

Sulphate concentration and S-SO₄²⁻ flux in soil solutions in the West Carpathians Mountains on an example of submontane beech forest stand

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ABSTRACT: The paper presents the evaluation of data on precipitation totals and on SO₄²⁻ concentrations and S-SO₄²⁻ fluxes in lysimetric waters in a submontane beech stand. The records cover continually a 19-year period. The site is situated in the Kremnické vrchy Mountains, belonging to the West Carpathians Mountains. The material was sampled on two plots. The first had been clear cut immediately before the research started (1989), the second was covered with the original forest stand. In total, the highest SO₄²⁻ concentrations on the open plot were measured four years after the intervention (1993) at the soil depth of 0.25 m (40.50 mg·l⁻¹). The lowest values were recorded in 1989 on the control plot at the soil depth of 0.25 m (4.54 mg·l⁻¹). The sulphate sulphur deposition was the highest in 1995 in the surface humus layer on the open plot (51.8 kg·ha⁻¹·year⁻¹). A very significant influence of precipitation totals on sulphur amounts deposited in the particular soil horizons was also confirmed. No interannual differences in SO₄²⁻ concentration and S-SO₄²⁻ flux were proved.

Keywords: sulphate concentrations; soil water; submontane beech forest; West Carpathians Mts

At present, we are facing three distinct crucial environmental issues. The most discussed one is global warming, followed by the ozone layer thinning and finally by air pollution causing soil acidification (PANNATIER et al. 2004; PAVLŮ et al. 2007; MONGEON et al. 2010). The negative impact of anthropic activities is their common feature and primary cause.

In this context, we focussed our research on an important factor in the forest soil acidification – sulphate concentrations in soil water. Sulphur, nitrogen, hydrogen ions and solid particles act as the major parts of the currently discussed forest soil development process.

Sulphur is an essential biogenic macroelement involved in protein synthesis and in material exchange pathways between them. The element is present in

some amino acids (cysteine, methionine), in plant fats and essential oils, vitamins, enzymes and coenzymes. It participates in redox processes occurring in plants. It supports atmospheric nitrogen fixation (FECENKO et al. 2010). Atmospheric sulphur entering the soil in precipitation (STACHURSKI, ZIMKA 2000) causes the displacement of basic ions and soil acidification. Soil acidification is a long-term, cumulative (HRUŠKA et al. 2001), dynamically developing process, the effect of which, mostly the negative one, needs some time to become identifiable. The alarming degradation of environment, primarily of forest soils, has required to establish limits for deposition in forest ecosystems.

Following the concept set by the UN Economic Commission for Europe (UN ECE), critical loads in the highest allowable deposition of acidifying

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substances not causing yet chemical modifications with permanent harmful impacts on the structure and performance of ecosystems have been defined. The main idea underlying this concept is the calculation of the ecosystem bearing capacity which can still buffer the atmospheric deposition (MINĎÁŠ et al. 2001; KALÚZ 2004).

The defined limits have become an important tool for designing strategies for national governments for reducing sulphur and nitrogen emissions in Europe and in North America (MATZNER, MEIWES 1994).

The territory of the Slovak Republic is medium sensitive to sulphur deposition. The critical value established for sulphur deposition in the Slovak Republic is 10–30 kg·ha⁻¹·year⁻¹. This value, however, has been exceeded on about one quarter of Slovak forest soils. In the years 1989–1999, the total amount of basic pollutants emitted across the SR was reduced by 57.9% – which represents an average yearly decrease by almost 6%. The data from 2000 (compared with the average values from 1985–1987) show an 83% (58.5 t·year⁻¹) reduction in particles, 77% (134.4 t·year⁻¹) in SO₂ and 42% (113.9 t·year⁻¹) in NO_x (KALÚZ 2004). The Report on the Health Condition of the Slovak Forests (<http://www.forestportal.sk>) shows that the atmospheric deposition values for sulphur were lower than for nitrogen on the all monitoring plots. In 2006, a drop in sulphur deposition by 50% (3.8 to 16.4 kg·ha⁻¹·year⁻¹) on average was recorded compared to 2001.

The data from the neighbouring Czech Republic comparing the emitted amounts between the years 1990 and 2000 show a decrease by 86% in SO₂ and by 53% in ammonium. The dry SO_x (SO₂ + SO₄²⁻ in aerosol) deposition dropped by 81%, the wet deposition of SO₄²⁻ by 32% (ZAPLETAL, CHROUST 2005; ZAPLETAL 2006). In NW Bohemia, FIALA et al. (2001) recorded a drop in SO₄²⁻ concentration from 7.5 mg·l⁻¹ in 1987 to 2.5 mg·l⁻¹ on average in 1997.

A decrease in SO₂ emissions across Western Europe was reported by PRECHTEL et al. (2001).

METHODS AND STUDY AREA

Research plots (RP) are situated in the Kremnické vrchy Mts (48°38'N, 19°04'E), in the central part of the West Carpathians Mts. The leading, highly dominant forest woody plant is beech, the stand age is 90–100 years, the average tree height is 28 m. The site is at an altitude of 450–510 m a.s.l., on a slope with an inclination of 17–20° (BARNA 2004,

2008; BARNA et al. 2009). The site climate is moderately warm, hilly district B5 with average annual temperature $t_{1951-1980}$ of 6.8°C and average annual precipitation total of 778 mm (SCHIEBER 2006).

The mean annual precipitation total in the growing season is 395 mm, the growing season length is 115–165 days.

