Acta Physica Universitatis Comenianae
Vol. L–LI, Number 1&2 (2009–2010) 155–161

Some Results of Application of INAA and AAS in the Environmental Research in Slovakia*

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Abstract: The concentrations more than 40 chemical elements (heavy metals, rare earths, and actinides) were determined in the atmosphere of Slovakia using bryophyte technique and membrane filters. The main goal of this study is the quantification of the atmospheric pollution and its trend in different parts of Slovakia. The elemental content in the sampling was measured using instrumental neutron activation analysis (INAA) at IBR-2 reactor in JINR Dubna and by atomic absorption spectrometry (AAS).

1. Introduction

Heavy metals are released into the environment from a great number of sources. Combustion of fossil fuels is the main anthropogenic source of Ni, V, Cd, As, and Zn. Such elements as Pb, Sb, Br, Cr and V are associated with automotive exhaust products and domestic heating. Non-ferrous smelters are the sources of Cu, Zn, Cd, and Pb. The largest source of airborne Cd in the environment is the burning of fossil fuels such as coal or oil, and incineration of municipal waste materials. Cd may also be emitted into the air from zinc, lead, or copper smelters. The current anthropogenic metal emissions are up to several orders of magnitude higher than their natural contents (Chmielewska et al., 2003).

The conventional method to study atmospheric deposition of heavy metals and other trace elements is precipitation analysis. An alternative method to measure integral trace element deposition is the use of terrestrial mosses growing in forests or other natural habitats. Mosses effectively accumulate the majority of metals and other trace elements from air and precipitation. More than three decades mosses are used as biomonitors. This technique is widely accepted at present as the method to assess the atmospheric deposition of heavy metals. The results from moss surveys are regularly published (each five years) in the Atlas of Heavy Metal Atmospheric Deposition in Europe by the UNECE ICP Vegetation (European Atlas, 2003, 2008).

2. Materials and methods

The Department of Nuclear Physics and Biophysics of Commenius University has participated in the two last moss surveys. The mosses *Pleurozium schreberi* and *Hylocomium splendens* were used as biomonitors to study the atmospheric deposition of trace elements over the territory of Slovakia performed during the first half of August

*) *Dedicated to Assoc. Professor Matej Florek on the occasion of his 70th birthday.*

2000 and 2006. Two complementary analytical techniques, instrumental neutron activation analysis (INAA) and atomic absorption spectrometry (AAS) were used for determination of the elemental content in the environmental samples (in moss samples and air filters). INAA is a direct and non-destructive method, its main advantages are high precision, high selectivity and sensitivity; small sample quantity needed, etc.

For INAA moss samples of about 0.3 g were packed in aluminum cups for long-term irradiation or heat-sealed in polyethylene foil bags short-term irradiation in the IBR-2 reactor, Dubna, described elsewhere (Frontasyeva, 2006). The element concentrations were determined on the basis of certified reference materials and flux comparators.

Flame atomic absorption spectrometry (VARIAN SPECTRA A-300 and mercury analyser AMA-254) was carried out in Zvolen and later in the Geological Institute of Comenius University.

3. Results and discussion

A total of 44 major and trace elements were determined (Florek, Maňkovská et al., 2001, 2007) in mosses samples collected from 86 localities (Fig. 1). The results of the measurements were presented in the form of maps and were published in review "Mapping of Main Sources of Pollutants and their Transport in Visegrad Space" (Suchara, Florek et al., 2007).

Comparison with the limit values from Norway (considered the pristine area) shows strong pollution of the examined areas of Slovakia with most of the heavy metals. The range of the ratio $K_i \quad \frac{C_{iSl}}{C_{iN}}$, where C_{iSl} is the median value of the element in the Slovak moss and C_{iN}, is the median value of the Norwegian one given in Table 1. The median values for Norway are taken from (Steinnes et al., 2000).

Table 1. Range of ratios of the median values of elements in the Slovak relative the Norwegian moss.

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

The part of the obtained results (only heavy metals) was submitted to the European Atlas "Heavy metals in European Mosses: 2000/2001 Survey". In the UNECE ICP Vegetation survey (UNECE ICP 2003) Slovakia is classified as a rather polluted European country.

The most significant anthropogenic sources are fossil fuels combustion (electric power stations) allocated in Upper Nitra and Vojany. From the other industrial activities metallurgy, nonferrous ores processing, and cement factories should be mentioned (Central Spiš, wider surroundings of Rožňava, Central Pohronie – Banská Bystrica – Brezno, Lower Orava).

