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AquaConSoil Copenhagen 2015

SpS 1C.23S.
Practical Experience with Nanoremediation

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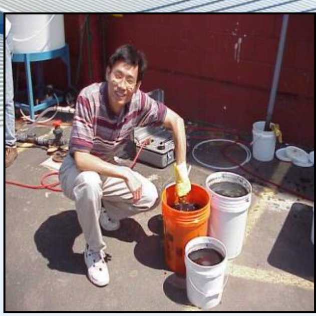

Pre-injection Batch Mixing of nZVI Slurry
(Photos: Dan Elliott)
First field-scale demonstration, Trenton, NJ, 2000

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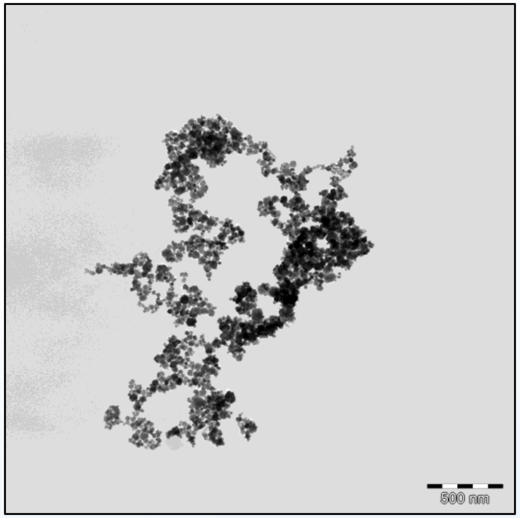
Agenda

I. Nanoremediation overview
II. Representative technologies with a focus on nZVI
III. Field use, lessons learned, and future outlook

Pre-injection Batch Mixing of nZVI Slurry
(Photo: Dan Elliott)
First field-scale demonstration, Trenton, NJ, 2000



5% Pd on Bio-Magnetite (Fe_3O_4)
TEM image (Photo: Merethe Kleiven)
NanoRem, 2014

I. Brownfield sites legacy in the U.S.

- Since the 1970s, hundreds of billions of $ have been spent to clean up contaminated sites in the U.S.[1]
- Scale of the problem (U.S.):
  - NAS (2012)[1]: >126,000 contaminated sites remain with a cost-to-cure of $110-127 billion USD
  - EPA (2004): >300,000 sites requiring remediation through 2033 at a cost exceeding $200 billion USD
- ~10% have “complex” hydrogeology and/or chemistry[1]:
  - Low permeability zones, deep aquifers, fractured bedrock, matrix diffusion, etc.
  - Recalcitrant contaminants, DNAPL, incompatible geochemistry, etc.
- Nanoremediation is a promising remedial option

1. Cavanaugh et al. Alternatives for Managing the Nation's Complex Contaminated Groundwater Sites. 2012. National Academy of Sciences

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I. Nanotechnology in the remediation market

- Primary goals for nanotechnology in remediation:
  - Degrade, transform, or sequester contaminants;
  - Detect chemicals which constitute a potential environmental threat
- Transformative anticipated benefits:
  - Extend the range of treatable contaminant classes
  - Increase remediation efficacy (e.g. speed & degree of completion)
  - Portability and access to low permeability zones (e.g. sediments)
- Key considerations:
  - Ensuring a “fit” with the site conceptual model, delivery method, and overall remediation approach
  - Assessing the cost-effectiveness of the nanoremediation approach
  - Characterizing the environmental *implications* (e.g. fate and transport, receptor analysis, etc.)