The prevailing soil-forming substrate consists of andesite tuff agglomerates from which a saturated variant of andosolic Cambisol with the skeleton content increasing with depth has been formed. The soil body is layered, composed of the main and the basal layer system (PICHLER 2003; PICHLER et al. 2009a,b). The soils were created in the Pleistocene period under active presence of solifluction processes and have these basic macromorphological characteristics:

Control plot – the soil is eutric andosolic Cambisol, the humus form is acid mull. Oo – 3 cm, layer of beech leaves and twigs. Oof – 0.5 cm, layer of partially decomposed beech leaves. Aoq – 0–8 cm, black-brown, freshly moist, with moderate amounts of roots, tiny andesitic gravel 10–15%. Bv1 – 8–45 cm, dark brown, clay loam, lumped, coarse andesitic gravel 20%. Bv2 – 45–75 cm, brown, clay loam to clayey, compact, moist, coarse tuffaceous gravel and stones 30–40%. C – 75–90 cm, parent rock with small layers of brown clay, moist, without roots. R – > 90 cm, solid tuff. Fieldes–Perrot's test for B horizons slightly positive.

Open plot – the soil is eutric andosolic Cambisol, the humus form is acid mull. Oo1 – 1–2 cm, layer of beech leaves and twigs. Oof – 0.5 cm, layer of partially decomposed leaves of beech and grasses (*Carex pilosa*). Aoq – 0–8 cm, black-brown, loamy, with fine moderate scrums, freshly moist, with moderate amounts of roots, tiny to coarse andesitic gravel 5%. Bv1 – 8–40 cm, dark brown, clay loam, lumped, coarse andesitic gravel 20%. Bv2 – 40–60 cm, dark brown, with grey and yellow stains of sandy clay around the tuffaceous skeleton, tiny to coarse gravel 40%. B/C – 60–85 cm, brown with fine yellow shade, clay-loam with sand admixture, lumped, strongly compact, moist, coarse gravel and stones 60%. R – 85–110 cm, soft tuff, rare with red colour. Fieldes–Perrot's test for B and B/C horizons slightly positive (KUKLA 2002).

From the viewpoint of forest typology, the plots belong to the 3rd forest vegetation zone, nutrient order B, group of forest types *Fagetum pauper inferiora* (ZLATNÍK 1959).

As for coenology and taxonomy, the central association is: *Dentario bulbiferae-Fagetum*, well distributed is also *Carici pilosae-Fagetum*.

Table 1. Basic data of beech stands on the plots after experimental cutting in February 1989. Ecological Experimental Site (EES), Kremnické vrchy Mts. (Western Carpathians Mts.)

Plots	Year	Stem density (No·ha ⁻¹)	Height (m)	Dbh (cm)	Stocking density	Basal area (m ² ·ha ⁻¹)	Area (m ²)	Height of beech seedling (cm)
C – control	1990	700	23.6	23.9	0.90	40.90	1,500	6
	1996	633			0.87	41.20		20
	2002		26.3	27.6	1.00			50
L – light cut	1990	397	25.4	29.4	0.70	28.80	3,500	7
	1996	363			0.78	33.10		10
	2002		28.6	34.5	0.90			30
M – medium cut	1990	243	26.9	31.3	0.50	18.60	3,500	8
	1996	229			0.62	23.80		90
	2002		29.5	38.5	0.70			200
H – heavy cut	1990	160	27.7	32.0	0.30	13.50	3,500	10
	1996	160			0.40			100
	2002		30.0	41.4	0.70	18.50		300
CC – clear cut	1990	0			0.00		4,000	15
	1996				0.00			210
	2002				0.00			480

Dbh – the mean diameter at breast height

In February 1989, the forest stands were subjected to regeneration cutting of different intensities – with the aim to adjust the stand stocking density. A series of partial plots differing in stocking density and also in ecological conditions has been created. In our study, we focussed on a comparison between the clear cut plot and the control plot left without silvicultural interventions (Table 1).

Lysimetric waters and throughfall

Lysimetric waters were sampled into plastic collectors with an area of 1,000 cm² in 3 soil horizons. The 1 series of collectors was installed in the 00 layer, that means in the surface horizon (organic layer), the 2 series at the depth of 0.1 m (upper mineral layer), and the 3 was placed at the depth of 0.25 m below the ground surface (lower mineral layer) (KUKLA 2002). The lysimeters and throughfall samplers were placed on the plots in 1988, three exemplars in each soil horizon.

Since 1989, the samples were taken monthly, at regular intervals, chemically processed in the laboratory, and subjected to statistical evaluation (LINDBERG, TURNER 1988). The measuring preci-

sion was 10⁻² l. The samplers for throughfall and wet deposition consisted of a bottle equipped with a funnel (660 cm² each) inserted into the cap of the bottle. Ten sampling devices were installed on each site (both open field and stand). The samples were collected monthly, and/or after a strong precipitation event. Samples of the open field and stand were individually pooled after each sampling period. These representative samples were analyzed (TUŽINSKÝ 2002).

Chemical analyses

The SO₄²⁻ concentrations were determined in a common way – by titration with lead nitrate in dythizone and conversion of the obtained value to sulphate sulphur. pH values, conductivity values, contents of fluorides, chlorides and nitrates were also measured.

Statistical methods

Statistical characteristics of measure and position were processed using the STATISTICA V 7

package. The hypothesis about normal distribution was tested by the Shapiro-Wilk W test. The significance of interannual differences was tested by Student's t -test. The obtained results were also verified by the two-sample test from the Statgraphics software package. Simple regression was used for an assessment of the influence of precipitation total on sulphate concentration in soil solutions taken from the particular soil horizons and in atmospheric precipitation.

