THE USE OF NATURAL SUBSTANCES AS A CONTRIBUTION TO SOLVING THE REVITALIZATION OF CONTAMINATED AREAS

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Abstract

The paper presents the results of experimental studies focused on possible solutions of the revitalization of soils contaminated by copper mining on the territory of Central Spiš (Slovakia). We have tested natural stimulator based on humic and fulvic acids - HUMAC Enviro in laboratory conditions. The test results showed that the copper content in the aqueous solution coming from the contaminated soils exceeded the permitted limits set out by the law 13 times. After the application of the natural stimulator the copper content has been significantly decreased in five days interval by 40% and the average value of Cu exceeded the limiting values set out by the law 8 times. In response to this finding, as well as numerous global researches aimed at exploring the impact of humic acids in environmental compartments, application of natural substance HUMAC Enviro seems to be important in addressing current environmental problems related to environmental contamination.

Key words: *soil, humic acid, aqueous solution, heavy metals, pH, copper*

1. INTRODUCTION

Soil, water and atmosphere can be contaminated with dangerous toxic substances, both as a result of natural processes or anthropogenic activities. Consequently, the contaminants can be released into the environment. The degree of contamination of the environment and its individual components, as well as the fate of the contaminant depends primarily on the physical and chemical properties of the contaminant. Knowledge about the behaviour of contaminants in the environment is essential for selecting the appropriate decontamination technology. The solid contaminants in their insoluble form are deposited predominantly in the surface layers of soil. They can reach the lower soil horizons only by transportation through the cracks via a rainfall (Pipíška & Remenárová 2014; Bárek *et al*. 2008). Inorganic contaminants are a serious problem in all components of the environment. The most important inorganic contaminants include also heavy metals.

Many of them act in terrestrial ecosystem as a toxic, even at low concentrations (a few mg kg^{-1} of soil). Effect of heavy metals on the environment is even heavier since they do not degrade. Cadmium, lead, copper and zinc are the elements with a high potential threat. Natural copper content in the soil determines the content of the parent rock and soil formation processes. Copper inlets to the soil from anthropogenic sources range from: the atmospheric deposition of 19%, the application of fertilizers and agricultural chemicals in the soil 35 - 45% of all the inputs. In terms of the profile differentiation copper is more strongly accumulated in the surface soil horizon due to its high affinity for organic matter and bioaccumulation, as well as anthropogenic deposition of copper (Fazekašová *et al*. 2014).

Humific soil organic matter is one of the main factors controlling the physical, chemical and biological soil properties. It affects the production of soil functions and plays an important role in soil hygiene (immobilization of heavy metals and organic pollutants). Humic acids are active in the interaction of various organic and inorganic contaminants, affecting their mobility, bio-accessibility, degradation and phytotoxicity (Fazekašová *et al*. 2014; Kondrlová *et al*. 2013). Metals tend to form distinct complexes with organic material (humic and fulvic acids) in the soil, depending on the nature of the metal. For example, copper is bonded inaccessibly, mainly with the formation of the humic acids (Makovníková *et al*. 2006; Skybová 2006).

In recent years, remediation of contaminated environment is in the centre of attention because soil and water contaminated with toxic substances constitute a serious danger to public health. Activated

carbon is one of the most widely used sorbent to remove contaminants due to high sorption capacity (Pipíška & Remenárová 2014).

The paper presents results of experimental studies focused on possible solutions to the revitalization of contaminated soils by copper mining in the Central Spiš region (Slovakia).

2. MATERIAL AND METHODS

The studied area is located in Rudňany - Gelnica area, which was based on environmental regionalization of the Slovak Republic, declared as a deteriorated and hygienically defective area. As a result of long and intensive mining and mineral processing operations, the area was polluted by heavy metals and the landscape was deformed by extensive anthropogenic forms. Rudňany - Gelnica burdened area has an extent of 357 km^2. The relief is mildly to moderately sloping. The geological structure of the area is built with Paleozoic (conglomerates, phyllites, schists), Paleogene (central Carpathian flysch in a typical development of sandstone and shale) and Quaternary (Holocene calcareous clays, sands and gravels) materials. Shallow, moderate loam and sandy loam soils have developed on these parent rocks. The dominant soil types are Cambisols from moderate to light and in a lesser extent, there are represented also fluvial and pseudogleys. The soils in this area can be characterized as moderately deep to shallow. The area belongs to the mild to moderately warm humid climates with average January temperatures of -2 to -5 °C and the average July temperature of 13-15 °C (Michaeli *et al*. 2015; Čech *et al.* 2011; Hronec *et al*., 2008).

