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In-situ bioprecipitation of heavy metals: sustainable approach for soil and groundwater remediation

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History of contamination

- Non-ferrous industry in Kempen, Belgium
  > 100 years exploitation
- Groundwater contamination:
  - Metals (Zn, Cd, Co, Ni, …)
  - Sulphates (1000 – 5000 mg/l) → acidic pH (3-5)
- Remediation:
  - Current technique: P&T → high cost

  (maintenance and energy), limited succes, long term…

⇒ Sustainable approach to ensure future of sector in Europe: *in-situ* bioprecipitation (ISBP)?

⇒ If ISBP successful: stability of formed precipitates?

Demonstration of IS(B)P

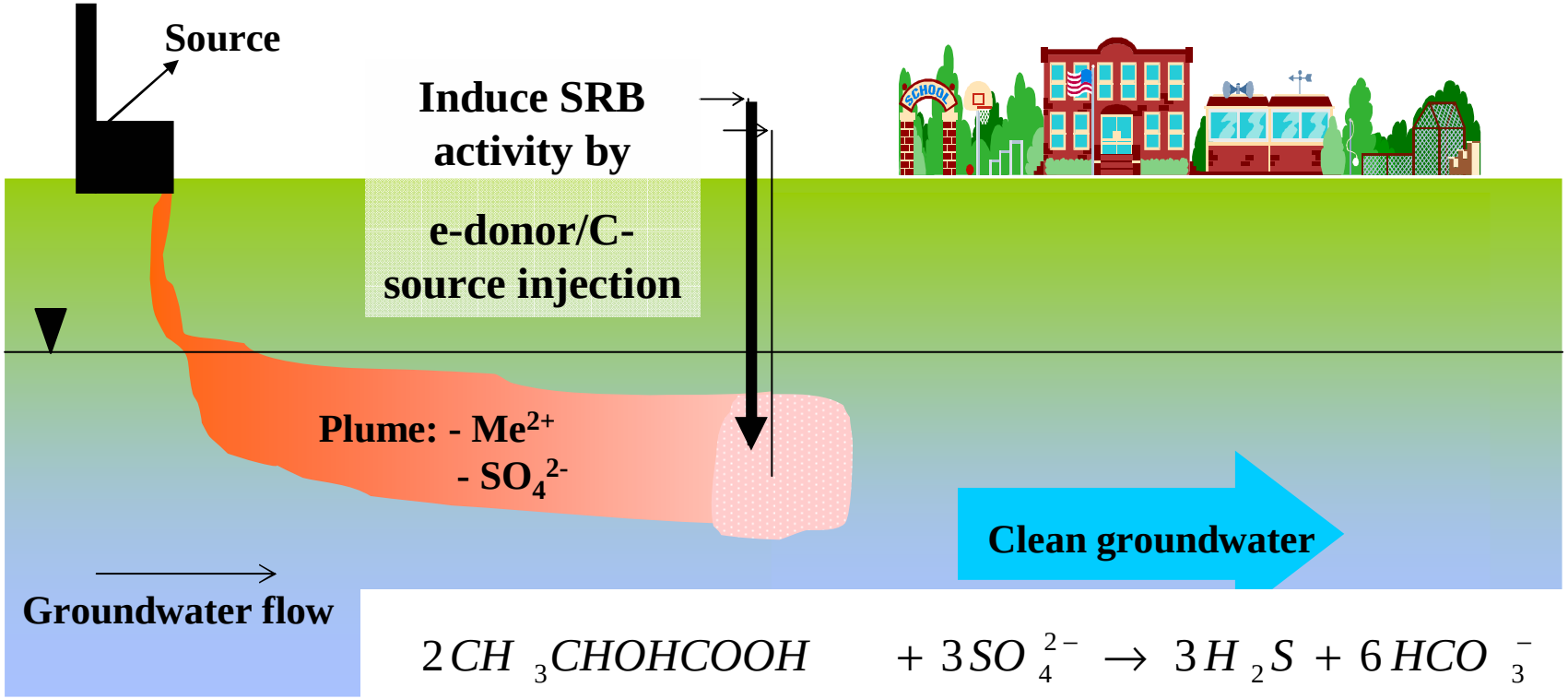
AIM:

1. Characterization of the sites (hydrogeology)
2. Screen for feasibility of IS(B)P in lab tests
   - » Screen for induction of biological (sulfidogenesis) or chemical precipitation in batch
     - » Biological:
       polylactate ester – soy oil – glycerol – Na lactate N/P – molasses – cheese whey
     - » Biochemical:
       ZVI and ZVI amended with Na lactate
     - » Chemical:
       CaSx and Na_2S
   - » Determine critical concentration for MeS formation in columns
3. Install field test and injection at pilot scale
4. Stability of formed precipitates in lab and field tests?

In-situ bioprecipitation (ISBP)

Demonstration of ISBP at pilot scale:

