POSSIBILITY OF REMEDIATION OF A HEAVY METAL POLLUTED SOIL

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Abstract

*Sustainable development presents important challenges to environmental research, such as developing perspectives and methods that clarify the links between social activities, resource use, and pollution. A typical territory polluted by human activities is situated in the area of the Gyöngyösoroszi metal mine. The mine of Gyöngyösoroszi worked with total capacity until 1950 and it was closed in 1986. Its slag sites are contaminated with residual toxic heavy metals (e.g. Zn, Cu, Pb, Hg, Cr). Location and degree of the contamination of this area have been studied in details earlier. Application of sheep manure compost (SM compost) was tested as a possible way for remediation of polluted soils in order to produce some special plants. Pot experiments were conducted to investigate the effects of the SM compost on the growth and the stress tolerance of maize (Zea mays L.) and Italian ryegrass (Lolium multiflorum L.)***.** *Our goal was to obtain detailed information about the feature of the compost which increases the stress tolerance of plants on the basis of experimental data originated from chemical analysis of the tested soil, the compost and the phosphorite. We carried out sorption and heavy metal leaching laboratory tests on the polluted soil, too. Additionally, adsorption of extracted humic–like components of the compost on the contaminated soil was studied. Langmuir-type isotherms were used to discover some details of sorption processes of the soluble organic fraction of the tested compost on the heavy metal polluted soil. We determined the effects of the applied compost on the solubility of soil pollutants by measuring the extent of salt leaching from the tested contaminated soil as well.*

Keywords: Mine sites of Gyöngyösoroszi, sheep manure compost, adsorption, leaching out of salts, metal uptake

INTRODUCTION

The slag sites of the metal mine at Gyöngyösoroszi were studied in details and a contamination map was constructed (Draskovits et al., 2002) before. The vegetations of these slag sites were mapped as well and different phytoremediation experiments were carried out there (Draskovits et al., 2002; Murányi and Ködöböcz, 2008; Papp, 2008). Application of composts for the purpose of increase the stress tolerance of plants is wide-spread in agricultural practice (Topcouglu et al., 2007; Ma del mar Delgado et al., 2002). However, the effect of composts is not completely clear in this respect. It is known that composts contain high amount of humic-like matters which are very good complex forming agents for some metal ions. Therefore we presume that composts can protect plants from the stress and the toxicity caused by different heavy metals (Keresztúri et al., 2008). For checking this assumption pot experiments were carried out with maize indicator plant. Effects of four different compost doses 0 (control), 50 g, 100 g, 200 g per pot (0, 30, 60, 120 t ha^{-1} compost doses respectively) were studied. Effect of phosphate on the growth of plants was also studied in other pot experiments. In order to clarify our assumption, we studied the adsorption of humic-like fraction of the compost on the tested slag site soil, and the leaching processes of heavy metal ions from the soil, treated with sheep manure compost. During the examination of leaching out processes we applied the method used by Esakku et al. (2008). The production technology of the compost applied in our experiments was developed by researchers of our institute (TERRASOL ® compost). In this paper we summarized the conclusions of our studies concerning to the abiotic stress moderating effect of the tested compost.

MATERIALS AND METHODS

Agricultural methods

Maize pot experiments

Maize *(Zea mays* L.*)* was grown in contaminated soil treated with *SM* compost in greenhouse. The soil was collected from the surface layer of the contaminated area of the former metal mine at Gyöngyösoroszi. Soil of 5 kg was put into plastic buckets. The following amounts of *SM* compost were added to the soil: 0 (control), 50 g, 100 g and 200 g per pot. The pots were arranged in completely randomized design with four replications. 20 maize seeds were sown in each pot as indicator plants.

Italian ryegrass experiments

Italian ryegrass (*Lolium multiflorum* L.) was grown in contaminated soil treated with *SM* compost and phosphorite mixture in a greenhouse. 2.5 kg of polluted soil were put into plastic buckets. Each combination of 0 (control), 25 g, 50 g and 100 g of *SM* compost and 0 g, 1 g, 2 g and 4 g of phosphorite was tested. The pots were arranged in completely randomized design with four replications. 40 seeds were sown in each pot as indicator plants.