Nine of contaminated sites in Central Spiš were monitored: Krompachy (1 – KR1, 2 – KR3, 3 – KR4), Slovinky (4 – SL1, 5 – SL4), Rudňany (6 – RD1, 7 – RD4) and Porac (8 – PR3, 9 – PR4) (Fig. 1). Soil samples for chemical soil properties and heavy metals content determination were sampled on permanent research sites, which are used as permanent grassland and are in immission field heaps and ponds, from A horizons the depth of 0.05 m to 0.15 m (Fig. 2). We studied and evaluated soil reaction in 1N solution KCl. The content of Cu in the soil and in aqueous solution was determined by x-ray fluorescence spectrometry (RFS) and by atomic emission spectrometry with inductively coupled plasma (AES – ICP) (Fiala *et al.* 1999). As sorbent was used 100% natural substance HUMAC Enviro made from net source oxihumolite (brown coal) in concentrations of 2% (Fig. 3). The active substance is humic acid, which has a high absorption capacity of binding to each different toxic substance. Humic acid content in the dry matter of preparation used was 62%.

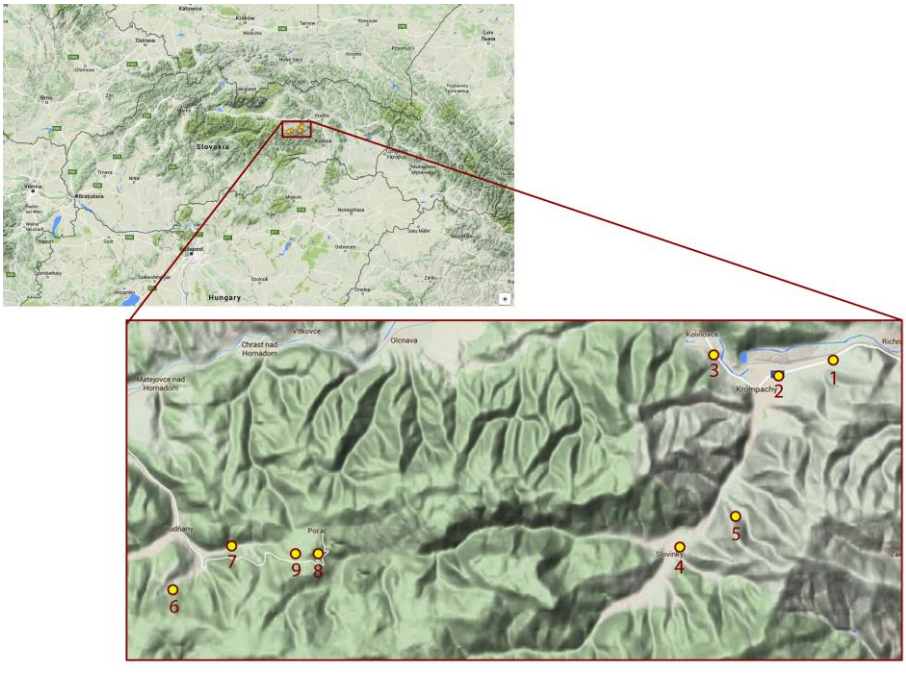

Fig. 1. Location of investigated areas in the Central Spis (Slovakia).



Fig. 2. Permanent grassland in the field of immission heap in the Central Spiš (Slovakia).



Fig. 3. HUMAC Enviro 100% natural substance (left – dust form, right – granula form).

3. RESULTS AND DISCUSSION

Former mining complex are problematic areas, especially with regard to environmental contamination by heavy metals (Manankovska & Steinnes 1995; Wilcke & Kaupenjohann 1998; Bálintová *et al*. 2013). In the Eastern part of Slovakia, copper concentration is mainly influenced by Fe-Cu-Hg-Ba mineralization (up to 495 mg kg^{-1}) near the village Rudňany (Urminská 2013). Human activities such as mining copper (Cu) contamination of soils, which must be removed Cu are non-degradable and toxic posing a threat to human health and ecosystem functioning (Alloway 1995). In the studied area, copper has been long mined and processed, therefore the measured values at seven sites exceeded the limit value (60 mg kg^{-1}) on average of more than 7 times the permanent grasslands. The largest copper pollution was recorded on permanent grasslands in the cadastral area Krompachy (1271 mg kg^{-1}, Table 1), due to the presence Kovohuty Krompachy, which was an important centre of colour metallurgy within Hungary at the beginning of the 19 century (Angelovičová & Fazekašová 2014; Takáč *et al.* 2008). According to our findings, Šefčík *et al.* (2008) categorized soils of Central Spiš as moderately to heavily contaminated with copper.

