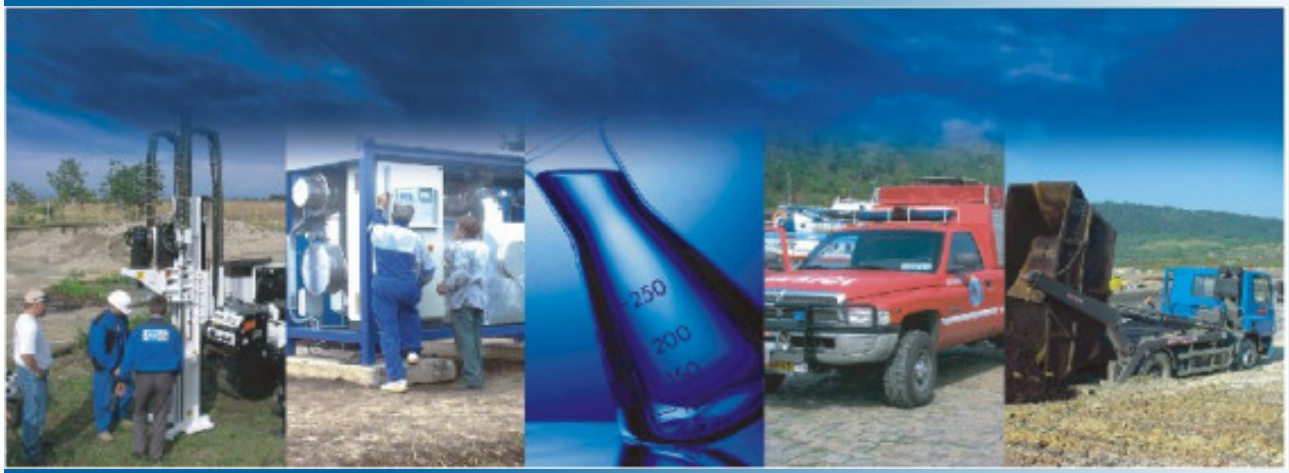

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IN-SITU ENHANCED REDUCTIVE DECHLORINATION OF CHLOROETHENES USING FOOD-PROCESSING WASTE – FROM LABORATORY TO FIELD APPLICATION

Lenka Vesela – Dekonta, a.s., Czech Republic

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Presentation objectives

- **Refers to a research study on biological reductive dechlorination enhanced by a suitable waste donor and its application possibilities in CZ and other CEE countries**

- **3 yrs, co-financed by the Czech Ministry of Industry and Trade**
- **Chlorinated ethenes – PCE, TCE, DCE, VC ⇒ ethene, ethane**
- **Alcohol wash, beet molasses, oil residue, whey and lactate**
- **Groundwater and soil (saturated zone)**
- **From laboratory to pilot-scale**
- ***Ex-situ* (laboratory, semi-pilot), *in-situ* (pilot)**

Biological reductive dechlorination (1)

- **Promising remediation technology for groundwater contaminated by chlorinated ethenes**

- **Based on a biological reaction in which bacteria gain energy and grow as one or more chlorine atoms on a CAH molecule are replaced with hydrogen in anaerobic environment**
- **Chlorinated compound serves as the electron acceptor and hydrogen serves as the electron donor**
- **Hydrogen is supplied via organic substrate fermentation**
- **Three types: direct (above-mentioned), cometabolic and abiotic (in practice all three reactions may occurring)**
- **Enhanced bioremediation applications (ERD) have targeted biotic dechlorination process**

Biological reductive dechlorination (2)

- **Generally, biological reductive dechlorination occurs by <u>sequential removal of chlorine ions</u>**

- Hydrogen is the electron donor, which is oxidised
- Chlorinated ethene is the electron acceptor, which is reduced
- Other fermentation products may serve as electron donor but hydrogen is the most important

