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Abiotic Degradation of Chlorinated Solvents in Subsurface Environments

November 19, 2020

SERDP DOD • EPA • DOE | ESTCP

Welcome and Introductions

Jennifer Nyman, Ph.D., P.E.
Webinar Facilitator

SERDP DOD • EPA • DOE | ESTCP

Webinar Agenda

- **Webinar Logistics** (5 minutes)
  Dr. Jennifer Nyman, Geosyntec Consultants
- **Overview of SERDP and ESTCP** (5 minutes)
  Dr. Andrea Leeson, SERDP and ESTCP
- **Abiotic Natural Attenuation by Reactive Minerals: Core Concepts** (25 minutes + Q&A)
  Dr. Paul Tratnyek, Oregon Health & Science University
- **Abiotic Natural Attenuation of Tetrachloroethene and Trichloroethene by Reactive Minerals** (25 minutes + Q&A)
  Dr. Michelle Scherer, University of Iowa
- **Final Q&A session**

Zoom Instructions

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  - Click the arrow next to the "Join Audio" button
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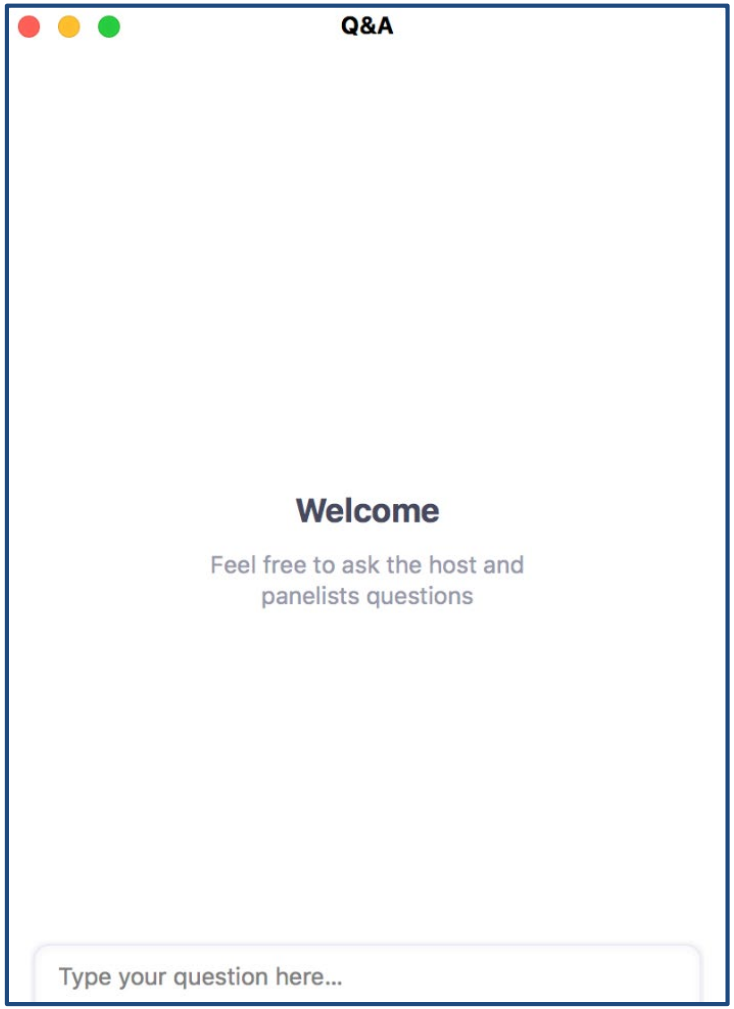

SERDP and ESTCP Overview

Andrea Leeson, Ph.D.
SERDP and ESTCP

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DoD's Environmental Technology Programs

Science and Technology

- Statutory program established 1991
- DoD, DOE, EPA partnership
  - Advanced technology development to address near-term needs
  - Fundamental research to impact real world environmental management

Demonstration and Validation

- Demonstrate innovative cost-effective environmental and energy technologies
  - Transition technology out of the lab
  - Establish cost and performance
  - Partner with end user and regulator
  - Technology transfer
    - Accelerate commercialization or broader adoption
    - Direct technology insertion

Environmental Drivers

Sustaining Ranges, Facilities and Operations

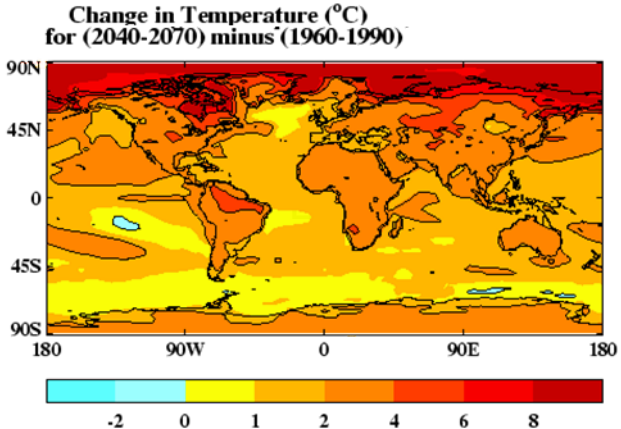
Maritime Sustainability
Threatened and Endangered Species

Toxic Air Emissions and Dust

UXO and Munitions Constituents

Noise

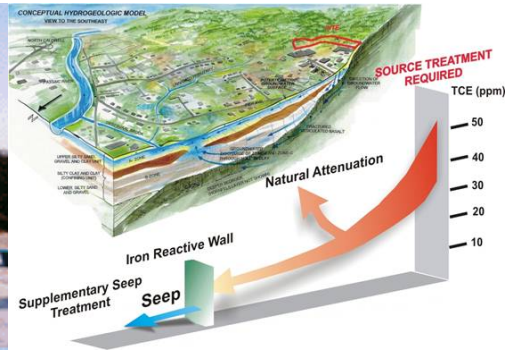
Sustainable FOB



Environmental Drivers

Reducing Current and Future Liability

Contamination from Past Practices



- Groundwater, soils and sediments
- Large UXO liability
- Emerging contaminants

Pollution Prevention to Control Life Cycle Costs

- Elimination of pollutants and hazardous materials in manufacturing, maintenance, and operations
- Achieve compliance through pollution prevention

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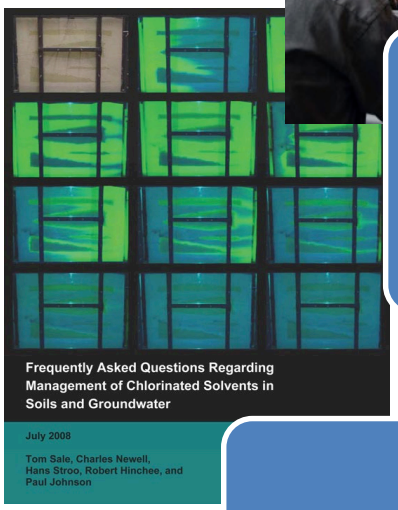

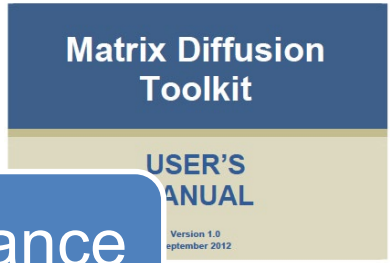

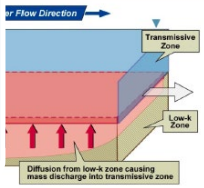

Webinars

In Person Training

EnviroWiki

Videos

Technology Transfer

Guidance and Manuals

SERDP and ESTCP Webinar Series

Date	Topic
December 10, 2020	Approaches for Managing Contaminated Sediments
January 14, 2021	Improving Energy Efficiency through Advanced Building Controls
January 28, 2021	Improved Approaches for PFAS Sampling and Treatment
February 11, 2021	Advances in the Detection of Submerged Unexploded Ordnance in Marine Environment
February 25, 2021	Managing Chlorinated Solvents in Groundwater Using Biological Treatment
March 11, 2021	New Resource Conservation Paradigms on DoD Lands
March 25, 2021	Safer Alternatives for Surface Engineering and Structural Materials in Weapons Systems and Platforms: A Fred Lafferman Tribute Webinar

For upcoming webinars, please visit

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Save the Date

SERDP • ESTCP
SYMPOSIUM

A three-day symposium showcasing the latest technologies that enhance DoD's mission through improved environmental and energy performance

November 30 - December 4, 2020

Registration for the virtual event is open!

Abiotic Natural Attenuation by Reactive Minerals: Core Concepts

Paul G. Tratnyek, Ph.D.
Oregon Health & Science University

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Agenda

Abiotic Attenuation by Reactive Minerals

- Core concepts – Paul Tratnyek (ER-2620)
  - Definition and scope of ANA* and ISCR*
    - Performance metrics
    - Enhancement by activation/mediation
    - Quantification of capacity/demand
  - Reactive Mineral Intermediates (RMIs)
- Case studies – Michelle Scherer (ER-2532)

Notes: *ANA = abiotic natural attenuation; ISCR = in situ chemical reduction*

Introduction

- Abiotic reduction of contaminants
  - Not new, but neglected until recently

Journal of Contaminant Hydrology, 1 (1986) 1—28
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

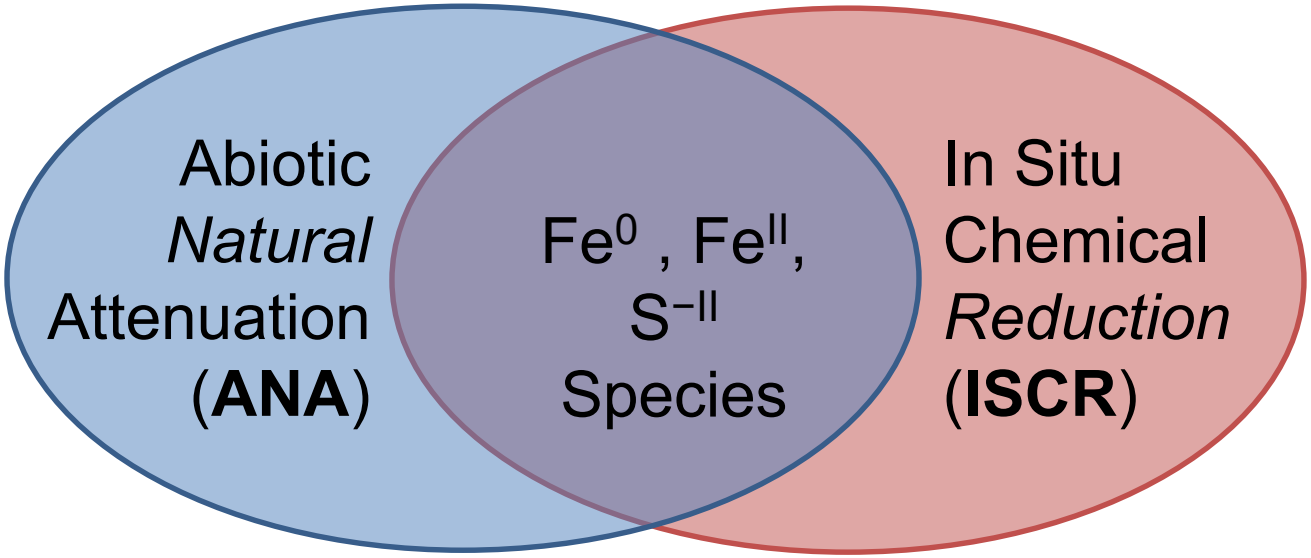
Review Paper

ABIOTIC REDUCTION REACTIONS OF ANTHROPOGENIC ORGANIC CHEMICALS IN ANAEROBIC SYSTEMS: A CRITICAL REVIEW

DONALD L. MACALADY, PAUL G. TRATNYEK and TIMOTHY J. GRUNDL
Colorado School of Mines, Department of Chemistry/Geochemistry, Golden, CO 80401

Introduction

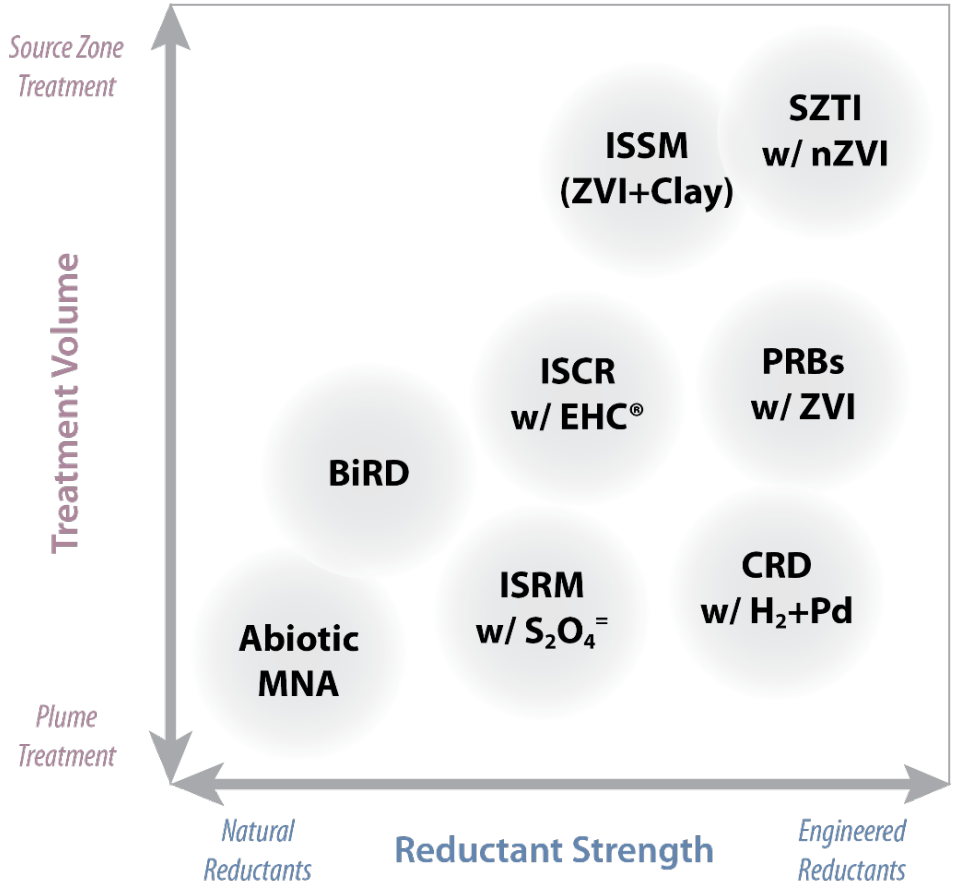
- Abiotic reduction of contaminants
  - Now widely recognized as means to improve remediation outcomes



