THE ORIGIN OF HEAVY METAL CONTENT IN SOILS OF AGGTELEK KARST (NE HUNGARY)

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ABSTRACT

The origin of the high heavy metal content in the soils near Lake Vörös on Aggtelek-Karst (NE Hungary) was studied by detailed examination of the elemental composition and distribution in a depth profile of the soil formed on slope sediments of red clay redzina. This work was focused on Cu, Zn and Pb contents because these elements can indicate supposed hydrothermal ore formation processes in this area. For examining the spatial distribution of Cu, Zn and Pb in the studied area we have extended our research further 13 soil samples. In addition, the elemental composition of limestone bedrock of the soils was also investigated. Our results show both natural and anthropogenic influence on heavy metal content in soils. However the results do not undoubtedly confirm the same geochemical origin of the studied elements.

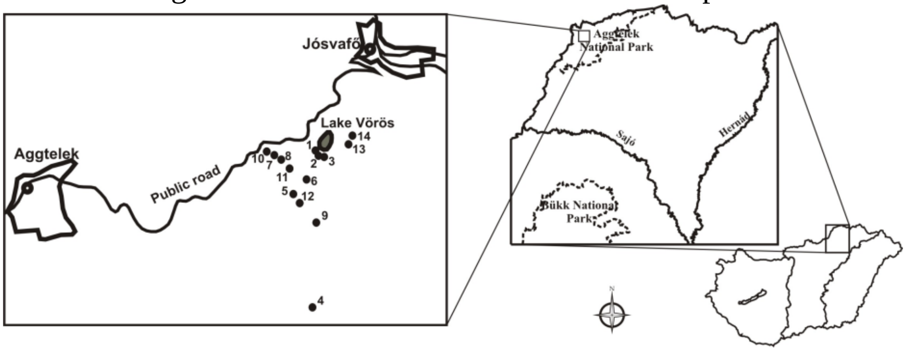
INTRODUCTION

Red clay rendzina is a rare soil type in Hungary which formed on Aggtelek Karst. Its parent material is composed of a mixture of weathered Mesosoic limestone and residuum of a relict soil formed from red clay. This relict residuum formed under tropic-subtropic weather condition in Triassic (Zámbó 1986).
Geochemical investigation of the collected sample near Lake Vörös on Aggtelek Karst was revealed anomalous elemental distribution in the soil of slope sediments of red clay rendzina. In the examined soil Zn concentration had increasing value with depth (Czirbus et al., 2010). Within 120 cm interval Zn content increased three times value to exceed Hungarian background (Gondi et al., 2004). This unusual Zn content originates from natural and/or anthropogenic sources. In this area the main anthropogenic effect can be the past mining of metal ores in Rudabánya, while the natural origin probably due to hydrothermal ore formation in Aggtelek Karst. The latter suggestion is confirmed by the presence of sulphide enrichments and sphalerite mineral deposits near the studied area pointed out by Németh et al. (2012) the high heavy metal content can origin from weathering of soil bedrock.

MATERIALS and METHODS

The examined soil formed on slope sediments of red clay rendzina and the further 13 soil samples were collected near Lake Vörös on Aggtelek-Rudabánya Mountain (Fig.1). This area belongs to Aggtelek National Park (Aggtelek Karst, NE Hungary) and has a natural protection. The examined profile of red clay rendzina is 120 cm deep and its bottom reaches an outcropping of carbonate bedrock. The examined rock sample is a part of this bedrock outcropping. Samples were taken from every 10 cm of the depth profile and the further 13 soil samples represent the deepest part of genetic horizons. These further 13 soil samples belong to 3 soil types formed on relict red clay: red clay rendzina, its soil of slope sediments and brown forest soil.

Figure 1 Location of the examined soil samples.

