TEMPORAL AND SPATIAL TRENDS (1990−2010) OF TRACE ELEMENT ATMOSPHERIC DEPOSITION IN SLOVAKIA: ASSESSMENT BASED ON MOSS ANALYSIS

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Abstract

The results of moss analysis by two complementary analytical techniques – neutron activation analysis and atomic absorption spectrometry – from the consequent moss surveys in 1990, 1995, 1996, 1997, 2000, 2005, and 2010 undertaken in the framework of the UNECE ICP Vegetation programme are reported. A total of 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, and Zr) were determined. S and N were determined by LECO analyzers. Temporal and spatial trends of atmospheric deposition of some selected trace elements are discussed.

Keywords: air pollution, bryomonitoring, heavy metals, neutron activation analysis, atomic absorption spectrometry.

Introduction

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 dyinig 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 bryomonitoring, was applied to the whole territory of the country in 1990, 1995, 1996, 1997, 2000, 2005, and 2010.

Experimental

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

Results and discussion

Slovakia joint the UNECE ICP Vegetation programme on actual deposition of elements using moss analysis 1990. The samples of mosses *Pleurozium schreberi* and *Hylocomium splendens* were collected at 58 permanent monitoring sites with the European network (16x16 km). Following elements were determined by atomic absorption spectroscopy (AAS): Cd, Cr, Cu, Fe, Mn, Ni, Pb, S, and Zn. Sulphur was also determined by LECO SC 132.

In the second moss survey in 1995 moss samples were collected at 78 permanent monitoring sites. In 1996 moss samples were collected at 69 and in 1997 at 74 permanent monitoring sites. The following elements were determined: As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V, and Zn by AAS and Hg by AMA-254.

The third moss survey at the European scale of atmospheric deposition of elements was realised within the ICP Vegetation in 2000. Collection of moss samples (*P. schreberi, H. splendens* and *Dicranum* sp.) was performed at 86 permanent monitoring sites in Slovakia. Neutron activation analyses (NAA) was carried out in the Frank Laboratory of Neutron Physics in 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). Varian Techtron atomic absorption spectrometer was used for analyses of Cd, Cr, Cu, Hg, Ni, Pb and Zn. Element determinators LECO SC 132 was used for sulphur determination and LECO SP 228 for nitrogen determination.

In the fourth European biomonitoring moss survey in 2005 moss samples (*P. schreberi, H. splendens, Dicranum* sp.) were collected at 77 permanent monitoring sites in Slovakia. They were analysed for contents of Cd, Cu, Fe, Hg, N, Ni, Pb, S, V, and Zn by AAS Varian Techtron, AMA-2454, LECO SC 132 and LECO SP 228. The results of analyses were published in the European reports (Harmens et al.,2010). The required and optionally monitored elements were evaluated in the context of neighbouring countries of Visegrad Four (Suchara et al., 2007).

So far, in the last fifth European biomonitoring survey in 2010 samples of mosses *P. schreberi, H. splendens, Dicranum s*p. were collected at 68 permanent monitoring sites in Slovakia. They were analysed for content of Al, Ca, Cd, Cl, Cu, Dy, I, K, Mn, Pb, S, Ti, V by means of AAS Varian Techtron, LECO SC 132 and LECO SP 228, and by use of NAA in Dubna, Russia. 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 (Fig. 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 (Tab.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) (Tab.2).

Table 2 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.

Table 1. 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).

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.

