MEASUREMENT OF THE ATMOSPHERE LOADING OF THE SLOVAK CARPATHIANS USING BRYOPHYTE TECHNIQUE

BLANKA MAŇKOVSKÁ, JÚLIUS OSZLÁNYI, PETER BARANČOK

Institute of Landscape Ecology, Slovak Academy of Sciences, Štefánikova 3, 814 99 Bratislava, Slovak Republic; e-mail: bmankov@stonline.sk

Abstract

Maňkovská B., Oszlányi J., Barančok P.: Measurement of the atmosphere loading of the Slovak Carpathians using bryophyte technique. Ekológia (Bratislava), Vol. 27, No. 4, p. 339–350, 2008.

Biomonitoring of multielement atmospheric deposition using terrestrial moss is a well-established technique in Europe. The moss samples of *Hylocomium splendens, Pleurozium schreberi* and *Dicranum* sp. were collected in the Slovak part of the Carpathian Mountains (sites of Geldek, Štefanová, Poľana, Východná, Stolíky, Morské oko). A total of 39 elements including a number of toxic metals and rare earths were determined by instrumental neutron activation analysis using epithermal neutrons at the IBR-2 reactor of FLNP JINR. In addition to NAA, atomic absorption spectrometry was applied to determine the content of Cd, Cu, Hg and Pb and elemental analyzer to determine the content of N and S. In comparison to the median northern Norway values of heavy metal contents in moss the Slovak atmospheric deposition loads of the elements were found to be higher than average. We found maximal concentrations of As (45 times), Cd (110 times), Cu (64 times), Fe (44 times), Hg (174 times), Pb (105 times) and Zn (14 times) in site Stolíky; Cr (218 times) and Mn (7 times) in site Morské oko; V (34 times) in site Štefanová in comparison to the Norway values. We find out statistical important decrease of concentration N on all sites by comparison 2000/2005. The obtained data can be useful as a reference level for comparison with the future measurements of air pollution in the examined area and also for biodiversity study.

Key words: air pollution, bryomonitoring, neutron activation analysis

Introduction

It is assumed that in Slovakia (SK) a large gradient of the atmospheric deposition load of elements exists because part of the Slovak territory belongs to the most polluted areas in central Europe known as the 'Black Triangle II'. In order to recognise the distribution of element deposition in SK, the moss monitoring technique, also known as bryomonitoring, was applied to the whole territory in 1990, 1995, 1996, 1997, 2000 and 2005 (Maňkovská, 1997). Bryomonitoring is a suitable technique using moss analyses to determine the levels of atmospheric deposition of the elements. As bryophytes' uptake of elements is primarily or solely from atmospheric deposition, a very close correlation can be found between the content of individual elements in mosses and the element's bulk deposition levels at the given site. This is why bryoindication of atmospheric deposition levels was introduced as early as in the late 1960s (Rűhling, Tyler, 1968, 1971). The technique has been highly standardised and international bryomonitoring programs coordinated by Nordic countries have a pan-European character (Rűhling, 1994; Harmens et al., 2008; Maňkovská, 1997; Maňkovská et al., 2003; Manning et al., 2002; Schröder et al., 2008; Sucharová, Suchara, 2004a, b; Zechmeister et al., 2003).

The objective of the paper was to find out the concentration of 45 elements in mosses (*Pleurozium schreberi, Hylocomium splendens* and *Dicranum* sp.) in six Slovak sites (Geldek, Štefanová, Poľana, Východná, Stolíky, Morské oko) as part of the Carpathian Mts; to compare the concentration in mosses with the concentration in Norway and to interpret their occurrence by factor analysis.

Material and methods

The sampling sites were established in Slovakia in December 1998 (Bytnerowicz et al., 2002; Fraczek et al., 2002). The mosses (*Pleurozium schreberi, Hylocomium splendens* and *Dicranum* sp.) were used as biomonitors to study the atmospheric deposition of trace elements on 6 sites (Malá Fatra Mts – Štefanová; Malé Karpaty Mts – Geldek; Vihorlat Mt. – Morské oko; Poľana; Stoliky; Kozie chrbty Mts – Východná). Moss samples were collected according to the procedures used in deposition surveys in the Scandinavian countries (Rühling, 1994). The collection of samples was performed during the first half of August 2000. The samples consisted of the last three years' annual segments and represented the deposition of heavy metals for the years 1998, 1999 and 2000.

The samples of soil were collected from two external layers of organic horizon: Oll /litter, and Ol /raw humus, on all 6 sites. Each site consisted of 5 circular areas of size 100 m^2 A homogenous area under canopy of stands in each of five circular areas inside of 6 plots was chosen. On each of these five places we made 20x20 cm square "outcrop" for collecting litter (Oll) and raw humus (Ol). Samples were collected from July to August 2000 (Niemtur et al., 2002).

Mosses. Neutron activation analysis (NAA) was performed in the Frank Laboratory of Neutron Physics, Dubna, Russia for 39 elements (Ag, Al, As, Au, Ba, Br, Ca, Ce, Cl, Co, Cr, Cs, Fe, Hf, I, In, K, La, Mg, Mn, Mo, Na, Ni, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, U, V, W, Yb, Zn, Zr). In the laboratory the samples were carefully cleaned from needles, leaves, soil particles and only the green, green-brown shoots representing the last three years growth were analyzed, after being air-dried to constant weight at 30–40 °C for 48 hours. The samples were neither washed nor homogenised. For short-term irradiation samples of about 300 mg were pelletized in simple press forms and heat-sealed in polyethylene foil. For epithermal neutron activation analysis samples prepared in the same manner were packed in aluminium cups for long-term irradiation. The samples were irradiated in the IBR-2 fast-pulsed reactor, in channels equipped with a pneumatic system. The neutron flux characteristics are shown in Table 1. Two kinds of analyses were performed: to determine short-lived radionuclides the samples were irradiated for 3 minutes in the second channel (Ch2) and to determine elements associated with long-lived radionuclides samples were irradiated for 100 hours in the cadmium screened Ch1. After irradiation gamma-ray spectra were recorded twice for each irradiation using a high-purity Ge detector: the first one after decay periods of 2–3 minutes for 5 minutes, the second one for 20 minutes, 9–10 minutes following the short irradiation. In case of long irradiation, samples were repacked into clean containers and measured after 4–5 days for 45 minutes and 20–23 after days for 3 hours (Frontasyeva, Pavlov, 2000).

