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# POSSIBILITY OF RECONSTRUCTION OF A HEAVY METAL POLLUTED SOIL

**Júlia BUDAI, Károly ANTAL*, Lajos BLASKÓ**
Karcag Research Institute, RISF, CAAES, University of Debrecen, Hungary

**ABSTRACT.** Ecological reconstruction of polluted sites are important scope of duties to ecological and agricultural researchers. A typical polluted territory is situated in the area of the Gyöngyösoroszi. Application of sheep manure compost and lime where tested as a possible way for remediation of the polluted habitat. These amendment materials are well-known in agricultural practice. Our goal was to obtain detailed information about the feature of these materials which increase the survival and help the growth of plants. We carried out pot experiments and chemical measurements too. In pot experiments we studied the effects of different doses of compost and lime with Italian ryegrass (*Lolium multiflorum L.*) as marker plant. In the chemical experiments we analyzed the polluted soil and we carried out heavy metal leaching laboratory tests on the polluted soil. We measured the pH changing effect of these substances too. We also determined the heavy metal content of Italian ryegrass which was grown in amended contaminated soil.

**Keywords:** compost, lime, flotation sludge, pot experiment, heavy metal uptake, salt leaching, immobilization

## INTRODUCTION

Gyöngyösoroszi was one of the most important mining regions in Hungary for many years. At mining period Gyöngyösoroszi large area were contaminated with flotation sludge which contain high quantities of heavy metals (e.g. Zn, Cu, Mn). The samples was collected from the flotation sludge. This area were studied in details by many researchers, e.g. Draskovits et al., 2002; Murányi and Ködöböcz, 2008; Papp, 2008. There are many possible ways for recultivation of these areas. One of possible method to reduce the toxic effect of polluted soil is immobilization of heavy metals (Zubillaga et al. 2008). Compost contains a high proportion of humic-like materials due to it can decrease the bioavailability of heavy metals in soil. In order to clarify this concept, we studied the adsorption of humic-like fraction of the compost in the tested sludge. In addition, we carried out leaching tests of heavy metal ions from the soil treated with compost similarly to the methods used by Esakku et al., 2008. We determined the heavy metal level in ryegrass like Tury és mtsi (2008). Application of composts for the purpose of increase the stress tolerance of plants is wide-spread in agricultural practice (Topcuoglu and Önal, 2007; Delgado Arroyo et al., 2002). Other amended materials used as chemical immobilizers include calcium-oxides. These amendment materials can increase the pH of the acidic soil. In this alkalization process form metal-oxides, metal-carbonates and other insoluble metal complexes.

The aim of work to study the efficiency of two amendment materials on plants which grow on Gyöngyösoroszi sludge.

## MATERIALS AND METHODS

### *Pot experiments with Italian ryegrass (Lolium multiflorum L.)*

Acidic, heavy metal polluted soil was used in all experiments. The soil was collected from the surface layer of the contaminated area of the former metal mine at Gyöngyösoroszi. Polluted soil was collected from spoil-bank and it was taken at a depth of 10-40 cm. Italian ryegrass was grown in plastic pots containing 0.6 kg of air-dried soil-compost mix. Treatments consisted of seven sheep manure compost doses, i.e. 0 (control), 1, 1.5, 2, 4, 6, 10 m/m % (30-300 t $ha^{-1}$). The treated with lime was carried out similarly to the experimental with the compost treatment. The $CaCO_3$ doses were 0, 0.5, 1, 2, 4, 6, 10 m/m % (7.5-300 t $ha^{-1}$). Italian ryegrass as test plant was grown in a greenhouse with supplemental lighting by "Cool White" fluorescent lamp to provide a 12 hour photoperiod. The pots were arranged in a completely randomized design with three replications. In each pot 45 seeds of the indicator plant were sown.

### *Chemical measurement*

Soil and plant analyses: The analyses was carried out according to the adequate Hungarian standards. The extractable toxic element from soil were extracted by KCl / EDTA solutions. For the determination total toxic element content of soil and plants were digested in $HNO_3$ / $H_2O_2$ mixtured by microwave technique with MarsXpress microwave digester. The concentrations of the metal ions were determined by atomic absorption spectrometry with SpectraAA 220FS spectrometer.

