An innovative remediation for metal polluted soils – combined chemical and phytostabilisation

Viktória Feigl\textsuperscript{1}, Katalin Gruiz\textsuperscript{1}, Attila Anton\textsuperscript{2}

\textsuperscript{1}Budapest University of Technology and Economics, Department of Applied Biotechnology and Food Science

\textsuperscript{2}Research Institute of Soil Science and Agrochemistry of the Hungarian Academy of Sciences
What is combined chemical and phytostabilisation?
Chemical stabilisers

- Stabilisation = immobilisation of metals
- Reduce metal mobility and solubility → reduce transport by water → lower the environmental risk
- Lower the bioavailable toxic metal content → enable germination and growth of plants → healthier plants, higher biomass
- A good stabiliser keeps its effect on long term
- Added before the settling of plants
Plants for phytostabilisation

- Metal tolerant plants
- Small metal accumulation in shoots
  → reduces metal amount that gets into food chain
  (≠ phytoextraction, when the aim is the removal of metals with hyperaccumulators)
- Increase complexity and humus-content
  → hinder leaching of metals
- Stop wind and water erosion

Reduce metal transport on all possible pathways
Site assessment

- Gyöngyösoroszi, Northern Hungary, former mine
  - Total metal concentrations in contaminated agricultural soil (mg/kg) and mine waste

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Cd</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>EQC</td>
<td>15</td>
<td>1</td>
<td>75</td>
<td>100</td>
<td>200</td>
</tr>
</tbody>
</table>

- 11–16% of total Cd and Zn is water soluble
- 17–34% of total Cd and Zn is acetate extractable (pH=4.6)
Objectives

- To develop an innovative remediation technology, which is able to reduce the risk of the former mining site, as a priority to ensure surface water quality at catchment scale
- CCP is a part of a complex risk management strategy, which uses GIS based, catchment scale risk assessment
- To select the best stabiliser and stabiliser–plant combination for Gyöngyösoroszi soil and waste material
Technological experiments

1. Microcosm
   - 2 kg Soil and amendments
   - Thermostate 25 °C
   - Irrigation every two months
   - Soilsampling and analysis

2. Lysimeter
   - 0.35 m³ Soil and amendments
   - Water collection and analysis
   - Irrigation when necessary
   - Plant collection and analysis

3. Field experiment
   - 90 m³ Soil and amendments
   - Soil sampling and analysis
   - Water collection and analysis
   - Irrigation when necessary
   - Plant collection and analysis

Green 5 Conference
Monitoring with integrated methodology

Integrated methodology

Chemical analytical methods
- Aqua Regia digest. + ICP-AES analyses
- Ammonium-acetate + EDTA extr. + ICP
- Ammonium-acetate extr. (pH=4.6) + ICP
- Water extraction + ICP analysis

Biological methods
- Plant bioaccumulation test

Environmental toxicity tests
- *Vibrio fischeri* bioluminescence inhibition
- *Azomonas agilis* dehydrogenase activity inhibition
- *Sinapis alba* root and shoot growth inhibition

Metal content of water by ICP-AES.
Metal content of plants by ICP-AES after nitric acid + hydrogen-peroxide (1:1) digestion.
Microcosms

- agricultural soil (1) and mine waste (2)

- traditional chemical stabilisers
  - hydrated lime, raw phosphate, alginite, lignite

- waste material for stabilisation
  - fly ashes (6) (pH=6.4–12.6) and their combination with lime
  - Fe-Mn-hydroxide precipitate from drinking water cleaning (3, 5)
  - red mud from bauxite processing (4)
**Microcosm results with alkaline fly ash**

Decrease in acetate extractable and water soluble Zn content in fly ash ‘A’ treated agricultural soil

