mineralization and complete NH_4^+ nitrification the amount of NO_3^- equivalents released from one weight unit of organic matter derived from conifer litter exceeds the amount of liberated SO_4^{2-} by a factor of 10 to 15 (Ulrich 1989). Additionally, a large part of mineralized SO_4^{2-} is almost instantaneously re-immobilized by soil microorganisms as ester sulfate (Ghani et al. 1992), thus diminishing net SO_4^{2-} mineralization. Finally, in contrast to NO_3^-, SO_4^{2-} can be retained in the mineral soil by adsorption to positively charged surfaces (amorphous and crystalline Fe and Al (hydr)oxides, clay minerals; Fuller et al. 1985; Harrison et al. 1989; MacDonald & Hart 1990) and by precipitation of sulfate minerals.

The effects of strong excess nitrification on the soil solution chemistry of severely disturbed forest ecosystems have been discussed in a number of papers (e.g. Likens et al. 1970; Stevens & Hornung 1990). Most of these publications were focussed on acidification effects caused by excess nitrification: An increase in cation concentrations in the seepage water and the resulting enhancement of cation export from the disturbed ecosystem. Little attention has been paid to interrelationships between anions. Yet, these interrelations are of great ecological interest, since it is the equivalent sum of anions in the soil solution which regulates the cation concentration and consequently the extent of unfavorable losses of nutrient cations and/or Al mobilization.

Based on theoretical considerations, four types of correlation between two anions can be inferred:

1. Independence (Fig. 1a)

The concentrations of two anions considered vary independently from each other. In this case, the anion equivalent sum can easily be predicted by simply

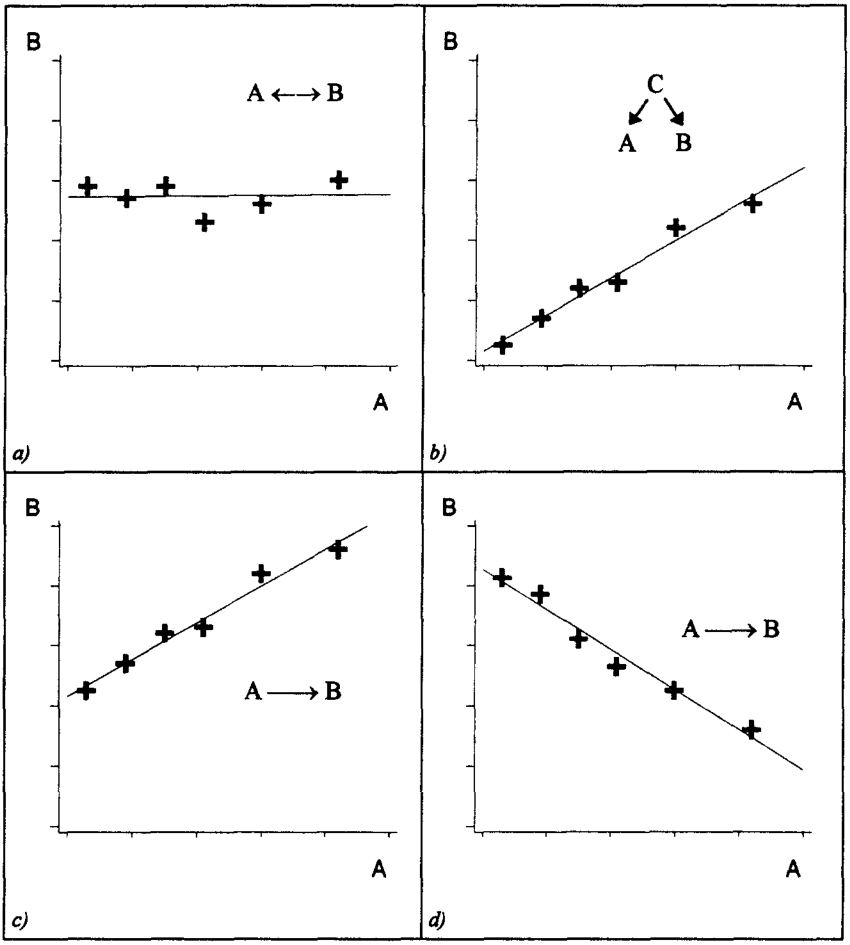

Fig. 1. 4 types of correlation between the concentrations of two anions (A and B). *a)* uncorrelated *b)* illusory correlation due to a master process (e.g. dilution/concentration) (C) *c)* positive correlation due to a causal relation between A and B *d)* negative correlation due to a causal relation between A and B.

adding the effects of all specific processes responsible for the variation of each anion.

2. *Illusory correlation due to a master process (Fig. 1b)*

This type of correlation between two anions exists, if their concentrations are changed by the same master process. This case is very common in soil biogeochemistry; it occurs e.g. when the soil solution is concentrated or diluted by changes in soil hydrology. The joint mobilization of two anions by mineralization of organic matter shows the same feature, if it proceeds congruently. The characteristic statistical feature of an illusory correlation is a constant quotient between the two concentrations and therefore a regression line through the origin of the coordinate system.

