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AIR POLLUTION WITH HEAVY METALS AND RADIONUCLIDES IN SLOVAKIA STUDIED BY THE MOSS BIOMONITORING TECHNIQUE

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Introduction

The conventional way of studying atmospheric deposition of chemical pollutants such as heavy metals and radioactive nuclides is the analysis of samples from bulk precipitation collectors and aerosol filters. The routine precipitation sampling is limited to a small number of sites, the concentrations of most elements in precipitation are very low, and contamination problems associated with the sampling are often encountered.

Another method to measure integrated heavy metal deposition is to use terrestrial mosses growing on the ground in forests and other natural habitats. The mosses concentrate most of heavy metals and other trace elements efficiently from air and precipitation by several orders of magnitude. The great majority of moss species have a special advantage, namely, they take nutrients almost exclusively from the atmosphere because they have no developed root system. Heavy-metal uptake, therefore, takes place through the surface of the plants, which are excellent 'catch organisms' for wet and dry deposition of heavy metals and radioactive isotopes. What is obtained by the moss method, as such, is a relative deposition pattern of the metals in question, but conversion to absolute deposition rates by calibration against the bulk precipitation data is rather straightforward.

Certain moss species are abundant in large parts of the temperate zone (*Hylocomium sp.* and *Pleurozium schreberi*, for example), and their growth pattern is such that the annual increment can be readily identified. Thus the sampling is easy, the analysis is far simpler than for precipitation samples, and the exposure period can be defined. Normally the last 3 years growth is taken for analysis. This technique has been used regularly for the last 20 years in the Scandinavian countries and has also been adapted in a number of additional European countries for routine monitoring of atmospheric deposition of metals with a very high spatial resolution [1].

In the Slovak Republic extensive studies in this direction have been done during the last decade by B. Mankovska from Forest Research Institute (FRI), Zvolen, within the frame of the program "Monitoring of metal atmospheric deposition in the Slovak Republic using analysis of mosses". Analysis of environmental samples is carried out by atomic absorption spectrometry (AAS). Activities of the laboratory include multielement analysis of soils, plants, mosses, tree bark, humus and other environmental matrices. External and internal rules of quality assurance are kept and based on intercalibration tests of plant and humus. The FRI Zvolen is involved in an international program of monitoring of metal atmospheric deposition in Europe co-ordinated by a group in the Nordic countries. Isoline maps of atmospheric deposition of metals including the Slovak Republic territory were presented in a report issued by the nordic Council of Ministers [1] and in the Goechemical atlas of Slovakia [2].

The present study was carried out within the framework of the agreement between Faculty of Mathematics, Physics and Informatics of the Comenius University and Frank Laboratory of Neutron Physics of the Joint Institute for Nuclear Research (JINR). The subject of agreement: to study atmospheric deposition of heavy metals and radinuclides in industrial areas of Slovakia by the moss biomonitoring technique in co-operation with the Forest Research Institute, Zvolen.

Experimental

The Pulsed fast reactor IBR-2 in FLNP JINR, equipped with the fast pneumatic transfer system REGATA and four irradiation channels for instrumental neutron activation analysis (INAA), provides activation with thermal, epithermal and fast neutrons [3]. Two channels are

cadmium screened for activation with epithermal neutrons [4]. The neutron flux density (for thermal or epithermal neutrons) inside channels of the order of 10^{12} cm^{-2}. s^{-1} [5]. The induced activity can be measured using γ-spectrometers with Ge(Li) and HPGe detectors and ORTEC electronics. The software developed at FLNP JINR is used for data processing [6]. The mentioned method can determine [7] up to 45 elements.

It should be added that the INAA technique does not require sample dissolution, and therefore has a great advantage if the total concentration is the aim of the analysis. Not all the above trace elements are strictly relevant as air pollutants, but they come additionally from the multi-element analyses with insignificant extra cost, and most of them can be used as air mass tracers. Previous experience in analysing environmental samples at JINR allows use of the epithermal neutron activation to determine a considerable number of rare-earth elements as tracers of geochemical processes. Epithermal neutron activation analysis is especially feasible at the pulsed fast reactor IBR-2 with its high fluxes of resonance and fast neutrons.

