

**DOCTORAL (PHD) DISSERTATION**

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**MITIGATION OF THE HEAVY METAL CONTENT OF WASTE HEAPS BY  
GROWING VARIOUS PLANT SPECIES**

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## **Introduction and aims of the study**

The surrounding area at the village of Gyöngyösoroszi is impacted by a metal load significantly exceeding what is regarded to be average. In the region, metal content of natural in origin springs from the geological settings as considerable ore-formation can be observed in the catchment area of the Toka Stream. Above-ground and near-surface ore-veins are present in the stream's burden originated from the denudation of the rocks in the catchment area. Due to the area's topography, the bed load of the stream is deposited in the valley. The subsequent concentration of heavy metals is further increased by stationary rocks.

The artificial metal load here is resultant from industrial activities. During the mining and beneficiation of ores, the emission of excess heavy metal volumes is unavoidable. Waste materials originating from the mine have a heavy metal content higher compared to that of the environment. Waste water discharged from the mine as well as the sewage sludge deposited during the clearing of this waste water also indicates a significant level of pollution.

## **Methods**

Setting-up of the open-field experiment began during the autumn of 2004. The units developed bordered by wooden frames, into which flotation sludge from the waste heap was deposited, were 50 cm in height. 12 various treatments, each with 4 repetitions, were set.

The treatments applied were as follows:

1. 30 kg compost, 2. 10 kg mordenite, 3. 10 kg sewage sludge + 2 kg synthetic zeolite, 4. 10 kg sewage sludge + 2 kg clinoptilolit (natural zeolite), 5. 10 kg lime dehydrate, 6. 10 kg lime sludge ( $\text{CaCO}_3$ ) + 5 kg wood-chips, 7. 10 kg 5% alginite, 8. 10 kg lime sludge ( $\text{CaCO}_3$ ) + 10 kg 5% alginite, 9. 10 kg lime sludge ( $\text{CaCO}_3$ ) + 2 kg clinoptilolit (natural zeolite), 10. 10 kg lime sludge ( $\text{CaCO}_3$ ) + 2 kg synthetic zeolite,

11. 30 kg lime sludge (CaCO<sub>3</sub>), 12. 15 kg lime sludge (CaCO<sub>3</sub>) + 15 kg lime dehydrate, 13. control.

In the first and second year of the experiment, Into half of the plots, *Paszadéna* variety of barley (*Hordeum vulgare*) was seeded whereas into the other half, *Viktória* variety of lucerne (*Medicago sativa*) was put in. In the third and fourth years, barley was replaced by *Keszthelyi 2* variety of Red Fescue (*Festuca rubra*).

The plots' distribution was randomised in the given repetitions. Therefore the likeliness that each treatment would partake the smaller or larger, positive or negative errors of experiment variant according to the plots was equal. As far as possible, it was intended to be achieved that treatments in the adjacent blocks should be different from each other. During the experiment, no soil disinfection or chemical weed control was applied in order to prevent any disorder in the experiment resultant from the potential phytotoxic effect of pesticides.

Both soil tests and plant analysis took place in the laboratory of the BÁLINT ANALITICS LTD.

To the mathematical and statistical evaluation of the data, one way analysis of variance (ANOVA) and two-sample t test were conducted. The values of significant difference were indicated on a P = 5% level of significance.

## **Conclusions and proposal**

### **Conclusions**

Among the three plant species grown on heavy metal loaded flotation sludge, the cadmium and lead uptake of barley is lower, compared to the other two species whereas the copper and zinc uptake was proved to be outstanding both in its roots and shoots.

The metal content (cadmium, copper, lead and zinc) of lucerne was lower both in the roots and the shoots compared to the barley and Red Fescue. The susceptibility of lucerne to soil acidity was revealed here.

Based on previous experiences, Red Fescue tolerates acidic pH which feature was also proved by the analyses carried out here as its stand was the most

significant of the three plant species even in the control plot. Its heavy metal uptake (of cadmium, copper, lead and zinc) was the most significant in both segments studied among the three plant species.

Of the 12 treatments applied, the sewage sludge + synthetic zeolite was proved to be the most effective as the highest level of decrease in the metal uptake of plants as well as the most intensive growth of plants were observed during this. This good result can be provided by sewage sludge as toxic elements make up a complex with the decomposed organic material. Thus, metal uptake of the plants will remain limited in extent.

As a consequence of the sewage sludge + clinoptilolit (natural zeolite) treatment, the amount of heavy metals taken up decreased to a similar level than during the sewage sludge + synthetic zeolite treatment; however, metal content was slightly higher in nearly all cases than in the case when the sewage sludge + synthetic zeolite treatment was applied. An explanation for this can be that the adsorption capacity of the synthetic zeolite exceeds that of the clinoptilolit and also has a better ion-binding capacity.

