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THE SLOVAK HEAVY METALS SURVEY BY MEANS THE BRYOPHYTE TECHNIQUE

MATEJ FLOREK[1], BLANKA MAŇKOVSKÁ[2], JÚLIUS OSZLÁNYI[2],
MARINA V. FRONTASYEVA[3], ELENA ERMAKOVA[3], SERGEJ S. PAVLOV[3]

[1] Department of Nuclear Physics and Biophysics of Comenius University, Mlynská dolina F-2, 842 48 Bratislava, Slovak Republic; e-mail: florek@fmph.uniba.sk
[2] Institute of Landscape Ecology of the Slovak Academy of Sciences, Štefánikova 3, P.O.Box 254, 814 99 Bratislava, Slovak Republic
[3] Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia

Abstract

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The results on atmospheric deposition of heavy metals and other trace elements in Slovakia using the moss biomonitoring technique are presented. INAA at the IBR-2 reactor has made it possible to determine 38 elements in mosses collected in 2000 at 86 sampling sites. In addition to NAA, flame AAS (atomic absorption spectrometry) was applied to determine the content of S, Cd, Cu, Hg and Pb. The level of elements determined in bryophytes reflects the relative atmospheric deposition loads of the elements at the investigated sites. Factor analysis was applied to determine possible sources of trace element deposition in the Slovakian moss. The geographical distribution of factor scores and some element distribution maps over the investigated territory are presented. Both approaches aim at simplifying a complex interpretation of the results obtained due to the overlapping of different pollution sources and endemic zones such as in Brezová pod Bradlom in Malé Karpaty Mts. The marginal hot spots were revealed in Volovské Mts (Central Spiš), Kremnické and Štiavnické Mts (nonferrous ores processing and factories) and near dumps of stone chips (Slanec). The trans-boundary 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 Small Black Triangle), known for metallurgical works, coal processing and chemical industries. 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.

Key words: atmospheric deposition, heavy metals, rare earth's elements, bryomonitoring, epithermal neutron activation analysis, atomic absorption spectrometry

Introduction

Air pollution sooner or later deposits on the Earth´s surface. A residential time of pollutants in the atmosphere depends on the physical and chemical properties of both the atmosphere and pollution. Between many pollutants heavy metals are the most toxic component for all living organisms. Heavy metals are present in the atmosphere in organic and also in inorganic forms, in the form of dust and aerosols. They can be transported to large distances from the source and where they fall out they have a very negative impact on the environment. The conventional method to study atmospheric deposition of heavy metals and other trace elements is precipitation analysis. As biological objects can respond more or less specifically to the influence of environmental factor intensities, including atmospheric deposition levels (sensitive, tolerant, bioaccumulative responses of organisms) suitable biotas are searched for use as biometers. In order to assess the relative or even absolute atmospheric deposition levels of elements, use is made of relationships between the element content of epiphytic lichens, tree bark, wood, algae, mushrooms, foliage, coniferous needle wax and other biological objects, on the one hand, and the local atmospheric deposition levels, on the other. Generally, passive and active methods of plant bioindication are used. Several surveys of biomonitoring methods and useable bioindicators are available in the literature (e.g., Buse et al., 2003; Maňkovská, 1997; Maňkovská et al., 2003; Steinnes et al., 2001; Markert et al., 2003; Sucharová, Suchara, 2004; Manning et al., 2002; Zechmeister 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 as bio-monitors. Mosses effectively accumulate the majority of metals and other trace elements from air and precipitation. In addition, they do not have a root system and the contribution from sources other than atmospheric is thus negligible in most cases.

The objective of paper was found out concentration of 44 elements in *Pleurozium schreberi* and *Hylocomium splendens*, to compare concentration in mosses with concentration in soil and to interpret their occurrence by factor analyses.

Materials and methods

The mosses *Pleurozium schreberi* and *Hylocomium splendens* were used as biomonitors to study the atmospheric deposition of trace elements over the territory of Slovakia. The samples of mosses were collected on 86 permanent plots situated in Slovakia at the intersections of 16x16 km pan–European network. Moss samples 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. The samples consisted of the last three years' annual segments and represented the deposition of heavy metals for the years 1998, 1999 and 2000.

Moss samples of about 0.3 g were packed in aluminum cups for long-term irradiation or heat-sealed in polyethylene foil bags for long-term and short-term irradiation in the IBR-2 reactor, Dubna. The used irradiation facilities are briefly described in Florek et al. (2001) and Maňkovská et al. (2003), together with our preliminary results.

The territory of Slovakia is situated in mild climatic zone with regular alternation of annual seasons, which is corresponding to moderate geographical conditions. Wind conditions are very complicated with aspect of the relief. This is due to spatial, particularly latitudinal variability of the territory. Mountainous zones that are forming crossing barriers for rainfall transition, subsequently affect also temperature changes and wind conditions. With this aspect different climatical character have lowlands, valleys, intra-mountain basins and high-mountainous regions.

The map of the sampling sites is shown in Fig. 1. Concerning fixation of moss species (*Pleurozium schreberi* and *Hylocomium splendens*) on forest ecosystem, was possible only marginality hypocrite pattern the other important pollution sources (Thermal power plant Zemianske Kostoľany and Vojany). The Danube and the Východoslovenská nížina lowland are almost uncovered. Slovnaft plant area was additionally inclusive to analyze and partial results provides conception of effect oil industry on environment. Sampling localities are arranged into groups I. – X. (Fig. 1) Characteristic mark of every group is dominant industrial pollution sources. Identification of originator pollution by element analyze obstruct mutual overlapping industrial, land and communal activity.

