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HEAVY METAL LOADING OF THE BELIANSKE TATRY MTS

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Abstract

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The contribution is dealing with heavy metal migration (Pb, As, Mn, Fe and Cu) within bedrock-soil-plant system in the Belianske Tatry Mts. Sampling was performed at the transect passing the Ždiarska vidla peak (1672–2005 m a.s.l.) including various geological-substratum complexes. Of the plant species, those as *Carex tatrorum*, *Carex firma*, *Juncus trifidus*, *Silene acaulis*, *Festuca versicolor* were included. Bedrock samples are presented by marly, red nodular, siliceous spotted, gray organodetrital and Gutenstein limestones, Baboš Quartzites, Carpathian Keuper and Ramsau Dolimite. Soil samples belong to Rendzic, Folic, Umbric, Cambic and Folic Rendzic Leptosols. On the base of analysis, distinct (and in some cases up to critical) contamination of individual system components is to be stated. The system is affected first of all by Pb, As, Mn and Cu.

Key words: heavy metal, contamination, loading, alpine environmental pollution, element migration, element concentration, Belianske Tatry Mts

Introduction

Geochemical research plays an important role at the high-mountain environment research from the point of view of its pollution and subsequent impact on biotic and abiotic components of nature. Geochemical aspect is involved in soil formation and its subsequent erosion. Geochemistry is focused mainly on explanation of mineral and chemical composition impact of bedrock, soil, pH, climate, water composition and hydrodynamics etc. Also heavy metal geochemical behaviour research linked to the soil is important, especially as for their migration, bond and availability for plants, through they are involved in food chain. Chemical plant composition may serve as an environment quality bioindicator and it is a reflection of geochemical environment. Element-intake by plants depends not only on their properties, but also on the element content in bedrock, soil and the processes running in the soil. Soil as a multifunctional natural body has a unique post as a basic production factor as well as a basic component of the environment.

Heavy metals are one of those basic contamination constituents being observed in various environment components. It concerns a wide group of contaminants of different properties, impacts and origin. Heavy metals input to the environment by natural as well as anthropogenous processes. Of the natural processes in the study area, weathering and atmospheric deposition should be mentioned. Anthropogenous sources include especially industry processes, fossil fuel burning to produce electric power, production and processing of ores etc.

Alpine environment pollution by heavy metals is an actual problem nowadays. It is linked not only to the forest ecosystem health state, but also possibly to Tatras chamois population decrease, as according to the analyses of biological materials of dead individuals (Chovancová, 2001a, b) there is a high concentration of Cd, Pb, As and Hg.

Soil loading by some hazardous metals was studied also by Bedrna, Račko (1999). They give information on As, Cd, Pb, Cr, Cu and Hg content in A horizon of 35 soil samples.

Element content, in whole Slovakia scale, was a subject of study of the Soil Science and Conservation Research Institute within Slovakia soil monitoring. There were sampled soils of agricultural land, forest and areas above the timber line (650 sites, some of them within the Belianske Tatry Mts) to monitor the content of elements such as Cd, Pb Cr, Zn, Cu, Hg, Ni, Co, Se, As, F.

Of other complex studies dealing with the space distribution of the element, Geochemical Atlas of Slovakia Soils (Čurlík, Šefčík, 1999) should be mentioned. It is based on 5200 soil sample analyses gathered from the whole area of Slovakia (network with density of about 1 sample per 10 km^2). Čurlík (2002) paid attention also to the trans-border pollution of Slovakia alpine areas.

Šoltés et al. (1992) evaluated the element contents (Cu, Cd, Zn, Pb and Cr) in vegetation focused on vascular plants, bryophytes and lichens in Tatras Mts when 2 of 6 transects were located in the Belianske Tatry Mts (Zadné Meďodoly and the valley of Dolina siedmich prameňov). The authors found the highest contents in the leaves sampled from the Zadné Meďodoly transect, where also an increased immission load was recorded by plant sample analysis. This area is affected mainly by fluorine reaching maximums in plant aboveground parts. The authors concluded, that immission load bioindication results observed on the base of vascular plants, lichens and bryophytes are corresponding and as the most loaded seems to be the area of Javorina, Podspády, Zadné Meďodoly etc.

Maňkovská (1996) performed the geochemical mapping of the forest tree assimilating organs in Slovakia-wide scale following the need to estimate the forest ecosystem decay. The samples included forest tree assimilating organs from 3062 sample sites in the 4x4 km grid network, while the density in industry areas was grid 1x1 km.

Marsina (1999) gives brief information on major and 26 additional element distribution within all Slovakia lithotypes (lihtological types)/ lithofacies. On the base of 3839 bedrock samples, 64 major bedrock types were distinct. Also the summary geochemical characteristic of 64 study main lithotypes/lithofacies is included.

Some information on plant, soil and bedrock analyses are to be found in the studies of Varšavová (2001), Varšavová et al. (1999; 2001; 2002), Mišovičová et al. (2002), Mišovičová (2003) and Ševc et al. (2002).

Of important factors concerning high heavy metal concentration, precipitation hand in hand with air quality should be taken into account. Northern and northwestern winds prevail in the Belianske Tatry Mts and therefore, polluting sources from west and north located within 150–200 km (Ostrava and Krakow region, Silesia) play crucial role.

The aim was to evalute (on the base of analysis) the concentration and migration of selected elements (Fe, Mn, Pb, As, Cu) in the bedrock-soil-plant system.