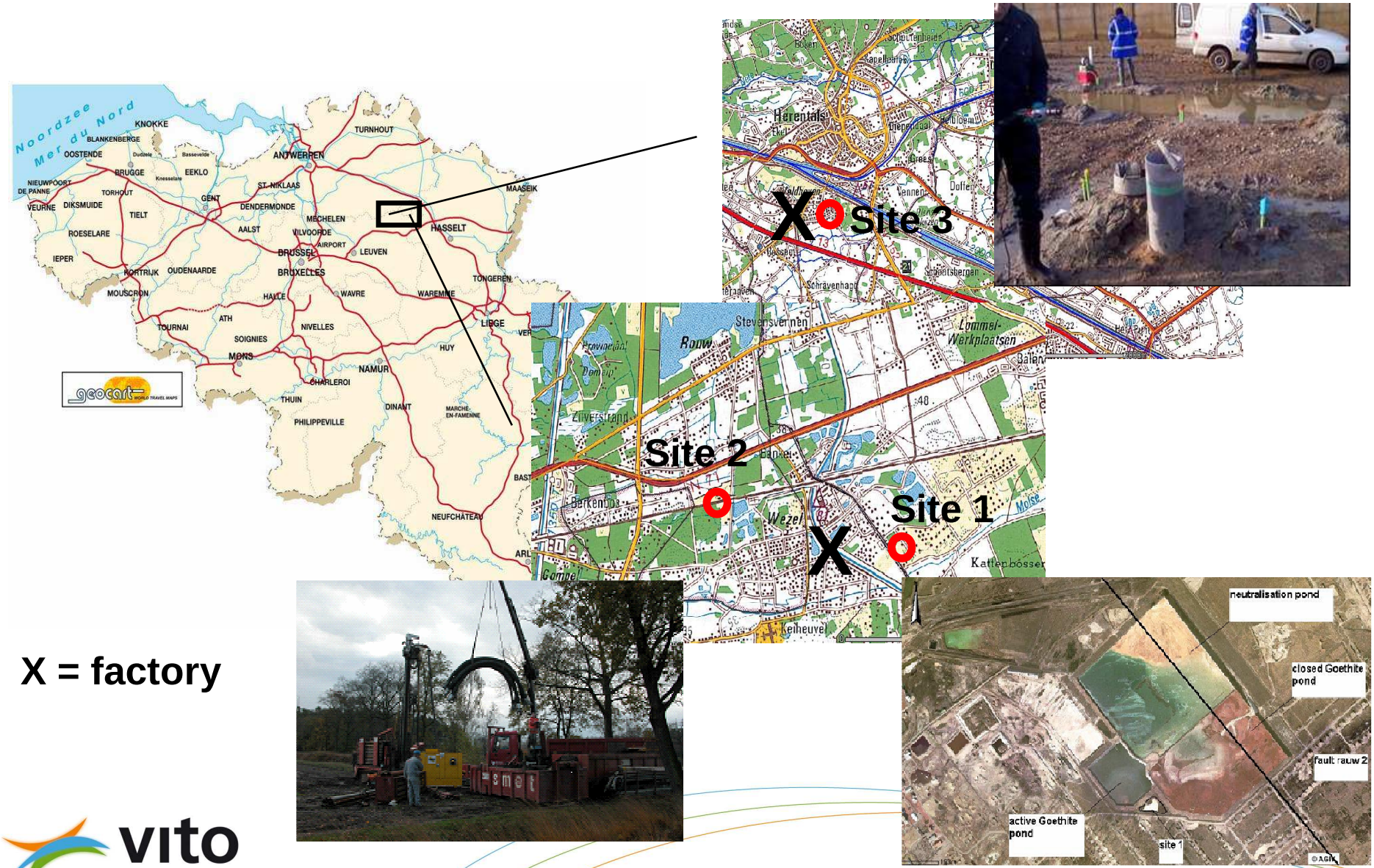
- Insimep project (Life project)
- study stability / irreversibility of precipitates



$$2\,CH_3CHOHCOOH + 3\,SO_4^{2-} \rightarrow 3\,H_2S + 6\,HCO_3^-$$

$$HS^- + Me^{2+} \rightarrow MeS\downarrow + H^+$$

Location of study sites



X = factory

Lab feasibility tests: BATCH

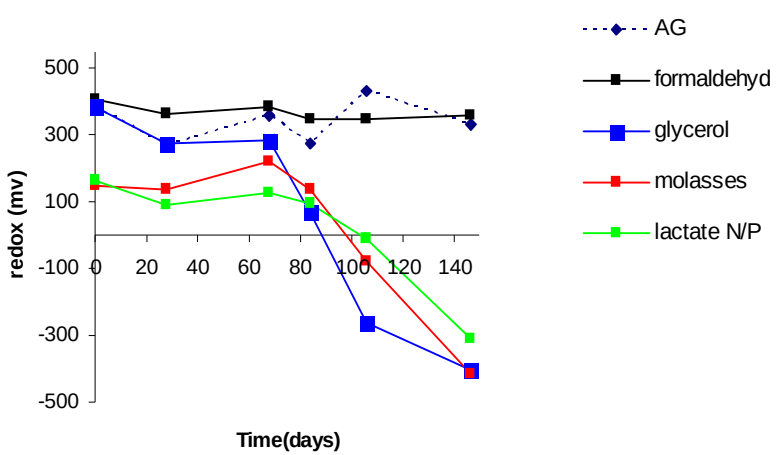
Sample site	Grondwater level (m-bg)	pH	SO_4^{2-} (mg/L)	Fe (mg/L)	Zn (mg/L)	Cd (mg/L)	Co (mg/L)
Site 3 (4-7 m-bg)	4.02	4,8	361	16			34,0
Site 2 (30m-bg)	0,78	4,8	1060	297	1983	2,1	
Site 1 (30m-bg)	5.10	4,2	1280	2	139	5,2	
Site 1 (65 m-bg)	5.11	4,5	1880	21	101	1,0	

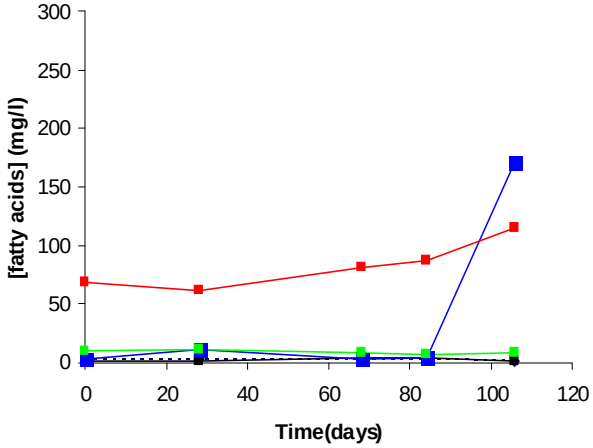
L/S 5/1

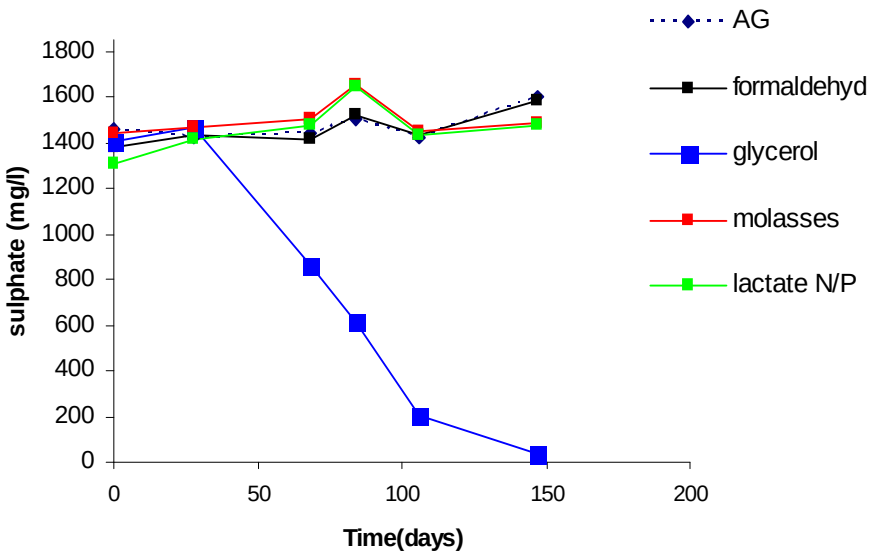
Vanbroekhoven *et al*. (2008). Hydrometallurgy

