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Modelling sulphate stream concentrations in the Black Forest catchments Schluchsee and Villingen

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Abstract

The sulphate (SO_4) released by mineralisation and desorption from soil can play an important role in determining concentrations of SO_4 in streams. The MAGIC model was calibrated for two catchments in the Black Forest, Germany (Schluchsee and Villingen) and SO_4 concentrations in the streams for the years 2016 and 2030 were predicted. Special emphasis was placed on the dynamics of soil sulphur (S) pools. At Schluchsee, 90% of soil S is stored in the organic S (S_{org}) pool, whereas at Villingen, 54% is in the inorganic (S_{inorg}) pool. The Villingen stream chemistry was modelled successfully by measured Langmuir isotherm parameters (LIPs) for S_{inorg}. Schluchsee data could not be modelled satisfactorily using measured or freely adapted LIPs only, as the S_{inorg} pool would have to be more than five times larger than what was measured. With 60.5 $mmol_c$ SO_4 m^{-2} yr^{-1} as internal soil source by mineralisation and the measured LIPs, stream data was modelled successfully. The modelling shows that in these two catchments pre-industrial concentrations of SO_4 in runoff can be reached in the next two decades if S deposition decreases as intended under currently agreed national and international legislation. S_{org} is the most likely dominant source of SO_4 released at Schluchsee. Mineralization from the S_{org} pool must be included when modelling SO_4 concentrations in the stream. As the dynamics and the controlling factors of S release by mineralisation are not yet clear, this process remains a source of uncertainty for predictions of SO_4 concentrations in streams. Future research should concentrate on dynamics of S mineralisation in the field, such that mathematical descriptions of long-term S-mineralisation can be incorporated into biogeochemical models.

Keywords: sulphate release, organic S, mineralisation, acidification, recovery, modelling, MAGIC, catchments, predictions, Germany, forest

Introduction

Since the industrial revolution, deposition of anthropogenic sulphate (SO_4) has led to SO_4 accumulation in forest soils and acidification of surface waters (Reuss and Johnson, 1985). Sulphur (S) is stored in the soil as inorganic SO_4 by adsorption and/or cycled through the organic S (S_{org}) pool before being released to soil solution and stream water (Alewell, 2001). The importance of these processes depends on soil characteristics. In the upper horizons of many soils, S_{org} is the dominant S fraction, and can comprise 60 – 90 % of total S pool (David *et al.*, 1984; Mitchell *et al.*, 1986; Autry *et al.*, 1990; Fitzgerald and Autry, 1992; Erkenberg *et al.*, 1996; Prietzel *et al.*, 2001).

SO_4 release from the S_{org} and other soil S pools has become of increasing importance as the atmospheric S input has declined during the last two decades. A study of the response of S dynamics to decreasing S deposition in several European catchments showed a net release of SO_4 in most catchments since the late 1980s and the early 1990s (Prechtel *et al.*, 2001). As the SO_4 released is accompanied in part by base cations, net SO_4 loss from soil enhances soil acidification and in acid soils increases acidification of soil solution and surface water. Therefore, understanding the S dynamics in soil and evaluating the relevant S sources is crucial for predicting the reversibility of acidification.

It has been hypothesised that mineralisation of soil estersulphates (E-S) is regulated by a biological requirement for S whereas mineralisation of carbon-bound S (C-S) is more closely associated with concomitant mineralisation of C and N as energy source for soil microbes (McGill and Cole, 1981). Norman *et al.* (2002) described S mineralisation as a two-step reaction during which C-S is converted slowly

Table 1a. Site characteristics of catchments studied: area, climate, catchment discharge, bedrock, soil and vegetation.

	SCHLUCHSEE	VILLINGEN
Area (ha)	11	46.3
Altitude (m a.s.l.)	1150-1290	810-945
Temperature (C°)*	4.4	6.3
Precipitation (m yr^{-1})**	1.87	1.33
Annual discharge (m yr^{-1})**	1.40***	0.47***
Bedrock	Granite	triassic sandstone
major soil types (FAO)	Haplic Podzol	Dystric cambisols (70%) Dystric Planosol (30%)
Forest	Norway Spruce	Norway Spruce
Natural forest species composition	beech, fir, spruce	fir, spruce, pine

*annual mean air temperature
**annual mean
***hydrological years

to E-S followed by fast hydrolysis of E-S. The factors controlling mineralisation rates in the field, however, are are poorly known.

