Remediation strategies overview – Remediation of metal contaminated sites

L. Diels
Flemish Institute for Technological Research, Vito, Mol, Belgium

NATO – CCMS meeting
Prevention and Remediation Issues
Non-ferrous mining sector

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Problems related to metals mining, metals processing or surface treatment

- Acid mine drainage
- Air emissions: heavy metals contaminated land
- Landfills containing jarosite, goethite, gypsum, slags, fines: Anaerobic or aerobic leaching especially in the presence of organics
  - Solubilisation of metals and metalloids
  - Contamination of surface water
  - Disasters
  - Leaching into groundwater

➔ Diffuse pollution

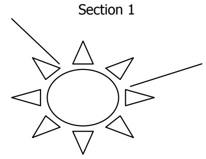
➔ Huge groundwater plumes (sometimes very deep)

➔ Surface water pollution

Integrated Management System (IMS) for Megasites

1. Megasite
   1. Definition of the site as a megasite
   2. Regulations and boundary conditions
   3. Definition of the organisatorial role and management of the megasite
2. Risks and risk reduction
   1. Megasite conceptual model
   2. Regional risk approach by clustering
   3. Risk reducing measures per risk cluster
3. Management scenarios or conceptual model
   1. Risk reduction scenarios at megasite scale
   2. Effects and uncertainties of the risk scenarios
   3. Cost effective calculation of the selected scenarios
   4. Priorities of the scenarios
4. Long term planning and management of a megasite
   1. Technical implementation- en monitoringplan
   2. Long term audit of the IMS

1. Megasite



1. Definition of the site as megasite
   - Large contaminated area, different pollutants
   - Many proprietaries or concession holders
   - Many stakeholders
   - Many end-users
   - Non-acceptable costs for the remediation
2. Regulatory directives and boundary conditions
   - EU - Framework directive Water
   - EU - Groundwater directive
   - Local legislation
3. Definition of the organisatorial role and management of the megasite
   - Future use of the site? (tourism, continuity of industrial activities?

2. Risks and risk reduction

Section 2

1. Megasite conceptual model

   1.1. Potential sources and contaminants

   - Open pit or underground mines
   - Waste heaps, lagunes, settling ponds, landfills
   - ➔ Solubilisation
   - ➔ Biological oxidation, reduction reactions
   - ➔ Metals, acids, cyanides

   1.2. Dominant fate and transport characteristics

   - Permeability
   - Impermeable clay or bedrocks
   - Fractures?
   - Retardation: ion-exchange, sorption, binding,….
   - Hydrogeological flows and flow rates

2. Risks and risk reduction

Section 2

1. Megasite conceptual model
   1.3. Potential receptors
   - Soil: residencial, natural areas
   - Groundwater
   - Surface water, rivers
   - Deeper aquifers, drinking water wells

   1.4. Final conceptual model
   - Flux to receptors
   - Interplanes related to measures
   - Source versus plume management

2. Risks and risk reduction

Section 2

2. Regional risk appraoch by clustering

2.1. Integration in the risk evaluation of:

- Transport modelling
- NA en immobilisation potential of the site
- Spatial planning issues

2.2. Definition of the basic elements for the IMS

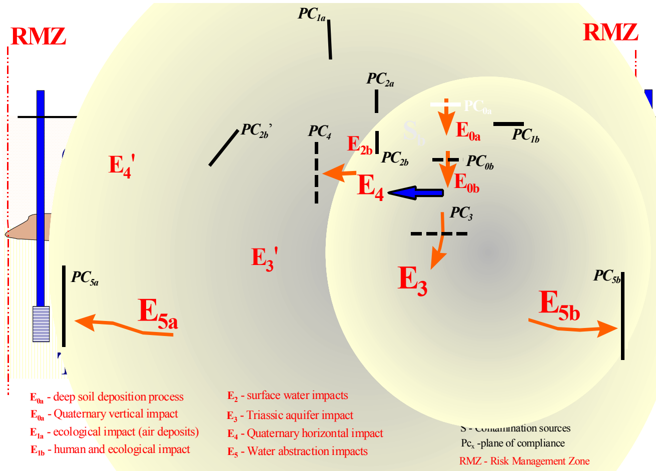
- Use GIS source-path-receptor analysis
- Definition of risk-clusters
- Understand the links between the clusters
- Confirm the risk clusters with the stakeholders