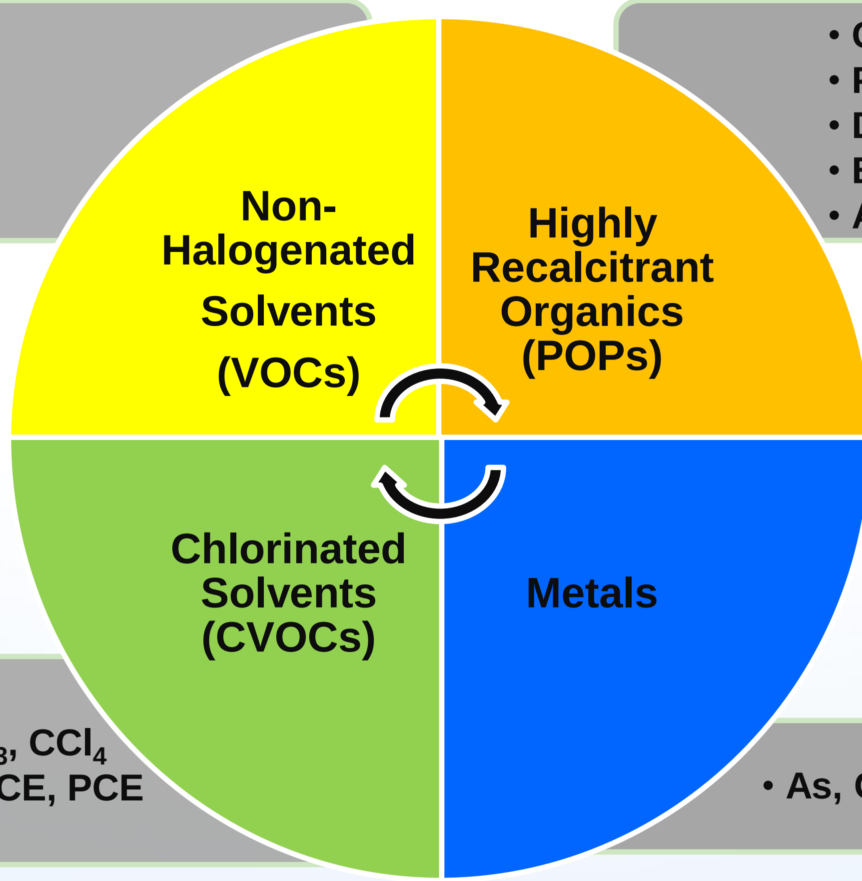
I. Amenable contaminant classes

- Acetone
- Benzene
- Toluene
- Xylene
- Napthalene

Labile, easy to treat

- Chlorinated benzenes
- PCBs
- DDT, DDE, DDD
- BHC (HCH)
- Aldrin, dieldrin, etc.

VERY difficult to treat!



- $MeCl_2$, $CHCl_3$, CCl_4
- VC, DCEs, TCE, PCE

- As, Cr, Pd, Hg, Ni, Zn

Recalcitrant, difficult to treat

Others: MTBE, ClO_4^-, PFCs

II. Types of NPs used in remediation

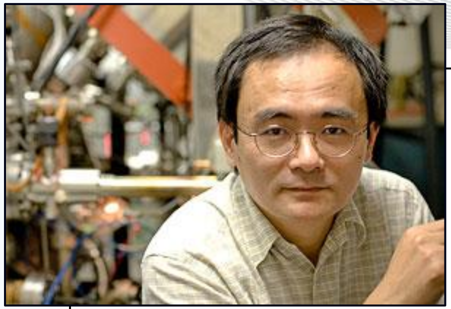
- **nZVI,** Fe^0
- Nano-Goethite, nFeO(OH)
- Carbo-iron®
- Fe-zeolites
- Bio-Magnetite, Fe_3O_4
- Biochar-nZVI*
- Barium ferrate**
- Zero-valent magnesium, Mg^0
- Nanoscale calcium peroxide*, CaO_2

NanoRem

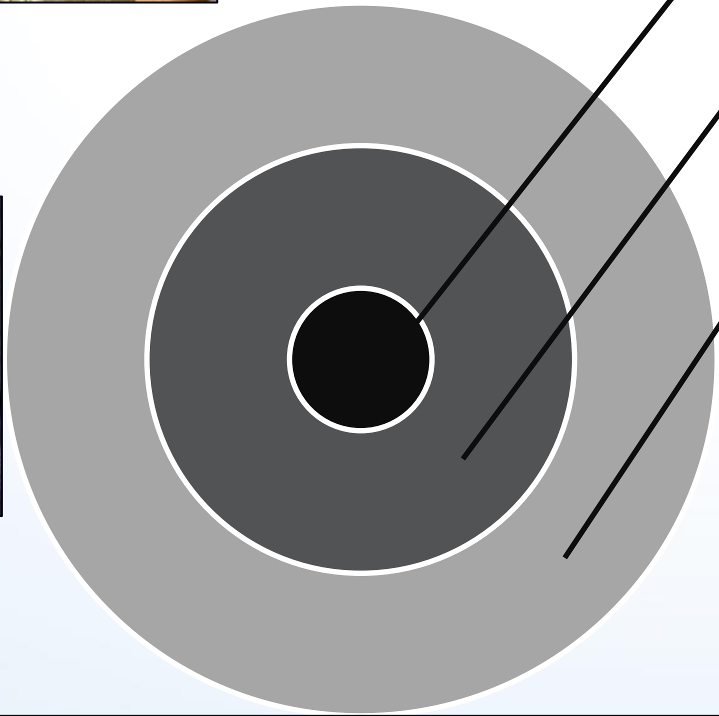
Reduction | Sorption | Oxidation | Sequestration

