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Temporal and Spatial Trends (1990–2010) of Heavy Metal Accumulation in Mosses in Slovakia

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1. Introduction

The multielement biomonitoring surveys, using suitable plant biomonitors [1] can provide information about long-term and large-scale atmospheric deposition rates of elements. The large-scale biomonitoring programs using selected bioindicators were introduced in Slovakia in the end of 1980s. The bioindicators are commonly available elsewhere in the landscape, and the bioindicated air quality parameters can be related to the particular sampling sites within the ecosystems. mosses and foliage of forest tree species [2,3] as biomonitors of atmospheric deposition of heavy metals began in Slovakia more than 30 years ago, in connection with the problems of dying forests.

Moss species such as *Pleurozium schreberi*, *Hylocomium splendens*, and *Dicranum* sp. can effectively adsorb deposited air pollutants on pectine and cell structures. Bryomonitoring method was validated and tested to large-scale estimate current atmospheric deposition rates of elements between 1970 and 2000 [4-6]. Since 2000, in the frame of UN ECE ICP-Vegetation program, more than 30 European countries have monitored the current element content in mosses at about 7000 sampling sites in 5-year intervals. The Slovak national moss surveys since 1990–2010 have mapped elemental content distribution within the whole country (16x16 km net).

2. Material

Two complementary analytical techniques, instrumental neutron activation analysis (INAA) and atomic absorption spectrometry (AAS) were used for determination of the elemental concentrations in the samples of moss for year 2000. 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 for short-term irradiation in the IBR-2 reactor, Dubna, described elsewhere [7]. The samples of mosses were not washed before analysis. Sulfur and nitrogen concentrations were determined using LECO corporation equipment (S: LECO SC 132 and N: LECO SC 228). Atomic absorption spectrometry (VARIAN SPECTRA A-300 and mercury analyzer AMA-254) was carried out in Forest Research Institute Zvolen (1990, 1995, 2000, 2005, 2010). The accuracy of data published in paper was verified by 109 individual laboratories and tested by the IUFRO program [8].

The monitoring studies have been undertaken in the framework of the international project Atmospheric Deposition of Heavy Metals in Slovakia Studied by the Moss Biomonitoring Technique Employing Nuclear and Related Analytical Techniques and GIS Technology. *Project REGATA (2003-2015)*.