T a b l e 1. Flux parameters of irradiation positions.

Irradiation position	Neutron flux density, [n× cm $^{-2}$ × s $^{-1}$]×1012		
	thermal	resonance	fast
	(E = 0÷0.55 eV)	(E = 0.55÷105 eV)	(E = 105÷25.106 eV)
Ch1 (Cd-screened)	0.023	3.3	4.2
Ch2	1.23	2.9	4.1

The atomic absorption spectrometer Varian Techtron was used to determine concentrations of Cd, Cu, Hg, and Pb. Elementary analyser LECO SC 132 was applied to determine concentration of sulphur. Elementary analyser LECO SP 228 was used to determine total concentration of nitrogen.

Soil. The samples of both soil layers were analysed. The atomic absorption spectrometer Varian Techtron was used to determine concentrations of Cd, Cr, Cu, Fe, Hg, Ni, Pb, V and Zn.

There is valid equation [concentration in moss] mg.kg^{-1} = [4x atmospheric deposition] mg.m^{-2}.year^{-1} (Steinnes et al., 2001). The analysis results were interpreted in the form of contamination factors K_F as the rates median value of element in Slovak mosses C_{iSl} vs. Norway mosses C_{iN} ($K_F = C_{iSl}/C_{iN}$). Median Norway value C_{iN} we take from Steinnes et al. (2001).

The accuracy of data was verified by an analysis of standard plant samples and by a comparison with the results obtained in 109 laboratories within the IUFRO working group for quality assurance (Hunter, 1994). The QC of NAA results were ensured by analysis of reference materials: trace and minor elements in lichen IAEA-336 (International Atomic Energy Agency), IAEA-SL-1 (Trace elements in lake sediment) and SRM-1633b (Constituent elements in coal fly ash, US NIST-National Institute of Standards and Technology), SRM-2709 (Trace elements in soil). For an assessment of vegetation and humus we used current statistical methods, factor and correlation analysis.

Results and discussion

The results of analysing the concentration of 45 elements in the mosses (*Pleurozium schreberi, Hylocomium splendens, Dicranum* sp.) are given in Table 2. We present separately loading for six sites (Malá Fatra Mts – Štefanová; Malé Karpaty Mts – Geldek; Vihorlat Mt. – Morské oko; Poľana; Stolíky; Kozie chrbty Mts – Východná) as Slovak part of the Carpathian Mts. For comparison with a pristine territory the corresponding data for northern Norway (Steinnes et al., 2001) are shown in the left-hand column. Comparison with the limit values from Norway (Table 2) shows strong pollution of the examined areas of Slovakia with most of the elements. For Au, N, S and Zr data from Norway were not available.

Exceedance of the concentration of elements in mosses in comparison with Norway we expressed by the coefficient of loading by air pollutants K_F and classified it into 5 classes: 1 – elements are in normal standard concentrations and coefficient does not exceed the value 1; 2 – light loading (coefficient of loading ranges from 1 to 10); 3 – moderate loading (coefficient ranges from 10 to 50); 4 – heavy loading (coefficient ranges from 50 to 100) and 5 – toxic (coefficient is higher than 100). As we can see in Table 3, coefficient of loading by air pollutants K_F for almost all elements is higher than one (except Geldek for I), it means the concentration of these elements in 6 Slovak sites is higher (Table 2 – Stolíky for Sb – 540 times higher) than in Norway.

T a b l e 2. Concentration of elements in the mosses of *Pleurozium schreberi. Hylocomium splendens* and *Dicranum* sp. in year 2000 (median in mg. $m^{-2}.year^{-1}$) and comparison of the results with Norway.

