‘Clustered’ remediation of Drycleaning Sites in Flanders

Presented by Leen Bastiaens

Richard Lookman, Ludo Diels

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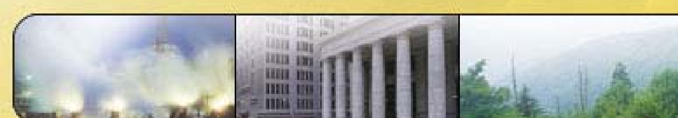
Flemish Institute for Technological Research (VITO) - Belgium

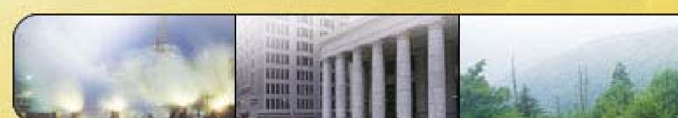


Problem

- **Drycleaner sites**: typical SME's with huge soil & groundwater pollution problems (**chlorinated aliphatic hydrocarbons: CAH**) but limited financial means for remediation
- **'Vlarebo' (Flemish soil remediation legislation)**:
  - 'the polluter pays' principle
  - CAH target concentrations are extremely low (sanitation limits PCE, TCE, DCEs, VC:

    40; 70; 50; 5 µg/L)
  - CAH-remediations are difficult (DNAPL; 'classical remediation technologies such as Pump & Treat fail)

→ **imminent bankruptcy for the sector?**



Flemish fund for drycleaner remediation

Ecolas-study for OVAM (March 2001) estimates:

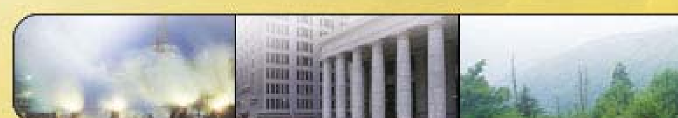
- 25 Keuro average costs per site for characterisation
- 250 Keuro average costs per site for remediation

VITO-study 2002-2003 for OVAM (finished 2004):

- More cost-effective remediation approach for drycleaning sites

Establiment of the fund (ongoing)

OVAM = Flemish Public Waste Agency



Goal

OVAM (Flemish Public Waste Agency) promoted projects to study the possibilities for a ‘standardized’ procedure for such sites, for both

Site characterization:

nature, 3-D dimensions, evolution in time (concentrations, mass, volumes) and risks

Remediation:

most attractive remediation technologies & methods (per city/ sector)

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Common charactarization & remediation protocol designed for drycleaner sites – considering the specific boundary conditions per city/sector. Demo-project: example City of Antwerp in Belgium

Step 1: Inventarisation stage

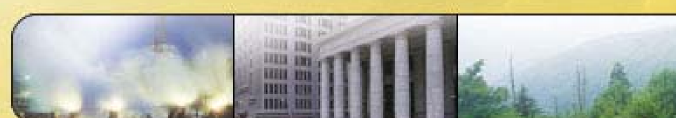
1. **Inventarisation of** drycleaner sites (locations)
2. Inventarisation of **regional geological/hydrological data**
3. **Inventarisation and study of existing consultant's soil investigation reports** (available at OVAM)
4. **Inventarisation of existing** (excavation, pump & treat, SVE, air sparging) **and innovative remediation technologies** – (bioremediation/bioaugmentation, (co)solventflushing, in-situ chemical oxidation, steam injection, reactive barriers, etc.-)

→ **"Desktop study"**

Inventarisation – info available in the USA

http://www.drycleancoalition.org/profiles/

> 100 **Site Profiles** downloadable of drycleaner remediations in the USA (pilot and full-scale) including:
- Description (location, historical info);
- Contaminants (type, amounts, concentrations) and Dimensions; DNAPL presence
- Hydrology, Depth to Groundwater, Lithology and Subsurface Geology; Conductivity; Gradient;
- Remediation Scenario (Cleanup Goals, Technologies Used..);
- Final remediation design;
- Date implemented);
- Results and Next Steps;
- Costs;
- Lessons Learned.



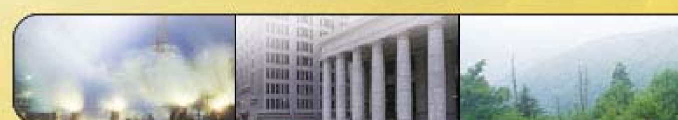
Inventarisation of drycleaners in City of Antwerp

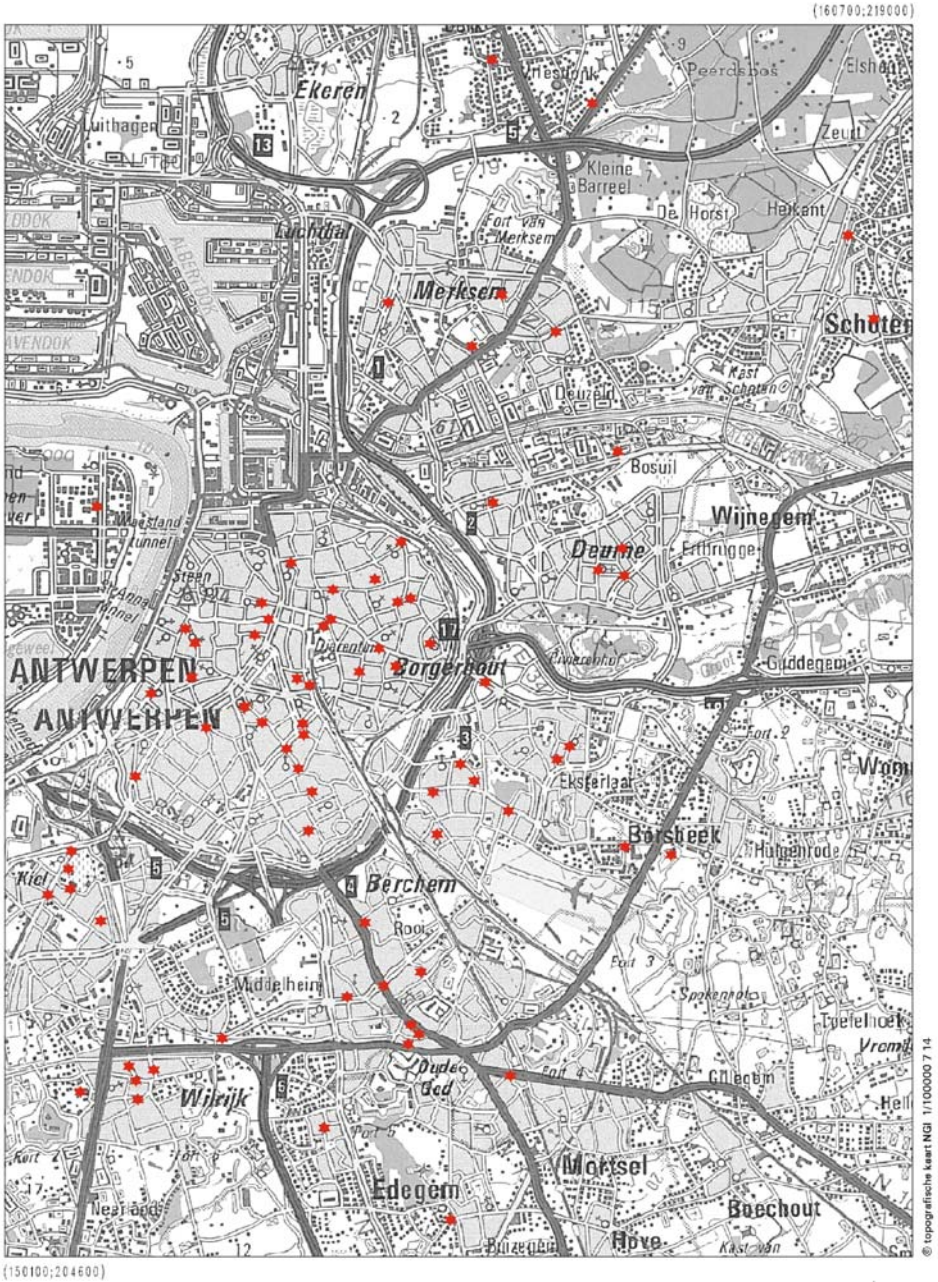
- **Operation licences** available at the Environmental Service of the City of Antwerp
- **Contacts** with a selection of drycleaner companies
- ‘**Golden Guide’** - search

