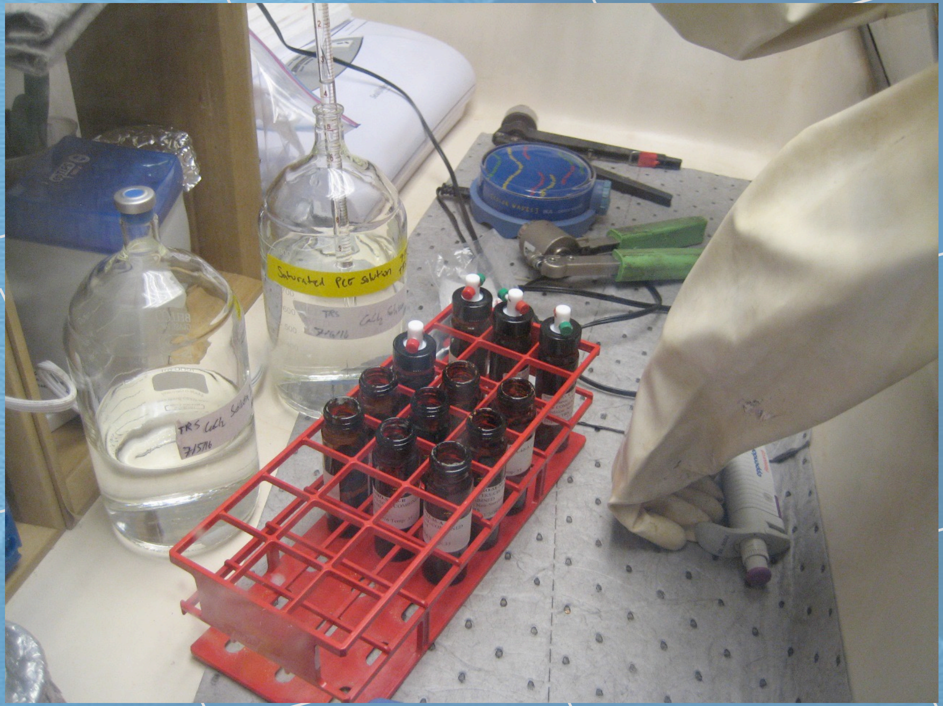
Naturally Occurring Dechlorination Reactions under Oxic and Anoxic Conditions in Natural Solids



CDM Smith

Charles Schaefer, Ph.D.

Paul Ho

University of Texas

Charles Werth, Ph.D.

Erin Berns

September 12, 2019

Abiotic Dechlorination via Ferrous Minerals

- Several studies have focused on abiotic dechlorination reactions facilitated by naturally occurring ferrous minerals
  - *Pyrite, magnetite, green rusts*

- Natural clays and rock matrices have received little attention
  - *Ferrous minerals are present in many natural clays and rock*

- Diffusion is a SLOW process, so even a slow dechlorination reaction within the clay or rock matrix can be an important attenuation mechanism

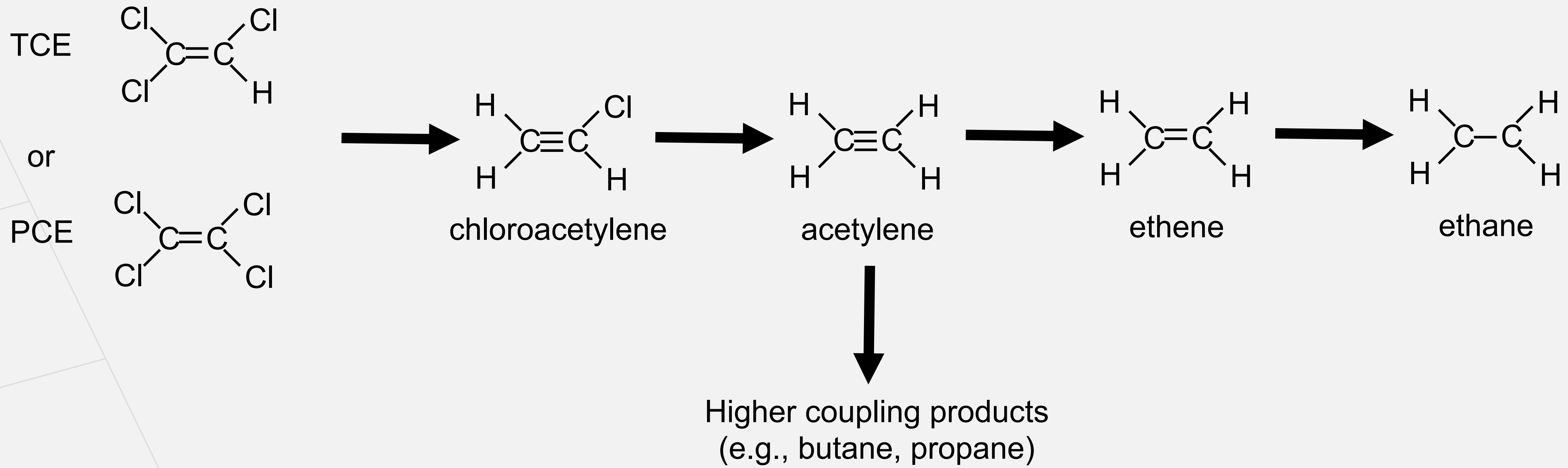
Outline

- Assess abiotic dechlorination mechanisms and pathways
- Determination of abiotic dechlorination rates in natural clay
  - Role of oxygen
- Potential importance at field sites
- Field-scale assessment of abiotic dechlorination

