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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Content

1. Non ferro industry in the ' Noorderkempen' (Belgium)

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 km^2 !!!

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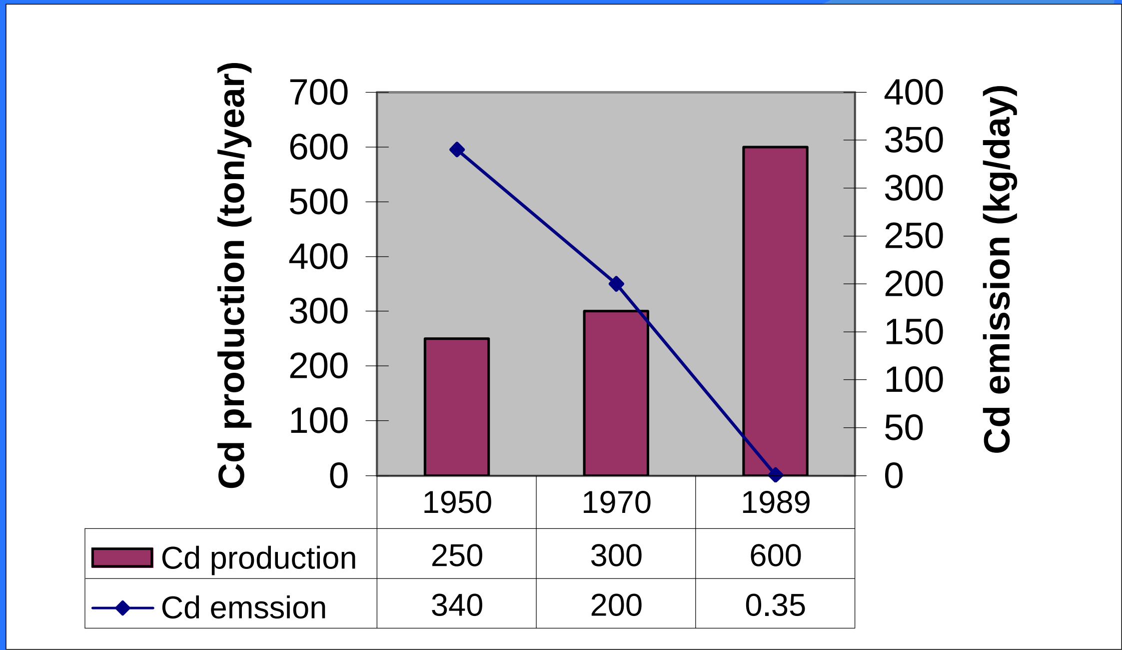
•Historic soil contamination: illustration



Source: Staessen et al., 1995

⇒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

2. Remediation options
for soils contaminated with heavy metals

Engeneering 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 engeneering approaches :

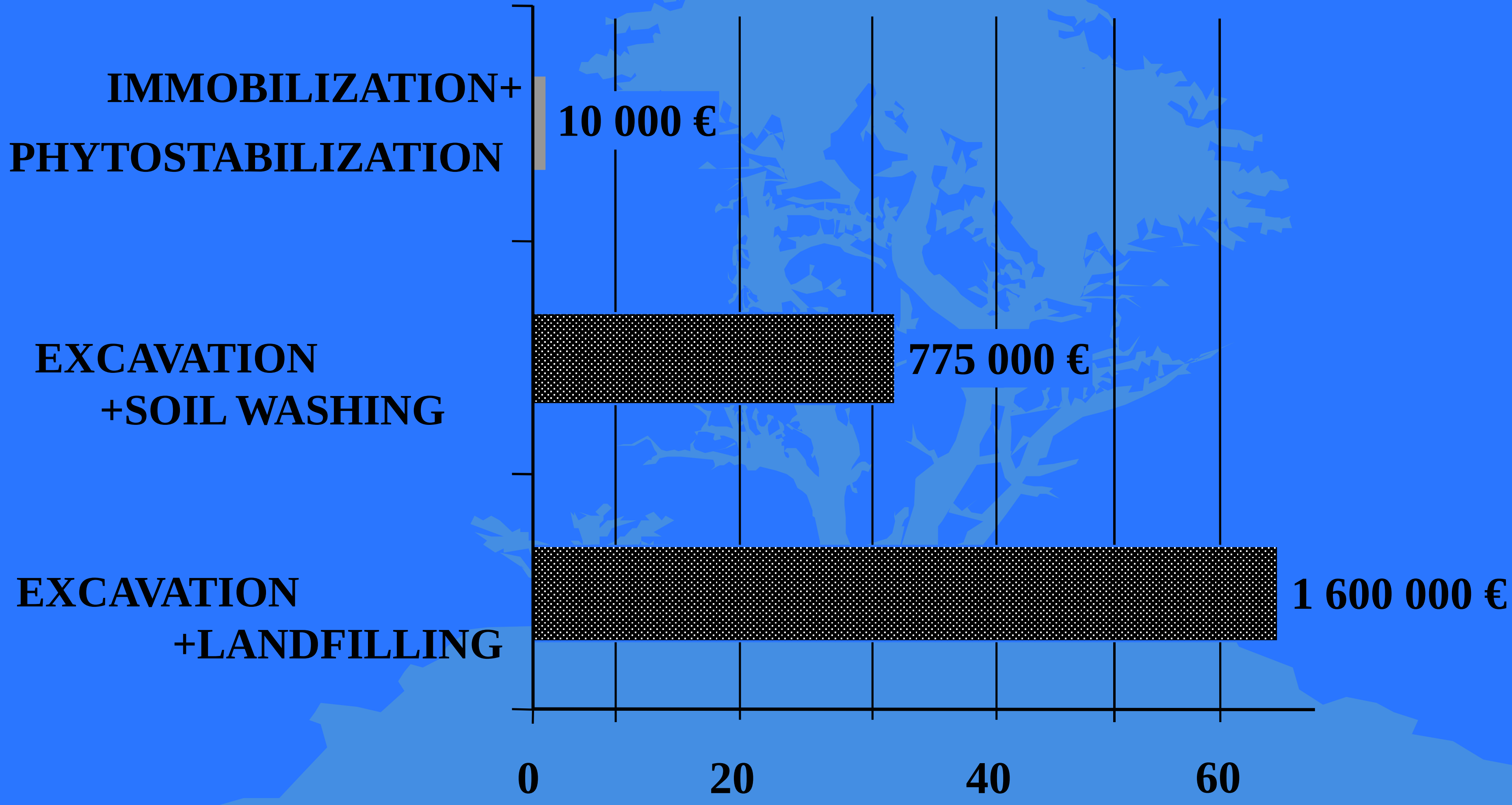
-clean soil for replacement?
-destruction of soil ‘quality’
-high cost (280 km2 !)

