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COMPARISON OF TWO EMPIRICAL MODELS FOR SOIL TO RYEGRASS TRANSFER OF METALS IN BAIA MARE MINING AREA

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Abstract. The concentrations of Pb, Cu, Cd and Zn were assessed in ryegrass (*Lolium perenne*) and adjacent soil, collected in urban area of Baia Mare, Northwestern Romania. Aqua regia and DTPA (diethylenetriaminepentaacetic acid) metal extractable fractions were investigated in order to evaluate the mobility of metals in soil. Linear (based on transfer factors) and nonlinear (based on Freundlich's equation) regression models were used to describe the transfer of Pb, Cu, Zn, Cd from soil to ryegrass. The obtained results showed that the soil of Baia Mare is highly polluted with heavy metals, the majority of the total concentrations of all the investigated metals exceeded the alert levels for sensitive soils, according to Romanian legislation. The mean values for transfer factors were: 0.049, 0.027, 0.453 and 0.034 for Pb, Cu, Cd and Zn, respectively.The results showed that Freundlich-type function was more suitable than linear regression to predict Pb, Cu and Zn concentrations in ryegrass from the DTPA-extractable metal concentrations.

Key words: metals, soil, *Lolium perenne*, transfer factor, Freundlich's equation

1. INTRODUCTION

Heavy metals are toxic for living systems and can alter a vast array of metabolic processes. For example, cadmium can attack kidney, liver, bone, while lead is neurotoxic (Peralta-Videa et al., 2009), along with other health-endangering effects, such as blood enzyme changes, anemia and hyperactivity. Copper and Zn are essential elements, but in high concentrations increase the risk of adverse health effects (Bakirdere & Yaman, 2008). Divalent metals (such as copper and lead) stimulate the human breast cancer cell proliferation (Martin et al., 2003). Cadmium, Pb and Cu are considered members of a new class of nonsteroidal environmental estrogens (Choe et al., 2003).

For plants, soil is the main source of metals that can act as nutrients or contaminants, in function of their species and their concentrations. The metals transfer from soil to plants is a very complex process, depending on natural and anthropic factors (Kubova et al., 2008). In soil, the mobile and the immobile metal fractions should be differentiated, due to the fact that metals could be bound to soil organic and inorganic matter.

The aqua regia extractable metal fraction is often considered equivalent to the total metal content, and is an important step in estimating the general level of soil pollution, but does not provide information on the chemical nature and mobility of metal (Levei et al., 2009; Black et al., 2011, Lopes et al., 2012). In order to evaluate the mobility of metals in soil, different single or sequential chemical extractions can be used, with satisfactory results, but no method has been recognized as general for the bioavailability prediction (Mourier et al., 2011). The DTPA (diethylenetriaminepentaacetic acid) extractable content could be an indicator of the metals availability to plants and reflects their mobility (He & Singh, 1993; Miclean et al., 2009; Șenilă et al., 2011) and can be used in order to assess toxic effects and to study geochemical pathways (Fuentes at al., 2004).

For the prediction of a metal concentration in plants, based on its concentration in soil, mechanistic and empirical models can be used. In the literature, a great variety of existing models approaches is described (Michel et al., 2007, Guala et al., 2010, Zheng et al., 2011, Lopes et al., 2012), the difficulty lies in choosing the model that is the best suited for the prediction of metal transport for a certain system, taking into consideration the type of soil, species of plants and physicochemical properties of heavy metals.