ANA and ISCR as Technologies

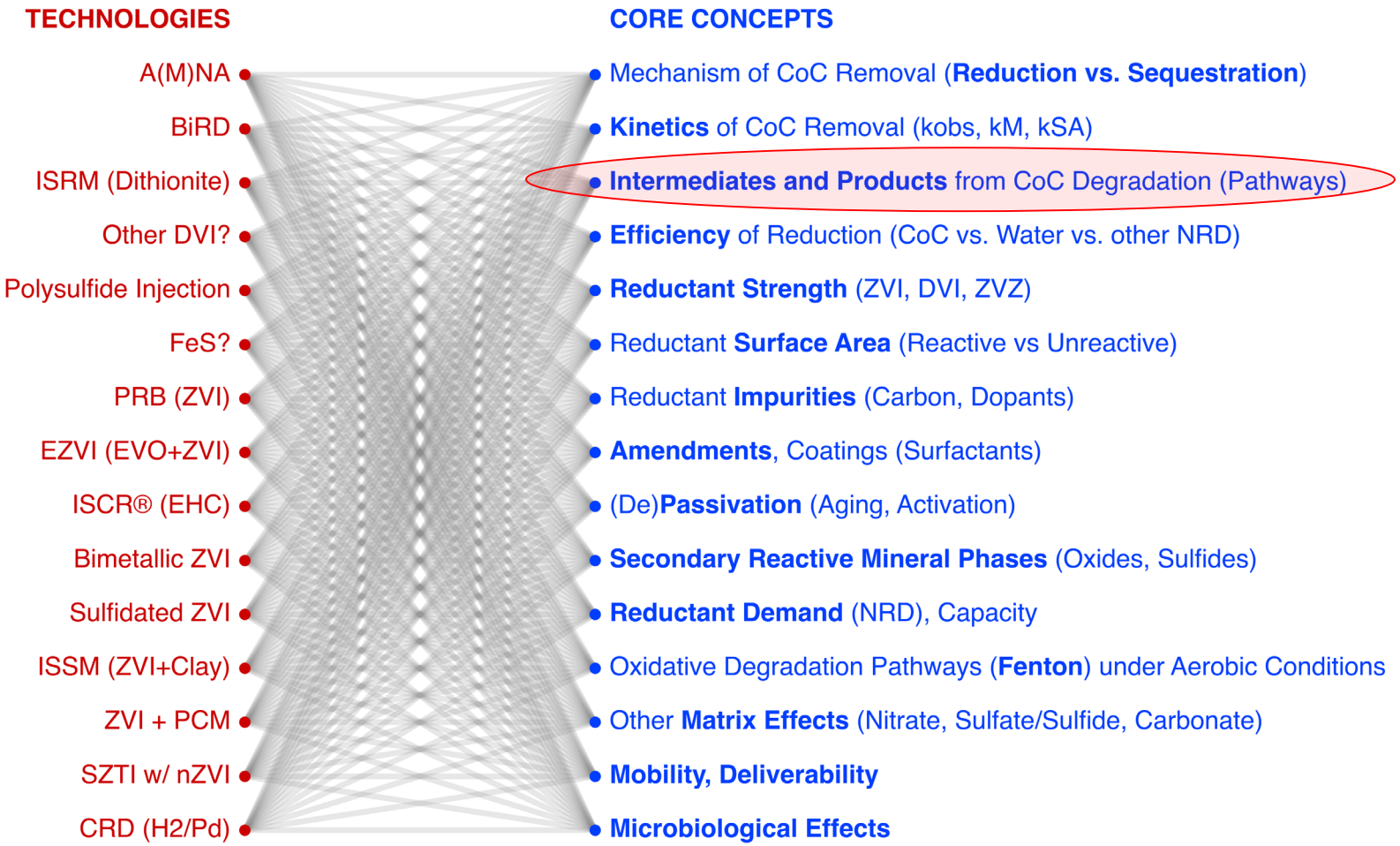
- Natural/intrinsic reductants
  - Abiotic Natural Attenuation (**ANA**)
  - Biogeochemical reductive dechlorination (**BiRD**)
  - In situ biogeochemical transformation (**ISBGT**)
- Mild chemical reductants
  - In situ redox manipulation (**ISRM**)
  - **EHC**®, Daramend®
- Strong chemical reductants
  - Zero valent iron (**ZVI**)
  - Catalytic reductive dechlorination (**CRD**) with H_2/Pd

ANA and ISCR as Technologies



***Notes**: ISSM = in situ soil mixing; SZTI = source zone targeted injection; PRB = permeable reactive barrier*

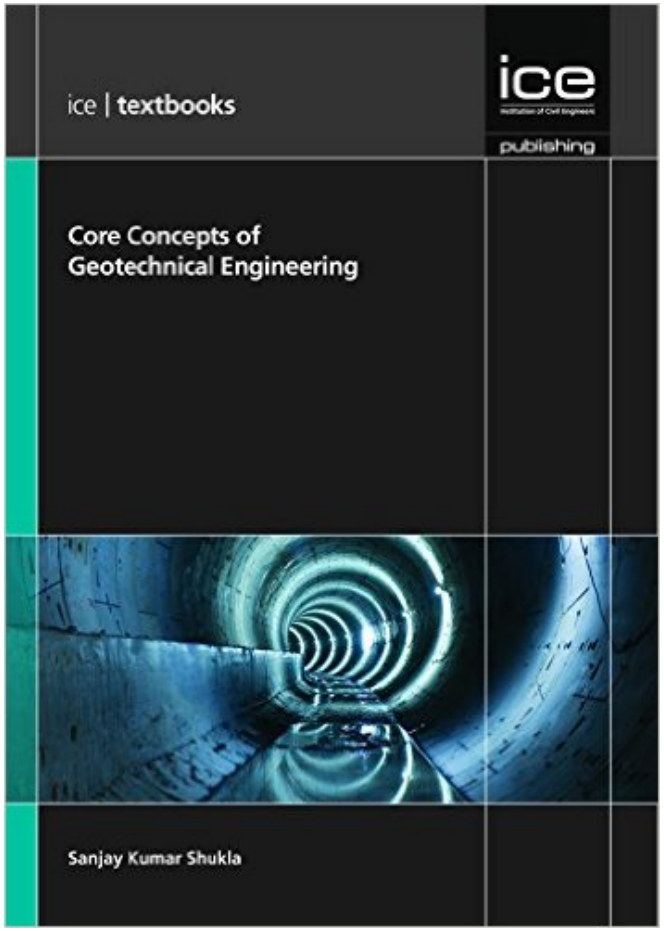
Introduction



***Notes**: DVI = divalent iron; NRD = natural reductant demand; PCM = pyrogenic carbonaceous matter; ZVZ = zero-valent zinc*

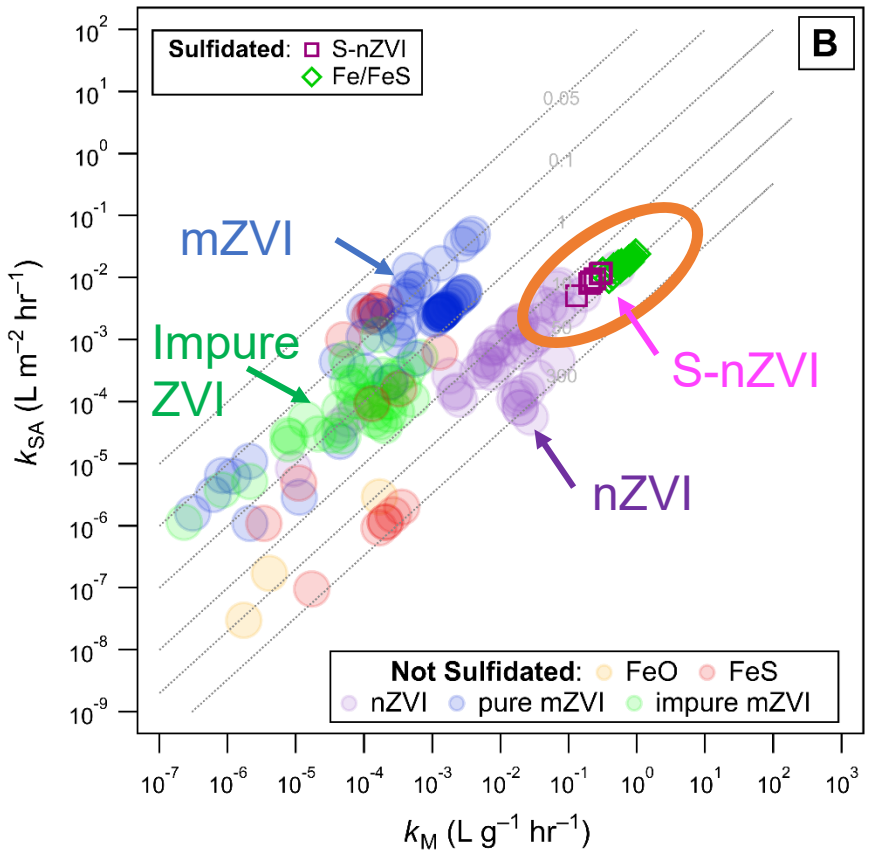
Technical Approach (ER-2620)

- Emerging core concepts
  1. Standardized metrics of remediation performance
     - Normalization of *k*'s
  2. Enhancement by activation or mediation
     - Secondary minerals (RMIs)
  3. Consideration of natural reductant demand
     - Electron efficiency (EEs)



Performance Metrics

- Reduction rate
  - Compile database
  - Fill data gaps
  - Normalize k_{obs}
    - Mass (k_M)
    - Surface area (k_{SA})
    - Magnetic susceptibility (k_{MS})?
    - Redox potential?



