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The biogeochemistry of two forested catchments in the Black Forest and the eastern Ore Mountains (Germany)

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Abstract. The biogeochemical input-output fluxes of two forested catchments with contrasting levels of atmospheric deposition were investigated in Germany. This paper focuses on the effects of recent changes in atmospheric inputs on the chemical composition in the soil solution and stream. The catchment 'Schluchsee' (Black Forest; SW Germany) is characterized by relatively low atmospheric inputs whereas 'Rotherdbach' (Ore Mountains; E Germany) received significant amounts of acid deposition (mainly originating from SO_2 emissions) until recent years. Both sites reveal decreases in H^+ and S deposition during the 1990s. This pattern is typical when compared to trends in Europe. In response to the reduced S deposition, soil solution and streamwater SO_4^{2-} concentrations decreased significantly. A net release of SO_4^{2-} (output > input) was observed at both sites due to the release of S previously stored in the soil. The level of N deposition was more or less constant at both sites. At Schluchsee, NO_3^- concentration in streamwater remained more or less unchanged, whereas a decrease at Rotherdbach was observed. A recovery from acidification was found in seepage water as indicated by increasing acid neutralizing capacity (ANC). Streamwater ANC increased only in the permanently acidified Rotherdbach. No change of ANC was observed in the Schluchsee stream, which was characterized by episodic acidification during high-flow conditions. Nevertheless, the key factor controlling the recovery from surface water acidification was the type, amount and distribution of stored S pools in the ecosystem. Thus, time series analysis of long-term data of input-output chemistry can be a valuable instrument in order to improve the understanding of linked terrestrial-aquatic systems and give useful clues for modeling efforts.

Introduction

The biogeochemical functioning of forest ecosystems has been in the focus of research since the 1970s. In this context, experimental catchments have proven to be ideal units for studying element fluxes both on the scales of landscapes and ecosystems (Likens et al. 1977; Swank and Crossley 1988; Hornung et al. 1990). Input-output budgets for a catchment can provide valuable information on the response of linked terrestrial-aquatic systems to changing environmental conditions (climate, air pollution) or land-management practices.

In recent years, anthropogenic emissions of SO_2 and mineral dust in Central Europe and subsequently deposition of protons (H^+), SO_4^{2-} and 'base cations' (Ca^{2+}, Mg^{2+}, Na^+, K^+) have substantially decreased (Tarrasón and Schaug 1999; Stoddard et al. 1999; Alewell et al. 2000a, 2001). In contrast, the temporal trends in N deposition tend to be more complex according to the regional emission pattern produced by industry, traffic, and agriculture. On average, N deposition during the last two decades has been more or less constant. However, N deposition is characterized by a distinct year-to-year variation, primarily due to varying meteorological conditions, thus complicating the detection of time trends (Wright et al. 2001).

The potential effects of such changes in the deposition pattern have been under debate. The extent and rapidity of the recovery of forest soils and related water chemistry and forest ecosystems from high rates of acidic deposition depends mainly on internal transformations. Previously-deposited SO_4^{2-} has accumulated in the soils, both in inorganic and organic forms, and can be released within an unknown time period. A regional analysis of data from the ICP-water program has shown an increase in alkalinity (which was defined as recovery from acidification) in streams and lakes allover Europe as a response to the significant reduction of sulfate deposition (Stoddard et al. 1999). This is mainly true for Northern Europe where soils normally are very shallow. However, numerous sites in Central Europe (with deeply developed soils) show a significant delay or even no reaction with respect to recovery from water acidification (Alewell et al. 2000b; Evans et al. 2001). Generally, it can be stated that ecosystems with a low storage capacity react relatively quickly to reduced S deposition with an increase in alkalinity. In contrast, recovery from acidification is delayed in systems where large amounts of S have been accumulated in the soil due to the continued release of SO_4^{2-} from soil sources (Alewell 1995).

During the last quarter of the 20th century many forested regions in Europe received elevated rates of N deposition (Wright et al. 2001). Hence it has been hypothesized that an excess of N deposition may lead to 'N saturation' of the forest ecosystems. However, it is difficult to forecast when an individual ecosystem would reach 'saturation'. In many forests, a previous massive export of organic matter (fuelwood coppicing, litter raking etc.) had lead to gross reduction in N availability (cf. Tamm 1991). Unfortunately, different definitions of 'N saturation' are used (cf. Ågren and Bosatta 1988, Nilsson 1986, Stoddard 1994) leading to contrasting perceptions of the actual N status of the same ecosystem (cf. Feger 1993, Moldan and Wright 1998). A commonly used definition is that ″the availability of ammonium (NH_4^+) and nitrate (NO_3^-) is in excess of the total combined plant and microbial nutritional demand″ (Aber et al. 1989). According to this definition N saturation leads to increased leaching of inorganic N (generally NO_3^-) below the rooting zone. Since NO_3^- is a strong acid anion, it significantly contributes to acidification of soils and surface waters (cf. Reuss and Johnson 1986; van Miegroet 1994). Notably, against the background of relatively high and more or less constant rates of N deposition and the observed reduction in S deposition, N transformations in the terrestrial systems will become more important for surface water acidification in the future. A release of the strong acid anions SO_4^{2-} and NO_3^- is always accompanied by cation leaching (Reuss and Johnson 1986). Therefore, temporal changes in SO_4^{2-} and NO_3^- concentrations will also influence the concentrations of cations in soil leachates and surface waters. In addition, reduced 'base cation' deposition may counteract the mitigation effects of reductions in S and N deposition.

Besides the varying site conditions, the deposition history should also be a key factor controlling the response to deposition changes. The effect of changed deposition during a distinct time period was examined in various manipulation experiments where deposition was experimentally altered (Cummins et al. 1995; Feger 1995; Wright and van Breemen 1995). The effect of 'deposition history' could be studied by comparing sites which ideally differ only in deposition climate. Correspondingly, in our study, we are primarily interested in: (1) the comparison of the biogeochemical flux characteristics of two forest ecosystems with analogous soil and bedrock conditions but contrasting deposition climate; and (2) the evaluation of the response of soil solution and streamwater chemistry to observed changes in deposition.

Material and methods

Site descriptions

Long-term data sets from two experimental catchments in Germany were analyzed. According to the objectives of our study catchments should have comparable bedrock, soils, and vegetation cover, but differ significantly in their element inputs from the atmosphere (Table 1). The catchment *Schluchsee* (47°49′ N; 8°06′ E) is located in the higher altitudes of the Black Forest (SW Germany, Figure 1) with elevation range between 1150 and 1250 m a.s.l. and an average slope of 22%. The whole catchment is covered with managed stands of Norway spruce (*Picea abies*) of an average age of 55 yrs. The natural mixed forest, dominated by beech (*Fagus sylvatica*), was replaced by monocultural spruce stands about 200 yrs ago (Feger 1993). The climate is cool and humid (Table 1). Severe symptoms of forest decline, which were observed during the early 1980s, were more a result of complex nutritional disturbances (notably acute Mg deficiency) than the direct effect of air pollution (Feger 1997).

The catchment *Rotherdbach* (50°47′ N; 13°43′ E) is located in the eastern Ore Mountains (E Germany) close to the border with Czech Republic with elevation range from 675 to 750 m a.s.l. and an average slope of 17%. A 90 yr-old managed Norway spruce covers 83% of the area while a small part of the catchment is stocked with a 15 yr-old Norway spruce plantation (Table 1). Generally, forests in the Ore Mountains had been intensively utilized since the middle age notably for mining purposes (Nebe et al. 1998). The present spruce stands are mainly 2nd to 3rd generation stands since regular forestry commenced in the 19th century. Since the 1980s, severe forest dieback has been observed in a vast area of the eastern Ore Mountains. The damages resulted from air pollution mainly characterized by ex-

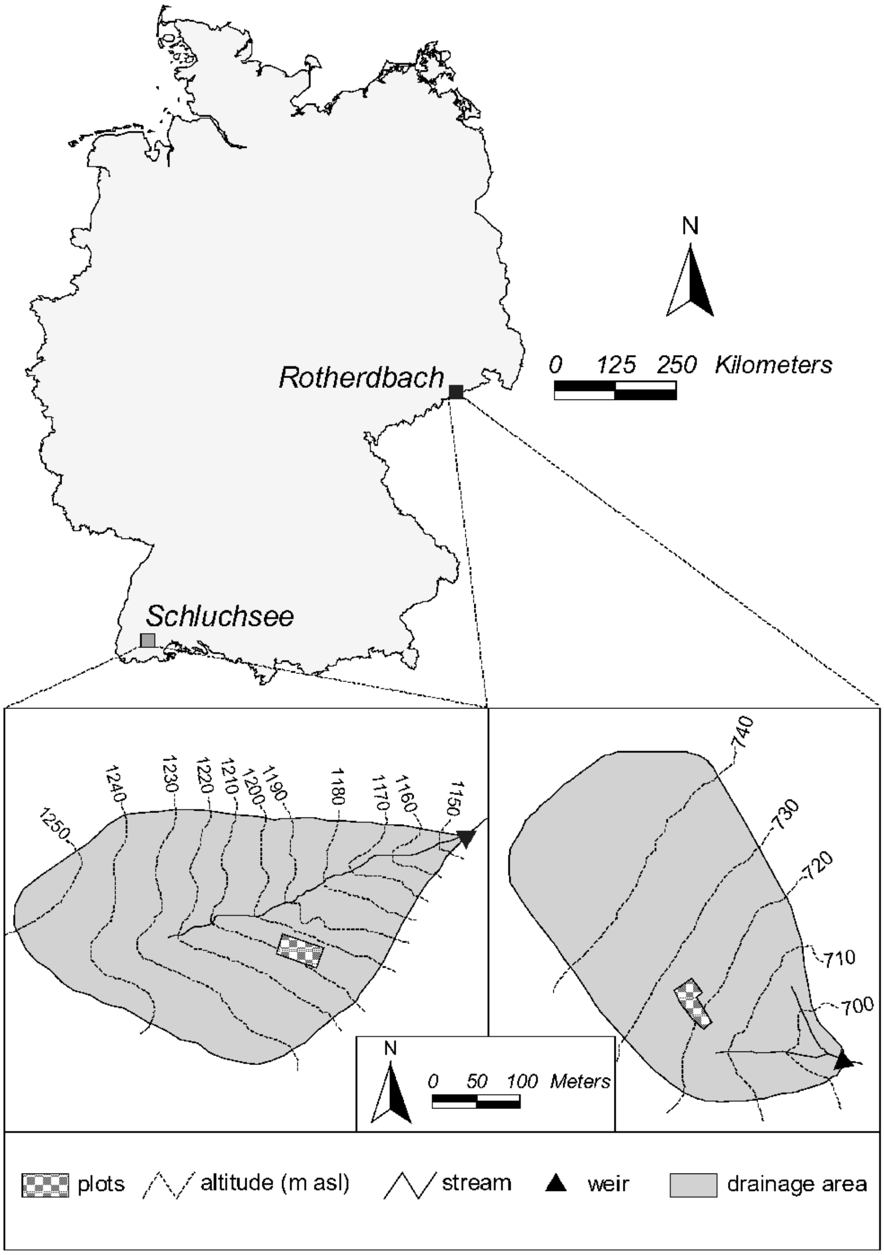

Figure 1. Location of the two catchments in Germany.

tremely high air concentrations of SO_2 from local combustion of S-rich brown coal. As a consequence of the introduction of abatement technologies in power plants and alternate use of gas and oil for heating, the emissions of SO_2 and related forest

Table 1. Characteristics of the studied catchments.