Technique	Cost per ha
Excavate + landfill	1 620 000 €
Excavate + soil washing	790 000 €

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

=> alternative option? PHYTOREMEDIATION?

Remediation: cost per hectare*



*Cunningham & Berti (1999)

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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

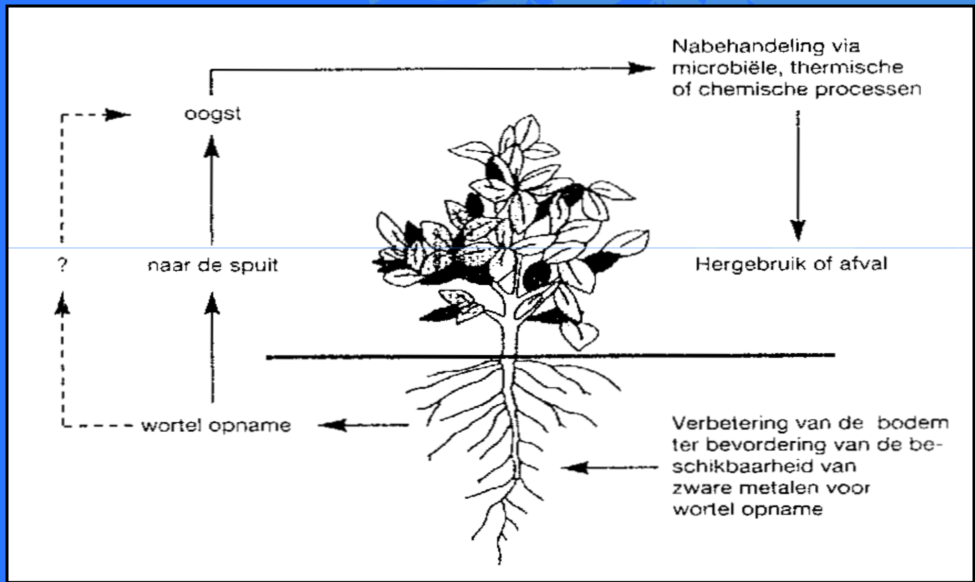
- **In case of metal contamined soils:**

  – PHYTOEXTRACTION: extraction of metals from the soil using metal accumulating plants (clean-up)

  – PHYTOSTABILIZATION: i*n 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



(adapted from Cuningham et al., 1995)

-removal of contaminants from the soil by plants

-root uptake and repeated harvesting (contaminant preferably to be translocated and concentrated in above-ground biomass)

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: <u>hyperaccumulators</u>

  => no further use of biomass, metal recuperation? dumping?

  => long clean up time due to low biomass

  -more and more: <u>high biomass producing species</u> with moderate metal content but with harvestable product/economic value!

  possibilities: -woody plants (eg willow) => 'green energy'

  -oil producing plants (eg rapeseed) => motor-oil

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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

mg/kg DS	Zn	Cd	Cu	Pb
field	223 ± 17	5.0 ± 0.3	32 ± 3	198 ± 17
Clean up value (type II)	600	2.0	200	200

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

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Maize

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

mg/kg DW	Zn	Cu	Cd	Pb
maize plant	339	16.1	2.7	21.4
limit value (KB 21/4/'99)	/	/	1.1	45.5

Soil depth of 25 cm	Cd removal g/ha/j	reduction Cd conc. mg/kg /j	'clean up' time (5=>2)
actual biomass	48.6	0.016	185 y

Rapeseed (winter)

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

mg/kg DW	Zn	Cu	Cd	Pb
	600	/	5.05	/

Soil depth of 25 cm	Cd removal g/ha/j	reduction Cd conc. mg/kg /j	‘clean up’ time (5=>2)
actual biomass	42	0.014	215

Sunflower

Screening 15 commercial varieties (Rolf HERZIG)

San Luca: good biomass production (12.6 ton/ha; 6 plants/m^2)

Other varieties: small or even absent

=>nutrients?

=>sowing data?

=>pH?

=>metal toxicity? YES!

*metal concentrations in sunflower (‘best cv’)

mg/kg DW	Zn	Cu	Cd	Pb
plant	657	/	6.75	/

*summary sunflower:

Soil depth of 25 cm	Cd removal g/ha/j	reduction Cd conc. mg/kg /j	‘clean up’ time (5=>2)
actual biomass	85	0.028	106 y

Remark:

-sunflowers seem more metal sensitieve than maize and rapeseed
-metal toxicity (Zn) can reduce phytoextraction succes 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:

mg/kg DW	Zn	Cu	Cd	Pb
Fop	525	24.6	21.0	49.9
NB CU 10-8	339	17.3	10.4	33.9

Soil depth of 25 cm (Fop/NB)	Cd removal g/ha/j	reduction Cd conc. mg/kg /j	'clean up' time (5=>2)
actual biomass	90 / 88	0.030/0.029	101 / 103

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Comparison of different species (best results)

