Combined chemical and phytostabilisation of metal polluted soil

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Introduction

Phytostabilisation can be combined with chemical stabilisation to lower the mobility and bioavailability of toxic metals in the soil. Immobilisation of metals enables settling of plants and consequently reduces the transport of pollution from soils. As a final result it lowers the environmental risk of the polluted soil on air, water and food chain. In our experiments the stabilising effect of five additives was modelled on metal polluted soils in laboratory microcosms. The stabilisation process was monitored by an integrated methodology, which combined physical-chemical analysis with biological and toxicological testing. We distinguished various mobilities: 1. Chemical extractability, measured after different solvent extractions; 2. Bioavailability, characterised by plant and bacterial toxicity of the soil; 3. Bioaccumulation in plants, measured by a self-developed rapid bioaccumulation test.

Objectives

The microcosm experiments aimed to select the suitable chemical stabilisers for metal polluted soils prior to vegetation and prove the environmental relevance of the integrated methodology.

Experimental

Microcosms

The treated and control soils were placed in 2 kg pots each. The moisture content was set to the 60% of the water capacity of the soil. The soil samples were incubated at 25°C, in a thermostat chamber. The soil was mixed and watered every two months.

The microcosm tests were monitored for 25 months by an integrated methodology, which combined physico-chemical analysis, biological and ecotoxicological testing.

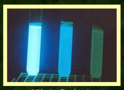
The contaminated soil originates from a hobby garden of Gyöngyösoroszi, Northern Hungary. The agricultural land was contaminated with metals due to former zinc and lead mining activity at the area.

The total metal concentrations in the aqua regia extracts show that As, Cd, Cu, Hg, Pb and Zn are above the limit. The mobile metal fraction extracted by acetate, contains 2,5 ppm Cd and 338 ppm Zn, equivalent with 34% and 24% of the total.

Table 1.: Metal contents of the Gyöngyösoroszi soil
(the mobile and water soluble part is in percentage of the total metal content = 100%)

	As	Cd	Cu	Hg	Pb	Zn
Total metal content (mg/kg)	333	7,25	338	3,09	1572	1396
Mobile (%)	~0%	34%	3%	~0%	~0%	24%
Water soluble (%)	~0%	13%	~0%	~0%	~0%	11%
Quality criteria for total (mg/kg)	15	1	75	0,5	100	200

The following chemical stabilisers were added to the soils in specific concentrations:
- Fly ashes „A” and „B” from the coal fuel power plant of Oroszlány, Hungary in three concentrations: 1 w%, 2 w%, 5w%,
- Lignite: 10 w%, alginite: 1,5 w%, raw phosphate: 1 w%, hydrated lime: 1 w% and the mixture of the four.


Vibrio fischeri


Azotobacter agile


Sinapis alba

Integrated methodology

The results of the integrated methodology give a more detailed picture on the environmental risk of polluted soil. The proper selection and combination of chemical and biological methods make the model able to characterise risk on soil flora and fauna, on agricultural products, on groundwater and surface water. Traditional extraction and leaching with water and acidic solvents is being used for modelling the transport of metals from soil to water. The risk of metal uptake into plants is often modelled by extraction with organic acids and EDTA. These „chemical models” simplify the real environment. To refine the risk model, we applied direct contact toxicity tests with soil living organisms for the characterisation of the bioavailability of the soil pollutants, and worked out and applied a rapid bioaccumulation test, which allows us to measure the amount of metals available for plant uptake.

Extractability of metals

The change of the mobility of the metals in the treated soil was followed by analysing metals in four different extracts and by testing their biological effects by toxicity testing.
The following extracts were analysed by ICP-AES.
- Soluble metals in water extract,
- Mobile metals in ammonium-acetate extract (pH=4,5)
- Mobile metals in a solvent mixture of ammonium-acetate, acetic acid and EDTA,
- Total metal content of the soil in aqua regia extract.

Toxicity and biaccumulation

To measure the adverse effects of the polluted soil and predict the environmental risk of the pollutants, the stabilisation process was followed also by ecotoxicity and bioaccumulation testing. The results of the chemical and the biological analyses were evaluated together.

Two microbial and a plant growth toxicity test were applied for whole soil, ensuring direct contact and interaction between soil and test organism during the test.
- *Vibrio fisheri* luminescence inhibition test,
- *Azotobacter agile* dehydrogenase enzyme-activity inhibition test,
- *Sinapis alba* (white mustard) root and shoot growth inhibition test.