	Schluchsee	Rotherdbach
Investigation period [a]	1988–1998	1994/95–1999 [b]
Location	47°49′ N; 8°06′ E	50°47′ N; 13°43′ E
Drainage area [ha]	10.98	9.43
Altitude [m a.s.l]	1150–1253	675–750
Mean slope [%]	21.9	16.7
Aspect	ENE	SE
Mean annual precipitation [mm]	1867	989 [c]
Mean annual runoff [mm]	1381	590 [c]
Mean annual air temperature [°C]	4.5	5.5
Vegetation	Norway spruce 55 yr (100%)	Norway spruce 90 yr (83%); Norway spruce 15 yr (17%)
Major soil types (FAO)	Haplic Podsol	Cambic Podsol
Bedrock	Granite	Rhyolithe

[a] hydrological years
[b] deposition 1994–1999; stream output 1995–1999
[c] period 1995–1999

damage symptoms have been decreasing considerably since 1990 (Abraham et al. 2000). The climate at *Rotherdbach* is also cold and humid but receives annual precipitation equivalent to only 50% of that measured at *Schluchsee* (Table 1).

The study catchments have a similar size (9.4 ha/11 ha) and are drained by perennial first-order streams. *Schluchsee* is underlain by a base-poor granite. SiO_2 and Al_2O_3 comprise 90% of the bedrock weight (Table 2). Soils are commonly loamy sands with high gravel content up to 60%. High hydraulic conductivity throughout the entire soil profile results into a predominant vertical water flow. Between the mineral soil and the solid granite bedrock there is a highly permeable layer of fine gravel from granite weathering (variable thickness up to 3 m). Thus, the soils (Haplic podzols) are well drained and highly acidic.

The bedrock of the *Rotherbach* catchment consists of rhyolite with a mineral composition similar to *Schluchsee*. However, there is a minor difference in Ca and Mg contents as they are somehow higher at *Rotherdbach* (Table 2). Soils at *Rotherdbach* are sandy loams to loams with a stone fraction of up to 70% in the subsoil (Abiy 1998). At sites protected from erosion soils are commonly underlain by a fossil layer of tertiary weathering material. These layers are rich in kaolinite and form the basement of the periglacial sediments from which the soils were formed (Nebe et al. 1998). As a result, hydraulic conductivity is lower compared to soils at *Schluchsee* and lateral flow paths prevail in soil drainage.

At *Rotherdbach*, de-icing salts are applied to a road crossing the ridge of the catchment during winter season (Abiy 1998, cf. Figure 1). Salts used are commonly a mixture of NaCl and $CaCl_2$, but unfortunately no data for applied amounts are

Table 2. Average element composition (mass%) of the bedrock at the two study catchments.

	Schluchsee ″Bärhalde″ granite (Brahmer 1990)	Rotherdbach ″Teplitz″ rhyolithe (Nebe 1964)
SiO_2	75.4	75.7
Al_2O_3	13.6	12.9
Fe_2O_3	1.21	–
MgO	0.17	0.46
CaO	0.31	0.70
Na_2O	3.38	2.30
K_2O	5.01	5.24
TiO_2	0.07	–
P_2O_5	0.19	0.01

available. In contrast at *Schluchsee*, which is located far away from traffic roads, there is no such an influence of de-icing salts.

Even though soil formation factors are quite similar (as reflected in comparable podzol soil types), there are distinct differences in soil chemical properties that can be attributed to recent air pollution impacts. Soils at *Schluchsee* are acidic and poor in base cations (Table 3). Values for pH (H_2O) range from 3.8 in the upper mineral soil to 4.4 in the subsoil. Base saturation is below 5% throughout the entire soil profile. In comparison, base saturation at *Rotherdbach* ranges from 3% minimum in 25–50 cm soil depth to 17% in the topsoil. This contrasting pattern clearly reflects higher deposition rates of base cations originating from mineral dusts (alkaline fly ash etc.). Effective cation exchange capacity (CEC_e), ranging from 35 μmol_c g^{-1} in the subsoil to 260 μmol_c g^{-1} in 20–25 cm depth, is higher as compared to *Schluchsee* (Table 4). As a result of higher SO_2 emissions in the Ore Mountains the contents of S_{tot} in the soil is distinctly higher at *Rotherdbach*. A detailed description of site properties is given by Armbruster (1998) for *Schluchsee* and by Abiy (1998) for *Rotherdbach*, respectively.

Methods

Sample collection and analyses

The catchments were monitored since 1987 (*Schluchsee*) and 1993 (*Rotherdbach*), respectively. Bulk precipitation and throughfall were collected weekly and bulked to monthly analyses at both catchments. From 1987 to 1990 precipitation samples were analyzed weekly at *Schluchsee*. Bulk precipitation was collected from reference points close to the catchments with sampling containers replicated three times at *Rotherdbach* and five times at *Schluchsee*. Throughfall was collected at sample plots (aprox. 50 × 50 m) within the catchment with containers replicated eight times at *Rotherdbach* and ten times at *Schluchsee* (cf. Figure 1). Stemflow was not col-

Table 3. Selected chemical properties of a typical soil profile at Schluchsee (Soil type: Haplic Podsol; texture: loamy sand/sandy loam).

Horizon	Depth	pH	C	N	S_{total}	CEC_e [a]	BS[b]
	(cm)	(H_20)	mg g^{-1}			μmol_c g^{-1}	%
Of	4–2	3.5	443	15.0	1.54		
Oh	2–0	3.4	238	8.7	0.85		
Ahe	0–30	3.8	24	1.7	0.14	71	3.7
Bsh	30–40	4.2	32	1.7	0.17	70	2.4
Bhs	40–60	4.9	30	1.1	0.15	43	2.1
Bhvs	60–80	4.9	30	1.3	0.11	42	1.9
Cv	80–100	4.4	5	0.4	0.03	20	4.1

[a] effective cation exchange capacity (0.5 M NH_4Cl)

[b] base saturation

Table 4. Selected chemical properties of a typical soil profile at Rotherdbach (Soil type: Cambic Podsol; texture: sandy loam/loam).

Horizon	Depth	pH	C	N	S_{total}	CEC_e [a]	BS [b]
	(cm)	(H_20)	mg g^{-1}			μmol_c g^{-1}	%
Of		4.9	433	20.0	2.91		
Oh		4.1	399	14.5	2.24		
Ahe	0–5	3.9	45	nd [c]	0.24	128	17.4
Ae	5–20	4.0	21	nd [c]	0.11	79	11.5
Bh	20–25	3.8	66	nd [c]	0.44	260	4.3
Bs1	25–50	4.3	56	nd [c]	0.46	107	3.0
Bs2	50–80	4.4	30	nd [c]	0.26	70	4.2
Cv	80–125	4.6	5	nd [c]	0.33	35	7.9

[a] effective cation exchange capacity (0.5 M NH_4Cl)

[b] base saturation

[c] nd = not detected

lected because this hydrologic component in Norway spruce stands comprises normally only 1 to 2% of canopy throughfall (Mitscherlich 1981). Simultaneously, soil leachates were collected on the same sample plots (weekly to fortnightly at *Schluchsee* and monthly at *Rotherdbach*) Soil water was collected from three depths (beneath the forest floor and at 30 cm and 80 cm in the mineral soil) at *Schluchsee*, and 6 depths (beneath the forest floor and at 10 cm, 20 cm, 40 cm, 60 cm and 80 cm in the mineral soil) at Rotherdbach using tension plate lysimeters and cups, respectively. Discharge was recorded permanently at V-notch weirs. Streamwater samples were taken weekly (*Schluchsee*) and monthly (*Rotherdbach*), respectively.

Specific electrical conductivity and pH-value were determined in the laboratory directly after sample collection. Samples for chemical analysis were filtered through 0.45 μm membrane filters. The anions Cl^-, NO_3^- and SO_4^{2-} were analyzed by ion chromatography at *Schluchsee* and flow injection analysis (FIA) and atomic adsorption with inductively coupled plasma (ICP) for S at *Rotherdbach*. Ammonium was determined photometrically. Cation elements Na, K, Ca, Mg, Al, Mn and Fe were measured by means of ICP (*Rotherdbach*) and AAS (*Schluchsee*), respectively. At *Schluchsee*, Al was fractionated with the cation exchange column percolation method developed by Discroll (1984). For *Rotherdbach* there were no Al speciation data available. Therefore, Al^{3+} calculated from Al_{tot} measured with ICP will be an overestimation of real values. Acid neutralizing capacity (ANC) was calculated according to Reuss and Johnson (1986) and van Miegroet (1994) from the charge balance:

$$ANC = [Na^{+}] + [K^{+}] + 2[Ca^{2+}] + 2[Mg^{2+}] + [NH_4{}^{+}] - [Cl^{-}] - [NO_3^{-}] \\ - 2[SO_4^{2-}][\mu mol^{l}]$$

Analytical methods are described in detail by Feger (1993) for *Schluchsee* and Langusch (1995) for *Rotherdbach*, respectively.

Calculation of total deposition

Estimating the total atmospheric deposition to forest ecosystems and its separation from wet deposition is still a problem (Marques 1999). A common approach, which was also used in our study, is the ’canopy budget model’ proposed by Ulrich (1983, 1991). This model, which compares open-land bulk deposition and throughfall, is mainly based on the assumption that Na does not interact with the canopy (no leaching, no uptake) and thus can act as an ’tracer’ for ’dry’ deposition. Dry deposition of an individual element is calculated from the canopy throughfall flux by means of the ratio $Na_{throughfall}/Na_{bulk}$. However, this implies that total deposition of other elements behave similar to Na. The application of the ’canopy budget model’ and specific extensions for our sites are described and critically discussed by Brahmer (1990) and Armbruster (1998) for *Schluchsee* and Abiy (1998) for *Rotherdbach*, respectively.