Abiotic Dechlorination via Ferrous Minerals

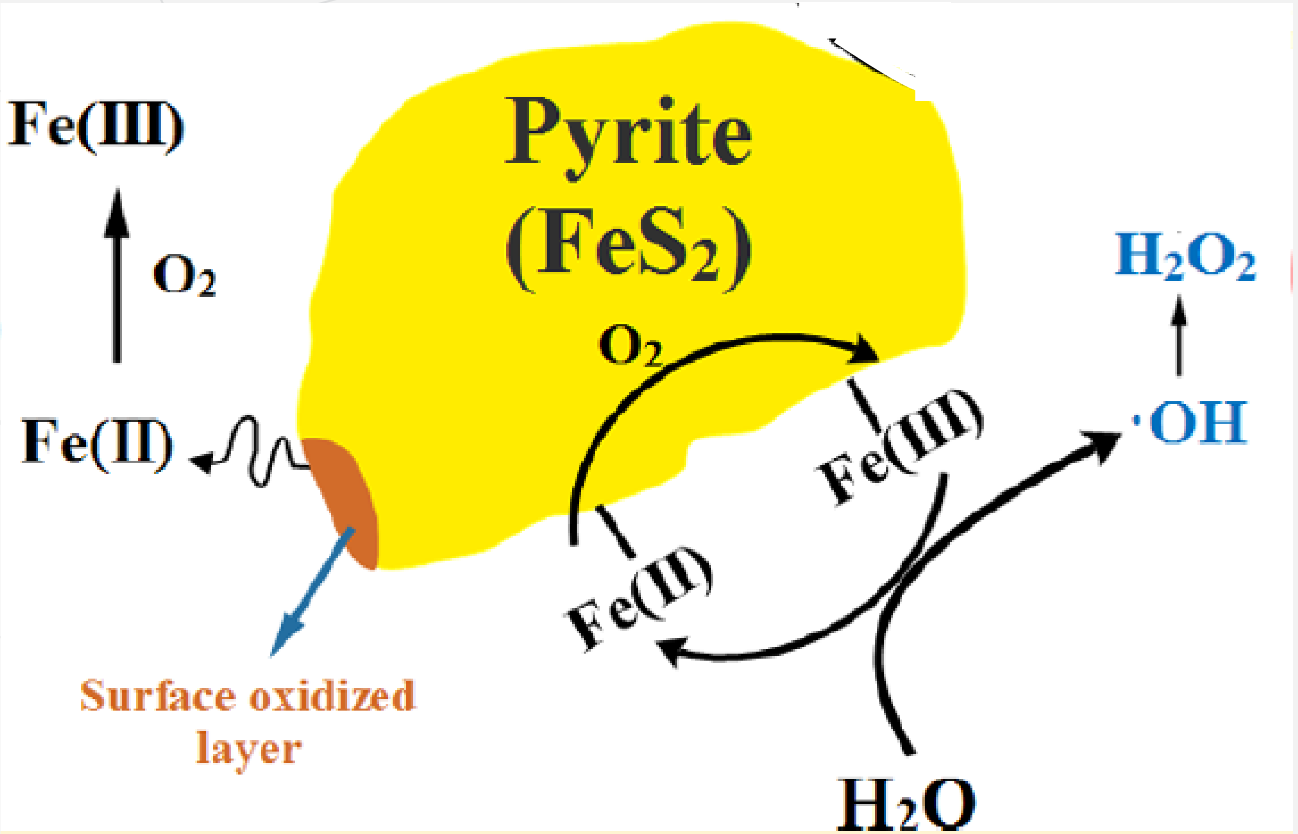
Anaerobic Conditions

- **FeS**
- **Pyrite (FeS_2)**
- **Magnetite (Fe_3O_4)**
- **Green rusts**



Abiotic Dechlorination via Ferrous Minerals

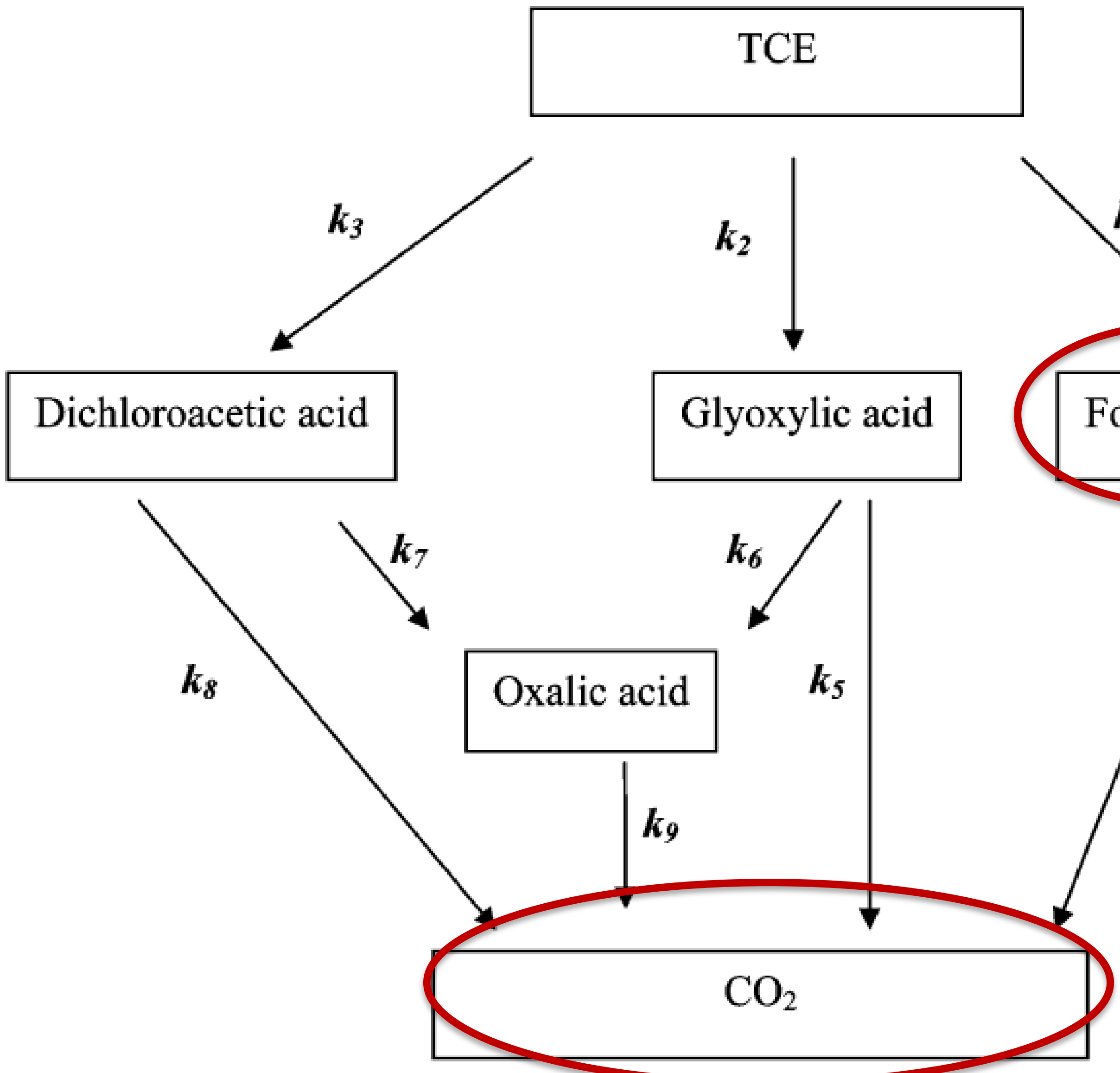
Aerobic Conditions – Hydroxyl Radical formation