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

*Remark: biomass production can influence metal removal strongly

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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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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

winderosion → **inhalation**

METALCONC in BLOOD ↑

METALCONC in BLOOD ↑

metals are solubilized in gastro intestinal tract

pica behaviour

rainfall

runoff

Metal leaching

soil

groundwater

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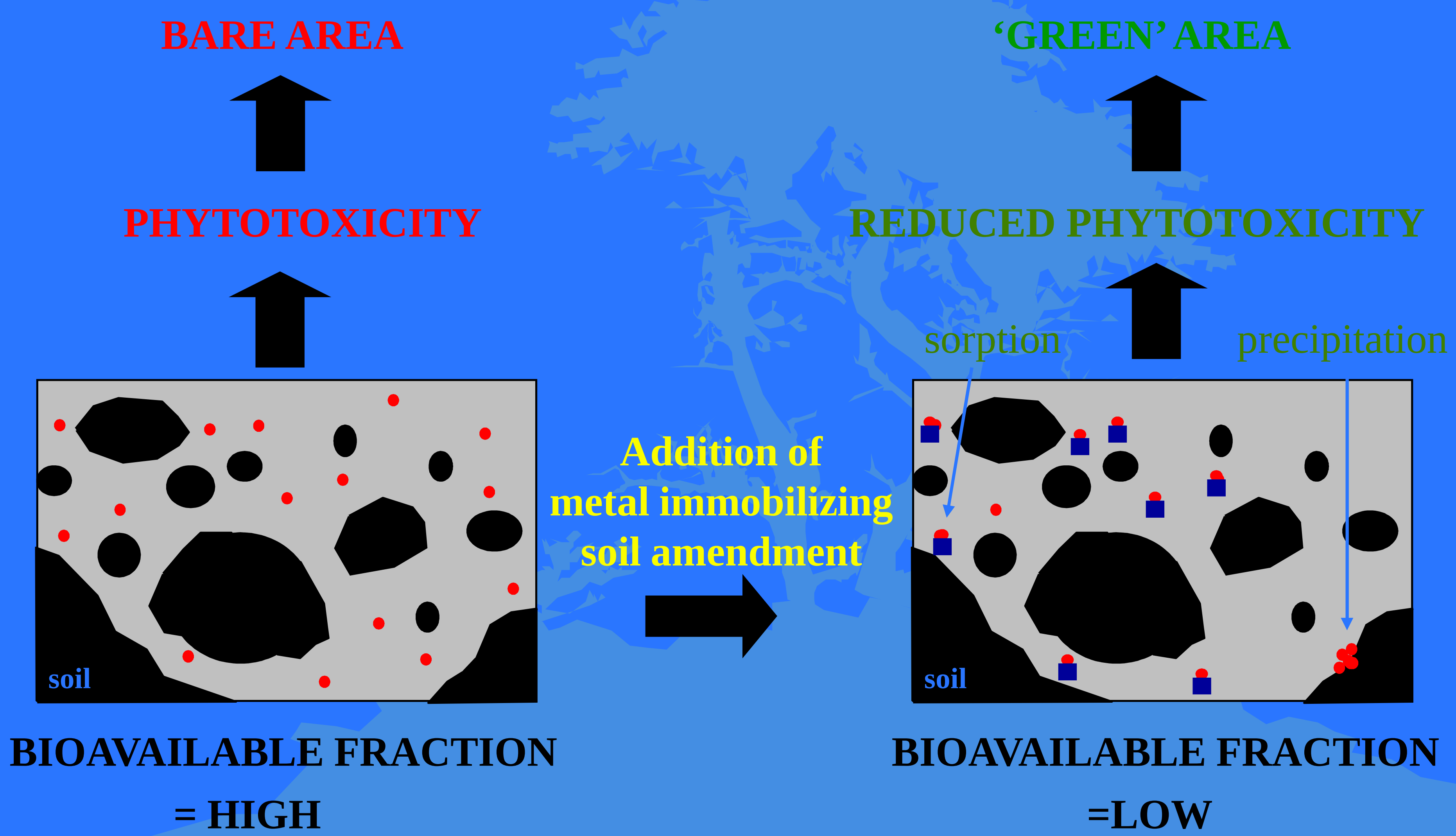
IMMOBILIZATION + PHYTOSTABILIZATION



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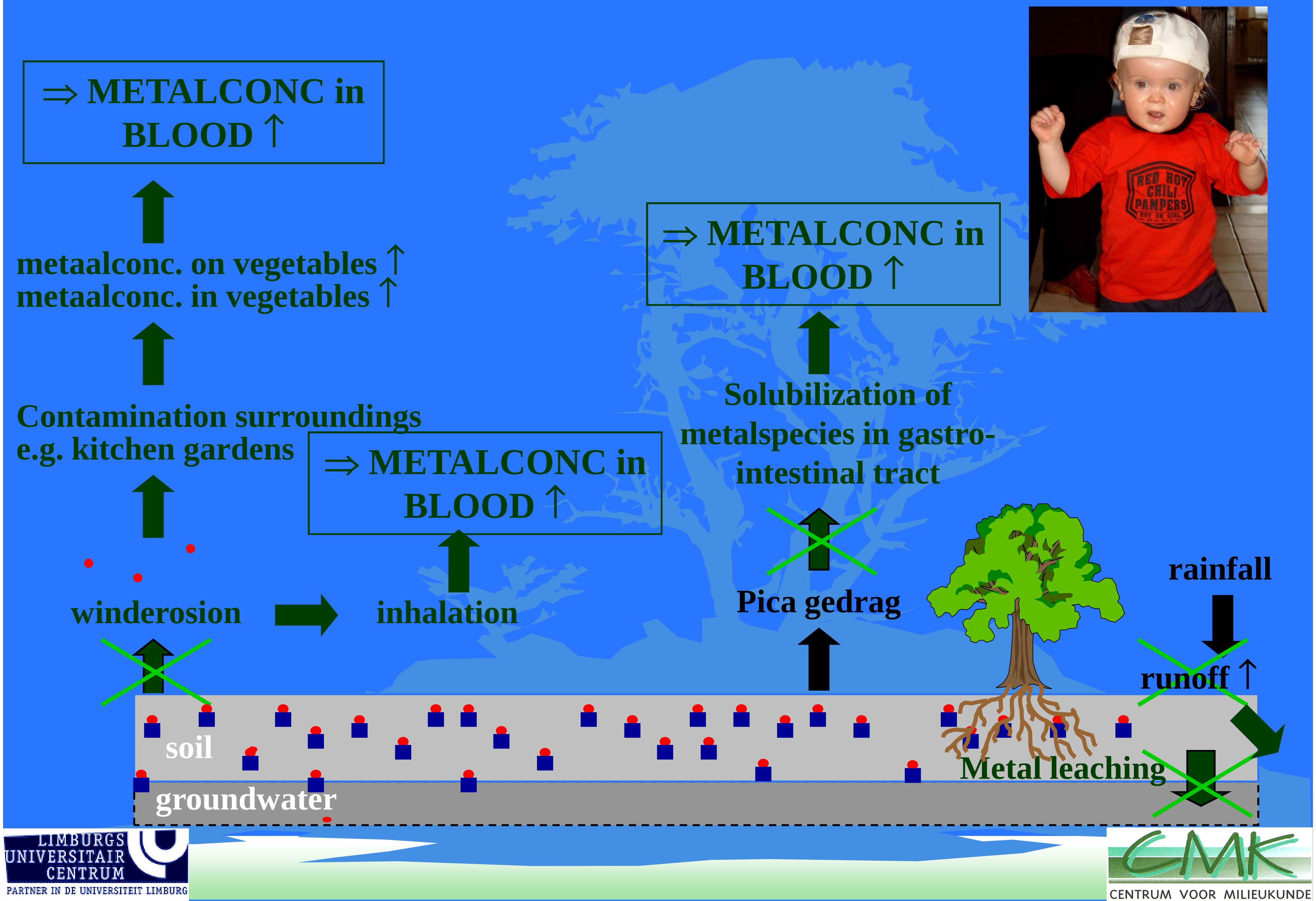