 # drycleaners

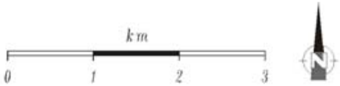
Found:

40	Drycleaner using PCE (‘hot’ drycleaner)
49	Drycleaner shop with external cleaning (‘cold’ drycleaner)
15	Former drycleaner
104	Total





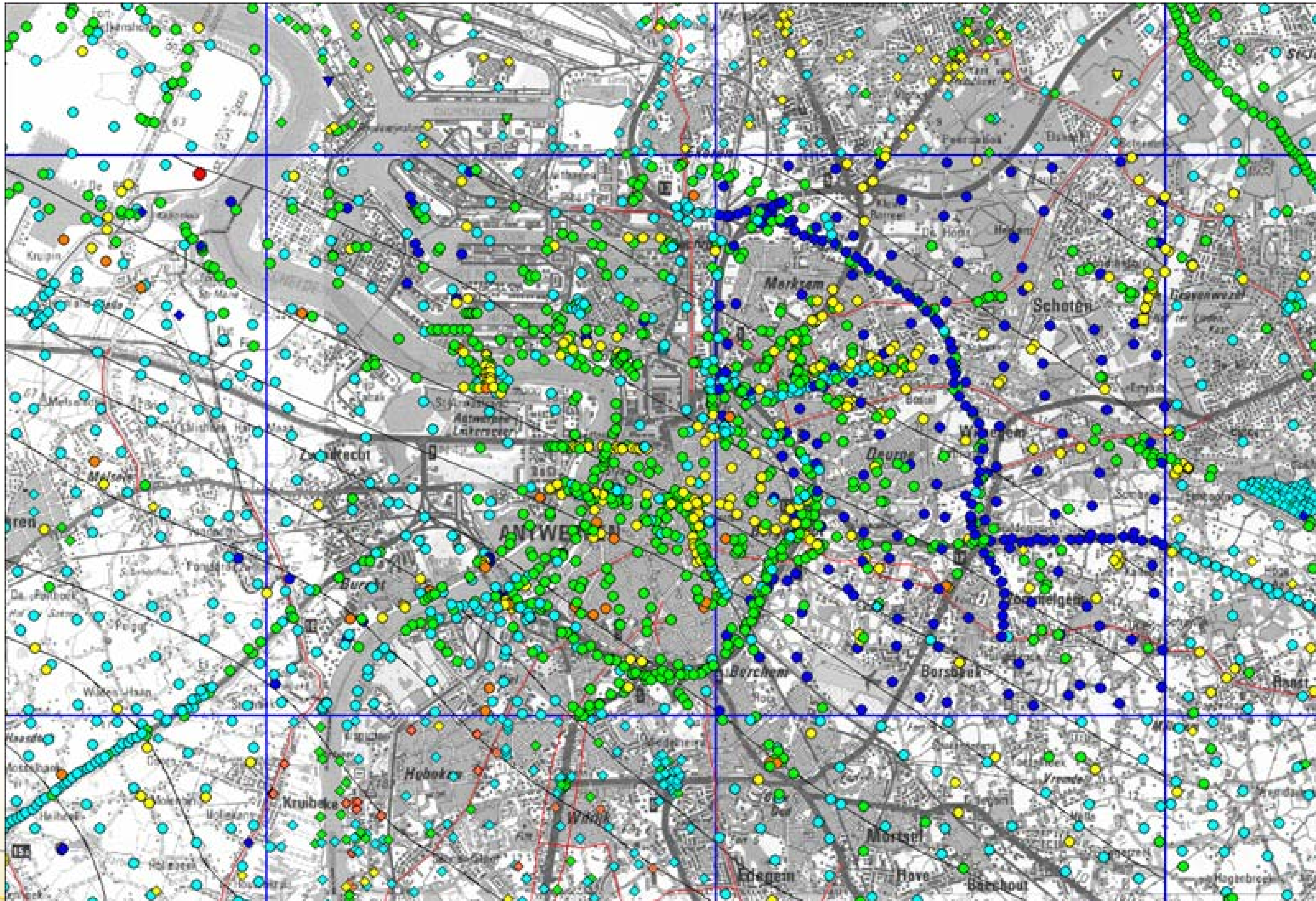
Locaties droogkuis regio Antwerpen



Problem: Drycleaner sites in urban environment

- 104 sites
- 40 hot PCE-treatments

Geological Service of Belgium – available soil drilling profiles



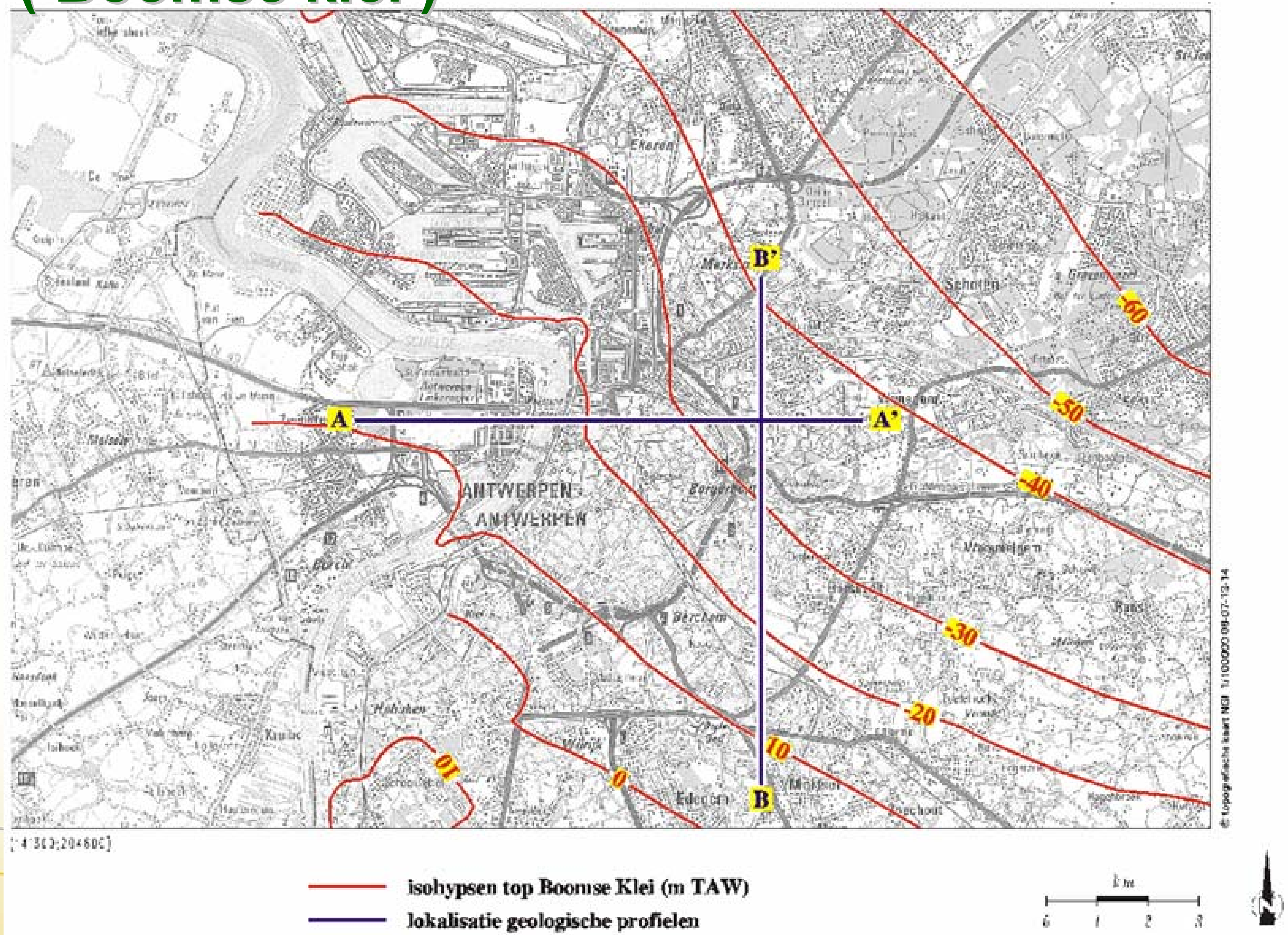
