

# Current Practice, Advances, & Challenges with nZVI Technology

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Groundwater Remediation Conference

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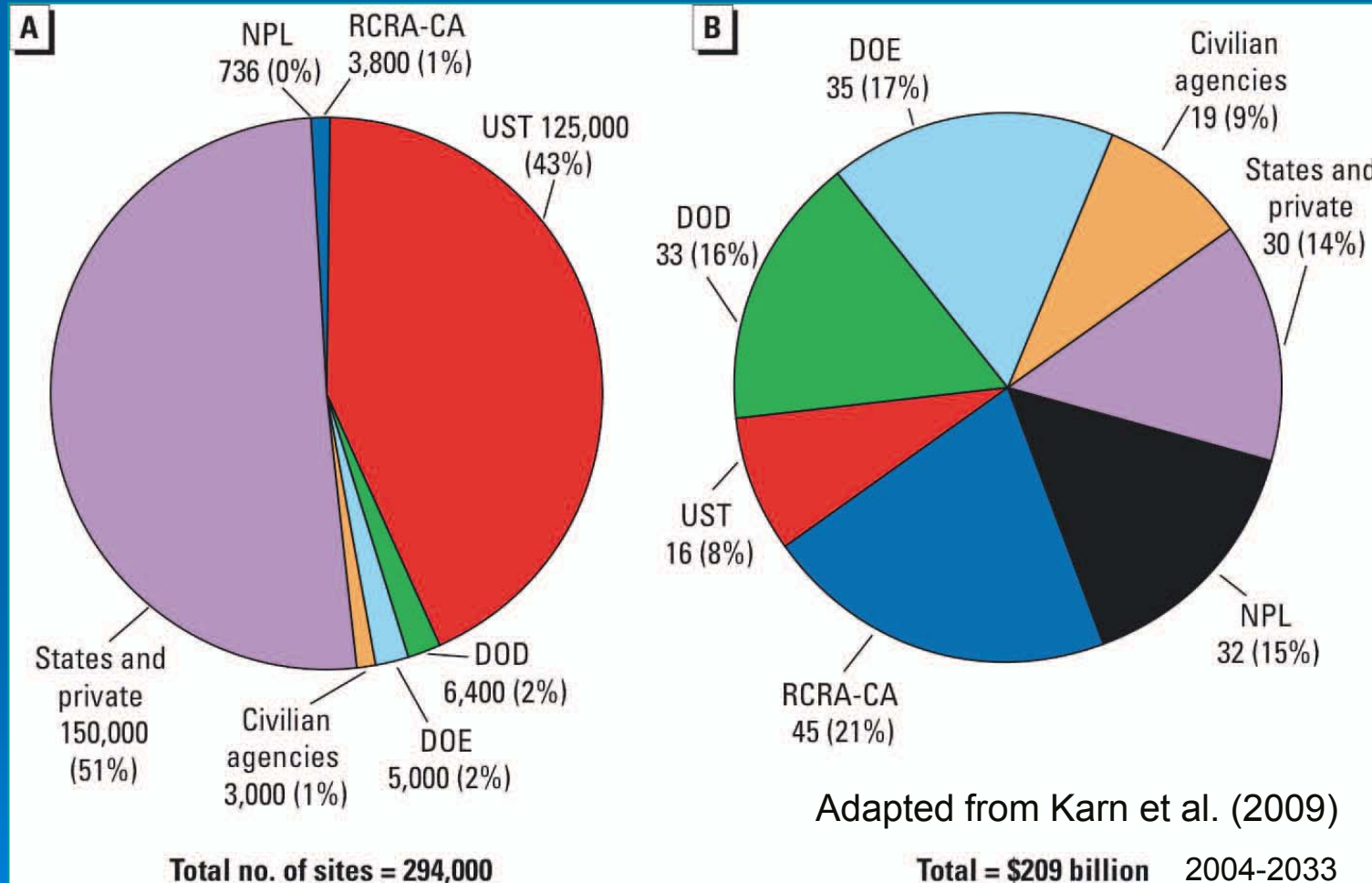
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# Outline

- i. Current state of the nZVI practice
- ii. Major challenges
- iii. Lindane, nZVI, and the need for QA/QC
- iv. Simplified QA/QC for nZVI
- v. Conclusions

# Setting the stage...

*"Better, cheaper, and faster site clean-ups"* USEPA (2004)



% in-situ RODs 1982-86 = 0; by 2005 = 31%

Upside potential of nanotech: reactivity & targeted delivery

# Factors favoring in-situ ZVI

- GW redox tends to be reducing
- Amenability of key contaminants
  - CHCs are relatively oxidized ( $\delta^+C-Cl^{\delta-}$ )
  - Many toxic metals are oxidized, e.g.  $CrO_4^{2-}$
- Synergies with anaerobic biodegradation
  - Splits water to form  $H_2$  and  $OH^-$
- Multiple treatment mechanisms
  - Abiotic reduction & sorption onto oxides
  - Formation of mixed Fe(II,III) minerals

# Development of nZVI

- 1996: Lehigh U., origins in PRB research
- Latter 1990s: bench-scale efficacy studies
  - CVOCs, PCBs, Cr(VI), etc.
- 2000: First field demonstration – Trenton, NJ
- Burgeoning interest since 2001
  - Research: synthesis, materials issues, fate and transport, human & ecotox
  - Applications: field-scale remediation, commercial availability