3. Results and discussion

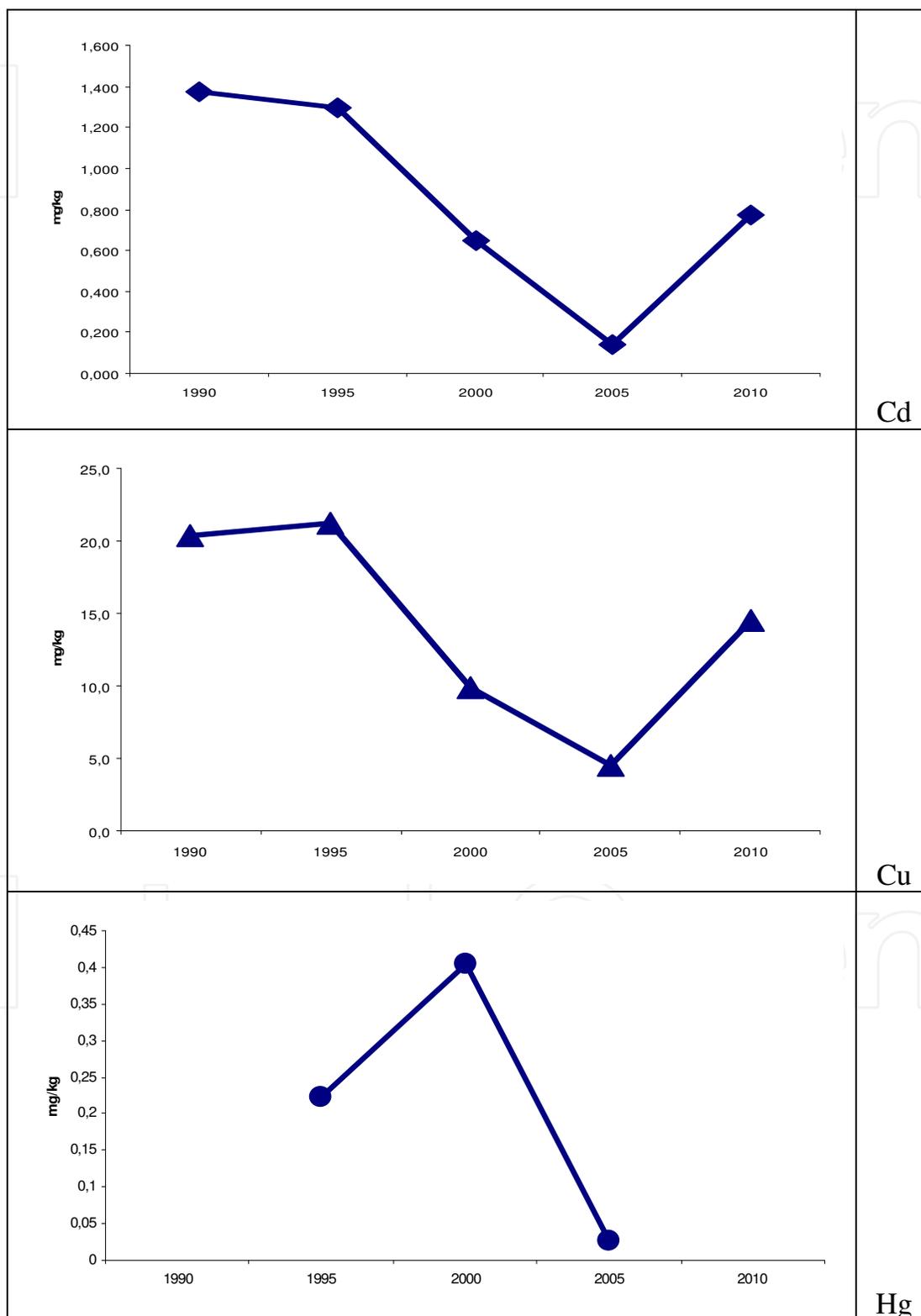
The principal investigator of the project, Dr. Maňkovská (at that time working in the Forest Research Institute in Zvolen, Slovakia) was invited by Scandinavian specialists (Finland, UNIDO, 1986) to join the existing European biomonitoring program focused on monitoring of actual deposition of selected set of elements using analyses of mosses in 1990. The first collection of moss samples of *Pleurozium schreberi* and *Hylocomium splendens* at 58 permanent monitoring sites in Slovakia was made in the same year in accordance with the European network. The following elements were analyzed by atomic absorption spectroscopy (AAS): Cd, Cr, Cu, Fe, Mn, Ni, Pb, S, and Zn.