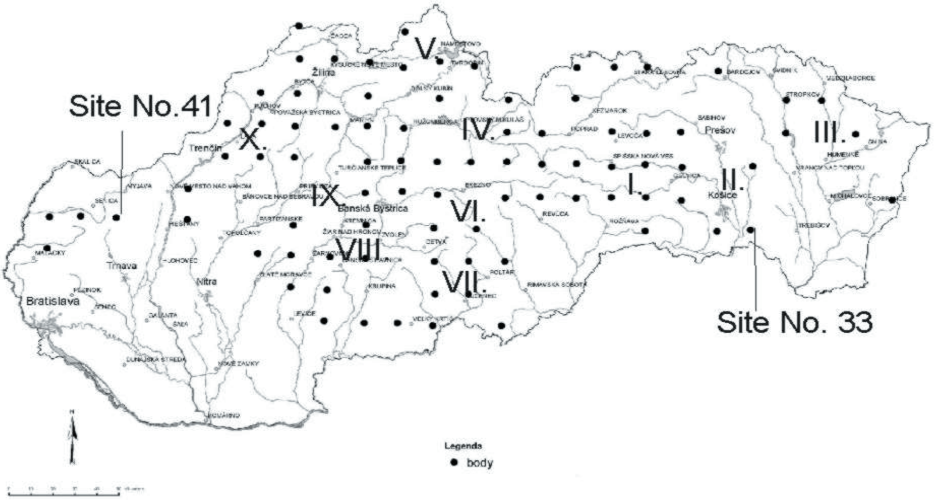

Fig. 1. The map of the sampling site.

Results and discussion

The total concentrations of 44 major and trace elements were determined in 86 samples of mosses. For each element the mean, median Ci, and range values were determined. Our results are presented on Table 1. The element concentrations were determined on the basis of certified reference materials and flux comparators (Frontasyeva, Pavlov, 2000). The element levels were shown in the form coloured maps using the coordinates of sampling points. Fig. 2. show the relative atmospheric deposition patterns of Cu and Mn on sampling site.

Table 1. Content of elements (average, median, minimum and maximum values) in environmental sampling collected over territory of Slovakia.

	Mosses (86 samples), mg/kg				Soil (5189 samples), mg/kg, data from (Čurlík, 1999)			
	Average	Median	Min.	Max.	Average	Median	Min.	Max.
Ag	0.1	0.12	0.04	0.65				
Al	3848	2470	751	17400	60000	58800	760	140000
As	0.8	0.71	0.34	2.21	10.4	7.2	0.3	732
Au	0.0	0.002	0.00	0.015				
Ba	61	51	11.9	343	395	380	25	460
Br	3.7	3.5	1.38	6.6				
Ca	5308	4925	2080	16400	14600	6100	500	263500
Cd	0.6	0.59	0.11	1.49	0.4	0.3	< 0.1	8.9
Ce	3.9	2.5	0.62	23	64	65	< 0.5	335
Cl	281	249	89	754				
Co	1.5	0.85	0.31	8.16	9	9	< 1	117
Cr	8.7	6.5	1.1	43	90	85	< 5	6096
Cs	0.5	0.41	0.14	5.44	5	5	< 1	100
Cu	9.8	8.8	3.9	37	17	17	< 1	22360
Fe	2211	1561	430	13750	27400	26400	3500	111800
Hf	0.7	0.39	0.10	3.95				
Hg	0.4	0.18	0.06	3.44	0.23	0.08	< 0.01	98
I	2.0	1.72	0.76	8				
In	0.2	0.11	0.01	1.6				
K	7075	6989	3464	15440	17100	16900	1400	67100
La	2.5	1.54	0.41	14	38	38	4	220
Mg	1734	1395	414.3	6000	8800	6400	800	106100
Mn	437	350	64	1510	760	680	20	8510
Mo	1.1	0.91	0.20	2.87	0.7	0.5	< 0.2	48.6
Na	514	361	131	2423				
Ni	3.9	3.2	0.7	12.6	28	25	1	2066
Pb	32.8	28	9.7	109	29	20	3	2122
Rb	16.9	13.4	4.8	53	84	84	3	327
S	2013	2030	1190	3280				
Sb	1.5	0.87	0.23	14.3	1.8	0.7	< 0.1	247
Sc	0.6	0.38	0.1	3.6				
Se	0.4	0.33	0.14	1.13	0.1	0.1	< 0.1	4
Sm	0.4	0.24	0.06	1.9				
Sr	86	62	7.9	328	104	93	21	706
Ta	0.1	0.06	0.02	0.50				
Tb	0.1	0.045	0.01	0.47				
Th	0.5	0.31	0.10	3.2				
Ti	57	35	10.2	304				
U	0.1	0.10	0.03	0.66				
V	7.4	5.7	1.8	30	78	74	6	403
W	0.3	0.25	0.06	0.70	< 1	< 1	< 1	45
Yb	0.3	0.16	0.02	1.36				
Zn	57	50	22	159	72	61	3	14925
Zr	92	54	14.7	512				

