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Temporal trends (1990-2005) in heavy metal accumulation in mosses in Slovakia

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Abstract. 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 Slovakia. Separately we evaluated the atmospheric deposition in the National Parks (Vysoké Tatry, Nízke Tatry, Západné Tatry -Jelenec, Slovenský raj) and in a landscape protection area (Veľká Fatra). In comparison to the median northern Norway values of heavy metal contents in moss, the Slovak atmospheric deposition loads of elements were found to be higher. The survey has been repeated and in this paper we report on the temporal trends in the concentration of Cd, Cr, Cu, Fe, Hg, Ni, Pb, V and Zn between 1990 and 2005. Metal- and sites-specific temporal trends were observed. In general, the concentration of Cd, Cr, Cu, Fe, Hg, Ni, Pb, V and Zn in mosses decreased between 1990 and 2005; the decline was higher for Pb than for Cd. The observed temporal trends for the concentrations in mosses were similar to the trends reported for the modelled total deposition of cadmium, lead and mercury in Europe. The level of elements, determined in bryophytes reflects the relative atmospheric deposition loads of elements at the investigated sites. Factor analysis was applied to determine possible sources of trace element deposition in the Slovakian mosses.

Keywords: air pollution, bryomonitoring, heavy metals; moss survey

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Introduction

The heavy metals in mosses biomonitoring network was originally established as a Swedish initiative (Rűhling & Tyler 1968, 1971). It is assumed that in the Slovakia (SK), a large gradient of the atmospheric deposition load of elements exists, because part of the SK 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 the SK, the moss monitoring technique, also known as bryomonitoring, was applied to the whole territory in 1990, 1995, 1996, 1997, 2000 and 2005 (Maňkovská & Oszlányi 2008). Bryomonitoring is a suitable technique, which use the moss analysis to determine the levels of atmospheric deposition of the elements. The technique has been highly standardised and international bryomonitoring programs coordinated by Nordic countries have a pan-European character (Harmens et al.

2008, Maňkovská 1997, Maňkovská et al. 2003, Maňkovská & Oszlányi 2008, Maňkovská et al. 2008, Schröder et al. 2008, Suchara et al. 2007, Zechmeister et al. 2003). The mosses are characterized by high concentration of toxic elements such as As, Cd, Cr, Cu, Hg, Fe, Mn, Ni, Pb, V and Zn.

The aim of this paper is to present actual data of the first survey of 9 elements, in mosses (*P. schreberi, H. splendens* and *Dicranum* sp.) in five Slovak sites: National parks (Vysoké Tatry, Nízke Tatry, Západné Tatry, Slovenský raj) and in the landscape protection area (Veľká Fatra). An additional aim of this report is to summarise changes in heavy metal concentrations in mosses in Slovakia between 1990 and 2005.

Materials and methods

The mosses *P. schreberi, H. splendens* and *Dicranum* sp. have been taken in compliance with the international methods (ICP 1994), in permanent areas situated on the intersections of a 16 x 16 km pan-European network. Moss samples were collected according to the procedures used in deposition surveys in the Scandinavian countries. The collection of samples was performed during the first half of August 1990, 1995, 1996, 1997, 2000 and 2005. The samples consisted of the last three years annual segments. Separate samples were taken in the National parks (Vysoké Tatry, Nízke Tatry, Západné Tatry-Jelenec, Slovenský raj) and in the landscape protection area (Veľká Fatra).

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 2000. 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 analysis 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 the 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).

The atomic absorption spectrometer Varian Techtron was used to determine concentrations of Cd, Cr, Cu, Hg, Ni, Pb and Zn. 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.

There is a valid equation [concentration in moss] mgkg^{-1} = [4x atmospheric deposition]

Table1 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

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} were taken 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 we used current statistical methods, factor and correlation analysis.

