

## Sulphate-mediated phosphorus mobilization in riverine sediments at increasing sulphate concentration, River Spree, NE Germany

DOMINIK ZAK\*, ANDREAS KLEEBERG and MICHAEL HUPFER

*Leibniz-Institute of Freshwater Ecology and Inland Fisheries (IGB), Central Chemical Laboratory, Müggelseedamm 301, 12587 Berlin, Germany; \*Author for correspondence (e-mail: zak@igb-berlin.de; phone: +49-30-64181-730; fax: +49-30-64181-682)*

Received 22 August 2005; accepted in revised form 8 January 2006

**Key words:** Eutrophication, Internal P load, Iron-bound P, P mobilization rates, Sulphate reduction

**Abstract.** The study focuses on the response of a sulphate rich lowland river (River Spree) to a further increase in sulphate concentration as a result of mining activities in its catchments. It was hypothesized that riverine sediments could be conservative against an increase in sulphate concentration relating to both the intensity of sulphate reduction and the accompanying P mobilization. The usually lower amount of organic matter, compared to lakes or wetlands, and the high contents of iron oxides in the Spree sediment from discharged mining waters should counteract an enhanced P mobilization. Three short-term incubation experiments were carried out to test the sensitivity of different sediment horizons (0–10, 10–20 and 20–30 cm), the influence of temperature (5 and 25 °C) and the effect of a rising sulphate concentration (2.6–7.8 mM) on P mobilization rates (PMR) and sulphate reduction rates (SRR). Contrary to our initial hypothesis sulphate played a key role for P mobilization in riverine sediments because (1) all sulphate treated horizons showed a significant increase in pore water P concentrations, (2) increasing sulphate concentrations led to rising SRR and PMR, (3) the highest response on sulphate-mediated P mobilization was observed by a temperature enhancement of 20 °C. PMR increased one order of magnitude at all tested sulphate concentrations, but these increases in PMR only slightly effected the P concentrations in the overlying water. In conclusions, an increase of internal P load is only expected in case of doubling the recent *in situ* sulphate concentrations, but extended warm periods as an effect of climate change or increasing temperature, respectively, could be of more importance.

### Introduction

In the middle of the last century, it was postulated that enhanced sulphate concentrations will increase the mobilization of phosphorus (P), consequently supporting the eutrophication of surface waters (Ohle 1938; Hasler and Einsele 1948). Several studies of marine systems, lakes and wetlands confirmed this relation (Caraco et al. 1993; Urban 1994; Roden and Edmonds 1997; Lamers et al. 1998; Lucassen et al. 2004). The sulphate-induced P mobilization is explained mainly by the formation of iron (Fe) reducing sulphides through sulphate reduction. As a result, soluble ferrous iron becomes fixed as insoluble iron sulphides, and formerly immobile phosphate is released. Along with this pathway, it is possible that P can be directly mobilized either from organic compounds via sulphate reduction or by microbial reduction of ferric oxides to ferrous oxides. Hence, the effects of sulphate on P mobilization depend on the saturation of Fe-hydroxides with P, the availability of both organic matter as electron donor and reducible Fe compounds or sulphate (as electron acceptors). Especially in deeper layers of the sediment, the mobilization of Fe and organic bound P can be limited by the penetration depth of sulphate or by the availability of decomposable organic matter (Holmer and Storkholm 2001).

The lack of knowledge regarding the sensitivity of inorganic and organic substances involved in P mobilization processes, along with simultaneous occurring complex retention processes, each of varying importance in different systems, complicates the prediction of the net P mobilization (Sinke et al. 1992; Holmer and Stockholm 2001). Furthermore, findings on sulphate-mediated P mobilization in riverine sediments are inadequate or absent. In particular, the small amounts of organic matter in riverine sediment compared to lacustrine or peaty sediments, lead to the assumption that sulphate reduction could be limited by the availability of organic matter. Moreover, the high contents of Fe-oxides/hydroxides in riverine sediments favour the adsorption of phosphates and other anions, at least at the sediment–water interface (Boström et al. 1988). For these reasons, we studied the lowland river Spree because it is strongly influenced

by a high loading of metals and sulphate from lignite mining activities in its catchment (Grünewald 2001; Gelbrecht et al. 2002). Current sulphate levels in the River Spree are already one order of magnitude higher than freshwaters regarded as sulphate-rich (Caraco et al. 1993; Holmer and Storkholm 2001). The sulphate concentration should increase further due to the discharge of sulphate-rich water originating from numerous recently emerged acid mining lakes (more than 400, with a total area of several thousand ha) in the catchment area of the river via ground water. The sulphate concentration into these newly formed lakes reaches more than 10.4 mM (Grünewald 2001). Thus, the objective of our study is to emphasize the influence of increasing sulphate concentrations on: (1) P mobilization in different sediment horizons with varying contents of organic matter, (2) P mobilization at two temperatures, and (3) the intensity of sulphate reduction and concomitant P mobilization.

## Materials and methods

### Sampling site

River Spree, NE Germany, is a medium-sized lowland river with a catchment area of about 10,000 km<sup>2</sup>. The river rises at an elevation of 580 m, and flows for 400 km to Berlin through several shallow lakes, and is affected by river regulation. A detailed description of River Spree and its tributaries and lakes, is given by Köhler (1994). The sampling site Kossenblatt (14° E, 52°07' N) belongs to a 21.1 km long sixth-order section of the river which, connects two lakes and represents a slower flowing (0.1–0.3 m s<sup>-1</sup>) stretch of the Krumme Spree (Figure 1). The slope of the trapezoid profile amounts to 0.01%, and the runoff ( $Q$ ) usually varies between 12 and 16 m<sup>3</sup> s<sup>-1</sup>. At average  $Q$  the mean water depth is 1.5–2.5 m (Bungartz and Wanner 2004). An overview about the chemical water parameters of the section Kossenblatt is given in Table 1. Since the abrupt decrease of coal mining in the Lusatia region (middle stream catchment area of the River Spree) the sulphate concentrations increased 1.4 times from 1.7 mM in 1991 to 2.4 mM in 2000 (Figure 2). Further distinct increases are expected once ground water returns to its original levels because discharge from adjacent mining lakes and formerly drained wetlands into the river will occur. Contrary to sulphate; the total input of P was reduced by 68% in the last two decades, due to an effective reduction of point sources. However, wastewater treatment plants are still the dominant pathway for P input (47%), followed by urbane areas (18%), groundwater (15%) and erosion (12%) (Behrendt 2002).

