TEMPORAL TRENDS IN THE CHEMICAL COMPOSITION OF PRECIPITATION, SOIL SEEPAGE AND STREAMWATER IN TWO FORESTED CATCHMENTS IN THE BLACK FOREST AND THE EASTERN ORE MOUNTAINS (GERMANY)

Martin Armbruster, Karl-Heinz Feger

Outline of contents: This paper focuses on the temporal trends in the composition of precipitation, throughfall affected by atmospheric deposition-load and the consecutive modifactions in soil seepage and stream water chemistry of two forested catchments in Germany. The catchment *'Schluchsee'* (Black Forest; SW Germany) has been exposed to relatively low atmospheric inputs lasting until a few years ago whereas *Rotherdbach* (Ore Mountains; E Germany) received considerable amounts of acid deposition (mainly originating from SO_2 emissions). Both sites reveal decreases in S deposition and cojoined acidity during the 1990s which ensue also the general trends in Europe. In response to the decline in atmospheric, S deposition, soil solution and stream-water SO_4^{2-} concentrations decreased significantly in the investigation period 1988-1998. In this time, the level of N deposition was more or less constant at both sites. At *Schluchsee*, NO_3^- concentration in stream water remained more or less unchanged, whilst a decrease at *Rotherdbach* was observed. Remarkable recovery of alkalinity was found in seepage water as indicated by increasing acid neutralizing capacity (ANC). Stream-water ANC increased only in the permanently acidified *Rotherdbach*. A 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.

Key words: atmospheric deposition, forested catchments, Norway spruce, recovery of alkalinity, seepage chemistry, stream-water chemistry, time-series analyses

Martin Armbruster, Karl-Heinz Feger, Institute of Soil Science and Site Ecology, Faculty of Forestry, Geosciences and Water Resources, Dresden University of Technology, D-01735 Tharandt, Germany

1. Introduction

In recent years, anthropogenic emissions of SO_2 and mineral dust in Central Europe and subsequently deposition of cojoined (potential) acidity (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 and the heterogeneity in the source functions of industry, traffic, and agriculture. Generally, atmospheric 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, mostly 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 with respect to e.g. possible recovery of resilience in forest-ecosystem functions. However, the extent and rapidity of developments in forest-soil properties, related water chemistry ecosystems after the successful abatement of high rates of acidic deposition depends mainly on ecosystem internal and adequately complex element transformations. Sulphate (SO_4^{2-}) deposited in former times has been accumulated in the soils, both in inorganic and organic forms, and can be released within an unknown time period after successful abatement of S emissions. A regional analysis of data from the ICP-water programhas shown an increase in alkalinity (which was defined as recovery of alkalinity) in streams and lakes allover Europe (Stoddard et al., 1999). This is mainly true for Northern Europe where soils normally are very shallow. However, numerous sites in Central Europe (with more deeply developed soils) show a significant delay or even no reaction with respect to recovery of alkalinity and relaxation after the effects of water acidification (Alewell et al., 2000b; Evans et al., 2001). Generally, it can be stated that ecosystems with a low pool capacities react quickly on decreased S deposition by an increase in alkalinity. In contrast, relaxation 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 increased 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 attain 'saturation'. In many forests, considerable exports of organic matter (fuel wood coppicing, litter raking etc.) had induced at large a reduction in N availability (Tamm, 1991). Unfortunately, different definitions of 'N saturation' are used (Agren and Bosatta, 1989; Nilsson, 1986; Stoddard, 1994) leading to contrasting perceptions of the actual N status of the same ecosystem (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 induces an 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 (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 play a more important role in surface-water acidification of the future. A release of the strong acid anions SO_4^{2-} and NO_3^- is inevitably 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' depositionmay counteract the mitigation effects of reductions in S and N deposition.

Besides varying site conditions, the history of atmospheric deposition and related acid load are suggested as keys for a deeper understanding of forest ecosystems and their response.. The effect of changed deposition during a distinct time period was recently examined in various manipulation experiments where deposition was experimentally altered (Cummins et al., 1995; Feger, 1995; Wright and van Breemen, 1995). Effects of the changes with time are studied by comparing sites which ideally differ only in deposition climate. The present study emphasis the response in soil solution and streamwater chemistry to changes in deposition by example of long-term data attained from two catchments

2. Material and Methods
1.1 Site descriptions
Long-term data sets from two experimental catchments in Germany were analyzed. According to the objective of our study catchments are quite similar in bedrocks, soils, and vegetation covers, but differ significantly by atmospheric element-deposition rates (Table 1, Table 4). The catchment *Schluchsee* (47°49' N; 8°06' E) is located in the greater altitudes of the Black Forest (SW Germany, Fig. 1, Table 1). The whole catchment is covered

with managed stands of Norway spruce *(Picea abies)* of 55 years in average. The pristine mixed forest, dominated by beech *(Fagus sylvatica),* was replaced by monoculture spruce stands about 200 yrs ago (Feger, 1993). The climate is cool and humid (Table 1). Severe symptoms of forest decline, 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).
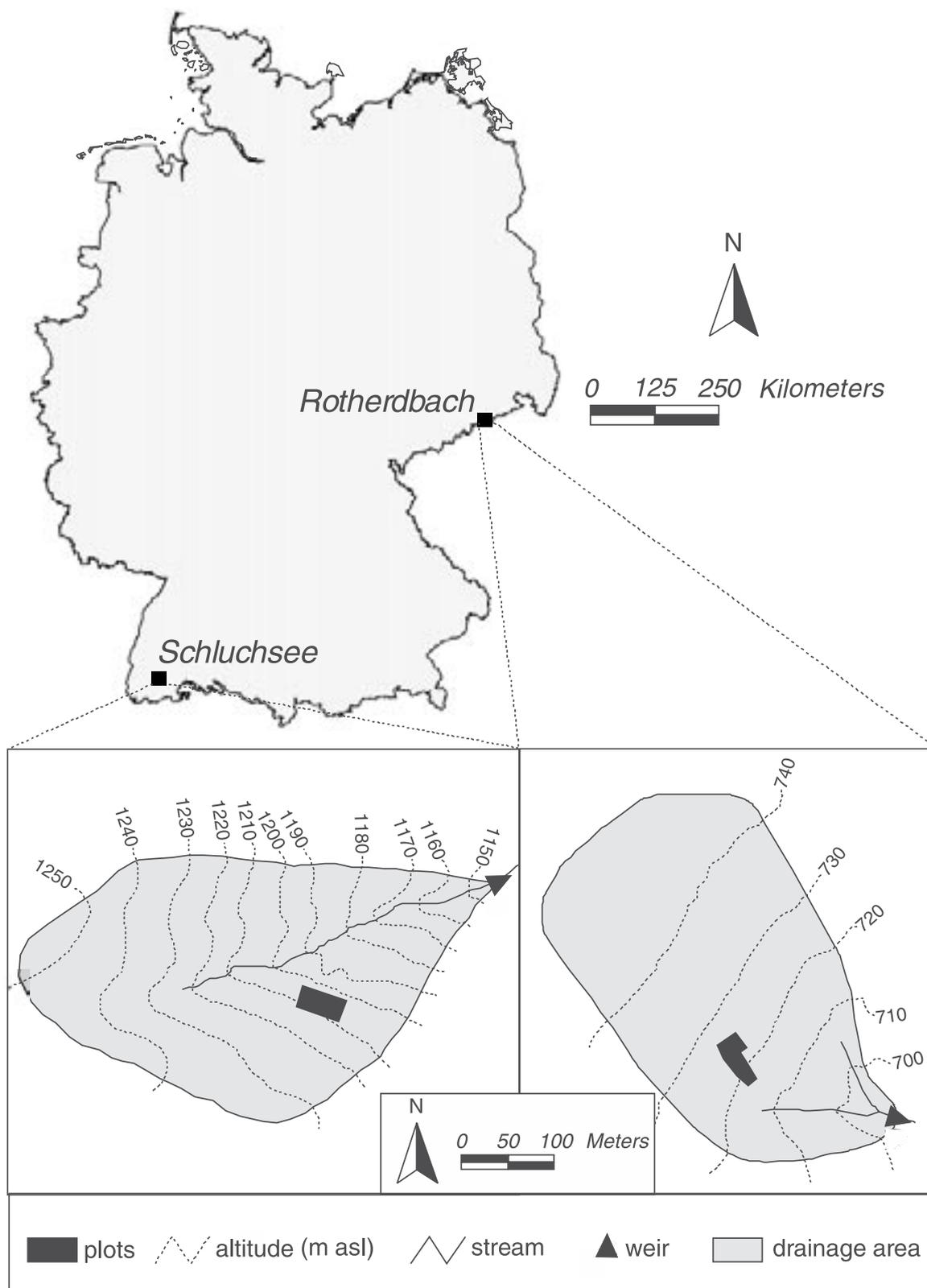