Element	**Norway**		**Geldek**		**Štefanová**		**Poľana**		**Východná**		**Stolíky**		**Morské oko**	
	median	exc.	median	exc.	median	exc.	median	exc.	median	exc.	median	exc.	median	exc.
Ag	0.005	1	0.065	13	0.143	28.6	0.070	14	0.182	36.4	0.278	55.6	0.123	24.6
Al	88	1	2100	23.9	5140	58.4	2070	23.5	2140	24.3	3495	39.7	6220	70.7
As	0.03	1	0.68	22.7	0.85	28.3	0.56	18.7	0.65	21.7	1.47	49	0.86	28.7
Au**	0.002	-	0.003	-	0.004	-	0.002	-	0.003	-	0.003	-	0.002	-
Ba	4.8	1	22	4.6	53	11	53	11	41	8.5	70	14.6	67	14
Br	1.25	1	3.65	2.9	3.92	3.1	3.68	2.9	4.03	3.2	3.46	2.8	5.43	4.3
Ca	780	1	5310	6.8	7230	9.3	3855	4.9	4070	5.2	4085	5.2	5420	6.9
Cd	0.02	1	0.40	20	0.57	28.5	0.74	37	0.30	15	0.88	44	0.88	44
Ce	0.086	1	0.525	6.1	1.275	2.4	0.401	0.3	0.602	1.5	0.875	1.5	1.175	1.3
Cl	50	1	197	3.9	263	5.3	264	5.3	459	9.2	346	6.9	295	5.9
Co	0.043	1	0.90	20.9	2.77	64.4	0.64	14.9	0.71	16.5	0.99	23	1.64	38.1
Cr	0.17	1	5.2	30.6	11.4	67.1	4.7	27.6	4.9	28.8	8.3	48.8	10.9	64.1
Cs	0.03	1	0.27	9	0.61	20.3	0.32	10.7	0.75	25	0.47	15.7	0.60	20
Cu	1.1	1	7.2	6.5	15	13.6	8.1	7.4	7.5	6.8	16.2	14.7	11.4	10.4
Fe	91	1	875	9.6	3108	34.2	1120	12.3	1206	13.3	2358	25.9	2961	32.5
Hf	0.002	1	0.42	210	0.76	380	0.28	140	0.41	205	0.47	235	0.92	460
Hg	0.013	1	0.108	8.3	0.203	15.6	0.143	11	0.144	11.1	0.343	26.3	0.234	18
I	0.50	1	0.105	0.2	2.99	6	1.49	3	1.46	2.9	3.09	6.2	2.12	4.2
In	0.05	1	0.105	2.1	0.097	1.9	0.141	2.8	0.109	2.2	0.195	3.9	0.157	3.1
K	750	1	5761	7.7	6786	9	6820	9.1	9732	13	8115	10.8	7137	9.5
La	0.07	1	1.4	20	4.0	57.1	1.1	15.7	1.3	18.6	1.9	27.1	3.3	47.1
Mg	386	1	945	2.4	2295	5.9	1330	3.4	1210	3.1	1775	4.6	1750	4.5
Mn	83	1	243	2.9	367	4.4	306	3.7	571	6.9	460	5.5	472	5.7
Mo	0.03	1	0.57	19	1.71	57	0.61	20.3	0.68	22.7	1.18	39.3	1.06	35.3
N*	5638	-	5763	-	5838	-	5488	-	5313	-	5625	-	6025	-
Na	50	1	321	6.4	692	13.8	344	7.1	357	7.1	528	10.6	707	14.1
Ni	0.28	1	1.8	6.4	4.8	17.1	3.4	6.4	1.8	6.4	3.9	13.9	4.8	17.1
Pb	0.7	1	14.5	20.7	33.1	47.3	23.1	23.1	16.2	23.1	59.8	85.4	33.9	48.4
Rb	2.48	1	17.3	7	13.7	5.5	16.5	16.9	41.8	16.9	11.8	4.8	15.6	6.3
S*	508	-	436	-	465	-	518	-	510	-	579	-	550	-
Sb	0.01	1	0.73	73	0.83	76	0.76	76	0.79	79	5.42	542	1.423	142.3
Sc	0.015	1	0.27	18	1.03	16	0.24	16	0.27	18	0.53	35.3	0.81	54
Se	0.093	1	0.25	2.7	0.43	2.9	0.27	2.9	0.22	2.4	0.45	4.8	0.70	7.5
Sm	0.086	1	0.043	13	0.120	28.6	0.035	28.6	0.045	36.4	0.070	55.6	0.090	24.6
Sr	2.9	1	84	29	51	27.6	80	27.6	31	10.7	103	35.5	108	37.2
Ta	0.001	1	0.044	44	0.115	39	0.039	39	0.046	46	0.071	71	0.120	120

T a b l e 2. (Continued)

Tb	0.001	1	0.038	38	0.111	25	0.025	25	0.030	30	0.076	76	0.083	83
Th	0.010	1	0.25	25	0.69	22	0.22	22	0.31	31	0.47	47	0.64	64
Ti	5.875	1	7.25	1.2	25	1.1	6.25	1.1	7.25	1.2	12.25	2.1	25.25	4.3
U	0.004	1	0.096	24	0.225	12.8	0.051	12.8	0.091	22.8	0.154	38.5	0.173	43.3
V	0.34	1	4.2	12.4	10.8	12.9	4.4	12.9	3.5	10.3	6.9	20.3	10.7	31.5
W	0.030	1	0.15	15	0.41	14	0.14	14	0.26	26	0.28	28	0.38	38
Yb	0.003	1	0.11	36.7	0.37	30	0.09	30	0.15	50	0.22	73.3	0.29	96.7
Zn	7.4	1	49	6.6	78	6.2	46	6.2	41	5.5	89	12	58.4	7.9
Zr**	0.50	-	55	-	89	-	39	-	58	-	67	-	129	-
K_F		1		20.3		42.5		18.8		22.5		45.4		43.7

Note: * Slovak median 2000 (Suchara et al., 2007); **Macedonia (Barandovski et al., 2006); Exc. – exceedance of element concentrations in mosses comparison with Norway; K_F – coefficient of loading by air pollutants

T a b l e 3. Coefficient of loading by air pollutants K_F.

