What nano-remediation is and what it can and cannot do

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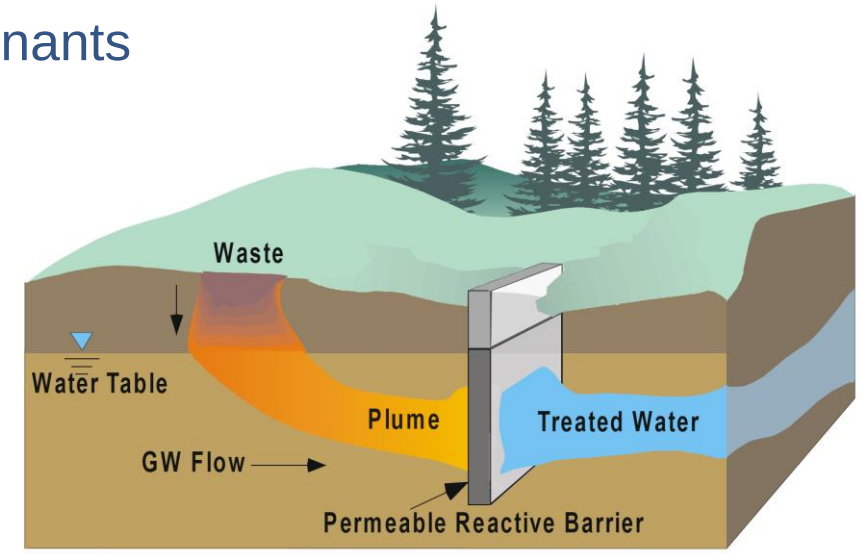
Outline

- What nano-remediation is
  - The application of materials in nanoscale or technologies working on nanoscale for treatment of contaminated water, soil, rock material.
- What it can do
  - Almost everything (in future), and many things now (treatment of contaminated groundwater, polluted wastewater, support bioremediation)
- What it cannot do
  - Miracles. It is only technology with its own limitations and restrictions.

Principles of nZVI

- Contaminant spills
- Permeable reactive barrier, Fe fillings = zero-valent iron
- CHC reduction → ethene
- nano-ZVI injection
  - Higher surface area
  - Higher reactivity with contaminants
  - Mobility in groundwater
- Technology:
- No space restrictions
- Simple to use?
- Broad applicability?
- Cheap and fast?



www.epa.gov

Chemical principles

- Chemically: a strong reducing agent
  interaction with water → gets (oxidized) rusty

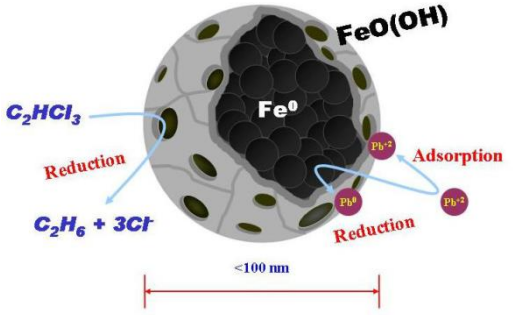
$$Fe^0 + 2H_2O = Fe^{2+} + H_2 + 2OH^-$$

- Similarly chemical reduction of chlorinated hydrocarbons, e.g. TCE:

$$3Fe^0 + C_2HCl_3 + 3H^+ = 3Fe^{2+} + C_2H_4 + 3Cl^-$$

- Precipitation on Fe-oxide reaction products

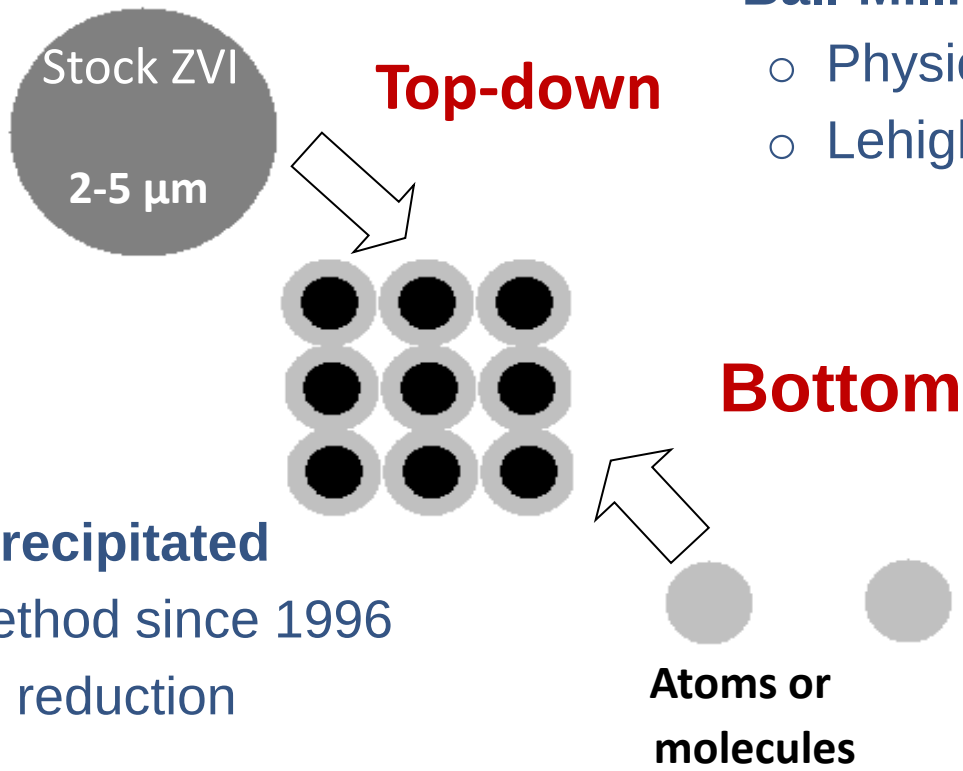
$$As \rightarrow Fe_xAs_{(2-x)}O_3$$



nZVI manufacturing

- **High temperature reduction**

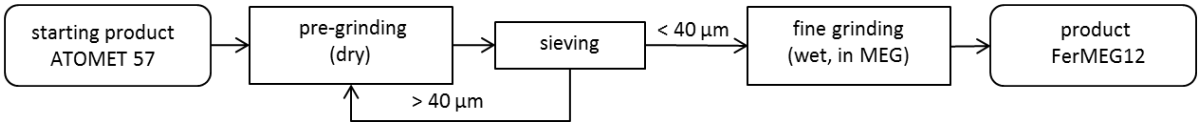
- **Mechanically Ground / Ball-Milling**
  - Physical size reduction
  - Lehigh University (2005)