2.3. Risk-reduction measures per risk cluster

- Mobility:bioavailability methods
- NA/MNA/INA
- Intervention technologies

Conceptual model of the Risk Management Zone (= mining site)

- E1. Spreading via the air to soil
- E2. Run off to surface water
- E4. Leaching in quaternary aquifer
- E3. Transport via windows in clay layer to deeper aquifer
- E5. Threatening drinking water wells



3. Management scenarios

Section 3

3.1. Risk reduction scenarios at megasite scale

Source mangement versus plume management:

- Source is very large and diffuse
- Source management is too expensive (unless economical interest)

➔ Plume management

3.2. Effects and uncertainties of the risk scenarios

3.3. Cost effective calculation of the selected scenarios

3.4. Prioritisation of the scenarios

4. Long term planning and management of a megasite

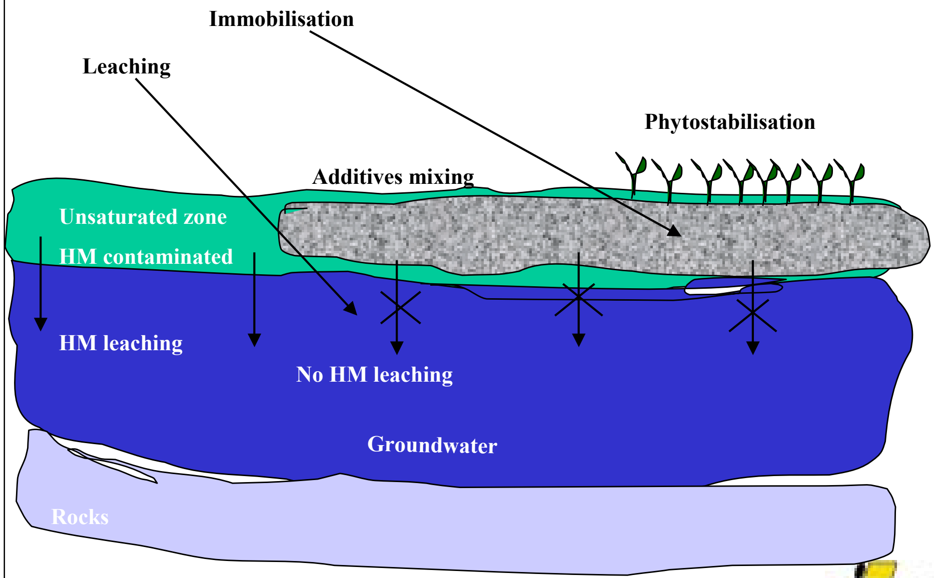
Section 4

1. Building of a technical implementation- and monitoring plan
2. Long term audit of the IMS

Measures at Interplanes of Risk Management Zones

- Unsaturated zone
  - Transport to soil (e.g. dust) and to groundwater (by rain) in residencial areas and natural areas
  - ➔(Phyto)stabilisation (short term)
  - ➔Phytoextraction (long term)

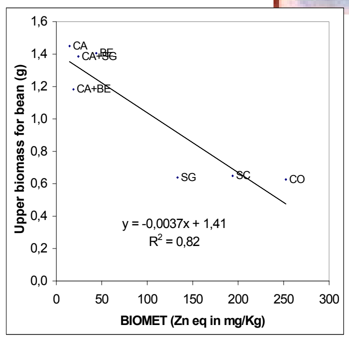
Immobilisation unsaturated zone



Evaluation of immobilisation tests

Mixing of contaminated soil with selected additives to reduce the bioavailability

- Batch tests
  - SEM/AVS:
  - BIOMET®:
  - Plants:
- Accumulation of metals by plants
- Lysimeter tests



Measures at Interplanes of Risk Management Zones

- Saturated zone
  - Transport to surface water or deeper groundwater layers (e.g. drinking water wells)

  ➔Pump & treat

  ➔Natural Attenuation

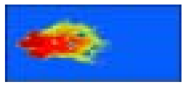
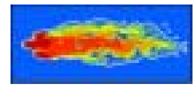
  ➔In situ bioprecpitation

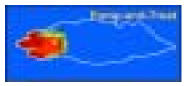
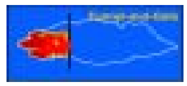
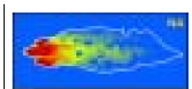
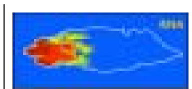
  ➔Reactive zones (e.g. in situ redox manipulation)