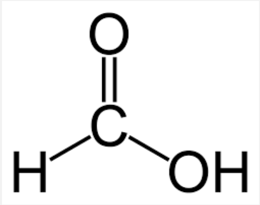


from Kong et al., *ES&T,* 2015

$$3Fe(II)_{min} + O_2 + 2H^+ \longrightarrow 3Fe(III)_{min} + OH^- + \bullet OH$$

Abiotic Dechlorination via Pyrite Minerals: Aerobic Pathway





from Pham et al., *ES&T,* 2009

Bench-Scale Testing to Determine Dechlorination Kinetics

- Gamma-irradiated clayey soils
- Anaerobic and aerobic test systems
- Triplicates
- Vary temperature

TCE spike

No
TCE spike

Analyze headspace for:
- VOCs
- Reduced gases
- O_2/CO_2

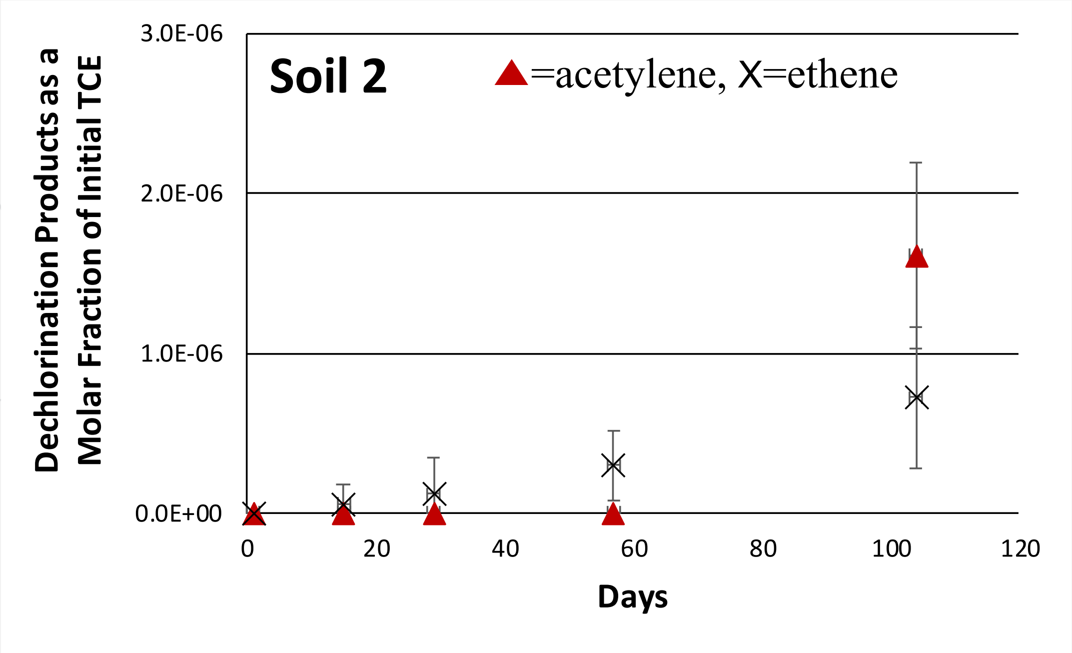
Analyze water for
- OAs
- Final pH

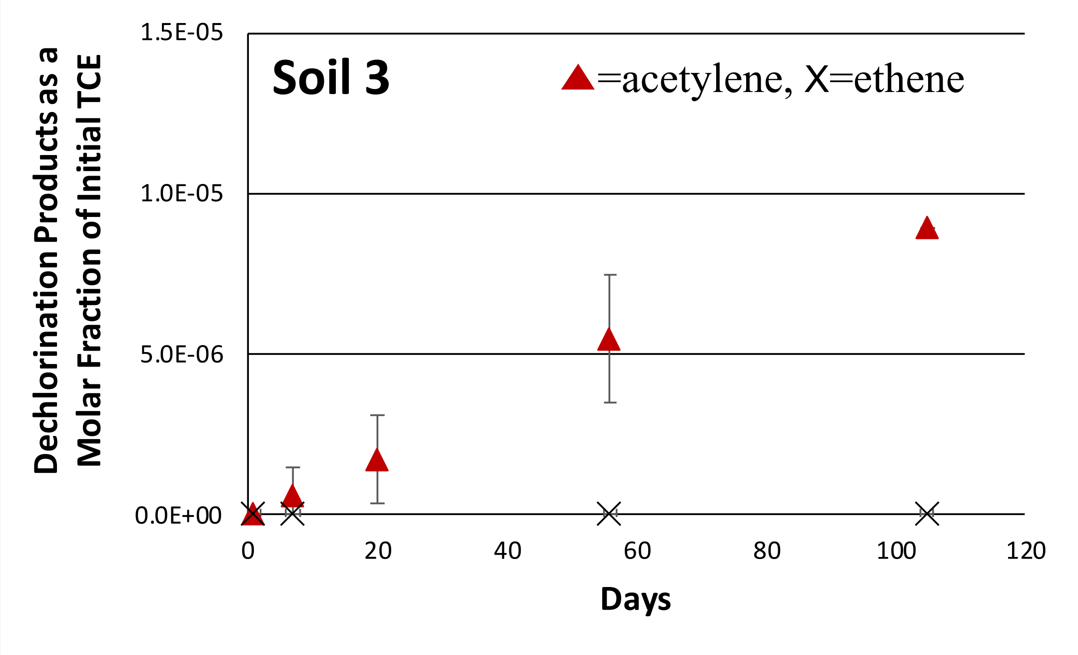
Natural Soils

Property	Soil 1	Soil 2	Soil 3***	Soil 4****	Soil 5
% Mineral Content (XRD)	illite (41); albite (30); quartz (25); siderite (1.6); anhydrite (1.5)	illite (33); quartz (27); ankerite (16); albite (16); kaolinite (3.5); calcite (3.0); siderite (1.0)	illite (29); quartz (23); ankerite (18); albite (17); kaolinite (6.9); calcite (5.4)	albite (42); illite (29); quartz (12); anhydrate (16);	Quartz (34); Albite (33); Orthoclase (22); biotite (9.3); apatite (1.5)
% Clay	37	23	23	2.1	13
% Silt	55	26	22	2.2	13
% Sand & Gravel	8	51	55	96	74
Magnetic Susceptibility (m^3/kg)	3.9×10^{-7}	3.5×10^{-7}	2.1×10^{-7}	6.1×10^{-7}	3.4×10^{-6}
Ferrous mineral content (mg/kg)	2570	160	337	45	3.3

Results – Anaerobic Conditions (<26μM O_2)

<u>Soils 4 & 5</u>: No transformation products detected (reduced gases, CO_2, OAs)