Results and discussion

The results of analysing the concentration of 45 elements in the mosses (P. *schreberi, H. splendens, Dicranum* sp.) are given in Table 2. We present separately loadings for National Parks (NP)-Vysoké Tatry, Nízke Tatry, Západné Tatry -Jalovec valley, Slovenský raj, Landscape protection area (LPA)-Veľká Fatra and Slovakia. For comparison with a pristine territory, the corresponding data for northern Norway (Steinnes et al. 2001) are shown in the left-hand column. The 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: class 1 - the elements are in normal standard concentrations and the coefficient does not exceed the value 1; class 2 - light loading (the coefficient of loading ranges from 1 to 10); class 3 - moderate loading (the coefficient ranges from 10 to 50); class 4 - heavy loading (the coefficient ranges from 50 to 100) and class 5 - toxic (the coefficient is higher than 100). As we can see in Table 3, the coefficient of loading by air pollutants K_F for almost all elements is higher than one, except for Au, Br, Ca, I, Se (Vysoké Tatry); Au, Br, I, Mg, S, Se, Sm, Ti (Nízke Tatry); Au, Br, Ca, Hg, I, In, Mg, S, Se, Sm (Západné Tatry-Jelenec); Au, Br, In Sm, Se (Slovenský raj) and Au, Br, In Sm (Veľká Fatra).

Spatial trends of heavy metal concentrations in mosses were metal-specific. However, in general, the lowest concentrations were observed in National Park Nízke Tatry and 10 times higher concentrations in Vysoké Tatry (Al, Cr, Hf, Sb, Ta, Yb, Zr), Západné Tatry (Cr, Hf, Sb, Yb, Ta, Zr), Slovenský raj (Ag, Hg, Hf, Mo, Pb, Ta, Tb, Yb, Zr), Veľká Fatra (Cr, Hf, Sb, Ta, Tb, Th, Yb, Zr), in comparison to the Norway values. The coefficient of loading by air pollutants K_F move from 4.2 (Nízke Tatry) to 11.8 (Slovenský raj). Since 1990, the metal concentration in mosses has declined for Cd, Cr, Cu, Fe, Hg, Ni, Pb, V, Zn (figure 1-3).

The examined Slovak territory shows that many regions have intense mining activity. They are characterized by high concentration of toxic elements such as As, Al, Mn, Cd, Cr, Cu, Hg, Pb and Sb. The most significant anthropogenic source is fossil fuels combustion (electric power stations), allocated in Upper Nitra and Vojany. From the other industrial activities, the metallurgy, nonferrous ores processing, and cement factories should be mentioned (Central Spiš, Central Pohronie, Orava). In Slovakia, many pollutants sources are overlapping, a fact which causes an obstruction in source identification (Maňkovská 1996, Suchara et al. 2007, Florek et al. 2008).

In comparison with the 1990 survey (Maňkovská 1997), the average values in 2005 (Fig. 1-3) for Cd, Cr, Cu, Fe, Hg, Ni, Pb, V and Zn were reduced. Decreasing concentrations are connected with decreasing production of steel and non-ferrous metals in Slovakia and with elimination from use of leaded gasoline.

The moss data from Slovakia were subjected to principal component factor analysis (Varimax with Kaiser Normalization). The result of analysis is in Table 4. The 8 factors explain 80% of the total variance in the data set. From the knowledge of the element composition of