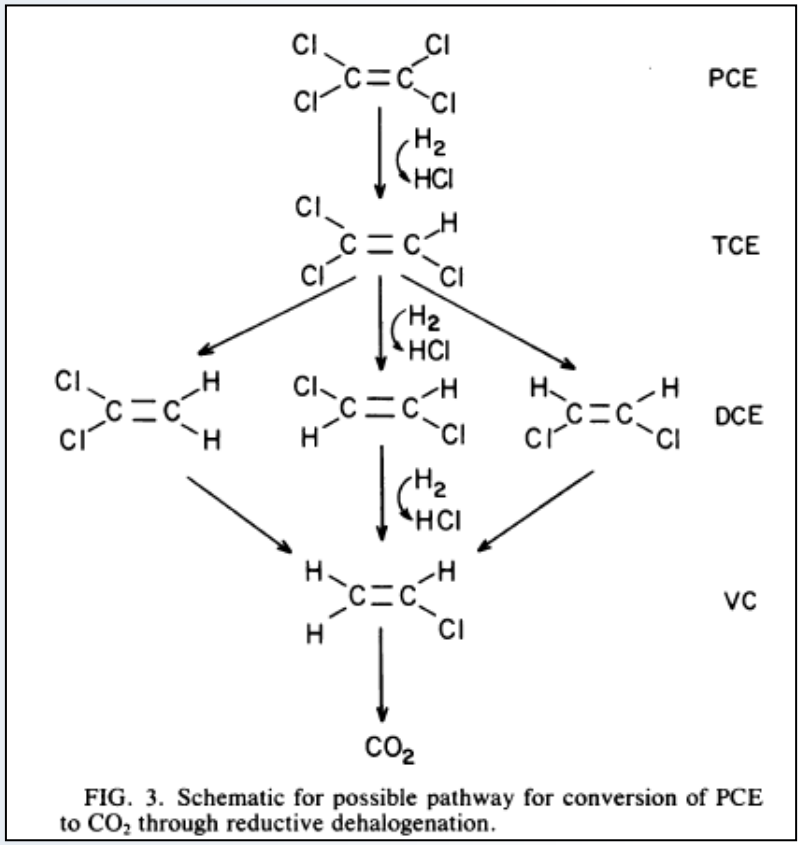


FIG. 3. Schematic for possible pathway for conversion of PCE to CO_2 through reductive dehalogenation.

Biological reductive dechlorination (3)

- **Similar to chloroethenes, the common chloroethanes and chloromethanes may be transformed as well**
  - Choroethanes – 1,1,1-TCA ⇒ 1,1-DCA ⇒ CA ⇒ ethane
  - Choromethanes – CT (carbon tetrachloride) ⇒ CF (chloroform) ⇒ MC (methylene chloride) ⇒ CM (chloromethane) ⇒ methane
- **Process depends on many environmental factors (e.g. anaerobic conditions, fermentable substrate presence, appropriate microbial population)**
  - Anaerobic dechlorination affects each of the chlorinated compounds differently (i.e. PCE and TCE are the most susceptible to anaerobic dechlorination, VC degrades at lower reaction rates ⇒ thus can accumulate in the environment)

ERD process application (1)

- **In practice, the technology consists in application of suitable substrate(s) and/or its (their) water solution into the contaminated ground (*in-situ*)**
  - **Biodegradation of injected organic substrate depletes DO and other terminal electron acceptors (i.e. nitrate, manganese, ferric ion, sulphate and carbon dioxide) and lowers groundwater ORP potential**
  - **Fermentation of injected substrate generates hydrogen ⇒ necessary for reductive dechlorination of CAHs (specific dechlorinators, but it is also consumed via other bacteria species)**

ERD process application (2)