Performance Metrics

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    - Surface area (k_{SA})
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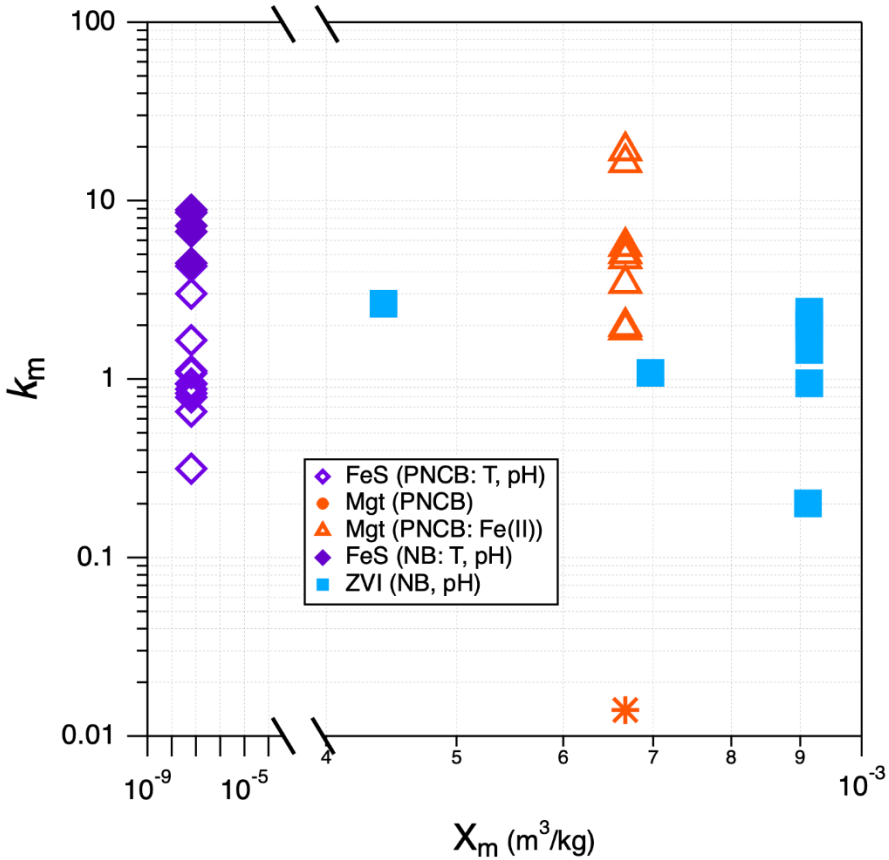
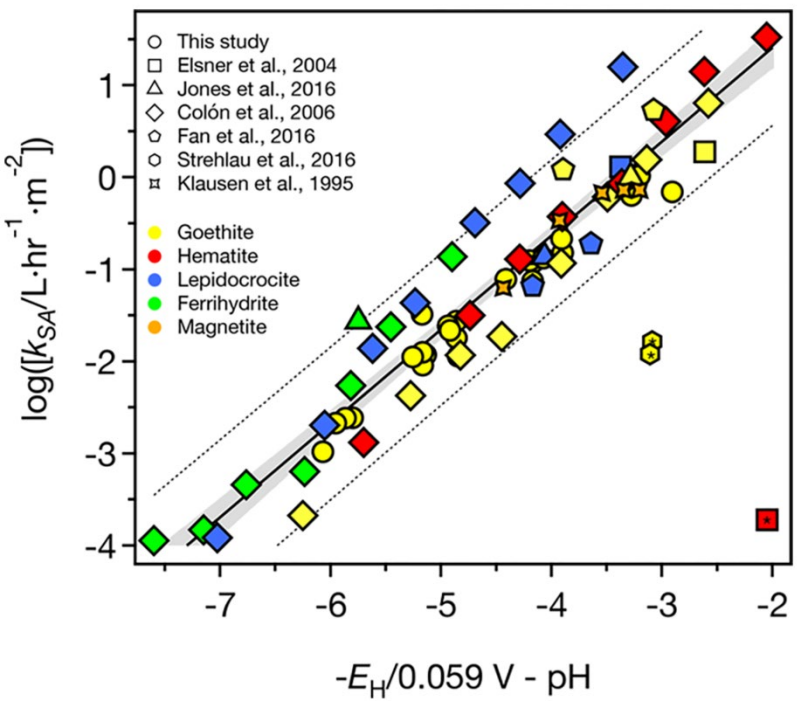
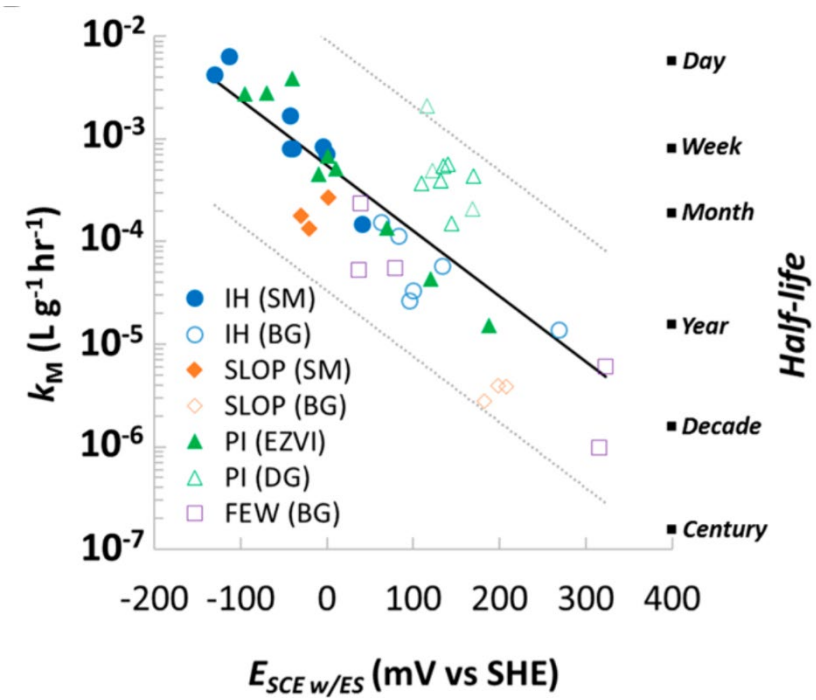


Mass Normalized
Magnetic Susceptibility (MS)

Performance Metrics

Normalize k_{obs} to redox potential?



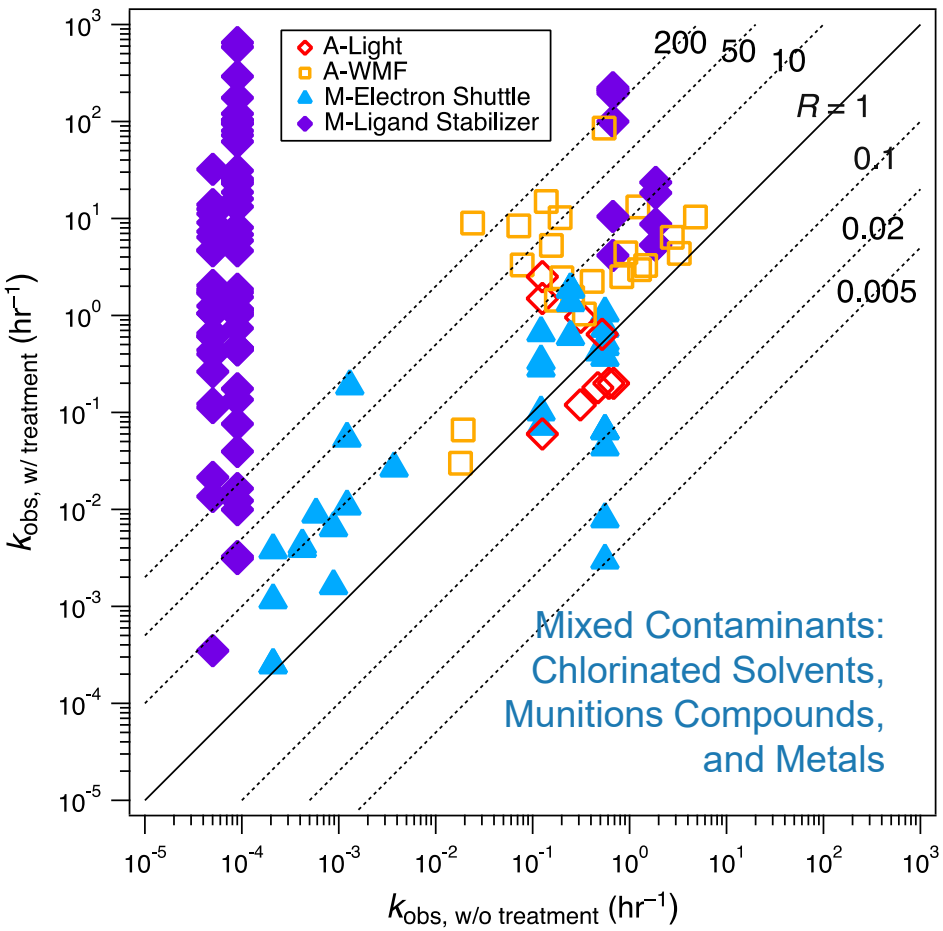


Not just E_H (ORP),
e.g., w/ electron shuttle (ES)

***Source**: Stewart/Gorski (2018) ES&T 52: 5600*

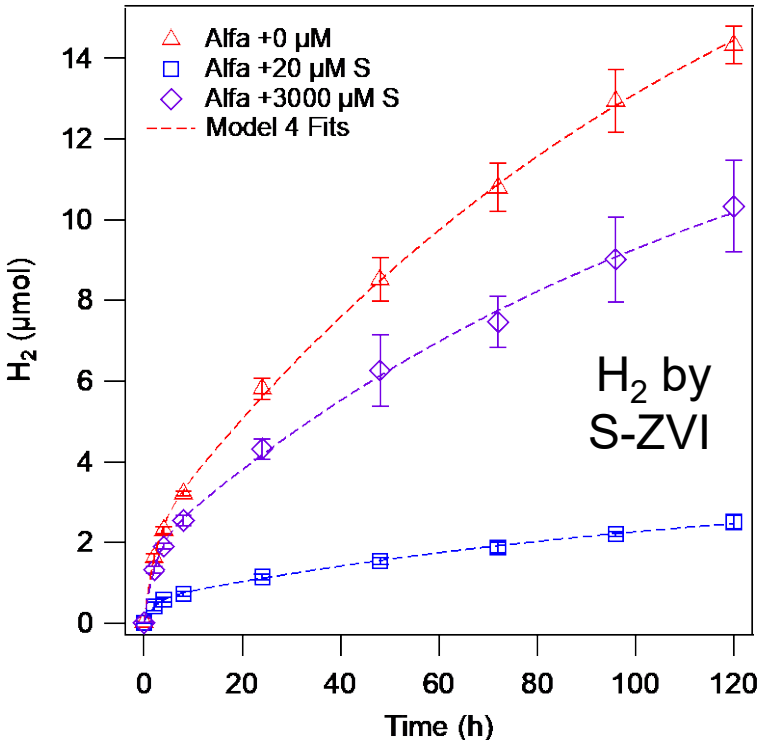
Activation/Mediation

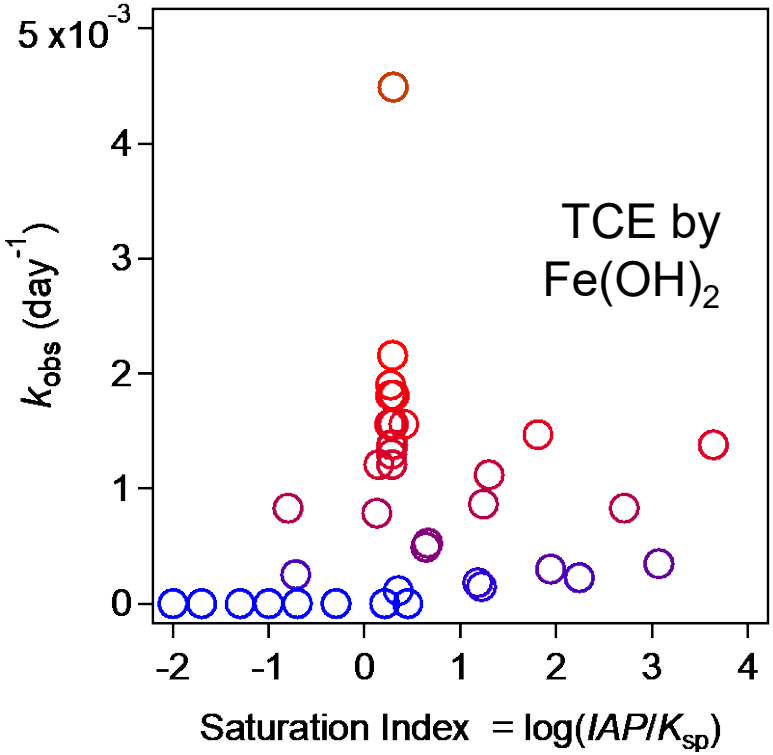
- Enhancement by:
  1. Heat, light
  2. Weak magnetic field (WMF)
  3. Electron shuttles
     - Vitamin B_{12}
     - Riboflavin
     - Quinones
     - Fe(II)-Ligands
  4. Reactive mineral intermediates (RMIs)