The simplest empirical model is the linear equation, assuming equilibrium conditions, according to equation (1):

$$C_p = K \cdot C_s \qquad (1)$$

where C_p is the metal concentration in plant, K is a factor of metal uptake from soil to plant and C_s is metal concentration in soil (Pusz, 2008). The linear equation represents the transfer factor (TF), defined as the ratio between the contaminant concentration in plant and in dry soil (Chojnacka et al., 2005, Lopes et al., 2012, Big et al., 2012). Due to the complicated biophysical processes involved in plant uptake, the metal transfer was considered nonlinear, described by curvilinear functions, such as Freundlich-type equations (equation 2):

$$C_p = K_F \cdot (C_s)^a \qquad (2)$$

where K_F and a are the empirical Freundlich coefficients (Krauss et al., 2002; Pusz, 2008). This equation can be linearized by log-transformation (equation 3), according to Krauss et al., (2002):

$$\log C_p = \log K_F + a \cdot \log C_s (3)$$

Taking into consideration that some studies revealed good relationships between transfer factors and DTPA extractable metal concentrations in soil (Lopes et al., 2012) and also that Freundlich-type model is preferred for the prediction of some metals transport in the acidic soils (Michel et al., 2007), the objectives of this study were: 1. the assessment of the total and DTPA extractable contents of Pb, Cu, Cd, Zn in soils from Baia Mare urban area; 2. the comparison of two simple empirical models (linear, using the transfer factors and nonlinear, using the Freundlich's equation) used to predict Pb, Cu, Cd and Zn concentrations in ryegrass based on DTPA extractable metal concentrations in soil.

2. EXPERIMENTAL

This study was conducted in Baia Mare city, Maramures County, Northwestern Romania, where centuries of ore extraction, processing and metallurgical activities resulted in contamination with heavy metals of the surrounding environment and particularly the soils, due to the acid rains and heavy metal emissions (Lăcătușu et al., 1995, Lăcătușu et al., 2003, Lăcătușu et al., 2008, Damian et al., 2008, Damian et al., 2010, Levei et al., 2009, Șenilă et al., 2012a, Șenilă et al., 2012b).

In autumn 2010, 35 ryegrass samples and the adjacent soil were randomly collected in Baia Mare, covering both industrial and residential areas. Thus, soil and vegetation are complementarily sampled.

The coordinates of sampling points were recorded with a 310 Magellan GPS and are presented in figure 1.

Lolium perenne (ryegrass) is one of the grass species frequently studied due to the fact that it is inexpensive and well accumulates metals (Bidar et al., 2007; Black et al., 2011).

The soil samples were air-dried, ground and sieved. To determine the total metal content, fraction below 2 mm was digested in aqua regia (HCl 37.5% and HNO_3 65%), for 16 hours at room temperature and then, 2 hours, at reflux conditions, according to SR ISO 11466:1999. The extract was analyzed by inductively coupled plasma optical emission spectrometer (ICP-OES) using a SPECTRO FLAME spectrometer (SPECTRO, Kleve, Germany).

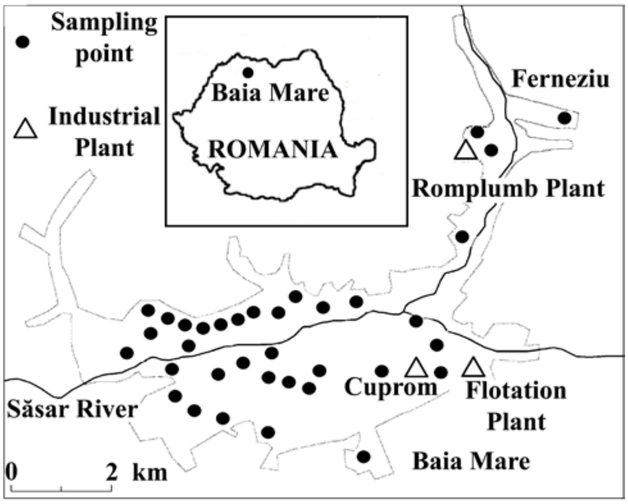

Figure 1. Sampling points in Baia Mare urban area

The available Pb, Cu, Cd, Zn contents in soil were determined by leaching the soil with DTPA solution (0.005 mol/L DTPA, 0.01 mol/L $CaCl_2$ and 0.1 mol/L triethanolamine (TEA), adjusted to pH 7.3 with 1 mol/L HCl solution) under continuous shaking for 2 h at 20ºC (SR ISO 14870:2002). The metal concentration extracted in DTPA was performed by inductively coupled plasma mass spectrometry, using ICP-MS ELAN DRC II spectrometer (Perkin Elmer, USA), that offers lower detection limits.