MAIN AIMS OF STRATEGY

- !! 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:

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Lommel-Maatheide 1990




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Lommel-Maatheide 1990-2003

1990, 2 weeks after sowing

1995

2003

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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 ($CaCO_3$), dolomite ($(Ca,Mg)CO_3$), anhydrite ($CaSO_4$), siderite ($FeCO_3$) and pyrite (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°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 toxicty ?

=>side-effects?

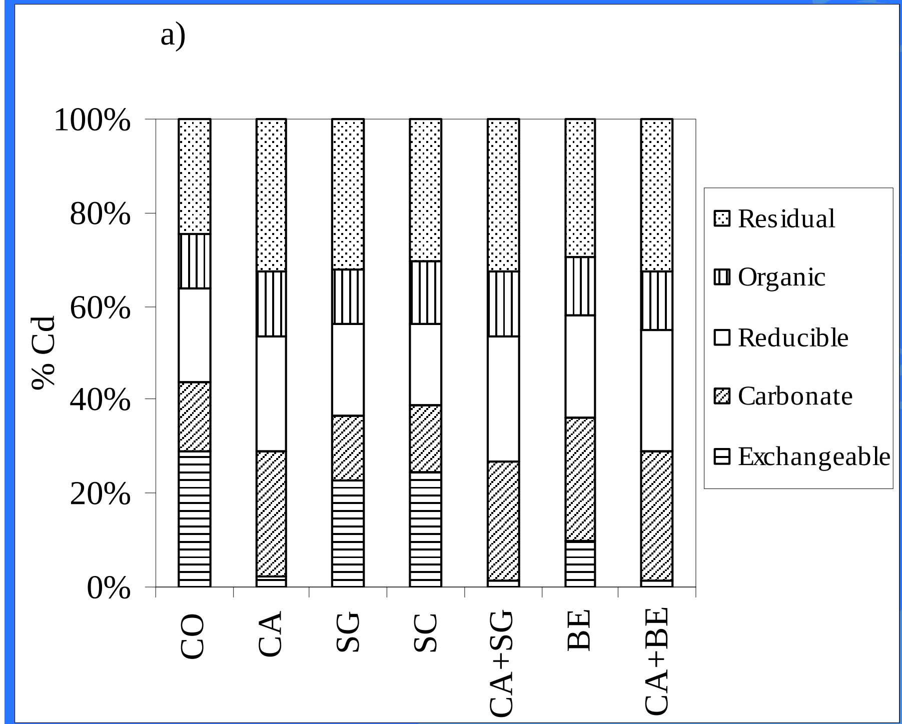
Long term evaluations: simulation experiment

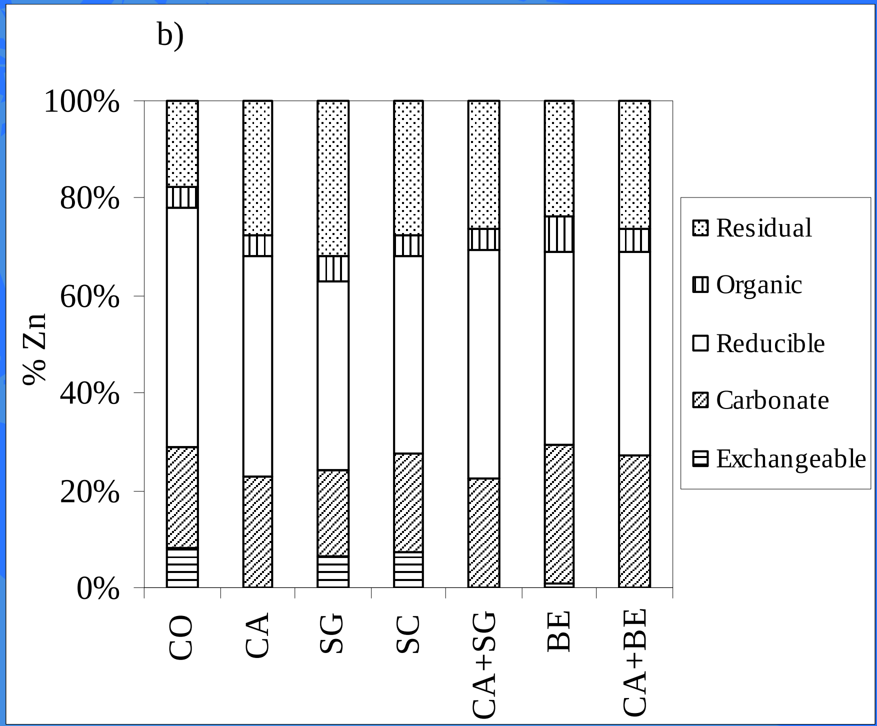
(results will be complemented with long term evaluation of the field)

