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LONG TERM AIR POLLUTION STUDIES (1990–2005) IN BÁB RESEARCH SITES USING THE MOSS BIOMONITORING TECHNIQUE

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Abstract

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Results on atmospheric deposition of 45 elements in Báb research sites using the moss biomonitoring technique are presented. Concentrations of Ag, Al, As, Au, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Fe, Hf, Hg, I, In, K, La, Mg, Mn, Mo, N, Na, Ni, Pb, Rb, S, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, U, V, W, Yb, Zn, Zr in the 3 year old segments of *Pleurozium schreberi, Hylocomium splendens* and *Dicranum* sp. are discussed in a context of their limit values. In comparison to the median Norway values of heavy metal contents in moss the Slovak atmospheric deposition loads of the elements were found to be higher on average. We find out statistical important decrease (20–90%) of concentration Cd, Fe, Ni, Pb and Zn by comparison 1990–2005. During the same period elements such as Mn, and S increased by approximately 107–198%. 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 too for biodiversity study.

Key words: air pollution, biomonitoring, mosses, elements

Introduction

Moss is the most effective type of organism for biomonitoring of metals from the atmosphere because of its ability to accumulate and retain chemical substances, including trace elements. Nowadays the moss biomonitoring technique is widely used all over Europe as a method to evaluate atmospheric deposition of metals (Harmens et al., 2008; Maňkovská, 1997; Maňkovská et al., 2003, Maňkovská, Oszlányi, 2008; Schröder et al., 2008; Steinnes et al., 2001; Steinnes et al., 2007; Suchara et al., 2007; Zechmeister et al., 2003). The use of mosses as biomonitors was introduced in Scandinavian countries more than three decades ago, and it is presently widely accepted as a method to assess the atmospheric deposition of metals (Rűhling, Tyler, 1968, 1971). Mosses have only a rudimentary root system and readily

take up elements from the atmosphere. The advantage of the method is in the simplicity of sample collection, although the determination of the species needs an experienced hand. Data from existing surveys of heavy metal concentrations in mosses are an invaluable resource for international negotiations on heavy metal pollution. Results from moss surveys allow examination of both spatial and temporal trends in heavy metal concentration/deposition, and identification of areas where there is high deposition of heavy metals from long-range transport and local sources. 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 using moss analyses to determine the levels of atmospheric deposition of the elements. There are characterized by high concentration of toxic elements such as As, Cd, Cr, Cu, Hg, Fe, Mn, Ni, Pb, V and Zn. In comparison with the 1990 survey the median values in 2005 for Cd, Fe, Hg, Pb and Zn were reduced by approximately 20–90%.

Tree and shrub species are dominant forms of the research area of the International Biological Programme at Báb. The ecosystem which represents the seminatural oak-hornbeam forest at loess is a typical climazonal unit in this part of Slovakia. Numerous studies were performed on the tree and shrub individuals (Biskupský, 1975; Oszlányi, 2001).

The primary task of the present study was to quantitatively characterize the deposition of trace elements, including some toxic metals, over the research area of the International Biological Programme at Báb and to assess the atmospheric transport of pollutants to this region from the strongly contaminated neighbouring regions. An additional aim of this report is to summarise changes in heavy metal concentrations in mosses in sites Báb between 1990 and 2005.

Material and methods

The mosses (*Pleurozium schreberi, Hylocomium splendens, Dicranum* sp.) have been taken in compliance with the international methods in permanent areas situated on the intersections of a 16x16 km pan-European network (Fig. 1). 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.

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 analyses were performed: to determine short-lived radionuclides the samples were irradiated for 3 minutes in

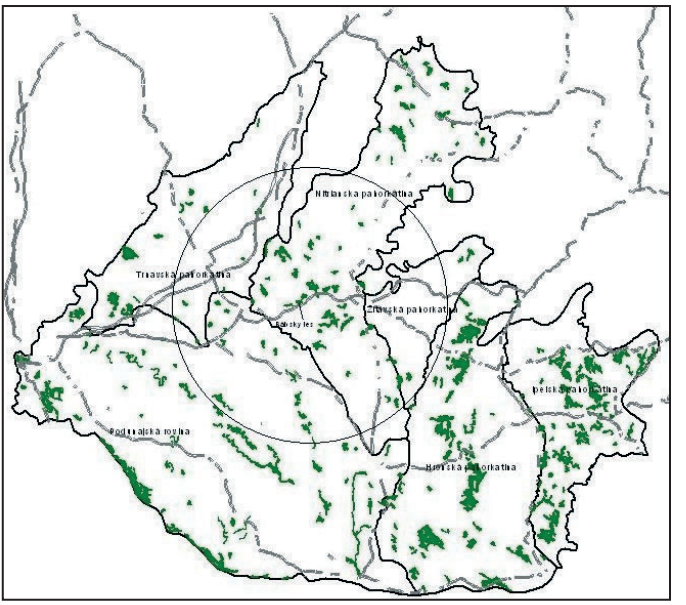

Fig. 1. Sampling area of Báb research sites.