The plants were washed in distilled water, dried at 40°C, until constant weight and grounded to obtain a homogenized powder. An amount of 0.5 g sample was digested in 5 ml HNO_3 and 2 ml H_2O_2 in closed PTFE vessel microwave digestion system, Berghof MWS-3+ (Eningen, Germany) (Sucharova & Suchara, 2006). Metals concentrations were measured by ICP-MS.

The quantification of ICP-OES and ICP-MS was performed using an external calibration with multi-elemental Merck (Darmstadt, Germany) standard solution. All chemicals used were of high-purity reagent grade. Throughout all analytical work, ultrapure water (Millipore, 18.2 MΩ/cm) was used, prepared by a Milli-Q system (Millipore, Watford, Hertfordshire, UK). A multielemental standard solution of 1000 mg/L Cd, Cu, Pb, Zn (Merck, Germany) was used for calibrations.

The accuracy of the methods was checked by analysis of Standard Reference Material 2709 San Joaquin Soil (New York, USA) and two vegetable certified reference materials IAEA-359 Cabbage and NCS ZC85006 Tomato (LGC PromoChem GmbH, Wessel, Germany) within the quality control of determinations.

3. RESULTS AND DISCUSSION

3.1 Metal concentrations in soils and plants

The quality assurance and quality control of the analytical procedures consisted in replicate and certified reference material analyses. All soil and plant samples were analyzed in triplicate. The quoted results therefore represent the averages of triplicate analyses. The analysis of reference soil and plants materials showed a good agreement between the obtained results and the certified values, with recoveries between 92% and 106%.

The obtained values of contents for the investigated metals in soil and ryegrass varied widely, over a large range of concentrations. Descriptive statistics for aqua regia and DTPA extractable metals content in soil and for metals content in ryegrass is presented in table 1.

In soil, the mean total content of the investigated elements decreased as follows: Zn>Pb>Cu>Cd. According to Romanian legislation (Ministerial Order 956/1997) for sensitive soils, total Pb content exceeded the intervention level (100 mg/kg) in all samples, while total Cu, Zn and Cd contents exceeded the corresponding alert levels (100 mg/kg; 300 mg/kg; 3 mg/kg) in 77%, 94% and 66%, respectively. The highest metal contents were recorded in the soils situated near the former flotation plant and cooper smelter. Similar contents were found also in soils from Ferneziu area, located in the North-Eastern part of the city, in the proximity of the Pb smelter. DTPA-extractable metal contents represent 24.1 ± 9.7 % (mean ± standard deviation), 10.2 ± 5.94 %, 46.2 ± 26.0 % and 20.3 ± 9.4 % from total extractable content for Cu, Zn, Cd and Pb, respectively. The obtained values were comparable with those obtained by Lăcătușu et al., (1996) by using EDTA-CH_3COONH_4 extraction, at pH=7. The obtained mean concentrations for the investigated metals in soils were generally higher than those previously reported for the same area (Lăcătușu & Lăcătușu, 2008, Levei at al., 2009; Damian et al., 2010; Șenilă et al., 2012a, Șenilă et al., 2012b), due to some punctual samples where excessive concentrations were recorded, situated close to the industrial area, as previously described. Concentrations of the same order of magnitude were recorded also by Damian et al., (2008) in samples collected near the industrial plants (Cuprom and Romplumb). The mean concentrations of metals in plants decreased in the following order: Zn>Cu>Pb>Cd. Therefore, micronutrients such as Zn and Cu recorded the highest concentrations in plants, whereas Pb and Cd presented the lowest ones.