51 usefull

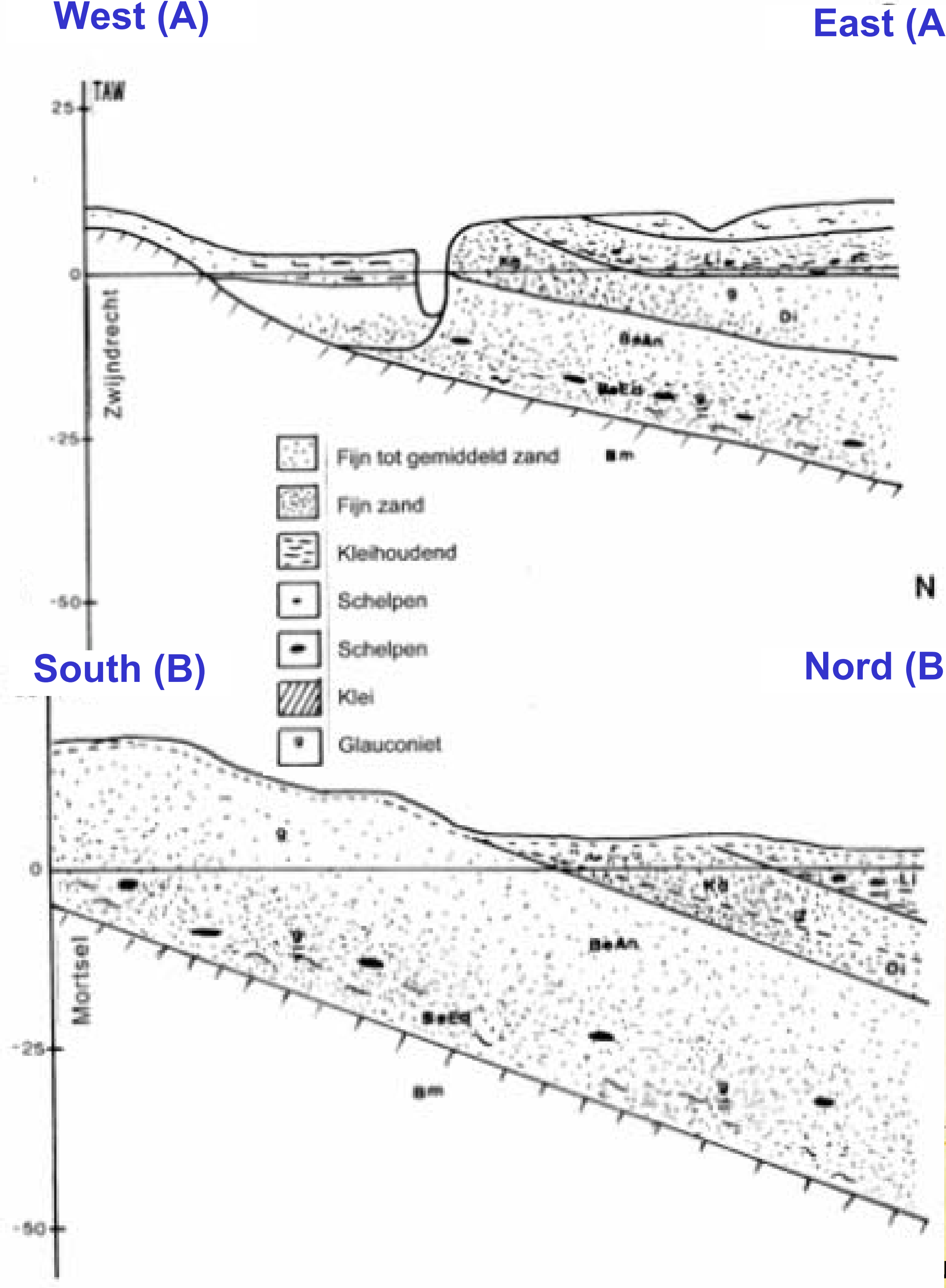
↓

Description of subsurface down to the clay layer

(Boomse klei)

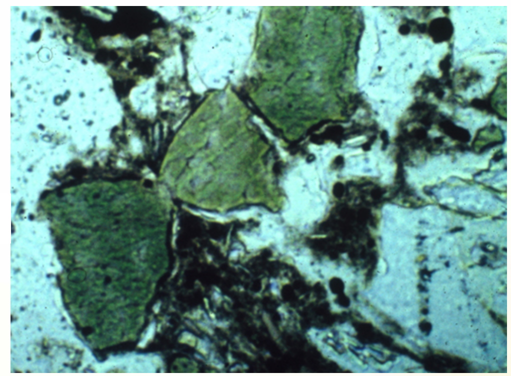
Extracted info: iso-lines of confining clay ('Boomse klei')





(hydro)geology

Geological Formation	Kh (m/d)
Sands of 'Lillo'	4 - 6
Sands of 'Kattendijk' and 'Diest'	6 -15
Sands of 'Antwerpen'	4 - 8



Tertiary deposits (sea) locally rich in shells, carbonates, GLAUCONITE!