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 (E = 0÷0.55 eV)	resonance (E = 0.55÷105 eV)	fast (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, 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 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 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 Báb and control one -the least polluted central part of Norway (Steinnes et al., 2001) in the year 2000. Table 2 presents also exceedance of 37 element concentrations in comparison with Norway. Central Norway belongs to the least polluted regions in Europe (Suchara et al., 2007). For Au, Ce, N, S , Sm and Ti 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 4 classes; class 1 – elements are in normal standard concentrations and coefficient does not exceed the value 1; class 2 – light loading (coefficient of loading ranges from 1 to 5); class 3 – moderate

T a b l e 2. Atmospheric deposition of elements (median in $mg.m^{-2}.year^{-1}$) in Báb area and Norway calculated from concentration of elements in 3 year old segments of *P. schreberi; H. splendens* and *Dicranum* sp. in the year 2000.

Element	**Norway**		**Báb**			Exceedance of Norway concentrations		
	Median	exc	Median	Maximum	Minimum	Median	Maximum	Minimum
Ag	0.005	1	0.021	0.036	0.009	4.20	7.20	1.80
Al	88	1	968	4200	485	11.00	47.73	5.51
As	0.03	1	0.205	0.292	0.107	6.83	9.73	3.57
Au**	0.002	1	0.0004	0.0008	0.0002	0.20	0.40	0.10
Ba	4.8	1	11.3	36.0	4.5	2.35	7.50	0.94
Br	1.25	1	1.16	1.64	0.56	0.93	1.31	0.45
Ca	780	1	1998	3775	575	2.56	4.84	0.74
Cd	0.02	1	0.201	0.259	0.034	10.05	12.95	1.70
Ce	0.086	1	1.04	3.79	0.50	12.09	44.07	5.81
Cl	50	1	53	131	42	1.06	2.62	0.84
Co	0.043	1	0.28	1.43	0.08	6.51	33.26	1.86
Cr	0.17	1	1.64	6.15	0.83	9.65	36.18	4.88
Cs	0.03	1	0.099	0.257	0.049	3.30	8.57	1.63
Cu	1.1	1	2.29	3.38	0.98	2.08	3.07	0.89
Fe	91	1	437	2495	166	4.80	27.42	1.82
Hf	0.002	1	0.163	0.470	0.073	81.50	235.00	36.50
Hg	0.013	1	0.0466	0.5625	0.0155	3.58	43.27	1.19

T a b l e 2. (Continued)

Element	**Norway**		**Báb**			Exceedance of Norway concentrations		
	Median	exc	Median	Maximum	Minimum	Median	Maximum	Minimum
I	0.50	1	0.745	2.005	0.198	1.49	4.01	0.40
In	0.05	1	0.020	0.042	0.007	0.40	0.84	0.14
K	750	1	1908	2813	1336	2.54	3.75	1.78
La	0.07	1	0.77	2.58	0.28	11.00	36.86	4.00
Mg	386	1	374	578	150	0.97	1.50	0.39
Mn	83	1	96	175	56	1.16	2.11	0.67
Mo	0.03	1	0.305	0.500	0.128	10.17	16.67	4.27
N*	5638	1	5500	6225	4900	0.98	1.10	0.87
Na	50	1	120	162	61	2.40	3.24	1.22
Ni	0.28	1	0.88	2.75	0.33	3.14	9.82	1.18
Pb	0.7	1	8.6	13.9	3.1	12.29	19.86	4.43
Rb	2.48	1	2.85	10.10	2.18	1.15	4.07	0.88
S*	508	1	464	770	298	0.91	1.52	0.59
Sb	0.01	1	0.193	0.538	0.058	19.30	53.80	5.80
Sc	0.015	1	0.165	0.868	0.065	11.00	57.87	4.33
Se	0.093	1	0.0875	0.2475	0.0475	0.94	2.66	0.51
Sm	0.086	1	0.115	0.458	0.040	1.34	5.33	0.47
Sr	2.9	1	22.5	46.3	7.0	7.76	15.97	2.41
Ta	0.001	1	0.024	0. 091	0.011	24.00	91.00	11.00
Tb	0.001	1	0.030	0.088	0.008	30.00	88.00	8.00
Th	0.010	1	0.133	0.545	0.04	13.30	54.50	4.00
Ti	5.875	1	9.5	22	6.0	1.62	3.74	1.02
U	0.004	1	0.028	0.120	0.018	7.00	30.00	4.50
V	0.34	1	1.575	2.925	0.825	4.63	8.60	2.43
W	0.030	1	0.078	0.130	0.038	2.60	4.33	1.27
Yb	0.003	1	0.093	0.200	0.025	31.00	66.67	8.33
Zn	7.4	1	15	19	7.5	2.03	2.57	1.01
Zr**	0.50	1	15	47	12	30.00	94.00	24.00
K_F		**1**				**8.84**	**26.88**	**3.78**

