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Metal/metalloïd immobilization and phytostabilization of contaminated sites:

theoretical background and field application at an As contaminated former goldmine site

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PHYTOREMEDIATION TECHNIQUES

- **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/metalloïd contaminated soils:

PHYTOEXTRACTION: remove metals from soil by the use of metal (hyper)accumulating plants (clean-up)

PHYTOSTABILIZATION: in situ metal inactivation by means of revegetation either with or without non-toxic metal-immobilizing soil amendments (immobilization/inactivation)

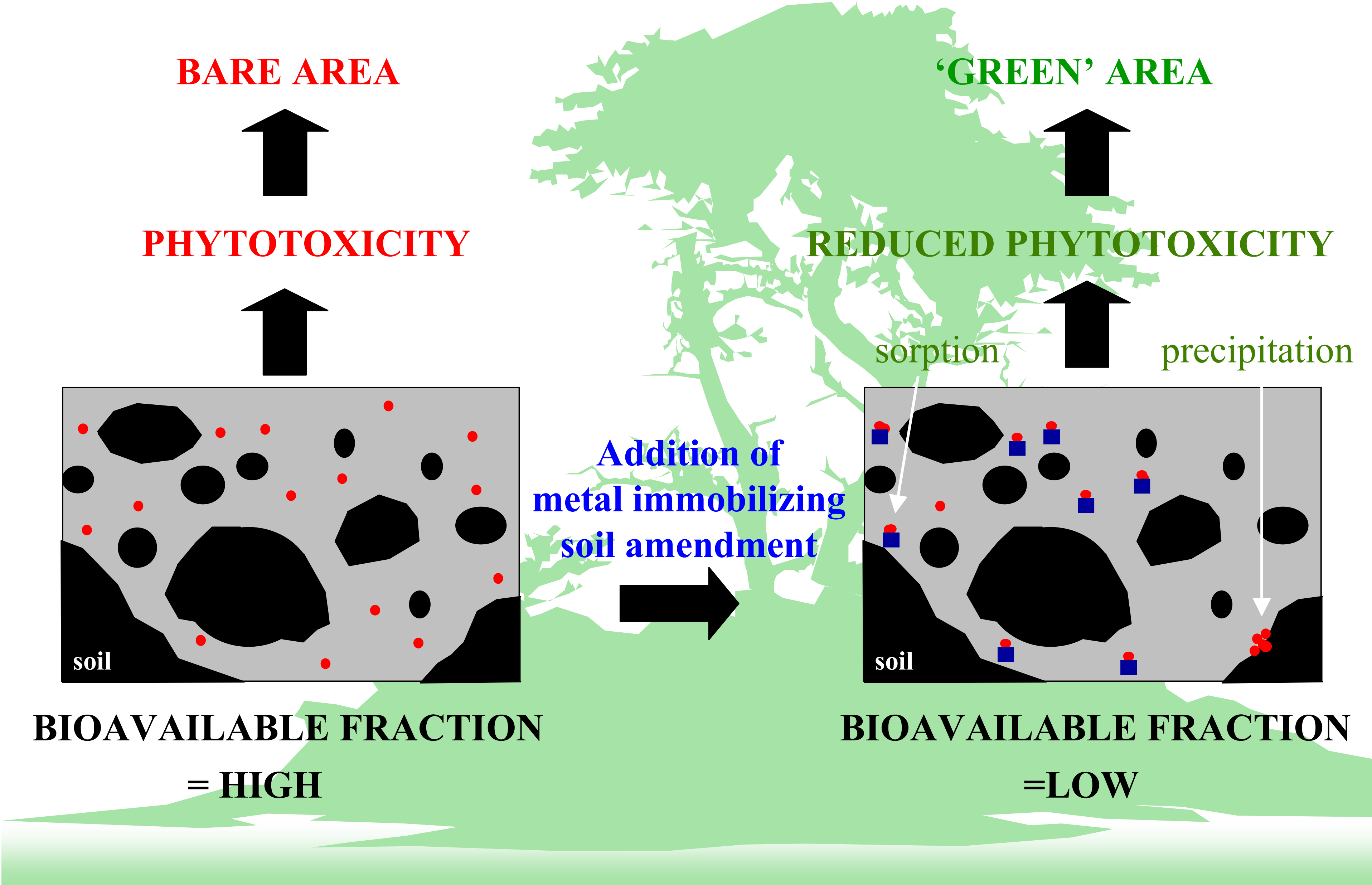
PHYTOSTABILIZATION: AIM

- reduce the risk presented by a contaminated soil by decreasing the metal bioavailability using a combination of plants and/or soil amendments (immobilization/inactivation)
- not a technology for real clean-up of contaminated soil but for stabilizing (inactivating) trace elements which are potentially toxic
- contamination is ‘inactivated’ in place preventing further spreading

PHYTOSTABILIZATION :TARGET AREA'S

large bare surfaces,
caused by mining
operations or by aerial
deposition of metals
from metal smelters

IMMOBILIZATION + PHYTOSTABILIZATION



ROLE OF SOIL AMENDMENTS IN PHYTOSTABILIZATION

- convert the soluble and exchangeable metals to more geochemically stable solid phases resulting in a reduced biological availability of heavy metals
- by consequence:
  - increase of biodiversity and evolution to normal functioning ecosystem
  - reduction of trace element transfer to surface- and groundwater
- Remarque: use of soil amendements to lower metal uptake in crops

ROLE OF PLANTS IN PHYTOSTABILIZATION