3. Positive correlation due to a causal relation (Fig. 1c)
This type of correlation is based on a causal interrelation between the concentrations of two anions, where the concentration change of one anion causes a concentration change of the other in the same direction. The result of this type of interrelation between two anions is an increased temporal variation of the anion equivalent sum in the soil solution.

4. Negative correlation due to a causal relation (Fig. 1d)
The characteristic feature of a negative correlation is an inverse relation between the concentrations of two anions in the soil solution. An increase in the concentration of one anion is coupled with a decrease of the other. Compared to the case of independence, this type of interrelation results in a decrease of the temporal variation of the anion equivalent sum in the soil solution.

In the following we shall demonstrate the relevance of these different types of interrelation between anions for the chemical composition of the soil solution, which characterizes bioelement cycling in forest ecosystems. Our demonstration is based on data sets of the soil solution chemistry of three forest ecosystems all characterized by strong excess nitrification due to stand breakdown by windthrow. The aim of our paper is (i) to give an example of a process-orientated interpretation of soil solution data, (ii) to clarify the importance of comprehensive approaches of perception in the assessment of ecological problems, and (iii) to stress the important role of excess nitrification as relevant process in the biogeochemistry of forest ecosystems.

Material and methods

Study sites

Table 1 informs about topography, climate and geology of the three sites discussed in this paper as well as about relevant chemical data of site-representative soil profiles. The presented sites have been chosen as examples from a larger number of studied forest ecosystems in Southern Germany; the reason being that for them the discussed correlation patterns are very pronounced. However, each of 10 more studied sites not shown in this paper exhibited one of the three types of interrelation between NO_3^- and SO_4^{2-} presented in this paper (Kölling 1993). Thus, a generalization of our statements seems feasible.

Table 1. Short description of the experimental sites (# denotes the installation depth of the lysimeters).

	Layer/ horizon	Boundary	pH	CEC (0.5 M NH_4Cl)	Percentage of exchangeable cations		
		[cm]	($CaCl_2$)	[μmol$_c$*g^{-1}]	Ca^{2+}	Mg^{2+}	Al^{3+}
Site "Eichstaett"	Ol	−1	4.3	410	65	8	0
Elevation: 505 m. a.s.l.	O2	0	3.5	236	55	5	3
Slope aspect: flat	Ah	2	3.3	98	31	4	26
Average annual temperature: 7.5 °C	EB	23	4.0	42	0	2	80
Average annual precipitation: 720 mm	BE	41	4.0	66	6	1	82
Bedrock: Loam with loess admixture above	BtBw	46	3.9	128	7	2	81
decarbonated cover from weathered dolomitic reef material (Jurassic Malm	#2 Bwl	80	4.3	162	44	22	29
Zeta3, Unterthiton layers)	Bw2	120	4.4	207	57	24	15
Soil type (FAO): Haplic Acrisol							
(USDA): Ochreptic Hapludult							
Site "Holzig"	O	0	3.7	294	53	7	2
Elevation: 420 m. a.s.l.	Ah	3	3.0	95	24	3	38
Slope aspect: E, inclined	Bwl	25	3.9	36	3	1	75
Average annual temperature: 7.5 °C	Bw2	45	4.1	24	3	1	76
Average annual precipitation: 800 mm	#2 BwC	75	4.0	25	3	1	78
Geological bedrock: loess-influenced cover	3 C	100	3.8	52	3	1	80
from triassic sandstone							
Soil type (FAO): Dystric Cambisol							
(USDA): Typic Haplumbrept							
Site "Kuehbruch"	O	0	3.5	194	56	9	8
Elevation:115 m. a.s.l.	Ah	4	3.2	60	22	4	48
Slope aspect: flat	Bw	20	4.4	11	7	1	76
Average annual temperature: 9.5 °C	BwC	30	4.6	6	7	1	69
Average annual precipitation: 660 mm	# CBtwl	70	4.6	4	9	1	50
Geological bedrock: Dune sand	CBtw2	140	4.4	4	9	1	51
Soil type (FAO): Dystric Cambisol							
(USDA) Quartzipsammentic Haplumbrept							

Soil solution chemistry

At each of the three sites we collected soil solution in a depth between 50 and 70 cm with at least three ceramic suction cups (Type P 80, Staatl. Porcellan Manufaktur Berlin, FRG). Sampling was carried out during 18 months in intervals of twenty days. The solution of each lysimeter was sampled and analyzed individually; in order to maintain a realistic calculation of mineral stability indices (see below) we did not pool samples from several lysimeters, which might represent chemically different micro-sites although being located at the same depth. All samples were membrane-filtered (0.45 μm cellulose acetate, not acid-treated). SO_4^{2-} and NO_3^- concentrations were measured colorimetrically with a Technicon auto analyzer; soluble Al and K were analysed by ICP-OES (KONTRON). H^+ activities were determined by using a glass electrode connected to a METROHM micro-voltmeter.

Table 2. Fractions of extractable soil Fe and Al.

