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The change in heavy metal content in soil profiles from various Slovak burden areas

Zmiany stężenia metali ciężkich w profilu glebowym z wybranych obszarów obciążonych środowiskowo na Słowacji

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Słowa kluczowe: metale ciężkie, Słowacja, gleba, obszary obciążone środowiskowo

Abstract

The aim of this work is to show the importance of monitoring the hygiene quality evaluation of soil profile in the Slovak Republic area. In the past, when no emphasis was laid on ecology, as it is nowadays, there was an uncontrolled emission of pollutants from different fields of anthropogenic activities. The consequences are manifested even today, and immediate and expensive solutions are much needed.

In this work, the results of the research on the degree of heavy metal contamination in the soil profile as well as plant availability have been presented, which depended on the soil reaction in the 'Štiavnica Hills' and 'Žitný ostrov' areas. The choice of these areas is related to specific areas mentioned above that are characteristic of anthropogenic activity, besides factors such as natural (geochemical) contamination and intensive agricultural activity.

All the soil samples were analysed to give a changeable soil reaction. Analyses on heavy metal in the aqua regia extract (total content) that is, risky elements in their mobile form contents in the NH_4NO_3 c = 1 mol•dm^{-3} leach and humus content according Tjurin were conducted.

Streszczenie

Celem pracy jest wykazanie konieczności monitorowania i szacowania jakości profili glebowych na obszarze Republiki Słowacji. W przeszłości, gdy nie kładziono nacisku na ekologię w takim stopniu jak obecnie, do atmosfery dostarczane były niekontrolowane ilości zanieczyszczeń pochodzących z różnych obszarów działalności człowieka. Konsekwencje tych działań znajdują swoje odzwierciedlenie także obecnie, zatem potrzebne są natychmiastowe i kosztowne rozwiązania.

W pracy zaprezentowano rezultaty badań nad stopniem zanieczyszczenia profili glebowych metalami ciężkimi, jak również ich biodostępność w zależności od odczynu gleby na obszarze Gór Szczawnickich (Štiavnicke Vrchy) i Wyspy Żytniej (Žitný ostrov). Obszary badań wybrano ze względu na ich specyficzny charakter wynikający z istnienia zanieczyszczeń antropogenicznych jak i naturalnych (geochemicznych) oraz intensywnej uprawy rolniczej.

Próbki badano przy zmiennym odczynie gleb. Analiza metali ciężkich obejmowała: określenie całkowitej zawartości w wodzie królewskiej, określenie mobilnych form poszczególnych metali w NH_4NO_3 c = 1 mol•dm^{-3} w odpływach oraz zawartość substancji organicznej wg Tjurina.

1. INTRODUCTION

One of the most important groups of hazardous substances in the environment is heavy metals [Póti et al. 2012]. Heavy metals are among nondegradable contaminants, which are characterised by different sources of origin, properties and action on living organisms [Tóth et al. 2005]. The risk elements are biologically irreplaceable microelements (eg, Cu, Zn, Mn and others) as well as numerous non-essential chemical elements (Cd, Pb, Hg, etc.). The risks lie in ecotoxicity and its accumulation in biotic and abiotic components of the environment [Vollmannová et al. 2007].

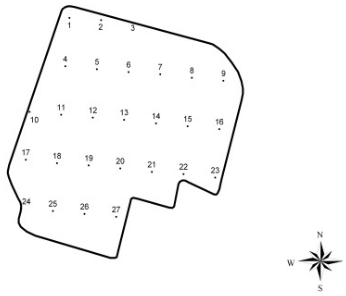
Heavy metals are an ubiquitous part of the environment as a result of the mutual natural and anthropogenic activities that cause an increased exposure of human populations to their effects through various channels [Poty et al. 2012; Wilson & Pyatt 2007]. Increasing concentrations of certain trace elements, especially their mobile forms, can cause serious environmental concern about contamination and accumulation in soil, vegetation, animals, surface and ground waters [Chopin & Alloway 2007].