* - Not being investigated as part of NanoRem (2013-2017)
** - Thus far, principally at the research scale

II. Types of ZVI used in remediation

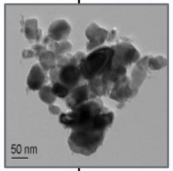


1996: nZVI studies begin



Nano, nZVI (<100 nm)

Application: In-situ inj for source area & dissolved plume

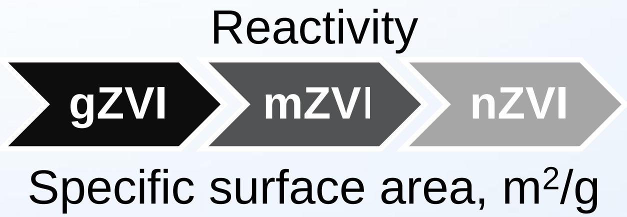


Micro, mZVI (1-100s μm)

Application: Backfill, limited in-situ inj.

Granular, gZVI (mm)

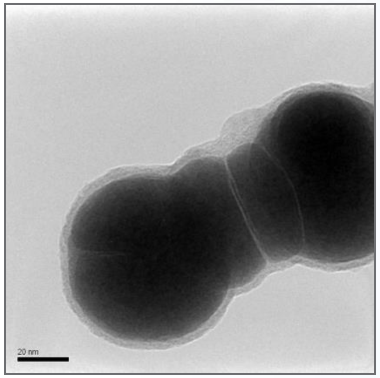
Application: PRBs, backfill, etc.

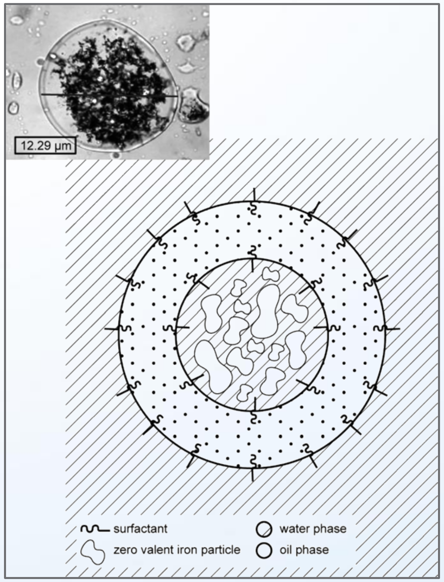


Dr. Wei-xian Zhang

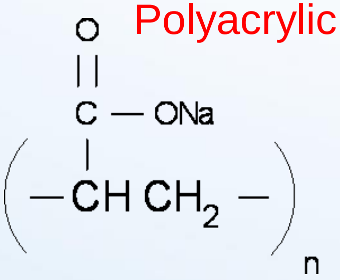
II. Variety of iron nanoparticles

- Bare nZVI & nFe-oxides
- Bimetallics (Fe/Pd, etc.)
- Supported nZVI
  - Carbon or polymeric bead substrate
- Emulsified ZVI (eZVI)
  - mZVI within emulsified oil micelles
- Surface-modified nZVI
  - Surfactant/polymeric surface architectures

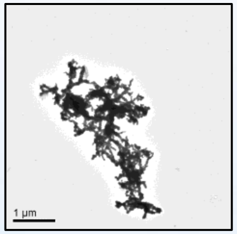




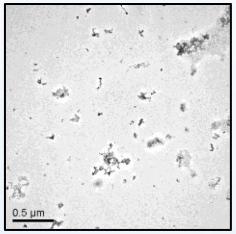
Polyacrylic acid (PAA) stabilized (others = NaHMP, CMC)



