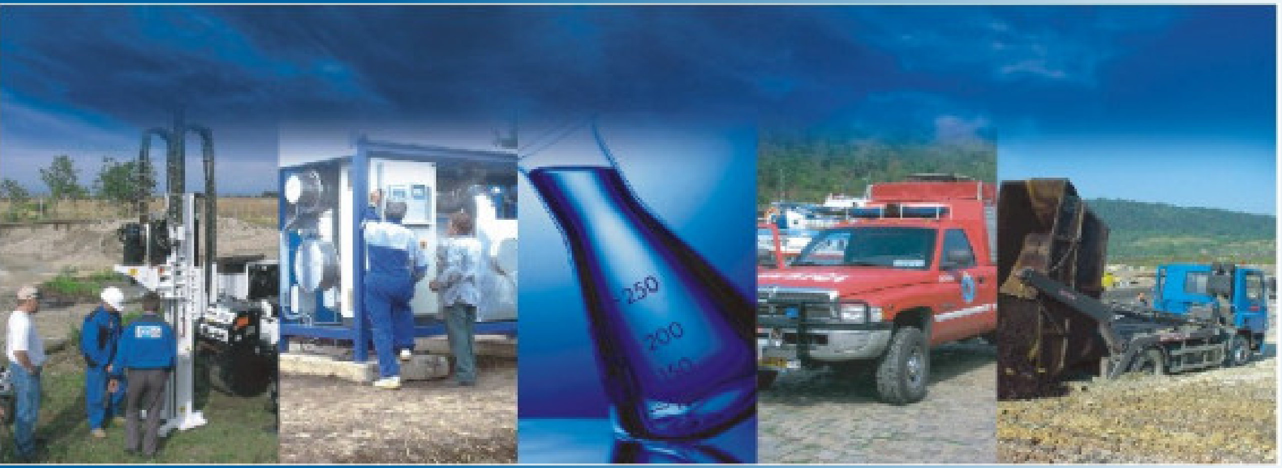

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IN-SITU ENHANCED REDUCTIVE DECHLORINATION OF CHLOROETHENES USING FOOD-PROCESSING WASTE – FROM LABORATORY TO FIELD APPLICATION

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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 <u>in anaerobic environment</u>**
- **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 sequential removal of chlorine ions**

- **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**

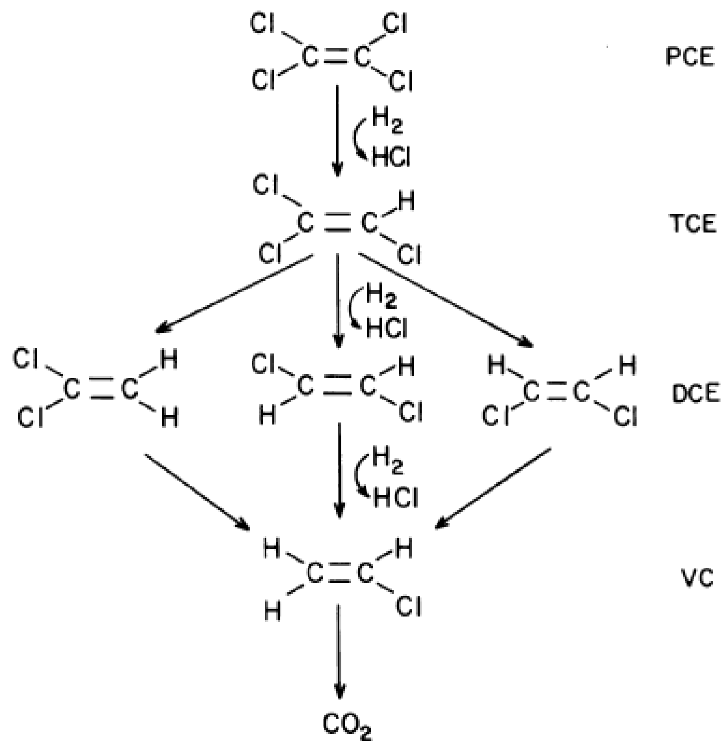


FIG. 3. Schematic for possible pathway for conversion of PCE to CO_2 through reductive dehalogenation.

