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Response of sulphur dynamics in European catchments to decreasing sulphate deposition

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Abstract

Following the decline in sulphur deposition in Europe, sulphate dynamics of catchments and the reversibility of anthropogenic acidification of soils and freshwaters became of major interest. Long-term trends in sulphate concentrations and fluxes in precipitation/throughfall and freshwaters of 20 European catchments were analysed to evaluate catchment response to decreasing sulphate deposition. Sulphate deposition in the catchments studied declined by 38-82% during the last decade. Sulphate concentrations in all freshwaters decreased significantly, but acidification reversal was clearly delayed in the German streams. In Scandinavian streams and Czech/Slovakian lakes sulphate concentrations responded quickly to decreased input. Sulphate fluxes in run-off showed no clear trend in Germany and Italy but decreased in Scandinavia, the Czech Republic and Slovakia. The decrease, however, was less than the decline in input fluxes. While long-term sulphate output fluxes from catchments were generally correlated to input fluxes, most catchments started a net release of sulphate during the early 1990s. Release of stored sulphate leads to a delay of acidification reversal and can be caused by four major processes. Desorption and excess mineralisation were regarded as the most important for the catchments investigated, while oxidation and weathering were of lesser importance for the long-term release of sulphate. Input from weathering has to be considered for the Italian catchments. Sulphate fluxes in German catchments, with deeply weathered soils and high soil storage capacity, responded more slowly to decreased deposition than catchments in Scandinavia and the Czech Republic/Slovakia, which have thin soils and relatively small sulphate storage. For predictions of acidification reversal, soil characteristics, sulphur pools and their dynamics have to be evaluated in future research.

Keywords: acidification reversal, sulphur, sulphate release, Europe, catchments, deposition, lake, stream

Introduction

From the beginning of the twentieth century, sulphur (S) emissions and deposition increased steadily (Erisman and Draaijers, 1995; Mylona, 1996) and sulphate (SO_4) deposition in forested ecosystems of north and central Europe reached more than 100 kg ha^{-1} yr^{-1} in the early 1980s (Erkenberg, 1991). Part of the deposited SO_4 has accumulated in the soils through adsorption processes (Johnson and Mitchell, 1998). When the SO_4 retention capacity of soils is exceeded, SO_4 is leached to deeper soil layers and freshwaters. Because SO_4 release is always accompanied by cation leaching, net loss from soils will cause soil acidification (depletion of calcium (Ca), magnesium (Mg), potassium (K) and sodium (Na) pools) as well as acidification of soil solutions and freshwaters (leaching of aluminum (Al), protons (H^+), iron (Fe) and manganese (Mn)) under conditions of low soil pH. Such conditions are common in acid forest soils of temperate regions.

Net release of SO_4 from forested soils can be caused by four major processes (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. Understanding and prediction of the reversal of soil and water acidification necessitates differentiation between these release processes. While SO_4 desorption is an abiotic process regulated by concentration gradients and binding partners for SO_4, mineralisation and oxidation are biologically controlled and thus dependent on parameters influencing the physiology of micro-organisms (e.g. temperature, water regime, availability of organic substrates etc.). In contrast, the release of S by weathering should be relatively stable in time as long as the climate does not show major changes.

Political initiatives such as the S Emissions Control Protocols of 1985 and 1994 of the United Nations Economic Commission for Europe (UNECE) have achieved a 60% decline in S emissions in Europe (1980–1997) (EMEP, 1999). As SO_4 deposition to ecosystems declined, questions concerning the reversibility of anthropogenic acidification of soils and waters and the dynamics of ecosystem recovery were raised. Generally, it can be stated that freshwaters from catchments with a low storage capacity for SO_4 react relatively quickly to reduced deposition with an increase in the acid neutralisation capacity (ANC) and pH as signs of acidification reversal (Stoddard *et al.*, 1999; Tipping *et al.*, 2000; Wright *et al.*, 1994). In contrast, reversal of water acidification can be delayed for decades in regions where previously stored SO_4 is released from deeply weathered soils with a high SO_4 storage capacity (Alewell *et al.*, 2000; Armbruster, 1998; Kopácek, *et al.* 2001a; Manderscheid *et al.* 2000; Veselý *et al.* 1998a).

As part of the EU project “RECOVER:2010 – Predicting recovery in acidified freshwaters by the year 2010 and beyond” (see Ferrier *et al.*, 2001) evaluated here are: (i) regional differences in long-term trends of SO_4 concentrations and fluxes in bulk precipitation/throughfall and freshwaters on a European scale; (ii) the catchment response to decreasing SO_4 deposition regarding SO_4 concentrations and fluxes as well as budgets; and (iii) the processes responsible for SO_4 release in the investigated catchments.

Methods

The long-term data used in this study were collected within national projects described elsewhere. This study includes 20 European catchments, covering a wide variety of bedrock, soils, and vegetation types as well as deposition and acidification levels (Tables 1a and 1b; Fig. 1). For the Czech and the Slovakian catchments, lake water was considered instead of catchment run-off. References for detailed descriptions of sampling methods and site characteristics as well as the time periods of the data used are listed in Table 1c.

Sulphate fluxes in throughfall were taken as total atmospheric SO_4 input for the forested catchments in Germany and Sweden, following the reasoning of Mayer and Ulrich (1974), Bredemeier (1988), Johnson and Mitchell (1998) and Alewell (2001a). At the Norwegian and UK sites, bulk precipitation was measured and total deposition (= wet and dry deposition) was calculated from chloride (Cl) mass balances (total SO_4 deposition = SO_4 fluxes with wet deposition multiplied by the ratio of Cl flux with run-off to Cl flux with wet deposition). For the Italian catchments, dry deposition was added as a fixed percentage of wet deposition to calculate total deposition (for details see Rogora *et al.*, 2001). Sulphate input fluxes to Czech catchments were based on fortnightly throughfall and precipitation measurements at Certovo Lake for the 1992-2000 period and on simulation from long-term SO_4 deposition in the Czech Republic before 1991 (Kopácek *et al.*, 2001b). For Lake Vysne Wahlenbergovo, SO_4 input was also simulated from long-term deposition trends at Chopok station (monthly data) (Kopácek *et al.*, 2001b).

Input flux calculations were based on samples collected daily (Birkenes, Langtjern, Storgama), weekly (Allt a’Mharcaidh, Risdalsheia, Schluchsee, and Villingen: weekly till 1990, after 1990 samples were combined to monthly bulk samples before analyses), fortnightly (Gårdsjön, Lehstenbach, Markungsgraben, Metzenbach) or monthly (Gårdsjön, Lange Bramke). Sulphate concentrations in bulk precipitation measured weekly at Pallanza (Italy) were taken to be representative for the Italian catchments Cannobino, Pellino, Pellesino, and Pescone where only the amount of precipitation was determined.

