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The Effect of Natural Substance HUMAC Enviro on Reducing the Concentration of Copper and Mercury in Contaminated Soils

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Abstract

The concentration of copper and mercury in soils that are found at immission field of mining dumps, heaps and ponds, as the remains of mining-industry activity in Central Spiš region (Slovakia), were investigated. The concentration of copper and mercury in the soils were in the range of 35-1271 and 0.4-32.7 mg kg^{-1}, which exceeded the upper limits of potentially toxic elements concentration for agricultural soils of Slovakia (Act No. 220/2004 Coll.). The result from this study demonstrated that the soils in the region of Central Spiš had endured severe copper and mercury pollution. Subsequently, the laboratory tested the effect of a natural substance HUMAC Enviro on the reduction of copper and mercury in contaminated soils. The statistical analysis methods used in this study, namely Wilcoxon Matched Pairs Test, proved a statistically significant influence of the natural substance HUMAC Enviro on the reduction of copper content in an aqueous solution, in the case of mercury, the statistical significance was not proved. The application of natural substance HUMAC Enviro based on humic acids seems to be important in addressing current environmental problems related to environmental contamination

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Introduction

The sources of soil contamination by heavy metals include atmospheric deposition, metallurgy, burning fossil fuels (especially coal), automobile sources (automotive industry), organic and mineral fertilisers, liming, pesticides, sludge from sewage treatment plants, household, and industrial waste. At the same time, soils have a natural content of heavy metals released from a parent rock in the process of pedogenesis. Extracting and processing of raw materials for copper production, electrical engineering industry and the manufacture of alloys belong to the most important sources of copper in the environment. Its natural content in soils ranges from 20 to 30 mg kg^{-1}. The recommended limit for carrying out decontamination is 500 mg kg^{-1} for soils and 500 mg l^{-1} for ground waters. In contaminated soils, it is present in the form of Cu^{2+} ions, often in the complexes with organic ligands [1]. Copper is bound inaccessibly, mainly as a result of the formation of complexes with humic acids which are characterized by a very slow speed of solubility and they are penetrating into such places in the structure of humic acids which they are very difficult to release from [2].

The most important sources of copper appearance in the environment include ore processing, electrochemical productions, electrical engineering industry, coal combustion and the manufacture of protection products in agriculture. All mercury compounds are extremely toxic to humans. The natural content of mercury in soils ranges from ones to tens of micrograms per a kilogram. The recommended limit for carrying out decontamination is 1500 mg kg^{-1} for soils and 500 mg l^{-1} for ground waters. Mercury has a strong tendency to form complexes with organic components of soils; it forms stable complexes with various organic ligands as a cysteine, amino acids and hydroxycarboxylic acids [1].

The main factors which influence the input of heavy metals from soils to a plant include soil reaction, granularity, content and quality of organic substance, redox potential, fertilization, the presence of other elements, sort and variety of a plant, as well as the method of cultivation [3, 4]. The maximum mobility of copper occurs by pH lower than 4.5 and higher than 7.0, the mobility of mercury is not dependent on pH [5]. Soil organic substance characterized by excellent absorption qualities influences bioaccessibility of metals, the increasing content of organic substance increases considerably the sorption of metals [3,5,6].

The ability of metal binding is one of the most important properties of humic substances. In natural systems, these substances can bind metals pollutants and significantly affect transport phenomena, toxicity, regeneration and cleaning processes. They have application in crop and animal production for increasing productivity. They are natural substances and environmentally friendly [7].

In recent years, the remediation of the 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 sorbents to remove contaminants due to high sorption capacity [1].

The paper presents results of the laboratory which tested the effect of a natural substance HUMAC Enviro on the reduction of copper and mercury in contaminated soils.

Materials 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

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extensive anthropogenic forms. Rudňany - Gelnica burdened area has an extent of 357 km^2. The relief is 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 from -2 to -5 °C and the average July temperature of 13-15 °C [8,9]. Climate and soil characteristics of investigated areas in the Central Spiš (Slovakia) are detailed in Table 1.