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 $\Rightarrow$ necessary for reductive dechlorination of CAHs (specific dechlorinators, but it is also consumed via other bacteria species)

ERD process application (2)

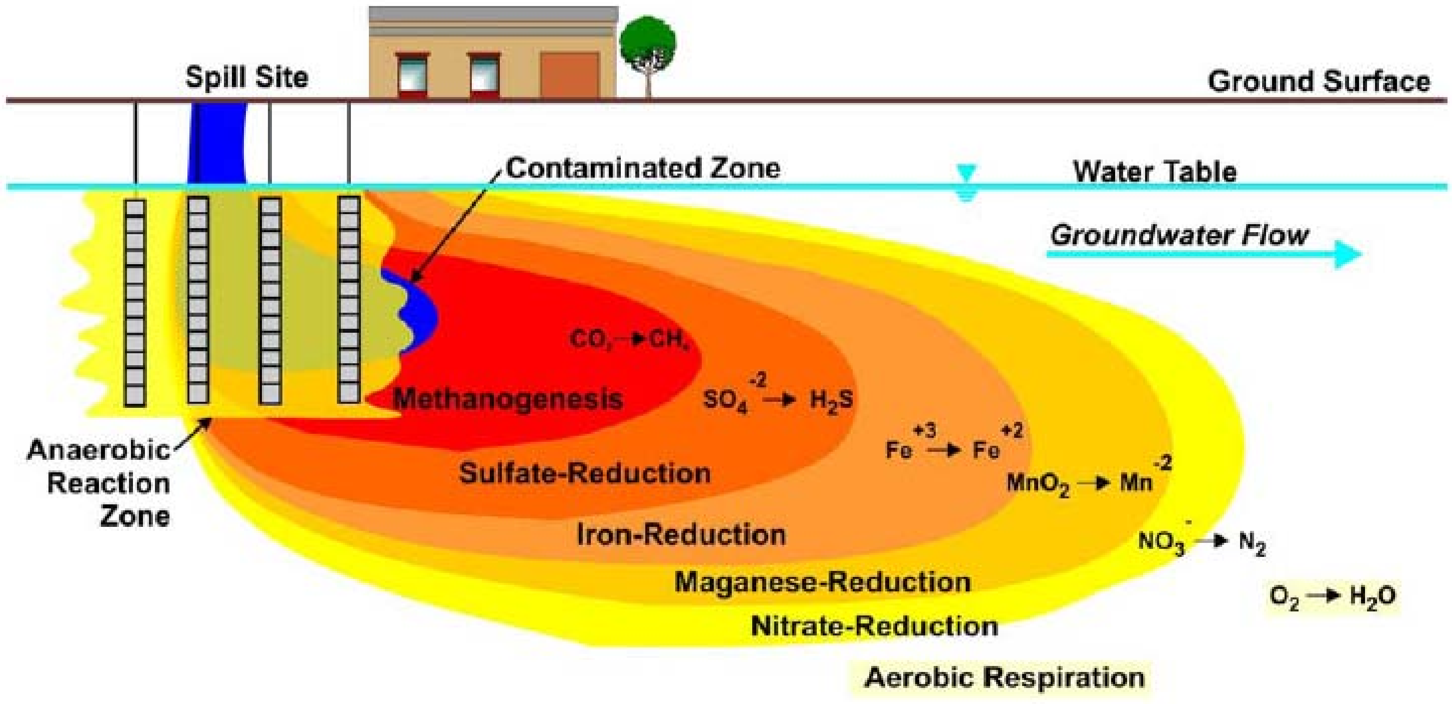


Figure 1.3 Reducing Zones Established Downgradient of Substrate Injection

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)