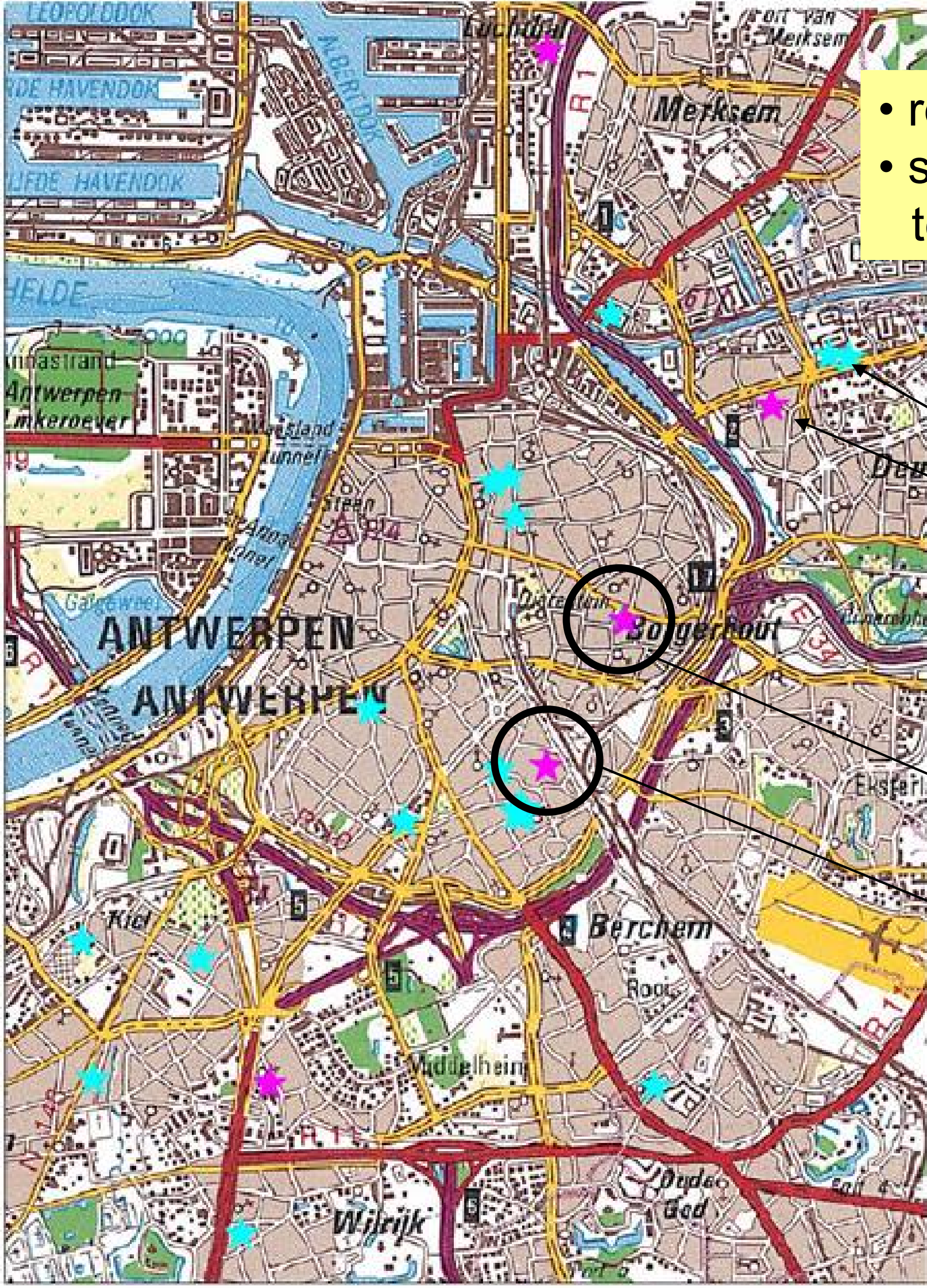
Li Formatie van Lillo (Li)

Kd Formatie van Kattendijk (Kd)

BeAn Formatie van Berchem (Be) - Lid van Antwerpen (BeAn)
BeEd - Lid van Edegem (BeEd)

Di Formatie van Diest (Di)

Bm Formatie van Boom (Bm)



- register of polluted sites at OVAM
- selection on Vlarebo-section 41.4 (chemical textile cleaning) and 46.3 (laundries)

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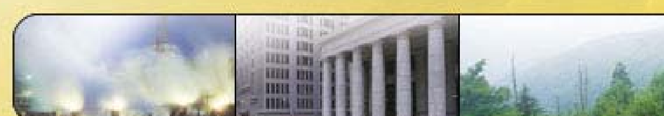
11 **preliminary** site investigations - 39
5 **descriptive** site investigations - 6
1 site **remediation** running/completed

(situation in 2002/2003) (2004)

'Borgerhout'
'Berchem'

detailed study (feasibility tests)



Study of site investigation reports available

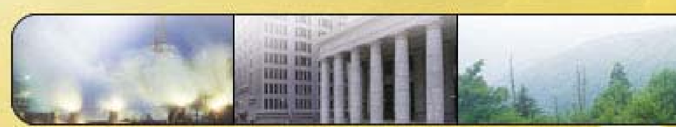
- Most cases → no use of innovative soil investigation techniques (only monitoring wells);
- 2 cases → CAH analyses on soil samples available
- No separate delineation of source zone NAPL (e.g. by Geoprobe liner drillings, DNAPL-detection, PID, soil-air analyses,…
- No idea of pollution mass
- Most cases → no idea of redox situation (electron acceptors, methane, DOC,…) and formation of final dechlorination products (natural attenuation/bioremediation?)
- Little info on hydraulic conductivity / organic matter content (plume migration)

General conclusion: soil investigation (site characterisation) is too much directed to deliniation of groundwater plume; not sufficient to assess optimal remediation approach.

Remediation technologies (2004)

- Excavation of source zone
- Soil Vapor Extraction (SVE) – Air injection
  - Very intensive treatment is required in source zone
  - Not suitable for low conductivity soils (→ fracturing)
- Multi-phase extraction (MPE)
- Pump & treat (P&T) → plume treatment

- Bioremediation (HRC, Melasse,…)
- In-situ chemical oxidation (MnO_4, H_2O_2, O_3)
- Soil flushing (surfactants, co-solvents)
- Reactive barriers (plume)/ zones
- (In situ termal treatment)

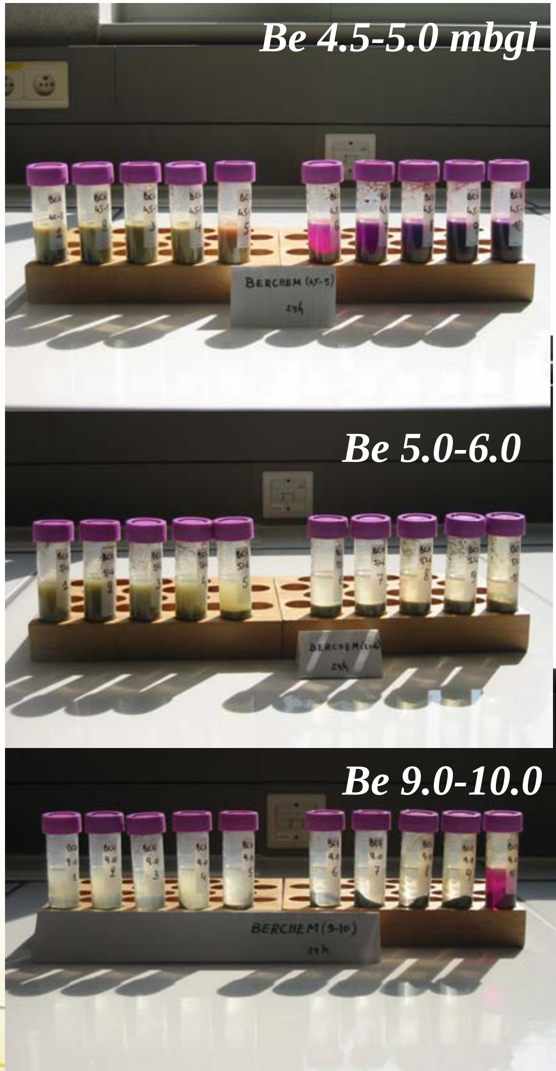


Step 2: Feasibility tests : key to *in-situ* remediation success?