Nine 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 Porač (8 – PR3, 9 – PR4) (Figure 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. We studied and evaluated soil reaction in 1N solution KCl. The content of Cu and Hg 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) [10].

As a sorbent, we used 100% natural substance HUMAC Enviro made from net source oxihumolite (brown coal) in concentrations of 2%. The active substance is a 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%.

Dell Statistica 13 software was used for all data analyses. The statistical analysis methods were used in this study, namely Wilcoxon Matched Pairs Test.

	Location name	GPS	Altitude	Climatic region	TS	Tjan	Tveg	Soil type
1	KR1	N48° 55' 19.4" E20° 53' 58.1"	576	mild warm – mild humid	2500 - 2200	- 5 - 2	13 - 15	Cambisols - loamy
2	KR3	N48° 55' 06.8" E20° 52' 51.6"	530	mild warm – mild humid	2500 - 2200	- 5 - 2	13 - 15	Cambisols - loamy
3	KR4	N48° 55' 23.3" E20° 51' 32.3"	450	mild warm – mild humid	2500 - 2200	- 5 - 2	13 - 15	Cambisols - loamy
4	SL1	N48° 52' 48.9" E20° 50' 51.1"	550	mild cold – mild humid	2200 - 2000	- 3 - 6	12 - 14	Cambisols - loamy
5	SL4	N48° 53' 14.1" E20° 51' 57.8"	568	mild cold – mild humid	2200 - 2000	- 3 - 6	12 - 14	Cambisols - loamy
6	RD1	N48° 52' 14.9" E20° 40' 27.1"	386	cold – humid	2000 - 1800	- 4 - 6	12 - 13	Cambisols - sandy loamy
7	RD4	N48° 52' 49.0" E20° 41' 38.1"	600	cold – humid	2000 - 1800	- 4 - 6	12 - 13	Cambisols - loamy
8	PR3	N48° 52' 43.6" E20° 43' 30.7"	599	very cold – humid	<1800	- 5 - 6	10 - 11	Cambisols - loamy
9	PR4	N48° 52' 44.3" E20° 43' 02.3"	603	very cold – humid	<1800	- 5 - 6	10 - 11	Cambisols – loamy

Table 1: Climate and soil characteristics of investigated areas in the Central Spiš (Slovakia).
TS - temperature sum TS >=10°C

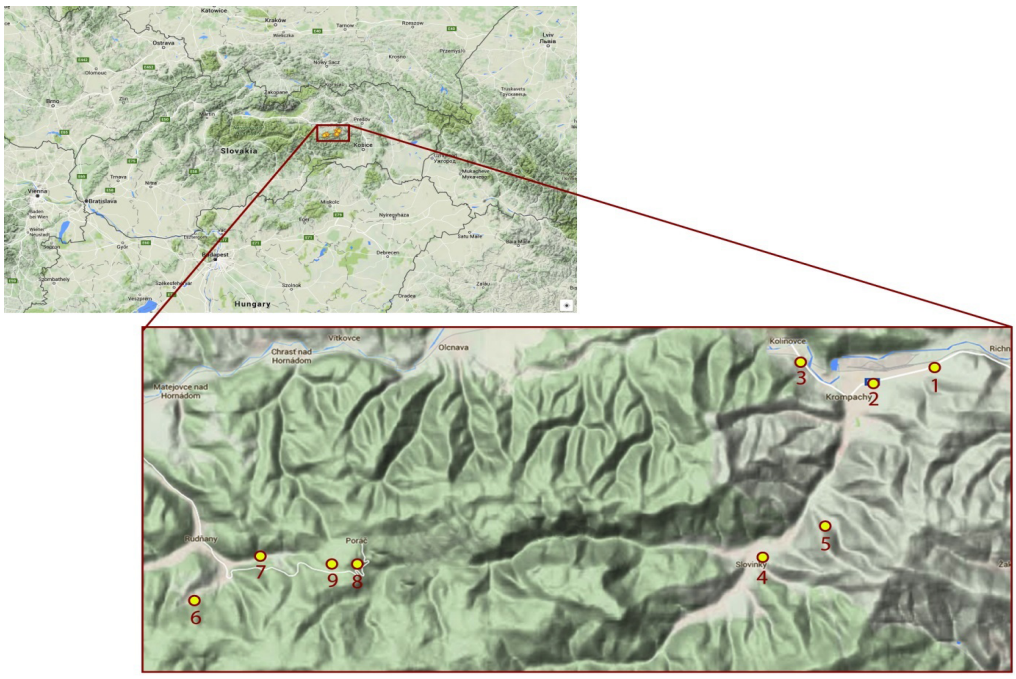

Figure 1: Location of investigated areas in the Central Spiš (Slovakia).