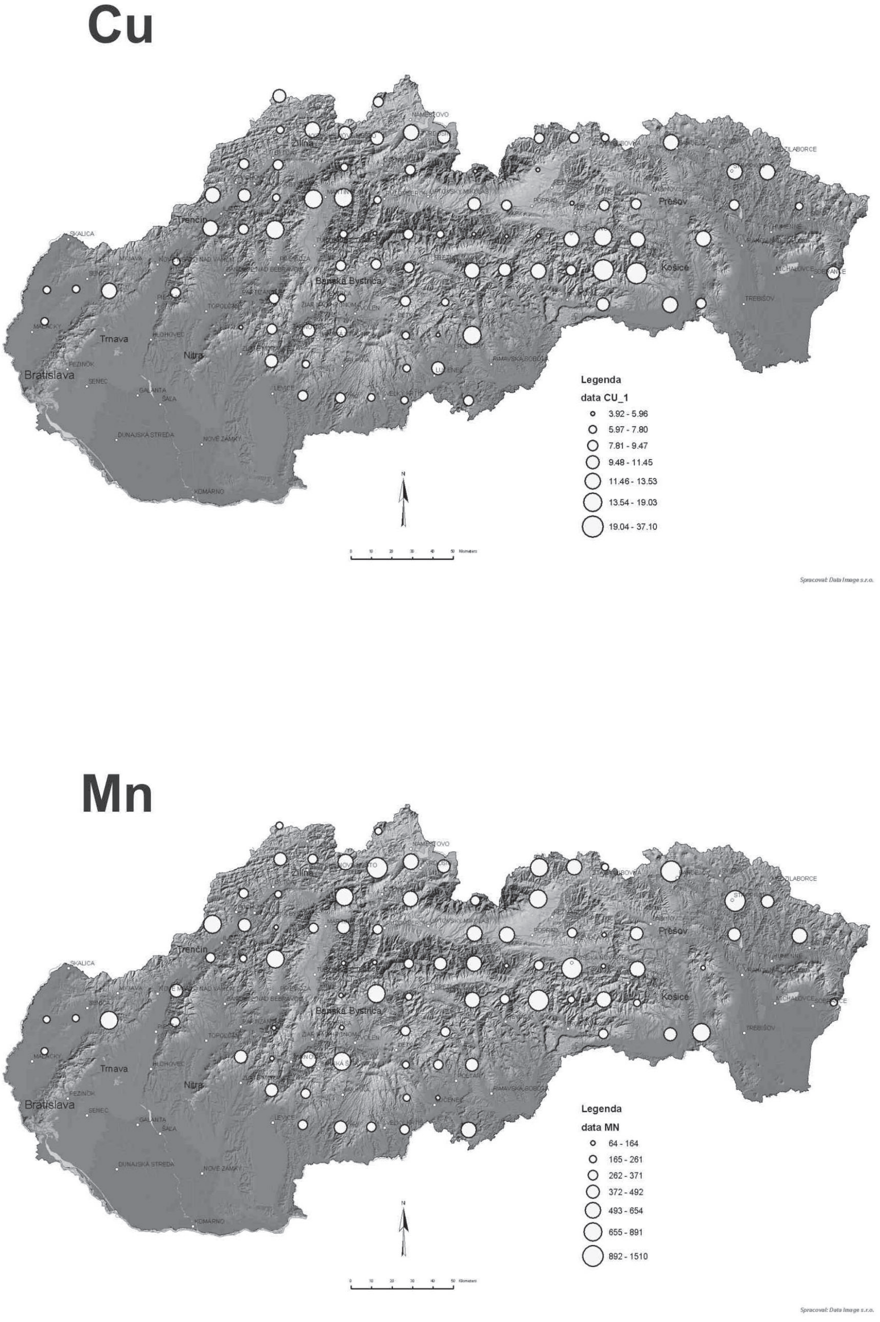

Fig. 2. Relative atmospheric deposition patterns of Cu and Mn.

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

	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

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 (Table 2). The analysis results were interpreted in the form of contamination factors Ki as the rates median value of element in Slovak mosses C_{iSl} vs. Norway mosses C_{iN} Median Norway value C_{iN} we take from (Steinnes et al., 2001).

$$K_i = \frac{C_{iSl}}{C_{iN}}$$

In comparison with the 1991 (Maňkovská, 1997) survey the median values 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.

Distribution of elements

A brief discussion of some elements often associated with air pollution is presented in the following, based mainly on the moss data:

Antimony is geochemically linked to As, but it is much more dispersed. Relatively marked Sb concentrations can be found in Volovské Mts, Štiavnica Mts and surroundings of nonferrous metals processing plants Krompachy, Vajsková, Rožňava, Banská Štiavnica, Banská Bystrica and Stropkov (II).

Arsenic. From natural sources of pollution zones in Volovské Mts, Beskydy Mts and Kremnica-Štiavnica Mts should be mentioned. The most significant anthropogenic sources are fossil fuels combustion (electric power stations and the burning of coal in private homes), which is particularly relevant in Upper Nitra, and regions with glass-ceramic production. From other industrial activities metallurgy, nonferrous ores processing, and cement factories could be mentioned (Upper part of Orava, Central Spiš, wider surroundings of Rožňava).

Cadmium. High cadmium concentrations were found almost all over the territory, mainly around Košice (manufacture of basic metals and fabricated metal products), Štiavnica Mts, where is a long tradition of ore mining and in Orava region affected by nonferrous metal industry. Low levels values were found in the Nízke Tatry Mts.