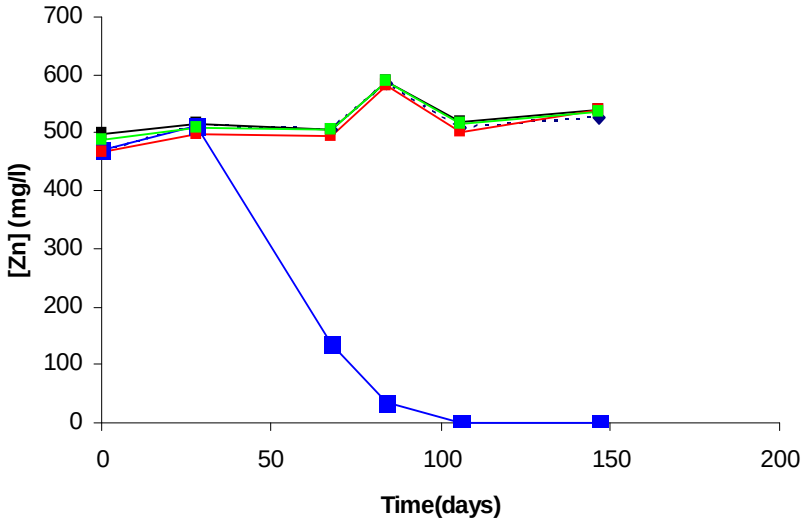
BATCH Site 1 (30 m bgs)

Only with glycerol removal of SO_4^{2-}, Zn, Cd, production of VFA









Overview BATCH tests

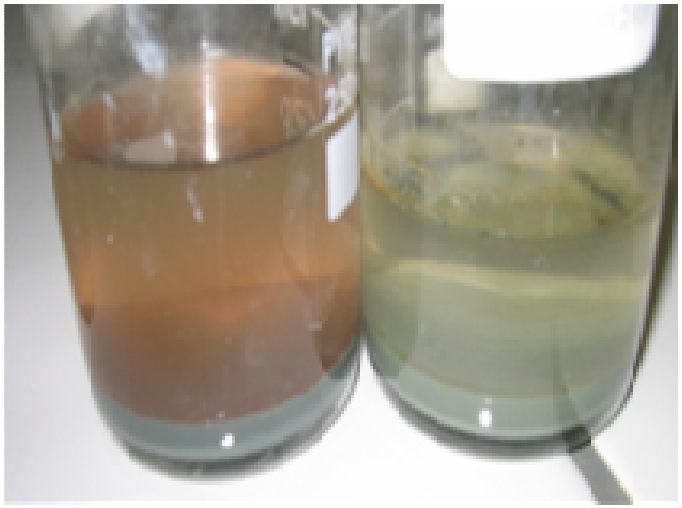
Site	Condition	Con-centration compound [g/l]	$pH_{initial}$	pH_{end}	$E_{initial}$ † [mV]	E_{end} † [mV]	Removal Me [%]	Removal SO_4^{2-} [%]	Removal tim [days]
site 3	Lactate N/P	**1**	5.5	6.3	10	-159	99,1	97.6	48
	Cheese whey	**24**	5.2	4.9	36	-170	97,5	100.0	48
site 2	Glycerol (87%)	**4**	4.1	5.1	215	-226	100	79.5	169
	Na_2S (35%)	**11**	5.9	9.6	-26	-423	99,6	-6.3*	=1
	CaSx (3.3g)	**17**	ND	6.3	ND	-37	99,9	ND	=1
site 1	Glycerol - 30m	**4**	3.9	6.0	387	-406	100	97	106
	Glycerol - 60m	**6**	3.7	3.7	386	37	96	14	215

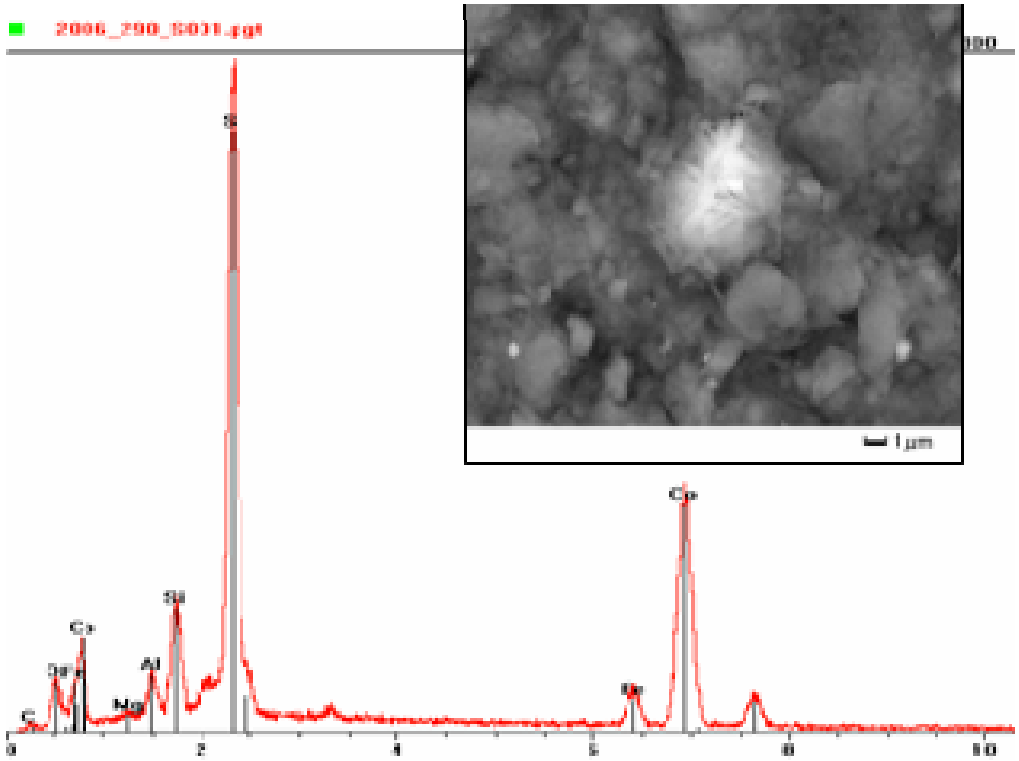
Vanbroekhoven et al., 2008. Hydrometallurgy