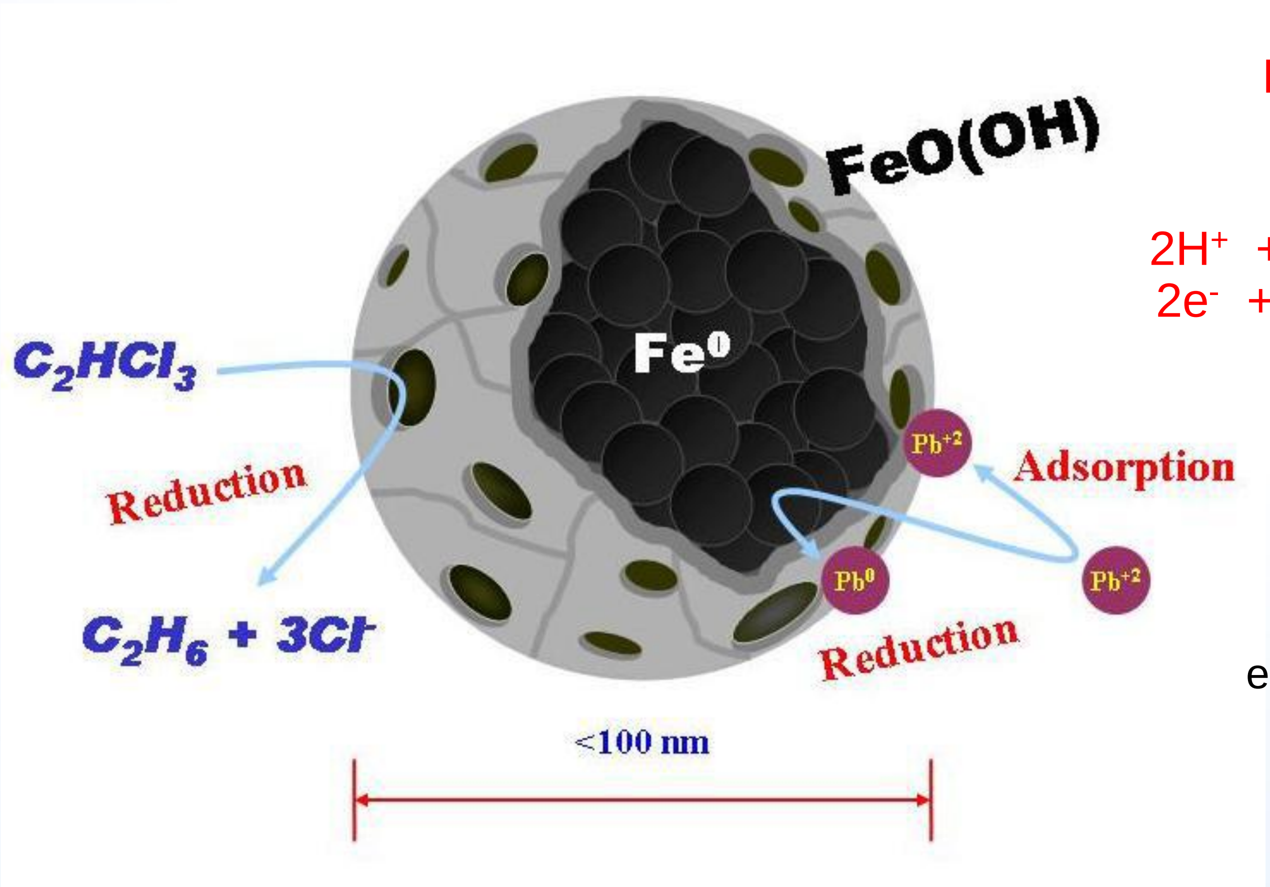
0% PAA



20% PAA



II. Conceptual model of nZVI action



Redox reactions

Anode

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

Cathode

$2H^{+} + ½ O_2 + 2e^{-} \rightarrow H_2O$

$2e^{-} + 2H_2O \rightarrow H_2 + 2OH^{-}$

Core-shell model