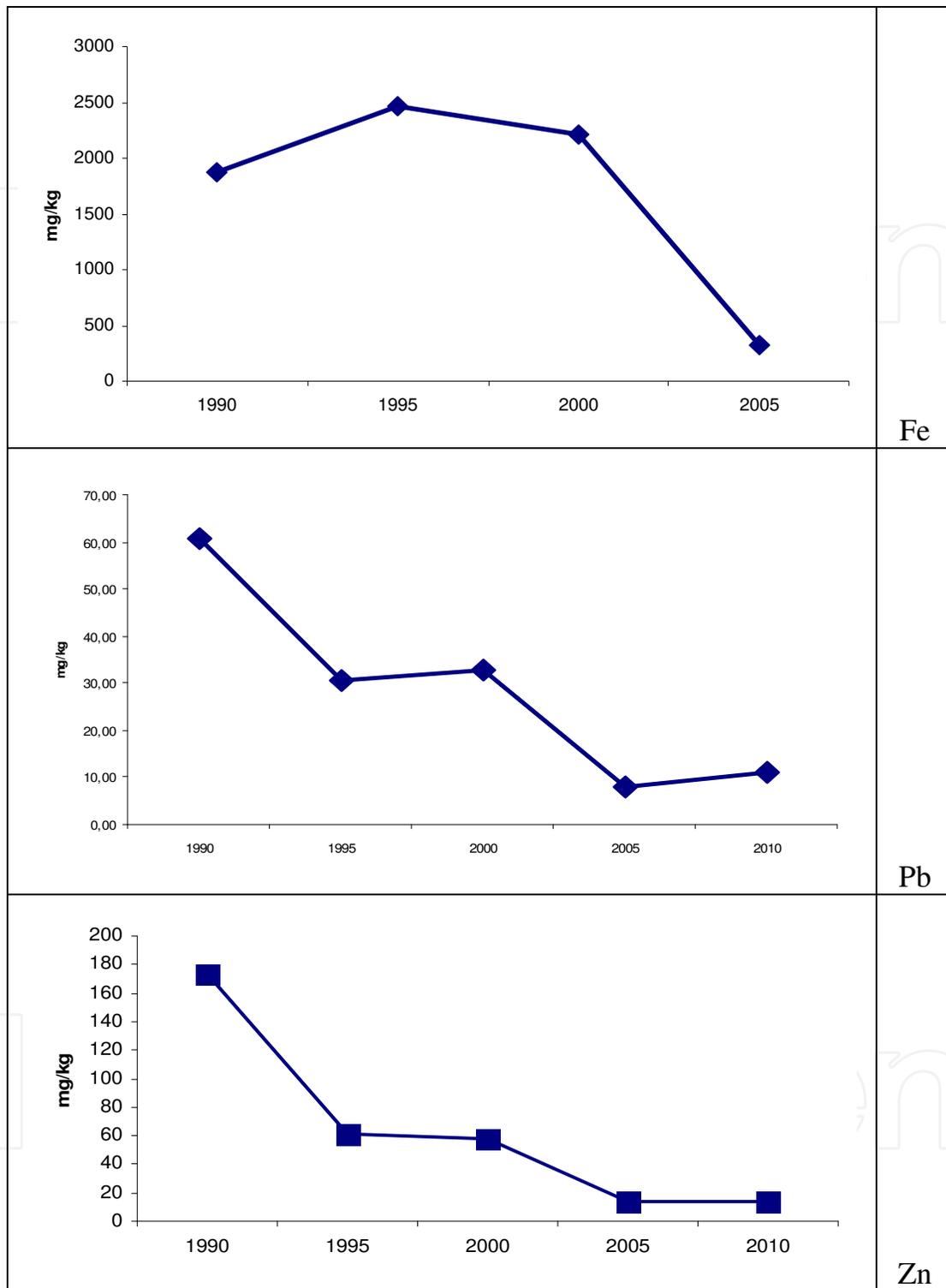
In the second European moss survey conducted in 1995, moss samples were collected at 78 permanent monitoring sites. In 1996, moss samples were collected at 69 and in 1997 at 74 permanent monitoring sites. The contents of As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V, and Zn were determined by AAS and Hg was determined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

The third moss survey at the European scale on actual levels of atmospheric deposition of elements was conducted within the ICP Vegetation in 2000. Collection of moss samples (*Pleurozium schreberi*, *Hylocomium splendens*, and *Dicranum* sp.) in Slovakia was performed at 86 permanent monitoring sites. NAA was carried out in the Frank Laboratory of Neutron Physics of the Joint Institute for Nuclear Research in Dubna, Russia. 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, Zr) were determined. Varian Techtron atomic absorption spectrometer was used for determination of Cd, Cr, Cu, Hg, Ni, Pb, and Zn. Sulfur and nitrogen determination was performed by LECO corporation equipment as earlier (see above).

In the fourth European moss survey in 2005, moss samples (*Pleurozium schreberi*, *H. splendens*, *Dicranum* sp.) were collected at 77 permanent monitoring sites in Slovakia. They were analyzed 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. Results from required monitoring elements were published

in the European reports [9, 10]. Results from required and optionally monitored elements from Slovakia were evaluated in the context of neighboring countries of Visegrad Four [11].





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

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

So far, in the last, that is, the fifth European moss survey in 2010 in Slovakia, collection of moss samples was made at 68 permanent monitoring sites (*P. schreberi*, *H. splendens*, *Dicranum* sp.). They were analyzed for contents of Al, Ca, Cd, Cl, Cu, Dy, I, K, Mn, Pb, S, Ti, V by use of AAS Varian Techtron, LECO SC 132, and LECO SP 228, and by use of NAA in the Frank Laboratory of Neutron Physics in Dubna, Russia. Results from required monitoring elements were published in European reports [12].

The concentration of Cd, Cr, Cu, Fe, Hg, Ni, Pb, V, and Zn in mosses between 1990 and 2010 are shown in Fig. 1.

