MŰEGYETEM 1782

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

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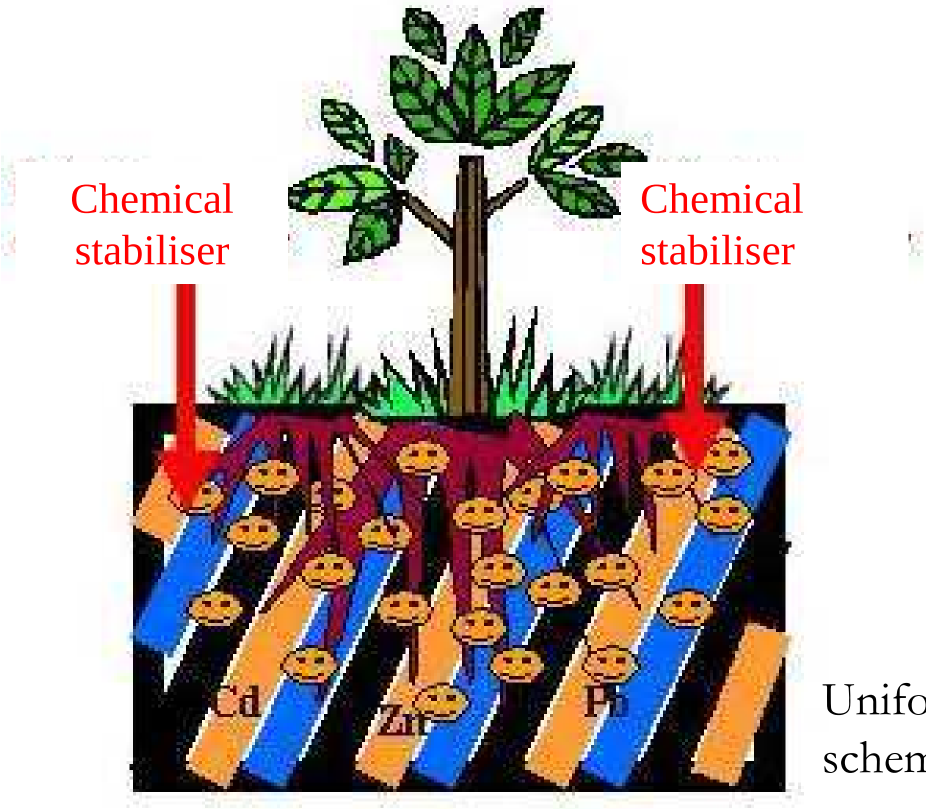
Introduction

What is combined chemical and phytostabilisation?