Soil as a conglomerate of mineral components, organic matter (humus, living organisms), air and water is vital for a healthy and viable population. In today's urban areas, the soil is shaken. The most affected are the roads and adjacent areas, industrially used areas and regions that are affected by emissions from metalworking companies. Anthropogenic material (exhaust, oil residue, particles of tire components, weathered surfaces of roads) together with the natural biogenic material (fallen leaves and other plant material) can adsorb dust on its surface and thus represent a potential vector for contamination in a larger area [Omar et al. 2007].

2. MATERIALS AND METHODS

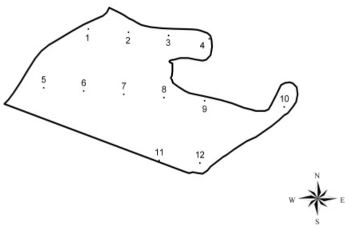
For the purpose of this paper, we selected two sites from different polluted areas of the Slovak Republic. The first is the site of ŠM-01 from the 'Žitný ostrov', namely Kameničná (Komárno District), which represents the area with a low level of contamination with high production potential, and the other is the dry meadow land, which is located within the boundaries of the village in the district Dudince – Krupina, which represents location with extremely high levels of contamination (particularly alluvial river area Štiavnica).

Land Hadovce 01 (ŠM-01) is located north of Komárno, in the urban district of Hadovce. It is in the report Agrodružstvo Kameničná. Loca-



tion coordinates are: 47°47.083' north latitude (φ) and 18°05.417' E (λ). Plot area is 40.9 hectares. Parcel identification number is 4703/1. Valuated soil-ecological unit of land is the 0024004th Soil type ČMCC – Chernozem – soil type and carbonate medium – silt-loam (ssh). Altitude of land ranged from 104.5 to 108.3 m n. m.

Dry meadows Land (SL) is located in the southwest corner of the urban village Dudince. It is under the administration of PD Agrohont Dudince. Location coordinates are: 48°10.386' north latitude



(φ) and 18°52.266' E (λ). Its area is 14.4 hectares. Parcel identification number was 2905/1. Valuated soil-ecological unit of land is the 0106005th Soil type HML – luvisem brown soil type and soil medium – loam (sh). Altitude of land was at the level of 138.9 m n. m.

The soil samples from the study plots were taken from a soil probe to a depth of 80 cm on the plot SL and 70 cm on the plot ŠM-01, and sampling was performed at intervals of 0.1 m from the soil surface. Soil probes are dug in the geometric centre of the plot. In all soil samples, analysis was performed to determine the exchange pH_{KCl} soil reaction, and the total content of mobile forms of studied heavy metals (Cd, Pb, Zn and Cu) in aqua regia extract and extract of NH_4NO_3. The limit values and critical risk elements monitored, by which we determine the level of contamination, are defined by law 220/2004 [Kobza et al. 2007]. For the purpose of finding cropping potential soil, analysis was performed to determine the content of humus by Ťjurina. Terminal was set up for detecting heavy metals in the extracts obtained by atomic absorption spectrometry on a Varian AA 240 FS. All obtained results were subjected to statistical analysis, mathematical program with STATISTICA 10.0 cz, at the level of basic descriptive indicators and regression analyses with confidence level $p < 0.05$.

3. RESULTS AND DISCUSSION

One of the most important agro-chemical indicators of sanitary quality of the soil is a soil exchange reaction, which greatly affects the performance and mobility of hazardous elements in the soil environment. As for the quality of soil structure and chemical composition of the land ŠM-01 between pointing and more valuable than land SL . Exchangeable soil reaction on the land stood at 7.55 ± 0.35 (median ± standard deviation), suggesting that the soil on the land environment is alkaline to strongly alkaline, the exact opposite of the situation in SL land where the soil exchange reaction stood at 6.74 ± 0.27. Such soil pH is defined as the plot which is slightly acidic to neutral. Figure 1 contains graphs that show the sequence of changes in the in-depth exchange of soil reaction and transfer regression curve. Different orientations of curves are mainly due to the bedrock on which the land is situated. The plot SL is a correlation between pH and depth of sampling negative, which is probably due to high ground water level and also high sulphates and sulphites. On the other hand, for the land ŠM-01 the situation is reversed, with the correlation depth and the pH positive, due to the high content of basic cations and clay minerals in the subsoil profile and high carbonate [Atlas krajiny SR, 2002].