Stability BATCH

I. Analyzed by microscopy

Site 3





Pink precipitate → freeze drying, analyses by SEM-EDX

Stability BATCH

II. Analyses by Bioassay

→ Aerobic conditions

→ Specific metal

Zn-biosensor (BIOMET®):

→ Host bacterium formerly *Ralstonia metallidurans*

→ Bioavailable concentrations of metals

→ Induced bioluminescence based on transcriptional fusion of metal resistance genes with lux genes

⇒ Indication of metal precipitate stability
in terms of “bio”availability under aerobic conditions

Stability BATCH

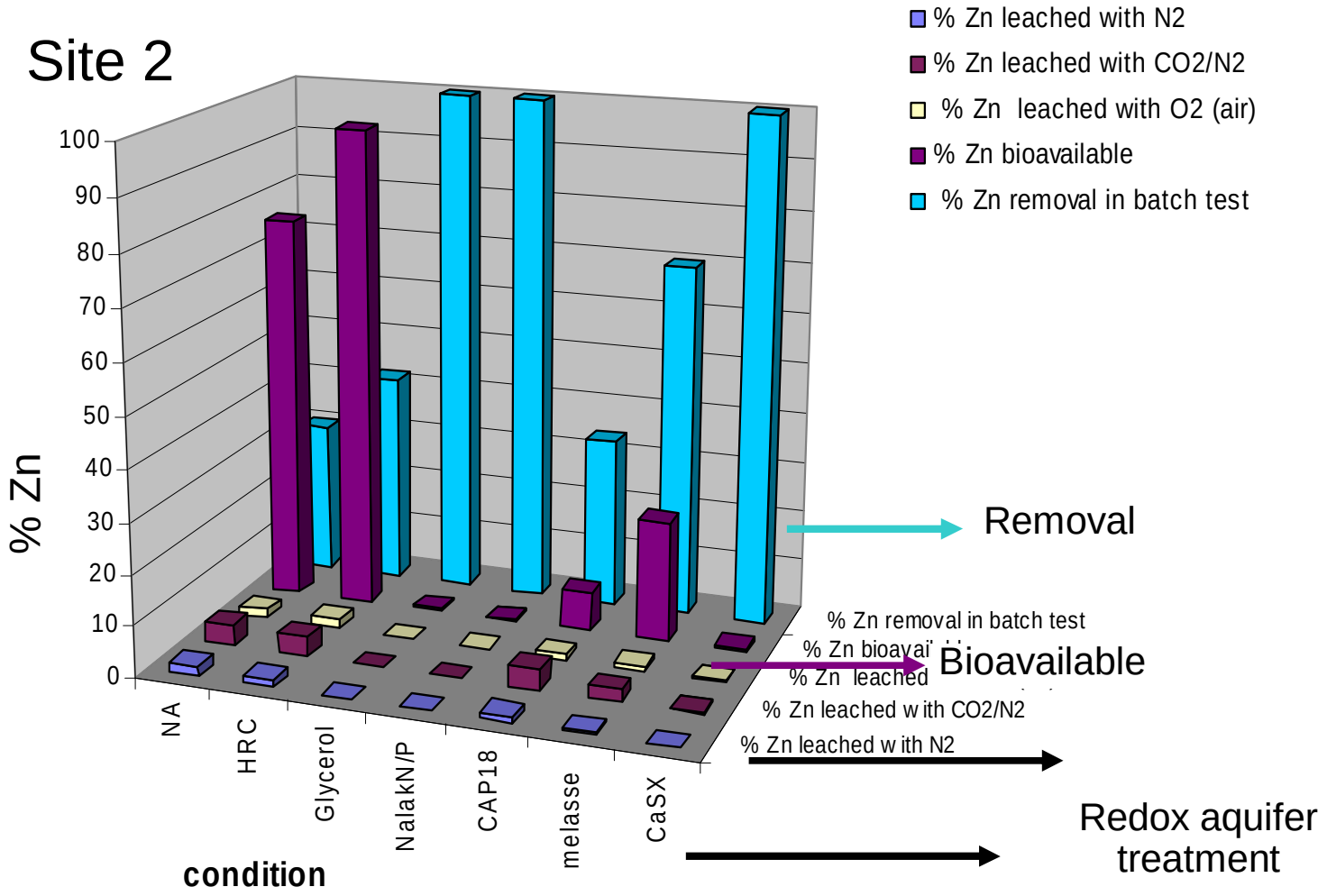
III. Analyzed by different wet-chemical methods

1. Redox aquifer treatment:
    1. Air gas phase (20% O_2)
    2. CO_2/N_2 (20%/80%) gas phase
    3. N_2 (100%) gas phase

L/S 4;