The $pH_w$ (active acidity) measurement was carried out by Inolab Multilevel 3P, Sen-Tix 81 pH electrode, in soil : water suspension (1:2.5) at room temperature after one day.

Salt leaching experiments: Soil samples of 100 g were suspended in 0.65-5 m% of compost of 0.5 $dm^3$ at room temperature for a month. The amount of leached

***Correspondence:** Károly Antal, University of Debrecen, RISF, CAAES, Karcag Research Institute, 166. Kisújszállási út, Karcag, Hungary, Tel. +36-(59)-500360, Fax. +36-(59)-500151, email: antal@dateki.hu
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out total salt content was gravimetrically determined in the liquid phase. At the end we determined the amount of heavy metals from the dried residue by AAS.

## RESULTS AND DISCUSSIONS

The effect of the different doses of compost on the growth of ryegrass seedlings on the polluted soil was studied in detail. The height of plants was measured after one month (figure 1). The plant heights increased by the increasing of the compost doses 0-4 m/m %, which is in good agreement with several published data (Topcouglu and Önal., 2007). This increase in the height of the plants can probably be caused by the improvement of phosphorus (P) supply and the complex forming ability (with metal ions) of the matter content of the compost. The positive effects of organic material have already been published by Dömsödi (1989), Máté-Gáspár and Anton (2005). Another possible explanation is the pH increase effect of the compost (figure 2). Increasing the compost content above 4 m/m % did not lead to a further increase in the height of the plants. We supposed that other chemical amendments can also be effective on the growth of plants particularly by pH increase. We applied lime, which is a classical, widely used agricultural amendment for neutralizing of acidic soils.

Figure 1 shows that the increasing lime content caused increases of height of the plants at 0-2 m/m % range, while increasing the lime content above 2 m/m % we experienced an similarly effect than compost. Figure 2 shows the effect of pH-change caused by liming on the plant heights.

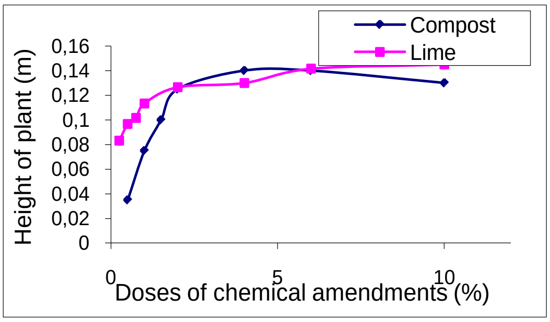


**Fig. 1** Effect of chemical amendments on the plants

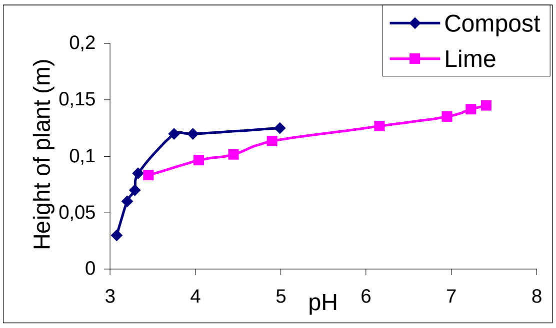


**Fig. 2** Effect of pH on the height of plants

Table 1 shows the unamended soil used for experiments. Th pH of soil is a very low pH (pH=2.83). The humic material content seems enough for plants, but the humic- content determination based on the chromate oxidation method not give adequate results in these high heavy metal concentration. The experimental date of soils are shown clearly the total phosphorus content is enough, but soluble phosphorus concentration is very low in the sludge. We supposed the small available phosphorus content caused by small solubility heavy metal-phosphorus salt (e.g. $K_{sp}$: $Cu_3(PO_4)_2$: 1,40 x $10^{-37}$, $Zn_3(PO_4)_2$: 9 x $10^{-33}$) (Lide, 2003-2004).

