Sulphate sorption characteristics of the Bohemian Forest soils

Jiří Kaňa* & Jiří Kopáček

Faculty of Biological Sciences, University of South Bohemia, and Hydrobiological Institute, AS CR, Na Sádkách 7, CZ-37005 České Budějovice, Czech Republic *jiri.kana@centrum.cz

Abstract

Sulphate (SO₄-S) sorption characteristics were determined in soils from catchments of three acidified mountain lakes, Plešné (PL), Čertovo (CT), and Černé (CN), situated in the Bohemian Forest. The SO₄-S desorption ranged between 0.07–0.73, 0.21–0.68, and 0.39–0.82 mmol.kg⁻¹ in the PL, CT, and ČN catchments, respectively. SO₄-S desorption was observed to be higher in horizon A than in mineral horizons below. The SO₄-S represented only 3.4% of total S pool in the catchments and did not explain a relatively high rate of terrestrial leaching of sulphate over last 10 years. This disproportion suggests that the soil SO₄-S pool is being replenished from internal soil processes from the pool of total S. Sulphate sorption maxima in soils in the catchments of the Bohemian Forest lakes varied between 1.5–11.7 mmol.kg⁻¹, being highest in A-horizon and lowest in E-horizon.

Key words: acidification, recovery, soil chemistry

INTRODUCTION

The chemistry (and, consequently, biology) of mountain lakes is determined by amount of precipitation and their composition, bedrock (PSENNER & CATALAN 1994), catchment soils and vegetation (e.g. BARON et al. 1994), and hydrology (WETZEL 2002). Soil sorption characteristics may significantly affect water composition, e.g. the sulphate-sulphur (SO₄-S) concentration. Increased inputs of SO₄²⁻ into catchments due to the processes of wet and dry atmospheric depositions are the main source of soil and freshwater acidification (HULTBERG et al. 1994, LINDBERG 1992). However, SO₄²⁻ concentrations in freshwaters largely depend on the soil ability to retain and release SO₄-S. The soil sorption capacity is a complex of functions of Al and Fe oxides pool, quality and quantity of soil organic matter and clay, pH, and other factors (SHANLEY 1992, COURCHESNE 1992, KAISER & KAUPENIOHANN 1996). While SO₄-S retention in soil maintains the soil solution pH during acidification, its subsequent release (due to desorption) has just the opposite effect and may delay the process of recovery of an ecosystem from acidification, so that it lasts several decades (GOBRAN et al. 1998, PRENZEL 1994, ALEWELL & MATZNER 1993). The latter situation currently occurs in the Bohemian Forest (KOPÁČEK et al. 2001a, b).

The objectives of this study are: (i) to determine and compare SO_4 -S sorption characteristics of soils in Bohemian Forest catchments and (ii) to evaluate soil properties, which predominantly determine the catchments soil capacity to retain and release SO_4 -S.

STUDY SITE DESCRIPTION

Plešné Lake (PL) is situated at 48°47' N, 13°52' E, at an altitude of 1090 m above the sea level (a.s.l.). The PL catchment covers an area of 66.6 ha (including the lake area of 7.5 ha; ŠVAM-BERA 1939), and is oriented northeast. The PL catchment is steep; its maximum local profile is 288 m. The PL bedrock is formed by granite (VESELÝ 1994). The forest (covering ~90% of the catchment) is on average 160 years old and dominated (99%) by Norway spruce.

Čertovo Lake (CT) and Černé Lake (CN) are situated at 49°10' to 11' N and 13°11' to 12' E, at altitudes of 1030 and 1008 m a.s.l., respectively, in the massive of Jezerní Hora Mt. (1343 m a.s.l.). The CT catchment covers an area of 87.5 ha (including the lake area of 10.3 ha), and is east oriented. The CN catchment covers an area of 129 ha (including the lake area of 18.4 ha), and is north oriented (ŠvAMBERA 1939). Both catchments are steep with the maximum local profiles of 313 m (CT) and 335 m (CN). Their bedrock is formed predominantly by mica-schist (muscovite gneiss) with quartzite intrusions in the CT catchment (VE-SELÝ 1994). The CT catchment vegetation is dominated by 90–150 years old Norway spruce forest (with sparse fir and beech) covering nearly completely the whole catchment. The forest in the CN catchment (VESELÝ 1994).