	Extractant	**Fraction of Al/Fe assumed to be extracted**
I	0.5 M NH_4Cl [Al]	Exchangeable Al (I)
II	0.05 M NH_4-EDTA [Al,Fe]	Organically bound Al/Fe (II–I)
III	NH_4-oxalate (pH 3.2) [Al,Fe]	Amorphous Fe- and Al oxides/hydroxides (III–II)
IV	Na-dithionite/citrate (pH 6) [Fe]	Crystalline Fe oxides/hydroxides (IV–III)

Determination of pedogenic Fe and Al minerals

For each site, soil samples of the horizon, where the suction cups have been placed, and of all superior horizons were taken from profiles within a 5 to 30 m distance from the lysimeters. Fine earth <2 mm was dried at 40 °C. For a selective extraction of different pedogenic Fe and Al minerals (Table 2), four aliquots of each sample were extracted (i) with 0.5 M NH_4Cl (Trüby & Aldinger 1989), (ii) with 0.05 M NH_4-EDTA (Farmer et al. 1980), (iii) with acidic NH_4 oxalate (Schwertmann 1959), and (iv) with dithionite-citrate buffer (McKeague et al. 1971). Fe and Al in the extracts were determined by ICP-OES.

Thermodynamical calculations

For calculation of saturation indices of relevant Al-bearing mineral phases and construction of a mineral phase stability diagram $p\mathrm{Al}^{3+}+3p\mathrm{OH}^-$ *vs.* $2p\mathrm{H}+p\mathrm{SO}_4^{2-}$, the activities of Al^{3+} were calculated using the thermodynamical equilibrium program WATEQF (Plummer et al. 1976). We did not consider Al-F- and Al-organical complexes in this calculation, because we unfortunately had no possibility to measure fluoride and the sample volume was not enough to perform Al fractionations. Thus, our calculations represent an upper bound for the solubility indices. However, Al-org-complexes should only comprise a minor portion of total Al in subsoil seepage water, where DOC concentrations were always lower than 30 mg/L. All activity coefficients were calculated by using the DAVIES equation; $p\mathrm{K} + p\mathrm{OH}$ was set to a constant value of 13.2.

Statistical calculations

Statistical treatment of our data was performed by using the procedure GLM of the statistical software package SAS (SAS Institute 1990).

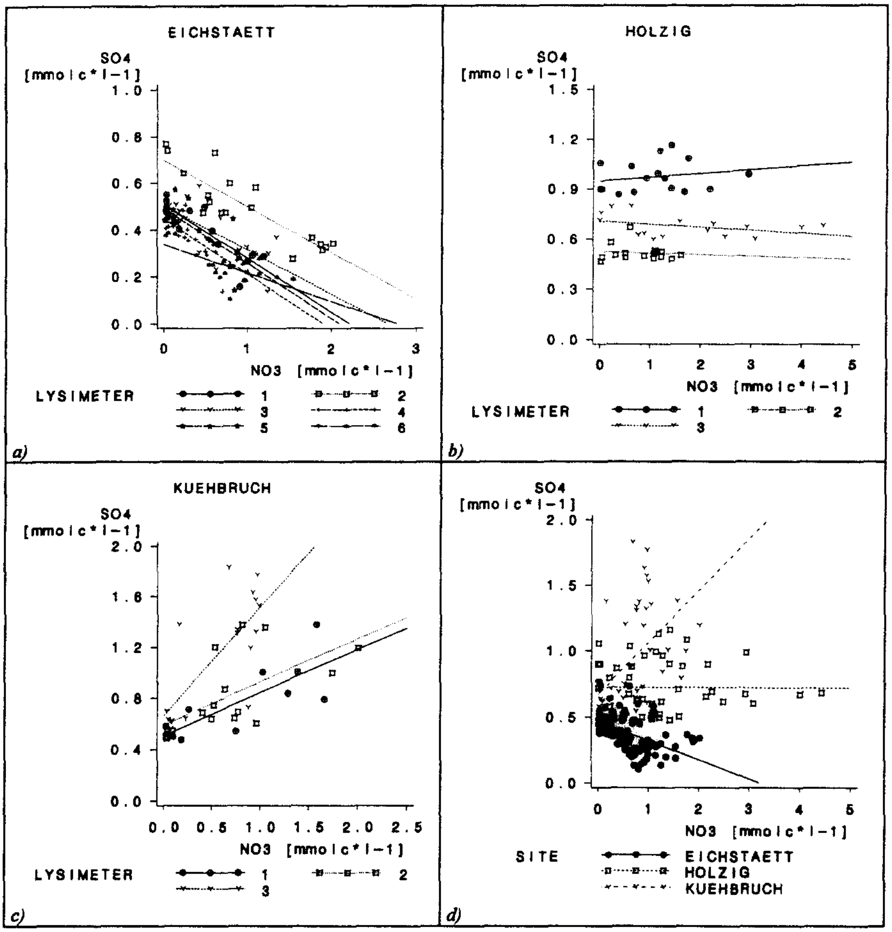

Fig. 2. a)–c) Linear models $SO_4^{2-} = b_0 + b_1 \cdot NO_3^-$ for the lysimeters of the three experimental sites. *d)* Linear model $SO_4^{2-} = b_0 + b_1 \cdot NO_3^-$ for the three experimental sites. EICHSTAETT: $SO_4^{2-} = 0.5 - 0.15\ NO_3^-$; HOLZIG: $SO_4^{2-} = 0.7$; KUEHBRUCH: $SO_4^{2-} = 0.7 + 0.4\ NO_3^-$.

