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Time trends of SO_4^{2-} concentration and deposition of S-SO_4^{2-} in precipitation, throughfall and soil solutions in a beech forest stand in the Štiavnické vrchy Mts.

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Abstract: Janík, R., Bublinec, E., Dubová, M. 2012: Time trends of SO_4^{2-} concentration and deposition of S-SO_4^{2-} in precipitation, throughfall and soil solutions in a beech forest stand in the Štiavnické vrchy Mts. – *Beskydy*, 5 (1): 79–86

The work summarises the data assembled and compared during a 22-year research on deposition and concentrations of sulphate sulphur in soil solutions in a submountain beech forest in the Štiavnické vrchy Mts. We also investigated the sulphur amounts in throughfall and in precipitation water in open area. The average sulphur concentration in atmospheric precipitation on the open plot was 14.92 mg.l^{-1}, in the forest stand 17.13 mg.l^{-1}. The sulphur deposition in soil increased with increasing depth: from the average of 18.9 kg.ha^{-1}.y^{-1} in the surface humus to 26.7 kg.ha^{-1}.y^{-1} in a depth of 0.25 m. The average concentration in the surface humus was 19.06 mg.l^{-1} , at a depth of 0.25 m it was 29.32 mg.l^{-1}. The total amount deposed in the soil over the whole study period was 587.1 kg.ha^{-1}S-SO_4^{2-}. The annual dynamics exhibited the highest SO_4^{2-} concentration values in the winter and spring, the lowest values were recorded in the summer and autumn. Regression analysis revealed that the sulphur content in soil solutions was very significantly influenced by sulphur content in atmospheric deposition. There has also been confirmed a major impact of rainfall total on sulphur content in precipitation water as well as in soil solutions. In general, it has been confirmed a decreasing trend for sulphur in atmospheric deposition

Keywords soil solutions, throughfall, amounts of S-SO_4^{2-}, Štiavnické vrchy Mts.

Introduction

Combustion of large amounts of rich-in-sulphur fossil fuels – facing the requirements from costumers as well as raising energy demands from industry and households, exerts a dramatic impact on rapidly increasing amounts of harmful substances emitted into the atmosphere.

As the most harmful have been classified nitrogen oxides, sulphur oxides and solid particles. These substances cause changes to soil sorption complex and affect its stability. Apart from nitrogen, the most important is sulphur and its compounds. Sulphur is an important biogenic macro-element embedded in the structure of proteins, amino-acids, vitamins, enzymes and coenzymes. It occurs in plant fats and oils, and promotes the fixation of atmospheric nitrogen. In emitted pollutants, sulphur is present mainly in form of SO_2, one of the most intensively monitored markers of emission load. Lindberg and Lovett (1992) report that sulphur present in form of SO_2 represents up to 60 % of the total sulphur.

In atmospheric precipitation, sulphur enters the soil (Stachurski and Zimka 2000) where it displaces alkaline ions and causes acidification. Acidification is a long, dynamically developing cumulative process (Hruška et al. 2001), the effect of which (mostly negative) requires some time to become evident.

The critical threshold for sulphur deposition in the Slovak Republic is 10–30 kg.ha^{-1}.year^{-1}. Since years 1989–1999, the total emissions of the basic polluting substances have been reduced by 57.9 %, which represents an average annual decrease by almost 6 %.

These facts seem optimistic, however, the danger of acidification maintains critically important, mainly due to the long-term character of this process and due to the sulphur's ability to penetrate vertically down to deeper soil horizons and to accumulate in them.

The aim of our work was to identify the trends in sulphate sulphur deposition and SO_4^{2-} concentration in the Štiavnické vrchy Mts, an area exposed to heavy load by airborne pollutants in the past.