Sampling frequencies for SO_4 concentrations in streams were weekly at Allt a’Mharcaidh, Birkenes, Langtjern, Storgama, Lange Bramke, Schluchsee and Villingen, fortnightly at Lehstenbach, Markungsgraben and Metzenbach, and monthly at Cannobino, Pellino, Pellesino and Pescone. At Risdalsheia run-off was sampled for each 10–20 mm and at Gårdsjön sampling frequency was proportional to flow. Lake waters in the Czech Republic and Slovakia were sampled once a year in July or August; for output fluxes at Czech and Slovakian sites concentrations were multiplied by annual discharge (see Kopácek *et al.*, 2001b). Weekly, fortnightly or monthly fluxes were

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

Catchments	Country	Location			Area ha	Climate		Annual discharge myr^{-1}
		Latitude N	Longitude E	Altitude m a.s.l.		temperature* °C	precipitation** myr^{-1}	
Černé (Bohemian Forest)	Czech Republic	49°11'	13°11'	1008	129	4.3	1.36	1.16
Čertovo (Bohemian Forest)	Czech Republic	49°10'	13°12'	1028	87.5	4.3	1.36	1.16
Plešné (Bohemian Forest)	Czech Republic	48°47'	13°52'	1090	66.6	4.3	1.36	1.16
Vysne Wahlenbergovo (High Tatras)	Slovakia	49°10'	20°01'	2145	32	-0.7 to -2.4	1.58	
Lange Bramke (Harz)	Germany	51°52'	10°26'	535-700	76	5.9	1.24	0.68
Lehstenbach (Fichtelgebirge)	Germany	50°09'	11°52'	694-871	420	6.0	1.00-1.10	0.46
Markungsgraben (Bavarian Forest)	Germany	48°57'	13°25'	890-1355	110	3.0-6.0	0.80 - 1.60	1.20
Metzenbach (Spessart)	Germany	49°54'	9°26'	385-586	240	6.0-7.0	0.70 - 1.10	0.17
Schluchsee (Black Forest)	Germany	47°49'	8°06'	1150-1290	11	4.4	1.87***	1.40***
Villingen (Black Forest)	Germany	48°03'	8°22'	810-945	46.3	6.3	1.33***	0.47***
Cannobino	Italy	46°04'	8°42'	193-2193	110.4		1.60-2.70	1.45
Pellino	Italy	45°47'	8°04'	290-942	17.5		2.00-2.10	1.67
Pellesino	Italy	45°48'	8°04'	290-1136	3.1		2.00-2.20	1.70
Pescone	Italy	45°48'	8°24'	290-1491	17.5		1.90-2.10	1.45
Birkenes	Norway	58°23'	8°15'	200-300	41	5.4	1.53	1.17
Storgama	Norway	59°01'	8°32'	580-690	60	5.1	1.21	0.95
Langtjern	Norway	60°22'	9°39'	510-750	480	3.0	0.86	0.61
Risdalsheia ROLF Reference	Norway	58°23'	8°19'	300	0.022	5.0	1.40	1.24
Gårdsjön F1 Control	Sweden	58°03'	12°01'	113-170	3.7	6.3	1.10***	0.55 ***
Allt a`Mharcaidh (Scotland)	United Kingdom	57°07'	3°50' **W**	350-1111	998	5.6	1.07	0.83

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

Table 1b. Site characteristics of catchments studied: dominant vegetation, geology and soils

Catchments	Forest /Vegetation	Bedrock	Soil type (FAO)
Černé	Norway Spruce	mica schist	Podzols, Cambisols
Čertovo	Norway Spruce	mica schist	Podzols, Cambisols
Plešné	Norway Spruce	granit	Podzols, Cambisols
Vysne Wahlenbergovo	Bare rocks, alpine meadow	granit	Leptosols
Lange Bramke	Norway Spruce	Lower Devonian Kahleberg sandstone	dystric Cambisols
Lehstenbach	Norway Spruce	granite deeply weathered	dystric Cambisols and Podzols
Markungsgraben	Spruce, mixed woodland	granite, gneiss	Cambisols
Metzenbach	Decidous Forest dominated by Beech	middle new red sandstone	Cambisols
Schluchsee	Norway Spruce	granite	haplic Podzol
Villingen	Norway Spruce	triassic sandstone	dystric Cambisols and dystric Planosols
Cannobino	Mixed Deciduous	orthogneiss and micaschist (60%)	
Pellino	Mixed Deciduous	white granite and granodiorite (50%), orthogneisses and micaschists (30%)	
Pellesino	Mixed Deciduous	white granite and granodiorite (80%)	
Pescone	Mixed Deciduous	white granite and granodiorite (35%), orthogneisses and micaschists (30%)	
Birkenes	Mixed Coniferous	granite	Podzols
Storgama	Individual trees, heather, moorgrass	granite	Podzols
Langtjern	Mixed Coniferous	gneiss	Podzols
Risdalsheia	Mixed Pine and Birch	granite	Podzols
Gårdsjön	Norway Spruce	gneiss	Podzols
Allt a`Mharcaidh	10% Native pine wood, Montane veg.	granite	dystric (fibric) Histosols, haplic and cryic Podzols

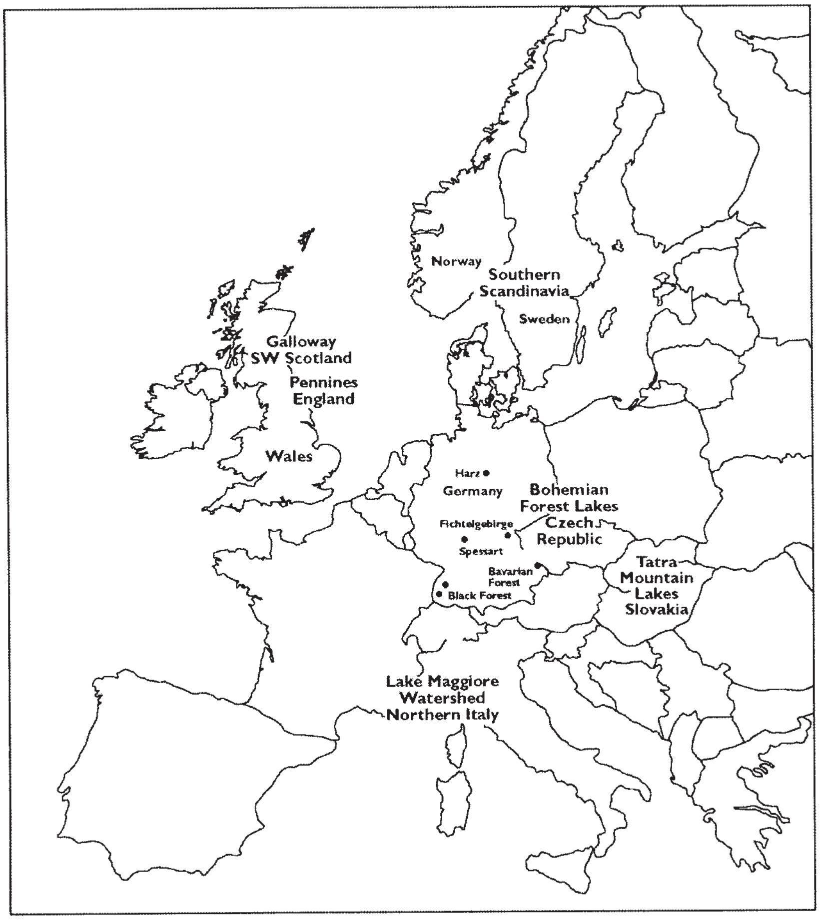

Fig. 1. *Map of European catchments included in this study*

Table 1c. Data periods and references for detailed descriptions of sampling methods and site characteristics of catchments studied