Soil characteristics

Representative soil profiles were taken in each catchment at different altitudes, i.e. between the lake surface and the ridge (KOPAČEK et al. 2002a, b). Podzol samples were taken from the following horizons: uppermost mineral horizon with accumulated humified organic matter (horizon A); grey eluvial horizon with low content of organic matter (horizon E); dark upper layer of horizon B rich in illuvial organic matter (horizon Bh); and rusty-brown low part of horizon B rich in illuvial Fe oxides (horizon Bs). In the CT catchment, the Bs and Bh were not always distinguishable and they were sampled together as horizon B. In spodo-dystric cambisol, samples were taken from horizon A (if well distinguishable from the following horizon Ae), horizon Ae (organic rich mineral horizon), and all existing distinguishable mineral horizons (Bsv). In the beech stands (cambisol), samples were taken from the uppermost mineral horizon with accumulated humified organic matter (horizon A) and 2 other distinguishable mineral horizons (AB1 and AB2).

The PL catchment is predominantly covered with ~0.2 m deep lithosol (38%), and ~0.45 m deep podzol (29%) or spodo-dystric cambisol (27%); the rest is covered with bare rocks (5%) and wetlands (~1%). Fine soil is sandy (sand content ~75%), low in clay (~2%), and its catchment weighted mean (CWM) pool is 92 kg.m⁻² (<2 mm, dry weight soil fraction). The concentrations of total C and S vary between 1.2–43.4 mol.kg⁻¹ and 3.1–74.8 mmol.kg⁻¹, respectively. Soil pH is low, with minimum pH_{CaCl2} values (2.5–3.1) in A-horizons and maximum (3.2–4.4) in the Bs and C horizons. The CWM cation exchange capacity is 129 meq. kg⁻¹ (one equivalent is mol of charge), 15% of which is base saturation, and is dominated by exchangeable Al³⁺ (57%) (KOPÁČEK et al. 2002a).

The CT catchment area is predominantly covered with ~0.5 m deep spodo-dystric cambisol (58%), podzol (21%), and shallow (~0.2 m) lithosol (17%); wetlands and bare rocks represent ~3% and 1%, respectively. Spodo-dystric cambisol and podzol are dominant soil types also in the CN catchment, but contributions of each of soil types were not evaluated in detail there. Fine soil is sandy (sand content 48–81%), with a low content of clay (1–4%), and its CWM pool is 225 and 143 kg.m⁻² (<2 mm, dry weight soil fraction) in the CT and CN catchment, respectively. Concentrations of total C and S vary between 0.8–45 mol.kg⁻¹ and 3.1–73.7 mmol.kg⁻¹, respectively. Soil pH is low, with minimum pH_{CaCl2} values (2.5–3.3) in the A horizons and maximum values (3.6–4.5) in the C-horizons. The CWM cation exchange capacity of the CT and CN catchment is 104 and 123 meq.kg⁻¹, respectively, and is dominated by exchangeable Al³⁺ (62% and 55%; respectively). The CWM base saturation of the CT and CN soils is 9% and 12%, respectively (KOPÁČEK et al. 2002b).

Soil analyses

Sulphate sorption characteristics were determined in 10 samples from the PL catchment, 10 samples from CT, and 5 samples from CN catchments. The experiments were performed with fresh samples (homogenised by using a 5-mm sieve) from podzol profile PL6 and mixed samples prepared for each catchment in May 2000. In the PL catchment, the mixed soil samples were prepared by mixing of equivalent amounts of soils from particular soil horizons(i) A, Ae and Bsv horizons of spodo-dystric cambisols (profiles PL9, PL10, and PL11) and (ii) A, AB1, and AB2 horizons from beech stand (profiles PL13 and PL14). For location of the soil profiles and chemical composition of individual soil horizons see KOPÁČEK et al. (2002a). The mixed samples for the CT catchment were prepared analogously to the PL catchment by mixing identical horizons from soil profiles of podzol (CT1, CT3, CT4, and CT7) and spodo-dystric cambisol (CT2, CT5, CT6, and CT8). Moreover, additional samples were prepared during grid sampling of CT catchment by gathering identical soil horizons from cores sampled as far down as to bedrock at 450 places distributed over a regular grid (KOPÁČEK et al. 2002b). The mixed samples for the CN catchment were prepared from soil profiles of podzol (CN1, CN3, CN5 and CN7) and spodo-dystric cambisol (CN2, CN4, CN6, and CN8). For location and chemical composition of individual soil horizons in the CT and CN catchments see KOPÁČEK et al. (2002b).