Uniform MOKKA scheme

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

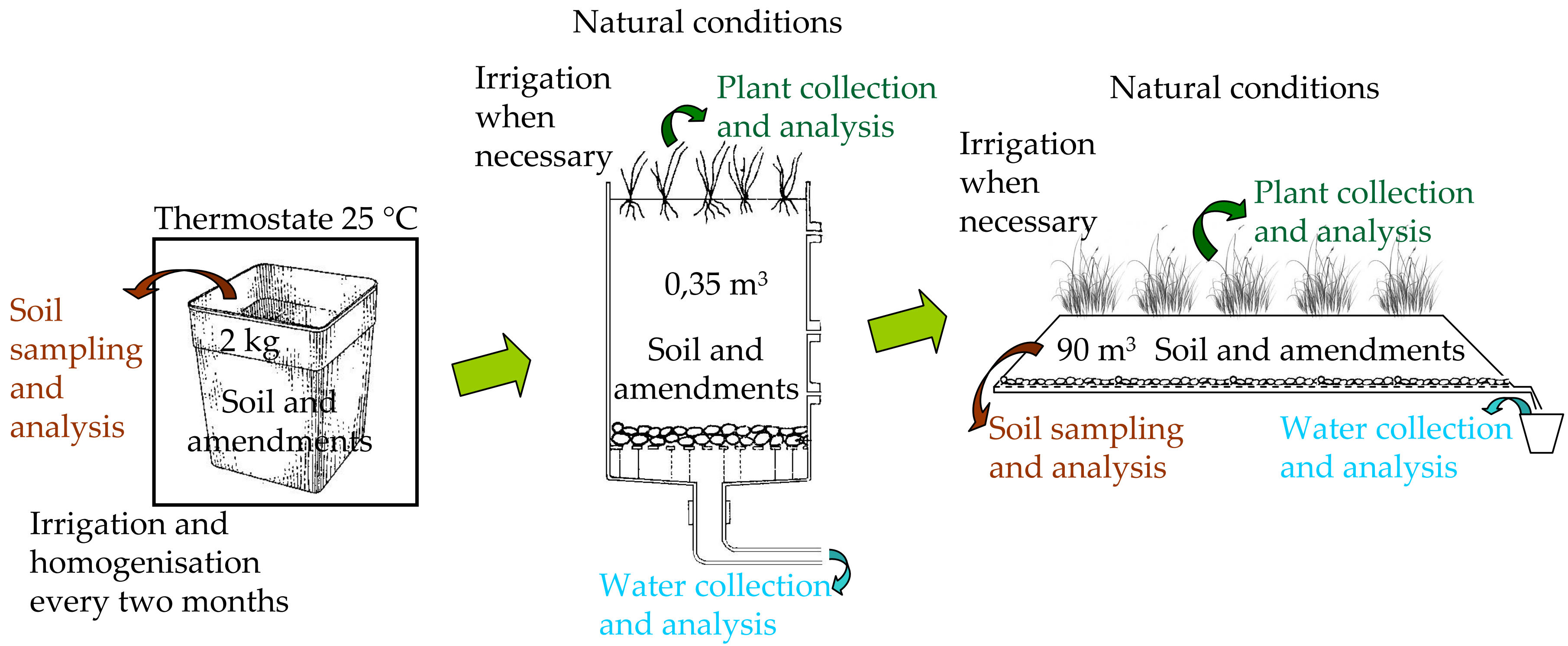
	As	Cd	Cu	Pb	Zn
soil	57–330	4.1–11.1	163–341	227–1589	871–1863
waste	298–390	4.9–22.4	36–374	1599–2050	1176–4361
EQC	15	1	75	100	200

  - 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. Lysimeter** **3. Field experiment**

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 activty 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.