Catchments	Data periods	References
Černé	1990-2000	Veselý et al. (1998a), Kopácek et al. (this issue)
Čertovo	1990-2000	Veselý et al. (1998a), Kopácek et al. (this issue)
Plešné	1990-2000	Veselý et al. (1998a), Kopácek et al. (this issue)
Vysne Wahlenbergovo	1980-2000	Kopácek et al. (1998), Kopácek et al. (this issue)
Lange Bramke	1983-1995	Hauhs (1989), Schmidt (1997)
Lehstenbach	1988-1998	LfW (1994), Manderscheid and Göttlein (1995), Alewell et al. (this issue)
Markungsgraben	1989-1998	LfW (1994), Alewell et al. (this issue)
Metzenbach	1988-1998	LfW (1994), Alewell et al. (this issue)
Schluchsee	1988-1996	Armbruster (1998)
Villingen	1988-1995	Armbruster (1998)
Cannobino	1985-1999	Boggero et al. (1996), Mosello et al. (1993), Rogora et al. (this issue)
Pellino	1985-1997	Boggero et al. (1996), Mosello and De Giuli (1982), Rogora et al. (this issue)
Pellesino	1986-1997	Boggero et al. (1996), Mosello and De Giuli (1982), Rogora et al. (this issue)
Pescone	1985-1997	Boggero et al. (1996), Mosello and De Giuli (1982), Rogora et al. (this issue)
Birkenes	1974-1999	Lydersen (1994)
Storgama	1975-1999	Lydersen (1994)
Langtjern	1974-1999	Lydersen (1994)
Risdalsheia ROLF Reference	1986-2000	Wright et al. (1993)
Gårdsjön F1 Control	1989-1999	Moldan (1999)
Allt a`Mharcaidh	1986-1994	Ferrier et al. (1990)

calculated by multiplying concentrations by the equivalent water fluxes; annual output fluxes were then calculated as the yearly sum of weekly, fortnightly or monthly SO_4 fluxes. All fluxes analysed are total SO_4 fluxes.

For the German catchments Lehstenbach, Markungsgraben and Metzenbach, yearly SO_4 fluxes with streams were calculated using the following formula:

$$\text{Yearly } SO_4 \text{ flux} = \frac{(\Sigma SO_4 \text{ flux of measurement days}) * \text{yearly discharge}}{\Sigma \text{discharge rate of measurement days}}$$

Yearly output fluxes in Villingen and Schluchsee were calculated according to Brahmer (1990, quoted from Armbruster, 1998), where the sum of water fluxes of a measurement period was multiplied by the arithmetic mean of element concentrations at the start and end point of the measurement period. Yearly element fluxes were calculated by summation of fluxes over all measurement periods. Output fluxes from the Italian streams were calculated according to the approach of Sonzogni *et al.* (1978) (also see Rogora *et al.*, 2001).

Annual output fluxes were subtracted from input fluxes to calculate the net retention or loss of SO_4 in the catchments. All fluxes are shown for calendar years with exception of Gårdsjön, Schluchsee, and Villingen which use hydrological years. For measurement periods see Table 1c.

Trend analysis on SO_4 concentrations in precipitation/ throughfall and surface water was done with the Seasonal-Kendall-Test except for the concentration trends for the Czech lakes and for bulk precipitation at Pallanza for which the Mann-Kendall-Test was used due to low sampling frequencies. Significance limit was set to $p<0.05$. The trend statistic T gives decrease (negative values) or increase (positive values) in $\mu mol_c\, l^{-1}\, yr^{-1}$. A detailed description of statistical methods is given in Evans *et al.* (2001). To distinguish changes in anthropogenic SO_4 from climate-related variations in sea-salt, deposition trends for Scandinavian catchments were calculated for non-marine sulphate (xSO_4) fraction only (total SO_4 minus marine SO_4). Marine SO_4 was calculated based on the SO_4/Cl ratio of seawater. For central Europe, where marine inputs are minor, non-marine SO_4 was considered equal to total SO_4.

Results

TRENDS IN SO_4 CONCENTRATIONS

Starting in the late 1980s, SO_4 concentrations in bulk precipitation decreased in most catchments (Figs. 2a and 2b). At Lange Bramke this decline started in the early 1980s. Only at Allt a'Mharcaidh in Scotland, UK, was there no significant trend (Mann-Kendall T = –0.74, $p > 0.05$; data not shown). The absolute decreases were largest in regions receiving the highest deposition (Figs. 2a and 2b). At the German catchments Lange Bramke, Markungsgraben, Metzenbach and Lehstenbach, the decrease in SO_4 concentration in bulk precipitation during the period 1988-1999 was 3.67, 3.85, 4.35 and 9.87 $\mu mol_c\, l^{-1}\, yr^{-1}$, respectively. In Villingen and Schluchsee (Black Forest, Germany) trends in SO_4 concentrations in bulk precipitation were lower (–1.58 and –1.4 $\mu mol_c\, l^{-1}\, yr^{-1}$, respectively). At those sites where throughfall data were available, throughfall concentrations (data not shown) generally decreased more than concentrations in bulk precipitation. Sulphate concentrations in throughfall are influenced by interception deposition where the relative decrease is more pronounced. At Lange Bramke, throughfall was measured at the north and south slope as well as at the ridge, and decreased by 9.9, 12.3 and 20.4 $\mu mol_c\, l^{-1}\, yr^{-1}$, respectively. For Markungsgraben, Metzenbach and Lehstenbach, decrease in throughfall concentrations was also greater than in bulk precipitation (–13.7, –9.3, –34.0 $\mu mol_c\, l^{-1}\, yr^{-1}$, respectively). Exceptions were Villingen and Schluchsee, where calculated throughfall trends were not significant even though bulk precipitation decreased significantly.

With the decline in SO_4 concentrations in precipitation, SO_4 concentrations in streams also decreased significantly at all but two sites (Figs. 2a and 2b). The absolute decrease was highest at Gårdsjön (Sweden) and Lehstenbach (Germany). These streams (together with Metzenbach (Germany)) also had the highest mean SO_4 concentrations in the 1990s of the sites included here. At Gårdsjön there was a decline in the general level of concentrations, whereas at Lehstenbach base flow concentrations were relatively stable over time and only the maximum concentrations decreased. The Lange Bramke stream showed a small increase for the whole period 1978-99 (1.2 $\mu mol_c\, l^{-1}\, yr^{-1}$) but a slight decrease since 1987 which, however, was not significant. There was no significant trend in stream concentrations at Allt a'Mharcaidh.

Concentrations in the lakes Cerné, Certovo and Plešné (Czech Republic) decreased significantly (Fig. 2b) and concentrations in lake Vysne Wahlenbergovo (Slovakia) decreased from 80 $\mu mol_c\, l^{-1}$ to around 35 $\mu mol_c\, l^{-1}$ (1987–1999) (trend statistics were not calculated due to major breaks in time series, Fig. 2b).