Material and methods

Pb and As are the subjects of our monitoring, as these are considered to be the most harmful and Fe, Mn and Cu, which can be poisonous too, especially in the case they are accumulated on a mass scale. The concentration of the mentioned elements was determined in samples of bedrocks, soils and plants. Moreover, general soil environment state was evaluated.

To follow the study goals, the sampling of bedrock, soils and plants was performed along the chosen transect of permanent monitoring site in the central part of the Belianske Tatry Mts in July, 2001 (Table 1, Fig. 1). The sampled sites are listed on Figs 1–6. Their characteristics and analyzed plant species are to be found in Table 1.

Table 1. Survey of samples from the Ždiarska vidla transect (ZV1 – ZV9b).

Locality	Altitude (m a.s.l.)	Bedrock samples	Soil samples	Plant species occurring on the sample site
ZV1	2005 m a.s.l. exp. – NE	marly limestone	Rendzic Leptosols	***Carex tatrorum***, *Festuca versicolor, Saxifraga paniculata, Aster alpinus, Oxytropis carpatica, Silene acaulis,* bryophytes
ZV2	1953 m a.s.l. exp. – NE	red nodular limestone	Rendzic Leptosols	***Carex tatrorum***, *Saxifraga paniculata, Saxifragy moschata, Dryas octopetala, Ranunculus alpestris, Carex fuliginosa, Saxifraga aizoides,* bryophytes
ZV3	1965 m a.s.l. exp. – E	siliceous spotted limestone	Folic Leptosols	***Carex tarorum***, *Saxifraga paniculata, Festuca versicolor, Helianthemum alpestre, Sesleria tatrae, Silene acaulis,* bryophytes
ZV4	1885 m a.s.l. exp. – SE	Baboš Quartzites	Umbric Leptosols up to Cambic Leptosols	***Juncus trifidus,*** *Vaccinium myrtillus, Vaccinium vitis-idaea, Oreochloa disticha, Campanula alpina, Homogyne alpina, Cetraria islandica,* bryophytes
ZV5	1849 m a.s.l. exp. – SE	gray organodetrital limestone	Rendzic Leptosols	***Silene acaulis,*** *Hedysarum hedysaroides, Myosotis alpestris, Trifolium repens* subsp. *orbelicum, Saxifraga paniculata, Ranunculus oreophilus*
ZV6	1838 m a.s.l. exp. – SW	dark-gray to black limestone	Rendzic Leptosols	***Festuca versicolor,*** *Trifolium repens* subsp. *orbelicum, Saxifraga paniculata*
ZV7	1805 m a.s.l. exp. – SW	Carpathian Keuper	Cambic Leptosols	***Juncus trifidus,*** *Vaccinium myrtillus, Pulsatilla alba, Vaccinium vitisidaea, Bistorta vivipara, Agrostis rupestris, Calluna vulgaris*
ZV8a	1756 m a.s.l. (ridge) exp. – SW	Ramsau Dolomite	Folic Rendzic Leptosols	***Carex tatrorum,*** *Festuca versicolor, Pedicularis verticillata, Saxifraga aizoides, Crepis jacquinii, Phyteuma orbiculare, Ranunculus oreophilus*
ZV8b	1745 m a.s.l. (slope) exp. – SW	Ramsau Dolomite	Folic Rendzic Leptosols	***Carex firma,*** *Crepis jacquinii, Carex tatrorum, Helianthemum grandiflorum, Festuca versicolor, Ranunculus oreophilus, Scabiosa lucida*
ZV9a	1675 m a.s.l. (ridge) exp. – SW	Gutenstein Limestone	Rendzic Leptosols	***Carex tatrorum,*** *Hieracium villosum, Anthyllis vulneraria* subsp. *alpestris, Festuca versicolor, Carex firma, Crepis jacquinii, Carlina acaulis, Ranunculus oreophilus, Scabiosa lucida*
ZV9b	1672 m a.s.l. (slope) exp. – SW	Gutenstein Limestone	Rendzic Leptosols	***Carex firma,*** *Ranunculus oreophilus, Gentianella lutescens, Arenaria ciliata, Scabiosa lucida, Bellidiastrum michelii, Thymus pulcherrimus, Carex tatrorum, Sesleria tatrae*