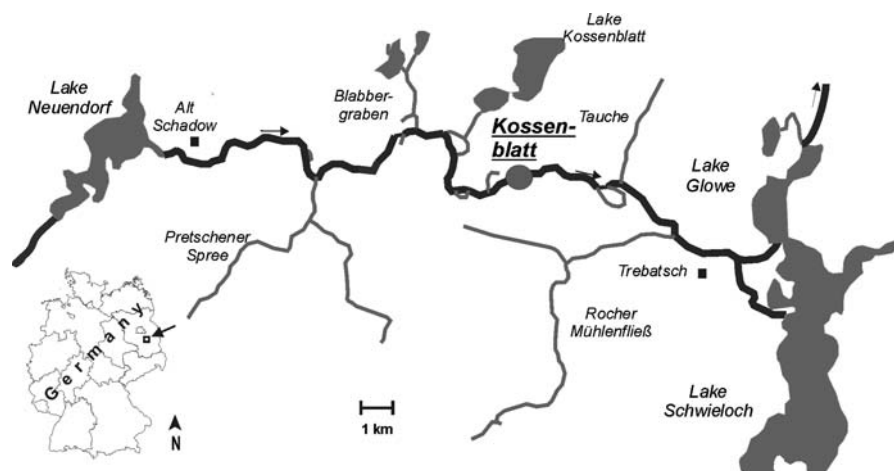


Figure 1. Sampling location Kossenblatt in the midstream section of River Spree.

Table 1. Water chemistry data of the study site Kossenblatt, which was sampled biweekly to monthly between 1993 and 2001 (Sulphate data from 1996 to 2001 were provided by the ‘Landesumweltamt Brandenburg’).

	SRP ( $\mu\text{M}$ )	Total P ( $\mu\text{M}$ )	$\text{SO}_4^{2-}$ (mM)	$\text{NO}_3^-$ (mM)	DOC (mM)	$\text{O}_2$ (%)	pH	Cond. ( $\mu\text{S cm}^{-1}$ )	Temp ( $^\circ\text{C}$ )
Min	0.1	1.1	1.1	<0.01 <sup>a</sup>	0.3	40	7.1	613	0
Max	1.6	6.5	3	0.1	0.8	142	9.2	867	26
Mean	0.9	3.8	2.1	0.05	0.6	91	8.2	740	13

DOC, dissolved organic carbon; Cond., electrical conductivity.

<sup>a</sup> Detection limit.

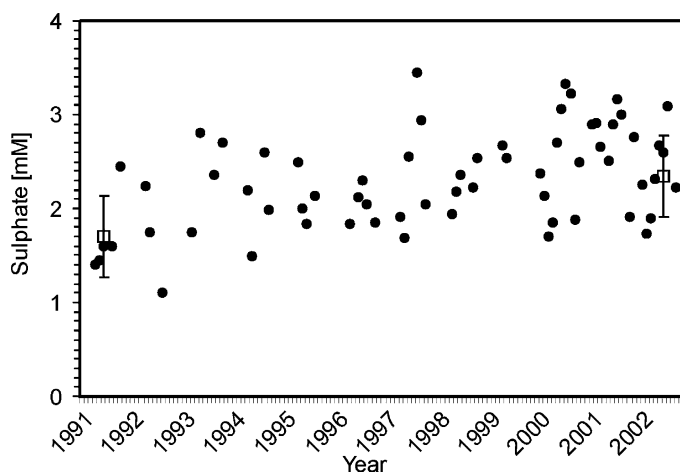


Figure 2. The increase of sulphate concentration in the midstream section of River Spree since 1991. For the years 1991 and 2001 the means  $\pm$  SD are given ( $n = 5; 10$ ).

### Sampling and experimental set-up

At each sampling occasion, between 20 and 30 sediment cores (diameter 5.5 cm) were collected with a modified Kajak sampler (UWITEC®) in autumn 2001 and in spring and autumn of 2002. Immediately after sampling, the sediment cores were either cut into 10 cm layers or the whole cores were pooled into containers.

Each wet sediment sample was placed into Perspex column together with river water from the sediment location (Figure 3). Before the treatment, the sediments were incubated for 2–3 weeks to compensate for possible disturbances. The three incubation experiments were run in darkness. The influence of varied conditions on the pore water were investigated by means of dialyses samplers, so called peepers (Hesslein 1976). Dialysis samplers are thin Perspex plates covered by a 0.2  $\mu\text{m}$  polysulfone membrane (HT-Tuffryn 200®, Pall®, Gelman Laboratory) with chambers filled with deionized water. The exposure time of the sampler in the sediment was at least 7 days to guarantee an equilibrium between the concentrations of dissolved substances in the pore water and the chamber water.

