# New Tools for Managing Chlorinated Solvents Sites: Concepts and Technologies

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Oregon Health & Science University

SERDP • ESTCP
SYMPOSIUM
2018 | Enhancing DoD's Mission Effectiveness

# Session Theme: Tools

- Tools for Site Management and Remediation
  - *John Wilson*: “Expand the *toolkit* to technologies, or combinations of technologies that remove…”
  - *Rob Hinchee*: “Do we have the *tools* we need? Do we know how to use them?”
  - SERDP/ESTCP *Workshop* on Chlorinated Solvents in GW (2018) Seattle, WA
  - SERDP *SON* on Plume Characterization for Transition Assessments (ERSON-20-C4)
- Toolkit Function
  - Manage (remediate) more sites better, faster, cheaper, etc.
  - Compete with others (companies and individuals)

tools
sites
site
remediation
processes
research
technology
information
approaches
needed
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long-term
guidance
technologies
contaminants
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management
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SERDP
CSMs
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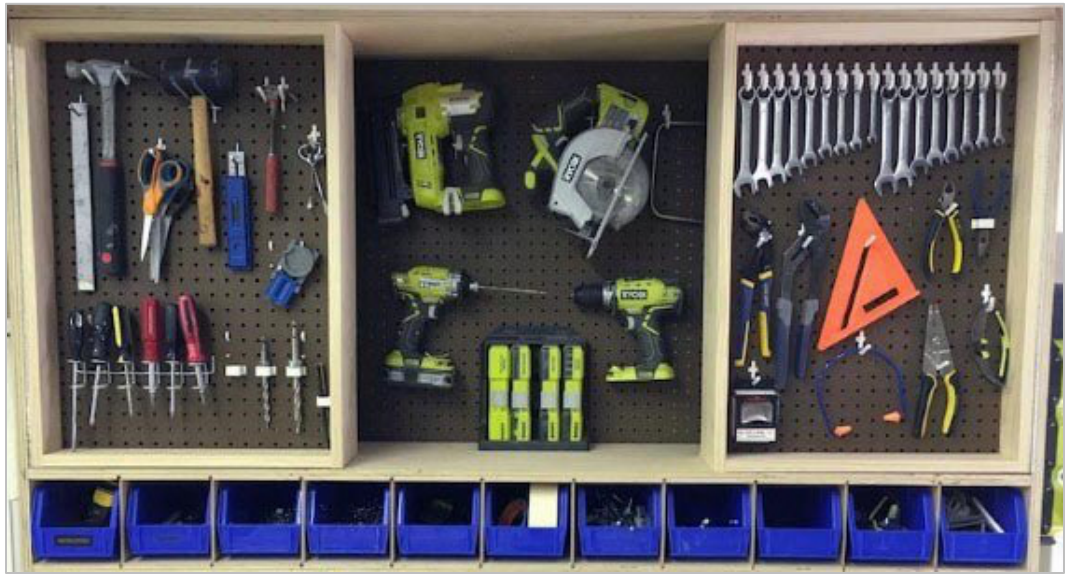
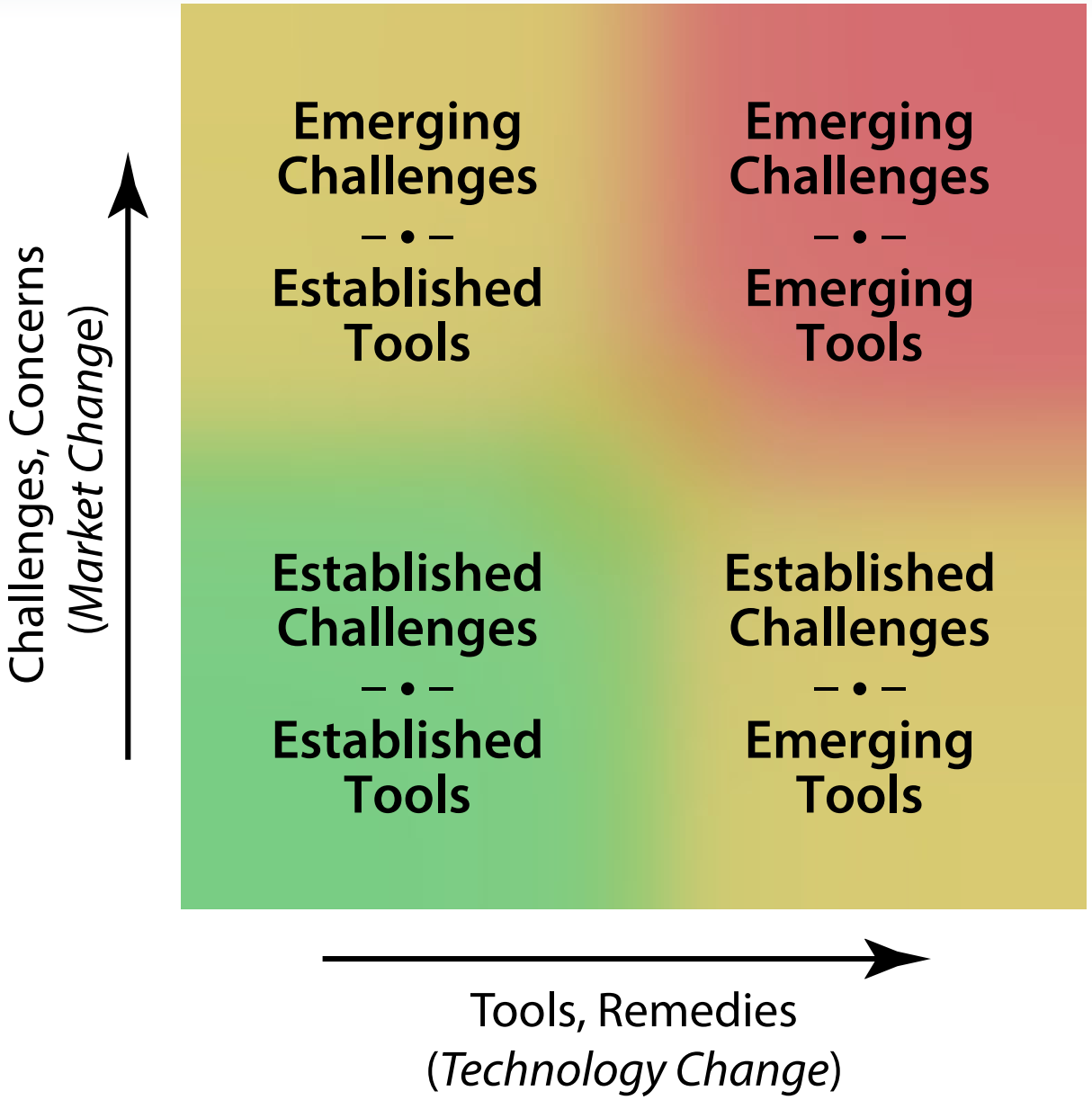
# Toolkit Characteristics

- Toolkit Optimization
  - Not big, but complete and balanced
  - Ready: organized and understood
  - Best available: proven and *new*