# Diversity of nZVI offerings

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

# nZVI-amenable reductates



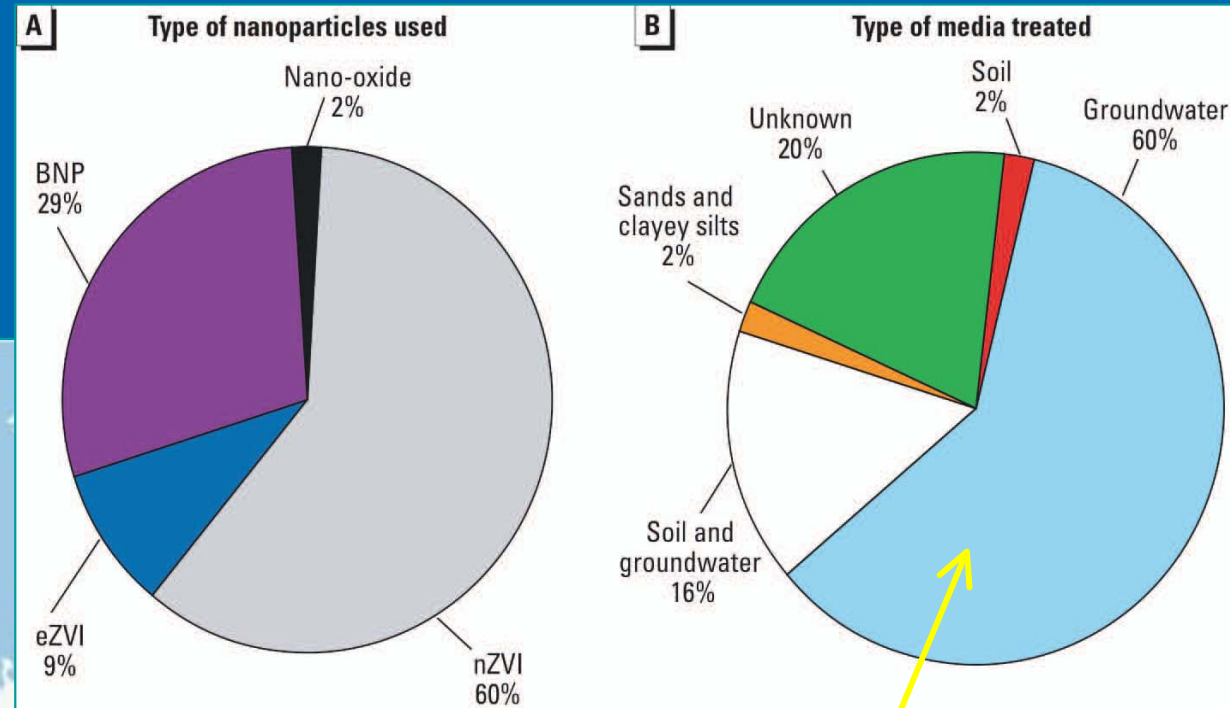
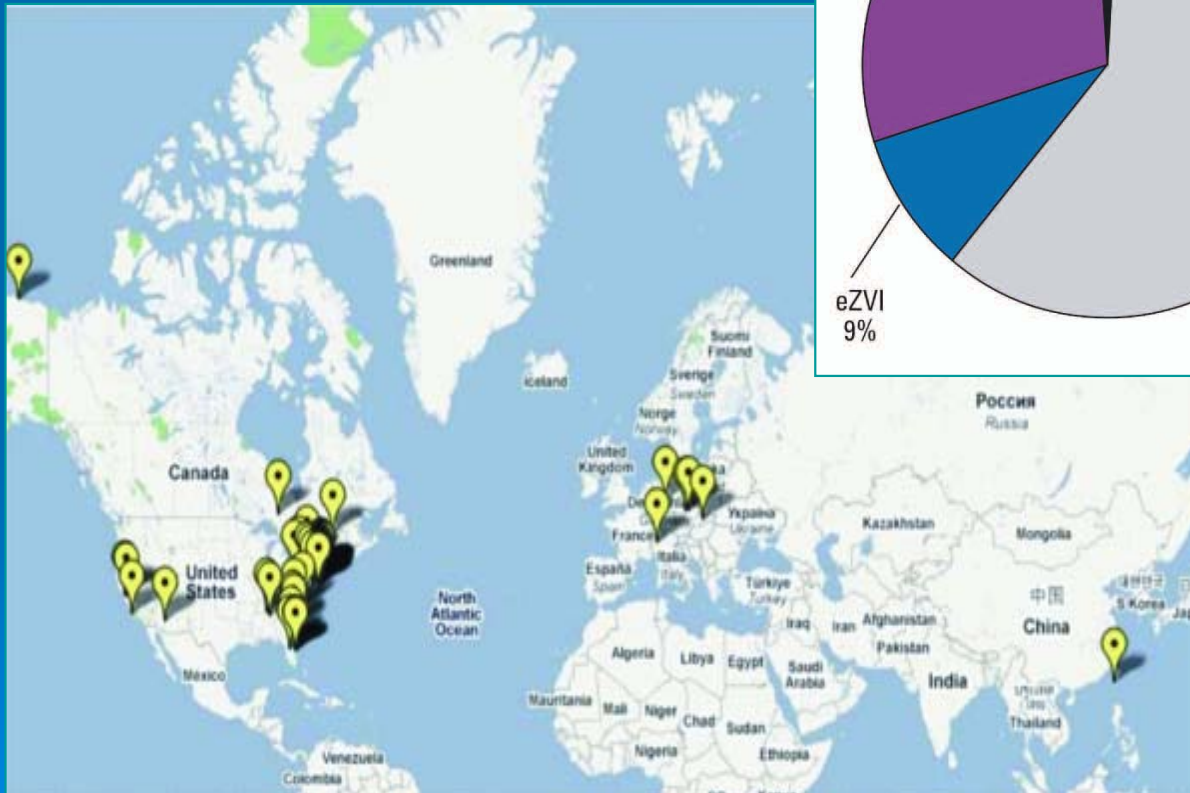
- Water
- Chlorinated aliphatics (CAHs)
  - TCE, CT
- Chlorinated aromatics
  - Chlorobenzenes, PCBs
- Pesticides/herbicides
  - DDT, Lindane
- Toxic metals
  - Cr(VI), Pb(II)
- Key anions
  - As(III,V),  $\text{ClO}_4^-$
  - Radionuclides (U, Te)

# nZVI issues to consider

- Performance vs. cost
  - Site specific dosing (typically 5-20 g/L)
  - ~\$30/lb vs. ~\$1-10/lb for mZVI
- Delivery issues
  - Hydrogeology, want  $K > 10^{-4}$
  - Injection well(s), recirc. loops, transects of borings
- Treatment objectives
  - Source areas (DNAPL) vs. dissolved-phase plumes
  - Proximity of receptors
- Regulatory issues
  - Permit-by-rule