RESULTS AND DISCUSSION

Amount of sulphates in the soil water of surface humus

In 1989, the average values of sulphate concentration in the soil surface horizon on the just deforested plot were almost three times higher than on the control plot with the original forest stand

(5.26/14.45 $\text{mg}\cdot\text{l}^{-1}$ – control plot, corresponding to 6.1/14.3 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{year}^{-1}$ $\text{S}\cdot\text{SO}_4^{2-}$). In that year we also recorded the lowest average concentration over the entire study period. During the next five years up to 1994, the sulphate concentration in the surface humus on the clear cut was lower by 3–4 $\text{mg}\cdot\text{l}^{-1}$ (Figs 1a, 1b) compared to the forest, and still somewhat below the critical limit of 14 $\text{mg}\cdot\text{l}^{-1}$ SO_4^{2-} (KUNCA 2007).

However, in 1994 this critical threshold was clearly exceeded by the value of 21.62 $\text{mg}\cdot\text{l}^{-1}$ (representing 33.4 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{year}^{-1}$ $\text{S}\cdot\text{SO}_4^{2-}$). The concentration in the stands was lower by more than 3 $\text{mg}\cdot\text{l}^{-1}$ at the same time. During the next six years up to the 2001, the concentration on the open plot was by 2–3 $\text{mg}\cdot\text{l}^{-1}$ lower again than in the forest stand, and still very near to the critical limit value.

Twelve years after the intervention, the development trend of $\text{S}\cdot\text{SO}_4^{2-}$ fluxes on the clear cut was getting similar to the parent stand; small differences were in favour of the clear cut plot. The

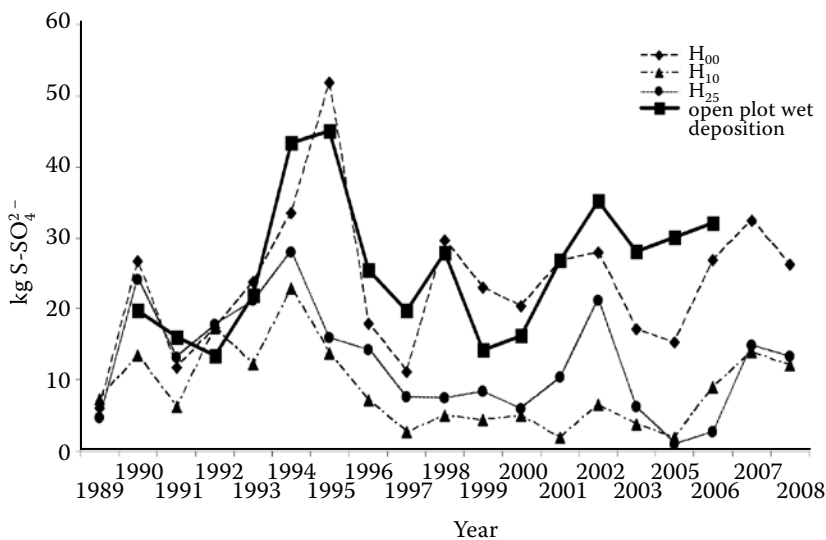


Fig. 1a. The flux of $\text{S}\cdot\text{SO}_4^{2-}$ in soil horizons on the H plot and precipitation on the open plot of Kremnické vrchy Mts. in 1988–2008

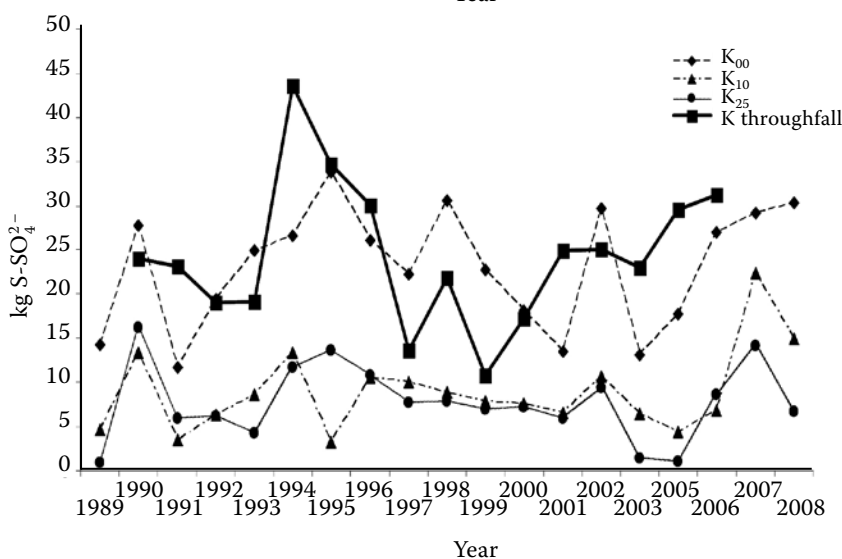


Fig. 1b. The flux of $\text{S}\cdot\text{SO}_4^{2-}$ in soil horizons on the K plot and forest throughfall of Kremnické vrchy Mts. in 1988–2008

Table 2. Descriptive statistics of SO_4^{2-} concentrations in the Kremnické vrchy Mts. (Western Carpathians Mts.) in 1989–2005