Open air experiments

Open air experiments were carried out in the Gyöngyösoroszi mine sites on the original polluted soil by some plants, for example: sunflower *(Helianthus annuus* L.*)*, millet *(Panicum miliaceum* L.*)*, chickling vetch *(Lathyrus sativus* L.*)*. The tested plants were harvested after two months. The harvested biomass was dried and analyzed by classical analytical methods.

Chemical methods

Soil analysis

Chemical parameters of the samples were determined by the actual Hungarian standard methods. We applied combined glass electrode to measure pH values in suspension of 1:2.5 soil mass/water volume ratio. Organic matter analysis was made with oxidative methods ($KCrO_4$ digestion), while $CaCO_3$ analysis was done by means of Scheibler-method. Soluble toxic elements were extracted by 0,1M KCl-0,05M EDTA solution. For determination of total toxic element contents the samples were digested in HNO_3 / H_2O_2 solution of 2:1 ratio while they were heated by microwave. The concentrations were determined by SpectraAA 220FS atomic absorption spectrometer.

Compost and phosphorite analysis

We determined N, P, K contents of compost and phosphorite by the Kjeldahl method.

Plant analysis

For determination of total toxic element contents the samples were digested in HNO_3 / H_2O_2 solution of 2:1 ratio while they were heated by microwave. The concentration was determined by SpectraAA 220FS atomic absorption spectrometer.

Adsorption measurements

Measures of the adsorption of the Extracted Humic Like Material (*EHLM*) on soil samples: For optimization of the adsorption experiments Kreoker-method was carried out by adding 0.5-5.0 g of soil samples to 15 cm^3 aqueous solution of *EHLM* of 3.7 gdm^{-3} concentration at room temperature. In this way the optimal amount of solid phase proved to be 1.5 g.

The validity of Langmuir isotherms was studied with the optimized soil weight in 0.3-4.1 gdm^{-3} *EHLM* concentration range. The equilibrium *EHLM* concentration was determined by Spekol 1100 VIS spectrophotometer, with using a calibration curve taken previously. The amount of specific sorbed *EHLM* was calculated by the following formula: $a = (C_0-C_e)V/m$, where: C_0: is the initial concentration,- C_e: is the equilibrium concentration of the sorbed material after the adsorption. *V* is the volume of the solution, *m* is the weight of the adsorbent(soil). By calculating $\Theta = a/a_{max}$, the coverage of the surface (%) the Langmuir-plots were analyzed.

Salt leaching experiments

Soil samples of 100 g were suspended in 0.65-5 m% aqueous solution of *EHLM* of 0.5 dm^3 at room temperature for a month. The amount of leached out total salt content was gravimetrically determined in the liquid phase.

RESULTS AND DISCUSSION

Some chemical features of the polluted soil were determined with the purpose of right valuation of our results. The analytical data show some troubles of the tested soil clearly *(Table 1).* The soil is very acidic. Both pH parameters (measured in H_2O and in KCl solution) are low. The readily available phosphate and nitrogen content of the soil are low, too. The humic content seems to be sufficient, but these data can be false, because the determination of humic-material content is based on the chromate oxidation method. The question arises whether this process is applicable in case of such high heavy metal concentration. Probably the high heavy metal concentration may affect other analytical results like results concerning humic matter contents. The *Table 1* shows that the sulphate content is very high and it can be toxic for plants.

Table 1.

Some chemical features of the tested soil

pH (H_2O)	2.65
pH (KCl)	2.62
Humus % (Tyurin-method)	1.24
P_2O_5 ($mgkg^{-1}$) (Ammonium lactate, AL)	<5
P_2O_5 ($mgkg^{-1}$) (Kjeldahl)	700
K_2O ($mgkg^{-1}$) (AL)	112
K_2O ($mgkg^{-1}$) (Kjeldahl)	7000
Ca ($mgkg^{-1}$) (AL)	21500
Mg ($mgkg^{-1}$) (AL)	1180
Na ($mgkg^{-1}$) (AL)	43
SO_4^{2-}($mgkg^{-1}$) (KCl)	25320
CO_3^{2-} ($mgkg^{-1}$) (Scheibler-method)	4000
NO_3^- -NO_2^- ($mgkg^{-1}$) (KCl)	<10
N ($mgkg^{-1}$) (Kjeldahl)	Under the detection limit

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 determined ratios of availability of each heavy metal (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)*.