e^{-} transfer across oxide layer

- Contaminant degradation by nZVI is *surface-mediated*

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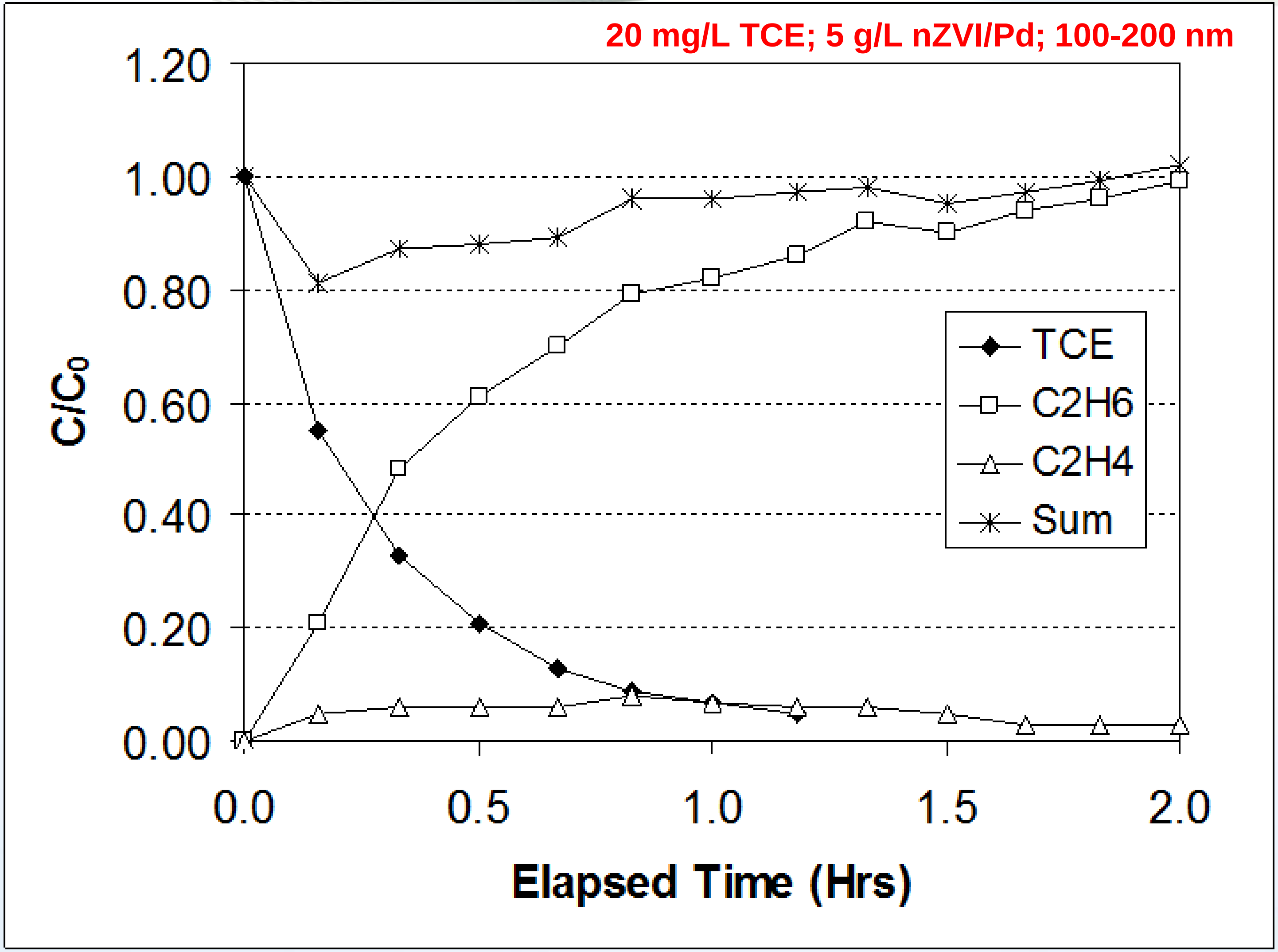
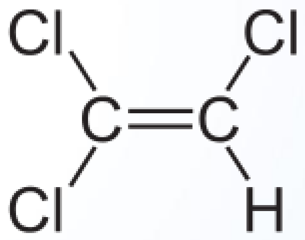
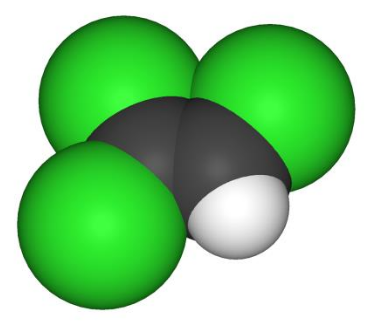
II. Upside potential – degradation of TCE by nZVI/Pd