Lysimeter	K_{00}	K_{10}	K_{25}	Forest through-fall	H_{00}	H_{10}	H_{25}	Precipitation on the open plot	Precipitation (mm)
Valid	19	19	19	16	19	19	19	16	16
Mean	15.52	15.93	17.33	15.41	13.99	15.83	15.41	11.39	751.05
Median	14.45	15.56	16.10	14.96	14.26	13.62	12.52	11.57	701.21
Min	7.74	7.07	4.53	8.47	5.26	5.68	6.62	6.38	354.90
Max	27.14	27.59	33.64	20.46	24.64	35.04	40.49	22.62	1,532.30
Range	19.40	20.52	29.11	11.99	19.38	29.37	33.87	16.24	1,177.40
V_x %	27.80	28.50	34.03	19.90	33.10	49.28	53.76	34.86	37.59
Variance	18.65	20.61	34.82	9.39	21.45	60.86	67.61	15.76	79,746.45
Std. dev.	4.32	4.54	5.90	3.07	4.63	7.80	8.28	3.97	282.39
Std. error	0.99	1.04	1.35	0.74	1.06	1.79	1.90	0.97	70.59
Lower quartile	13.67	13.36	15.11	12.58	11.14	10.29	10.36	8.40	552.35
Upper quartile	17.82	18.51	19.20	16.13	16.52	22.09	19.09	12.33	893.25
Percentile 10,00000	9.34	10.29	11.41	11.58	6.97	8.37	7.96	7.35	507.70
Percentile 90,00000	20.53	21.55	24.00	19.04	21.62	30.48	29.52	16.51	1,035.50

K_{00} – K_{25} – lysimeter in the forest, H_{00} – H_{25} – lysimeter in the open plot

cause may consist in the advance growth on this plot – exceeding a height of 12 m in 2006. In that year, the mean annual sulphate concentrations on both plots reached their maxima: $24.64 \text{ mg}\cdot\text{l}^{-1}$ ($26.8 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{year}^{-1} \text{ S}\cdot\text{SO}_4^{2-}$) on the former clear cut, and $27.14 \text{ mg}\cdot\text{l}^{-1}$ ($27.0 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{year}^{-1} \text{ S}\cdot\text{SO}_4^{2-}$) in the forest stand. In both cases, the critical threshold established for forest soils in the Slovak Republic was exceeded by almost 100%. On the other hand, the lowest mean SO_4^{2-} concentrations in the surface humus on the clear cut plot were $5.26 \text{ mg}\cdot\text{l}^{-1}$ and more than $6 \text{ mg}\cdot\text{l}^{-1}$ recorded in 1989 and 1991, respectively. In the forest stand, the lowest value was $7.74 \text{ mg}\cdot\text{l}^{-1}$, representing more than $17.0 \text{ kg}\cdot\text{ha}^{-1}$ per year $\text{S}\cdot\text{SO}_4^{2-}$ sulphates deposited in the layer of surface humus. Since 2006, the differences between the plots were very small (less than $1.0 \text{ mg}\cdot\text{l}^{-1}$). During this period, the critical limit values were not exceeded on the former clear cut plot any more. The sulphate concentration in soil can also be influenced (HRUŠKA et al. 2001) by the type and intensity of silvicultural measure – driving the following base cations depletion. Indirect but significant factors influencing the sulphur amounts in soil solutions are: precipitation amount (LINDROOS et al. 2006), soil depth (MANDERSCHIED et al. 2000),

composition of surface humus layer (KATUTIS et al. 2008), atmospheric sulphur deposition (NOVOTNÝ et al. 2008), altitude (PICHLER et al. 2006), and physical and chemical properties of forest soils.

The variability in SO_4^{2-} concentrations was found lower in the forest stand where it did not exceed 28% (Table 2).

The critical sulphur amount in throughfall – $30 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{year}^{-1}$ established for the Slovak Republic by KALÚZ (2004) was not exceeded either on the open cut or in the forest stand until 1994. The amounts of sulphur deposition recorded until 1996 were lower on the open plot than on the control plot with the original forest stand. From that year to the year 2008, the sulphur flux entering the soil on the former clear cut was higher compared to the control – which could be explained by the total precipitation amounts that were higher on the former clear cut. The highest depositions of the throughfall sulphate sulphur on the study plots were recorded in 1994, with very similar values of $43.58 \text{ kg}\cdot\text{ha}^{-1}$ per year, that means exceeding the critical threshold more than twice. These facts are in contradiction with the above-mentioned information about a very significant general decrease in sulphur oxides. A possible explanation is the quality of emit-

ted substances and dispersion conditions (a 204 m tall chimney) favourable for transport from distant important pollution sources – the aluminium plant in Žiar nad Hronom and the thermal power station in Nováky. Our measurements show that the critical SO_4^{2-} loads were exceeded both in soil solutions and in atmospheric deposition during almost the entire period of study. The year 2007 with only $12.03 \text{ mg}\cdot\text{l}^{-1} \text{ SO}_4^{2-}$ in atmospheric precipitation on the open plot was the only exception. In the surface soil horizon, we also measured the highest values of $\text{S}\cdot\text{SO}_4^{2-}$, which corresponds to the findings reported by KÁŇA and KOPÁČEK (2005) for soils in selected forest stands in the Czech Republic. Interesting is also the fact that four, five and six years after the cut, the sulphur flux in the soil water in the surface horizon was higher than the amount of this substance in the throughfall. NOVÁK et al. (2007) explained this fact by comparatively higher values of sulphur concentrations, and so also amounts present in horizontal precipitation (mists, dew, also stemflow) that have not been included in the precipitation summaries. Another possible cause is sulphur in litter and surface humus.

The throughfall on the plot without intervention manifested the lowest value of the coefficient of variation (19.20%) – revealing relatively stable and balanced conditions on this plot. The respective value on the open plot did not exceed 35%.

The tests of differences in SO_4^{2-} concentrations in the surface humus did not confirm significance of these differences. The regression analysis unveiled a close dependence of concentrations of SO_4^{2-} and $\text{S}\cdot\text{SO}_4^{2-}$ on the total precipitation amount: the correlation coefficient was 0.85 and 0.93 on the open plot and in the forest stand, respectively.