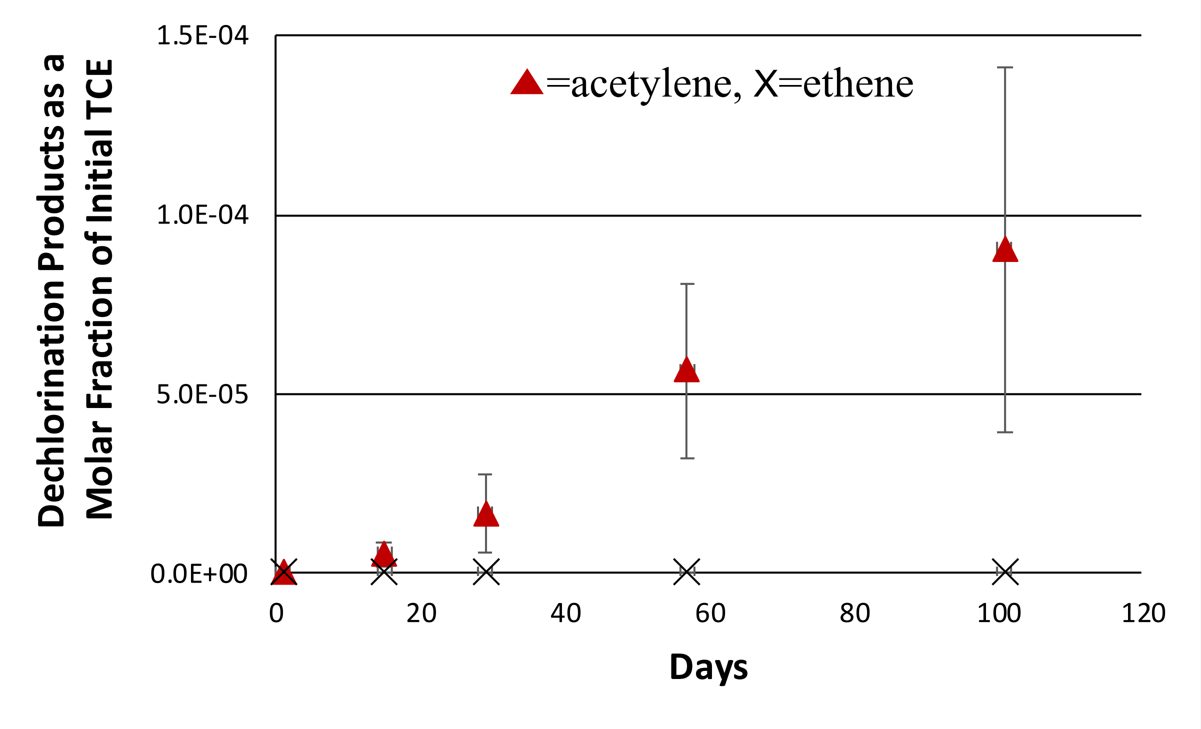


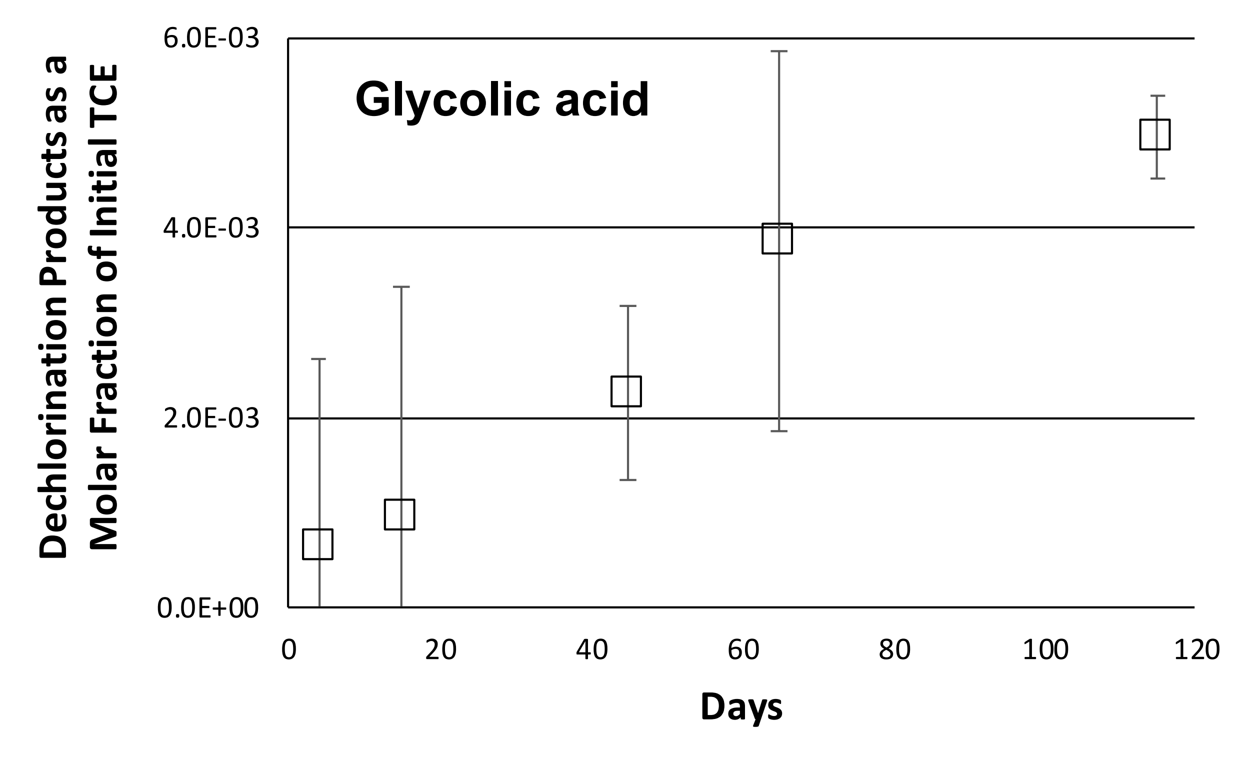


As expected, clayey soils with ferrous iron have reduced gas transformation products

Results – Anaerobic Conditions (<26µM O_2)

Soil 1





- *More reactive than the other soils*
