THE MODELING OF PHYTOREMEDIATION PROCESS FOR SOILS POLLUTED WITH HEAVY METALS

Carmen Cristina ELEKES[1], Gabriela BUSUIOC[1]
E-mail: cristina_elekesh@yahoo.com

Abstract

The state of bioavailability of heavy metals in soil is influenced by their concentration in soil solution. Some trace elements are involved in key metabolic activities such as respiration, photosynthesis and nutrient uptake and fixation. Transition metal group elements are known as enzyme activators or are incorporated in metallo-enzymes as electronic transfer systems. These metals can also serve as catalysts to change valence in the substrate. A basic requirement for optimal growth and development of plant is the chemical equilibrium, based on the interaction of elements found in the body. Each metallic element is accumulated differently by plants; the factors influencing their absorption are the species and metal content of soil. The absorption of Cu is strongly influenced by metal concentration in substrate and less by the species. Among other heavy metals, Ni and Cr in soil strongly influence the absorption of copper, and among the macronutrients, P has a synergistic effect. Zinc absorption is also dependent on the species and the metal concentration in soil. Among heavy metals, the Pb content in soil has the greatest synergistic effect on the absorption of Zn, as Mn and Cr in soil. The Sn absorption in plants is influenced most strongly by species than the presence of Sn in soil. Among the macronutrients, Ca and P have the greatest influence on the absorption of Sn in plants. Absorption of lead in plants is dependent on metal concentration in soil and is very strongly influenced by the content of Zn, Cr and Mn in the soil.

Key words: bioavailability, heavy metals, absorption

The perennial grasses are known to be metal-tolerant if they grow on a polluted soil (Rosselli et al., 2003) and were frequently studied in the last decade about them capacity to uptake heavy metals from soil and about the possibility to use them in the heavy metals polluted soil bioremediation (Palazzo et al., 2003; Caggiano et al., 2005; Schnoor et al., 2005; Bidar et al., 2007; Jankaitė and Vasarevičius, 2007). Near this characteristic, the perennial grasses has the advantage to produce a rich yield with high percent of dry matter (Pichtel and Salt, 1998), and also the possibility to reduce metal toxicity in soil (Schnoor et al., 2005).

Because of high heavy metals tolerance, the perennial grasses uptake these elements from the soil and accumulate them in roots and shoots (Scragg, 2005) so that the metal concentration in soil is decreasing. The usage of plants in the bioremediation is a favorable option, with minimal negative effects on the soil, have the advantage of removing metals from soil and is a 50-80% cheaper method comparing with classical methods (Salt et al., 1995). The disadvantage is that the method is slow, can spend many growing seasons, the pollutants can reduce the growing process of plants and the accumulating plants become toxic for environment and have to be treated in consequence.

For a plant to be used in phytoremediation have to be metal tolerant, to develop high amount of yield in a short time, to accumulate the metals in the harvestable parts and to have a high bioaccumulation factor (BF). Most of plants have a BF lower than 1, but for a species to be efficient in phytoremediation, the amount of metal in plant should be higher than the concentration of metal in soil, so need a Bf higher than 1 or better higher than 5. Using a plant with a BF of 20, the soil contamination will be reduced with 50% in 10 crops (Chaney et al., 1997; Scragg, 2005).

To improve the plant capacity to accumulate heavy metals from soil can apply some supplements to increase the metal bioavailability in the soil solution. This method has the disadvantage of high costs and the risk of increasing metals leaching to the ground water. The bioavailability of heavy metals in soil is influenced by them concentration in soil solution and by the (Ginocchio et al., 2002). The base requirement for an optimal growing of plants is the chemical balance in the soil solution, based on the metallic elements interactions. Each metal is accumulated in a different way by plants and the factors that

[1] University Valahia of Târgovişte

influence them uptake are the species, metal content in soil, macronutrients concentration in soil and pH (Kabata-Pendias, 2004).

The aim of this paper is to highlight those species of perennial grasses which are accumulators or hyperaccumulators for Cu, Zn, Sn or Pb, and also the factors which has the most important influence on the heavy metals uptake and accumulation in plants.