• Selection of a seed mixture

Illustration of laboratory evalutions: 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

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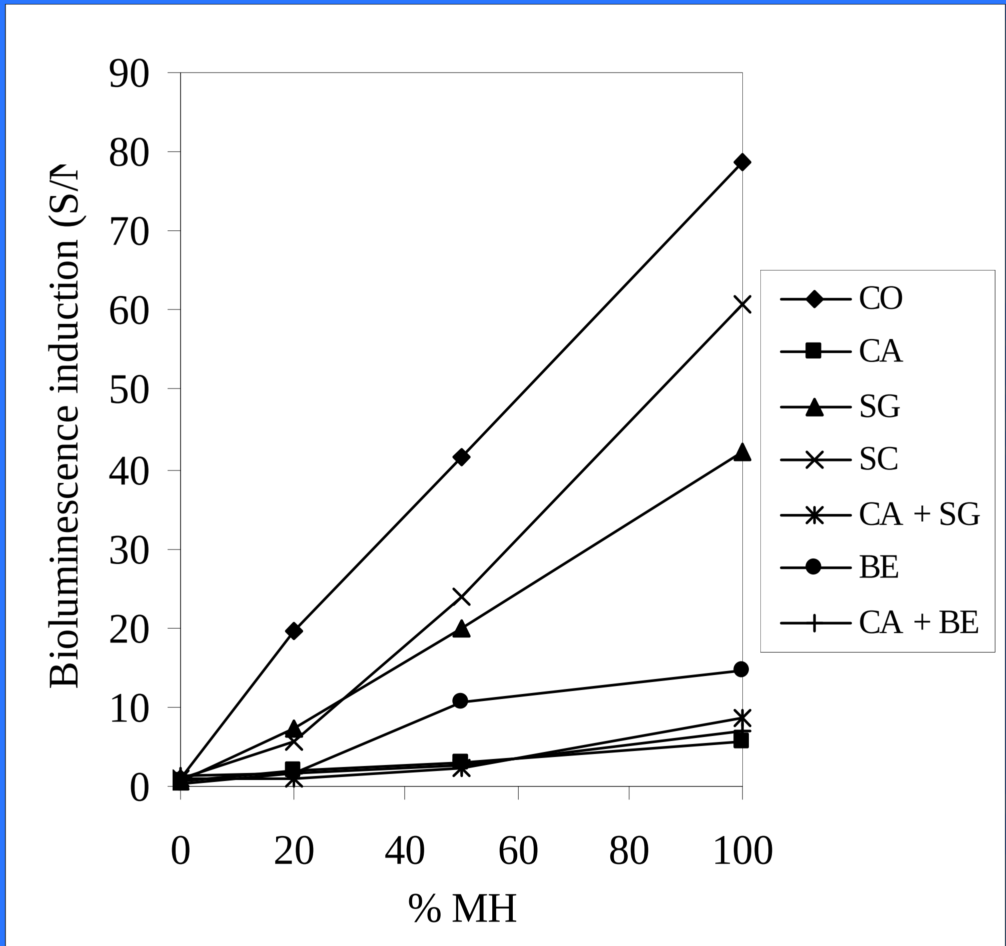
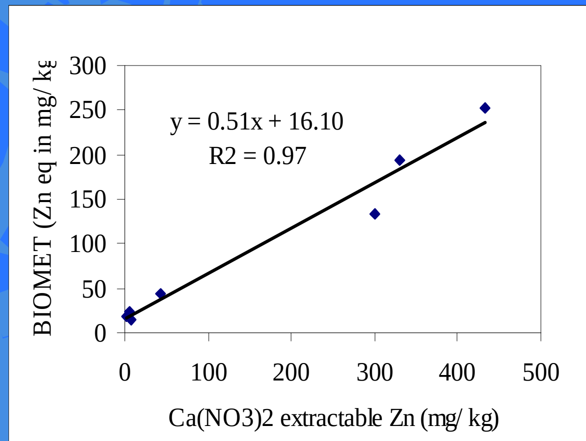
• bacterial availability test (BIOMET)



Correlation with chemical:



Conclusion: CA reduces bacterial Zn availability almost to control level even in 100%MH soil