Alewell (2001) and Gbondo-Tugbawa *et al.* (2002) among others suggested that SO_4 released from mineralisation can play an important role in concentrations of SO_4 in streams. The discrepancy between measured and modelled SO_4 concentrations was reduced considerably when biotic processes such as plant uptake and mineralisation were included in the model (PnET-BGC) (Gbondo-Tugbawa *et al.*, 2002). They suggested that under conditions of decreasing S deposition, mineralisation in excess of immobilization and plant uptake becomes more important in controlling SO_4 losses than SO_4 desorption and that models which only describe abiotic processes will not be suitable for predicting long-term recovery of stream water from acidification. Most biogeochemical models for soil and water acidification consider inorganic SO_4 adsorption and desorption only. Thus, specific results from forecasts are highly dependent on the assumptions made concerning the S sources to and within the catchment (Gbondo-Tugbawa *et al.*, 2002).

S pools and SO_4 dynamics of the Black Forest, Germany, catchments Schluchsee and Villingen (Table 1a) have been analysed by Feger *et al.* (1990), Feger (1993a,b), Armbruster (1998) and Prietzel (1998a). These detailed data, the proximity of the catchments to each other (same deposition history), and their differences in soil S pools and S release make these catchments well-suited for this attempt to model the past and future concentrations of SO_4 in streamwater. At Schluchsee, 90% of total S is found in the organic fraction (S_{org}), whereas at Villingen only 54% is in this pool (Table 1b). The absolute amounts of S_{org}, however, are similar in both catchments. While at Schluchsee the SO_4 net loss (input minus output) was 50 mmol$_c$ SO_4 m^{-2} yr^{-1} (mean 1988–1996), the SO_4 budget at Villingen was almost balanced (1988-1995). Feger *et al.* (1990) suggested that mineralisation of the S_{org} pool is the most likely SO_4 source at Schluchsee. Furthermore, a comparison of soil S pools (forest floor and 0-80 cm) with the cumulative SO_4 net

Table 1b. Pools of total S (S_{tot}), organic S (S_{org}), inorganic S (S_{inorg}), carbon-bound S (C-S) and estersulphate-S (E-S) in the main soil types (O-horizon and 0–100 cm) of the studied catchments Schluchsee and Villingen (after Prietzel, 1998a) (pools were determined in samples from 1986). Measured values and percentages of total S.

mmol S m^{-2}	*Podzol*										
SCHLUCHSEE	*Depth [cm]*	*S_{tot}*		*S_{org}*		*S_{inorg}*		*C-S*		*E-S*	
O	5-0	372	12%	363	12%	9	0%	281	9%	84	3%
A	0-30	928	30%	872	29%	56	2%	506	17%	366	12%
B	30-80	1534	50%	1338	44%	197	6%	819	27%	519	17%
C	80-100	225	8%	175	5%	50	2%	19	1%	156	5%
	Sum	**3059**	**100%**	**2744**	**90%**	**316**	**10%**	**1625**	**53%**	**1125**	**37%**
mmol S m^{-2}	*Cambisol*										
VILLINGEN	*Depth [cm]*	*S_{tot}*		*S_{org}*		*S_{inorg}*		*C-S*		*E-S*	
O	6-0	422	9%	409	9%	13	0%	331	7%	75	2%
A, AB	0-20	975	20%	856	18%	119	3%	569	12%	288	6%
B, BC	20-70	2447	51%	859	18%	1584	33%	369	8%	491	10%
C	70-100	922	19%	438	9%	484	10%	166	3%	272	6%
	Sum	**4766**	**100%**	**2563**	**54%**	**2203**	**46%**	**1434**	**30%**	**1125**	**24%**

release (1988–1995) showed that the release at Schluchsee cannot be explained by losses from the inorganic SO_4 pool (Alewell, 2001). The catchment received 253 mmol_c S m^{-2} yr^{-1} and released 550 mmol_c S m^{-2} yr^{-1} with seepage water. With an inorganic S pool of 263 mmol_c S m^{-2} and a S_{org} pool of 2572 mmol_c S m^{-2}, the net release of 297 mmol_c S m^{-2} yr^{-1} most likely originates from the S_{org} pool.