- protect the contaminated soil from wind and water erosion
- reduce water percolation through the soil to prevent leaching of the contaminants
- alter the chemical form of the contaminants by changing the soil environments (e.g. pH, redox potential) around plant roots
- accumulate and precipitate heavy metals in the roots or adsorb metals to the roots
- micro-organisms living in the rhizophere of plants may have an important role in these processes

PLANTS FOR PHYTOSTABILIZATION

should:

- be tolerant to metals and/or tolerant to specific growing conditions for a given site
- not accumulate contaminants in above-ground parts which could be consumed by humans or animals
- have shallow roots to stabilize soil and take up soil water
- be easy to care for once established

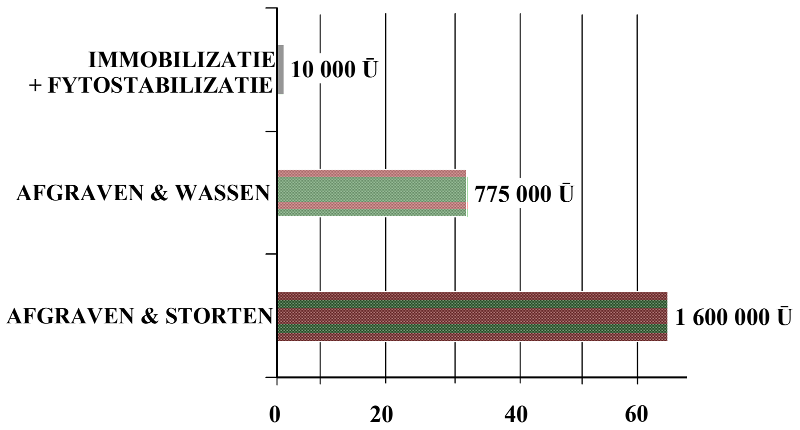
INTEGRATION OF METAL IMMOBILIZATION AND SUBSEQUENT PHYTORESTORATION RESULTS IN:

- the installation of a normal or almost normal functioning ecosystem
- an inhibition of lateral wind erosion, and reduction of trace element transfer to surface- and groundwater
- an attenuation of the impact on site and to adjacent ecosystems

ADVANTAGES OF IN SITU INACTIVATION AND PHYTOSTABILIZATION

- aesthetic profit (for heavily contaminated industrial sites)
- soil structure not disturbed
- no by-products
- cost effective:

KOST PER HECTARE*



*Cunningham & Berti (1999)

LIMITS OF IN SITU INACTIVATION AND PHYTOSTABILIZATION

- soils which can not (or only with extensive efforts, time and money) be made suitable for plant growth (soil structure, high salinity, toxic substances other than metals)

- sometimes conflicting results between plant growth and metal leaching (organic matter addition, P-fertilisation,...)

