RESULTS OF COOPERATION BETWEEN SLOVAKIA AND FLNP JINR IN THE ENVIRONMENTAL RESEARCH (2000–2013)

Florek M., Holý K., Masarik J., Sýkora I.

Department of Nuclear Physics and Biophysics, Comenius University, Bratislava, SR

Maňkovská B., Oszlányi J.

Institute of Landscape Ecology of the SAS, Bratislava, SR

M.V. Frontasyeva, S.S. Pavlov, T.M. Ostrovnaya, S.F. Gundorina, Y.V. Aleksiayenak

Frank Laboratory of Neutron Physics, JINR, Dubna, RF

Abstract

During last twelve years cooperation between Slovakia and FLNP JINR focused on the environmental studies. The moss and airborne particulate matter were the objects of investigations. INAA at the IBR-2 reactor and flame AAS were applied in order to determine 44 elements in moss collected in 2000, 2005, and 2009. Factor analysis was applied to determine possible sources of trace element deposition in the Slovakian moss. The transboundary contamination with Hg through dry and wet deposition from Czech Republic and Polish is evident in the bordering territory in the north-west part of Slovakia (The Second Black Triangle), known for metallurgical works, coal processing and chemical industries. Knowledge of the current contents of individual elements in the moss-biomonitors allowed us estimating their absolute atmospheric deposition levels. The concentrations of trace metals, rare earths, and actinides were evaluated in the atmospheric aerosols, too.

The moss samples collected in Slovakia and Belarus were assayed with respect to gamma-emitting radionuclides (^{137}Cs and ^{210}Pb) using the low-level background facilities of in the Comenius University in Bratislava. Moss was employed for the first time in Belarus as a biological indicator of radioactive environmental pollution in consequence of the Chernobyl accident in 1986. Using the results for ^{137}Cs and ^{210}Pb concentration in surface air in Slovakia, the median values of moss activity in Slovakian and Belarus samples we estimate, that the inhalation dose for man (from ^{210}Pb and ^{137}Cs) in Slovakia was shown to be more than twice as higher as in Belarus in spite of the initially very high ^{137}Cs exposure in the latter country.

Introduction

Trace 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).

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. This technique is widely accepted at present as method to assess the atmospheric deposition of trace 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.

Materials and Methods

We have analyzed more than 600 environmental samples from Slovakia. The main part of them was mosses. The mosses (*Hylocomium splendens, Pleurozium schreberi,* and *Dicranum* sp.) were used as biomonitors to study the atmospheric deposition of trace elements over the territory of Slovakia performed during the first half of August 2000, 2006 and 2009.

The second part of samples was aerosol filters. Nitro-cellulose membrane filters (PRAGOPOR, pore size 0.85 μm) with collection efficiency approximately 100 % were used. A sampling device with an air-flow rate 30 $m^3 \cdot h^{-1}$ was installed at a height of 2.85 m above the ground. At other sampling stations the glass-fibre filters MILLIPORE were used and the volume of air sampled was about 55 m^3. Further details can be found in (Sýkora et al., 2007).

The third part was samples of the vegetation organs of forest tree species (foliage, spruce needles, lime and spruce wood, soil, and roe deer teeth). The environmental samples were not washed before analysis.

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. 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, 2011). 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 in Geological Institute of Comenius University.

Results and discussion

a. Concentration of elements in mosses

A total of 44 major and trace elements were determined (Florek et al., 2001, 2007; Maňkovská et al., 2003) in mosses samples collected at 86 sites (Fig. 1). The results of measurements were presented in the form of maps and were published in the review "Mapping of Main Sources of Pollutants and their Transport in Visegrad Space" (Suchara et al., 2007). Our data (only trace metals) were incorporated into the European programme "Atmospheric heavy metal deposition in Europe – estimation based on moss analysis". In the UNECE ICP Vegetation survey (UNECE ICP, 2003). Slovakia is classified as a rather polluted European country.

The most signi-ficant 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). 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 negative effect on the environment of different level of toxicity. Machine--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 atmospheric transport form the Katowice-Ostrava region also known as the Second Black Triangle. The huge amount of coal is mined here and, accompanied by metallurgical, chemical industries, as well as mechanical engineering, significantly affects the environment.