- *Unexpected: OAs>>reduced gases*
- *Trace O_2 levels likely responsible*

CDM Smith

Results – Aerobic Conditions (>120 µM O_2)

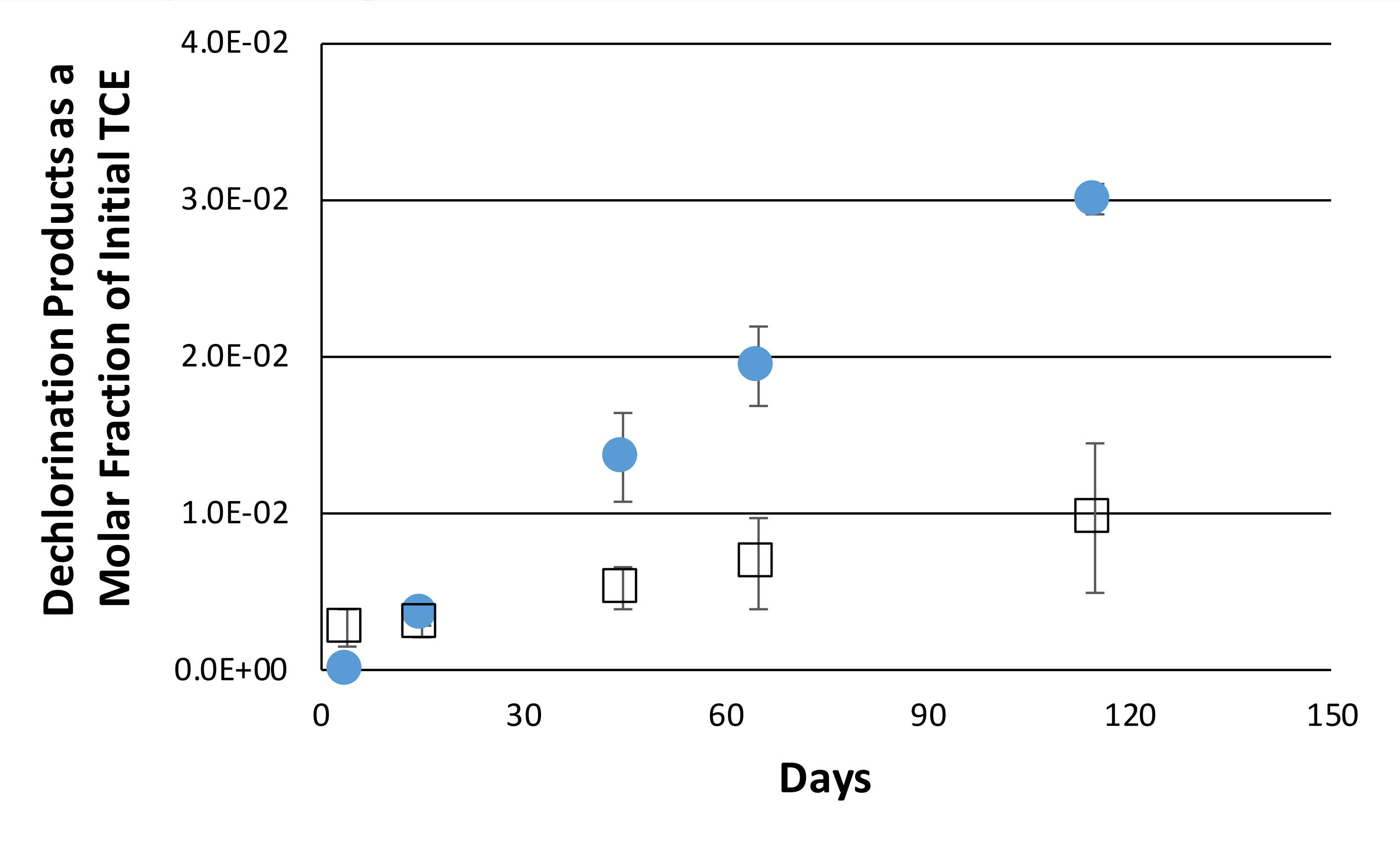
Soils 4 & 5: No transformation products detected (reduced gases, CO_2, OAs)

