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Temporal and spatial trends (1990 -2010) of heavy metal accumulation in mosses in Slovakia

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Abstract

The use of mosses as biomonitor of atmospheric deposition of heavy metals in Slovakia started more than 30 years ago in connection with the problems of the forest dying in Slovakia.1990s, within the framework of UNECE ICP Vegetation programme, systematic studies using moss were carried on in Slovakia (net 16x16 km), and the results were presented in the European Atlas *Atmospheric Heavy Metal Deposition in Europe – Estimations Based on Moss Analysis*. 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 biomonitoring, was applied to the whole territory in 1990, 1995, 1996, 1997, 2000, 2005 and 2010. The application of mosses as biomonitors of trace elements in selected Slovak industrial areas, mining country, and National parks affected by anthropogenic activity is reviewed. Moss was successfully used also to study temporal and spatial deposition of N and S. A combination of analytical data (NAA, and AAS in our case) with principle component analysis and correlation factor allowed pollution source characterization and apportioning in the sampled areas: Central Spiš (effect of heavy metals); Aluminium plant Žiar nad Hronom; Thermal power plant Horná Nitra; Central Slovakia (mining area of Staré Hory, Ľubietová, Špania dolina); Beskydy (north part of Slovakia- influence of Poland and Czech pollutants); High Tatra National Park (TANAP) and Low Tatra National Park (NAPANT).

Key words: air pollution, biomonitoring, heavy metals

1. Introduction

Heavy metals, such as lead and cadmium, can be toxic to both humans and wildlife, in adition nitrogen pollution can lead to eutrophication, damaging aquatic ecosystems. Previous studies have demonstrated that the level of these pollutants found in mosses, due to air pollution from vehicle emissions, for example, can be used as an indicator of the amount of heavy metal and nitrogen being deposited from the atmosphere to the ground (Suchara et al., 2007; Schröder et al., 2008; Maňkovská and Oszlányi, 2010; Harmens et. al., 2012). The use of mosses as biomonitor of atmospheric deposition of heavy metals in Slovakia started more than 30 years ago in connection with the problems of the forest dying in Slovakia 1990s, within the framework of UNECE ICP Vegetation programme, systematic studies using moss were carried on in Slovakia (net 16x16 km), and the results were presented in the European Atlas *Atmospheric Heavy Metal Deposition in Europe – Estimations Based on Moss Analysis*. 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 Second Black Triangle. In order to recognise the distribution of elemental deposition in the SK, the moss monitoring technique, also known as biomonitoring, was applied to the whole territory of the country in 1990, 1995, 1996, 1997, 2000, 2005, and 2010.

2. Materials and methods

The samples of mosses were not washed before analysis. For INAA moss samples of about 0.3 g were packed in aluminium cups for long-term irradiation or heat-sealed in polyethylene foil bags short-term irradiation in the IBR-2 reactor, Dubna, described elsewhere (Frontasyeva, 2011). Atomic absorption spectrometry (VARIAN SPECTRA A-300 and mercury analyser AMA-254) was carried out in FRI Zvolen. The accuracy of the results was verified by 109

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separate laboratories and tested by the IUFRO programme (Maňkovská and Oszlányi, 2010). The concentrations of S and N were determined by LECO SC 132 and LECO SC 228 analyzers, respectively.

3. Results

Slovakia joint the UNECE ICP Vegetation programme on actual deposition of elements using moss analysis 1990- 2010. The samples of mosses *Pleurozium schreberi* and *Hylocomium splendens* were collected at permanent monitoring sites with the European network (16x16 km). The results for the required monitoring elements were published in the European reports (Harmens et al., 2012).

In general, the concentration of Cd, Cr, Cu, Fe, Hg, Ni, Pb, V, and Zn in mosses decreased between 1990 and 2010; 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 (Figure 1).