Sites	Contamination factor K_F					K_F
	< 1	1–10	10–50	50–100	> 100	
Geldek	I	Ba, Br, Ca, Cl, Cs, Cu, Fe, Hg, In, K, Mg, Mn, Na, Ni, Rb, Se, Zn	Ag, Al, As, Cd, Co, Cr, La, Mo, Pb, Sc, Sr, Ta, Tb, Th, U, V, W, Yb	Sb	Hf	20
Štefanová		Br, Ca, Cl, In, K, Mg, Mn, Rb, Se,	Ag, As, Ba, Cd, Cs, Cu, Fe, Hg, I, Mo, Na, Ni, Pb, Sc, Sr, V, W Zn	Al, Co, Cr, La, Sb, Sc, Th, U	Hf, Ta, Tb, Yb	43
Poľana		Br,Ca,Cl,Cu, In, K, Mg, Mn,Na, Rb, Se, Zn	Ag, Al, As, Ba, Cd, Co, Cr, Cs, Fe, Hg, I, La, Mo, Ni, Pb, Rb, Sc, Sr, Ta, Tb, Th, U, V, W, Yb	Sb	Hf	19
Východná		Ba, Br, Ca, Cl, Cu, I, K, Mg, Mn, Na, Ni Rb, Se, Zn	Ag, Al, As, Cd, Co, Cr, Cs, Fe, Hg, I, La, Mo, Pb, Sc, Sr, Ta, Tb, Th, U, V, W, Yb	Sb	Hf	23
Stolíky		Br, Ca, Cl, In, K, Mg, Mn, Rb, Se,	Al, As, Ba, Cd, Co, Cr, Cs, Cu, Fe, Hg, I, La, Mo, Na, Ni Sc, Sr, Th, U, V, W, Zn	Ag, Pb, Ta Tb, Yb,	Hf ,Sb	45
Morské oko		Br,Ca, Cl, In, K, Mg, Mn, Rb, Se, Zn	Ag, As, Ba, Cd, Co, Cr, Cs, Cu, Fe, Hg, I, La, Mo, Na, Ni, Pb, Sr, U, V, W	Al, Sc, Tb, Th, Yb	Hf, Sb, Ta	44

In comparison with the 1990 survey (Maňkovská, 1997), the median values in 2005 (Fig. 1) for Cd, Fe, Hg, Pb and Zn were reduced by approximately 20–90%. Decreasing concentrations are connected with decreasing production of steel and non-ferrous metals in Slovakia and with facing out leaded gasoline. During the same period elements such as Cu, Mn, Ni and V increased by approximately 50–100%. The main source of increase in air

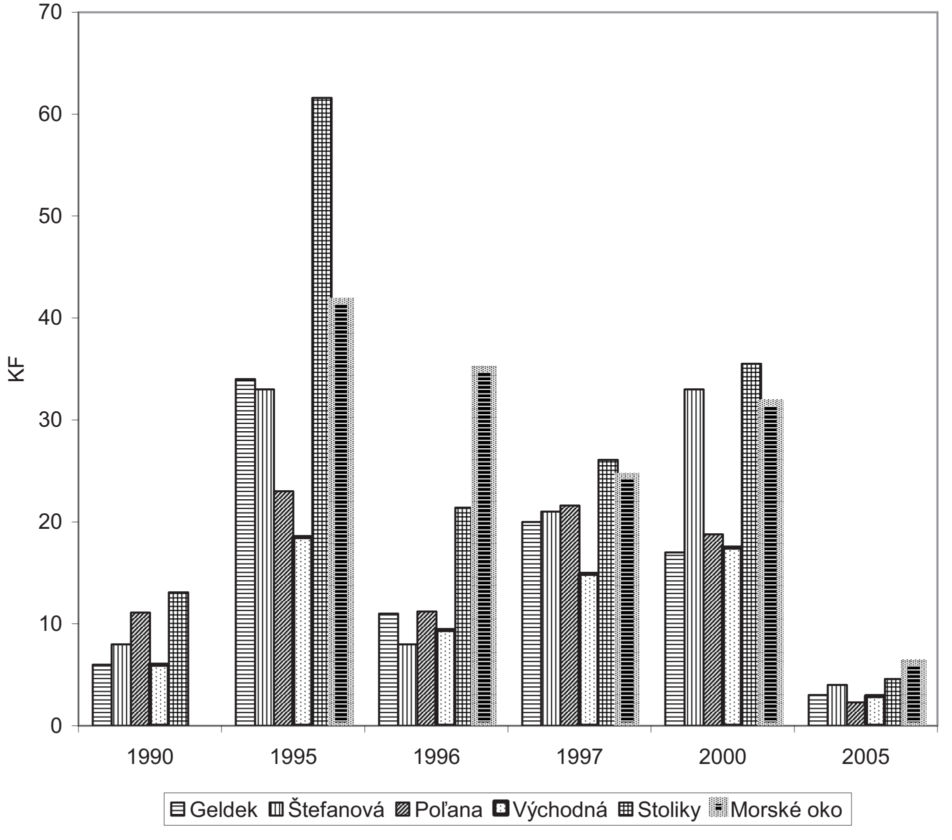

Fig. 1. Exceedance of element concentration (K_F) in mosses in the years 1990–2005.
Note: K_F for Cd, Fe, Hg, Pb and Zn

is gradually growing heavy oil combustion. Increasing concentrations are connected also with transboundary transmission from the Czech Republik (Geldek, Štefanová), Poland (Východná) and Ukraine (Morské oko).

