

## THE MIGRATION OF CADMIUM AND LEAD FROM SOIL TO PLANTS IN AREA OF HEAVY METAL INDUSTRY PRODUCTION

TOMAS J.<sup>1</sup>, KOPERNICKÁ M.<sup>1</sup>, BYSTRICKA J.<sup>1</sup>, TOTH T.<sup>1</sup>, SLAVIK M.<sup>1</sup>,  
MUSILOVA J.<sup>1</sup>, ZUPKA S.<sup>1</sup> and VOLNOVA B.<sup>1</sup>

<sup>1</sup> Slovak University of Agriculture in Nitra, Faculty of Biotechnology and Food Sciences,  
Department of Chemistry, Tr. A. Hlinku 2, 949 76 Nitra, Slovakia  
E-mail: m.kopernicka@gmail.com

### ABSTRACT

The transition of cadmium and lead compounds from the organic soil layer into the local plants represents a significant risk of contamination of the food chain and can affect the health of the population. We have focused on the determination of the content of cadmium and lead in soil and biomass. The measured values were compared with the limit values laid down by the legislation of hazardous substances in the soil (Act No. 220/2004 Coll.). Samples of soil ( $n = 37$ ) and plants ( $n = 37$ ) were taken in the northern part of the Slovak Republic in the south to south-easterly direction from the source of contamination, which is an company in city Istebné. This company is the diversified manufacturer of ferroalloys in central Europe. The history of company is dated back to the year 1952, when first ferroalloys were manufactured in Slovakia. Soil samples were taken from a depth of 0.10 m and samples of plant material sampling were collected from the same sampling sites. We have defined the basic parameters that affect the mobility of heavy metals in soil (pH active, pH exchange, humus and oxidizable carbon). Analyzes to determine a bioavailable forms of cadmium and lead was performed by extraction of soil leachate in 50 cm<sup>3</sup> of NH<sub>4</sub>NO<sub>3</sub> (1 mol/dm<sup>3</sup>). Samples of the dried plant samples were mineralized by acid digestion using microwave digestion device MARS X-press. The end of determining the cadmium and lead content in the samples was performed by atomic absorption spectrometer Varian 240 FS. The average value of the active soil reaction was  $7.02 \pm 0.67$  and exchange soil reaction was  $5.91 \pm 0.79$ . Based on analyses of soil from the area could be described as a weakly acidic to neutral. The total content of cadmium and lead in soil and plants depends on the content of humus and oxidizable carbon. Median humus content in soil samples was  $3.27 \pm 3.41$  % in the case of oxidizable carbon  $1.90 \pm 1.98$  %. The cadmium and lead content in biomass increases with the content of heavy metals in soil and humus. The content of cadmium in soil samples was  $0.11 \pm 0.05$  mg/kg, which exceeded the limit value by 2.4 times. The lead content in soil samples was  $0.36 \pm 0.14$  mg/kg, which exceeded the limit value by 6.8 times. In the case of plant material, the average of cadmium content was  $0.20 \pm 0.27$  mg/kg and lead content was  $1.20 \pm 1.13$  mg/kg. The results are set out in the fresh biomass conversion of dry matter, whose average content was 30%. The limit values were exceeded in 22 ( $n = 37$ ) soil samples in the case of cadmium and lead in all 37 ( $n = 37$ ) samples.

**Keywords:** heavy metals, cadmium, lead, soil contamination, local biomass.

### 1. Introduction

Heavy metals present in soil and water naturally or as contaminants from human activities can cause bioaccumulation affecting the entire ecosystem and pose harmful health consequences in all life forms. Application of phytoextraction can reduce phyto-available metals in the soil and thereby diminish toxic metal contents in agricultural products (Zhi *et al.*, 2015). The most emissions come from industrial chimneys, heavy traffic emissions and population density (Feszterová *et al.*, 2012). The high metal content in tailings constitutes a primary environmental pollution source that affects soils, water and potentially the atmosphere (Pascaud *et al.*, 2015). Heavy metals, such as cadmium and lead are major environmental pollutants, particularly in

areas with high anthropogenic pressure. Heavy metal accumulation in soils is of great concern in agricultural production due to the adverse effects on food safety and marketability, crop growth due to phytotoxicity, and environmental health of soil organisms (Gill, 2014). Food safety is a major public health concern worldwide and food consumption has been identified as the major pathway for human exposure to certain environmental contaminants (Fries, 1995, Akinyele *et al.*, 2015). Plant species vary significantly in their ability to accumulate metals from contaminated soils and water. Metal hyperaccumulating plants are those that can accumulate unusual amounts of specific metals (Raskin *et al.* 1994). Baker *et al.* (1989), Baker *et al.* (2000) and Reeves *et al.* (2000) summarized research on hyperaccumulator plants. In addition the solution pH also affects the mobility and availability of metal ions with cationic species being more soluble at pH below 7.0 and anionic forms more soluble at pH above 7.0 (Chojnacka, 2010). Therefore, the pH of polluted solution becomes a crucial factor of the metal biosorption process in both non-living and living plants (Rajkumar *et al.*, 2009, Chocobar Ponce *et al.*, 2015). Addition of organic amendments, such as sewage sludge and green waste composts to soils enhances the physicochemical and biological conditions of soils, thereby improving plant growth. Some of these amendments are known to have immobilizing effects on metal(loid)s. The organic amendments can directly or indirectly alter the distribution and availability of metal(loid)s in soil (Hudec *et al.*, 2013, Bolan *et al.*, 2014).