Table 2

Heavy metal content of the examined soil

Metal content	**Mobile fraction (mg kg^{-1})**	**Total amount (mg kg^{-1})**	**Mobile fraction ratio from total amount (%)**	**Threshold limit* (mg kg^{-1})**
Zn	**648**	**1720**	**38**	**200**
Cu	**230**	**675**	**34**	**75**
Fe	258	42600	0,6	no date
Mn	270	964	28	no date
Cr	<4.00	33.0	<12	75
Co	2.40	10.0	24	30
Ni	<2. 00	7.00	<29	40
Cd	6.30	7.00	90	1
Pb	356	473	75	100

Some chemical features of the applied compost and phosphorite are shown in the Table 3 respectively. Contrary to the investigated soil, the compost provided a good phosphorus source for the plants.

Table 3.

The analytical data of the applied sheep manure compost

Determined material	**Phosphorite (mgkg $^{-1}$)**	**Compost * (mgkg $^{-1}$)**
N	Under the detection limit	19800
P_2O_5	270000	17500
K_2O	2700	37900
Total organic material	Under the detection limit	480000

* TERRASOL ®

The maize was sowed in soil treated with different amount of compost. We measured the height of plants after one month. We found that the increasing amount of compost resulted in monotonously increasing height of maize *(Figure 1)*. This increase of height can probably be caused by the improving phosphorus (P) supply and the complex forming ability (with metal ions) of the *SM* compost (Dömsödi 1989; Máté-Gáspár and Anton, 2005).

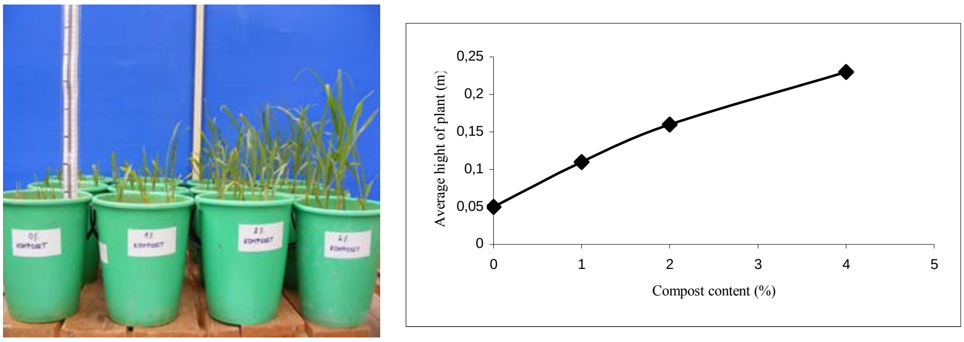

Figure 1 : Effect of compost doses for high of maize in pot experiments

We carried out another pot experiments with Italian ryegrass because we wanted to verify the effect of phosphate content of compost. We mixed the compost and the phosphorite in different ratio and added them to the pots. We determined the average height of plants *(Figure 2-3)*.