The aims of this study were to (i) apply the model MAGIC to the two catchments Schluchsee and Villingen and predict concentrations of SO_4 in the streams in the years 2016 and 2030 and (ii) to evaluate the role of soil S pools for modelling SO_4 stream concentrations. The year 2016 was chosen as it is the year by which 'good surface water status' is to be achieved in the implementation of the Water Framework Directive (European Commission, 2000), and 2030 was chosen as a further forecast target year.

Methods

DESCRIPTION OF CATCHMENTS

The catchments, Schluchsee (47°49′ N, 8°06′ E) and Villingen (48°03′ N, 8°22′ E) are located in the higher altitudes of the Black Forest (Table 1a). Both catchments are completely forested and have not been affected by agricultural activities, fertilization or road salts. Research in the catchments started in 1988 (Feger, 1993a) and deposition and stream chemistry data has been collected from 1988 until 1995 and 1996 at Villingen and Schluchsee, respectively. A detailed description of the catchments is given in Feger *et al.* (1990), Feger (1993a), and Mayer *et al.* (1995).

The Schluchsee catchment is covered by well-drained Podzols of 60–100 cm depth. Prevailing soil types at Villingen are dystric Cambisols (70% of catchment area) and dystric Planosols (30% of catchment area) of about 70 cm depth (Feger, 1993a). S pools in the catchments differ greatly (Table 1b).

Elemental ratios in the organic matter of the soils also differ between the catchments (Table 1c). According to Prietzel (1998a), mineralisation of humus and adsorption of E-S explain the higher C_{org}/S_{org}-ratios in the Schluchsee Ahe- and Bsh-horizon, respectively, than in the organic layers. Due to this, four times more S_{org} is adsorbed to the soil than SO_4-S. In contrast at Villingen, all of the adsorbed S in the deeper mineral soil is SO_4-S. The small C_{org}/S_{org}-ratio in the Bv2 might be a result of the very low C_{org}- and S_{org}-contents. Removed S-rich organic matter from the organic layers is also stored in the upper mineral soil at Villingen.

Atmospheric SO_4 input of 56–59 mmol_c SO_4 m^{-2} yr^{-1} (mean 1988–1995/1996) to the catchments Schluchsee and Villingen is low to moderate as compared with other German and central European forested catchments (Prechtel *et al.*, 2001). The Black Forest catchments are relatively remote; long-range transport of air-pollutants is more important than emissions from local sources and the inputs are very similar to the levels measured in southern Scandinavia (Feger *et al.*, 1990).

Average SO_4 concentrations in streamwater (1988-1995/1996) were 75 (Schluchsee) and 115 (Villingen) μmol_c SO_4 l^{-1}; these levels are similar to those of the Norwegian streams Birkenes, Langtjern and Storgama (same time period) and are much lower than in streams of other low mountain ranges in Germany, e.g.: Lehstenbach (341 μmol_c SO_4 l^{-1}) and Lange Bramke (252 μmol_c SO_4 l^{-1}) (same time period) (Prechtel *et al.*, 2001).

Model set-up

MODEL DESCRIPTION

The MAGIC (version 7) model is a simplified process-oriented model for forecasting effects of acidic deposition on water quality and is described in detail by Cosby *et al.* (1986, 2001). Many applications of MAGIC aim to forecast

Table 1c. C/N- and C_{org}/S_{org}-ratios in the main soil types (O-horizon and 0-45/80 cm) of the studied catchments Schluchsee and Villingen (after Prietzel, 1998a) (pools were determined in samples from 1986).

SCHLUCHSEE *Horizon*	*Podzol* *Depth [cm]*	*C/N*	*C_{org}/S_{org}*	VILLINGEN *horizon*	*Cambisol* *depth [cm]*	*C/N*	*C_{org}/S_{org}*
Of		30	277	Of		37	286
Oh		27	190	Oh		40	247
Ahe	0-30	20	159	Ah	0-12	17	163
Bsh	30-40	19	167	Ah-Bv	12-20	13	162
Bs	40-60	27	242	Bv1	20-28	11	175
Bvs	60-80	23	247	Bv2	28-45	9	104

timescales of reversibility of acidification of lakes and streams. As a lumped-parameter model it is assumed that a set of 'average' physical and chemical parameters can be found to describe effectively the response of a whole catchment (Cosby *et al.*, 1986). Major soil processes in MAGIC are cation exchange, weathering, plant uptake and SO_4 sorption which is described by a Langmuir isotherm. The Langmuir isotherm parameters (LIPs) E_{max} (maximum SO_4 adsorption capacity, in $mmol_c\ kg^{-1}$) and C (half saturation constant, in $mmol_c\ m^{-3}$) are MAGIC input parameters which have to be set for calibrating the model to the observed stream SO_4 data. Further, the model requires a number of fixed parameters to describe the stream and soil physically and chemically.