We found the following metal ions in the soil written in decreasing order of concentration: Fe>Zn>Mn>Cu>Pb>Cr>Co>Ni,Cd. However, the total metal content is not available for plants. Therefore we determined the metal content which can be extracted by ammonium-lactate. We suppose that this type of metal content is available for plants. The results in decreasing order of concentration are as follows: Zn>Pb>Mn>Fe>Cu>Cd>Cr>Co>Ni. On the basis of the previous data we calculated the ratios of availability of each heavy metals (Walker et al, 2004; Topcouglu, 2004). The “available” (mobile fraction of total amount (%) heavy metals in decreasing order of concentration are: Cd>Pb>Zn>Cu>Ni>Mn>Co>Cr>Fe (table 2).

We measured the pH changing of the treated soils at different doses of compost and lime. We plotted the pH as against of different doses of compost and lime. Figure 3 shows increase doses of the amendment materials are enhance the pH of the differently treated soils. It is clear that lime is more efficient in the pH enhancement than compost. However, similar doses of compost is not resulted the same height of the grass seedlings than lime. One of the possible explanation of the decrease the toxicity of soils is the pH increase effect of the compost and lime. Well known, the pH increase is decrease the solubility of the heavy metal salts.

In addition, we performed some salt leaching experiments by compost. Figure 4 shows that the compost application linearly decreases the solubility of salts from the tested soil. Decrease of amount of solubility salt caused by pH increase effect and complex forming ability of compost. This observation could be explained by the complex formation of heavy metal ions with compost which adsorbed on the soil particles. We studied the sorption of compost on this soil earlier. The Langmuir-type plotting showed a good linearity of adsorption of compost on the tested soil. It means that the soluble organic fraction of compost (humic-like materials) forms a monomolecular layer on the surface of the soil particles and the process is reversible (Antal et al., 2008)

Furthermore, we analyzed the heavy metal content of these salt. Figure 5-6 show for demonstration the decrease of Zn and Cu content of salts.

*Table 1*

**Some mean features of examined soil**

| | |
|---|---|
| pH ($H_2O$) | 2.83 |
| Humic material (%) | 1.24 ? |
| $P_2O_5$ (mg $kg^{-1}$) (Soluble) | <5 |
| $P_2O_5$ (mg $kg^{-1}$) (Total) | 700 |

*Table 2*

**Heavy metal content of tested soil**

| Metal content | Extractable (mg/kg) | Total (mg/kg) | Available % |
|---|---|---|---|
| Zn | 648.0 | 1715.0 | 37.8 |
| Cu | 230.0 | 675.0 | 34.1 |
| Fe | 258.0 | 42661.0 | 0.6 |
| Mn | 270.0 | 964.0 | 28.0 |
| Cr | <4.0 | 33.0 | <12.1 |
| Co | 2.4 | 10.0 | 24.0 |
| Ni | <2.0 | 7.0 | <28.6 |
| Cd | 6.3 | 7.0 | 90.0 |
| Pb | 356.0 | 473.0 | 75.3 |

