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INFLUENCE OF SOIL CHEMISTRY ON THE PHYTOREMEDIATION PROCESS

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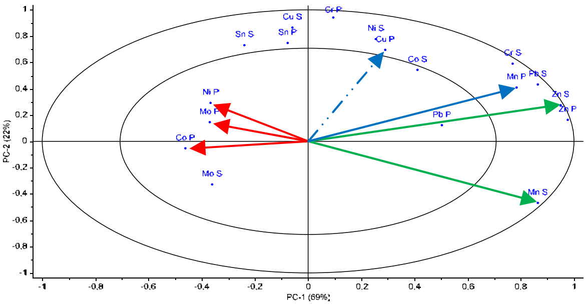
The perennial grasses are known as good accumulators for heavy metals, because of the tolerance to these elements in soil. The plants can accumulate heavy metals in roots and shoots so that the metal concentration in soil is decreasing under the risk limit. We analysed the heavy metals bioaccumulation in perennial grasses and in soil and correlations between the soil chemistry and bioaccumulation factor. The heavy metals concentration in studied perennial grasses varies in a wide range. The mean concentrations were 35.07 mg/kg, 204.57 mg/kg, 220.39 mg/kg and 11.84 mg/kg for Cu, Zn, Sn and Pb. Zinc and lead bioaccumulation showed similarities concerning the correlations with the metal content of soil. We observe strong correlations between Ni – Cu, Cr – Cu, Zn – Zn, Mn – Zn, Cr – Zn, Pb – Pb, Mn – Pb and Cr – Pb. Calcium, magnesium and potassium showed strong and very strong positive correlations with the zinc and lead bioaccumulation.



INTRODUCTION

Responsible for the migration of contaminants into soil (such as dust or leachate) are the metallurgical activities, controlled or uncontrolled waste disposal, mining and smelting of metalliferous ores. From soil, the pollutants contribute towards to the contamination of entire ecosystem. Some heavy metals are considered important environmental pollutants, especially in areas with high anthropogenic activities,[1] because they cannot be broken down and can accumulate in plant cells above optimal levels. This accumulation can cause direct toxicity by damaging cell structure, because of the oxidative stress caused by reactive oxygen species, or can inhibit a number of cytoplasmic enzymes.[2] The indirect toxic effects of heavy metals can be produced by replacing the essential nutrients at cation exchange sites in plants.[3]

As an optimal solution for all these aspects, some researchers stated that the use of some heavy metal-tolerant plant species are important tools for the phytoremediation of heavy metal polluted soils. Phytoremediation is an integrated multidisciplinary approach to clean up metal polluted soils, which combines the disciplines of plant physiology, soil chemistry and soil microbiology.[4,5] Certain species of higher plants are able to accumulate high concentration of heavy metals in their tissues without showing any morphological changes specific of metal toxicity.[6,7] These plants can be successfully used in the remediation of heavy metal polluted soils if their biomass and metal content are large enough to complete the remediation within a reasonable period.[8]

The efficacy of phytoremediation treatments might firmly rely on the settlement of appropriate vegetation which constitutes one of the critical steps and closely depends on the metal tolerance of plants and the associated microbiota for the in-situ treatment of heavy metal polluted soils.[9] The phytoremediation is the best approach to remove heavy metals from polluted soils and isolate them, without destroying the soil structure and fertility.[6]

The perennial grasses were studied in phytoremediation experiments, due to their metal-tolerant characteristic[10] and their capacity to absorb heavy metals from polluted soils.[11-15] Using the perennial grasses in phytoremediation has the advantage of a rich yield with high percentage of dry matter[16] and due to their capacity to reduce metal toxicity in soil – phytostabilization.[13]

Besides species, the soil chemistry is a very important factor in the phytoremediation. Heavy metals exist in colloidal, ionic, particulate and dissolved phase.[17] The soluble forms of metals are generally ions or unionised organometallic chelates or complexes. Solubility of heavy metals in soil and groundwater is predominantly controlled by pH,[18-20] by the amount of metal in soil,[21] cation exchange capacity, organic carbon content, the oxidation state of the mineral components and the redox potential of the system.[22-24] A high soil pH determines a greater metal retention and a lower solubility of metal cations.[25] In previous experiments was observed a competition for absorption between various metals. For examples, cadmium absorption was decreased by the addition of Pb or Cu.[26]

The metal uptake by plants is defined by three processes: (1) sequestration of metals inside root cells, (2) symplastic transport into the shoots and (3) release into xylem.[27] Non-essential heavy metals compete for the same transmembrane carriers used by essential metals.[17] This lack of selectivity in transmembrane ion transport explains why non-essential heavy metal can be absorbed in plants tissues, even against a concentration gradient.

