

## Immission-load-related dynamics of $\text{S-SO}_4^{2-}$ in precipitation and in lysimetric solutions penetrating through beech ecosystems

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### Abstract

KUKLA, J., BUBLINEC, E., SCHIEBER, B., KELLEROVÁ, D., BIČAROVÁ S., JANÍK, R., 2017. Immission-load-related dynamics of  $\text{S-SO}_4^{2-}$  in precipitation and in lysimetric solutions penetrating through beech ecosystems. *Folia Oecologica*, 44: 96–106.

The paper presents the results of a 23-year study of sulphate sulphur dynamics in beech ecosystems exposed to different immission loads. The amounts of  $\text{S-SO}_4^{2-}$  in precipitation water entering the ecosystems were: the Kremnické vrchy Mts, a clear-cut area  $519 \text{ kg ha}^{-1}$  ( $24.7 \text{ kg ha}^{-1}$  per year), a beech forest  $476 \text{ kg ha}^{-1}$  ( $22.7 \text{ kg ha}^{-1}$  per year); the Štiavnické vrchy Mts an open place  $401 \text{ kg ha}^{-1}$  ( $24.6 \text{ kg ha}^{-1}$  per year), a beech forest  $324 \text{ kg ha}^{-1}$  ( $19.1 \text{ kg ha}^{-1}$  per year). The average  $\text{SO}_4^{2-}$  concentrations in lysimetric solutions penetrating through surface humus to a depth of Cambisol 10 and 25 cm were increased as follows: in the Kremnické vrchy Mts from  $12.71$  to  $16.17 \text{ mg l}^{-1}$  and in the Štiavnické vrchy Mts from  $18.73$  to  $28.80 \text{ mg l}^{-1}$ . The  $\text{S-SO}_4^{2-}$  amounts penetrating the individual soil layers in the Kremnické vrchy Mts were as follows: in case of surface humus on clear-cut area  $459 \text{ kg ha}^{-1}$  ( $20.9 \text{ kg ha}^{-1}$  per year), in beech forest  $433 \text{ kg ha}^{-1}$  ( $19.7 \text{ kg ha}^{-1}$  per year); below 10 cm organo-mineral layer of the mentioned plots penetrated  $169$ – $171 \text{ kg ha}^{-1}$  ( $7.7$ – $7.8 \text{ kg ha}^{-1}$  per year), and below 25 cm mineral layer  $155$ – $255 \text{ kg ha}^{-1}$  ( $7.1$ – $11.6 \text{ kg ha}^{-1}$  per year) – a higher amount was found on clear-cut area with an episodic lateral flow of soil solutions. In beech forest of the Štiavnické vrchy Mts penetrated below surface humus  $424 \text{ kg ha}^{-1}$   $\text{S-SO}_4^{2-}$  ( $18.9 \text{ kg ha}^{-1}$  per year), below 10 cm mineral layer  $458 \text{ kg ha}^{-1}$   $\text{S-SO}_4^{2-}$  ( $19.9 \text{ kg ha}^{-1}$  per year), and below 25 cm mineral layer as much as  $599 \text{ kg ha}^{-1}$   $\text{S-SO}_4^{2-}$  ( $26.0 \text{ kg ha}^{-1}$  per year). This fact was caused by frequent lateral flow of soil solutions. The results indicate that the assumption about lower immission load of the beech ecosystem in the Kremnické vrchy Mts is wrong, at least in the case of  $\text{S-SO}_4^{2-}$ . The testing has revealed that the studied beech ecosystems differ very significantly in sulphur amounts penetrating under 0.10 m and 0.25 m. The inter-annual differences were insignificant.

### Keywords

beech ecosystems, immissions, lysimetric solutions, precipitation, sulphate sulphur, throughfall

### Introduction

Sulphuric compounds (oxides, sulphides) and sulphur are present almost in all components of all Earth's ecosystems (FECENKO et al., 2010). Sulphur (S) is an im-

portant biogenic macro-element occurring in various amino-acids (cysteine, methionine), plant oils and vitamins. It participates in redox processes in plants, promotes activation of enzymes and metabolism of proteins (LOŠÁK et al., 2010, 2011). Sulphur in the soil is organic

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and mineral but the organic form clearly prevails (over 90%). From organic substances, S is released owing to decomposition by microorganisms. Sulphate anions are very poorly adsorbed in the soil, and therefore they are more easily subject to leaching into the lower soil layers (FECENKO and LOŽEK, 2000).

Sulphur is soluble in water (including atmospheric precipitation, soil water) with which it reacts and forms sulphuric acid – influencing significantly leaching of iron from leaf chloroplasts and inhibiting assimilation of carbon dioxide from atmosphere. Entering the soil in emitted pollutants and in atmospheric precipitation, sulphur displaces basic cations and causes soil acidification (QUILCHANO et al., 2002). Soil acidification is a long-term, cumulative and dynamically developing process with usually negative effect on sensitive species of forest phytocoenoses (KOPÁČEK and VRBA, 2006; LOŠÁK et al., 2012). The total amount of basic pollutants emitted across the Slovak territory in years 1989–99 has dropped by 57.9%, which represents an annual decline by almost 6%. Sulphur dioxide (SO<sub>2</sub>) emissions in the Slovak Republic showed greatest values in the 1990s, (more than 500,000 tons). In 2003 it was already less than 200,000 tons. The decreasing trend has also been observed at local scales. For example, the sulphur deposition in the locality Tatranská Lomnica compared to 2001 decreased by 64% (to 5.7 kg ha<sup>-1</sup> year) and in the locality Jasenie by 53% (6.5 kg ha<sup>-1</sup> year), while in the locality Grónik only by 24% (16.4 kg ha<sup>-1</sup> year). In other areas, the decrease in sulphur deposition was recorded in 2006 by approximately 50% compared to 2001 (MINISTRY OF ENVIRONMENT OF THE SLOVAK REPUBLIC, 2010). The same trend has also been recorded in the surrounding lands (HRKAL et al., 2006). All these indicators seem optimistic, however, as noted also by ALEWELL et al. (2000) the danger of acidification is really urgent – primarily because of its either long-term character or ability to penetrate vertically down to deep soil layers and accumulate there.