Results and discussion

In the Figs. 2a–c information is given about relations between NO_3^- and SO_4^{2-} concentrations in the seepage water of the studied sites EICHSTAETT, HOLZIG and KUEHBRUCH. Linear regression graphs are presented for each single one of the 12 lysimeters. The regression lines for the three sites reflect the correlation types 4 (EICHSTAETT), 3 (KUEHBRUCH) and 1 (HOLZIG) mentioned in the introduction. Analysis of covariance (Table 3; factors: NO_3^-, lysimeter, interaction NO_3^- x lysimeter) reveals a significant effect of NO_3^-

Table 3. Results of the analysis of covariance for the model: SO_4 = Lysimeter + NO_3 + Lysimeter * NO_3. *** : P |H_0| < 0.001; * : P |H_0| < 0.05.

Experimental site	Source		
	Lysimeter	NO_3^-	Lysimeter x NO_3^-
EICHSTAETT	***	***	–
HOLZIG	***	–	–
KUEHBRUCH	***	***	*

to SO_4^{2-} concentration for the sites EICHSTAETT and KUEHBRUCH, but not for HOLZIG. For all sites, the effect of the single lysimeters is highly significant, probably due to microscale variation of soil chemistry. We did not find any significant interaction "lysimeter x NO_3^- concentration" (0.01 level). Consequently, the same global slope parameter β_1 can be used for the curves of all lysimeters on a study site. The global interrelation "SO_4^{2-} *vs.* NO_3^-" for the three sites is shown in Fig. 2d.

As already mentioned, the interrelation between the concentrations of NO_3^- and SO_4^{2-} in the soil solution of EICHSTAETT corresponds to the interrelation type 4 (negative correlation). High concentrations of NO_3^- in the seepage water are accompanied by low SO_4^{2-} concentrations. This interrelation can be interpreted causally: High excess nitrification increases the proton concentration of the soil solution. In the subsoil of acidic forest soils, the protons are only partly an immediate reaction product of nitrification. Moreover, the percolation of a solution highly enriched in nitrate through the soil profile induces the mobilization of Al^{3+}, which in turn liberates protons due to hydrolysis (Reuss & Johnson 1986). The increases in (i) proton concentration as well as (ii) ionic strength enhance sulfate adsorption (Bruggenwert et al. 1989). Co-sorption of H^+ and SO_4^{2-} leads to the formation of outer-sphere complexes (Sposito 1984; Zhang & Sparks 1990). Thus, sulfate is removed from the soil solution as protons are mobilized by an increased nitrate concentration. This process seems to be characterized by fast reaction kinetics, since the correlation between the concentrations of NO_3^- and SO_4^{2-} is strong.

The contents of dithionite/citrate-extractable Fe in the subsoil horizons of EICHSTAETT exceed those of the other studied soils by far (Fig. 3). Thus it is suggested that variable charges of crystalline Fe oxides and hydroxides are of major relevance (cf. Fuller et al. 1985) for the effective and fast SO_4^{2-} sorption and desorption observed.

The site KUEHBRUCH is an example for the correlation type 3 (positive correlation between NO_3^- and SO_4^{2-} concentration in the soil solution). The soil is characterized by a low content of pedogenic Fe minerals (Fig. 3).

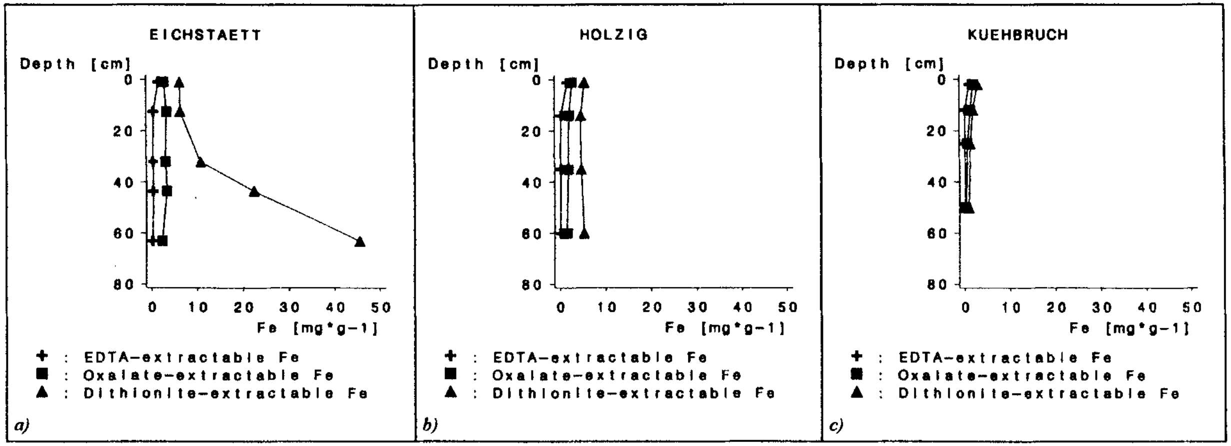

Fig. 3. Depth profiles for extractable Fe.