Activation/Mediation

Enhancement by RMI formation

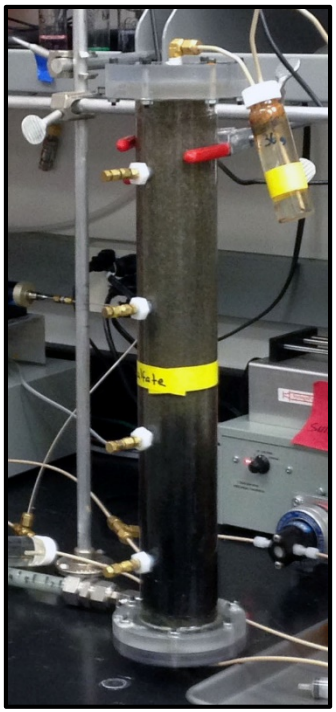


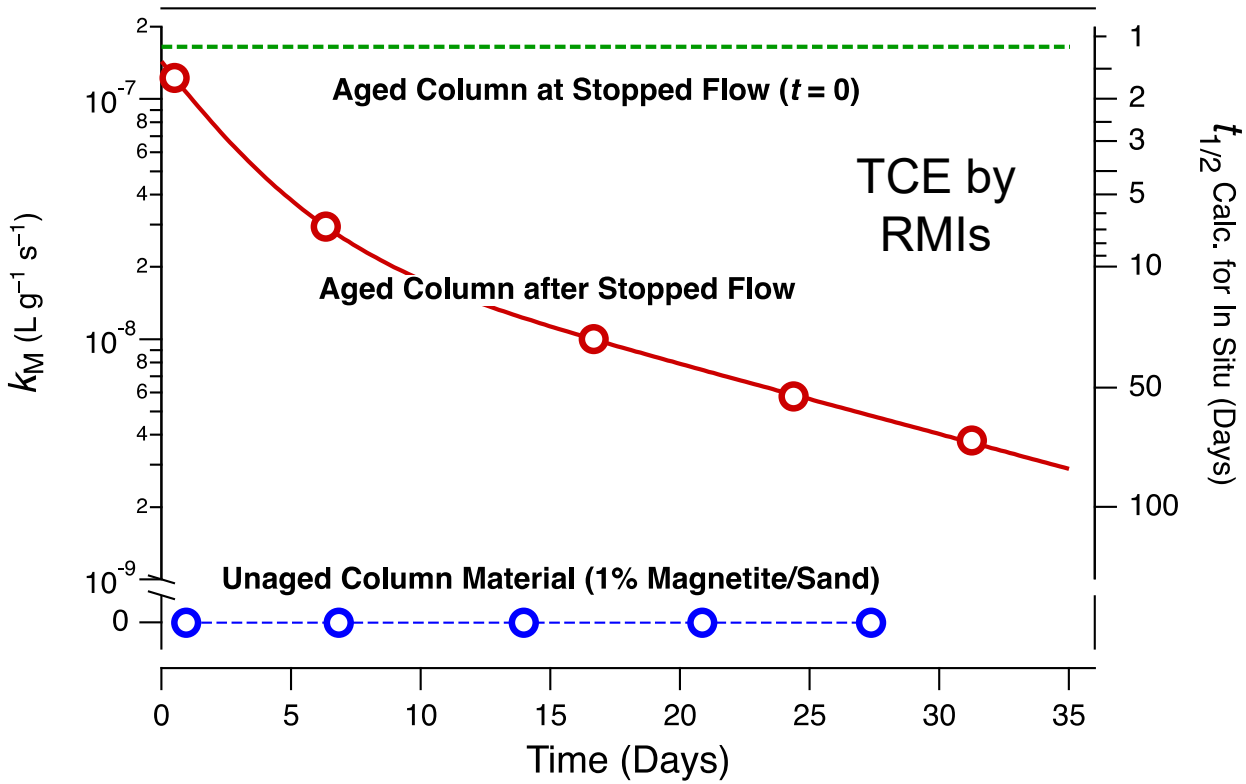


***Source**: Culpepper/Scherer (2018) ESPI 20: 1340*

Activation/Mediation

Enhancement by RMI formation

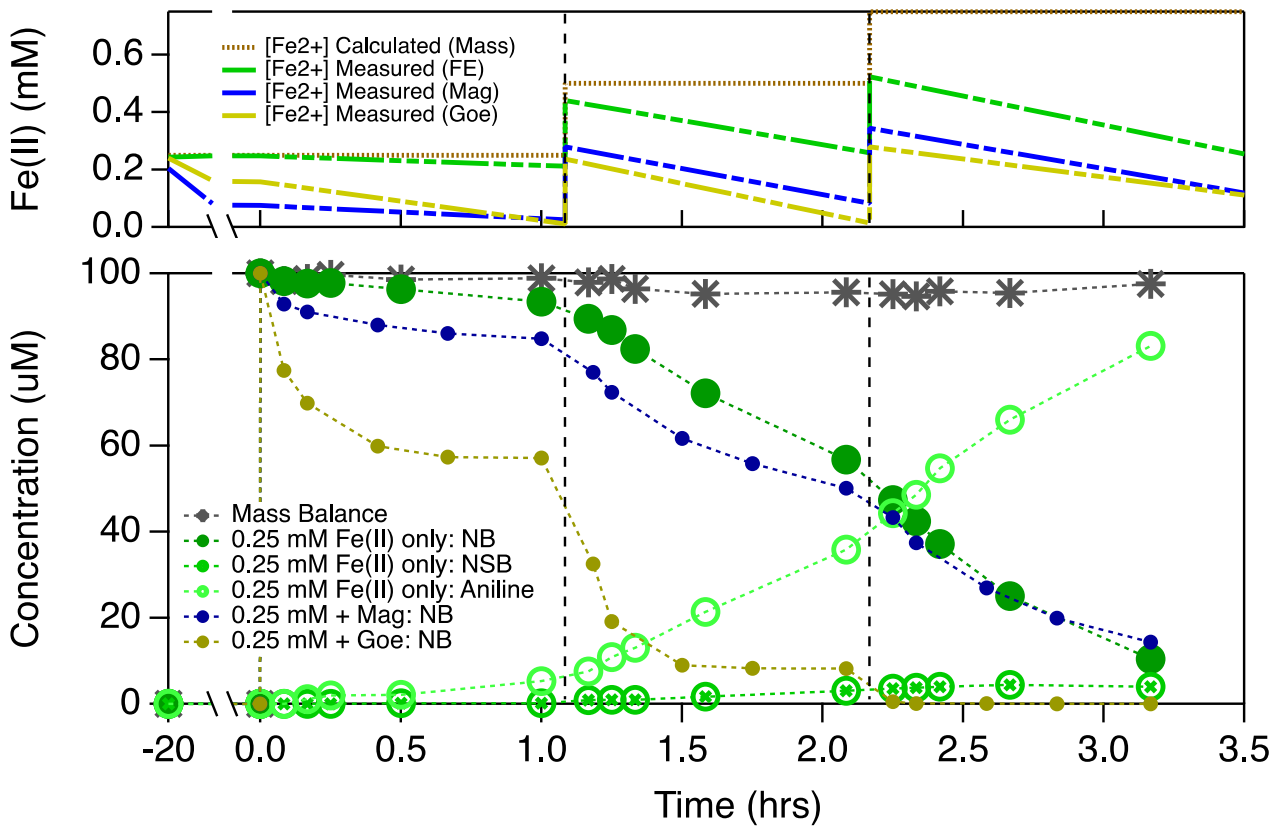


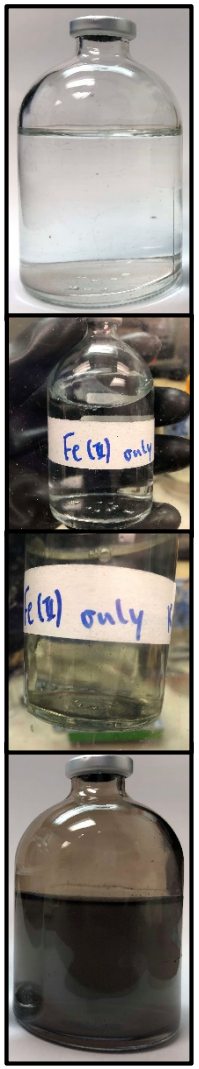


***Source**: Johnson (2018) ER-2621*

Activation/Mediation

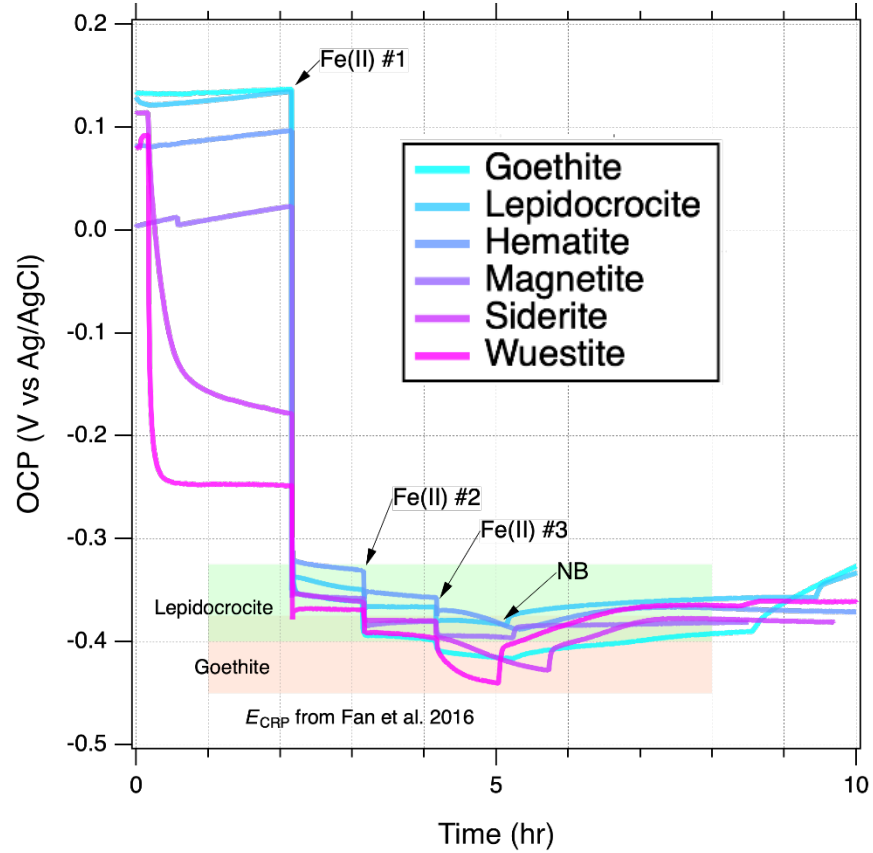
Enhancement by RMI formation





Metrics for Enhancement

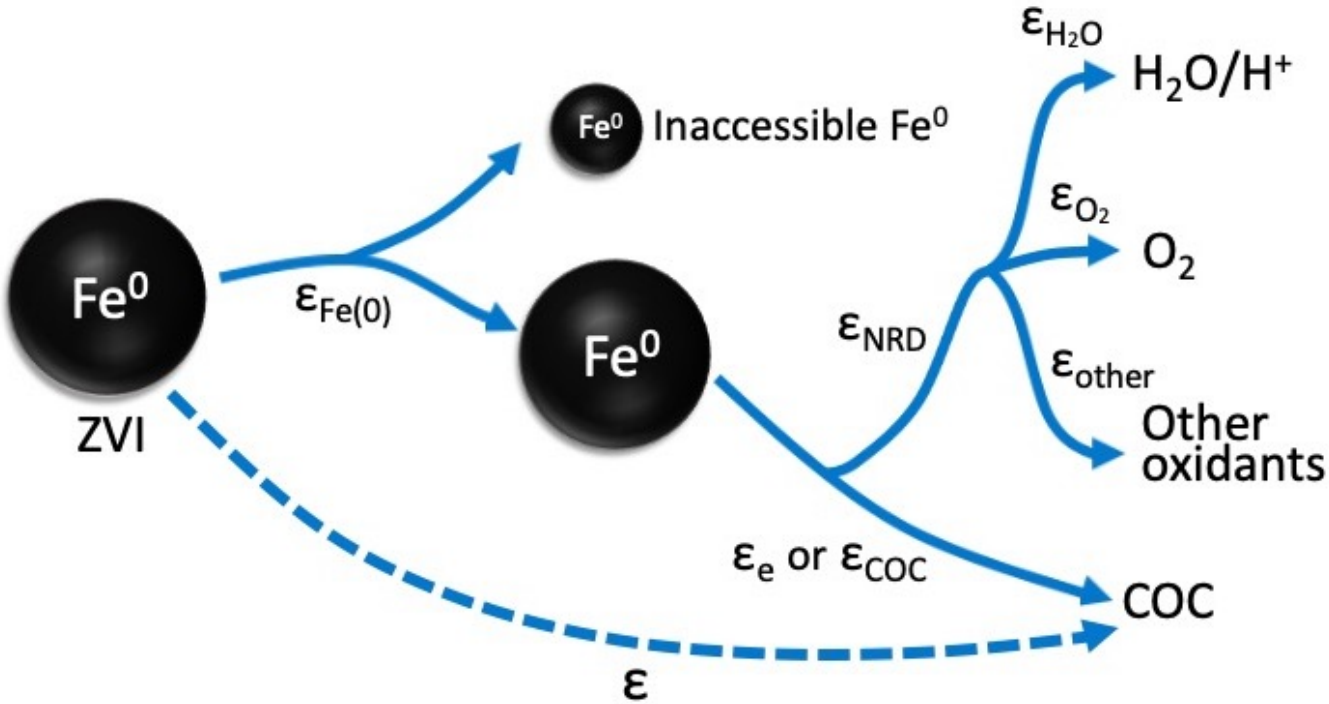
- Reduction rate
  - Compile database
  - Fill data gaps
  - Normalize k_{obs}
    - Mass (k_M)
    - Surface area (k_{SA})
    - Magnetic susceptibility (k_{MS})?
    - Redox potential? (Eh ≈ ORP ≈ OCP)



***Note**: OCP = open circuit potential*

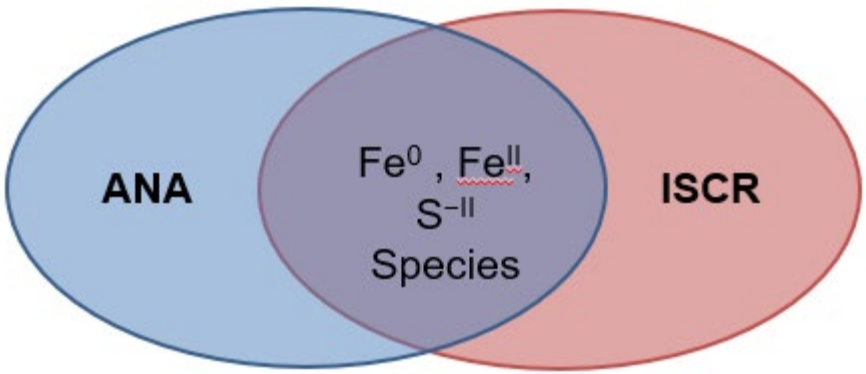
Reductant Demand

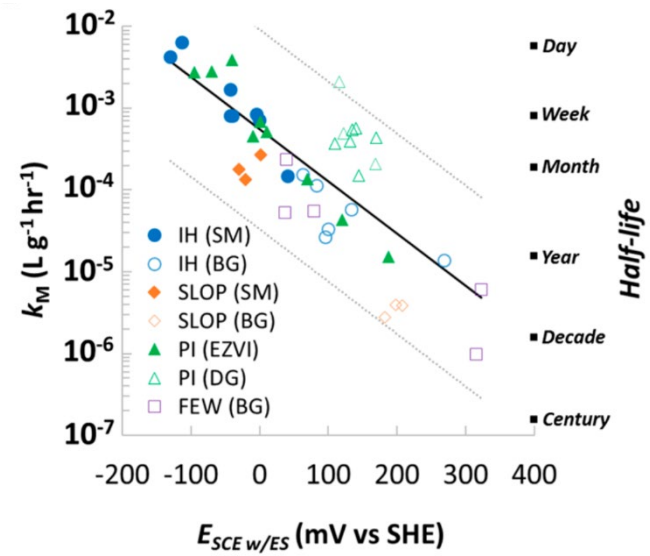
- Natural Reductant Demand (NRD)
- Capacity, efficiency (EE)
  - Definition, measurement
  - Sulfidation of ZVI



