Phytoremediation of heavy metal contaminated sites:

a focus on field experiments in a heavy metal contaminated region in Belgium (‘Noord-Limburg’)

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Ludo Diels (VITO)
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2. Remediation options for soils contaminated with heavy metals

3. Phytoremediation of heavy metal contaminated soils
   3.1 Phytoextraction
   3.2 Phytostabilisation

4. Conclusions
1. Non ferro industry in ‘Noord-Limburg’

- since the end of 19th century zinc smelters have been active:
  - Lommel
  - Overpelt
  - Balen
  - (Budel-NL)

- Poor sandy soils (limited agricultural productivity)
  => open area + need for economic activities
  - presence of several channels => easy transport of ores and products

- Result of the activities: widespread soil contamination with metals (Zn, Cd, Pb)
  => related to the production technology
  => diffuse contamination + point sources
  => area: by estimation >280 km² !!!
• Historic soil contamination: illustration

⇒ emissions became lower and lower in the course of time: first because of shift from pyrometallurgic to electrolytic process technology, later due to improved filter systems

Source: Staessen et al., 1995
2. Remediation options
for soils contaminated with heavy metals

Engineering approaches:

-Metal removal:
  - excavation and landfilling
  - excavation and soil washing techniques

-Metal stabilization:
  - vitrification (heat 1600-200°C)
  - physical caps
  - addition of stabilizing materials (e.g. cement)
Disadvantages engineering approaches:

- clean soil for replacement?
- destruction of soil ‘quality’
- high cost (280 km² !)

<table>
<thead>
<tr>
<th>Technique</th>
<th>Cost per ha</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excavate + landfill</td>
<td>1 620 000 €</td>
</tr>
<tr>
<td>Excavate + soil washing</td>
<td>790 000 €</td>
</tr>
</tbody>
</table>

=> contaminated area in ‘Noord-Limburg’ too large to be treated with engineering techniques (= 45 360 000 000 €, excavate and landfill)

=> alternative option? PHYTOREMEDICATION?
Remediation: cost per hectare*

- IMMobilization + PHYtostabilization: 10,000 €
- EXCAVATION + SOIL WASHING: 775,000 €
- EXCAVATION + LANDFILLING: 1,600,000 €

*Cunningham & Berti (1999)
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4. Conclusions
3. Phytoremediation of metal contaminated soils

- Phytoremediation of contaminated soils
  = the use of plants to reduce the negative impact of a contaminated site, or for soil clean up

- In case of metal contaminated soils:
  - PHYTOEXTRACTION: extraction of metals from the soil using metal accumulating plants (clean-up)
  - PHYTOSTABILIZATION: in situ metal inactivation by means of revegetation often in combination with metal-immobilizing and/or fertilizing soil amendments (immobilization/inactivation)
3.1 PHYTOEXTRACTION

MAIN AIM OF THE STRATEGY

-removal of contaminants from the soil by plants
-root uptake and repeated harvesting
(contaminant preferably to be translocated and concentrated in above-ground biomass)

(adapted from Cuningham et al., 1995)
DESIRABLE CHARACTERISTICS IN AN EFFECTIVE PHYTOEXTRACTION SPECIES

• High metal accumulation in easily harvested plant parts

• Tolerance to elevated soil metal levels that may be coupled with low macronutrient and soil organic matter content

• Potential ‘use’ of the biomass:
  -originally: hyperaccumulators
    => no further use of biomass, metal recuperation? dumping?
    => long clean up time due to low biomass

  -more and more: high biomass producing species with moderate metal content but with harvestable product/economic value!
    possibilities: -woody plants (eg willow) => ‘green energy’
    -oil producing plants (eg rapeseed) => motor-oil
TARGET AREA’S

– Agricultural soils
– Abandoned agricultural land
– Kitchen gardens

Metal concentrations in crops often above consumption limits!
=> solution needed for the area!
PHYTOEXTRACTION APPROACH LOOKS ATTRACTIVE

=>alternative land use scenario’s (non food crops delivering some economic benefits)

=>combined with soil clean up?

=>system of sustainable land management

=>long clean up times not really problematic
FIELD IN BALEN

- 500 m from UMICORE in Balen
- former maize field
- sandy soil
- pH-KCL 5.5 ±0.1
- metal content (aqua regia): cfr. table

<table>
<thead>
<tr>
<th>mg/kg DS</th>
<th>Zn</th>
<th>Cd</th>
<th>Cu</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>field</td>
<td>223</td>
<td>5.0</td>
<td>32</td>
<td>198</td>
</tr>
<tr>
<td></td>
<td>± 17</td>
<td>± 0.3</td>
<td>± 3</td>
<td>± 17</td>
</tr>
<tr>
<td>Clean up value</td>
<td>600</td>
<td>2.0</td>
<td>200</td>
<td>200</td>
</tr>
</tbody>
</table>
PLANT SPECIES TESTED