- metal concentrations in vegetables not sufficiently reduced

SOIL AMENDMENTS

*Alkaline materials

lime

* Phosphate minerals

Thomas basic slags (TBS)

(hydroxy)apatite

phosphoric acid

*Iron and manganese oxides

(+ iron and manganese bearing amendments)

hydrous Mn oxides (HMO)

hydrous Fe oxides (HFO)

birnessite

red mud (from aluminium industry)

sludge from drinking water industry

bog iron ore

Fe-rich (du Pont de Nemours™)

steel shots

steel shot waste from descaling of treated steel plate

*Organic compounds

biosolids

compost

*Aluminosilicates

bentonite

montmorillonite

Al-montmorillonite

gravel sludge

cyclonic ashes (beringite)

zeolites (natural and synthetic)

Steel shots

* iron rich material (97 % metallic iron,
containing 3% impurities-Mn)

*commercially available

*intended for shaping metal surfaces prior to coating

*literature background:

-As in soil is mainly retained by Fe-oxides

-data reporting strong As immobilising properties in some cases

mechanism: sorption of arsenate by Fe- (and Mn-) oxides

IN SITU IMMOBILIZATION AND PHYTOSTABILIZATION: CASE STUDIES

CASE 1: As contaminated kitchen gardens (Belgium)

CASE 2: As contaminated former goldmine site (France)

CASE 1: As contaminated kitchen gardens

- North of Belgium (Reppel): former As refinery
  =>contamination of surroundings
- Soil characteristics (sandy soil)

	As_{tot}	pH-H_20	OM(%)
Garden 1	98	6.6	7.3
Garden 2	166	6.7	7.9
Garden 3	72	6.0	5.0
Garden 4	76	6.0	4.1
Garden 5	88	6.5	2.7
Reference	4	7.0	5.7
CCR*	2-20		
Clean up value			

*CCR= Common concentration range

- As concentration in vegetables without and with SS treatment

Case 2: Phytostabilisation at an As contaminated former gold mine site

- mining district of Salsigne, situated in the south of France (200 km^2)
- exploitation of gold started in beginning of 20th century
- ores extracted for more than 100 years were rich in As
- borders to river Orbiel =>spread of contamination
- remediation of Site 'La Combe du Saut' (120 ha)

is under responsibility of ADEME:

AIM= reduce pollutant fluxes in air and water

Part of DIFPOLMINE PROJECT:

Evaluate possibilities of phytostabilisation
at the site of La Combe du Saut

focussing on
the reduction of As contaminated surface water runoff

METHODOLOGY

STEP 1. Evaluation of soil phytotoxicity, and reduction of As mobility by steel shots

STEP 2. Selection of a seed mixture

LAB

STEP 3. Installation and follow up of field plots

FIELD

STEP 1: Evaluation of soil phytotoxicity, and reduction of As mobility by steel shots (laboratory)

*Soil samples collected at different locations in the field

*Physico-chemical soil characterisation

mg/kg DW	As total	pH	available P
CAU1	14200		
CYAN 4	380		
CYAN 10	1250		
FONDE 13	815		
MON 16	115		

=> phytotoxicity test with *Phaseolus vulgaris* (bean)
=> chemical extractions

without and with SS (1%w/w)

Water extractions

	Location	Total As (aqua regia) (mg/kg DW)[1]	Water-soluble As (mg/kg DW)	% reduction
Control			<0.25	
CAU 1 * CAU 1+SS	(location 1)	14200	584 ± 112 360 ± 44	39%
CYAN 4 CYAN 4+SS	(location 2)	380	1.6 ± 0.1 0.29 ± 0.07	82%
CYAN 10* CYAN 10+SS	(location 3)	1250	7.1 ± 0.3 4.5 ± 0.4	36%
FONDE 13 FONDE 13+SS	(location 4)	815	17.6 ± 0.4 3.6 ± 0.6	79%
MON 16 MON16+SS	(location 5)	115	8.3 ± 0.2 0.4 ± 0.1	95%