This approach is based on the fact that the concentrations of heavy metals in mosses correlate very well with the atmospheric concentrations. It was proven that the calibration of the concentration of a given element in mosses can be done using the concentration of the same element in the atmospheric deposition. The concentration of individual elements was recalculated to the time of moss exposure for 3 years. A good linear relation between the concentrations of a given element in mosses and in precipitation was observed. It follows the equation [concentration in moss] mg/kg = [4x atmospheric deposition] mg/(m^2·year) (Steinnes et al., 2007). Excess of the concentration of elements in mosses in comparison with Norway (Table 1) we expressed by means of the coefficient of loading by elements K_F and classified into 4 classes; class < 1 – elements are in norm and do not exceed the value 1; class 2 – slight loading (elements range from 1 to 10); class 3 – moderate loading (elements range from 10 to 50); class 4 – heavy loading (elements are higher than 50 times higher value) (Table 1).

Table 1. Coefficient of loading by elements K_F in the year 2000

Sites	Coefficient of loading by elements K_F				K_F
	< 1	1 -10	10-50	>50	
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**
Žiar basin	Au, Br, Cl, I, In, Mn	Ag, Al, As, Ba, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Hg, K, La, Mg, Mo, Na, Ni, Rb, Sc, Se, Sm, Sr, Tb, Th, Ti, U, V, W, Zn	Hf, Pb, Sb, Ta, Yb	F	**6.2**
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**
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**
Báb	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	**8.8**
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**
Poľana	Au	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**
Morské oko	Au	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, Hf, Sb, Sc, Ta, Tb, Th, Yb	**44**
Central Spiš	Au	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, Hf, Pb, Sb Ta Tb, Yb	**45**
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**

The marginal hot spots were revealed in Volovské Mts (Central Spiš), Kremnické and Štiavnické Mts (nonferrous ores processing and aluminium factories) and near dumps of stone chips (Slanec). In comparison to the average Austrian and Czech values of heavy metal contents in moss, the Slovak atmospheric deposition loads of the elements were found to be 2–3 times higher on average. The transboundary contamination by Hg through dry and wet deposition from Czech Republic and Poland is evident in the bordering territory in the north-western part of Slovakia (The Second Black Triangle), known for its metallurgical works, coal processing and chemical industries. Spatial trends of trace element concentrations in mosses were metal-specific. Since 1990, the metal concentration in mosses has declined for cadmium, chromium, cooper, iron, lead, mercury, nickel, and zinc.

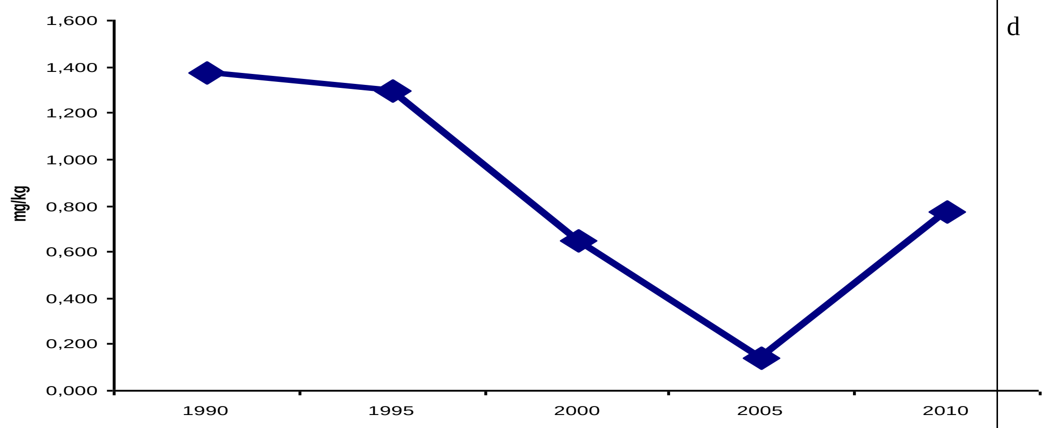
The temporal trends in the concentration of Cd, Cr, Cu, Fe, Hg, Ni, Pb, V, and Zn between 1990 and 2010 were observed. In general, the concentration of Cd, Cr, Cu, Fe, Hg, Ni, Pb, V, and Zn in mosses decreased between 1990 and 2010; the decline was higher for Pb than for Cd. The observed temporal trends 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 the elements at the investigated sites. In comparison with the Norwegian low concentration values (Central Norway is a relatively pristine area) for Al, As, Ca, Cd, Cl, Co, Fe, K, Mn, Sb, Sm, Sr, W, and Zn, those in the industrial area of Central Spiš considerably exceed them (Table 2).