Time series analyses

A major aim of time series analysis is to detect patterns in temporal variation in order to develop a model, which describes such variations in a given data set. Typical systematic patterns in time series are seasonal fluctuations and overlaying trends. In our study, a summation time series model was used to analyze and to describe time series consisting both of deposition and solution chemistry data (Equation 1). The trend component, which is the special emphasis in our study, was calculated by using a seasonal, multiple regression model (Flieger and Toutenburg 1995), (Equation 2). Furthermore, dependence of deposition and solution chemistry on water flux was included in the regression. Unfortunately, water flux data for seepage water were not available for *Rotherdbach*. As a result, the model included only 'seasonal variation' and 'long-term trend' components for soil water at *Rotherdbach*. Monthly element inputs (g ha^{-1} $month^{-1}$) were taken for the analysis of deposition trends (bulk precipitation, throughfall). For time series analysis of soil leachates and streamwater, we took concentration data. The temporal resolution for the analysis in streamwater and soil water was selected according to temporal resolution of measurements (monthly at *Rotherdbach*; fortnightly for soil water at *Schluchsee*; weekly for streamwater at *Schluchsee*). Normal distribution of regression residual was checked by comparing standardized residuals with normal distribution and cumulative probabilities. Auto-correlation of residuals was checked through computing the Dubin-Watson coefficient. Data points with residuals greater than 3 standard derivations were replaced by smoothed data (linear interpolation) to improve normal distribution of residuals and reliability of trend component (cf. Flieger and Toutenburg 1995). The significance threshold for the trend component was set to $p < 0.05$. All statistical analyses were performed with SPSS for Windows 10.0. Details of the statistical analysis are given in Armbruster (1998).

$$x_t = s_t + q_t + t_t \tag{1}$$

x_t = observed value of time series at time t
s_t = seasonal component of time series
q_t = component related to water flux
t_t = trend component of time series

$$x(t) = s(t) + a \times q(t) + b \times t \tag{2}$$

x(t) = observed value of time series at time t
s(t) = seasonal component of time series
q(t) = water flux at time t
a = regression variable related to water flux
b = regression variable related to time (= temporal trend)
t = time

Results

Solute chemistry

Going through the various ecosystem strata, significant changes in hydrochemical composition can be seen in both catchments (Figure 2). Bulk precipitation, throughfall and streamwater concentrations are volume-weighted means, and seepage waters are arithmetic means. Organic anions (Org^-) are calculated numbers representing ion deficits derived from the charge balance. In both catchments, throughfall concentrations were higher than in bulk precipitation. At *Schluchsee* (Figure 2a) the leachates beneath the O-layer revealed the highest total ion concentrations, with Org^- being the dominating anion. In all mineral soil depths and the streamwater,

SO_4^{2-} was the dominant anion. With increasing soil depth the percentage of protons (H^+) decreased while Al^{3+} increased. Comparing seepage water at 80 cm depth with streamwater revealed an increase in Na^+ and Ca^{2+} and a decrease in Al^{3+}. At *Rotherdbach* (Figure 2b) SO_4^{2-} clearly predominated both in the O-layer and the mineral soil with Al^{3+} (calculated from Al_{tot}) being the major cation in the mineral soil. An increase of Al^{3+} concentrations with soil depth can be seen. The highest solute concentration at *Rotherdbach* occurred in 80 cm mineral soil depth. Notably, SO_4^{2-} concentrations increased from 60 cm to 80 cm mineral soil depth. Similar to *Schluchsee*, a marked increase in Na^+ and Ca^{2+} also occurred from 80 cm soil depth to streamwater at *Rotherdbach*. Nevertheless, Al^{3+} still dominated the cation composition (28% of cation sum; whereas at Schluchsee: only 6%).

Streamwater patterns

In both catchments, SO_4^{2-} was the dominant ion in streamwater (Figures 3 and 4). The major base cation was Na^+ at *Schluchsee* and Ca^{2+} at *Rotherdbach*. At *Schluchsee*, streamwater pH varied between 4.6 and 7.1, and ANC between −55 and 109 µmol l^{-1} (Figure 3; Table 5). In contrast, pH-values in the *Rotherdbach* stream varied between 4.2 and 4.7 and ANC between −524 and −79 µmol l^{-1} (Figure 4; Table 5). As a consequence, streamwater in the *Rotherdbach* catchment was characterized by elevated concentrations of Al_{tot} (1.3–4.2 mg l^{-1}).

Streamwater chemistry at both sites was characterized by distinct temporal variations (Figures 3 and 4). At *Schluchsee*, Na^+ and Al_{tot} (total Al) concentrations and ANC were strongly related to discharge (data not shown here, cf. Brahmer 1990, Armbruster 1998). This relationship was less pronounced at *Rotherdbach*. Comparing average concentrations of all samples with samples collected at high discharge rates exhibits the fact that the acidification status in the *Schluchsee* stream depended on water flow (Table 5). At high discharge rates the concentrations of Na^+ decreased whereas H^+, NO_3^- and Al_{tot} concentrations showed distinct increases. This led to negative ANC values at high discharge rates at Schluchsee whereas average ANC was slightly positive. This episodic acidification during high-flow conditions was primarily due to the mobilization of NO_3^- (Armbruster et al. 2000). In the *Rotherdbach* catchment the relationship between acidification status and discharge was less pronounced. In contrast to the episodically acid *Schluchsee* stream, the stream in the *Rotherdbach* catchment could therefore be characterized as ’permanently acid’.

Input-output fluxes

Evapotranspiration (bulk precipitation minus stream output) was 490 mm at Schluchsee and 430 mm at *Rotherdbach* (Table 6). At *Schluchsee*, 66% of evapotranspiration was attributed to interception whereas 44% of evapotranspiration was attributed to interception at Rotherdbach.

Open land bulk deposition (BD) of the two sites was comparable for most elements. The lower input rates in Na^+ and Cl^- at *Rotherdbach* are typical for the more continental-type climate in the Ore Mountains. Total N and SO_4^{2-} in bulk

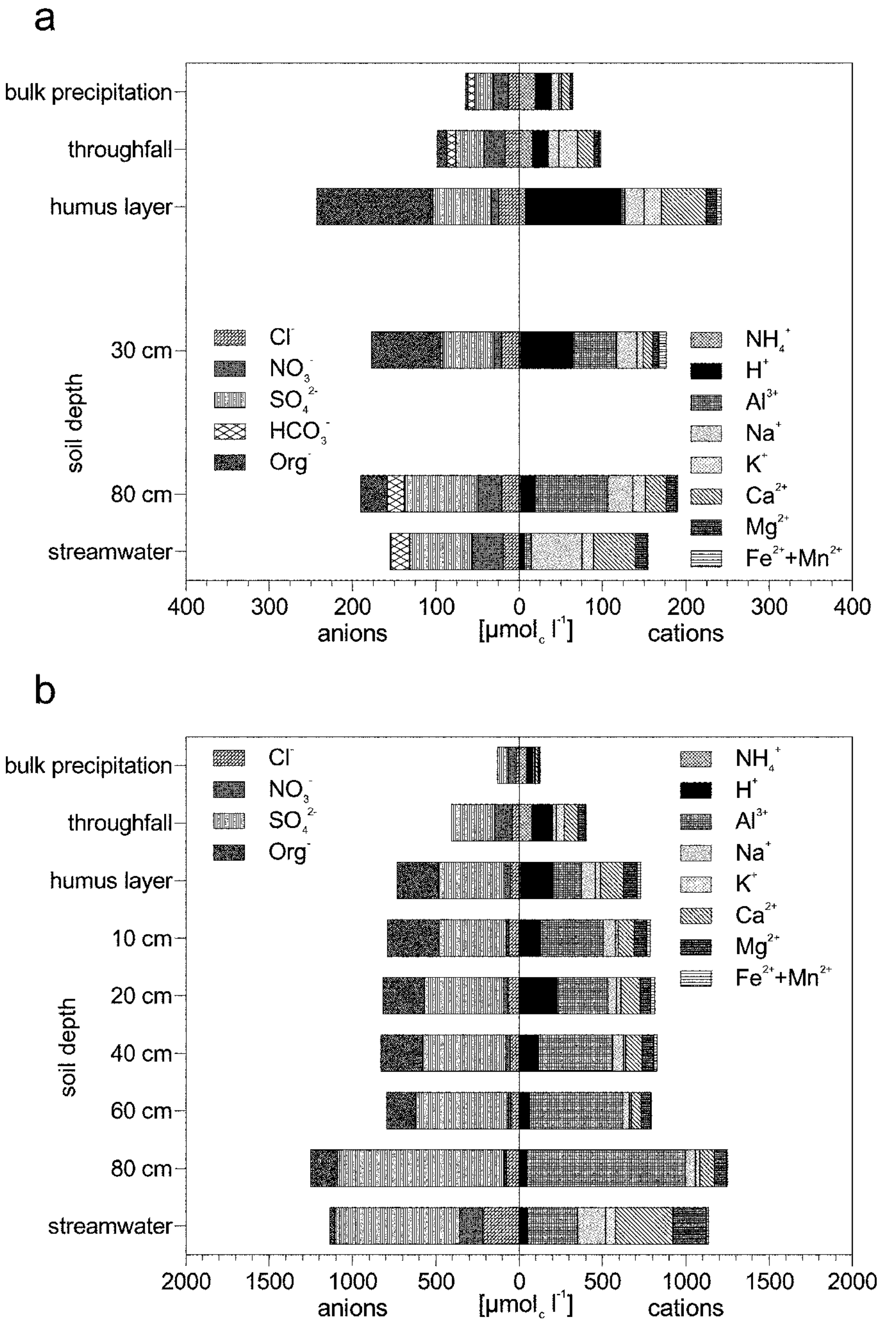

Figure 2. Charge balances in different compartments of the study sites Schluchsee (a) and Rotherdbach (b).

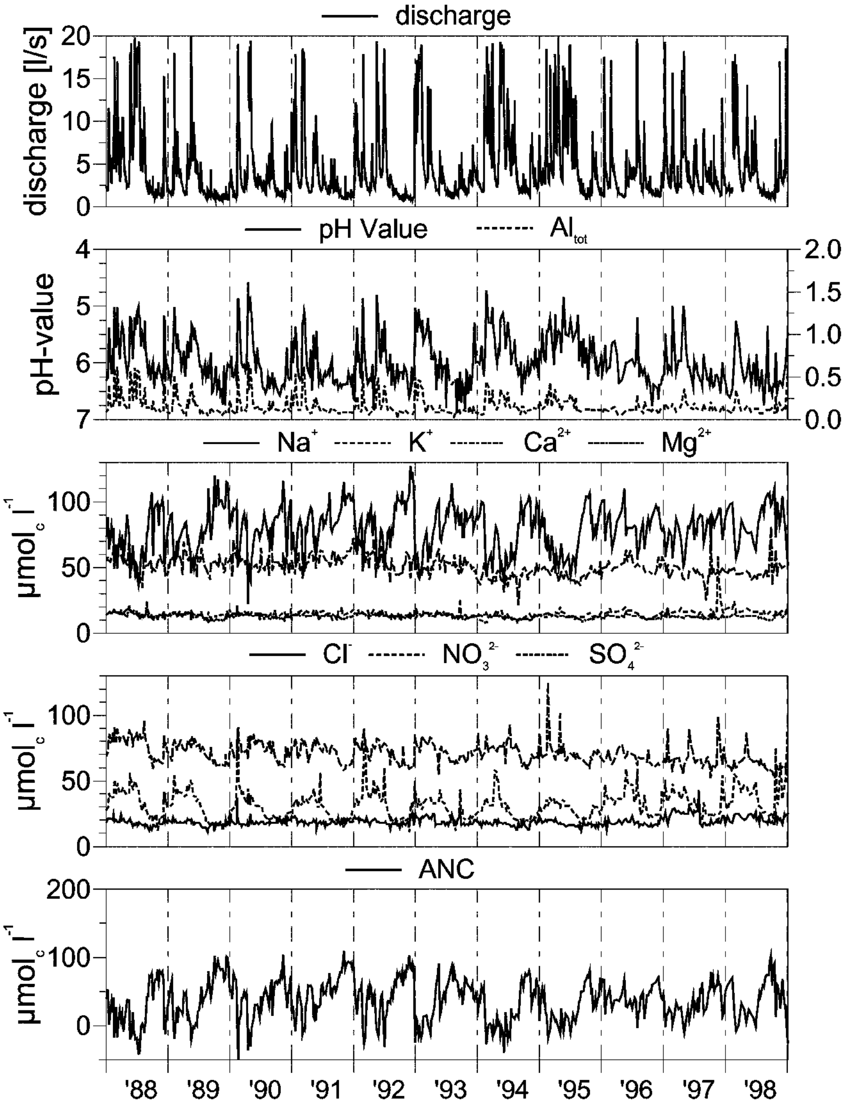

Figure 3. Temporal patterns in streamwater concentrations (Schluchsee catchment; year numbers correspond to hydrological years).