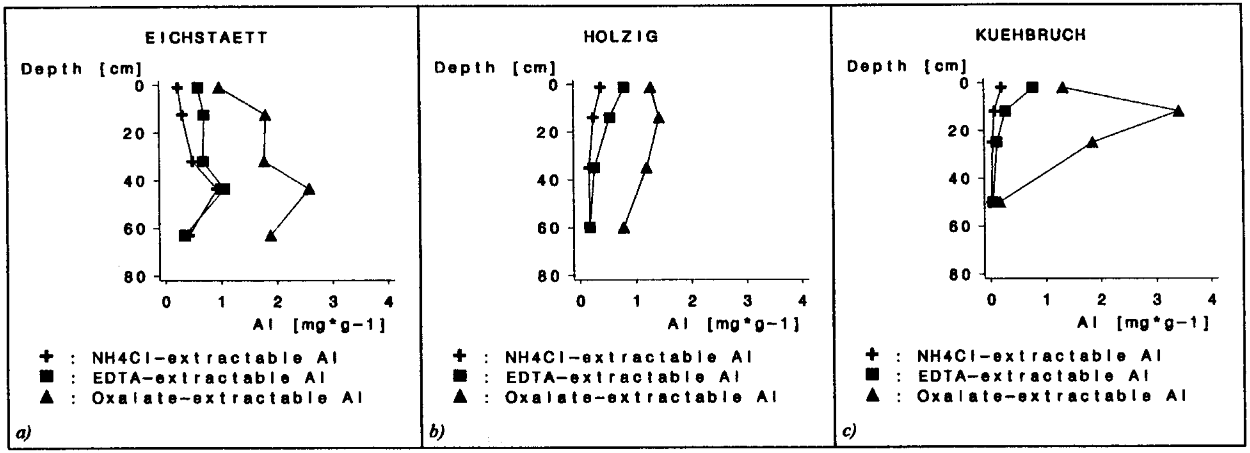

Fig. 4. Depth profiles for extractable Al.

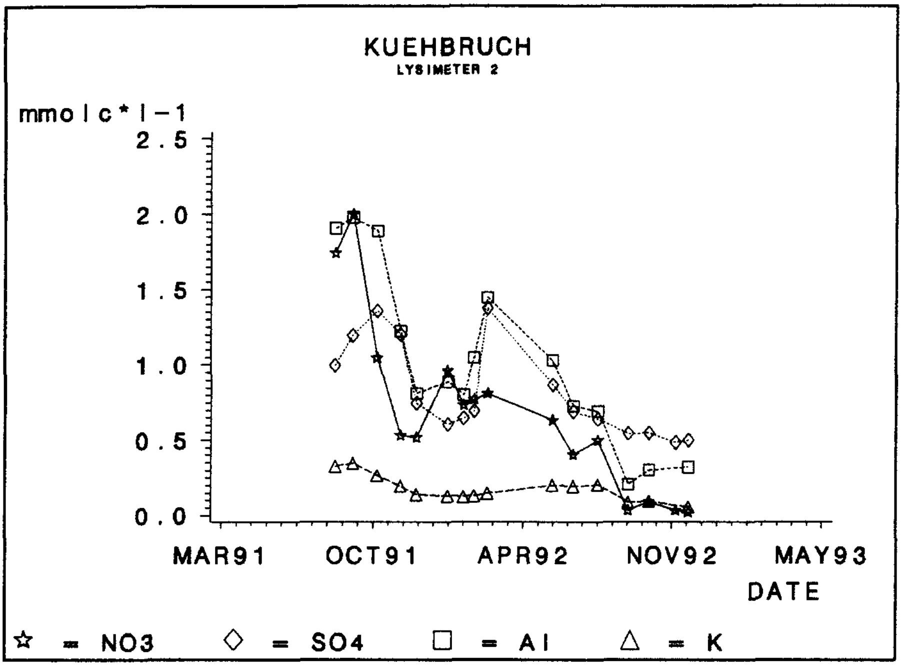

Fig. 5. Time curves for the SO_4^{2-}, NO_3^-, Al^{3+}, and K^+ concentrations of lysimeter 2 (experimental site KUEHBRUCH).

Contrarily, the contents of oxalate-extractable Al are very high compared to the other sites studied (Fig. 4). The concentrations of NO_3^-, SO_4^{2-}, Al^{3+} and to a lower degree also K^+ in the soil solution show a remarkable conformity during the one-year period of investigation (Fig. 5).