MATERIAL AND METHOD

Sampling and preparation

The studied plant species were harvested nearby the metallurgical units of Targoviste city. When the plants were harvested together with the radicular system, also the soil they grew on was sampled. After harvesting, the fresh plants sample were cleaned with deionized water to remove the soil particles, dried at 60°C for few hours, ground to fine powder and analyzed to establish the metal concentrations. The plants' soil samples were dried at 40°C for 24 hours, ground to fine powder, sieved at 250 μm (conform SR ISO 11464), then analyzed to establish the metal concentrations and pH.

Analytical procedure

Determination of heavy metals, in both plants and soil they grew on, was done by Inductively Coupled Plasma - Atomic Emission Spectrometry method (ICP-AES). For analyze, the samples were mineralized in Berghof microwave digester, plants by mixture with 10 ml of nitric acid concentrated 65% and 2 ml of hydrogen peroxide, and soil in mixture 1:1 with nitric acid (according with Berghof method). The advantage of this method is the multielementale detection, which give the possibility, in one shot, to read a wide range of elements.

For this research, analyze was done with Liberty 110 spectrometer of Varian brand. The minimal detection limits of device range according to the analyzed element and is 0.4 mg/kg for Zn, and Cu; 0.6 mg/kg for Sn and Pb. The concentrations values for analyzed metals are expressed in milligrams of metal per kilogram of dry soil or fungi (mg/kg).

The soil pH determination was done with portable pH-meter WTW 3110 SET 2, with a precision of 0.01 units. For pH analyze, 5 g of each soil sample were mixed with 50 ml KCl 0.1N, F 1000, Tt 0.0056 g/ml and homogenized for 15 minutes with a magnetic stirrer.

Data analysis

The bioaccumulation factor for studied plants was calculated with formula:

$$BF = \frac{C_{pl}}{C_{soil}}$$

where: BF represents the bioaccumulation factor; C_{pl} represents the metal concentration in plants; and C_{soil} represents the metal concentration in soil.

Statistical interpretation of results was done with Microsoft Office Excel (2007) and CAMO UnscramblerX, 10.1 version software. The first software was used to calculate the Pearson's coefficient of correlation between the soil content and metal concentration in plants, and the second one for descriptive statistics of metal concentrations and for a multivariate Principal Component Analysis (PCA) of the correlation between the metallic content of the soil and metal concentrations in studied plants.

RESULTS AND DISCUSSIONS

The soil that the perennial grasses grew on was sampled nearby the metallurgic unit of Targoviste city, from the surface to 10 cm deep. In terms of macronutrients, the soil is well supplied, but also has high concentrations of heavy metals (tab. 1). The average content of Cu, Sn and Pb in soil exceeds the alert threshold for agricultural soils, 100, 35, 50 mg/kg respectively, but in some sampling points the concentrations exceed even the alert threshold for industrial soils, 250, 100, 250 mg/kg. For Zn, the mean concentration in soil is normal, but in sampling points exceeds the alert threshold of 700 mg/kg.

Table 1

Statistical results for the metal concentration in soil and pH (mg/kg)

Metal	Soil concentration				
	min	max	mean	SD	unit
Fe	8.27	43.65	22.03	15.03	g/kg
Ca	6.93	24.99	13.05	5.41	g/kg
Mg	1.19	9.06	2.68	2.65	g/kg
P	0.40	4.42	1.12	1.35	g/kg
K	0.51	3.35	1.15	0.85	g/kg
Cu	21.98	600.38	152.43	177.73	mg/kg
Zn	42.64	870.32	194.26	231.71	mg/kg
Sn	24.58	125.41	65.68	30.70	mg/kg
Pb	0.60	294.28	65.17	87.22	mg/kg
pH	6.47	7.89	7.30	0.42	

For the present study were chosen seven species of perennial grasses from *Juncaceae* and *Poaceae* family, usually found in natural grasslands (tab. 2).