### Sulphate sensitivity of different sediment horizons (INC I)

Three sediment horizons (0–10, 10–20 and 20–30 cm) were separately incubated in two columns each. Dialysis samplers were introduced into the homogenized sediments so that three chambers with a total distance of 10 cm were exposed in the sediment (Figure 3a). The chambers of dialysis sampler were filled

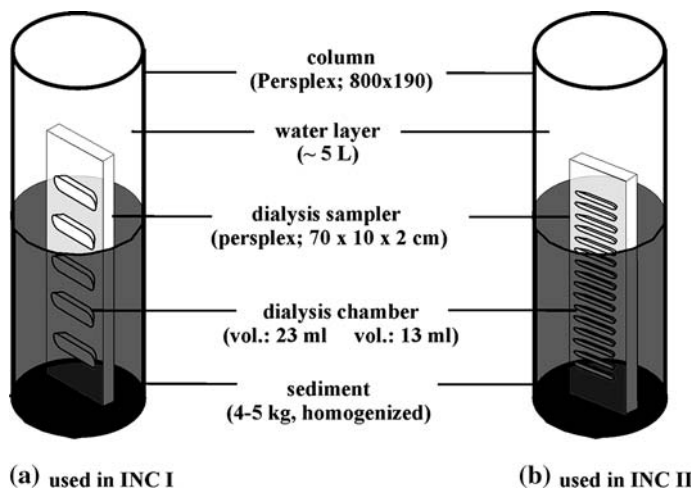


Figure 3. Sediment columns for the two incubation experiments to test the sulphate-mediated P mobilization: (a) in different sediment horizons (0–10, 10–20, 20–30 cm); three sediment chambers as source of sulphate and to control the P concentration; (b) testing different sulphate concentration in the surface water at water temperatures of 5 and 25 °C. Dialysis samplers allow determination of vertical concentration profiles (1 cm scale) of sulphate and phosphate for further calculations.

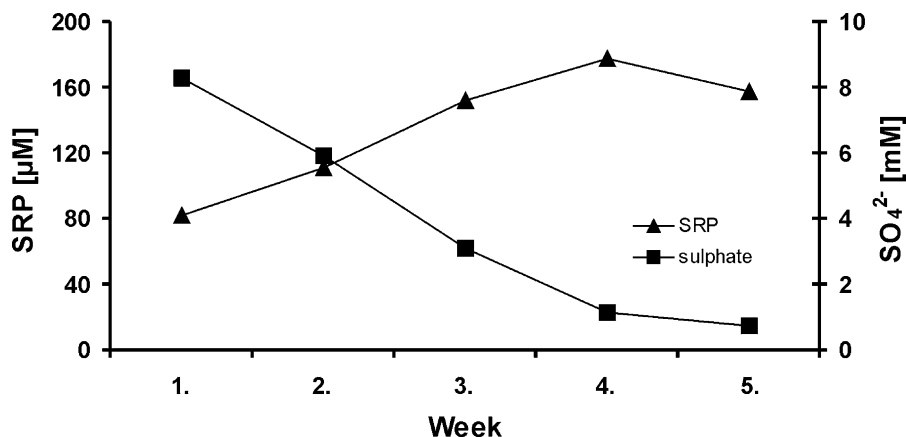


Figure 4. Preliminary investigations on the course of SRP and sulphate concentrations in the pore water in sulphate amended sediments for the 0 to 30 cm horizon (mean,  $n = 2$ ) over an incubation period of 5 weeks. Sampling started 1 week after sulphate treatment (introduction of the dialysis samplers with five chambers as ‘sulphate batteries’: Vol.:  $5 \times 23$  ml, sulphate concentrations:  $\sim 10$  mM). According to these results, the incubation period for INC I was set up 4 weeks.

either with deionized water (control) or with  $\text{Na}_2\text{SO}_4$  solution (sulphate approach). Sulphate application via dialysis chambers allowed a direct and consistent supply throughout sediment layer. Sulphate concentrations of the single chambers were about 7 mM. Following the preliminary investigations, where the soluble reactive P (SRP) concentrations and sulphate were measured once a week for 5 weeks (Figure 4), the samplers were recovered after 4 weeks and the three ‘sediment chambers’ were sampled. A recovery of samplers for the weekly sampling in the time course experiment, as proposed by Jacobs (2002) through the use of rechargeable dialysis samplers, was not necessary.

#### *Influence of temperature and rising sulphate concentrations (INC II a, INC II b)*

Sediment from the 0 to 30 cm horizon (taken in spring of 2002) was placed in 8 columns: 4 different sulphate concentrations at 5 and 25 °C, respectively (INC II a). 12 columns, 3 replicates of 4 different

sulphate concentrations, were also prepared with the sediment from the 0 to 30 cm horizon collected in autumn 2002 (INC II b). The initial sulphate concentrations in the overlying water were adjusted between 1.6 and 6.8 mM in INC II a and between 2.6 and 7.8 mM in INC II b. The penetration depth of sulphate and of SRP into the pore water was determined by a 2 week incubation with dialysis samplers with a vertical resolution of 1 cm (Figure 3b).

### *Chemical analysis*

The chamber water of dialysis samplers was taken with a multipipette (Eppendorf). Oxidative changes of the redox-sensitive samples were avoided through fast sampling and fixation. SRP was measured by the molybdenum blue method (Varian, Cary 1E). Total dissolved Iron ( $\text{Fe}_T$ ) was analysed by flame atomic absorption spectrometry (Perkin Elmer, 3300) and  $\text{SO}_4^{2-}$  by ion chromatography (Shimadzu).

Before the single incubation experiments were started, sedimentary P species were determined by a sequential extraction scheme according to Psenner et al. (1984) with slight modifications (Hupfer et al. 1995). With this procedure, the following P binding forms are separated: Loosely-adsorbed P ( $\text{NH}_4\text{Cl-P}$ ); reductant-soluble P mainly bound to Fe-hydroxides (BD-P); P bound to Fe- or Al-oxides (NaOH-SRP), organic P and Poly-P (NaOH-NRP) and Ca bound P (HCl-P). Concentrations of non-reactive P (NRP) in the NaOH extract were calculated as the difference between total P and SRP. Total P content of solid material was determined as SRP after digestion in a solution of 2 ml 10 M  $\text{H}_2\text{SO}_4$ , 2 ml 30%  $\text{H}_2\text{O}_2$ , and 20 ml deionized water at 160 °C for 8 h. The organic content of sediment was determined as loss on ignition (450 °C, 3 h).