Conclusions

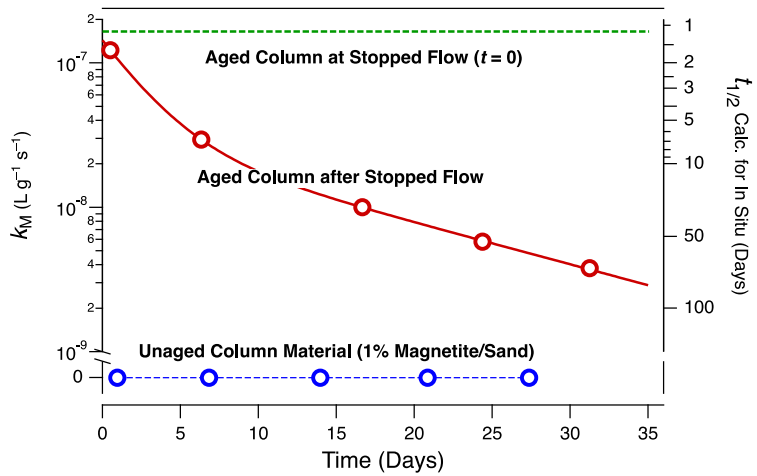
- ANA and ISCR overlap and share core concepts
- Performance metrics
  - k_M and k_{SA} (yes), k_{MS} (no), $k_{ORP/ES}$ (maybe)

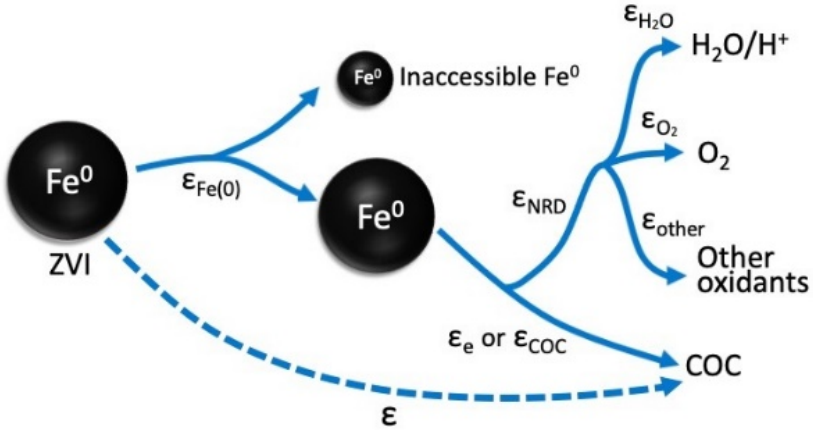




Conclusions

- Mediation/activation
  - Soluble mediators (no), RMIs (yes)
- Demand/capacity
  - EE improved by sulfidation





Benefits to DoD

- ANA and ISCR applicable to most DoD priority COCs
  - Energetics
  - Chlorinated solvents
  - Some metals
  - Not 1,4-dioxane or PFAS
- Core concepts applicable to all ANA/ ISCR technologies
  - Synergy with ISCO
- Predict reduction rates at specific field sites using $k_{ORP/ES}$
  - Development continuing
- Enhance ANA/ISCR by stimulation of RMI formation
  - Active, dynamic and transient
- Improve EE of ISCR via sulfidation

Additional Resources

1. Tratnyek et al. (2014) **In situ chemical reduction for source zone remediation**. In: Kueper et al. (eds.), Chlorinated Solvent Source Zone Remediation. SERDP and ESTCP Monograph Series, Vol. 7, DOI: 10.1007/978-1-4614-6922-3_10
2. Kocur et al. (2020) **Predicting abiotic reduction rates using cryogenically collected soil cores and mediated reduction potential measurements**. Environmental Science & Technology Letters 2020, 7(1), 20-26. DOI: 10.1021/acs.estlett.9b00665
3. Qin et al. (2018) Modeling the **Kinetics of hydrogen formation by zerovalent iron: Effects of sulfidation on micro- and nano-scale particles**. Environmental Science & Technology 52(23), 13887-13896. DOI: 10.1021/acs.est.8b04436
4. Fan et al. (2017) **Sulfidation of Iron-Based Materials: A Review of Processes and Implications for Water Treatment and Remediation**. Environmental Science & Technology Letters 51(22), 13070-13085. DOI: 10.1021/acs.est.7b04177
5. He et al. (2020) **Quantifying the efficiency and selectivity of organohalide dechlorination by zerovalent iron**. Environmental Science: Processes & Impacts 22, 528. DOI: 10.1039/C9EM00592G

For additional information, please visit
https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Persistent-Contamination/ER-2620

Speaker Contact Information

tratnyek@ohsu.edu; 503-346-3431

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Q&A Session 1

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Abiotic Natural Attenuation (**ANA**) by Reactive Minerals: Two Case Studies

Michelle Scherer, Ph.D.
The University of Iowa

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Agenda

Abiotic Natural Attenuation (ANA)

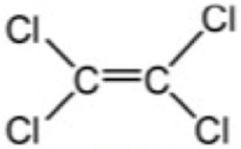
Two Case Studies of Reactive Mineral Intermediates (RMIs)

1. Magnetite
2. Clay Minerals

Two Case Studies

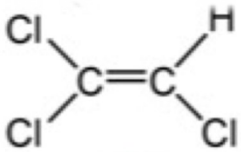
#1
Magnetite

The presence of these Fe containing minerals is unlikely to be sufficient for **ANA**



PCE

#2
Structural Fe(II) in clay minerals



TCE

Active precipitation of **reactive mineral intermediates** may be more relevant

Is ANA Likely?

- We suggest that rather than looking for specific minerals, aquifer/groundwater properties may be more predictive of whether ANA is likely at a site

Evidence for **ANA** by Fe Minerals

Plume and column CE **removal patterns**

e.g., TCE removal without DCE or VC accumulation

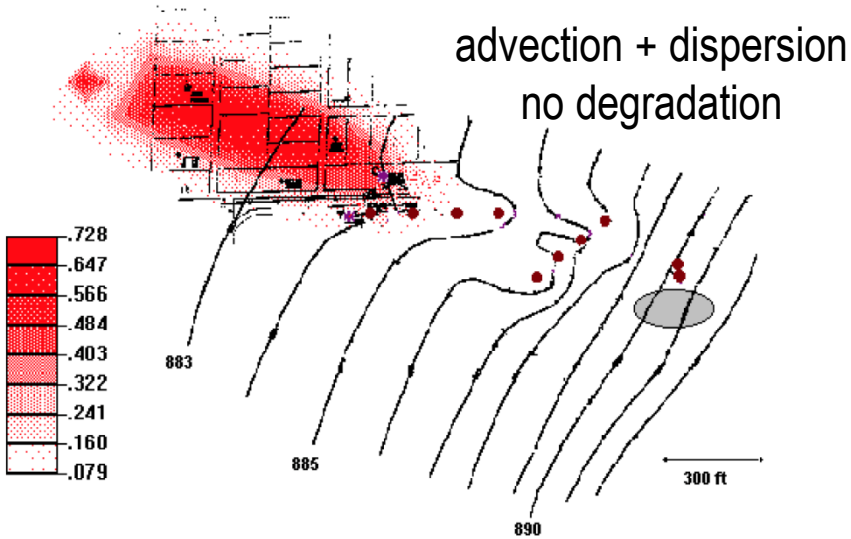
Presence of Fe minerals in many aquifers

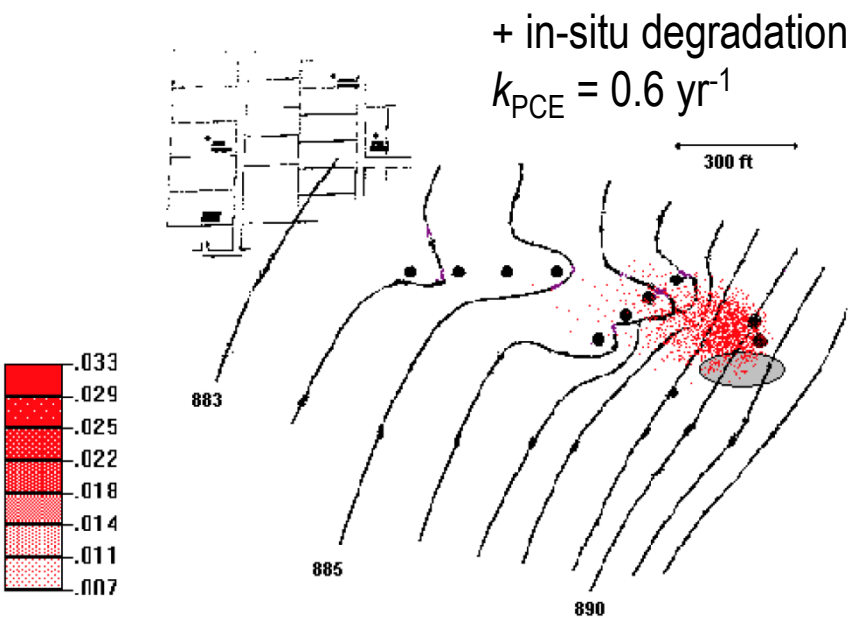
e.g., magnetite, clay minerals, Fe sulfides, hematite

Some Fe minerals **reduce CEs (in lab)**

e.g., Fe sulfides, green rusts

The **Trifecta** at Twin Cities Army Ammunition Plant (TCAAP)





Nonbiological Removal of *cis*-Dichloroethylene and 1,1-Dichloroethylene in Aquifer Sediment Containing Magnetite

MARK L. FERREY,*,†
RICHARD T. WILKIN,‡
ROBERT G. FORD,‡ AND
JOHN T. WILSON‡

Minnesota Pollution Control Agency, 520 Lafayette Road, St. Paul, Minnesota 55155-4194, National Risk Management Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, 919 Kerr Research Drive, Ada, Oklahoma 74820

But, little to no reduction of PCE/TCE by magnetite in laboratory studies

Abiotic Reductive Dechlorination of Chlorinated Ethylenes by Iron-Bearing Soil Minerals. 1. Pyrite and Magnetite

WOOJIN LEE*,† AND BILL BATCHELOR‡

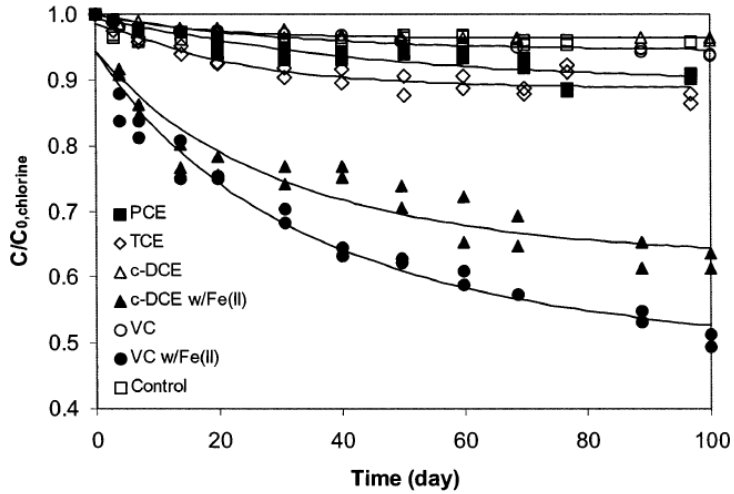
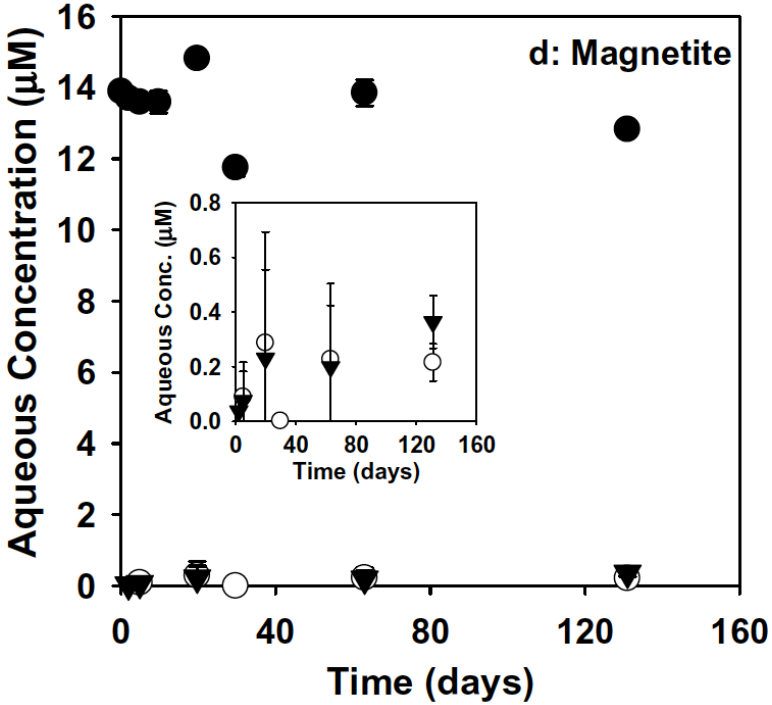