Desorption isotherms were measured according to ALEWELL (1998). Field-moist soil (5 g of <5 mm soil fraction) was shaken with distilled water in 8 consequent steps. The 1st, 2nd and 3rd steps were done with the soil-water ratio of 1:1, and the following steps with the 1:4 ratio. Extracts were centrifuged at ~1000 g for 15 min and filtered (glass fibre filters Macherey-Nagel, porosity of 0.4 μ m), and SO₄²⁻ was determined by ionic chromatography (Thermo Separation Products, USA) in each extract. A total amount of SO₄-S released from the soil was the total quantity released in all steps and it was recalculated per dry weight (at 105 °C) of the sample.

 SO_4 -S sorption isotherms were measured using mixed samples from CT and CN (except CN-A) catchments and in the profile PL6, using the method by ALEWELL (1998). The same samples that had been extracted in establishing desorption isotherms, were shaken in 6 successive steps (18 h each) with increasing SO_4 concentrations (up to 1000 µmol.l⁻¹) at 25 °C. The amount of SO_4 -S sorbed by soil in each step was determined as a difference between the original and equilibrium SO_4 -S concentration in the solution. Resulting values served to calculate the SO_4 -S sorption maximum assuming that the sorption characteristics follow the Langmuir isotherms described by the following equation:

$$X = (c.X_{max}.k)/(1+c.k) \tag{1}$$

where X represents sorbed SO₄-S, c equilibrium SO₄-S concentration, X_{max} sorption maximum, and k is constant.

Soil subsamples used in chemical analyses were air-dried, homogenised, and sieved (<2 mm). In addition, subsamples for organic carbon (C) and sulphur (S) analyses were dried at 105 °C and finely ground. Concentrations of C and S were determined using CN analyser (NC 2100, ThermoQuest, Italy) and Eschka method (ISO 334 International Standard), respectively. The pH value was measured in 0.01M CaCl₂ solution (pH_{CaCl2}), with a mass ratio of

the air dried <2 mm soil to liquid phase of 1:5 after 2.5-hour extraction (horizontal shaker).

Oxalate-extractable Fe (Fe_o), Al (Al_o) and citrate-dithionite extractable Al and Fe (Al_{cd}) Fe_{cd}) were determined by extraction of 0.5 g of air-dried <2 mm soil with 50 ml of acid ammonium oxalate solution $(0.2M H_2 C_2 O_4 + 0.2M (NH_4)_2 C_2 O_4 \text{ at pH 3})$ and citrate-dithionite solution $(0.09M Na_2 S_2 O_4 + 0.57M Na_3 C_6 H_5 O_7 2 H_2 O)$, respectively, according to CAPPO et al. (1987). The original method has been modified as follows: the extraction process was carried out in three successive steps, each with fresh extracting solution, lasting together 17 hours (for details see KOPAČEK et al. 2002a). Fe and Al concentrations were determined from the extracts using the method by KOPAČEK et al. (2001c). The results were recalculated on a dry weight soil basis.

RESULTS AND DISCUSSION

Chemical composition of mixed samples is given in Table 1 and for details on other parameters or chemical and physical characteristics of individual soil profiles see KOPÁČEK et al. (2002a, b). Concentrations of S in the samples from PL catchment varied between 3.1–53.1 mmol.kg⁻¹. The highest concentrations were observed in A-horizons, while the lowest in lower mineral horizons. Similar pattern was observed also in the CT and CN catchments, where concentrations of S varied between 3.1–56.5 and 6.9–46.9 mmol.kg⁻¹, respectively. Concentrations of Al_o, Al_{ed}, Fe_o, and Fe_{ed} in the samples from all catchments varied between 25-688, 8-530, 5-354, and 16-528 mmol.kg⁻¹, respectively (Table 1). Highest concentrations of metals were observed in lower mineral horizons (both in podzols and spodo-dystric cambisols), whereas lowest concentrations were typical for E-horizons of podzol. While concentrations of Al_{o} and Al_{cd} were comparable, concentrations of Fe_{cd} were significantly (P<0.001) higher than Fe concentrations, due to redox conditions during the process of citrate-dithionite extraction. Because the soil ability to adsorb SO_4 -S is associated with concentrations of both Al and Fe oxides (e.g., ALEWELL 1998), we used the sum of Al, and Fe_{cd} as a measure of the metal oxides concentrations for the further evaluation of soil sorption characteristics. The sum of Al_o and Fe_{ed} concentrations ranged between 41–916, 112–580, and 220–683 mmol.kg-1 in the samples from PL, CT and CN catchments, respectively. The highest concentrations were observed in the B-horizons, while the lowest in E- and A-horizons.