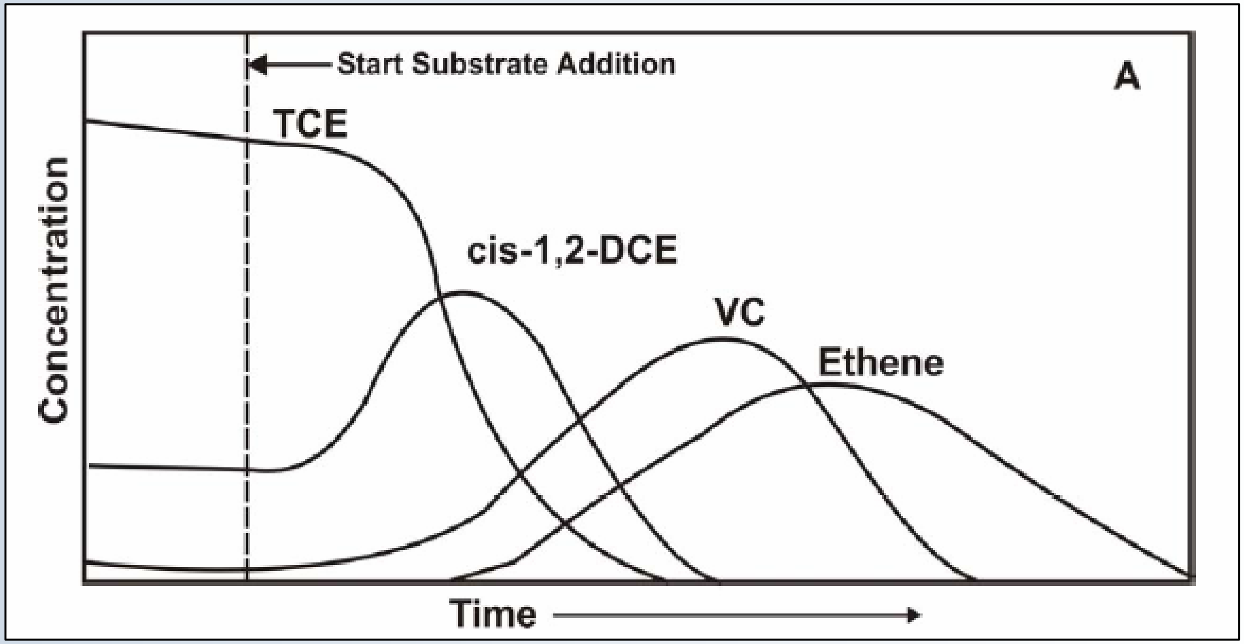
➢ Results of the experiments

- 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)

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➢ **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**

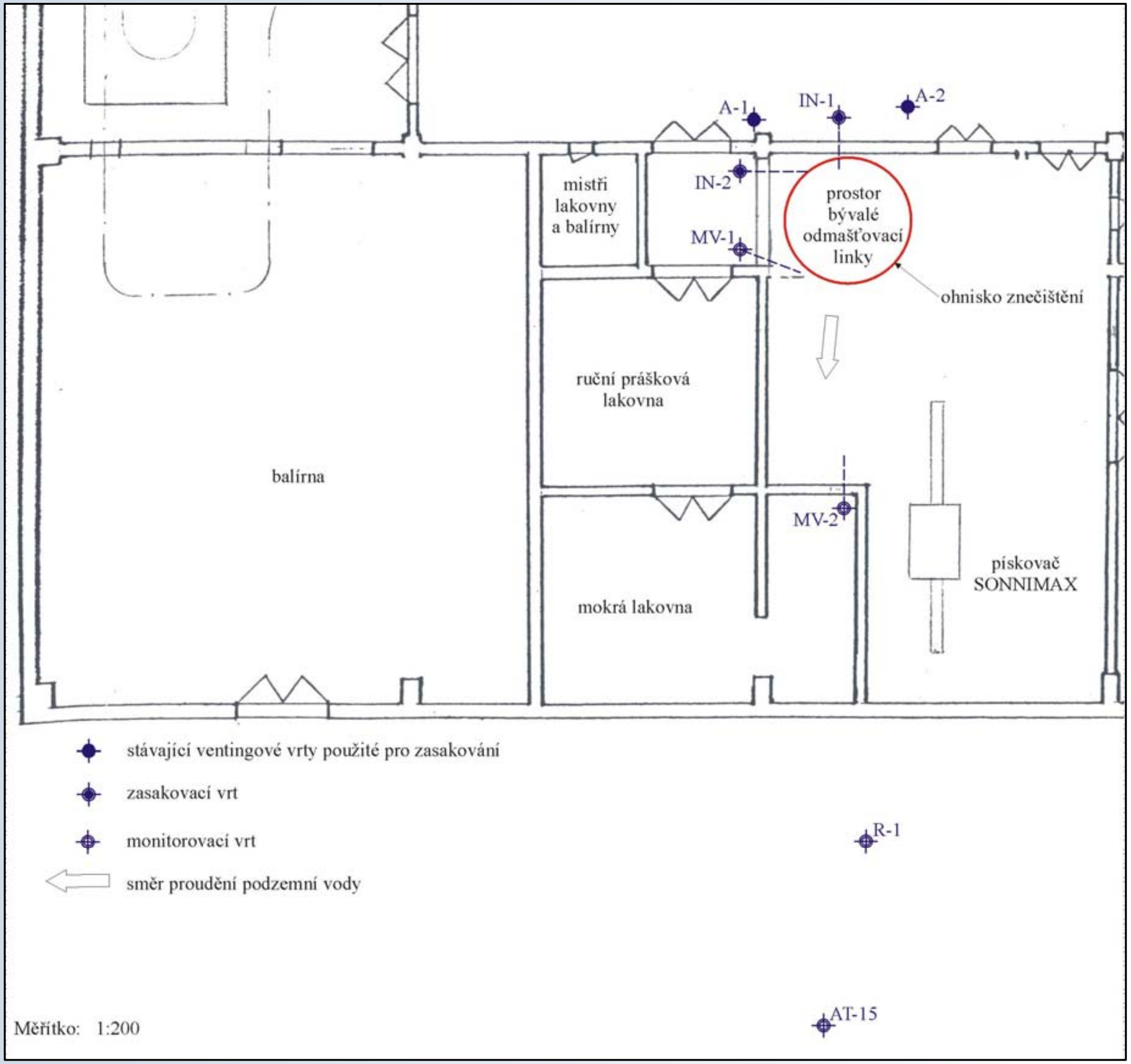
- **From left – biotic controls (B1, B2), alcohol wash (LV1, LV2), beet molasses (M1, M2) and whey (S1, S2)**