In the year 2000 we compared the concentration of N, S in the mosses (*Pleurozium schreberi, Hylocomium splendens, Dicranum* sp.); foliage of *Fagus sylvatica*, 1-year-old needles of *Picea abies* (Maňkovská et al., 2002); letter (Oll) and raw humus (Ol) (Niemtur et al., 2002). Sulphur and nitrogen are essential plant nutrients. S and N air pollutants as SO_2, H_2S, NO_2, NH_3, or HNO_3 can cause increased foliar concentrations of both elements in plants. With regard to damage to forest ecosystems, three main reasons of S toxicity should be considered: damage to roots from elevated concentrations of S in humus complex, damage to foliage by S metabolites resulting from excessive SO_2 and H_2S uptake and redistribution and accumulation of S in older organs (older leaves, wood, etc.). Sulphur is an important

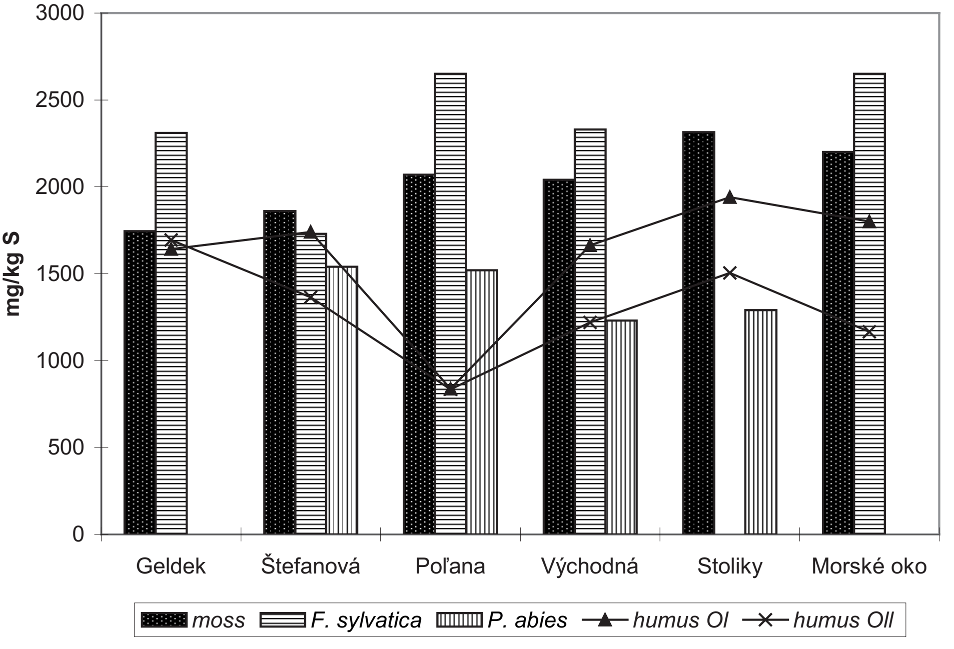

Fig. 2. Concentration of S in the mosses (*Pleurozium schreberi, Hylocomium splendens, Dicranum* sp.), foliage of *Fagus sylvatica*, 1-year-old needles *Picea abies;* letter (Oll) and raw humus (Ol) (median in mg.kg^{-1}) in the year 2000.
Note: limit value in mg.kg^{-1}: *F. sylvatica (* S-1000); *P. abies (*S-1000); Mosses (S-2032)

nutrient limiting the growth of plants – both excess and deficiency of S may cause growth reduction. Our results (Fig. 2) show that concentrations of S in 1-year-old spruce needles ranged from 1230 to 1540 mg.kg^{-1}; in beech leaves from 1730 to 2650 mg.kg^{-1}; in mosses from 1745 to 2315 mg kg^{-1}; in humus Ol from 838 to 1940 mg.kg^{-1}; and humus Oll from 835 to 1694 mg.kg^{-1}. According to Innes (1995), S concentrations in spruce needles range from 800 to 1000 mg.kg^{-1}, what corresponds with our previous data (Maňkovská, 1988). In polluted regions the S concentration in spruce and fir needles increases markedly up to 5000 mg.kg^{-1}. The values from 1100 to 1800 mg.kg^{-1} for coniferous trees and 1000 to 2000 mg.kg^{-1} for broadleaved trees are considered as sufficient. Higher concentrations should be considered undesirable. These high values confirm marked impact of sulphur oxides in the entire range of the Carpathian Mountains. The highest values of S were found in spruce in Štefanová, in beech in Poľana and Morské oko, in mosses in Morské oko, in humus Ol in Stolíky and in humus Oll in Geldek.

Concentrations of N in 1-year-old spruce needles in the Carpathian Mts ranged from 11700 to 13100 mg.kg^{-1}, in beech leaves from 19800 to 29700 mg.kg^{-1}, in mosses from 21250 to 24100 mg.kg^{-1}; in humus Ol from 14000 to 20933 mg.kg^{-1}; and humus Oll from

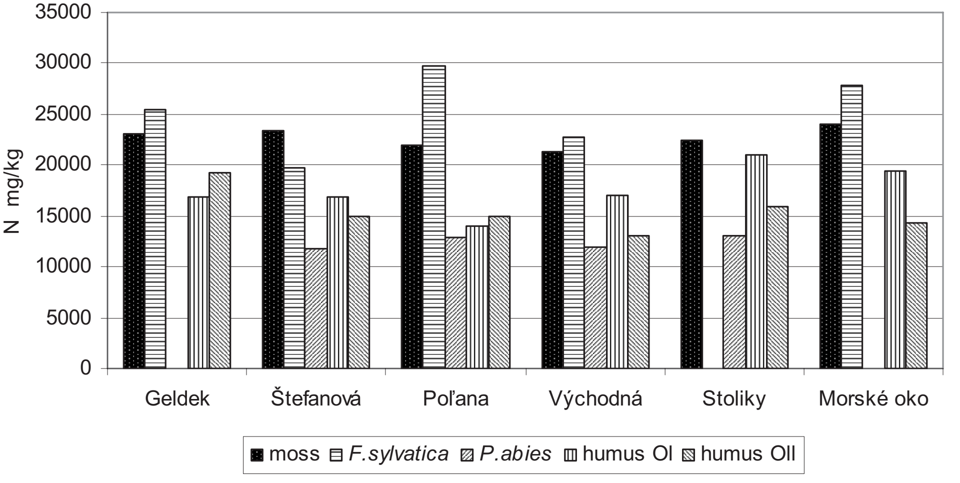

Fig. 3. Concentration of N in the mosses (*Pleurozium schreberi, Hylocomium splendens, Dicranum* sp.), foliage of *Fagus sylvatica*, 1-year-old needles *Picea abies;* letter (Oll) and raw humus (Ol) in the year 2000 (median in mg.kg^{-1}).
Note: Limit value in mg.kg^{-1}: *F. sylvatica (N* -18000-25000); *P. abies (N*-12000-20000); mosses (N-18900)