Table 2. The rate of median values of element in Slovak vs. Norway mosses in year 2000

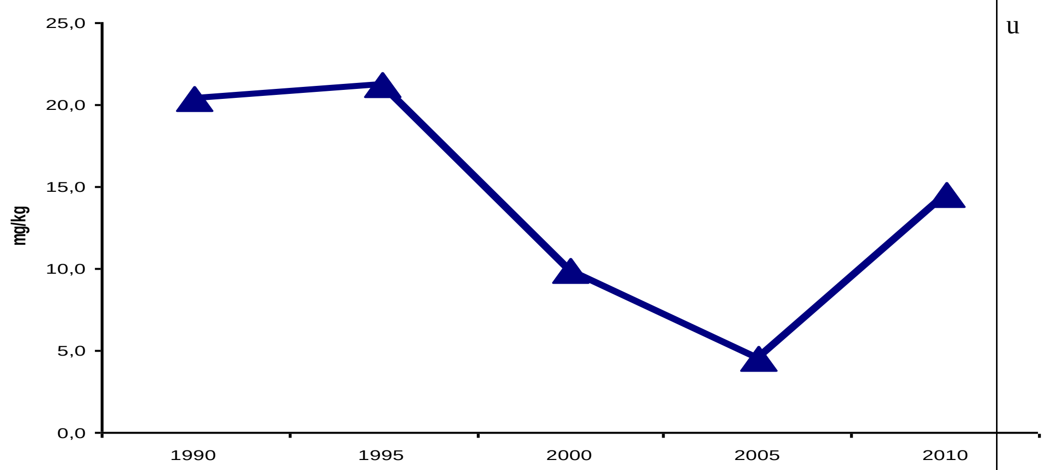
Contamination factor Kz				
>1	1-2	2-5	5-10	>10
Br, I	Cl, Mn, Na, Ni, Se, Rb, U, Zn,	Ba, Ca, Co, Cr, Cu, Fe, Hg, K, Sm, Tb, Th, Ti, V	Al, Au, Ce, La, Sb, Se, Sr, Yb, Pb	Ag, Cd, Mo, Ta, W

Note: Kz= contamination factor as the rates median value of element in Slovak mosses vs. Norvay mosses (Steinnes et al., 2007).

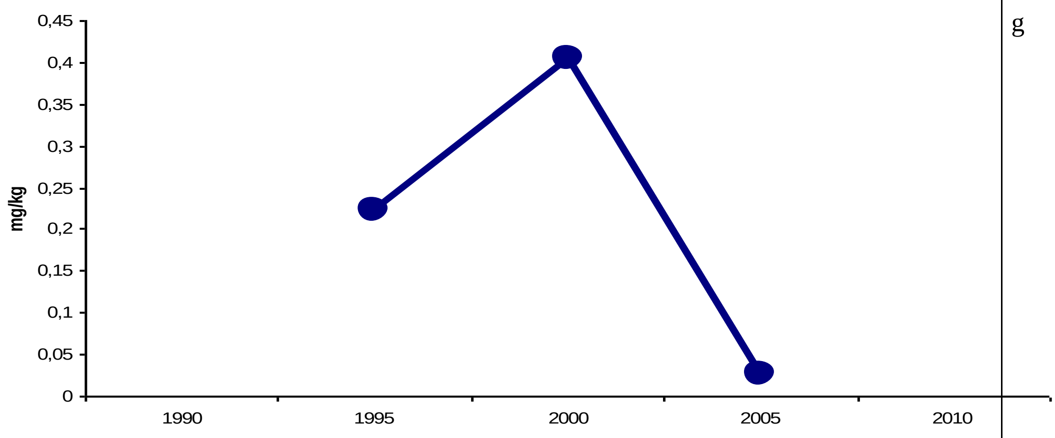
Figure 1. Concentration of Cd, Cu, Hg, Fe, Pb, and Zn (average in mg/kg) in mosses for Slovakia in 1990, 1995, 2000, 2005, 2010.