The main contaminants produced by the local sources in the Žiarska kotlina basin (Aluminium Company in the Žiar nad Hronom; Thermal power plant in Nováky town; transportation on nearby highway; waste disposal) in the past were: fluorine, sulphur and nitrogen oxides, arsenic, cadmium, ozone, solid particles and others (KUKLOVÁ et al., 2015). Atmospheric pollutants entering the ecosystem of the Štiavnické vrchy Mts for many years had been modifying the ecological conditions which had negative impact on the quality of beech stands. Unfavourable for forest ecosystems was mainly the effect of airborne pollutants based on fluorine and SO<sub>2</sub>. The area close to the aluminium plant belonging long-time to the most heavily polluted areas of the Slovak Republic was classified in 1990s to the pollution degree II.–III. The updated technology as well as new legislation measures applied since 1990s have resulted in a conspicuous reduction in amount of emitted pollutants. The fluorine concentration, for example, has

dropped below the allowable limit of 1 µg m<sup>-3</sup> (URMINSKÁ et al., 2000). On the other hand, the beech ecosystems situated on the southern slopes of the Kremnické vrchy Mts with relatively low load of atmospheric pollutants originating from anthropogenic sources could provide a good comparative standard for our research.

The aim of this paper is to evaluate the dynamics of sulphate sulphur in vertical structure of two contrast ecosystems: in the segments of relatively slightly polluted beech ecosystems situated in the Kremnické vrchy Mts, and in the beech ecosystems situated in the Štiavnické vrchy Mts, segments of which were mainly in the past (1970–2000) heavily loaded by emitted and airborne pollutants.

The null hypothesis works with the assumptions that the sulphur concentrations in lysimetric soil solutions are mostly influenced by the momentary sulphur content in atmospheric precipitation and by the precipitation amount, and that the highest sulphur amounts in soil solutions occur in localities more loaded by atmospheric pollutants.

## Materials and methods

The first set of research plots (RP), which is slightly influenced by atmospheric pollutants, is situated in the southern part of the Kremnické vrchy Mts (48°38'N and 19°04'E, 450–510 m asl, slope inclination 17–20°), (BARNA, 2004). The climate district is B5 – moderately warm, moderately moist, hilly, with a mean annual temperature  $t_{1951-1980} = 6.8$  °C and total mean annual precipitation 778 mm (SCHIEBER, 2006). The mean annual rainfall in the growing season is 395 mm (DUBOVÁ and BUBLINEC, 2006) and the length of growing season is 115–165 days. The dominant tree species of 80–110 year old stand is the European beech (*Fagus sylvatica* L.) with an average height of 28 m. The parent rock is tuffaceous andesite agglomerates on which Eutric Andic Cambisol have developed with a proportion of skeleton increasing with the soil depth to 30–40 (60)% (KUKLA, 2002). From geobiocoenological point of view (ZLATNÍK, 1959, 1976; HANČINSKÝ, 1972), the partial plots of the beech ecosystem in the Kremnické vrchy Mts belong to the 3<sup>rd</sup> forest vegetation grade, mesotrophic edaphic-trophic order of geobiocoenes, group of forest types *Fagetum pauper inferiora* and forest type *Carex pilosa-nudum* (KUKLA, 1988, 2002; KUKLA et al., 1998).

The second set of research plots loaded with pollutants is situated in the north-western part of the Štiavnické vrchy Mts (48°35'N, 18°51'E, 470 m asl, slope inclination 15°). The locality with the mean annual temperature of 8.0–8.5 °C (in the growing season 14.5–15.5 °C) belongs to the warm climatic area of Slovakia. The total mean annual precipitation is 700–750 mm, with the maximum 1,005–1,020 mm and the minimum 430–450 mm (KELLEROVÁ, 2005). The parent

rock is rhyodacite tuffs covered with almost skeleton-free Dystric Gleyic Cambisol with gleyic colour pattern in a depth under 30 cm (KUKLA, 1990). From geobio-coenological point of view, the segment of 110-year-old beech forest belongs to the 3<sup>rd</sup> forest vegetation grade, waterlogged edaphic-hydric order of geobiocoenes, mesotrophic edaphic-trophic order of geobiocoenes, group of forest types *Fagetum pauper inferiora* and forest type *Dentaria bulbifera-nudum* (KUKLA, 1990). Waterlogging of soil is currently indicated only by the gradation of the species *Athyrium filix-femina* and the rare occurrence of the species *Dryopteris dilatata*. The open plot is located in vicinity of beech forest.

Lysimetric solutions were collected into plastic collectors (each 1,000 cm<sup>2</sup> in area) installed below organic horizons of surface humus, 0.10 m and 0.25 m thick mineral layer in 1987. Lysimetric solutions were sampled as a rule in monthly intervals or after heavy rainfall, subjected to chemical analyses and evaluated in years 1988–2003 by KUKLA (unpublished data) and in years 2004–2011 by JANÍK et al. (2012a, 2012b).

Throughfall solutions were captured using 10 funnels (each 660 cm<sup>2</sup> in area) and collected into closed collectors regularly situated in the beech stand and on adjacent open area. The sampling was made at regular 2-week intervals and after each appropriately intense precipitation event. The representative samples consisted of the mixture of solutions taken from all the collectors placed in the beech stand or in the open

plot. The samples were subjected to chemical analysis and evaluated by BUBLINEC (to 2003) and JANÍK (after 2004). Concentrations of SO<sub>4</sub><sup>2-</sup> anions were determined by titration with lead nitrate at presence of dithizone and recalculated to the amount of sulphate sulphur (S-SO<sub>4</sub><sup>2-</sup>, kg ha<sup>-1</sup>).

Data were processed with using the Statistica-7 software package. Normality was tested with Shapiro-Wilk W test. The significance of differences was tested using the Student's t-test for dependent variables. Influence of total precipitation on amount of sulphate sulphur in throughfall and in soil solutions was assessed by simple regression.