Maize  Rapeseed  Sunflower  Tobacco

=> performance of different species in ‘Noord-Limburg’ conditions?
=> ’best species’ and ’best’ cultivars of a species? (highest metal removal)
=> economic aspects and potential ‘use’ of biomass
Maize

*2 cultivars
*growth and biomass production OK (18 ton/ha)
*metal concentrations in plant (‘best cultivar’):

<table>
<thead>
<tr>
<th>mg/kg DW</th>
<th>Zn</th>
<th>Cu</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>maize plant</td>
<td>339</td>
<td>16.1</td>
<td>2.7</td>
<td>21.4</td>
</tr>
<tr>
<td>limit value</td>
<td>/</td>
<td>/</td>
<td>1.1</td>
<td>45.5</td>
</tr>
<tr>
<td>(KB 21/4’/99)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Soil depth of 25 cm</th>
<th>Cd removal g/ha/j</th>
<th>reduction Cd conc. mg/kg /j</th>
<th>‘clean up’ time (5=&gt;2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>actual biomass</td>
<td>48.6</td>
<td>0.016</td>
<td>185 y</td>
</tr>
</tbody>
</table>
Rapeseed (winter)

*10 varieties
*growth and biomass production OK (8.3 t/ha)
*metal concentrations ‘beste’ cv:

<table>
<thead>
<tr>
<th>mg/kg DW</th>
<th>Zn</th>
<th>Cu</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>/</td>
<td>5.05</td>
</tr>
</tbody>
</table>

Soil depth of 25 cm

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</tr>
</thead>
<tbody>
<tr>
<td>actual biomass</td>
<td>42</td>
<td>0.014</td>
<td>215</td>
</tr>
</tbody>
</table>
Screening 15 commercial varieties (Rolf HERZIG)

San Luca: good biomass production (12.6 ton/ha; 6 plants/m²)

Other varieties: small or even absent

=> nutrients?

=> sowing data?

=> pH?

=> metal toxicity? YES!
*metal concentrations in sunflower (‘best cv’)

<table>
<thead>
<tr>
<th>mg/kg DW</th>
<th>Zn</th>
<th>Cu</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>plant</td>
<td>657</td>
<td>/</td>
<td>6.75</td>
<td>/</td>
</tr>
</tbody>
</table>

*summary sunflower:

<table>
<thead>
<tr>
<th>Soil depth of 25 cm</th>
<th>Cd removal g/ha/j</th>
<th>reduction Cd conc. mg/kg /j</th>
<th>‘clean up’ time (5=&gt;2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>actual biomass</td>
<td>85</td>
<td>0.028</td>
<td>106 y</td>
</tr>
</tbody>
</table>

Remark:

-sunflowers seem more metal sensitive than maize and rapeseed
-metal toxicity (Zn) can reduce phytoextraction success of sunflower (pH!=>liming)!
**Tobacco**

*Fop (Forchheim Pereg) (4.3 ton/ha):

=> NF Cu 7-15; NF Cu 10-2

Bag (Badisher Geudertheimer)

=> NB Cu 10-8; NB Cu 10-4 (8.4 ton/ha)

*growth and biomass OK *(except. Bag)

*metal concentrations in ‘best’ variants:

<table>
<thead>
<tr>
<th></th>
<th>mg/kg DW</th>
<th>Zn</th>
<th>Cu</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fop</td>
<td></td>
<td>525</td>
<td>24.6</td>
<td>21.0</td>
<td>49.9</td>
</tr>
<tr>
<td>NB CU 10-8</td>
<td></td>
<td>339</td>
<td>17.3</td>
<td>10.4</td>
<td>33.9</td>
</tr>
</tbody>
</table>

Soil depth of 25 cm (Fop/NB)

Cd removal g/ha/j       reduction Cd conc. mg/kg /j ‘clean up’ time (5=>2)

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>actual biomass</td>
<td>90 / 88</td>
<td>0.030 / 0.029</td>
<td>101 / 103</td>
<td></td>
</tr>
</tbody>
</table>
## Comparison of different species (best results)