Amount of sulphates in soil water of the upper mineral layer

The mean SO_4^{2-} concentration in this horizon over the entire study period reached $15.83 \text{ mg}\cdot\text{l}^{-1}$, more by almost $2 \text{ mg}\cdot\text{l}^{-1}$ than in the surface horizon. Converted to the sulphate sulphur, the amount having reached this depth on the open plot was $9.0 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{year}^{-1}$, representing 38.3% of the flux of $23.4 \text{ kg}\cdot\text{ha}^{-1} \text{ S}\cdot\text{SO}_4^{2-}$ measured in the surface horizon on this plot. The cause was in lower soil water volumes at this depth. The highest percolation of $23.0 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{year}^{-1} \text{ S}\cdot\text{SO}_4^{2-}$ to the depth of 0.10 m was recorded in 1994, when the annual precipitation total was one of the highest (1,035 mm) and the SO_4^{2-} concentration in the soil ($43.37 \text{ mg}\cdot\text{l}^{-1}$)

was three times higher than the critical limits. In the same forest stands in the Kremnické vrchy Mts, DUBOVÁ and BUBLINEC (2006) recorded $25 \text{ kg}\cdot\text{ha}^{-1}$ per year of sulphur in the atmospheric deposition on the open plot and $24.9 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{year}^{-1}$ in the stand. The authors also confirmed the maximum values of sulphur in precipitation in the years 1994–1995. They reported increased sulphur amounts in atmospheric deposition and also in soil water across the whole Europe in those years. Another cause according to these authors and backed-up by the emission monitoring in Europe was a rising emission amount ($> 20.0 \text{ kg S}\cdot\text{SO}_4^{2-}\cdot\text{ha}^{-1}\cdot\text{year}^{-1}$) in SE Great Britain and in Central-European industrial areas. In 1996, VRBEK (2000) recorded $22 \text{ kg}\cdot\text{ha}^{-1}$ per year of sulphur at the 0.1 m depth in Calcocambisol on limestone in submontane beech forests in Croatia (Zavižan – C Croatia). In the same year, a sulphur amount of $10.6 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{year}^{-1}$ was recorded in the corresponding soil horizon in the Kremnické vrchy Mts. The same author reported the maximum sulphur concentration in emissions ranging from 3 to $15 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{year}^{-1}$, and he classified Croatia as belonging to low endangered regions in terms of soil acidification. The amount of sulphur in the open area in the discussed Croatian locality did not exceed $13 \text{ kg}\cdot\text{ha}^{-1}$ (compared to $7.2 \text{ kg S}\cdot\text{SO}_4^{2-}$ per $\text{ha}^{-1}\cdot\text{year}^{-1}$ in the Kremnické vrchy Mts.). The highest mean annual SO_4^{2-} concentration ($35.04 \text{ mg}\cdot\text{l}^{-1}$) was recorded in 1993. The SO_4^{2-} values in the stand reached the maximum ($27.60 \text{ mg}\cdot\text{l}^{-1}$) in 1997. Interesting is the trend of higher SO_4^{2-} concentration in the stand in this soil horizon on the control plot since 1996, that means seven years after the silvicultural intervention. Until that year, higher concentrations were recorded on the clear cut, which could be considered as open area at that time, because the developing succession stand could not yet act as a filter for atmospheric deposition. The higher coefficient of variation (49.28%) and the higher value of standard deviation (7.80) on the plot treated with the clear cut also reveal a comparatively high variability in the values within the seasons and a high variability in the mean annual SO_4^{2-} concentrations at this depth.

The critical sulphate concentration levels were exceeded more frequently in the forest stand (Figs 1a, 1b). Since 1996 the sulphate concentrations on the former clear cut were under the critical limit, with the only exception in 2002 ($15.78 \text{ mg}\cdot\text{l}^{-1}$).

The differences among the years were not found significant, the differences between the plots were significantly higher ($P < 0.05$) in the first five years following the clear cut.

Amount of sulphates in soil water of the lower mineral layer

The development trend of SO_4^{2-} concentrations in the horizon 0.25 m under the ground surface on the former clear cut was as follows: the mean annual concentrations until 1996 (eight years after the cutting) were higher than in the surface layer and in most cases also lower than at the depth of 0.1 m. During the following period 2004–2008, the concentrations at the depth of 0.25 m were lower than in the other two soil layers. However, the soil water amount considerably influenced the sulphur amount percolating to this depth ($14.0 \text{ kg}\cdot\text{ha}^{-1}$ per year) – up to 62% of sulphur in the surface humus layer. It follows that the sulphur accumulation is the highest exactly on this plot. A similar trend was also recorded on the control plot, without any differences but in absolute sulphur units per 1 ha – from which the ability of the stand to filter atmospheric sulphur deposition was evident (VRBEK

2000). On the former clear cut, the SO_4^{2-} concentration range was the widest ($33.88 \text{ mg}\cdot\text{l}^{-1}$), and, at the same time, the standard deviation was the highest ($8.28 \text{ mg}\cdot\text{l}^{-1}$). The average variability of the values on the open plot was 53.76%, reflecting diverse conditions within the studied soil horizon (diversity in physical and chemical properties of forest soils, highly variable values of total precipitation and soil water content).

The highest SO_4^{2-} concentration on the open plot was recorded in 1993: the value of $40.50 \text{ mg}\cdot\text{l}^{-1}$, in the stand, it was $33.65 \text{ mg}\cdot\text{l}^{-1}$ recorded in 1990. However, the maximum flux of sulphate sulphur in the 0.25 m soil layer $27.8 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{year}^{-1}$ was observed in 1994 (Figs 1c, 1d).