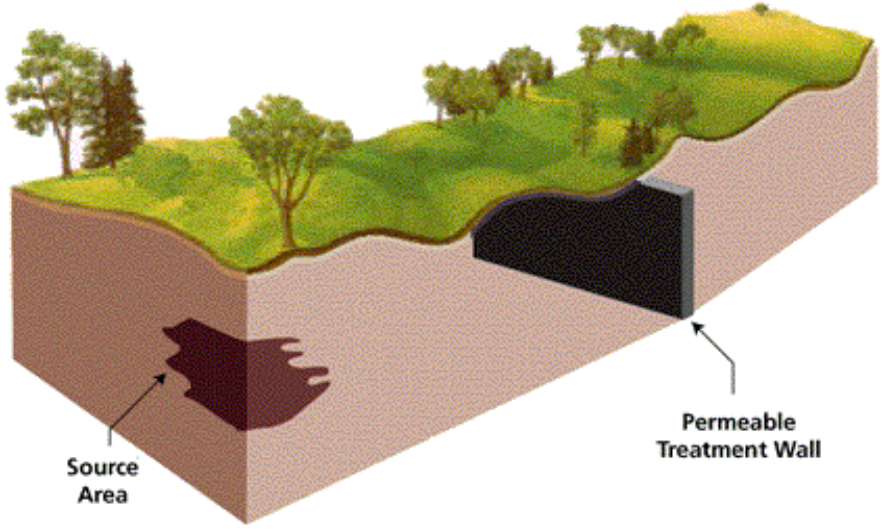
# Toolkit Characteristics

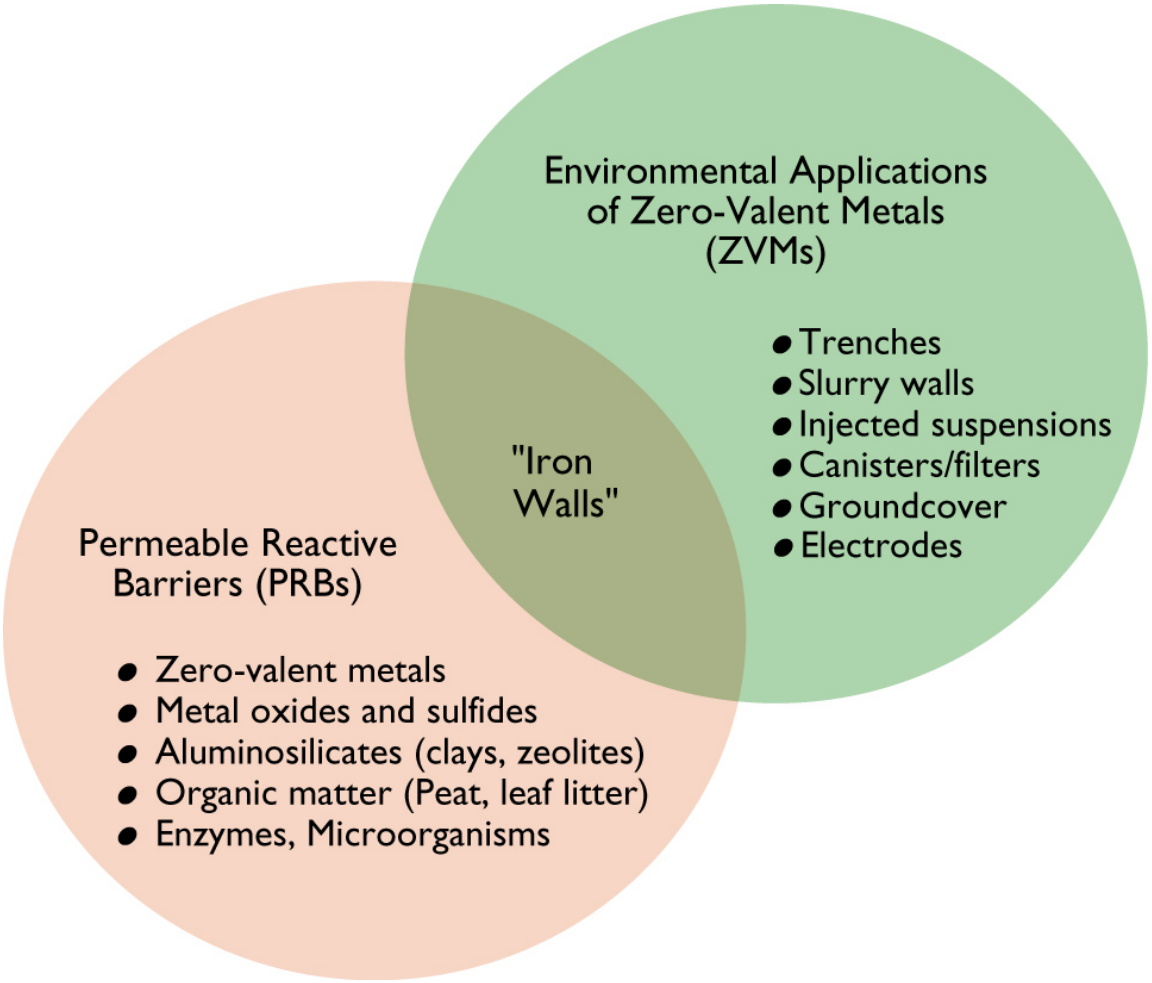
- Toolkit Optimization
  - Not big, but complete and balanced
  - Ready: organized and understood
  - Best available: proven and *new*
- Toolkit Change
  - Tools/remedies change
    - Established, new, emerging
  - Challenges/concerns change
    - Contaminants and priorities
- Tools/Toolkits are Transferable
  - Across quadrant interfaces
  - Among colleagues



# Established Tools (Technological): **ZVI PRBs**

- Zerovalent Iron (ZVI)
  - Gillham and O'Hannesin (1994)
- Permeable Reactive Barriers (PRBs)
  - Blowes, Cherry, et al. (1995)
- Envirometal Technologies Inc. (ETI)
  - http://www.eti.ca (1992)