Table 1. Descriptive statistics for aqua regia and DTPA extractable metals content in soil and for metals content in ryegrass (mg/kg dw)

Metals		Min	Max	Mean	Standard deviation	Skewness	Kurtosis
Pb	aqua regia extractable	114	16230	1591	3073	3.96	16.7
Cu		38.1	1770	314	342	2.68	9.02
Cd		<0.5	29.9	6.60	7.44	1.68	2.48
Zn		114	9769	1829	2488	2.14	3.78
Pb	DTPA extractable	8.67	353	119	85.2	1.30	1.33
Cu		6.49	228	59.2	49.3	1.93	3.89
Cd		<0.01	14.4	2.52	2.98	2.87	8.85
Zn		16.3	351	96.9	85.6	1.94	3.43
Pb	ryegrass	0.16	10.8	4.86	3.000	0.50	-0.83
Cu		1.11	15.1	6.02	4.18	0.62	-0.91
Cd		0.16	2.86	0.61	0.62	2.35	5.37
Zn		16.0	217	75.8	48.6	1.34	1.48

The same order was found for metals in soil, except for Cu which occupied an intermediate position between Pb and Cd. These results suggest that plant uptakes more easily metals like Zn and Cu, since these elements are essential for plant growth (Lopes et al., 2012).

The mean concentration of Cd in ryegrass was below the maximum level (1 mg/kg) established by the European Directive 2002/32/EC allowed in animal feed, with 14% of samples exceeding this concentration. The maximum admitted level for Pb (10 mg/kg) was exceeded in only one ryegrass sample collected near lead smelter. Generally, the highest metal concentrations were recorded also near the industrial facilities. Relatively high lead concentrations were found also in the samples collected near the roads, probably due to the leaded gasoline formerly used by cars. The obtained values were comparable with those reported by Șenilă et al., (2012b) for native vegetation (*Agrostis, Agropirum, Trifolium repens, Urtica dioica*) collected in Baia Mare area.

Although the smelting activities in the area have generally ceased, the metals concentrations still remain high, especially in the sites where the metal containing airborne particulates from sedimentation ponds erosion or emissions were carried by winds.

The relationship between contaminant concentration in vegetation (ryegrass) and the concentration in soil is described using transfer factor (TF). The TF values quantify the relative differences in bioavailability of metals to plants and identify the efficiency of a plant species to accumulate a given metal (Pusz, 2008).

In our study, the mean obtained values for TFs were: 0.049, 0.027, 0.453 and 0.034 for Pb, Cu, Cd and Zn, respectively. These values were of the same order of magnitude with those reported by Miclean et al., (2009) and Șenilă et al., (2012b) for Cu, Cd and Zn calculated for vegetables collected in Baia Mare area, except for Pb which was one order of magnitude higher for ryegrass.

3.2 Transfer functions

The concentration of extractable metals in soil is considered to be a better parameter than total metal concentration to predict the transfer of metals from soil to plants (Lopes et al., 2012). Due to the fact that the percent of DTPA-extractable metal can be used as an indicator of metal and availability for plants, further in this study, we will apply the transfer function to DTPA extractable metal contents.

The graphical representations of the DTPA-extractable contents for Pb and Cu, and also for Cd and Zn, related to their contents in ryegrass samples are shown in figures 2 and 3, respectively, as linear functions. The relationships between the concentrations of DTPA-extractable Pb, Cu and Cd, Zn, respectively in soil and vegetation (ryegrass), as logarithmic nonlinear functions (Freundlich-type functions) are graphically represented in figures 4 and 5.

Linear regression analysis with simultaneous conversion through logarithms of concentrations of metals in plants and soil (DTPA extractable) is equivalent to a Freundlich-type model (equation 3).

The linear and Freundlich-type functions parameters describing the transfer of Pb, Cu, Cd and Zn from soil to ryegrass are shown in table 2.