Material and Methods

The research was carried out on two parallel study plots in the northern part of the Štiavnické vrchy Mts (48°33´ N,18°52´ E), at 470 m altitude. The first plot was covered with a 110-year-old beech forest stand with a stocking density of 0.9, the second was an open plot without forest cover. The Štiavnické vrchy Mts belong to the warm regions of Slovakia. The annual mean air temperature is 8.0–8.5 °C, in the growing season 14.5–15.5 °C (Table 1).

The mean annual precipitation total is 700–750 mm, with a maximum of 1005–1020 mm and minimum of 430–450 mm, the slope is NW facing (Kellerová 2005). The main contaminants in the Štiavnické vrchy Mts in the past were fluorine, sulphur and nitrogen oxides, arsenic, cadmium, ozone, solid particles and other, generated primarily by the regional point pollution sources (aluminium plant, power plant, transport, waste disposal). The airborne pollutants, entering in large amounts the ecosytem of the Štiavnické vrchy Mts for several years, caused changes to its ecological conditions. The result was impaired quality of the discussed beech ecosystems. Adverse effect to the ecosystems was primarily due to fluorine and SO_2. The part of the Štiavnické vrchy Mts close to the aluminium plant was for many years belonging to the heaviest polluted areas in the former Czechoslovakia. Since the late 1990s, there has been recorded an evident decrease in pollutants generation, because of innovations to the industrial structure and to implementation of the new legislation. The fluorine concentration has dropped to a tolerable level of 1 µg m^{-3} (Urminská et al. 2000).

Soil solution, bulk precipitation and throughfall

Soil solution was sampled by plate plastic lysimeters (1000 cm^2 each). The first set of the lysimeters were instaled in the forest plot in the organic layer (F_{00}). The second and third set were located at 0.1 m (upper mineral layer) and 0.25 m dephts (lower mineral layer) at both study areas (Kukla 2002). The samples had been collected monthly since 1988. The samplers for bulk precipitation and throughfall consisted of a bottle equipped with a funnel (660 cm^2 each) inserted into the cap of the bottle. Ten sampling devices

Tab. 1: Basic characteristics of the locality EES Kremnické vrchy Mts and Štiavnické vrchy Mts.

Orographic unit	Štiavnické vrchy Mts
Partial research plot	Research monitoring plot Žiar nad Hronom
Localisation	N – 48° 35' 08", E – 18° 51' 10"
Altitude [m a.s.l.]	470
Exposition	NW
Slope [°]	15
Geological substrate	ryolites tufits
Soil type	cambisol luvisol
Humus form	not done
Throughfall [mm] *	750
Temperature [°C] *	7.6
Forest type groups	Fagetum pauper
Tree composition of total EES [%]	beech 100
Age of mature stand [years]	100–105
Area of total EES [ha^{-1}]	0.15

* Throughfall and Temperature: average values from 2003–2005

were installed on each site (both open field and stand). The samples were collected monthly, eventually after a strong precipitation events. Samples of the open field and stand were individually pooled after each sampling period.

Chemical analyses

We determined SO_4^{2-} by titration with lead nitrate in dithizone and conversion (by calculation) into sulphate sulphur.

Statistical methods

For calculation of statistical characteristics of measure and position and for performing the tests, we used a Statistica v 7 Package. The significance of differences between the statistical data sets of the two localities was evaluated with using Student's t test for dependent variables. Influence of rainfall totals on sulphate sulphur deposition in precipitation and in soil solutions was assessed with simple regression.