gas flushing at 0 and 24h; analyses after 48h

Stability BATCH



⇒ Up to 5% release of Zn for control in CO_2/N_2

⇒ Up to 70 - 90% bioavailable Zn in control, HRC; up to 20% in molasses

Stability BATCH

2. Sequential extraction
(adapted Tessier protocol)

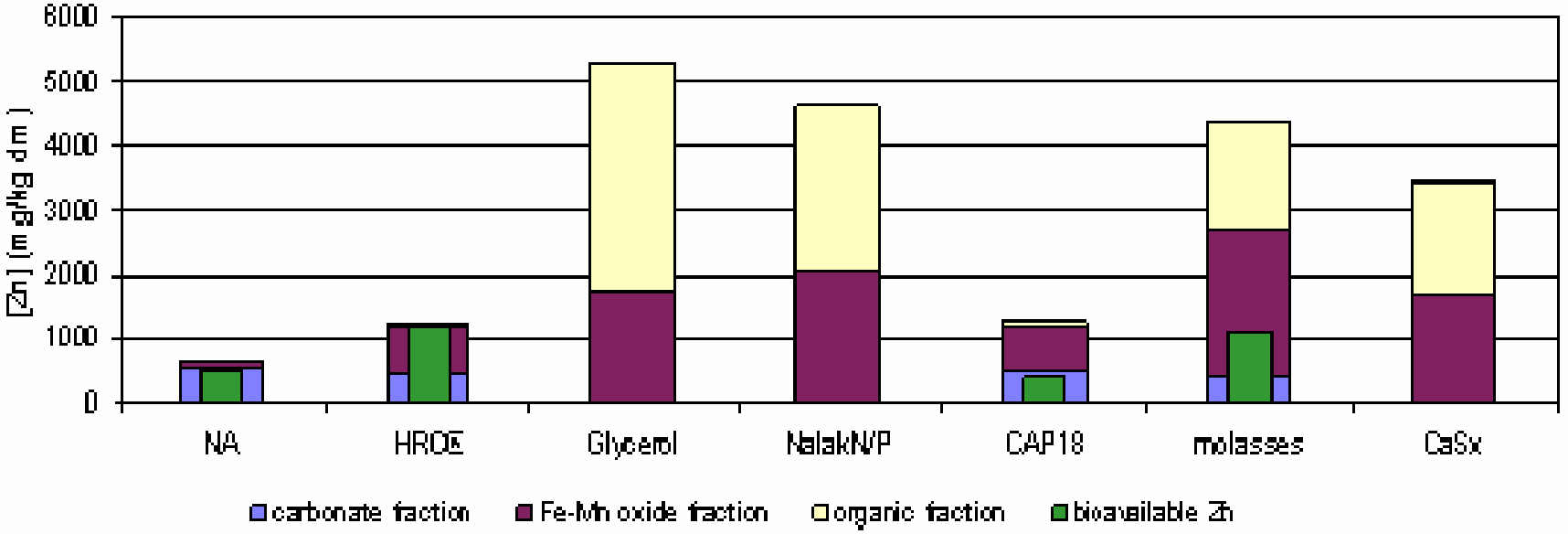
1. Labile fraction (carbonate)
2. Fe-Mn oxide
3. Organic fraction

Increasing stability

Stability BATCH

Site 2

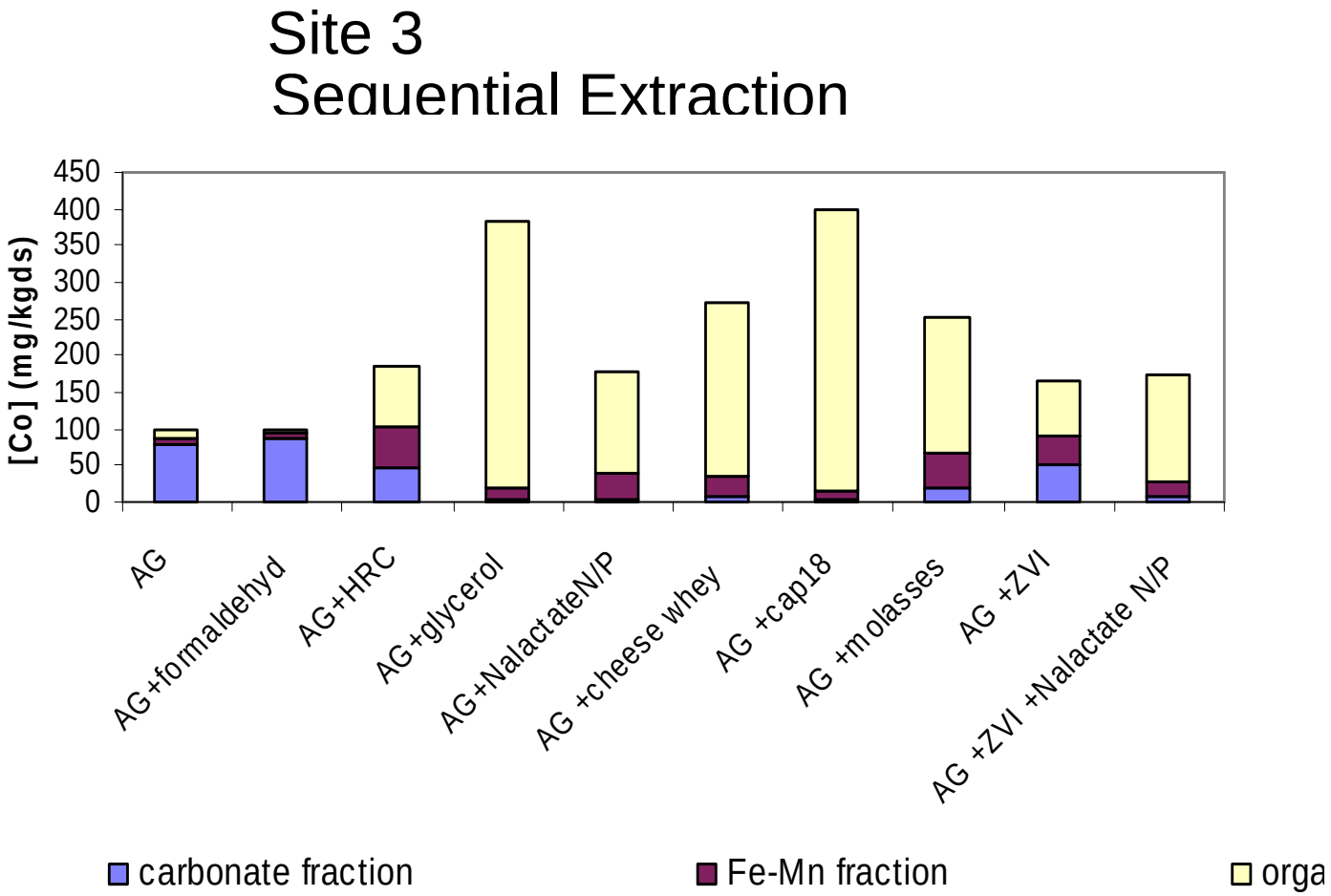
Sequential extraction - Bioassay



⇒ similar results as for redox treatment (Control, HRC)