This amount represented up to 83.44% of the sulphur amount in the surface horizon ($33.4 \text{ kg}\cdot\text{ha}^{-1}$ per year). Also in this case, there was a significant effect of the total precipitation amount – reaching in that year its maximum values (1,035 mm) over the entire study period. Not the least significant

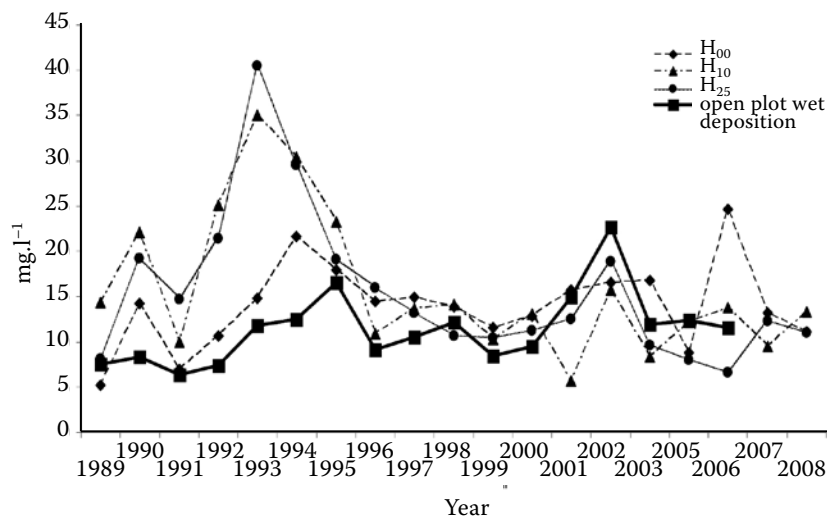


Fig. 1c. The concentration of SO_4^{2-} in soil horizons on the H plot and precipitation on the open plot of Kremnické vrchy Mts. in 1988–2008

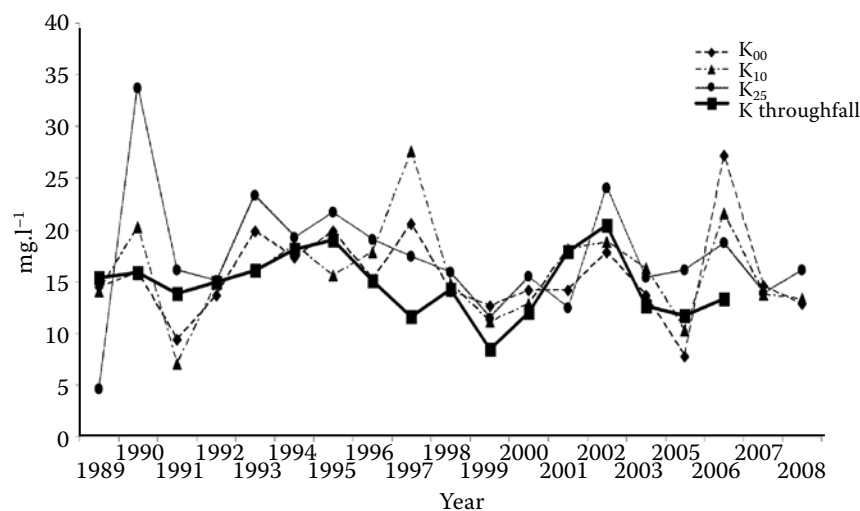


Fig. 1d. The concentration of SO_4^{2-} in soil horizons on the K plot and forest throughfall of Kremnické vrchy Mts. in 1988–2008

was the influence of the succession stand age and height. At that time, the stand was five years old, and the root system had been developed much less compared to the year 2006. In that year, the total precipitation amount of 1,530 mm containing 32.1 kg S-SO₄²⁻·ha⁻¹·year⁻¹ decreased on the plot, the SO₄²⁻ concentration at the depth of 0.25 m was only 6.62 mg·l⁻¹, after conversion 2.7 kg S-SO₄²⁻·ha⁻¹ per year. The maximum flux of sulphur deposited on the two plots was observed in autumn and winter. The summer values were lower, and they depended on the precipitation totals in the given periods. In the autumn and winter months, the occurrence of maximum sulphate sulphur amounts in atmospheric precipitation and in soil water was similar (DUBOVÁ, BUBLINEC 2006). PICHLER et al. (2006) reported maximum S-SO₄²⁻ amounts in precipitation in mixed forests in winter. KAISER and GUGGENBERGER (2005) recorded even 53% of bulk organic sulphur in the soil of 90-year-old beech forests in NE Bavaria in the autumn months.

The testing results show that the most evident differences – at a 99% significance level – were recorded mainly in this horizon. The flux of sulphur in the 0.25 m horizon was mostly influenced by the treatment intensity.

For comparison: in spruce forest stands in N Finland, PIIRAINEN et al. (2004) recorded an average sulphur deposition of 1.5 kg·ha⁻¹·year⁻¹ on a clear cut where the deposition amounted up to 4.6 kg·ha⁻¹ per year before the cutting. The critical value for coniferous stands reported by ÅGREN (1992) is 3–8 kg·ha⁻¹·year⁻¹. In spruce stands in the Krušné hory Mountains in N Bohemia, NOVÁK et al. (2007) measured 56 kg·ha⁻¹·year⁻¹ of bulk sulphur in 1994. This fact agrees with the statement that the sulphur amounts in coniferous stands are higher compared to the broadleaved ones. For spruce forests in Slovenia, ŠIMONČIČ (1996) reported a sulphur amount of about 33 kg·ha⁻¹. BUBLINEC and DUBOVÁ (1995) measured 44.5 kg·ha⁻¹ S-SO₄²⁻ in the forest and 32.7 g S-SO₄²⁻ atmospheric deposition on the open plot in spruce stands in the ridge part of the Low Tatras Mts.