Figure 1. Location of the two catchments in Germany
Ryc.1. Lokalizacja dwu badanych zlewni w Niemczech

Table 1. Characteristics of the studied catchments
Tab.1. Charakterystyka badanych zlewni

	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 basin [ha]	10.98	9.43
Altitude [m asl]	1150 - 1253	675-750
Mean slope [%]	21.9	16.7
Exposition	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 (main tree species)	Norway spruce 55 yr (100%)	Norway spruce 90 yr (83%); Norway spruce 15 yr (17%)
Major soil type (FAO)	Haplic Podsol	Cambic Podsol
Bedrock	Granite	Rhyolithe

[a] Hydrological years; rok hydrologiczny
[b] Deposition 1994-1999; stream output 1995-1999; depozycja 1994-1999, odpływ ze strumieniem 1995-1999
[c] Period 1995-1999; okres 1995-1999

The catchment *Rotherdbach* (50°47' N; 13°43' E) is located in the eastern Ore Mountains (E Germany) close to the frontier of the Czech Republic. A 90 yr-old managed Norway spruce stand 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 especially by harvesting wood 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 die-back has been observed in a vast area of the eastern Ore Mountains. The damages resulted from air pollution mainly characterized by extremely high air concentrations of SO_2 from local combustion of S-rich brown coal which lasted until a few years ago. 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 damage symptoms have been decreasing considerably since 1990 (Abraham et al., 2000). The climate at *Rotherdbach* is also cold and humid but receives an annual precipitation of only 50% measured at *Schluchsee* (Table 1).

The both study catchments have similar extents (9.4 ha and 11 ha) and are drained by perennial first-order streams. The *Schluchsee* area is underlain by base-poor granite. SiO_2 and Al_2O_3 dominate by 90% in the bedrock composition. The soils (Haplic podzols) are habitually developed from loamy sands owing gravel contents up to 60% and are well drained and intensely acidic.

The bedrock of the *Rotherbach* catchment consists of rhyolite with a mineral composition similar to *Schluchsee*. However, there are minor differences in Ca and Mg contents as they are somehow greater at *Rotherdbach*. Soils at *Rotherdbach* developed from sandy loams and loams owing a stone fraction of up to 70% in the subsoil (Abiy, 1998). Hydraulic conductivity is lower compared to soils at *Schluchsee* and lateral flow paths prevail in soil drainage.

Even though soil formation factors are quite similar (as reflected by the podzol soil type), there are distinct differences in soil chemical properties attributed to recent air pollution impacts. Soils at *Schluchsee* are acidic and poor in base cations (Table 2). Base saturation is below 5% all over the entire soil profile. In comparison, base saturation at *Rotherdbach* ranges from a minimum of 3% in 25-50 cm soil depth to a maximum of 17% in the topsoil (Table 3). This contrasting pattern clearly reflects the influence of greater atmospheric deposition rates of base cations originating from min-

132

eral dusts (alkaline fly ash etc.). Effective cation exchange capacity (CEC_e) is greater as compared to *Schluchsee*. As a result of greater SO_2 emissions in the Ore Mountains, the contents of S_{tot} in the soil are distinctly increased at *Rotherdbach*. A detailed description of site properties is given by Armbruster (1998) for *Schluchsee* and by Abiy (1998) for *Rotherdbach,* respectively.

Table 2. Selected chemical soil properties of the Haplic Podsol (texture: loamy sand/sandy loam) in the Schluchsee catchment

Tab.2. Wybrane chemiczne właściwości gleby bielicowej właściwej (uziarnienie: piasek gliniasty / glina piaszczysta) w zlewni Schluchsee

Horizon Poziom	Depth Gębokość (cm)	pH (H₂0)	C	N	S_{total}	CEC_e [a]	BS [b]
			——— 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 NH₄Cl); efektywna pojemość wodna kationowa (0.5 M NH₄Cl)

[b] Base saturation; wysycenie zasadami

Table 3. Selected chemical properties of the Cambic Podsol (texture: sandy loam/loam) in the Rotherdbach catchment

Tab.3. Wybrane chamiczne właściwości gleby rdzawej bielicowej (uziarnienie: glina piaszczysta/glina) w zlewni Rotherdbach

Horizon Poziom	Depth Głebokość (cm)	pH (H₂0)	C	N	S_{total}	CEC_e [a]	BS [b]
			——— 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 NH₄Cl); efektywna pojemość wodna kationowa (0.5 M NH₄Cl)

[b] Base saturation; wysycenie zasadami

[c] nd = not detected; = nie oznaczano

2.2. Methods

2.2.1. Sample collection and analyses

The catchments were monitored for atmospheric deposition and water chemistry since 1987 *(Schluchsee)* and 1993 *(Rotherdbach)*. At both catchments, bulk precipitation and throughfall were sampled weekly and bulked for analyses of the monthly flux rates. From 1987 to 1990 precipitation samples were analyzed weekly for *Schluchsee*. Bulk precipitation was sampled from reference points in the open close to the catchments by open-top samplers replicated three times at *Rotherdbach* and five times at *Schluchsee*. Throughfall was collected at sample plots (aprox. 50 x 50 m) within the catchment by the same typ of samplers replicated eight times at *Rotherdbach* and ten times at *Schluchsee* (Fig. 1). Stemflow was not sampled because this hydrologic component in Norway spruce stands typically comprises 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 sampled from three depths (beneath the forest floor, at 30, and 80 cm in the mineral soil) at *Schluchsee,* and 6 depths (beneath the forest floor, at 10, 20, 40, 60, and 80 cm in the mineral soil) at *Rotherdbach* using tension plate lysimeters and cups, respectively. Discharge of the catchments was recorded permanently at V-notch weirs. Stream-water samples were taken weekly *(Schluchsee)* and monthly *(Rotherdbach)*.

Electrical conductivity and pH-value were determined in the laboratory directly after sample collection. Samples for chemical analysis were filtrated through 0.45 µm membrane filters. Mayor anions (Cl^-, NO_3^- and SO_4^{2-}) and cations (NH_4 Na, K, Ca, Mg, Al, Mn and Fe) of all water samples were analyzed. Analytical methods are described in detail by Feger (1993) for Schluchsee and by Langusch (1995) for Rotherdbach.