⇒ up to 5 g/kg dm Zn immobilised with glycerol

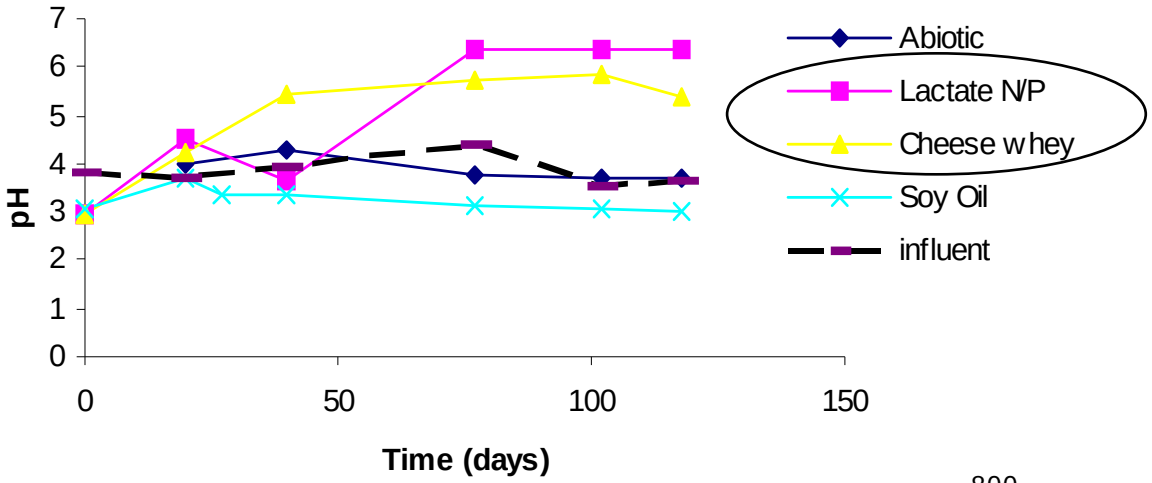
Stability BATCH



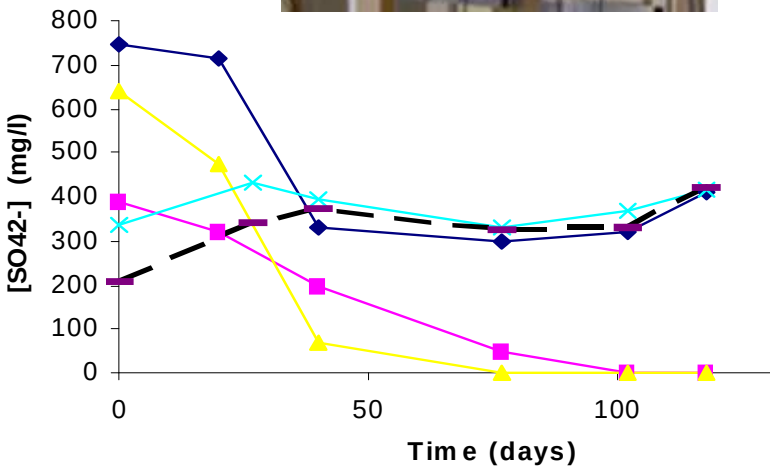
Lab feasibility tests: Columns

Site 3

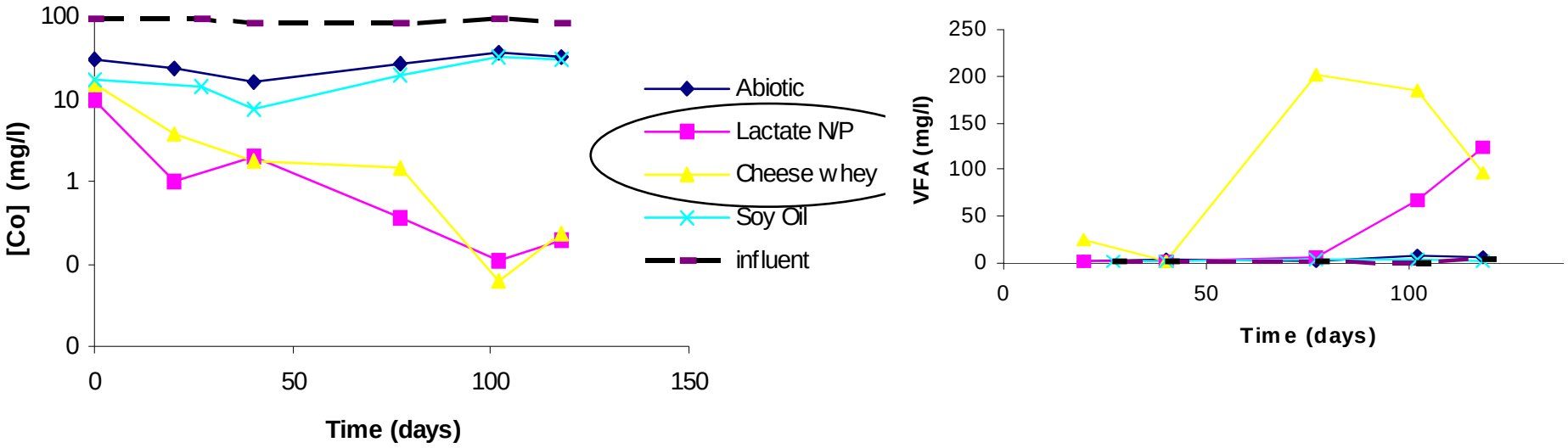
L/S 0,1/1



- pH increase after 50 days for Nalactate and cheese whey fed columns
- Simultaneous sulfate removal
- No effect for soy oil or control