Chromium is used as alloying element in metallurgy in alloys production. Relative enhanced concentrations are located also in surroundings of magnesite works (Ľubeník – Jelšava). Elevated content of chromium we found near of Ferro-alloys works (Orava), works for metal chromium plating (Považská Bystrica), town Martin (manufacture of machinery and equipment) at affected area II (Snina-Stropkov-Strážske (manufacture of chemicals, chemical products, pulp and paper products), in surrounding town Svit and Ružomberok (IV) with chemical and pulp manufactures. Low levels values were found in the Nízke Tatry Mts and Krupinská vrchovina Mts.

Cobalt. The median and maximum values of cobalt in Slovakia mosses are comparable with corresponding values in other areas, with the exception of Serbian mosses (Frontasyeva et al., 2004). High Co concentrations are observed near Martin, Dubnica, Detva (manufacture of machinery and equipment), Poltár (glass industry) and Banská Štiavnica (old mining and smelters).

Copper. To the main pollution sources belong metallurgy of nonferrous metals industry (75% according to Burda et al., 1999), and ores reworking facilities surroundings of Krompachy, Gelnica, Slovinky, Slovník (affected area I) and Hnúšťa-Ľubeník-Miková (affected area VII with magnesite ores and reworking facities). High local value of copper we found near the town of Martin (metal working factories).

Indium. To the knowledge of the authors, Indium in atmospheric deposition has been studied by the bryomonitoring in Slovakia for the first time. This was possible due to the very high sensitivity offered by NAA for the determination of In, in particular when the epithermal variant was used. High concentration was observed in affected area I (cooper mining and smelters) and area V (ferro-alloy plant Orava, magnesite plant Ľubeník-Jelšava, Košice manufacture of basic metals and fabricated metal products).

Iron has many biotic functions, the most important being functions in photosynthesis, in life processes of the cells and in many catalytic reactions. High iron concentrations in the moss are most often observed at sites associated with Factor 1. In addition an area Snina-Stropkov, Košice and near town Martin and Dubnica (various metal-working industry) show elevated Fe level. Median value for iron is considerably higher in Slovakia than in neighbouring countries Austria, Czech Republic and Poland (Buse et al., 2003).

Lead. Increased concentrations of Pb are related to soils of mineralized zones, areas in which ore and smelters processing facilities (of base metals) were situated. Above all it is Volovské Mts (affected area I) and near Banská Štiavnica (VIII), Kysuce, Ľubenik-Jelšava-Poltár. Elevated Pb content was found in area Pb-mine Lovinobaňa (VII).

Mercury. Mainly sources of contamination territory of Slovakia with Hg are related to metals processing industries (50%) and combustion domestic waste (23%) according to (Burda et al., 1999). In addition to contamination by atmospheric transport is current process. The Hg-map in Slovakia mosses confirm Hg dispersion in polluted areas of metallurgic

Table 3. Number and name affected areas in Slovakia.

No.	Name	Elements with content Ci > 2*Cmediana
I	Central Spiš region (Volovské Mts), industrial activity metallurgy, nonferrous ores and processing factories	Na, Mg, **Al, Cl, K, Sc**, Ti, V, **Cr**, Co, Ni, **Mn, Fe, Ni, As, Se, Br, Rb, Sr, Zr**, Mo, **Ag, Sb**, I, Cs, **Ba, La, Ce, Sm, Tb, Yb, Hf, Ta, W, Th, U, Cu, Zn**, Cd, Pb, S, Hg
II	Region Košice-Prešov (manufacture of basic metals and fabricated metal products)	Na, Al, Cl, Cr, As, Se, Br, Mo, Ag, In, Sb, W, Cu, **Zn, As, Cu**, Zn, **Cd, Pb**, S, Hg
III	Snina-Stropkov-Strážske (manufacture of basic metals and fabricated metal product, chemical products)	Na, Al, Cl, K, Sc, Ti, V, Cr, Mn, Co, Ni, Se, Sr, Zr, Mo, Sb, Ba, Hf, Ta, W, U, Cd, S, Hg
IV	Ružomberok-Svit (pulp, paper products, chemical and fiber industry)	Mg, Al, Cl, K, Sc, Ti, V, Cr, **Co**, Ni, Se, Br, **Rb**, Sr, Zr, **Mo**, Ag, Hf, Ta, W, Th, S,
V	Orava (ferro-alloys smelters, fabricated metal product)	K, Mn, As, Se, Br, Mo, In, I, Sm, W,. Zn, S, Hg
VI	Detva-Brezno (manufacture of basic metals and fabricated metal products)	K, Br, Zr, Sb, Hf, **Zn**, S, Hg
VII	Jelšava-Lučenec-Poltár (magnesite works, glass-ceramic production)	Na, Mg, Al, Sc, Ti, V, Cr, Co, **Ni**, Se, Sr, Zr, La, Sm, Hf, Ta, U, Pb, S, Hg,
VIII	Kremnicko-Štiavnické Mts (non-ferrous ores and smelters, old mining districts)	Na, Al, Sc, Ti, V, Mn, Co, Ni, Se, Br, Rb, **Sr, Zr**, La, Ce, Sm, Tb, Yb, Hf, Ta, W, Th, U, Cd, S, Hg
IX	Upper Nitra and Martin (thermal power stations, manufacture of machinery and equipment).	**Na, Mg**, Al, Ca, Sc, Ti, V, Cr, Co, **Ni**, Se, **Br,** Zr, **Mo**, Ag, I, La, Sm, Tb, Hf, Ta, **W, Au**, Th, U, Zn, **Cd, Pb**, S, Hg
X	Kysuce and Považská valley (engineering and instrument industry, glass, tire and rubber industry (Small Black Triangle)	Al, Cl, Ca, Sc, Ti, V, Mn, Cr, Co, Ni, As, Se, **Br**, Rb, Sr, Zr, Mo, I, Ce, La, Sm, Tb, Yb, Hf, **W**, Th, U, Cd, S, **Hg**
Anomalous zones		
Site 41	Brezová pod Bradlom, (geogenic anomalous zones)	**Na, Mg,Al, Sc, Ti, V,** Cr, Fe, Co, Ni, Zn, As, Se, **Br**, Rb, **Zr**, Mo, **I**, Ba, La, Ce, **Sm**, Tb, Yb, Hf, Ta, W, Th, **U**, S(?)
Site 33	Slanec (output and crumbled of stone)	Na, Mg,Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, As, **Se**, Br, Rb, Sr, Zr, Mo, Ba, La, Ce, Sm, Tb, Yb, **Hf**, Ta, W, Th, U, S