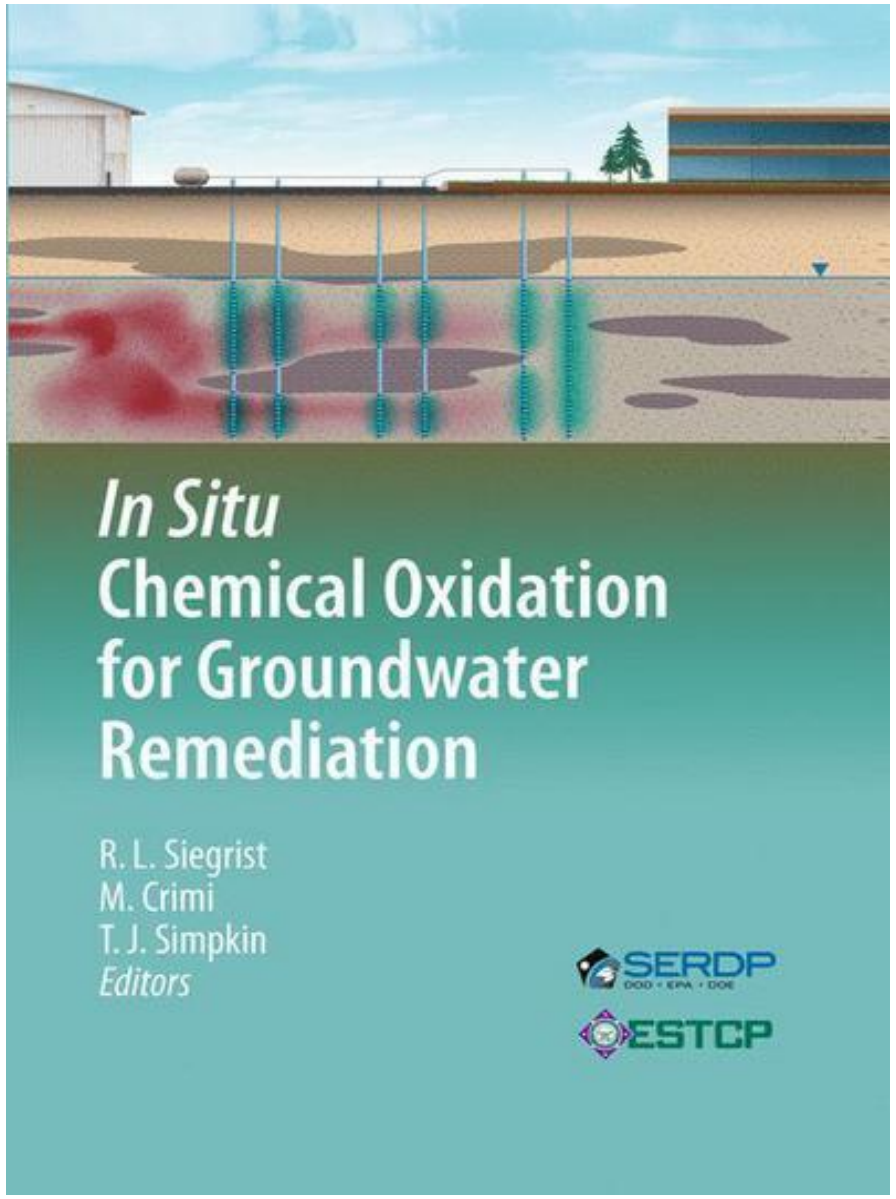



http://cgr.ieh.ohsu.edu/iron/ (2005)

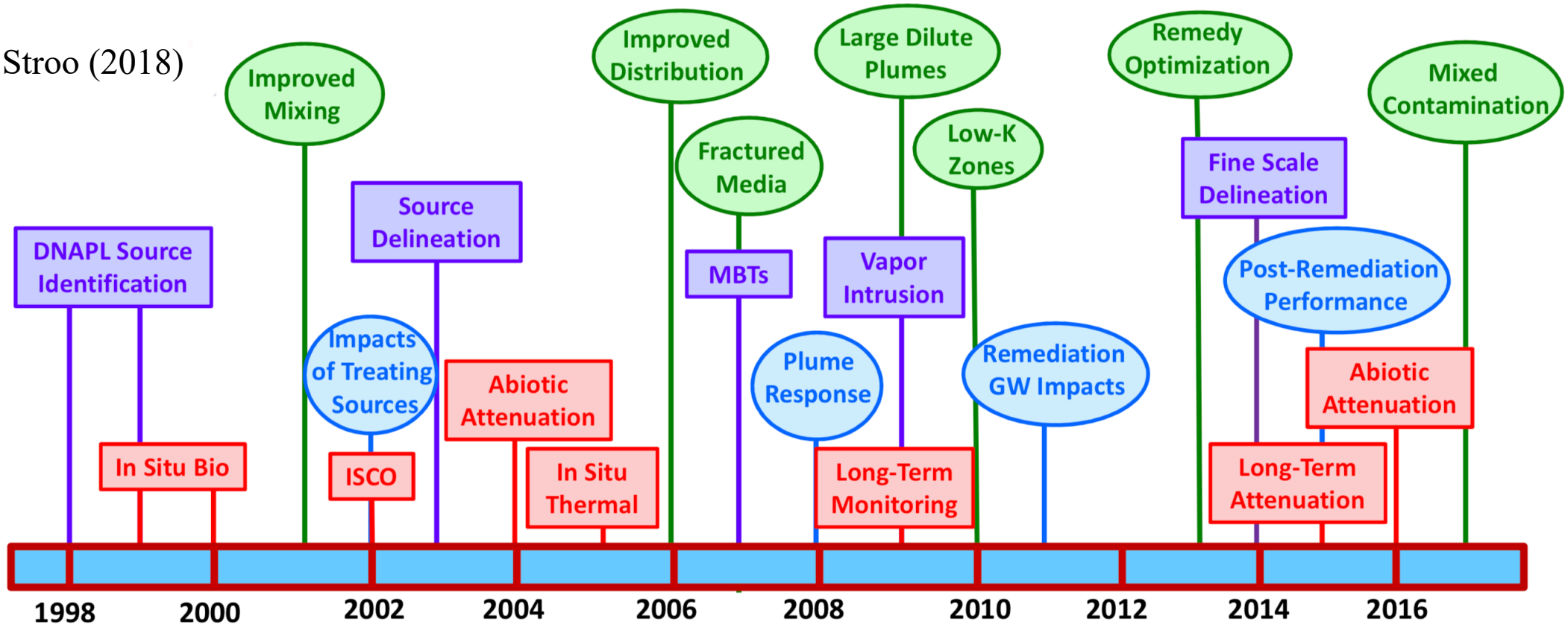
# Established Tools (Technological): **Chemical Oxidation**

- Peroxide/Fenton
  - Brown 1984 (FMC Patent)
  - Vella 1993, Watts 1993, Siegrist 1995
- Permanganate
  - Early 1990's: Vella, Siegrist, Farquhar,
  - Later 1990's: Schwartz, Hoag, Brown
- Persulfate
  - Early 2000's: Hoag, Liang, Block/Brown
  - Late 2000's: Tratnyek etc.
- "ISCO"
  - 1990's Various
  - 2001 Volumes by Siegrist and ITRC
  - 2011 SERDP/ESTCP Book



# **Timeline of Tool Development** (by SERDP SONs)

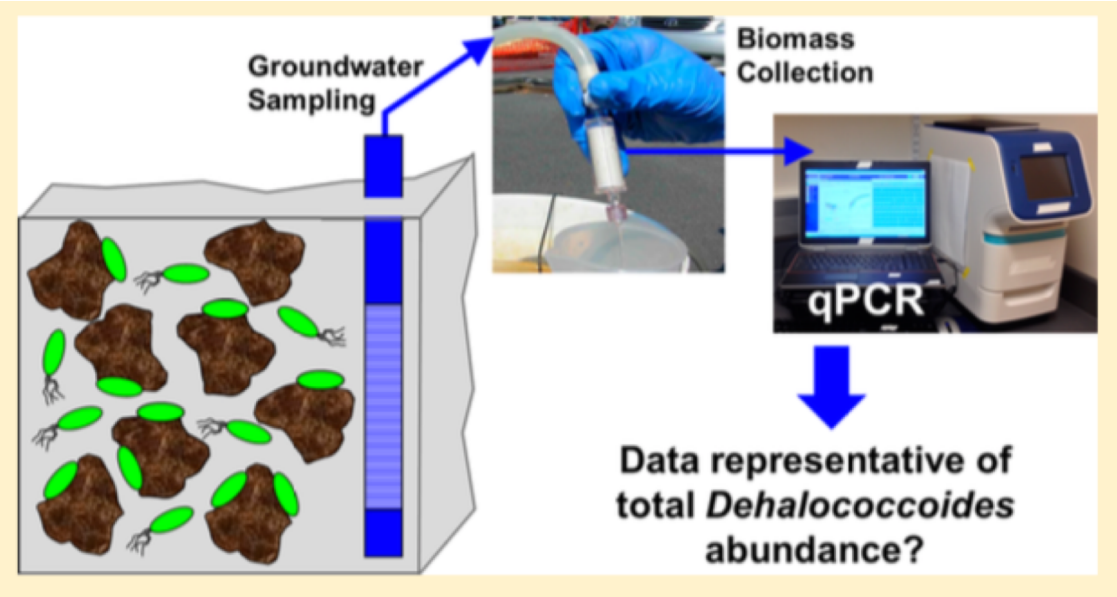
Hans Stroo (2018)