Column tests site 3



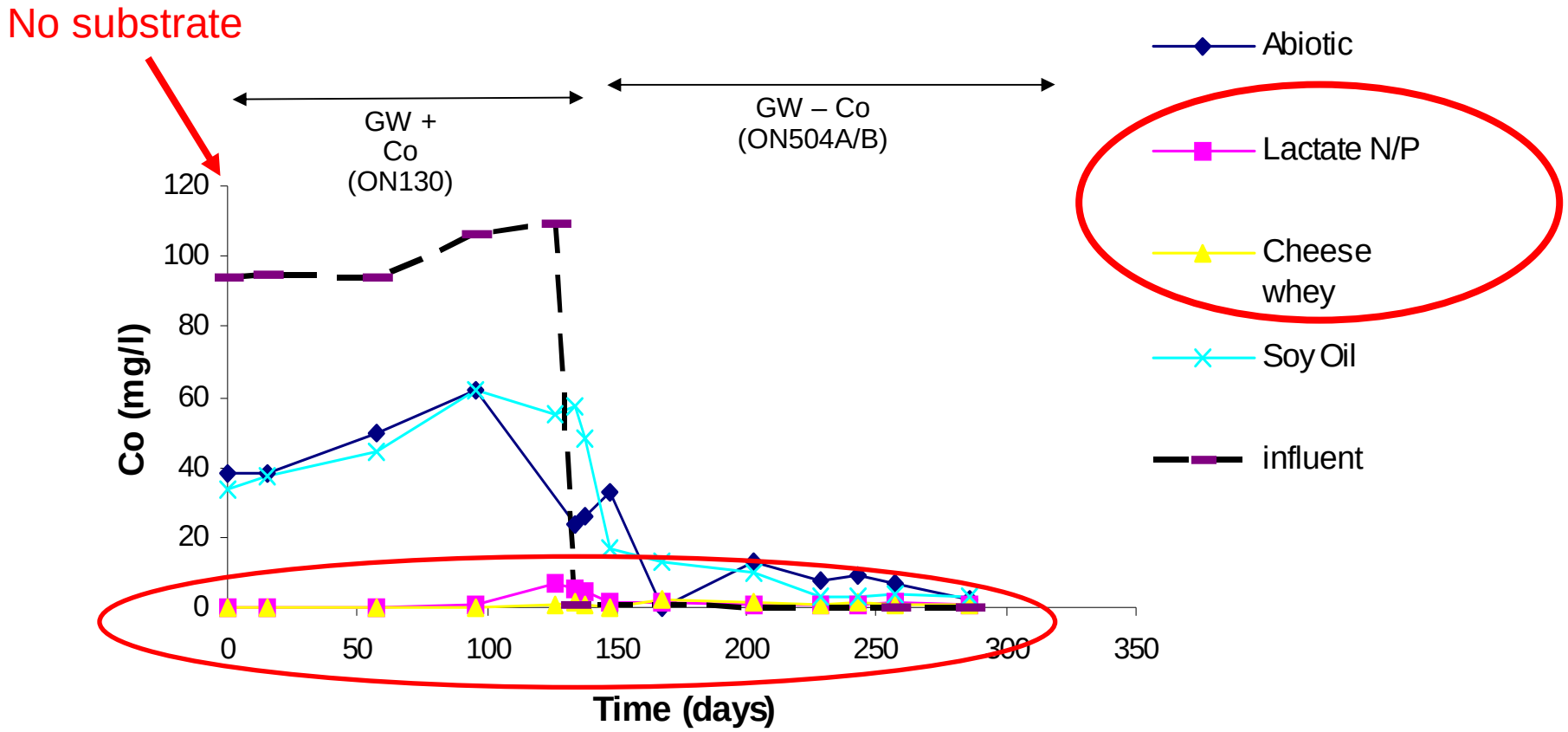
- Efficient Co removal within 100 days for Nalactate and cheese whey fed columns
- Serious VFA production for both columns

Overview column tests

Site	Condition	Removal Me [%]	Removal SO_4^{2-} [%]	ISBP induced after [days]	Remarks
site 3	Lactate N/P	>99	50	45	
	Cheese whey	>99	83	45	
site 2	Glycerol	>99	60	100	diluted groundwater
site 1	Glycerol	>99	35	167	

Stability column tests

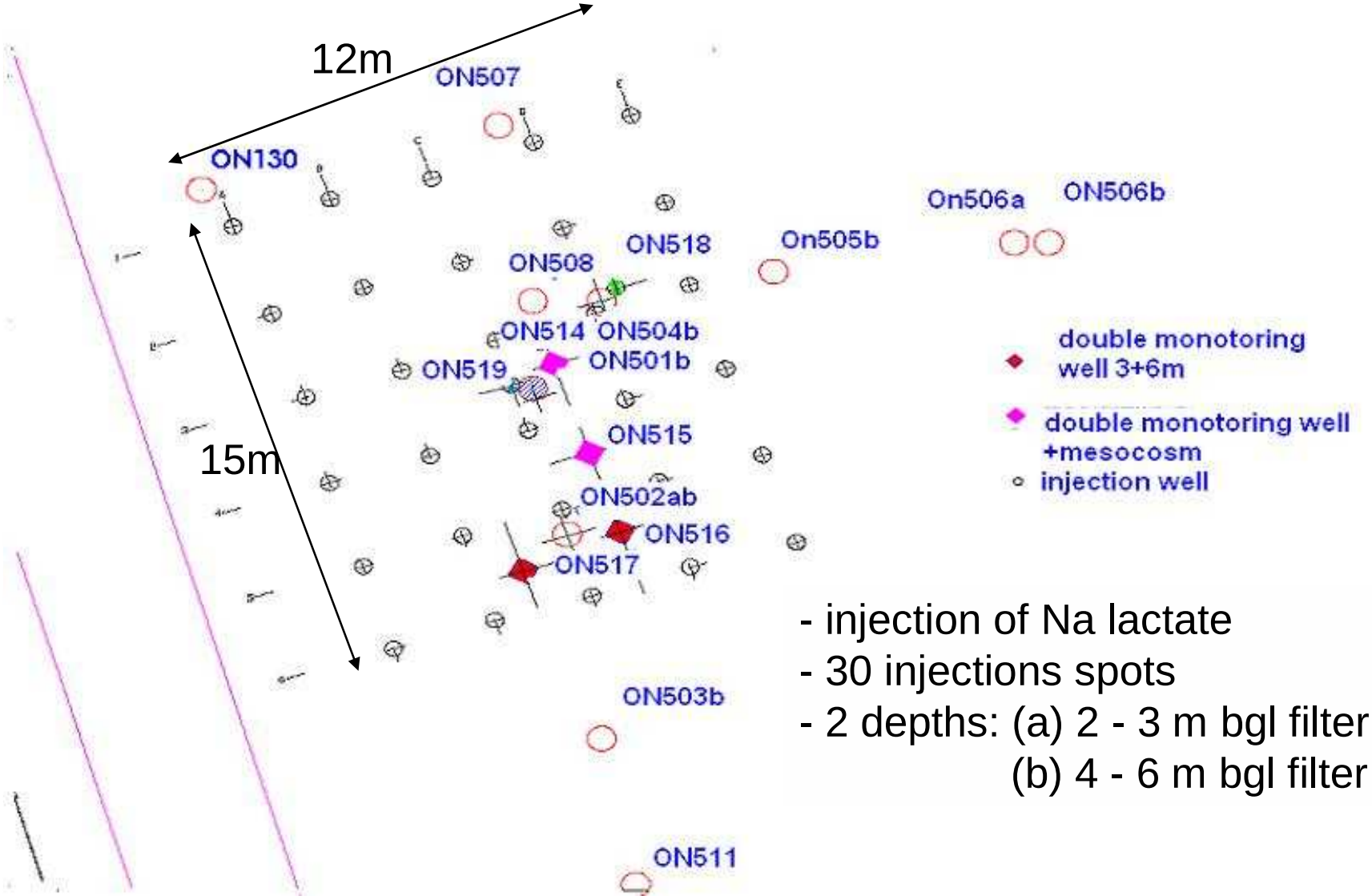
Post-substrate impact in column tests site 3