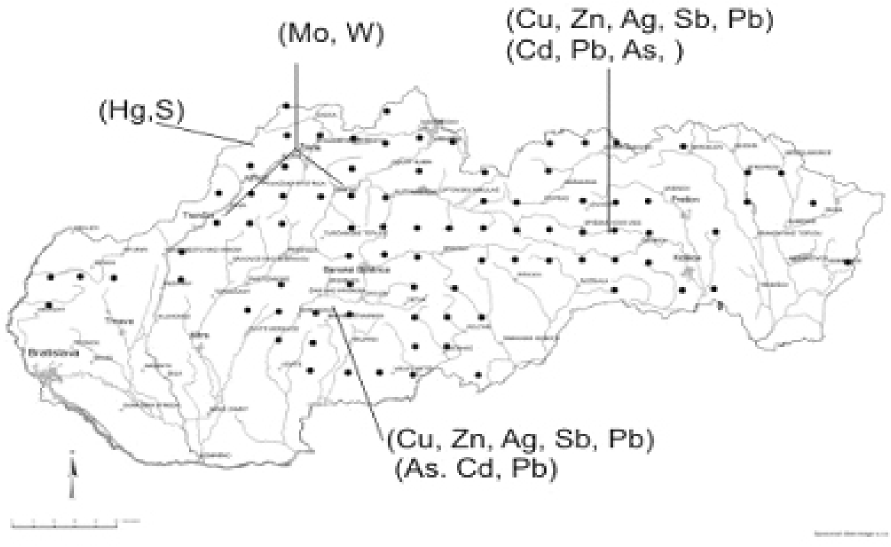

Fig. 1. The map of sampling sites on territory SR.

The examined territory is known for its numerous regions with intense mining activity (Slovenské Rudohorie, Kremnické and Štiavnické vrchy). They are characterized by high concentration of toxic elements such as As, Al, Mn, Cd, Cr, Cu, Hg, Pb, and Sb. Many of them rank to the past, but their presence in waste heap produces the negative effect on the environment of different level of toxicity. Instrument- producing industry is responsible for Mo, W contamination near the town of Martin and in the Považská valley (Považská Bystrica, Dubnica). In the north-northwest border areas of Slovakia the elevated concentration of Hg was determined. Most probably, it reflects the long-range transport form the Katowice-Ostrava region also known as the 2-nd Black Triangle. The huge amount of coal is mined here and, accompanied by metallurgical, chemical industry and mechanical engineering, they significantly influence the environment.

INAA and AAS were employed in order to evaluate the concentrations of up to 43 chemical elements in the atmospheric aerosol filters, too (Merešova, Florek et al., 2007). Two sampling sites in Bratislava were examined. The first site Líščie údolie is a quite pristine location with a low traffic density. The second sampling site is close to the crude oil processing plant Slovnaft. The influence of the steel industry in Veľká Ida and thermal power plant in Prievidza were investigated. Most heavily contaminated sampling site in the vicinity of surface coal mine Tušimice in the Czech Republic was also included in this study. Sampling of atmospheric aerosol particles was performed in the period 2004–2006. The levels of pollutant concentrations were compared to those in the atmosphere of other five European sites: Krakow; Budapest; Ispra, Ponzone, and Milan.

Figure 2 shows a decreasing trend of air pollution with heavy metals in Bratislava since 1981. The emissions of Pb have decreased, reflecting the shift from leaded to unleaded gasoline. The further explanation of this decreasing trend is the declination of industry in Slovak Republic after the year 1989, since the fuel burning processes in thermal power plants and industry factories are the major source of atmospheric pollution