# Snapshot of ZVI in remediation (2008)

- 44 Field applications
- >90% [CAH]<sub>0</sub> > 1 mg/L
- None are complete



39% PCE, 84% TCE  
55% c-DCE, 27% VC

# Major hurdles facing the technology

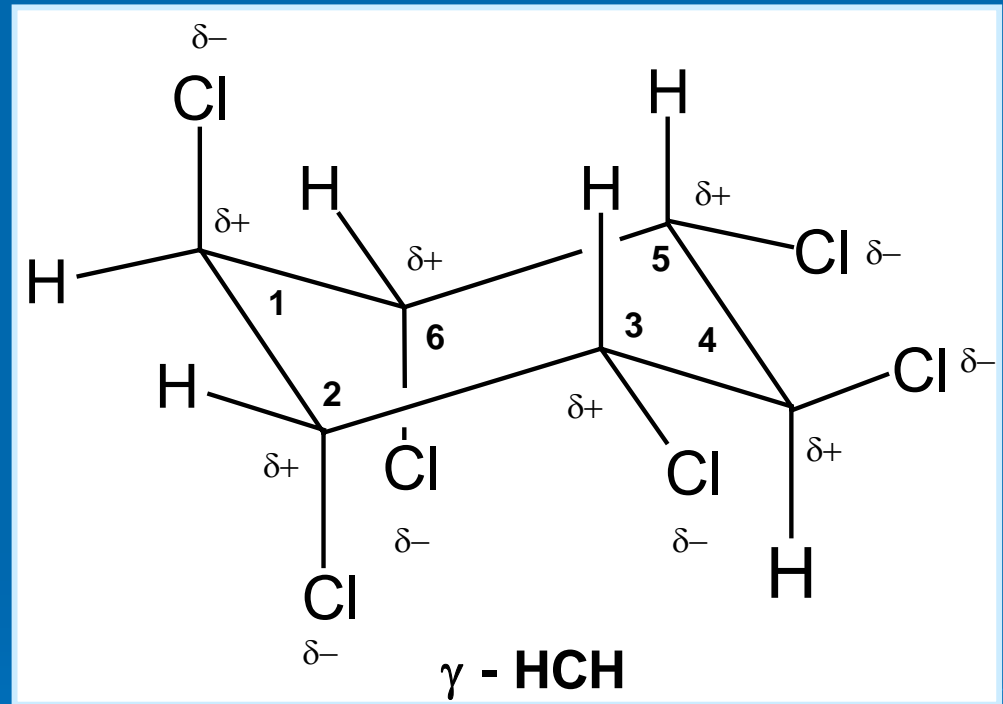
- Still relatively expensive
- Mixed track record of performance
- User selection & regulator reservations
- Subsurface mobility
- Human exposure & toxicological concerns
- **nZVI variability – lack of QA/QC**

# Sources of nZVI variability

- Multiple vendors
  - Variety of nZVI products
- Different synthetic methods
  - Chemical and physical
- Intrinsic nZVI reactivity
  - Properties change over time
  - Storage prior to use
  - Implications for contaminants

# Lindane as test case

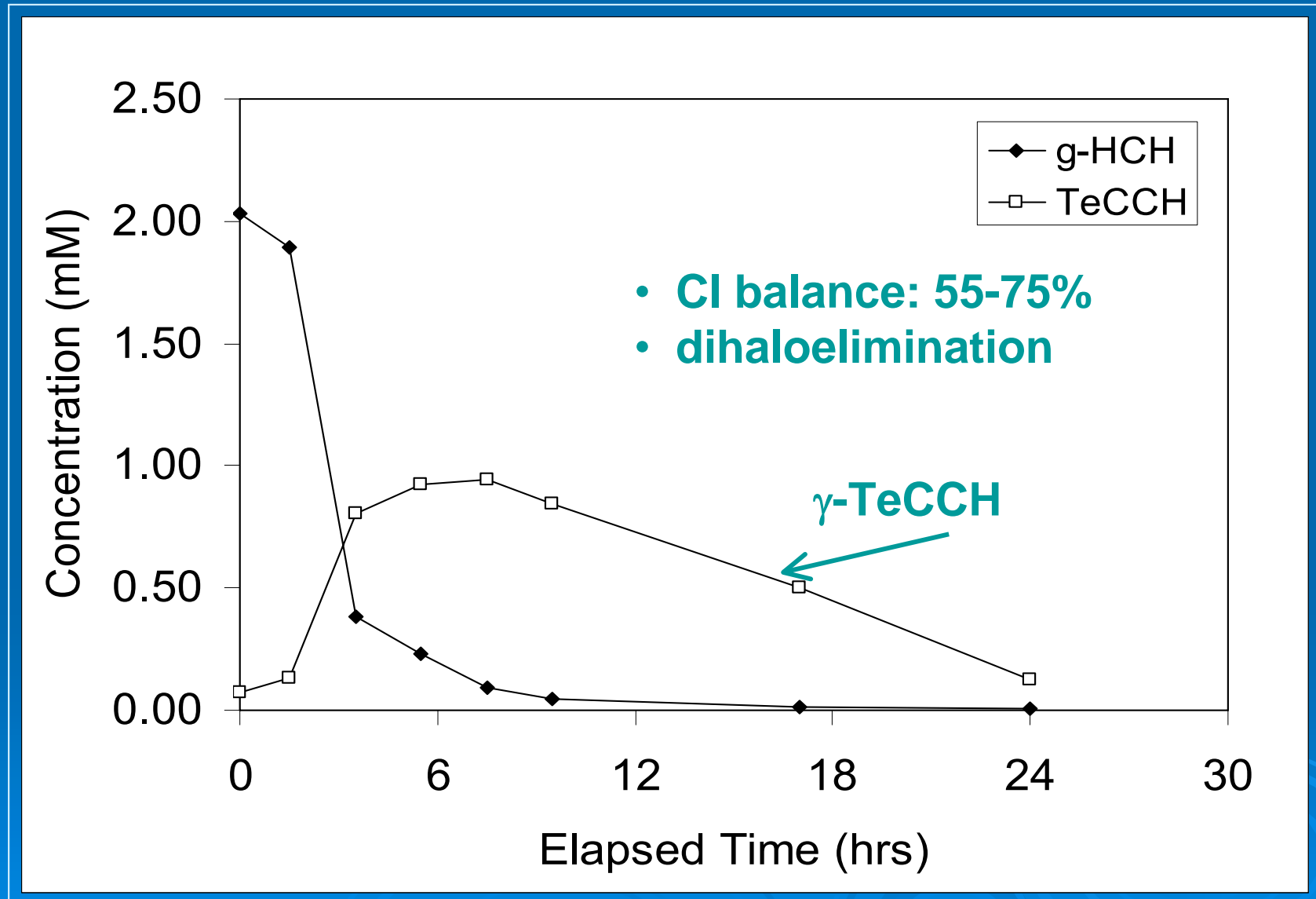
- Org-chlorine pesticide
  - 10MM tons tech HCH used globally from the 1940s into the 1990s
  - Relatively recalcitrant
- Capable of multiple degradation pathways
  - Dehydrohalogenation
  - Dihaloelimination