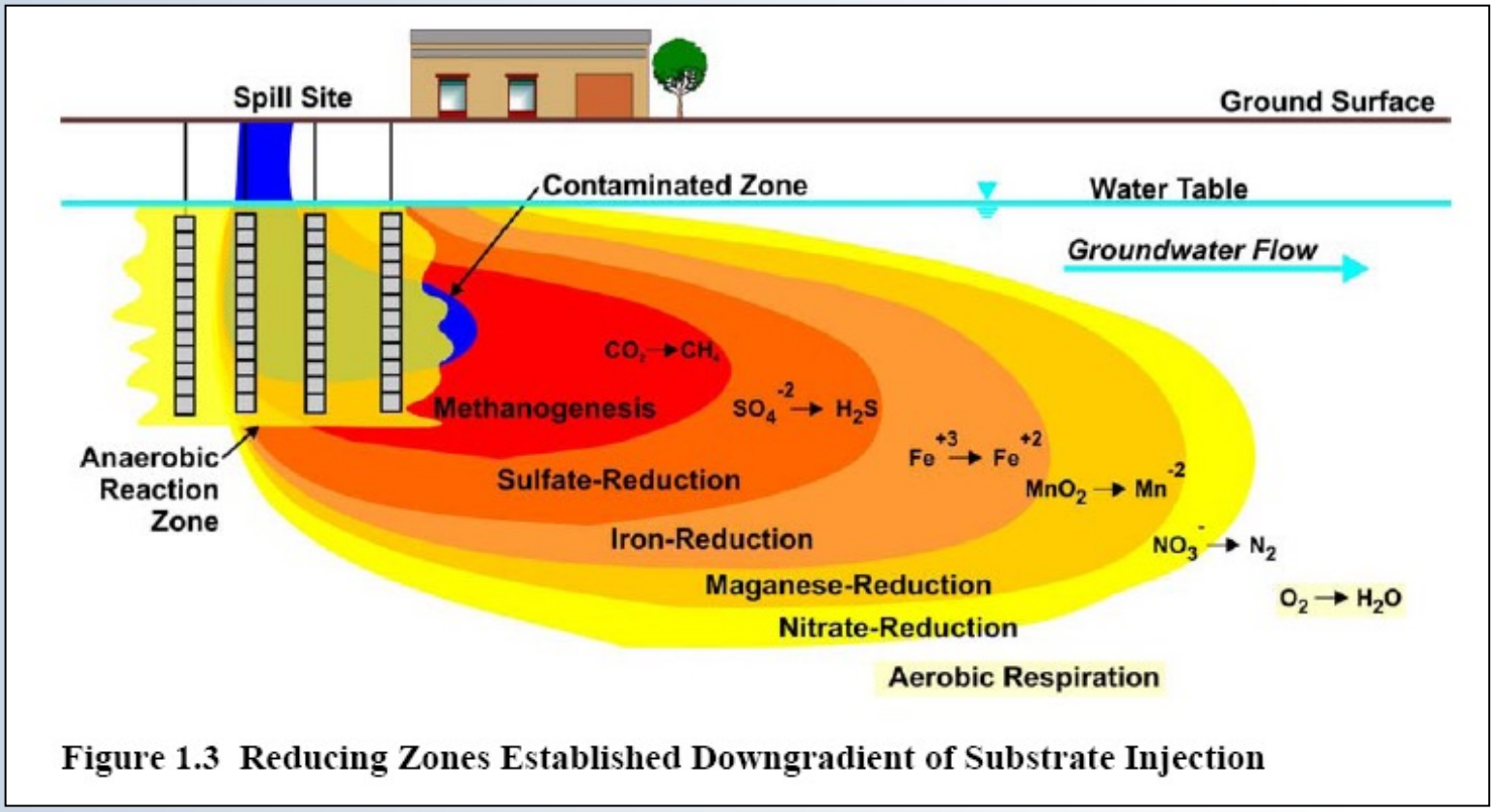


Figure 1.3 Reducing Zones Established Downgradient of Substrate Injection

ERD process application (3)

- **The most common substrates: acetates, alcohols (ethanol, methanol), carbohydrates, chitin, HRC®, lactates, molasses, propionate, vegetable oils, whey…**
- **Microbial population (= specific dechlorinators) mainly *Dehalococcoides* sp.**
  - **Compete dechlorination of PCE to ethene demonstrated only for *Dehalococcoides ethenogens* (common, not ubiquitous)**
  - **Other microbes may facilitate dechlorination of PCE to *cis*-DCE**
  - **In nature, the process is typically carried out by mixed cultures**
  - **In 2000 Flynn et al. demonstrated complete dechlorination with a mixed culture that did not contain the *Dehalococcoides* sp.**

ERD process application (4)

- **The ERD technology applied at various range**
  - **Hydrogeological conditions – from silts and clays to alluvial sand and gravel deposits to fractured bedrock**
  - **Geochemical conditions – in some cases DO may create an oxygen electron acceptor demand that cannot be overcome with substrate addition**
  - **Contaminant levels – average CAHs from 0.01 to 100 mg/L, but also residual or sorbed DNAPL above 100 mg/L**
- **Available methodologies**
  - **U.S. EPA – Engineered Approaches to *In-Situ* Bioremediation of Chlorinated Solvents (EPA 542-R-00-008, Jul 2000)**
  - **ESTCP – Final Technical Protocol RABITT (Dec 2002)**
  - **U.S. Air Force, NAVFAC, ESTCP – Final Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents (Aug 2004)**

Waste substrate properties (1)

- **4 types of food-processing waste – alcohol wash, beet molasses, oil residue and whey**

- **Using food-processing waste as an alternative electron donor is an object of discussion among environmentalists due to possible residual contents of pesticide, herbicide, phosphates, sulphates and other inorganic salts**
- **Therefore detailed analyses of their chemical and physical properties were carried out before the experiment start**