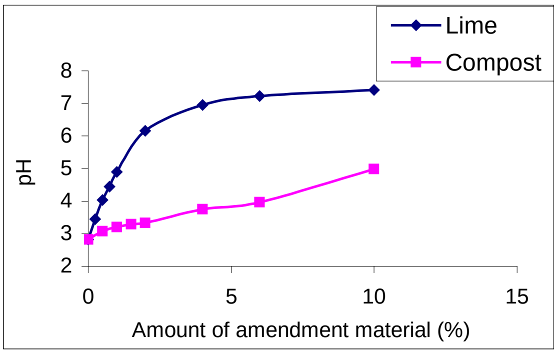


**Fig. 3** The effect of the chemical amendments on pH

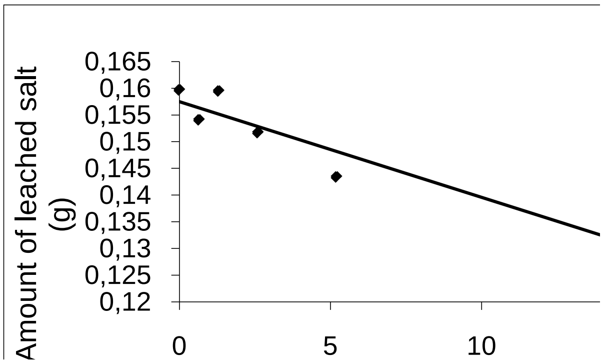


**Fig. 4** Effect of the compost content on the amount of salt leached out from the soil

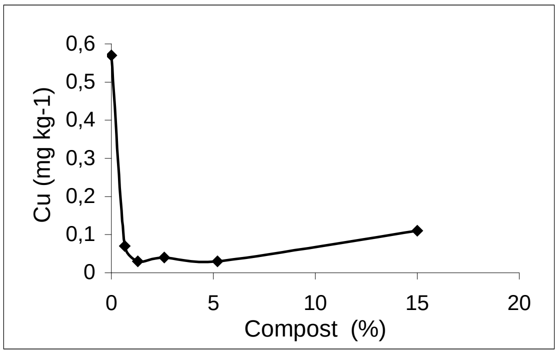


**Fig. 5** Effect of the compost content on the concentration of Cu leached out from the soil

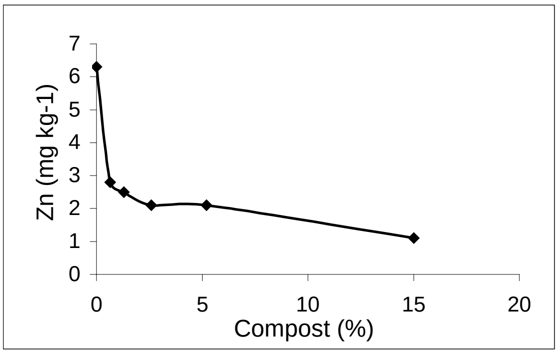


**Fig. 6** Effect of the compost content on the concentration of Zn leached out from the soil

We analyzed the heavy metal content in the plants which grown in pots. After one month we harvested and dried the grass. We analyzed them by Hungarian standard. We summarized the results in table 3.

Table 3 and figure 7-10 show the concentration of heavy metals (Cu, Mn, Fe, Zn) in the shoots (leaves and stem) of the Italian ryegrass which grown in the different soil samples. The compost employed were very efficient at reducing heavy metal uptake by the plants. We plotted the dates of table 3 in figure 7-10. The heavy metal content of plant decrease with increasing compost doses. Hence their availability for plants decreased as well in polluted soil by compost too.

We also analyzed the metal uptake of grasses which grown in polluted soil treated with lime. The data of the analyses similarly to compost treatment, the lime also reduced the heavy metal concentration in plants (table 4).

*Table 3*

**The effect of compost on the pH and metal content of the tested plants**

| Compost | | Metal content of plants mg kg$^{-1}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Doses % | Resulted pH | Cu Mean | Cu SD | Zn Mean | Zn SD | Mn Mean | Mn SD | Fe Mean | Fe SD |
| 0.00 | 2.84 | * | * | * | * | * | * | * | * |
| 0.50 | 3.08 | 225.0 | 50.1 | 350.0 | 41.9 | 450.0 | 33.5 | 1575.0 | 102.4 |
| 1.00 | 3.20 | 75.0 | 15.4 | 181.3 | 17.3 | 237.5 | 11.6 | 606.3 | 75.6 |
| 1.50 | 3.29 | 43.3 | 5.6 | 170.0 | 18.6 | 223.3 | 13.2 | 573.3 | 80.9 |
| 2.00 | 3.33 | 33.3 | 3.7 | 168.8 | 21.7 | 222.9 | 14.7 | 337.5 | 74.5 |
| 4.00 | 3.75 | 25.0 | 3.5 | 132.1 | 16.4 | 216.4 | 12.8 | 246.4 | 48.1 |
| 6.00 | 3.97 | 22.8 | 2.2 | 91.3 | 10.8 | 187.0 | 9.1 | 139.1 | 36.7 |
| 10.00 | 4.99 | 22.4 | 2.1 | 71.4 | 9.9 | 155.1 | 8.8 | 211.2 | 48.2 |