Tools: Conceptual | Tools: Technologies

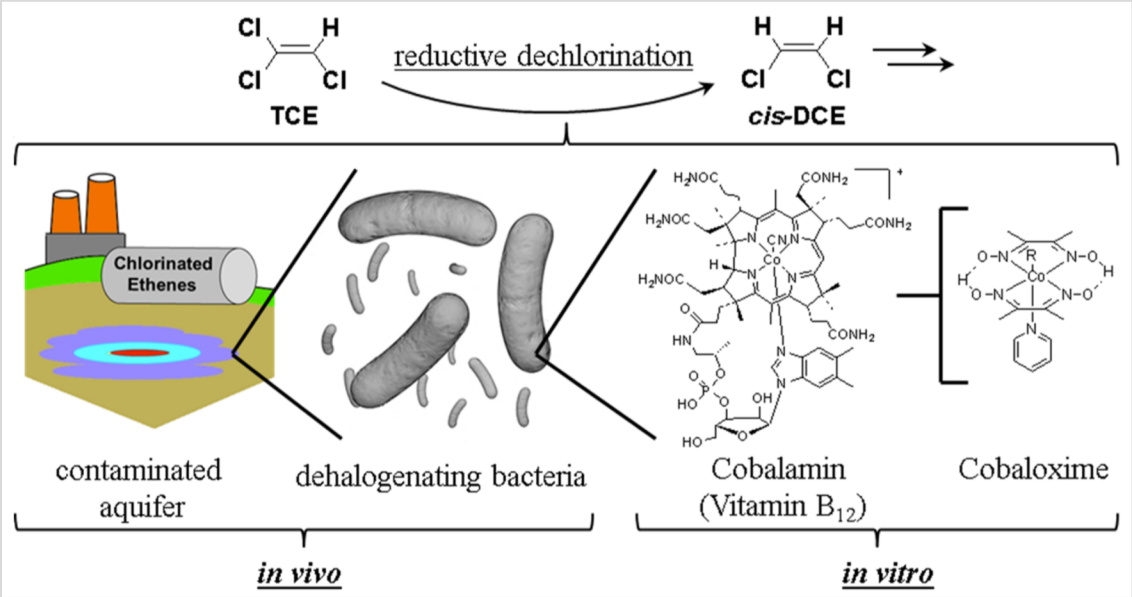
# **Other New Tools** (Technological/Conceptual)

- Molecular Biological Tools (MBTs)
  - Major et al. (2002) semiquantitative PCR on KB-1 augmented field site
  - Lendvay, Loeffler et al. (2003) qPCR on in situ Biobarriers
  - SOPs for qPCR in SERDP ER-1561




Capiro et al. (2014)

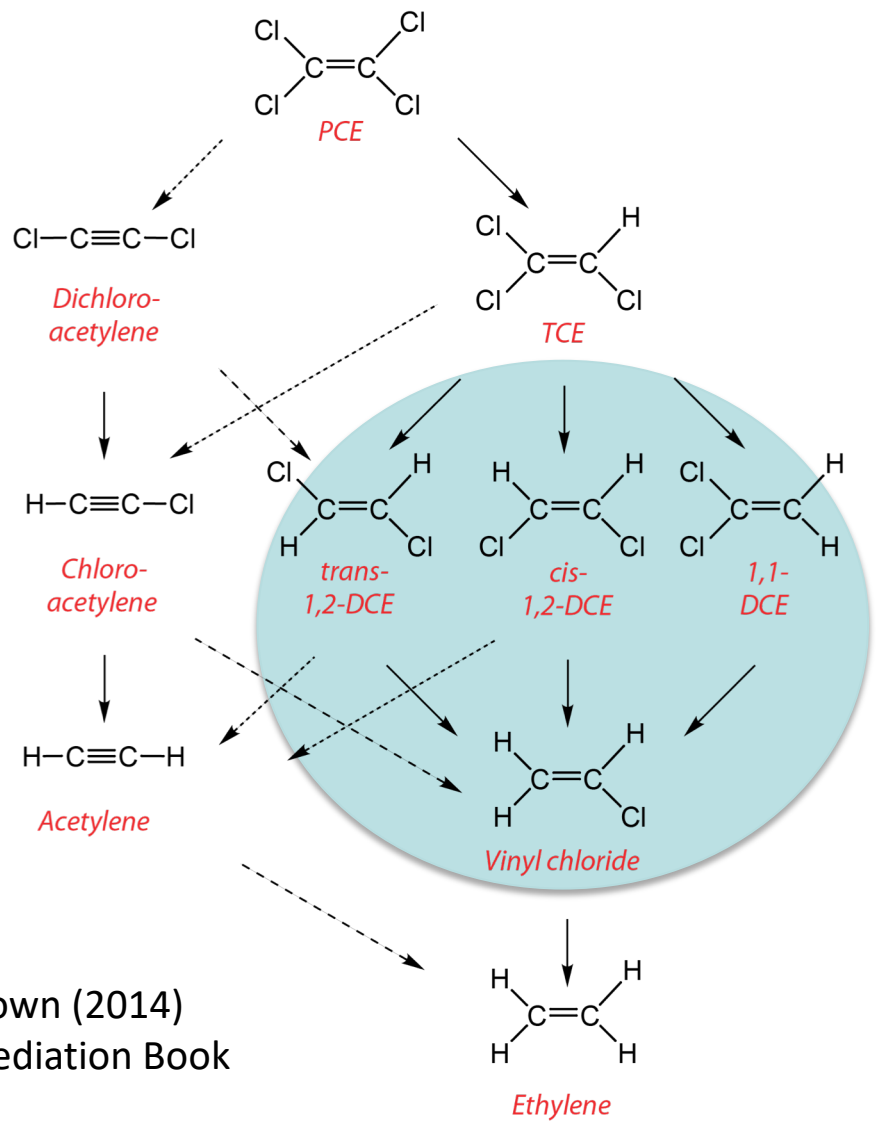
- Compound-Specific Stable Isotope Analysis (CSIA)
  - Aravena et al. (1999)
  - Slater, Sherwood-Lollar (2001)
  - Schwarzenbach: Elsner (2005), Hofstetter (2006)




Cretnik | Elsner (2013)