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

Element	Norway		Vysoké Tatry (n=3)		Nízke Tatry (n=4)		Západné Tatry (n=14)		Slovenský Raj (n=5)		Veľká Fatra (n=6)		Slovakia (n=86)	
	average	exc.	average	exc.	average	exc.	average	exc.	average	exc.	average	exc.	average	exc.
Ag	0.005	1	0.031	6.2	0.027	5.4	0.033	6.6	0.072	14.4	0.032	6.4	0.038	7.6
Al	88	1	888	10.1	345	3.9	735	8.4	708	8.0	769	8.7	966	11.0
As	0.03	1	0.2	6.7	0.15	5.0	0.18	6.0	0.28	9.3	0.19	6.3	0.2	6.7
Au**	0.002	-	0.001	0.5	0.001	0.5	0.001	0.5	0.001	0.5	0.001	0.5	0.001	0.5
Ba	4.8	1	8.8	1.8	8.8	1.8	12.5	2.6	21.5	4.5	11	2.3	15.4	3.2
Br	1.25	1	1.03	0.8	0.78	0.6	0.85	0.7	0.81	0.6	0.95	0.8	0.91	0.7
Ca	780	1	722	0.9	1006	1.3	113	0.1	1036	1.3	1485	1.9	1322	1.7
Cd	0.02	1	0.1	5.0	0.12	6.0	0.15	7.5	0.14	7.0	0.16	8.0	0.16	8.0
Ce	0.086	1	0.45	5.2	0.463	5.4	0.61	7.1	0.68	7.9	0.765	8.9	0.98	11.4
Cl	50	1	68	1.4	99	2.0	80	1.6	74	1.5	52	1.0	70	1.4
Co	0.043	1	0.283	6.6	0.133	3.1	0.345	8.0	0.405	9.4	0.315	7.3	0.378	8.8
Cr	0.17	1	1.83	10.8	0.8	4.7	1.8	10.6	1.41	8.3	2.33	13.7	2.18	12.8
Cs	0.03	1	0.13	4.3	0.2	6.7	0.12	4.0	0.11	3.7	0.11	3.7	0.13	4.3
Cu	1.1	1	2.1	1.9	1.6	1.5	5.5	5.0	4.1	3.7	2.1	1.9	2.5	2.3
Fe	91	1	425	4.7	186	2.0	377	4.1	455	5.0	497	5.5	555	6.1
Hf	0.002	1	0.128	64.0	0.055	27.5	0.131	65.5	0.125	62.5	0.125	62.5	0.168	84.0
Hg	0.013	1	0.034	2.6	0.032	2.5	0.01	0.8	0.147	11.3	0.039	3.0	0.102	7.8
I	0.50	1	0.3	0.6	0.4	0.8	0.4	0.8	0.7	1.4	0.5	1.0	0.5	1.0
In	0.05	1	0.05	1.0	0.12	2.4	0.04	0.8	0.04	0.8	0.02	0.4	0.04	0.8
K	750	1	2362	3.1	2269	3.0	1936	2.6	1753	2.3	1674	2.2	1770	2.4
La	0.07	1	0.23	3.3	0.32	4.6	0.35	5.0	0.51	7.3	0.58	8.3	0.62	8.9
Mg	386	1	373	1.0	262	0.7	354	0.9	393	1.0	387	1.0	436	1.1
Mn	83	1	114	1.4	89	1.1	135	1.6	141	1.7	92	1.1	110	1.3
Mo	0.03	1	0.17	5.7	0.24	8.0	0.28	9.3	0.3	10.0	0.26	8.7	0.27	9.0
N*	5638	-	6642	1.2	5494	1.0	6268	1.1	5520	1.0	5407	1.0	5927	1.1
Na	50	1	81	1.6	107	2.1	82	1.6	109	2.2	90	1.8	129	2.6
Ni	0.28	1	0.78	2.8	0.38	1.4	0.84	3.0	0.53	1.9	0.98	3.5	0.99	3.5
Pb	0.7	1	5.1	7.3	4	5.7	5.3	7.6	12.9	18.4	6.3	9.0	8.3	11.9
Rb	2.48	1	7.5	3.0	9	3.6	5.1	2.1	3.15	1.3	4.13	1.7	4.26	1.7
S*	508	-	492	1.0	404	0.8	473	0.9	596	1.2	511	1.0	502	1.0
Sb	0.01	1	0.17	17.0	0.13	13.0	0.2	20.0	2.06	206.0	0.24	24.0	0.38	38.0
Sc	0.015	1	0.118	7.9	0.048	3.2	0.105	7.0	0.11	7.3	0.143	9.5	0.153	10.2
Se	0.093	1	0.08	0.9	0.055	0.6	0.08	0.9	0.07	0.8	0.098	1.1	0.095	1.0
Sm	0.086	1	0.038	0.4	0.053	0.6	0.051	0.6	0.058	0.7	0.07	0.8	0.088	1.0
Sr	2.9	1	13.5	4.7	7	2.4	15.8	5.4	14	4.8	14.5	5.0	21.6	7.4
Ta	0.001	1	0.017	17.0	0.008	8.0	0.017	17.0	0.016	16.0	0.02	20.0	0.023	23.0
Tb	0.001	1	0.007	7.0	0.005	5.0	0.01	10.0	0.013	13.0	0.017	17.0	0.02	20.0
Th	0.010	1	0.05	5.0	0.05	5.0	0.08	8.0	0.09	9.0	0.11	11.0	0.13	13.0
Ti	5.875	1	16	2.7	3.8	0.6	11.6	2.0	9.3	1.6	10.3	1.7	14.3	2.4
U	0.004	1	0.018	4.5	0.033	8.3	0.025	6.3	0.025	6.3	0.028	7.0	0.035	8.8
V	0.34	1	1.13	3.3	0.71	2.1	1.48	4.4	1.24	3.6	1.88	5.5	1.85	5.4
W	0.030	1	0.05	1.7	0.08	2.7	0.07	2.3	0.08	2.7	0.08	2.7	0.07	2.3
Yb	0.003	1	0.038	12.7	0.016	5.3	0.038	12.7	0.043	14.3	0.05	16.7	0.063	21.0
Zn	7.4	1	16.3	2.2	9.5	1.3	15	2.0	19	2.6	11.5	1.6	15.4	2.1
Zr**	0.50	-	24	48.0	7.5	15.0	20	40.0	16	32.0	17	34.0	23.1	46.2
KF		1		6.7		4.2		7.0		11.8		7.6		9.5