  ➔Permeable Reactive Barriers

  ➔Wetlands

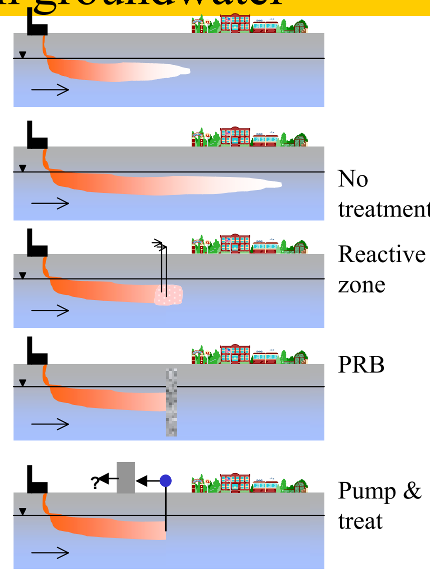
Plume management options

Contaminated Site  No measures → No NA Future Situation 

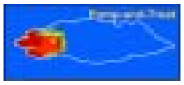
Options				
Technical Complexity	**moderate**	**high**	**low**	**high**
Investment Costs	**low**	**high**	**low**	**moderate**
O & M Costs	**high**	**low**	**low**	**moderate**
Land Use	**low**	**low**	**high**	**moderate**

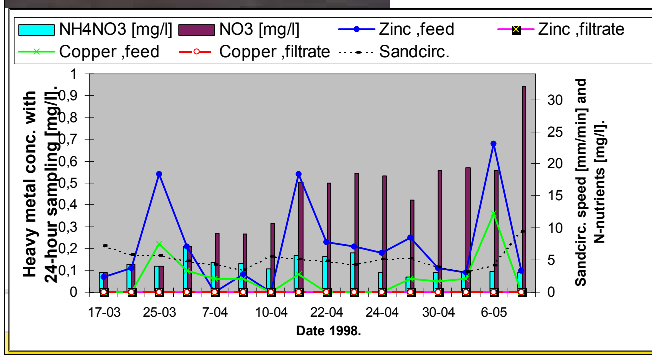
Heavy metals in groundwater

- Nature of heavy metals:
  - Can not be degraded,
  - Only immobilized or transferred
- Mechanisms:
  - Bioremediation
    - Biosorption
    - Bioprecipitation
  - Chemical technologies
    - reduction (zero valent Fe)
    - cementation (zero valent Fe)
    - oxidation ($KMnO_4$, $Na_2S_2O_8$)
  - Physical technologies
    - Electroreclamation
    - Adsorption
    - Precipitation
- Techniques:



“Pump & treat”: SAND FILTER INOCULATION





Removal of heavy metals from:

- **Non-ferrous waste water**
- **Mine water**
- **Groundwater**

Removal of:

Zn (100%)

Cu (100%)

Co (95%)

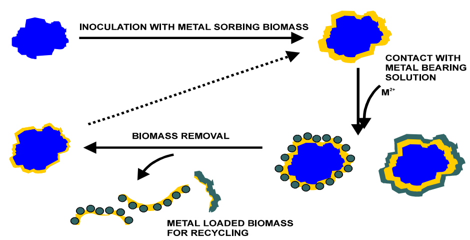
Ni (90%)

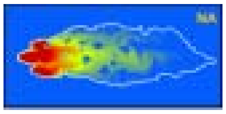
Ag, As, Se, Cr, Tl, Pb

Moving bed sand filter concept

SORPTION AND DESORPTION OF METALS BY INOCULATED SAND FILTERS

1. Inlet distributor
2. Outlet
3. Dirty sand
4. Air-lift pump
5. Sand washer
6. Washer labyrinth
7. Wash water outlet
8. Cleaned sand