# New Tools (Conceptual): **Diagnostic Pathway/Product Branching**

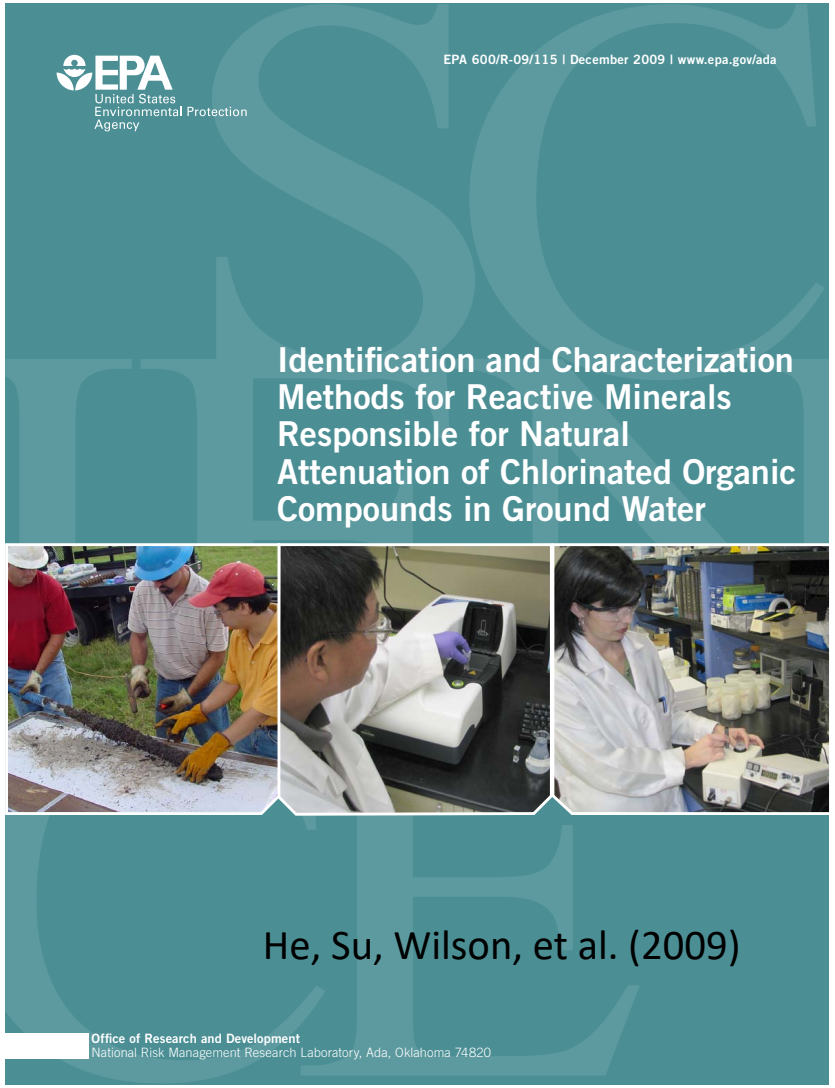
- Hydrogenolysis ($+1e^- +H^+ -Cl^-$)
  - Anaerobic *biodegradation* generally occurs by hydrogenolysis.
  - Sequential steps via *stall intermediates* (DCE, VC)
  - Solid arrows
- Reductive elimination ($+2e^- -2Cl^-$)
  - Anaerobic *abiotic natural attenuation* generally involves reductive elimination.
  - Bypasses stall intermediates
  - Dashed arrows




Tratnyek, Johnson, Lowry, Brown (2014)
SERDP/ESTCP Source Zone Remediation Book

# New Tools (Conceptual): **Abiotic Natural Attenuation**

- In Situ Chemical Reduction (ISCR)
  - Since mid 2000's
  - Analogous to ISCO
  - ZVI, nZVI, ISRM (Dithionite), etc.
  - In situ, biogeochemical reductive dechlorination (ISBGT, BiRD)
- Abiotic Natural Attenuation (ANA)
  - Late 2000's
  - Macalady (1986) "Abiotic reduction of contaminants…" J. Contam. Hydrol. 1(1): 1
  - Mackinawite, Green rust, Magnetite
  - Fe(II) sorbed to Fe(III) oxides
  - Oxidative ANA? Schaefer et al. (2018)

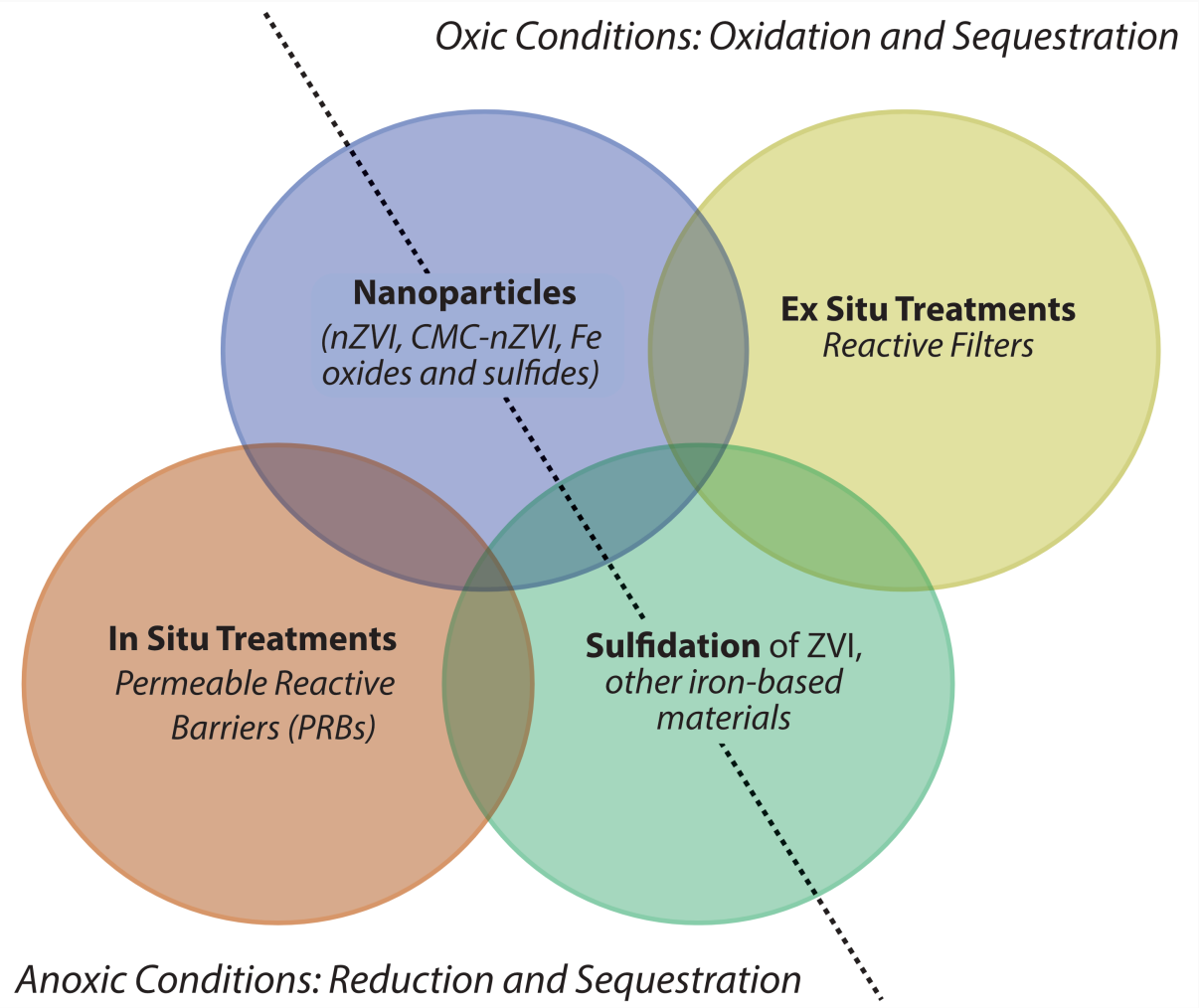



He, Su, Wilson, et al. (2009)