The fraction available for plant uptake was measured by a new, self-developed, rapid bioaccumulation test. The amount taken up by the plants was analysed in the 5 day old seedling by ICP-AES after $H_2O_2 + HNO_3$ digestion of the biomass.

Results and discussion

Fly ash treatment

Both the chemical and toxicological results showed the good immobilising efficiency of fly ash. The decrease in the extractable metal content was observed already 21 days after fly ash addition and became significant after 4 months of treatment. According to the chemical analytical results the stabilizing efficiency of the two types of fly ashes were nearly the same, although the type „A” was slightly better. After the addition of 5 w% fly ash to the soil the mobile Cd and Zn concentration decreased by **45–49%** in the acetate extract, while by **99%** in the water extract. The stabilising effect of a single treatment has remained unchanged for more than 2 years.

The stabilizing effect of fly ash

The applied fly ashes (pH_A=12,6; pH_B=9,66) has an alkalising effect on the Gyöngyösoroszi soil (pH_{soil}=5,54 —> $pH_{soil+5\%"A"ash}$=7,15), which gives explanation to a certain extent on the changes in the toxic metal mobility in the soil. Its long term stabilising effect – compared to the lime-treatment – can be explained by the additional effect of fly ash on the formation of secondary silicates (reverting the weathering processes) and binding metals into the molecular lattice.

➢ The fly ash treatment diminished the acetate extractable (Fig.1) and water soluble (Fig.2) zinc and cadmium concentration in the soil.
➢ The higher amount of fly ash was added (1, 2, 5 w%), the decrease in the mobility was bigger (Table 2). The addition of 5 w% „A” fly ash diminished the acetate extractable Zn and Cd concentrations with 45–49% and the water soluble amount with 99%.
➢The fly ash kept its stabilising effect on long term (more, than 2 years).
➢The extractable concentrations of other, less mobile metals also decreased. The best results showed 68% decrease for lead and 30% for copper in the acetate extract. The water soluble amount of lead was not measurable, the copper was lowered by 66%.

Effect of fly ash on acetate and water soluble zinc concentration

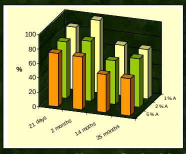


Fig. 1: Acetate extractable zinc in fly ash stabilised soil compared to the non-treated control = 100%.

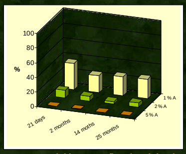


Fig. 2: Water soluble zinc in fly ash stabilised soils compared to the non-treated control = 100%.

Table 2: Decrease in acetate extractable metal concentrations in soils treated with fly ash „A” compared to the non-treated control.

	As	Cd	Cu	Hg	Pb	Zn
1% fly ash A	<DL	25%	29%	<DL	58%	32%
2% fly ash A	<DL	29%	31%	<DL	56%	33%
5% fly ash A	<DL	45%	30%	<DL	68%	49%

Effect of fly ash on the toxicity of soil

The results of the toxicity and bioaccumulation tests have proved that the fly ash is able to immobilize the mobile metals therefore reduce the toxicity of the soil. The bacterial *Vibrio fisheri* and *Azotobacter agile* test showed that the toxicity decreased particularly after 2 and 5 w% of fly ash treatment. The plant tests showed reduced toxicity even after 1 % fly ash treatment. According to the results of the rapid bioaccumulation test the most efficient was the 5 w% „B” fly ash, which diminished the Cd and Zn uptake of the plant by 58% and 74%.

The result of the plant tests gives direct information on the suitability of the chemical stabiliser from the point of view of the following phytostabilisation process, which has to fulfil three basic requirements: good plant growth, high biomass production and no metal accumulation.

The plant toxicity tests showed that the addition of fly ash decreased the toxicity of the soil, since the growth of plants was increased (Fig. 3).

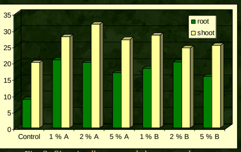


Fig. 3: *Sinapis alba* root and shoot growth
(in mm, 25 months after the treatment)

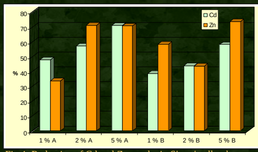


Fig.4: Reduction of Cd and Zn uptake in *Sinapis alba* shoot
(control = 0%; 25 months after treatment)

The Zn and Cd uptake of the plant decreased after the addition of fly ash to the soil (Fig. 4). This was observed already two months after the treatment and remained the same after 25 months.

