

THE CONCENTRATION OF HEAVY METALS IN GRASSLAND ECOSYSTEMS OF THE CENTRAL SLOVAKIA NATIONAL PARKS

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Abstract: In the contribution we evaluate a concentration of heavy metals in grass ecosystems (in soil and plant biomass). Monitoring was carried out during the years 2009 – 2011 on permanent grassland, in the region of Starohorské vrchy (habitat Radvaň), National park Nízke Tatry (habitat Panský diel) and National park Veľká Fatra (habitat Kráľova studňa). The habitats had different altitude (habitat Radvaň, 480 m a.s.l., Panský diel, 1000 m a.s.l., Kráľová studňa, 1300 m a.s.l.). We specified following elements of heavy metals in soil and plant samples (root biomass and above-ground part of vegetation): Cd, Co, Cr, Pb, Zn, Mn, Cu, Fe and Ni (atomic absorption method spectrometry). We recorded the highest concentrations of Fe (1351.45 – 3569.37 mg.kg⁻¹) and Mn (330.28 – 589.27 mg.kg⁻¹) and the lowest concentrations of Cr (3.93 – 7.62 mg.kg⁻¹) and Cd (1.61 – 2.35 mg.kg⁻¹) in all three evaluated environments (soil, roots, aboveground sward). Based on achieved results, we can state that heavy metals are mostly concentrated in plant roots and in soil. Significantly lower content was determined in biomass of above-ground parts of vegetation. The grasslands are as excluder of a large group of heavy metals - Cd, Co, Cr, Pb, Mn, Fe and Ni in view of the heavy metals transport in soil - root - aboveground biomass, (bio-concentration factor BCF <1). This strategy is very suitable for bulk feed production, heavy metals concentration is relatively low in aboveground parts of sward, and there is no contamination of the food chain. Translocation factor (TF) is for all assessed heavy metals less than 1, what is documenting their significant accumulation in root system of grasslands. Also was confirmed a significant effect of years and evaluated habitats on the concentration of heavy metals. The concentration of heavy metals is significantly increasing with higher altitude of habitats.

Keywords: environment, heavy metals, grassland ecosystem, soil, plant biomass, national park

1. INTRODUCTION

Environmental contamination currently presents a serious environmental and social problem with a marked global dimension. The heavy metals are one of the most serious groups of hazardous substances in the environment. They belong to the non-degradable contaminants which are characterized by a different source of origin (geochemical anomalies and anthropogenic sources such as industrial and municipal waste, fertilizers, pesticides, etc. are sources of heavy metals in the soil), characteristics and effect to the living organisms (Tóth et al., 2005). Biologically irreplaceable microelements (Cu, Zn, Mn and others), as well as numerous non-essential chemical elements (Cd, Pb, Hg and others) belong to the risk elements, and their risks consist in eco-toxicity and accumulation

in biotic and abiotic components of the environment (Lahučký et al., 2009). Gray et al., (2006) & Big et al., (2012) state that persistence and cumulating of heavy metals in the environment is adversely reflected at all levels of the food chain, soil quality and present an impact on the overall burden of the environment. Lăcătușu et al., (1996) & Lăcătușu et al., (2008) state, that systematic consumption of vegetables and fruits polluted with heavy metals by the inhabitants of polluted zones is leading to the healthiness state altering and to appearance of some chronically diseases with unpredictable final.

In this paper, we present the results of the concentration of heavy metals in soil and plant biomass of perennial grasslands and we compare their contents with the permitted legislative limits.

2. MATERIALS AND METHODS

Content monitoring of heavy metals in soil and in grass biomass we realized during the years 2009 - 2011 on semi-natural grass swards in the central Slovakia – a region Starohorské vrchy (habitat Radvaň), in the National park Nízke Tatry (habitat Panský diel) and in the National park Veľká Fatra (habitat Kráľova studňa), within three locations at different altitudes (Fig 1):

- Location Radvaň, the lowest altitude (480m) had the northern exposure with a slope 12-15°; the soil type is humus carbonate (rendzinas) on limestone.