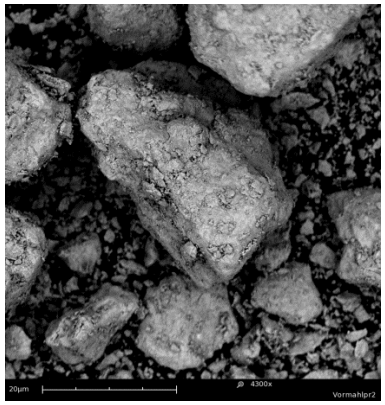


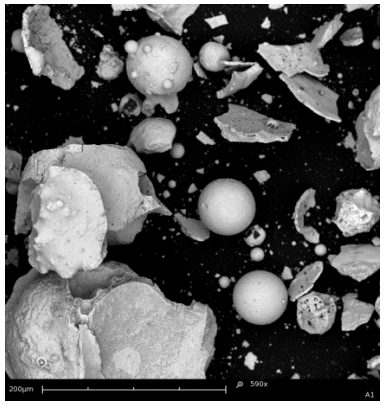
Chemically Precipitated

- Classical method since 1996
- Borohydride reduction

Milling of ZVI nanoparticles



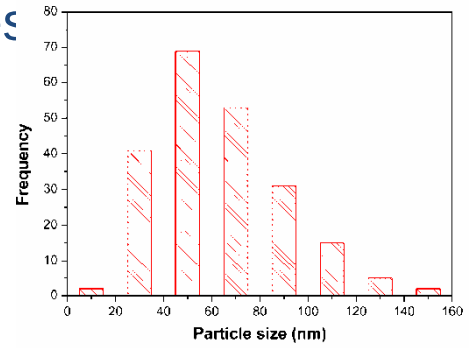


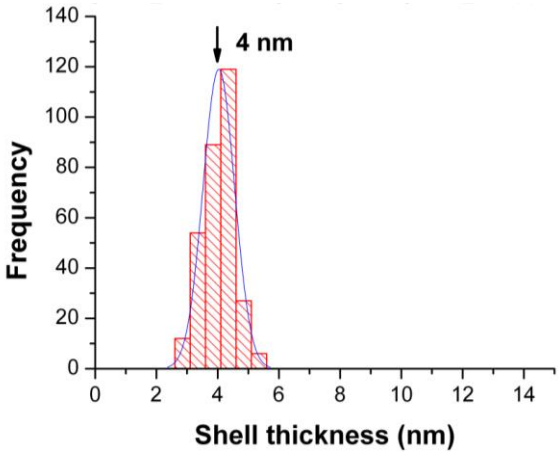


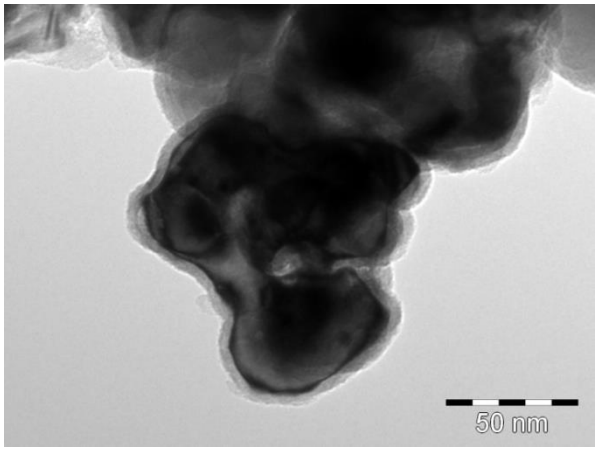
SEM pictures: starting product ATOMET57, pre-milling product, FerMEG final nZVI

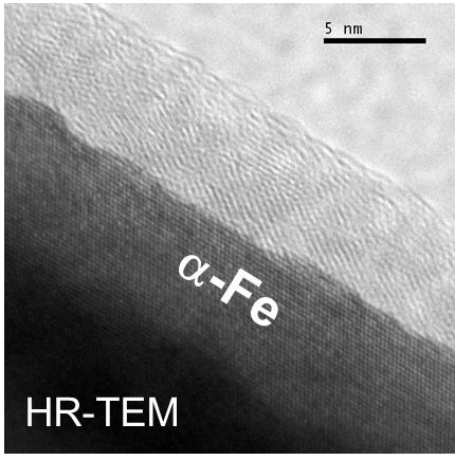
Dry NANOFER STAR particles

- High temperature hydrogen reduction of Fe-oxides
- Large scale production: n.100 kg/month
- Large surface area > 20 m^2/g
- 80 nm particles
- 90% Fe(0)
- Dry powder
- Protective oxidic layer → storage in air, transportability, storability,
- Activation process + surface stabilization prior to use