ENAA for air pollution studies

The dominant part of air pollution studies on the reactor IBR-2 is based on the use of the moss biomonitoring technique [7]. This technique is widely spread in Western Europe, is presently applied in Dubna to air pollution studies in some industrial areas of Russia [8], Central Russia [9]) and in the country-members of JINR (Poland [10] and Romania [11]) as well as in non-member countries (Norway [12], China [13]). In the present paper we report the result of analyses of mosses collected from different parts of Slovakia.

Epithermal neutron activation analysis (ENAA) has certain advantages over conventional instrumental activation analysis for many trace elements in terms of improvement in precision and lowering of detection limits and reduction of high matrix activity. The technique is based on the fact that some elements have isotopes with very high resonance activation integral relative to the thermal neutron activation cross-section (I_o/σ_o ratio). This ratio is of the order of 0.5 for a majority of nuclides but may be as high as 100 in other cases. This means that the radionuclide distribution originating from epithermal activation may deviate strongly from that apparent when the whole reactor spectrum is employed.

Sampling

The samples of mosses were collected on 86 permanent plots situated in Slovakia at the intersections of 16x16 km pan–European network. Moss samples *(Pleurozium schreberi, Hylocomium splendes and Dicranum scoparium)* 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 2000 and was executed by a specialist of the Forest Research Institute in Zvolen. The samples were subjected to analysis without preceding washing, after drying at a temperature not exceeding 60 °C for 24 hours.

The samples consisted of the last three years' annual segments and represented the deposition of heavy metals for the years 1998, 1999 and 2000. The concentration of Pb, Cd, Cu, and Hg was determined (with a precision of ~ 5%) in the Forest Research Institute, Zvolen, by flame atomic absorption spectrometry with VARIAN SPECTRA A-300 and by the mercury analyser AMA-254 manufactured by ALTEC, Prague.

The other 38 elements were determined by neutron activation analysis at the reactor IBR-2, Dubna. Moss samples of about 0.3 g were packed in aluminium cups for long-term irradiation and samples of about 0.3 g were heat-sealed in polyethylene foil bags for short-term irradiation. To determine the short-lived isotopes of Na, Mg, Al, Cl, K, Ca, Mn, I and Br, channel 2 was used (conventional NAA). Samples were irradiated for 5 min and measured twice after 3-5 min of decay for 5 and 15 min, respectively.

Elements yielding long-lived isotopes were determined using the Cd-screened channel 1 (ENAA) at the reactor IBR-2. Samples were irradiated for 4 days, re-packed, and then measured twice after 4-5 days and 20 days of decay, respectively. Measurement time varied from 1 to 5 hours. The concentration of elements was determined with a precision of 8% - 18% (dependending on the element), only for Br it was as high as 25 %.

Results and discussion

Heavy metals

The total concentrations of individual elements (median, arithmetical mean, standard deviation, coefficient of variation, range) were determined. Comparison with background values from Norway shows strong pollution of the examined areas of Slovakia with most of the heavy metals (Fig.1). The maximum level of pollution by heavy metals was observed in a region named Spish ($48^0$46' N, $20^0$07' E).

Mosses were sampled in their natural habitats in 58 localities in 1991, 78 in 1995 and 86 localities in 2000. In comparison with the 1991 survey [14] the median values (Table 1) in 2000 for Cd, Cu and Pb were reduced by approximately 50 % and for Zn even ~70 %. During the same period elements such as Ni and V increased by approximately 50 %. Fe and Hg showed practically no change. Decreasing concentrations are connected with decreasing production of steel and non-ferrous metals in Slovakia and with facing out leaded gasoline. The main source of increase of nickel and vanadium in air is gradually growing heavy oil combustion.

Table 1. Concentrations of heavy metals in mosses collected in 1991,1995, and 2000.

Median [mg/kg]									
Years	Cd	Cr	Cu	Fe	Ni	Pb	Zn	Hg	V
1991	1.35	3.4	19	1571	1.7	41	162		
1995	1.2	13.2	16	1483	2.0	23	49	0.11	1.2
2000	0.6	6.5	9	1560	3.2	28	50	0.18	5.6

Radionuclides

Before activation of the mosses sampled, part of them (11 out of 86) were measured in the low-level counting laboratory of Department of Nuclear Physics of Comenius University by gamma-ray spectrometry, using an ORTEC HPGe detector (40 cm^3) with Be window, placed in a low-level background shield. The measuring time was usually ~ 50 hours.