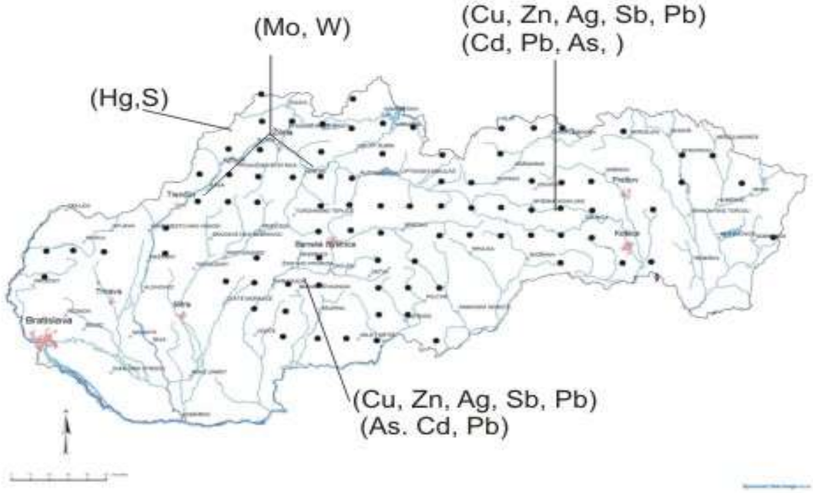

Fig. 1. Sampling map in the territory of SR with marks of high concentrations of relevant elements

Comparison with the limit values from Norway, considered the pristine area, shows strong pollution of the examined areas of Slovakia with most of heavy metals. Median values of concentrations of some elements (Al, Ag, Au, Ce, Cd, La, Mo, Sb, Pb, Sc, Sr, Ta, Yb, and W) in moss samples is 5–10 times higher in comparison to the Norwegian median values. In comparison to Austrian, Hungary, Poland, Czech, and Ukraine the median values of trace elements were found to be 2–3 times higher in the Slovakian mosses (Florek et al. 2007).

Metal- and site-specific temporal trends were observed. In general, the concentrations 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 (Harmens, H., et al, 2010).

b. Results on elemental concentrations in atmospheric aerosol

INAA and AAS were employed in order to evaluate the concentrations of up to 43 chemical elements in the atmospheric aerosol filters, too (Merešova et al., 2008). 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 the thermal power plant in Prievidza were investigated. Most heavily contaminated sampling site in the vicinity of surface coal mine Tušimice in Czech Republic was also included in our study. Sampling of atmospheric aerosol particles was performed in the period 2004–2009. A significantly increased airborne pollution was observed in the area of Tušimice affected by the surface mine and combustion of coal by the thermal power plant Tušimice II.

Since the year of 1981 a decreasing trend of air pollution with such elements as Cd, Cu, Pb, and Zn was observed in Bratislava. The emissions of Pb have decreased, reflecting the shift from the leaded to unleaded gasoline. The other reason of this decreasing trend is the decline of the industrial production in Slovak Republic after the year of 1989, since the fuel burning processes in thermal power plants and industrial plants are the major sources of atmospheric pollution with heavy metals. The emissions of pollutants were reduced also due to more strict requirements in the environmental legislation.

The levels of pollutant concentrations were compared to those in atmosphere of the other five European sites: Krakow; Budapest; Ispra, Ponzone, and Milan. The low-level atmospheric pollution in Bratislava may be caused by a small number of pollution sources, and, in particular, by the high number of windy days per year, typical for this location. The complete table of results was published (Merešova et al., 2008).

The sixteen filter samples were exposed during 7−10 days regularly within the whole year of 2004. Atmospheric concentrations of some elements indicate seasonal variations over the year with elevated values in summer. Most of them are crustal components (Ca, Ti, Mn, Ba, U), although they may also be emitted as fly-ash from the combustion of coal, and as dust from other mineral-related activities. Only Cu was classified as an anthropogenic element. Thus, we can conclude that the seasonal variations of elements are not significantly influenced by human activities. The variations may be governed by atmospheric transport processes and circulation. For some elements (Ba, Ca, Cu, Mn, Ti, and U) the seasonal variations in concentration were observed, for the other ones the concentration is relatively stable over the year.

c. Measurement of ^{137}Cs and ^{210}Pb activity in mosses and aerosol filters

Part of moss samples from Slovakia and Belarus were measured in the low-level counting laboratory of Department of Nuclear Physics and Biophysics of Comenius University, Bratislava on presence ^{137}Cs and ^{210}Pb (Sykora I., 2011).

The measurements of nuclides ^{137}Cs in Slovakian moss samples collected in 2000, 2006 and 2009 years demonstrate a decrease of activity over the time period. It follows from the measurements of ^{137}Cs using aerosol filters in Bratislava air from 1977 till 2010 that in Slovakia the annual average activity of ^{137}Cs in surface air decreased consequently from 130 $\mu Bq/m^3$ in 1977 down to 0.3 $\mu Bq/m^3$ in 2009, except for a significant increase of activity level during the years 1986–1987 due to the Chernobyl accident. The observed decrease in the ^{137}Cs activity in the air follows the exponential law with an apparent ecological mean half-life of 41 months (3.4 years). However, during 2007-2010 the yearly averaged ^{137}Cs activity was almost constant, with except seasonal variation. In contrast to the pre-Chernobyl period, in seasonal variations we have observed a shift of maximum ^{137}Cs activity from the summer season to the winter season. This is might be due to the changes in sources of anthropogenic radionuclides in the surface air.