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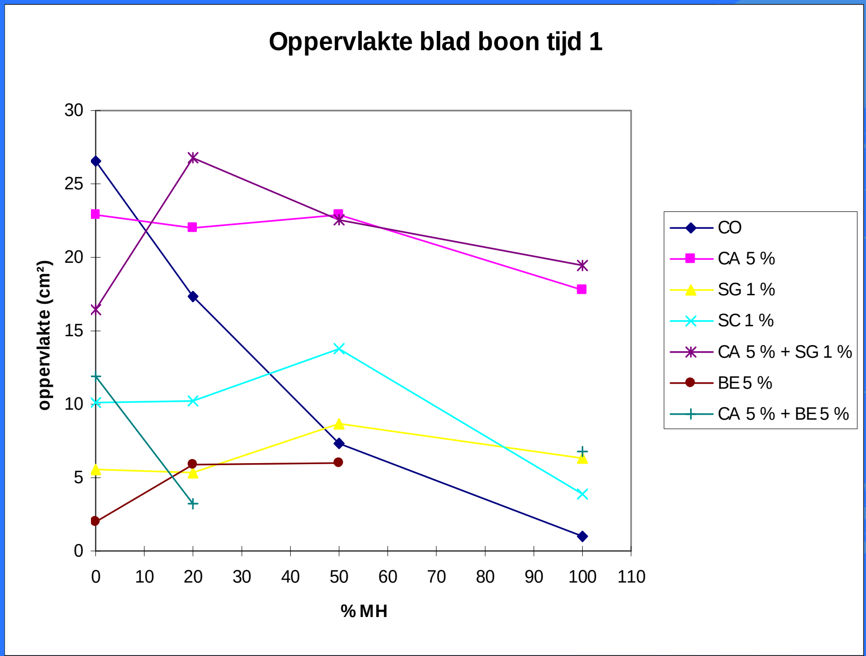
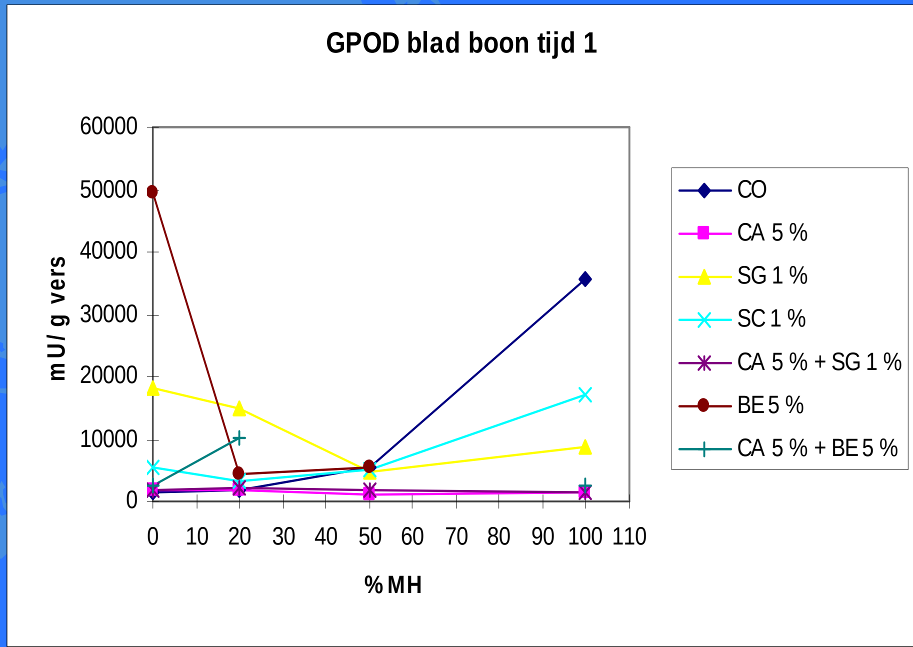
• toxicity test with plants

growth response



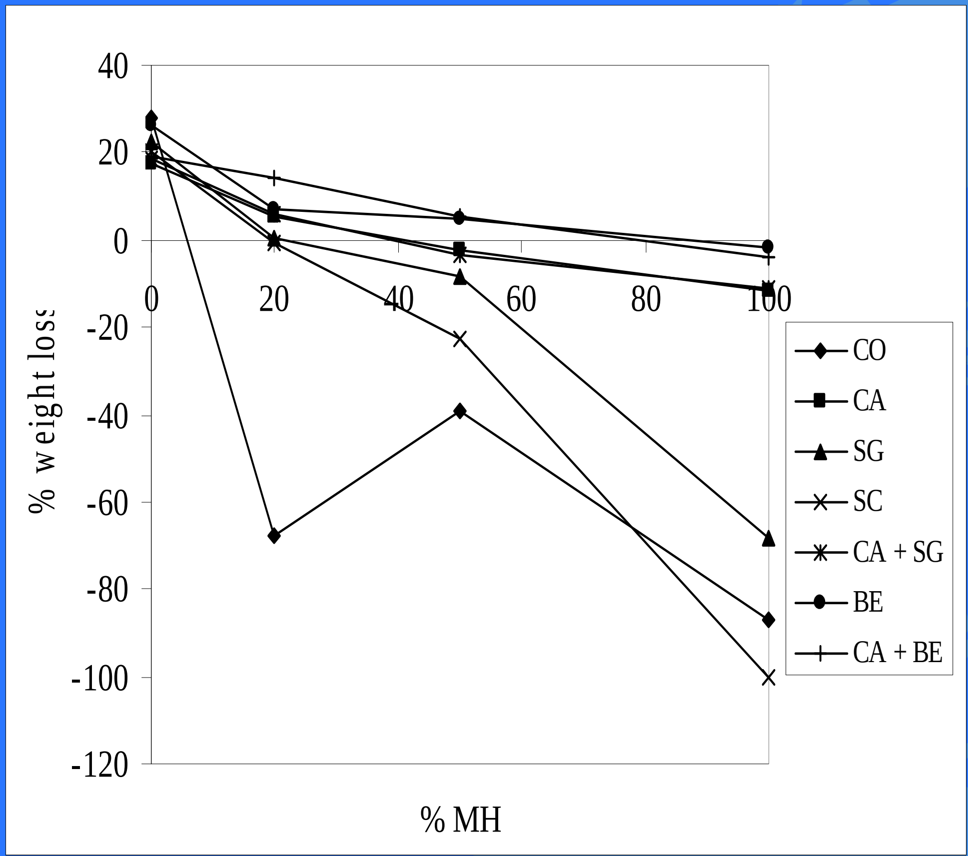
stress-enzyme (GPOD)



Conclusion: CA eliminates/reduces phytotoxicity in MH soil

Remark: BE results⇔Ca-nitrate extractions

• toxicity test with invertebrates (earthworm Eisenia fetida)