ROUTING PARAMETERS – SOIL BOXES

The model represents the catchment soil as a homogeneous unit that can be described in 'soil boxes' of which one (Schluchsee: Podzol) or two (Villingen: Cambisol and Planosol) can be defined. Soil boxes can be arranged horizontally (as soil layers) or vertically (as soil types); for the latter version the percentage of covered area or rather of flow fractions through the soils must be set (used at Villingen; see Table 1). Parameters for these soil boxes include bulk density, CEC (cation exchange capacity), dissolved organic carbon (DOC) and the LIPs and were weighted over soil depth (Table 2a). The LIPs chosen for the different calibrations are shown later (see Calibration).

DEPOSITION AND STREAM DATA

The last year of the data set was used as reference year for calibration, which was 1995 and 1996 at Villingen and Schluchsee, respectively (Armbruster, 1998). Data for deposition and stream chemistry for these years are given in Tables 2b and 2c. Deposition of Na^+, NO_3^-, NH_4^+ and SO_4^{2-} was set equal to measured throughfall in the catchments. Ca^{2+}-, Mg^{2+}-, K^+- and Cl^--bulk deposition was multiplied by the $Na_{throughfall}$ to $Na_{bulk\ deposition}$ ratio to calculate total deposition (Prechtel *et al.,* 2001).

For the hindcast, SO_4 deposition was estimated from S emissions data in Europe (Mylona, 1996) combined with currently calculated data for the period since 1960 (Schöpp *et al.*, 2003). As both catchments are situated in the same EMEP grid square the hindcast deposition scenario was the same for Schluchsee and Villingen.

Table 2a. MAGIC input: Soil characteristics of the catchments (soil depth, bulk density, cation exchange capacity (CEC), base saturation and DOC).

	SCHLUCHSEE*	VILLINGEN** soil box 1#	soil box 2##
Soil depth (m)	0.8	0.7	0.7
Bulk density (kg m^{-3})	1083	1335	1661
CEC (meq kg^{-1})	55.8	60.2	23.3
Base saturation (% of CEC)	3	3.3	4.6
DOC (mmol m^{-3})	55.3	32.8	32.8

*profile weighted over 80 cm (A- and B-horizons)
**profile weighted over 70 cm (A- and B-horizons)
[#] Cambisol
[##] Planosol

Table 2b. MAGIC input: Deposition chemistry in reference year.

Deposition Concentration	SCHLUCHSEE* $\mu mol_c\ l^{-1}$	VILLINGEN** $\mu mol_c\ l^{-1}$
Ca	9.8	10.8
Mg	2.8	3.5
Na	10.2	8.8
K	4.4	5.4
NH_4	15.2	11.5
SO_4	29.8	22.5
Cl	16.8	14.6
NO_3	23.3	15.5

* 1996
**1995

Table 2c. MAGIC target values: Stream chemistry in reference year.

Stream Concentration	SCHLUCHSEE* $\mu mol_c\ l^{-1}$	VILLINGEN** $\mu mol_c\ l^{-1}$
Ca	51.5	39.8
Mg	12.7	26.6
Na	78.2	35.8
K	15.1	12.0
NH_4	0.2	0.2
NO_3	37.6	4.4
Cl	17.9	29.0
SO_4	67.0	96.5
ANC[X]	35.1	–15.5
BC[XX]	157.4	114.2
Ph	5.6	4.5

* 1996
**1995
[X] Acid Neutralising Capacity
[XX] Sum of base cations

SINKS AND SOURCES

In MAGIC the S sink 'net uptake' is defined as uptake necessary for tree biomass increment. Feger (1993b) reported annual element uptake rates for increment of 45-year and 100-year old spruce trees at Schluchsee (14 $mmol_c$ SO_4 m^{-2} yr^{-1}) and Villingen (6 $mmol_c$ SO_4 m^{-2} yr^{-1}), respectively (Feger, 1993b). Assuming that during tree growth element uptake increases and reaches a maximum sometime after the juvenile phase a 'sink sequence' for base cations and also S was constructed to reflect forest history in the catchments: At Schluchsee the natural forest was clearcut in 1750 and a pure spruce forest was planted. After another clearcut in 1943, 100% spruce was planted again. At Villingen, the old coniferous forest (see Table 1a) was clearcut in 1887 and replanted with 100% spruce.