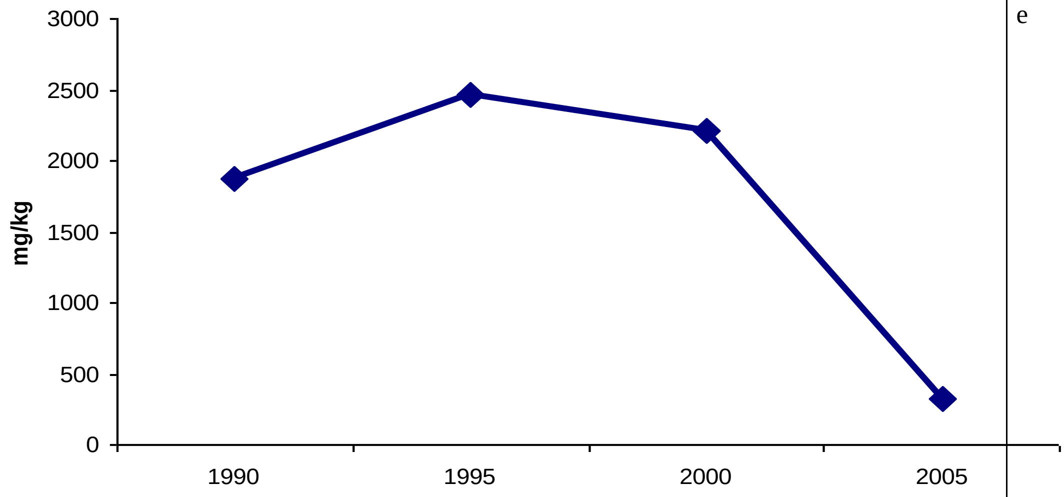
d



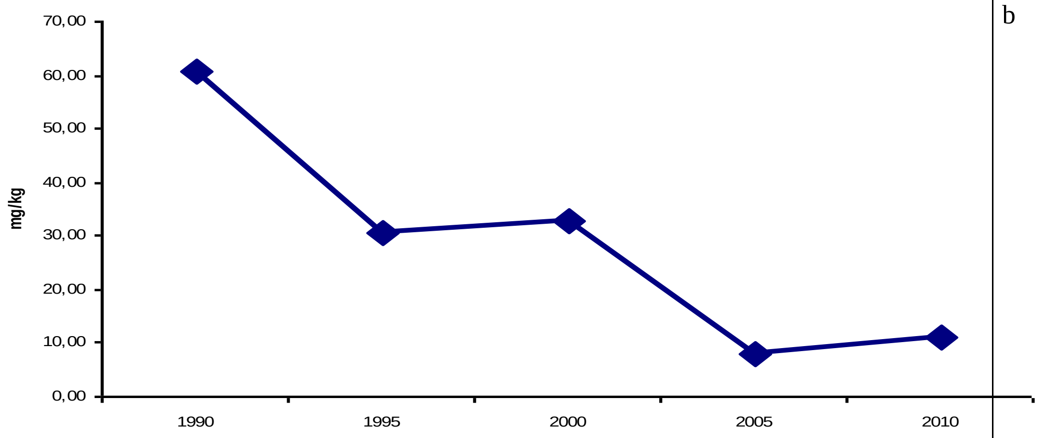
u


0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
mg/kg
1990
1995
2000
2005
2010