- **Inorganic parameters: SO_4^{2-}, Cl^-, PO_4^{3-}, Ca, Mg, Na, K, Fe, Mn, NH_4^+ and metals (As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sn, V, Zn)**
- **Organic parameters: chlorobenzenes, chloroethenes, chlorophenols, AOX, EOX, PCBs, pesticides (organic, triazine), PAHs, TPH and TOC**
- **Others: density, viscosity and water solubility**

Waste substrate properties (2)

➢ Analytical results

- All substrates contain significant concentration of inorganic ions (K, Na, Ca, Fe, Mg, Mn, Zn) and salts (sulphates, chlorides) – mainly alcohol wash, beet molasses
- Pesticide and herbicide not detected in any of tested waste
- Rather high content of TPH (but not classical petroleum) – mainly oil residue
- Differences in physical properties – mainly water solubility and viscosity of oil residue (better to use oil-water emulsion with lecithin)

Waste substrate properties (3)

Parameter	Alcohol wash	Beet molasses	Oil residue	Whey
Viscosity (mm^2/s)	3.16	28.00	67.30	1.15
Water solubility	soluble (1 g sub. in >1 ml water)	soluble (1 g sub. in >1 ml water)	non-soluble (1 g sub. in <10 L water	soluble (1 g sub. in >1 ml water)
Sulphates (mg/kg)	5 240	5 170	963	760
Chlorides (mg/kg)	13 800	3 770	193	1 180
Phosphates (mg/kg)	990	321	6.26	1 070
K (mg/kg)	26 000	24 900	0.4	1 610
Na (mg/kg)	11 400	4 780	22.7	434
Ca (mg/kg)	7 740	729	7.81	1 020
Fe (mg/kg)	934	155	0.582	2.83
Mg (mg/kg)	1 340	75.30	0.199	101
TPH (mg/kg)	67	59	640 000	140
TOC (%)	11.40	23.60	62.60	2.18

Laboratory and semi-pilot tests (1)

➢ Experiment description

- Groundwater and soil (TCE and PCE up to 30 mg/L)
- Two arrangements: 2 L reaction bottles, 30 L reaction vessels
- Various substrates (alcohol wash, beet molasses, oil residue – rape and whey)
- Tested substrate added on basis of TOC levels ⇒ <200 mg/L
- Substrates added with and without yeast extract (20 mg/L)
- Prepared abiotic and biotic control variants
- Nitrogen used for displaying DO
- Resazurin (1 mg/L) added for anaerobic process control
- Variants cultivated at 21 °C and atmospheric pressure
- Regularly sampled (every 30 to 60 days)

Laboratory and semi-pilot tests (2)

➢ Reaction bottles

- 2 L (soil 400 g, water 800 ml)

➢ Monitored parameters:

- Soil phase – PCE, TCE, *cis*-1,2-DCE, *trans*-1,2-DCE, 1,1-DCE, VC, TOC
- Water phase – ditto, methane, ethene, ethane, nitrates, sulphates, Fe, Mn plus K, Na, Ca, Mg, Zn, chlorides, phosphates
- Gas phase – ditto, methane, ethene, ethane, chlorine

Laboratory and semi-pilot tests (3)

➢ Reaction vessels

- 30 L (soil 10 kg, water 20 L)

➢ Monitored parameters:

- Soil – PCE, TCE, *cis*-1,2-DCE, *trans*-1,2-DCE, 1,1-DCE, VC (not regularly)
- Water – ditto, methane, ethene, ethane, nitrates, sulphates, Fe, Mn plus K, Na, Ca, Mg, Zn, chlorides, phosphates, anaerobic and SR bacteria, pH, ORP, temperature, conductivity

Laboratory and semi-pilot tests (4)