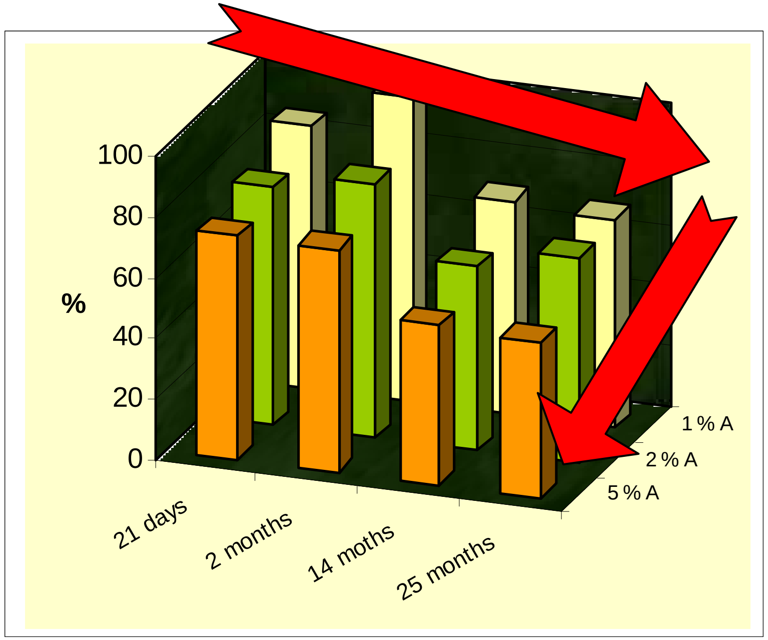
Microcosms

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

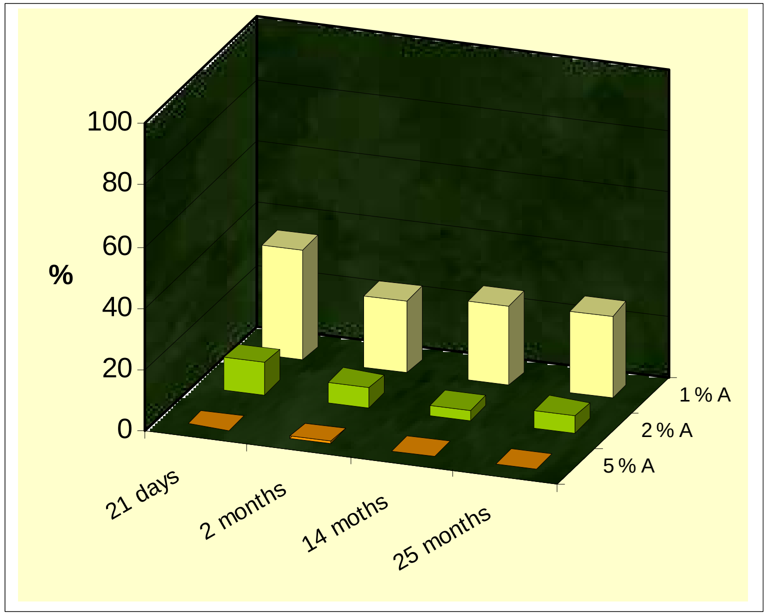
- traditional chemical stabilisers
  - hydrated lime, raw phosphate, alginite, lignite
- waste material for stabilisation
  - fly ashes (6) (pH=6.4–12.6) and their combination with lime
  - Fe-Mn-hydroxide precipitate from drinking water cleaning (3, 5)
  - red mud from bauxite processing (4)

Microcosm results with alkaline fly ash

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



Acetate extractable



Water soluble

Compared to non-treated = 100%

Best stabilisation with amendments

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

Test method	Fly ash ‘A’	Fly ash ‘B’	Fly ash ‘T’	‘T’ + lime	Lime	Algi nite	Phos phate	Lig nite	Mixt of 4	Prec. “R”	Prec. “C”	Red mud
Water extractable Cd and Zn	**99**	**98**	78	**99**	**99**	92	97	-142	**99**	71	79	83
Acetate extractable Cd and Zn	**49**	**34**	12	**68**	**53**	31	21	-9	**68**	53	64	62
Bioaccumulated Cd and Zn	**70**	**74**	10	**57**	**70**	70	48	-33	**70**	~0	~0	~0
Plant toxicity	**70**	**60**	62	10	20	31	20	-15	30	60	56	~0