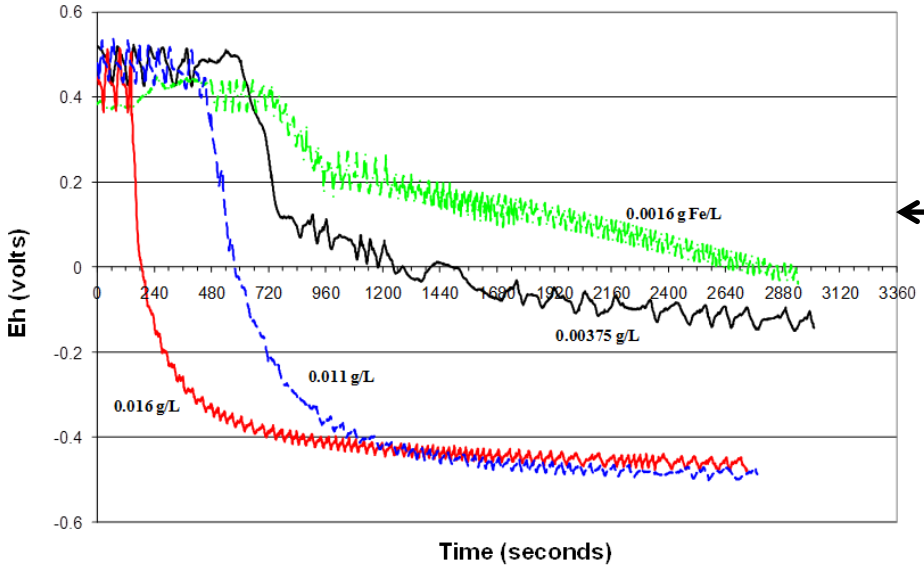






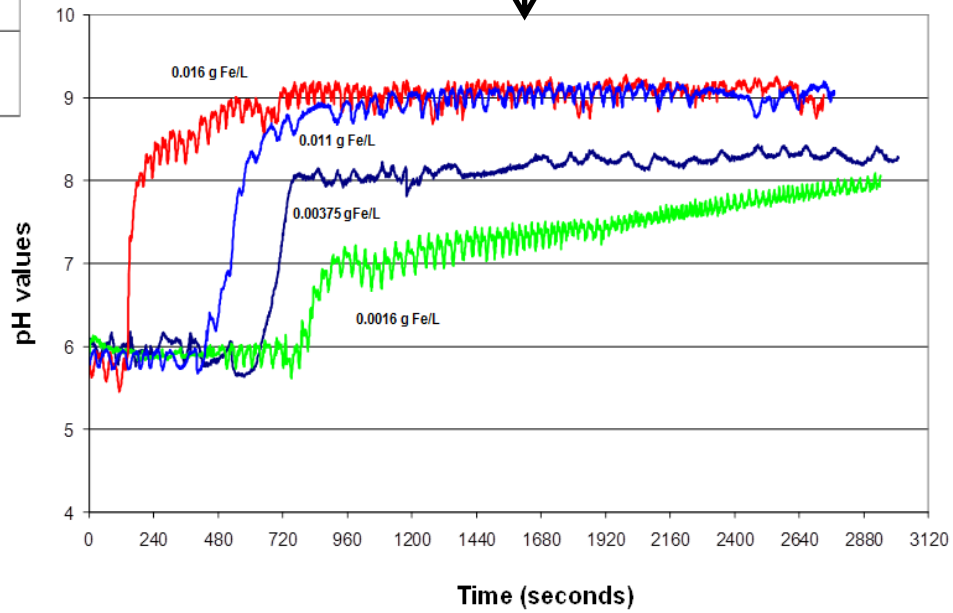


Reaction in water



$Fe^0 + 2H_2O \rightarrow Fe^{2+} + 2e^-$

$2\ H_2O + 2e^- \rightarrow H_{2(g)} + 2\ OH^-$



