IMPACT OF SOIL PROPERTIES ON SORPTION OF HEAVY METALS IN BELIANSKE TATRAS MTS.

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ABSTRACT

Our objective was to evaluate the impact of selected chemical properties of Leptosols soil type on sorption of mobile forms of heavy metals lead (Pb) and cadmium (Cd) in soils´ Belianske Tatras Mountains. The content of heavy metals in the soil is impacted by the content of total organic carbon and humic acids. The results also show a high complexion capacity of humic acid for the heavy metals. The strength of binding of the two metals is in the sequence of Pb > Cd. Based on discovered attributes of humic acids (HA) and fulvic acids (FA) in analysed soils dominate fulvic acids and it is about low-class humate-fulvic humic. Average content of fulvic acids represented approximately double content of humic acids. Between HA and FA was detected positive correlation, where $r = 0.985$ on importance level $\alpha = 0.01$. Positive correlation was detected between TOC and content of humic acids ($r = 0.873$; $p < 0.01$) and humic substances ($r = 0.833$; $p < 0.01$). Content of humic fraction fulvic acids was negatively correlated with content of TOC ($r = 0.792$; $p < 0.01$). Content of heavy metals in soils´ Belianske Tatras Mountains is probably influenced by anthropogenic factors of environment and structure of rocks.

Key words: cadmium, lead, soil, humic acids, fulvic acids.

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INTRODUCTION

Carbonates contain, according to Alloway (1990), 0.03 mg Cd.kg^{-1} of soil and 5.7 mg Pb.kg^{-1} of soil. Marsina (1999) stated its limestones and dolomite content sa 0.5-14.0 mg Pb.kg^{-1}, while Alloway (1990) as 7 mg Cd.kg^{-1} of soil. Primary carbonate rock to weathered carbonate rock and from primary carbonate rocks to the soil coexisting with carbonate rocks, the contents of the heavy metal elements Cd and Pb show increasing tendencies (Ni et al., 2009) and limestone has by Aziz et al. (2008) significantly removed more than 90 % of most metals at a final pH of 8.5. Grupe and Kuntze (1988) argue, that metals of anthropogenic origin are generally considered as more available from soils than those originating from parent rock. On the absorption of trace elements are involved not only organic matter (Kabata-Pendias and Pendias, 1984), soil biota (Styk, 2001), soil properties, according to the variability in organic and inorganic soil constituents (Alloway, 1995), as well as carbonates, phosphates, sulfates, clay particles (Kabata-Pendias and Pendias, 1984; Styk, 2001), most of the Pb in sediments occurs in clays (Wedepohl, 1956). Effects of heavy metal pollution are most long lasting in soils due to relatively strong adsorption of many metals onto the humus and clay colloids (Alloway and Ayres, 1994). Heavy metals may be bound or sorbed by particular natural substances, which may increase or decrease mobility (Hulanicki, 2000). Organic amendments such as composts or peat, which contain a high proportion of humified organic matter, can decrease the bioavailability of heavy metals in soil by adsorption and by forming stable complexes with humic substances (Schuman, 1999). Humic acids (HA) contain acidic groups such as carboxyl and phenolic OH functional groups (Hofrichter et al., 2001) and, therefore, provide organic macromolecules with an important role in the transport, bioavailability, and solubility of heavy metals (Lagier et al., 2000).

The objective of work is to detect selected soil´s chemical properties and to sum up their impact on sorption of mobile forms of heavy metals (Pb, Cd) in Belianske Tatras Mountains´ soils.

MATERIAL AND METHODS

Soil samples were taken from the randomly selected sites in Belianske Tatras Mts. (Tab. 1). This is a limestone area, Fatricum of Krizna Nappe, build up of limestones, quartzites and sandstones. The main geochemical rock types are limestones and dolomites (Bedrna, 2002). The analyzed soil samples were taken in the autumn of 2011 from a depth of 0 - 30 cm (Leptosols soil type).