*= shorter equilibration period)

Conclusion: -strong reductions in water soluble As by steel shots

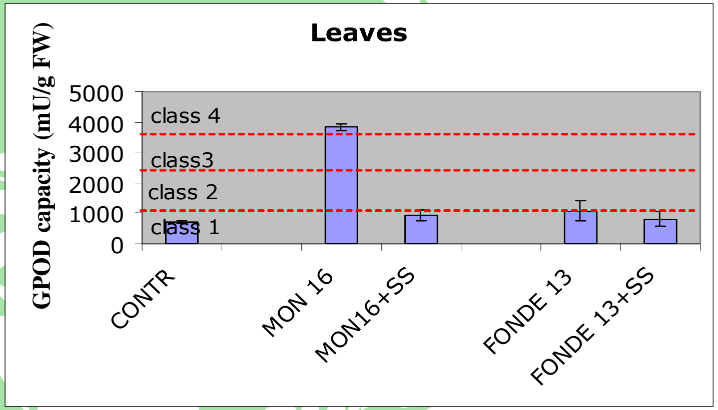
-very high water soluble As at location 1

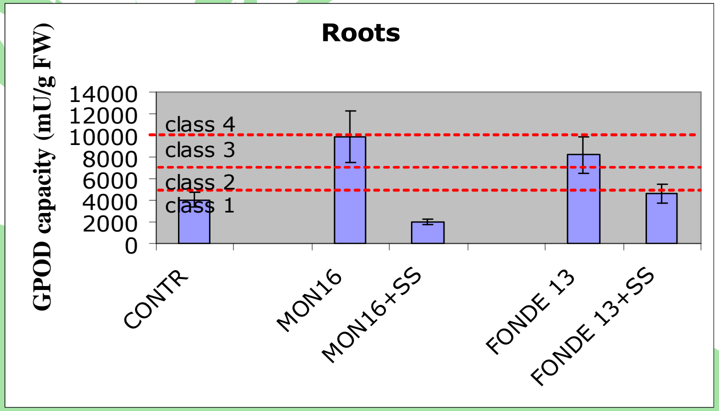
Phytotoxicity test

e.g. GPOD capacity

strong induction of stress enzymes in leaves and /or roots at location 4 and 5

-reduction to control level in leaves and roots after application of SS





⇒Steel shots can eliminate phytotoxicity of some substrates

⇒Revegetation looks realistic=>field

STEP 2: Selection of a seed mixture (laboratory + field)

Basis of the selection

- 3 groups: grasses, leguminosae and other species
- an inventory of the relevant and most characteristic species of the site+nearby area
- commercial availability of the seeds
- observations on the digue and comments by ‘Phytosem’
- Results of greenhouse experiments

18 species selected:

grasses


Arrhenatherum elatius
(Avoine élevée/Fromental)


Agrostis tenuis
(Agrostide)


Dactylis glomerata
(Dactyle vulgaire)


Festuca ovina
(Fétuque ovine)

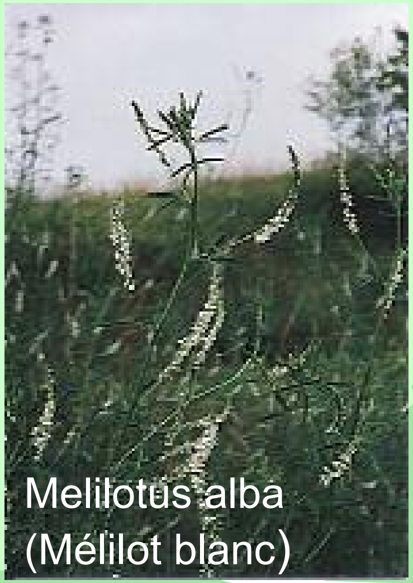

Festuca rubra
(Fétuque rouge)

Leguminosae

Lotus corniculatus
(Lotier corniculé)

Coronilla glauca
(Coronille glauque)

Onobrychis sativa
(Sainfoin)