Results and Discussion

Former mining complexes are problematic areas, especially with regard to environmental contamination by heavy metals [11-13]. In the Eastern part of Slovakia, copper and mercury concentration are mainly influenced by Fe-Cu-Hg-Ba mineralization [14]. Human activities such as mining copper and mercury contamination of soils which must remove Cu and Hg are non-degradable and toxic posing a threat to human health and ecosystem functioning [6]. In the studied area, copper and mercury have been long mined and processed; therefore, these heavy metals reach the highest values area-wide.

The largest copper pollution was recorded on permanent grasslands in the cadastral area Krompachy (1271 mg kg^{-1}), due to the presence of Kovohuty Krompachy which was an important centre of colour metallurgy within Hungary at the beginning of the 19 century [3,15]. The copper limit values were exceeded at seven investigated localities (Table 2). According to our findings, [16] the categorized soils of Central Spiš are moderately to heavily contaminated with copper.

The presence of mercury in soils of the loaded area results from a long-term ore extracting and processing in Rudňany. The measured values of ore exceeded the limit values at six localities (Table 2). The most serious contamination was found in the territory of Poráč close to which there are many heaps of mining waste which come from the production of mercury in Rudnaňy situated. The measured values of mercury were exceeded up to 66 times. The mentioned findings were published also in papers [15,17]. Our previous researches also showed a considerable increase in the mercury appearance in plants [18].

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 [19]. The solubility of copper compounds is lowest in the range of pH 7 to 8 [2]. The maximum mobility of copper occurs by pH lower than 4.5 and higher than 7.0, the mercury mobility is not dependent on pH [5]. The pH/KCl values ranged from 4.8 (strongly acidic) to 7.6 (alkaline) in investigated areas (Table 2).

	Location name	Copper [mg kg^{-1}]	Mercury [mg kg^{-1}]	pH/KCl
1	KR 1	718	4.57	7.7
2	KR 3	436	3.39	5.1
3	KR 4	1271	6.74	4.8
4	SL 1	89	0.45	5.3
5	SL 4	166	0.43	7.3
6	RD 1	47	8.46	5.7
7	RD 4	35	0.35	6.0
8	PR 3	104	18.9	4.8
9	PR 4	257	32.7	5.5
	Threshold value*	60	0.5	

Table 2: The copper, mercury content and values of soil reaction to the investigated areas in the soil of Central Spiš (Slovakia).
*Threshold values according to Act No. 220/2004 Coll. of Laws.

The results of experimental measurements showed that also in the aqueous solution which was made from the samples containing the Cu contents over limits, the Cu content was over limits in all samples (0.03 – 0.87 mg l^{-1}, limit 0.02 Government regulation n. 269/2010 of surface water) which represent 13 times the limit values. Followed by the application of 2% of HUMAC Enviro substance into an aqueous solution, we found 0.03 – 0.32 mg l^{-1} Cu after 5 days. The average value was 0.16 mg l^{-1} Cu and its excess was 8 times. By comparing with the control samples, we found out 35% reduction of Cu content. The allowed limit was met by 2 samples (Figure 2).