** The plant did not grow*

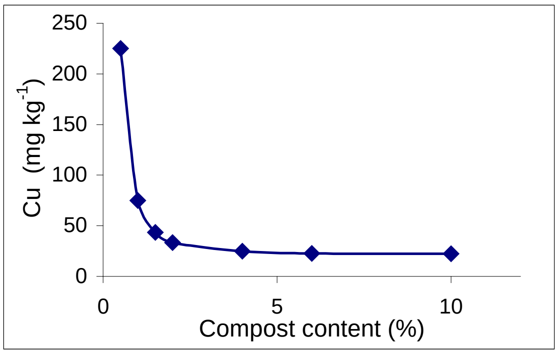


**Fig. 7** Effect of compost on Cu content of plant

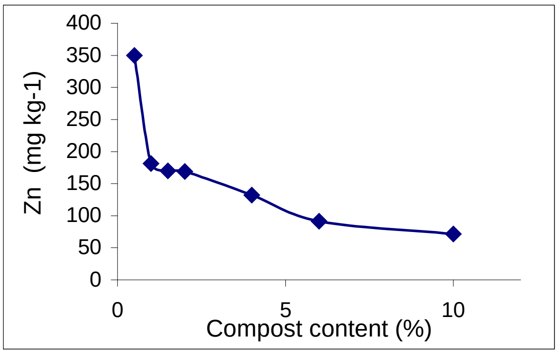


**Fig. 8** Effect of compost on Zn content of plant

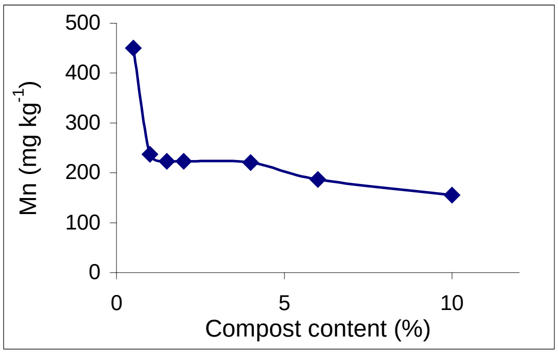


**Fig. 9** Effect of compost on Mn content of plant

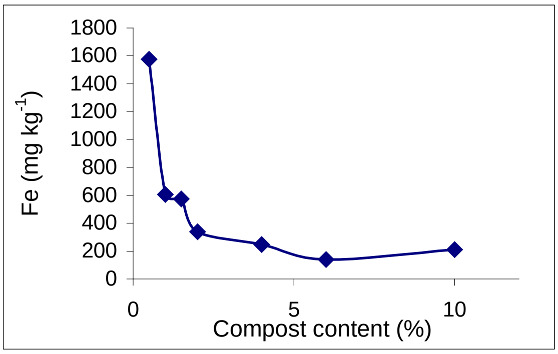


**Fig. 10** Effect of compost on Fe content of plant

*Table 4*

**The effect of lime on the pH and metal content of the tested plants**

| Lime | | Metal content of plants mg kg$^{-1}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Doses % | Resulted pH | Cu Mean | Cu SD | Zn Mean | Zn SD | Mn Mean | Mn SD | Fe Mean | Fe SD |
| 0.00 | 2.82 | * | * | * | * | * | * | * | * |
| 0.50 | 4.04 | 34.0 | 4.1 | 138.1 | 11.5 | * | 36.6 | 526.6 | 94.1 |
| 1.00 | 4.90 | 23.5 | 3.5 | 127.8 | 16.7 | * | 12.4 | 249.5 | 113.8 |
| 2.00 | 6.16 | 17.1 | 3.7 | 60.2 | 13.2 | 426.3 | 103.9 | 248.8 | 54.3 |
| 4.00 | 6.95 | 16.1 | 0.6 | 46.5 | 4.5 | 134.0 | 12.6 | 243.3 | 60.4 |
| 6.00 | 7.22 | 19.9 | 2.4 | 51.6 | 3.2 | 85.5 | 5.8 | 300.0 | 101.9 |
| 10.00 | 7.41 | 24.2 | 3.4 | 56.3 | 8.1 | 71.8 | 13.4 | 290.0 | 56.9 |

** The plant did not grow*

We plotted the dates of table 4 in Figure 11-14. These figures show the amount of heavy metals in the aboveground parts of the examined plants. In this case, the lime also reduce the heavy metal uptake. One of explanation of this phenomenon is the metal precipitation in the soil by lime (Lombi et al., 2001).