works Detva, trans-boundary contamination by Hg through dry and wet depositions from the Czech Republic. Geochemical anomalies are found in mining areas (Rudňany, Slovinky).

Nickel is considered for risk element. The median concentration of Ni in Slovakian mosses (3.2 mg/kg) is higher than in neighboring countries (1.26–2.06 mg/kg). A high correlation (R ~ 0.8) with Al, Sc, Ti, V, Fe and Co may be noted. Association with Factor 1 indicates that the generally high Ni level in Slovakia mainly reflects the geochemistry of the area (Košice basin and around the old mining districts). During weathering Ni is released and migrates in environment, often over long distance. Relatively high values at sites near Petrochema Dubová, towns Dubnica and Svit, Košice, Strážske (associated with the industry), around towns Lučenec–Poltár–Fiľakovo (engineering industry) and at sites North Slovakia – transport from Poland. Main Slovak source (> 60%) of Ni atmospheric pollution is burning of fossil fuel and automotive gases (Burda et al., 1999).

Vanadium. The highest values in moss however were observed in the vicinity of the industrial towns Jeľšava–Ľubeník–Rožňava. Higher V contents are observed surrounding of town Martin (manufacture of machinery and equipment) and Lučenec–Poltár–Fiľakovo, Košice and Martin (engineering industry), Strážske and Svit with chemical and fiber industry (affected area IV). Probably, main source pollution is great incineration waste. Low content of V were found in the area of the Nízke Tatry Mts. Element V shows strongly correlation ($r > 0.9$) between elements Al, Sc, Ti, Ta and it have r between 0.8 and 0.9 with elements Mg, Fe, Co, Ni, Se, Zr, La, Ce, Yb, Tb, Hf and Th.

Zinc. The contamination by Zn is usually related to nonferrous and ferrous metals industry (~ 60%). Secondary main sources are combustion of coal and oil. Relative considerable input of Zn to moss is via atmospheric dust transport. High concentrations of Zn are observed in the vicinity of Martin, Piešťany, Košice, Banská Štiavnica, Podbrezová and area of Kysuce and Orava.

The results of measurements were presented in the form of maps. So far we cannot present the contour maps for 44 elements in the present paper, we restrict ourselves to Table 3, showing presence (occurrence) of elements in different polluted area if their content (in arbitrary locality included to given area) is 2 times higher as compared to Slovak median values. The bold font are marked elements, which content is near maximum value (in range uncertainty of measurement). The localities Brezová pod Bradlom (site 41) and Slanec (site 33) are listed separately. The first locality is wellknown for its anomalous geological-rock composition (influence on moss). The second locality (Slanec) is situated near the stone breakage and stone granulator. Elements from the earth crust (factor I), and also elements from wear metal frame granulator emitted to atmosphere in the process of stone granulation in the form of rock stone particles.

The moss data compared with soil data are shown in Table 1. We used soil data obtained by Čurlík and Ševčík (Čurlík, Ševčík, 1999). The atlas was elaborated on the results of chemical analyses from 5200 soil profiles (grid 1.5x1.5 km^2) all over the territory of Slovakia. Sampling was made from A and C-horizons. We used data only from A horizons, which correspond to the humus horizon. All the soil analyses were made in the Soil Science and Conservation Research Institute (VÚPOP) Bratislava, by routine soil methodologies.

Median values for Se, Mo, Cd, Sb, and Hg are advanced in mosses look like at pattern soil. Concentrations of Ca, Zn, Sr, and P are identical. Concentrations of another elements in soil exceed their concentrations in moss. In order to better distinguish between contribution from air pollution and from a crustal component associated with windblown soil particles enrichment factors (EF = (X/Al)moss/(X/Al)soil were calculated from the moss and soil data from Slovakia (Čurlík, Ševčík, 1999) and plotted in Fig. 3. Typical crustal elements show EF values near unity. The elements Cd, Cu, Hg, Mg, Mn, Mo, Pb, Sb, Se, Sr, and Zn are significantly enriched in the moss, clearly indicating that these elements represent