Amounts of SO₄-S desorbed from soils of the PL, CT, and CN catchments were similar ranging from 0.07 to 0.73, from 0.21 to 0.68, and from 0.39 to 0.82 mmol.kg⁻¹, respectively. Desorption of SO₄-S was higher in A-horizons than in lower mineral horizons (0.32–0.82 vs. 0.07–0.46 mmol.kg⁻¹) and exhibited steeper desorption isotherms (Fig. 1). The successive SO₄-S release in B-horizons and quicker desorption in A-horizon are in concordance with other studies (GIESLER et al. 2000, LISCHEID et al. 2000). Amounts of SO₄-S released in A-horizons of the Bohemian Forest soils were similar to results reported by ALEWELL (1998) on spruce forest soils in the Fichtelgebirge (North Bavaria) and the Ore Mountains (Czech Republic). In contrast, SO₄-S concentrations in lower mineral horizons of the Bohemian Forest soils were similar to results presented by ALEWELL (1998).

Based on previous studies we expected that there would be a noticeable correlation between concentrations of SO_4 -S and Al_9 + Fe_{cd} (COURCHESNE 1992, ALEWELL 1998) or between concentrations of SO_4 -S and organic matter (STANKO-GOLDEN et al. 1994, COURCHES-NE et al. 1999, KAISER & ZECH 1998). However, the only significant correlation observed was between desorbed amounts of SO_4 -S and soil organic C concentrations (R²=0.83; P<0.001), and negative correlation between desorbed amounts of SO_4 -S and pH in samples from the PL catchment (R²=0.65; P<0.05). No other significant relationship between SO_4 -S and other variables was observed in the Bohemian Forest soils, despite the strong correlation (R²=0.93; P<0.001) between concentrations of total S and organic C. The lack of correlation between SO₄-S concentrations and other soil characteristics in our study may result from the low number of samples analysed and from surprisingly higher SO₄-S desorption in A-horizons with low concentrations of metal oxides.

 SO_4 -S concentrations were by two orders of magnitude lower than concentrations of total S. Percent contribution of SO_4 -S to the total S pool (SO_4 -S:S ratio) increased with depth and was higher in CT soils than in PL soils. The SO_4 -S:S ratio of PL soils was <0.8% in A-hori-

Table 1. Chemical characteristics of soil samples from catchments of the Plešné (PL), Čertovo (CT), and Černé (CN) lakes. SO₄-S, water extractable sulphate; and X_{max} , SO₄-S adsorption maximum capacity determined according to ALEWELL (1998). Not determined, n; GS, samples from catchment grid sampling (KOPÁČEK et al. 2002b); mix., mixed samples; beech, samples from the beech stands.