### *Calculations*

The net sulphate reduction rates (SRR) and P mobilization rates (PMR) were determined from the vertical concentration profiles of sulphate and phosphate, assuming that phosphate equals SRP. The rates are yielded by the statistical program Profile V1 (Berg et al. 1998). The program uses Fick's first law of diffusion, and it also considers the biodiffusivity and bioirrigation. The sediments used were free of macrozoobenthos, so that these variables could be set up to zero. Diffusion constants for phosphate and sulphate at defined conditions (5 and 25 °C; pH:  $\sim 7$ ) are obtained from Li and Gregory (1974) and Furrer and Wehrli (1996), respectively. The porosity of the sediment layer was estimated from its percentage of water, and inorganic and organic constituents (Lewandowski et al. 2002). Statistical tests were done by ANOVA (Excel 2000; *t*-test: two-sample assuming unequal variances).

## **Results**

### *Sediment characteristics*

The P fractionation of the sediment used for the laboratory experiments reveals the dominance of metal bound P (Figure 5). The proportion of organic P (NaOH-NRP) ranged only between 2 and 5% of TP. Loosely-adsorbed P ( $\text{NH}_4\text{Cl-P}$ ) was in most cases below 1% of TP and is thus no longer considered. Comparing the different sediment layers (0–10, 10–20 and 20–30 cm), it is apparent that concentrations of P bound to Fe-hydroxide (BD-P) and, to minor extent, the organic P (NaOH-NRP) were higher in the upper horizon than in the horizon below. The P fractions of the two deeper layers are rather similar (Figure 5). The relative proportion of metal oxide bound P (NaOH-SRP) increased with depth. Organic matter content decreased from 11% in the upper layer to 5% in the lowest layers (November 2001; Table 2).

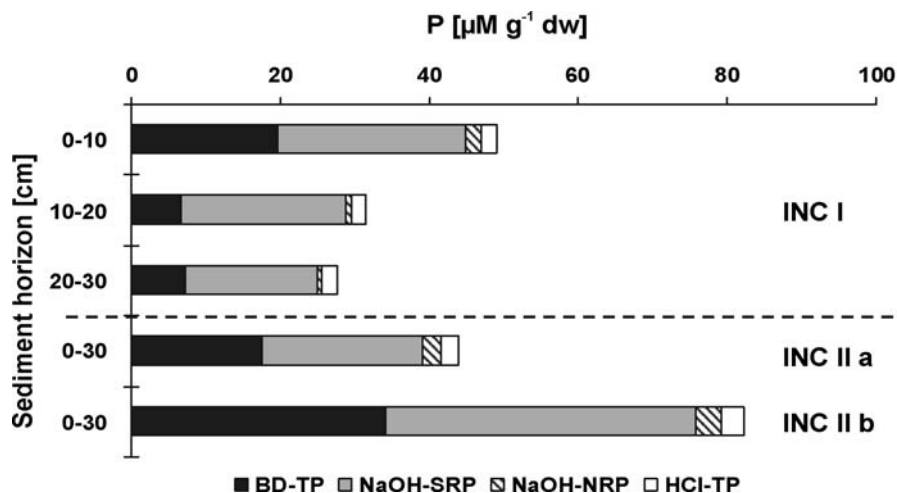


Figure 5. Fractional P composition of sediments from the Kossenblatt section of River Spree taken in November 2001 (INC I), April (INC II a) and November 2002 (INC II b) (BD-P, NaOH-SRP, NaOH-NRP, HCl-P; for an explanation of fractions, see methods).

Table 2. Content of Fe(III)-hydroxides (BD-Fe) and crystalline Fe(III)-oxides (HCl-Fe) in the sediments used in incubation experiments (INC I, INC II a + b).

Experiment	Sampling date	Horizon (cm)	Fe ( $\mu\text{mol g}^{-1} \text{ dw}$ )		Fe:P (molar)		OM <sup>a</sup> (%)
			BD	HCl	BD	HCl:NaOH	
INC I	Nov./01	0–10	101	340	5.1	13.5	11
		10–20	30	230	4.6	10.5	6
		20–30	33	190	4.6	10.7	5
		Mean $\pm$ SD	55 $\pm$ 40	285 $\pm$ 78	4.8 $\pm$ 0.3	11.6 $\pm$ 1.7	7 $\pm$ 3
INC II a	Apr./02	0–30	62	273	3.4	12.4	9
	Nov./02	0–30	91	451	2.7	10.8	13

The molar Fe:P ratio of amorphous Fe(III)-hydroxides (BD-Fe:BD-P) and of crystalline Fe(III)-oxides (HCl-Fe:NaOH-SRP) are also given.

<sup>a</sup> Content of organic matter (OM) determined as loss on ignition.

The total P content of the homogenized sediments collected in autumn 2002 was nearly twice as high as those taken in spring 2002 (Figure 5). Furthermore, the highest organic matter content was found in the sediment taken in autumn 2002, 13% as compared to 9% for sediment taken in spring 2002 (Table 2). Molar Fe:P ratios of amorphous Fe(III)-hydroxides from the sediment BD extracts ranged from 2.7 to 5.1, with lowest values in the autumn 2002 sediment. Compared to amorphous Fe(III)-hydroxides, a higher proportion of Fe (about 3- to 8-fold more) was found in the HCl extracts, which represent the crystalline Fe(III)-oxides (Table 2). The Fe:P ratios of the crystalline Fe species are slightly higher than 10.

The composition of the P binding forms, as well as other sediment characteristics of the experimental sediments, are representative for other middle stream locations of the River Spree (data not shown).