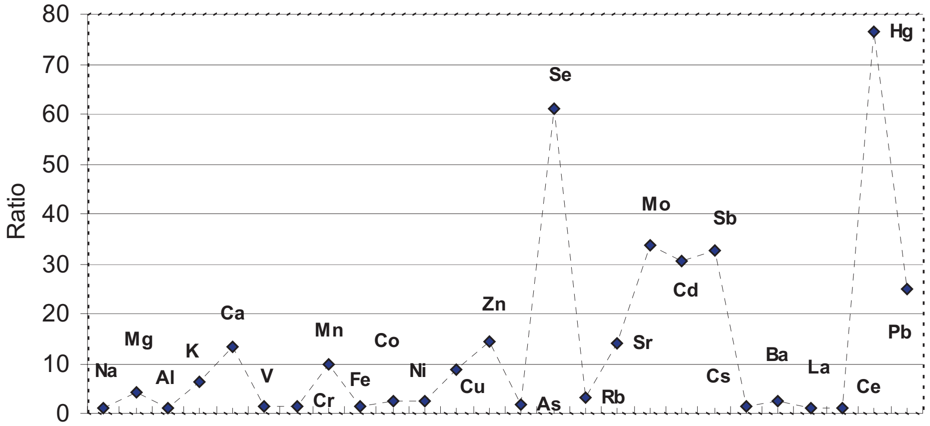

Fig. 3. Enrichment factors calculated from Slovak moss and soil.

a regional pollution problem. The higher values of EF for K and Ca are connected with active biological processes in moss. Clearly the moss is a far better medium to express regional contamination from atmospheric deposition than the surface soil.

Factor analysis

The moss data from Slovakia were subjected to principal component factor analysis (Varimax with Kaiser Normalization). The result of analysis is in Table 4. The geographical distributions of some factor scores are shown in Fig. 4. The 8 factors explain 80% of the total variance in the data set. From the knowledge of the element composition of each factor and values of factor loadings, the major sources can be identified. Below is the interpretation of 8 factors in the sequence of their significance:

Factor 1 is responsible for 40% of total variance and is characterized by the presence all typical crustal elements and it can be explained by elements associated with mineral particles, mainly windblown dust and include 13 elements Al, Sc, Ti, V, Fe, Zr, Re, Hf, Ta, and Th have loading higher than 0,9. Next ten elements (Na, Mg, Cr Co, Ni, Se, Sr, Cs, Ba, and U) have loading factor between 0.70–0.89. This factor has maximum in Volovské Mts. High value is observed in the area Kremnica -Štiavnica Mts (Fig. 4).

Factor 2 is industrial component, with very high loadings for Cu, Zn, Ag, Sb, Pb and explains 10% of total variance with the factor loading from 0.52 to 0.87. Maximum value is in area Krompachy–Smolnícka Huta–Zlatá Idka. Factor 2 reflects the impact from metallurgical plants.

Table 4. WARIMAX rotated PC solution for the 86 moss samples collected in the territory of Slovakia. Eight main source types were identified. Characteristic elements for the sources types are marked in bold type.

Element	F1	F2	F3	F4	F5	F6	F7	F8
Ag	0.14	**0.68**	0.15	0.04	0.12	–0.02	–0.20	–0.15
Al	**0.94**	0.06	0.06	0.10	–0.02	0.06	0.18	–0.06
As	0.17	0.36	0.26	**0.61**	0.34	–0.04	0.10	0.16
Au	0.35	0.32	0.43	–0.05	0.24	0.16	0.02	–0.02
Ba	**0.74**	0.35	0.29	–0.01	–0.06	0.16	–0.13	0.01
Br	0.42	–0.12	0.05	0.29	0.24	**0.45**	0.33	0.23
Ca	0.28	–0.03	0.08	0.20	0.07	–0.11	**0.65**	0.11
Cd	0.13	0.21	–0.04	**0.76**	0.14	–0.08	0.12	0.04
Ce	**0.95**	0.08	0.08	–0.06	0.10	0.16	0.01	0.06
Cl	0.08	0.08	**0.82**	0.29	–010	0.20	–0.03	0.14
Co	**0.84**	0.14	0.13	0.01	0.11	–0.04	0.09	0.16
Cr	**0.75**	0.00	0.24	0.26	0.15	–0.12	–0.03	–0.10
Cs	0.59	0.21	0.36	–0.11	–0.10	**0.52**	0.00	0.00
Cu	0.15	**0.76**	–0.03	0.24	0.17	–0.05	0.22	0.18
Fe	**0.93**	0.14	0.14	0.08	0.04	0.17	0.07	0.02
Hf	**0.92**	0.06	0.11	0.04	–0.03	0.11	–0.03	0.00
Hg	0.01	0.03	0.11	0.05	0.14	–0.06	0.09	**0.85**
I	0.30	0.13	0.10	0.11	0.23	0.05	**0.75**	0.09
In	0.02	0.06	**0.59**	–0.14	–0.14	0.06	0.36	–0.11
K	0.14	–0.03	0.52	0.11	0.21	**0.62**	–0.11	–0.09
La	**0.88**	0.07	0.03	–0.11	0.23	0.22	0.14	0.07
Mg	**0.78**	0.13	0.12	0.22	0.01	0.03	0.37	–0.16
Mn	0.38	0.12	**0.57**	–0.21	0.10	–0.05	0.07	0.20
Mo	0.21	0.21	–0.07	0.26	**0.77**	0.13	0.13	–0.06
Na	**0.80**	0.03	0.03	0.00	0.20	0.13	0.08	–0.17
Ni	**0.84**	0.02	0.09	0.11	0.03	–0.18	0.09	0.12
Pb	0.12	**0.55**	–0.22	**0.51**	0.15	–0.11	0.27	–0.17
Rb	0.28	–0.03	0.08	–0.18	0.10	**0.77**	–0.04	–0.03
S	0.06	0.33	–0.13	0.42	–0.33	0.27	0.18	0.46
Sb	0.09	**0.87**	0.09	0.05	–0.05	0.06	–0.02	0.06
Sc	**0.94**	0.08	0.06	0.01	0.08	0.15	0.16	0.01
Se	**0.85**	0.13	–0.03	0.28	0.17	0.10	0.02	0.04
Sm	**0.88**	0.01	–0.02	–0.06	0.25	0.22	0.10	0.01
Sr	**0.84**	–0.03	0.11	0.20	–0.10	–0.08	–0.06	0.13
Ta	**0.95**	0.08	0.09	0.04	0.04	0.11	0.05	0.01
Tb	**0.94**	0.11	0.05	–0.03	0.12	0.11	0.15	0.09
Th	**0.94**	0.12	0.11	–0.02	0.10	0.19	0.06	0.03
Ti	**0.90**	–0.01	0.03	0.11	0.02	0.00	0.22	–0.02
U	**0.78**	0.10	0.01	–0.05	0.27	0.32	0.24	–0.03
V	**0.90**	0.03	–0.06	0.17	0.09	0.00	0.25	–0.03
W	0.23	0.19	–0.01	0.11	**0.77**	0.13	0.15	0.22
Yb	**0.94**	0.10	0.02	–0.02	0.11	0.09	0.03	0.11
Zn	–0.04	**0.52**	0.22	0.33	0.28	–0.02	0.20	0.14
Zr	**0.93**	0.03	0.10	0.06	0.00	0.09	0.06	–0.05