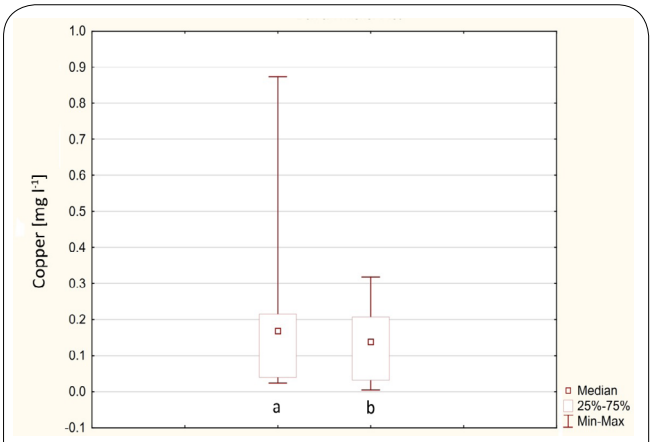

Figure 2: The range of monitored copper content (mg l^{-1}) in an aqueous solution of the control samples (a) and with the addition of 2% HUMAC Enviro after 5 days (b).

In aqueous solutions, the mercury content also exceeded the limits. The average Hg value in an aqueous solution was 0.0014 mg l^{-1} which represent 14 times the limit values (limit 0.0001 mg l^{-1} Government regulation n. 269/2010 of surface waters). The allowed limit was met by 2 samples 5 days after applying 2% of HUMAC Enviro substance into an aqueous solution, we found out the reduction of the limit values of mercury only in two tested samples (Figure 3).

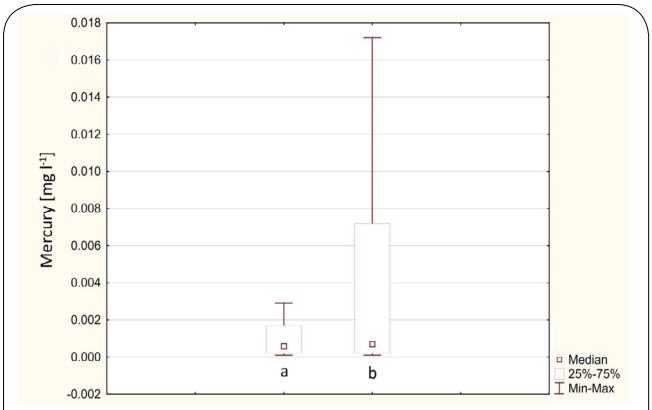

Figure 3: The range of monitored mercury content (mg l^{-1}) in an aqueous solution of the control samples (a) and with the addition of 2% HUMAC Enviro after 5 days (b).

Using the statistical analysis methods used in this study, namely Wilcoxon Matched Pairs Test, we found out statistically significant influence of natural substance HUMAC Enviro on the reduction of copper content in aqueous solution what confirmed our assumption that the increasing content of organic substance in soil significantly increases the sorption of metals, mainly the metals with high affinity to organic substance. In the case of mercury, our results were not statistically significant.

The results of Wilcoxon Matched Pairs Test are shown as p-value (Table 3). In compliance with our findings, numerous studies show that natural substances based on humic acids are considered highly effective sorbents of various contaminants [20-24].

Parameter	Valid N	T	Z	p-value
p <.05000				
p <.01000				
Copper (in an aqueous solution) [mg l^{-1}] & Copper (in an aqueous solution with 2% HUMAC Enviro after 5 days) [mg l^{-1}]	9	0	2.66557	0.007686
Mercury in an aqueous solution [mg l^{-1}] & Mercury (in an aqueous solution with 2% HUMAC Enviro after 5 days) [mg l^{-1}]	6	4	1.362773	0.172956

Table 3: The results of Wilcoxon Matched Pairs Test.
Valid N - the total number of pairs, T - Test statistic, Z - Z-score

Conclusion

The result from this study demonstrated that the soils in the region of Central Spiš (Slovakia) had endured severe copper and mercury pollution. The results of the 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), caused a considerable reduction of copper content. Using the statistical analysis methods, namely Wilcoxon Matched Pairs Test, in this study, we found out a statistically significant influence of a natural substance HUMAC Enviro on the reduction of copper content in an aqueous solution, in the case of mercury, the statistical significance was not proved. 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 the natural substance HUMAC Enviro seems to be important in addressing current environmental problems related to environmental contamination.

Competing Interestes

The authors declare that they have no competing interestes

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