TRENDS IN SO_4 FLUXES AND BUDGETS

Input fluxes with total deposition at all European catchments started to decrease significantly during the late 1980s parallel to the decrease in concentrations (Figs. 3a and 3b). The

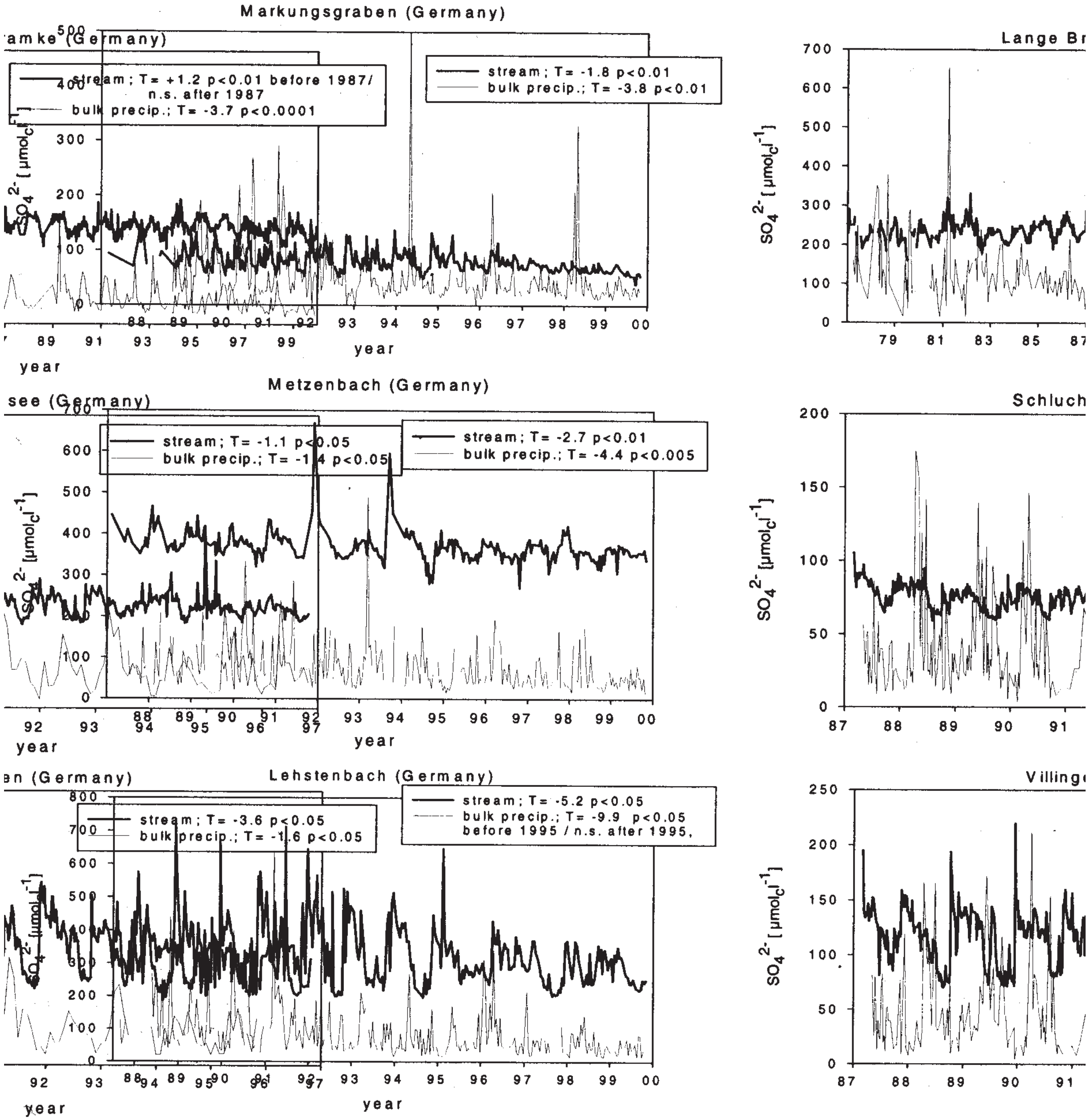

Fig. 2a. *Sulphate concentrations in stream and bulk precipitation – German catchments. Kendall-Tau (T) values for significant trends in* $\mu mol_c\, l^{-1} yr^{-1}$*; negative T= decrease, positive T= increase; n.s.= not significant* $(p>0.05)$

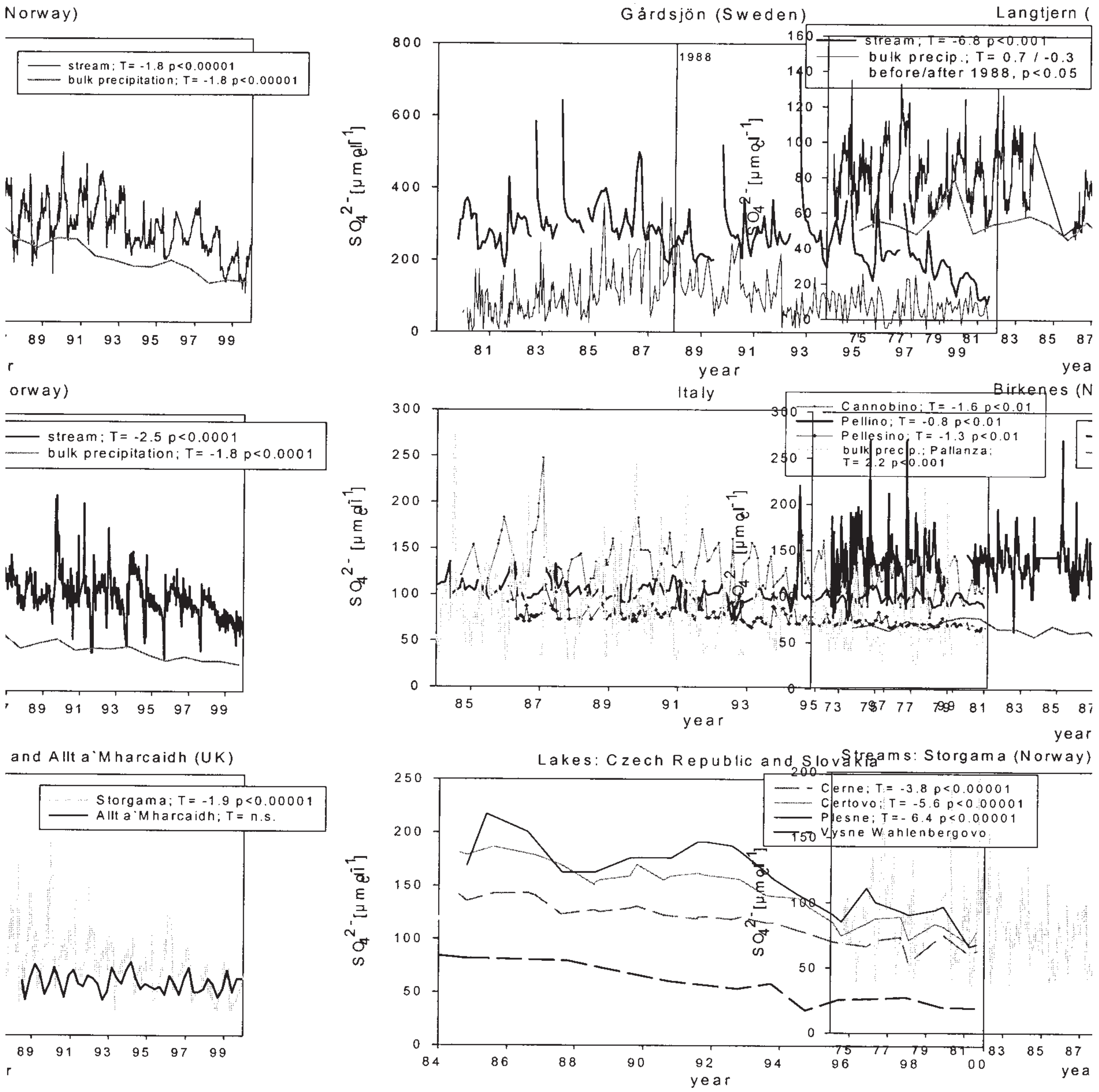

Fig. 2b. *Sulphate concentrations in stream and bulk precipitation – Norwegian, Swedish, Italian and Czech catchments. Kendall-Tau (T) values for significant trends in* $\mu mol_c\ l^{-1} yr^{-1}$; *negative T= decrease, positive T= increase; n.s.= not significant (p>0.05)*