Notes: * – Slovak median 2000 (Suchara et al., 2007); ** – Macedonia (Barandovski et al., 2006); Exceedance (exc) – of element concentrations in mosses comparison with Norway.

T a b l e 3. Coefficient of loading by air pollutants K_F in the year 2000.

Contamination factor K_F				
< 1	1–10	10–50	>50	K_F
Au, Br, In, Mg, N, S, Se,	Ag, As, Ba,Ca, Cl, Co, Cr, Cs,Cu, Fe,Hg, I, K, Mn, Na, Ni, Rb, Sm, Sr, Ti, U, V, W, Zn	Al, Cd, Ce, La, Mo, Pb, Sb, Sc, Ta, Tb, Th, Yb, Zr	Hf	**8.84**

loading (coefficient ranges from 5 to 10); class 4 – heavy loading (coefficient is higher than 10. As we can see in Table 3, coefficient of loading by air pollutants K_F for almost all elements is higher than one, it means the concentration of these elements in Báb is higher (sometimes 10 up to 50 times higher; Hf – 235 times) than in Norway. Only the concentration of Au, Br, In, Mg, N, S, Se is lower in Báb as Norway.

In comparison with the 1990 survey (Maňkovská, 1997), the median values in 2005 (Table 4) for Cd, Fe, Ni, Pb and Zn were reduced by approximately 20–90%. Decreasing concentrations are connected with decreasing production of non-ferrous metals in Slovakia and with facing out leaded gasoline. During the same period elements such as Mn, and S increased by approximately 107–198%. The main source of increase in air is gradually growing heavy oil combustion. Increasing concentrations are connected also with transboundary transmission from the Czech Republic and Austria.

Conclusion

It was determined on the basis of bryomonitoring performed in 3year old segments of *Pleurozium schreberi, Hylocomium splendens* and *Dicranum* sp.; on Báb research sites that:

a. coefficient of loading by air pollutants K_F for almost all elements is higher than one, it means the concentration of these elements in Báb is higher (sometimes 10 up to 50 times higher): 1990 (Fe, Pb, Zn); 1995 (Cd, Cr, Fe, Ni, Pb); 1997 (Ni, Pb); 2000 (Al, Cd, Ce, La, Mo, Pb, Sb, Sc, Ta, Tb, Th, Yb, Z and for Hf -235 times) in comparison to the Norway values. Only the concentration of Au, Br, In, Mg, N, S, Se is lower in Báb research sites as Norway.

Table 4. Concentration of elements in mosses (*Pleurozium schreberi,. Hylocomium splendens* and *Dicranum* sp.) in the years 1990–2005 (median in mg. m^{-2}.$year^{-1}$) and comparison with Norway.

	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	S	V	Zn
1990	-	0.480	1.7	8.9	1008	-	88	1.20	27.1	221	-	142
1995	-	1.452	13.1	16.0	1248	0.0118	-	9.68	14.0	-	0.16	34
1996	0.295	0.143	3.99	21.0	413	0.0405	-	1.64	2.5	-	3.06	23.6
1997	0.085	0.315	4.67	10.7	563	0.0830	-	6.58	7.3	-	2.15	22.4
2000	0.821	0.803	6.56	9.2	1747	0.1865	384	3.50	34.5	1855	6.30	60
2005	-	0.143	-	3.4	186	0.0219	94	1.05	4.05	437	0.34	14.1
Norway	0.135	0.087	0.69	4.2	91	0.0540	83	0.28	0.7	508	0.34	7.4
%1990–/2005	-	29.8	-	37.9	18.5	-	106.8	87.5	14.9	197.7	-	9.9

b. coefficient of loading by air pollutants K_F move from 1990(6.5); 1995(8.7), 1996(3.2); 1997(5.0); 2000 (8.8) and 2005(1.5).
c. we find out statistical important decrease (20–90%) of concentration Cd, Fe, Ni, Pb and Zn by comparison 1990–2005. During the same period elements such as Mn, and S increased by approximately 107–198%.
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.

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