CALIBRATION

With the parameters and assumptions described above, MAGIC was calibrated to target year values of stream and soil chemistry and further by comparing the long-term trends of element concentrations with the measured data set. Strong acid anion concentrations (NO_3^-, Cl^- and SO_4^{2-}) were calibrated first. Base cation concentrations were then calibrated by adjusting base cation exchange selectivity coefficients and base cation weathering in an interactive procedure until the model simulations matched the observed data. Finally, pH and concentrations of organic anions in the stream were calibrated by adjusting parameters controlling weak acid-base chemistry (Sullivan and Cosby, 1998).

For calibrating SO_4 in the stream, LIPs have to be set in the parameter file. For Schluchsee Podzol, Villingen Cambisol and Villingen Planosol E_{max} and C have been determined in the A- and B-horizons by Kurth *et al.* (1989) in a batch extraction. For the first calibration, these LIPs were used (Table 3). At Schluchsee different calibrations were run: For calibration 2, E_{max} was calculated from the measured soil S pool (Prietzel, 1998a) (Table 3). In calibration 3, LIPs were the result of an interactive procedure: the best approach to the measured SO_4 stream concentration was modelled by adjusting freely chosen LIPs (Table 3). After that, calibrations 4a and 4b were run with an additional S source term that is attributed to net mineralisation of the soil S_{org} pool (Table 3).

FORECAST

The so-called 'current legislation scenario' for the decrease in S deposition was used. This scenario assumes implementation of the Gothenburg protocol and relevant EU Directives (Schöpp *et al.*, 2003) and entails a 55, 57 and 60% reduction of SO_4 deposition for 2010, 2016 and 2030, respectively, compared to the reference year 1995/1996. Scale factors for the deposition in the future in relation to the reference year were calculated and the forecast was run with (calibrations 4a and 4b) and without (calibrations 1 and 3) the additional soil S source for Schluchsee (see above).

Results

ACIDIFICATION HISTORY

The generalised historical deposition (hindcast scenario) well matched the measured deposition data since the mid-1980s for Schluchsee and Villingen catchments (Fig. 1). Over the 140-year hindcast period the SO_4 fluxes in runoff increased as a result of the increasing S deposition.

Table 3. MAGIC input: Soil parameters for S dynamics (Langmuir isotherm parameters and additional SO_4 source) for the different calibration procedures.

Calibrations	*Langmuir parameters*	*half sat* $meq\ m^{-3}$	*max cap* $meq\ kg^{-1}$	*add.* SO_4 *source* $mmol_c\ m^{-2} yr^{-1}$
calibration 1	measured*	790	1.85	none
calibration 2	measured + calculated**	790	0.27	none
calibration 3	result of calibration	100	9.70	none
calibration 4a	measured*	790	1.85	*c.* 60.5
calibration 4b	measured*	790	1.85	const. 60.5

* Kurth *et al.*, 1989
** Kurth s.o., Prietzel,1998a

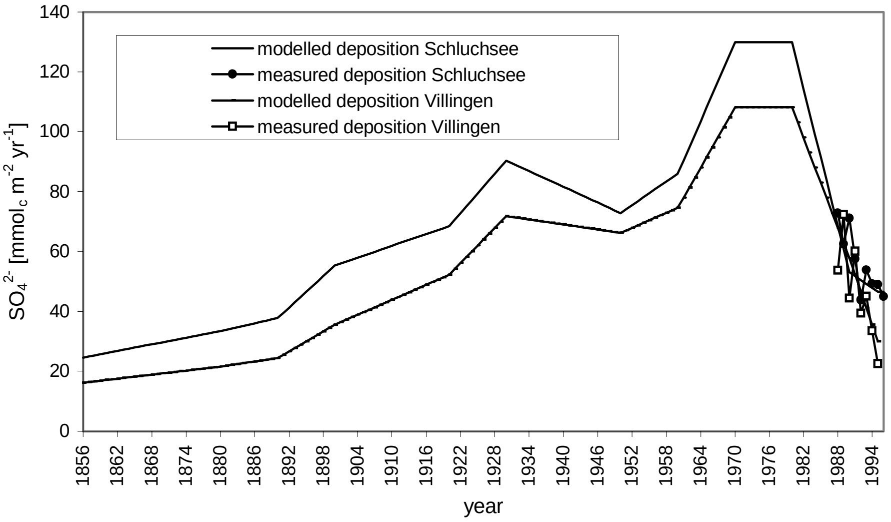

Fig. 1. *Modelled and measured SO$_4$ fluxes with input (total deposition) at Schluchsee and Villingen.*