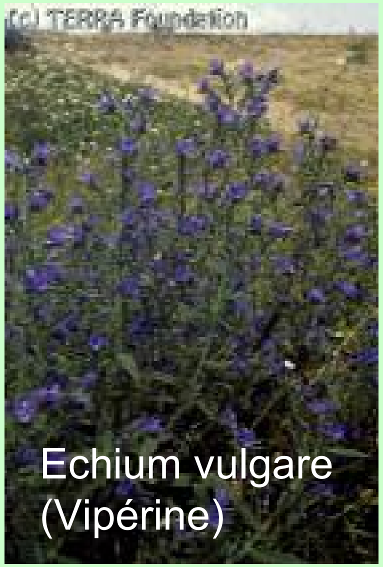
Melilotus alba
(Mélilot blanc)

Medicago lupulina
(Minette)

Psoralea bituminosa
(Psoraléé bitumineuse)

Spartium junceum
spartier à tiges
de jonc

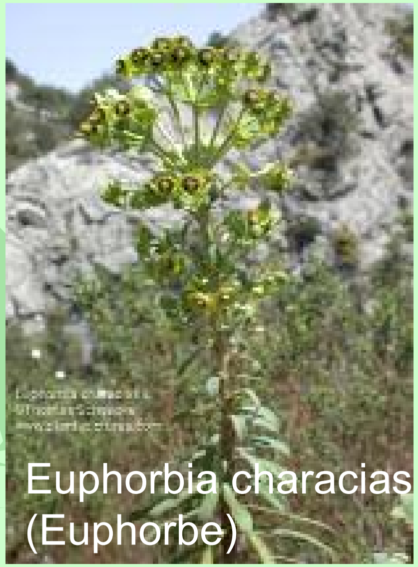
Other species



Echium vulgare
(Vipérine)

Daucus carota
(Carotte sauvage)

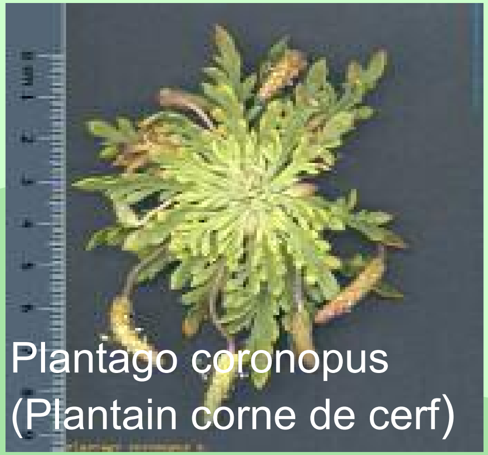
Sanguisorba minor
(Petit pimpernelle)



Euphorbia characias
(Euphorbe)

Inula viscosa
(Inule visqueuse)

Plantago lanceolata
(plantain lanéolé)



Plantago coronopus
(Plantain corne de cerf)

Evaluation of species and cultivars in greenhouse experiments

- 2 different cultivars or origines of the species were tested
- Small pots of 100g were filled with soil
- 8 seeds of each cultivar were sown
- 4 weeks
- 5 different soils were used (5 field plots)

MON 16 (Location 5)

Remark: Chlorosis on Lotus, Medicago and Onobrychis in UNT soil

Conclusion laboratory tests:

- Good growth of most species and cultivars, sometimes even without SS (except CAU 1) => substrates not very phytotoxic =>revegetation looks realistic

- SS can reduce chlorotic symptoms at two locations (reduction of toxicity)

- The two tested cultivars of most species gave similar results except for Agrostis, Onobrychis (second cv better growth on CAU1, no chlorosis on FONDE 13, MON 16)

  =>mixture of cv's used on field plots for most species

  =>Agrostis and Onobrychis: second cultivar used in field

- Of course: field check is important! (exposure period, climate)

STEP 3: Installation and follow up of field plots

*5 field plots

*during installation it came out that pollution degree of samples was different from pollution level of field plots (site = hetergeneous)