Acid neutralizing capacity (ANC) was calculated according to Reuss and Johnson (1986) and van Miegroet (1994) from the ionic charge balance:

$$ANC\ [\mu mol\ l^{-1}] = [Na^+] + [K^+] + 2[Ca^{2+}] + 2[Mg^{2+}] + [NH_4^+] - [Cl^-] - [NO_3^-] - 2[SO_4^{2-}]$$

2.2.2. Time series analyses

Typical systematic patterns in time series are seasonal fluctuations and blanketing trends. 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 time-series. In our study, a summation time series model was used to describe and analyse time series consisting of both deposition and aqueous 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, interdependences between deposition rates, related waterfluxes and the chemical speciation of water composition were included into the regression. Unfortunately, water flux data for seepage water were not available for *Rotherdbach*. Consequently, the model included only 'seasonal variation' and 'long-term trend' components for soil water at *Rotherdbach* but not for atmospheric deposition Monthly element inputs (g ha^{-1} month^{-1}) were taken for the analysis of deposition trends (bulk precipitation, throughfall). Time series analysis for soil leachates and streamwater were carried out for concentration data. The temporal resolution for the analysis in stream water 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).

$$x_t = s_t + q_t + t_t \qquad (1)$$

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

$$x(t) = s(t) + a \cdot q(t) + b \cdot t \qquad (2)$$

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

3. Results

3.1. Temporal development of element fluxes and concentrations

1.1.1. Deposition

Temporal trends in deposition indicate significant decreases in bulk deposition and throughfall for SO_4^{2-} at both sites during the 1990s (Table 5, Fig. 2). In Fig. 3, the results from time series analysis are presented for SO_4^{2-}. Calculated annual de-
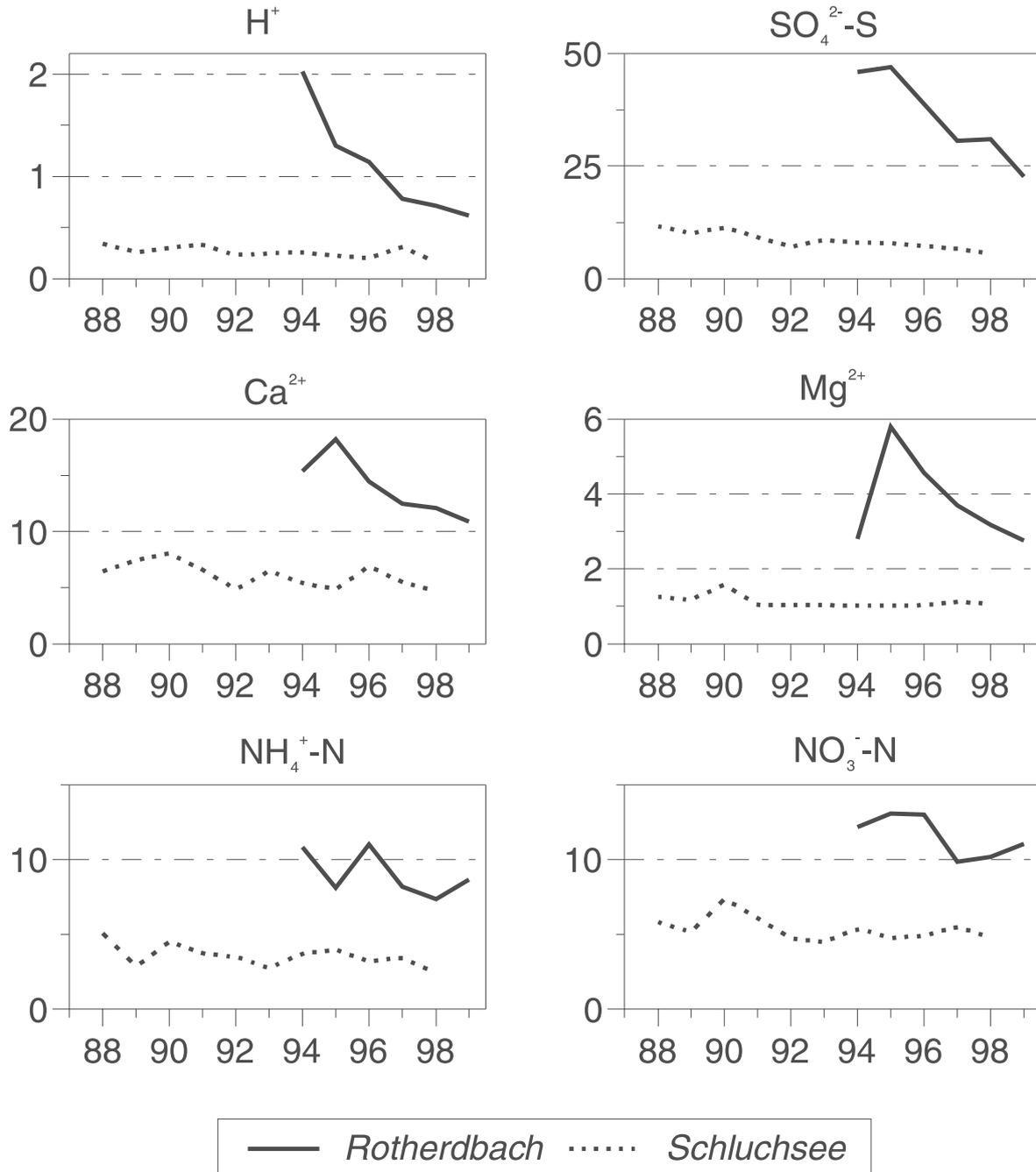

Figure 2. Annual throughfall deposition (kg ha⁻¹ yr⁻¹) of both catchments. X-axis units represent hydrological years
Ryc. 2. Roczny opad podkoronowy (kg ha⁻¹ rok⁻¹) w obu badanych zlewniach; osie x jednostek reprezentują lata hydrologiczne