The results show that for vegetation like *Lolium perenne*, the Freundlich-type functions describe better the transfer of heavy metals (Pb, Cu, Zn) from soil to plants than linear functions, indicating a nonlinear transfer process of these metals.

The significant linear correlation for Cd can be explained by the high degree of homogeneity for Cd versus Pb, Cu and Zn in soil.

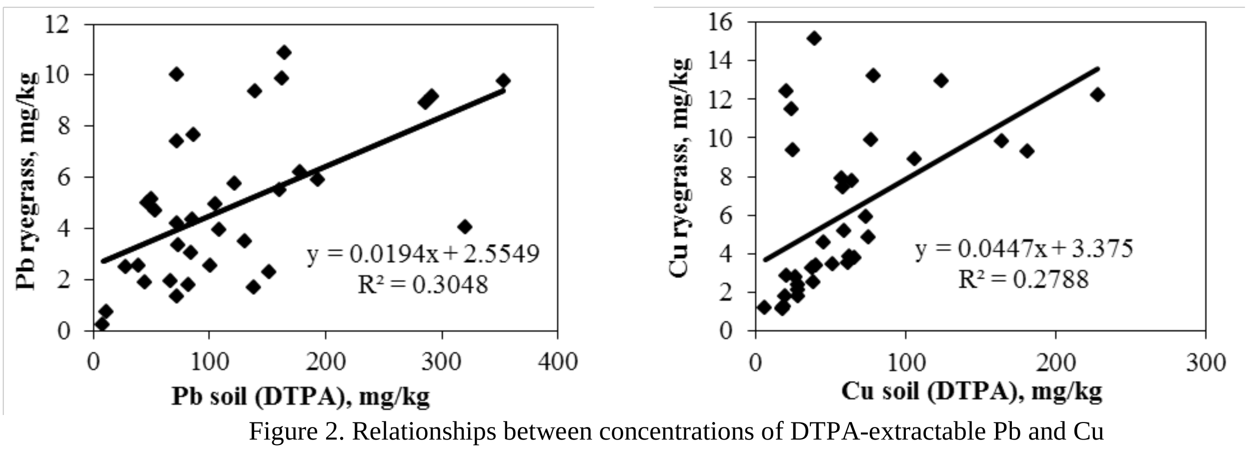

Figure 2. Relationships between concentrations of DTPA-extractable Pb and Cu in soil and ryegrass – linear functions

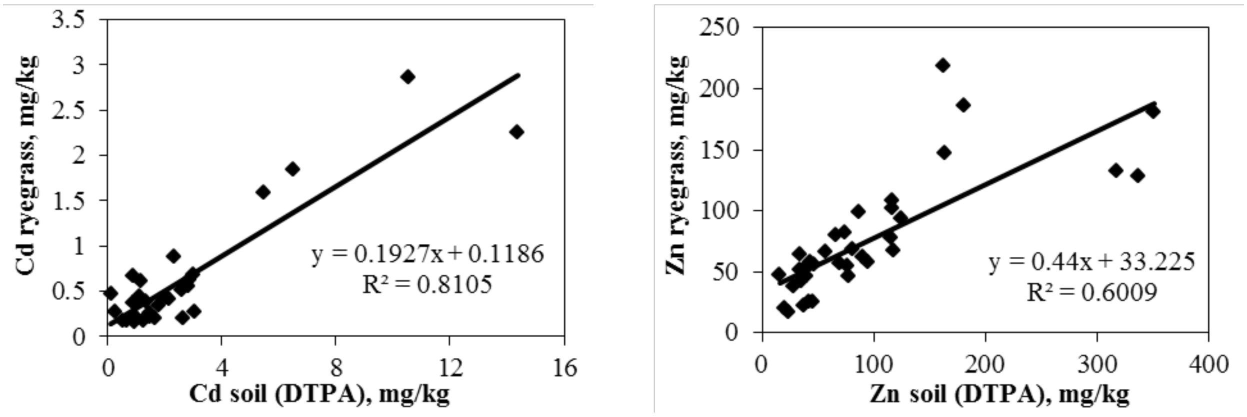

Figure 3. Relationships between concentrations of DTPA-extractable Cd and Zn in soil and ryegrass – linear functions