Figure 2 graphically shows the total contents of heavy metals observed in the extract of aqua regia and their depth sequence. The total content of cadmium in grounds SL stood at 15.85 ± 3.85 $mg \bullet kg^{-1}$, Lead: 1565.0 ± 311.17 $mg \bullet kg^{-1}$, Zinc: 2097 ± 8.83 $mg \bullet kg^{-1}$ and Copper: 115.8 ± 6.73 $mg \bullet kg^{-1}$. In the case of Cd and Zn, the highest concentration of sme was found in the layer 0.8 to 0.9 m, in the case of lead in the layer 0.5 to 0.6 m and in the case of copper in layer 0.3 to 0.4 m, which is probably due to the long copper intensive application of plant protection products. According to the Kabata-Pendias – Pendias [2001], clark content in normal agricultural soils is around 20 $mg\ Cu \bullet kg^{-1}$ soil. A similar issue was addressed by a number of authors, for example, when Chopin et al. [2008] found that in Champagne (France), the copper content after long-term application of copper fungicide "Bordeaux" in topsoil term stood at around 230 $mg \bullet kg^{-1}$, and such an amount exceeds the natural content by more than 10-fold. Cadmium, lead and zinc values obtained a range of high clark content, and the average concentration over the entire horizon was well above the limit values of the relevant standard. The contents of Cd, Pb and Zn are positively correlated, and the copper content slightly negatively correlated with the depth of sampling.

Mobile fractions studying the risk elements for SL plot (Fig. 5) are closely correlated with their total content. The only exception is copper, which is strongly negatively correlated (compared to the overall content) with the depth of sampling. The data obtained are moving in the following levels: Cd: 0.29 ± 0.25, Pb: 0.19 ± 0.06, Zn: 8.63 ± 8.83 and Cu: 0.25 ± 0.15. In the case of cadmium, critical values exceeded nearly three times the median, Pb: two times, Zn more than fourfold, and copper was not exceeded.

The situation on the land ŠM-01 in the overall content of the monitored elements of risk is vastly different in almost all studied factors. Hazardous elements are significantly lower owing to the absence of sources of potential environmental contamination (excluding transport and application of plant protection products), other soil-forming factors that operate in the development of land in this area (naplaveniny rivers Váh and Danube) as well as other physical, physico-chemical and chemical properties of soil [Atlas krajiny SR, 2002].

The content of all monitored elements (except cadmium) is negatively correlated with depth of sampling soil samples, with the highest content found in the upper two sampling layers. This situation is caused by long-term application of phosphate fertilisers and long-term use of agrochemicals. Low subsoil horizon points out the fact that the natural content of elements in the soil is substantially lower and is not influenced by soil-forming substrate [Linkeš 1997]. Cadmium content, the only element of the positive correlation is around 1.05 ± 0.34, and the maximum level was found in

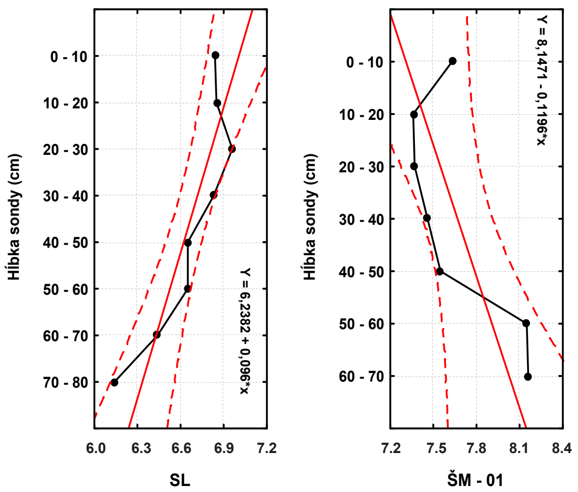


Fig. 1. The changeable soil reaction graphs in soil profile on monitored plot with the regression curves and significance level ($p < 0.05$) in mg•kg^{-1}