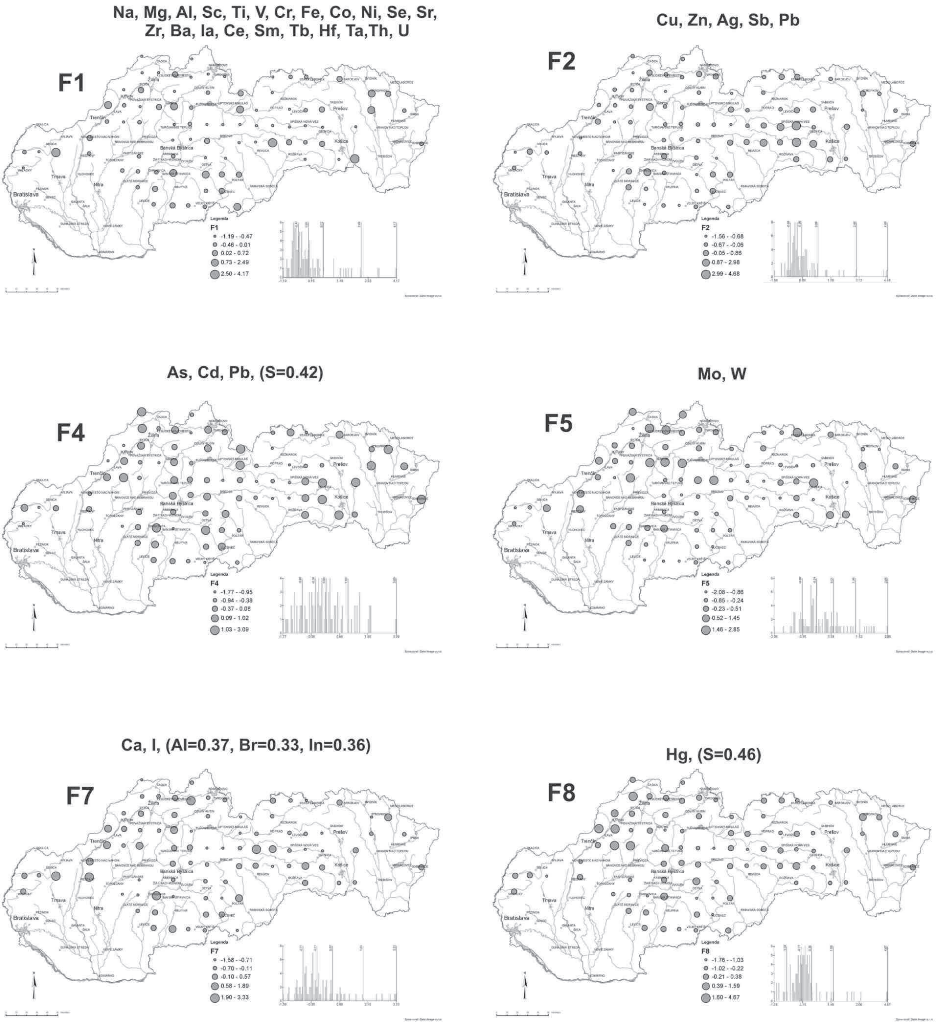

Fig. 4. Geographical distribution of the factor scores (see text).

Factor 3 includes mainly Cl, Mn, In and **Factor 6** contains K, Rb, and Cs. These elements are likely to be mainly of natural origin.