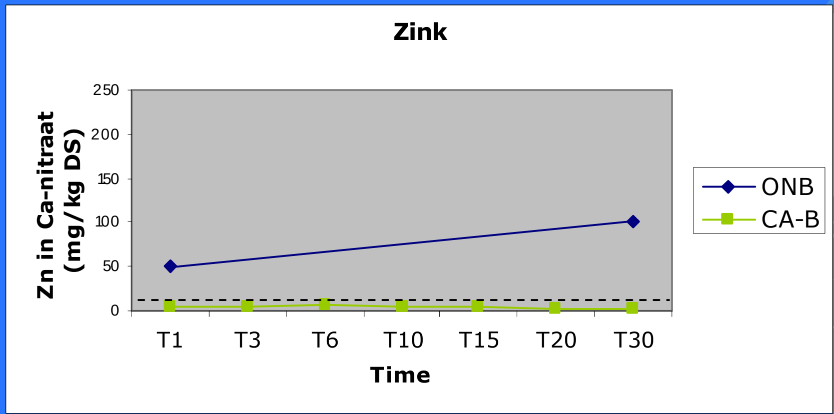
Conclusion: no significant weight loss of Eisenia fetida after treatment of MH soil with CA

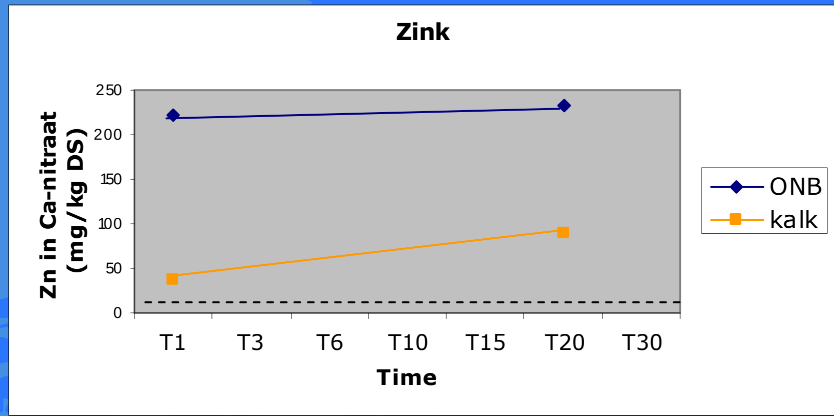
Illustration of laboratory evaluation: long term simulation

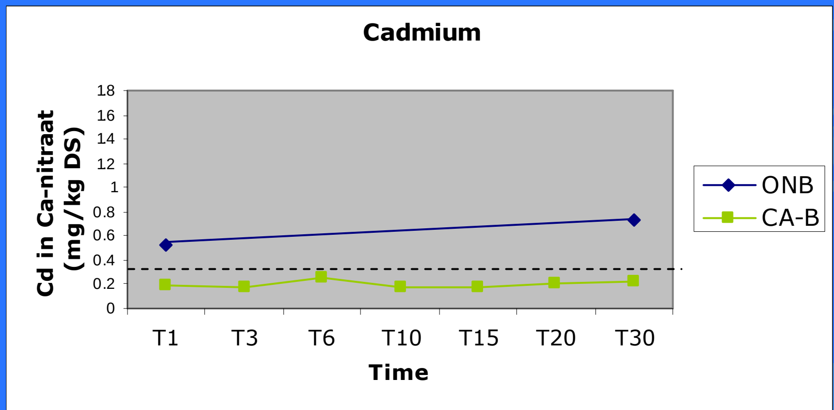
- columns (Ǿ25 cm), filled with 1m soil
- simulation of rainfall (destilled water) (annual rainfal of 600mm, simulated in 1 week)
- follow up of metal leaching and soil parameters (pH, exchangeable metals)

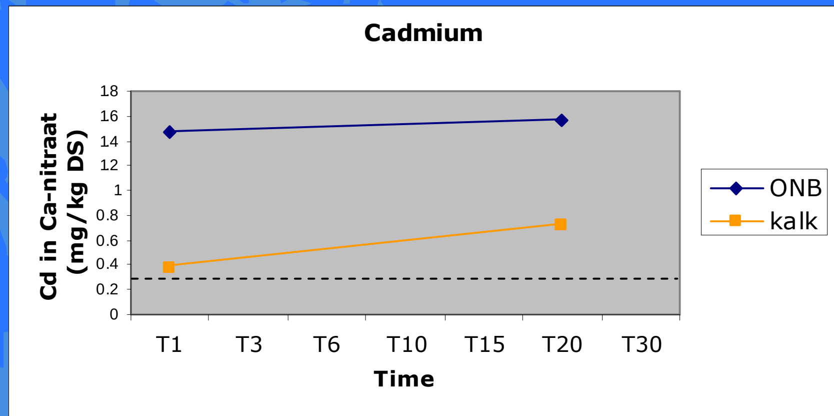
CA-B (5%)
Bodem Lommel
Zn tot= 730; Cd tot =8 ppm; pH = 6.5

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









Conclusion:-with CA-B exchangebale 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

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Conclusion laboratory tests:

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

↓

Field-experiment

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Lommel-Maatheide 1990-2003

1990, 2 weeks after sowing

1995

2003

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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

	Zn_{tot}	Zn_{H20}	Ratio tot/H_20
5 year			
13 year			

OVERPELT 1997-2003:

amendment tested ‘compost+beringite’