Tab. 1 Characteristics of sampling sites of soil samples

Number of samle	Locality	Slope	Exposure	Altitude [m n. m.]	Forms of reliéf
P1	Hlúpy	10°	north/northeast	2049	Flat
P2	Pod Hlúpmi	15°	south/southeast	2010	slightly
P3	Belianska Kopa	15°	north/northeast	1828	Flat
P4	Zadné Meďodoly	30°	south	1724	Convex
P5	Ždiarska Vidla	45°	south/southeast	2133	slightly
P6	Predné Jatky	25°	north/northeast	1964	slightly
P7	Bujačí vrch	35°	north/northwest	1943	Flat
P8	Muráň	45 - 59°	north/northeast	1834	Convex
P9	Nový	40 - 45°	southwest/west	1959	Flat
P10	Havran	35°	north/west	2047	slightly

The soil was air-dried at room temperature and sieved (< 2 mm) using standard procedures. The soil reaction in distilled water was determined to be an active soil reaction (pH_{H2O}) and in a solution of 1 mol l^{-1} KCl an exchange soil reaction (pH_{KCl}). The ratio of soil to solution was 1:2.5 (van

Reeuwijk, 2002). Total organic carbon (TOC) was measured via Tyurin method modified by Nikitina according to Orlov and Grišina (1981). The total nitrogen (N_T) was determined by the Kjeldahl method (Bremner, 1960). The content of humic substances (HS), as well as the ratio HA:FA were determined by group composition of humic substances using the Belčiková - Kononová method (Kononová and Belčiková, 1962). Humic substances were extracted into 0.1 M solution sodium pyrophosphate adjusted to pH 13 with 1 M sodium hydroxide and the samples were left for infusion for 24 hours at room temperature. The humification degree (DH) of humified substances was calculated from the relation DH = HA/TOC.100 [%] (Grišina, 1986).

Quantitative determination of lead (Pb) and cadmium (Cd) in leachate 2 M nitric acid in a 1:10 (soil/2 M nitric acid) was performed by ET-AAS technique on an atomic absorption spectrometer SpectrAA–200 (Varian, Mulgrave Virginia, Australia) equipped with deuterium background correction with GTA-100 module.

The measured data was statistically processed with the software Statistics 8. To determine the correlation relationships between chemical parameters, we used Spearman's test of serial correlation.

RESULT AND DISCUSSION

By analysis and evaluation of selected chemical soil properties of Belianske Tatras Mountains, we detected high content of total organic carbon (TOC) in the soil, which was in interval 8,89 – 29,59 %. Average content was 15,57 % (Tab. 2). The soils are integrated into neutral soils based on values of active soil reaction and into slightly acid based on the values of exchanging soil reaction. Total nitrogen in soil was not correlated with content of TOC (Tab. 3), what does not correspond with contention of Pan et al. (2013). Positive correlation was detected between content of TOC and content of humic acids ($r = 0{,}873$; $p < 0{,}01$) and humic substances ($r = 0{,}833$; $p < 0{,}01$) (Tab. 3). Content of fulvic acids´ humic fraction was negatively correlated with content of TOC ($r = 0{,}792$; $p < 0{,}01$). Positive correlation was detected between individual fractions of humic (HA and FA), where $r = 0{,}985$ on importance level $\alpha = 0{,}01$ (Tab. 3). Based on detected values of humic acids (HA) and fulvic acids (FA) in analysed soils dominate fulvic acids and it is low class humate-fulvic humic.

Tab. 2 Samples collected and chemical properties (Belianske Tatras Mts.)

Number of sample	pH_{H2O}	pH_{KCl}	TOC	Humic	N_T	C/N	HA	FA	HS	DH	Cd	Pb
			%		$mg.kg^{-1}$		%				$mg.kg^{-1}$	
P_1	6,8	6,4	11,73	20,23	5600	21,0	1,293	3,142	4,435	11,02	0,40	57,28
P_2	6,8	6,4	10,78	18,59	5775	18,7	0,739	2,318	3,057	6,86	0,11	37,70
P_3	6,8	6,2	29,59	51,01	6650	44,5	2,549	4,252	6,801	8,61	0,83	139,41
P_4	7,0	6,4	8,89	15,32	4900	18,1	0,645	2,142	2,787	7,26	0,08	32,12
P_5	6,9	6,4	15,31	26,39	7875	19,4	1,235	2,934	4,169	8,07	0,12	67,30
P_6	6,9	6,4	19,21	33,12	8575	22,4	1,324	2,873	4,197	6,89	0,29	79,13
P_7	6,9	6,4	14,51	25,01	6300	23,0	0,712	2,294	3,006	4,91	0,08	39,75
P_8	6,7	6,3	21,50	37,06	7000	30,7	2,134	4,045	6,179	9,93	0,14	123,48
P_9	6,8	6,1	14,26	24,58	6825	20,9	1,326	3,098	4,424	9,30	0,24	54,55
P_{10}	7,0	6,4	9,91	17,09	5600	17,7	1,273	3,123	4,396	12,85	0,20	46,44
Average	**6,9**	**6,3**	**15,57**	**26,84**	**6510,0**	**23,6**	**1,32**	**3,02**	**4,35**	**8,57**	**0,25**	**67,71**