Table 3 Coefficient of loading by air pollutants KF

Sites	Contamination factor K_F					KF
	< 1	1 -10	10-50	50-100	>100	
Vysoké Tatry	Au, Br, Ca, I, Se	Ag, As, Ba, Cd,Ce, Cl, Co, Cs, Cu, Fe, Hg, In, K, La, Mg, Mn, Mo, N,Na, Ni, Pb, Rb, S, Sc, Se, Sm, Sr, Tb, Th, Ti, U, V, W, Zn	Al, Cr, Sb, Ta, Yb,Zr	Hf		6.7
Nízke Tatry	Au, Br, I, Mg, S, Se, Sm,Ti	Ag, Al, As, Ba, Ca, Cd,Ce, Cl, Co, Cr, Cs, Cu, Fe, Hg, In, K, La, Mn, Mo, N,Na, Ni, Pb Rb, Sb, Sc, Sr, Ta, Tb, Th, U, V, W, Yb, Zn, Zr	Hf			4.2
Západné Tatry	Au, Br,Ca, Hg, I, In, Mg, S,Se, Sm	Ag, Al, As, Ba, Cd,Ce, Cl, Co, Cs, Cu, Fe, K, La, Mn, Mo, N,Na, Ni, Pb Rb, Sc, Sr, Tb, Th, Ti, U, V, W, Zn	Cr, Sb, Yb, Ta, Zr	Hf		7
Slovenský raj	Au, Br, In Sm, Se	Al, As, Ba, Ca, Cd,Ce, Cl, Co, Cr, Cs, Cu, Fe, I, K, La, Mg, Mn, N,Na, Ni, Rb, S, Sc, Sr, Th, Ti, U, V, W, Zn	Ag, Hg, Mo, Pb, Ta, Tb, Yb, Zr	Hf	Sb	11.8
Veľká Fatra	Au, Br,In Sm	Ag, Al, As, Au, Ba, Ca, Cd,Ce, Cl, Co, Cs, Cu, Fe,Hg, I, K, La, Mg, Mn, Mo, N,Na, Ni, Pb Rb, S, Sc, Se, Sr, Ti, U, V, W, Zn	Cr, Sb, Ta, Tb, Th, Yb, Zr	Hf		7.6
Slovakia	Au, Br, In	Ag, As, Ba, Ca, Cd, Cl, Co, Cs, Cu, Fe, Hg, K, La, Mg, Mn, Mo, N,Na, Ni, Rb, S,Sb, Sc, Sm, Sr, Ti, U, V, W, Zn	Al, Ce, Cr, Hf, Pb, Sb, Se, Ta, Tb, Th, Yb, Zr			9.5