During the pre-Chernobyl period the main source of global fallout radionuclides in the surface air was stratospheric radioactive air. During the post-Chernobyl period the stratospheric reservoir of ^{137}Cs has not been anymore its dominant source, but a resuspension of global and Chernobyl fallout ^{137}Cs from soil has become important source of ^{137}Cs in the surface air.

The results of measurements of ^{137}Cs and ^{210}Pb in moss samples were compared with the results of air monitoring of ^{137}Cs and ^{210}Pb carried out in Slovakia since 1977 till 2010. Measurements of the ^{210}Pb concentration in moss samples collected over the territory of Slovakia showed that the median value exceed 2.3 times median value of ^{210}Pb obtained for the Belarus moss. For that reason, the inhalation dose for man (from ^{210}Pb and ^{137}Cs) in Slovakia (7.3 μSv/a in 2005) was shown to be more than twice as higher as in Belarus (3.2 μSv/a) in spite of the initially very high ^{137}Cs exposure in the latter country. In the relatively higher contaminated areas of Belarus the concentration of ^{137}Cs in moss (assigned to 2005) is around 500 times higher. Thus, the natural ^{210}Pb is currently much more important than the anthropogenic ^{137}Cs for the inhalation dose to man in both countries. To estimate the total dose knowledge of the external irradiation and activity consumed with food is needed.

d. Concentration of elements in roe deer teeth and annual growth rings in spruce and lime wood

The region Central Spiš is historically linked with exploitation and processing of non-ferrous metals known for the maximum level of pollution with trace metals. The concentrations of 19 elements were determined in the teeth of roe deer from the three polluted areas of the Žiarska dolina valley, the Central Spiš and the Upper Orava region, and also in the Nízke Tatry National Park control area (NAPANT) which is far removed from the industrial pollutant sources. A statistically significant difference was established between the concentration of As, Cd, Co, Cu, Hg, Na, Pb, Rb, Sr, and Zn in roe deer teeth among the mentioned regions (Maňkovska, et al., 2012). In comparison with limit values the concentration of Ba, Co, Hg, Mg, Mn, and Sr in the teeth of roe deers increased markedly. The other determined elements (Al, As, Ca, Cd, Cu, Fe,Na, Pb, and Rb) did not exceed the limits (Maňkovská, 2012).

In order to get a chronological record of trace element pollution in the Central Spiš, we used the 10-year-old segments of one hundred-old lime *Tilia cordata* Mill and of 90-old spruce wood *Picea abies Karst.* Trees usually form visible annual growth rings. Sampling was conducted in May 2001. We had available bores from both sides stem of lime (NW and SW at angle 180^o) and from one side of spruce. The bores we subdivided into 10-year-old segments. To avoid contamination, the wood samples were prepared with a hard metal corer.

No correlation of elements was observed between two sides of a lime. Correlation of elements in relevant rings of two types of wood was not evident (Maňkovska, Popierová, 2003). Maximal concentrations of metals are apparently mobile in the stem wood. Therefore, the current locations of these maxima are not reliable markers for the dating of pollution events in the forest environment. The radial distribution of heavy metals in wood rings should be cautiously used as a tool for chronological record of the environmental pollution.

Conclusion

In the frame work of cooperation between Slovakia and Frank Laboratory of Neutron Physics JINR the moss samples, aerosol filters and the vegetation organs of forest tree species from territory of Slovakia were analyzed. We have evaluated separately the industrial area and the Landscape protection area. Up to 44 elements were determined in the examined samples. Such a large association of elements has never been studied before in the environmental samples from Slovakia. It was shown that Slovakia has been affected by an intense atmospheric depositional load of elements. It is assumed that a large gradient of the atmospheric deposition load of elements exists in Slovakia because the part of its territory occurs in the most polluted area of the Central Europe known as the Second Black Triangle. Partly, it is connected with geochemical peculiarities of Slovakia and intense mining activity in several regions. Many of them rank to the past, but the present-day waste heaps produce negative effect of various levels of toxicity on the environment.

The results of cooperation were reported at the ISINN periodically starting from 2001. The full dataset was published in *“Mapping of Main Sources of Pollutants and their Transport in Visegrad Space”* (a printed publication + CD-edition), which was distributed among different environmental institutions of Slovakia in 2007.