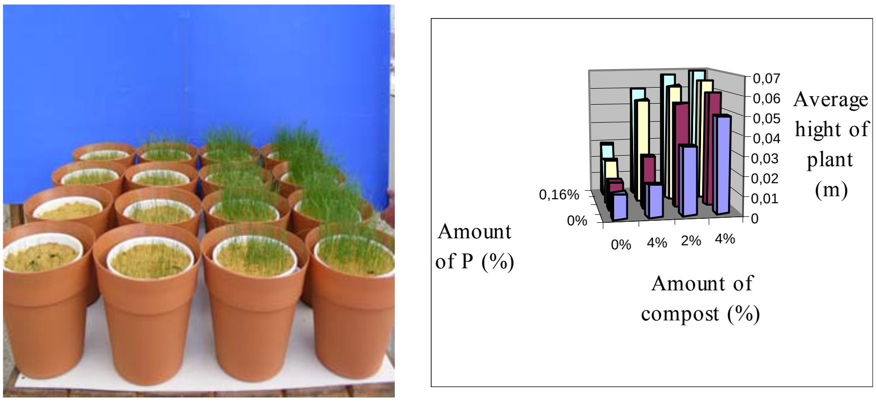

Figure 2-3: Common effect of compost and phosphorite for grass growth

We observed that phosphorite is beneficial to the growth of grass. Moreover, we experienced the compost is more effective than the natural phosphorite in equivalent amount. The phosphate can affect the growth of plants in two different ways. It is either a good nutrient for plants or it decreases the biological availability of heavy metals by reducing their solubility (Lide, 2003-2004). Therefore we may conclude that other components of the compost can take effect on growth of plants. In heavy metal tolerance of plants the humic fraction content of the compost can play important role. In order to clarify the chemical mechanism of heavy metal retention of the compost we studied the adsorption features of humic fraction on the soil.

We also determined the amounts of some heavy metal ions of the maize plants. The analytical data supported our assumption, because the increasing compost doses decreased the heavy metal contents of aboveground parts of the tested plants *(Figure 4-5).* Our results corroborate the finding of Tury et al. (2008) and Morrison (2000).

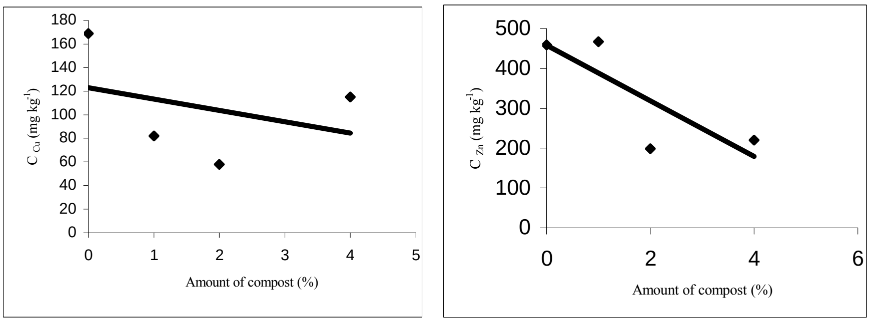

Figure 4-5: Cu and Zn content on aboveground parts of maize

Analytical data of the roots do not show such an obvious results. The copper content decreased, but the zinc did not decrease by compost addition (Figure 6-7). Probable reason is that, copper forms strong complexes with humic materials while zinc does not (Wei et al., 2004).

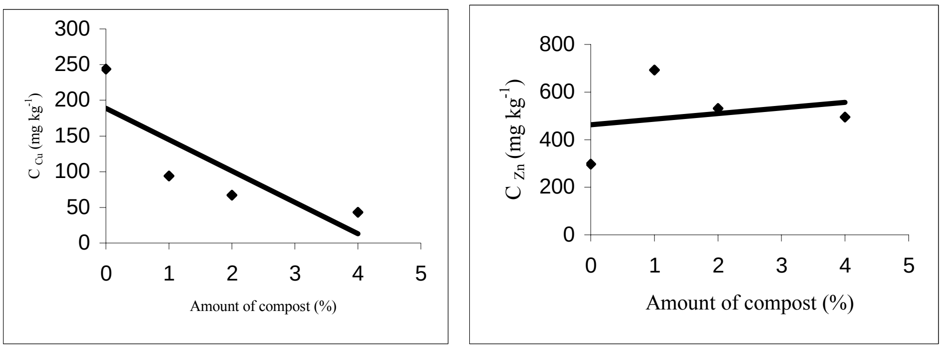

Figure 6-7: Cu and Zn content on root of maize

The reduction of heavy metal uptake caused by the compost application was confirmed in open air experiments as well. We compared the metal contents and the average height of stalks of plants produced on treated and untreated soils. We found that the compost treatment increased the height of plants and decreased the metal concentration in the plants *(Table 4)*.

Table 4

Metal concentrations of plants stalk amended with compost in open air experiments

Tests		Average Height (m)	Heavy metal content ($mg\ kg^{-1}$)	
			Cu	Zn
Sunflower *Helianthus annuus*	Untreated	0.30	7	706
	Treated	0.80	0	224
Chickling vetch *Lathyrus sativus*	Untreated	0.30	21	106
	Treated	0.50	8	175
Millet *Pariculum miliaceum*	Untreated	0.25	32	97
	Treated	0.60	0	116

We amended our plant tests with chemical experiments. We studied the salt leaching from tested soil by different doses of compost. *Figure 8,9,10* show that application of the compost decreases the leach out of salts and heavy metals ions. Hence their availability for plants decreases in soil-*SM* compost suspensions. This observation can be explained by the complex formation of heavy metal ions with *SM* compost adsorbed on the soil particles.