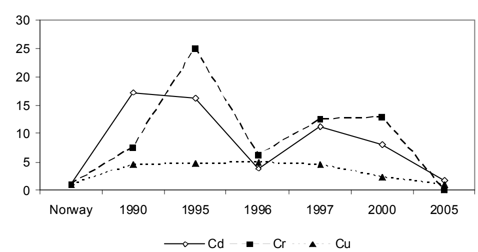

Figure 1 Concentration of Cd, Cr and Cu (average) in mosses for Slovakia in all survey years

Note: Year (number of PMP): 0(58);1995(79); 1996(69); 1997 (74); 2000 (86); 2005(82), PMP- Permanent monitoring plots.

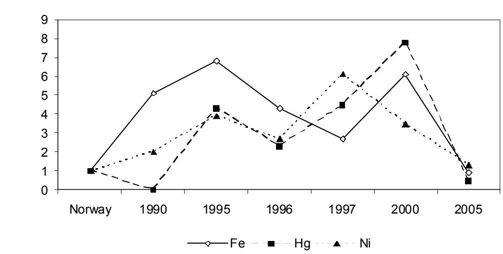

Figure 2 Concentration of Fe, Hg and Ni (average) in mosses for Slovakia in all survey years

Note: Year (number of PMP): 1990(58);1995(79); 1996(69); 1997 (74); 2000 (86); 2005(82), PMP- permanent monitoring plots

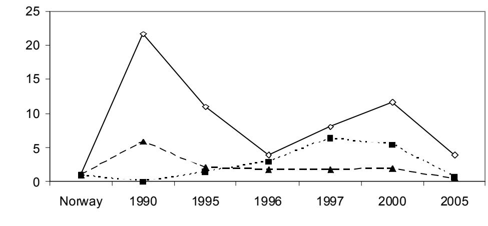

Figure 3 Concentration of Pb, V and Zn (average) in mosses for Slovakia in all survey years

Note: Year (number of PMP): 1990(58);1995(79); 1996(69); 1997 (74); 2000 (86); 2005(82), PMP- permanent monitoring plots

each factor and values of factor loadings, the major sources can be identified. Below is the interpretation of 8 factors in the sequence of their significance.

Factor 1 is responsible for 40% of total variance and is characterized by the presence of all typical crustal elements and it can be explained by elements associated with mineral particles, mainly windblown dust and include 13 elements Al, Sc, Ti, V, Fe, Zr, Re, Hf, Ta, and Th have loading higher than 0.9. Next ten elements (Na, Mg, Cr Co, Ni, Se, Sr, Cs, Ba, and

Table 4 WARIMAX rotated PC analysis of the first eight factors on 86 moss samples collected in the territory of Slovakia in 2000