135

a

kg ha^{-1} month^{-1}

Schluchsee bulk deposition

$r^2 = 0,46$

Schluchsee throughfall

$r^2 = 0,50$

'88 '89 '90 '91 '92 '93 '94 '95 '96 '97 '98

—— measured ······ time series model

b

kg ha^{-1} month^{-1}

Rotherdbach bulk deposition

$r^2 = 0,65$

Rotherdbach throughfall

$r^2 = 0,50$

'94 '95 '96 '97 '98 '99

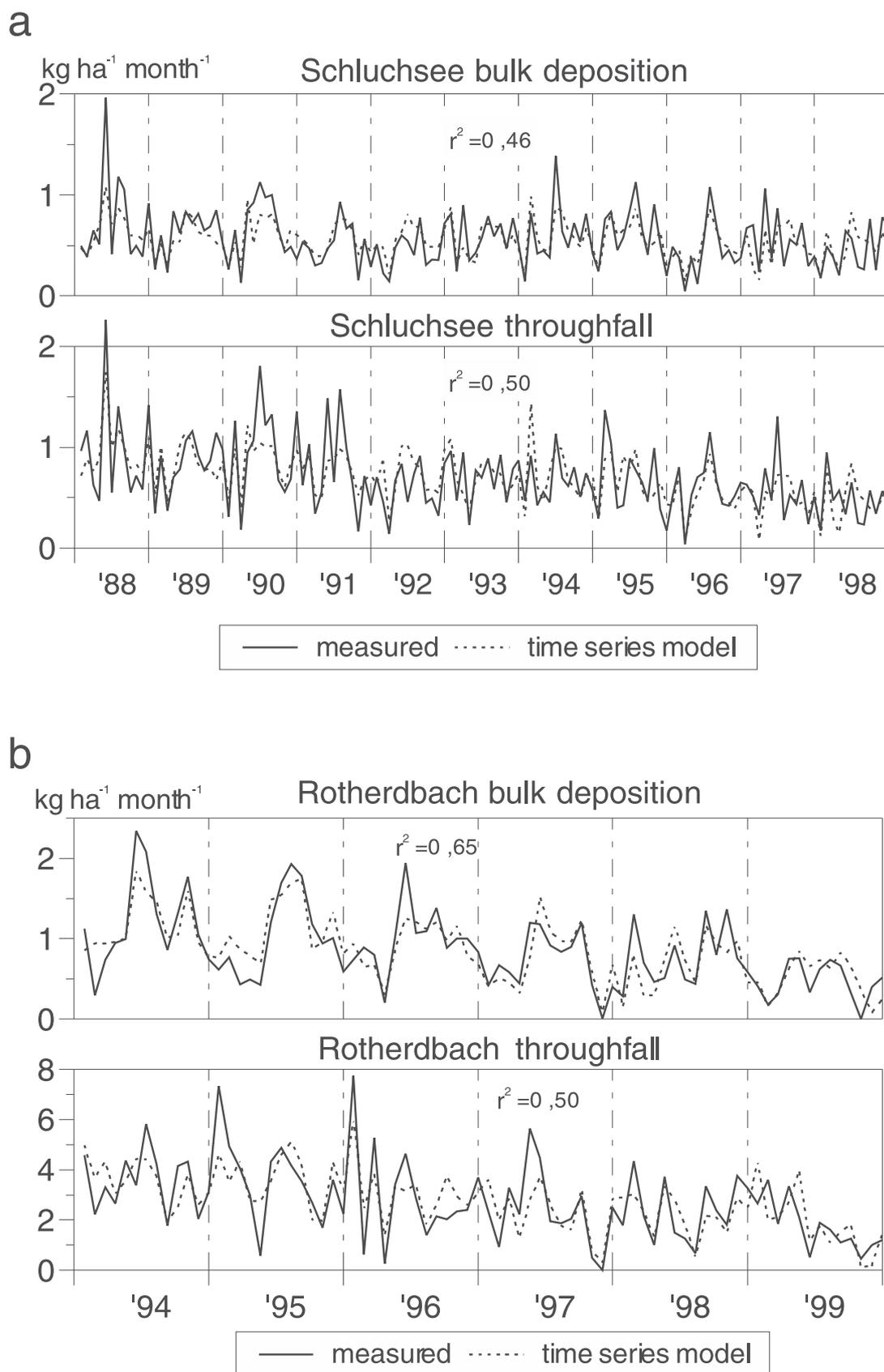—— measured ······ time series model

Figure 3. Comparison between measured and predicted (time series model) values of monthly S-deposition in the
Schluchsee (a) and Rotherdbach (b) catchment
Ryc.3. Porównanie pomierzonych i przewidywanych (model serii czasowych) wartości miesięcznego depozytu S
w zlewniach Schluchsee (a) i Rotherdbach (b)

136

creases in SO_4^{2-} were approximately 10 times higher at *Rotherdbach* than at *Schluchsee*. Measured S depositon in throughfall at *Rotherdbach* decreased from 46 kg ha^{-1} yr^{-1} in the hydrological year 1994 to 23 kg ha^{-1} yr^{-1} in 1999 (Fig. 2). In contrast, summing-up the estimated annual decrease provided by application of the time series model (2.6 kg ha^{-1} yr^{-1}; Table 5) in the total 6-years-period resulted in a decrease of 16 kg ha^{-1}. The absolute decline in S deposition was much lower at *Schluchsee* due to the also 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 (Fig. 2). The yearly decrease in S deposition calculated from the time series (0.28 kg ha^{-1} yr^{-1}; Table 5) 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 (Table 4). 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 5). 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.

Table 4. Mean values of water and element fluxes with bulk deposition (BD) throughfall (TF), total deposition (TDP, calculated by the canopy interaction models after Ulrich 1983 and 1991) and stream output (SO). All fluxes in L m^{-2} and kg ha^{-1} yr^{-1} respectively (investigation periods consist of hydrological years)

Tab.4. Średnie wartości przepływów wody i elementów w depozycji bezpośredniej (BD), opadzie podkoronowym (TF), depozycji całkowitej (TDP), obliczonej przy pomocy modelu interakcji koronowej wg Ulricha 1983 i 1989) oraz wymycia przez rzekę (SO); wszystkie przepływy w l m^{-2} i kg ha^{-1} yr^{-1} (okresy badań składają się z lat hydrologicznych)

Component Składnik	Schluchsee (1988-1998)				Roterdbach (1995-1999)			
	BD	TF	TDP	SO	BD	TF	TDP	SO
Water	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}); w Rotherdbach pomierzono w S_{calk} (SO_4^{2-}-S + S_{org})

	H⁺			Ca²⁺			Mg²⁺			SO₄²⁻-S			N$_{tot}$ [a]		
	Trend	p	r²	Trend	P	r²	Trend	p	r²	Trend	p	r²	Trend	p	r²
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$_{tot}$ = NH₄⁺-N + NO₃⁻-N
[b] ns = not significant; nie istotne