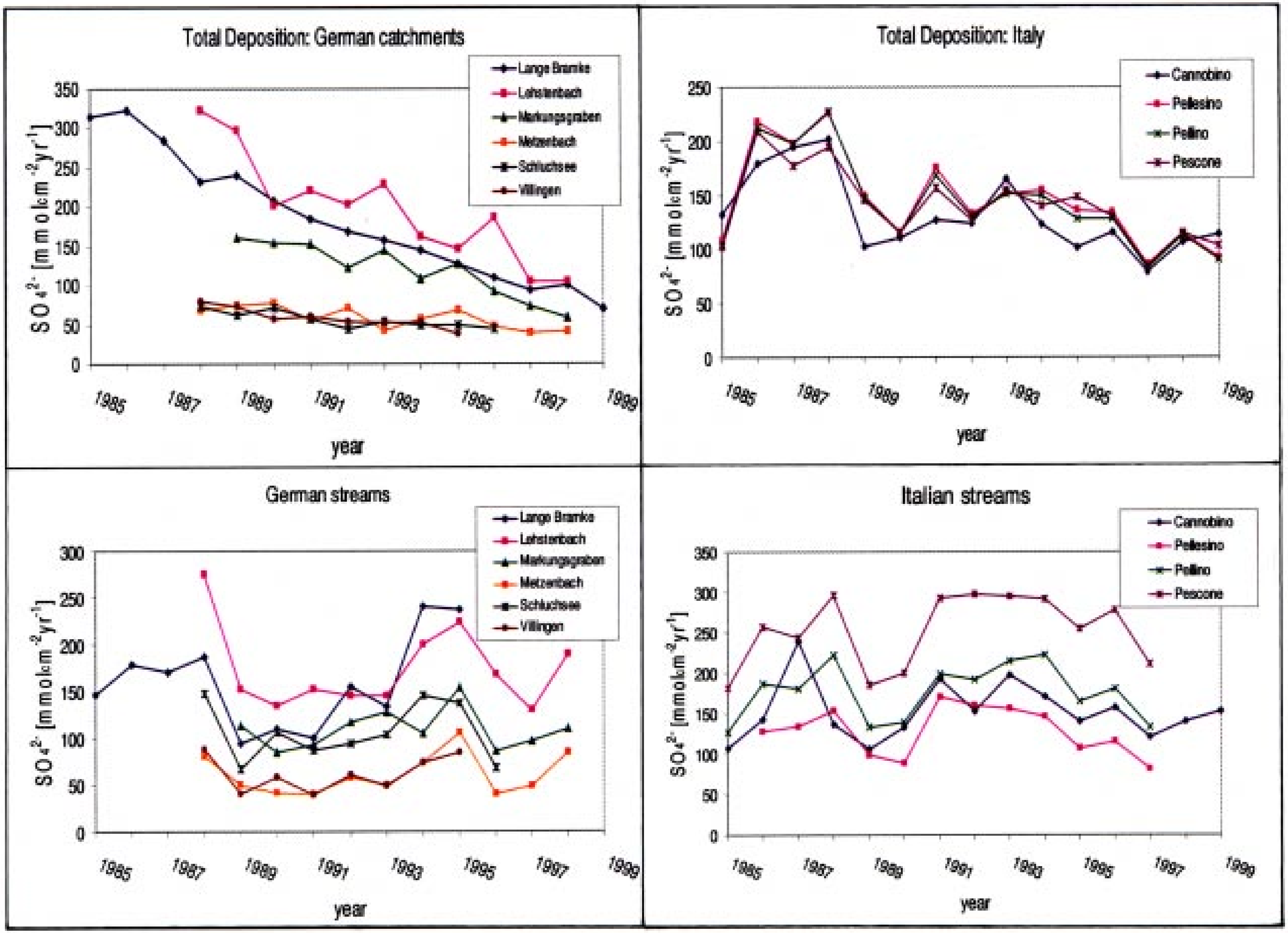

Fig. 3a. *Sulphate input and output fluxes – German and Italian catchments*

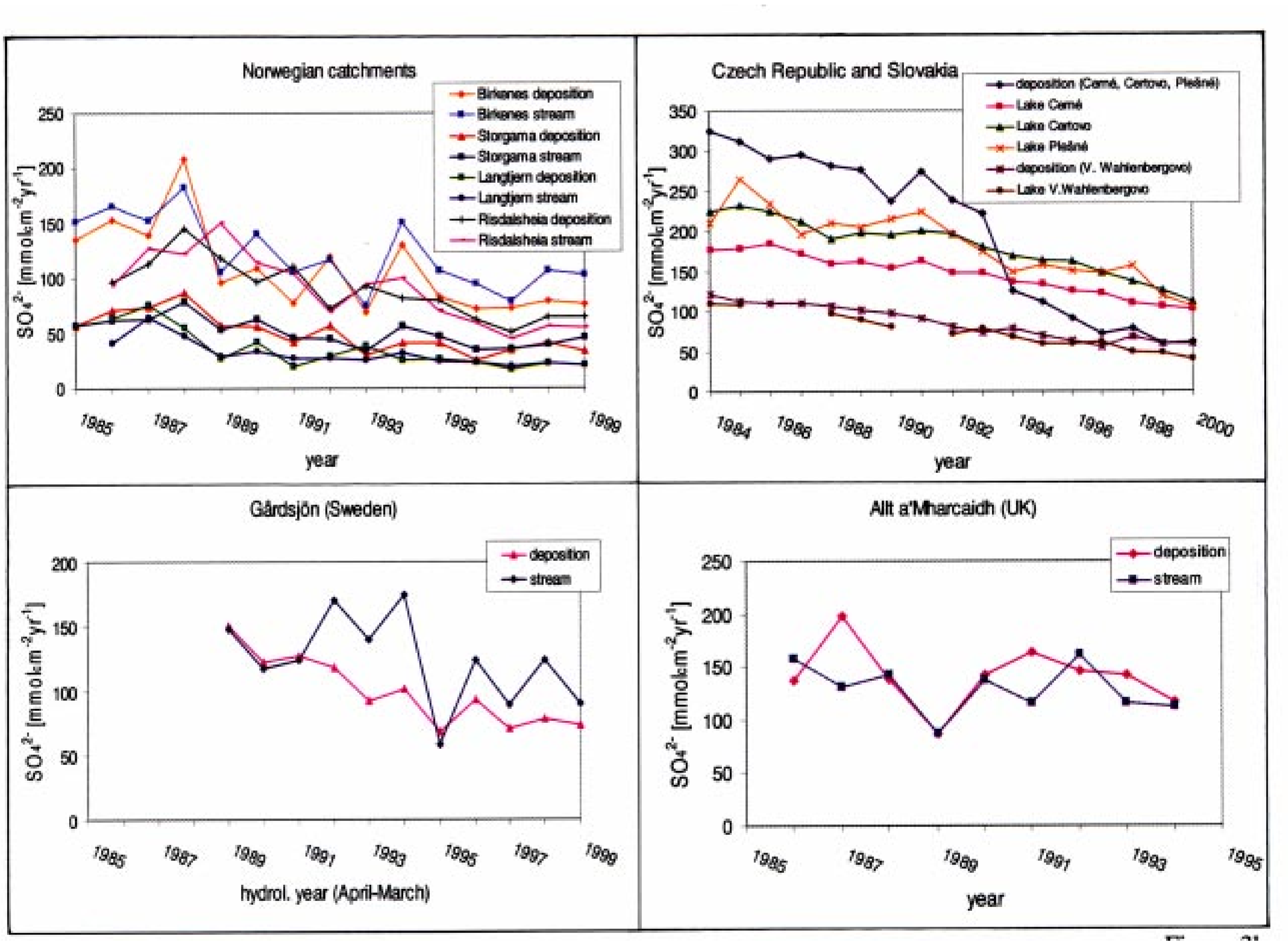

Fig. 3b. *Sulphate input and output fluxes – Norwegian, Swedish, Czech and UK catchments*

decrease in input fluxes for the period 1988/89 (reference year) to 1998/99 ranged between 38% (Metzenbach, Schluchsee (1988–1996)) to 70% (Lange Bramke) at the German catchments, between 43–60% (Pellino - Cannobino) in Italy, between 53–64% in Norway and between 78–82% in the Czech Republic (for the Czech Republic reference year was 1990). The decreases at Slovakian (1980–1999) and Swedish sites (Gårdsjön, 1989–1999) were 48% and 51%, respectively (Figs. 3a and 3b).

The German catchments Lange Bramke and Lehstenbach along with the Czech lakes were impacted by the highest SO_4 deposition throughout the whole measurement period (for mean input fluxes see Fig. 4). Lehstenbach and Lande Bramke and the Czech lakes also had the highest output fluxes. The catchment wiht he lowest input and outpput fluxes was Langtjern (Norway). There was a positive relationship between yearly mean input load and yearly mean output flux (Fig. 4). An exception is the Italian catchment Pescone which had a higher output relative to input; this is probably due to weathering of S-containing minerals. Another exception is the catchment Schluchsee (Germany) with a medium output (106 $mmol_c\ m^{-2}\ yr^{-1}$) and only a low input (56 $mmol_c m^{-2}\ yr^{-1}$). Finally, Lange Bramke had a relatively low output compared to input values.

Although the general long-term levels of SO_4 input and output fluxes are correlated (Fig. 4), the temporal dynamics of the output fluxes was not parallel to input dynamics. Compared to the major decrease in input fluxes, output fluxes of German and Italian catchments showed no trend (Fig. 3a), partly caused by a high variability