- **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 $\Rightarrow$ <100 mg/L**
- **Regularly sampled (every 60 or 90 days)**

Pilot testing (2)



Pilot testing (3)

Pilot testing (4)

Pilot testing (5)

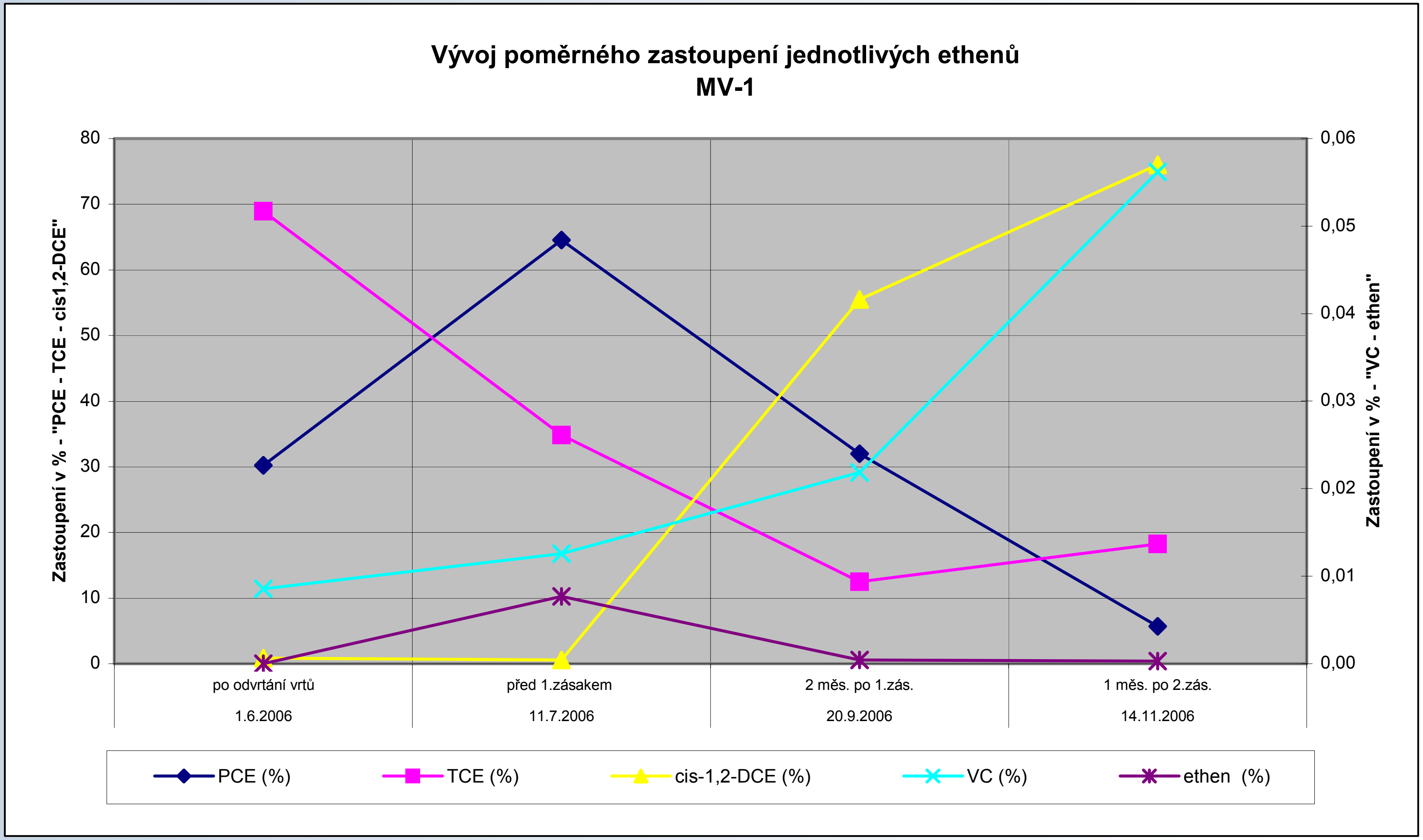
- **Monitored parameters: only groundwater**
  - **PCE, TCE, *cis*-1,2-DCE, *trans*-1,2-DCE, 1,1-DCE, VC**
  - **Ethene, ethane, methane, chlorides**
  - **TOC**
  - **Nitrates, sulphates, Fe, Mn**
  - **pH, ORP, temperature, conductivity**
  - **Groundwater level**
  - **Anaerobic and SR bacteria**