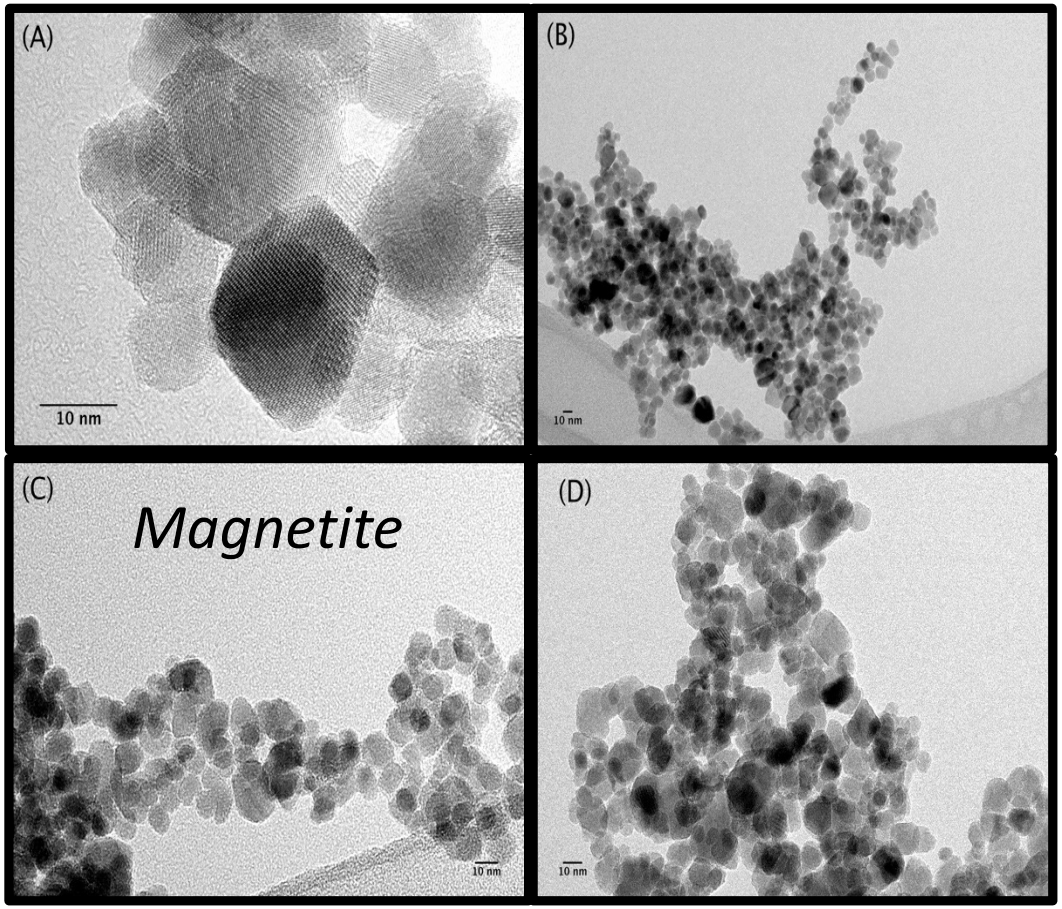
FIGURE 3. Reductive dechlorination of chlorinated ethylenes in magnetite suspension (0.063 g/g) with and without 42.6 mM Fe(II) addition. Curves represent kinetic model fits. Control is the control sample for PCE.

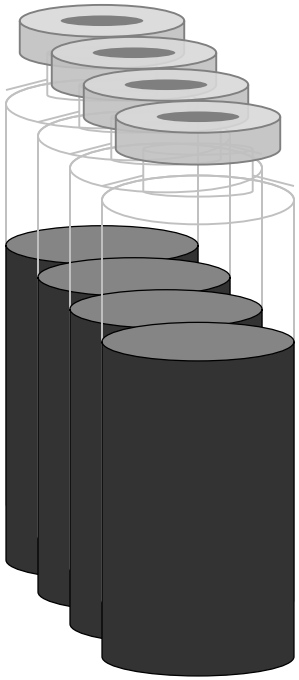
Kinetic and isotope analyses of tetrachloroethylene and trichloroethylene degradation by model Fe(II)-bearing minerals

Xiaoming Liang [a], R. Paul Philp [b], Elizabeth C. Butler [a]



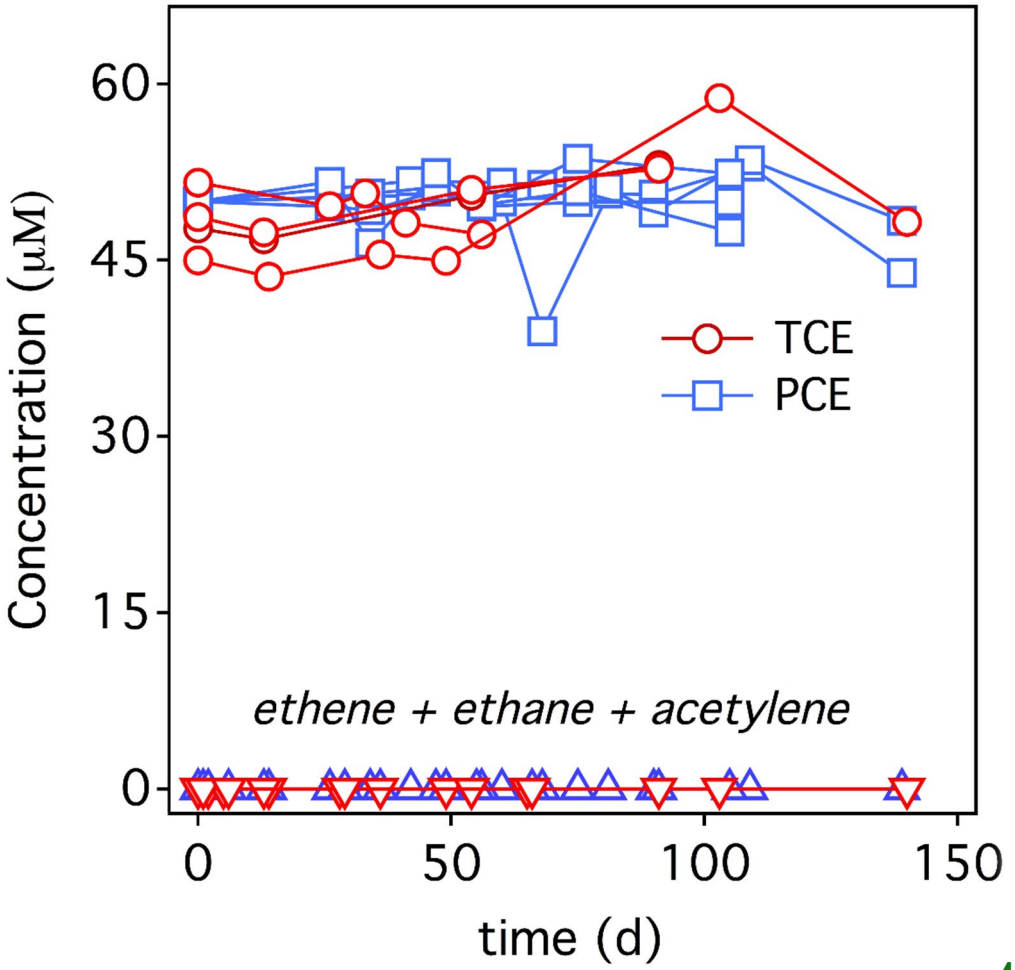
Therefore, we reacted magnetite with PCE and TCE in the laboratory to check





Magnetite alone does not reduce PCE or TCE under our conditions

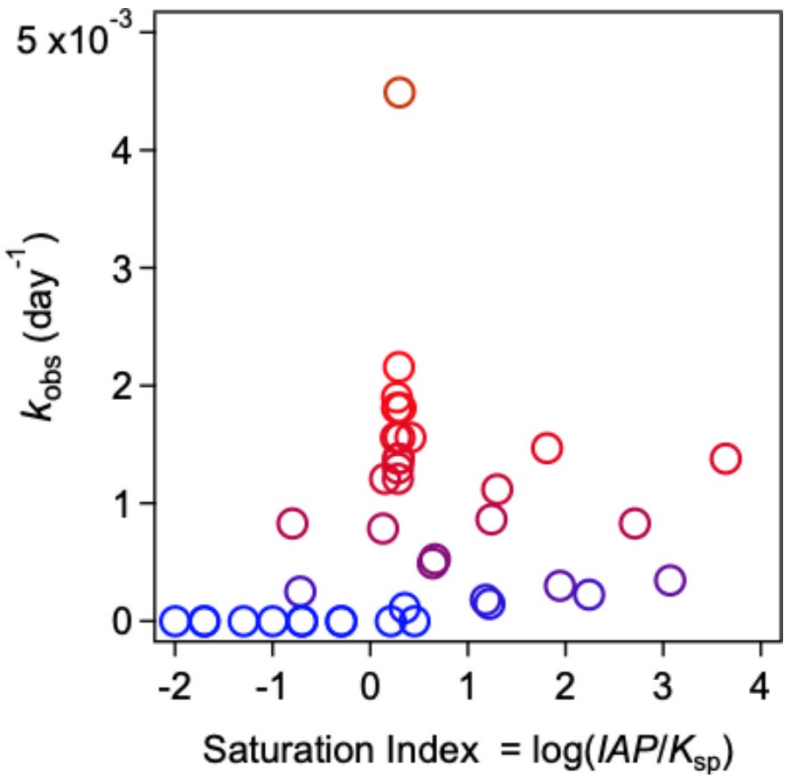
synthesized magnetite
varying stoichiometries
freeze-dried
anaerobic
60 m^2/g
pH 6 to 9
5 to 20 g/L

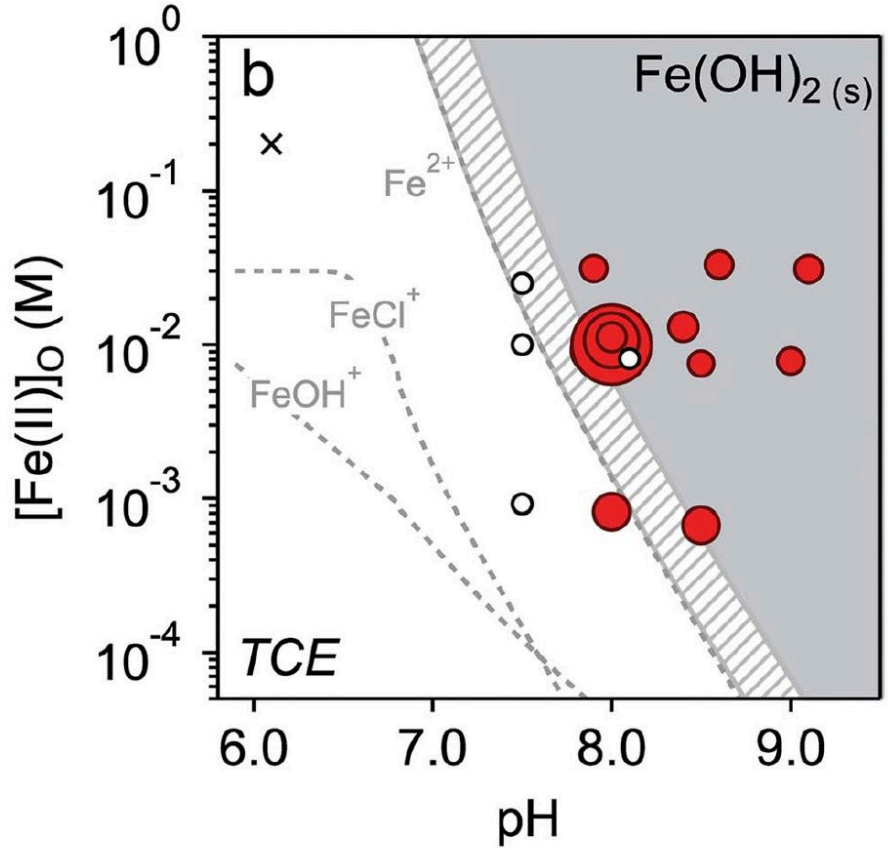


Magnetite + Fe(II) does reduce PCE and TCE, *sometimes*

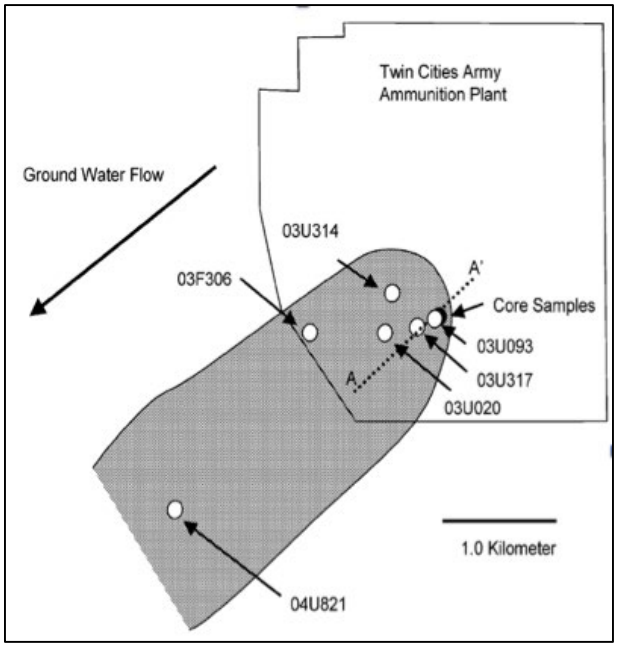
$$Fe(OH)_2(s) = Fe^{2+} + 2OH^-$$

Reduction occurs when saturated (SI > 0) with respect to $Fe(OH)_2(s)$





Estimate aquifer first order decay coefficients



<u>Magnetite + Fe(II) in **bottle**</u>
60 m^2/g
5 – 33 g/L

<u>*Assume* **aquifer** properties</u>
bulk density = 1700 kg/m^3
porosity = 0.2

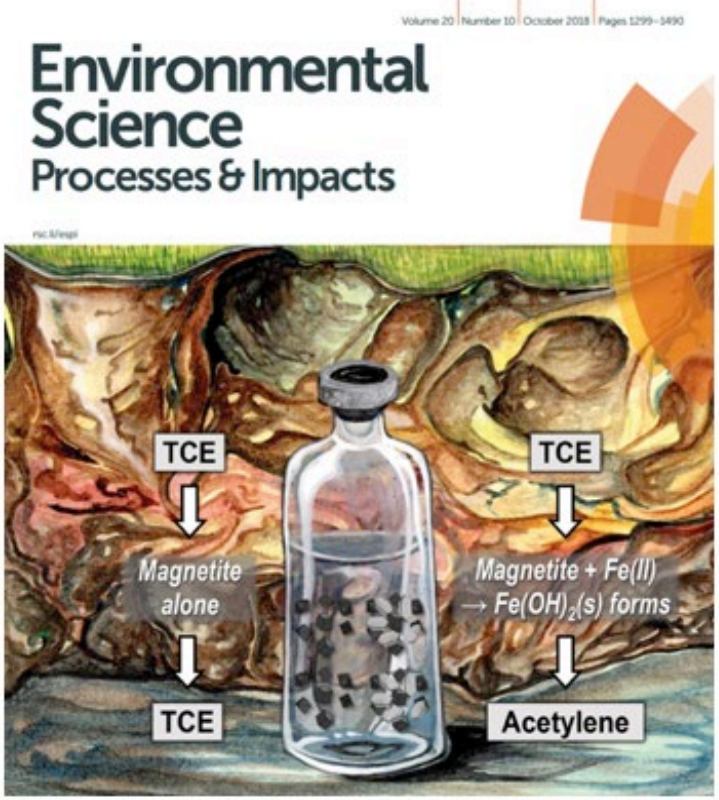
<u>*Assume* Magnetite in **sediments**</u>
60 m^2/g; 0.1 to 10 mg/kg