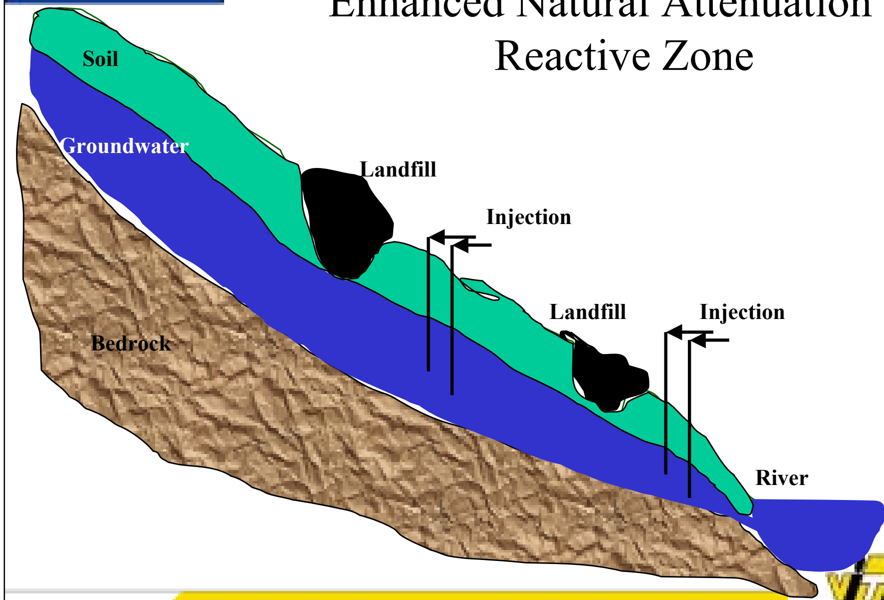


Natural processes of metal removal in soil and aquifer

- Adsorption and complexation of metals by organic substrates
  - Binding to carboxylic, phenolic groups of humic acids
  - Fe = Cu >> Zn >> Mn
- Microbial sulphate reduction followed by precipitation of metal sulfides
- Precipitation of Fe2O3, MnO2
- Adsorption to Fe(OH)3
- Metals uptake by plants
- Filtration of suspended and colloidal materials
- Alkalinity generation

In situ remediation activities

Enhanced Natural Attenuation or Reactive Zone



In situ bioprecipitation

Sulfate Reducing Bacteria (or iron reducing bacteria) must be available in the aquifer

Sulfate must be available sufficiently

An organic substrate as methanol, ethanol, molasse, acetate, lactate, HRC, compost leachate must be present or added.

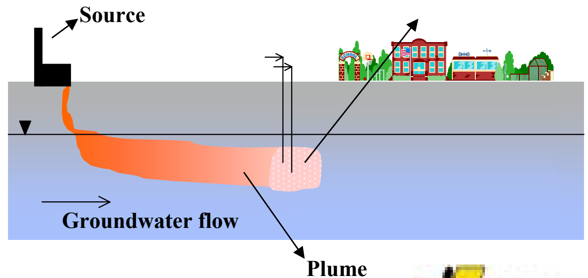
Not too extreme pH (5 – 9), minimal content of nutrients (N en P), no oxygen and a low ORP.

$SO_4^{2-} + 8\,e + 8\,H^+ \Longrightarrow S^{2-} + 4\,H_2O$

$CH_3COOH + 2H_2O \Longrightarrow 2CO_2 + 8\,H^+ + 8\,e$

$CH_3COOH + SO_4^{2-} \Longrightarrow 2HCO_3^- + HS^- + H^+$

$H_2S + Me^{++} \Longrightarrow MeS + 2H^+$



Metal processing, site 1a: groundwater + low sulfate content

Zn	T0	T4	T8	T12
aquifer + groundwater	1870	1400	1510	644
aquifer +groundwater+ 0.5 mM $HgCl_2$	1840	1630	1940	2270
aquifer + groundwater + 1 ml K-acetate (25%)	1350	922	1200	1500
aquifer + groundwater + 5 ml K-acetate (25%)	1570	884	1160	434
aquifer + groundwater + 1 ml K-acetate (25%) + Dd8301	38	14	14	25
aquifer + groundwater + 5 ml K-acetate (25%) + Dd8301	16	144	118	14
aquifer + groundwater + Postgate C medium + Dd8301	1170	51	20	26

74 mg sulfate/l

Metal processing, site 1a: groundwater + low sulfate content

	T0	T1	T4	T8	T12	T20
groundwater	-68					
aquifer + groundwater	156	57	161	-95	-32	86
aquifer +groundwater+ 0.5 mM $HgCl_2$	393	389	418	345	358	361
aquifer + groundwater + 1 ml K-acetate (25%)	129	93	191	-118	-149	141
aquifer + groundwater + 5 ml K-acetate (25%)	189	-140	280	211	191	259
aquifer + groundwater + 1 ml K-acetate (25%) + Dd8301	-224	-60	-28	-295	-219	-152
aquifer + groundwater + 5 ml K-acetate (25%) + Dd8301	-173	-165	217	107	-102	-188
aquifer + groundwater + Postgate C medium + Dd8301	-276	-172	-287	-354	-331	-337