Reduced gases: none observed for any soil

OAs: observed in Soils 1 through 3

Results – Aerobic Conditions (>120 µM O_2)

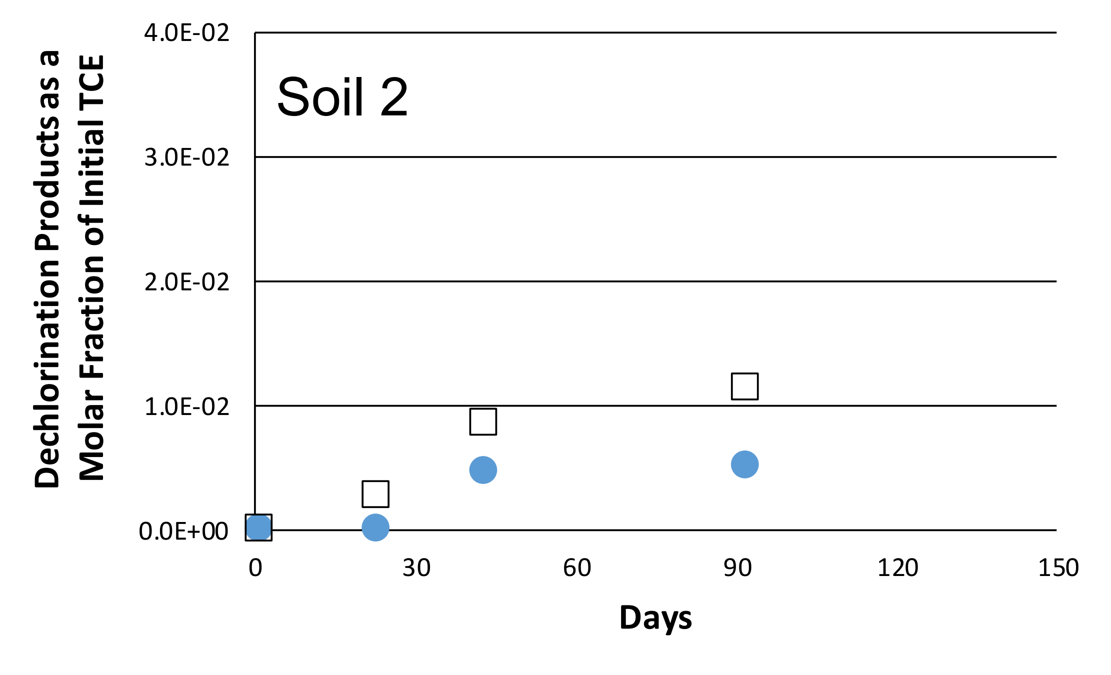
Soil 1

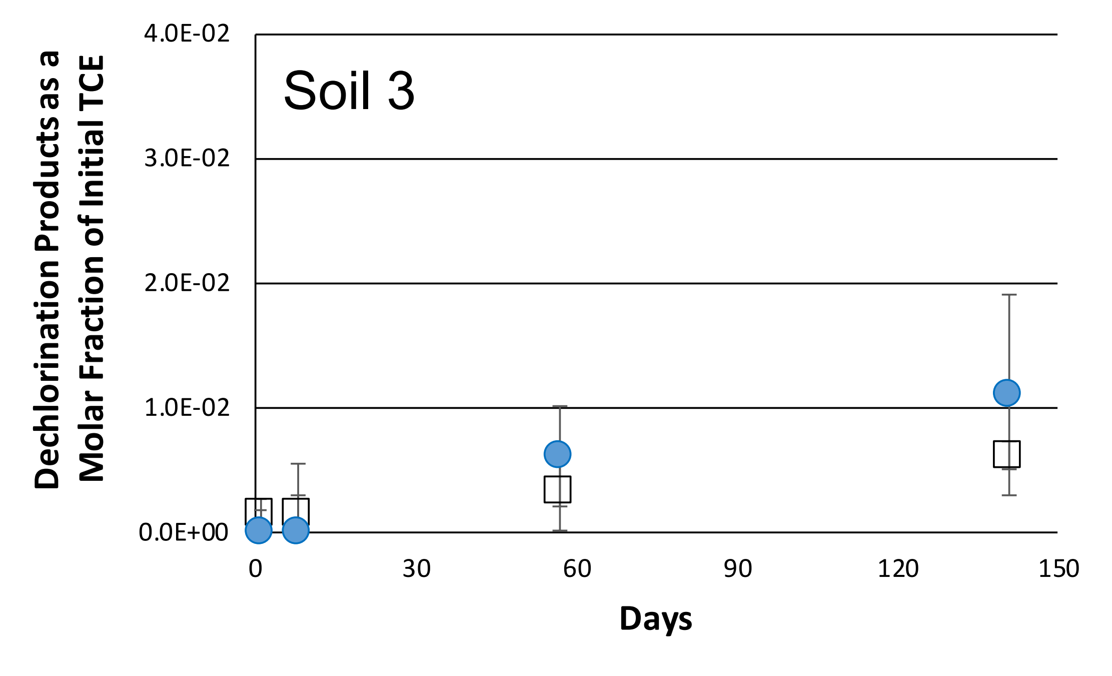


●=formic acid, □=glycolic acid

- ~8-times more OAs generated than under "anaerobic" conditions
- Formic acid formation dominates