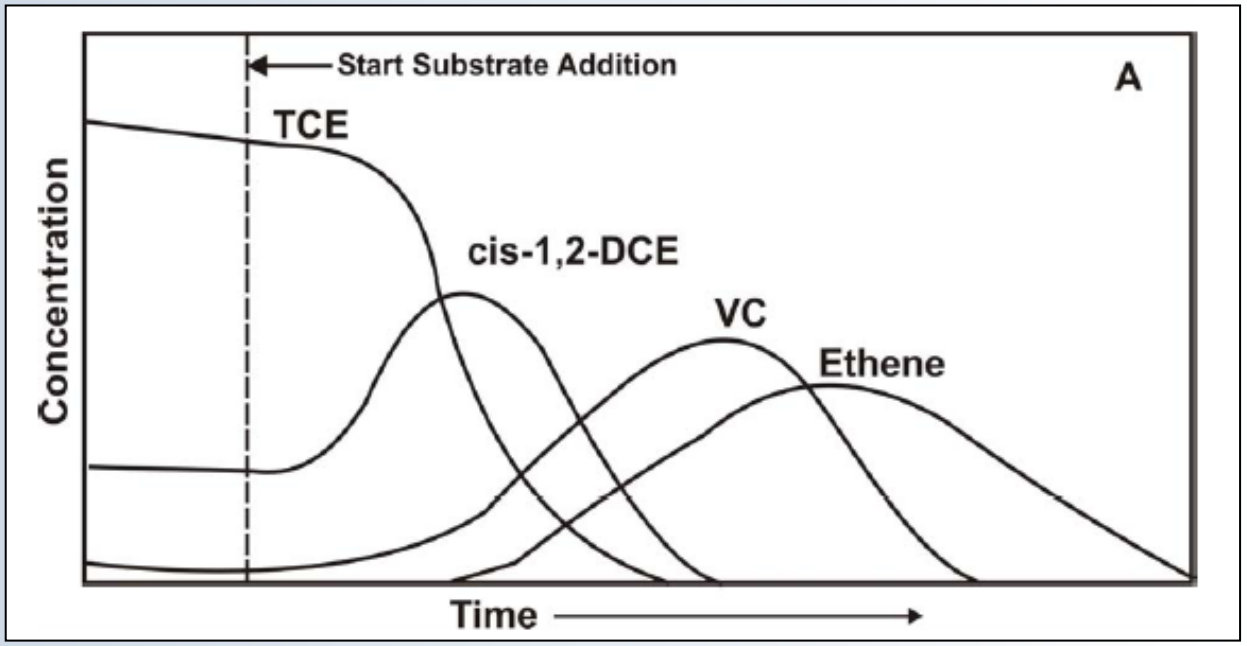
➢ Results of the experiments

- Possible to use all tested food-processing waste as alternative electron donors
- Significant decrease of PCE and TCE (up to 95%) and massive increase of *cis*-1,2-DCE and VC reached; in some variants ethene detected
- Methane observed in the most variants
- The highest rate of ERD reached with alcohol wash and whey; beet molasses showed a longer lag-phase; oil residue had problems with its dissolving
- Using waste materials led to low increase of K, Na, Ca, Mg and Fe content as well as phosphates and sulphates – mainly beet molasses
- Yeast extract no effect on ERD process

Laboratory and semi-pilot tests (5)

➢ Future activities

- Testing will be carried out till Jun 2007 (approx. 350 days)
- Hopefully, further decrease of *cis*-1,2-DCE plus VC and increase of ethene will be reached



Laboratory and semi-pilot tests (6)

- **Reaction bottles after 114 days**
- **From left – abiotic control (1), biotic controls (2, 3), alcohol wash (4, 5), beet molasses (6, 7) and oil residue (8, 9)**