#### *Sulphate sensitivity of different sediment horizons (INC I)*

The enhanced availability of sulphate led to a significant increase in SRP concentrations in the pore water. For all three horizons, the increase was in the range of 18–33  $\mu\text{M}$  compared to the controls (Figure 6). The average increase of SRP concentrations in the upper horizon was slightly higher, but surprisingly, it was not significantly different from the increase in the lower horizons. This indicated a similar net P mobilization in

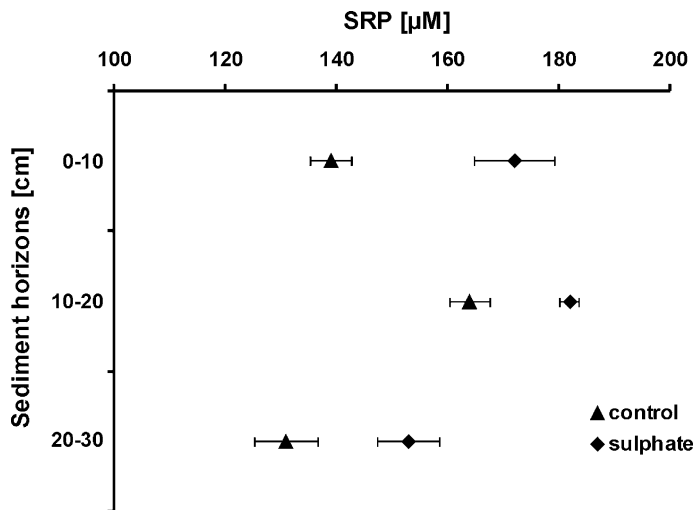


Figure 6. SRP concentration (means  $\pm$  1 SE;  $n = 3$ ) in the pore water of sulphate amended horizons (squares) compared to the controls (triangles). SRP concentrations in the controls are always significantly lower ( $p < 0.05$ ).

all horizons during the incubation period. In all approaches, the SRP concentrations reached 180  $\mu\text{M}$  on average, which is in good accordance with the preliminary investigation about the time course of P and sulphate concentrations (Figure 4). However, the sulphate concentrations were about 0.01 mM at the end of the experiment, in contrast to the relatively high concentrations (1 mM) found in the preliminary investigation.

#### *Influence of temperature and rising sulphate concentrations (INC II a, INC II b)*

For the vertical SRP concentration profiles at 5 and 25  $^{\circ}\text{C}$ , the effect of enhanced sulphate concentrations in the overlying water is shown for INC II a in Figure 7. The resulting PMR are one order of magnitude higher at 25  $^{\circ}\text{C}$  compared to 5  $^{\circ}\text{C}$  (Table 3). Temperature effects aside, the PMR were only slightly enhanced with increasing sulphate concentrations. A significant increase was observed only at highest tested sulphate concentration of 7.8 mM (Table 4). It is worth mentioning that the PMR at highest sulphate concentrations in INC II a (6.8 mM, 25  $^{\circ}\text{C}$ ) is still lower than the rates of the INC II b at much lower sulphate concentrations (2.6 mM, 25  $^{\circ}\text{C}$ ; see Tables 3 and 4).

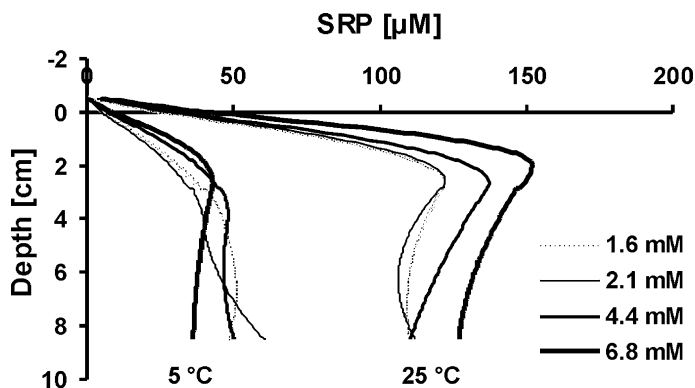


Figure 7. Statistically tested SRP concentration profiles with increasing sulphate concentrations in the overlying water (1.6–6.8 mM) as basis for calculation of P mobilizing rates by Profile VI (Berg et al. 1998) at 5 and 25  $^{\circ}\text{C}$ .

Enhanced sulphate concentrations in the overlying water of INC II a and INC II b did not lead to any substantial enlargement of the penetration depth (only about 1 cm) and had no significant effects on extending the P mobilizing horizon at temperature of 25 °C (Tables 3 and 4). Furthermore, a significant increase of the net sulphate consumption (about 3-fold higher compared to the initial concentrations) was observed only at highest sulphate concentrations of 7.8 mM.

The Fe:P ratios in the pore water of the upper sediment layer (0.5–1.5 cm), which is closed to the redox interface, were similar in all approaches, ranging from 2.2 to 2.7. The P concentrations in the overlying water, which remained aerobic during incubation period, tended to increase with enhanced sulphate concentrations; however, the increases were not significant (Table 5).

*Table 3.* Net P mobilization rate (= PMR; integrated over the P mobilizing horizon), extension of the P mobilizing horizon and penetration depth of sulphate ( $\geq 0.01$  mM) depending on the water temperature at different sulphate concentrations in the overlying water (INC II a).

Sulphate (mM)	Net PMR <sup>a</sup> (mmol P m <sup>-2</sup> d <sup>-1</sup> )		Extension of P mobilizing horizon <sup>a</sup> (cm)		Penetration depth of sulphate (cm)	
	5 °C	25 °C	5 °C	25 °C	5 °C	25 °C
	1.6	0.03	0.32	4.3	2.8	4.5
2.1	0.03	0.34	4.3	2.8	4.5	2.5
4.4	0.05	0.35	4.3	2.8	4.5	2.5
6.8	0.06	0.48	2.8	2.1	6.5	2.5

<sup>a</sup> Values are calculated with Profile V1 (Berg et al. 1998).

*Table 4.* Net P mobilization rate (= PMR; integrated over the P mobilizing horizon) and net SO<sub>4</sub><sup>2-</sup> consumption rates (integrated until the penetration depth of sulphate), the extension of the P mobilizing horizon and the penetration depth of sulphate ( $\geq 0.01$  mM) depending on different initial sulphate concentrations in the overlying water (INC II b).