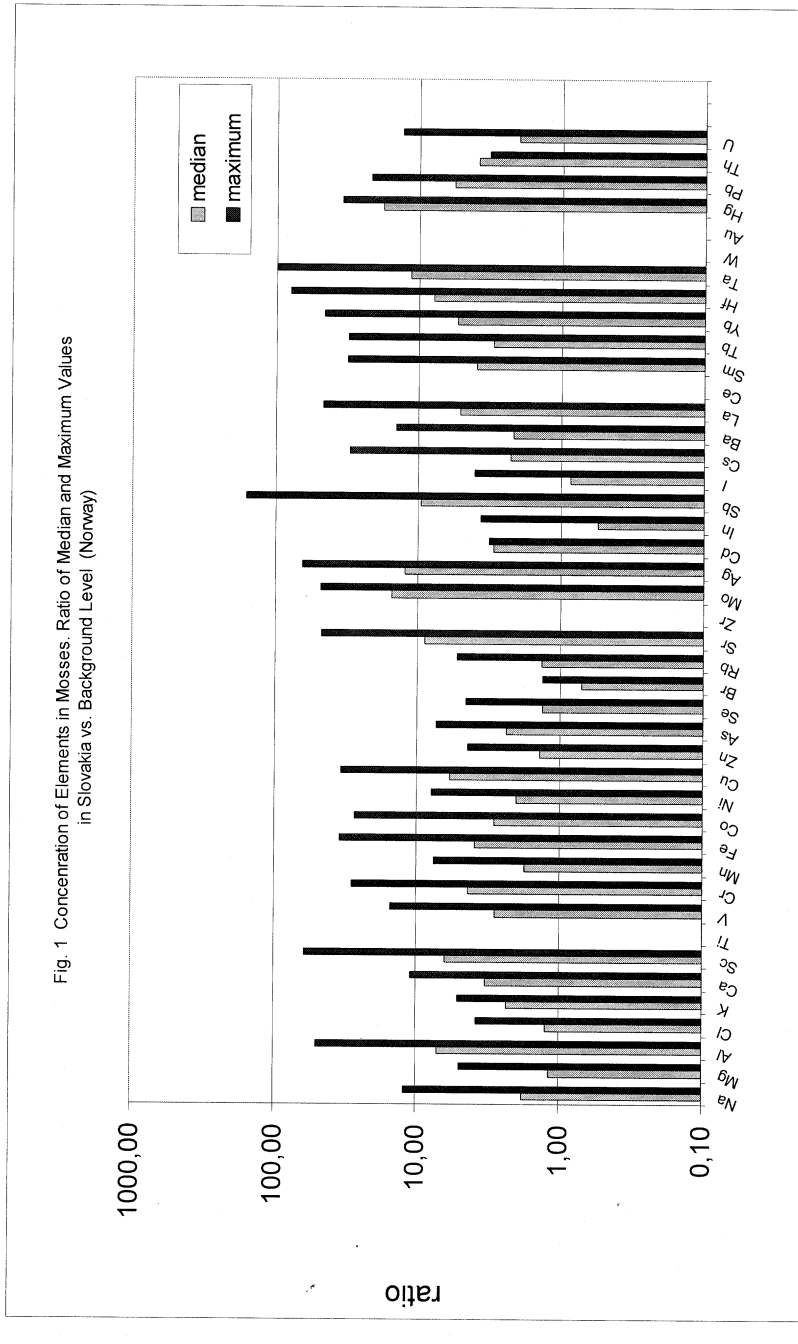
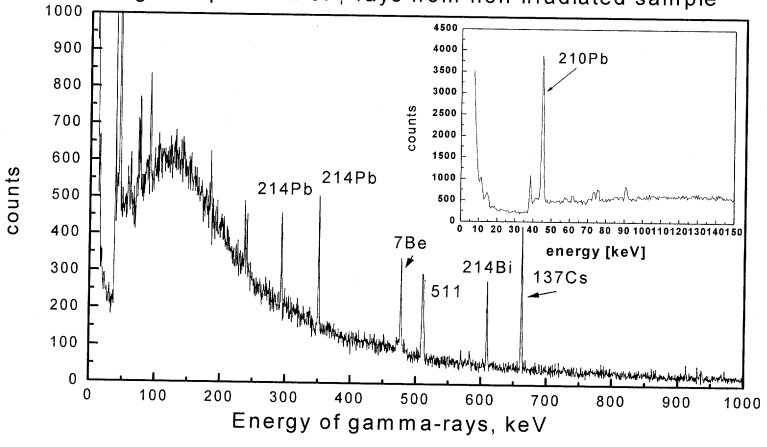