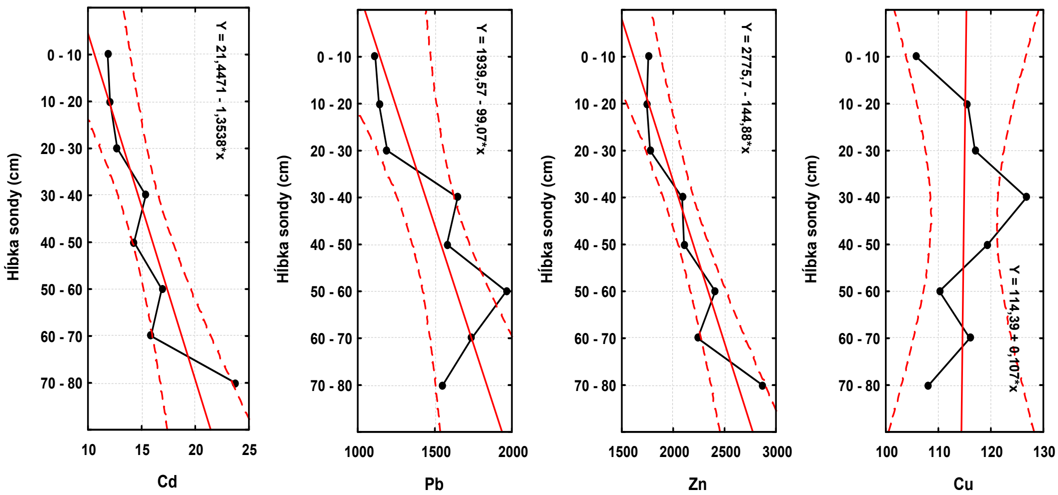


Fig. 2. The total content of heavy metal graphs in soil profile on the monitored plot *SL*

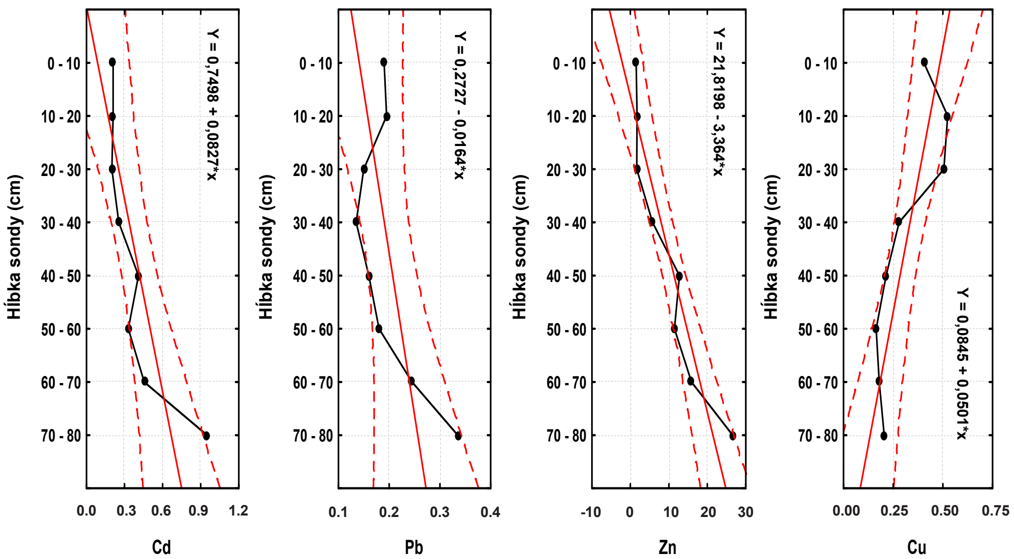


Fig. 3. The mobile fraction content of heavy metal graphs in soil profile on the monitored plot *SL* with the regression curves and significance level ($p < 0.05$) in mg•kg^{-1}