in water fluxes (data not shown). The Scandinavian streams, however, showed an overall decrease of output fluxes by 33% (Birkenes), 40% (Storgama and Gårdsjön) to 60% (Risdalsheia) between 1986-1999 (Fig. 3b) parallel to the decrease in deposition. Sulphate output fluxes in the investigated Czech and Slovakian lakes also decreased clearly by between 40–50% (Fig. 3b).

The dynamics of SO_4 budgets (defined as flux in total deposition minus flux out in run-off) indicated a trend towards negative values (i.e. net loss) in most of the catchments since the late 1980s (Fig. 5). Many sites switched from net retention to net loss, except Pescone (Italy) and Schluchsee (Germany) which lost SO_4 since the beginning of measurements in 1985 and 1988 (average loss rates 107.6 $mmol_c\ m^{-2}\ yr^{-1}$ and 49.9 $mmol_c\ m^{-2}\ yr^{-1}$, respectively). The Italian catchments Cannobino and Pellino started releasing SO_4 in 1989 and 1990, respectively. Most German catchments started losing SO_4 in the early 1990s. The catchments with the highest annual loss rates were Pescone and Lange Bramke with –108 and –102 $mmol_c\ m^{-2}yr^{-1}$, respectively. Villingen, Gårdsjön, Cannobino, Lehstenbach, Pellino and Schluchsee showed annual loss rates between 34 and 49 $mmol_c\ m^{-2}yr^{-1}$. Lower annual loss rates were observed at Markungsgraben, Birkenes, Metzenbach, Pellesino and Storgama (release 24 $mmol_c\ m^{-2}yr^{-1}$ or less).

At Pellesino (Italy), input fluxes exceeded the output fluxes in run-off in most years, thus showing a net retention of SO_4 (14.9 $mmol_c\ m^{-2}\ yr^{-1}$). Retention of SO_4 was also observed at Risdalsheia from 1995 to 2000. The accumulation rate at Risdalsheia, however, was only around

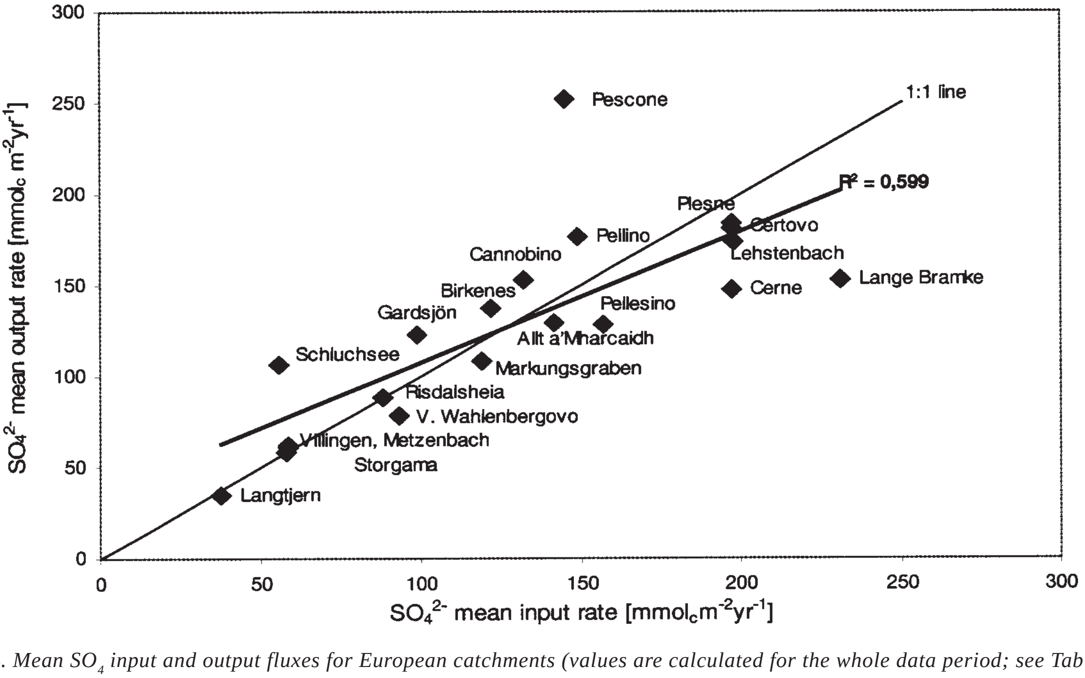

Fig. 4. *Mean SO_4 input and output fluxes for European catchments (values are calculated for the whole data period; see Table 1c)*