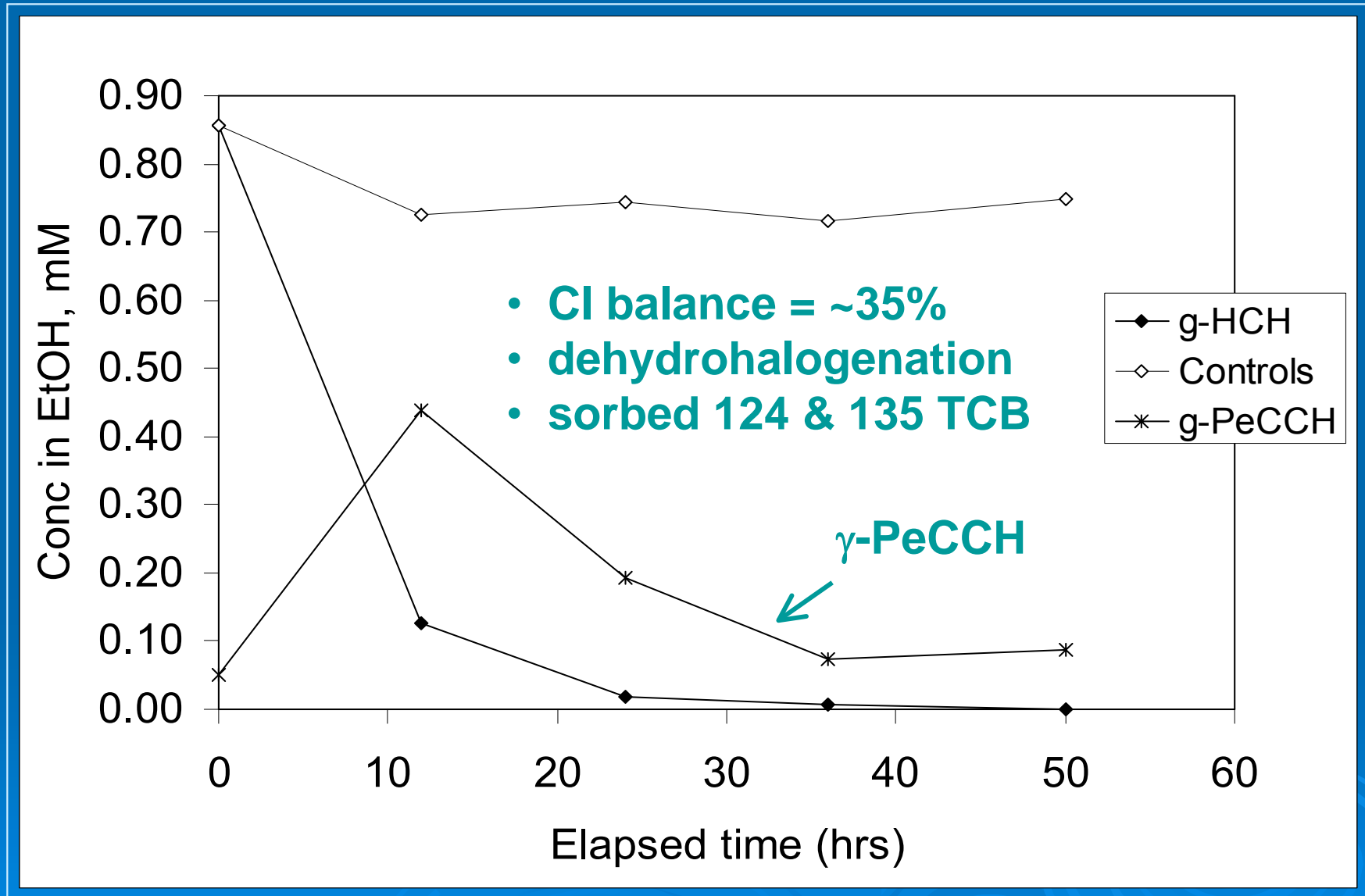
# nZVI-mediated degradation of lindane

- Testing with two types of nZVI
  - Type II ( $\text{SO}_4^{2-}$ ), 70-80 nm
  - Type III ( $\text{SO}_4^{2-}$ ), <50 nm
- $[\gamma\text{-HCH}]_0 \sim 300\text{-}600 \text{ mg/L}$ 
  - Studies in 95% EtOH
- nZVI: 9.4-26.5 g/L

# Results with Type II nZVI



# Results with Type III nZVI



# nZV QA/QC – Major data gaps

- Bench-scale efficacy  $\neq$  field success
- How do you know if the nZVI is any good?
  - Minimal product lifecycle analyses
  - Variable mfg methods and storage periods
- What performance or quality data is needed from vendor?
- Need more than the MSDS!