## Results

### The Kremnické vrchy Mts

The mean SO<sub>4</sub><sup>2-</sup> concentrations found in precipitation taken from clear-cut area ranged from 2.18 to 22.62 mg l<sup>-1</sup> (in average 10.10 mg l<sup>-1</sup>) and in 1989–1996 were lower compared with SO<sub>4</sub><sup>2-</sup> concentrations in throughfall, where the average was 12.60 mg l<sup>-1</sup> (Fig. 1a, Table 1). The average SO<sub>4</sub><sup>2-</sup> concentrations found in lysimetric solutions on clear-cut area ranged between 12.71–14.53 mg l<sup>-1</sup> and in beech stand from 14.00 to 16.17 mg l<sup>-1</sup>, with a maximum in a depth of 0.25 m (Fig. 1b, 1c, Table 1).

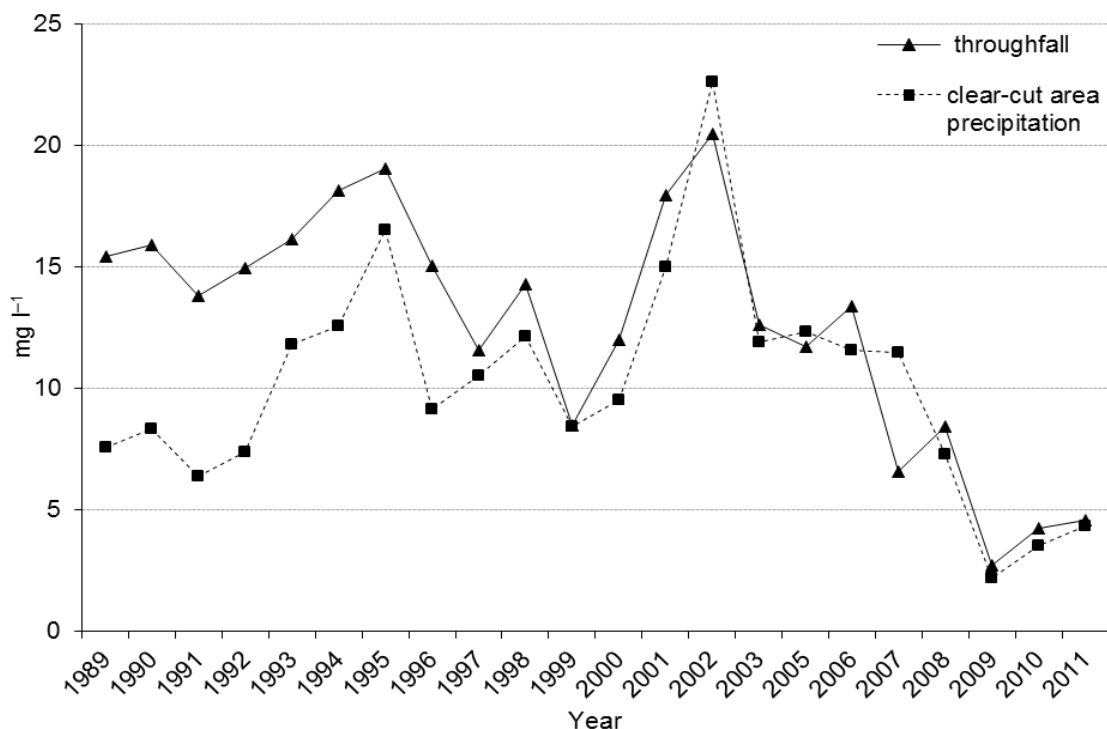


Fig. 1a. The dynamics of SO<sub>4</sub><sup>2-</sup> concentrations in throughfall and precipitation taken from the beech ecosystem in the Kremnické vrchy Mts.

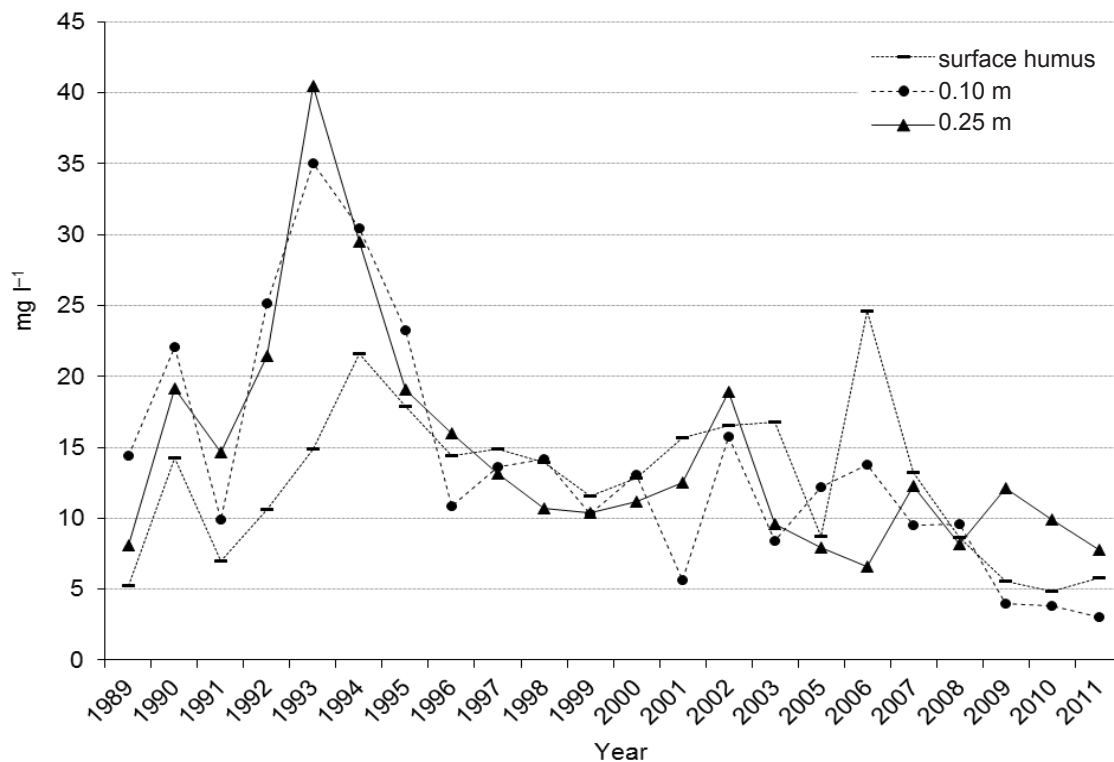


Fig. 1b. The dynamics of  $\text{SO}_4^{2-}$  concentrations in lysimetric solutions collected below surface humus and 0.10 and 0.25 m layer of Cambisol in clear-cut area of the Kremnické vrchy Mts.