The positive correlation between NO_3^- and SO_4^{2-} concentrations in the soil solution of KUEHBRUCH can be neither explained by dilution/enrichment processes (in this case the intercept of the regression line in Fig. 2c should not be distinctly different from zero) nor by simultaneous mineralization of N and S. Assuming a N/S ratio in soil organic matter of 15, congruent mineralization would result in a slope β_1 of 0.07, which is much lower than the observed value 0.4 (Fig. 2c).

Based on these considerations, we hypothesize the existence of a reactive $(K)Al_x(OH)_y(SO_4)_z$ mineral phase in the soil KUEHBRUCH as *e.g.* alunite $(KAl_3(OH)_6(SO_4)_2)$. According to our hypothesis the increase in proton concentration in the soil solution as a consequence of excess nitrification induces a partial dissolution of that mineral phase, thus increasing the concentration of the reaction products Al^{3+}, SO_4^{2-}, and K^+ in the soil solution. According to current scientific knowledge, there is no possibility directly to identify and

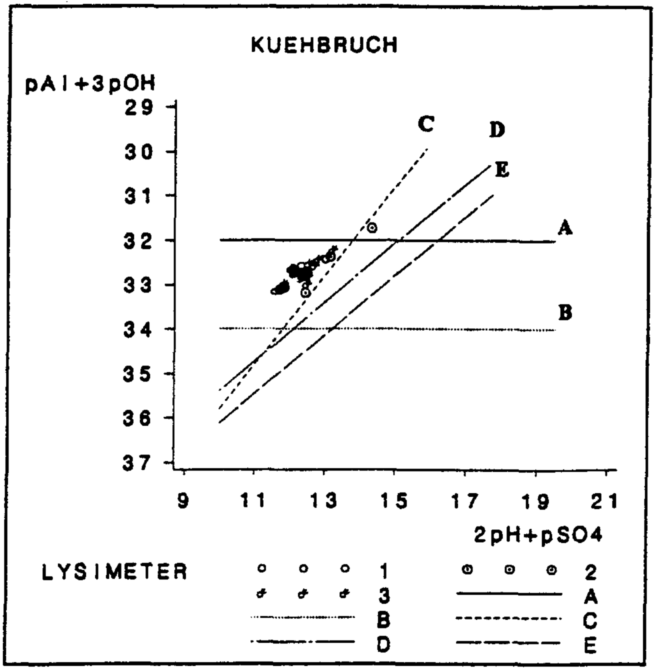

Fig. 6. Stability diagram for the Al-containing minerals A = amorphous $Al(OH)_3$ [$\log K_{sp}^{o}$ = −32.0], B = gibbsite [$\log K_{sp}^{o}$ = −34.0], C = jurbanite [$\log K_{sp}^{o}$ = −17.8], D = alunite [$\log K_{sp}^{o}$ = −83.4], E = alunite [$\log K_{sp}^{o}$ = −85.6] ($\log K_{sp}^{o}$ for C to E according to Nordstrom (1982), $pK + pOH = 13.2$).

Table 4. Saturation indices (SI) calculated by use of WATEQF for alunite, gibbsite and amorphous $Al(OH)_3$ in the soil solution (70 cm) of the lysimeters of the experimental site KUEHBRUCH. Ref.: Plummer et al. 1976; SD: standard deviation.

	SI Alunite			SI Gibbsite			SI $Al(OH)_3$ (amorphous)		
	n	Mean	SD	n	Mean	SD	n	Mean	SD
Lysimeter 1	2	3.86	0.58	2	−0.47	0.09	2	−1.69	0.09
Lysimeter 2	13	3.35	0.88	13	−0.82	0.56	13	−2.04	0.57
Lysimeter 3	14	3.74	0.55	14	−0.80	0.29	14	−2.02	0.29
	$KAl_3(SO_4)_2(OH)_6 \Leftrightarrow K^+ + 3\,Al^{3+} + 2\,SO_4^{2-} + 6\,OH^-$			$Al(OH)_3 \Leftrightarrow Al^{3+} + 3OH^-$			$Al(OH)_3 \Leftrightarrow Al^{3+} + 3OH^-$		
ΔH^* [$kJ \cdot mol^{-1}$]	124.85			60.58			54.39		
$\log K_{Sp}^*$ (25 °C)	−85.32			−32.77			−31.61		

quantify Al hydroxy sulfates in soils. However, our hypothesis is supported by (i) positive saturation indices (Table 4) and (ii) and the results of the phase diagram (Fig. 6, cf. Nordstrom 1982). The distinct oversaturation of the subsoil solution of KUEHBRUCH with respect to alunite might be due to kinetic constraints of alunite dissolution (Arp and Ouimet 1986) or due to the fact that our method of Al determination (ICP-OES) includes not only Al^{3+} and hydroxy Al cations, but as well Al-F- and organical Al complexes. However, the soil solution of KUEHBRUCH would be still (over)saturated with respect to alunite, even if Al-F and Al_{org} species should contribute to 90% of total Al. Support for our hypothesis is provided by the fact that the stoichometric relation of the ions Al^{3+}, SO_4^{2-}, and H^+ exactly resembles the solution activities of these ions which would result from congruent dissolution of a mineral phase with the chemical constitution $KAl_3(SO_4)_2(OH)_6$. Additional support for our hypothesis is provided by the comparably high amounts of oxalate-extractable Al in the KUEHBRUCH soil (Fig. 4c), which can be attributed to alunite, whereas the existence of $Al(OH)_3$ seems unlikely according to the negative saturation index of this mineral (Table 4).