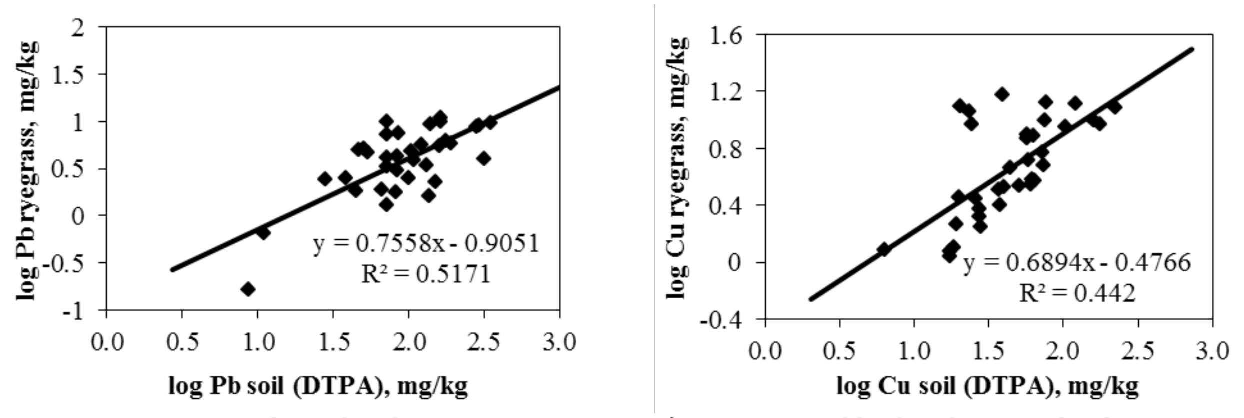

Figure 4. Relationships between concentrations of DTPA-extractable Pb and Cu in soil and ryegrass, transformed by logarithms – Freundlich-type function

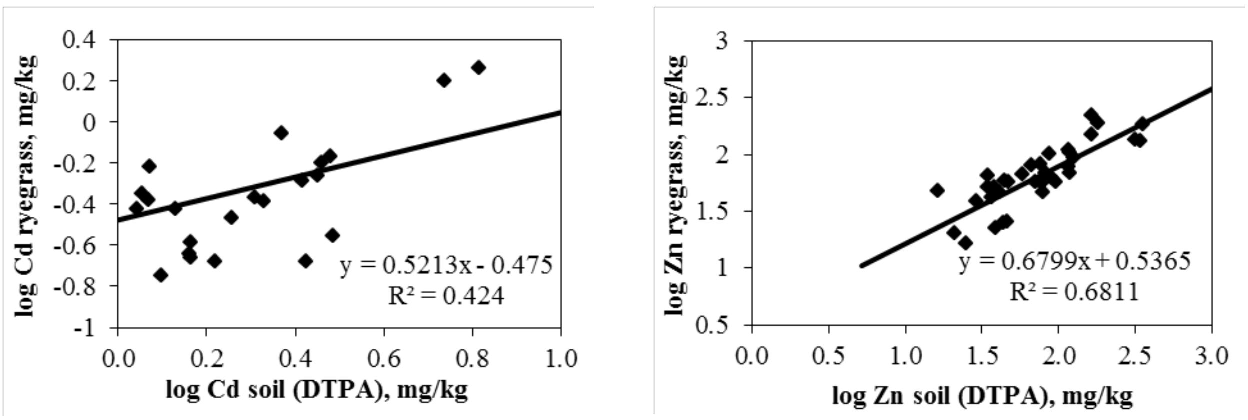

Figure 5. Relationships between concentrations of DTPA-extractable Cd and Zn in soil and ryegrass, transformed by logarithms – Freundlich-type function

The Cu and Pb contents in plants were poorly correlated with their content in soil. A possible explication for Pb could be its low mobility and bioavailability (Streit et al., 1993; Damian et al., 2008) and for Cu, its active regulation and easy translocation in the plant (Krauss et al., 2002).