Table 6 presents the results from time series analysis using ion concentrations in seepage water and stream water in the *Schluchsee* catchment. In Fig. 4, results 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 stream water. The calculated decrease in SO_4^{2-} was lower in stream water (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 the concentrations of Ca^{2+} and Mg^{2+} decreased significantly in all compartments. Opposite to these elements, Na^+ showed a significant increase in 30 cm seepage water whilst 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 compared to ΣBC in soil leachates, ANC increased significantly. In contrast to soil solution, stream water 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 Na^+, K^+, NO_3^-. For these, r² (indicating the part of data variability explained by model) calculated by the model is very low and, as a consequence probability of the time series model, is lower than 0.05. In most cases model r² 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 7, Fig. 5). Decreases in seepage water (55-68 μmol_c L⁻¹ yr⁻¹) were somewhat higher than in streamwater (41 $\mu molc$ 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 (NO_3^-) and Al_{tot} concentrations also declined significantly in all monitored compartments in the *Rotherdbach* catchment. Acid neutralization capacity (ANC) increases 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 stream water clearly differed at the two study sites (Fig. 6). At *Schluchsee,* which is characterized by a decreasing N deposition (Table 5), a slight increase in stream-water NO_3^- concentrations occurred (Fig. 6 a). At *Rotherdbach,* N fluxes decreased only slightly in bulk deposition (Table 5) whereas a strong decrease in streamwater NO_3^- concentration was observed (Fig. 6 b). At *Rotherdbach* the seasonal variability of stream water NO_3^- concentration was less pronounced as compared to *Schluchsee.*
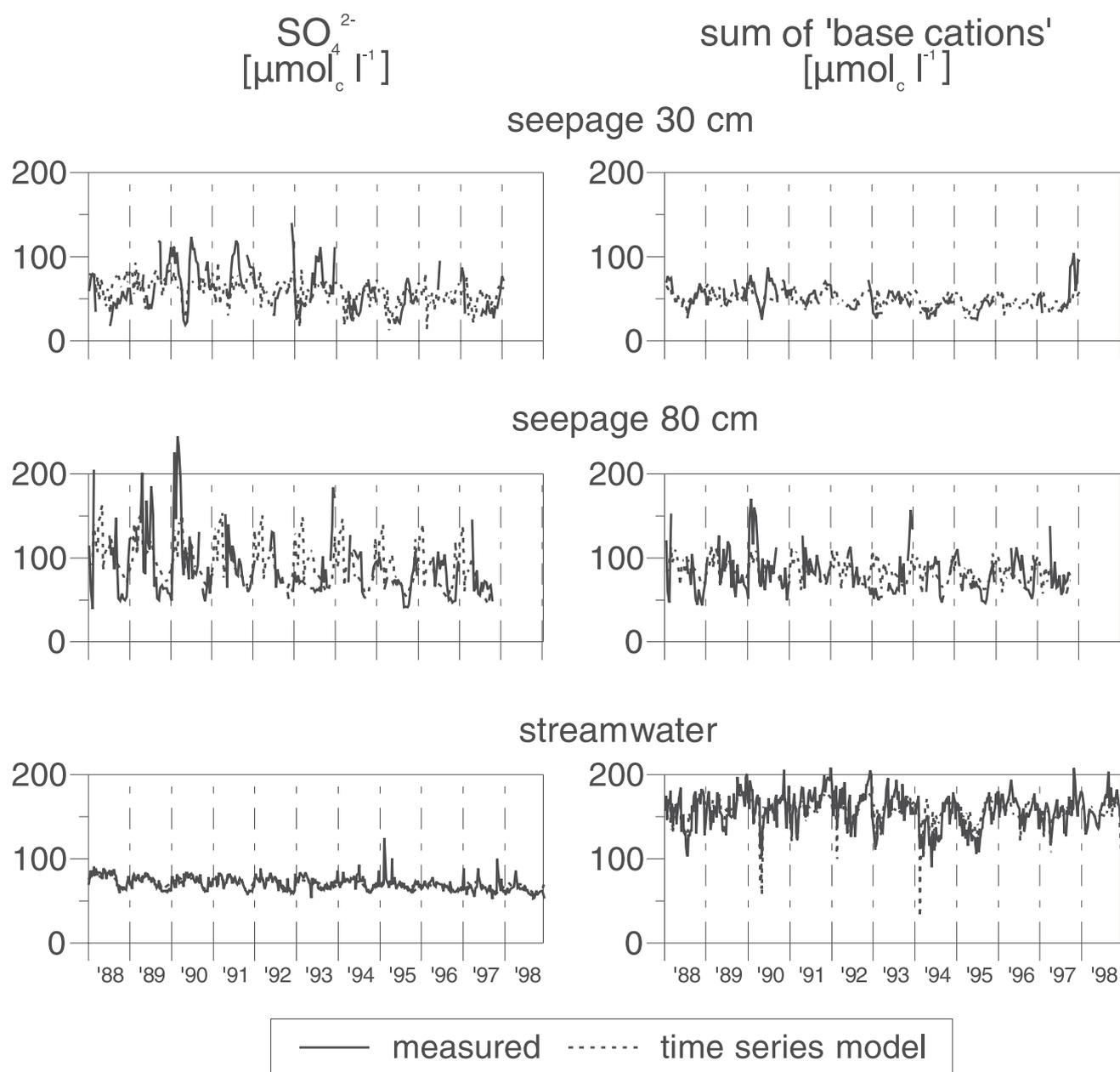
Figure 4. Comparison between measured and predicted (time series model) values of SO_4^{2-} and sum of 'base cations' ($[Na^+] + [K^+] + [Ca^{2+}] + [Mg^{2+}]$) concentrations in soil leachates and streamwater (Schluchsee catchment)

Ryc.4. Porównanie pomierzonych i przewidywanych (model serii czasowych) wartości stężeń SO_4^{2-} i sumy kationów zasadowych ($[Na^+] + [K^+] + [Ca^{2+}] + [Mg^{2+}]$) w roztworach glebowych i wodach strumienia (zlewnia Schluchsee)

Table 6. Annual concentration trends in streamwater and in leachates from two selected soil depths in the Schluchsee catchment during hydrological years of the 1987-1998 period

Tab.6. Trendy roczne stężeń w wodach strumienia i w roztworach glebowych na dwu wybranych głebokościach w zlewni Schluchsee w latach hydrologicznych 1987-1998

Component		Seepage water [d] Wody glebowe						Stream water Wody strumienia		
		30 cm depth			80 cm depth					
Składnik		Trend	P	r^2	Trend	p	r^2	Trend	p	r^2
H^+	(μmol_c L^{-1})	+2.9	***	0.23	+0.7	***	0.16	-0.04	**	0.80
NH_4^+	(μmol_c L^{-1})		Ns	0.14		ns	0.14			[a]
Na^+	(μmol_c L^{-1})	+0.5	**	0.36			[a]		ns	0.70
K^+	(μmol_c L^{-1})	-0.6	***	0.10			[a]	+0.1	***	0.25
Ca^{2+}	(μmol_c L^{-1})	-1.0	***	0.50	-0.5	*	0.16	-1.0	***	0.25
Mg^{2+}	(μmol_c L^{-1})	-0.4	***	0.29	-0.9	***	0.48	-0.1	***	0.36
NO_3^-	(μmol_c L^{-1})	-1.4	***	0.33			[a]	+0.3	***	0.60
SO_4^{2-}	(μmol_c L^{-1})	-2.4	***	0.18	-2.7	***	0.29	-1.0	***	0.54
Cl^-	(μmol_c L^{-1})	+0.6	*	0.14		ns	0.25	+0.2	***	0.22
Al_{tot}	(μg L^{-1})	-25.1	***	0.30	-16.0	*	0.19	-3.6	***	0.81
Mn_{tot}	(μg L^{-1})	-1.6	***	0.45	-1.6	***	0.29	-0.5	***	0.76
Fe_{tot}	(μg 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	(μmol L^{-1})	+1.7	**	0.22	+2.4	***	0.33		ns	0.68
ΣBC [b]	(μmol_c L^{-1})	-1.6	***	0.27	-1.2	*	0.12	-0.7	***	0.51
ΣA [c]	(μmol_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; ns nie istotne

[a] Model not significant; model nie istotny

[b] Sum of 'base' cations ($[Na^+] + [K^+] + [Ca^{2+}] + [Mg^{2+}]$); suma kationów zasadowych

[c] Sum of strong acid anions ($[Cl^-] + [NO_3^-] + [SO_4^{2-}]$); suma anionów silnych kwasów