# New Tools (Technological): **Sulfidation**

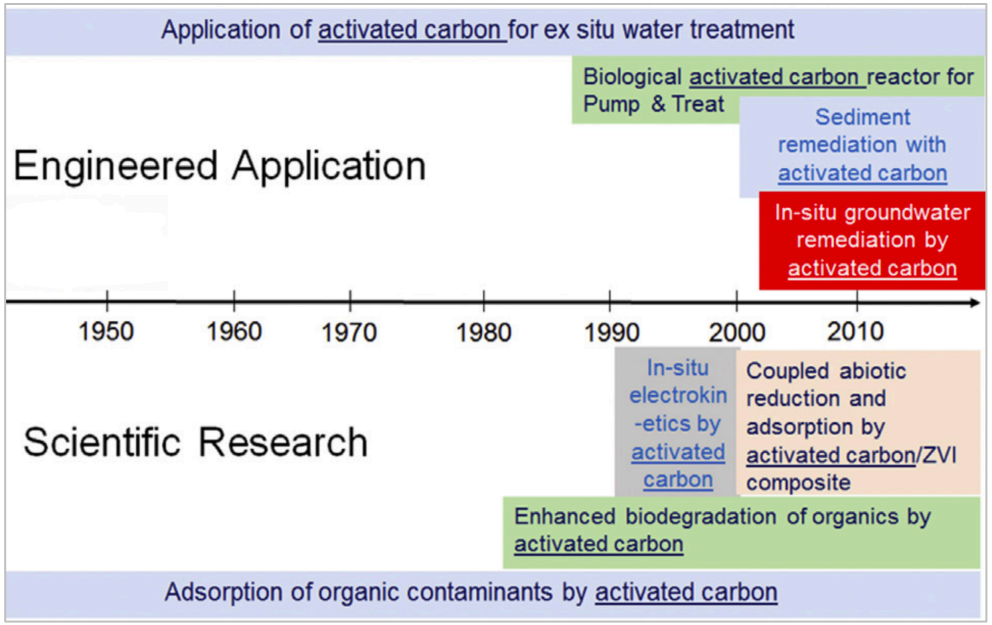
- Precursors to Sulfidation
  - S-impurities in ZVI (Wolfe, Lipczynska)
  - FeS minerals (Hayes, Reinhard, etc.)
- Benefits of Sulfidated ZVI
  - Contaminant reduction kinetics/products
  - Efficiency of CoC vs. water reduction
- Technology Transfer
  - Replaced bimetallic and nano ZVI in academic research
  - Already several vendors of sulfur modified ZVI
  - Vendors of other FeS amendments
  - Consultant Toolkits?

Fan, Tratnyek, et al. (2017) Env. Sci. Technol. 71: 13070-13085



# New Tools (Technological): **Black Carbon Amendments**

- Varieties of black carbon
  - Granular Activated Carbon (GAC)
  - Pyrogenic Carbonaceous Matter (PCM)
    - Includes AC, biochars, etc.
- Traditional Applications (ex situ)
  - Adsorption of contaminants
  - Support in biofilm reactors
- Established Applications (in situ)
  - Adsorption of sediment contaminants
  - GAC supported ZVI (micro-scale)
- Emerging Applications
  - Colloidal AC blends
  - PCMs modified for reactivity




Fan, Gilbert, Fox (2017) J. Env. Manag. 204: 793-803

| Product | Property | Target Contaminant | Degradation Pathway |
|---|---|---|---|
| BOS-100® | Granular AC (GAC) impregnated by ZVI | Chlorinated solvents | Abiotic reductive dechlorination |
| BOS-200® | Powder AC (PAC) mixed with nutrients, electron acceptors, and facultative bacteria mix | Petroleum Hydrocarbons | Aerobic and anaerobic bioaugmentation |
| CAT-100® | BOS-100® and reductive dechlorination bacterial strains | Chlorinated solvents | Abiotic and biotic reductive dechlorination |
| COGAC® | GAC or PAC mixed with calcium peroxide, and sodium persulfate | Chlorinated solvents or petroleum hydrocarbons | Chemical oxidation, aerobic and anaerobic biostimulation |
| PlumeStop® | Colloidal AC suspension with an organic stabilizer, co-applied with hydrogen or oxygen release compounds, and/or corresponding bacterial strains | Chlorinated solvents or petroleum hydrocarbons | Enhanced biotic reductive dechlorination for chlorinated solvents and aerobic biodegradation for petroleum hydrocarbons |
| Carbo-Iron® | Colloidal AC impregnated with ZVI | Chlorinated solvents | Abiotic reductive dechlorination |

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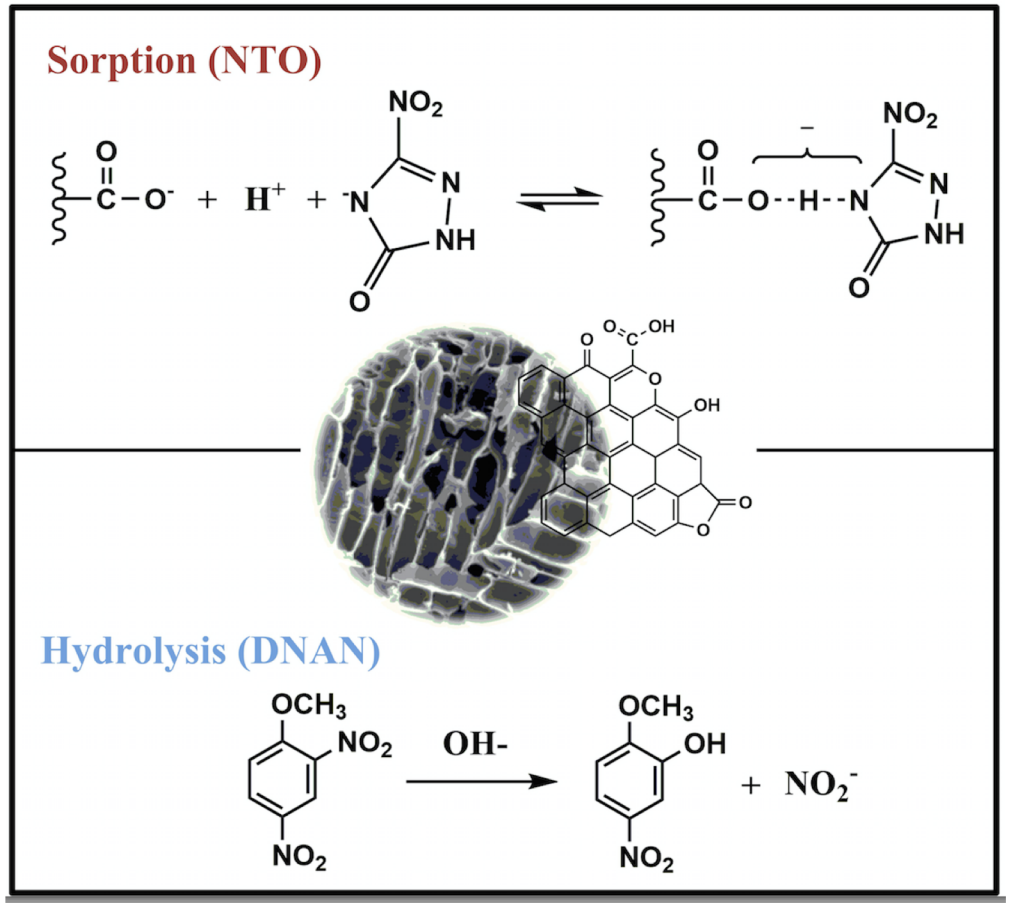
ER19-1239: "Optimizing Carbon Amendments that Simultaneously Adsorb and Transform Legacy and Insensitive High Explosives" Wenqing Xu (Villanova), Joe Pignatello (CAES), Paul Tratnyek (OHSU), Eric Bylaska, (PNNL), Sam Beal (ERDC-CRREL)