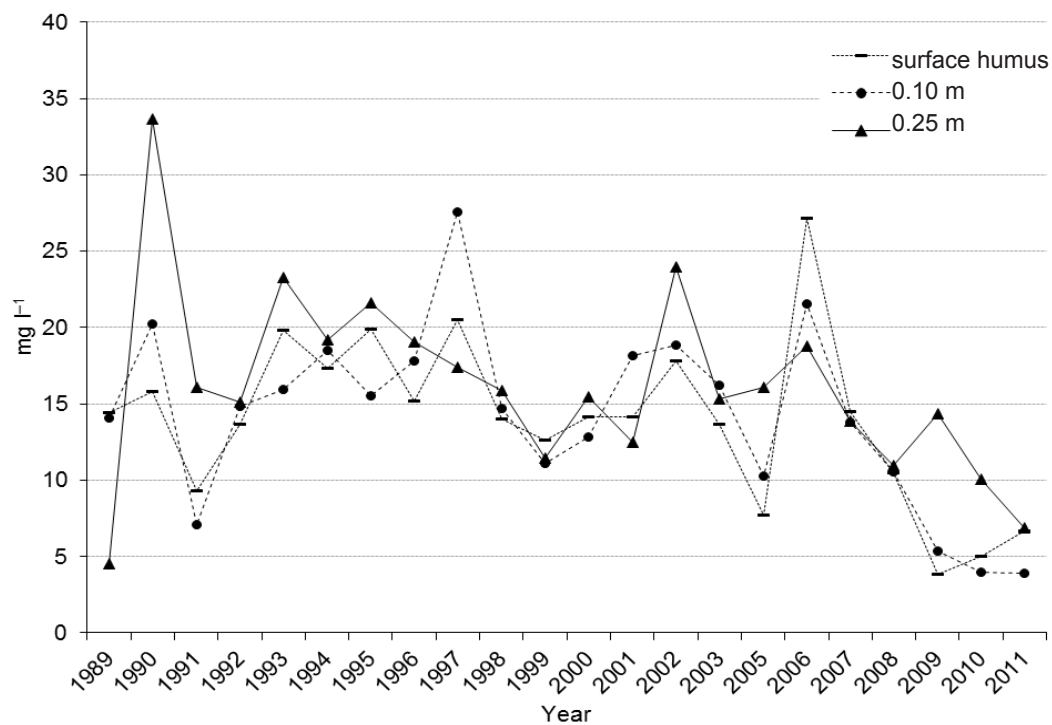


Fig. 1c. The dynamics of  $\text{SO}_4^{2-}$  concentrations in lysimetric solutions collected below surface humus and 0.10 and 0.25 m layer of Cambisol in beech ecosystem of the Kremnické vrchy Mts.

Table 1. Descriptive statistics of S-SO<sub>4</sub><sup>2-</sup> amounts and SO<sub>4</sub><sup>2-</sup> concentrations found in years 1988–2011

Locality	Kremnické vrchy Mts								Štiavnické vrchy Mts					
	Clear-cut area				Beech stand				Open plot		Beech stand			
	Parameter	Lysimeter			Throughfall	Lysimeter			Precipitation	Throughfall	Lysimeter			
		below (m)				below (m)					below (m)			
SH		0.10	0.25	SH		0.10	0.25	SH			0.10	0.25		
S-SO <sub>4</sub> <sup>2-</sup> (kg ha <sup>-1</sup> )														
Average	24.7	20.9	7.7	11.6	22.7	19.7	7.8	7.1	23.6	19.1	18.5	19.9	26.0	
Min	5.4	5.6	0.9	0.9	3.7	1.5	1.4	0.8	12.1	7.2	8.9	5.9	11.8	
Max	53.4	51.8	22.8	27.9	47.2	33.9	22.4	16.2	45.2	33.3	35.1	38.0	52.6	
Variance	190.4	116.9	37.2	57.3	172.9	83.3	21.1	19.6	94.9	35.7	53.4	86.9	139.6	
V x %	55.9	51.7	79.2	65.5	57.7	46.2	58.9	61.9	36.9	31.4	39.5	46.7	45.4	
Std. Dev.	13.8	10.8	6.1	7.6	13.1	9.1	4.6	4.4	9.7	6.0	7.3	9.3	11.8	
Std. Error	3.0	2.3	1.3	1.6	2.9	1.9	1.0	0.9	2.4	1.4	1.5	1.9	2.5	
SO <sub>4</sub> <sup>2-</sup> (mg l <sup>-1</sup> )														
Average	10.10	12.71	14.00	14.53	12.60	14.00	14.23	16.17	14.41	16.83	18.73	23.16	28.80	
Min	2.18	4.88	3.01	6.62	2.70	3.87	3.91	4.53	3.25	9.64	8.02	10.69	15.16	
Max	22.62	24.64	35.04	40.50	20.46	27.14	27.59	33.65	25.33	24.68	30.18	39.73	42.03	
Variance	20.46	28.16	71.53	64.28	24.56	29.89	34.72	38.42	32.56	16.98	34.44	64.83	70.59	
V x %	44.75	41.78	60.43	55.20	39.37	39.07	41.39	38.34	39.63	24.50	31.34	34.76	29.17	
Std. Dev.	4.52	5.31	8.46	8.02	4.96	5.47	5.89	6.20	5.71	4.12	5.87	8.05	8.40	
Std. Error	0.96	1.13	1.80	1.71	1.06	1.17	1.26	1.32	1.38	1.00	1.22	1.68	1.75	

SH, surface humus.