- Location Panský diel, the middle altitude (1000 m) had the south-western exposure with a slope more than 20°; the soil type is cambisol from weathered crystalline-acidic rocks.

- Location Kráľova studňa, the highest altitude (1300 m) had the south-eastern exposure with a slope 20-25°; the soil type is shallow humus carbonate on limestone.

Permanent grasslands belong to a plant community *Poa-Trisetum* (alliance *Arrhenatherion*). The community determined grasses, especially the dominant *Trisetum flavescens* and other valuable grasses *Poa pratensis*, *Dactylis glomerata* and *Arrhenatherum elatius*. Fabaceae plants, *Trifolium repens*, *Trifolium pratense* and *Lotus corniculatus* increase stand value. *Taraxacum officinale* is the most significant species of herbs.

Samples of soil and grass biomass (root and above-ground biomass of the sward) were regularly collected at monthly intervals (May to September) during the growing season. We present average results of five samplings. Samples of soil and plant biomass were taken from identical sampling sites (area 0.2 x 0.2 m, sampling depth from 20 to 150 mm) by a spade. The soil samples were dried at laboratory temperature and sieved through a sieve having a pore size 0.125 mm, and processed under the regular methodologies (Linkeš, 1997). Basic physical-chemical soils properties of assessed locations are presented in table 1.



Figure 1. Situation map of sample sites in soil and plant samples in the surrounding of Banská Bystrica (the central Slovakia)

Table 1. Physical-chemical characteristic of soil

Location	pH (KCl)	N _t (g)	C _{ox} (g)	Humus (%)	Nutrients (mg.kg ⁻¹)			Type of soil
					P	K	Mg	
Radvaň (480 m a.s.l)	7.02	13.19	101.6	17.52	7.26	26.00	841.6	Rendzina
Panský diel (1000 m a.s.l)	4.24	3.67	47.3	8.16	8.58	31.00	166.6	Cambisol
Kráľova studňa (1300 m a.s.l)	6.99	4.87	57.2	9.86	21.83	42.00	698.0	Rendzina

Plant samples were divided into root and ground part, the samples were homogenized after drying to constant weight. Soil was extracted with $2\text{mol}\cdot\text{dm}^{-3}$ HNO_3 solution, and biomass in $10\text{mol}\cdot\text{dm}^{-3}$ HNO_3 solution. Extracts were analysed by atomic absorption spectrophotometer using flame atomisation (acetylene-air). Soil and plant samples were analysed at the laboratory of the Grasslands and Mountain Agriculture Research Institute (GMARI) in Banska Bystrica (Slovakia). Concentration of nine heavy metals elements (Cd, Co, Cr, Pb, Zn, Mn, Cu, Fe, Ni) were determined in each sample. For the evaluation of uptake and accumulation of heavy metals by grassland were used bio-concentration factor (BCF) and translocation factor (TF):

$\text{BCF} = \text{concentration of heavy metals in the aboveground phytomass} / \text{heavy metal content in soil (mg}\cdot\text{kg}^{-1})$

$\text{TF} = \text{heavy metal content in aboveground phytomass} / \text{heavy metal content in the root (mg}\cdot\text{kg}^{-1})$

The coefficients make a possibility to assess the ability of grassland to accumulate up taken heavy metals from the soil in their tissue and to classified stand into one of the heavy metals tolerance groups (excluders, indicators, accumulators and hyper-accumulators) Baker (1981), Staňová et al., (2010) indicate the following groups of strategy:

- a value of $\text{BCF} < 1$, excluders,
- a value of $\text{BCF} = 1$, indicators,
- a value of $\text{BCF} > 1$, accumulators – hyper-accumulators

The results of heavy metals concentration were processed by mathematical-statistical methods using PC (software Statgraphics ver. 5.0, a method of multifactor analyse of variance, $\text{LSD}_{0.05}$ test).