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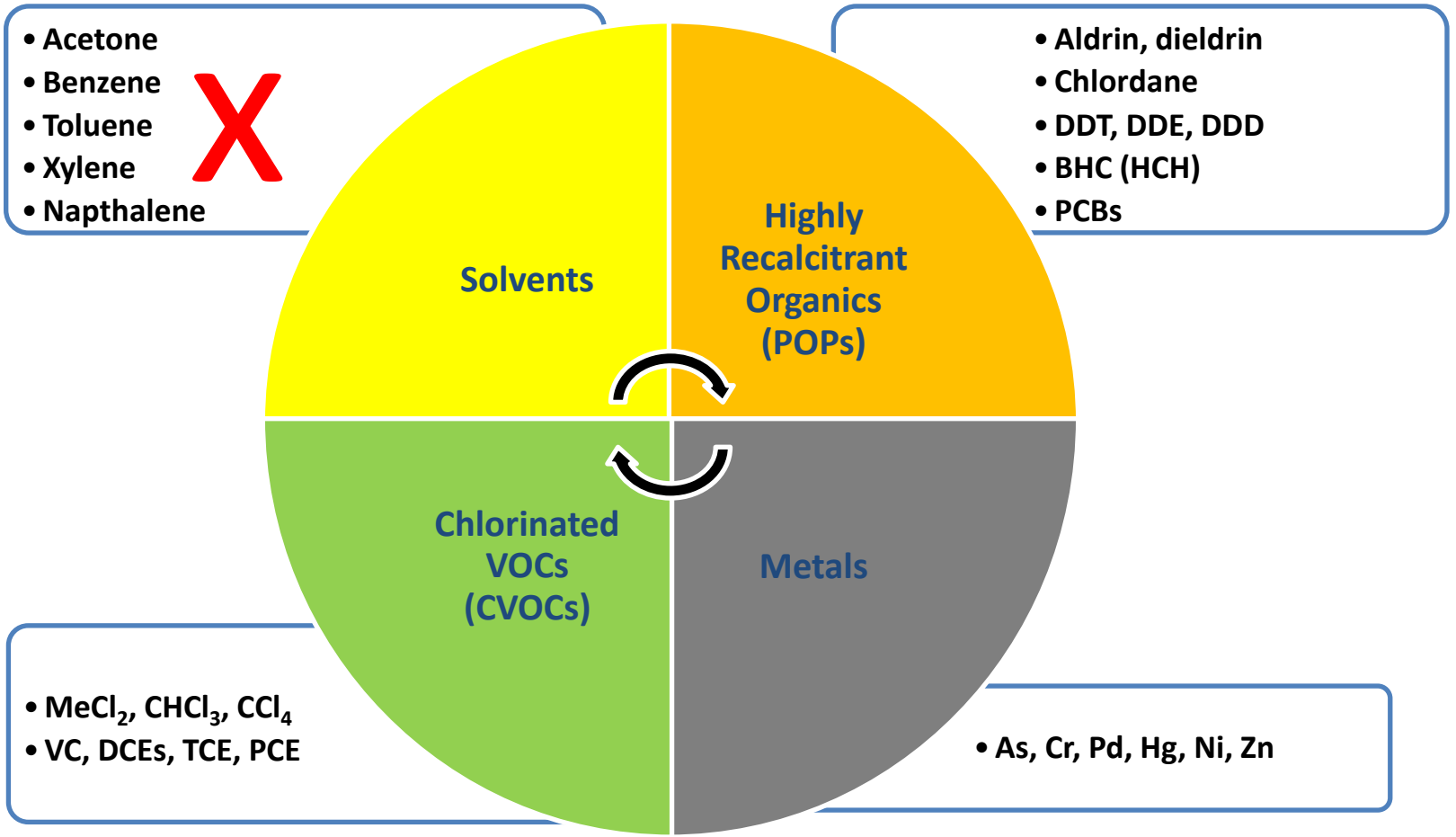
nZVI migration

In situ application

- Dry powder transported to the site
- On site surface stabilization
- Advantage → high reactivity, >95% Fe0
- Improved mobility