The average amount of S-SO<sub>4</sub><sup>2-</sup> deposited on clear-cut area reached 24.7 kg ha<sup>-1</sup>yr<sup>-1</sup>. Below crown layer of beech forest penetrated a little lower average amount of S-SO<sub>4</sub><sup>2-</sup>, only 22.7 kg ha<sup>-1</sup>yr<sup>-1</sup>. The average amounts of S-SO<sub>4</sub><sup>2-</sup>, which penetrated below surface humus and 0.10 and 0.25 m mineral soil layers reached in the clear-cut area 20.9, 7.7 and 11.6 kg S ha<sup>-1</sup>yr<sup>-1</sup> (due to occasional occurrence of subsurface lateral flows in 0.25 m), in case of beech forest 19.7, 7.8 and 7.1 kg ha<sup>-1</sup>yr<sup>-1</sup> (Table 1). The amounts of S-SO<sub>4</sub><sup>2-</sup> accumulated in-, or leached from these layers were as follows: on the clear-cut area 2.8, 13.2 and –3.9 kg of S ha<sup>-1</sup>yr<sup>-1</sup>, and in the beech stand 3.0, 11.9 and 0.7 kg of S ha<sup>-1</sup>yr<sup>-1</sup>.

As for the annual dynamics of S-SO<sub>4</sub><sup>2-</sup>, the highest values were recorded in autumn months, the lowest in spring and summer months. The S values on clear-cut area varied from 51.7%–79.2%, which corresponds to the course of biological processes and climatic characteristics over the year. In the beech stand, the variability of S values was narrower: 46.2–61.9% (Table 1).

The highest average amounts of S-SO<sub>4</sub><sup>2-</sup> penetrated below surface humus in 1995 and reached 51.8 kg ha<sup>-1</sup> on the clear-cut area and 33.9 kg ha<sup>-1</sup>yr<sup>-1</sup> in the beech stand. On the other hand, the lowest amount of S-SO<sub>4</sub><sup>2-</sup>, representing 5.6 kg ha<sup>-1</sup>yr<sup>-1</sup> on clear-cut area and only 1.5 kg ha<sup>-1</sup>yr<sup>-1</sup> in beech forest was found in 2011 (Table 2).

Under 0.1 m penetrated the highest average amounts of S-SO<sub>4</sub><sup>2-</sup> on clear-cut area in 1994 (22.8 kg ha<sup>-1</sup>yr<sup>-1</sup>) and in the beech stand in 2007 (22.4 kg ha<sup>-1</sup>yr<sup>-1</sup>), representing 68–77% of the S-SO<sub>4</sub><sup>2-</sup> amounts penetrating in the same years below surface humus. The lowest average amounts of S-SO<sub>4</sub><sup>2-</sup> (0.9–1.4 kg ha<sup>-1</sup>yr<sup>-1</sup>) were found in 2011 (Table 2).

Under 0.25 m, the highest average amounts of S-SO<sub>4</sub><sup>2-</sup> penetrated on clear-cut area in 1994 (27.9 kg ha<sup>-1</sup>yr<sup>-1</sup>) and in the beech stand in 1990 (16.2 kg ha<sup>-1</sup>yr<sup>-1</sup>), representing 121–122% of the S-SO<sub>4</sub><sup>2-</sup> amounts penetrating in the same years below 0.1 m layer of soil. The lowest values (0.8–0.9 kg ha<sup>-1</sup>yr<sup>-1</sup>) were found in 2005 and 2011 (Table 2).

There have not been found significant differences ( $p < 0.01$ ) between the individual soil layers on clear-cut area and in the beech stand. Neither the differences between the years were significant. The regression analysis, however, unveiled an important influence of precipitation amount on amount of sulphate sulphur penetrating through the SH on clear-cut area. The value of correlation coefficient in case of the beech stand was 0.93, documenting a very important dependence of sulphur contents penetrating through the surface humus on the sulphur content in precipitation total.

Table 2. Amount of S-SO<sub>4</sub><sup>2-</sup> in the lysimetric solutions and precipitation collected in years 1988–2011

Locality.	Kremnické vrchy Mts								Štiavnické vrchy Mts							
	Clear-cut area				Beech stand				Open plot		Beech stand					
	Year	Lysimeter				Throughfall	Lysimeter			Precipitation	Throughfall	Lysimeter				
		Precipitation	below (m)				SH	0.10	0.25			SH	0.10	0.25		
			SH	0.10	0.25										SH	0.10
S-SO <sub>4</sub> <sup>2-</sup> (kg ha <sup>-1</sup> )																
1988	n. c.	n. c.	n. c.	n. c.	n. c.	n. c.	n. c.	n. c.	n. c.	n. c.	22.0	29.5	52.6			
1989	n. c.	6.1	7.2	4.6	n. c.	14.3	4.7	0.9	n. c.	n. c.	10.8	13.5	20.1			
1990	19.8	26.6	18.4	24.1	25.5	27.7	13.4	16.2	n. c.	n. c.	22.2	31.2	33.3			
1991	16.1	11.7	6.2	13.2	23.7	11.7	3.5	5.9	n. c.	n. c.	11.1	17.5	27.3			
1992	13.5	17.2	17.3	17.8	19.1	19.4	6.3	6.2	n. c.	n. c.	11.1	17.1	33.1			
1993	21.9	23.8	12.1	21.2	19.2	24.9	8.6	4.2	n. c.	n. c.	11.7	14.1	15.6			
1993	21.9	23.8	12.1	21.2	19.2	24.9	8.6	4.2	n. c.	n. c.	11.7	14.1	15.6			
1994	43.4	33.4	22.8	27.9	43.6	26.6	13.4	11.6	12.4	7.2	21.9	32.2	47.4			
1995	45.0	51.8	13.8	16.0	34.8	33.9	3.2	13.7	25.0	23.9	21.4	24.4	33.8			
1996	25.4	17.8	7.2	14.2	30.1	26.1	10.6	10.8	32.3	19.8	26.8	34.5	37.2			
1997	19.7	11.1	2.6	7.5	13.6	22.2	10.0	7.8	28.4	19.5	21.8	15.0	22.0			
1998	27.9	29.6	4.9	7.4	21.9	30.6	8.9	7.8	23.6	15.8	17.3	26.6	29.4			
1999	14.2	23.0	4.4	8.4	10.8	22.8	7.8	6.9	26.6	18.4	21.8	15.9	26.1			
2000	16.2	20.4	4.8	5.8	17.2	18.1	7.6	7.1	20.8	12.9	16.1	16.8	18.2			
2001	26.8	26.6	1.8	10.4	24.9	13.5	6.6	5.9	45.3	25.1	35.1	38.0	37.6			
2002	47.2	27.9	6.5	21.1	47.2	29.7	10.7	9.4	27.8	19.5	33.8	32.3	41.1			
2003	29.1	17.2	3.7	6.2	23.0	13.1	6.5	1.4	39.0	22.3	18.8	17.5	22.7			
2005	41.3	15.3	1.9	0.9	37.0	17.8	4.4	1.0	18.1	16.2	20.4	14.2	11.8			
2006	53.4	26.8	9.0	2.7	46.2	27.0	6.8	8.6	30.4	14.9	22.8	10.8	12.2			
2007	16.2	32.5	13.9	14.8	8.4	29.2	22.4	14.2	13.6	13.7	16.5	9.7	17.2			
2008	17.5	13.2	3.8	4.8	12.1	12.9	6.8	1.9	20.7	18.1	8.8	9.1	14.1			
2009	5.4	11.2	1.9	3.5	3.7	3.9	2.9	5.2	12.5	22.3	9.5	9.9	12.5			
2010	12.6	10.1	4.1	16.6	7.9	6.2	4.6	8.0	12.8	33.3	13.3	22.2	21.9			
2011	6.7	5.6	0.9	5.9	6.2	1.5	1.4	0.8	12.1	18.4	9.6	5.9	11.9			
Mean	24.7	20.9	7.7	11.6	22.7	19.7	7.8	7.1	23.6	19.1	18.5	19.9	26.0			
Total	519.3	458.9	169.2	255.0	476.1	433.1	171.1	155.5	401.2	324.3	424.5	457.8	598.9			