MODELLING OF MEASURED STREAM SO$_4$ CONCENTRATION

Modelling SO$_4$ concentrations in streamwater at Schluchsee using the measured LIPs (calibration 1) was not successful; the measured SO$_4$ concentrations stream were greatly underestimated (Fig. 2). As a result, additional calibrations with various sets of input parameters for the S dynamics were tried. Calibration 2 was run with a smaller E_{max} and the same C as calibration 1 (Table 3), but resulted in the same or lower SO$_4$ concentrations in the stream (Fig. 2). Calibration 3 attempted to reach the measured SO$_4$ concentration level by adjusting freely chosen LIPs in an interactive procedure. The best LIP was 9.7 (E_{max}) and 100 (C), but still resulted in a 22% underestimation of SO$_4$ concentrations. In calibration 3, MAGIC calculated a soil S_{inorg} pool of 1295 mmol S m^{-2} in 1986, whereas the measured S_{inorg} pool in 1986 was only 253 mmol S m^{-2} (0–80 cm; Table 1b). For modelling SO$_4$ stream concentrations with this 'ad-/desorption only' approach, a more than five times larger E_{max} and soil S_{inorg} pool compared to measured values must be assumed.

For calibration 4a an additional S source meant to comprise net mineralisation from the S_{org} pool was included

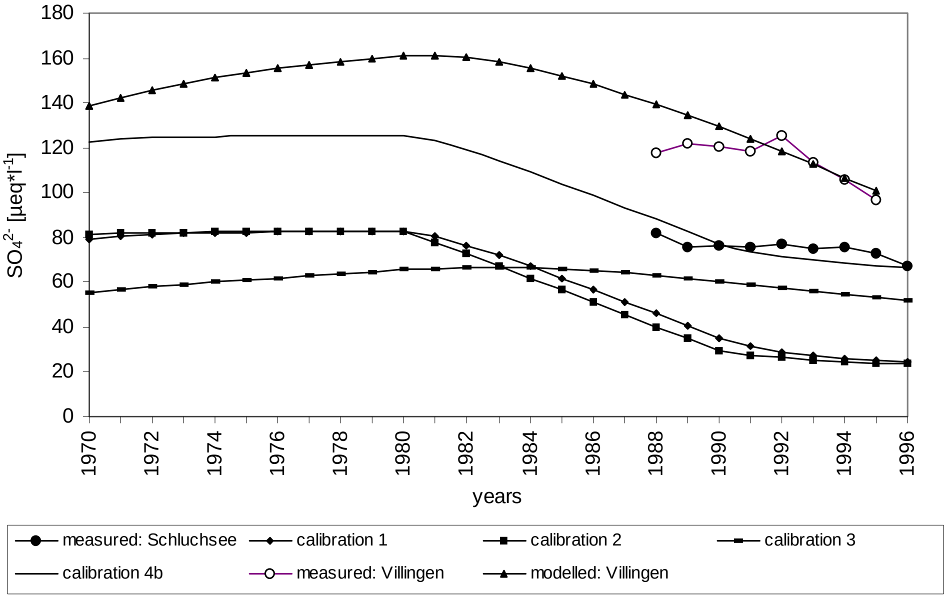

Fig. 2. Schluchsee and Villingen: Modelled compared to measured SO$_4$ stream concentrations.

in the same parameter file used in calibration 1 (measured LIPs). Measured data could be modelled by adding up the 'missing' SO$_4$ with a variable S source which varied from year-to-year such that the modelled and measured stream SO$_4$ concentrations matched. The average S source for these years (60.5 mmol$_c$ SO$_4$ m^{-2} yr^{-1}) was then used as a constant soil S source in calibration 4b. With these additional 60.5 mmol$_c$ SO$_4$ m^{-2} yr^{-1}, measured data were matched by the model with a correlation coefficient of 0.98.