In non-treated decrease = 0%

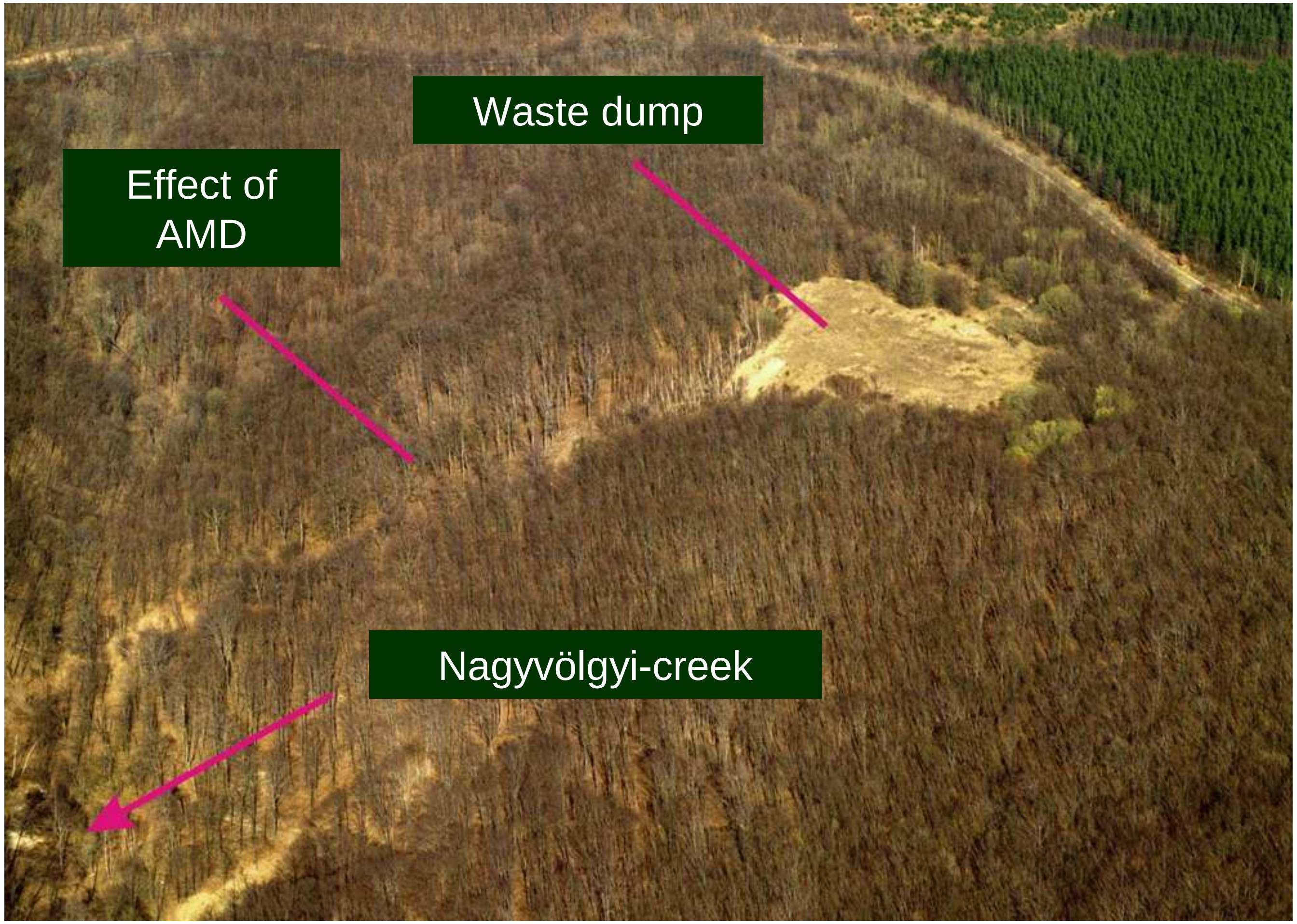
Construction of lysimeters

Stabilising effect of fly ashes in lysimeters

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

Treatment	Cd (µg/l)	Zn (µg/l)	Decrease Cd (%)	Decrease Zn (%)
Non-treated	311	53 677		
Fly ash, type ‘T’	30.4	6 405	90.2	88.0
Fly ash, type ‘V’	0.2	72.5	>99.9	99.9
Fly ash, type ‘A’	0.1	15.2	>99.9	>99.9
‘A’ as reactive barrier	0.1	26.7	>99.9	>99.9
EQC for GW	5.0	200		