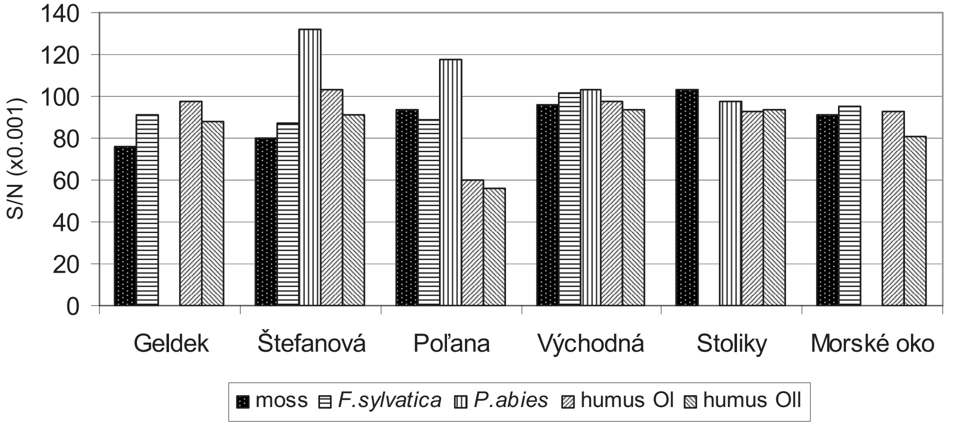

Fig. 4. Ratio of S/N in the in the mosses (*Pleurozium screberi, Hylocomium splendens, Dicranum* sp.), foliage of *Fagus sylvatica*, 1 year old needles *Picea abies;* letter (Oll) and raw humus (Ol) in the year 2000.

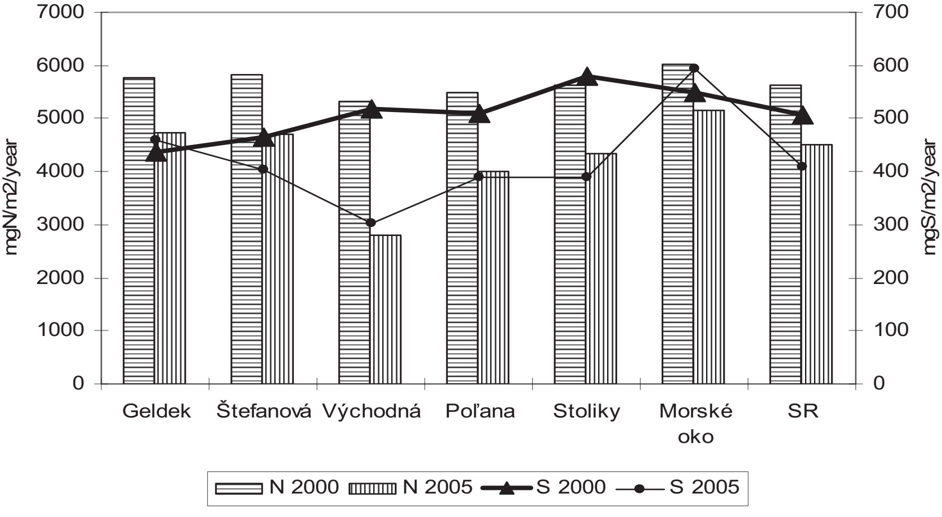

Fig. 5. Concentration of N and S in the mosses (*Pleurozium schreberi, Hylocomium splendens, Dicranum* sp.) in the years 2000 and 2005 (in mg.m^{-2}.year^{-1}).

14320 to 19200 mg.kg^{-1} (Fig. 3). Maňkovská (1996) considers 13500–17000 mg.kg^{-1} as sufficient foliar concentrations for tree species. The highest values of N were found in spruce in Stolíky, in beech in Poľana, in mosses in Morské oko, in humus Ol in Stolíky and in humus Oll in Geldek. One of the most complicated issues related to forest health is nitrogen deposition. Nitrogen is not only a major atmospheric and terrestrial constituent but also the most common growth- limiting plant nutrient (Lorenz et al., 2008; Maňkovská, Oszlányi, 2008).

The S/N ratio in the foliage of spruce needles ranged from 0.099 to 0.132, in beech leaves from 0.087 to 0.102, in mosses from 0.076 to 0.103; in humus Ol from 0.060 to 0.103; and humus Oll from 0.056 to 0.094 (Fig. 4). The S/N ratio is a sensitive indicator of S accumulation in the foliage of forest trees subjected to atmospheric pollution. Molar ratio of protein S and protein N ranges from 0.05 to 0.15 (Stefan et al., 1997) and it is relatively constant for all tree species. The S/N ratio is no optimally balanced in all study samples when compared with the limit ranges.

Concentrations of N and S in the mosses (*Pleurozium schreberi, Hylocomium splendens, Dicranum* sp.) in the years 2000 and 2005 are given in Fig. 5. We find out statistically important decrease of N concentration on all sites by comparison 2000/2005. Concentrations of S were lower on 4 sites and increased on sites Geldek and Morské oko by comparison 2000/2005. Differences in concentrations of S were not statistically significant between 2000/2005.