The measured LIPs led to a successful calibration at Villingen (Fig. 2). No changes of LIPs or soil sources and sinks were necessary to achieve satisfactory simulation of SO$_4$ concentrations in the stream. The modelled SO$_4$ concentrations were on average 1.14 times higher than measured. The modelled soil S$_{inorg}$ pool (maximum in 1980: 1145 mmol S m^{-2}) compared relatively well with the measured (Table 1b).

FORECAST

At Schluchsee stream SO$_4$ concentrations predicted using calibration 1 decreased to 5.6 µmol$_c$ SO$_4$ l^{-1} in 2016, a level near the modelled pre-industrial level (calibration 1, before 1856) (Fig. 3a). Calibration 3 resulted in 29.0 µmol$_c$ SO$_4$ l^{-1} in 2016. With the additional S source, SO$_4$ in the stream was 48.5 µmol$_c$ SO$_4$ l^{-1} in 2016 compared to 67 µmol$_c$ SO$_4$ l^{-1} in 1996 (measured value). At Villingen, a SO$_4$ stream concentration of 39.8 µmol$_c$ SO$_4$ l^{-1} was predicted for 2016, which is equivalent to the hindcast for 1904 (Fig. 3b).

Discussion

The modelling indicated that in these two catchments pre-industrial conditions of SO$_4$ concentrations in runoff can be reached in the next two decades, if S deposition declines as agreed in current legislation. The forecast concentration at Schluchsee depends highly on the magnitude of S$_{org}$ released from mineralisation. The difference in the forecasts with and without an additional S source at Schluchsee was 43 µmol$_c$ SO$_4$ l^{-1} in 2016/2030 (Fig. 3a). Theoretically, and in dependency of the mineralisation dynamics, the S$_{org}$ pool could, as 'worst case scenario', release the same amount of SO$_4$ as in calibration 4a/4b constantly for decades. Without considering SO$_4$ release from mineralisation, a faster reversibility of stream SO$_4$ concentration was predicted at Schluchsee (Fig. 3a).

At Villingen the model suggested a relatively quick reversibility of SO$_4$ concentrations to less than half the 1995 value in 2016 and another 50% reduction by 2030 (Fig. 3b). the Uncertainty with respect to the relevant processes for SO$_4$ release and the S$_{org}$ source, however, is quite large (Fig. 3a). Therefore, it is crucial to identify the sources of SO$_4$ release from catchments soils for modelling future trends of stream SO$_4$ concentrations.

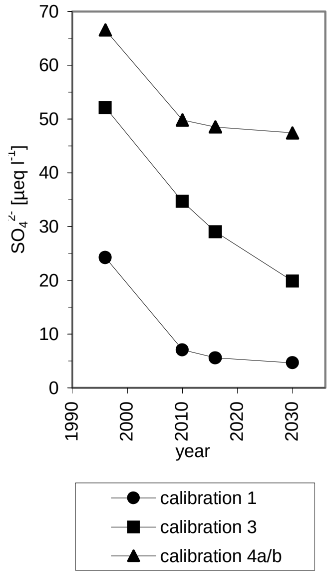

Fig. 3a. Schluchsee: Modelled SO$_4$ stream concentration in 1996, 2010, 2016 and 2030 depending on calibration.

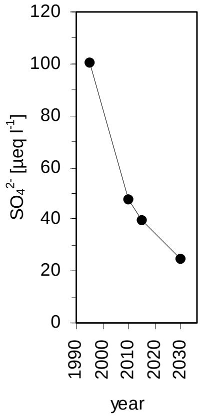

Fig. 3b. Villingen: Modelled SO$_4$ stream concentration in 1995, 2010, 2016 and 2030.

In general, four major processes can be responsible for S release from soil: (i) desorption of inorganic SO$_4$, (ii) oxidation of reduced S species, (iii) excess mineralisation of organically bound S, and (iv) weathering of S-containing minerals. Feger *et al.* (1990) and Mayer *et al.* (1995) assumed that oxidation and weathering are negligible (max. 0.013 mmol$_c$ SO$_4$ m^{-2} yr^{-1}; Prietzel, 1998b) in the two catchments.

At Schluchsee, a high percentage of the annual precipitation is falls as snow. Due to this, a 10% underestimation of the SO$_4$ input fluxes is possible (Feger *et al.*, 1990). This might account for part of the 'missing' SO_4 in the stream. But, increasing the amount of precipitation and the SO_4 input to the catchment was not sufficient to account for the measured SO_4 concentrations in the stream.