The value of the exchange soil reaction (pH in KCl or pH in $CaCl_2$) is considered in the literature as one of the most important parameters which influence the soil, in particular the metals of bio-friendly manner, and the sorption parameters of sorbents (Fazekašová *et al.* 2014; Igaz *et al*. 2009). The solubility of copper compounds is lowest in the range of pH 7 to 8 (Makovníková *et al.* 2006). The pH/KCl values ranged from 4.5 (strongly acidic) to 7.7 (alkaline) in investigated areas (Table 1).

Table 1. The copper content and values of soil reaction to the investigated areas in the soil of Central Spiš (Slovakia).

	Location name	Copper [mg kg^{-1}]	pH/KCl
1	KR 1	718	7.7
2	KR 3	436	5.1
3	KR 4	1271	4.8
4	SL 1	89	5.3
5	SL 4	166	7.3
6	RD 1	47	5.7
7	RD 4	35	6.0
8	PR 3	104	4.8
9	PR 4	257	5.5
	Threshold value*	60	

* Threshold values according to Act No. 220/2004 Coll.

The results of experimental measurements have shown that in an aqueous solution which has been taken from samples containing the above-limit content of Cu, the Cu content is over limit in all samples (0.04 - 0.87 mg l^{-1}, 0.02 Governmental limit no. 269 /2010 surface water) which represents 13 times the limit values. Followed by application of 2% HUMAC Enviro substances in aqueous solution, we found Cu in samples from 0.03 to 0.30 mg l^{-1} after 5 days. The average value was 0.15 mg l^{-1} Cu and its excess was 8 times. We found 40% reduction of Cu by comparison with control samples. Allowed limit has been met by 2 samples (Fig. 4).

In compliance with our findings, numerous studies show that natural substances based on humic acids are considered highly effective sorbents of various contaminants (Xu & Zhao 2013; Cattani *et al*. 2009; Olu-Owolabi, Popoola & Unuabonah 2010; Sounthararajah *et al.* 2015; Xu *et al*. 2013; Igaz *et al*. 2011).

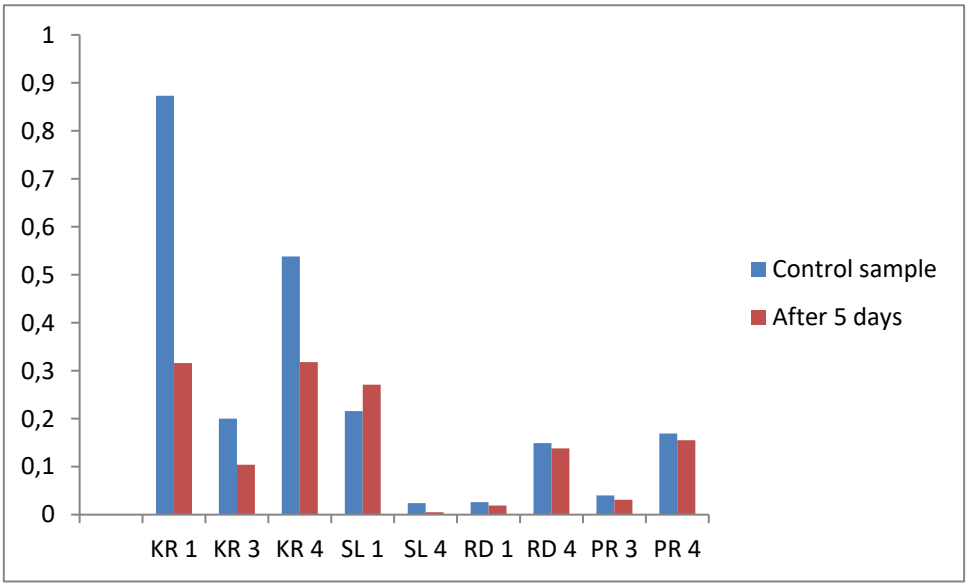

Fig. 4. Copper content (mg 1^{-1}) in an aqueous solution of the control samples and with the addition of 2% HUMAC Enviro after 5 days.

4. CONCLUSIONS

The results of experimental measurements have shown that the application of 2% of a natural substance HUMAC Enviro into the aqueous solution prepared from the samples of contaminated soils from Central Spiš (Slovakia), there was a reduction of the Cu by 40% after 5 days in comparison with the control samples. In response to this finding, as well as numerous global researches aimed at exploring the impact of humic acids in environmental compartments, the application of natural substance HUMAC Enviro seems to be important in addressing current environmental problems related to environmental contamination.

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