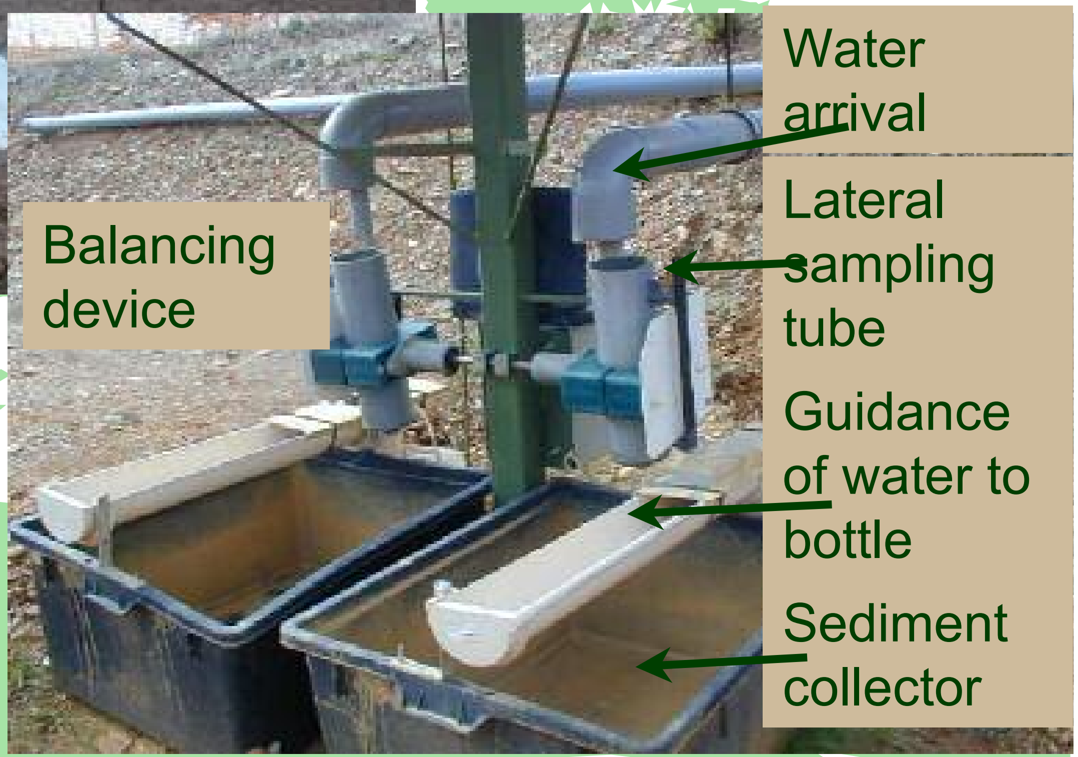
mg/kg DW	As_{total} samples	As_{total} field plots
CAU1	14200	9550/6261
CYAN 4	380	1814/4578
CYAN 10	1250	4283/3192
FONDE 13	815	2236/4193
MON 16	115	124/164

⇒results to be expected in the field are impredictable!

⇒(no SS applied at cyan 10)

Application of steel shots in the field

- last week of january 2004
- applied at a rate of 1% w/w (manual fertilisation device)
- mixed with rotary tiller to a depth of 15 cm...



=>Follow up of:
-vegetation
-runoff water

Results vegetation:

General vegetation view:

•Location 1: only locally plant growth (toxicity confirmed)
•Location 3: (without SS): no plant growth
=> greenhouse exp. in progress