We determined a concentration of the following heavy metals: Cd, Co, Cr, Pb, Zn, Mn, Cu, Fe a Ni, in the soil, root biomass and aboveground biomass of grassland, at three locations in the central Slovakia (Radvaň, Panský diel a Kráľová studňa). We also determined bio-concentration and translocation factor. The results are presented in table 2.

The heavy metals concentration in soil, roots and aboveground biomass was compared with the set limit values for heavy metals (Table 3).

3. RESULTS AND DISCUSSION

The highest values of heavy metals us determinate in four cases: Cd – 2.35, Co – 13.17, Pb – 151.09, Mn – 589.27 $\text{mg}\cdot\text{kg}^{-1}$, so a soil is an environment where the heavy metals are concentrated significantly. The mean values were determinate for Cr - 5.99, Fe - 2192.9, Ni -

11.24 $\text{mg}\cdot\text{kg}^{-1}$. The lowest concentration for Zn – 48.71 and Cu – 11.42 $\text{mg}\cdot\text{kg}^{-1}$. The total content of Cd and Pb exceeded 3.36 resp. 2.16 times the permissible legislative limits established by Act No. 220/2004 on Agricultural land Protection and Use, which is in conjunction with the current European Union legislation. Concentration of Co, Cr, Zn, Cu a Ni didn't exceed the set limit values.

Heavy metals are significantly concentrated in roots of analysed plant parts, with the highest level of Cr – 7.62, Zn – 208.21, Cu – 39.25, Fe – 3569.37, Ni – 12.52 $\text{mg}\cdot\text{kg}^{-1}$. Significantly lower values of heavy metals were determinate in aboveground plant parts. The lowest values were determinate in seven cases (Cd, Co, Cr, Pb, Mn, Fe, Ni). The concentration of Co, Pb, Mn was higher in soil than in roots. Elements like Cd, Co, Cr, Pb, Mn, Fe, Ni had higher content in aboveground sward. Concentration of Cr, Zn, Cu, Fe was significantly higher in roots than in soil, and concentration of Cd, Cr, Zn, Cu, Fe, Ni was higher in aboveground part of grass biomass. The total content of Cd, Cr and Ni in aboveground plant biomass (bulk feed) slightly exceeded the maximum limits of heavy metals in feed (Decree of MASR No.2080/2005 on Feed Materials for the Production of Compound Feed and Animal Feed). Concentration of Pb didn't exceed the maximum levels of heavy metals in feed.

We recorded the highest concentrations of Fe (1351.45 – 3569.37 $\text{mg}\cdot\text{kg}^{-1}$) and Mn (330.28 – 589.27 $\text{mg}\cdot\text{kg}^{-1}$) and the lowest concentrations of Cr (3.93 – 7.62 $\text{mg}\cdot\text{kg}^{-1}$) and Cd (1.61 – 2.35 $\text{mg}\cdot\text{kg}^{-1}$) in all three evaluated environments (soil, roots, aboveground sward).

Soil:

$\text{Fe} > \text{Mn} > \text{Pb} > \text{Zn} > \text{Co} = \text{Cu} = \text{Ni} > \text{Cr} > \text{Cd}$

Roots:

$\text{Fe} > \text{Mn} > \text{Zn} > \text{Cu} > \text{Pb} > \text{Ni} > \text{Cr} = \text{Co} > \text{Cd}$

Aboveground sward:

$\text{Fe} > \text{Mn} > \text{Zn} > \text{Pb} > \text{Cu} > \text{Ni} > \text{Co} > \text{Cr} > \text{Cd}$

Samples analyses results of soil and plant biomass allow assessing the ability of individual plant organs accumulate heavy metals and examine the process of transport of these elements in the system soil - root - aboveground biomass, using as a bulk feed for polygastric livestock. The average results of BCF, which we have obtained during the three years and at three locations in the central Slovakia, can define for evaluated grasslands the following characteristics regarding their strategies to accumulate heavy metals: grasslands have been shown as excluder of a large group of heavy metals: Cd, Co, Cr, Pb and Ni, ($\text{BCF} < 1$). This strategy is very suitable for bulk feed production, heavy metals concentration is relatively low in aboveground parts of sward, and there is no contamination of the food chain:

- grasslands have demonstrated as zinc accumulator, value of 2.13 doesn't mean a serious risk of sward is actively concentrating metals in contamination of above-ground biomass production, aboveground parts of phytomass (BCF> 1), but the - grasslands are expressing as Cu indicator (BCF = 1).