Compared to non-treated = 100%
## Best stabilisation with amendments

### Decrease (%) in metal mobility and toxicity of mine wastes and soil after treatment

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Water extractable Cd and Zn</td>
<td>99</td>
<td>98</td>
<td>78</td>
<td>99</td>
<td>99</td>
<td>92</td>
<td>97</td>
<td>-142</td>
<td>99</td>
<td>71</td>
<td>79</td>
<td>83</td>
</tr>
<tr>
<td>Acetate extractable Cd and Zn</td>
<td>49</td>
<td>34</td>
<td>12</td>
<td>68</td>
<td>53</td>
<td>31</td>
<td>21</td>
<td>-9</td>
<td>68</td>
<td>53</td>
<td>64</td>
<td>62</td>
</tr>
<tr>
<td>Bioaccumulated Cd and Zn</td>
<td>70</td>
<td>74</td>
<td>10</td>
<td>57</td>
<td>70</td>
<td>70</td>
<td>48</td>
<td>-33</td>
<td>70</td>
<td>~0</td>
<td>~0</td>
<td>~0</td>
</tr>
<tr>
<td>Plant toxicity</td>
<td>70</td>
<td>60</td>
<td>62</td>
<td>10</td>
<td>20</td>
<td>31</td>
<td>20</td>
<td>-15</td>
<td>30</td>
<td>60</td>
<td>56</td>
<td>~0</td>
</tr>
</tbody>
</table>

In non-treated decrease = 0%
Construction of lysimeters
## Stabilising effect of fly ashes in lysimeters

Effect of fly ashes on Cd and Zn in drain water from heavily weathered waste material

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Cd (µg/l)</th>
<th>Zn (µg/l)</th>
<th>Decrease Cd (%)</th>
<th>Decrease Zn (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-treated</td>
<td>311</td>
<td>53 677</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fly ash, type ‘T’</td>
<td>30.4</td>
<td>6 405</td>
<td>90.2</td>
<td>88.0</td>
</tr>
<tr>
<td>Fly ash, type ‘V’</td>
<td>0.2</td>
<td>72.5</td>
<td>&gt;99.9</td>
<td>99.9</td>
</tr>
<tr>
<td>Fly ash, type ‘A’</td>
<td>0.1</td>
<td>15.2</td>
<td>&gt;99.9</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>‘A’ as reactive barrier</td>
<td>0.1</td>
<td>26.7</td>
<td>&gt;99.9</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>EQC for GW</td>
<td>5.0</td>
<td>200</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Waste dump in Bányabérc

Effect of AMD

Waste dump

Nagyvölgyi-creek
Construction of field plots
Construction of field plots
Construction of field plots
The plots
Water collection
### Field experiments with mine waste

#### Cd and Zn content of drain water from field plots

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Cd</th>
<th>Zn</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-treated (µg/l)</td>
<td>441</td>
<td>89 079</td>
<td>2.9</td>
</tr>
<tr>
<td>Fly ash (µg/l)</td>
<td>138</td>
<td>30 380</td>
<td>4.1</td>
</tr>
<tr>
<td>Fly ash + lime (µg/l)</td>
<td>2.3</td>
<td>226</td>
<td>7.2</td>
</tr>
<tr>
<td>EQC for GW</td>
<td>5</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>Fly ash (% decrease)</td>
<td>68.8</td>
<td>65.9</td>
<td></td>
</tr>
<tr>
<td>Fly ash + lime (% decrease)</td>
<td>98.5</td>
<td>99.7</td>
<td></td>
</tr>
</tbody>
</table>
Effect of fly ash + lime on mine waste

Effect of fly ash + lime treatment on the characteristics of heavily weathered mine waste

<table>
<thead>
<tr>
<th>Decrease in</th>
<th>Fly ash</th>
<th>Fly ash + lime</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water extracted metal conc.</td>
<td>99%</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>Acetate extracted metal conc.</td>
<td>80%</td>
<td>85%</td>
</tr>
<tr>
<td>Bioaccumulated metal conc.</td>
<td>59%</td>
<td>84%</td>
</tr>
<tr>
<td>Toxicity</td>
<td>67%</td>
<td>75%</td>
</tr>
<tr>
<td>Soil activity (increase)</td>
<td>10×</td>
<td>100×</td>
</tr>
</tbody>
</table>
Effect of treatment on the growth of grass

0.16 ppm Cd (FQC=1 ppm)
58 ppm Zn (FQC=100 ppm)
The growth of *Sorghum* species

*Sorghum sudanense*
- 0.43 ppm Cd (FQC=1 ppm)
- 59 ppm Zn (FQC=100 ppm)