Notes: Highlighted species represent sample

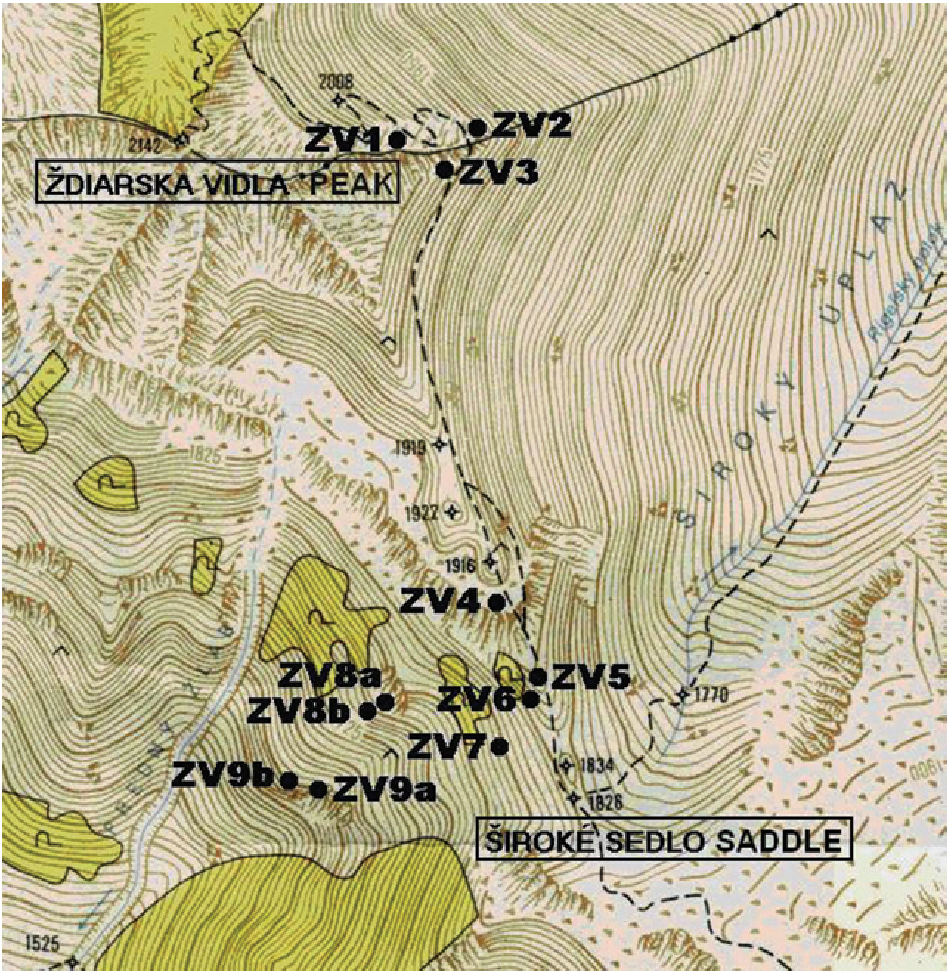

Fig. 1. Transect Ždiarska vidla peak – scheme of site situation ZV1 up to ZV9b.

The detailed sampling method and processing of the samples are offered in the study of Varšavová et al. (1999, 2001, 2002). The samples were analyzed at the Department of Analytical Chemistry, Faculty of Natural Sciences, Comenius University, Bratislava. The following methods were used to analyze the samples: AAS-P (flame atomic absorption spectrometry, AAS Model by Perkin Elmer instrument.) for Cu, Fe, Mn, Pb, while As content was evaluated by hydride generation by FIAS-200 device.

The observed values were compared with the limits for hazardous constituents according to Act No. 220/2004 and data of Varšavová et al., 2001; Čurlík, Ševčík, 1999; Zaujec, 1999; Bedrna, Račko, 1999; Marsina, 1999; Ištoňa, 1993; Šoltés et al. 1992; Kabata-Pendias, Pendias, 1992; Alloway, 1990; Holobradý, Kalúz, 1987 and Bowen, 1979.

Table 2. Lead concentration.

Site	Bedrock	Lead content (Pb) [mg.kg^{-1}]					
		Ždiarska vidla transect			Hlúpy transect **		
		bedrock	top soil	plant	Bedrock	top soil	plant
ZV1	marly limestone	4.05	96.2	9.21	27.8	100	8.5
ZV2	red nodular limestone	< 0.055*	129.0	8.74	26.5	136	22.0
ZV3	siliceous spotted limestone	1.26	188.0	6.12	–	–	–
ZV5	gray organodetrital limestone	< 0.055*	45.3	5.94	–	–	–
ZV6	dark-gray to black limestone	5.56	45.8	6.34	–	–	–
ZV9a	Gutenstein Limestone	–	186.0	7.58	25.8	170	14.4
ZV9b	Gutenstein Limestone	21.20	199.0	5.37	26.9	176	13.8
ZV8a	Ramsau Dolomite	1.92	147.0	5.46	17.3	105	12.8
ZV8b	Ramsau Dolomite	1.43	171.0	4.08	18.5	88	13.8
ZV7	shales of Carpathian Keuper	9.20	80.3	1.66	–	–	–
ZV4	Baboš Quartzites	3.49	78.3	0.53	25.3	445	49.4

Notes: * valid for 0.5 g/50 ml; ** according to Varšavová et al. (2001)

Results and discussion

Lead (Pb)

As for limestone, lead content was found to be in the range of > 0.055 up to 21.2 mg.kg^{-1}, while for dolomite 1.43 and 1.92 mg.kg^{-1}, quartzite 1.26 mg.kg^{-1} and shale 9.2 mg.kg^{-1} (Table 2). Compared with the data of Varšavová et al. (2001), the content is relatively low except for Gutenstein limestone (Hlúpy transect, Table 2). Marsina (1999) stated its limestone and dolomite content as 0.5–14.0 mg.kg^{-1}, while Alloway (1990) as 7 mg.kg^{-1}.

Limestone soils yield Pb content ranging from 45.3 to 199 mg.kg^{-1} (the highest value at all), those of dolomite 147 and 171 mg.kg^{-1}, quartzite 78.3 mg.kg^{-1} and shale 80.3 mg.kg^{-1} (Varšavová et al., 2001). Hazardous element limits in soil were exceeded in 7 samples (the limit for sandy-loamy and loamy soils is 70 mg.kg^{-1} and for clay-loamy, clay is 115 mg.kg^{-1}).