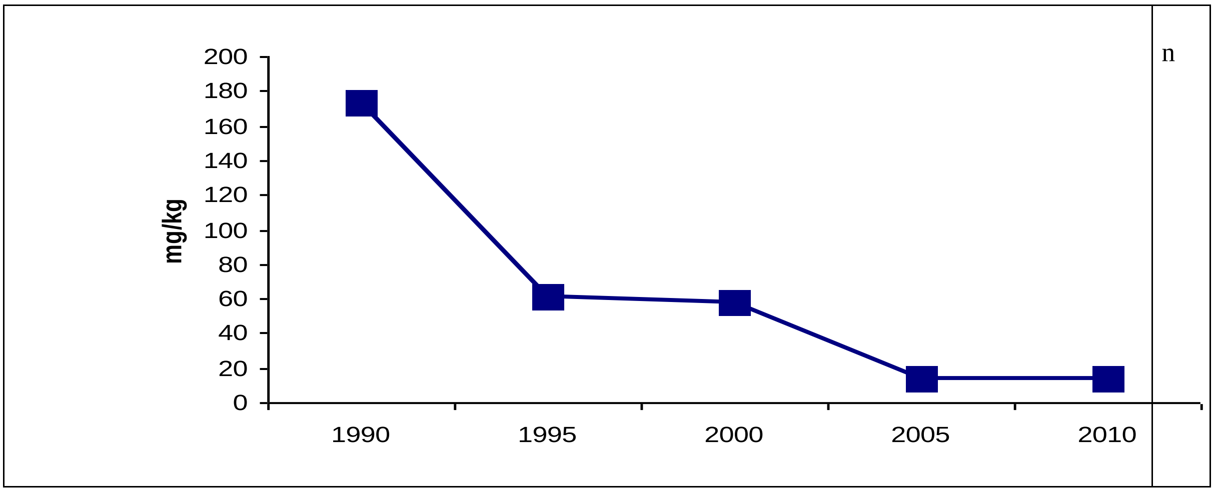
g


3000
2500
2000
1500
1000
500
0
mg/kg
1990
1995
2000
2005

e


70,00
60,00
50,00
40,00
30,00
20,00
10,00
0,00
mg/kg
1990
1995
2000
2005
2010

b



Note: Year (number of PMP): 1990(58);1995(79); 1996(69); 1997 (74); 2000 (86); 2005(82), 2010(67); PMP-permanent monitoring plots.

4. Conclusions and discussion

The Slovakian moss surveys play an important role in identifying spatial and temporal trends in atmospheric trace element pollution across Europe. This work is essential for monitoring atmospheric deposition of trace elements with a high spatial resolution. It provides useful data for additional validation of modelled atmospheric deposition fluxes. The environmental monitoring programmes such as moss surveys are appropriate tools for the regulatory bodies to protect the environment from deteriorating or ensure that its quality is improved.

The biomonitoring based on analysis of 3year old segments of *Pleurozium schreberi, Hylocomium splendens* and *Dicranum* sp. collected at 10 sites in the Slovakia showed that:

a. Concentration of elements is more than 50 times higher at sites Báb (Hf), Poľana (Hf, Sb); Vysoké Tatry (Hf); Slovenský raj (Hf, Sb); Veľká Fatra (Hf); Central Spiš (Ag, Hf, Pb, Sb Ta Tb, Yb); Žiar basin (F) and site Morské oko (Al, Hf, Sc, Sb, Ta, Tb, Th, Yb) in comparison to the Norwegian values.
b. Coefficient of loading of air pollutants K_F varies from 4.2 - Nízke Tatry; 6.2 - Žiar basin; 6.7 - Vysoké Tatry; 7.6 - Veľká Fatra; Báb - 8.8; 11.8 - Slovenský raj; 19 -Poľana; 44 - Morské oko to 45 - Central Spiš.

The obtained data can be used as a reference level for future measurements of air pollution in the examined areas and also serve for the biodiversity study. The significance of transboundary atmospheric transport in this region remains to be studied in the future.

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