	С	S	SO_4 -S	X _{max}	Al	Al _{cd}	Fe _o	Fe _{cd}	pН
	mol.kg ⁻¹	mmol.kg ⁻¹							
PL-6-A	32.8	53.1	0.48	3.4	76	50	21	33	3.26
PL-6-E	5.5	6.3	0.07	n	25	8	5	16	3.71
PL-6-Bh	3.2	15.6	0.15	2.0	316	367	225	290	3.82
PL-6-Bs	9.4	9.4	0.28	3.2	688	530	223	227	4.37
PL-A	23.1	40.6	0.32	n	76	76	39	56	3.43
PL-Ae	4.7	9.4	0.18	n	72	67	29	42	3.87
PL-Bsv	1.3	3.1	0.10	n	73	56	63	73	4.10
PL-A (beech)	20.0	42.2	0.36	n	93	125	31	51	3.52
PL-AB1 (beech)	4.2	7.8	0.26	n	126	120	107	139	3.99
PL-AB2 (beech)	1.6	6.3	0.24	n	137	132	110	148	4.37
CT-A (mix.)	20.1	56.5	0.68	5.2	104	100	95	113	3.59
CT-Ae (mix.)	6.6	21.7	0.48	3.7	102	223	116	332	3.95
CT-E (mix.)	1.8	4.3	0.24	3.1	51	43	42	64	3.94
CT-B (mix.)	2.9	8.7	0.50	3.3	137	242	133	347	4.25
CT-C (mix.)	1.0	8.7	0.38	2.4	147	136	120	244	4.50
CT-A (GS)	21.4	43.2	0.66	n	115	105	103	119	3.75
CT-Ae (GS)	6.8	16.1	0.50	3.2	130	196	130	302	4.10
CT-E (GS)	1.8	3.1	0.24	2.6	33	43	21	79	4.15
CT-B (GS)	2.9	6.4	0.55	2.3	157	304	130	413	4.35
CT-C (GS)	1.0	6.3	0.61	1.5	135	116	117	270	4.60
CN-A	23.6	46.9	0.82	n	90	78	107	130	3.50
CN-Ae	7.6	19.8	0.48	4.6	155	152	349	434	3.99
CN-E	5.1	9.4	0.39	2.9	34	48	66	193	3.76
CN-B	4.7	11.6	0.61	11.7	154	178	354	528	4.12
CN-C	2.1	6.9	0.69	3.6	163	172	262	417	4.43



Fig. 1. SO_4 -S desorption isotherms in mixed samples of dominant soil horizons from catchments of the Plešné (PL) and Čertovo (CT) Lakes. Black triangles – observed data, solid line – calculated desorption isotherm.



Fig. 2. SO_4 -S sorption isotherms in mixed soil samples taken from major soil horizons (A, Ae, E, B, and C) in the catchment of the Čertovo Lake. Black triangles – observed data, solid line – calculated sorption isotherm.

zons (despite the highest SO₄-S concentrations; Table 1) and increased up to 3.7% in lower mineral horizons. In the CT and CN catchments, the SO₄-S:S ratio was <2% in A-horizons and increased up to 9% in B- or up to 12% in C-horizons.

The CWM pool of SO₄-S was ~30 times lower (3.4%) than the pool of total S in the CT catchment (0.096 and 2.8 mol.m⁻², respectively).

Examples of SO₄-S sorption isotherms (CT soils) are given in Fig. 2. SO₄-S sorption maxima (X_{max}) in the Bohemian Forest catchments varied between 1.5–11.7 mmol.kg⁻¹ (Table 1), with the maximum observed in the sample CN-B (Table 1). Other X_{max} values did not vary significantly either between catchments or horizons and were <5.2 mmol.kg⁻¹. All X_{max} values were by one or two orders of magnitude higher than amounts of SO₄-S desorbed before, suggesting that the SO₄-S sorption capacity of soils was not saturated.

The X_{max} values observed in the Bohemian Forest soils are similar to results reported by

ALEWELL (1998) on spruce forest soils in the Fichtelgebirge (North Bavaria) and the Ore Mountains (Czech Republic). However, ALEWELL (1998) observed that X_{max} values increased from A-horizons to lower mineral horizons, whereas we observed slightly higher X_{max} in A-horizons than in other horizons (with the exception of CN-B sample; Table 1). The X_{max} values in the PL catchment were comparable to data obtained by CAMPS ARBESTAIN et al. (1999) for soils on granite parent material. The study of CAMPS ARBESTAIN et al. (1999) showed a decreasing SO_4 -S sorption capacity in the order amphibolite > biotitic schist > granite > phyllite, with values from 17 to 0.4 mmol.kg⁻¹. A comparison to these data suggests that sulphate sorption capacity of the Bohemian Forest soils is relatively low. Moreover, the pools of soils in the studied catchments are low (KOPAČEK et al. 2002a, b). Therefore, the ability to adsorb and release SO_4 -S in the catchments is weak. We suppose that this low SO_4 -S sorption capacity resulted in a more straightforward response of the water quality in catchments of the Bohemian Forest lakes to acid deposition than in other Czech mountainous areas (HRUŠKA & MAJER 1996).