TOC was positively correlated with content of lead´s and cadmium´s mobile forms too. Based on correlation´s analysis lead has the highest sorption attribute on TOC ($r = 0{,}941$; $p < 0{,}01$), compared to cadmium ($r = 0{,}718$; $p < 0{,}05$). On the other hand, the correlation was found between soil HA and heavy metals (Pb>Cd). According to Liu and Gonzaley (2000) Cd is the metal which is the most difficult to be completed by HA. Content of heavy metals´ Pb and Cd mobile forms is correlated only with humic fraction of humic acids (Tab. 3), probably because humic acids contain a wide variety of functional groups, which may react with metals (Livens, 1991). Content of heavy metals in soil is impacted by one another too, what is acknowledged by the correlation between Pb and Cd ($r = 0{,}672$; $p < 0{,}05$).

The detected values of lead´s and cadmium´s mobile forms in leachate 2 $mol.l^{-1}$ HNO_3 are judged by a decision of the Ministry of Agriculture of the Slovak Republic nb. 531/1994-540 „Limitarian values of danger inorganic substances in soil“. The limitarian value for content of lead is 30 $mg.kg^{-1}$ and of cadmium is 0,3 $mg.kg^{-1}$ of dry solid, based on it can be said that content of lead was over limited in every sample of soil, probably because according to Jomová et al. (2002) region long burdened waste metallurgical and mining activity causes high levels of heavy metals until today. In the course of weathering, the heavy metals are continuously accumulated (Ni et al., 2009), and hence the heavy metals deposition in Tatras mountain relates with automobility and on northern aspects there is evident the effect of transboundary air pollutants from Polland (Katowice) (Končok et al., 1973) and by Barančoková et al. (2009) are polluting sources from west and north located within 150-200 km (Ostrava and Krakow region, Silesia). In case of samples P_1 (Hlúpy) and P_3 (Belianska Kopa) there was found to be an overlimited content of cadmium. (Tab. 2).

Tab. 3 Correlation between of chemical properties (Belienske Tatras Mts.) (n=10)

	pH_{H2O}	pH_{KCl}	TOC	N_T	C/N	HA	FA	HS	DH	Cd
pH_{H2O}	x									
pH_{KCl}	0,492	x								
TOC	-0,513	-0,490	x							
N_T	-0,237	-0,158	0,543	X						
C/N	-0,505	-0,509	0,935**	0,213	X					
HA	-0,559	-0,555	0,873**	0,353	0,865**	x				
FA	-0,582	-0,547	-0,792**	0,305	0,792**	0,985**	X			
HS	-0,574	-0,553	0,833**	0,329	0,829**	0,996**	0,997**	X		
DH	-0,063	-0,163	-0,085	-0,225	-0,007	0,398	0,519	0,464	x	
Cd	-0,294	-0,464	0,718*	0,109	0,798**	0,691*	-0,371	0,100	-0,340	X
Pb	-0,586	-0,451	0,941**	0,461	0,896**	0,916**	-0,416	0,201	-0,627	0,672*

* $p < 0{,}05$ ** $p < 0{,}01$

CONCLUSIONS

Sorption of heavy metals in soil is impacted not only by the soil´s chemical properties, but also by the anthropogenic effect and geological sub-soil, which contribute to soil enriching with heavy metals. The content of heavy metals is impacted by the content of TOC and is controlled by the soil matrix and the composition of the soil solution. The results also show a high complexation capacity of humic acid for the heavy metals. The strength of binding of the two metals is in the sequence of Pb > Cd. Content of mobile form of lead is positively correlated with content of cadmium in Belianske Tatras Mountains soil. ($r = 0{,}672$; $p < 0{,}05$). The problem with heavy metals in soil is their lack of degradability. That is why the monitoring of soils´ encumbrance by heavy metals is an important aspect by evaluating the quality of soil and searching for ways to prevent soil contamination by heavy metals.

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