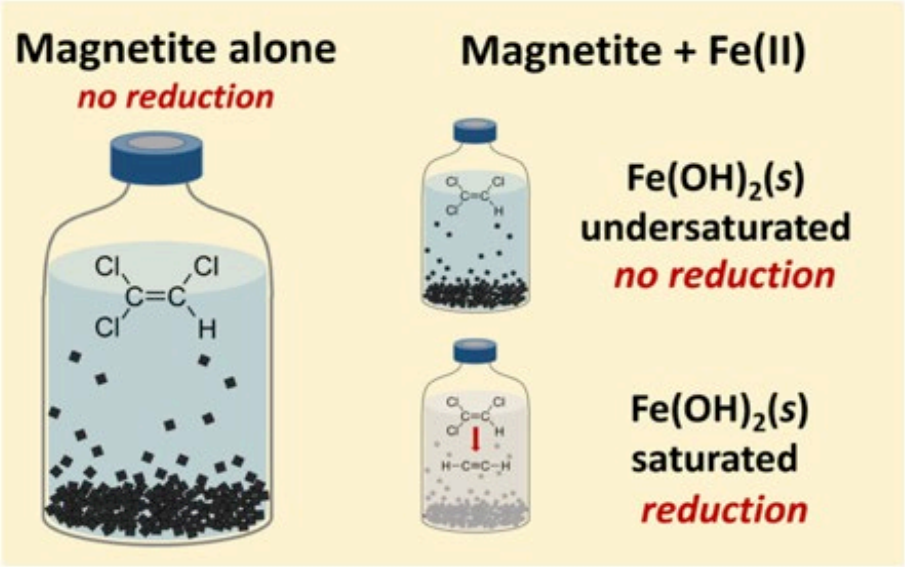
For magnetite + Fe(II) aquifer first order decay coefficients

$k_{aquifer}$ = 0.11 to 4.2 yr^{-1}

$t_{1/2}$ = 2 months to 6.3 years

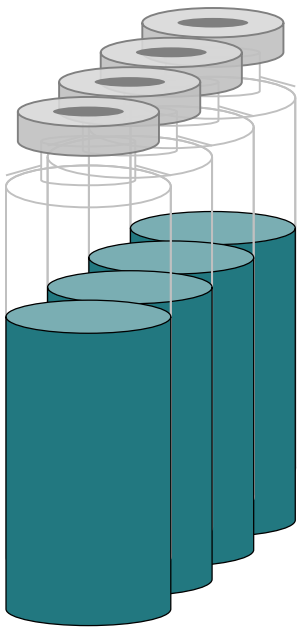
#1 Magnetite

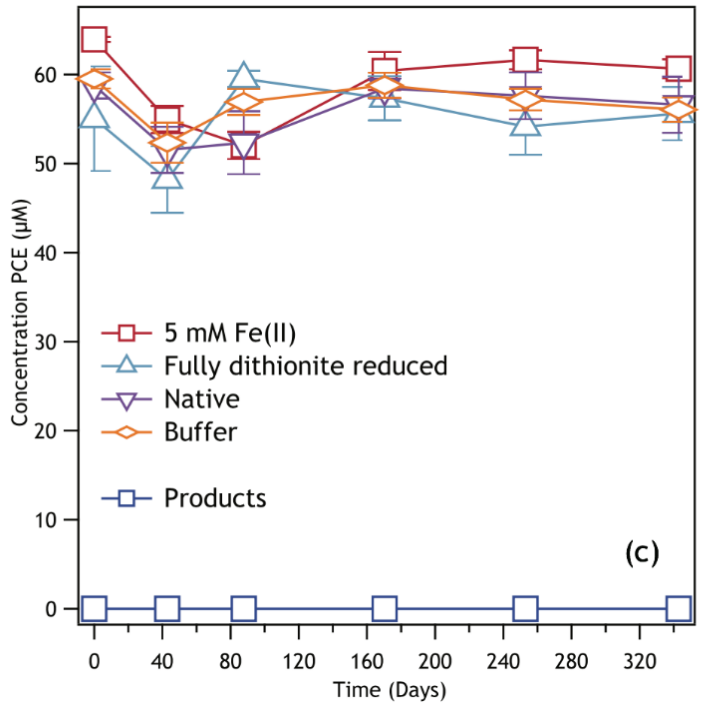


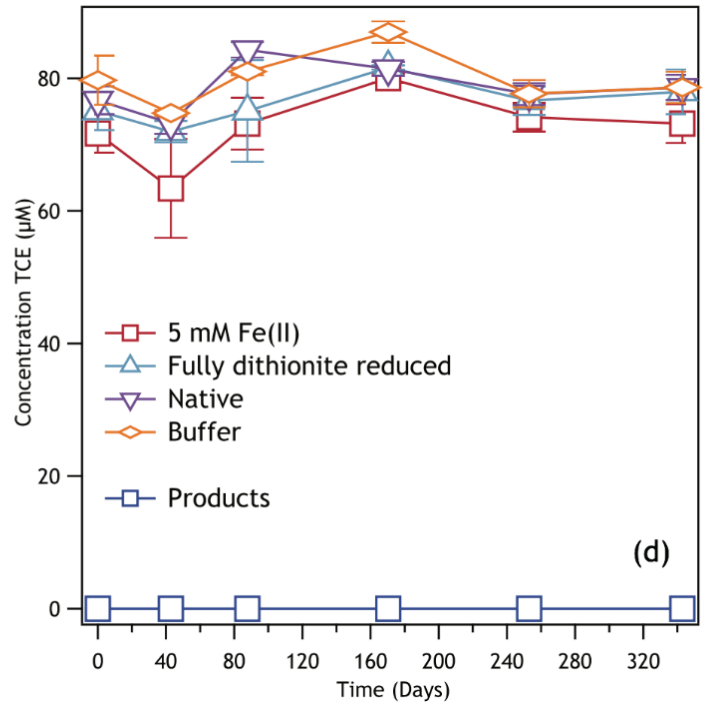


Magnetite is unlikely to be as important as previously thought for abiotic reduction of PCE and TCE in anoxic groundwater plumes.

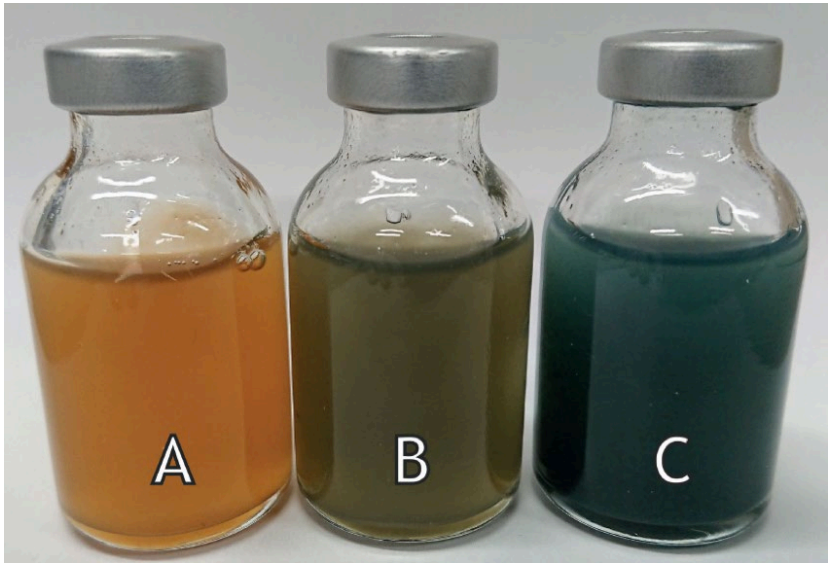
2 Structural Fe(II) in Clay Minerals

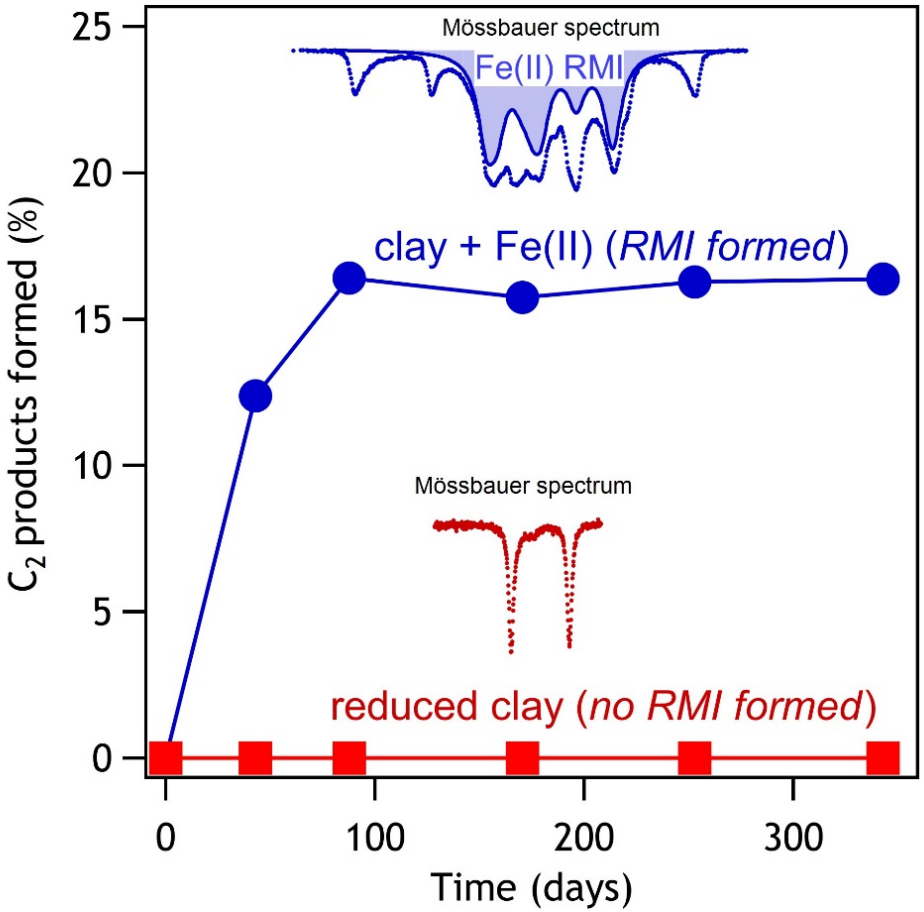






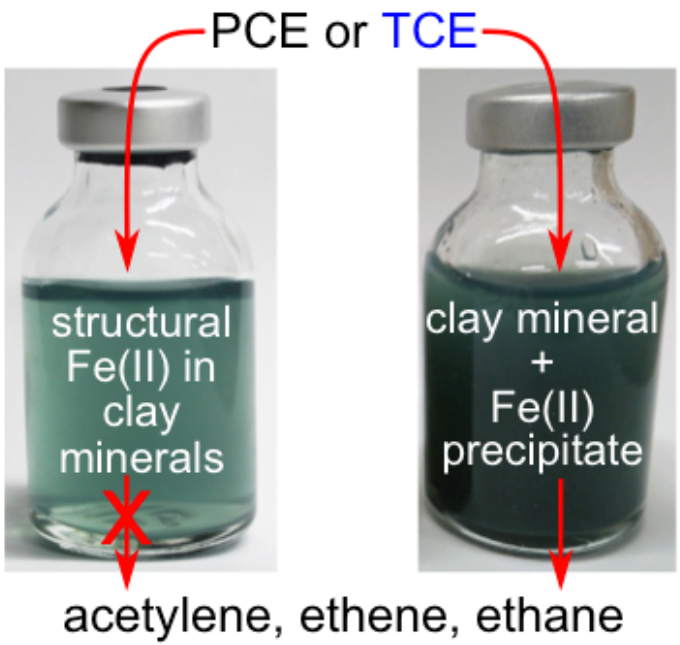
Fe clay + Fe(II) does reduce PCE and TCE *sometimes*