SH, surface humus; n. c., not collected.

### The Štiavnické vrchy Mts

The average SO<sub>4</sub><sup>2-</sup> concentrations found in precipitation taken from clear-cut area ranged between 3.25–25.33 mg l<sup>-1</sup> (in average 14.41 mg l<sup>-1</sup>) and were slightly lower compared with concentrations in throughfall, which ranged from 9.6 to 24.7 mg l<sup>-1</sup> with average 16.83 mg l<sup>-1</sup> (Fig. 1d, Table 1). The mean SO<sub>4</sub><sup>2-</sup> concentrations found in lysimetric solutions on beech plot

ranged between 19–29 mg l<sup>-1</sup> and, due to occasional occurrence of lateral flows, they were increasing toward lower soil layers (Fig. 1e, Table 1).



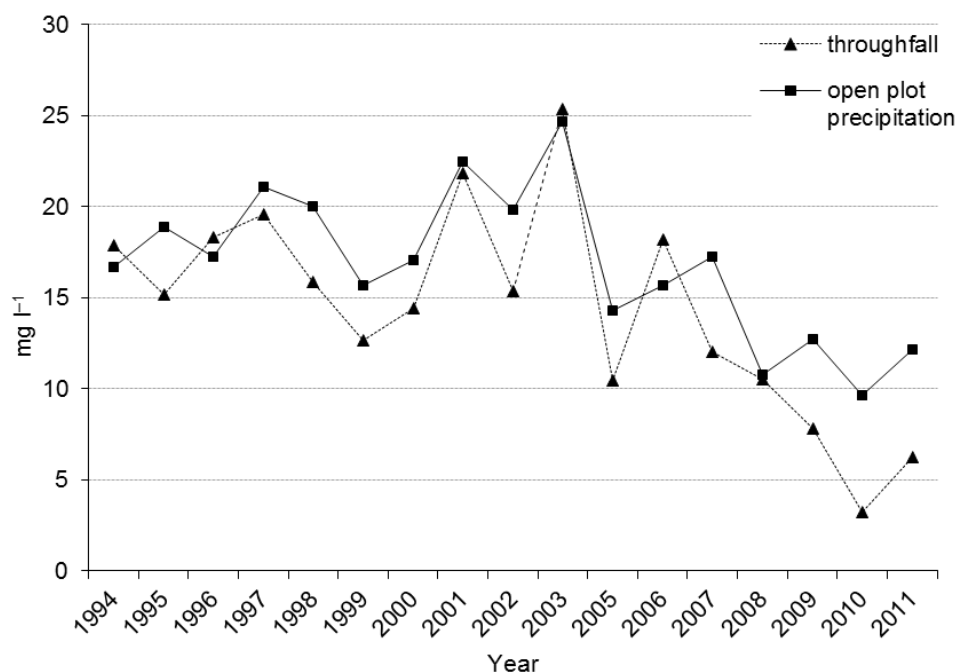


Fig. 1d. The dynamics of  $\text{SO}_4^{2-}$  concentrations in throughfall and precipitation taken from the beech ecosystem in the Štiavnické vrchy Mts.