deposition were higher at *Rotherdbach*. Throughfall fluxes and total deposition fluxes (TDP) at the two sites differed significantly for all elements. Dry deposition (TDP – BD) is 10 to 20% of TDP at *Schluchsee* and thus played only a minor role. In contrast, TDP was controlled by increased fluxes of H^+ and SO_4^{2-} at *Rotherdbach*. For other components, 50% of the total deposition resulted from dry deposition. The fluxes of the conservative tracer Cl^- through the entire system were nearly equal at *Schluchsee* indicating plausible water fluxes in this catchment. In

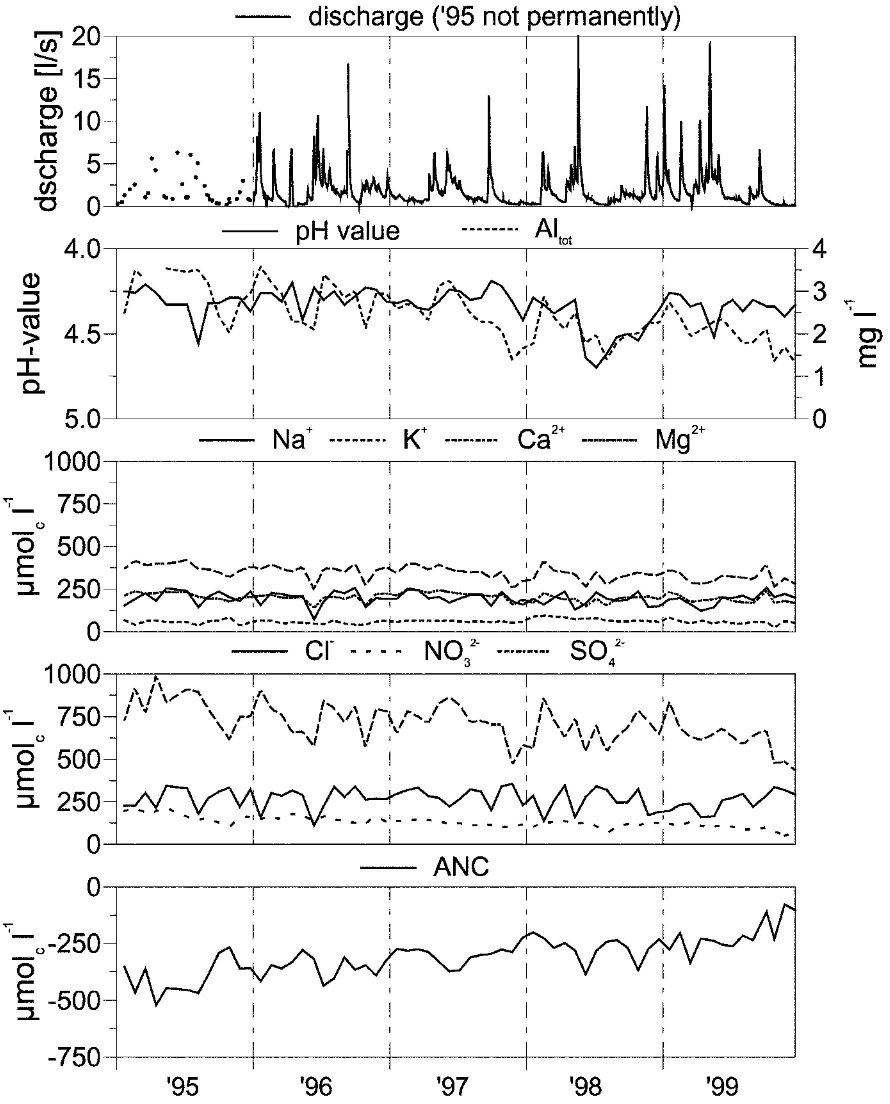

Figure 4. Temporal patterns in streamwater concentrations (Rotherdbach catchment; (year numbers correspond to hydrological years).

the *Rotherdbach* catchment however, a negative Cl^- budget can be seen which was due to the use of de-icing salts.

Both sites demonstrated a net release of SO_4^{2-}. Average output fluxes with streamwater at both sites were approximately twice as high as input with total deposition. Calculation of net release (stream output minus total deposition) led to an average S net release of 8 kg ha^{-1} yr^{-1} from *Schluchsee* and 34 kg ha^{-1} yr^{-1} from *Rotherdbach*.

Table 5. Statistical analysis of streamwater chemistry in the two catchments studied (year numbers represent hydrological years).

		Schluchsee (1988–1998)				Rotherdbach (1995–1999)			
		min.	max.	mean [a] n = 554	mean hd [b] n = 119	min.	max.	mean [a] n = 64	mean hd [b] n = 13
pH		4.59	7.09	5.27	5.09	4.19	4.70	4.31	4.30
H^+	$\mu mol_c \; l^{-1}$	< 0.1	25.7	5.4	8.1	20.0	64.6	49.2	49.6
NH_4^+	$\mu mol_c \; l^{-1}$	< 1	4	< 1	< 1	< 1	7	2	1
Na^+	$\mu mol_c \; l^{-1}$	22	127	61	49	70	257	169	143
K^+	$\mu mol_c \; l^{-1}$	7	58	14	14	22	92	58	58
Ca^{2+}	$\mu mol_c \; l^{-1}$	21	81	50	49	248	419	344	337
Mg^{2+}	$\mu mol_c \; l^{-1}$	8	24	14	14	134	250	201	196
NO_3^-	$\mu mol_c \; l^{-1}$	11	91	37	41	50	213	136	136
SO_4^{2-}	$\mu mol_c \; l^{-1}$	52	125	75	77	434	989	749	763
Cl^-	$\mu mol_c \; l^{-1}$	11	43	19	19	108	354	219	177
Al_{tot}	$\mu g \; l^{-1}$	10	668	303	412	1319	4229	2709	2806
Mn_{tot}	$\mu g \; l^{-1}$	< 1	52	21	29	144	323	247	252
Fe_{tot}	$\mu g \; l^{-1}$	< 1	38	9	11	< 1	210	38	30
DOC	$Mg \; l^{-1}$	< 0.1	5.8	1.4	1.6	3.6	5.7	4.6	4.8
ANC	$\mu mol \; l^{-1}$	– 55	109	8	–11	–524	–79	–331	–341
Σ BC [c]	$\mu mol_c \; l^{-1}$	90	209	138	126	498	960	771	735

[a] volume-weighted mean

[b] volume-weighted mean at high discharge (samples collected at upper 20% of discharge: Schluchsee discharge rate > 7.1 $l \; s^{-1}$; Rotherdbach discharge rate > 2.9 $l \; s^{-1}$)

[c] sum of ″base cations″ ($[Na^+] + [K^+] + [Ca^{2+}] + [Mg^{2+}]$)

Both sites were characterized by a net retention of N (*Schluchsee*: 4 kg ha^{-1} yr^{-1} N; *Rotherdbach*: 15 kg ha^{-1} yr^{-1} N). According to the higher output of the anions Cl^-, NO_3^- and SO_4^{2-} output rates of 'base cations' (Na^+, K^+, Ca^{2+}, Mg^{2+}) and Al_{tot} were markedly higher at *Rotherdbach* as compared to *Schluchsee*. At *Schluchsee*, approximately 50% of Al_{tot} in streamwater consisted of inorganic Al^{3+} as a result of Al speciation (Prietzel and Feger 1996; Armbruster 1998). However, according to the given solution chemistry it is plausible that the overwhelming portion of Al_{tot} in the Rotherdbach stream consisted of Al^{3+} ions.

Temporal development of element fluxes and concentrations

Deposition

Temporal trends in deposition revealed significant decreases in bulk deposition and throughfall for SO_4^{2-} at both sites during the 1990s (Table 7, Figure 5). In Figure 6, the results from time series analysis are presented for SO_4^{2-}. Calculated annual decreases in SO_4^{2-} were roughly 10 times higher at *Rotherdbach* as compared to *Schluchsee*. Measured S depositon in throughfall (which can be assumed as TDP)

Table 6. Average values of water and element fluxes with bulk deposition (BD) throughfall (TF), total deposition (TDP) and stream output (SO). All fluxes in kg ha^{-1} yr^{-1} (year numbers represent hydrological years).

	Schluchsee (1988–1998)				Roterdbach (1995–1999)			
	BD	TF	TDP	SO	BD	TF	TDP	SO
Water [mm]	1867	1543		1381	989	803		563
H^+	0.34	0.26	0.43	0.05	0.32	0.91	1.43	0.42
Na^+	4.1	4.7	4.7	21.2	2.3	4.6	4.6	26.6
K^+	2.1	13.3	2.4	7.8	1.0	14.6	2.0	13.3
Ca^{2+}	3.9	6.1	4.6	13.6	3.5	13.6	7.0	41.3
Mg^{2+}	0.7	1.1	0.8	2.2	1.3	4.0	2.6	14.5
NH_4^+-N	5.0	3.6	5.7	0.1	6.7	8.7	13.4	0.2
NO_3^--N	4.5	5.4	5.5	6.9	6.4	11.4	12.8	10.9
N_{tot} [a]	9.5	8.9	11.2	7.0	13.1	20.1	26.2	11.1
SO_4^{2-}-S [b]	6.8	8.4	8.3	16.3	10.7	34.0	34.0	68.1
Cl^-	8.4	9.1	9.0	9.4	6.1	11.7	12.2	55.9
Al_{tot}	0.16	0.25	0.20	3.3	0.26	0.98	0.52	14.9
Mn_{tot}	0.06	0.41	0.07	0.23	0.05	0.35	0.10	1.40
Fe_{tot}	0.10	0.14	0.12	0.11	0.14	0.47	0.28	0.41
DOC	21.4	57.0		18.9				26.8

[a] $N_{tot} = NH_4^+$-N + NO_3^--N

[b] Rotherdbach measured as S_{tot} (SO_4^{2-}-S + S_{org})

at *Rotherdbach* decreased from 46 kg ha^{-1} yr^{-1} in the hydrological year 1994 to 23 kg ha^{-1} yr^{-1} in 1999 (Figure 5). In contrast, summing-up the estimated annual decrease provided by application of the time series model (2.6 kg ha^{-1} yr^{-1}; Table 7) over the total 6-yrs-period resulted in a decrease of 16 kg ha^{-1}. The absolute decline in S deposition was much lower at *Schluchsee* due to the lower deposition rates. Measured S throughfall deposition declined from 12 kg ha^{-1} yr^{-1} in 1988 to 5.6 kg ha^{-1} yr^{-1} in 1998 (Figure 5). The yearly decrease in S deposition calculated from the time series (0.28 kg ha^{-1} yr^{-1}; Table 7) model can be summed-up to 3.1 kg ha^{-1} for the total 11 yr period at *Schluchsee*. Nitrogen in bulk deposition decreased significantly at both sites. The reduction rate was higher at *Schluchsee*, which has the lower N deposition (cf. Table 6). A significant decrease in throughfall was observed only at *Schluchsee*. Ca^{2+} and Mg^{2+} deposition in bulk deposition and throughfall also decreased significantly at *Schluchsee*. Magnesium deposition decreased only slightly (0.02 kg ha^{-1} yr^{-1}; average throughfall deposition: 1.1 kg ha^{-1} yr^{-1}; cf. Table 6). In contrast at *Rotherdbach*, Ca^{2+} decreased by 0.2 kg ha^{-1} yr^{-1} in bulk deposition and 0.46 kg ha^{-1} yr^{-1} in throughfall. Time series analysis with the *Rotherdbach* data yielded no significant decrease in Mg^{2+} deposition.