1997

1998, 2 months after sowing

1999

2002

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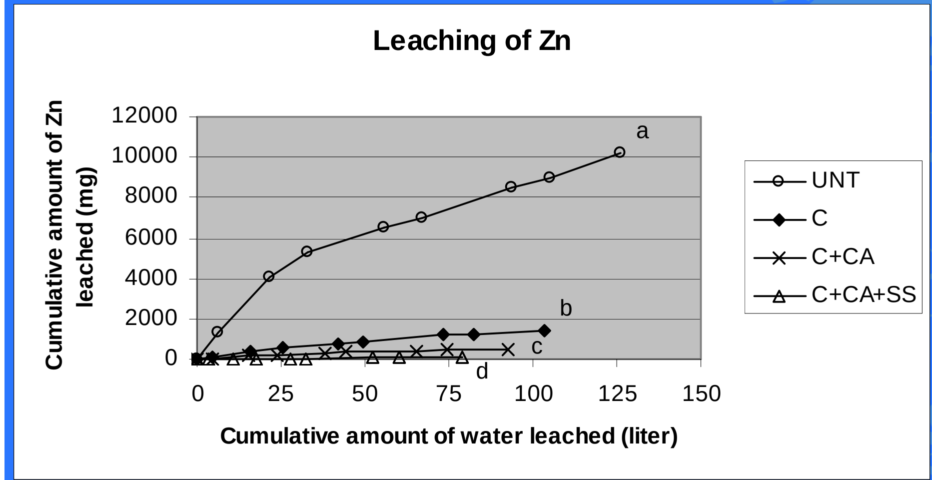
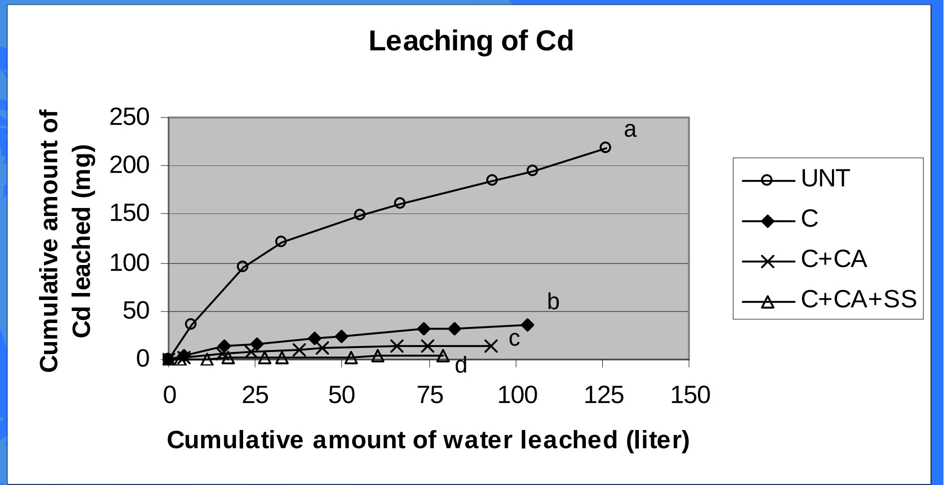
EFFECT OF SOIL ADDITIVES ON METAL PERCOLATION





$\Rightarrow$Reduction of Zn and Cd leaching after all treatments

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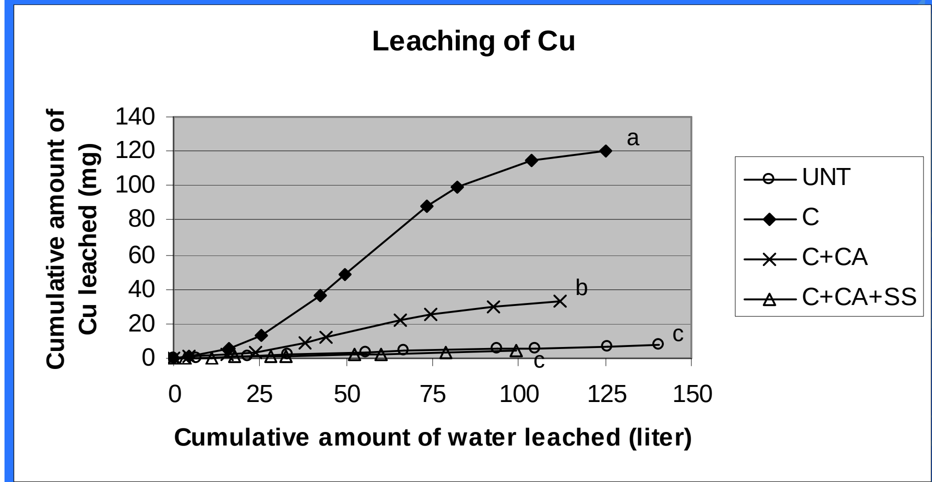

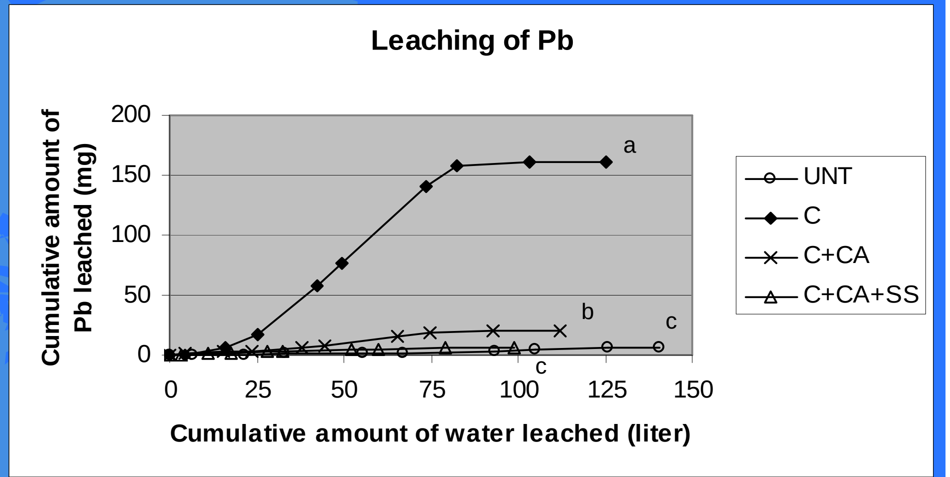

⇒increase of Cu and Pb leaching after compost addition!

⇒partly compensated by combination with CA

⇒completely compensated by combination with CA+SS

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Cyclonic ashes from Beringen not available anymore: search for alternative cyclonic ashes:

<u>Methodolgy:</u>

•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)

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4. General conclusions

- In case studies on field scale phytostabilization has been shown to be succesful
- 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

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