High Pb soil concentration of all sites can be documented also by comparing the data of other studies. Ištoňa (1993) states a normal-like Pb concentration in non-polluted soils to 50 mg.kg^{-1}. According to Holobradý a Kalúz (1987), toxic Pb content limit is 100 mg.kg^{-1}. Bowen (1979) states a normal-like Pb soil concentration range from 2–300 mg.kg^{-1}. Kabata-Pendias, Pendias (1992) consider the range of 100–400 mg.kg^{-1} to be the critical concentration.

Intake of Pb by plants depends on soil properties (redox potential, pH, mineral composition, organic matter content, moisture). It is stated, that only about 0.05% of soil Pb is accessible for plants (Zaujec, 1999). Natural Pb content in plants is, according to Chreneková (1982), 2.7 mg.kg^{-1}, however, it is usually ranging from 0.1 to 9.0 mg.kg^{-1}. The content we found is from 0.539 mg.kg^{-1} (*Juncus trifidus*, ZV4 site) to 9.21 mg.kg^{-1} (*Carex tatrorum,* ZV1

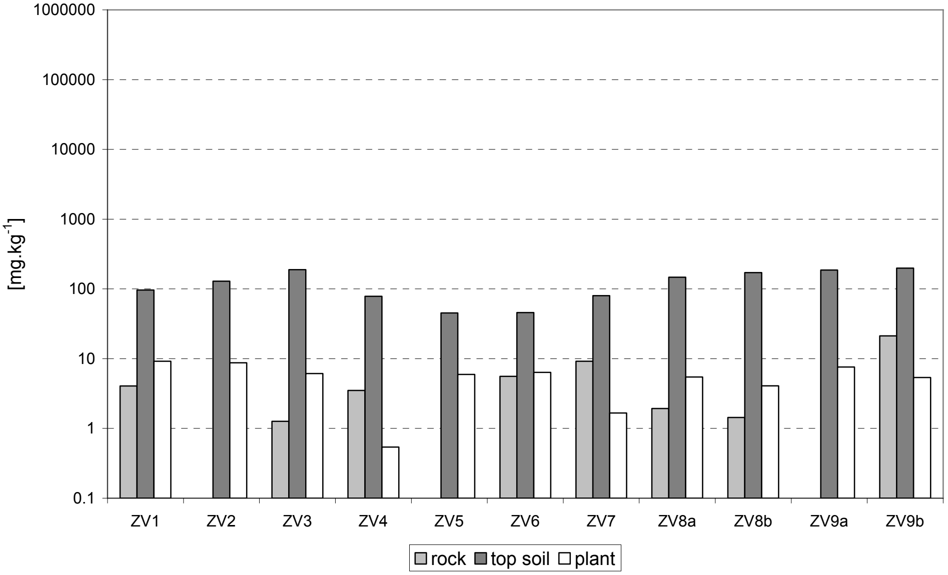

Fig. 2. Lead concentration in the Ždiarska vidla transect.

site), (Fig. 2). Acidophilous species (e.g. *Juncus trifidus*) contain much less lead compared to calciphilous species. Comparing this value, the Pb content we found is much higher.

According to Šoltés et al. (1992), allowable Pb content in plants is estimated to be 15 mg.kg^{-1}. This threshold was not exceeded in the samples. Bowen (1979) states its normal range 0.2–10 mg.kg^{-1} and Kabata-Pendias, Pendias (1992) set critical value of 30–300 mg.kg^{-1}.

Arsenic (As)

Arsenic content in limestone was ranging from 0.59 to 2.73 mg.kg^{-1}, while in dolomite 0.43–0.72 mg.kg^{-1}, quartzite 0.78 mg.kg^{-1} and shale 8.82 mg.kg^{-1}. Marsina (1999) mentioned its content for dolomite and pure limestone about 1.7–1.8 mg.kg^{-1}, while for limestone with clay or sandy addition 2.1–2.9 mg.kg^{-1}. Alloway (1990) considers its typical concentration in carbonates to be 1 mg.kg^{-1}.

Much higher As content is reflected in soils. It was ranging from 4.55 do 19.6 mg.kg^{-1}. For dolomite soils, we found its concentration from 7.97 to 102 mg.kg^{-1}. The lowest value was determined for quartzite soils 4.24 mg.kg^{-1}. Arsenic content can be stated to be rather variable. Its content from ZV8b site exceeded legal limits (Fig. 3, Table 3).

Bedrna, Račko (1999) states, that 8.5% of the Belianske Tatry Mts soil samples exceeded B indication according to the Decree of Ministry of Agriculture, 1994 (in force until 2004). The most distinct pollution is stated for its utmost parts.