⇒ ongoing Co removal >100 days

⇒ no release, neither with Co or without Co in groundwater

Site 3 pilot test in field

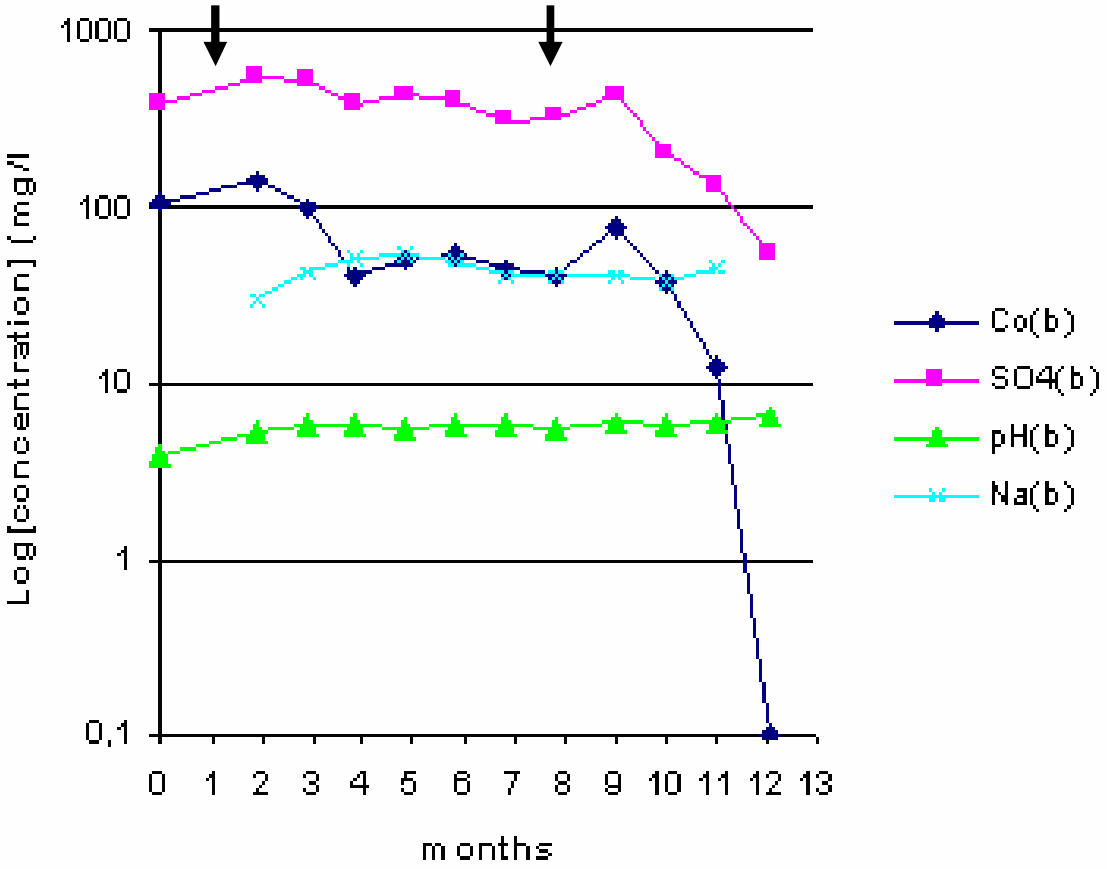


- injection of Na lactate
- 30 injections spots
- 2 depths: (a) 2 - 3 m bgl filter
  (b) 4 - 6 m bgl filter

Site 3 pilot test in field

Monitoring of well ON501b (4-6 m bgs)

↓ Injection of lactate



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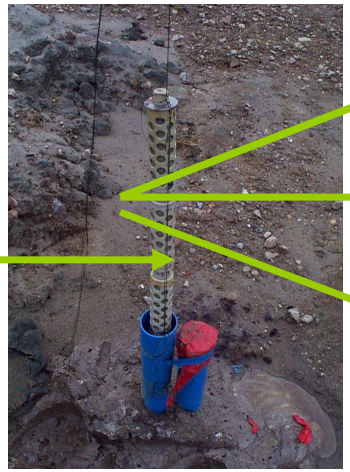
Site 3 pilot test in field

Mesocosm systems to study stability

Site 3 pilot test in field

» **Study approach:**

Before and after injection of the C-source



1. Total metal analysis

2. Co sorption (exchange tests)

3. Co leaching tests

Site 3 pilot test in field

1. Total metal analysis: mesocosm sediment

sample date	25/01/2008	9/04/2008	8/09/2008	9/04/2008	8/09/2008
sample	T0 5-6m site3	Meso ON514b 6m	Meso ON514b 6m	Meso ON501b 6m	Meso ON501b 6m
dry matter%	83,7	91,4	84,9	92,6	85,3
Co (mg/kgdm)	810	220	190	3200	2500
Fe (mg/kgdm)	16000	9700	8800	8100	7400
Ni (mg/kgdm)	16	5,8	<5	49	44
S (mg/kgdm)	2200	<500	<50	1600	1800
SO4(mg/kgdm)			<150		5500
		After 6 months injection	**After 12 months injection**	**After 6 months injection**	**After 12 months injection**

ISBP → high Co concentration in soil

Site 3 pilot test in field

2. Co exchange → sorbed Co?

Mesocosm sample	% DS	Co (mg/kgdm)	% sorbed (exchangeable Co)
ON514 B (6m)	85,53	200	64,50
ON501b	85,56	2900	0,11
To staal	83,7	810	66,67

ISBP → only 0,1% Co is exchangeable

Site 3 pilot test in field

3. Co leaching in column tests?

condition	%Co released after 122 days	%Co released after 148 days	%Co released after 175 days	%Co released after 290days
T0 site 3 25/01/2008	146	165	184	248
ON501b 6m 09/04/2008	**0**	**0**	**0**	**1**
ON514b 6m 09/04/2008	**76**	86	94	137
ON515a 3m 09/04/2008	3	ND	ND	ND
ON515b 6m 09/04/2008	**0**	**0**	**0**	**0**

ISBP → only 1% Co can be leached

Conclusions & Perspectives

- ISBP is feasible technology
  - determined by lab tests (batch and column)
  - Up-scaling to field implementation: successful
- Stability of formed precipitates
  - control conditions: no stable metal fraction on aquifer
  - strongly depending on substrate injected
    lactate N/P/ Glycerol > molasses
  - depending on metal to be treated
    Co > Zn, Cd
  - Co immobilized by ISBP = stable
  - BUT distinguish between sorption and precipitation

⇒ Stable precipitates based on lab tests

⇒ Evaluation of stability of precipitates in long term leaching tests with field material for Co = OK

Partners

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