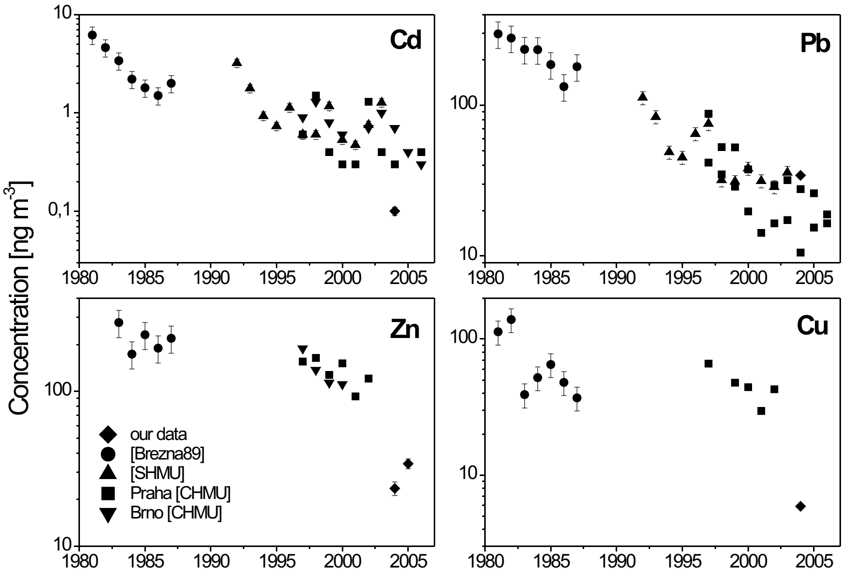

Fig. 2. The temporal variations of atmospheric concentrations (ng·m^{-3}) of Cd, Pb, Zn, and Cu in Bratislava; circle – (Brežná, Závodský, 1989), triangle – (SHMU), diamond – our data. For comparison also elemental concentrations in Prague (square) and Brno (reverse triangle) (CHMU) are shown.

with heavy metals. The emissions of pollutants were reduced also via utilization of more rigid requirements in the environmental legislation and employment of new more effective filtration techniques.

For several environmentally meaningful elements (Cr, Fe, Ni, Cu, Zn, As, Cd, Pb) our results are compared (Tab. 2) to the relevant data from some European cities. The complete table of the results was published in paper by Florek, Merešova et al., 2008.

A small town of Ponzone (Rizzio et al., 2001) in Italy is famous for its wool industries and Ispra (Rizzio et al., 1999) is a residential settlement in the northern Italy. The city of Milan (Gallorini et al., 1999) is the industrial centre of the northern Italy, thus concentrations of almost all elements are obviously the highest in relevant aerosols. The main objective of the Krakow research study (Wróbel et al., 2000) was to determine the contribution of traffic to the particulate air pollution, and to characterize transport of aerosols in urban area that are close (5 m) to the main road. Also, the location of Szena Square in Budapest (Salma et al., 2002) has a more closed downtown character and is affected by heavy traffic. It is worth to note that concentration of such elements as Mn, Ni, Cu, As, Sb, and Pb in low atmospheric layers of large cities (Budapest, Milan) is comparable or exceeds that one in strongly contaminated areas like the territory of the thermo power electrical station in Tušimice.

The concentrations of almost all elements are lower in Bratislava-Líščie údolie compared to the other localities, or comparable to the Italian sites of Ponzone and Ispra, which are typically low pollution areas. The low-level atmospheric pollution in Bratislava may be caused by a small number of pollution sources, and in particular by for this location typical high number of windy days per year.

Table 1. Contents of stable elements [ng·m^{-3}] in the atmosphere for 10 European locations.

	Líščie údolie	Slov-naft	Veľká Ida	Prievidza	Tušimice	Krakow	Buda-pest	Ponzone	Ispra	Milan
	Slovakia				CR	Poland	Hungary	Italy		
Cr	1.1	2.8	1.1	1.2	150		3.4	7	6.5	38.6
Mn	4.9				13	17	27	23	14	98
Fe	252		643	435		788	1969	807	511	5800
Co		0.3	0.42	0.19	1.37					
Ni	0.45	5.1	1.6*	1.0*	4.4		2.9	20.5	12.2	25.1
Cu	8.0	41	18	21	9.0	18	33	21	10	185
Zn	28		1294	1515	26122	61	147	98	119	392
As	0.3		1.7*	7.9*	1.5		1.6	0.8	0.99	2.3
Cd	0.11	2.2	1.1*	0.4*	7.1			0.75	0.51	3.4
Sb	1.0		1.37	5.5	2.4			4.9	4.5	68
Hg	0.064		< 4.2	< 4.2						
Pb	22	42	90	29	45	46	29	36	98	475
Th	0.042				1.4			0.22	0.05	0.5

**Data taken from Burda et al., 2006*

For the first time more than 40 elements in the Slovak atmosphere using mosses samples and aerosol filters were determined (Merešova, Florek et al., 2008). The obtained data can be useful as a reference level for comparison with the future measurements of heavy metal pollution in the examined area.

Acknowledgements

The authors express their deep gratitude to B. Mankovska and J. Ozslanyi from the Institute for Landscape Ecology of SAS, Bratislava, and the Department of NAA of FLNP JINR for their participation in this study. This work was supported by the grant of the Plenipotentiary of the Slovak Republic at the Joint Institute for Nuclear Research, Dubna, with support of S. Dubnicka.

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