T a b l e 4. Concentration of elements in samples (humus, mosses) from sites with different tree species (in $mg.kg^{-1}$).

Sites	Samples	Forest types	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn
Geldek	humus	d	0.92	21	18	7337	0.120	10	52	3.2	119
Štefanová	humus	d	0.64	23	26	12528	0.151	41	49	12.9	90
Poľana	humus	a	0.86	9	18	9967	0.162	11	59	5.2	106
Východná	humus	c	0.76	18	20	10399	0.299	16	75	11.4	68
Stolíky	humus	b	1.78	17	89	14970	0.853	17	156	6.6	206
Morské oko	humus	d	1.79	12	17	6934	0.088	29	29	4.1	80
Geldek	mosses	d	1.30	12	15	650	0.055	10	9	1.63	45
Štefanová	mosses	d	1.30	20	15	2475	0.163	8	27	1.08	48
Poľana	mosses	a	1.52	5.2	12	1089	0.099	1.1	26	0.11	48
Východná	mosses	c	0.81	8.3	14	686	0.095	1.1	11	0.10	33
Stolíky	mosses	b	1.84	10	47	3354	0.479	2.4	64	1.52	98
Morské oko	mosses	d	0.70	19	17	2965	0.101	2.3	11	1.02	56

Note: Forest types: a – spruce forest (*Picea abies*); b – fir-beech forest (*Abies alba-Fagus sylvatica*); c – spruce-fir forest (*Picea abies-Abies alba);* beech forest *(Fagus sylvatica*).

T a b l e 5. Results of Student test for significance of difference among average concentrations of elements into humus and mosses, resp. between humus-mosses and coefficient (r) of linear correlation between concentration of the same elements into humus and mosses.

Material	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn	t_{tab}
H – humus	5.299*	7.679*	2.699*	8.275*	2.352^{n}	4.203*	3.836*	4.427*	5.492*	2.571
M – mosses	7.085*	5.128*	3.656*	3.799*	2.573*	2.640*	2.878*	3.340*	2.571*	2.571
H/M	0.436^{n}	1.307^{n}	0.900^{n}	6.310*	0.841^{n}	3.199*	2.254*	3.817*	2.551*	2.228
r	0.0695	0.4093	**0.9854**	0.4519	**0.9467**	0.2182	**0.8772**	-0.3309	**0.9122**	-

Note: * – statistical significance at $p < 0.005$; n – non statistical significance, values in bold face are significant correlation at $p < 0.005$

The concentration of elements in samples (humus, mosses) from sites with different tree species for year 1995 is given in Table 4. The results of Student test for significance of difference among average concentrations of elements into humus and mosses, respectively between humus-mosses and coefficient (r) of linear correlation between concentration of the same elements into humus and mosses are in Table 5. We find out statistical significant difference between concentration of Cd, Cr, Cu, Fe, Hg, Ni, Pb, V and Zn in humus and mosses. We find out statistically significant difference between humus/mosses for Fe, Ni, Pb, V and Zn and significant correlation r ($p < 0.005$) for Cu, Hg, Pb and Zn.

Conclusion

It was determined on the basis of bryomonitoring performed in 3year old segments of *Pleurozium schreberi, Hylocomium splendens* and *Dicranum* sp., and humus on 6 sites in the Slovakian part of Carpathian Mts forests that:

a. We found concentration of elements more than 50 times higher: site Geldek, Poľana, Východná (Sb, Hf); site Štefanová (Al, Co, Cr, Hf, La, Sb, Sc, Ta, Tb, Th, U, Yb); site Stolíky (Ag, Hf, Pb, Sb, Ta, Tb, Yb), and site Morské oko (Al, Hf, Sc, Sb, Ta, Tb, Th, Yb) in comparison to the Norway values.
b. Coefficient of loading by air pollutants K_F move from 19 – Poľana, 21 – Geldek, 22 – Východná, 45 – Štefanová to 46 – Stolíky and Morské oko.
c. The highest values of S and N were found in mosses in Morské oko, in humus Ol in Stolíky and in humus Oll in Geldek. We find out statistical important decrease of concentration N on all sites by comparison 2000/2005. Concentration of S was lower on 4 sites and increased on sites Geldek and Morské oko by comparison 2000/2005. Differences in concentrations of S were not statistically significant between 2000/2005.
d. The obtained data can be useful as a reference level for comparison with the future measurements of air pollution in the examined area and also for biodiversity study. The significance of transboundary atmospheric transport in this region remains to be studied in the future.

Translated by the authors

References

Barandovski, L., Frontasyeva, M.V., Pavlov, S.S., Stafilov, T., Steinnes, E., Urumov, V.M., 2006: Air pollution studies in Macedonia using the moss biomonitoring technique, NAA, AAS and GIS technology. Preprint of the Joint Institute for Nuclear Research, Dubna, p. 19.

Bytnerowicz, A., Szaro, R., Karnosky, D.F., Manning, W., McManus, M., Musselmann, R., Muzika, R.M., 2002: Importance of international research cooperative programs for better understanding of air pollution effects on forest ecosystems in central Europe. Effects of air pollution on forest health and biodiversity in forests of the Carpathian Mountains. IOS Press, p. 13–20.

Fraczek, W., Postelnicu, D., Bytnerowicz, A., Černý, M., Vasile, C., 2002: GIS as a tool for evaluating air pollution and biological resources of Carpathian forests. IOS Press, p. 121–137.

Frontasyeva, M.V., Pavlov, S.S., 2000: Analytical investigation at the IBR-2 Reactor in Dubna: preprint JINR E14-2000-177, Dubna, p. 5–32.