To improve the results of phytoremediation treatments, the heavy metal absorption by plants need to be increased by fertilization, conditioning and soil acidification which increase the metal bioavailability in the soil solution. This research starts from the hypothesis that the soil chemistry is the most important factor, beside species, which control the heavy metal bioabsorption and accumulation in perennial grasses.

RESULTS AND DISCUSSION

The soil samples consist in the upper layer of soil, down to 20 cm, where the most of the roots can be found. The content of soil in macronutrients, was about 13 g/kg for Ca, 3 g/kg for Mg, and 1 g/kg for P and K (tab. 1). Heavy metal concentration in soil was high when comparing with the agricultural soils. 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.[28] For Zn, the mean concentration in soil is normal range for agricultural soil, but in some sampling points exceeds the alert threshold of 700 mg/kg.

For this study we chose seven species of perennial grasses from *Juncaceae* and *Poaceae* family, usually found in natural grasslands and meadows: *Lolium perenne, Festuca pratensis, Stipa capillata, Agrostis alba, Agrostis tenuis, Cynodon dactylon, Luzula campestris*. The heavy metal concentration in perennial grasses was widely different between the species for all studied metals (Table 2). Copper concentration range between 1 and 114 mg/kg, with the highest value for *F. pratensis*. In the same species was found the highest value for the tin concentration, 379 mg/kg, while the lower value was for *L. campestris*, 8 mg/kg. Zinc concentration range for studied species between 62-922 mg/kg, and lead concentration varies between not detectable level of concentration in most of studied species and 201 mg/kg. The maximum values of zinc and lead concentration were found for *L. perenne* species, 922 mg/kg and 201 mg/kg respectively.

The bioaccumulation capacity of plants was estimated as the ratio of metal content in soil and the metal concentration in plant. This ration is called bioaccumulation factor (BF)[29] and we evaluated as weak accumulators the species which have a BF value between 1.0-1.5, as good accumulators the species with a value of BF between 1.5-5.0 and hyperacumulators those species with higher BF than 5.0 (Table 3). Even *F. pratensis* and *L. perenne* showed the highest values of metal concentration, they did not show the highest accumulation capacity for those metals. The best accumulator for Cu, Zn and Sn were the plants of *C. dactylon* species which showed BF values of 1.12, 1.37 and 6.06 respectively for Cu, Zn and Sn. Lead was very well accumulated by *L. campestris* which show a very high level of metal bioaccumulation, 12.3. Tin was the metal with best bioaccumulation in perennial grasses.

Table 1

Soil chemistry: essential and non-essential metal content and pH (mg/kg)

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

Table 2

Heavy metals concentration in species of perennial grasses (mg/kg)

Species	**Cu**	**Zn**	**Sn**	**Pb**
L. perenne	61.95±15.7	921.67±136.2	217.83±40.1	201.23±14.9
F. pratensis	113.83±22.8	130.62±48.2	379.23±103.2	ND
S. capillata	10.04±3.9	88.22±2.8	265.25±17.4	ND
A. alba	31.83±5.5	85.34±7.12	250.04±74.2	5.21±3.2
A. tenuis	0.99±0.6	72.33±3.8	235.94±12.1	2.72±0.1
C. dactylon	25.11±2.4	62.09±2.0	186.13±31.4	ND
L. campestris	1.76±0.4	71.69±2.9	8.38±0.9	7.38±0.5

ND – not detected

Table 3

Accumulator and hyperaccumulator species of perennial grasses

Metal	**Mean± SD**	**Accumulation gradient**
Cu	0.88±0.2 1.12±0.1	*A. alba* – weak *C. dactylon* – good
Zn	1.00±0.1 1.31±0.3 1.37±0.1	*A. alba* – weak *L. perenne* – good *C. dactylon* – good
Sn	4.11±0.6 4.10±0.8 2.43±0.1 3.00±0.8 5.85±0.1 6.06±0.3	*L. perenne* – good *F. pratensis* – good *S. capillata* – good *A. alba* – good *A. tenuis* – hyper *C. dactylon* – hyper
Pb	1.04±0.1 4.54±0.2 12.3±0.9	*L. perenne* – good *A. tenuis* – good *L. campestris* – hyper