CONCLUSION

The SO₄²⁻ concentrations and amounts in the particular forest soil horizons mostly depend on the total amount of atmospheric precipitation and its sulphur content, on physicochemical properties of soils, on the parent rock material, and on the forest management intensity. The influence of human

management (forest management, state of the environment) activities on sulphur content and concentration has been found evident in the deepest soil horizons on both study plots.

In spite of the declared decrease in emitted sulphur oxides, the values on the study plots frequently markedly exceeded the critical SO₄²⁻ concentration values established for soils in Slovak Republic. Possible causes are multiple: accumulation during the preceding periods, parent rock type and soil-forming process, distance from the pollution source (Žiar nad Hronom, Nováky), prevailing wind direction, stand composition, silvicultural methods and others.

References

- ÅGREN CH. (1992): Acidification still a major problem in Sweden. *Enviro*, **13**: 28–32.
- BARNA M. (2004): Adaptation of European beech (*Fagus sylvatica* L.) to different ecological conditions leaf size variation. *Polish Journal of Ecology*, **52**: 35–45.
- BARNA M. (2008): The effect of cutting regimes on natural regeneration in submountain beech forests: species diversity and abundance. *Journal of Forest Science*, **54**: 533–544.
- BARNA M., SCHIEBER B., CÍČÁK A. (2009): Effect of post cutting changes in site conditions on the morphology and phenology of naturally regenerated beech seedlings (*Fagus sylvatica* L.). *Polish Journal of Ecology*, **57**: 461–472.
- BUBLINEC E., DUBOVÁ M. (1995): Wet deposition in the crest part of the Low Tatras. *Acta Facultatis Forestalis*, **37**: 85–95.
- DUBOVÁ M., BUBLINEC E. (2006): Evaluation of sulphur and nitrate-nitrogen deposition to forest ecosystems. *Ekológia*, **25**: 366–376.
- FECENKO J., LOŽEK O., KULICH S. (2010): Importance of Application of Sulphur Fertilizers in Slovak Republic. Available at <http://www.agris.cz> (accessed May 20, 2010).
- FIALA J., RIEDER M., DVOŘÁKOVÁ M., LIVOROVÁ H. (2001): Trends in the atmospheric and hydrological cycle of sulphur at catchments in the Czech Republic. *Atmospheric Environment*, **35**: 55–62.
- HRUŠKA J., CIENCIALA E., MORAVČÍK P., NAVRÁTIL T., HOFFMEISTER J. (2001): Dlouhodobá acidifikace a nutriční degradace lesních půd, limitující faktor současného lesnictví. [The long-term acidification and nutrient degradation of forest soils.] *Lesnická práce*, **80**: 24–32.
- KAISER K., GUGGENBERGER G. (2005): Dissolved organic sulphur in soil water under *Pinus sylvestris* (L.) and *Fagus sylvatica* (L.) stands in northeastern Bavaria, Germany variations with seasons and soil depth. *Biogeochemistry*, **72**: 337–364.