Factor	F1	F2	F3	F4	F5	F6	F7	F8
% of cumulative variability	43.9	53.3	59.8	64.5	68.2	71.4	74.4	76.9
Element								
Ag	0.14	**0.68**	0.15	0.04	0.12	–0.02	–0.20	–0.15
Al	**0.94**	0.06	0.06	0.10	–0.02	0.06	0.18	–0.06
As	0.17	0.36	0.26	**0.61**	0.34	–0.04	0.10	0.16
Au	0.35	0.32	0.43	–0.05	0.24	0.16	0.02	–0.02
Ba	**0.74**	0.35	0.29	–0.01	–0.06	0.16	–0.13	0.01
Br	0.42	–0.12	0.05	0.29	0.24	**0.45**	0.33	0.23
Ca	0.28	–0.03	0.08	0.20	0.07	–0.11	**0.65**	0.11
Cd	0.13	0.21	–0.04	**0.76**	0.14	–0.08	0.12	0.04
Ce	**0.95**	0.08	0.08	–0.06	0.10	0.16	0.01	0.06
Cl	0.08	0.08	**0.82**	0.29	–010	0.20	–0.03	0.14
Co	**0.84**	0.14	0.13	0.01	0.11	–0.04	0.09	0.16
Cr	**0.75**	0.00	0.24	0.26	0.15	–0.12	–0.03	–0.10
Cs	0.59	0.21	0.36	–0.11	–0.10	**0.52**	0.00	0.00
Cu	0.15	0.76	–0.03	0.24	0.17	–0.05	0.22	0.18
Fe	**0.93**	0.14	0.14	0.08	0.04	0.17	0.07	0.02
Hf	**0.92**	0.06	0.11	0.04	–0.03	0.11	–0.03	0.00
Hg	0.01	0.03	0.11	0.05	0.14	–0.06	0.09	**0.85**
I	0.30	0.13	0.10	0.11	0.23	0.05	**0.75**	0.09
In	0.02	0.06	**0.59**	–0.14	–0.14	0.06	0.36	–0.11
K	0.14	–0.03	0.52	0.11	0.21	**0.62**	–0.11	–0.09
La	**0.88**	0.07	0.03	–0.11	0.23	0.22	0.14	0.07
Mg	**0.78**	0.13	0.12	0.22	0.01	0.03	0.37	–0.16
Mn	0.38	0.12	**0.57**	–0.21	0.10	–0.05	0.07	0.20
Mo	0.21	0.21	–0.07	0.26	**0.77**	0.13	0.13	–0.06
Na	**0.80**	0.03	0.03	0.00	0.20	0.13	0.08	–0.17
Ni	**0.84**	0.02	0.09	0.11	0.03	–0.18	0.09	0.12
Pb	0.12	**0.55**	–0.22	**0.51**	0.15	–0.11	0.27	–0.17
Rb	0.28	–0.03	0.08	–0.18	0.10	**0.77**	–0.04	–0.03
S	0.06	0.33	–0.13	0.42	–0.33	0.27	0.18	0.46
Sb	0.09	**0.87**	0.09	0.05	–0.05	0.06	–0.02	0.06
Sc	**0.94**	0.08	0.06	0.01	0.08	0.15	0.16	0.01
Se	**0.85**	0.13	–0.03	0.28	0.17	0.10	0.02	0.04
Sm	**0.88**	0.01	–0.02	–0.06	0.25	0.22	0.10	0.01
Sr	**0.84**	–0.03	0.11	0.20	–0.10	–0.08	–0.06	0.13
Ta	**0.95**	0.08	0.09	0.04	0.04	0.11	0.05	0.01
Tb	**0.94**	0.11	0.05	–0.03	0.12	0.11	0.15	0.09
Th	**0.94**	0.12	0.11	–0.02	0.10	0.19	0.06	0.03
Ti	**0.90**	–0.01	0.03	0.11	0.02	0.00	0.22	–0.02
U	**0.78**	0.10	0.01	–0.05	0.27	0.32	0.24	–0.03
V	**0.90**	0.03	–0.06	0.17	0.09	0.00	0.25	–0.03
W	0.23	0.19	–0.01	0.11	**0.77**	0.13	0.15	0.22
Yb	**0.94**	0.10	0.02	–0.02	0.11	0.09	0.03	0.11
Zn	–0.04	**0.52**	0.22	0.33	0.28	–0.02	0.20	0.14
Zr	**0.93**	0.03	0.10	0.06	0.00	0.09	0.06	–0.05

Note: Eight main source types were identified. Characteristic elements for the sources types are marked in bold type

U) have a loading factor between 0.70-0.89.