Acknowledgements

This work was supported by Scientific Grant Agency of Ministry of Education of Slovak Republic (VEGA project 1/0143/14),by the Slovak Grant Agency APVV under the grant VV-

0420-10 and by the grant of the Plenipotentiary of the Slovak Republic at the Joint Institute for Nuclear Research.

References

1. Aleksiayenak Yu. V., Frontasyeva M.V., Florek M., Sykora I., Holy K., Masarik J., Brestakova L., Jeskovsky M., Steinnes E., Faanhof A., Ramatlhape K. I. (2013): Distributions of ^{137}Cs and ^{210}Pb in moss collected from Belarus and Slovakia. Journal of Environmental Radioaktivity, 117 19-24.
2. Buse, D. Norris, H. Harmens, G. Mills, B. Mankovska, M. Florek et al. (2003): Heavy metals in European Mosses: 2000/2001 Survey UNECE ICP Vegetation, Centre for Ecology and Hydrology, ISBN 1 870393 70 8,
3. Florek M., Mankovska B., Frontasyeva M. V., Oprea K., Pavlov S. S., Sykora I.. Steinnes E. (2001). Air Pollution with Heavy Metals and Radionuclides in Slovakia Studied by the Moss Biomonitoring Technique. Preprint JINR E3-2001-155
4. Florek M., Maňkovská B., Oszlányi, J., Frontasyeva M. V., Ermakova E. E., Pavlov S. S. (2007): The Slovak Heavy Metals Survey by Means the Bryophyte Technique. Ekologia (Bratislava), 22, 1, p. 99 - 114,
5. M.V. Frontasyeva. Neutron activation analysis for the Life Sciences. A review. “Physics of Particles and Nuclei”, 2011, Vol. 42, No. 2, p. 332-378 (in English). http://www.springerlink.com/content/f836723234434m27/
6. Harmens H., Norris D. and the participants of the moss survey, (2008): Spatial and temporal trends in heavy metal accumulation in mosses in Europe (1990-2005). Centre for Ecology and Hydrology, Environmental Centre Wales, United Kingdom, ISBN: 978-1-85531-239-5
7. Harmens, H., Frontasyeva, Maňkovská, B., et al, (2012). Country-specific correlations across Europe between modelled atmospheric cadmium and lead deposition and concentrations in mosses. Environmental Pollution 166: 1-9
8. Harmens, H., Frontasyeva, M., Maňkovská, B., et al . (2010). Mosses as biomonitors of atmospheric heavy metal deposition: spatial and temporal trends in Europe. Environmental Pollution 158: 3144-3156
9. Chmielewska, E., Spiegel, H., (2003): Some control of an amplified heavy metal distribution at immission sites of Danube lowland refineries. Environment Protection Engineering, *29*: 23-32
10. Maňkovská B., Florek M., Frontasyeva M.V., Ermakova L., Oprea K., Pavlov S. S.. (2003) Atmospheric Deposition of Heavy Metals in Slovakia Studied by the Moss Biomonitoring Technique, Neutron Activation Analysis and Flame Atomic absorption Spectrometry. Ekologia (Bratislava), vol. 22, Supplement 1/2003. p. 157-162.
11. Mankovska B., Oszlanyi J., Goryanova Z. I., Frontasyeva M. V., Kaštier P., (2012): Regional Variation in Environmental Element Concentration in Slovakia Derived from Analysis of Roe Deer Teeth. Ekológia (Bratislava), 31, No. 2, p. 138–149
12. Maňkovská B., Popierová D., Florek M., Frontasyeva M.V., Ermakova L., Antoni J. (2003): Elemental composition of lime wood response to atmospheric deposition. Ekologia (Bratislava), 22, Supplement 1/2003. p. 152-156
13. Meresova J., Florek M., Holy K., Jeskovsky M., Sykora I., Frontasyeva M.V., Pavlov S.S., (2008): Evaluation of Elemental Content in Airborne Particulate Matter in Low-level Atmosphere of Bratislava (Slovakia), Atmospheric Environment, 42 8079-8085. (see too: JINR Preprint, E18-24-2008, Dubna, , pp. 18).

14. Suchara I., Florek M., Godzik B., Maňkovska 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.
15. Sýkora I., Povinec P., Bresťáková L., Florek M., Holý K., Masarik J., Frontasyeva M.V., Steinnes E. (2011): Variations of ^{137}CS and ^{40}K in the Surface Air of Bratislava (Slovakia) — Iidications for Soil Resuspension Processes. Preprint JINR E14-2011-85.