- KALÚZ K. (2004): Kvalita ovzdušia na Slovensku a poškodzovanie ekosystémov. [Imission situation in Slovakia and ecosystems deterioration.] Nitra, Slovenská poľnohospodárska univerzita: 8.
- KÁŇA J., KOPÁČEK J. (2005): Sulphate sorption characteristics of the Bohemian Forest soils. *Silva Gabreta*, **11**: 3–12.
- KATUTIS K., REPSIENE R., BALTRAMAITYTE D. (2008): The effects of different soil genesis on the concentration of biogenic elements in lysimetric water. *Agronomijas Vēstis (Latvian Journal of Agronomy)*, **10**: 37–41.
- KUKLA J. (2002): Variability of solutions percolated through cambisol in a beech ecosystem. *Ekológia (Bratislava)*, **21**: 13–25.
- KUNCA V. (2007): Atmosférická depozícia a kritické záťažové klimaxovej dubiny v Štiavnických vrchoch. [Air deposition and critical load of climax oak in the Štiavnické vrchy Mts.] In: STŘELCOVÁ K., ŠKVARENINA J., BLAŽENEC M. (eds): *Bioclimatology and Natural Hazards. International Scientific Conference 17.–20. September 2007. Poľana nad Detvou, Slovak Republic*: 1–4.
- LINDBERG S., TURNER R. (1988): Factors influencing atmospheric deposition, stream export in forested watersheds. *Water, Air and Soil Pollution*, **39**: 123–156.
- LINDROOS A.J., DEROME J., DEROME K., LINDGREN M. (2006): Trends in sulphate deposition on the forest and forest floor and defoliation degree in 16 intensively studied forest stands in Finland during 1996–2003. *Boreal Environment Research*, **11**: 451–460.
- MANDERSCHIED B., SCHWEISSER T., LISCHIED G., ALEWELL C., MATZNER E. (2000): Sulphate pools weathered substrata of a forested catchment. *Soil Science Society of America Journal*, **64**: 1078–1082.
- MATZNER E., MEIWES K.J. (1994): Long-term development of element fluxes with bulk precipitation and throughfall in two German forests. *Journal of Environmental Quality*, **23**: 162–166.
- MINĎÁŠ J., ŠKVARENINA J., ZÁVODSKÝ J., KREMLER M., MOLNÁROVÁ H., PAVLENDÁ P., KUNCA V. (2001): Present results of critical levels/loads estimation in Slovakia. Zvolen, National Forest Centre: 11.
- MONGEON A., AHERNE J., WATMOUGH A.S. (2010): Steady-state critical loads of acidity for forest soils in the Georgia Basin, British Columbia. *Journal of Limnology*, **69**: 193–200.
- NOVÁK M., MITCHEL M.J., JAČKOVÁ I., BUZEK F., SCHWEISTILLOVÁ J., ERBANOVA L., PŘIKRYL R., FOTTOVÁ D. (2007): Processes affecting oxygen isotope ratios of atmospheric and ecosystem sulphate in two contrasting forest catchments in Central Europe. *Environmental Science & Technology*, **41**: 703–709.
- NOVOTNÝ R., LACHMANOVÁ Z., ŠRÁMEK V., VORTELOVÁ L. (2008): Air pollution load and stand nutrition in the Forest District Jablunkov, part Nýdek. *Journal of Forest Science*, **54**: 49–54.
- PANNATIER G.E., WALTHERT L., BLASER P. (2004): Solution chemistry in acid forest soils: Are the BC: Al ratios as critical as expected in Switzerland? *Journal of Plant Nutrition and Soil Science*, **167**: 160–168.
- PAVLŮ L., BORŮVKA L., NIKODEM A., ROHOŠKOVÁ M., PENÍŽEK V. (2007): Altitude and forest type effects on soils in the Jizera mountain region. *Soil & Water Research*, **2**: 35–44.
- PICHLER V. (2003): *Ekologicko-produkčné a environmentálne aspekty vodného režimu pôdy po zmene denzity stromovej zložky bukoveho ekosystému*. [Production Ecology and Environmental Aspects of the Soil Water Regime Due to Change of Beech Ecosystem Density.] [Habilitation Thesis.] Zvolen, TU Zvolen: 142.
- PICHLER V., BUBLINEC E., GREGOR J. (2006): Acidification of forest soil in Slovakia—causes and consequences. *Journal of Forest Science*, **52**: 23–27.
- PICHLER V., ĐURKOVIČ J., CAPULIAK J., PICHLEROVÁ M. (2009a): Altitudinal variability of the soil water content in natural and managed beech (*Fagus sylvatica* [L.]) forests. *Polish Journal of Ecology*, **57**: 313–319.
- PICHLER V., HOMOLÁK M., CAPULIAK J. (2009b): Long-term soil reaction in a temperate beech forest subject to past alkaline pollution. *Water, Air and Soil Pollution*, **204**: 5–18.
- PIIRAINEN S., FINÉR L., MANNERKOSKI H., STARR M. (2004): Effects of forest clear cutting on the sulphur, phosphorus and base cations fluxes through podzolic soil horizons. *Biogeochemistry*, **69**: 405–424.
- PRECHTEL A., ALEWELL C., ARMBRUSTER M., BITTERSÖHL J., CULLEN J.M., EVANS C.D., HELLIWELL R., KOPÁČEK J., MARCHETTO A., MATZNER E., MEESENBERG H., MOLDAN MORITYŽ K., VESELÝ J., WRIGHT R.F. (2001): Response of sulphur dynamics in European catchments to decreasing sulphate deposition. *Hydrology and Earth System Sciences*, **5**: 311–326.
- SCHIEBER B. (2006): Phenology of leafing and yellowing of leaves in selected forest trees in Slovakia. *Journal of Forest Science* **52**: 29–36.
- STACHURSKI A., ZIMKA J.R. (2000): Atmospheric input of elements to forest ecosystems: a method of estimation using artificial foliage placed above rain collectors. *Environmental Pollution*, **10**: 345–356.
- ŠIMONČIČ P. (1996): *Odziv gozdnega ekosistema na vplive kislich odložen s poudarkom na preučevanje prehranskih razmer za smreko (*Picea abies* [L.] Karst.) in bukev (*Fagus sylvatica* L.) v vplivnem območju TE Šoštanj*. [The response of the forest ecosystem to the influences of acid depositions, with the emphasis on the study of nutrition conditions for spruce (*Picea abies* [L.] Karst.) and beech (*Fagus sylvatica* L.) in the area affected by the Sostanj thermal power plant.] [Ph.D Thesis.] Ljubljana, Biotehniška fakulteta, Univerzita v Ljubljani: 85.
- TUŽINSKÝ L. (2002): Soil moisture in mountain spruce stand. *Journal of Forest Science*, **48**: 27–37.

VRBEK B. (2000): A method for monitoring deposited matter in forest ecosystems. Archives of Industrial Hygiene and Toxicology, **51**: 207–216.

ZAPLETAL M. (2006): Atmospheric deposition of nitrogen and sulphur in relation to critical loads of nitrogen and acidity in the Czech Republic. Journal of Forest Science, **52**: 92–100.

ZAPLETAL M., CHROUST P. (2005): Nelineární vztah mezi emisemi oxidu siřičitého a mokrou a suchou depozicí síry ve vybraných oblastech České republiky. [The nonlinear relationship between SO₂ and wet and air deposition of

sulphur in the selected localities of the Czech Republic.] In: HOLOUBKOVÁ I. (eds): Program a sborník konference O vzduší, Brno, 9.-11.5. 2005, Masarykova univerzita Brno: 100–108.

ZLATNÍK A. (1959): Přehled slovenských lesů podle skupin lesních typů. [The review of Slovak forests by groups of forests types.] Brno, Vysoká škola zemědělská v Brně, Lesnická fakulta: 195.

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