An additional soil S source was necessary. About 60.5 $mmol_c$ SO_4 m^{-2} yr^{-1} were needed to yield SO_4 stream concentrations at the measured level (calibrations 4a, 4b). This amount is consistent with those reported by Feger *et al.* (1990), Mayer *et al.* (1995) and Prietzel (1998b) (62–94 $mmol_c$ SO_4 m^{-2} yr^{-1}) to balance S flux budgets. The modelling shows that SO_4 release from the catchment cannot be explained solely with ad-/desorption. Kurth *et al.* (1989) found that adsorption in the humus-rich podzol is largely blocked by organic anions even in the subsoil. From depleted $\delta^{18}O_{sulphate}$-values in soil leachates Mayer *et al.* (1995) concluded that a considerable portion of SO_4 in the subsoil seepage must be derived from excess mineralisation of C-S. On basis of SO_4 fluxes and soil S pools (Table 1b) together with results on N dynamics Feger *et al.* (1990) and Feger (1993a) assumed that microbial turnover of relict subsoil humus pools (originating from the former deep-rooting beech-fir forest stand) might be responsible for the nitrate and SO_4 release at Schluchsee (Table 2c). This is supported by the fact that half of the S_{org} pool is stored in the B-horizon (Table 1b).

When the model was calibrated without the additional S source (calibration 3), MAGIC calculated a S_{inorg} pool that was five times larger than the measured S_{inorg} pool in 1986. Thus, MAGIC gives an additional indication that the S_{org} rather than S_{inorg} pool is the dominant soil SO_4 source at Schluchsee.

In contrast to Schluchsee, at Villingen adsorption/desorption processes can explain the concentrations and isotope composition of SO_4 in seepage water of the subsoil (Mayer *et al.*, 1995). This is due to the high sesquioxide content in the soil (Kurth *et al.*, 1989). This was confirmed by the successful calibration of MAGIC to the measured stream data with the measured LIPs (Fig. 2). Thus, S release from mineralisation of S_{org} played only a minor role, although the S_{org} pool still accounts for 54% of S_{tot} (Table 1b).

Consideration of the modelling results and S dynamics for these catchments leaves some questions open. This study only indicated that net mineralisation is a probable SO_4 source at Schluchsee. It remains open, if the relict humus and a high microbial activity in this humus actually are the reasons for SO_4 net release there as suggested by Feger *et al.* (1990). The question why the S_{org} should be mineralised in excess at Schluchsee and not at Villingen cannot be answered based on the available information. Mayer *et al.* (1995) concluded that at Villingen immobilization and mineralisation most likely occur concurrently at the same rate, resulting in more or less balanced S budgets and depleted $\delta^{18}O_{sulphate}$-values in soil leachates. How the S_{org} pool in these catchments will react in the future, and whether it might also become a net source at Villingen remain unanswered questions. Similar uncertainties on the future behaviour of S_{org} were indicated for the Gårdsjön catchment in Sweden (Torssander and Mörth, 1998). There, excess mineralisation of S_{org} in the B-horizon (where most of it is stored) is currently not important as a SO_4 source but could prolong acidification processes for centuries.

Sulphur mineralisation might increase with decreasing SO_4 concentration in soil solution (Maynard *et al.*, 1985; Simon *et al.*, 1989). If this happens for the soil S_{org} pool in the studied catchments, an increasing S release from mineralisation in the future is likely. In addition, it is quite possible that other factors which control mineralisation (e.g. temperature, moisture) are may change in the future and could therefore influence S release from the S_{org} pool. The excess mineralisation of S_{org} remains a source of uncertainty for predictions of the future concentrations of SO_4 in streamwater.

Conclusions

The model calibrations and S budgets from earlier studies indicated that the soil organic S pool most likely is the dominant source for SO_4 release from the Schluchsee catchment. Thus, S_{org} and S mineralisation have to be considered when modelling SO_4 stream concentrations there. Excess mineralisation can be modelled with MAGIC by implementing a soil S source. As the future dynamics of S release from mineralisation and the controlling factors are not clear, this process has to be taken into account as a source of uncertainty when predicting SO_4 concentrations in catchments. Future research should concentrate on dynamics of S mineralisation to be able to implement a more precise description of long-term S mineralisation into biogeochemical models.

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