# Future Tools (Conceptual): **Reactive Mineral Intermediates**

- Hypothesis:
  - Active precipitation leads to
  - Metastable phases that serve as
  - Reactive mineral intermediates (**RMIs**), which may cause
  - Abiotic natural attenuation
- Characteristics of RMIs:
  - Formed *in situ* +
  - Highly reactive =
  - Metastable intermediates
  - Transient or steady-state
  - Can't be isolated
  - Can degrade contaminants

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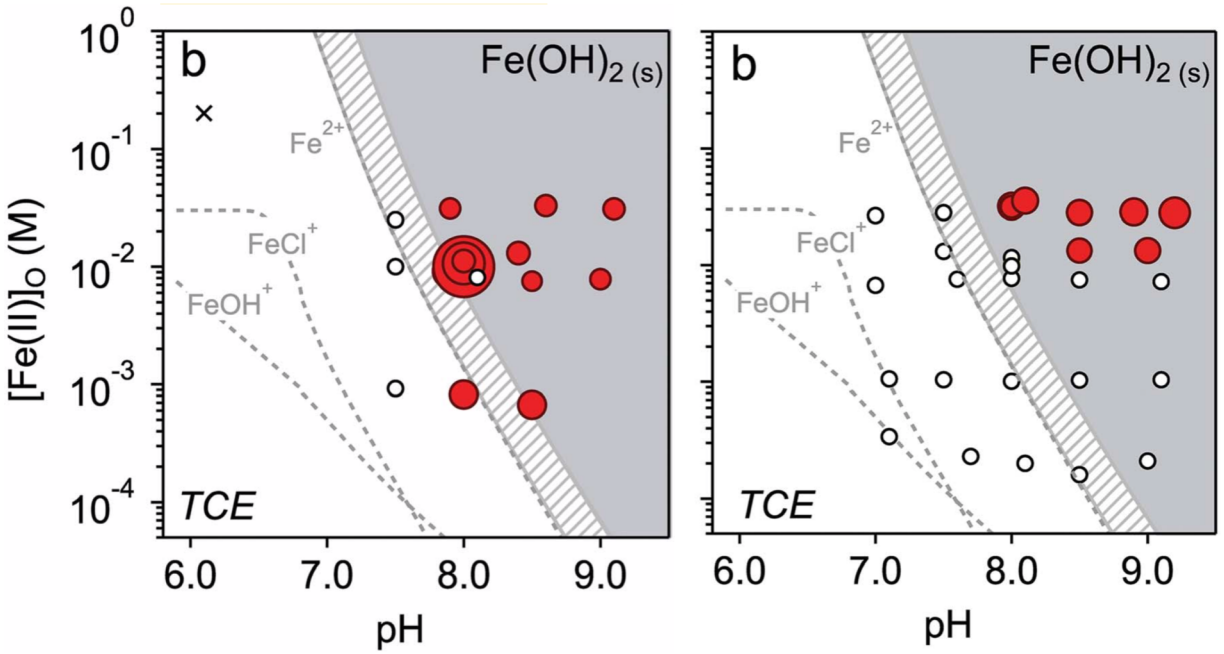
**Reduction of PCE and TCE by magnetite revisited†**

Johnathan D. Culpepper,[a] Michelle M. Scherer,[a] Thomas C. Robinson,[a] Anke Neumann,[b] David Cwiertny[a] and Drew E. Latta[*a]



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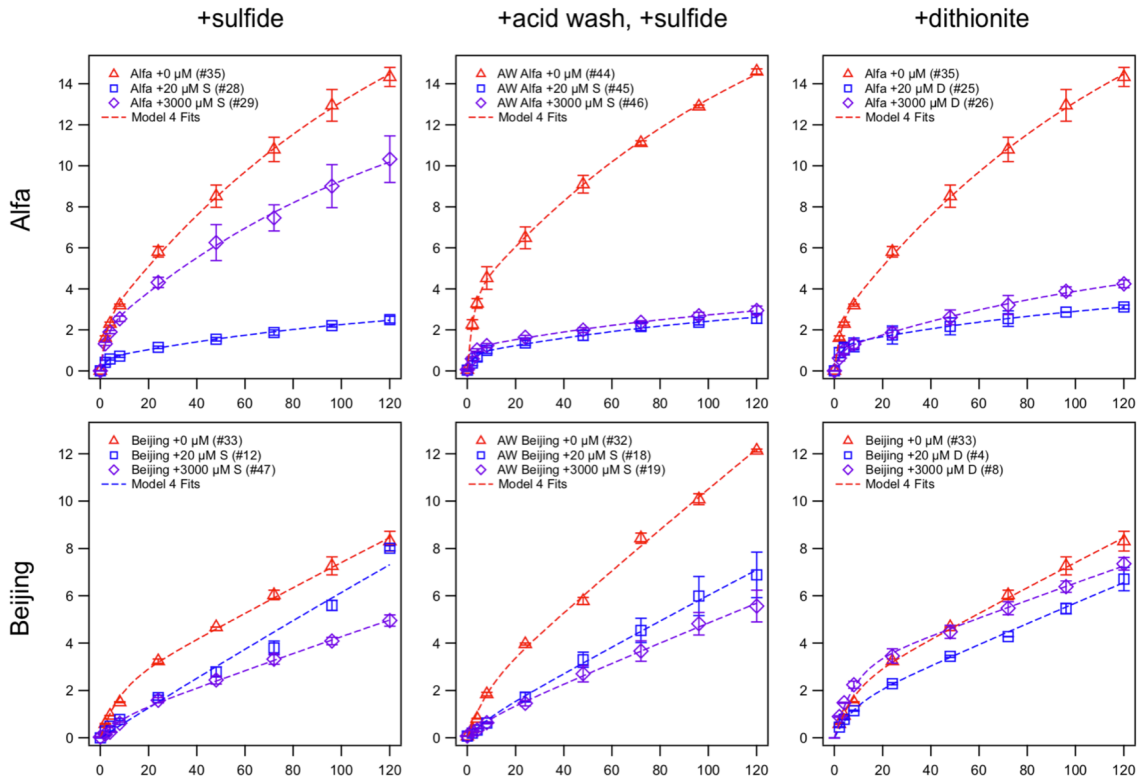
Environmental Science & Technology
Article
Cite This: *Environ. Sci. Technol.* XXXX, XXX, XXX–XXX
pubs.acs.org/est