74 mg sulfate/l

Metal processing, site 1b: high sulfate concentration

Zn (µg/l)	T0	T8	T20
Aquifer + GW	101000	79200	49000
+ $HgCl_2$	109000	94200	62400
+ acetate	109000	82800	15
+ 5 x acetate	103000	109000	90000
+ acetate + Dd	93100	77200	12
+ 5x acetate + Dd	96100	91600	72800

ORP (mV)	T0	T8	T20
Aquifer + GW	-117	- 60	-36
+ $HgCl_2$	232	-50	-104
+ acetate	-146	-70	-229
+ 5 x acetate	-65	-78	-90
+ acetate + Dd	-194	-78	- 259
+ 5x acetate + Dd	-103	-96	-88

initial sulfate concentration: 506 mg SO_4^{2-}/l

Metal processing, site 1c: Toxic metals

	Control	+ Molasse	+ methanol
pH	5.3	5.6	6.3
Eh	- 93	-185	-344
SO4	1260	430	67
Cd	22900	4	2
Zn	131000	99	26
Ni	45400	11300	29
Co	11200	1620	< 5
Fe	24900	9640	652

Time: 30 weeks

Industrial landfill, site 2, evolution As concentration (µg/l)

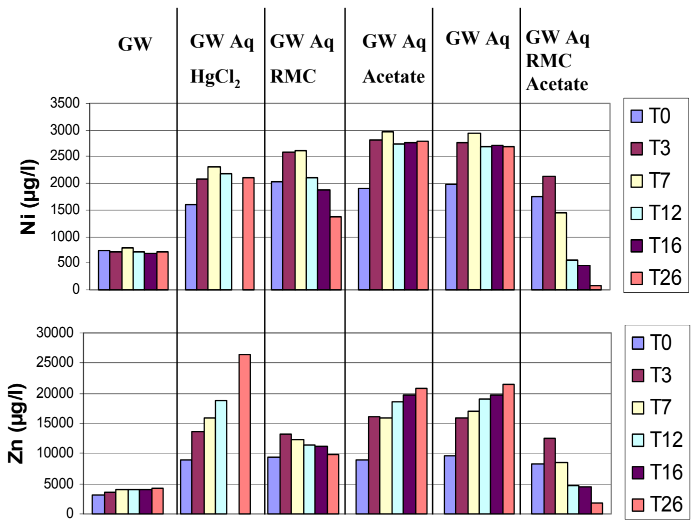
aquifer PB11 + groundwater PB11	T0		T4	T6	T8	
	Total	In solution	Total	Total	Total	
groundwater	8480	5190				
aquifer + groundwater	7170	3130	*3780*	*971*	*4940*	
aquifer +groundwater+ 0.5 mM $HgCl_2$	5910	2070	*1560*	*1030*	*2060*	
aquifer + grondwater + 1 ml K-acetate (25%)	5750	2100	*3190*	*817*	*481*	
aquifer + groundwater + 1 ml K-acetate (25%) + Dd8301	5560	1340	*3420*	*679*	*145*	
aquifer + groundwater + Postgate C medium 10x + 1 ml K-acetate (25%) + Dd8301	5750	5630	*1610*	*608*	*61*	
aquifer + groundwater + Postgate C medium 10x + 1 ml K-acetate (25%)	5230	5090	*1770*	*591*	*281*	
aquifer + groundwater + Fe-A4	5290	3840	*2740*	*2250*	*1460*	
aquifer + groundwater + 0,5 mM $HgCl_2$ + Fe-A4	5730	2810	*1550*	*1190*	*547*	
aquifer + groundwater + Fe-A4 + 1 ml K-acetate (25%)	5070	3740	*2710*	*805*	*140*	
aquifer + groundwater + Fe-A4 + 1 ml K-acetate (25%) + Dd8301	6230	4260	*2140*	*60*	*113*	