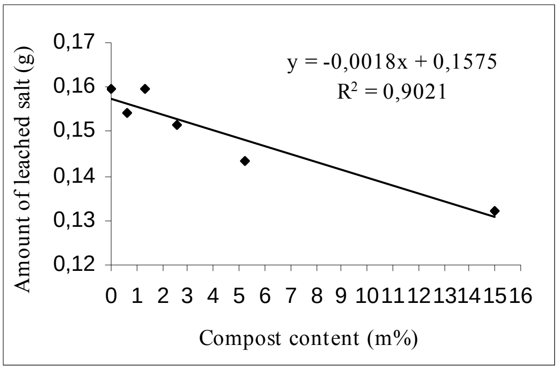

Figure 8: The amount the leached salt from soil versus o f SMC compost content

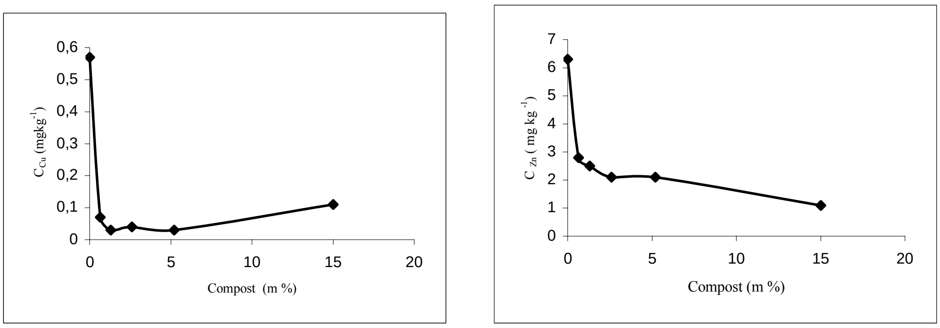

Figure 9: The leached concentration of Cu and Zn versus of SMC compost content

We studied the adsorption features of the *EHLM* on the tested soil because we wanted to know the way of the metal-soil-humic complex formation. The Langmuir-type plot *(Figure 10)* shows a good linearity of adsorption of *EHLM* on the tested soil. It means that the *EHLM* forms a monomolecular layer on the surface of the soil particles and the process is reversible. The type of this bond is probably electrostatic with binding constant of 2.9 $\pm$ 0.3 dm^3g^{-1}, which represents a remarkably strong interaction between the surface of soil particles and *EHLM.*

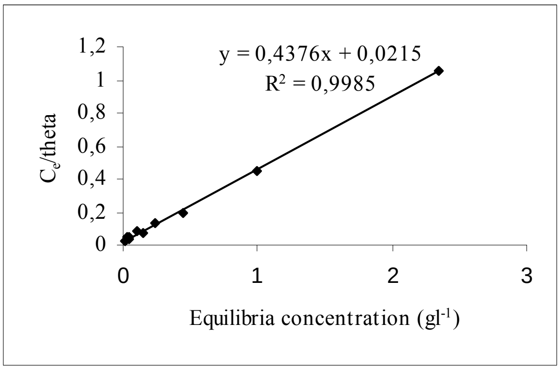

Figure 10*: Linearized Langmuir-type isotherm of EHLM extract on the tested soil*

CONCLUSION

This study suggests that the sheep manner compost is good protecting agent for survival and growing of plants in polluted soil. We suppose that the following reasons explain the results:

1., The compost makes up for phosphorus which is absent from soil.

2., The water soluble fraction of compost strongly adsorbs to the contaminated soil, and as a very good complex forming material holds back the heavy metals.

3., The *SM* compost reduces the mobility of salts and heavy metals in polluted soil suspensions.

4., Increasing the amount of compost unambiguously helps the growing the maize in pot experiments.

5., According to greenhouse tests the added compost results higher plants.

6., The *SM* compost treatment decrease the Cu and Zn concentrations in the stalk of the different plants.

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