This mean effect of this soil treatments was increased insoluble fraction of heavy metals. The insoluble fraction, which named residual fraction too, not available for plants caused probably form strong bonds between the compost and soil and on the other hand the metal precipitation in the lime and soil.

We compared the effect of compost with lime. We experienced the compost more effective than lime at retention of Cu, Zn, Mn and Fe in the polluted soil (figure 15).

These results corresponded with the results of several other researchers (Topcouglu and Önal, 2007; Castaldi et al., 2005).

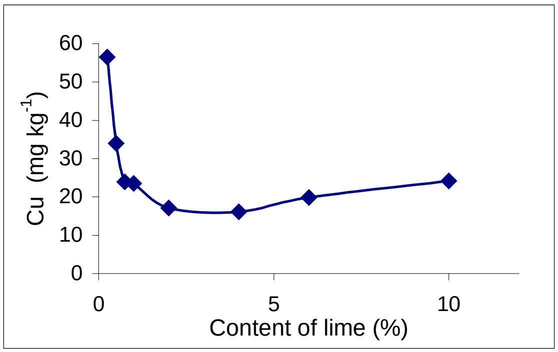


**Fig. 11** Effect of lime on Cu content of plant

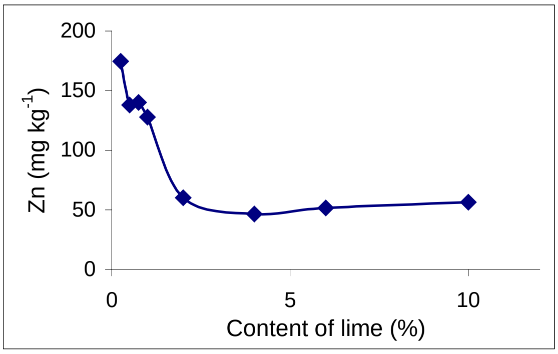


**Fig. 12** Effect of lime on Zn content of plant

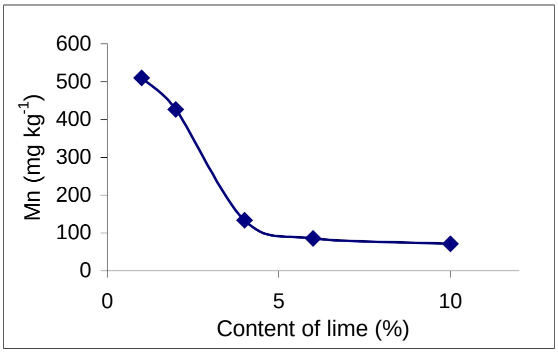


**Fig. 13** Effect of lime on Mn content of plant

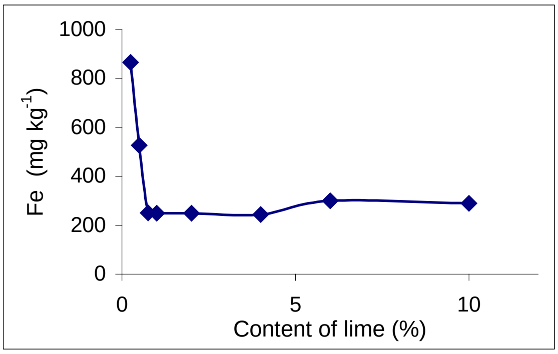


**Fig. 14** Effect of lime on Fe content of plant

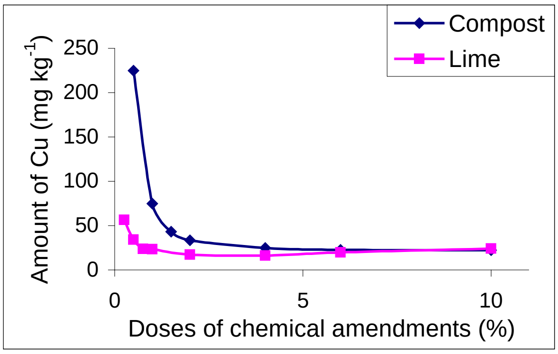


**Fig.15** The effect of the chemical amendments the Cu-content of plants

## CONCLUSIONS

We have studied the effect of compost and lime on the growth and the metal uptake of ryegrass in an acidic, heavy metal polluted soil in pot experiment. In this pot experiment we established that the increasing doses of compost and lime help the survival of the Italian ryegrass under these inauspicious living conditions. The different amendment materials immobilize the examined heavy metals. The compost is good complex forming agent with soil and metal due to bond the metal adsorbing surface of soil. The effect of lime to originate the forming of precipitate with heavy metals. This processes result a decrease in the toxic heavy metal content of the plants.