<table>
<thead>
<tr>
<th></th>
<th>Maize</th>
<th>Rapeseed</th>
<th>Sunflower</th>
<th>Tobacco</th>
</tr>
</thead>
<tbody>
<tr>
<td>N° of cultivars</td>
<td>2</td>
<td>10</td>
<td>15</td>
<td>2(+4)</td>
</tr>
<tr>
<td>Range Cd mg/kg DS</td>
<td>2.2-2.7</td>
<td>3.9-8.3</td>
<td>5.9-12.9</td>
<td>9.2-22.2</td>
</tr>
<tr>
<td>Cd conc. ‘Best’ extractor</td>
<td>2.7</td>
<td>5.05</td>
<td>6.75</td>
<td>15.96</td>
</tr>
<tr>
<td>Biomass* kg/ha</td>
<td>18t/ha/j (14pl/m2)</td>
<td>8.3 t/ha/j (4pl/m2)</td>
<td>12.6 t/ha/j (6 pl/m2)</td>
<td>8.4 t/ha/j (4 pl/m2)</td>
</tr>
<tr>
<td>Cd removal</td>
<td>48.6g/ha/j</td>
<td>42 g/ha/j</td>
<td>85 g/ha/j</td>
<td>90 g/ha/j</td>
</tr>
<tr>
<td>Clean up time (5ppm=&gt;2ppm)</td>
<td>185 y</td>
<td>215 y</td>
<td>106 years</td>
<td>101 years</td>
</tr>
</tbody>
</table>

*Remark: biomass production can influence metal removal strongly*
Conclusion phytoextraction

- tobacco most promising in terms of metal removal, but ‘economics’?
- for all crops: clean up time = long
  => Realistic?? Yes, for low to moderate contaminations and if...
  (other aspects to be involved)

How to improve efficiency of phytoextraction?

- Genetic transformation of high biomass producing plants
- Increase mobility/plant availability of metals in soils, using (1) metal chelating agents (f.i. EDTA), (2) adjusting pH of soils (3) siderophore producing rhizosphere bacteria
- Increase metal accumulation and translocation capacity in plants: metal accumulating endophytic bacteria
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4. Conclusions
3.2 PHYTOSTABILIZATION

TARGET AREA’S

large bare surfaces, caused by smelting activities (aerial deposition of acids and metals from zinc smelters)
HEALTH RISKS

METALCONC in BLOOD ↑

metalconc. on vegetables ↑
metalconc. in vegetables ↑

contamination surroundings e.g. kitchen gardens

METALCONC in BLOOD ↑

metals are solubilized in gastro intestinal tract

metal conc. in vegetables ↑

inhalation

pica behaviour

runoff

rainfall

winderosion

soil

groundwater

Metal leaching
IMMOBILIZATION + PHYTOSTABILIZATION

BARE AREA

PHYTOTOXICITY

Addition of metal immobilizing soil amendment

BIOAVAILABLE FRACTION

= HIGH

‘GREEN’ AREA

REDUCED PHYTOTOXICITY

sorption

precipitation

BIOAVAILABLE FRACTION

= LOW
Contamination surroundings e.g. kitchen gardens

⇒ METALCONC in BLOOD ↑

metaalconc. on vegetables ↑
metaalconc. in vegetables ↑

⇒ METALCONC in BLOOD ↑

Contamination surroundings e.g. kitchen gardens

⇒ METALCONC in BLOOD ↑

Solubilization of metalspecies in gastro-intestinal tract

⇒ METALCONC in BLOOD ↑

Pica gedrag

⇒ METALCONC in BLOOD ↑

Metal leaching

groundwater

soil

winderosion

inhalation

runoff

rainfall
MAIN AIMS OF STRATEGY

• "is not a technology for real clean-up of contaminated soil but for stabilizing (inactivating) trace elements that are potentially toxic
• restoring plant cover and installation of a functioning ecosystem
• inhibition of lateral wind erosion, and reduction of trace element transfer to surface- and groundwater
• attenuation of the impact on site and to adjacent ecosystems
PHYTOSTABILIZATION AT LOMMEL-MAATHEIDE (BELGIUM)

- Old pyrometallurgical zinc smelter site (1904-1974) - bare area
- Poor, acid, sandy soil
  Zn: 2800-20000 mg/kg
  Pb: 700-2000 mg/kg
  Cd: 10-70 mg/kg
  Cu: 400-2000 mg/kg
- Based on laboratory tests
  amendement selected: cyclonic ashes from Beringen:
Lommel-Maatheide 1990-2003

1990, 2 weeks after sowing

1995

2003
Cyclonic ashes (from Beringen) 
origin and production

- cyclonic ashes originate from the fluidized bed burning of coal refuse
- minerals present in the schists are: quartz, illite, kaolinite, chlorite, calcite ($\text{CaCO}_3$), dolomite ($\text{(Ca,Mg)}\text{CO}_3$), anhydrite ($\text{CaSO}_4$), siderite ($\text{FeCO}_3$) and pyrite ($\text{FeS}_2$); illite is the most dominant clay present
- the schists are burned by heating in an electronically guided fluidized bed oven at ca. $800^\circ\text{C}$
Cyclonic ashes (from Beringen) : some physico-chemical characteristics

- The pH of the product is strongly alcaline (± 11). The high pH can be explained by the presence of MgO and CaO which are formed during the heating of CaCO$_3$ and (Ca,Mg)CO$_3$ minerals present in the schists. The oxides form hydroxides (Ca(OH)$_2$ and Mg(OH)$_2$) when they come in contact with water.