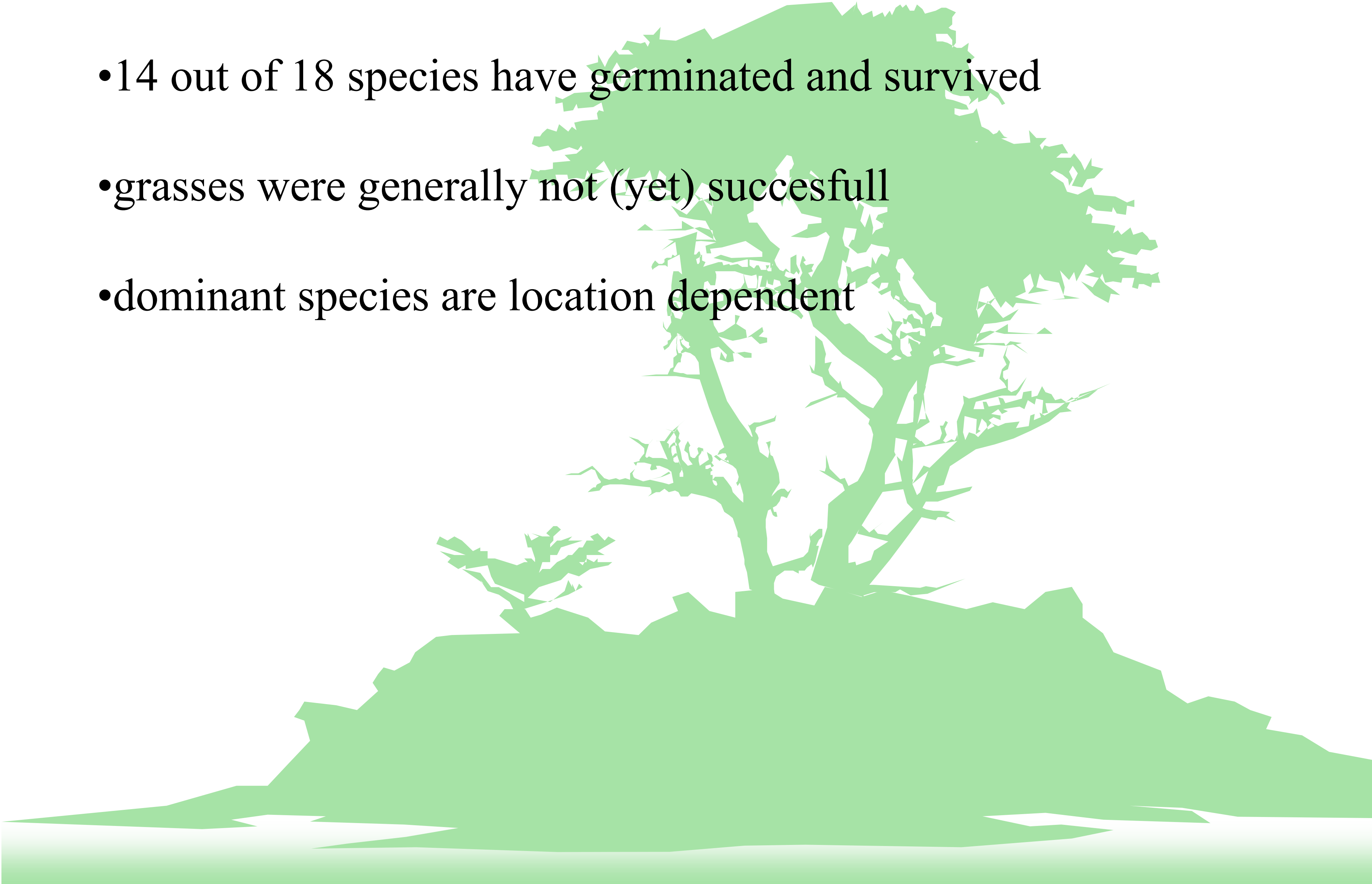
•Location 2, 4 and 5:
-rather succesfully revegetated
-however uncovered spots present (heterogeneity - local toxicity)

Specific species results:

•14 out of 18 species have germinated and survived

•grasses were generally not (yet) succesfull

•dominant species are location dependent



Results Runoff water

- As concentrations
- Amount of Runoff water

data treatment in progress

Actual measurements:

-As uptake in different species

-effective results of SS application in field plots (water-extractions)

CONCLUSION

In situ inactivation (immobilization) and/or phytostabilization can be valuable alternatives for the reclamation of vast metal-contaminated sites.

* Heavily contaminated soils: immobilization and phytostabilization reduce further spreading of metal to the surroundings and limit transfer of metals from metal enriched soils to the biotic trophic levels of ecosystems.

* 'Moderately' contaminated soils (gardens, agricultural soils): Immobilization limits the transfer of metals from soil to consumers. In this case, also phyto-extraction can be a valuable alternative.

ACKNOWLEDGEMENTS

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