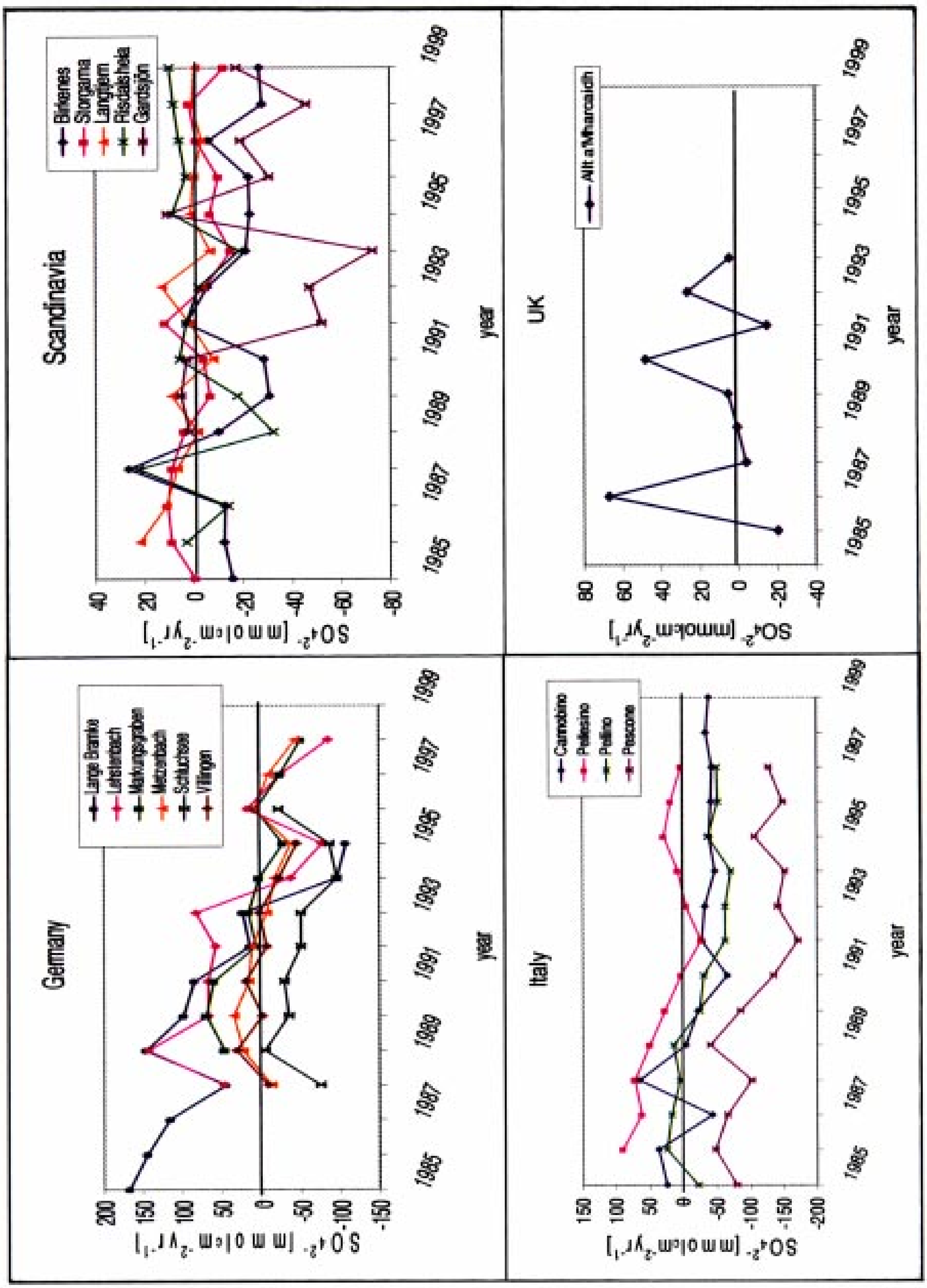

Fig. 5. *Sulphate net retention (+) or loss (-) – German, Italian, Scandinavian and UK catchments*

10 mmol$_c$ m^{-2} yr^{-1} and might be within the errors associated with flux measurements. The Scandinavian sites show no major changes in budgets and outputs track inputs closely. At Allt a'Mharcaidh (UK) the budgets showed no clear trend (Fig. 5).

Discussion

TRENDS IN SO_4 CONCENTRATIONS AND FLUXES

The decrease in SO_4 deposition during the 1990s in the European catchments investigated ranged between 38 and 82% (reference year 1988/1989). The catchments with the highest inputs in 1988/1988, such as Lange Bramke, Lehstenbach (Germany) and the Czech catchments also had the greatest decrease (70–82%) in deposition. At the Italian catchments with high inputs in 1988, the decline was less pronounced (43–60%). The decreases in deposition at these sites falls into the general pattern for Europe and corresponds to the decline in emissions (Barrett *et al.*, 2000).

All stream sites, with the exception of Lange Bramke and Allt a'Mharcaidh, had significant decreasing trends in SO_4 concentrations during the 1990s (Figs. 2a and 2b). Clearly, recovery from high SO_4 deposition has occurred but changes in stream concentrations were lower than those in deposition in most catchments. Sulphate was still the dominant strong-acid anion in many of the streams (also see Alewell *et al.*, 2001), even though the relative importance of nitrogen (N) deposition is increasing in Europe with decreasing SO_4 deposition.

With the exception of the Scandinavian and Slovakian catchments, the response of SO_4 fluxes in run-off to reduced deposition has been delayed in most catchments. Despite decreased SO_4 concentrations and fluxes in input, several streams had no clear trend in annual output fluxes (e.g. the German, Italian and Scottish streams) or the decrease was less than the reduction in input fluxes, such as at the Czech lakes. This could be due partly to the fact that output fluxes are controlled by hydrology with short-term hydrological variations masking long-term trends in annual SO_4 fluxes. However, the results of SO_4 fluxes combined with the precipitation and stream concentration trends showed a delayed response in SO_4 output in catchments to decreased deposition.

This delay was due to a net release of SO_4 from the catchments. At most sites a change in net retention occurred in the late 1980s or early 1990s. The consequences of SO_4 release into the waters are ongoing cation leaching from soils and thus a delay of acidification reversal of soils and waters. These results confirm studies by Alewell *et al.* (2000), Veselý *et al.* (1998b) and Kopácek *et al.* (2001a) who reported a widespread delay in acidification reversal in ecosystems with a high soil SO_4 and proton storage capacity.

The data clearly demonstrate that there is a general relationship between mean SO_4 input and mean SO_4 output from catchments (Fig. 4). This implies that despite a net release of stored SO_4, a reduction in deposition will eventually lead to a reduction in SO_4 output.