Sulphate (mM)	Net PMR <sup>A</sup> (mmol m <sup>-2</sup> d <sup>-1</sup> )	Net SO <sub>4</sub> <sup>2-</sup> consumption <sup>A</sup> (mmol m <sup>-2</sup> d <sup>-1</sup> )	Extension of P mobilizing horizon <sup>A</sup> (cm)	Penetration depth of sulphate (cm)
2.6	0.53 ± 0.04 <sup>a</sup>	10.4 ± 2.1 <sup>a</sup>	3.7 ± 0.5 <sup>a</sup>	3.2 ± 0.3 <sup>a</sup>
3.6	0.55 ± 0.06 <sup>a, c</sup>	15.6 ± 3.1 <sup>a</sup>	3.4 ± 0.7 <sup>a</sup>	3.5 ± 0 <sup>a</sup>
5.2	0.58 ± 0.03 <sup>a</sup>	13.5 ± 2.1 <sup>a</sup>	3.6 ± 0.6 <sup>a</sup>	4.5 ± 0 <sup>b</sup>
7.8	0.66 ± 0.03 <sup>b, c</sup>	28.1 ± 4.2 <sup>b</sup>	2.9 ± 0.3 <sup>a</sup>	4.5 ± 0 <sup>b</sup>

Means ± 1SE,  $n = 3$ . Within columns, values with the same letters are not significantly ( $p < 0.05$ ) different from each other.

<sup>A</sup> Values are calculated with Profile V1 (Berg et al. 1998).

*Table 5.* Concentration of soluble reactive P (SRP) and initial SO<sub>4</sub><sup>2-</sup> concentration in the overlying water at 25 °C (means ± 1SE,  $n = 3$ ) as well as the molar Fe:P ratio of the pore water of the upper sediment (0.5–1.5 cm) of incubation experiment INC II a and b.

Experiment	Overlying water		Pore water
	SO <sub>4</sub> <sup>2-</sup> (mM)	SRP (μM)	Fe:P ratio (molar)
INC II a	1.6	2.9	2.7
	2.1	3.6	2.3
	4.4	4.6	2.4
	6.8	5.2	2.5
INC II b	2.6	1.0 ± 0.06 <sup>a</sup>	2.5 ± 0.2 <sup>a</sup>
	3.6	1.2 ± 0.13 <sup>a</sup>	2.5 ± 0.2 <sup>a</sup>
	5.2	1.1 ± 0.05 <sup>a</sup>	2.2 ± 0.1 <sup>a</sup>
	7.8	1.5 ± 0.22 <sup>a</sup>	2.4 ± 0.1 <sup>a</sup>

Within columns, values with the same letters are not significantly ( $p < 0.05$ ) different from each other.



## Discussion

Sulphate-mediated P mobilization is the finding of several studies focusing mainly on lakes and wetlands (Caraco et al. 1989; Roden and Edmonds 1997; Lamers et al. 1998; Lucassen et al. 2004). In contrast to these systems, the riverine sediments studied here are poor in organic matter (5–13%) and thus decomposition processes, such as sulphate reduction and concomitant P mobilization, were hypothesized to be limited by the availability of decomposable organic matter. However, the SRR determined in this study are within the range of those of other systems such as lakes and wetlands (Table 6).

Contrary to the initial assumption, the sulphate reduction in the investigated sediment of River Spree was not limited by the availability of decomposable organic matter. First, sulphate had disappeared nearly completely in all investigated horizons of INC I within the incubation period, and second, the penetration depth of sulphate was not further enhanced despite strongly elevated sulphate concentrations in the overlying water of INC II a and INC II b. Consequently, the sulphate reduction during the incubation periods was limited by diffusion of sulphate, rather than controlled by the availability of decomposable organic matter, which is consistent to the findings of Sinke et al. (1992).

Although strongly elevated sulphate concentrations generally led to comparatively low increases of the PMR, the results clearly confirm the dependence of P mobilization on sulphate reduction processes. First, P concentrations increased significantly in all sulphate-treated horizons of INC I. Second, the P mobilizing horizon is in good accordance to the penetration depth of sulphate (Tables 2 and 3). Thus, in the lower, sulphate free horizons, negative PMR were calculated (results are not shown).

The weak P response under enhanced sulphate concentrations does not seem to be reasonable. According to the findings of Gunnars et al. (2002), the Fe(III)-hydroxides in River Spree sediments (molar Fe:P ratios in the BD-extract range between 2.7 and 5.1) are more or less saturated with P. Consequently, a further reduction of these compounds through hydrosulphides (as a product of sulphate reduction) should be accompanied by a 'very effective' mobilization of the Fe bound P. In other words, the sediments studied, should be very sulphate (or sulphide) sensitive regarding P mobilization. Indeed, we found high PMR (0.32–0.53 mmol P m<sup>-2</sup> d<sup>-1</sup>) at the high initial experimental sulphate concentrations (*in situ* concentrations), which is consistent to other studies (Caraco et al. 1993; Smolders and Roelofs 1993; Kleeberg 1997). The reasons, that sulphate increases had only a slight impact on the PMR can be manifold. Thus, large portions of the gross mobilized P may be retained, for example, by adsorption to reactive surfaces of metal oxides and/or microbial uptake (e.g. Boström et al. 1988). Additionally, only part of the hydrosulphide formed is able to react with the redox-sensitive Fe compounds, because these compounds can be preserved, for example by coating with Fe sulphides (De Vitre et al. 1988).

Overall, significant increases of PMR were found only in samples with the highest sulphate concentrations and/or higher temperature of 25 °C. The observed temperature effect is in good accordance to the rule of van't Hoff (RGT-rule); thereafter, an increase of 10 °C enhances turnover rates by a factor of about 2–3,

Table 6. Span of benthic sulphate reduction rates (SRR) at different concentrations of sulphate (SO<sub>4</sub><sup>2-</sup>) in marine and acid as well as neutral freshwater systems.