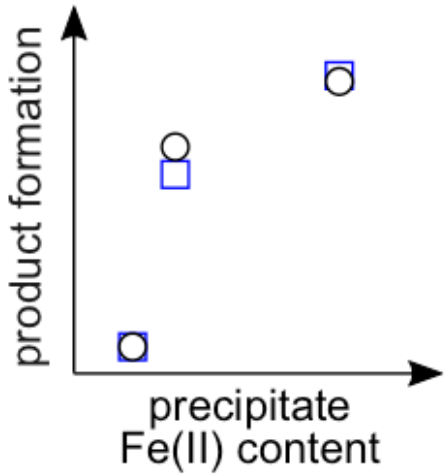




Source: Whiting (2014) GWMR

2 Structural Fe(II) in Clay Minerals

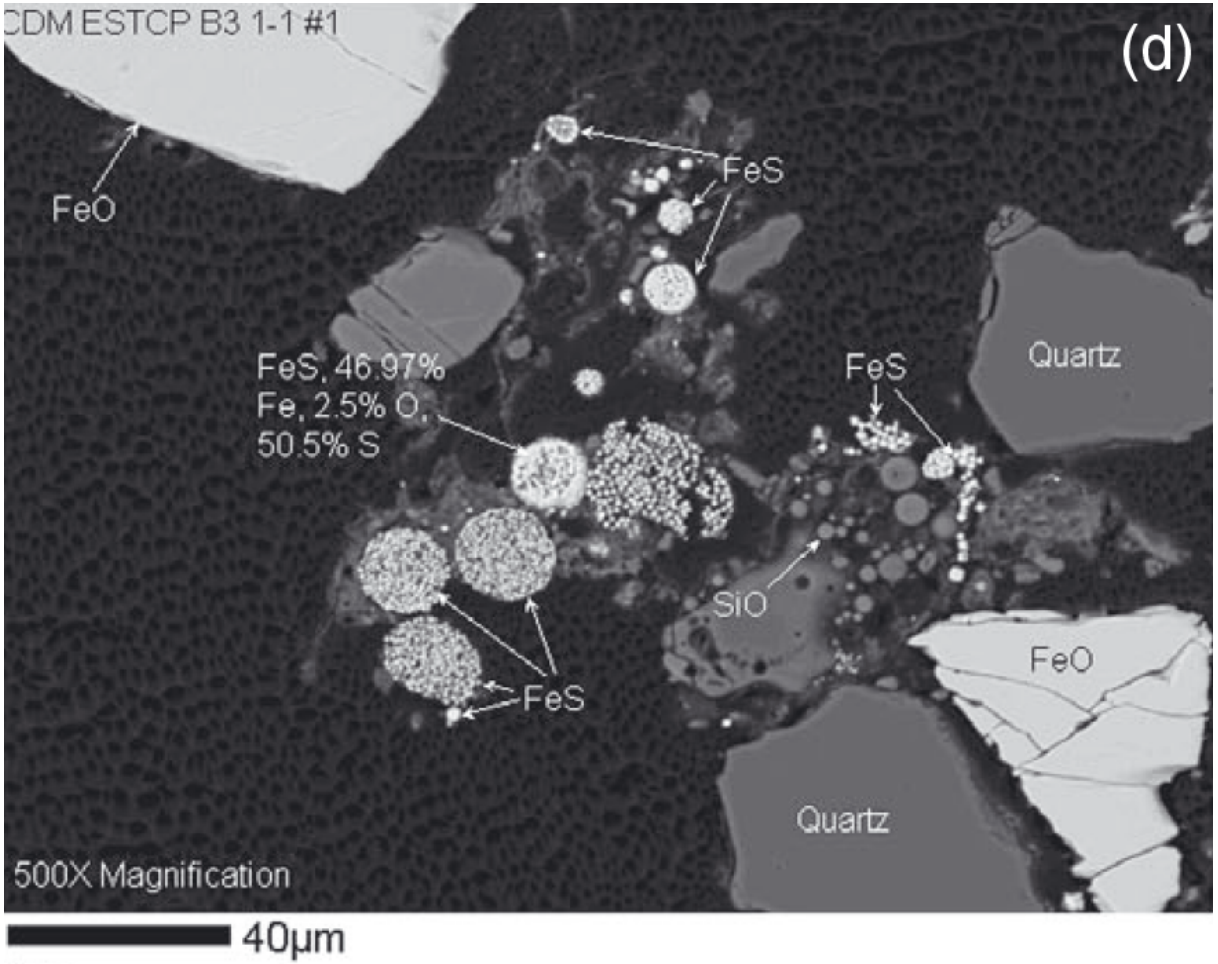




Structural Fe(II) in clay minerals is unlikely to be important for abiotic reduction of PCE and TCE in anoxic groundwater plumes.

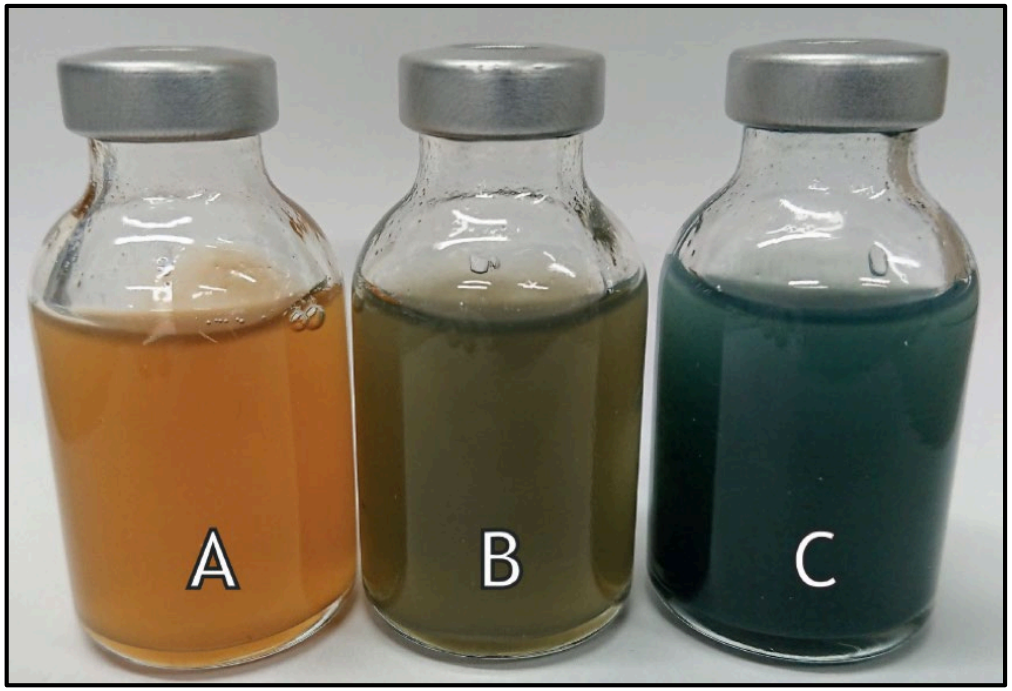
In the presence of dissolved Fe(II), however, clay minerals containing low or no Fe appear to enable the formation of a reactive mineral intermediate that does slowly reduce PCE and TCE.

The presence of these Fe-containing minerals is unlikely to be sufficient for **ANA**

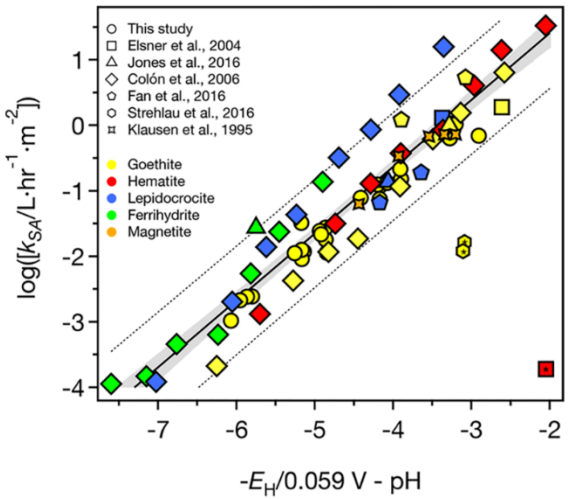


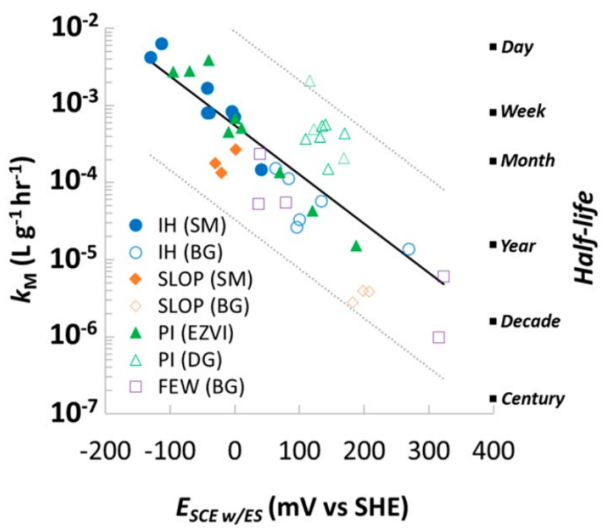
***Source**: Whiting (2014) GWMR*

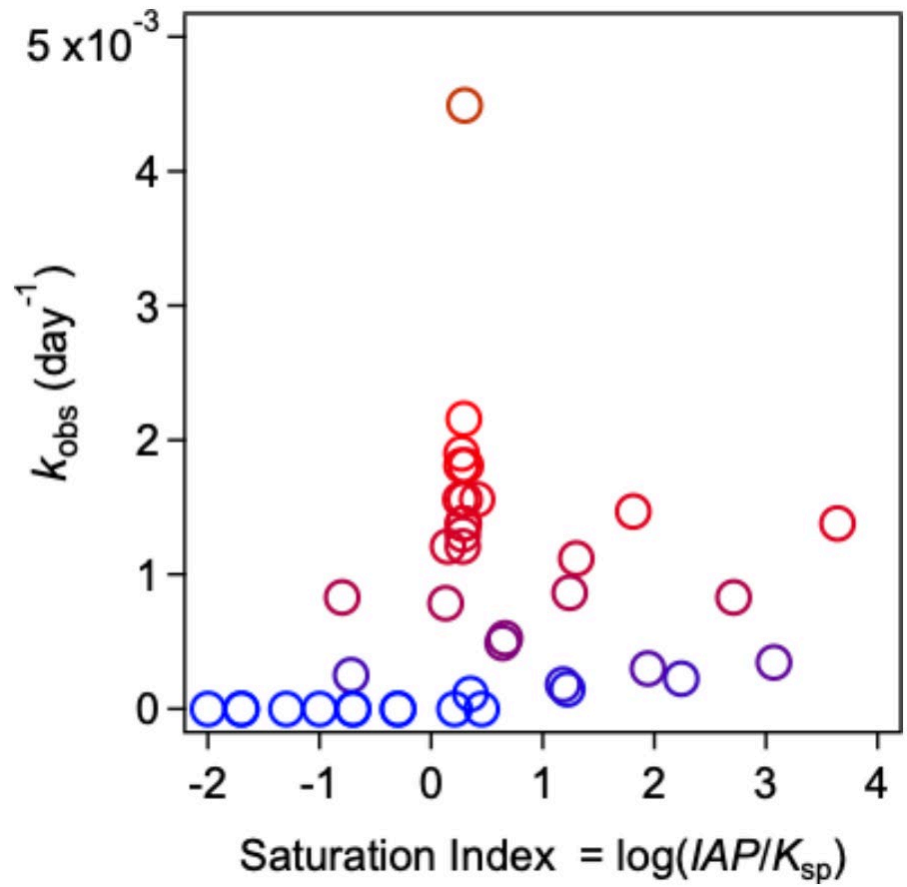
Active precipitation of **Reactive Mineral Intermediates** may be more relevant



Saturation indices and redox potentials may be useful as indicators of **RMI** formation







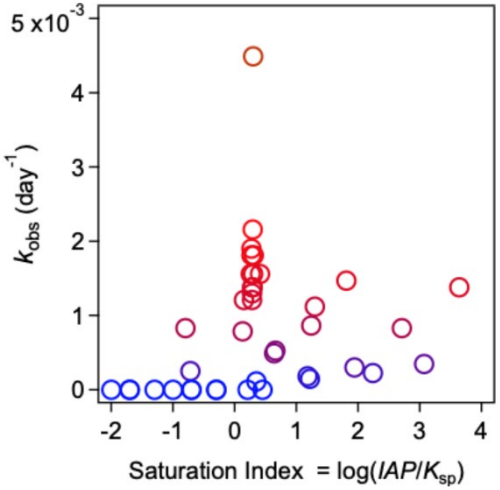
Sources: *Stewart/Gorski (2018) ES&T 52: 5600; Kocur/Johnson/Tratnyek (2019) ES&TL 7: 20*

Is ANA Likely?

- We suggest that rather than looking for specific minerals, aquifer/groundwater properties may be more predictive of whether ANA is likely at a site

Conclusions

- **Magnetite** unlikely to directly reduce PCE and TCE in anoxic aquifers
  - Therefore, magnetite presence likely not sufficient for ANA evidence
- **Fe(II) in clays** also unlikely to directly reduce PCE and TCE in anoxic aquifers
- **Reactive mineral intermediates** (RMIs) may contribute to ANA and SI and redox measurements may be good indicators



Benefits to DoD

- ANA applicable to most DoD priority COCs
  - Energetics, chlorinated solvents, some metals, not 1,4-dioxane or PFAS
- Predict reduction rates at specific field sites using SI analysis and $k_{ORP/ES}$
  - Development continuing
- Enhance ANA by stimulation of RMI formation based on SI analysis
  - Active, dynamic, and transient

Additional Resources

- Culpepper, J., M. Scherer, T. Robinson, A. Neumann, D. Cwiertny, and D. Latta. **2018**. Reduction of PCE and TCE by magnetite revisited. *Environ. Sci. Proc. Impacts* 20(10): 1340-1349 [DOI: 10.1039/c8em00286j]

- Entwistle, J., D. E. Latta, M. M. Scherer, and A. Neumann. **2019**. Abiotic degradation of chlorinated solvents by clay minerals and Fe(II): Evidence for reactive mineral intermediates. *Environ. Sci. Technol.* 53(24): 14308-14318 [DOI: 10.1021/acs.est.9b04665]

For additional information, please visit

https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Persistent-Contamination/ER-2532

Speaker Contact Information

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Q&A Session 2

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The next webinar is on December 10, 2020

Approaches for Managing Contaminated Sediments

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