- A mean specific surface of ± 20 m$^2$ g$^{-1}$ was measured.

- The cation exchange capacity was found to be about 20 meq/100 g
Cyclonic ashes (from Beringen): working mechanism

- increased adsorption on binding sites of the original soil components freed due to a ‘liming effect’ (presence of (Ca(OH)$_2$ and Mg(OH)$_2$))
- precipitation reactions due to increased soil pH
- adsorption reactions on the surface of the modified clay
- coprecipitation of metals with Al, Fe and Mn oxides (hypothetic)
- possibly also formation of metal silicates
Laboratory tests before start of a field experiment

- Evaluation of one or several soil amendments:
  - Short term evaluations:
    - physico chemical test (soil parameters, selective or sequential extractions)
    - biological tests (bacteria, plants, invertebrates):
      => elimination of toxicity?
      => side-effects?

- Long term evaluations: simulation experiment
  (results will be complemented with long term evaluation of the field)

- Selection of a seed mixture
Illustration of laboratory evaluations: short term

- soil pH and conductivity
- selective or sequential extractions (Tessier)

**Conclusion:** CA reduces exchangeable metal fraction in favour of carbonate bound and residual fraction.
• bacterial availability test (BIOMET)

Conclusion: CA reduces bacterial Zn availability almost to control level even in 100%MH soil
• toxicity test with plants

growth response

stress-enzyme (GPOD)

Conclusion: CA eliminates/reduces phytotoxicity in MH soil
Remark: BE results $\Leftrightarrow$ Ca-nitrate extractions
Conclusion: no significant weight loss of *Eisenia fetida* after treatment of MH soil with CA.
Illustration of laboratory evaluation: long term simulation

- columns (Ø25 cm), filled with 1m soil
- simulation of rainfall (destilled water) (annual rainfall of 600mm, simulated in 1 week)
- follow up of metal leaching and soil parameters (pH, exchangeable metals)
CA-B (5%)
Bodem Lommel
Zn tot = 730; Cd tot = 8 ppm; pH = 6.5

Lime (2%)
Bodem Budel
Zn tot = 170; Cd tot = 2.3, pH = 4.1

**Conclusion:**
- with CA-B exchangeable soil metal content stays at a constant low level
- Increase of the difference with untreated soil
- with lime: exchangeable soil metal content increases with time
- decrease of the difference with UNT
Conclusion laboratory tests:

CA are able to consistently reduce metal mobility and toxicity in MAATHEIDE soil; long term effect expected

Field-experiment
Lommel-Maatheide 1990-2003

1990, 2 weeks after sowing

1995

2003
FOLLOW-UP EVALUATIONS

- **physico-chemical**: general soil parameters, selective or sequential extractions, pore water...
- **biological**: bacteria, plants, invertebrates
  - toxicity and availability tests
  - biodiversity in the field (plants, mycorrhizas, nematodes)
Total zinc concentration (mg/kg dry soil), water-extractable zinc (mg/kg dry soil) and ratio water-extractable zinc on total zinc concentration at different moments after the treatment

<table>
<thead>
<tr>
<th></th>
<th>Zn_{tot}</th>
<th>Zn_{H20}</th>
<th>Ratio tot/H_{20}</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 year</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13 year</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
OVERPELT 1997-2003: amendment tested ‘compost+beringite’

1997

1998, 2 months after sowing

1999

2002
EFFECT OF SOIL ADDITIVES ON METAL PERCOLATION

⇒ Reduction of Zn and Cd leaching after all treatments
⇒ increase of Cu and Pb leaching after compost addition!
⇒ partly compensated by combination with CA
⇒ completely compensated by combination with CA+SS
Cyclonic ashes from Beringen not available anymore: search for alternative cyclonic ashes:

Methodology:

• Analysis of the product itself (pH, conductivity, metal content, ...)

• **Short term** evaluations on treated soils:
  - physico-chemical tests (extractions)
  - biological tests (organisms of different trophic levels)
    (= evaluate reduction in toxicity, possible-side effects)

• **Long term** evaluations on treated soils:
  - simulation experiments + effect on metal leaching
  - field validation + follow up (physical + biological)
4. General conclusions

- In case studies on field scale phytostabilization has been shown to be successful.
- Phyto-extraction will only be realistic when incorporated in a long-lasting system of sustainable agricultural/sylvicultural use of contaminated soils (economical aspects!!)
- Plant-based strategies are promising, attractive and easily acceptable for the remediation of soils contaminated with heavy metals.
Acknowledgements

- OVAM (Public Waste Agency of the Flemish Region)
- EU project QLRT-2001-00429 (PHYTAC)
- European Fund for Regional Development