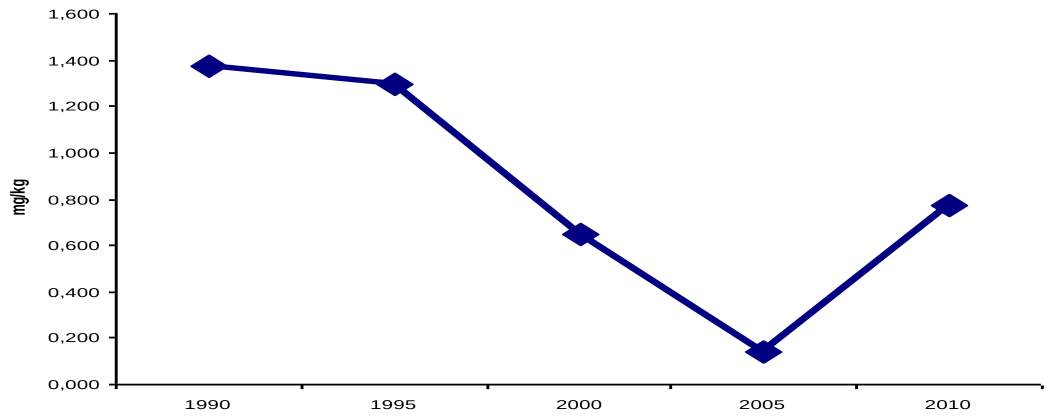
Conclusion

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.

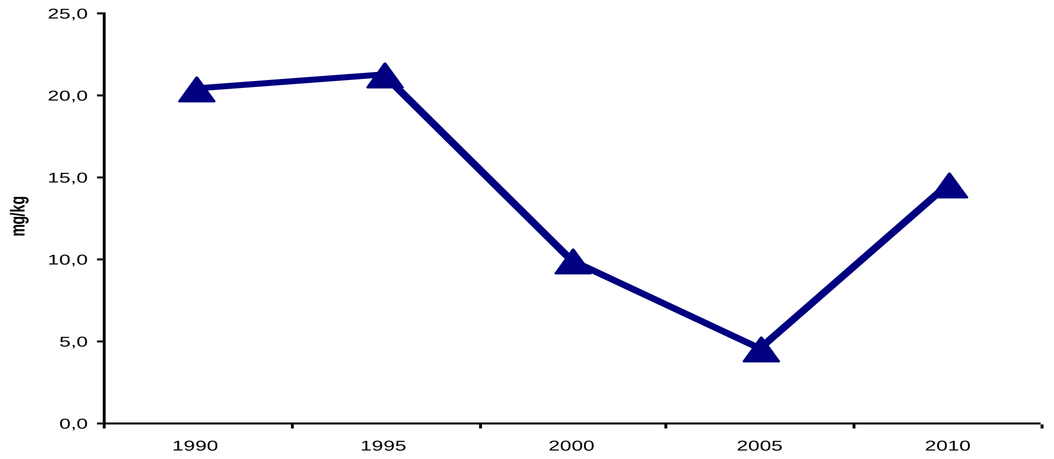
The bryomonitoring based on analysis of 3year old segments of *Pleurozium schreberi*, *Hylocomium splendens* and *Dicranum* sp. collected at 10 sites in the Slovakia showed that:

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.
c. 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.