Redox zone: In situ redox manipulation

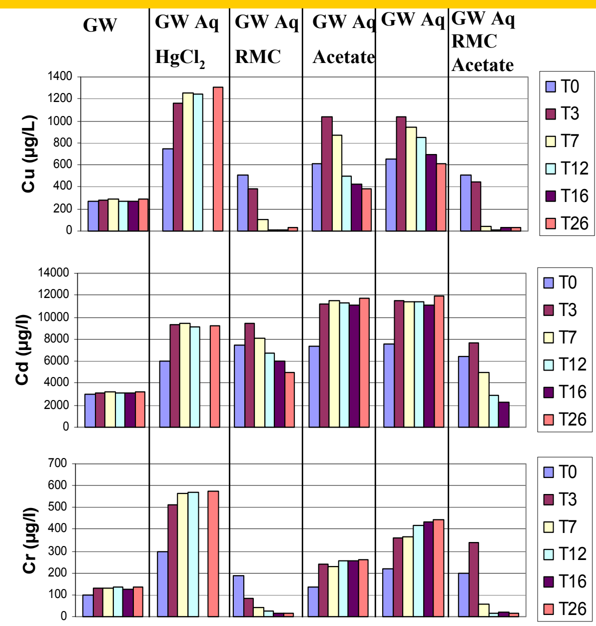
Conditions **pH**	T0	T3	T7	T12	T16	T26
Groundwater	3.1	3.3	3,2	3.2	3.0	3.1
Aquifer + groundwater + $HgCl_2$	3.3	3.4	3.5	3.4	ND	3.3
Aquifer + groundwater + RMC	3.5	3.8	3.9	4.1	4.4	4.4
Aquifer + groundwater + acetate	3.8	3.9	3.6	3.6	3.6	3.6
Aquifer + groundwater	3.3	3.2	2.0	3.2	3.3	2.3
Aquifer + groundwater + acetate + RMC	3.9	4.0	4.2	5.4	5.4	5.5
Conditions ORP	T0	T3	T7	T12	T16	T26
Groundwater	440	455	402	262	167	300
Aquifer + groundwater + $HgCl_2$	392	380	280	292	ND	329
Aquifer + groundwater + RMC	339	363	57	32	- 80	205
Aquifer + groundwater + acetate	294	336	215	280	188	294
Aquifer + groundwater	321	441	409	340	208	320
Aquifer + groundwater + acetate + RMC	287	315	274	-58	-123	-12

Redox zone: In situ redox manipulation

Evolution heavy metal concentration:

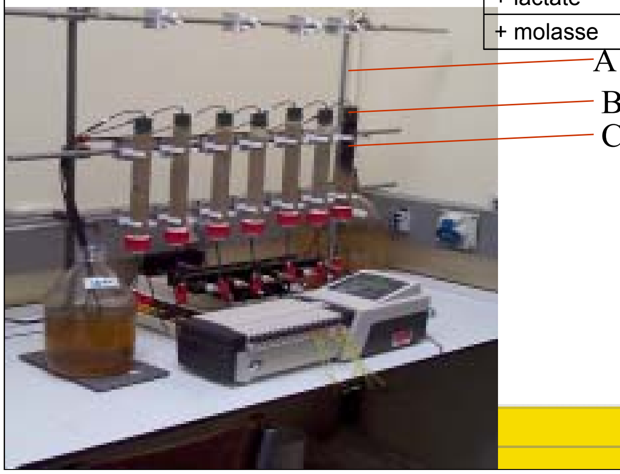


Redox zone: In situ redox manipulation



Column experiments

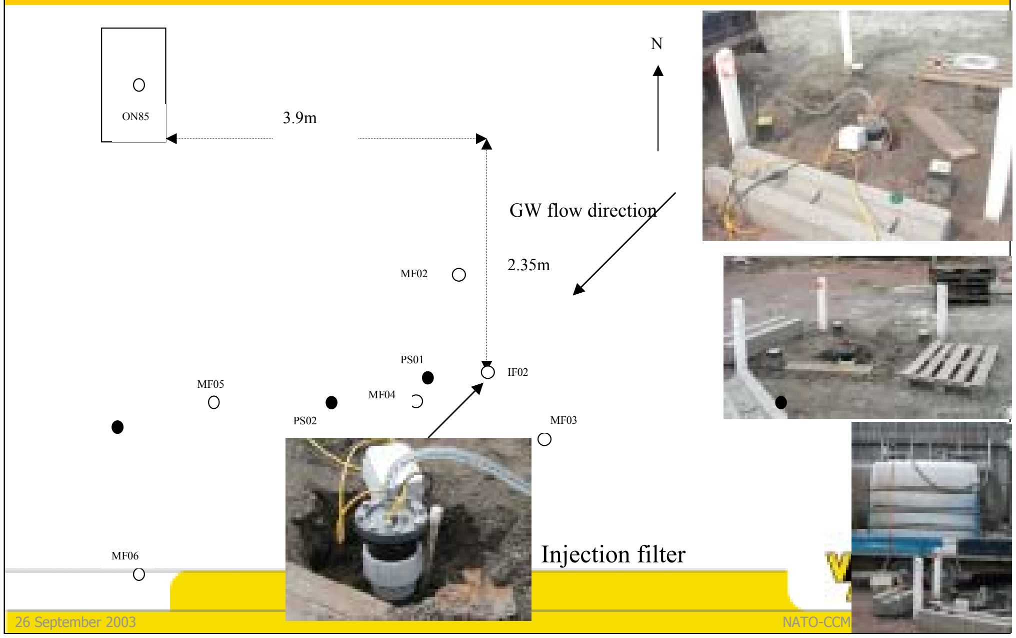
	Cd (mg/l)	Zn (mg/l)
Input	0.20	146
Control	0.18	152
+ $HgCl_2$	0.18	148
+ methanol	0.03	< 0.001
+ ethanol	0.01	< 0.001
+ acetate	0.02	40.6
+ lactate	0.01	< 0.010
+ molasse	0.01	0.8*