Tests performed in Drycleaners Remediation Study Antwerp:

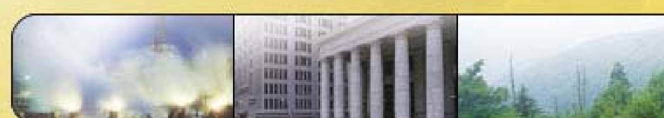
- ISCO
- Co-solvent/detergent flushing
- Anaerobic bioremediation

1A. ISCO / permanganate tests

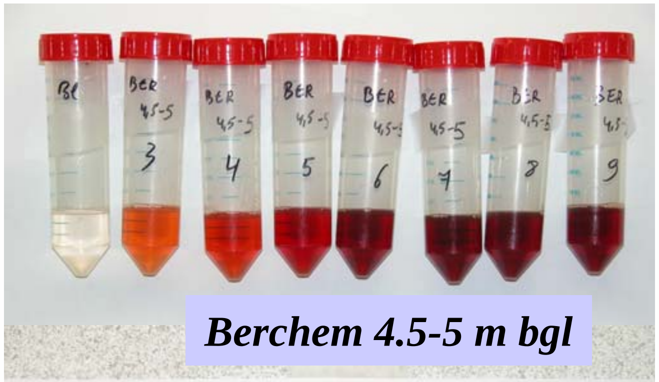


	Berchem/ m bgl.	OM (%)	Fe-II (mg/kg ds)	MD (g/kg)
Location 1	Be 4,5-5	1,84	168	0,34
	Be 5-6	2,32	2090	8,5
	Be 7-8	1,93	9166	8
	Be 8-9	1,82	9256	7
	Be 9-10	2	8901	7
Location 2	Bo 7-8	2,2	4652	8,5
	Bo 5-6	1,14	807	1
	Bo 6-7	1,56	1076	2,5
	Bo 7-8	2,05	3219	8,5
	Bo 8-9	2,37	5641	8,5

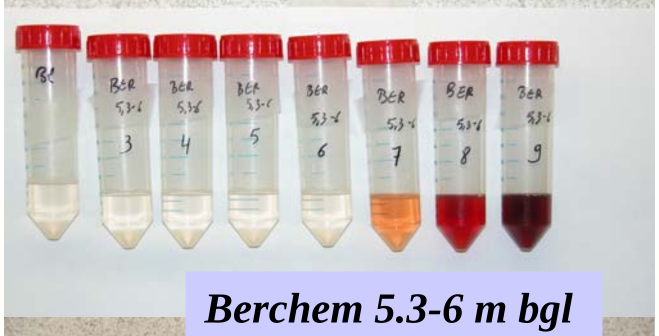
2 weeks



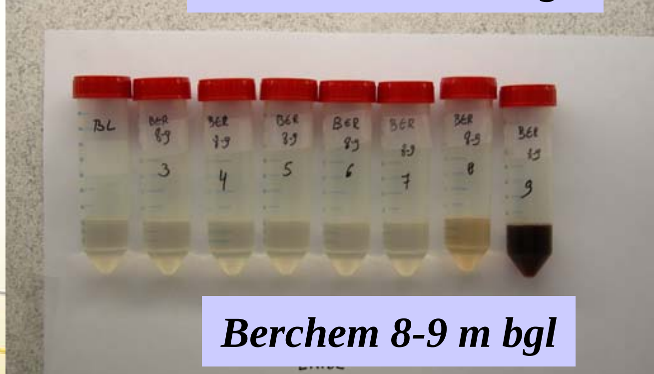
1B. ISCO / persulfate tests



Berchem 4.5-5 m bgl



Berchem 5.3-6 m bgl

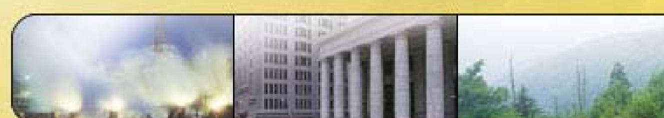


Berchem 8-9 m bgl

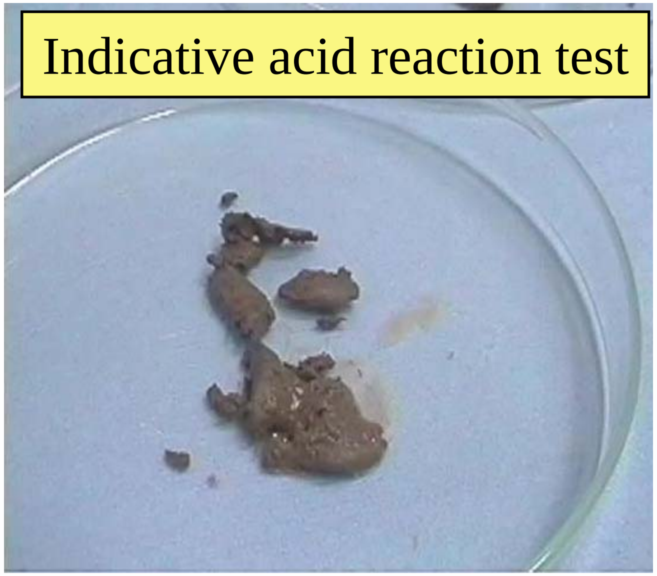
Sample	Oxidant demand (g ox/kg wet soil material)
Be 4.5-5m	< 0.2
Be 5-6m	2.8 – 5.6
Be 8-9m	Ca. 11.3

Sample	Oxidant demand (g ox/kg wet soil material)
Bo 5-6m	< 0.2
Bo 6-7m	< 0.3
Bo 7-8m	5.65 – 11.3

3 weeks



1C. ISCO / Fenton's tests



H_2O_2

Fe (II)

H_2SO_4

(pH 4,5)

before

After Fenton's oxidation

After incineration at 550°C

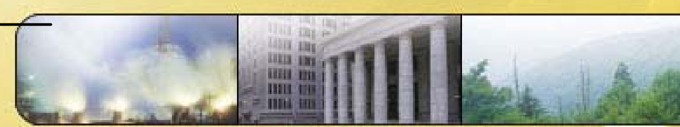
ISCO / Fenton's tests – PCE destruction 'Berchem'

Sample	Reaction time	PCE	PCE
		µg/L	%
Be (8-9) 0.5MD	0 min	11853	100
Be (8-9) 1MD	0 min	16050	100
Be (8-9)1.5MD	0 min	13378	100
Be (8-9) 0.5MD	15 min	2372	17
Be (8-9) 1MD	18 min	1174	9
Be (8-9)1.5MD	26 min	682	5
Be (8-9) 0.5MD	24u	522	4
Be (8-9) 1MD	24u	383	3
Be (8-9)1.5MD	24u	36	0

PCE ↓
⬆
Time ↑
dose ↑

MD=45g /kg!