Table 2. Heavy metals concentration (mg.kg⁻¹), BCF a TF of grass ecosystems

Year	Location	Environment	Heavy metals concentration (mg.kg ⁻¹)								
			Cd	Co	Cr	Pb	Zn	Mn	Cu	Fe	Ni
2009	Radvaň	soil	3.06	7.05	3.58	68.88	41.87	963.03	10.50	615.56	7.84
		roots	1.09	4.03	8.20	5.92	188.07	249.81	28.80	1433.94	6.29
		sward	0.78	2.49	1.70	4.71	36.82	166.65	6.94	182.82	4.24
		BCF	0.25	0.35	0.47	0.07	0.88	0.17	0.66	0.30	0.54
		TF	0.72	0.62	0.21	0.80	0.20	0.67	0.24	0.13	0.67
	Panský diel	soil	0.87	10.73	3.21	54.38	35.36	1161.52	13.97	4557.43	15.40
		roots	1.88	7.26	15.29	15.03	252.13	696.32	23.66	3417.40	25.96
		sward	0.82	2.40	3.26	5.32	54.09	439.12	7.64	348.68	7.66
		BCF	0.94	0.22	1.02	0.10	1.53	0.38	0.55	0.08	0.50
		TF	0.44	0.33	0.21	0.35	0.21	0.63	0.32	0.10	0.30
	Kráľova studňa	soil	4.20	7.76	3.50	84.32	62.47	1169.06	11.09	1636.97	9.50
		roots	2.38	5.27	10.39	19.20	230.57	274.12	17.27	1927.11	7.06
		sward	0.79	2.98	2.38	6.20	61.07	232.61	8.34	494.34	4.15
		BCF	0.19	0.38	0.68	0.07	0.98	0.20	0.75	0.30	0.44
		TF	0.33	0.57	0.23	0.32	0.26	0.85	0.48	0.26	0.59
2010	Radvaň	soil	1.77	17.71	6.64	42.55	29.16	416.21	12.22	144.47	7.76
		roots	2.27	8.13	4.37	17.15	215.43	153.03	29.15	2454.52	6.57
		sward	2.32	10.57	7.20	21.87	211.33	333.66	21.18	2711.04	11.58
		BCF	1.31	0.60	1.08	0.51	7.25	0.80	1.73	18.77	1.49
		TF	1.02	1.30	1.65	1.28	0.98	2.18	0.73	1.10	1.76
	Panský diel	soil	0.59	32.26	9.66	62.94	33.36	655.53	13.32	3256.24	17.92
		roots	3.55	13.31	11.04	31.71	269.43	556.97	27.19	6257.96	25.50
		sward	3.10	12.37	9.80	23.30	203.68	744.17	22.71	5137.56	22.09
		BCF	5.25	0.38	1.01	0.37	6.11	1.14	1.70	1.58	1.23
		TF	0.87	0.93	0.89	0.73	0.76	1.34	0.84	0.82	0.87
	Kráľova studňa	soil	3.62	16.22	10.33	173.06	110.71	678.93	12.96	1861.15	9.53
		roots	4.98	10.75	5.86	55.17	302.60	278.62	22.49	3061.48	7.10
		sward	3.19	11.13	5.71	34.58	230.43	383.12	19.51	2827.68	6.67
		BCF	0.88	0.69	0.55	0.20	2.08	0.56	1.51	1.52	0.70
		TF	0.64	1.04	0.97	0.63	0.76	1.38	0.87	0.92	0.94
2011	Radvaň	soil	2.30	8.77	6.93	222.59	27.45	66.90	8.97	277.03	9.66
		roots	1.43	4.04	3.44	16.40	135.55	264.22	33.27	3867.60	6.77
		sward	1.05	3.84	1.55	5.18	37.33	124.65	5.68	156.09	4.35
		BCF	0.46	0.44	0.22	0.02	1.36	1.86	0.63	0.56	0.45
		TF	0.73	0.95	0.45	0.32	0.28	0.47	0.17	0.04	0.64
	Panský diel	soil	0.77	10.14	4.21	255.88	34.25	85.57	9.79	3979.37	12.47
		roots	1.44	5.73	6.57	18.54	113.67	416.00	66.92	6454.06	19.99
		sward	1.17	4.01	1.97	4.61	44.49	336.05	5.12	146.80	7.79
		BCF	1.52	0.40	0.47	0.02	1.30	3.93	0.52	0.04	0.62
		TF	0.81	0.70	0.30	0.25	0.39	0.81	0.08	0.02	0.39
	Kráľova studňa	soil	4.01	7.88	5.87	395.19	63.75	106.71	10.00	3407.86	11.11
		roots	1.41	3.75	3.39	40.95	166.42	295.39	104.49	3250.26	7.42
		sward	1.29	3.58	1.80	5.68	56.09	212.45	6.34	158.00	5.10
		BCF	0.32	0.45	0.31	0.01	0.88	1.99	0.63	0.05	0.46
		TF	0.91	0.95	0.53	0.14	0.34	0.72	0.06	0.05	0.69
Average data (3 years, 3 locations)		soil	2.35	13.17	5.99	151.09	48.71	589.27	11.42	2192.90	11.24
		roots	2,27	6.92	7.62	24.45	208.21	353.83	39.25	3569.37	12.52
		sward	1,61	5.93	3.93	12.38	103.93	330.28	11.50	1351.45	8.18
		BCF	0.68	0.45	0.66	0.08	2.13	0.56	1.01	0.62	0.73
		TF	0.71	0.86	0.52	0.51	0.50	0.93	0.29	0.38	0.65