The moss biomonitoring technique is based on the fact that the concentration of heavy metals in mosses correlates with the atmospheric concentration. It was proven that it is possible between the concentration of the given element in mosses and the concentration of the same element in the atmosphere. The concentration of individual elements in precipitation was calculated to the time of exposure of mosses (3 years). In case of each element, there was a good linear relationship between the concentrations of a given element in mosses and in precipitation. There is a valid equation [concentration in moss] $\text{mg.kg}^{-1} = [4x \text{ atmospheric deposition}] \text{mg.m}^{-2}.\text{year}^{-1}$ [13]. The concentration of elements in mosses in comparison with Norway (Table 1 and Table 2) is expressed by means of the coefficient of loading by elements K_F and classified into 4 classes; class < 1 – elements are within 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).

Contamination factor K_F				
⊙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: K_F = contamination factor as the rate of median values of element in Slovak mosses vs. Norway mosses (Steinnes et al., 2007). K_F Slovakia= 9.5; K_F Norway=1.

Table 1. The rate of median values of element in Slovak vs. Norway mosses in year 2000

The marginal 2 hot spots were shown in Central Spiš (metallurgical plants), Žiar basin (nonferrous ores processing and aluminium plant). The protected area of Morské oko (chemical industry) is also of great interest. In comparison with the mean Austrian and Czech values of heavy metal contents in moss, the Slovak atmospheric deposition loads of these 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 (Black Triangle II), known for metallurgical works, coal processing, and chemical industries. Spatial trends of heavy metal concentrations in mosses were metal-specific. Since 1990, the metal concentration in mosses has declined for cadmium, chromium, copper, iron, lead, mercury, nickel, and zinc.

Sites	Coefficient of loading by elements K_F				K_F
	< 1	1 -10	10-50	>50	
Hot Spots					
Žiar basin	Au, Br, Cl, I, Ag, Al, As, Ba, Ca, Cd, Ce, Co, Cr, Cs, In, Mn,	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
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
National Parks					
Nízke Tatry	Au, Br, I, Mg, S, Se, Sm, Ti	Ag, Al, As, Ba, Ca, Cd, Ce, Cl, Co, Cr, Cs, Hf, 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			4.2
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
Protected Area					
Veľká Fatra	Au, Br, In, Sm	Ag, Al, As, Au, Ba, Ca, Cd, Ce, Cl, Co, Cs, Cr, Cu, Fe, Hg, I, K, La, Mg, Mn, Mo, N, Na, Ni, Pb, Rb, S, Sc, Se, Sr, Ti, U, V, W, Zn	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, Hg, I, K, La, Mg, Mn, N, Na, Ni, Rb, S, Sc, Sr, Th, Ti, U, V, W, Zn	Ag, 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, Sc, Ta, Tb, U, V, W	Al, Hf, Sb, Th, Yb	44

Table 2. Coefficient of loading by elements K_F in the year 2000

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 modeled 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. Factor analysis was applied to determine possible sources of trace element deposition in the Slovakian moss. In the industrial area of Central Spiš, in comparison with the Norwegian limit values (Central Norway is considered a relatively pristine region), exceeded levels for Al, As, Ca, Cd, Cl, Co, Fe, K, Mn, Sb, Sm, Sr, W, and Zn were found.

4. Conclusion

Moss surveys can provide quick and cheap information about spatiotemporal changes of the current deposition rates of about 40 chemical elements across the country. Figures from the moss surveys may be the only data about elemental deposition rates that have not been determined at measurement stations of air quality (e.g., Be, Li, Se, Tl, Th, and REEs).

Moss biomonitoring is an effective tool for detecting effects of new technologies on deposition zones in the vicinity of emission sources. All results of the Slovak moss surveys were accepted and stored in the UN ECE ICP-Vegetation database for checking of deposition loads in Europe and their environmental effects.

On the basis of biomonitoring using 3-year-old segments of *Pleurozium schreberi*, *Hylocomium splendens*, and *Dicranum* sp. at 10 sites in Slovakia, it was determined that:

- a. The concentration of elements (in parentheses) 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) compared to the Norwegian values.
- b. Air pollutants K_F varies in the range of 4–45 (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; and 45 – Central Spiš). Results of biomonitoring campaigns serve as a reliable basis for planning and long-term exploitation of the landscape of the country and for further environmental investigations.

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