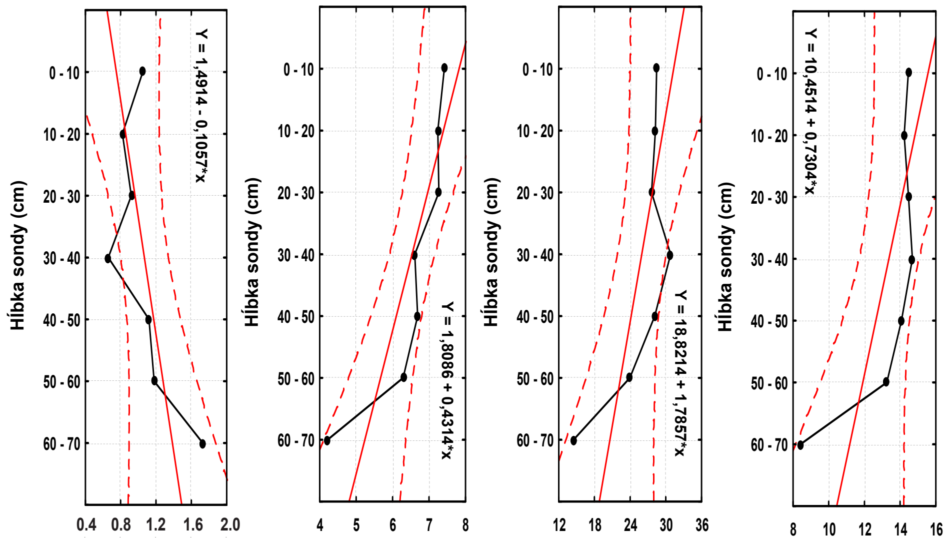


Fig. 4. The total content of heavy metals graphs in soil profile on monitored plot *ŠM-01* with the regression curves and significance level (p < 0,05) in mg • kg^{-1}

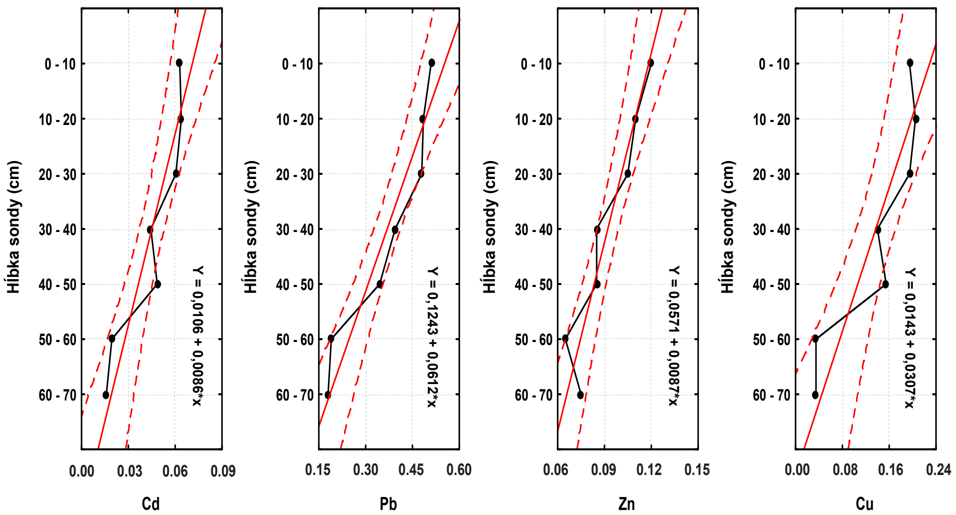


Fig. 5. The mobile fraction content of heavy metals graphs in soil profile on monitored plot *ŠM-01* with the regression curves and significance level (p < 0.05) in mg • kg^{-1}

the lower run (1.73 mg • kg^{-1}). The content of the other elements studied were in the following levels Cd: 0,58 ± 0,18 mg • kg^{-1}, Pb: 6.69 ± 1.10 mg • kg^{-1}, Zn: 28.15 ± 5.45 mg • kg^{-1} and Cu: 14.23 ± 2.23 mg • kg^{-1}. The limit values for the total content of elements studied were exceeded only by cadmium (at the median level of 5%).

The content of cellular fractions of all studied risk elements in the grounds ŠM-01 is negatively correlated with the depth of soil sample collection, which is probably due to the increasing exchangeable soil reaction in relation to depth. Most mobile forms of heavy metals are found in the upper three sampling layers, which are the most active area for the reception of all elements in plant roots.

The content of mobile forms of elements studied ranged in the following levels: Cd: 0.048 ± 0.02 mg • kg^{-1}, Pb: 0.395 ± 0.14 mg • kg^{-1}, Zn: 0.085 ± 0.02 mg • kg^{-1} and Cu: 0.155 ± 0.07 mg • kg^{-1}, which exceeded the critical value at the median level was only for lead, by almost 300%.

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