SULPHUR POOLS AND PROCESSES REGULATING SO_4 RELEASE

The net retention and release of SO_4 from the catchments raises the question as to which pools and processes within the ecosystems are involved. Understanding of the sizes of soil S pools and their dynamics will play an important role in the prediction of future SO_4 concentrations in streams and, thus, prediction of reversibility of soil and water acidification.

The different development of soils in central and north Europe is reflected in the catchment response of SO_4 dynamics. The German catchments Lange Bramke and Lehstenbach have old, deeply-weathered soils and a high soil storage of adsorbed SO_4, whereas the Scandinavian, Czech and Slovakian catchments have young, thin soils and thus low SO_4 storage capacity. The latter reacted relatively quickly to a decrease in deposition with large decreases in SO_4 output flux.

Previous investigations have shown that inorganic soil SO_4 pools are sufficiently large to explain a net release by *desorption processes* for several decades in the catchments Villingen (Armbruster, 1998; Alewell, 2001b), Lange Bramke (Malessa, 1995; Lükewille *et al.*, 1995), Lehstenbach (Manderscheid *et al.*, 2000; Alewell, 1995) and Gårdsjön (Moldan, 1999). Manderscheid *et al.* (2000) evaluated the SO_4 storage in the weathered substrata (0.5–10 m depth) of the Lehstenbach catchment and found approximately 90 kmol ha^{-1} Na_2HPO_4-extractable SO_4. This SO_4 is highly mobile and could be partly released to seepage and run-off for more than 75 years. An interesting result of this analysis is the increasing or constant stream SO_4 concentrations at Lange Bramke despite decreasing deposition. Model simulations for Lange Bramke indicated that SO_4 concentrations in the stream should increase until 2020 (Lükewille *et al.* 1995). This prediction was based on measured SO_4 pools and an assumed reduction of deposition of 40% between 1988 and 1993 (Lükewille *et al.*, 1995). The increase in stream water SO_4 concentrations is due to net release of adsorbed SO_4 from large pools in the deeper soil layers (down to 2.4 m depth) which function as a long-term memory of the high deposition regime of the past. The relatively low SO_4 output at Lange Bramke compared to the input flux (Fig. 4) probably reflects SO_4 adsorption in deeper soil layers and thus net retention. In contrast to Lange Bramke and Lehstenbach, at Schluchsee (Germany) and Risdalsheia (Norway), the comparison of S fluxes and pools demonstrated that inorganic S pools are too small to explain SO_4 release within the last few decades (Wright *et al.*, 1988; Prietzel, 1998; Armbruster, 1998; Alewell, 2001a). Furthermore, even if inorganic S pools are large enough to explain a cumulative net loss, this does not exclude underlying SO_4 release from other processes.

Excess *mineralisation* of organic S (mineralisation > immobilisation and uptake) in soils is another process leading to net release of SO_4 to soil solution and run-off. The factors regulating excess mineralisation and the influence of decreased deposition is not yet clear. Stable S isotopes, however, provide a tool for distinguishing between flow paths and processes within ecosystems. Stable isotope investigations have shown a contribution of S mineralisation to stream water SO_4 in several of the catchments; Lehstenbach (Alewell and Gehre, 1999), Gårdsjön (Torssander and Mörth, 1998), Villingen and Schluchsee (Mayer *et al.*, 1995) as well as in two catchments in the Czech Republic (Novak *et al.*, 1995). The stable isotope signature of S, however, can only point to the occurrence of processes and will not yield quantitative estimates of net loss or retention rates. Excess S mineralisation must certainly be considered for the catchments Schluchsee and Risdalsheia, where a comparison of cumulative fluxes over the last decade demonstrated that the organic pool most likely functions as a SO_4 source (Alewell, 2001b). In the Schluchsee catchment, however, snowfall is an important part of the total precipitation and SO_4 input fluxes in snow are difficult to quantify. This might lead to an underestimation of input fluxes and, thus, account partly for the negative budgets observed at Schluchsee.

Reduction of S compounds is another mechanism by which S can be stored in catchments. The *oxidation* of these compounds can provide a net release of SO_4 to run-off. Reduction is a significant sink at Lehstenbach (Alewell and Gehre, 1999) and Schluchsee (Feger *et al.*, 1999). Oxidation of reduced S takes place when the water table decreases and oxygen-saturated water infiltrates formerly anaerobic zones. The result is a high temporal variability of SO_4 retention and release throughout the year. According to Dillon and LaZerte (1992) oxidation of formerly reduced S can function as a long-term source, thus delaying a reduction of SO_4 concentrations in stream water at sites with significant pools of reduced S. As long as climate conditions (water regime and soil temperature) are stable, however, S reduction/oxidation cycles should not influence the long term trends of SO_4 concentrations and fluxes in streams.

Sulphate release from *weathering* of S-containing minerals is a significant source in some areas and might have been underestimated in the past as has been shown for eastern North America (Mitchell *et al.*, 2001). Weathering probably supplies a significant fraction of the S in the Italian catchments investigated. Boggero *et al.* (1996) suggested that weathering is a S source at Cannobino. Since the bedrock in Pescone and Pellino are similar to Cannobino (Table 1b), a contribution of weathering of S-containing minerals to SO_4 net loss from these catchments is also likely. This might explain the relatively high output flux compared to the input flux at Pescone (Fig. 4). A quantitative estimate of the relative importance of S weathering rates versus the contribution of mineralisation and desorption will be important for a prediction of SO_4 release from the Italian catchments. The relatively high uncertainty of the input fluxes to Italian catchments (estimation of dry deposition) makes S budgets difficult to estimate.

The contribution of weathering of S-containing minerals to the overall SO_4 net loss from catchments should not influence trends as long as weathering rates can be assumed to be stable over time. An increase in S weathering rates would be expected with higher temperatures due to, for example, global warming. A soil survey is planned for the Italian catchments in the year 2001 which will give more insight to S pools and dominant processes regulating SO_4 release at these catchments.

Conclusions

The 20 European catchments in this study indicated a delayed reduction in stream water SO_4 concentration and fluxes in central Europe in response to decreased SO_4 deposition with the exception of the Scandinavian catchments where the response in stream water concentrations and fluxes is relatively quick. Although most catchments showed a significant reduction in SO_4 concentration in surface waters (and thus reversal of acidification), at several central European catchments this reduction is not yet reflected in the annual SO_4 output fluxes. These catchments, with deeply weathered soils and high SO_4 storage, have a net release of S in response to decreased levels of deposition. Sulphate output fluxes at these sites respond later to the deposition change than in catchments with thin soils and relatively low storage capacity, such as those in Scandinavia and the Czech Republic/Slovakia. Sulphate release exceeded input in most catchments since the late 1980s and the early 1990s and this net loss continues. As a consequence, loss of base cations from soils as well as soil and water acidification, can be expected to continue in acidified catchments.

Predictions of time scales of reversibility of acidification are dependent on soil S pools and their dynamics. At present it remains difficult to differentiate clearly between processes and pools responsible for net SO_4 release into surface waters. Investigation of inorganic and organic S pools and fluxes, weathering rates of S-containing minerals and the contribution of wetland areas (S reducing zones) to stream run-off are required.

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