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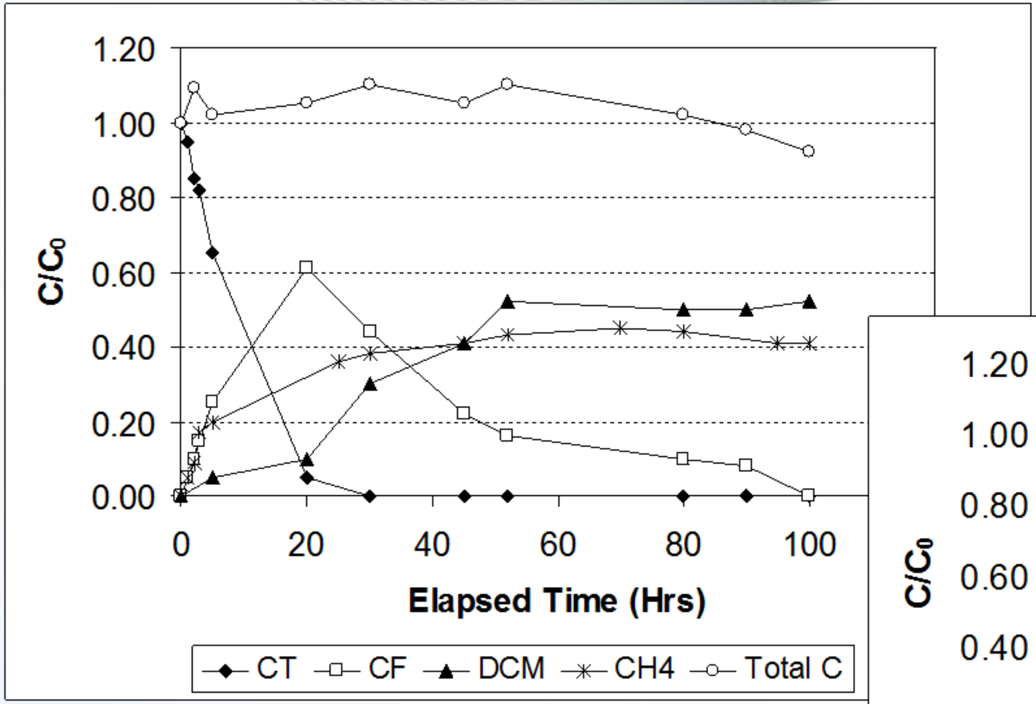
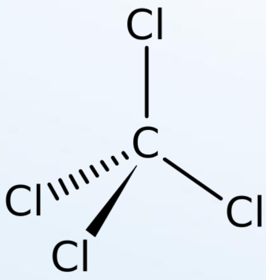
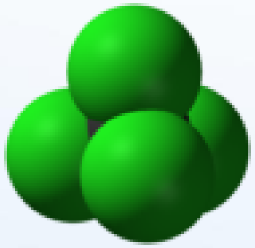
II. Upside potential – degradation of CT by nZVI and nZVI/Pd