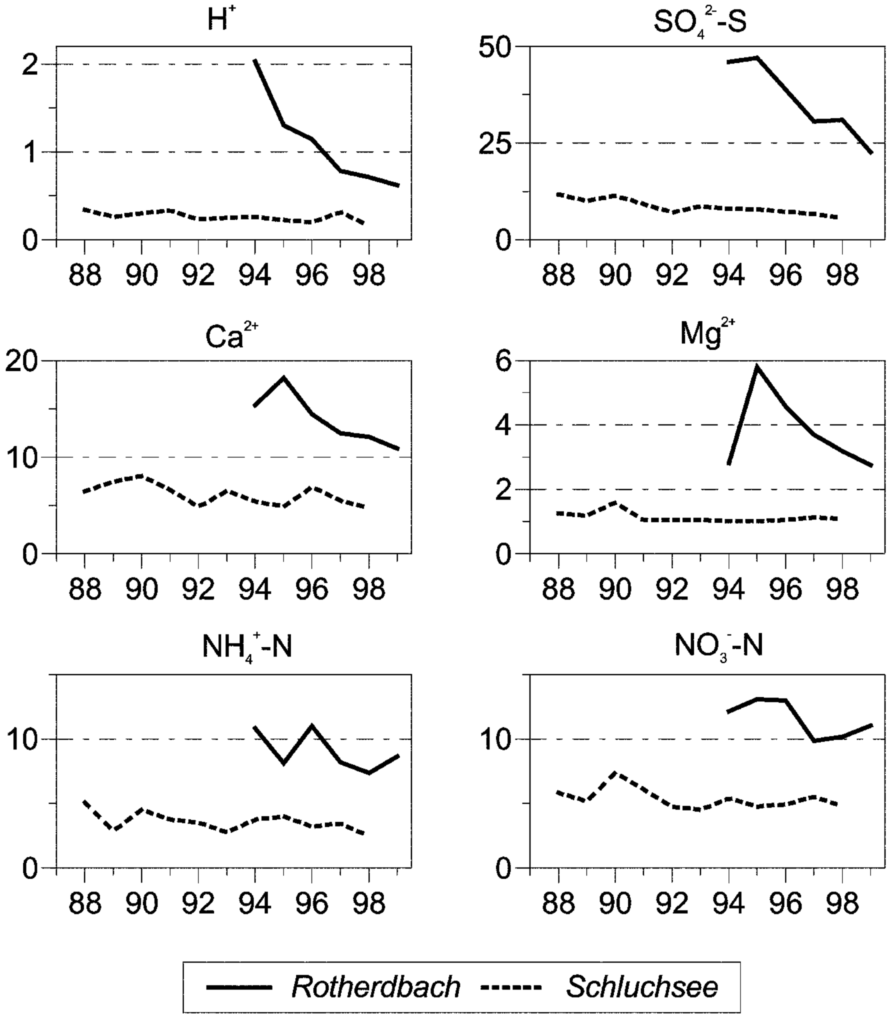

Figure 5. Annual throughfall deposition (kg ha^{-1} yr^{-1}) of both catchments. X-scale units represent hydrological years.

Soil solution and streamwater

In Table 8 the results from time series analysis using ion concentrations in seepage water and streamwater in the *Schluchsee* catchment are presented. In Figure 7, the predictions from the time series model are compared with actual measurements for SO_4^{2-} and sum of 'base cations'. The decreasing SO_4^{2-} deposition resulted in reduced concentrations in soil and streamwater. The calculated decrease in SO_4^{2-} was lower in streamwater (1 µmol$_c$ l^{-1} yr^{-1}) compared to seepage water (2.4–2.7 µmol$_c$ l^{-1} yr^{-1}). However, the temporal trend for 'base cations' was not uniform for all individual elements. Only Ca^{2+} and Mg^{2+} concentrations decreased significantly in

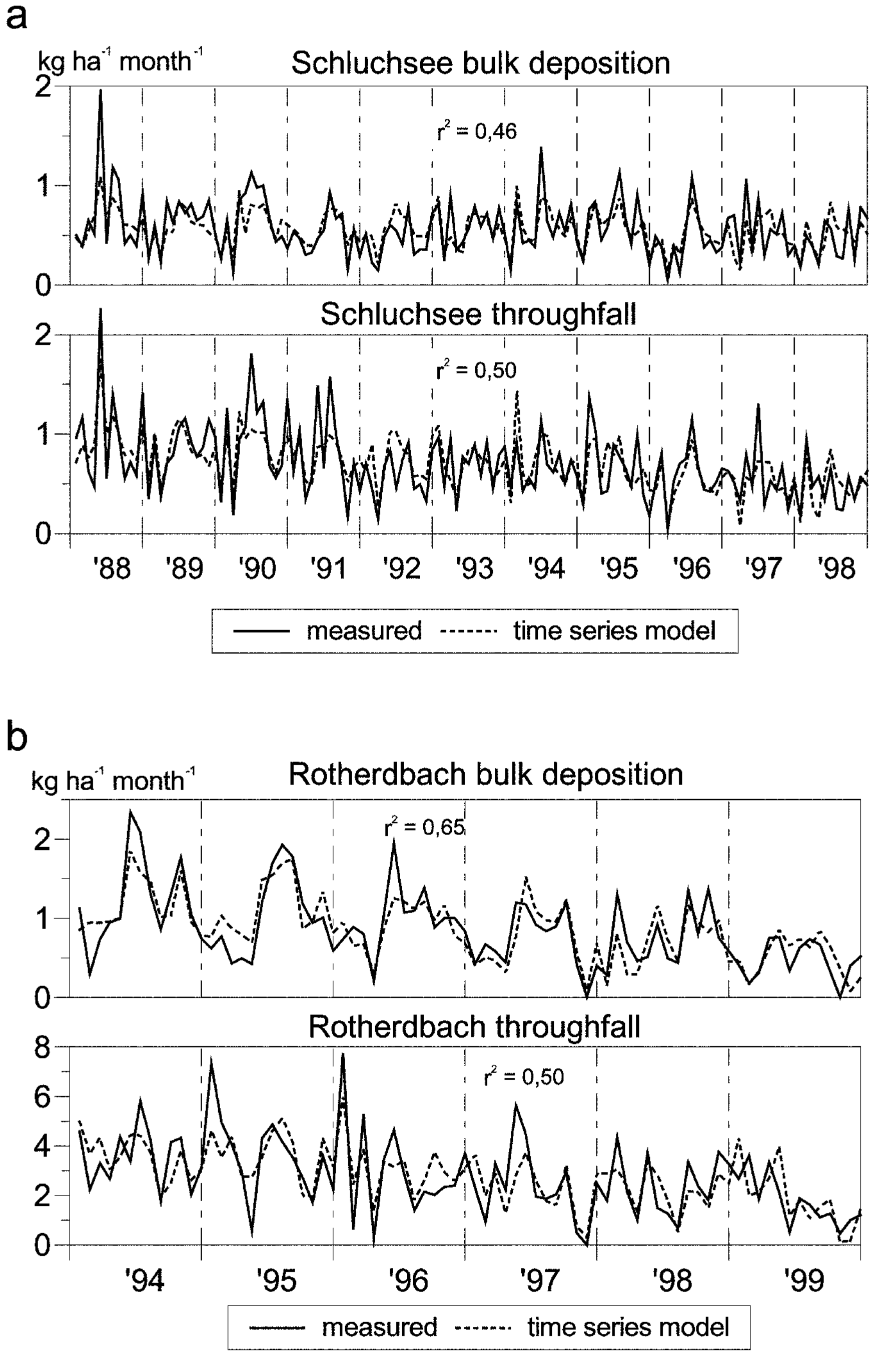

Figure 6. Comparison between measured and predicted (time series model) values of monthly S-deposition in the Schluchsee (a) and Rotherdbach (b) catchment.

Table 7. Trends in bulk deposition (BD) and throughfall (TF) of study sites. All numbers are annual trends in g ha^{-1} yr^{-1} (year numbers represent hydrological years).

	H^+			Ca^{2+}			Mg^{2+}			SO_4^{2-}-S			N_{tot} [a]		
	trend	p	r^2	trend	p	r^2	trend	p	r^2	trend	p	r^2	trend	p	r^2
	Schluchsee (1988–1998)														
BD		ns [b]	0.53	−82	**	0.29	−16	***	0.53	−88	*	0.46	−103	*	0.61
TF	−5	*	0.49	−132	**	0.37	−18	**	0.40	−281	***	0.50	−166	**	0.46
	Rotherdbach (1994–1999)														
BD	−37	**	0.19	−181	**	0.29		ns [b]	0.19	−983	**	0.65	−54	**	0.54
TF	−116	***	0.44	−455	*	0.32		ns [b]	0.38	−2621	**	0.50		ns [b]	0.30

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$

[a] $N_{tot} = NH_4^+$-N + NO_3^--N

[b] ns = not significant

all compartments. In contrast, Na^+ showed a significant increase in 30 cm seepage water whereas no trend was detected in other compartments. Potassium decreased in 30 cm seepage water whereas an increase in streamwater was noted. The sum of 'base cations' (ΣBC) decreased in all compartments. Similarly, concentrations of Al_{tot}, Mn_{tot} and sum of strong acid anions (ΣA) declined in all compartments. As a result of larger decreases of ΣA than ΣBC in soil leachates, ANC increased significantly. In contrast to soil solution, streamwater ANC was not significantly altered. The application of the time series model to subsoil leachates (80 cm) does not fit with the measured concentrations of some solutes (Na^+, K^+, NO_3^-). In these cases model r^2 (indicating the part of data variability explained by model) is very low and, as a consequence, probability of the time series model is lower than 0.05. In most cases model r^2 is higher in streamwater than in soil leachates.

The decreases in SO_4^{2-} concentrations were more pronounced at *Rotherdbach* as compared to *Schluchsee* (Table 9, Figure 8). Decreases in seepage water (55–68 μmol_c l^{-1} yr^{-1}) were somewhat higher than in streamwater (41 μmol_c l^{-1} yr^{-1}). The temporal trend for 'base cations' at *Rotherdbach* is significant only for Ca^{2+} concentrations in all compartments. Correspondingly, the sum of 'base cations' (ΣBC) is reduced. Only the seepage in 80 cm soil depth (characterized by the lowest Ca^{2+} decrease) failed to show a significant trend in ΣBC concentrations. Nitrate and Al_{tot} concentrations also declined significantly in all monitored compartments in the *Rotherdbach* catchment. ANC increased significantly in all compartments. Cases in which the prediction model does not yield a good fit with the measured values are more abundant at *Rotherdbach* than at *Schluchsee*.