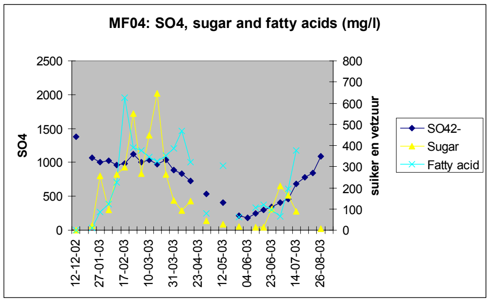
Sustainability of the heavy metals precipitation in column tests

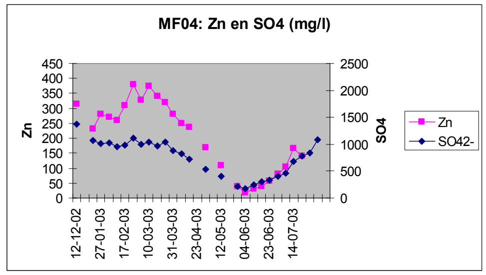
	Zn	Cd	As	Ni
Input water	146	0.2	0.03	0.06
+ HgCl2	122	0.2	0.05	0.09
+ ethanol	0.12	<0.002	0.03	0.02
- ethanol	80	< 0.002	0.08	0.08

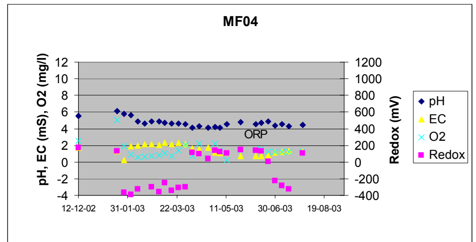
In situ bioprecipitation: Pilot plant



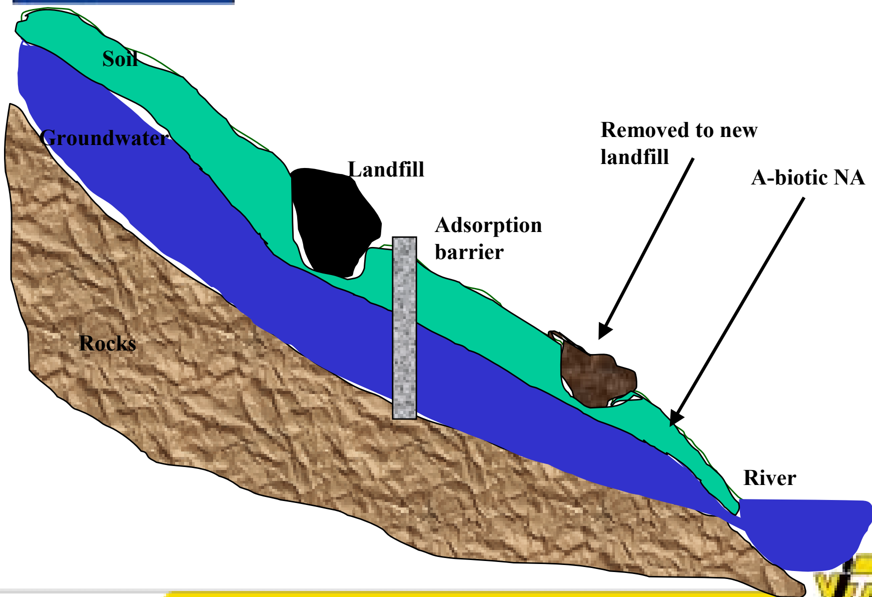
Pilot tests: MF04



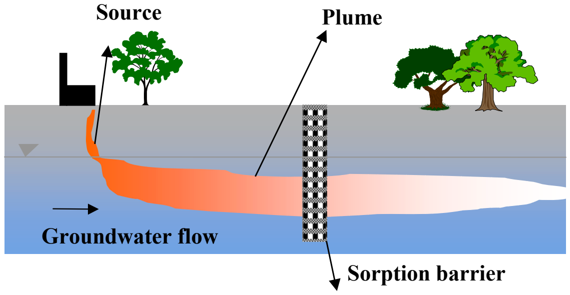




In situ remediation activities



Physical techniques: sorption barriers



Metal + Sorption material --> adsorbed metal

Sorption barriers: Zn removal

Adsorbent	Zn concentration				
Initial concentrations	**0**	**5**	**20**	**50**	**100**
Activated coal	**0,01**	**0,06**	**1,02**	**7,44**	**24,82**
Synthetic zeolite	**0,02**	**0,01**	**0,06**	**0,13**	**0,45**
Ironoxide-hydroxide	**0,04**	**0,06**	**0,13**	**0,44**	**1,43**
Silicate	**0,02**	**0,03**	**0,01**	**0,12**	**0,23**
Mordenite	**0,03**	**0,08**	**0,31**	**1,23**	**5,84**
Zeolite X	**0,00**	**0,16**	**0,16**	**0,35**	**0,25**
Anaerobic compost	**0,23**	**0,30**	**1,30**	**5,84**	**23,5**
As-adsorbent	**0,06**	**0,06**	**0,35**	**2,18**	**13,21**
Zerovalent iron	**0,06**	**1,71**	**13,23**	**14,30**	**59,52**

Concentrations in mg Zn/l

Sorption bariers: metal removal