Fig. 1 Concentration of Elements in Mosses. Ratio of Median and Maximum Values in Slovakia vs. Background Level (Norway)

The counting rates in the full-energy peaks of ^{210}Pb, ^{7}Be, ^{137}Cs and ^{40}K were corrected for the background of the measurement system and for self-absorption effect. The calculated activity

Fig. 2 Spectrum of γ-rays from non-irradiated sample

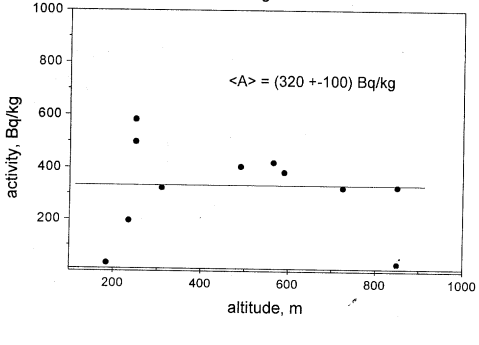


of ^{7}Be was corrected for decay. A typical gamma-ray spectrum of non-irradiated mosses is shown in Fig.2. The peaks corresponding to the 46.5 keV, 477 keV, 662 keV and 1461 keV of gamma rays of ^{210}Pb, ^{7}Be, ^{137}Cs and ^{40}K, respectively, were significantly high to allow a reasonable activity determination. The uncertainty in determination of radionuclide activities was estimated at 30%.

Beryllium-7 is a relatively short-lived (53.3 days) naturally occurring nuclide of cosmogenic origin, which is formed by reaction processes of light nuclei (C, N, O) after absorbing protons or neutrons from the primary components of cosmic rays. The long-lived ($T_{1/2}$= 30,14 years) artificial radionuclide ^{137}Cs originates from the nuclear weapons tests and from nuclear accidents. ^{40}K is a very long-lived naturally occurring nuclide.

Regular collection of the aerosol samples for routine environmental air monitoring in Slovakia has been provided in six Measuring Points of Air Contamination (MPAC). The concentration of ^{7}Be in the surface air was measured only at one of these sites (Hurbanovo; 47°52'N, 18°12'E). During the period 1993-1996 the concentration of ^{7}Be varied between 1.0 and 7.7 mBq/m^3 [15] with an annual average of 2.8 mBq/m^3. This average is consistent with the value of 3.0 mBq.m^{-3} recommended by UNSCEAR for the

Fig. 3



region of Middle Europe [16]. On the other hand, our measurements show that the median value of ^{7}Be activity is (320±100) Bq/kg for moss samples collected in different parts of Slovakia at the same time. Because of the absence of requested moss types in the vicinity of Hurbanovo, we used this median value to compare the activity of ^{7}Be in moss and air.

These sampling sites were located at different altitudes from 180 to 850 m. Dependence of ^{7}Be concentration (expressed in activity units) on altitude is shown in Fig. 3. Besides two marginal points, data are near to the mean activity value A=(320±100) Bq/kg. This allows determining a coefficient to establish the correlation between measured activity of ^{7}Be in moss A_{moss} and its concentration in air A_{air} [Bq/m^3].

$$A_{air} = 8.7 \cdot 10^{-6}\ [m^{-3} \cdot kg] \cdot A_{moss}\ [Bq \cdot kg^{-1}]$$

The maximum concentration of ^{137}Cs in surface air was registered on May 1, 1986 (1 Bq/m^3) and then it decreased with an effective half-life of 15 month. In 1996 [15] it was was equal to 1.4 μBq/m^3 and at present it is lower than the detection limit of the conventional spectrometers. Our measurements show that this information can be easily obtained using moss data over large areas by establishing a connection between ^{137}Cs activity in moss and its activity in air per m^{-3}.