What nZVI can do



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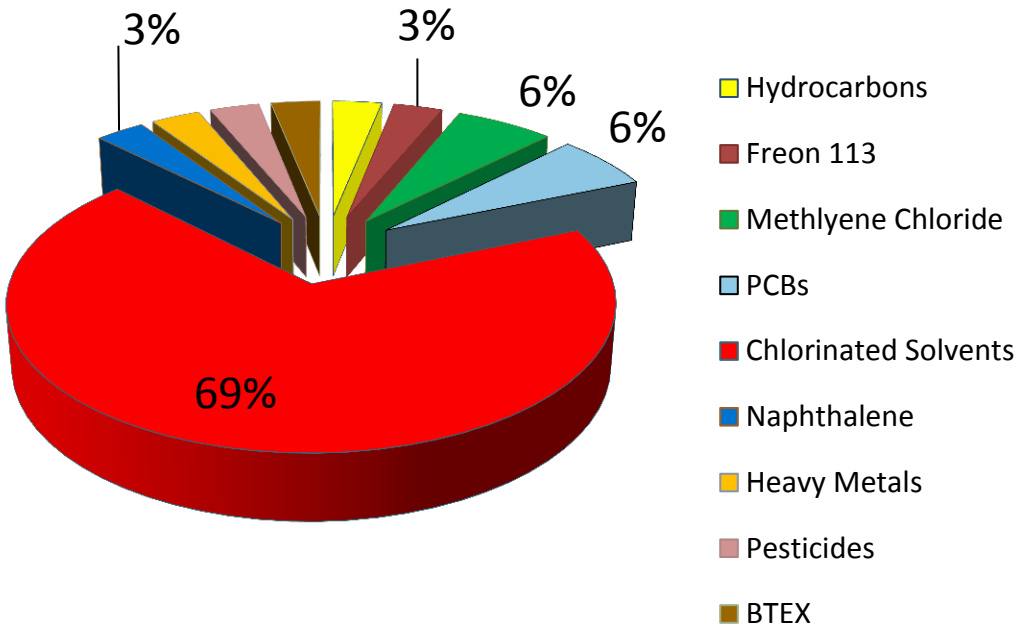
Target contaminants

- Chlorinated solvents
  - PCE, TCE, DCE, VC, 1,1,1-TCA
- Freon 113
- Hydrocarbons (C8 to C50)
- Metals (Chromium, nickel)
- Methylene chloride
- Naphthalene
- PCBs
- Pesticides (Metoalchlor, Chlorpyrifos, Lindane)



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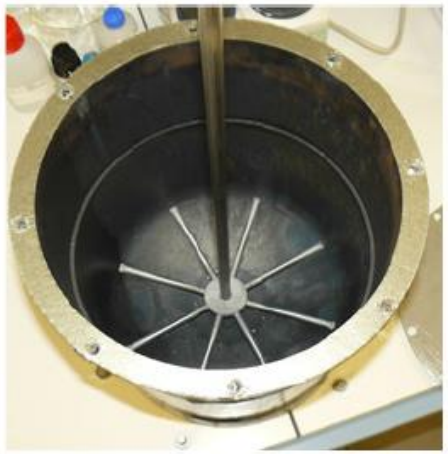
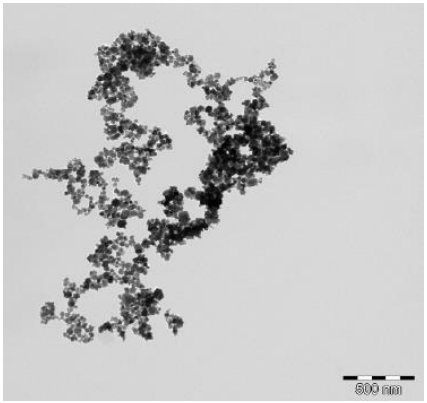
Carbo-Iron

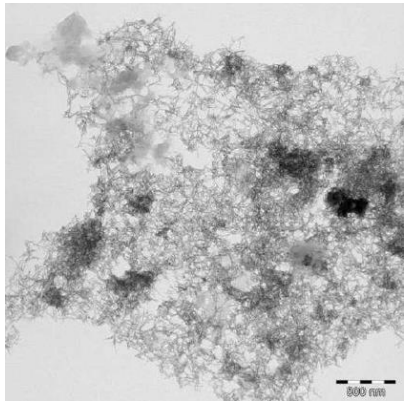
- Composite material of colloidal activated carbon and nZVI
- Sorption properties → enhance the effectiveness
- Combination of both materials – iron and carbon → enrichment of pollutants in the vicinity of nanoparticles
- Support biological degradation processes
- For more info contact: Helmholtz-zentrum für Umweltforschung – UFZ (K. Mackenzie)