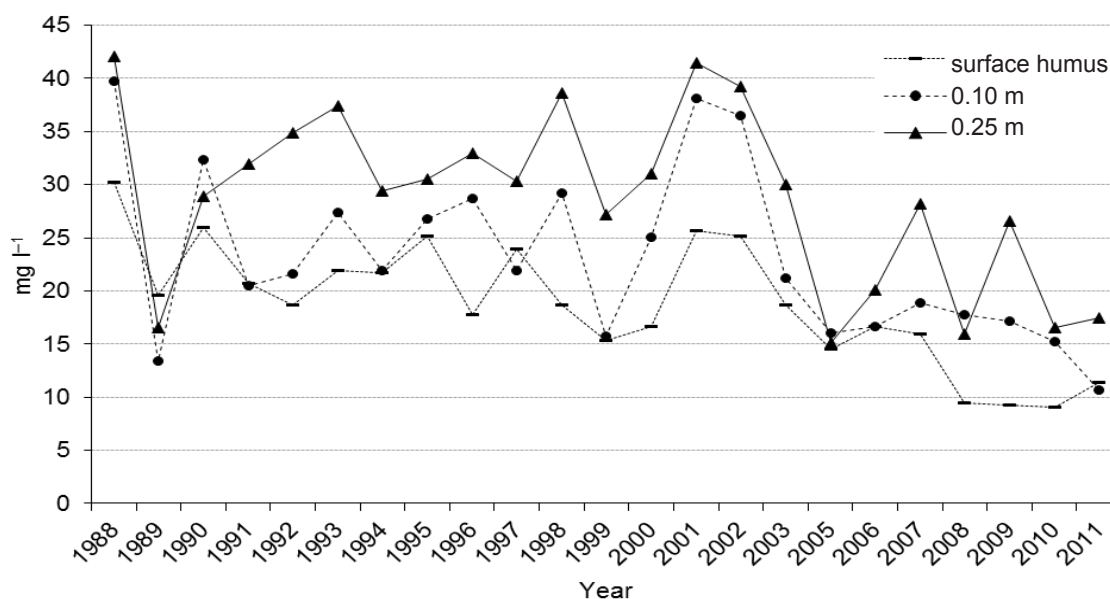


Fig. 1e. The dynamics of  $\text{SO}_4^{2-}$  concentrations in lysimetric solutions collected below surface humus and 0.10 and 0.25 m layer of Cambisol in beech ecosystem of the Štiavnické vrchy Mts.

The average amount of  $\text{SO}_4^{2-}$  deposited on open plot reaches  $23.6 \text{ kg ha}^{-1} \text{ yr}^{-1}$ , i.e. about 1 kg less compared with open plot in the Kremnické vrchy Mts. Below crown layer of beech forest, there penetrated a slightly lower amount of  $\text{S-SO}_4^{2-}$  ( $19.1 \text{ kg ha}^{-1} \text{ yr}^{-1}$ ; Table 1). The average amounts of  $\text{S-SO}_4^{2-}$ , which penetrated below surface humus and 0.10 and 0.25 cm mineral soil layers in the beech forest reached 18.5, 19.9 and

$26.0 \text{ kg ha}^{-1} \text{ yr}^{-1}$  (Table 1). The amounts of  $\text{S-SO}_4^{2-}$  accumulated in-, or leached from these layers were: 0.6,  $-0.8$  and  $-6.9 \text{ kg ha}^{-1} \text{ yr}^{-1}$ .

As for the annual dynamics of  $\text{S-SO}_4^{2-}$ , the highest values of sulphur input were recorded in autumn. In case of throughfall and precipitation in open area, the trend was decreasing both in  $\text{SO}_4^{2-}$  concentration and in  $\text{S-SO}_4^{2-}$  amounts. The variability of  $\text{S-SO}_4^{2-}$  values

reached 31.4%–46.7% and was narrower compared with beech ecosystem in Kremnické vrchy Mts (Table 1).

The highest average amounts of  $\text{S-SO}_4^{2-}$  penetrated below surface humus was observed in 2001 ( $35.1 \text{ kg}^{-1} \text{ ha}^{-1}$ ) and the lowest value ( $8.8 \text{ kg}^{-1} \text{ ha}^{-1} \text{ yr}^{-1}$ ) in 2008. Under 0.1 m, the highest average  $\text{S-SO}_4^{2-}$  amounts penetrated in 2001 ( $38.0 \text{ kg}^{-1} \text{ ha}^{-1} \text{ yr}^{-1}$ ), representing 108% of the  $\text{S-SO}_4^{2-}$  amounts penetrating in the same year below surface humus. The lowest average amount of  $\text{S-SO}_4^{2-}$  ( $5.9 \text{ kg}^{-1} \text{ ha}^{-1} \text{ yr}^{-1}$ ) was found in 2011. Under 0.25 m, the highest average amounts of  $\text{S-SO}_4^{2-}$  penetrated in 1988 ( $52.6 \text{ kg}^{-1} \text{ ha}^{-1} \text{ yr}^{-1}$ ), representing 178% of the  $\text{S-SO}_4^{2-}$  amounts penetrating in the same years below 0.1 m layer of soil. The lowest values ( $11.8$ – $11.9 \text{ kg}^{-1} \text{ ha}^{-1} \text{ yr}^{-1}$ ) were found in 2005 and 2011 (Table 2).

Neither in the case of beech ecosystem in the Štiavnické vrchy Mts were observed significant differences between the individual soil layers. It was found the sulphur content in precipitation influenced the sulphur content in soil solution. There were no significant differences in sulphur content in throughfall and in open area between the studied beech ecosystems. Significant differences ( $p < 0.001$ ) were recorded in contents of  $\text{S-SO}_4^{2-}$  penetrating through 0.10 and 0.25 m layers of beech ecosystems in the Kremnické and Štiavnické vrchy Mts.

## Discussion

Today, the strong influence of so called anthropic factors on many, not only forest, ecosystems has been recognised undisputable. This fact has also been confirmed by the variability of the results of our research focused on sulphur and its compounds distribution, primarily concerning the deposition of all substances in many, not only forest, ecosystems. The research was conducted in areas with different atmospheric pollution and revealed presence of several determining factors. Important is the nature of parent rock material and soil depth. Some authors point at influence of surface humus structure and the associated stands composition (HRUŠKA et al., 2001, PICHLEK et al., 2006, KATUTIS et al., 2008). However, the composition of the stands did not affect the amount of sulphur entering the soil in our case, because the research was done in more or less homogeneous beech stands aged of 110 years. The biggest fluctuations in sulphur amounts were observed in the 1990s in close connection with fluctuations of sulphuric emissions from the local sources. In indirect way, the sulphur amount in soil solutions is significantly dependent on precipitation amount (LINDROOS et al., 2006, ŽALTAUSKAITĖ and JUKNYS, 2009) and on amount of sulphur in atmospheric deposition (NOVOTNÝ et al., 2008). The last in these “natural” determining factors is altitude (HRUŠKA et al., 2006).