The long-lived natural nuclide ^{210}Pb has half-life of 22.2 years and emits gamma rays with very low energy (46.5 keV). It is of natural origin from the decay of ^{222}Rn. The threshold of gamma- ray registration by our spectrometric system is below 40 keV (see inserted part in Fig.2). From the direct measurement of activity in surface air in Slovakia we obtained value of 0.5 mBq/m^3. In mosses activity of ^{210}Pb varied from 367 Bq/kg up to 1100 Bq/kg with median value 666 Bq/kg (Table 2.).

Table 2. Activity of radionuclides [Bq/kg] in mosses. Uncertainty ≤ 30 %

Nuclide	^{210}Pb	^{7}Be	^{137}Cs	^{40}K
Median	666	320	30	137
Minimum	367	30	0.7	76
Maximum	1100	500	103	210

Conclusion

By a combination of epithermal and conventional activation analysis, and supplemented by atomic absorption spectrometry, 42 elements (Al, Ag, As, Au, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Fe, Hf, Hg, I, K, La, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Sc, Se, Sm, Sr, Ta, Ti, Tb, Th, U, V, W, Yb, Zn, and Zr,) were determined in 86 samples of mosses. To the best of our knowledge, such a large association of elements has never been studied before in environmental samples from Slovakia. The results of these investigations will be further

presented in the form coloured contour maps for each element using GIS (geographical information systems) technology.

The most important feature of the sampling is that it correlates with the European Moss-Survey-2000, and the results obtained will be incorporated in the Atlas of Heavy Metal Atmospheric Deposition in Europe.

Collected samples contained 3-year-old segments of mosses and it represented a deposition of heavy metals for the years 1998, 1999 and 2000. During this period 47 t of arsenic, 11 t of cadmium, 9 t of chromium, 64 t of copper, 3.4 t of mercury, 35 t of nickel, 84 t of lead and 73 t of zinc were emitted annually in Slovakia [17]. The region near the border between Slovakia, Poland and the Czech Republic is considered as the second "black triangle" of Central Europe with substantially higher concentrations of heavy metals than the first "black triangle" near the borders of the Czech Republic, Poland and Germany. Information about the air pollution status in different parts of the Slovakia is essential for a better understanding of environmental stresses. Biomonitoring techniques allow monitoring of atmospheric deposition of heavy metals with a very high spatial resolution.

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Изучение атмосферных выпадений тяжелых металлов
и радиоактивных изотопов в Словакии
с использованием мхов-биомониторов

Применение метода биомониторирования атмосферных выпадений позволило определить концентрации тяжелых металлов, редкоземельных элементов, актинидов (U и Th) и радиоактивных изотопов на территории Словакии в рамках европейского сбора мхов в 2000 году. Основная часть элементов в 86 образцах мхов-биомониторов определялась методом эпитеплового нейтронного активационного анализа на реакторе ИБР-2 в Дубне. Такие элементы, как In, Cu, Cd, Hg и Pb, были определены методом атомной абсорбции в Научно-исследовательском институте лесного хозяйства в г. Зволен (Словакия). Сообщаются также результаты измерений концентраций радиоактивных изотопов ^{210}Pb, ^{7}Be, ^{137}Cs и ^{40}K в 11 образцах мхов. Сравнение с результатами сбора мхов в 1991 и 1995 годах позволило определить тенденцию загрязнений исследованной территории.

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Florek M. et al.
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Air Pollution with Heavy Metals and Radionuclides in Slovakia Studied
by the Moss Biomonitoring Technique

Applying the moss biomonitoring technique to air pollution studies in Slovakia, heavy metals, rare-earth elements, actinides (U and Th) were determined in 86 moss samples from the European moss survey 2000 by means of epithermal neutron activation analysis at the IBR-2 reactor (Dubna). Such elements as In, Cu, Cd, Hg and Pb were determined by AAS in the Forest Research Institute, Zvolen (Slovakia). The results of measurement of the natural radionuclides ^{210}Pb, ^{7}Be, ^{137}Cs and ^{40}K in 11 samples of moss are also reported. A comparison with the results from moss surveys 1991 and 1995 revealed previously unknown tendencies of air pollution in the examined areas.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR, at the Department of Nuclear Physics of Faculty of Mathematics, Physics and Informatics, Comenius University, Bratislava and at the Forest Research Institute, Zvolen, Slovakia.

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