Harmens, H., Norris, D.A., Koerber, G.R., Buse, A., Steinnes, E., Rühling, A., 2008: Temporal trends (1990–2000) in the concentration of cadmium, lead and mercury in mosses across Europe. Environ. Pollut., *151*: 368–376.

Hunter, I.R., 1994: Results from the Interlaboratory sample exchange. IUFRO, Working Group S1.02 –08 Foliar Analysis. Natural Resources Institute, Kent, 18 pp.

Innes, J., 1995: Influence of air pollution on the foliar nutrition of conifers in Great Britain. Environ. Pollut., *88*: 183–192.

Lorenz, M., Sheppard, L., Johnson, D., 2008: Monitoring forest condition in Europe: concentrations of nitrogen and sulphur in bulk deposition and defoliation of main tree species. International Journal of Environmental Studies, *65*, 3: 297–308.

Maňkovská, B., 1988: The accumulation of atmospheric pollutants by *Picea abies* K a r s t. Ekológia (ČSFR), *7,* 1: 95–108.

Maňkovská, B., 1996: Geochemical atlas of Slovakia – forest biomass (in Slovak, English). Geologická služba Slovenskej republiky, Bratislava, 87 pp.
Maňkovská, B., 1997: Deposition of heavy metals in Slovakia – assessment on the basis of moss and humus analyses. Ekológia (Bratislava), *16* : 433–442.
Maňkovská, B., Černý, M., Moravčík, P., Godzik, B., Grodzińska, K., Badea, O., Barančok, P., Oszlányi, J., Varšavová, M., Fleischer, P., Blum, O., Parpan, V., Bytnerowicz, A., Szaro, R., 2002: Chemical and morfological changes in Carpathian mountains trees caused by air pollution. In Szaro, R.C., Bytnerowicz, A., Oszlányi, J. (eds), Effects of air pollution on forest health and biodiversity in forests of the Carpathian Mountains. NATO Science Series I. Life and Behavioural Sciences *345*, IOC Press, Amsterdam, p. 173–184.
Maňkovská, B., Florek, M., Frontasyeva, M.V., Ermakova, E., Oprea, K., Pavlov, S.S., 2003: Atmospheric deposition of heavy metals in Slovakia studied by the moss biomonitoring technique, neutron activation analysis and lame atomic absorption spectrometry. Ekológia (Bratislava), *22*, Suppl. 1: 157–162.
Maňkovská, B., Oszlányi, J., 2008: Mosses and foliage of forest tree species as biomonitors of nitrogen pollution. International Journal of Environmental Studies, *65*, 3: 377–388.
Manning, W.J., Godzik, B., Musselman, R., 2002: Potential bioindicator plant species for ambient ozone in forested ountain area s of Central Europe. Environ. Pollut., *11*: 283–290.
Niemtur, S., Maňkovská, B., Godzik, B., Grodzińska, K., 2002: Changes in Carpathian forest soils caused by air pollution and other factors. In Szaro, R.C., Bytnerowicz, A., Oszlányi, J. (eds), Effects of air pollution on forest health and biodiversity in forests of the Carpathian Mountains. NATO Science Series I. Life and Behavioural Sciences *345*, IOC Press, Amsterdam, p. 225–235.
Rühling, A, Tyler G., 1968: An ecological approach to the lead problem. Bot. Not., *121*: 321–342.
Rühling, A, Tyler G., 1971: Regional differences in the deposition of heavy metals over Scandinavia. J. Appl. Ecol., *71*, 8: 497–507.
Rühling, A., 1994: Monitoring of atmospheric heavy-metal deposition in Europe using bryophytes and humus samples as indicators. Proposal for an international programme 1995. Lund: Environ. Monitor. and Data Group of the Nordic Countries:1–14.
Schröder, W., Pesch, R., Englert, C., Harmens, H., Suchara, I., Zechmeister, H.G., Thöni, L., Maňkovská, B., Jeran, Z., Grodzinska, K., Alber, R., 2008:Metal accumulation in mosses across national boundaries: Uncovering and ranking causes of spatial variation. Environ. Pollut., *151*: 377–388.
Stefan, K., Fűrst, A., Hacker, R., Bartels, U., 1997: Forest Foliar Condition in Europe. Technical Report. EC and UN/ECE, Brussels, Geneva, 207 pp.
Steinnes, E., Berg, T., Sjobak, T.E., Uggerud, H. Vadset, M., 2001: Atmospheric deposition of heavy metals in Norway (in Norwegian). Nation-wide survey 2000. Report 838/01, State Pollution Control Authority, Oslo, 28 pp.
Suchara, I., Florek, M., Godzik, B., Maňkovská, B., Rabnecz, G., Sucharová, J., Tuba, Z., Kapusta, P., 2007: Mapping of main sources of pollutants and their transport in the Visegrád space. Project 11007-2006-IVF, Průhonice, 127 pp.
Sucharová, J., Suchara, I., 2004a: Bio-monitoring the atmospheric deposition of elements and their compounds using moss analysis in the Czech Republic. Results of the international-monitoring programme UNECE ICP-Vegetation 2000. Acta Průhoniciana, *77*: 1–135.
Sucharová, J., Suchara, I., 2004b: Current multi-element distribution in forest epigeic moss in the Czech Republic. A survey of the Czech national biomonitoring programme 2000. Chemosphere, *57*: 1389–1398.
Zechmeister, H.G., Grodzińska, K., Szarek-Lukaszewska, G., 2003: Bryophytes. In Markert, B.A., Breure, A.M., Zechmeister, H.G. (eds), Bioindicators and biomonitors. Elsevier, Amsterdam, p. 329–375.