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## REFERENCES

Antal, K., Budai, J., Szabó, How to Protect the Plants from Heavy Metal Stress in Contaminated Mine Sites with Sheep Manure Compost? Cereal Research Comm., 37, 549-552, 2009.

Delgado Arroyo, M. M., Porcel Cots, M. Á., Miralles De Imperal Hornedo, R., Beltrán Rodríguez, E., Beringola Beringola, L., Martín Sanchez, J. V., Sewage Sludge Compost Fertilizer Effect on Maize Yeld and Soil Heavy Metal Concentration, Rev. Int. Contam. Ambient, 18, 147-150, 2002.

Dömsödi J., Talajjavítás és komposztálás a házikertben. Mezőgazdasági Kiadó, Budapest, 56, 91- 92, 105, 1989.

Draskovits, P., Magyar, B., Jánosi, M., Report of OMFB-02453/2000 project. 2002.

Esakku, S., Kurian Joseph, O. P., Nagerendran, R., Heavy Metal Fractionation and Leachability Studies on Fresh and Partially Decomposed Municipal Solid Waste. 12, 127-132, 2008.

Lide D. L. (ed.), Handbook of chemistry and physics. 84th edition, CRC Press, 1313-1319, 2003-2004.

Lombi, E., Zhao, F-J., Zhang, G., Sun, B., Fitz, W., Zhang, H., P. McGrath S., In situ fixation of metals in soils using bauxite residue: chemical assessment. Environmental Pollution, 118, 435-443, 2002.

Máthé-Gáspár, G.-Anton, A., Phytoremediation Study: Factors Influencing Heavy Metal Uptake of Plants. Proceedings of the 8$^{th}$ Humgarian Congress on Plant Physiology and the 6$^{th}$ Hungarian Conference on Photosyntesis, Acta Biologica Szegediensis, 49, 69-70, 2005.

Murányi A., Ködöböcz L., Heavy Metal Uptake by Plants in Different Phytoremediation Treatments. Cereal Research Communication, 36, 387-390, 2008.

Papp M., Juhász L., Botanikai állapotfelméres szennyezett talajfelszíneken Gyöngyösoroszi térségében a volt Országos Érc- és Ásványbányák Gyöngyösoroszi ércelőkészítőjének területén. Debrecen, 2008.

Topcuoglu, B., Effects of Rereated Applications of Sewage Sludge and MSW Compost on the Bioavailability of Heavy Metals in Greenhouse. Soil Polish Journal of Environmental Studies, 14, 217-222, 2004.

Topcouglu, B.-Önal, M. K., Heavy metal Accumulation in the Eggplant *(Solanum melongena)* Grown in MSW compost applied soil Utilization of diversity in land use systems. Sustainable and organic approaches to meet human needs Tropentag 2007, October 9 - 11, Witzenhausen, Germany, 2007.

Tury R., Szakál P., Szegedi L., A tavaszi árpa *(Hordeum vulgare* L.*)* növekedése és nehézfém-akkumulációja a gyöngyösoroszi bányameddőn különböző kezelések hatására. Talajvédelem, Talajtani vándorgyűlés, 2008. május 29-29. Nyíregyháza, Talajvédelmi Alapítvány, Bessenyei György Könyvkiadó, Nyíregyháza, 2008.

Zubillaga, M.S., Bressan, E.L., Raul, S., Heavy Metal Mobility in Polluted Soils: Effect of Different Treatment. American Journal of Environmental Science, 341-348, 2008.

Walker, D.J., Clemente, R., Bernal, M.P., Contrasting effects of manure and compost on soil pH, heavy metal availability and growth of *Chenopodium album* L. in a soil contaminated by pyritic mine waste. Chemosphere, 52, 215-224, 2004.