Pilot testing (6)

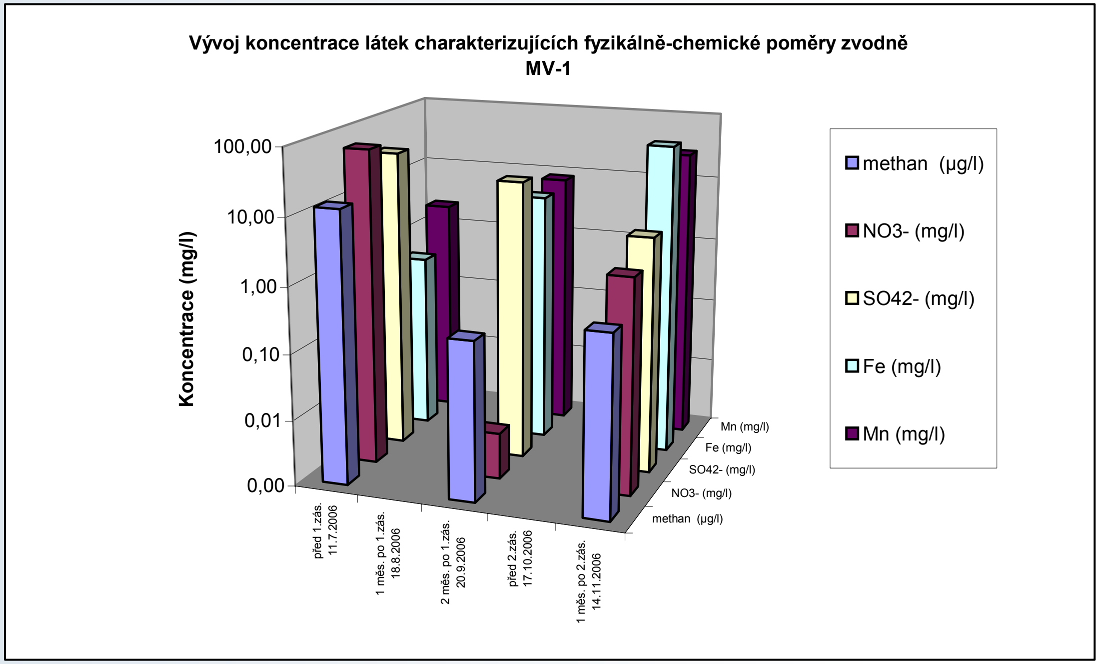
➢ Results of the pilot test

- 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

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!

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