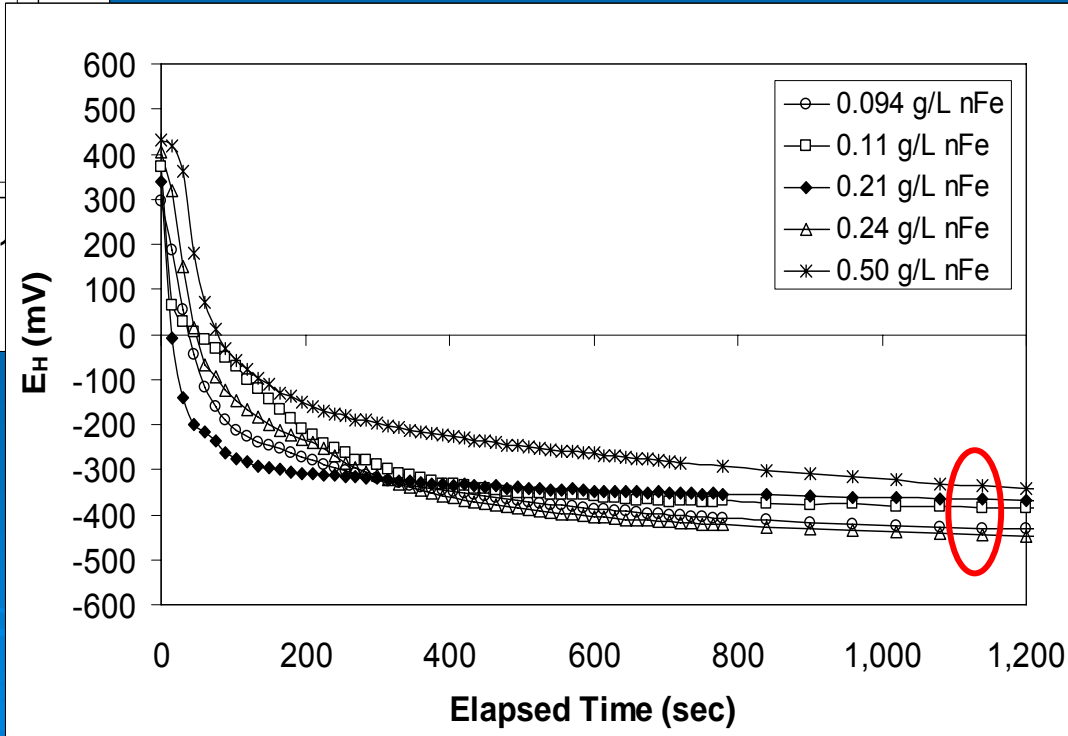
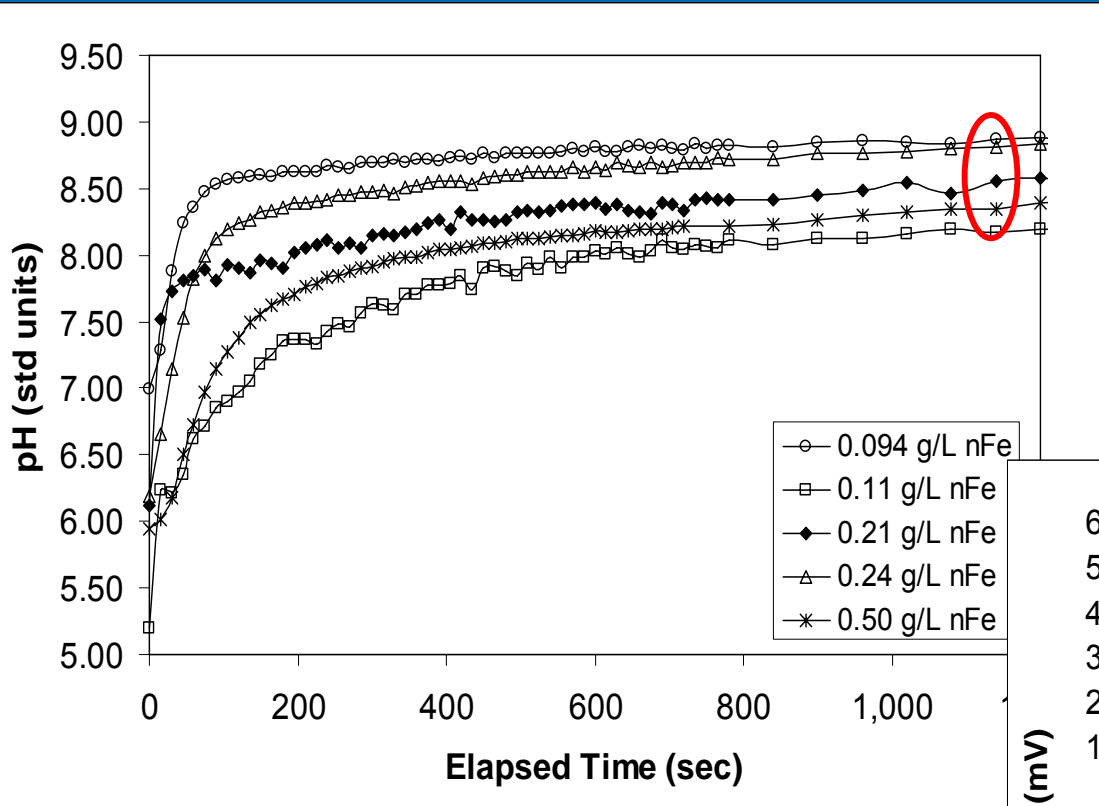
# Potential QA/QC parameters

- pH/ORP profile
- Particle size distribution (PSD)
- Specific surface area (SSA)
- Zeta potential ( $\zeta$ ) & Isoelectric point (IEP)
- Batch reactivity test