[d] Concentrations in soil water only measured until October 1997; koncentracje w wodach glebowych mierzono tylko do października 1997
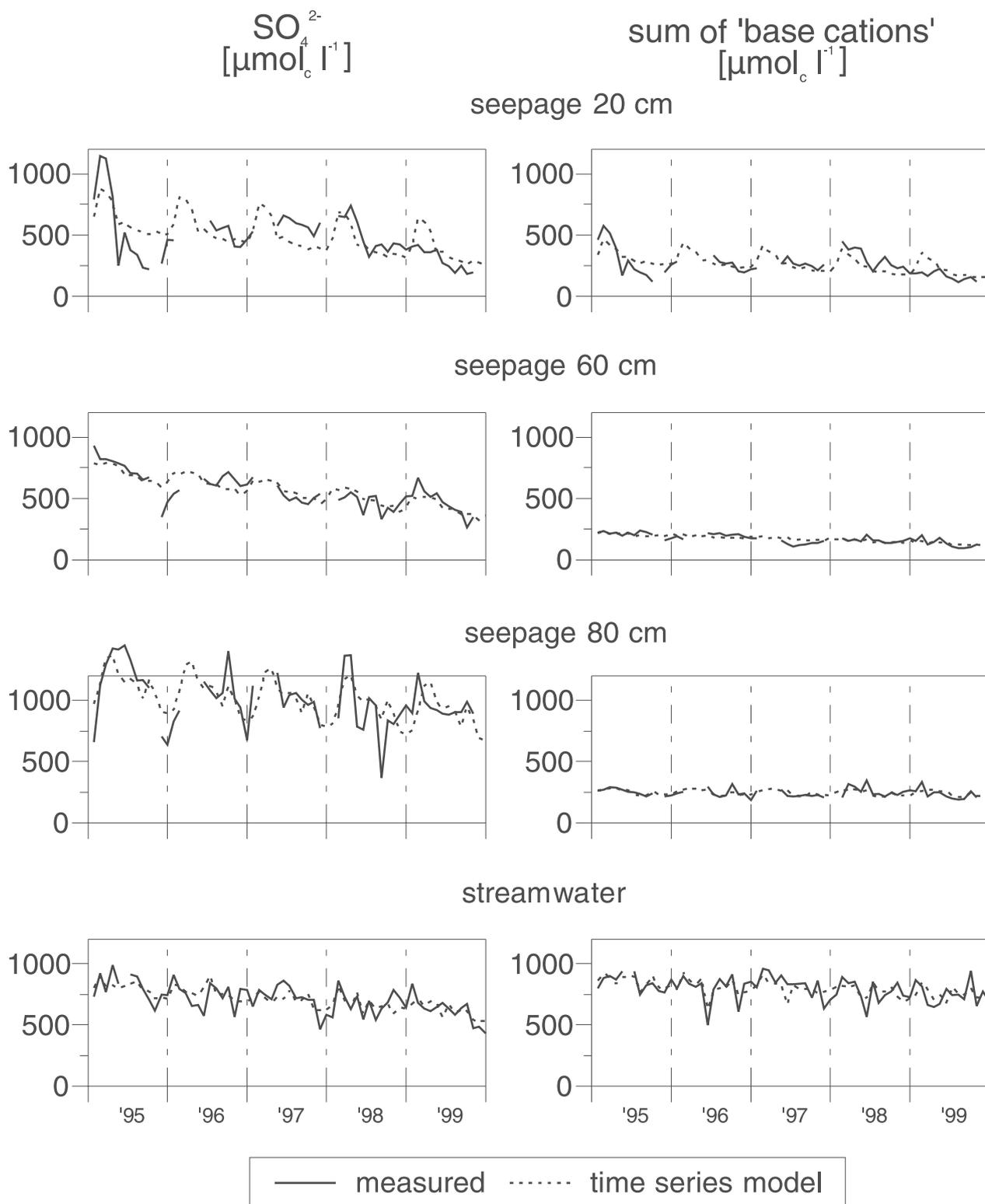
Figure 5. *Comparison between measured and predicted (time series model) values of SO₄²⁻ and sum of 'base cations' ([Na⁺] + [K⁺] + [Ca²⁺] + [Mg²⁺]) concentrations in soil leachates and streamwater (Rotherdbach catchment)*

Ryc.5. Porównanie pomierzonych i przewidywanych (model serii czasowych) wartości stężeń SO₄²⁻ i sumy kationów zasadowych ([Na⁺] + [K⁺] + [Ca²⁺] + [Mg²⁺]) w roztworach glebowych i wodach strumienia (zlewnia Rotherdbach)

141

Table 7. Annual concentration trends in streamwater and in leachates from three selected soil depths in the Rotherdbach catchment during hydrological years of the 1987-1999 period

Tab.7. Trendy rocznych stężeń w wodach strumienia i w roztworach glebowych na wybranych trzech głębokościach w zlewni Rotherdbach podczas lat hydrologicznych 1987-1999

| | | **Seepage water** Wody glebowe | | | | | | | | | **Stream water** Wody strumienia | | |
| | | **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; ns nie istotny

[a] Model not significant; model nie istotny

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

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

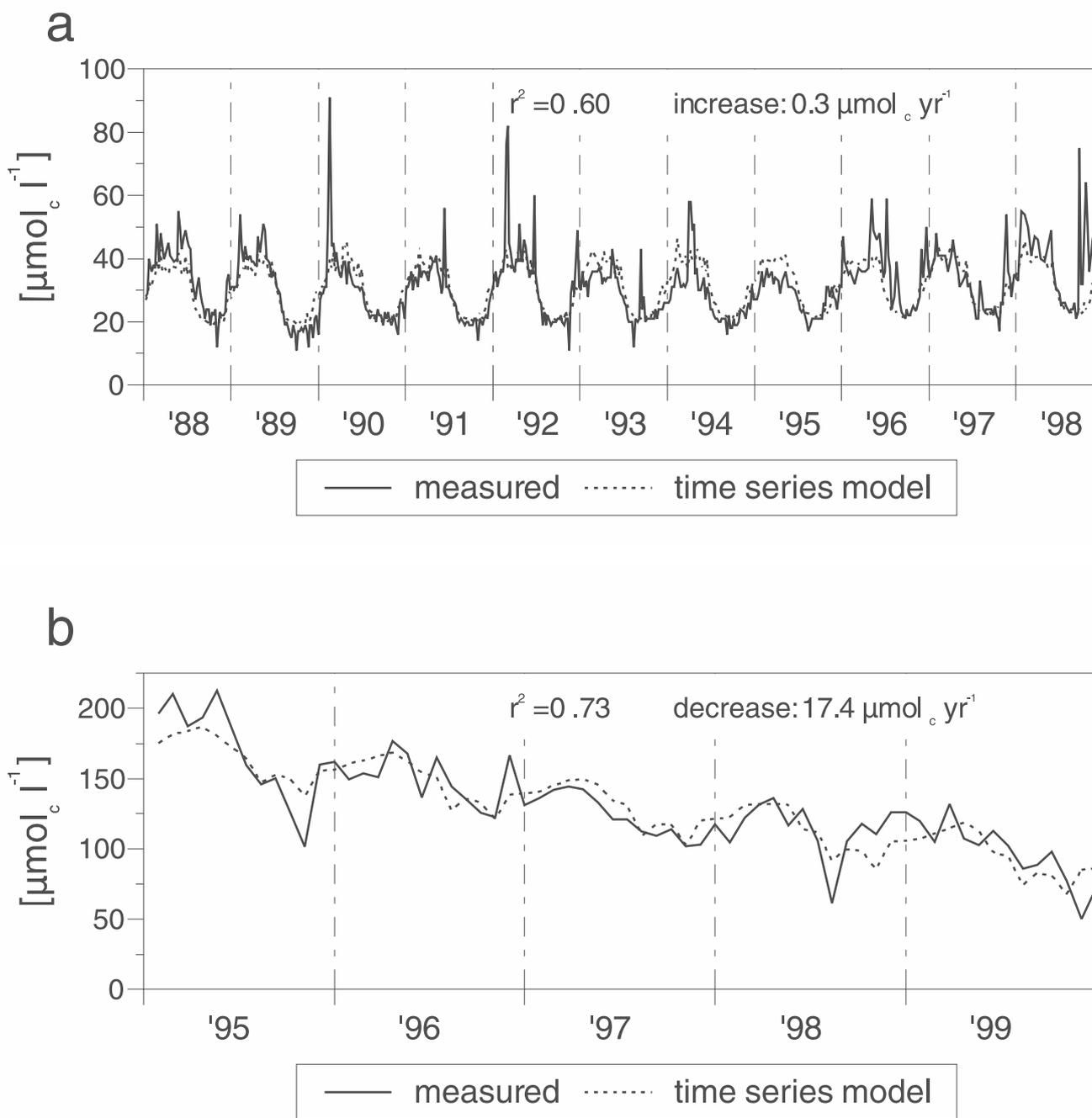*Figure 6. Temporal pattern of NO_3^- concentrations in stream water. Comparison between measured and predicted (time series model) values (a) Schluchsee catchment; (b) Rotherdbach catchment*