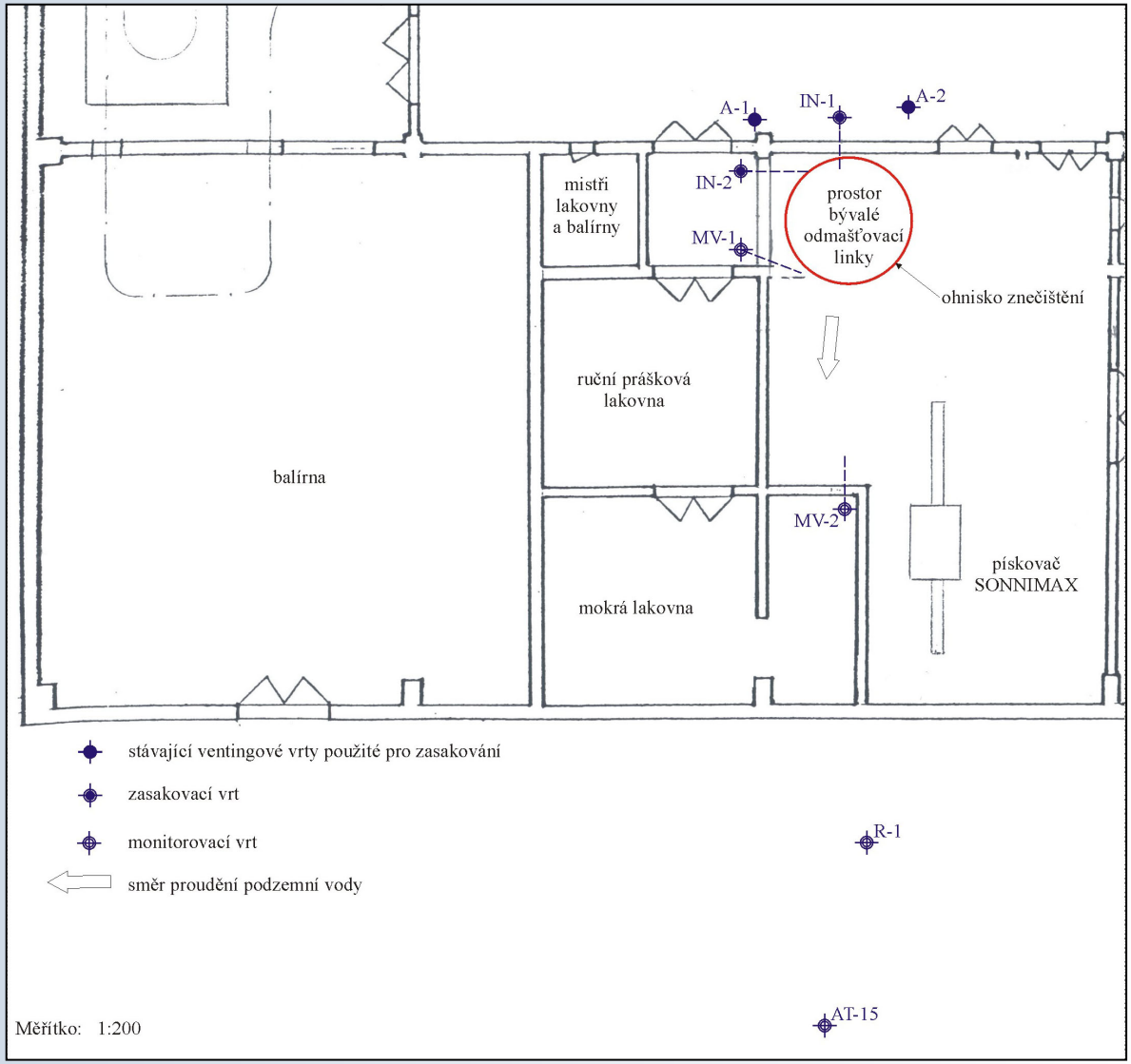
Laboratory and semi-pilot tests (7)

- **Reaction vessels after 114 days**
- From left – biotic controls (B1, B2), alcohol wash (LV1, LV2), beet molasses (M1, M2) and whey (S1, S2)
- Anaerobic and SR bacteria content 10^4 to 10^5 CFU/ml
- ORP –100 to –200 mV

Pilot testing (1)

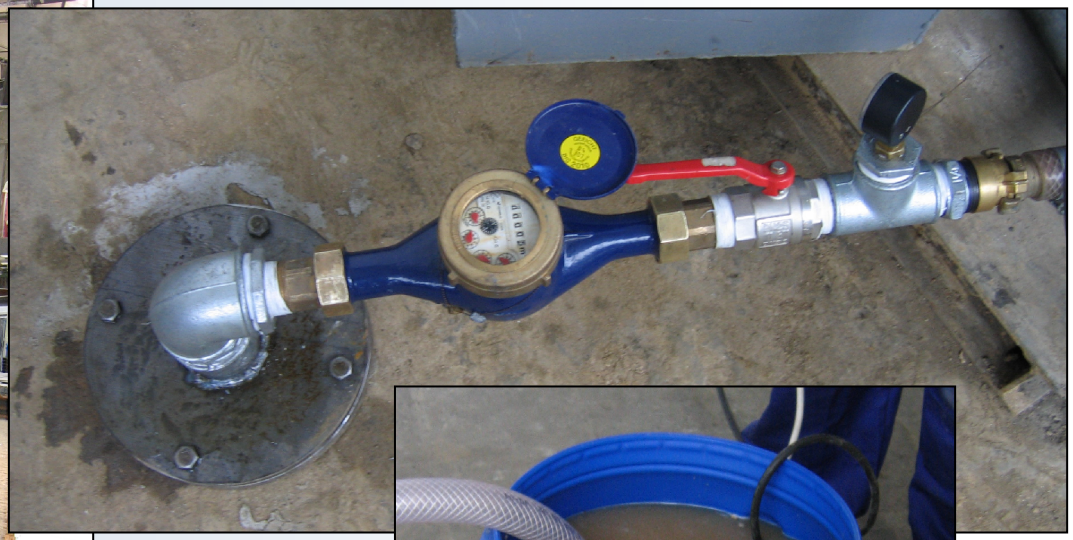
- **Testing *in-situ* carried out simultaneously with the laboratory experiments**
- **Carried out on a model site from Jul 2006**
- **Historical accidental release of TCE, PCE**
- **CAHs plume reaches up to 400 mg/L (PCE, TCE)**
- **Evaluation of the site for ERD suitability before starting**
- **4 injection wells IN-1, IN-2, A-1, A-2**
- **4 monitoring wells MV-1, MW-2, R-1, AT-15**
- **Used substrate – whey with beet molasses (till now 4 m^3, pressure application)**
- **Tested substrate added on basis of TOC levels ⇒ <100 mg/L**
- **Regularly sampled (every 60 or 90 days)**