MD = Matrix Demand



ISCO / Fenton's tests – PCE destruction 'Borgerhout'

Sample	Reaction time	PCE	PCE
		µg/L	%
Bo (6-7) 0.5MD	0 min	11481	100
Bo (6-7) 1MD	0 min	12542	100
Bo (6-7) 1.5MD	0 min	12464	100
Bo (6-7) 0.5MD	3 min	6128	50
Bo (6-7) 1MD	5 min	5947	49
Bo (6-7) 1.5MD	6 min	4904	40
Bo (6-7) 0.5MD	24u	3074	25
Bo (6-7) 1MD	24u	1860	15
Bo (6-7) 1.5MD	24u	997	8

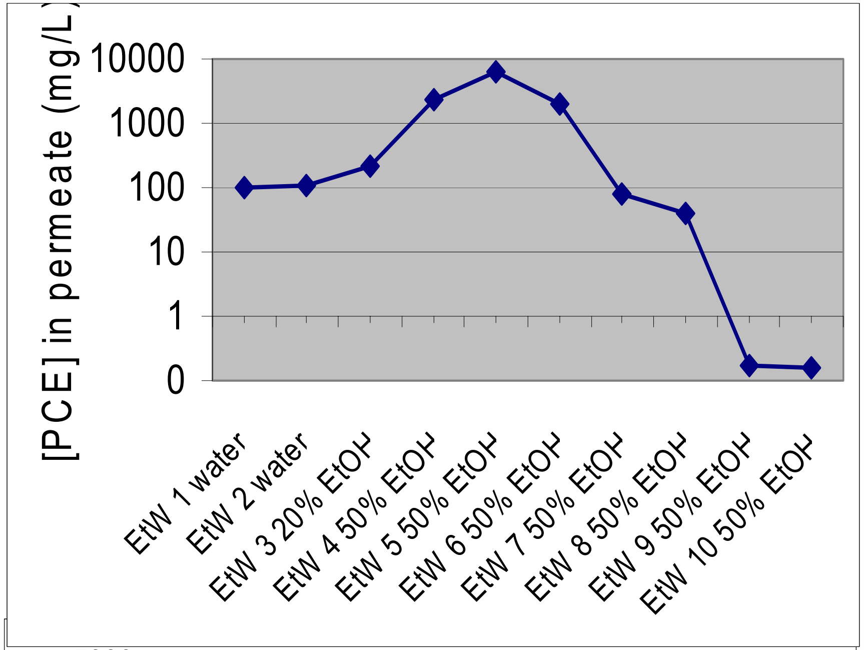
MD = 1.4g /kg!

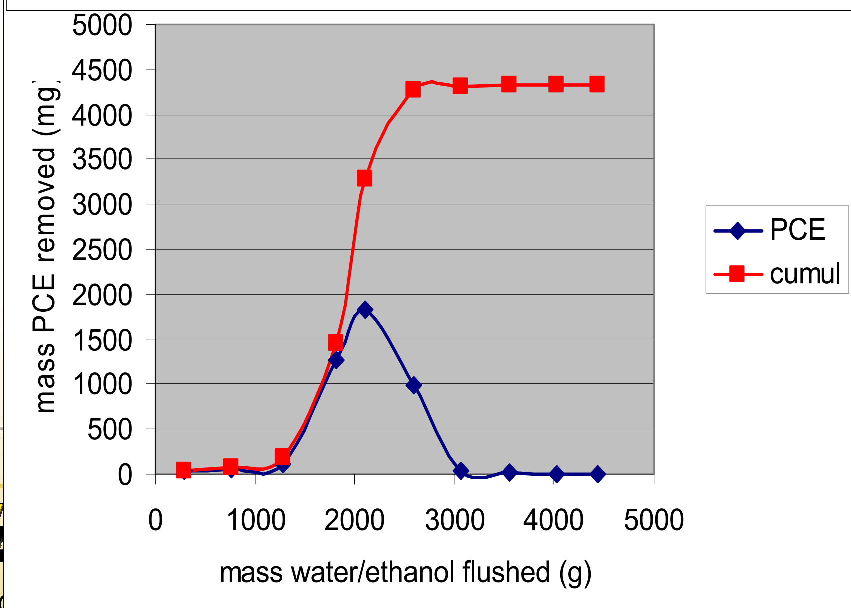
ISCO- conclusions

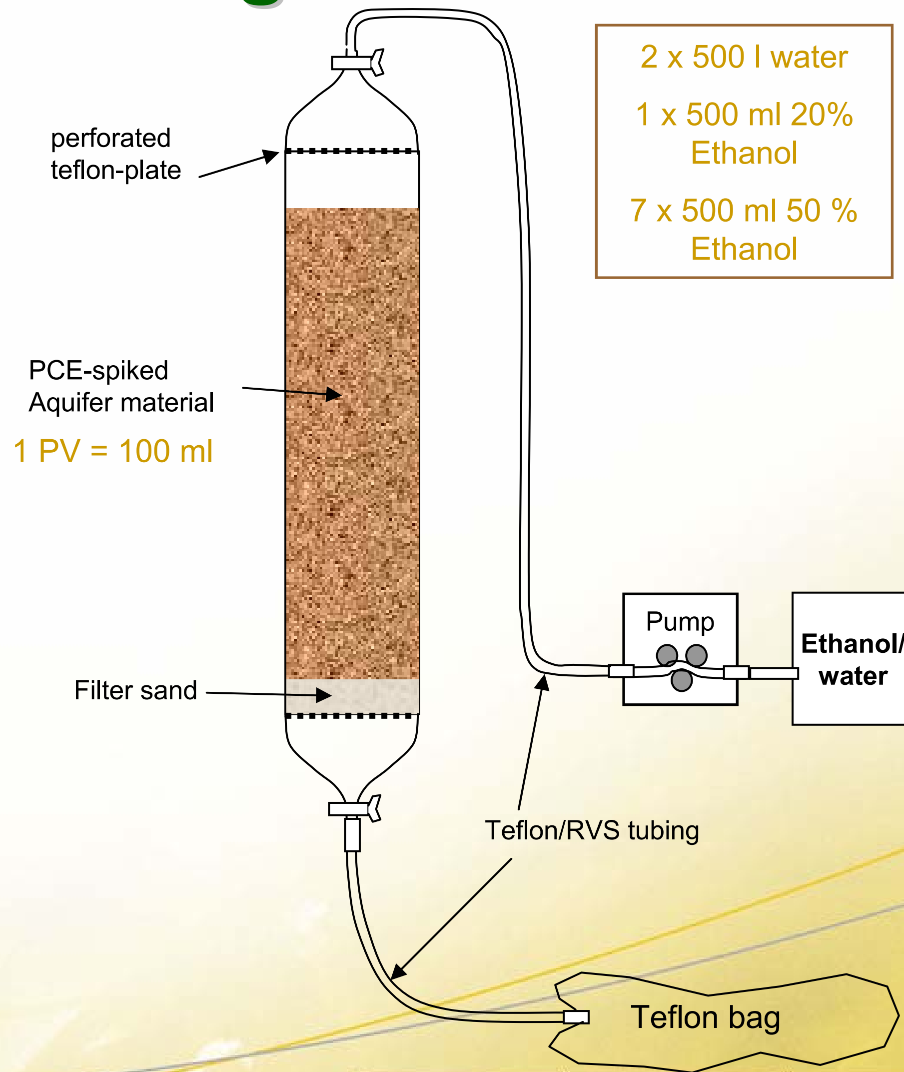
- **Matrix demand (MD) determined by type of aquifer**
- MD of investigated samples: very variable with depth (need to study several samples at relevant depths)
- Permanganate: if MD=1-5 g/kg: ISCO feasible; larger MD = too much oxidant needed (costly)
- MD positively related to OM and Fe(II) contents
- Persulfate: about same MD as permanganate
- Fenton’s reagent: strong acid reaction; large volume of gas produced (risks)

Conclusion: ISCO with permanganate or persulfate might be locally feasible but strong variability between soil layers and between the two sites investigated (not applicable as full scale at the sites)

2A. Ethanol flushing tests







2B. Surfactant flushing tests

- Dried soil sample spiked with PCE to 4860 mg/kg,
- Homogenized and rewetted to 20% moisture; homogenized again.
- Analysis: [PCE] 3584 mg/kg.
- 500 g of soil in glass column (**PV = 100 mL**).