Results – Aerobic Conditions (>120 µM O_2)

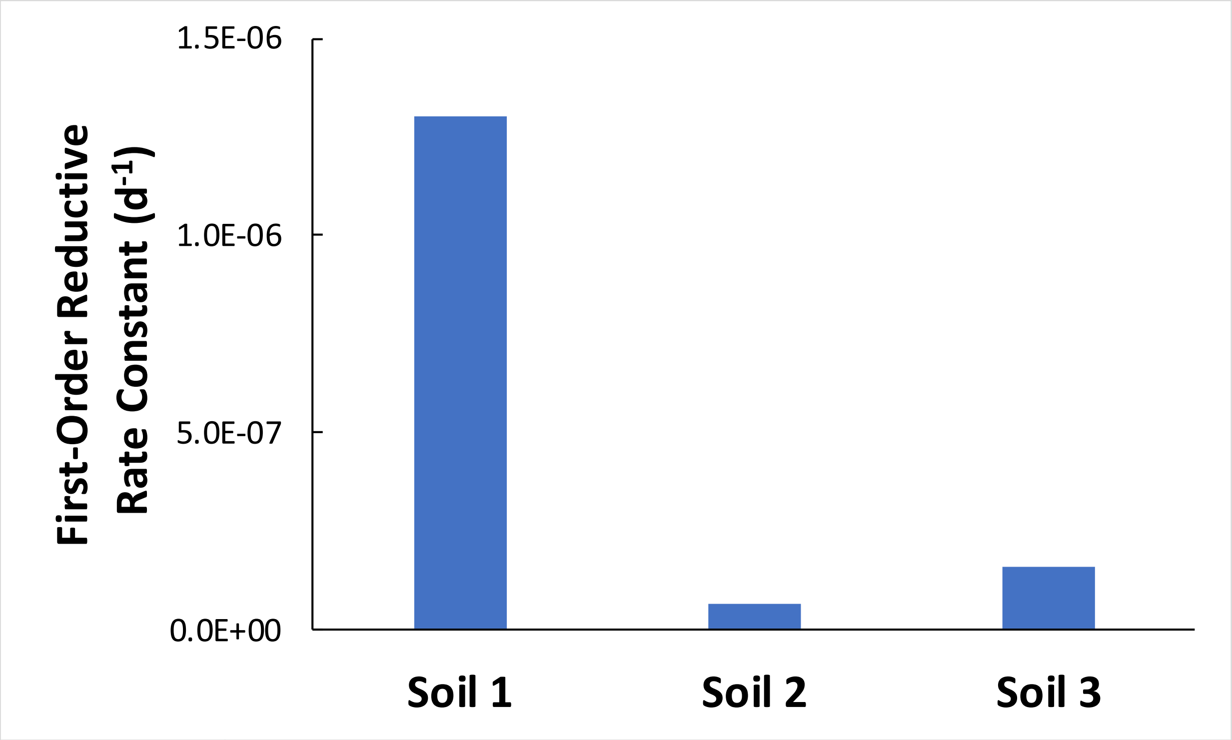


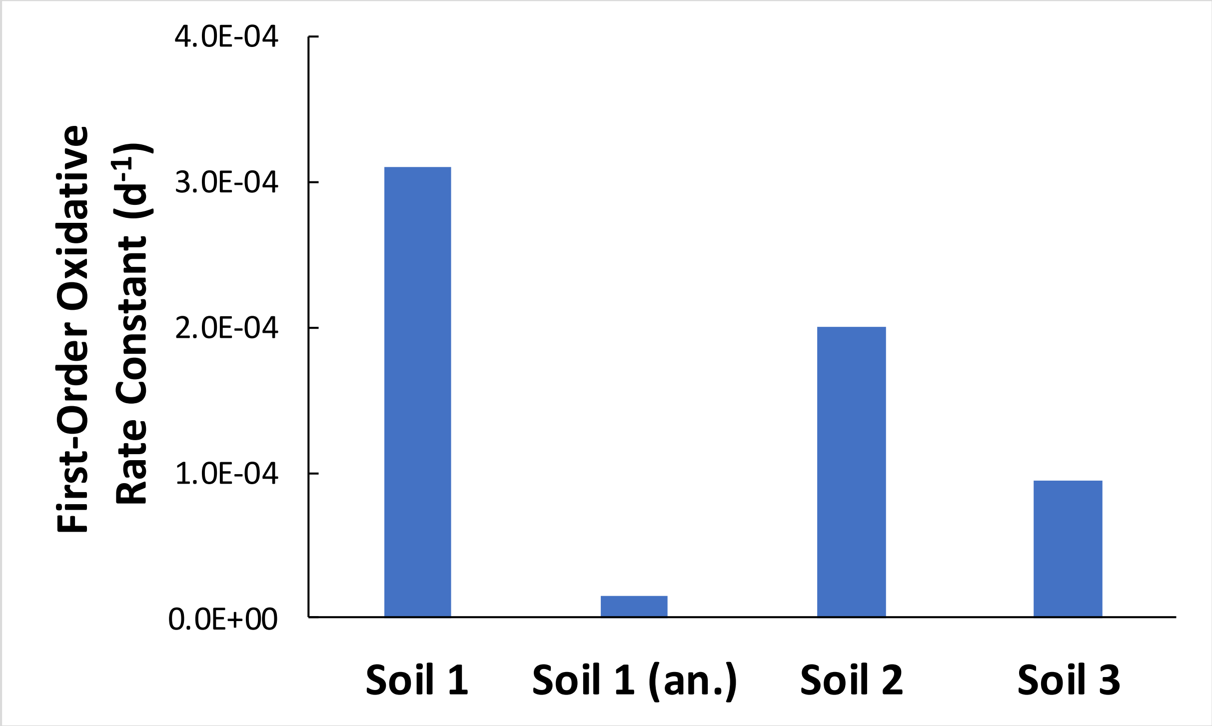


● =formic acid, □ =glycolic acid

CDM Smith

Reductive and Oxidative First-Order Rate Constants





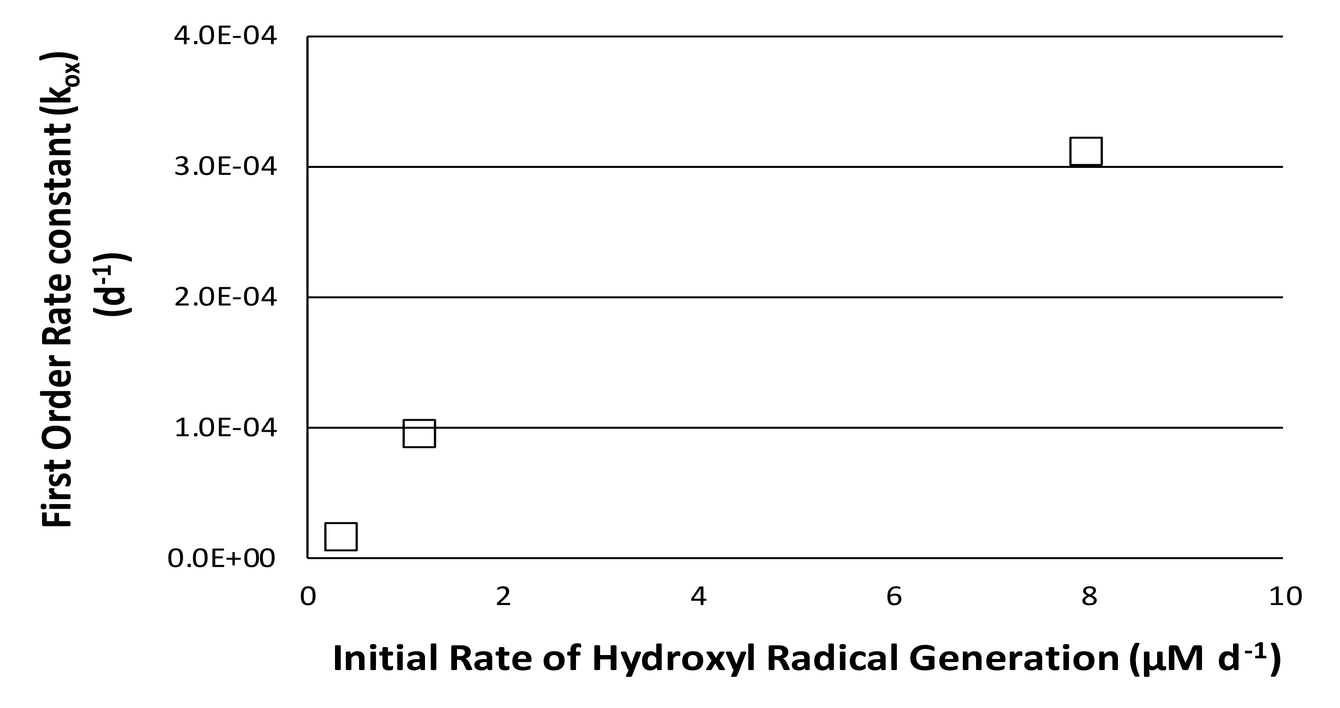
Anaerobic conditions only