*QA/QC should be low cost, rapid, and easy to develop*

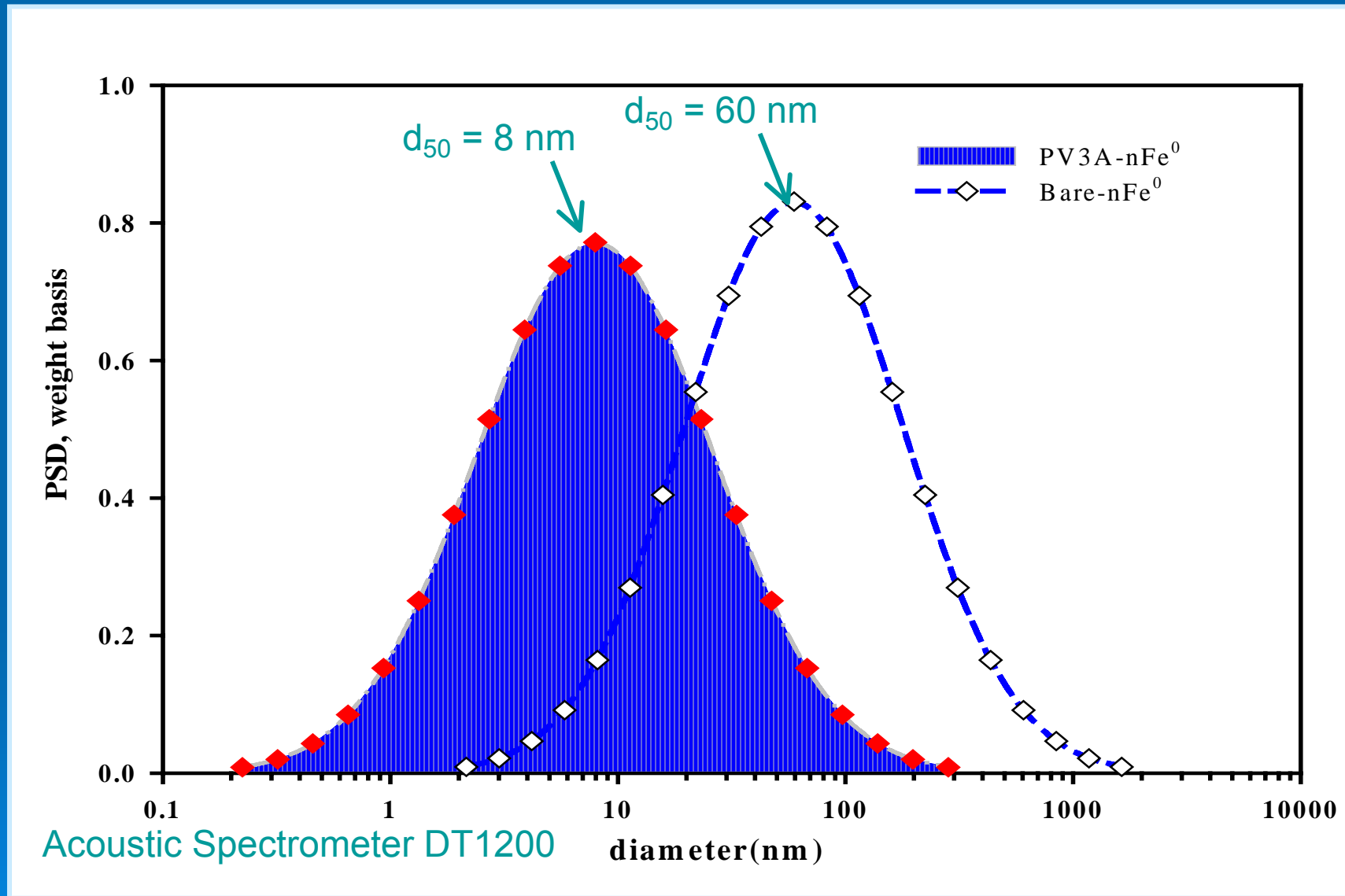
# pH-ORP profile

*If your nZVI doesn't behave like this, you may have problems in the field!*

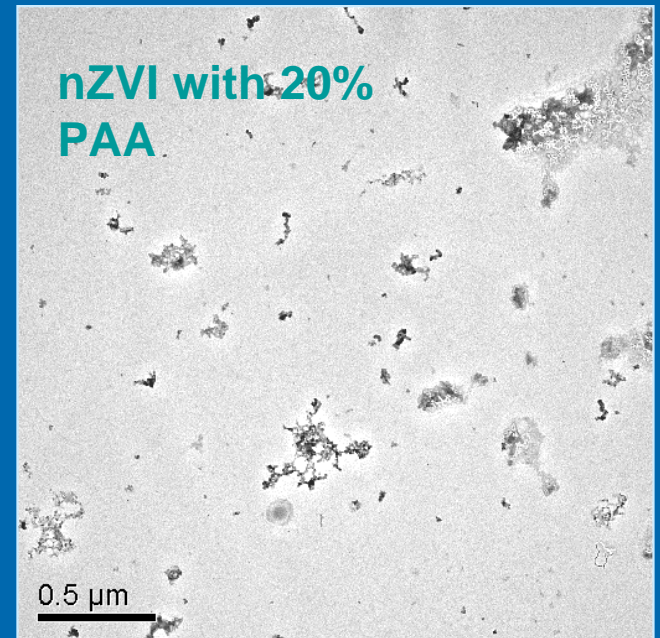
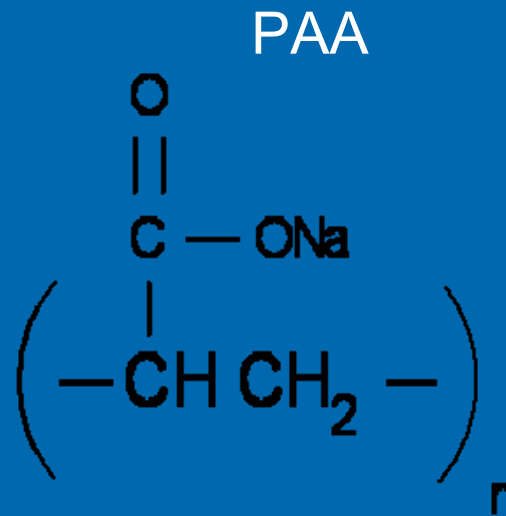
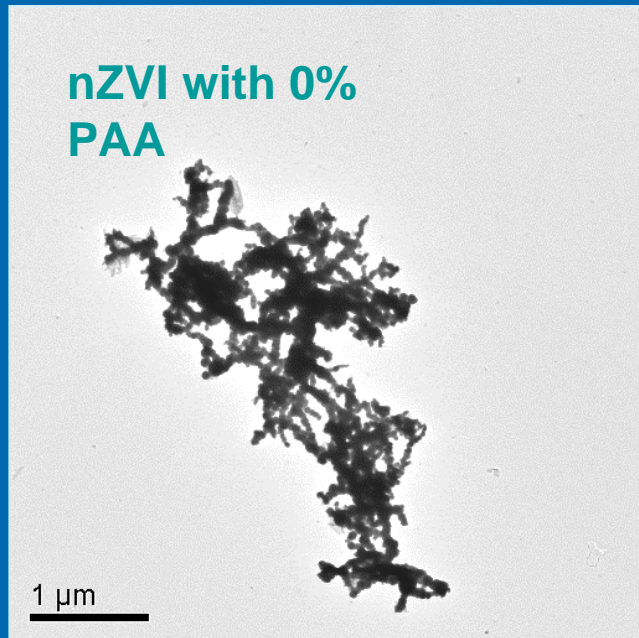