Flushing test:

- 2 x 500 mL tapwater,
- 2 x 500 mL 0,1% Faliten (biodegradable surfactant)
- 2 x 500 mL 0,2% Faliten (sulfonated vegatable oil)
- Flushed at 500 mL/h using a peristaltic pump.
- Leached solute collected in Teflon bag.
- Solutes analysed by headspace GC-FID after 1/10 and 1/100 dilution.

Results

Faliten%	mL	conc.(mg/L)	PCE mass (mg)
0	500	187	93,5
0	500	187	93,5
0,1	500	255	127,5
0,1	500	201	100,5
0,2	500	197	98,5
0,2	500	243	121,5
			635 mg

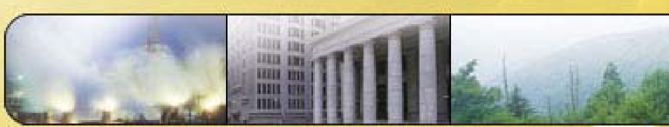
- Soil analysis after flushing (10 PVs water; 10 PVs 0.1% Faliten; 10 PVs 0.2% Faliten): **PCE 2013 mg/kg** (3584 mg/kg was initally present)

→ **44% of PCE removed**

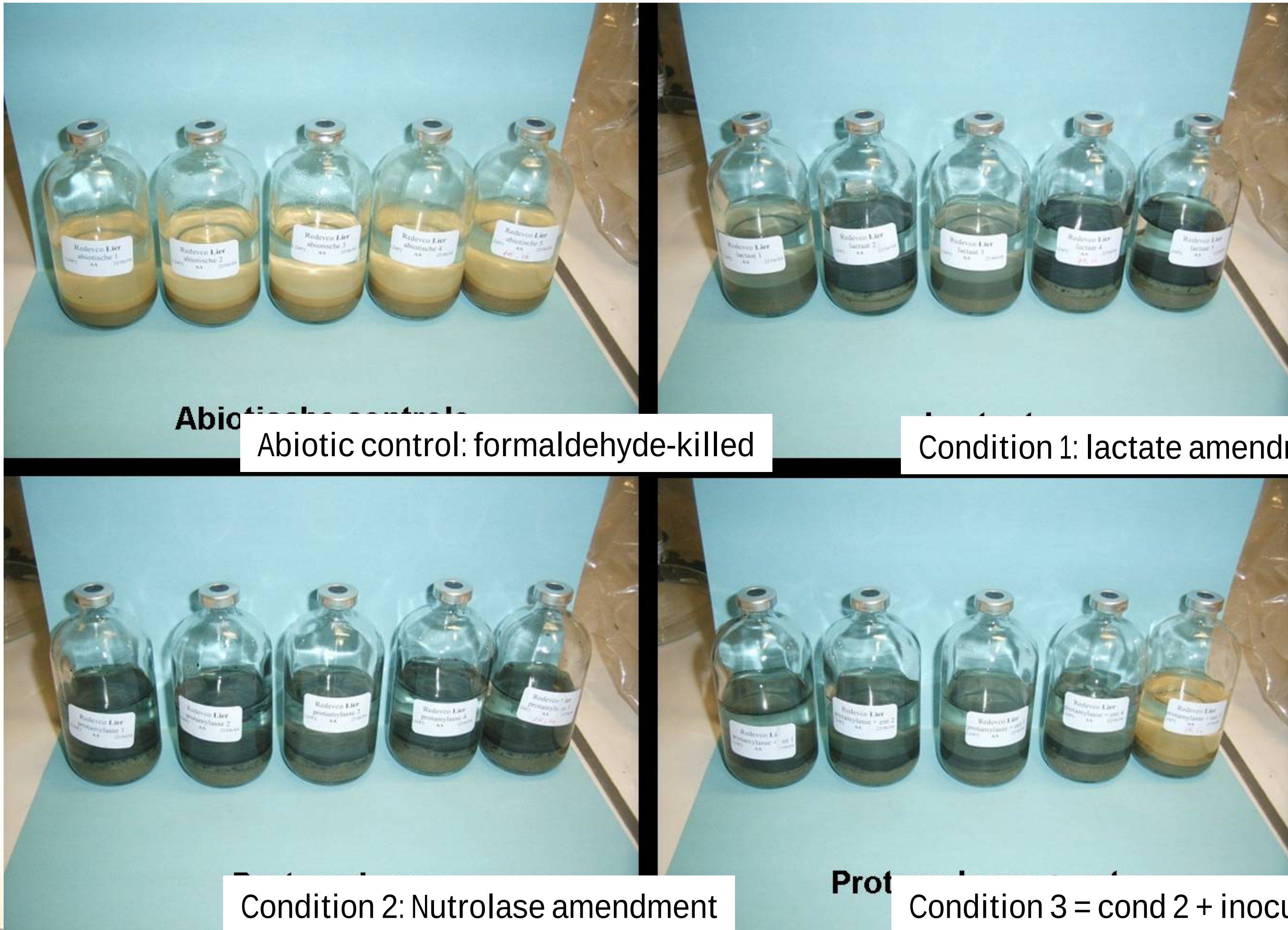
- 635 mg PCE (18%) removed via water phase according to water phase analyses
- 'missing' 44-18=26% of PCE removed as **PCE droplets**?

→ headspace GC-FID analysis not suitable to quantify total water phase conc.

→ Faliten has PCE-DNAPL phase mobilizing effect and only minor concentration-enhancing effect in the water phase



Anaerobic batch degradation tests (microcosms)



Aquifer & GW from the site

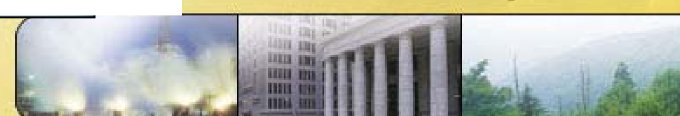
<u>Testconditions:</u>
(triplo, 20°C, static)

- **Abiotic control**
- **NA condition**
- **Addition of electron donor**

<u>Monitoring:</u>

CAHs, ethane, DOC, ethene, ORP, pH, …

(Nutrolase = potato-derived molassis)



Studied sites

Site		Pollutants
1	Microchip production	PCE
2	Industrial site (F)	cDCE, DCM, 111TCA, TCE, 12DCA, 11DCE, 11DCA, TCM
3	Industrial site (F)	PCE, DCM
4	Electronics	PCE, TCE, cDCE
5	Industrial site	111TCA
6	Dry cleaner	PCE, TCE, cDCE
7	Dry cleaner	PCE, TCE, 111TCA
8	Industrial site	TCE, cDCE
9	Industrial site	TCE, cDCE, VC
10	Surface treatment	TCE, 111TCA, 11DCA, 11DCE
11	Industrial site	VC
12	Super market	PCE, TCE, cDCE, VC
13	Industrial site	TCE, DCE
14	Dry cleaner	PCE

Degradation pathway

Site	Degradation of chlorinated ethenes					Chlorinated ethanes	
	PCE	TCE	cDCE	VC	ethene	111TCA	DCA
1	d	F,d	F,-				
2	d	F,-				-	F?
3	d	F,d	F, -				
4	d	F,d	F,d	F,d	F		
5						+	-
6	d	F,d	F,(d)	(F),(d)			
7	d	F, d	F, (d)	(F),(d)			
8		d	F, d	F,d	F,d		
9	d	F,d	F,d	F,d	F,d		
10		-	F?			+	-
11				d	F		
12	d	F, d	F,d	F,d	F		
13		-	-				
14	d	F, d	F				
	9/9	9/12	4/10	5/7	2/5	2/3	0/3