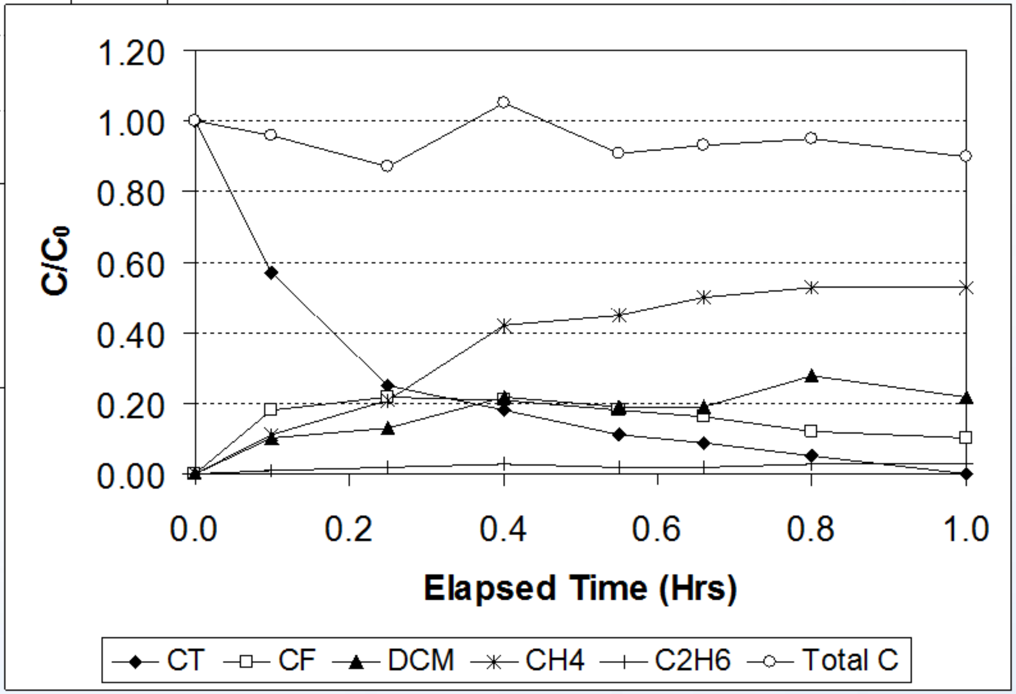


15.86 mg/L CT; 12.5 g/L nZVI; 100-200 nm





15.4 mg/L CT; 12.5 g/L nZVI/Pd; 100-200 nm



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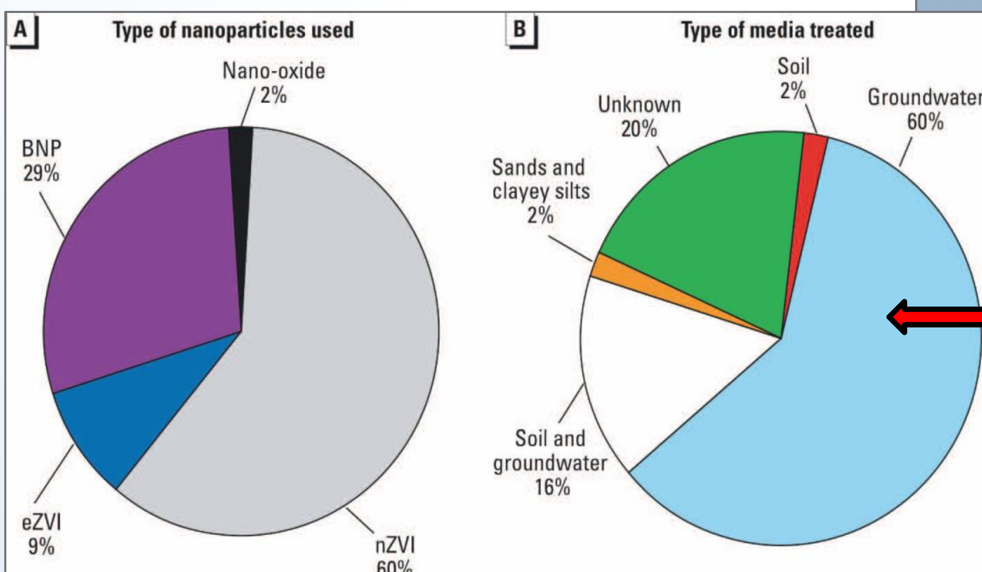
II. Field-scale nZVI applications

Field demonstrations (2000, 2007)
Photo: Dan Elliott



~70 Field-scale projects (thru 2014)