Adsorbent	Cd	Zn	Ni	Cr	As
Activated coal	++	-	-	-	-
Synthetic zeolite	++	++	+	-	++
Ironoxide-hydroxide	+	++	++	-	++
Silicate	+	++	++	-	-
Mordenite	+	+	++	-	-
Zeolite X	+	++	-	-	-
Anaerobic compost	+	-	-	-	-
As-adsorbent	-	+	+	-	++
Zerovalent iron	-	-	-	++	++

Measurements after 24 hour

Sorption test (columns)

Objective:

Evaluation of the use of compost for the immobilisation of heavy metals

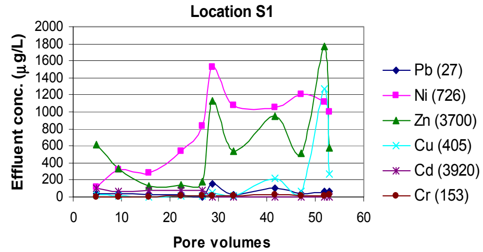
Set-up:

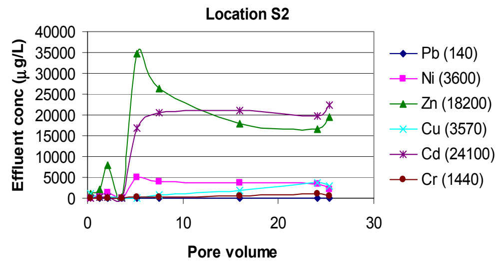
- Column test
- 18 g compost
- Room temperature
- 17-18 cm/day
- Monitoring:
  Zn, Cr, Cd, Ni, Cu, Pb
  pH, ORP

Conclusion:

- Fast breakthrough after 3 - 25 PVs
- pH-effect: pH_{in}: 2.5; pH_{out}: 6.5 --> 3.85
- Sorption barrier with compost is not a good alternative for bioprecipitation.

Results:





CONCLUSIONS

- Large measures as prevention of disasters (e.g. dikes, slurry walls)
- IMS approach can be used on Mining sites
- Source – path – receptor: risk evaluation
- Clustering (old mining, new activities)
- Conceptual model
- Measures:
  - Natural Attenuation
  - Pump & treat
  - In *situ* heavy metal bioprecipitation in groundwater
  - *In situ* groundwater redox manipulation
  - Permeable Reactive Barriers
    ➔MULTIBARRIER (e.g. treatment of cyanides and metals)
  - Wetlands