KOPÁČEK et al. (2001d) evaluated the S amount accumulated in the CT soils due to the elevated S contribution from atmospheric deposition over the period of 1930–2000. This amount (0.8 mol.m⁻²) represented \sim 30% of the current pool of total S in the catchment. Accumulated S in soils delayed the process of water acidification during the period of increasing S deposition, but currently (after ~80% decline in S deposition) SO₄-S released from soils significantly delays the process of water recovery in the Bohemian Forest (MAJER et al. 2003). Soils in the CT catchment became a net source of SO₄-S around 1993–1994 (KOPÁČEK et al. 2001d), similar to the most damaged Central European region (the Ore Mountains; Novák et al. 2000). The average annual SO_4 -S leaching rate from CT soils was 31 mmol. m⁻².yr⁻¹ in the period of 1994–2000 (Kopáček et al. 2001d) and 29 mmol.m⁻².yr⁻¹ in the period of 2000–2003 (Kopáček unpubl. data). Based on the amount of water extractable SO_4 -S in the CT soils in 2000 (96 mmol.m⁻²), we can estimate that the S leaching of this rate level would continue next 1-3 years only. However, S leaching in the CT catchment has continued till present, which supports the hypothesis suggesting that the soil SO_4 -S pool is being replenished from the process of mineralisation of organic S (Novák et al. 1996) and inorganic S (e.g., Al-SO, complexes; Nordstrom 1982). Therefore, if all of the S accumulated in the Bohemian Forest soils over the 1930–2000 period was available and could be transported at the present leaching rate (and the present level of atmospheric S deposition), the process of S wash out would last 10–25 years. Provided that the S leaching rate will gradually decrease in future, it may last even longer to remove S completely.

The SO₄-S desorption from PL soils was studied only using one soil profile (PL-6) and mixed samples. This limited number of samples was not sufficient to estimate the CWM SO₄-S pool in the PL catchment. Nevertheless, SO₄-S amounts desorbed from individual samples were comparable to results obtained for CT soils. Also SO₄-S leaching in the PL catchment (31 mmol.m⁻².yr⁻¹ in the 2000–2003 period; KOPAČEK unpubl. data) is similar to leaching in the CT catchment. Based on this we assume that S removal estimates made for the CT catchment are applicable also to the other Bohemian Forest catchments. Such assumptions are supported also by dynamic modelling of sulphate cycling in the Bohemian Forest catchment-lake ecosystems (MAJER et al. 2003).

CONCLUSION

The SO₄-S pool represented on average 3.4% of the pool of total S. We have observed a positive correlation between desorbed SO₄-S and organic C concentration (P<0.001) and a negative correlation between desorbed SO₄-S and soil pH (P<0.05) in PL soils. These relationships, however, were not significant in CT and CN catchments. No significant relationships have been observed between desorbed SO_4 -S and concentrations of extractable Al and Fe in soils.

Soil sorption maxima of SO_4 -S varied between 1.5–11.7 mmol.kg⁻¹ among the catchmets studied, being slightly higher in the A than lower mineral horizons, and with the highest values in the CN catchment.

The amount of SO₄-S desorbed by water extraction ranged between 0.06–0.73, 0.21–0.68, and 0.39–0.82 mmol.kg⁻¹ in the PL, CT, and CN catchments, respectively. The maximum SO₄-S desorption was observed in A-horizons.

The amounts of SO_4 -S desorbed from the Bohemian Forest soils were comparable to other central European forest sites (Fichtelgebirge and Ore Mountains; ALEWELL 1998) in A-horizons, but were one order of magnitude lower in the lower mineral horizons.

The observed SO_4 -S desorption characteristics (successive desorption from B-horizon vs. quick desorption from A-horizon) were similar to other published studies (GIESLER et al. 2000, LISCHEID et al. 2000).

Acknowledgement. We acknowledge the laboratory and field assistance provided to us by our colleagues from the Hydrobiological Institute ASCR and Faculty of Biological Sciences USB (H. Šantrůčková, P. Porcal, T. Picek, J. Šetlík, and K. Murtinger). This study was sponsored by the Grant Agency of the Czech Republic, Project No. 206/00/0063 (sampling), No. 206/03/1583 (analysis, evaluation, and publication), and partly by Institutional Research Plan CAS No. Z 6017912 (laboratory equipment and facilities) and MSM 123100004 (field sampling).