System	pH	SO <sub>4</sub> <sup>2-</sup> (mmol l <sup>-1</sup> )	SRR (mmol m <sup>-2</sup> d <sup>-1</sup> )	<i>n</i>	Reference
Mining lakes	3–6	3.3–21.0 <sup>a</sup>	1.2–5.2	4	Blodau et al. (1998)
Lakes	8–9	1.1–3.1 <sup>b</sup>	0.9–8.3 <sup>c</sup>	8	Kleeberg (1998)
Lakes	–	0.03–20.0 <sup>b</sup>	0.02–450	27	Cook and Kelly (1992)
Lakes	7–9	0.03–20.0 <sup>b</sup>	0.1–35.6	835	Urban (1994)
Lakes	8–9	0.07–0.2 <sup>b</sup>	0.1–7.4	6	Holmer and Storkholm (2001)
Marine systems	~7	28 <sup>b</sup>	0.2–438	103	Urban (1994)
River Spree	7–8	2.6–7.8 <sup>b</sup>	10.4–28.1	4	Table 3, this study

<sup>a</sup> Sediment pore water.

<sup>b</sup> Water overlying sediment.

<sup>c</sup> Hypolimnetic – benthic SRR, i.e. mass balance approach.

considering that mobilizing processes are not further limited. In our case, at 20 °C increased temperature, the rates increased by the factor 7–10.

It is also interesting to compare the PMR of INC II a and INC II b. The times of sediment collection (spring sediment vs. autumn sediment) had a higher impact on PMR than the increasing sulphate concentrations. The PMR in INC II b at the lowest considered sulphate concentration was distinctly higher than the PMR in INC II a, which had a 4.2 mM higher sulphate concentration. Two possible explanations are a significantly higher organic and inorganic P content of the autumn sediment, or the very low molar Fe:P ratio (2.7) of the sediment. However, it supports explicitly the important role of the specific sediment for the intensity of P mobilization processes (Sinke et al. 1992).

Despite the high PMR in sulphate treated sediments, the P concentrations in the overlying water are only slightly influenced. Likewise, at significantly enhanced PMR, only slight increases of phosphate concentration were observed. Apparently, there is still sufficient ferrous iron at the sediment–water interface to effectively retain P through precipitation of Fe-oxides/hydroxides. Accordingly, the critical values for Fe:P ratios in Spree sediment pore water are about 3 and less (Nürnberg 1988; Jensen et al. 1992). In the case of further high sulphate reduction, the surplus of hydrosulphides could diminish the already low pore water Fe:P ratio (Caraco et al. 1993; Smolders and Roelofs 1993). This would result in an acceleration of P release at the sediment–water interface. However, the Fe:P ratios in our experiments are similar at all tested sulphate concentrations, which may be attributed to the short incubation time.

In conclusion, contrary to the initial hypothesis, the sediment of the studied river section was found to be sensitive against increasing sulphate concentrations and concomitant P mobilization. It can be explained by both the presence of sufficient amounts of decomposable organic matter (also in deeper sediment layers) as a basis for sulphate reduction and the saturation of redox-sensitive Fe compounds with P. For a short-term, an increase of internal P load is likely only in the case of distinctly rising sulphate concentrations, which are more than double the recent *in situ* conditions. The long-term effect of slightly increasing sulphate concentrations remains hypothetical. However, the already critical Fe:P ratios in the sediment pore water ( $\leq 3$ ) could be further diminished and consequently lead to an enhanced P release into the surface water. Rather than changes of sulphate concentrations, extended warm periods or increasing average temperature could be of more importance.

## Acknowledgements

The authors thank all the colleagues of the Chemical Laboratory of the IGB supporting the comprehensive analysis of the major dissolved constituents: Hans-Jürgen Exner for the assistance of the AAS analyses, Christiane Herzog for the help with the P-fractionation procedure and Thomas Rossoll for the ion chromatographic measurements. Furthermore, we offer thanks to Bernd Schütze for his technical assistance during field work. Brian Payer (University of Stanford) is acknowledged for linguistic improvements of the text and two anonymous reviewers for the helpful comments to a previous version of the manuscript. The study was supported by the German Federal Ministry of Educations and Research (BMBF).

## References

- Behrendt H. 2002. Nutrient emissions from the Spree catchment – past and present. In: Köhler J., Gelbrecht J. and Pusch M. (eds), Die Spree – Zustand, Probleme und Entwicklungsmöglichkeiten. Limnologie aktuell, Bd. 10, Schweizerbarth, Stuttgart, pp. 62–73.
- Berg P., Risgaard-Petersen N. and Rysgaard S. 1998. Interpretation of measured concentration profiles in sediment pore water. *Limnol. Oceanogr.* 43(7): 1500–1510.
- Blodau C., Hoffmann S., Peine A. and Peiffer S. 1998. Iron and sulfate reduction in the sediments of acidic mine lake 116 (Brandenburg, Germany): rates and geochemical evaluation. *Water Air Soil Poll.* 108: 249–270.
- Boström B., Anderson J.M., Fleischer S. and Jansson M. 1988. Exchange of phosphorus across the sediment–water interface. *Hydrobiologia* 170: 229–244.