The concentration of heavy metals in these perennial grass species varies in a wide range for all four metals, Cu, Zn, Sn and Pb (tab. 3). Mean concentrations of Cu and Sn found in the plant samples was 35.07 mg/kg and 220.39 mg/kg, respectively, and the maximum values for both metals were found in the species *F. pratensis*. For Zn and Pb, maximum concentration was found in L. perenne species, and the mean concentrations in all studied samples were 204.57 mg/kg and 11.84 mg/kg, respectively.

Table 2
Species of wild growing perennial grasses

Species	Popular name	Observation
Lolium perenne	Iarbă de gazon	found in meadows
Festuca pratensis	Păiuşul de livadă	component of pastures and meadows
Stipa capillata	Năgară, păiuş	found in steppe and forest steppe
Agrostis alba	Iarba câmpului	found in meadows
Cynodon dactylon	Pirul gros	found in meadows and as weed in crops
Agrostis tenuis	Iarba câmpului	found in meadows
Luzula campestris	Mălaiul cucului	found in meadows and pastures

Table 3
Statistical results of heavy metals concentration in perennial grasses (mg/kg)

Metal	Metal concentration in plants				
	min	max	mean	SD	Species max conc.
Cu	0.40	135.20	35.07	39.64	*F. pratensis*
Zn	59.94	1009.87	204.57	304.19	*L. perenne*
Sn	7.45	491.05	220.39	114.42	*F. pratensis*
Pb	0.00	202.83	11.84	43.86	*L. perenne*

Bioaccumulation factor is the ratio of metal concentrations found in plant and soil (Scragg, 2005) and we considered weak accumulators the species which have a BF value between 1.0 - 1.5, good accumulators species with a value of BF between 1.5 - 5.0 and hyperacumulators those with higher BF than 5.0 (tab. 4). Among the studied species, the best accumulators are *C. dactylon* for Cu, Zn and Sn, *L. perenne* for Zn, Sn and Pb, *L. campestris* for Pb. Sn is very well accumulated by most of the studied species, except for *L. campestris*.

Table 4
Statistical results of the bioaccumulation factor for perennial grasses

Metal	Bioaccumulation factor				
	min	max	mean	SD	Accumulators sp.
Cu	0.01	1.21	0.40	0.42	*A. alba* – weak *C. dactylon* – good
Zn	0.58	1.65	0.97	0.29	*A. alba* – weak *L. perenne* – good *C. dactylon* – good
Sn	0.16	6.29	3.67	1.98	*L. perenne* – good *F. pratensis* – good *S. capillata* – good *A. alba* – good *A. tenuis* – hyper *C. dactylon* – hyper
Pb	0.00	13.27	2.47	4.41	*L. perenne* – good *A. tenuis* – good *L. campestris* – hyper

Absorption and accumulation of metals in perennial grasses is influenced both by species and the soil that plants grow on, pH, moisture and metal content in soil (fig. 1). The absorption of Cu is influenced primarily by the metal concentration in soil and less by the species, and the difference in absorption can be well observed in *F. pratensis* and *S. capillata* species. Zn absorption is influenced almost equally by species and metal content in soil, with variations in absorption both within species and between species.