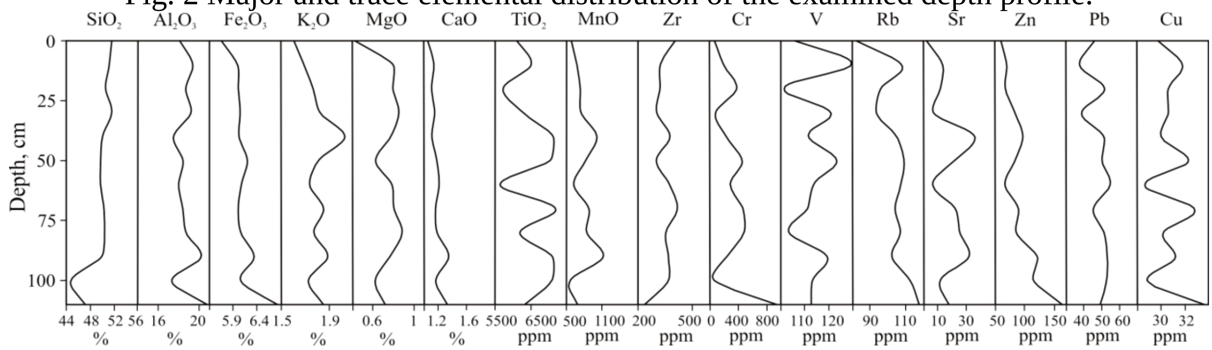


The major and trace elements of soil and rock samples were measured by Horiba Jobin-Yvon XGT-5000 X-ray fluorescence spectrometer (30 kV excitation voltage, Rh X-ray source, 100 μm spot diameter, 900 sec measuring time, 5 parallel measurements). Soil bedrock was solubilized by 10 % hydrochloric acid to examine the insoluble residue. Spatial distribution of Cu, Zn and Pb content of all investigated soil samples were visualized by Surfer for Windows.

RESULTS

The results of the elemental distributions in soil profile are shown in Fig. 2. The change of Zn concentration in profile shows intense increase with the depth. Its value in 120 cm deep is three times higher than on the surface of profile. Cu and Pb contents do not show increasing concentration along the profile but their average values in the soil exceeds the Hungarian background (Gondi et al., 2004).

Fig. 2 Major and trace elemental distribution of the examined depth profile.



The Cu content ranges between 28 ppm and 34 ppm and the Pb concentration varies between 38 ppm and 55 ppm in 120 cm interval. These values indicate polluted area. The evaluating of depth profile of the major and trace elements shows a strong correlation only between Zn, Fe and Al. These observations indicate that certain adsorption processes can play role in the elemental distribution because heavy metals have strong affinity to the surface of the Fe- and Al-oxide-hydroxide formed by weathering processes (Bohn, 1985).

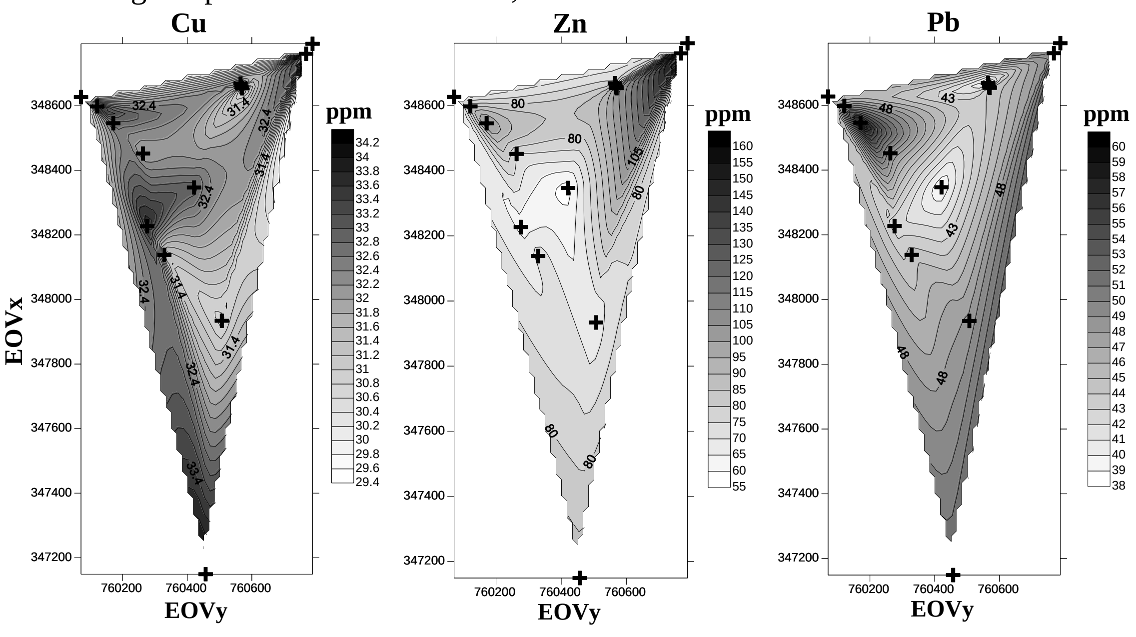
Results of elemental composition of the soil bedrock and its insoluble residue are shown in Table 1. This table contains also the element composition of soil sample from lowermost interval (110-120 cm) of depth profile. For determining the Cu, Zn and Pb adsorption on carbonate or sulfide minerals the carbonates were dissolved by acidic treatment. The Ca content decreased below 1 %. Mg and S content remained the same value, while Al, Si, K, Fe, Ti, Mn, V, Cr, Rb, Sr and Zr have a relative enrichment in the insoluble residue.