Waste dump in Bányabérc



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

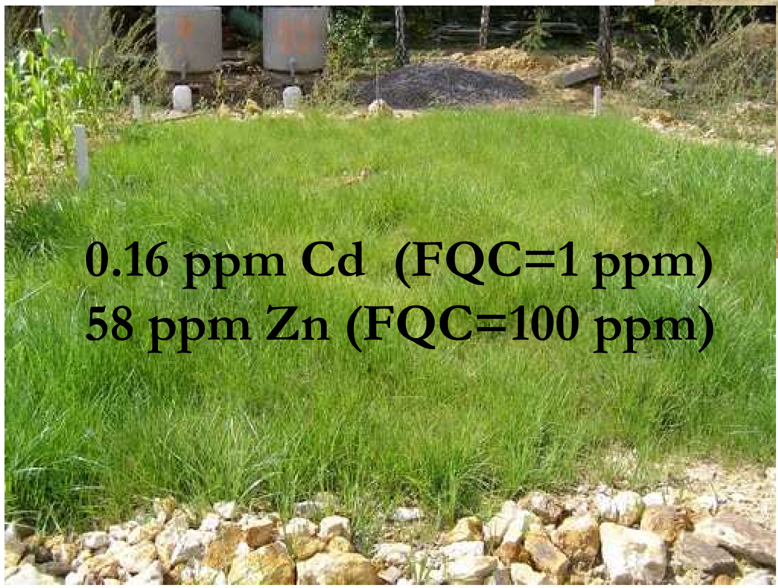
Treatment	Cd	Zn	pH
Non-treated (µg/l)	441	89 079	2.9
Fly ash (µg/l)	138	30 380	4.1
Fly ash + lime (µg/l)	2.3	226	7.2
EQC for GW	5	200	
Fly ash (% decrease)	68.8	65.9	
Fly ash + lime (% decrease)	98.5	99.7	

Effect of fly ash + lime on mine waste

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

Decrease in	Fly ash	Fly ash + lime
Water extracted metal conc.	99%	>99%
Acetate extracted metal conc.	80%	85%
Bioaccumulated metal conc.	59%	84%
Toxicity	67%	75%
Soil activity (increase)	10×	100×

Effect of treatment on the growth of grass



The growth of *Sorghum* species

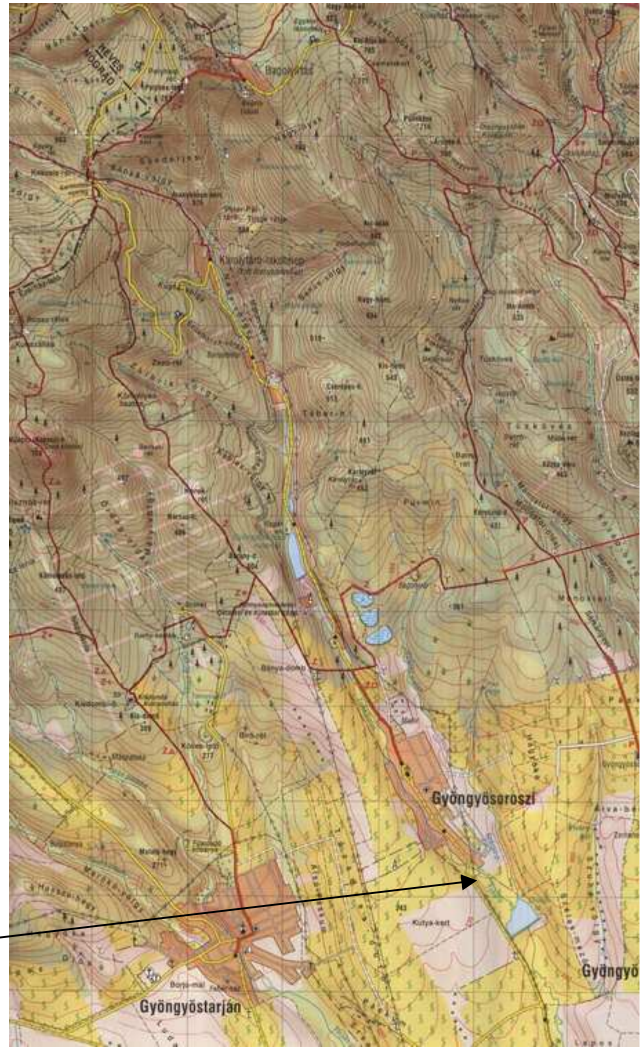
Sorghum vulgare

0.27 ppm Cd
(FQC=1 ppm)
43 ppm Zn
(FQC=100 ppm)