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



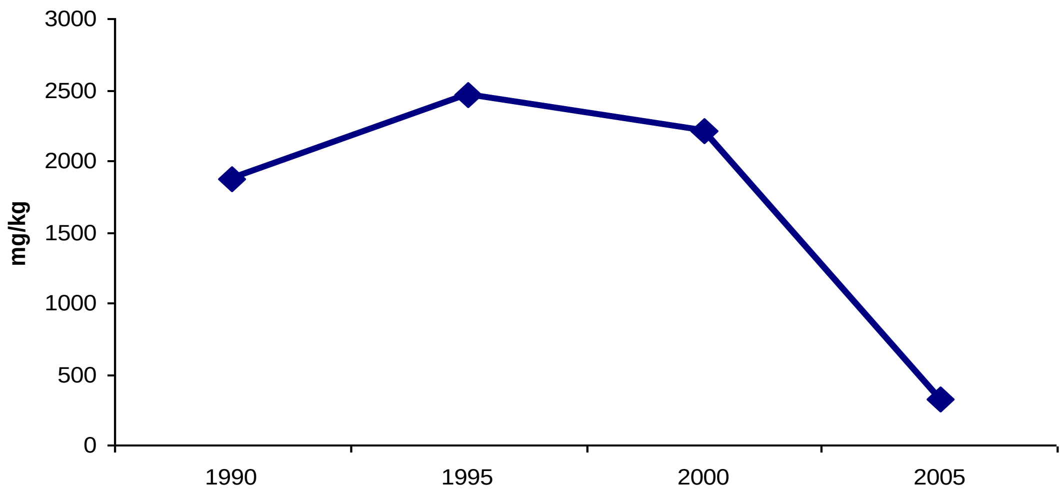
Cd



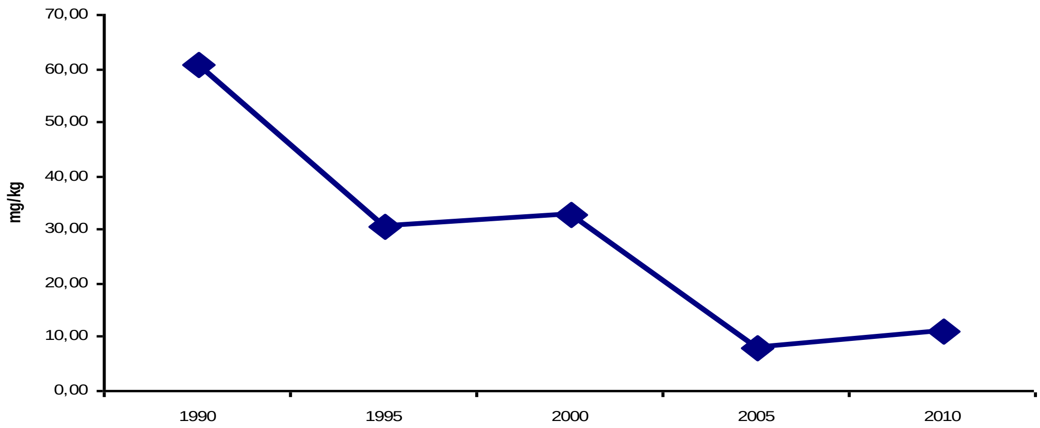
Cu


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

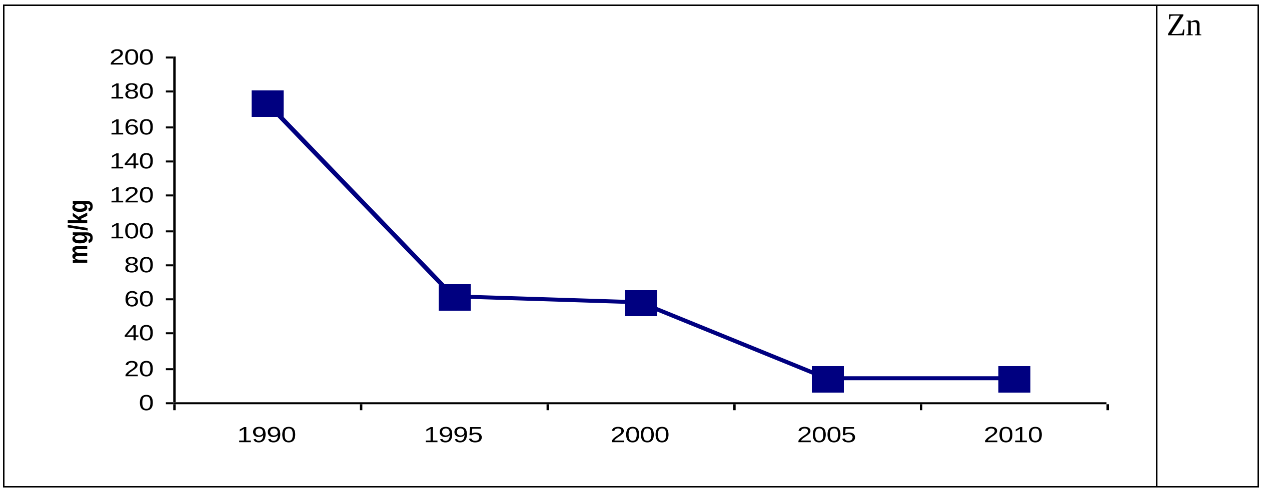
Hg


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

Fe


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

Pb



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

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