Results and Discussion

The average $S\text{-}SO_4^{2-}$ in deposition in the soil cover humus in this part of the Štiavnické vrchy Mts was 18.9 $kg^{-1}.ha^{-1}.y^{-1}$ (Table 3). The maximum values, representing 35.1 $kg^{-1}.ha^{-1}.y^{-1}$, were measured in year 2001. In the same year, the sulphate deposition in atmospheric precipitation was also the highest: 45.3 $kg^{-1}.ha^{-1}.y^{-1}$, corresponding to a concentration of 21.84 $mg.l^{-1}$ SO_4^{2-}. The minimum $S\text{-}SO_4^{2-}$ values, representing 10.79 $kg^{-1}.ha^{-1}.y^{-1}$, were measured in year1989. The sulphate sulphur deposition values measured in the Štiavnické vrchy Mts displayed much less (only 30%) variability than the values obtained in the neighbouring Kremnické vrchy Mts. The deposition in the forest stand, in the 0.10 m layer was by 6.8% higher than in the cover humus (on average 20.5 $kg^{-1}.ha^{-1}.y^{-1}$). This provides evidence for sulphur accumulation in deeper soil layers. This trend was pronounced mainly in years 1988–1999 (Fig. 1a). The variability of these values was 43.8%. Almost over the whole study period, the highest sulphur amounts across the soil profile were found at 0.25 m, with an average value of 26.7 $kg^{-1}.ha^{-1}.y^{-1}$ (by 28.8% more than in F_{00}). The highest $S\text{-}SO_4^{2-}$ values were measured at the beginning of study in year 1988: 52.6 $kg^{-1}.ha^{-1}.y^{-1}$ (36.10 $mg.l^{-1}$), the lowest ones, 11.8 $kg^{-1}.ha^{-1}.y^{-1}$, were recorded in 2005. All soil solutions exhibited decreasing $S\text{-}SO_4^{2-}$ trends, except years 2001 and 2002 with maximum values occurring at almost all depths. This fact is possible to explain by continuing performance of the brown-coal-fired power station in Nováky. Comparing with the Kremnické vrchy Mts where $S\text{-}SO_4^{2-}$ deposition was decreasing with depth, the Štiavnické vrchy Mts exhibited an opposite trend. As for the annual dynamics, the maximum values of sulphur input were recorded in the winter or spring months.

Also the SO_4^{2-} concentration values show an increasing trend downwards deeper soil layers: from an average of 19.06 $mg.l^{-1}$ SO_4^{2-} in the humus cover to 29.32 $mg.l^{-1}$ in 0.25 m layer. The average sulphur concentration in atmospheric precipitation on the open plot was 14.92 $mg.l^{-1}$, in the forest stand 17.13 $mg.l^{-1}$. This means that the vegetation in the forest stands exerts an enhancing effect on SO_4^{2-} concentration in the throughfall. The maximum SO_4^{2-} concentration

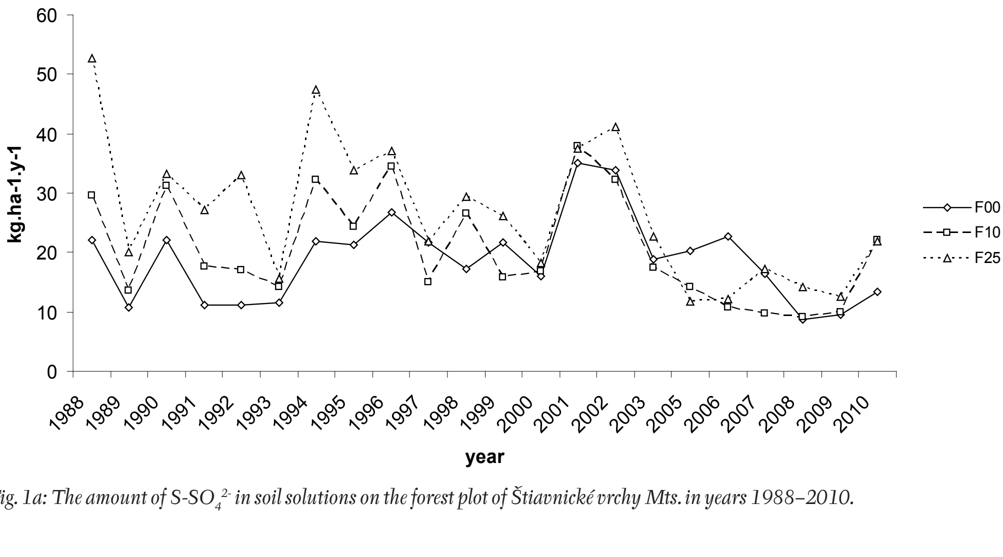

Fig. 1a: The amount of $S\text{-}SO_4^{2-}$ in soil solutions on the forest plot of Štiavnické vrchy Mts. in years 1988–2010.