Table 1 Major and trace element contents in bedrock of the studied soil, its insoluble residue and in the lowermost part of the soil.

Sample	**MgO**	**Al_2O_3**	**SiO_2**	**K_2O**	**CaO**	**Fe_2O_3**	**SO_3**	**TiO_2**	**MnO**	**V**	**Cr**	**Cu**	**Zn**	**Rb**	**Sr**	**Zr**	**Pb**
	%							ppm									
bedrock	1.482	0.15	1.3	0.012	44.7	0.055	0.22	35	94	6	0	0	14	66	133	15	23
insoluble residue	1.891	23.9	50.5	4.407	0.94	2.979	0.27	5844	177	99	51	0	0	101	233	232	38
soil	0.718	20.9	47.1	1.850	1.33	6.84	0.11	6350	692	113	929	34	162	117	28	238	49

For further analyze was focused those elements (Ca, S, Cu, Zn and Pb) which play an important role in the hydrothermal ore formation of sedimentary environment (Hartai, 2008). Cu was not determined in the bedrock. During acidic treatment zinc dissolved so this element was in strong association with carbonate minerals, whereas the Pb accumulated in the insoluble residue. Therefore, we suppose that the Pb was as sulfide mineral in the bedrock. The Zn did not derive only bedrock as it is show by dissimilar Pb and Zn ratio observed in soil and bedrock together with higher value than expected value from the bedrock.

Fig. 3 Spatial distribution of Cu, Zn and Pb contents of the studied area.



Spatial distributions of Cu, Zn and Pb content in samples from the bottom layer of the 14 soil samples are shown in Fig. 3. The aim of the mapping was to show any relationship between spatial distributions of these three elements. Distribution of Cu content does not show any similarity with distribution of the other two elements. Zn and Pb distributions are comparable. Pb concentration is higher than Hungarian background in every soil samples. The highest Cu content and the lowest Zn and Pb concentration are observed in the east and the middle part of the studied area. The highest Zn concentration was determined in the NE area and the highest Pb concentration was detected in the NW part of the studied area. Taken together our results suggested that Zn associated with carbonate and Pb presence as sulfide mineral in bedrock. The difference between the zinc and lead distributions is due to the different accumulation processes and the different way of immobilization.

CONCLUSIONS

- Cu, Zn and Pb content in the studied soil of slope sediments of red clay rendzina is higher than Hungarian background. Zn content distribution in the examined profile shows a strong correlation with Fe and Al concentration which refers to adsorption processes of zinc in the soil.
- Unusual values of Cu, Zn and Pb content in the studied soil come probably from different sources. Whereas the main source of the Pb is the bedrock, the Cu content does not likely originate from the bedrock. Origin of Zn and Pb content from hydrothermal ore formation cannot be excluded in this area.
- The spatial distributions of Zn and Pb are similar in this area while the Cu conspicuously differs from them. The slight difference between spatial distributions of Zn and Pb due to the different concentration of adsorbing compounds in bedrock and the different adsorption processes of the elements.

ACKNOWLEDGEMENT

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