The study site HOLZIG can be attributed to the correlation type 1 (independence). The variation of SO_4^{2-} concentration in the soil solution is weak and cannot be explained by the variation of NO_3^- concentration. With respect to the sulfate dynamics of that soil, either both dissolution/precipitation and sorption/desorption reactions are of negligible importance or their effects are mutually extincted by the antagonism of the two processes. However, the latter alternative seems rather unlikely, since both reactive Al and Fe (hydr)oxides and Al hydroxy sulfate minerals (which could be extracted with acidic NH_4 oxalate) are missing in this soil (Figs. 3 and 4).

The increase in sulfate sorption at variable charge positions as an effect of the pH decrease associated with excess nitrification has been described by Nodvin et al. (1986), Fuller et al. (1987) and Mitchell et al. (1989), who studied a clear cutting experiment at the Hubbard Brook Experimental Forest. In general, SO_4^{2-} adsorption is assumed to be of great importance for S retention in acidic forest soils with the sesquioxide and clay mineral content being the major factor determining their sulfate adsorption capacity (Johnson 1984; Prietzel et al. 1995). If the sesquioxide and clay mineral content of a soil is very low, as it is the case for the study sites HOLZIG and KUEHBRUCH, sulfate adsorption is not likely to be a relevant factor of S retention. On the other hand, low sesquioxide contents in acidic forest soils together with high Al^{3+} (and K^+) concentrations in the soil solution promote the formation of (K)-Al-hydroxy sulfates due to the absence of sesquioxides as competitors for soil solution SO_4^{2-}. The relevance of Al hydroxy sulfates for the retention of SO_4^{2-} in soils is discussed controversially (Nordstrom 1982; Prenzel 1983;

Khanna et al. 1987; von Freiesleben 1988; Prietzel & Feger 1990; Böttcher 1992). The results of our study suggest that, for a given S input situation, the formation of a (K-) $Al_x(OH)_y(SO_4)_z$ solid phase (alunite ?) is favored if sesquioxide contents are low and consequently SO_4^{2-} concentration in the soil solution is high due to missing sulfate sorption. The formed solid phase is highly labile; it is easily resolubilized when soil solution chemistry changes.

The mobile anion concept (Reuss & Johnson 1986) stresses the relevance of anions in the process of soil acidification. The dynamics in anion concentrations in the soil solution is associated by a parallel dynamics in cation concentrations. In that model the crucial input term is the anion equivalent sum: Under a given chemical environment a fixed anion equivalent sum always results in the same cation composition irrespective of the anion distribution in the soil solution. In this context the results of our study are of particular importance. It was shown that the three types of interrelations between NO_3^- and SO_4^{2-} concentrations can induce very different types of anion equivalent sum dynamics:

- under conditions of intensive SO_4^{2-} adsorption at Fe oxohydroxide surfaces, the anion sum will be lower than expected, since the SO_4^{2-} concentration is diminished by intensified sulfate adsorption, when the NO_3^- concentration in the soil solution increases. Consequently, peaks of the anion equivalent sum will be reduced (under-additive effect; Fig. 7) comparable to the anion shift effect (Krug & Frink 1983).
- under conditions of missing or low adsorption of SO_4^{2-} to sesquioxides, but present Al hydroxy sulfates, the anion sum will be higher than expected, since in addition to the NO_3^- formed by excess nitrification SO_4^{2-} is released to the soil solution due to dissolution reactions. Consequently, peaks of the anion equivalent sum will be exaggerated (over-additive effect; Fig. 8).
- if both SO_4^{2-} adsorption and Al hydroxy sulfates are missing (or adsorption and dissolution processes go on in the same magnitude, but in opposite direction) the concentrations of NO_3^- and SO_4^{2-} can be predicted indepenently from each other and the anion equivalent sum can be calculated by simple addition of the two concentrations (additive effect; Fig. 9).

Conclusions

The fluctuating amount of the anion equivalent sum is the crucial factor governing the dynamics of soil solution chemistry. Different processes are

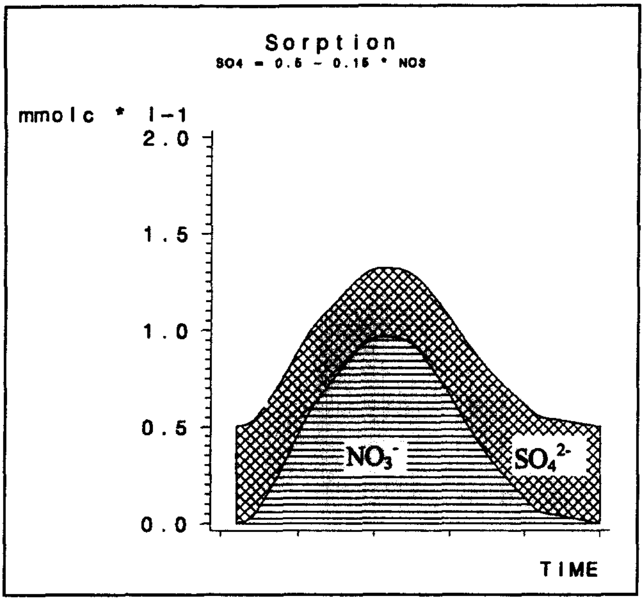

Fig. 7. Modeled sum of anions (case of SO_4^{2-} adsorption). The NO_3^- concentration is varied from 0 to 1 $mmol_c \cdot L^{-1}$.