values were measured in year 2001 at almost all the studied depths: from 25.62 mg.l^{-1} in the surface humus (with the maximum at this depth reached in 1990, representing 25.97 mg.l^{-1}) to 41.46 mg.l^{-1} at 0.25 m. The minimum values were recorded in 2005: 14.53 mg.l^{-1} in the surface layer and 15.16 mg.l^{-1} at the depth of 0.25 m (Table 2).

Similar decreasing trends were observed the in throughfall and in atmospheric precipitation on open plot, equally in SO_4^{2-} concentration and S-SO_4^{2-} deposition, except the year 2001 in which were recorded maximum S-SO_4^{2-} values (with 45.3 kg^{-1}.ha^{-1}.r^{-1} S-SO_4^{2-} on the open plot).

The performed tests did not reveal significant differences among the individual horizons. There was clearly manifested influence of sulphur content in precipitation water on sulphur content in soil solutions (Fig. 1b).

Comparing the data on soil sulphur deposition between heavy loaded areas and areas less disturbed by airborne pollutants, we can identify several determining factors. Very important is soil depth (Manderscheid et al. 2000). Katutis et al. (2008) point at surface humus composition and the associated stand structure Pichler et al. (2006). Here can be considered also other physical and chemical soil properties.

The current governing factors are so called anthropic factors the influence of which is also reflected in results obtained in research dealing with deposition of sulphur and sulphur compouds into all components of all ecosystem types, not only forest ones.

Dubová and Bublinec (2006) recorded in forest stands in the Kremnické vrchy Mts 25 kg of sulphur in atmospheric deposition in open area. The authors have also confirmed that the maximum sulphur amounts in precipitation occurred in years 1994–1995. The highest content of soil sulphate sulphur recorded by these authors was in the H_{00} horizon. Similar results were obtained by Káňa and Kopáček (2005) in soils of selected forest stands in the Czech Republic. Interesting is the fact that in certain years after the management intervention (4, 5, 6), the sulphur amounts in soil solutions in the horizon H_{00} were higher than in the throughfall. According to Škvarenina (1998), Tesař et al. (2004), this is because the high concentration and content values of sulphur in horizontal precipitation (mists, dew) have not been included in our summarisation. Nevertheless, the annual sulphur deposition in form of mist can reach 1436.88 kg.km^{2}.y^{-1}, representing 79.6% of the total amount. In such a way, the overall sulphur amount deposed on soil surface in spruce forest stands can reach 49–80 kg S ha^{-1} .y^{-1} (Novák et al. 2007). Total sulphur deposition amounted to 8.1, 8.3 and 6.7 kg S.ha^{-1} at Rájec and to 14.8, 16.9 and 15.4 kg S.ha^{-1} at Beskids for the three years studied, respectively in the spruce stands (Drápelová et al.2010). Kunca (2007) reports for 180–190-year-old oak forest stands growing in the Štiavnické vrchy Mts at 680 m asl 23 kg.ha^{-1} of pure sulphur in the throughfall. Novotný et al. (2008) measured in the Silesian Beskids Mts 14.73 kg.ha^{-1}.y^{-1} S-SO_4^{2-} in beech forest stands and 12.86 kg.ha^{-1}.y^{-1} on open plot. For atmospheric precipitation, the same authors give up to 20.52 kg ha^{-1}.y^{-1} S-SO_4^{2-}. Pichler et al. (2006) declare that the maximum S-SO_4^{2-} values in precipitation in mixed forests occur in winter months.

Fig. 1b: The amount of S-SO_4^{2-} in forest throughfall and in wet deposition of Štiavnické vrchy Mts. in years 1988–2010.