## 2. Material and methods

The sampling was conducted in the district of Dolný Kubín, northern Slovakia. The samples of soil ( $n = 37$ ) and plant material ( $n = 37$ ) were taken in the south to south-easterly direction from the emission source. It is located in the catchment area of the emission source of processing plant in Istebné. Sampling points were defined by a hand-held navigation device Garmin 60 Cx, with an accuracy of  $\pm 2$  m. Samples of soil were collected from the depth of 0.00 to 0.10 m. The soils were sieved to  $<2$  mm, dried at room temperature and homogenized. Biomass material was taken from the same sampling sites. The samples were collected in June 2014. Cadmium and lead concentrations were measured in the soil and plant mineralization, obtained by treating the samples by  $10 \text{ cm}^3$  of aqua regia ( $2.5 \text{ cm}^3 \text{ HNO}_3$  and  $7.5 \text{ cm}^3 \text{ HCl}$ ) using microwave digestion unit Mars X-press 5 (CEM Corp., USA). The mineralization was carried out in teflon vessels at elevated temperature. The concentrations of metals were measured using atomic absorption spectrometry (AAS) in a Varian AA 240 Z (Varian, Australia) with GTA120 graphite furnace. Statistical analyses were performed using descriptive data analysis (minimum value, maximum value, median and standard deviation) by STATISTICA 12.0 software (Statsoft, USA). The significance of each variable was verified by LSD test. We used Pearson correlation coefficients at significance level of  $p < 0.05$  (weak statistical significance) and  $p < 0.01$  (very strong statistical significance) available at STATGRAPHICS Plus 5.1. We have created the graphs displayed as the 3D surface plot for statistical evaluation of results and program STATISTICA 12.0 was used to process gained data.

## 3. Results

Relatively wide range of active and exchangeable reaction in soil samples indicate different quality parameters of samples, which is reflected on the level of Cd and Pb contamination and content of heavy metals in biomass. The values of the active reaction and exchange reaction in soil indicate the high variability of the measured values. The soil samples are slightly acidic to strongly alkaline. Total content of Pb in soil and biomass correlated with the humus content and oxidizable carbon. These values indicate high level of organic matter of sampling points (Table 1).

Between content of monitored heavy metals in soil and pH value is a high positive correlation, content of organic mass is a low positive correlation. It shows a high impact of the monitored parameters because between content of Cd and Pb in biomass and content of Cd and Pb in soil is a high positive correlation (Table 2). The cadmium content in biomass increases with the cadmium content in the soil and humus content (Figure 2), despite the alkaline pH (Figure 1) as well as in the case of lead content in biomass (Figure 3, Figure 4).

**Table 1:** Cadmium and lead content in samples of soil and biomass and characteristics of monitored parameters of soil from study area.

Parameter	Unit	Minimum	Maximum	Median	RSD
pH (KCl)	-	3.91	7.20	5.91	0.79
pH (H <sub>2</sub> O)	-	5.64	8.25	7.02	0.67
humus	%	0.54	15.49	3.27	3.41
Cox	%	0.32	8.99	1.90	1.98
Cd in soil	mg/kg	0.05	0.25	0.11	0.05
Cd in biomass	mg/kg	0.00	0.93	0.20	0.27
Pb in soil	mg/kg	0.14	0.68	0.36	0.14
Pb in biomass	mg/kg	0.00	3.60	1.20	1.13

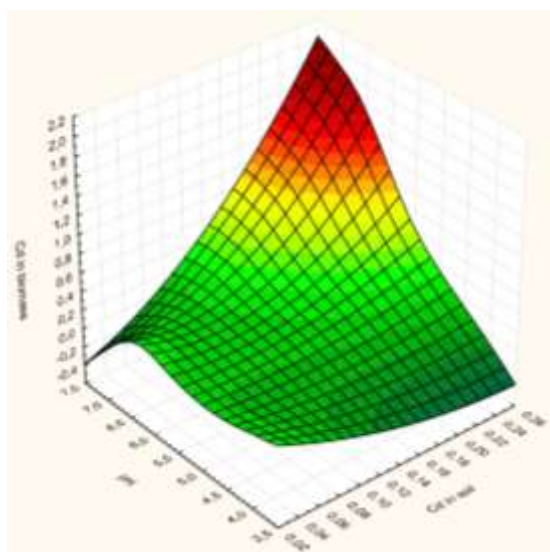
RSD – relative standard deviation (%)

**Table 2:** Statistical analysis of Cd and Pb content in soil and plant material and their relationship to the selected parameters.