Table 4

The influence of soil chemistry on heavy metals bioabsorption

Soil chem.	**Heavy metals in plants**			
	Cu	**Zn**	**Sn**	**Pb**
Ca	0.4474^{c}	0.7340^{c}	0.1232^{c}	0.7134^{c}
Mg	0.4388^{c}	0.9755^{c}	0.0668^{c}	0.9688^{c}
P	-0.0746^{c}	-0.1028^{b}	-0.1451^{b}	-0.0857^{c}
K	0.3830^{c}	0.9484^{c}	0.0088^{c}	0.9527^{c}
Fe	0.6325^{c}	0.6150^{c}	0.4966^{c}	0.5503^{c}
Cu	0.6475^{b}	0.0283	0.5343	-0.1091^{b}
Zn	0.4608^{b}	0.9617^{a}	0.1158	0.9412^{b}
Sn	0.3094^{b}	-0.1285	0.6164^{c}	-0.2049^{c}
Pb	0.5213	0.9018^{a}	0.2460^{c}	0.8841^{b}

Table 4 (continued)

Co	0.6424[a]	0.4479[b]	0.3231[c]	0.4019
Ni	0.9075[c]	0.3263[a]	0.6829[c]	0.2047[b]
Mn	-0.0361[c]	0.7434[c]	-0.4041[c]	0.8230[c]
Cr	0.7274[b]	0.8314[a]	0.3804[c]	0.7469[c]
Mo	-0.5239[a]	-0.459[b]	-0.3458[c]	-0.4061
pH	0.5691[b]	0.5842[b]	0.3736[c]	0.5305

[a] – $p < 0.05$; [b] – $p < 0.01$; [c] – $p < 0.001$

Absorption and accumulation of metals in perennial grasses is influenced by both species and the soil underneath, pH, moisture and metal content in soil.[30] The bioaccumulation of the four studied metals is differently influenced by pH of soil and metal content (Table 4). The metal bioaccumulation in plants was correlated with the metal concentration in soil for each sample. Copper bioaccumulation has a strong positive correlation with the Ni and Cr content of the soil. The synergic relation between Zn and Pb[30] is demonstrated by the strong positive correlation of Pb in soil and Zn bioaccumulation and very strong correlation between Zn in soil and Pb bioaccumulation. Strong correlations were observed also between Zn – Zn, Mn – Zn, Cr – Zn, Pb – Pb, Mn – Pb and Cr - Pb. The tin bioaccumulation is less influenced by the heavy metal content of the soil (weak to moderate-strong correlations).

The macronutrients content of the soil has different influences on the heavy metal bioaccumulation. The correlation between macronutrients and the accumulation of Cu and Sn are weak. The zinc and lead bioaccumulation is similar influenced by the macronutrients content of the soil. Ca, Mg and K showed strong and very strong positive correlations with the zinc and lead bioaccumulation, while P has very weak negative correlation with these metals. The pH of soil showed moderate influences on the bioaccumulation of studied heavy metals.

EXPERIMENTAL

The studied plant species were harvested nearby the metallurgical units of Târgovişte city. When the plants were harvested, we sampled also the soil underneath. 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 a fine powder and analysed to establish the metal concentrations. The soil samples were dried at 40 °C for 24 hours, ground to a fine powder, sieved at 250 µm (conform SR ISO 11464), then analysed to establish the metal concentrations and pH.

Determination of metal concentration (heavy metals and macronutrients), in both plants and soil underneath, was done by Inductively Coupled Plasma – Atomic Emission Spectrometry method (ICP-AES). For analyse, 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 multielemental detection, which gives the possibility, in one shot, to read a wide range of elements. For this research, analyse was done with Liberty 110 spectrometer of Varian brand. The minimal detection limits of device range according to the analysed element and is 0.4 mg/kg for Zn, and Cu; 0.6 mg/kg for Sn and Pb. The concentrations values for analysed metals are expressed in milligrams of metal per kilogram of dry soil or fungi (mg/kg).

The soil pH was determined with a portable pH-meter, WTW 3110 SET 2, with 0.01 units precision. For pH analyse, 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.

The bioaccumulation factor (BF) for studied plants was calculated as the ratio: $BF = C_{pl} / C_{soil}$, where: C_{pl} represents the metal concentration in plants and C_{soil} represents the metal concentration in soil.

CONCLUSIONS

The metal content of soil is the most important factor which influences the heavy metal bioaccumulation in perennial grasses. The presence/absence of a metal in the soil can activate/inhibit the heavy metal absorption and accumulation by these plant species. The phytoremediation process can be controlled by controlling the metal content of soil.

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