Tab. 2: The concentration of SO_4^{2-} in ($mg.l^{-1}$) the Štiavnické vrchy Mts. in years 1988–2010.

Lysimeter/Year	F_{00}	F_{10}	F_{25}	Forest throughfall	*Open plot wet deposition*
1988	30.18	39.73	42.03		
1989	19.56	13.44	16.57		
1990	25.97	32.32	28.86		
1991	20.69	20.54	31.89		
1992	18.68	21.62	34.88		
1993	21.86	27.41	37.42		
1994	21.66	21.91	29.42	17.88	*16.68*
1995	25.17	26.76	30.51	15.20	*19.90*
1996	17.74	28.71	32.96	18.32	*17.24*
1997	23.95	21.93	30.30	19.59	*21.09*
1998	18.72	29.24	38.62	15.85	*20.04*
1999	15.28	15.70	27.20	12.66	*15.67*
2000	16.65	25.07	31.01	14.44	*17.08*
2001	25.62	38.15	41.46	21.84	*22.46*
2002	25.19	36.51	39.23	15.38	*19.85*
2003	18.72	21.25	30.03	25.33	*24.68*
2005	14.53	15.99	15.16	10.48	*14.28*
2006	16.62	16.60	20.09	18.20	*15.67*
2007	15.95	18.92	28.23	12.03	*17.23*
2008	9.42	17.78	15.90	10.50	*10.79*
2009	9.23	17.13	26.62	7.82	*12.70*
2010	8.02	15.21	16.59	3.25	*9.64*
Mean	*19.07*	*23.72*	*29.32*	*14.92*	*17.13*

F_{00}-F_{25} – Lysimeter in the Forest

Tab. 3: Descriptive statistics of Sulphate in the Štiavnické vrchy Mts. in years 1988–2010.

Lysimeter	F_{00}	F_{10}	F25	Forest throughfall	*Open plot wet deposition*
Valid	22	22	22	16	*16*
Mean	18.9	20.5	26.7	19.1	*24.3*
Median	19.6	17.3	24.4	18.9	*24.3*
Min	8.9	9.1	11.8	7.2	*12.4*
Max	35.1	37.9	52.6	33.2	*45.2*
Range	26.2	28.8	40.8	26.0	*32.8*
V x %	38.3	43.9	43.8	32.5	*39.5*
Standard deviation	7.2	9.0	11.7	6.2	*9.6*
Standard Error	1.5	1.9	2.5	1.5	*2.4*

F_{00}-F_{25} – Lysimeter in the Forest , V x %-coefficient of variation

Conclusions

Deposition and concentration of sulphate ions in particular soil horizons in forest stands depend on the total precipitation amount, sulphur content in precipitation water, physical and chemical properties of soils, parent rock material and on the intensity of forest management activities. In the area of the Štiavnické vrchy Mts, the lowest average values of $S\text{-}SO_4^{2-}$ deposition were measured in the surface humus 18.9 kg.ha^{-1}.y^{-1}, the highest at the depth of 0.25m: 26.7 kg.ha^{-1}.y^{-1}. The total $S\text{-}SO_4^{2-}$ amount deposed at this depth was 587.1 kg.ha^{-1} To notice is the fact that the sulphur deposition in the throughfall was lower than in the soil water – possibly the filtering effect of the forest stand.

There were also observed significant differences in sulphur deposition in soil, primarily between the depths of 0.10 and 0.25 m. One of possible causes is surely the sulphur accumulation in bottom soil horizons, mainly up to the year 1990. Without doubts, we may declare that the precipitation total and sulphur presence in atmospheric deposition exert considerable effects on sulphur deposition and concentration levels in individual soil horizons.

The annual dynamics exhibited maximum values mainly in the winter and spring, with the minima occurring more frequently in the summer or autumn. The measured SO_4^{2-} concentration values are in accordance with this fact.

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