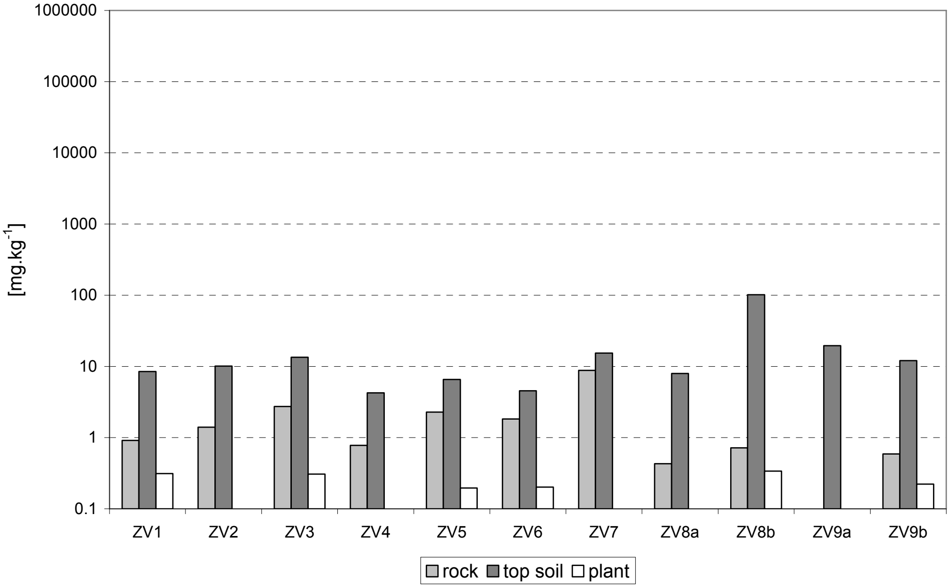

Fig. 3. Arsenic concentration in the Ždiarska vidla transect.

Table 3. Arsenic concentration.

Site	Bedrock	Arsenic content (As) [mg.kg^{-1}]					
		Ždiarska vidla transect			Hlúpy transect **		
		bedrock	top soil	plant	bedrock	top soil	plant
ZV1	marly limestone	0.91	8.47	0.312	0.298	13.4	0.602
ZV2	red nodular limestone	1.40	10.10	0.078	0.275	16.9	0.428
ZV3	siliceous spotted limestone	2.73	13.50	0.307	–	–	–
ZV5	gray organodetrital limestone	2.29	6.56	0.196	–	–	–
ZV6	dark-gray to black limestone	1.82	4.55	0.202	–	–	–
ZV9a	Gutenstein Limestone	–	19.60	0.084	2.280	120.7	0.907
ZV9b	Gutenstein Limestone	0.59	12.10	0.222	2.130	49.8	2.080
ZV8a	Ramsau Dolomite	0.43	7.97	0.049	0.322	30.6	0.906
ZV8b	Ramsau Dolomite	0.72	102.00	0.338	1.150	19.5	0.758
ZV7	shales of Carpathian Keuper	8.82	15.40	< 0.005*	–	–	–
ZV4	Baboš Quartzites	0.78	4.24	< 0.005*	1.110	43.8	1.200

Notes: * valid for 0.5 g/50 ml; ** according to Varšavová et al. (2001)

Almost all of our samples yielded higher As concentration as those offered by Čurlík, Šefčík (1999). According to the criteria proposed by Ištoňa (1993) considering its normal range from 10 up to 30 mg.kg^{-1}, the values we found are exceeded in 5 samples. As for Holobradý, Kalúz

(1987) evaluation, 5 samples exceeded the limit, of which one as much as doubly. According to this evaluation, the As content is increased but not reaching the level of toxicity. According to Bowen (1979), normal As content in soil is ranging from 0.1 to 40 mg.kg^{-1} and the critical value is, complying with Kabat-Pendias, Pendias (1992), 20–50 mg.kg^{-1}.

The range of arsenic content in plant samples is from > 0.005 up to 2.08 mg.kg^{-1} (Table 3). Its normal range (Bowen, 1979) is 0.02–7 mg.kg^{-1}, while critical value is between 5–20 mg.kg^{-1} (Kabata-Pendias, Pendias, 1992).

Soil pollution by As is frequently affected by emissions containing products of fossil fuel. In alpine areas it is caused by long-distance transport from outside of Slovak Republic.

Manganese (Mn)

The Ždiarska vidla transect site on the limestone was ranging from 17.2 to 1 188 mg.kg^{-1}, while on dolomite from 43.9 to 47.2 mg.kg^{-1}, on quartzite > 0.005 mg.kg^{-1} and shale 585 mg.kg^{-1}. High Mn content in bedrock is reflected in the soils and vice versa, except for ZV8b site, where low Mn content in dolomite does not correspond to its high content in the soil. As referenced by Marsina (1999), Mn content in pure limestone and dolomite is in the range of 101 to 155 mg.kg^{-1} and in siliceous limestone up to 1141 mg.kg^{-1}. Zaujec (1999) reported the value of 950 mg.kg^{-1} in bedrock and Alloway (1990) 620 mg.kg^{-1} in carbonates.

Soils formed on limestone contained from 139 to 282 mg.kg^{-1} of Mn, on dolomite from 150 to 1156 mg.kg^{-1}. Its value for quartzite soil was found to be 28.6 mg.kg^{-1} and 213 mg.kg^{-1} for the soils on shale. Comparing the values with Hlúpy transect soils it is obvious that soils on quartzite and nodular limestone yields lower Mn content (Table 4). Those values can be handled as increased comparing the values documented by Čurlík, Šefčík (1999) and Zaujec (1999) – they reached double up to triple values. Mn soil concentration, according to Bowen (1979) is 20–10000 mg.kg^{-1} and the critical value, according to Kabata-Pendias, Pendiasa (1992) is 500–3000 mg.kg^{-1}.

Table 4. Manganese concentration.