17 in the EU: DE, CZ, and IT

Primary target: CVOCs

39% PCE, 84% TCE, 55% DCEs, 27% VC

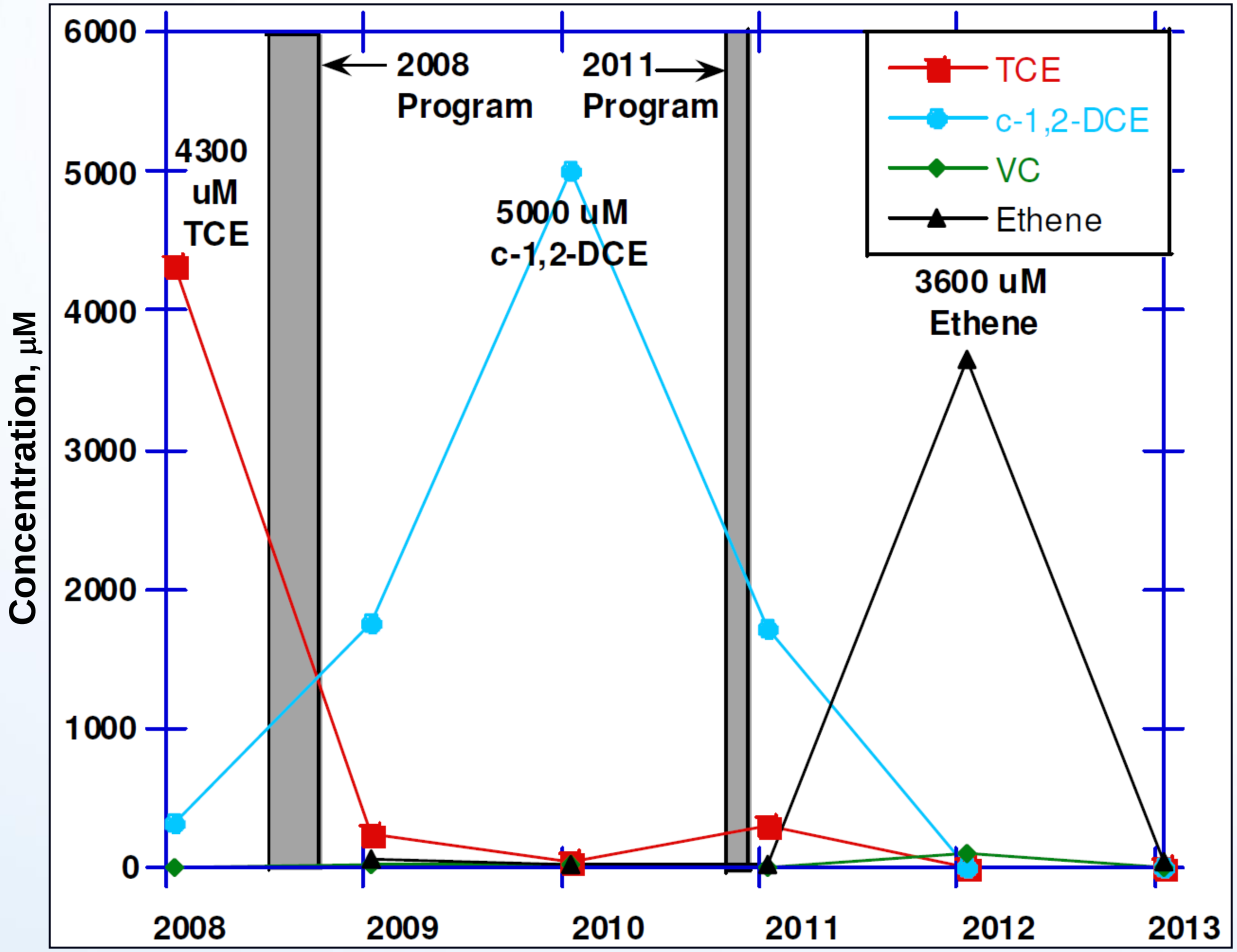
Typically 50-150 kg nZVI, 10-20 g/L

7,375 kg nZVI at Stephenville, TX

Data from Karn et al. (2009) *Environ. Health Perspect*. Vol. 117(12), pp. 1823-1831.

II. Representative case study – Stephenville, TX

CVOCs at Source Area Well MW-1



Courtesy of Dr. John Freim, On Materials, LLC

Site Overview:

- Active industrial facility
- TCE release from a degreaser
- 30 x 15m source area, 100m dissolved plume
- Source area $[TCE]_{aq}$ ~500 mg/L
- Lithology: 1m coarse fill on native silty sand, depth to groundwater ~2m

Remediation Program:

- 2008-09: 4,875kg Z-Loy™ nZVI + 43,000kg EVO + 150,000L deoxygenated H_2O
- 60 Injection wells in source area, depth to 3.5m
- 2011: 2,500kg Z-Loy™ + 75,000L EVO slurry + 50L Dhc

III. Nanoremediation – a mixed track record for nZVI

- Site characterization shortcomings:
  - GW flow direction & hydrogeology not well understood
  - Presence of low K zones or preferential pathways
  - Elevated CO_3^{2-}, pH, or incompatible geochemistry, etc.
- Insufficient iron dosing:
  - Iron to saturated soil ratio[1] >0.004
  - Multiple nZVI injections are generally needed
  - Natural reductant demand too high
- Issues regarding the iron quality, storage, or subsurface delivery
  - nZVI is intrinsically reactive
  - Very short shelf-life if stored as an aqueous slurry
  - Plugging of injection well screens & poor mobility

1 – Gavaskar et al. Cost and Performance Report Nanoscale Zero Valent Iron Technologies for Source Remediation. 2005. U.S. Navy (NAVFAC)

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III. Nanoremediation – hurdles to broader utilization

Manufacturing & materials characterization

- Stabilize intrinsically reactive nZVI
- Lessen variability in production & storage
- Standardized QA/QC

Fate and transport

- nZVI reactive longevity & potential for regeneration
- Selectivity enhancement
- Increase subsurface transport
- Focus on more complex recalcitrant contaminants
- Implications for potential receptors

nZVI effectiveness with other RA technologies

- Couple with bioaugmentation, EK

Site characterization

- Thorough site conceptual models
- Match NPs to site geochemistry, hydrogeology, & contaminants

Applications & costing tools

- NP dosage guidance
- Detailed cost-to-cure assessments

Permitting & risk issues

- Normalizing permitting requirements
- Assessing potential exposures
- Balancing remediation requirements, technology capabilities, & risks

NanoRem designed to probe many of these areas

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NanoRem

III. Nanoremediation – pivotal role of NanoRem

- What is NanoRem?
  - A consortium of 28 partners: universities, national research labs, consultants, and contaminated site owners
  - 4-yrs beginning April 2013 with €14MM funding (FP7)
- Major goal:
  - Identify cost-effective nanotechnology solutions and develop them to commercially relevant scales at EU Brownfield sites
- Outlook for nanoremediation:
  - NanoRem offers a crucial opportunity to overcome 15 yrs of mixed results and user experiences with nZVI
  - Leverage global research into novel NPs and applications
  - Develop additional large, multi-year, well-studied field projects
  - Good if cost-benefit and risk analyses are favorable

Questions?

Thank you!