Pilot testing (2)



Pilot testing (3)

Pilot testing (4)



Pilot testing (5)

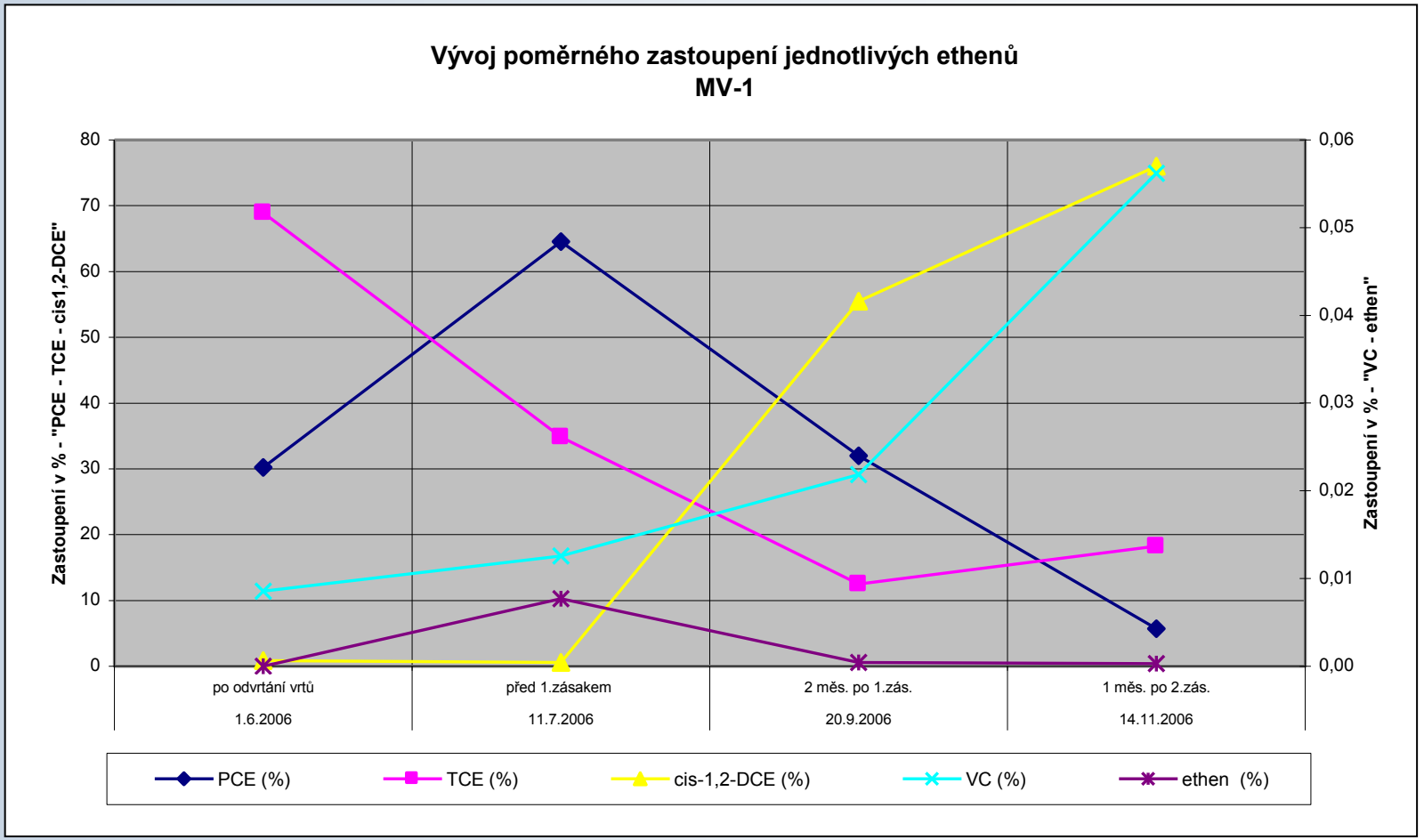
- **Monitored parameters: only groundwater**
  - PCE, TCE, *cis*-1,2-DCE, *trans*-1,2-DCE, 1,1-DCE, VC
  - Ethene, ethane, methane, chlorides
  - TOC
  - Nitrates, sulphates, Fe, Mn
  - pH, ORP, temperature, conductivity
  - Groundwater level
  - Anaerobic and SR bacteria