Seasonal patterns and long-term trends in NO_3^- concentrations in streamwater clearly differed at the two study sites (Figure 9). At *Schluchsee*, which is characterized by a decreasing N deposition (Table 7), a slight increase in streamwater NO_3^- occurred (Figure 9a). At *Rotherdbach*, N deposition decreased only slightly in bulk deposition (Table 7) whereas a strong decrease in streamwater NO_3^- concentration

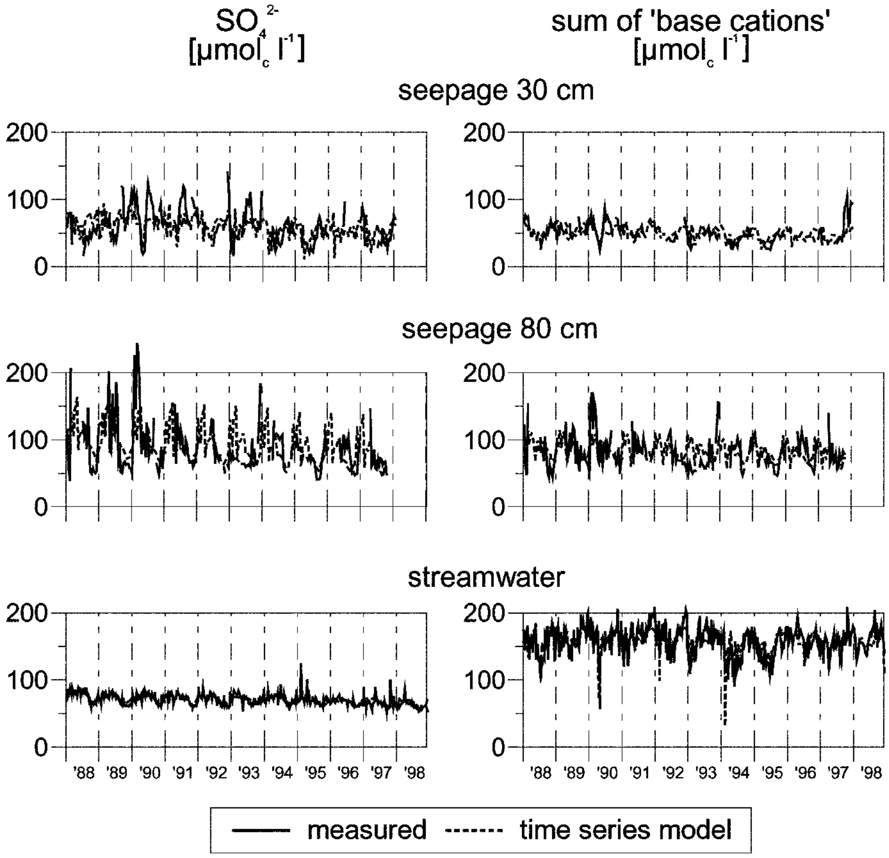

Figure 7. Comparison between measured and predicted (time series model) values of SO_4^{2-} and 'base cations' ($[Na^+] + [K^+] + [Ca^{2+}] + [Mg^{2+}]$) concentrations in soil leachates and streamwater (Schluchsee catchment).

was observed (Figure 9b). At *Rotherdbach* the seasonal variability of streamwater NO_3^- was less pronounced as compared to *Schluchsee.*

Discussion

In our study, we used a seasonal, multiple regression model (SMRM) for the determination of temporal trends. Compared with other statistical methods for time trend analysis of seasonally fluctuating water quality data (Seasonal Kendall test (SKT): Hirsch et al. 1982, Hirsch and Slack 1984) the SMRM requires attention with regard to normality, data quality and serial correlation. As an advantage, model predictions and measured data can be compared, and the statistical significance of the trend component and the percentage of variability explained by the model are

Table 8. Annual concentration trends in streamwater and in leachates from selected soil depths in the Schluchsee catchment.

		seepage water [d]						streamwater		
11/1987–10/1998		30 cm depth			80 cm depth					
		trend	p	r^2	Trend	p	r^2	trend	p	r^2
H^+	($\mu mol_c\ l^{-1}$)	+2.9	***	0.23	+0.7	***	0.16	−0.04	**	0.80
NH_4^+	($\mu mol_c\ l^{-1}$)		Ns	0.14		ns	0.14			[a]
Na^+	($\mu mol_c\ l^{-1}$)	+0.5	**	0.36			[a]		ns	0.70
K^+	($\mu mol_c\ l^{-1}$)	−0.6	***	0.10			[a]	+0.1	***	0.25
Ca^{2+}	($\mu mol_c\ l^{-1}$)	−1.0	***	0.50	−0.5	*	0.16	−1.0	***	0.25
Mg^{2+}	($\mu mol_c\ l^{-1}$)	−0.4	***	0.29	−0.9	***	0.48	−0.1	***	0.36
NO_3^-	($\mu mol_c\ l^{-1}$)	−1.4	***	0.33			[a]	+0.3	***	0.60
SO_4^{2-}	($\mu mol_c\ l^{-1}$)	−2.4	***	0.18	−2.7	***	0.29	−1.0	***	0.54
Cl^-	($\mu mol_c\ l^{-1}$)	+0.6	*	0.14		ns	0.25	+0.2	***	0.22
Al_{tot}	($\mu g\ l^{-1}$)	−25.1	***	0.30	−16.0	*	0.19	−3.6	***	0.81
Mn_{tot}	($\mu g\ l^{-1}$)	−1.6	***	0.45	−1.6	***	0.29	−0.5	***	0.76
Fe_{tot}	($\mu g\ l^{-1}$)		ns	0.32	−0.3	*	0.13	+0.2	***	0.24
DOC	($mg\ l^{-1}$)	+0.8	***	0.59	+0.3	***	0.39	+0.1	***	0.37
ANC	($\mu mol\ l^{-1}$)	+1.7	**	0.22	+2.4	***	0.33		ns	0.68
ΣBC [b]	($\mu mol_c\ l^{-1}$)	−1.6	***	0.27	−1.2	*	0.12	−0.7	***	0.51
ΣA [c]	($\mu mol_c\ l^{-1}$)	−2.2	***	0.19	−4.6	**	0.24	−0.3	*	0.65

*** $p < 0.001$; ** $p < 0.01$; * $p < 0.05$; ns not significant

[a] model not significant

[b] sum of 'base' cations ($[Na^+] + [K^+] + [Ca^{2+}] + [Mg^{2+}]$)

[c] sum of strong acid anions ($[Cl^-] + [NO_3^-] + [SO_4^{2-}]$)

[d] soil water only measured until October 1997

calculated. Furthermore, a flow adjustment of concentrations (fluxes), which might be necessary for SKT (Hirsch et al. 1982), is already included in the SMRM. As a consequence, SMRM should enable to detect trends related to water fluxes. However, SMRM like SKT is only able to detect monotonic trends within time series. Comparison of temporal trends determined with differing methods is not completely possible. As a consequence, trends for the *Schluchsee* site which were presented earlier by Alewell et al. (2001) differ somewhat from results presented in our study. In general, SMRM calculates significance for more elements than SKT.

Our results provide clear evidence for a significant decrease in recent S deposition at both sites. A net release of SO_4^{2-} is observed at both sites when comparing SO_4^{2-} input with output on average or yearly basis. This net release can be caused by four major processes (i) desorption of inorganic SO_4^{2-}, (ii) oxidation of reduced S species, (iii) excess mineralization of organically bound S (mineralization > immobilization and uptake) and (iv) weathering of S-containing minerals (Prechtel et al. 2001). However, the influence of the weathering of S-containing minerals and the oxidation of reduced S species is minimal at our two sites. It is quite clear that

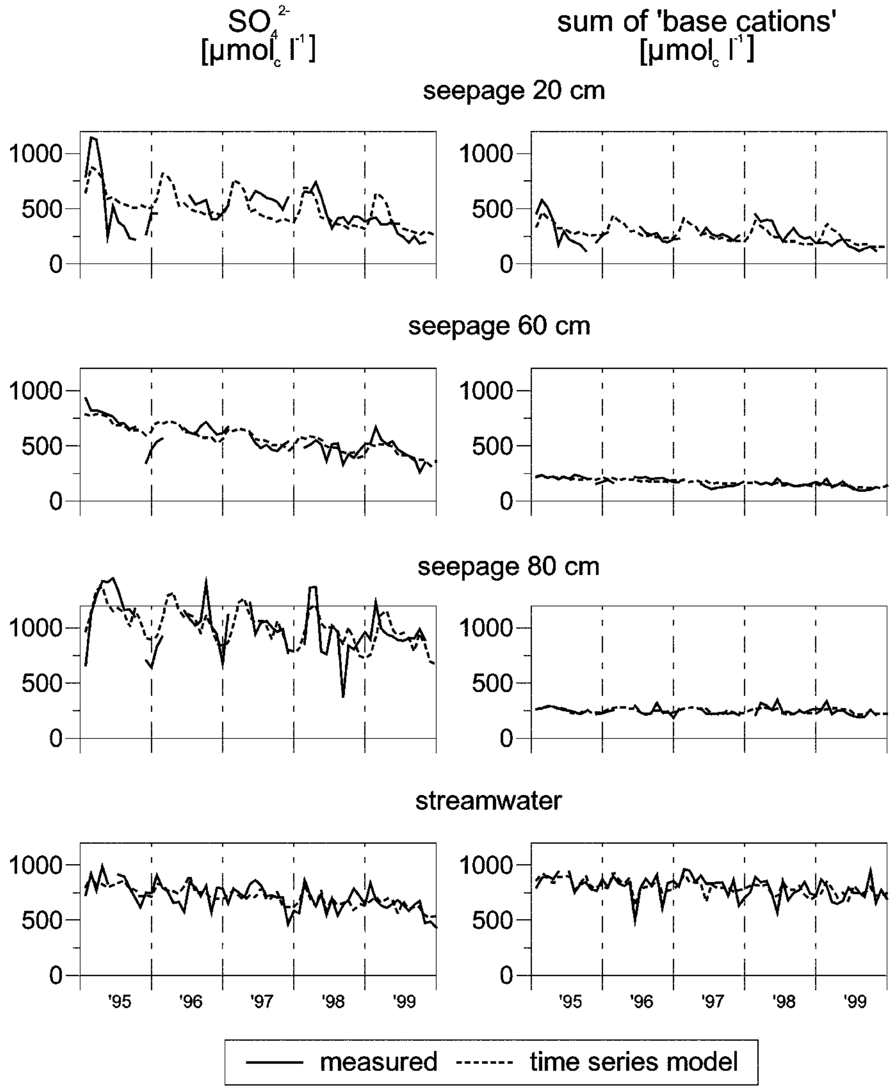

Figure 8. Comparison between measured and predicted (time series model) values of SO_4^{2-} and 'base cations' ($[Na^+] + [K^+] + [Ca^{2+}] + [Mg^{2+}]$) concentrations in soil leachates and streamwater (Rotherdbach catchment).

in waterlogged boggy soils, considerable amounts of reduced S species can be stored and potentially be released after the water table decreases and oxidation products are flushed during subsequent rainfalls. However, the percentage of such plots is very low at both sites. Excess mineralization of organic S must be considered at *Schluchsee*. At this site, the major part of the S pool in the soil is organically bound (90% of S pool, cf. Prietzel (1998)). In addition, stable isotope inves-

Table 9. Annual concentration trends in streamwater and in leachates from selected soil depths in the Rotherdbach catchment.