Ryc.6. Czasowe przebiegi stężeń NO_3^- w wodach strumieni ; porównanie pomierzonych i przewidywanych wartości (model serii czasowych) w zlewni (a) Schluchsee i (b) Rotherdbach

4. Discussion

In our study, we used a seasonal, multiple regression model (SMRM) for determination of temporal trends. In comparison with other statistical methods for analyses of time-trends analysis and seasonality in water quality data (Seasonal Kendall test (SKT): Hirsch et al., 1982; Hirsch and Slack, 1984) the SMRM requires special attention of normality, data quality and serial correlation. Especially supported by the specific properties of the model, the predictions can be compared and thus partly validated with measured data, The model calculates the statistical significance of the trend component and the degree of explained variability. 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 possible to completion. 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 clearly evidence for a significant decrease in recent S deposition at both sites. In addition, 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 (Table 4). This net release may be due to four major processes (i) desorption of inorganic SO_4^{2-}, (ii) oxidation of reduced S species, (iii) net-mineralization of organically bound S (mineralization > immobilization and uptake) and (iv) weathering of S-containing minerals (Prechtel et al., 2001). However, options of S-weathering from minerals and the oxidation of reduced S species are negligible for the two sites. It is obvious that 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. Net-mineralization of organic S are to be consid-

ered at *Schluchsee,* where the major portion of the soil-S pool is organically bound (78% of S pool, cf. Prietzel, 1998). In addition, stable isotope investigations at this site yielded clear evidence for the key role of organic S mineralization as an important source for SO_4^{2-} in stream-water (Mayer et al., 1995). In contrast, at *Rotherdbach* about 50% of the S pool consist of inorganic species (Prietzel pers. comm.). As a consequence, observed net releases of SO_4^{2-} at *Rotherdbach* are mainly the result of a remobilization from atmospherically deposited and accumulated inorganic S. However actually it is not clear which process (e.g. desorption, dissolution of mineral phases ($Al(OH)SO_4$ type)) are emergent in the phenomenon. Furthermore, at both sites the decease in S deposition has resulted in distinct decreases of SO_4^{2-} concentrations in soil leachates and stream water. 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 stream-waters and groundwater was outlined recently by Manderscheid et al. (2000). Thus, an influence of the large organic S pool has to be considered when assessing the influence of decreased S input at *Schluchsee.* It is most probable that organic mineralization rates are not constant during the whole investigation period and therefore time trends in the control of mineralization by e.g. temperature and soil moisture attain uncertain emergence in S-dynamics. which is yet not quite clear.

N atmospheric deposition at *Schluchsee* and *Rotherdbach* ensued a slightly decreasing trend which complied with regional-scale developments in Europe (Wright et al., 2001). Surprisingly, the *Schluchsee* site, where N deposition declines 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, NO_3^- concentrations begun only to increase in the hydrological year 1997 (Fig. 6a). These fea-

tures may be due to a significant snow break event, which damaged a large number of trees during the winter season 1996/97 (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 is not explained by changes in climate or management practices but effective reduction of acidic deposition and notably SO_2 concentrations in the ambient air at this formerly highly impacted site which have resulted in an increased vitality of the forest ecosystem. Thus, an improved capability for N retention is most probable. A long-term change in NO_3^- streamwater concentrations is also observed at the Lange Bramke catchment in the Harz Mountains (North Germany). After an increase up to the 1980s level, NO_3^- concentrations decreased again in the 1990s (Wright et al., 2001). On the regional scale an unexplained extensive decrease of NO_3^- in streamwater during the 1990s is reported for the Czech Republic (Vesleý et al., 2002). Until now substantial explanations for such trends (which appear to be in contradiction with recent hypotheses on a gradual loss of N retention capacity) are still missing.

Compared to relatively low mean N deposition rates (11 kg ha^{-1} yr^{-1}), the N output with streamwater at Schluchsee was unexpectedly high (7 kg ha^{-1} yr^{-1}; cf. Table 4). 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 the 'stage 2' (annual N cycle dominated by N loss). However, Feger (1993) ascribes 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 which consists of planted shallow-rooting Norway spruce, the pristine 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 is elevated due to an 'imbalance' between mineralization and uptake of N in the mineral soil, where mixed stands have formerly been converted into monocultural spruce (Kreutzer, 1994). This emphasizes that land-use history is an important issue in understanding the spatial patterns and time trends related to N cycling in forested ecosystems (Tamm, 1991). At *Rotherdbach*, NO_3^- concentrations in streamwater exceeded 50 μmol_c l^{-1} during the entire study period (cf. Figure 6b). 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 considerably reduced in this stage. With respect to the formerly high impact of SO_2 in ecosystem functions and the effective recovery observed in of forest-stands vitality, for the coming years a return to the 'stage 2' is imageable. Temporal changes in leaching of anions NO_3^- and SO_4^{2-} are inevitably associated with adequate effects in the cation composition of seepage. As a consequence of the observed trends in the dynamics of anions, concentrations of the sum of basic cation equivalents and and Al_{tot} in streamwater also decreased in our study. However, also depositions of 'base cations' (mainly Ca) have decreased simultaneously with the rates of SO_4^{2-} at both sites and probably counteract the reversibility of water acidification by missing alkalinity in the flux budget of the ecosystem (Meesenburg et al., 1995; Evans et al., 2001). It can be summarized, the concentrations of strong acid anions in seepage water decreased more than that of base cations; as a consequence, seepage water ANC increased significantly and therefore, 'base cation' deposition decrease did not offset the decreases in S (N) deposition. Opposite, in the stream in the Schluchsee catchment, there was no significant change in ANC due to remobilization of SO_4^{2-} from the pools accumulated 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 of mean concentrations in streamwater. This is in contrast to *Rotherdbach* where streamwater ANC significantly 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 this site leading to the observed ANC increase.

5. Conclusions

Both sites demonstrated typical decreases in S deposition and conjoined acidity which is generally consistent with the European-scale trend. Differences in the absolute extent of such changes at different sites appear to reflect specific features of atmospheric deposition history. At both sites, the observed reduction of the atmospheric deposition rates resulted in recovery of alkalinity in seepage and stream-waters which in the past declined due to atmospheric deposition load. Essential keys for understanding the changes and trends observed are the accumulation of soil-S by former atmospheric deposition, the amounts and speciation of the pools and its distribution 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 S cycling and the importance of interactions with N-transfers in production of acidity in the soil environment of forest ecosystems. 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.

6. Acknowledgements

7. References

Aber J.D., Nadelhofer K.J., Steudler P., 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.* Ph.D. thesis, Dresden University of Technology.