Pilot testing (6)

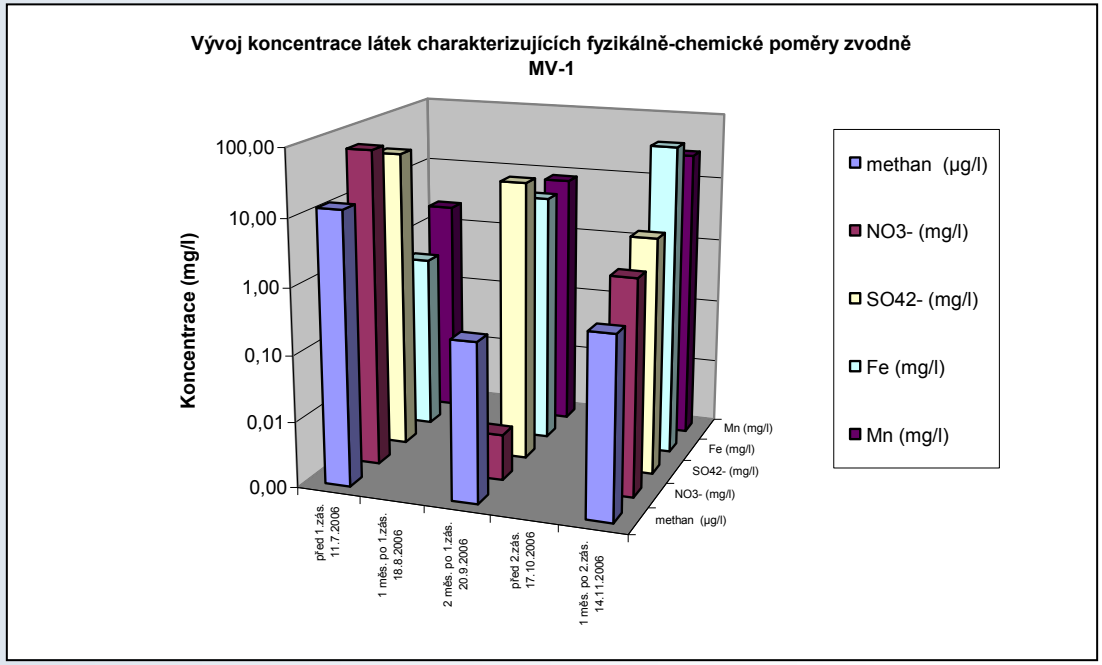
➢ Results of the pilot test

- Significant decrease of PCE and TCE below 40 and 22 mg/L
- Massive increase of *cis*-1,2-DCE up to 150 mg/L and also VC
- Ethene detected up to 2 mg/L, methane to 0.4 mg/L
- Anaerobic and SR bacteria content 10^3 to 10^4 CFU/ml
- ORP below –100 mV
- pH 6 to 6.5
- Temperature 16.5 to 19 °C
- Conductivity around 1 to 2 mS/cm

Pilot testing (7)



Pilot testing (8)



➢ Future activities

- **Testing will be carried out till Dec 2007 (approx. 1.5 years)**
- **Hopefully, further decrease of *cis*-1,2-DCE and VC together with increase of ethene will be reached**
- **If the pilot is successful, the full-scale application will be carried out**

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Conclusions

- Tested food-processing waste may be used as alternative electron donors
- Rather long lag-phase can be seen with some substrates
- ERD is a valuable and effective technology for treatment of contaminated sites with CAHs (including the heavily ones)
- The technology is (may be) also cost effective (depending on a site)

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Thank you for your attention!

➢ Contact details

- Lenka Vesela

Dekonta, a.s., Volutova 2523, 158 00 Prague 5, Czech Republic

Tel.: +420 312 292 967, Fax: +420 312 292 966

Mobile: +420 724 289 804, E-mail: vesela@dekonta.cz

www.dekonta.cz