Factor 2 is an industrial component, with very high loadings for Cu, Zn, Ag, Sb, Pb and explains 10% of total variance with the factor loading from 0.52 to 0.87. Maximum value is in the area Krompachy-Smolnícka Huta-Zlatá Idka. Factor 2 reflects the impact from metallurgical plants.

Factor 3 includes mainly Cl, Mn, In and factor 6 contains K, Rb, and Cs. These elements are likely to be mainly of natural origin.

Factor 4 includes As, Cd, Pb and S. The pollution with mentioned metals is probably caused mainly by the long range transport. High levels of precipitation are strongly correlated with the heavy metals deposition, and seems to be the main source of heavy metal fallout at higher altitudes

Factor 5. Elements Mo and W are the main constituents. Their loading to the factor is 0.77. The factor components originate from engineering and instrument industry placed in the towns of Brezno, Martin, Dubnica, Košice and in triangle Stará Turá-Piešany-Nové Mesto n/V.

The major elements in factor 7 are Ca, I, Br and In. In Slovakia there are 1626 registered mineral water springs of different chemical composition, part of them contain I and Br in adequate quantity.

Finally, factor 8 explains 3% of the total variance. The dominating element is mercury. Sources of contamination with Hg are related to metals processing industries, combustion fossil fuels and municipal solid wastes and trans-boundary contamination in the NW wind directions.

Conclusions

Mosses provide an effective method for monitoring trends in heavy metal pollution in Slovakia at a high resolution.

Spatial trends of heavy metal concentrations in mosses were metal-specific. Coefficient of loading by air pollutants KF moves from 4.2 (Nízke Tatry) to 11.8 (Slovenský raj). Since 1990, the metal concentration in mosses has declined for Cadmium, Chromium, Cooper, Iron, Lead, Mercury, Nickel, Vanadium and Zinc.

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.

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References

Barandovski L., Cekova M., Frontasyeva M.V., Pavlov S.S., Stafilov T., Steinnes E., Urumov V., 2006. Air Pollution Studies in Macedonia Using The Moss Biomonitoring Technique, NAA, AAS and GIS Technology. JINR Preprint E18-2006-160, Dubna 2006, pp. 5-15.

Florek M., Maňkovská B., Oszlányi J., Frontasyeva V.M., Ermakova E., Pavlov S.S.,2007. The Slovak heavy metals survey by means the bryophyte technique. Ekológia (Bratislava), 26 (1): 99-114.

Frontasyeva M.V., Pavlov S.S., 2000. Analytical investigation at the IBR-2 Reactor in Dubna: preprint JINR E14-2000-177, Dubna, pp. 532.

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 p.

ICP, 1994. Manual on Methods and Criteria for Harmonized Sampling, Assessment, Monitoring and Analysis of the Effects of Air Pollution on Forest. 3rd edition Programme Coordinating Centre West, BHF, Hamburg, 45 p.

Maňkovská B., 1996. Geochemical atlas of Slovakia forest biomass (in Slovak, English). Geologická služba slovenskej republiky, Bratislava, 87 p.

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., 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. Ekológia (Bratislava) 22 (1): 211-217.

Maňkovská B., Oszlányi J., 2008a. Mosses and foliage of forest tree species as biomonitors of nitrogen pollution. International Journal of Environmental Studies, 65 (3): 377-388.

Maňkovská B., Oszlányi J., Barančok P. 2008b. Measurement of the atmosphere loading of the Slovak Carpathians using bryophyte technique. Ekológia (Bratislava), 7 (4): 339-350.

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.

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

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 p.

Suchara I., Florek M., Godzik B., Maňkovská B., Rabnecz G., Sucharova J., Tuba Z., Kapusta P. 2007. Mapping of Main Sources of Pollutants and their Transport in Visegrad Space. Silvia Taroucy Institute for Landscape and Ornamental Gardering Průhonice, CZ, ISBN 978-80-85116-55-7, p.78.

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 pp. 329-375.