- pH  $\Delta$  = incr. >1 std units
- ORP  $\Delta$  = decr. >500 mV

# Particle Size Distribution (PSD) Sun, 2006



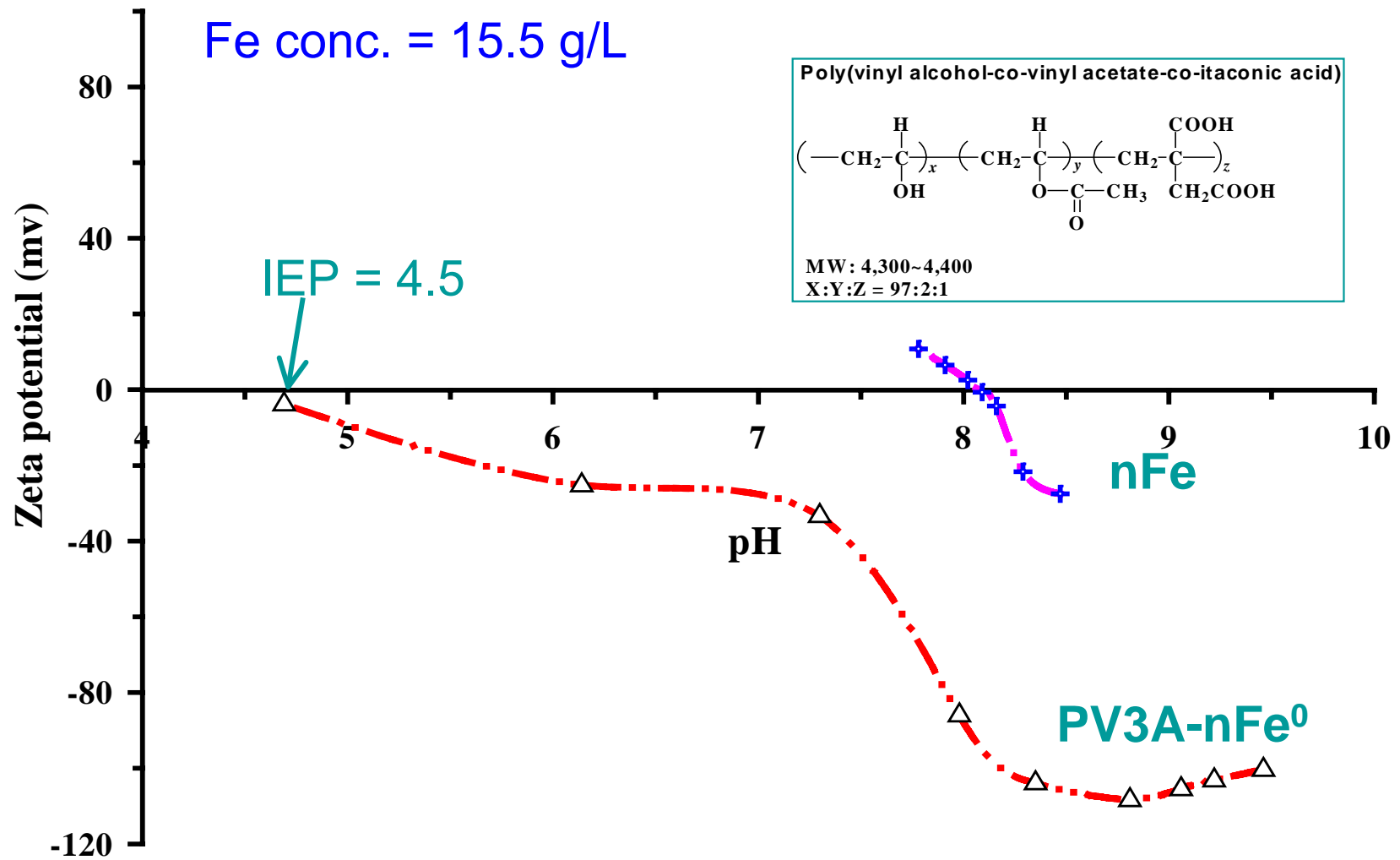
# Specific Surface Area (SSA)



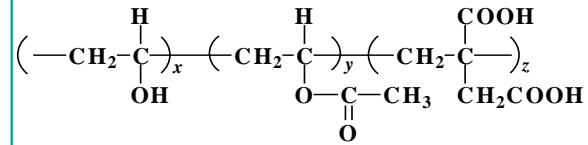
- SSA for “plain” nZVI  $\sim 35 \text{ m}^2/\text{g}$
- Commercial surface area analyzers, BET
- Surface modifiers like PAA increase the SSA, may impact reactivity

# Zeta potential ( $\zeta$ )/ISE

Fe conc. = 15.5 g/L



Poly(vinyl alcohol-co-vinyl acetate-co-itaconic acid)