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

Agren G.I., 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 19, 185 p.

Alewell C., Armbruster M., Bittersohl J., Evans C., Meesenburg H., Moritz K., Prechtel A., 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(3): 367-378.

Alewell C., Manderscheid B., Gerstberger P., 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.

Alewell C., Manderscheid B., Bittersohl J., Meesenburg H.; 2000b: I*s acidification still an ecological threat?* Nature 407: 856-857.

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

Armbruster M., Köhler H., 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. 25, 295 p.

Cummins T., Beier C., Blanck K., de Visser P.H.B., Farrell E.P., Rasmussen L., Kreutzer K., Weis W., Bredemeier M., Lamersdorf N., 1995: *The EXMAN project. Biogeochemical fluxes in plantation forests on acid soils.* Water Air Soil Pollut. 85: 1653-1658.

Evans C.D., Cullen J.M., Alewell C., Kopácek J., Marchetto A., Moldan F., Prechtel A., Rogora M., Veselý J., Wright R., 2001: *Recovery from acidification in European surface waters.* Hydrol. and Earth Syst. Sci. 5(3): 283-297.

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

Feger K.H., 1995: *Solute fluxes and sulfur cycling in forested catchments in SW Germany as influenced by experimental (NH$_4$)$_2$SO$_4$ treatments.* Water Air Soil Pollut. 79: 109-130.

Feger K.H., 1997: *Biogeochemistry of Mg in forest ecosystems (Chapter 3).* - In: Hüttl RF and Schaaf W (Eds.): Magnesium deficiency in forest ecosystems. Nutrients in Ecosystems 1, Kluwer Academic Publishers – Dordrecht, 67-99.

Fink S., Feger K.H., Gülpen M., Armbruster M., 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., Toutenburg H., 1995: S*PSS Trends für Windows. Arbeitsbuch für Praktiker.* Prentice Hall - München.

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

Hornung M., Roda F., 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., Wright R.F. (eds.). Acidification of freshwater ecosystems: Implications for the future. Dahlem Workshop Reports. Environmental Sciences Research Report 14., Wiley and Sons – Chichester, 67-99.

Langusch J., 1995: *Untersuchungen zum Ionenhaushalt zweier Wassereinzugsgebiete in verschiedenen Höhenlagen des Osterzgebirges.* Ph.D. thesis. Dresden University of Technology.

Likens G.E., Bormann F.H., Pierce R.S., Eaton J.S., Johnson N.M., 1977: *Biogeochemistry of a forested catchment.* Springer - New York.

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

Mayer B., Feger K.H., Giesemann A., 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., 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.* Band 2: Waldklima und Wasserhaushalt. Sauerländer - Frankfurt.

Moldan F., 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., Roloff A., 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 Miljřrappord 11, Nordic Council of Ministers - Copenhagen.

Prechtel A., Alewell C., Armbruster M., Bittersohl J., Cullen J., Evans C.D., Helliwell R., Marchetto A., Matzner E., Meesenburg H., Moldan F., Moritz K., Vesely J., Wright R.F., 2001: *Response of sulphur fluxes in European freshwater to decreasing sulphate deposition.* Hydrol. and Earth Syst. Sci. 5(3): 311-325.

Prietzel J., 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., 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, 375-386.

Reuss J.O., 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., Forsius M., Johannessen M., Kahl J.S., Kellog J.H., Kemp A., Mannio J., Monteith D.T., Murdoch P.S., Patrick S., Rebsdorf A., Skjelkvale B.L., Stainton M.P., Traaen T., van Dam H., Webster K.E., Wieting J., Wilander A., 1999: *Regional trends in aquatic recovery from acidification in North America and Europe.* Nature 401: 575-578.

Stoddard J.L., Traaen T.S., 1995: *The stages o nitrogen saturation: classification of catchments included in "ICP on Waters".* In: Hornung M., Sutton M.A., 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 - Edingburg, UK, 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, 223-284.

Swank T.S., 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., 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., Pankrats J. (eds.). Effects of air pollutants in forest ecosystems, Reidel Publ. Co, - Dortrecht, 33-45.

Ulrich B., 1991: *Rechenweg zur Schätzung der Flüsse in Waldökosystemen. Identifizierung der sie bedingenden Prozesse.* In: Volker G., Friedrich J. (eds.). Beiträge zur Methodik der Waldökosystemforschung. Ber. d. For. Zentr. Walökosysteme (B) 24: 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., Wright R.F. (eds.). Acidification of freshwater ecosystems: Implications for the future. Dahlem Workshop Reports. Environmental Sciences Research Report 14, Wiley and Sons – Chichester, 33-49.

Veselý J., Majer V., Norton, S.A., 2002: *Heterogenous response of central European streams to decreased acidic atmospheric deposition.* Environmental Pollution 120(2): 275-281.

Wright R.F., Alewell C., Cullen J.M., Evans C.D., Marchetto A., Moldan F., Prechtel A., Rogora M., 2001: *Trends in nitrogen deposition and leaching in acid-sensitive streams in Europe.* Hydrol. and Earth Syst. Sci. 5(3): 299-310.

Wright R.F., van Breemen N., 1995: *The NITREX project: an introduction.* Forest Ecol. Manage. 71: 1-6.

CZASOWE TRENDY SKŁADU CHEMICZNEGO OPADÓW, ROZTWORÓW GLEBOWYCH I WÓD STRUMIENI W DWU ZALESIONYCH ZLEWNIACH W CZARNYM LESIE I WE WSCHODNICH RUDAWACH (NIEMCY)

Podsumowanie

Praca dotyczy czasowych trendów składu opadów i wód opadu podkoronowego zmienionych ładunkami depozycji atmosferycznej i związanych modyfikacji roztworów glebowych oraz chemii wód strumieni w dwu zalesionych zlewniach w Niemczech. Zlewnia Schluchsee (Czarny Las, SW - Niemcy) była wystawiona na relatywnie niskie atmosferyczne wejścia trwające od kilku lat, gdy zlewnia Rotherdbach (Góry Rudawy, E - Niemcy) otrzymywała znaczące ilości kwaśnej depozycji (głównie powodowanej przez emisje SO_2). W obu siedliskach nastąpiło zmniejszenie depozycji S i związanej kwasowości w ciągu lat 90-ych, co odpowiada ogólnemu trendowi w Europie. W następstwie malejącej depozycji atmosferycznej zmalały stężenia SO_4^{2-} w roztworach glebowych i w wodach strumieni w okresie badań 1988-1998. W tym okresie poziom depozycji N był bardziej lub mniej stały w obu siedliskach. W Schluchsee stężenia NO_3^- w wodach strumienia pozostawały mniej lub więcej niezmienione, gdy w zlewni Rotherdbach zaobserwowano ich zmniejszenie. Zauważalna odbudowa alkaliczności została stwierdzona w roztworach glebowych, co wykazał wskaźnik pojemności zobojętniania kwasów (ANC). ANC w wodach strumieni wzrastał tylko w trwale zakwaszonym Rotherdbach. Zmianę ANC zaobserwowano w strumieniu Schluchsee, który charakteryzował się epizodycznym zakwaszeniem podczas sytuacji wysokich przepływów. Analiza serii czasowej długookresowych danych chemizmu wejścia i wyjścia może być przydatnym instrumentem w porządkowaniu i doskonaleniu zrozumienia powiązanych systemów terestryczno-wodnych i dostarczyć pożyteczne klucze dla prób modelowania.