Site	Bedrock	Manganese content (Mn) [mg.kg^{-1}]					
		Ždiarska vidla transect			Hlúpy transect **		
		bedrock	top soil	plant	bedrock	top soil	plant
ZV1	marly limestone	617.0	612.0	493.0	378.0	654	105.0
ZV2	red nodular limestone	707.0	956.0	700.0	811.0	1 772	317.0
ZV3	siliceous spotted limestone	1 188.0	1 282.0	346.0	–	–	–
ZV5	gray organodetrital limestone	65.6	139.0	291.0	–	–	–
ZV6	dark-gray to black limestone	77.2	159.0	52.6	–	–	–
ZV9a	Gutenstein Limestone	-	608.0	158.0	83.9	553	90.9
ZV9b	Gutenstein Limestone	17.2	180.0	108.0	44.3	784	108.0
ZV8a	Ramsau Dolomite	43.9	150.0	181.0	98.9	296	53.2
ZV8b	Ramsau Dolomite	47.2	1 156.0	101.0	81.4	252	79.0
ZV7	shales of Carpathian Keuper	585.0	213.0	325.0	–	–	–
ZV4	Baboš Quartzites	<0.005*	28.6	131.0	228.0	1 024	223.0

Notes: * valid for 0.5 g/50 ml; ** according to Varšavová et al. (2001)

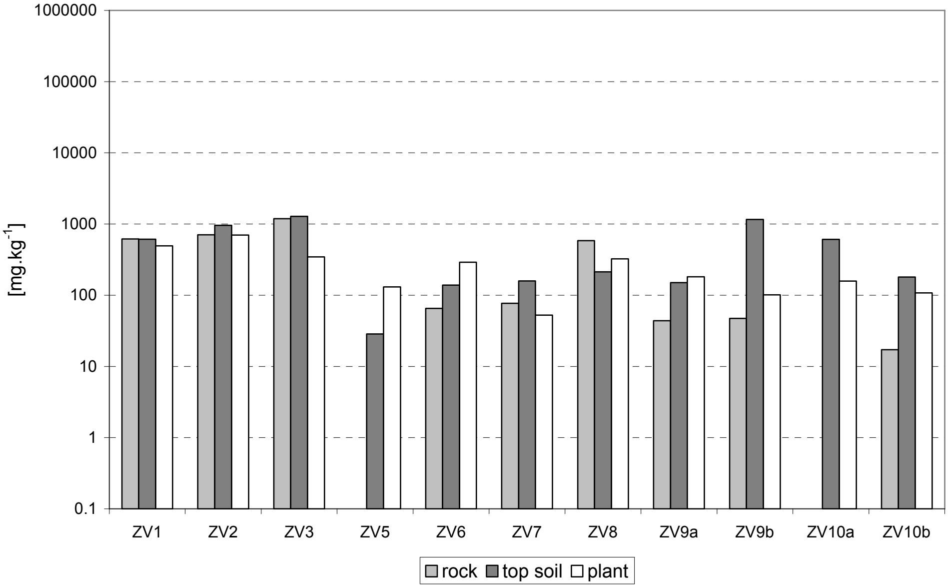

Fig. 4. Manganese concentration in the Ždiarska vidla transect.

As reported by Šoltés et al. (1992), allowed Mn concentration for plant is 300 mg.kg^{-1}. We recorded its exceeding for 4 samples. The highest value for ZV2 site was found for *Carex tatrorum*, where it reached 700 mg.kg^{-1} (Fig. 4, Table 4). To compare with Chreneková (1982), Mn natural content in plants is about 630 mg.kg^{-1}. Normal range is referenced to be 20–1000 mg.kg^{-1} (Bowen, 1979), while that of critical concentration 300–500 mg.kg^{-1} (Kabata-Pendias, Pendias, 1992).

Iron (Fe)

Fe content of the Ždiarska vidla transect site for limestone was found to be from 290 to 9710 mg.kg^{-1}, in dolomite over 600 mg.kg^{-1}, quartzite 300 mg.kg^{-1} and shale 42 660 mg.kg^{-1}. Of these, the highest values were reached for shales, about 4 up to 12 times more than the limestone. Much lower value was observed for Gutenstein limestone, dolomite and quartzite. Marsina (1999). Referred Fe content for pure limestone and dolomite ranging from 1 554 to 1710 mg.kg^{-1}, while its content for other limestone type from 5207 to 12 980 mg.kg^{-1}.

As for the soils, Fe content was recorded to be from 3100 mg.kg^{-1} (ZV4 site) to 26 630 mg.kg^{-1} (ZV7 site, Fig. 5). Compare to bedrock, its content is higher here confirming known fact, that Fe is reconcentrated during soil formation progress (Beneš, Pabianová, 1986).

The limit of plant Fe concentration (2500 mg.kg^{-1}) specified by Šoltés et al. (1992) was not recorded at all both for Ždiarska vidla and Hlúpy transect sites (Table 5).