**Modeling the Kinetics of Hydrogen Formation by Zerovalent Iron: Effects of Sulfidation on Micro- and Nano-Scale Particles**

Hejie Qin,[†,‡] Xiaohong Guan,[*,†,‡] Joel Z. Bandstra,[§] Richard L. Johnson,[∥] and Paul G. Tratnyek[*,∥]



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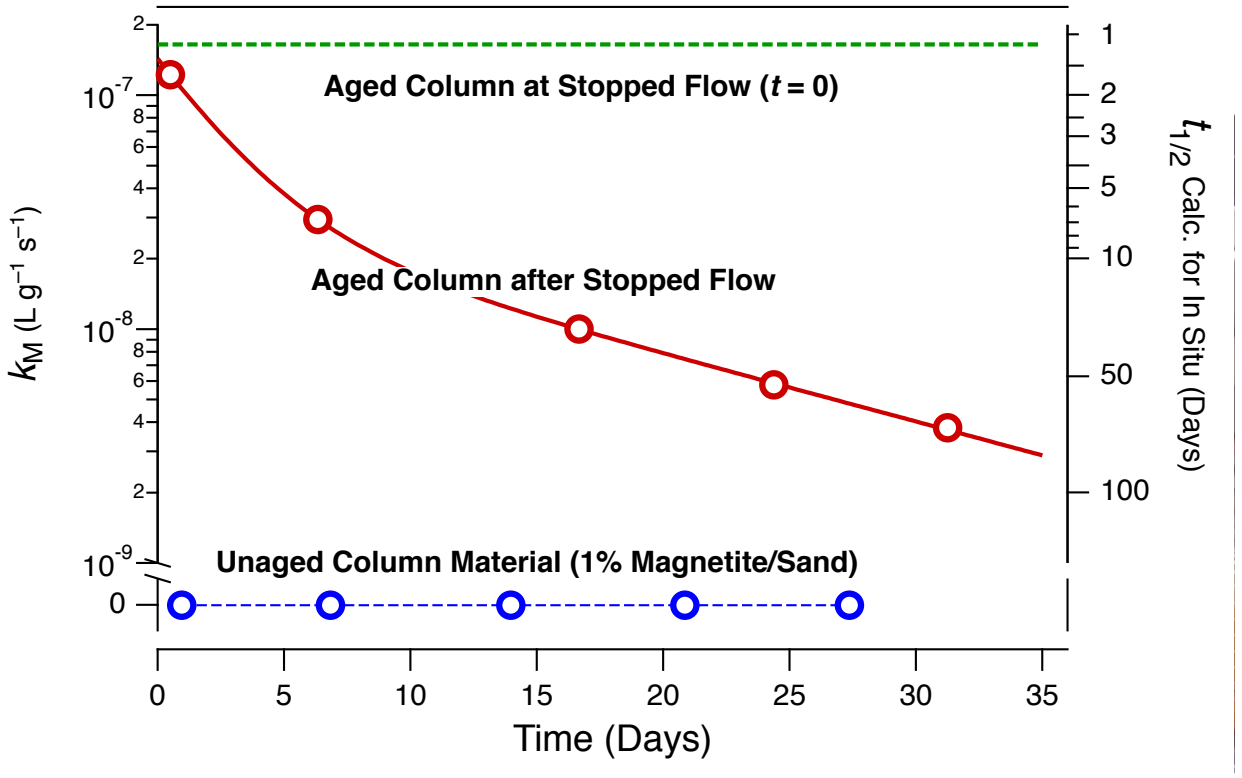
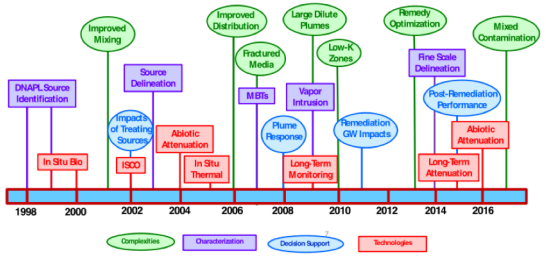
Home > Program Areas > Environmental Restoration > Contaminated Groundwater > Persistent Contamination > ER-2621 Project Overview

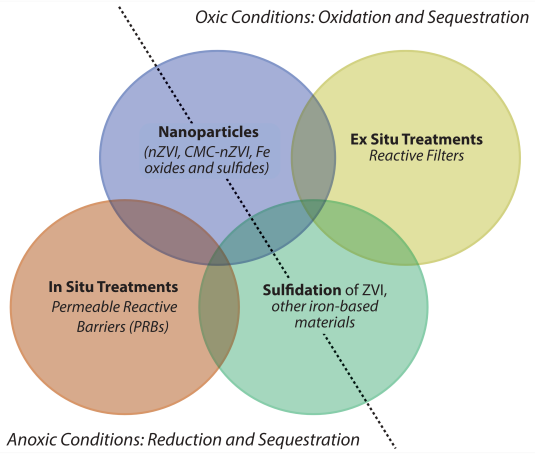
## Field Assessment of Abiotic Attenuation Rates using Chemical Reactivity Probes and Cryogenic Core Collection

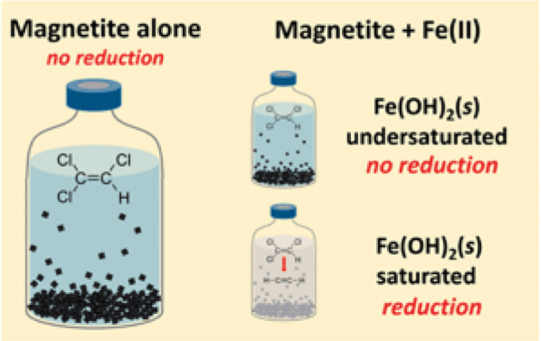


# Summary

- Toolkit is the currency of this field
  - Clean up sites + Compete with others
  - Includes technologies and concepts
- Toolkit change is essential
  - Challenges (contaminants, priorities)
  - Competition (companies, individuals)
  - Established, new, emerging, future
- Toolkit development is an investment
  - CVOCs → (I)MCs, PFAS, etc.
  - CSIA → Dechlorination, Nitro reduction
  - Training the next generation of practitioners




Tools: Conceptual

Tools: Technologies

# Acknowledgements and Disclaimer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  - Michelle Scherer, Drew Latta, Frank Loeffler, Bob Siegrist, Pamela Dugan, Hans Stroo, Wenqing Xu
- Others
  - Jacobs, Geosyntec, Regenesis, Carus, Peroxychem, Hepure/ARS, Peerless


*Nothing in this talk was reviewed or approved by any of the above.*