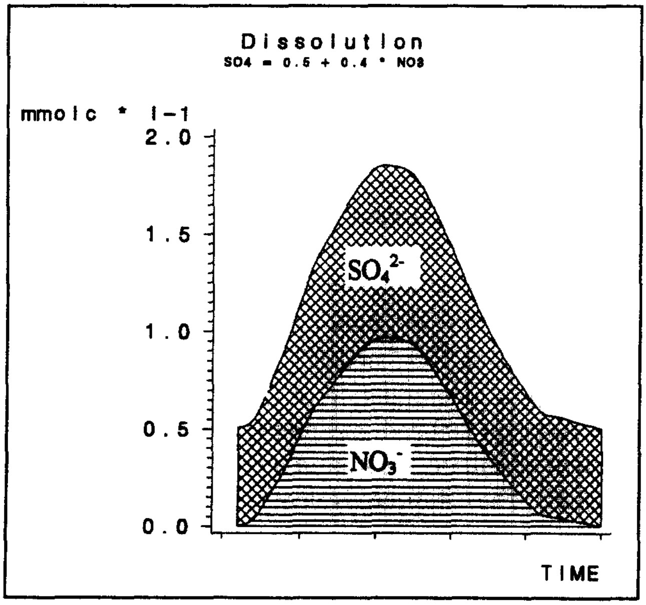

Fig. 8. Modeled sum of anions (case of dissolution of an Al hydroxy sulfate mineral). The NO_3^- concentration is varied from 0 to 1 $mmol_c \cdot L^{-1}$.

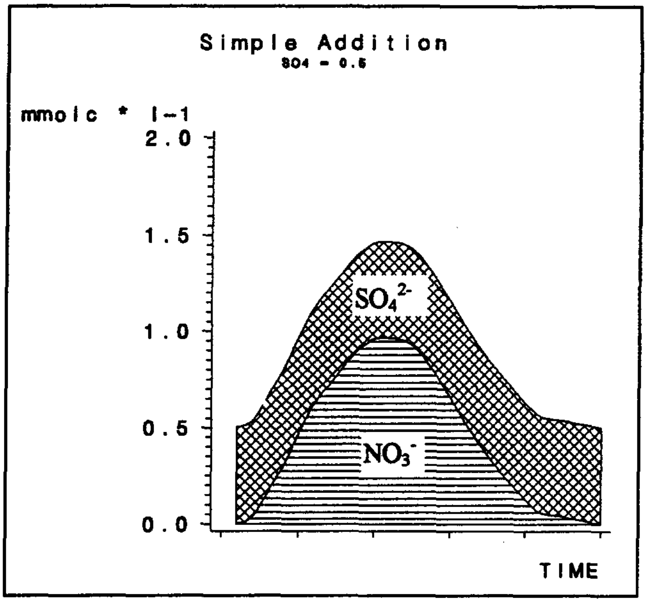

Fig. 9. Modeled sum of anions (without SO_4^{2-} adsorption or Al hydroxy sulfate dissolution). The NO_3^- concentration is varied from 0 to 1 $mmol_c \cdot L^{-1}$.

responsible for the enrichment of the soil solution with NO_3^-, SO_4^{2-}, Cl^-, and HCO_3^-. Even if all processes are known, the resulting anion equivalent sum can only in particular cases be predicted by simply adding the effects of the processes involved. A causal interpretation of soil solution chemistry data by explanation models (e.g. linear models) is faciliated, if existing interrelations have been identified. Additionally, in our example of alunite dissolution during periods of high NO_3^- concentrations in the soil solution (Fig. 8), the variation in the cation equivalent sum of the soil solution could be explained satisfactorily by either the variation in NO_3^- concentration or the variation in SO_4^{2-} concentration. However, only knowledge of the obvious one-sided causal dependence between NO_3^- and SO_4^{2-} concentrations in the soil solution allows a meaningful interpretation of data stressing excess nitrification as driving force. Also, an isolated interpretation of soil solution data in our case of enforcement of sulfate adsorption by excess nitrification would lead to wrong conclusions: The cation equivalent sum is positively correlated with the NO_3^- concentrations, but negatively with the SO_4^{2-} concentrations. Again, only knowledge of the causal interrelation leads to the right interpretation: Excess nitrification is the key process, sulfate adsorption is a dependent process, and the resulting anion equivalent sum finally is the governing factor of the cation equivalent sum.

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