Other types of nanoparticle

- Biomagnetite: bacterial reduction of, small amounts, only for lab. Studies (till now)
- Other metallic nanoparticles: commercially available Al, Mg (micro → nano; milling process)
- Nano-Goethite: oxidation + sorbent for aliphatic hydrocarbons
- Fe-Zeolites: commercially available, sorbent + oxidation catalysts (particle size ~ 1nm)
- Ferrates: in dissolved form → stabilization?





Zeolites Bio-Magnetite FeOx NP

What nano-remediation cannot do

- MIRACLES. Do not expect:
- Fast, cheap, total removal of all types of contaminants.
- Easy deployment without an experienced user
- Effective performance without preparation work: conceptual model, lab + pilot tests, plan of remediation, repeated actions,….
- So just like many other remediation technologies!

- Disadvantages:
- Cost, migration, lifetime
- Solution?
- Method combinations

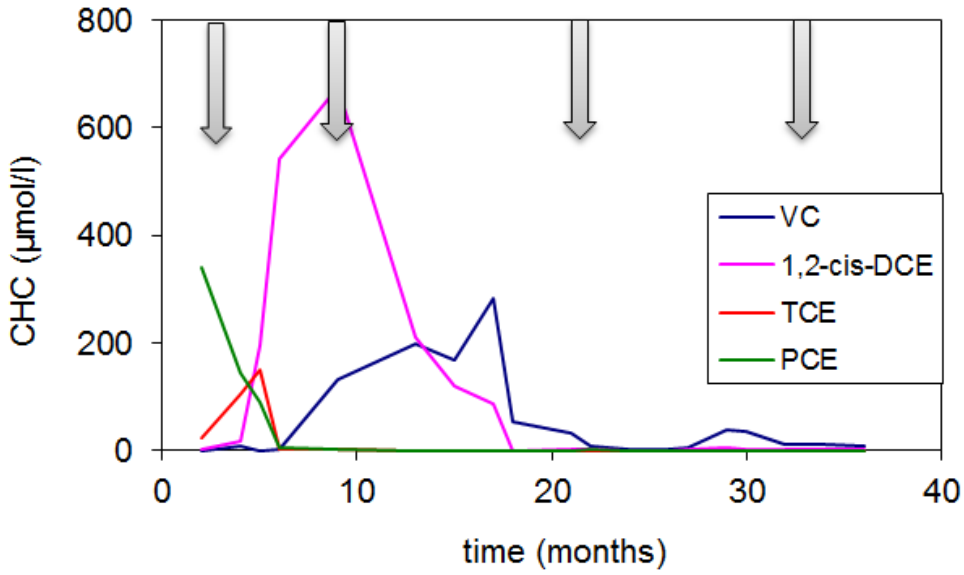
Combination of nano and bio

- Lactate → fermentation→ source of electrons for bioreduction

- Bioremediation: cheap, good migration

  BUT: less-Cl CHC, lower ORP → 1,2-c-DCE commulation

- Horice(CR) site
- Low hydraulic conductivity
- Aplication of lactate
- 3x aplication nZVI



Combination of nano and EC

Quternary aquifer $T=10^{-7}$ m^2s^{-1}
electrodes:

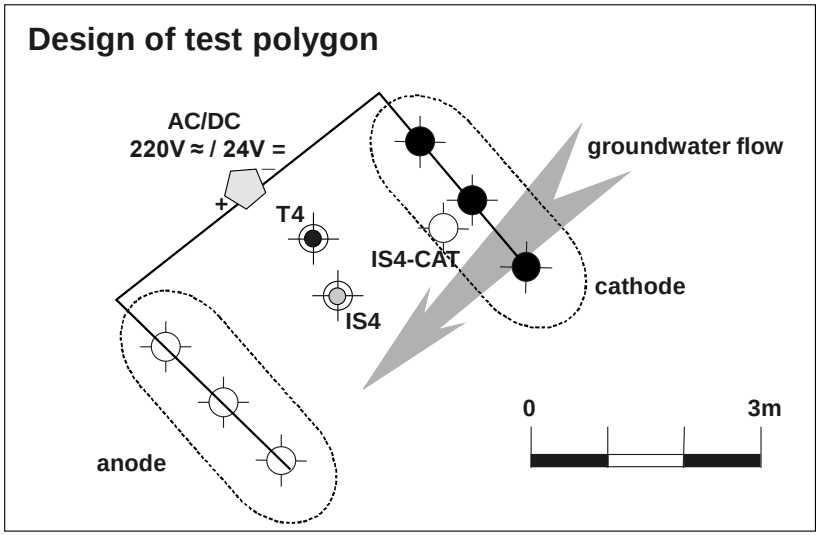
- 10m long,
- 20 mm in diameter
- 24V a 7-15A
- exchange every 6 months

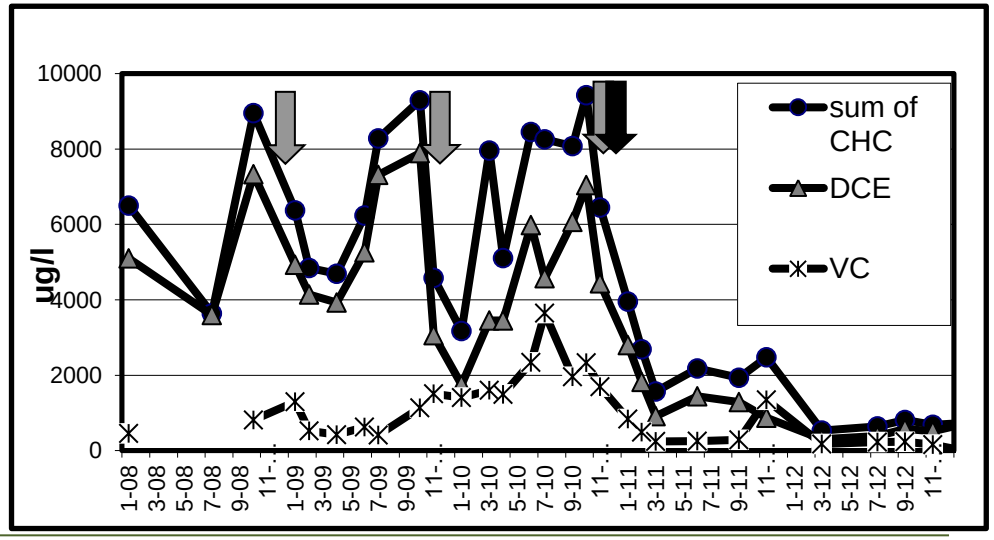
Cathode:

- Eh ≈ -600 mV
- pH > 12
- reduction od CHC

Anode:

- no effect





nZVI, ZVI and oxidation

Parameter	nZVI (in-situ)	ZVI (PRB)	Oxidation (in-situ)
Reactivity	high	low	very high
Mobility in soil	few meters	no	tens of meters
Longevity	few months	few years	hours → days
Toxicity	Nanoparticles? Surfactants?	Non-toxic	significant
Instalation costs	Low	High	Low
Operation costs	Low	Low	Low
Permission	Moderate	low	Problematic
Applicability	High (below build)	Limited	high
By-products	H2	H2	ROS, heavy metals
Environ. Effect	ORP drops Microbial changes	ORP drops (slight) Microbial changes	ORP increase from reducing; depletion of org. Mirobial changes;

The next challenges

- Demonstrate the method more widely on European sites
- Continuous improvement of nanoparticle properties (migration → lower amount needed)
- Reduction of production costs
- Widen the spectrum of applications
- Combinations with other remediation methods

Thank **you for your interest**
and
the **EU for the funding**

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