References

- ALEWELL C. & MATZNER E., 1993: Reversibility of soil solution acidity and of sulphate retention in acid forest soils. Water, Air, and Soil Pollution, 71: 155–165.
- ALEWELL C., 1998: Investigating sulphate sorption and desorption of acid forest soils with special consideration of soil structure. Zeitschrift für Pflanzenernährung und Bodenkunde, 161: 73–80.
- BARON J.S., OJIMA D.S., HOLLAND E.A. & PARTON W.J., 1994: Analysis of nitrogen saturation potential in Rocky Mountain tundra and forest: implications for aquatic systems. *Biogeochemistry*, 27: 61–82.
- CAMPS ARBESTAIN M., BARREAL M.E. & MACÍAS F., 1999: Parent Material Influence on Sulphate Sorption in Forest Soils from North-western Spain. Soil Science Society of America Journal, 63: 1906–1914.
- CAPPO K.A., BLUME L.J., RAAB G.A., BARTZ J.K. & ENGELS J.L., 1987: Analytical Methods Manual for the Direct/ Delayed Response Project Soil Survey. US EPA, Las Vegas, USA, Sections 8–11.
- COURCHESNE F., 1992: Relationships between soil chemical properties and sulphate sorption kinetics in podzolic soils from Quebec. *Canadian Journal of Soil Science*, 72: 467–480.
- COURCHESNE F., LABERGE J.-F. & DUFRESNE A., 1999: Influence of soil organic matter on sulfate retention in two podzols in Quebec, Canada. *Canadian Journal of Soil Science*, 79: 103–109.
- GIESLER R., ILVESNIEMI H., NYBERG L., VAN HEES P., STARR M., BISHOP K., KAREINEN T. & LUNDSTRÖM U.S., 2000: Distribution and mobilization of Al, Fe and Si in three podzolic soil profiles in relation to the humus layer. *Geoderma*, 94: 249–263.
- GOBRAN G.R., COURCHESNE F. & DUFRESNE A., 1998: Relationships between sulphate retention and release, solution pH and DOC in the Gårdsjön soils. In: *Experimental reversal of acid rain effects: The Gårdsjön roof project*, HULTBERG H. & SKEFFINGTON R. (eds) Wiley & Sons, Chichester, pp. 207–229.
- HRUŠKA J. & MAJER V., 1996: Retence antropogenní síry v půdách: faktor bránící okyselení šumavských povrchových vod [Retention of human-induced sulphur in soils: a factor preventing acidification in surface water of Bohemian Forest]. Silva Gabreta, 1: 143–149 (In Czech).
- HULTBERG H., APSIMON H., CHURCH R.M., GRENNFELT P., MITCHELL M.J., MOLDAN F. & ROSS H.B., 1994: Sulphur. In: *Biogeochemistry of small catchments*, MOLDAN B. & ČERNÝ J. (eds) Wiley & Sons, Chichester, pp. 229–254.
- KAISER K. & KAUPENJOHANN M., 1998: Influence of the soil solution composition on retention and release of sulphate in acid forest soils. Water, Air, and Soil Pollution, 101: 363–376
- KAISER K. & ZECH W., 1998: Rates of dissolved organic matter release and sorption in forest soils. Soil Science, 163: 714–725.
- KOPÁČEK J., HEJZLAR J., KAŇA J. & PORCAL P., 2001a: Element budgets in three Bohemian Forest lakes and their