The acidic extracts do not model well the metal uptake of plants, since the calculated bioconcentration factors ($BCF_{LE} = c_{plant}/c_{acidic\text{-}extract}$) vary between 0.3–5.9, instead of 1 in case of a true model.

Hydrated lime, alginite, raw phosphate and lignite

The additives are ranked from 1-5: the 1st was the most efficient stabilizer

1. *The mixture of the four stabilisers*, lime, alginite, phosphate and lignite: Its best efficiency was proved by both the chemical analytical and the toxicity test results.
2. *Hydrated lime (1 w%):* Based on the chemical analytical measurements the lime reduced the extractable metal content of the soil on long term with 47–64%. Bacterial test showed high immobilizing effect, but the plant test showed slight reduction in toxicity, influenced by soil type. The bioaccumulation test showed 60–70% reduction in Cd and Zn uptake.
3. *Alginite (1,5 w%):* According to the chemical analytical results the alginite reduced the amount of extractable metal with 25–31%, while the bioaccumulation test showed as good results as for the lime. The bacterial toxicity test did not show any change, but for the plants it was the very best amendment in reducing the toxicity.
4. *Raw phosphate (1 w%):* The analytical and bioaccumulation results showed only a slight decrease in metal mobility, while the toxicity results showed stimulation on the effect of phosphate addition. If it is due to the reduction of the inhibition of the toxicant or the growth stimulating effect of the P: is still a question.
5. *Lignite (10%):* The analytical results showed decrease in metal mobility right after the addition of lignite, but this effect did not remained on long term. For bacteria, and especially for plants the soil became more toxic after the addition of lignite, and the bioaccumulation of metals was enhanced.

Effect of the amendments on metal mobility and toxicity

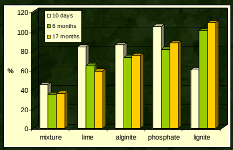


Fig. 5: Decrease in the acetate soluble Cd in the treated soils compared to the non-treated control (100%).

Table 3: Ranking of the stabilizers according to the toxicity and bioaccumulation tests

Test	**Ranking of stabilisers**
Bacterial	1st: hydrated lime 2nd: raw phosphate 3rd: mixture of four
Plant	1st: alginite 2nd: raw phosphate 3rd: mixture of four (3rd)
Bioaccumulation	1st: hydrated lime 1st: alginite, 1st: mixture of four

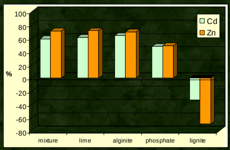


Fig. 6: Change in Cd and Zn uptake in *Sinapis alba* shoot, control = 0%

The analytical results do not always agree with the toxicological results. That is why chemical analysis has to be integrated with toxicity measurements.
According to the analytical measurements the best stabiliser is the four amendment together (Fig. 5), while the bioaccumulation (Fig. 6) test indicates the good stabilising effect of alginite, lime and the mixture of four. Considering toxicity (Table 3) alginite, lime and raw phosphate is even better than the four together.
Lignite was proved to be inefficient by all measurements.

Conclusions

The results of the **stabilisation microcosm** experiments indicate that it is possible to reduce the mobility of toxic metals such as Cd, Zn, Pb, Cu and As by the treatment of the soil with chemical stabilisers.
The fly ash treatment reduced the amount of the mobile metals on long term (2 years). The addition of 5 w% fly ash decreased the acetate extractable Cd and Zn by 45–49% and the water soluble Zn and Cd by 99%. The results of the chemical analyses and the biological testing fully agrees with each other in case of fly ash treatment, which reduced plant toxicity with 40-60%, and bioaccumulation by 58% (Cd) and 74% (Zn).
Other stabilisers, as hydrated lime, alginite, raw phosphate and lignite were also examined as possible stabilizers. Applying the four together showed the best stabilizing effect. The addition of hydrated lime decreased the mobile metal content of the soil on long term (17 months) with 47–64%, and it also reduced the toxicity of the soil for bacteria. The stabilizing effect of alginite was mainly proved by the bioaccumulation and the plant toxicity tests, while raw phosphate resulted in stimulation, in spite of low reduction in extractability. Lignite had no stabilizing effect, it increased the toxicity of the soil and the metal accumulation of the test plant.
The integrated methodology, used for the monitoring of the stabilisation process was able to distinguish between extractability, bioavalilability and accessibility for plant uptake. These indicators were in agreement in the best cases, but in the contradictory cases it caleld our attention on the complexity of the process and the necessity of further studies.

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