Sorghum sudanense

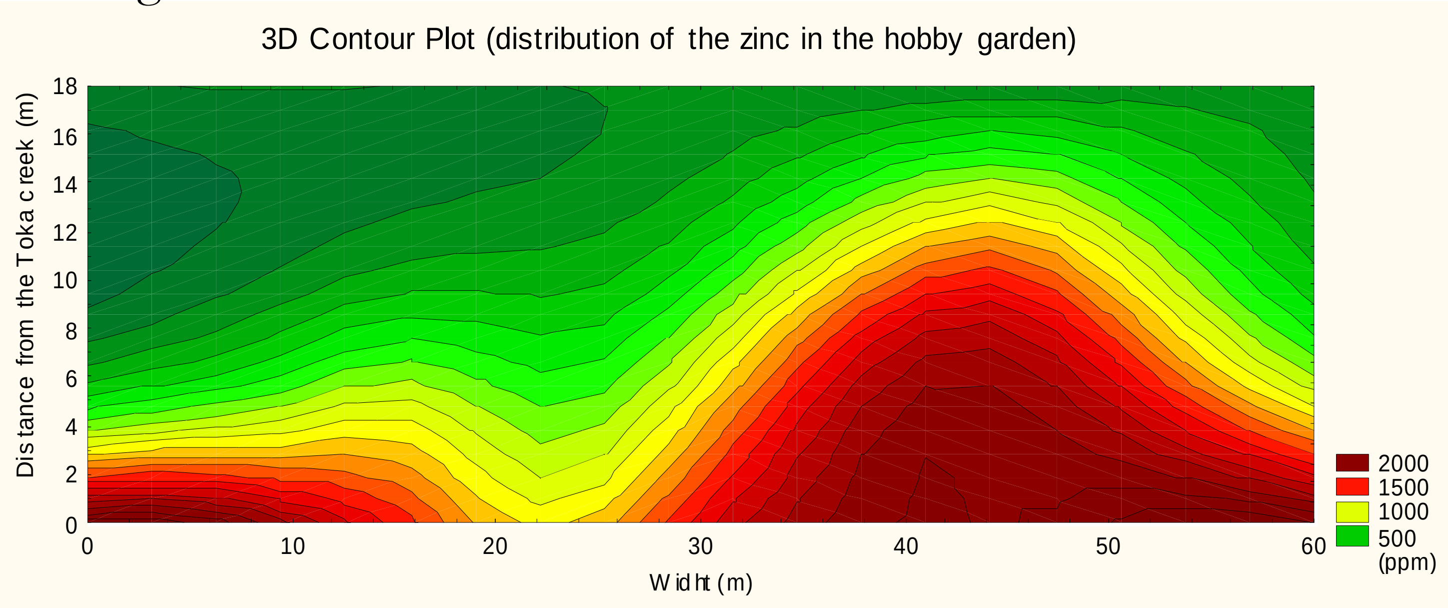
0.43 ppm Cd
(FQC=1 ppm)
59 ppm Zn
(FQC=100 ppm)

Agricultural experimental area



Contamination distribution

Gyöngyösoroszi
mining area



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

Effect of fly ash treatment on agricultural soil

Decrease in metal mobility and bioavailability in agricultural soil

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

EQC and FQC in blue brackets.

Plant growth

Zea mays

Sorghum sudanese

Technology verification

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

Risk and cost compared with alteranatives

	„0”	D&D	D&DTD	Soil washing	CCP
Risk score	1291	192	110	149	44
Specific cost (euro/t, 2006)	3.4	91.7	12.1	52.1	2.4

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),
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  GVOP 3.1.1-2004-05-0261/3.0 (www.eugris.info/projects),
- “MOKKA” Hungarian R&D Project

  NKFP-020-05 (www.mokka.hu),
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Thank you for your attention!

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Combined chemical and phytostabilisation of metal polluted soils – From microcosms to field experiments