watersheds in the 2000 hydrological year: Čertovo Lake. Silva Gabreta, 6: 35–52

- KOPAČEK J., HEJZLAR J., KAŇA J. & PORCAL P., 2001b: Element budgets in three Bohemian Forest lakes and their watersheds in the 2000 hydrological year: Plešné Lake. Silva Gabreta, 6: 73–86
- KOPAČEK J., BOROVEC J., HEJZLAR J. & PORCAL P., 2001c: Parallel spectrophotometric determinations of iron, aluminium, and phosphorus in soil and sediment extracts. *Communications in Soil Science and Plant Analysis*, 32: 1431–1443.
- KOPAČEK J., VESELÝ J. & STUCHLÍK E., 2001d: Sulphur and Nitrogen Fluxes and Budgets in the Bohemian Forest and Tatra Mountains during the Industrial Revolution (1850–2000). *Hydrology and Earth System Sciences*, 5(3): 391–405.
- KOPÁČEK J., KAŇA J., ŠANTRŮČKOVÁ H., PORCAL P., HEJZLAR J., PICEK T. & VESELÝ J., 2002a: Physical, chemical, and biochemical characteristics of soils in watersheds of the Bohemian Forest lakes: I. Plešné Lake. Silva Gabreta, 8: 43–66.
- KOPÁČEK J., KAŇA J., ŠANTRŮČKOVÁ H., PORCAL P., HEJZLAR J., PICEK T. & VESELÝ J., 2002b: Physical, chemical, and biochemical characteristics of soils in watersheds of the Bohemian Forest lakes: II. Čertovo and Černé Lake. Silva Gabreta, 8: 67–94.
- LINDBERG S.E., 1992: Sulphur distribution and cycling in forest ecosystems. In: Atmospheric Deposition and Forest Nutrient Cycling. A synthesis of the integrated forest study, JOHNSON D.W. & LINDBERG S.E. (eds) Springer – Verlag, New York, pp. 74–90.
- LISCHEID G., MORITZ K., BITTERSOHL J., ALEWELL C. & MATZNER E., 2000: Sinks of anthropogenic nitrogen and sulphate in the Lehstenbach catchment (Fichtelgebirge): lessons learnt concerning reversibility. *Silva Gabreta*, 4: 41–50.
- MAJER V., COSBY B.J., KOPÁČEK J. & VESELÝ J., 2003: Modelling Reversibility of Central European Mountain Lakes from Acidification: Part I – The Bohemian Forest. *Hydrology and Earth System Sciences*, 7(4): 494–509.
- NORDSTROM D.K., 1982: The effect of sulphate on aluminium concentrations in natural waters: some stability relations in the system Al₂O₃-SO₃-H₂O at 298 K. *Geochimica et Cosmochimica Acta*, 46: 681–692.
- NOVÁK M., BOTTRELL S.H., FOTTOVÁ D., BUZEK F., GROSCHEOVÁ H. & ŽÁK K., 1996: Sulphur isotope signals in forest soils of Central Europe along an air pollution gradient. *Environmental Science and Technology*, 30: 3473– 3476.
- NOVÁK M., KIRKNER J.W., GROSCHEOVÁ H., HAVEL M., ČERNÝ J., KREJČÍ R. & BUZEK F., 2000: Sulphur isotope dynamics in two Central European watersheds affected by high atmospheric deposition of SO_x. *Geochimica et Cosmochimica Acta*, 64: 367–383.
- PRENZEL J., 1994: Sulphate sorption in soils under acid deposition: Comparison of two modelling approaches. Journal of Environmental Quality, 23: 188–194.
- PSENNER R. & CATALAN J., 1994: Chemical composition of lakes in crystalline basins: a combination of atmospheric deposition, geologic background, biological activity and human action. In:. *Limnology now: A paradigm* of planetary problems, MARGALEF R. (ed.) Elsevier science B.V., pp. 255–314.
- SHANLEY J.B., 1992: Sulphate retention and release in soils at Panola Mountain, Georgia. Soil Science, 153: 499– 508.
- STANKO-GOLDEN K.M., SWANK W.T. & FITZGERALD J.W., 1994: Factors affecting sulphate adsorption, organic sulphur formation, and mobilization in forest and grassland spodosols. *Biology and Fertility of Soils*, 17: 289–296.
- ŠVAMBERA V., 1939: Jezera na české straně Šumavy [Lakes in the Czech part of the Bohemian Forest]. Sborník české společnosti zeměpisné, 45: 15–23 (in Czech).
- VESELÝ J., 1994: Investigation of the nature of the Šumava lakes: a review. *Časopis Národního Muzea, Praha, Řada přírodovědná*, 163: 103–120.
- WETZEL R.G., 2002: Limnology. Lake and River Ecosystems. Academic Press, San Diego, 850 pp.

Received: 15 July 2004 Accepted: 2 November 2004