DUBOVÁ and BUBLINEC (2006) recorded on the same plots in the Kremnické vrchy Mts  $25.0 \text{ kg S ha}^{-1}$

$\text{yr}^{-1}$  in precipitation on the open plot and  $24.9 \text{ kg S ha}^{-1} \text{ yr}^{-1}$  in the beech stand. The results of these authors match our results according to which maximum amounts of sulphur in precipitation were recorded in years 1994–1995. The authors mentioned that in these years were recorded increased sulphur amounts across the whole Europe – both in atmospheric deposition and in soil water. The results of emissions monitoring in Europe document an increase in emitted pollutants ( $>20.0 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ ) also in SE part of Great Britain and in industrial areas of Central Europe (TARRASON et al., 2006).

The highest amounts of sulphate sulphur in the Kremnické vrchy Mts were found in surface humus, which is in accordance with the results obtained by KAŇA and KOPÁČEK (2005) in soils of selected forest stands in the Czech Republic. TEJNECKÝ et al. (2013) found in the Jizerské hory Mts the lowest amount of  $\text{SO}_4^{2-}$  in the organo-mineral A soil horizons, and this was true under each of two analysed vegetation types.

The mean input of  $\text{S-SO}_4^{2-}$  into the studied beech ecosystems was within a limit value of  $10$ – $30 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ , for mountain nature forests stated by UN ECE (1993, in TUČEK et al., 2004). However, in some years, there were recorded also significantly higher  $\text{S-SO}_4^{2-}$  inputs – in the Kremnické vrchy Mts ranging from  $41.3$ – $53.4 \text{ kg ha}^{-1} \text{ yr}^{-1}$  (in 1994, 1995, 2002, 2005 and 2006) and in the Štiavnické vrchy Mts ranging from  $30.4$ – $45.3 \text{ kg ha}^{-1} \text{ yr}^{-1}$  (in 1996, 2001, 2003 and 2006), Table 1.

The regression analysis unveiled an important influence of precipitation amount on amount of sulphate sulphur penetrating through the SH on clear-cut area. The value of correlation coefficient in case of the beech stand was 0.93, documenting a very important dependence of sulphur contents penetrating through the surface humus on the sulphur content in precipitation total.

Remarkable is also the fact that in some years, after thinning intervention, the sulphur amount was found higher in soil solution sampled below SH than in the throughfall. MINĚŠ et al. (2001) explain this phenomenon by high sulphur concentration values, that means also amounts of sulphur in horizontal precipitation (mist, dew), not involved in precipitation totals. The same results were also found by TESAŘ et al. (2004) in forests of the Šumava Mts, with  $\text{SO}_4^{2-}$  concentrations in horizontal precipitation (mist and cloud water) ranging between  $0.31$ – $77.60 \text{ mg l}^{-1}$ , and in bulk precipitation  $0.25$ – $27.73 \text{ mg l}^{-1}$ . At the same time, the annual sulphur deposition in mist can reach up to  $1,436.88 \text{ kg km}^2 \text{ yr}^{-1}$  and share by even 79.6% in the total deposition. Another important factor balancing sulphur deposition in forest stands is stemflow. KANTOR and LOCHMAN (1985) found higher sulphur concentrations in throughfall and stemflow than in open area in the Orlické vrchy Mts.

The total annual amount of sulphur reaching the soil surface in spruce stands can be  $49$ – $80 \text{ kg S ha}^{-1} \text{ yr}^{-1}$  (NOVÁK et al., 2007). In the Sliezske Beskydy



Mts, NOVOTNÝ et al. (2008) recorded  $14.7 \text{ kg ha}^{-1} \text{ yr}^{-1}$   $\text{S-SO}_4^{2-}$  in beech stands and  $12.9 \text{ kg ha}^{-1} \text{ yr}^{-1}$  on open plot. For atmospheric precipitation, the authors reported even  $20.5 \text{ kg ha}^{-1} \text{ yr}^{-1}$   $\text{S-SO}_4^{2-}$ . According to results presented by DUBOVÁ and BUBLINEC (2006), the maximum amounts of sulphate sulphur in autumn and winter precipitation are similar. On the other hand, PICHLER et al. (2006) found in mixed forests maximum values of  $\text{S-SO}_4^{2-}$  in winter precipitation. KAISER and GUGGENBERGER (2005) studying soils in 90-year-old beech stands in NE Bavaria recorded in autumn up to 53% of the total annual amount of organic sulphur.

The deposition of sulphur in forests is usually higher than in the adjacent forestless areas. We are aware only of few exceptions reported in literature sources from deciduous forests. For example, PAVLENDA et al. (2012) found lower values of sulphur deposition in beech stands compared with open plots.

## Conclusions

The testing has corroborated the null hypothesis about significant influence of precipitation amount and sulphur content in atmospheric deposition on concentration of sulphur in percolating soil solutions. The studied ecosystems differ in mean sulphur amounts penetrated through 0.10 m soil layer and even through 0.25 m soil layer. The cause may be the large amounts of sulphur accumulated in the soils of the beech ecosystems in the Štiavnické vrchy Mts by year 1990. No differences in sulphur contents in precipitation collected on studied plots have been found, nor the inter-annual differences in sulphur contents were statistically significant. The annual dynamics shows maximum  $\text{S-SO}_4^{2-}$  values primarily in autumn, minimum in summer or spring. This is also in accordance with  $\text{SO}_4^{2-}$  concentration values.

The results indicate that the assumption about lower immission load on the beech ecosystem located in the southern part of the Kremnické vrchy Mts is not in line with reality, at least in the case of  $\text{S-SO}_4^{2-}$ . The input of sulphur by atmospheric precipitation and throughfall was in fact by about  $120 \text{ kg ha}^{-1}$  and  $150 \text{ kg ha}^{-1}$  higher in the southern part of the Kremnické vrchy Mts compared with the beech ecosystems in the Štiavnické vrchy Mts.

## Acknowledgement

This investigation was supported by the Scientific Grant Agency of the Slovak Academy of Sciences Nos. 2/0089/14, 2/0120/17, and 2/0126/16.

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Received January 25, 2017  
Accepted November 14, 2017