After having the impacts of lime sludge + synthetic zeolite and lime sludge + clinoptilolit (natural zeolite) treatments compared, it can be concluded that here the addition of the synthetic zeolite mitigated the uptake of heavy metals to a more significant level, too. This can also be the result of the differences in the ion-binding capacities and adsorption features already mentioned. Having the effect of lime sludge compared to that of the sewage sludge, based on the experiences, it can be claimed that plants grew more intensively in plots treated with sewage sludge and they also had a lower metal concentration. An explanation for this can be that lime sludge influenced only the pH of the sludge, whereas sewage sludge while binding metals also supplied nutrients (nitrogen, phosphor) to the plants.

The effect of compost treatment also indicated good results for all three plant species, as it is likely that due to the decomposed organic material, the uptake of toxic elements by plants decreased, thus their growth became intensive.

Compared to the treatments already mentioned, the mordenite (natural zeolite) and alginate treatments did not deliver good results. As a result of the

treatments, no improvement was observed in the nutrient-supplying capacity of the sludge; basic conditions to the growth of plants therefore were not established.

Treatments with lime sludge when combined with other substances (wood-chips, alginite) did not indicate as good results as the treatments mentioned earlier. By them, heavy metal accumulation could be reduced to a limited extent, only. The plants indicated a slight growth only, and remained extenuate until the end of the vegetation period, with many of them becoming decayed. Their metal uptake was more significant in comparison to when synthetic zeolite and clinoptilolite were added. As a result of these treatments, an increase of the sludge's pH was observed.

The uptake of heavy metals was the most significant, compared to the control, when lime dehydrate, lime sludge and lime sludge + lime dehydrate were applied. Plants hardly grew in the plots mentioned above, without growing generative organs at all. Presumably, the growth of plant here was inadequate partly due to nutrient deficiency; although the lime applied reduced the acidity of the waste heap but did not supply nutrients indispensable to the growth of plants.

### **Proposals**

Flotation sludge, as with an acidic pH, demands liming. It is suggested to add the adequate amount of lime to alter the sludge's pH to be neutral or alkaline.

Nutrients indispensable to the growth of plants have also to be supplemented as the waste heap has a nutrient deficiency. This could take place by applying either fertilizer or manure.

The use of sewage sludge could be a good solution to the supply of organic material, and in the meantime, the emplacement of the sewage sludge arisen can also be tackled however, it is suggested for use only after composting.

The effect of zeolites can be regarded positive as having advantageous impacts on the features of the flotation sludge. They improve its structure, air and water balance as well as contribute to a better exploitation of nutrients.

### New scientific results

1. When flotation sludge is treated with synthetic zeolite and sewage sludge, the amount of toxic material can be significantly reduced, compared to the control, both in the roots and in the part of the plants above-ground. The nutrient supplying and structure improving capacities of sewage sludge were enhanced by adding synthetic zeolite.
2. Natural zeolite when combined with sewage sludge and lime sludge, significantly reduced the cadmium, copper, lead and zinc accumulation of barley, lucerne and Red Fescue both in their roots and shoots. By this, the mobility of toxic elements was detained. The ion-binding capacity of clinoptilolite further decreased the availability of toxic elements. Sewage sludge advanced the supplement of nutrients and the binding of toxic elements as complexes. The transition of the sludge's acidic reaction to the alkaline province was advanced by adding lime sludge. Decrease in the metal uptake was as follows: for barley: Cd: 49 %, Cu: 56 %, Pb: 58 %, Zn: 45 %; for lucerne: Cd: 46 %, Cu: 40 %, Pb: 50 %, Zn: 50 %; for Red Fescue: Cd: 49 %, Cu: 39 %, Pb: 60 %, Zn: 39 %.
3. *Lime sludge* combined with synthetic zeolite or clinoptilolite (natural zeolite) indicated good results, however was not proved to be as efficient as the sewage sludge. Lime sludge only increased the pH of the flotation sludge and has no metal-binding capacity unlike the sewage sludge. Decrease in the metal uptake was as follows: for barley: Cd: 47 %, Cu: 56 %, Pb: 58 %, Zn: 45 %; for lucerne: Cd: 46 %, Cu: 43 %, Pb: 50 %, Zn: 50 %; for Red Fescue: Cd: 49 %, Cu: 39 %, Pb: 60 %, Zn: 49 %.
4. *Compost* had a positive effect on the features of the flotation sludge. It improved its air, heat and water balance thus the nutrients supplied were exploited and a contribution was also made to the establishment of a more active soil life. Decrease in the metal uptake was as follows: for barley: Cd: 35 %, Cu: 49 %, Pb: 58 %, Zn: 45 %.

Pb: 51 %, Zn: 45 %; for lucerne: Cd: 46 %, Cu: 40 %, Pb: 45 %, Zn: 46 %; for Red Fescue: Cd: 49 %, Cu: 30 %, Pb: 45 %, Zn: 37 %.

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