Chlorinated ethenes:

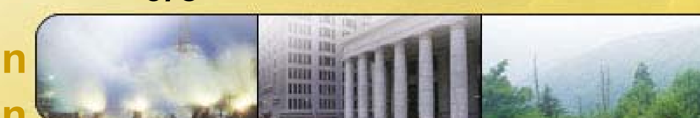
No degradation: 2/13

Stagnation on:
TCE: 3/13 (23%)
cDCE: 5/13 (39%)
VC 0/13 (0%)
ethene: 3/13 (23%)

Degradation up to ethane: 2/13 (15%)

PCE/TCE → ethene 5/13 (39%)

d = degradation
F = formation



Electron donor & inoculation

Site	NA	Supplied electron donor	testperiod months	Inoculation
1		Lactate, methanol	5	
2	slowly	Lactate + YE	6	
3		molasses > lactate,	4	
4		ethanol > Lactate + YE > molasses	8	
5		Lactate = Molasses	10	
6	+	ethanol > Lactate > Molasses	10	
	slowly	Molasses > lactate > ethanol	10	+
7	slowly	Lactate > molasses > ethanol	10	
8	slowly	Lactate	6	
9		Lactate > ethanol > isopropanol	4	
	+	Lactate		
10		Lactate	6	+
11	+	-	8	
12		nutrolase > lactate	3	++
13		Lactate = nutrolase	6	+
14		Lactate > ethanol	6	+

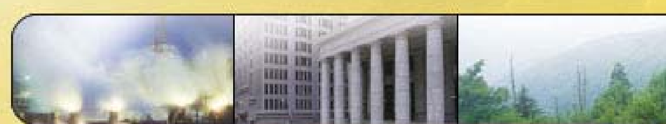
Electron donor:

Addition required in most cases

No generalisation concerning best additive (Lactate)

Inoculation:

Offers possibilities



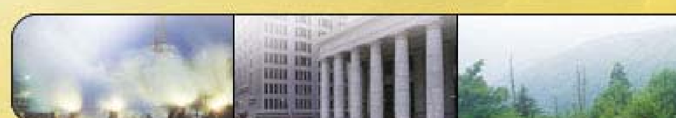
Conclusions anaerobic biodegradation

- CAH-biodegradation capacity is present at both sites, but:
  - Fast degradation from PCE → TCE → cDCE
  - Only very slow conversion of cDCE to VC and ethene

  → Accumulation of cDCE and VC
- Carbon-source:
  - Addition required in most cases
  - The 'Best' carbon source is site depending
- Bio-augmentation has potential for the realisation/accelleration of biodegradation at the sites

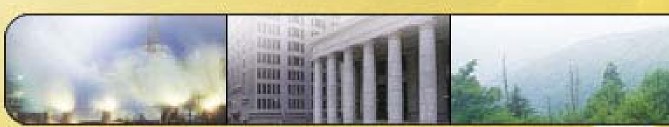
Conclusion faesibility tests

Location/ tested technology	Chemical oxidation	Co-solventfushing /detergent flushing	Bio-remediation/ augmentation
Berchem	Not optimal	**Possible** ethanol > detergent A lot of ethanol needed!	**Possible** carbon source & inoculum needed
Borgerhout	Not optimal	**Possible** ethanol > detergent A lot of ethanol needed!	**Possible** carbon source & inoculum needed



Step 3: Proposed protocol for common site investigation and remediation strategy for drycleaner's sites in a city such as Antwerp

- Subdivide into '**clusters**' of 4-6 neighbouring sites (with comparable soil/groundwater geochemical characteristics)
- **Site investigation** per cluster
- **Remediation feasibility study** per cluster
- **Remediation plan** and **execution** per cluster
  - General part (hydrogeology, potentially relevant remediation technologies)
  - Site specific part (detailed description of proposed remedial actions per individual pollution spot within the cluster)



Common soil investigation systematics

Subject	Includes…
Overview map of cluster; map of individual sites	▪ Street names, infrastructure (buildings), metalling types of ground surface; reference hights (ground surface) ▪ Location of conduits, sewers, subsurface structures ▪ Location of spill areas (e.g. laundry machines; subsurface storage tanks,…) ▪ Photographs
Soil geology	▪ Stratigraphy; texture analyses at relevant depths; hydraulic conductivities; organic matter content - profile in depth; …
Hydrology	▪ depth to groundwater; gradient; seasonal fluctuations ▪ Flow direction and flow velocity
Pollution situation	Historical info
	Soil investigation source zone deliniation (PID/Oil Red/Liner/MIP) – unsaturated and saturated soil!
	Groundwater investigation: plume (monitoring wells), MIP, groundwater probe

Common soil investigation systematics (continued)

Subject	Includes…
	Soil air - PID/Dräger/activated carbon samplers/passive samplers
	Analysis of (expected) spontaneous evolution of pollution situation – analysis of electronacceptors/donors; final dechlorination products; DNA analyses (e.g. presence of dehalogenases) – groundwater velocities, pollutants retardation factors
Risk-evaluation	Indoor Air analyses – inventarisation of potential vapour influx locations (cellars, former pipes, sewers, ringen, hollow walls, openings in paved floors…)
conceptual modelling	• 3-D mapping of source and plume zones of pollution with indication of concentrations in soil, groundwater (and soil air) • horizontal and vertical drawings • estimate of pollutant mass (air/water/solid/NAPL phases)

Common remediation protocol – combine technologies!

Source removal technologies

- full or partial **excavation** if possible!
- Larger unsaturated zones: **SVE** for permeable soils; **multi-phase extraction** in less permeable or stratified soils
- Saturated zone: **chemical oxidation**, **detergent/cosolvent flushing** or **nano-iron**
- Execute laboratory and field feasibility tests first (extrapolate within each cluster!) – **stepwize up-scaling** to full-scale remediation

Plume treatment technologies

- use **biological pollutant degradation** processes in plume zones!
- Investigate per cluster **Natural Attenuation** and possibilities to stimulate NA (**bioremediation** by substrate injection) or **bioaugmentation**:
  - Trend analysis
  - Geochemical and biochemical indicators
  - Microcosms: type of carbon source, kinetics, complete or partial dechlorination (bioaugmentation)

Common remediation protocol – combine technologies!

Per cluster:

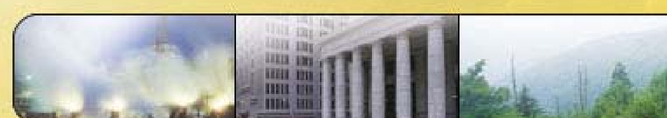
- Options for source removal
- Plume treatment methodologies
- Feasibility and pilot test(s)
- Common cleanup goals (realistic) need to be determined
- Common monitoring strategy – determination of remediation end-point
- Financing via FUND
- Timing/planning: risk based

Per cluster:

- ONE Co-ordinator (appointed by FUND managing board)
- ONE consultant & consortium (soil/groundwater monitoring, reporting)
- ONE contractor & consortium (execution, maintenance, operational follow-up)

→ Equipment/hardware can be used consecutively at all sites within each cluster
→ **GOOD PLANNING ESSENTIAL**

CLUSTER-APPROACH WILL SAVE MONEY



More information

Richard.lookman@vito.be
VITO
Environmental and Process Technology
Boeretang 200
2400 MOL, Belgium

www.ovam.be