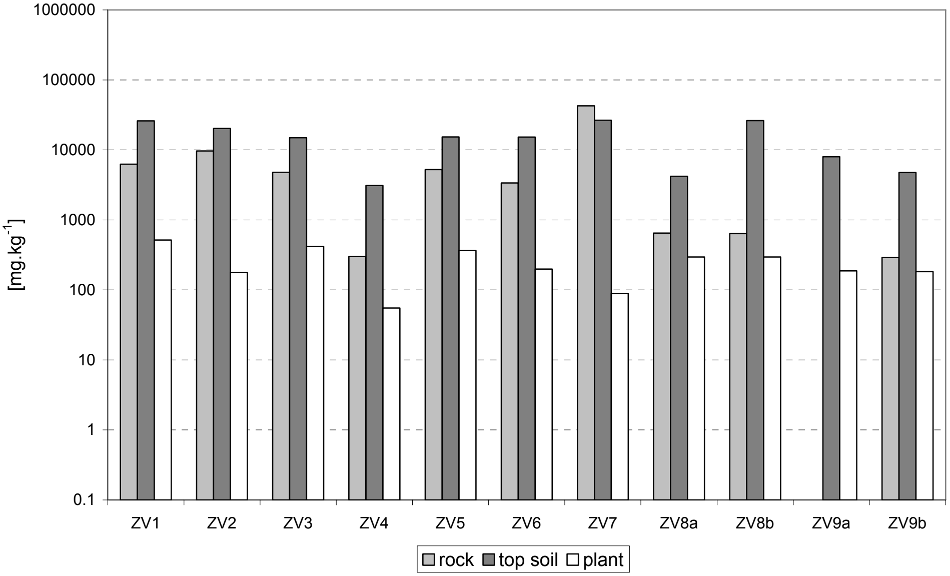

Fig. 5. Iron concentration in the Ždiarska vidla transect.

Table 5. Iron concentration.

Site	Bedrock	Iron content (Fe) $[mg.kg^{-1}]$					
		Ždiarska vidla transect			Hlúpy transect **		
		bedrock	top soil	plant	bedrock	top soil	plant
ZV1	marly limestone	6 240	26 070	518	9 168	32 700	969
ZV2	red nodular limestone	9 710	20 290	178	5 356	31 500	1 782
ZV3	siliceous spotted limestone	4 790	14 940	419	–	–	–
ZV5	gray organodetrital limestone	5 250	15 330	364	–	–	–
ZV6	dark-gray to black limestone	3 370	15 250	199	–	–	–
ZV9a	Gutenstein Limestone	–	8 000	187	681	21 500	622
ZV9b	Gutenstein Limestone	290	4 740	183	712	28 600	919
ZV8a	Ramsau Dolomite	650	4 200	124	2 073	17 300	708
ZV8b	Ramsau Dolomite	640	26 220	295	5 742	17 700	1 455
ZV7	shales of Carpathian Keuper	42 660	26 630	89	–	–	–
ZV4	Baboš Quartzites	300	3 100	55	8 480	18 400	1 111

Notes: ** according to Varšavová et al. (2001)

Copper (Cu)

Copper content was found to reach from 2.5 up to 27.5 $mg.kg^{-1}$ (the highest value). Its value in dolomites reached 2.18 and 3.2 $mg.kg^{-1}$, quartzite 0.13 $mg.kg^{-1}$ (the lowest value) and shale 19.2 $mg.kg^{-1}$. According to Beneš, Pabianová (1986), the highest values within

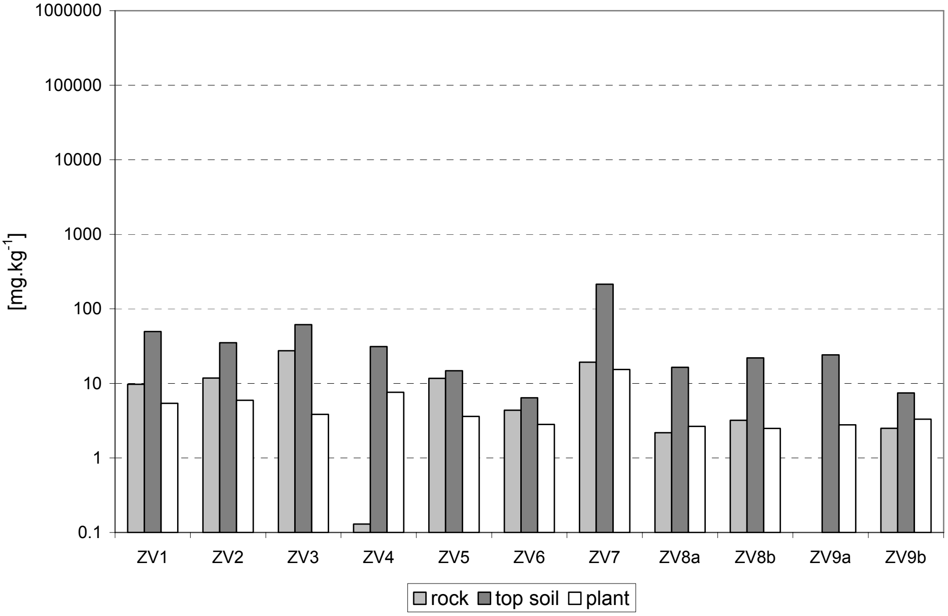

Fig. 6. Copper concentration in the Ždiarska vidla transect.

sedimentary bedrocks are contained (20-60 mg.kg^{-1}) in shale and clays, while the range for carbonate bedrock is 5–20 mg.kg^{-1}. Marsina (1999) referred Cu content for pure dolomite and limestone to be 4.4–5.7 mg.kg^{-1} and 13.4–16 mg.kg^{-1} for clay and siliceous limestone. Alloway (1990) published Cu content for carbonate bedrocks 5.5 mg.kg^{-1}.