MW: 4,300~4,400

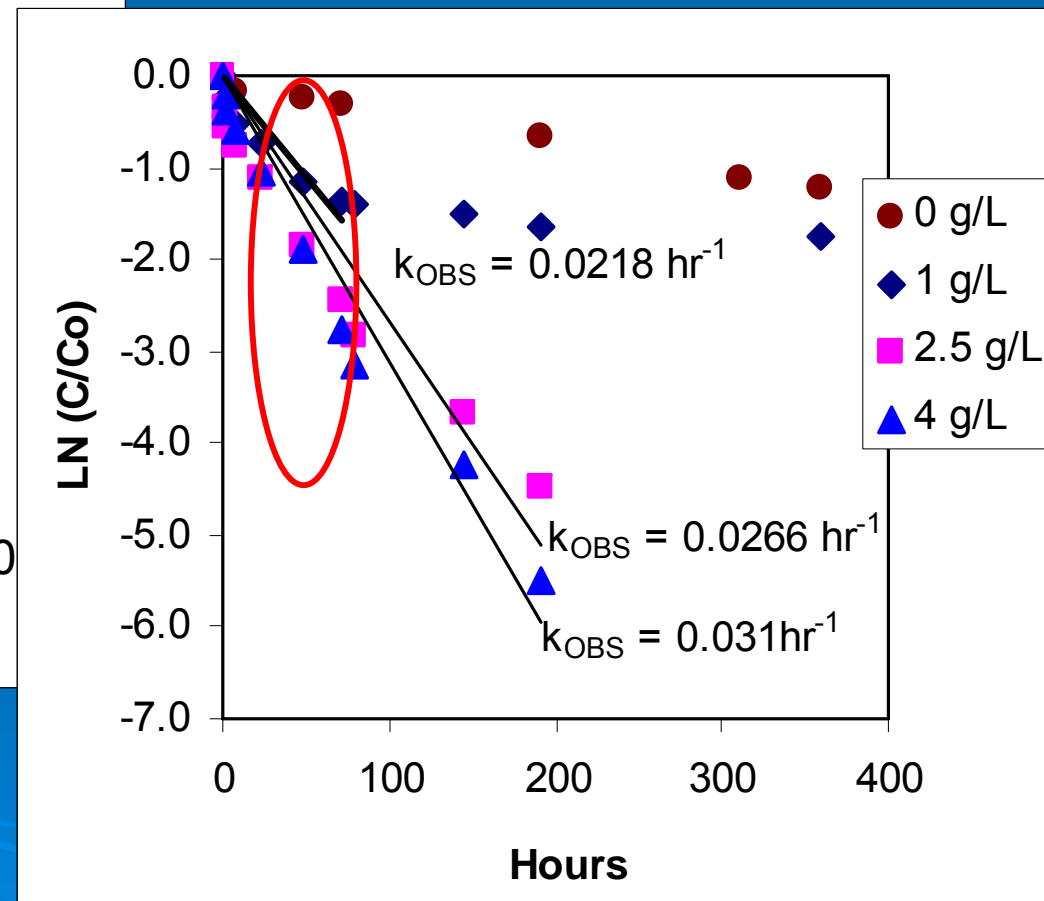
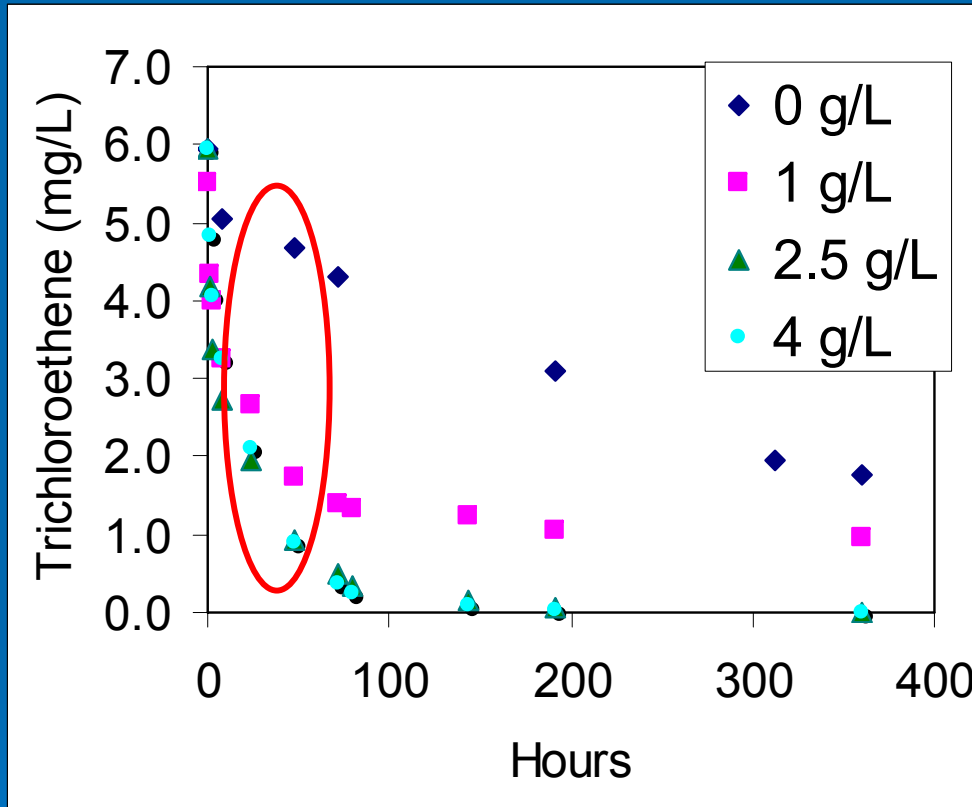
X:Y:Z = 97:2:1

Malvern Zetasizer 3000HSA PCS: PSD,  $\zeta$

# Batch Reactivity Test – TCE

Andrews AFB Site 282 Groundwater

- nZVI dose effects & kinetics
- Reactivity & degradation prods



- 24-48 hr batch test
- 1 mg/L TCE, 1-10 g/L nZVI

# Other important data

- “Born-on” dating for nZVI batches/lots
- Details regarding manufacturing method
  - Chemical synthesis vs. size reduction
  - Presence of impurities
- Storage details
  - Is material dry/wet?
  - Stored under water, EtOH, or a glycol?
  - Duration of storage prior to use?

# Conclusions

- nZVI is a great complementary technology
  - Best for hot-spots or source areas
  - Teams exceptionally well with anaerobic bioprocesses
- Despite promise, not yet a prime-time player
  - +/- 50 field sites worldwide – none 100% cleaned up
  - Cost, fate/transport issues, user/regulator reservations
  - nZVI can be highly variable: material & performance
- Need for standard nZVI QA/QC
  - pH/ORP, PSD, SSA, ZP/ISE, TCE test
  - Born-on dating, mfg and storage details

# Questions?