Factor 4 includes As, Cd, Pb and S. The pollution with mentioned metals is probably caused mainly by the long large transport. This conclusion is confirmed by the correlation between the altitude and the deposition of As and Pb in the Slovak region. We used soil

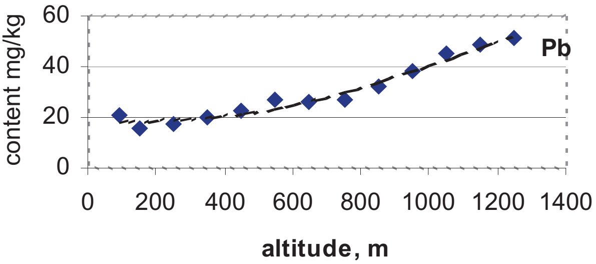

Fig. 5. Dependence of lead deposition vs altitude in Slovakia.

data (Čurlík, Ševčík, 1999) for evaluation of the dependence of heavy metal content with altitude in soil. The concentrations of Pb and As increase with altitude (Fig. 5). The points are average values of content Pb in soil samples situated on localities between one hundred meters. High levels of precipitation are strongly correlated with the heavy metals deposition, and seem to be main source of heavy metal fallout at higher altitudes.

Factor 5. Elements Mo and W are the main constituents. Their loading to the factor is 0.77. The factor components originate from engineering and instrument industry placed in the towns of: Brezno, Martin, Dubnica, Košice and in triangle Stará Turá–Piešťany–Nové Mesto n/V.

The major elements in **Factor 7** are Ca, I, Br and In. The map of the factor scores shows elevated values near: a) the roads crossing of the mountains (one possible candidate is the technical salt used on gravel roads during winter periods) b) sources iodo-bromic mineral water. In Slovakia there are 1626 registered mineral water springs of different chemical composition, part of them contain I and Br in adequate quantity.

Finally, **Factor 8** explains 3% of the total variance. The dominating element is mercury. Sources of contamination with Hg are related to metals processing industries, combustion fossil fuels and municipal solid wastes and trans-boundary contamination in the NW wind directions.

The total pollution coefficient

The total pollution coefficient Zi was calculated for all sampling sites to identify the most heavy metal polluted areas:

$$Z_i = \frac{1}{n}\sum_{k=1}^{n}\frac{C_{ik}}{C_{k\_bg}} = \frac{1}{n}\sum_{k=1}^{n} f_{ik},$$

where $\mathbf{f}_{\mathbf{ik}}$ is content of k-pollutant (C_{ik}) in i-sampling site divided by baseline level $\mathbf{C}_{\mathbf{k\ bg}}$. For value of background level we used the current median value in Norway (Steines et al.,

2001) and **n** is the number of pollutants considered. The following pollutants were selected: As, Cd, Co, Cr, Ni, Cu, Fe, Hg, Pb, and Zn (n = 10). Distribution map shows that most high Zc values are related to the above mentioned industrial areas in the metal industry in area Stropkov, Košice, Martin, Dubnica, where is 10–15 times high in comparison with Norway limit value and lowest (~ 2 times) at eastern part of the Vysoké Tatry Mts.

Assessment of deposition rates

The distribution of element content in moss reflects current distribution of atmospheric deposition loads of individual elements. The mean absolute deposition rates of elements (over territory of Slovakia) are practically absent, and they may be estimated from the data of concentrations of elements in moss.

The mean absolute deposition rate D_k of k-element [mg m^{-2} per year] for the individual zones of the contour maps have been assessed in accordance with the following formula (Suchara, Sucharová, 1999):

$$D_k = \frac{C_k . A}{E_k},$$

where C_k is the concentration of the element in a moss sample [mg kg^{-1}], A is the biomass production of the moss at given locality (kg m^{-2} per year), and E_k is the efficiency of element income in the moss in decimal expression. The available published coefficients for element uptake for the investigated elements in *Pleurozium schreberi* (Berg, Steinnes, 1998) were used (Table 5). The mean of the annual production (biomass) of the moss in the area was taken as 129 g of dry weight per year (Suchara, Sucharová, 1999). In accordance with the formula, the computed average bulk atmospheric deposition values for the individual elements in the SR are presented in Table 5. The deposition values D_k were estimated for median, minimum and maximum contains individual elements in mosses.

Conclusion

- In comparison to the median Austrian and Czech values of heavy metal contents in moss (Zechmeister et al., 2003; Sucharová, Suchara, 2004) the Slovak atmospheric deposition loads of the elements were found to be 2–3 times higher on average. It is connected partly with geochemical peculiarities of Slovakia.
- The examined territory shows that many regions have intense mining activity. 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.

Table 5. Estimation of mean bulk deposition [mg m^{-2} per year] for the some elements in Slovakia in 1998–2000.

Element	coefficient **E**	D median	D min	D max
Al	0.7	700	140	3200
As	0.35	0.24	0.12	800
Cd	0.6	0.1	0.02	0.3
Co	0.5	250	0.08	2.1
Cr	0.7	0.25	0.2	7.9
Cu	0.4	2.5	1.3	12
Fe	0.6	335	0.9	2900
Mo	0.5	0.22	0.05	0.75
Ni	0.5	0.9	0.18	3.3
Pb	1	3.6	1.2	14
S	0.3	670	500	1400
V	0.5	1.2	0.45	7.8
Th	0.43	0.09	0.03	0.9
U	0.86	0.015	0.005	0.1
Zn	0.65	8	4	31

- 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). In Slovakia many pollutants sources are overlapping, which it cause an obstruction to identify source.
- Part of the results obtained (only heavy metals) were submitted to the European Atlas “Atmospheric heavy metal deposition in Europe – estimation based on moss analysis.” (2003).
- The obtained data can be useful as a reference level for comparison with the future measurements of heavy metal pollution in the examined area.

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