Soils formed on limestone yielded its content ranging from 6.42 to 61.4 mg.kg^{-1}, while those on dolomite Cu 16.5 up to 22.0 mg.kg^{-1}, quartzite 31.2 mg.kg^{-1} and shale as much as 214 mg.kg^{-1} (the highest recorded value). Cu content is variable in the soils. Čurlík, Šefčík (1999) stated 17 mg.kg^{-1} to be a medium value in Slovakia soils for A and C horizons. The values we found from Ždiarska vidla site exceeded it in 7 cases. Bedrna, Račko (1999) reported also higher values in A horizon of the Belianske Tatry Mts. ZV7 site soils offered interesting value exceeding limit values specified for hazardous elements in soils complying with Act No. 220/2004 (for sandy, loamy-sandy, it is 30 mg.kg^{-1}, for sandy-loamy and loamy 60 mg.kg^{-1}, and for clay-loamy and clay 70 mg.kg^{-1}), (Fig. 6, Table 6). Normal range of Cu content in soil is 2–250 mg.kg^{-1} (Bowen, 1979) and its critical value is 60–125 mg.kg^{-1} (Kabata-Pendias, Pendias, 1992).

As for Cu content in plant samples, it was observed from 2.49 mg.kg^{-1} in *Carex firma* (ZV8b site) to 15.4 mg.kg^{-1} in *Juncus trifidus* (ZV7 site). Markert (1992) published its average values for plants 5–15 mg.kg^{-1} and Chreneková (1982) stated its natural content in plants 14 mg.kg^{-1}. As referred by Bowen (1979), its normal range in plants is 5–20 mg.kg^{-1} and the critical one 20–100 mg.kg^{-1} (Kabata-Pendias, Pendias, 1992). Allowable value 100 mg .kg^{-1}, according to Šoltés et al. (1992), was not exceeded at all.

Table 6. Copper concentration.

Site	Bedrock	Copper content (Cu) [mg.kg^{-1}]		
		bedrock	Top soil	plant
ZV1	marly limestone	9.74	49.7	5.41
ZV2	red nodular limestone	11.80	35.1	5.93
ZV3	siliceous spotted limestone	27.50	61.4	3.85
ZV5	gray organodetrital limestone	11.70	14.8	3.61
ZV6	dark-gray to black limestone	4.38	6.4	2.81
ZV9a	Gutenstein Limestone	–	24.2	2.78
ZV9b	Gutenstein Limestone	2.50	7.4	3.32
ZV8a	Ramsau Dolomite	2.18	16.5	2.66
ZV8b	Ramsau Dolomite	3.20	22.0	2.49
ZV7	shales of Carpathian Keuper	19.20	214.0	15.40
ZV4	Baboš Quartzites	0.13	31.2	7.63

Conclusion

On the base of analytical evaluation of bedrock-soil-plant system results, distinct (and in some cases up to critical) contamination of individual system components is to be stated. The system is affected first of all by Pb, As, Mn and Cu.

For all soil samples, lead limit concentration values were exceeded distinctly. The highest values were found for 6 sites exceeding the highest limit value (115 mg.kg^{-1}, complying with Act No. 220/2004), namely that of ZV 2 (Rendzic Leptosol – 129 mg.kg^{1}), ZV 3 (Folic Leptosol – 188 mg.kg^{-1}), ZV 8a, ZV 8b (Folic Rendzic Leptosol – 147 and 171 mg.kg^{-1}), ZV 9a, ZV 9b (Rendzic Leptosol – 186 a 199 mg.kg^{-1}). Until 2004, limit values for hazardous elements in soils specified by the Ministry of Agriculture were in force according to which if the value exceeds 150 mg.kg^{-1}. It falls within B indication value, i.e. contamination was confirmed analytically and additional study is needed in the case, if formation, area and concentration can have negative impact on human health or other environment components.

High arsenic concentration was recorded mainly for soils. One sample value exceeded more than triple (102 mg.kg^{-1} – ZV 8b) limit specified for hazardous elements in soil (it is 30 mg.kg^{-1}for clay-loamy and clay soils). In plants, even if the concentration was higher, it still was not toxic.

Manganese concentrations in soil samples exceeded twice up to threefold compare to other authors. Čurlík, Šefčík (1999) published for the Belianske Tatry Mts values ranging from 20 to 520 mg.kg^{-1}. This range was exceeded in 5 samples. The highest values (over 1000 mg.kg^{-1}) were recorded in 2 sites; ZV3 – Folic Leptosol (1282 mg.kg^{-1}) and ZV8b – Folic Rendzic Leptosol (1156 mg.kg^{-1}). Mn concentration exceeding was recorded also for 4 plant samples, especially on the ZV2 site (*Carex tatrorum*), where allowable value

(300 mg.kg^{-1} setup by Šoltés et al., 1992) was exceeded in 2 cases. Observed value reached 700 mg.kg^{-1} here.

Limit for hazardous elements in soil was exceeded also for copper (70 mg.kg^{-1}). Soil sample of the ZV7 site (Umbric Leptosol) contained 214 mg.kg^{-1}, i.e. threefold exceeding.

Summarily we can state the most distinct heavy metals loading for limestone bedrock and quartzite. In quartzite, marly limestone and Gutenstein limestone accumulation and high concentration of lead were recorded. Soils formed on limestone bedrock seem to be the most hazardous (Rendzic Leptosol – high Pb, As and Mn concentration, Rendzic Leptosol – high Mn and Cu concentration, Folic Rendzic Leptosol – high Pb, As and Mn concentration) hand in hand with those on quartzite (Umbric Leptosol ranker – high Pb, As and Mn contents). High hazardous element concentrations (Pb, Mn) were estimated for *Carex firma*, *Carex fuliginosa* and *Silene acaulis*.

Results point at high concentration of some elements, especially in soil and plant samples, what could be the reason of increased heavy metal concentration observed in chamois.

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