		seepage water									streamwater		
11/1994–10/1999		30 cm depth			60 cm depth			80 cm depth					
		trend	p	r^2	trend	p	r^2	trend	p	r^2	trend	p	r^2
H^+	($\mu mol_c\ l^{-1}$)			[a]			[a]			[a]			[a]
NH_4^+	($\mu mol_c\ l^{-1}$)			[a]			[a]			[a]			[a]
Na^+	($\mu mol_c\ l^{-1}$)	+5.5	***	0.40			[a]			[a]	−5.1	*	0.56
K^+	($\mu mol_c\ l^{-1}$)			[a]			[a]			[a]			[a]
Ca^{2+}	($\mu mol_c\ l^{-1}$)	−24.6	***	0.47	−11.6	***	0.72	−8.0	***	0.46	−24.7	***	0.38
Mg^{2+}	($\mu mol_c\ l^{-1}$)			[a]	−6.3	***	0.46			[a]	−4.9	*	0.12
NO_3^-	($\mu mol_c\ l^{-1}$)	−6.3	**	0.43	−3.9	*	0.27	−9.0	***	0.49	−17.4	***	0.73
SO_4^{2-}	($\mu mol_c\ l^{-1}$)	−59.6	***	0.30	−68.0	***	0.58	−55.1	**	0.28	−41.2	***	0.41
Cl^-	($\mu mol_c\ l^{-1}$)		ns	0.24			[a]			[a]	−9.2	**	0.77
Al_{tot}	($\mu g\ l^{-1}$)			[a]	−559	***	0.64	−667	***	0.34	−290	***	0.58
Mn_{tot}	($\mu g\ l^{-1}$)	−4.1	*	0.23			[a]		ns	0.42	−14.2	***	0.46
Fe_{tot}	($\mu g\ l^{-1}$)		ns	0.22			[a]			[a]		ns	0.19
DOC	($mg\ l^{-1}$)			[a]		ns	0.38	−0.9	***	0.52		ns	0.27
ANC	($\mu mol\ l^{-1}$)	+45.8	**	0.33	+57.0	***	0.52	+59.9	***	0.35	+44.5	***	0.61
ΣBC [b]	($\mu mol_c\ l^{-1}$)	−26.1	**	0.31	−18.4	***	0.45		ns	0.19	−23.2	**	0.29
ΣA [c]	($\mu mol_c\ l^{-1}$)	−67.6	**	0.38	−76.4	***	0.60	−62.5	**	0.34	−67.8	***	0.50

*** $p < 0.001$; ** $p < 0.01$; * $p < 0.05$; ns not significant

[a] model not significant

[b] sum of 'base' cations ($[Na^+] + [K^+] + [Ca^{2+}] + [Mg^{2+}]$)

[c] sum of strong acid anions ($[Cl^-] + [NO_3^-] + [SO_4^{2-}]$)

tigations at this site yielded clear evidence for the key role of organic S mineralization as an important source for streamwater SO_4^{2-} (Mayer et al. 1995). In contrast, at *Rotherdbach* about 60% of the S pool is inorganically bound (Prietzel pers. comm.). As a consequence, observed net releases of SO_4^{2-} at *Rotherdbach* should mainly be the result of a remobilization from previously stored inorganic S. At the moment however, it is not clear what process (e.g., desorption, dissolution of mineral phases ($Al(OH)SO_4$ type)) is behind that phenomenon. Furthermore, at both sites the decease in S deposition has resulted in distinct decreases of SO_4^{2-} concentrations in soil leachates and streamwater. Comparing the decrease in SO_4^{2-} concentrations in the deeper seepage (80 cm soil depth) with the decrease in streamwater a higher trend is observed in the soil seepage at both sites. In addition to the mineral soil, the weathered substrata appear also to contain considerable amounts of adsorbed SO_4^2 in both catchments. The importance of SO_4^{2-} stored in the weathering zone below the rooted soils with respect to the release of S to the streamwater and groundwater was outlined recently by Manderscheid et al. (2000). Besides the influence of decreased S input at Schluchsee an influence of the large organic S pool should be considered, too. It is quite possible that organic mineralization rates

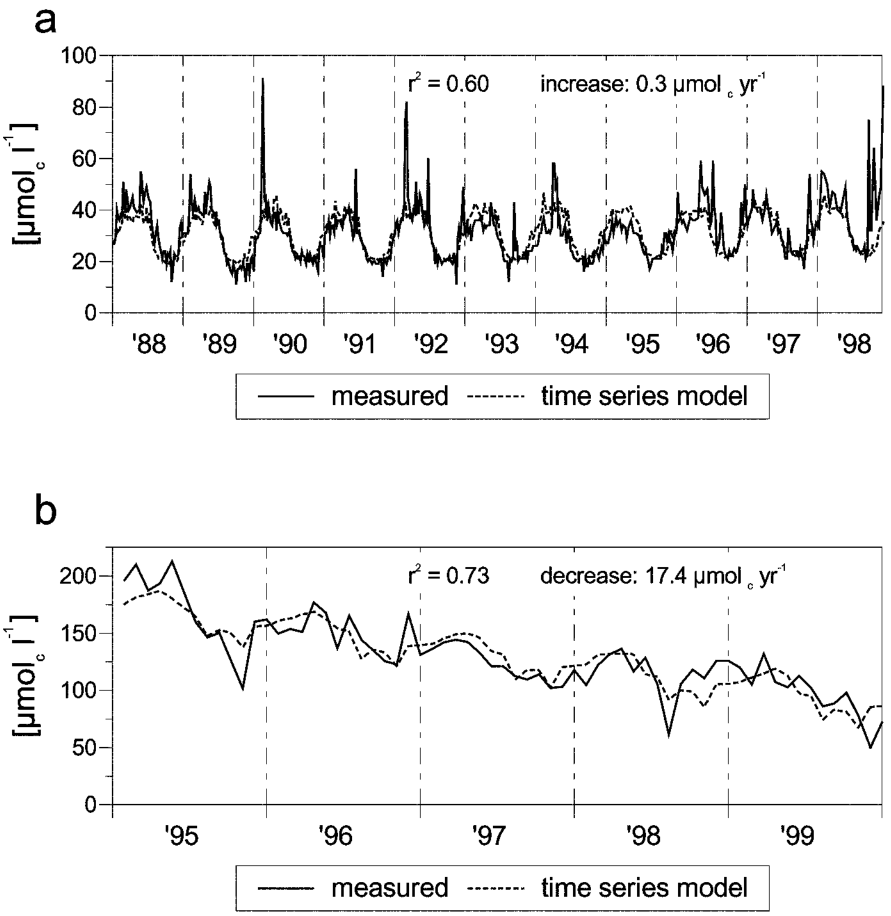

Figure 9. Temporal patterns of NO_3^- concentrations in streamwater. Comparison between measured and predicted (time series model) values (a) Schluchsee catchment; (b) Rotherdbach catchment.

are not constant during the whole investigation period. A temporal trend in factors supposed to control mineralization (*e.g.*, temperature, moisture) would also influence time trends, but the factors controlling S-mineralization are not yet clear.

N deposition at *Schluchsee* and *Rotherdbach* displayed a slightly decreasing trend with regional-scale trends in Europe (cf. Wright et al. 2001). Surprisingly, the *Schluchsee* site, where N deposition diminishes much stronger as compared to *Rotherdbach*, shows even a slight increase of NO_3^- concentrations in streamwater. However, this trend is not uniform because time series analysis of a shorter period (1988–1995) has resulted in a slightly decrease of NO_3^- (Armbruster 1998). According to time series data (Figure 9a), NO_3^- concentrations started to increase with the hydrological year 1997. This pattern may represent the complex result of a significant snow break event, which damaged a large number of trees during the winter season 1996/97 (cf. Fink et al. 1999). In contrast, at *Rotherdbach*, N deposition remained more or less constant. Nevertheless, a large decrease of streamwater NO_3^- concentrations was observed. This temporal pattern is not explained by changes in climate or management practices. An explanation could be that the effective reduction of acidic deposition and notably SO_2 concentrations in the ambient air at this formerly highly impacted site have resulted in an increased vitality of the forest ecosystem. This could have resulted in an improved capability for N retention. A long-term change in NO_3^- streamwater concentrations is also observed at the Lange Bramke catchment in the Harz Mountains (N Germany). After an increase up to the 1980s NO_3^- concentrations decreased again in the 1990s (Wright et al. 2001). On a regional scale an unexplained extensive decrease of NO_3^- in streamwater during the 1990s is reported for the Czech Republic (Veselý et al. 2002). Until now a clear explanation for such trends (which appear to be contradictory to the hypothesis of a gradual loss of N retention capacity) is lacking.

Compared to the relatively low N deposition (11 kg ha^{-1} yr^{-1}), the N output with streamwater at *Schluchsee* was surprisingly high (7 kg ha^{-1} yr^{-1}). This site should therefore be characterized as 'N saturated' or 'partly N saturated' depending on definition. According to the definition of Stoddard (1994), which uses changes in the seasonal and long-term pattern of surface water concentrations, *Schluchsee* would be in 'stage 2' (annual N cycle dominated by N loss). However, Feger (1993) ascribed the elevated NO_3^- losses with streamwater at *Schluchsee* mainly to microbial turnover of relic subsoil humus pools originating from the former deep-rooting beech-fir stand. In contrast to the present stand consisting of planted shallow-rooting Norway spruce, the natural beech-fir forests in the Black Forest are characterized by an abundance of fine roots in the mineral soil. As a consequence, N leaching from forests where mixed stands have formerly been converted into monocultural spruce is elevated due to an 'imbalance' between mineralization and uptake of N in the mineral soil (cf. Kreutzer 1994). This underlines that land-use history is an important issue in understanding the spatial patterns and time trends related to N cycling in forested ecosystems (cf. Tamm 1991). At *Rotherdbach*, NO_3^- concentrations in streamwater exceeded 50 μmol_c l^{-1} during the entire study period (cf. Table 5). Also a coherent seasonal pattern in NO_3^- concentrations was not evident. This situation corresponds to 'stage 3' of N saturation according to Stoddard (1994); (see also Stoddad and Traaen 1995). Nitrogen retention mechanisms (uptake by vegetation and microbes) are much reduced in this stage. With respect to the formerly high impact of SO_2 and the effective recovery of forest stands one may postulate that in future years this site may come back to 'stage 2'.

Temporal changes in the leaching of anions NO_3^- and SO_4^{2-} have strong effects on cation losses. As a consequence, concentrations of ΣBC and Al_{tot} in streamwater also decreased in our study. In addition, deposition of 'base cations' (mainly Ca) has decreased in parallel to SO_4^{2-} at both sites. This may counteract the reversibility of water acidification (cf. Meesenburg et al. 1995, Evans et al. 2001). However, concentrations of strong acid anions in seepage water decreased more than that of base cations. As a consequence, seepage water ANC increased significantly. Therefore, 'base cation' deposition decrease did not offset the decreases in S (N) deposition. In the stream in the *Schluchsee* catchment, there was no significant change in ANC. One reason for this could be the remobilization of SO_4^{2-} stored in the deeper weathered substrata. On the other hand, episodic acidification during high-flow conditions is primarily due to the mobilization of NO_3^- (Armbruster et al. 2000) showing a slight increase in streamwater. This is in contrast to *Rotherdbach* where streamwater ANC clearly increased. Also at this site a remobilization of SO_4^{2-} in the deeper weathering zone (potentially counteracting the recovery from acidification) can be postulated. Streamwater NO_3^- concentration distinctly decreased at *Rotherdbach* leading to the observed ANC increase.

Conclusions

Both sites demonstrated typical decreases in proton and S deposition which is consistent with European-scale trends. Differences in the absolute extent of such changes appear to reflect deposition history. At both sites, the observed reduction in deposition inputs resulted in a recovery of water from acidification. The key factor for the extent and temporal dimension of recovery is the type, amount and distribution of stored S pools in the ecosystem. Furthermore, our results indicate that site-specific conditions such as land-use history and hydrologic pathways are important contributing factors. This is especially true with regard to the N cycling pattern. Thus, the identification and prognosis of ″N saturation″ is still highly uncertain. Coupling with other approaches, time series analysis of long-term ecosystem data can be a valuable instrument in order to improve the understanding of ecosystems and give useful hints for modeling efforts.

Acknowledgements

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References

Aber J.D., Nadelhofer K.J., Steudler P. and Melillo J.M. 1989. Nitrogen saturation in northern forest ecosystems. BioScience 39: 378–386.