Table 3. Heavy metals concentration in soil and plant biomass (mg.kg⁻¹)

Environment	Heavy metals concentration (mg.kg ⁻¹)								
	Cd	Co	Cr	Pb	Zn	Mn	Cu	Fe	Ni
Soil	2.35 b	13.17 b	5.99 b	151.09 b	48.71 a	589.27 b	11.42 a	2192.90 b	11.24 b
	Limit value of heavy metals (mg.kg ⁻¹) (The Act No. 220/2004)								
	0.7	15	70	70	150	-	60	-	50
	Exceeding the limit value (multiple)								
	3.36	< limit	< limit	2.16	< limit	-	< limit	-	< limit
Roots	2.27 b	6.92 a	7.62 c	24.45 a	208.21 c	353.83 a	39.25 b	3569.37 c	12.52 b
Sward	1.61 a	5.93 a	3.93 a	12.38 a	103.93 b	330.28 a	11.50 a	1351.45 a	8.18 a
	The maximum levels of heavy metals in feed (mg.kg ⁻¹) (The Decree of MASR č.2080/2005)								
	1	-	3	40	-	-	-	-	5
	Exceeding the limit value of heavy metals in feed (multiple)								
	1.61	-	1.31	< limit	-	-	-	-	1.64
LSD _{0.05}	0.413	2.423	1.088	24.740	18.899	61.180	14.513	813.807	1.900

a, b, c, – significant differences

Translocation factor (TF) is for all assessed heavy metals less than 1, what is documenting their significant accumulation in root system of grasslands.

We can conclude that the heavy metals are most concentrated in the roots of plants and soil. Root biomass and upper part of soil as a part of grass sod have a great importance in protection of the environment. The grass sod provides a protection of aboveground part production against increased concentration of heavy metals that would otherwise enter to the food chain. The similar results were presented in the works: Klobošický & Balcar (1997), Klobošický & Kopec (1997), Petříková (1990), Hecl et al., (2005). The cultivated plants have different abilities to accept and accumulate risk elements. We can conclude that the grass species don't accumulate excessive amounts of heavy metals (in comparison with the soil and roots) in the aboveground part of biomass. It is considered that the transport of hazardous elements to the aboveground plant parts blocks Caspari's strips in endodermic cells of the root (Wenzel et al., 1999). The concentration of

heavy metals in plant tissues also researched Andráš et al., (2007). They state that the highest content of metals is in the roots, then in the leafs and in the stalks. The flowers, seeds and fruits contain heavy metals at least.