*Sorghum vulgare*
- 0.27 ppm Cd (FQC=1 ppm)
- 43 ppm Zn (FQC=100 ppm)
Agricultural experimental area

Flood-plain
Contamination distribution

Gyöngyösoroszi mining area

3D Contour Plot (distribution of the zinc in the hobby garden)

Toka-creek

See poster:
M. Tolner, G. Nagy, E. Vaszita and K. Gruiz: In situ delineation of point sources and high resolution mapping of polluted sites by field-portable X-ray Fluorescence measuring device

Green 5 Conference
## Effect of fly ash treatment on agricultural soil

Decrease in metal mobility and bioavailability in agricultural soil

<table>
<thead>
<tr>
<th>Test method</th>
<th>Non-treated (mg/kg)</th>
<th>Fly ash treated (mg/kg)</th>
<th>Decrease (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water extracted Cd</td>
<td>0.051</td>
<td>&lt;0.004</td>
<td>92</td>
</tr>
<tr>
<td>Acetate extracted Cd</td>
<td>1.54</td>
<td>0.275</td>
<td>82</td>
</tr>
<tr>
<td>Total Cd</td>
<td>5.23 (200)</td>
<td>5.23 (1)</td>
<td></td>
</tr>
<tr>
<td>Bioaccumulated Cd</td>
<td>6.63</td>
<td>0.72 (1)</td>
<td>89</td>
</tr>
<tr>
<td>Water extracted Zn</td>
<td>4.106</td>
<td>0.315</td>
<td>92</td>
</tr>
<tr>
<td>Acetate extracted Zn</td>
<td>237.4</td>
<td>47.7</td>
<td>80</td>
</tr>
<tr>
<td>Total Zn</td>
<td>1102 (200)</td>
<td>1102 (100)</td>
<td></td>
</tr>
<tr>
<td>Bioaccumulated Zn</td>
<td>503</td>
<td>108 (100)</td>
<td>79</td>
</tr>
</tbody>
</table>

EQC and FQC in blue brackets.
Plant growth

Zea mays

Non-treated

Treated

Sorghum sudanese

Non-treated

Treated

Green 5 Conference
Technology verification

- Technology efficiency:
  - Mass balance based on mobile metal fraction
- Environment efficiency:
  - Assessment of risk, RQ calculation
- Cost evaluation
- SWOT analysis

### Risk and cost compared with alternatives

<table>
<thead>
<tr>
<th></th>
<th>„0“</th>
<th>D&amp;D</th>
<th>D&amp;DTD</th>
<th>Soil washing</th>
<th>CCP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Risk score</td>
<td>1291</td>
<td>192</td>
<td>110</td>
<td>149</td>
<td>44</td>
</tr>
</tbody>
</table>
| Specific cost  | 3.4    | 91.7  | 12.1   | 52.1         | 2.4 | (euro/t, 2006)
Conclusions

- Combined chemical and phytostabilisation is an effective technology for the remediation of diffusely metal polluted soils.
- Fly ash and the combination of fly ash + lime is effective in reducing metal mobility in agricultural soil and mine wastes: below EQC for GW.
- On the stabilised, previously barren mine waste material a healthy, closed vegetation was able to develop, with metal content under FQC.
- The verification gave good result, therefore hopefully the trust and confidence towards this technology will improve and this useful and smart innovation will get into the market.
Aknowledgements

- “DIFPOLMINE” EU Life 02 ENV/F000291 Demonstration Project (www.difpolmine.org),
- “BANYAREM” Hungarian R&D Project GVOP 3.1.1-2004-05-0261/3.0 (www.eugris.info/projects),
- “MOKKA” Hungarian R&D Project NKFP-020-05 (www.mokkka.hu),
- Albert Apponyi programme

Established by the support of the National Office for Research and Technology.
Thank you for your attention!

For further information send an e-mail to

vfeigl@mail.bme.hu or
gruiz@mail.bme.hu

and see poster

V. Feigl, A. Anton, F. Fekete, K. Gruiz:
Combined chemical and phytostabilisation of metal polluted soils – From microcosms to field experiments

Green 5 Conference