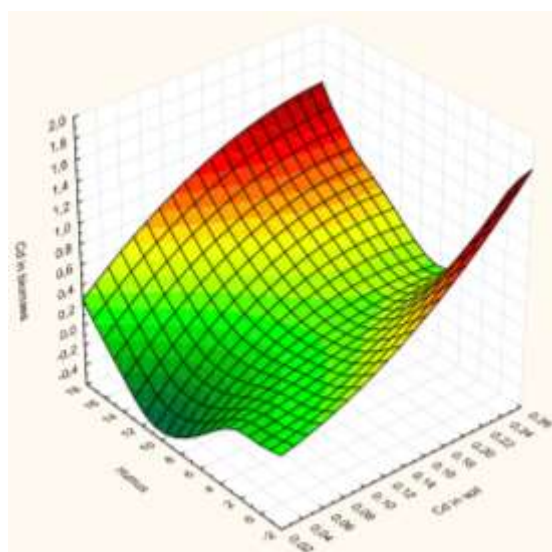
Parameter		Correlation coefficient (r)
Dependent	Independent	
Cd in soil	pH (KCl)	0.2548**
	pH (H <sub>2</sub> O)	0.3120**
	humus	0.5343*
	Cox	0.5346*
Cd in biomass	Cd in soil	0.4582**
Pb in soil	pH (KCl)	0.3749**
	pH (H <sub>2</sub> O)	0.4223**
	humus	0.5176*
	Cox	0.5179*
Pb in biomass	Pb in soil	0.3623**

\* weak statistical significance of the correlations ( $p < 0.05$ )

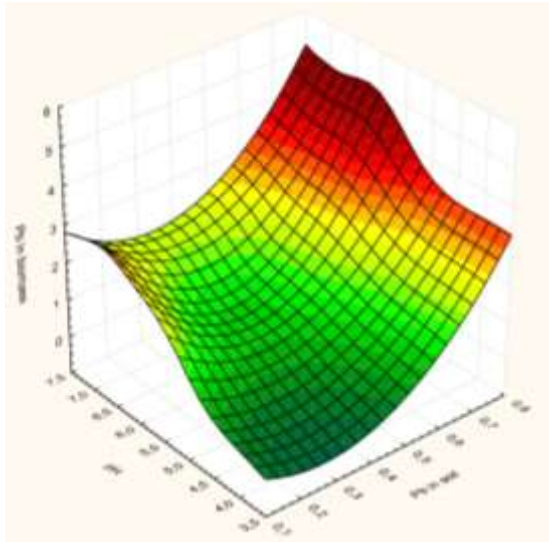
\*\* very strong statistical significance of the correlations ( $p < 0.01$ )



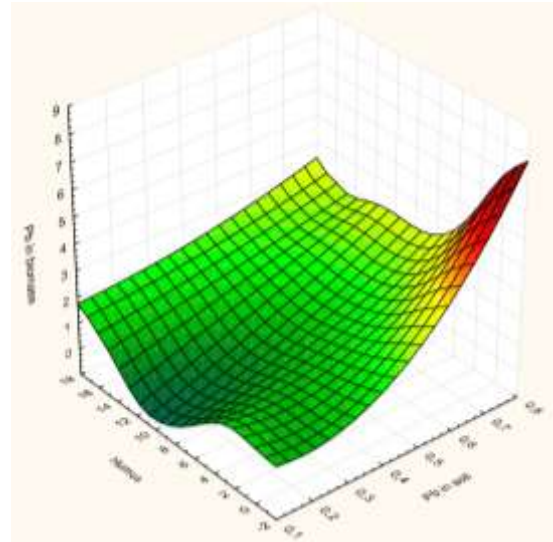
**Figure 1:** Evaluation of the effect of the Cd content in soil and pH to content of Cd in biomass



**Figure 2:** Evaluation of the effect of the Cd content in soil and humus to content of Cd in biomass



**Figure 3:** Evaluation of the effect of the Pb content in soil and pH to content of Pb in biomass



**Figure 4:** Evaluation of the effect of the Pb content in soil and humus to content of Pb in biomass

#### 4. Conclusions

The aim of our work was the determination of cadmium and lead content in soil and local biomass. The measured values were compared with the limit values set out legislation for the maximum quantity of hazardous elements in soil (according to Act No. 220/2004 Coll.). To evaluate of the quality of heavy metals in samples can be concluded that collected soil and plant samples were contaminated with cadmium and lead. The effect of pH and content of organic matter in soil on the concentration of cadmium and lead in biomass was confirmed. The contaminated plants pose a risk of heavy metal entry into the feed and food chain and thus a threat for population.

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