The year of evaluation had also influence on heavy metals concentration. The results of heavy metals concentration in particular years are presented in table 4. The heavy metals concentration was at balance in the years 2009 and 2011, a significantly higher in 2010 (only exception was the concentration of Pb, Mn and Cu). We have also confirmed the impact of altitude of evaluated locations on heavy metal concentration (Table 5).

The lowest concentration of all evaluated heavy metals was recorded in location of Radvaň with the lowest altitude, significantly higher concentration in locations with higher altitudes (Panský diel, Kráľova studňa). Hronec (1996) states, that the tendency may be related to accumulation of gaseous immissions, which contain large contents of heavy metals.

Table 4. Heavy metals concentration in years 2009 - 2011

Year	Heavy metals concentration (mg.kg ⁻¹)								
	Cd	Co	Cr	Pb	Zn	Mn	Cu	Fe	Ni
2009	1.76 a	5.55 a	5.72 b	29.33 a	106.94 b	594.69 c	14.25 a	1623.81 a	9.79 a
2010	2.82 b	14.72 b	7.85 c	51.37 a	178.46 c	466.69 b	20.08 a	3079.12 b	12.75 b
2011	1.65 a	5.75 a	3.97 a	107.22 b	75.44 a	211.99 a	27.84 a	2410.79 ab	9.41 a
LSD _{0.05}	0.413	2.423	1.088	24.740	18.899	61.180	14.513	813.807	1.900

a, b, c, – significant differences

Table 5. Heavy metals concentration at research sites (mg.kg⁻¹)

Location	Heavy metals concentration (mg.kg ⁻¹)								
	Cd	Co	Cr	Pb	Zn	Mn	Cu	Fe	Ni
Radvaň	1.79 a	7.40 a	4.85 a	45.03 a	102.56 a	304.24 a	17.41 a	1315.90 a	7.23 a
Panský diel	1.58 a	10.91 b	7.22 b	52.41 a	115.61 a	565.69 c	21.15 a	3728.39 b	17.20 b
Kráľova studňa	2.87 b	7.70 a	5.47 a	90.48 b	142.68 b	403.45 b	23.61 a	2069.43 a	7.52 a
LSD _{0.05}	0.413	2.423	1.088	24.740	18.899	61.180	14.513	813.807	1.900

a, b, c, – significant differences

4. CONCLUSIONS

We recorded the highest concentration of heavy metals in soil (Cd - 2.35, Co - 13.17, Pb - 151.09, Mn – 589.27 mg.kg⁻¹) and root biomass (Cr – 7.62, Zn – 208.21, Cu – 39.25, Fe – 3569.37, Ni – 12.52 mg.kg⁻¹), considerably lower content of heavy metals was determined in tissues aboveground parts of the swards. The lowest values were determinate in seven cases (Cd, Co, Cr, Pb, Mn, Fe, Ni).

The grasslands are as excluder of a large group of heavy metals - Cd, Co, Cr, Pb, Mn, Fe and Ni in view of the heavy metals transport in soil - root - aboveground biomass, (bio-concentration factor BCF < 1). This strategy is very suitable for bulk feed production, heavy metals concentration is relatively low in aboveground parts of sward, and there is no contamination of the food chain. Translocation factor (TF) is for all assessed heavy metals less than 1, what is documenting their significant accumulation in root system of grasslands.

From the perspective of environmental functions, the root system of grassland is a certain physiological barrier that restricts the movement of heavy metals from roots to aboveground parts of sward and eliminates contamination of harvest. The content of heavy metals in grass ecosystem is significantly changing during the years. A different altitude of locations has a big impact on concentration of heavy metals. The content of heavy metals is increasing with growing of altitude.

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