- Bungartz H. and Wanner S.C. 2004. Significance of particle interaction to the modelling of cohesive sediment transport in rivers. *Hydrol. Process.* 18(9): 1685–1702.
- Caraco N.F., Cole J.J. and Likens G.E. 1989. Evidence for sulphate-controlled phosphorus release from sediments of aquatic systems. *Nature* 341: 316–318.
- Caraco N.F., Cole J.J. and Likens G.E. 1993. Sulfate control of phosphorus availability in lakes. *Hydrobiologia* 253: 275–280.
- Cook R.B. and Kelly C.A. 1992. Sulphur cycling and fluxes in temperate dimictic lakes. In: Howarth R.W., Stewart J.W.B. and Ivanov M.V. (eds), *Sulphur Cycling on the Continents: Wetlands, Terrestrial Ecosystems and Associated Water Bodies*. J. Wiley & Sons, Chichester, pp. 145–188.
- De Vitre R.R., Buffle J., Perret D. and Baudat R. 1988. A study of iron and manganese transformations at the O<sub>2</sub>/S(-II) transition layer in a eutrophic lake (Lake Bret, Switzerland): a multimethod approach. *Geochim. Cosmochim. Acta* 52(6): 1601–1613.
- Furrer G. and Wehrli B. 1996. Microbial reactions, chemical speciation, and multicomponent diffusion in porewaters of a eutrophic lake. *Geochim. Cosmochim. Acta* 60(13): 2333–2346.
- Gelbrecht J., Exner H.J., Conradt S., Rehfeld-Klein M. and Sensel F. 2002. Water chemistry. In: Köhler J., Gelbrecht J. and Pusch M. (eds), *Die Spree – Zustand, Probleme und Entwicklungsmöglichkeiten*. *Limnologie aktuell*, Bd. 10, Schweizerbarth, Stuttgart, pp. 74–85.
- Grünwald U. 2001. Water resources management in river catchments influenced by lignite mining. *Ecol. Eng.* 17: 143–152.
- Gunnars A., Blomqvist S., Johansson P. and Andersson C. 2002. Formation of Fe(III) oxyhydroxide colloids in freshwater and brackish seawater, with incorporation of phosphate and calcium. *Geochim. Cosmochim. Acta* 66(5): 745–758.
- Hasler A.C. and Einsele W.G. 1948. Fertilization for increasing productivity of natural inland waters. *Trans. North. Amer. Wildl. Conf.* 13: 527–555.
- Hesslein C.H. 1976. An in situ sampler for close interval pore water studies. *Limnol. Oceanogr.* 21: 912–914.
- Holmer M. and Storkholm P. 2001. Sulphate reduction and sulphur cycling in lake sediments: a review. *Freshw. Biol.* 46: 431–451.
- Hupfer M., Gächter R. and Giovanoli R. 1995. Transformation of Phosphorus species in settling seston and during early sediment diagenesis. *Aquat. Sci.* 57(4): 505–524.
- Jacobs P.H. 2002. A new rechargeable dialysis pore water sampler for monitoring sub-aqueous *in-situ* sediment caps. *Wat. Res.* 36: 3121–3129.
- Jensen H.S., Kristensen P., Jeppesen E. and Skytthe A. 1992. Iron:Phosphorus ratio in surface sediment as an indicator of phosphate release from aerobic sediments in shallow lakes. *Hydrobiologia* 235/236: 731–743.
- Kleeberg A. 1997. Interactions between benthic phosphorus release and sulfur cycling in Lake Scharmützelsee (Germany). *Water Air Soil Poll.* 99: 391–399.
- Kleeberg A. 1998. The quantification of sulfate reduction in sulfate-rich freshwater lakes – a means for predicting the eutrophication process of acidic mining lakes? *Water Air Soil Poll.* 108(34): 365–374.
- Köhler J. 1994. Origin and succession of phytoplankton in a river–lake system (Spree, Germany). *Hydrobiologia* 289: 93–100.
- Lamers L.P.M., Tomassen H.B.M. and Roelofs J.G.M. 1998. Sulphate-induced eutrophication and phytotoxicity in freshwater wetlands. *Environ. Sci. Technol.* 32: 199–205.
- Lewandowski J., Rüter K. and Hupfer M. 2002. Two-dimensional small-scale variability of pore water phosphate in freshwater lakes: results from a novel dialysis sampler. *Environ. Sci. Technol.* 36: 2039–2047.
- Li Y.H. and Gregory S. 1974. Diffusion of ions in sea water and in deep-sea sediments. *Geochim. Cosmochim. Acta* 38: 308–313.
- Lucassen E.C.H.E.T., Smolders A.J.P., Van de Crommenacker J. and Roelofs J.G.M. 2004. Effects of stagnating sulphate-rich groundwater on the mobility of phosphate in freshwater wetlands: a field experiment. *Arch. Hydrobiol.* 160: 117–131.
- Nürnberg G.K. 1988. The prediction of phosphorus release rates from total and reductant soluble phosphorus in anoxic lake sediments. *Can. J. Fish. Aquat. Sci.* 45: 453–462.
- Ohle W. 1938. Die Bedeutung der Austauschvorgänge zwischen Schlamm und Wasser für den Stoffwechsel der Gewässer. *Vom Wasser* 13: 87–97.
- Psenner R., Pucsko R. and Sager M. 1984. Die Fraktionierung organischer und anorganischer Phosphorverbindungen von Sedimenten – Versuch einer Definition ökologisch wichtiger Fraktionen. *Arch. Hydrobiol. Beih.* 30: 43–59.
- Roden E.E. and Edmonds J.W. 1997. Phosphate mobilization in iron-rich anaerobic sediments: microbial Fe(III) oxide reduction versus iron-sulfide formation. *Arch. Hydrobiol.* 139(3): 347–378.
- Sinke A.J.C., Cornelese A.A., Cappenberg T.E. and Zehnder A.J.B. 1992. Seasonal variation in sulfate reduction and methanogenesis in peaty sediments of eutrophic Lake Loosdrecht, The Netherlands. *Biogeochemistry* 16: 43–61.
- Smolders A. and Roelofs J.G.M. 1993. Sulphate-mediated iron limitation and eutrophication in aquatic ecosystems. *Aquat. Bot.* 46: 247–253.
- Urban N.R. 1994. Retention of sulphur in lake sediments. In: Baker L.A. (ed.), *Environmental Chemistry of Lakes and Reservoirs*. *Adv. Chem. Ser.* 237: 323–369.