Abiy M. 1998. Standortskundliche und hydrochemische Untersuchungen in zwei Wassereinzugsgebieten des Osterzgebirges. PhD Thesis, Dresden University of Technology.

Abraham J., Cichanowicz-Kusztal R., Drüeke M., Jodlowska-Opyd G., Kallweit D., Keder J. et al. 2000. Common report on air quality in the black triangle region 1999.

Ågren G.I. and Bosatta E. 1988. Nitrogen saturation of terrestrial ecosystems. Environmental Pollution 54: 185–198.

Alewell C. 1995. Sulfat-Dynamik in sauren Waldböden – Sorptionsvermögen und Prognose bei nachlassenden Depositionen. Bayreuther Forum Ökologie, Vol. 19, 185 p.

Alewell C., Armbruster M., Bittersohl J., Evans C., Meesenburg H., Moritz K. et al. 2001. Are there signs of acidification reversal after two decades of reduced acid input in the low mountain ranges of Germany? Hydrol. and Earth Syst. Sci. 5: 367–378.

Alewell C., Manderscheid B., Bittersohl J. and Meesenburg H. 2000b. Is acidification still an ecological threat? Nature 407: 856–857.

Alewell C., Manderscheid B., Gerstberger P. and Matzner E. 2000a. Effects of reduced atmospheric deposition on soil solution chemistry and elemental contents of spruce needles in NE-Bavaria, Germany. J. Plant Nutr. Soil. Sci. 163: 509–516.

Armbruster M. 1998. Zeitliche Dynamik der Wasser/ – und Elementflüsse in Waldökosystemen. *Freiburger Bodenkundl. Abh* Vol. 38., 331 p.

Armbruster M., Köhler H. and Feger K.H. 2000. Chemical composition of first-order streams in the upper Black Forest – Variability related to runoff dynamics and soil liming (in German). Forstw. Cbl. 119: 249–262.

Brahmer G. 1990. Wasser- und Stoffbilanzen bewaldeter Einzugsgebiete im Schwarzwald unter besonderer Berücksichtigung naturräumlicher Ausstattung und atmogener Einträge. *Freiburger Bodenkundl. Abh* Vol. 25., 295 p.

Cummins T., Beier C., Blanck K., de Visser P.H.B., Farrell E.P., Rasmussen L. et al. 1995. The EXMAN project. Biogeochemical fluxes in plantation forests on acid soils. Water Air Soil Pollut. 85: 1653–1658.

Discroll C.T. 1984. A procedure for the fractionation of aqueous aluminum in dilute acidic waters. Int. J. Environ. Anal. Chem. 16: 267–283.

Evans C.D., Cullen J.M., Alewell C., Kopácek J., Marchetto A., Moldan F. et al. 2001. Recovery from acidification in European surface waters. Hydrol. and Earth Syst. Sci. 5: 283–297.

Feger K.H. 1993. Bedeutung von ökosysteminternen Umsätzen und Nutzungseingriffen für den Stoffhaushalt von Waldökosystemen. *Freiburger Bodenkundl. Abh* Vol. 31., 237 p.

Feger K.H. 1995. Solute fluxes and sulfur cycling in forested catchments in SW Germany as influenced by experimental $(NH_4)_2SO_4$ treatments. Water Air Soil Pollut. 79: 109–130.

Feger K.H. 1997. Biogeochemistry of Mg in forest ecosystems (Chapter 3). In: Hüttl R.F. and Schaaf W. (eds), Magnesium Deficiency in Forest Ecosystems. Nutrients in Ecosystems 1. Kluwer Academic Publishers, Dordrecht, pp. 67–99.

Fink S., Feger K.H., Gülpen M., Armbruster M. and Lorenz K. 1999. Magnesium-Mangelvergilbung an Fichte – Einfluss von frühsommerlicher Trockenheit und Dolomit-Kalkung. FZKA-BWPLUS-Berichtsreihe 25, http://bwplus.fzk.de/berichte/SBer/PEF197001SBer.pdf.

Flieger A. and Toutenburg H. 1995. SPSS Trends für Windows. Arbeitsbuch für Praktiker. Prentice Hall, München.

Hirsch R.M., Slack J.R. and Smith R.A. 1982. Techniques of trend analysis for monthly water quality data. Water Resour. Res. 18: 107–121.

Hirsch R.M. and Slack J.R. 1984. A non-parametric test for seasonal data with serial dependence. Water Resour. Res. 20: 727–732.

Hornung M., Roda F. and Langan S.J. 1990. A review of small catchment studies in western Europe producing hydrochemical budgets. CEC Air Pollution Report 28.

Kreutzer K. 1994. The influence of catchment management processes in forests on the recovery in fresh waters. In: Steinberg C.E.W. and Wright R.F. (eds), Acidification of Freshwater Ecosystems: Implications for the Future. Dahlem Workshop Reports. Environmental Sciences Research Report 14. Wiley and Sons, Chichester, pp. 325–344.

Langusch J. 1995. Untersuchungen zum Ionenhaushalt zweier Wassereinzugsgebiete in verschiedenen Höhenlagen des Osterzgebirges. PhD Thesis, Dresden University of Technology.

Likens G.E., Bormann F.H., Pierce R.S., Eaton J.S. and Johnson N.M. 1977. Biogeochemistry of a Forested Catchment. Springer, New York.

Manderscheid B., Schweisser T., Lischeid G., Alewell C. and Matzner E. 2000. Sulfate pools in the weathered bedrock of a forested catchment. Soil Sci. Soc. Am. J. 64: 1078–1082.

Marques C.M. 1999. Eintrag von luftgetragenen partikelgebundenen Spurenstoffen in Wälder durch die trockene Deposition. Wissenschaftlicher Verlag, Berlin.

Mayer B., Feger K.H., Giesemann A. and Jäger H.J. 1995. Interpretation of sulfur cycling in two catchments in the Black Forest (Germany) using stable sulfur and oxygen isotope data. Biogeochemistry 30: 31–58.

Meesenburg H., Meiwes K.J. and Rademacher P. 1995. Long term trends in atmospheric deposition and seepage output in northwest German forest ecosystems. Wat. Air and Soil Poll. 85: 611–616.

Mitscherlich G. 1981. Wald, Wachstum und Umwelt. Vol. 2. Waldklima und Wasserhaushalt, Sauerländer, Frankfurt.

Moldan F. and Wright R.F. 1998. Changes in runoff chemistry after five years of N addition to a forested catchment at Gardsjön, Sweden. Forest Ecol. and Management 101: 187–197.

Nebe W. 1964. Die chemische Zusammensetzung der wichtigsten Grundgesteine Sachsens als Grundlage für eine Beurteilung der Nährstoffverhältnisse in Waldböden. Jb. Staatl. Mus. Mineral. Geol. Dresden 10: 351–386.

Nebe W., Roloff A. and Vogel M. (eds) 1998. Untersuchungen von Waldökosystemen im Erzgebirge als Grundlage für einen ökologisch begründeten Waldumbau. Forstwiss. Beiträge Tharandt (Contributions to Forest Science) 4. Department of Forest Sciences, Technical University of Dresden, Tharandt.

Nilsson J. (ed.) 1986. Critical Loads for Nitrogen and Sulphur. NORD Miljørapport 11. Nordic Council of Ministers, Copenhagen, 232 p.

Prechtel A., Alewell C., Armbruster M., Bittersohl J., Cullen J., Evans C.D. et al. 2001. Response of sulphur fluxes in European freshwater to decreasing sulphate deposition. Hydrol. and Earth Syst. Sci. 5: 311–325.

Prietzel J. and Feger K.H. 1996. Dynamik von Aluminium und ökotoxischen Al-Bindungsformen in kleinen Fließgewässern nach Forstdüngung mit sulfatischen Magnesiumsalzen. Vom Wasser 87: 387–408.

Prietzel J. 1998. Untersuchungen zum S-Haushalt – Zusammenfassende Diskussion. In: Raspe S., Feger K.H. and Zöttl H.W. (eds), Ökoystemforschung im Schwarzwald. Auswirkungen von atmogenen Einträgen und Restabilisierungsmaßnahmen auf den Wasser- und Stoffhaushalt von Fichtenwäldern. Verbundprojekt ARINUS. Umweltforschung in Baden-Württemberg. ecomed Verlag, Landsberg, pp. 375–386.

Reuss J.O. and Johnson D.W. 1986. Acid deposition and the acidification of soils and waters. Ecological studies 59. Springer, New York.

Stoddard J.L., Jeffries D.S., Lükewille A., Clair T.A., Dillon P.J., Driscoll C.T. et al. 1999. Regional trends in aquatic recovery from acidification in North America and Europe. Nature 401: 575–578.

Stoddard J.L. and Traaen T.S. 1995. The stages o nitrogen saturation: classification of catchments included in ″ICP on Waters″. In: Hornung M., Sutton M.A. and Wilson R.B. (eds), Maping and modelling of critical loads for nitrogen – a workshop report. Proceedings of the Grange-over-Sands Workshop 24–26 Oct. 1994. Institute of Terrestrial Ecology, Edinburgh, UK, pp. 69–76.

Stoddard J.L. 1994. Long-term changes in watershed retention of nitrogen: its causes and aquatic consequences. In: Baker L.A. (ed.), Environmental Chemistry of Lakes and Reservoirs. Advances in Chemistry 237. American Chemical Society, Washington, pp. 223–284.

Swank T.S. and Crossley D.A. (eds) 1988. Forest Hydrology and Ecology at Coweeta. Ecological Studies 66. Springer, New York.

Tamm C.O. 1991. Nitrogen in terrestrial ecosystems. Questions of productivity, vegetational changes, and ecosystem stability. Ecological Studies 81. Springer, New York.

Tarrasón L. and Schaug J. (eds) 1999. Transboundary acid deposition in Europe. EMEP (Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air pollutants in Europe) summary report 1999. Norwegian Meteorological Institute Research Report 83.

Ulrich B. 1983. Interactions of forest canopies with atmospheric constituents: SO_2 alkali and earth alkali cations and chroride. In: Ulrich B. and Pankrath J. (eds), Effects of Air Pollutants in Forest Ecosystems. Reidel Publ. Co., Dordrecht, pp. 33–45.

Ulrich B. 1991. Rechenweg zur Schätzung der Flüsse in Waldökosystemen. Identifizierung der sie bedingenden Prozesse. In: Volker G. and Friedrich J. (eds), Beiträge zur Methodik der Waldökosystemforschung. Ber. d. For. Zentr. Walökosysteme (B) Vol. 24,, pp. 204–210.

van Miegroet H. 1994. The relative importance of sulfur and nitrogen compounds in the acidification of fresh water. In: Steinberg C.E.W. and Wright R.F. (eds), Acidification of Freshwater Ecosystems: Implications for the Future. Dahlem Workshop Reports. Environmental Sciences Research Report 14. Wiley and Sons, Chichester, pp. 33–49.

Veselý J., Majer V. and Norton S.A. 2002. Heterogenous response of central European streams to decreased acidic atmospheric deposition. Environmental Pollution 120: 275–281.

Wright R.F., Alewell C., Cullen J.M., Evans C.D., Marchetto A., Moldan F. et al. 2001. Trends in nitrogen deposition and leaching in acid-sensitive steams in Europe. Hydrol. and Earth Syst. Sci. 5: 299–310.

Wright R.F. and van Breemen 1995. The NITREX project: an introduction. Forest Ecol. Manage. 71: 1–6.