Deviation from linearity could be explained by the complexity of the metal transfer from soil to plant. The content of metal in plant is influenced by a variety of factors, including: plant species, type of soil and its physico-chemical properties, weather conditions, type of cultivation, etc. Also, metals are taken up by plants not only from soil, but also from air deposition and water (Chojnacka et al., 2005).

The equation (3) can be simplified expressed as equation 4:

$$y = \log b + a \cdot x \qquad (4)$$

The Freundlich-type correlations allow the interpretation of the values of the coefficents *a* and *b* (equation 4).

Table 2. Linear and Freundlich-type function parameters showing the transfer of Pb, Cu, Cd and Zn from soil to ryegrass

Metal	Equation	Regression coefficient, R^2
Pb	y=0.0032x+0.4299	0.3048
log Pb	y=0.649x-1.4613	0.5171
Cu	y=0.0447x+3.375	0.2788
log Cu	y=0.6894x-0.4766	0.4420
Cd	y=0.1927x+0.1186	0.8105
log Cd	y=0.5213x-0.475	0.4240
Zn	y=0.44x+33.225	0.6009
log Zn	y=0.6799x+0.5365	0.6811

The coefficient *b* is a measure of the capability of the plant to accumulate metals from soil and can be used to identify the accumulating plants for soil remediation. The coefficient *a* reflects the plant's ability to influence the accumulation of metal. A low coefficient *a* indicates an increased uptake of metals at low concentrations of the metals in soil and/or a low absorption at high concentrations in soil. A value of the coefficient *a*=1, indicates that the transfer function is a linear function (Krauss et al., 2002). The parameters of Freundlich-type function (equation 4) describing the relationship between DTPA-extractable Pb, Cu, Cd and Zn in soil and ryegrass are presented in table 3.

Table 3. Parameters of Freundlich-type function for describing the relationship between DTPA-extractable Pb, Cu, Cd and Zn in soil and ryegrass

Metal	Coefficient *a*	Coefficient *b*
Pb	0.6490	0.0346
Cu	0.6894	0.3337
Cd	0.5213	0.3350
Zn	0.6799	3.4395

4. CONCLUSIONS

The soil of Baia Mare is highly polluted with heavy metals; the majority of the total concentrations of all the investigated metals (Pb, Cu, Cd, Zn) exceeded the alert levels for sensitive soils, according to Romanian legislation. The highest metals contents were recorded in the industrial area, and also in Ferneziu district. The DTPA-extractable contents have the potential risk to enter the food chain, among them the highest risk is posed by Cd and Pb, due to their toxicity.

Freundlich-type function is easy to apply and is suitable to describe better the transfer of Pb, Cu, Zn from soil to *Lolium perenne* plant, than linear function, represented by the transfer factor. The poor correlation for Cu and Pb between their concentration in plant and DTPA-extractable content could be attributed also to the atmospheric depositions. The transfer function could be used to predict the extractable metal concentrations in soil, knowing the concentrations in plant and also, the metal concentrations in plant based on the concentration in soil.

The Freundlich type function provides the opportunities for interpretation: the coefficients *a* and *b* reflect the ability of the plant to control heavy metal concentrations in plant tissue. However, the coefficients are influenced by atmospheric deposition of the metals.

The study of metal transfer from soil to spontaneous grown vegetation is thus necessary for the selection of the appropriate plant species which limits metal dispersion in the environment for the successful phytomanagement of the polluted sites. Also, the modelling can be valuable in evaluating the potential risks that heavy metals may pose to the environment.

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