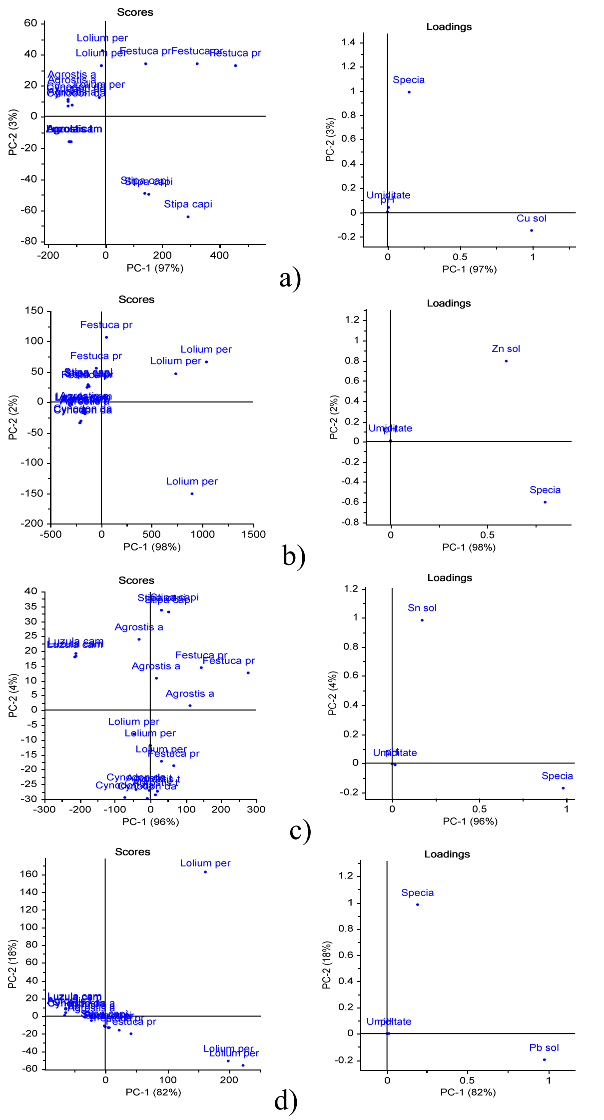

Figure 1 **Dominant factors of heavy metals uptake in perennial grasses: a) Cu; b) Zn; c) Sn; d) Pb**

Absorption of tin is determined to a greater extent by the species; the analyzed samples had similar concentrations regardless of metal concentration in soil. For Pb, the metal content in soil is an important factor, which is observed best in the *L. perenne* species. Moisture and soil pH have less influence on the absorption of heavy metals compared with the first two factors, species and metal content of soil.

Regarding the effect of heavy metals in soil on the absorption of the four studied metals (tab. 5) can be observed that between two elements there is a positive correlation in most cases. The correlations were stronger between Zn and Pb content in soil and their concentration in plants, between the two metals being a synergistic correlation. Mo content in the soil has antagonistic effects on the absorption of all studied metals.

Table 5

Effect of heavy metals in soil on the absorption of Cu, Zn, Sn and Pb (C. Pearson)

		Heavy metals in plants			
		Cu	Zn	Sn	Pb
Heavy metals in soil	Fe	0.6325	0.6150	0.4966	0.2651
	Cu	0.6475	0.0283	0.5343	-0.1091
	Zn	0.4608	0.9617	0.1158	0.9412
	Sn	0.3094	-0.1285	0.6164	-0.2049
	Pb	0.5213	0.9018	0.2460	0.8841
	Co	0.6424	0.4479	0.3231	0.4019
	Ni	0.9075	0.3263	0.6829	0.2047
	Mn	-0.0361	0.7434	-0.4041	0.8230
	Cr	0.7274	0.8314	0.3804	0.7469
	Mo	-0.5239	-0.4595	-0.3458	-0.4061

Macronutrients in soil have a low and very low influence on the accumulation of heavy metals in perennial grasses, and there are moderate correlations only between P content in soil and Cu accumulation (tab. 6). Soil pH has a weak influence on the accumulation of Cu, Zn and Sn, and a weak-moderate influence on Pb accumulation.

Table 6

Effect of pH and macronutrients in the soil on the bioaccumulation factor (C. Pearson)

		Cu	Zn	Sn	Pb
	pH	-0.0069	-0.0004	0.0724	-0.2127
Macronutrients in soil	Fe	-0.0549	-0.0664	0.0008	-0.2499
	Ca	-0.086	-0.1893	0.1299	-0.1937
	Mg	-0.0077	-0.1728	0.0154	-0.0773
	P	0.5393	0.3804	0.2621	-0.0621
	K	-0.0296	-0.2517	0.0048	-0.0479
		Bioaccumulation factor			

CONCLUSIONS

In addition to species, metal content of soil and pH play an important role in activating or inhibiting the uptake and the accumulation of heavy metals by perennial grasses, so that he soil remediation process can be streamlined by controlling the ratio of minerals in the soil. Heavy metals in soil have generally synergistic effects on the accumulation of heavy metals in plants, while the macronutrients have, in most cases, antagonistic effects on the accumulation of heavy metals by perennial grasses.

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