Abiotic Oxidative Dechlorination Rate Constant a Function of Hydroxyl Radical Generation Rate

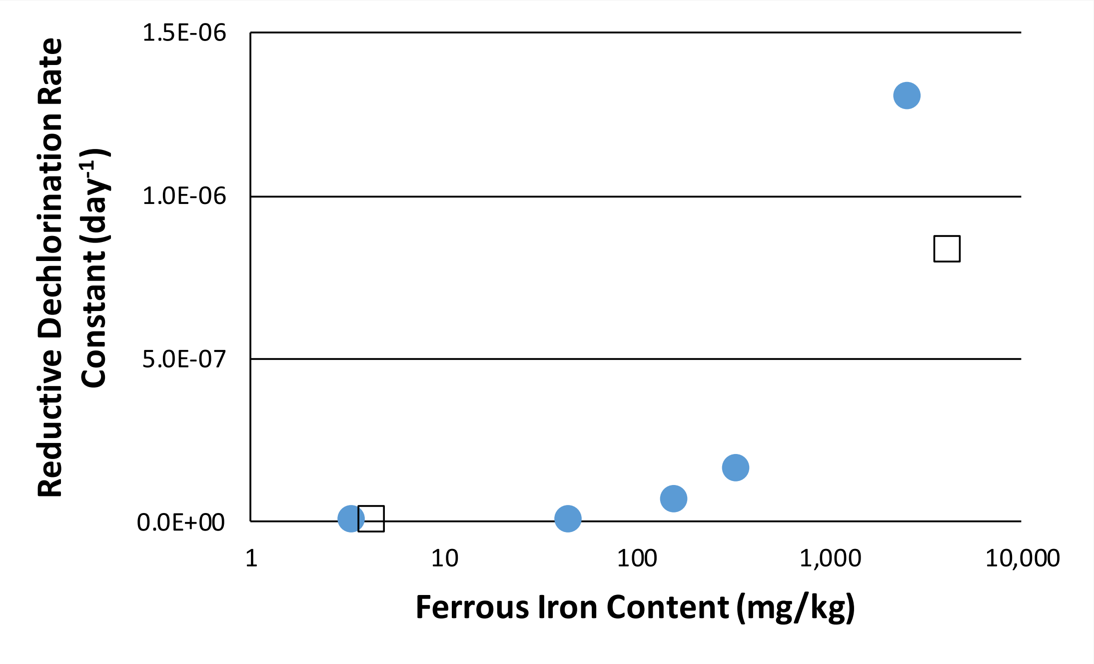
Available online at www.sciencedirect.com
SCIENCE DIRECT
Analytica Chimica Acta 527 (2004) 73–80
ANALYTICA CHIMICA ACTA
www.elsevier.com/locate/aca

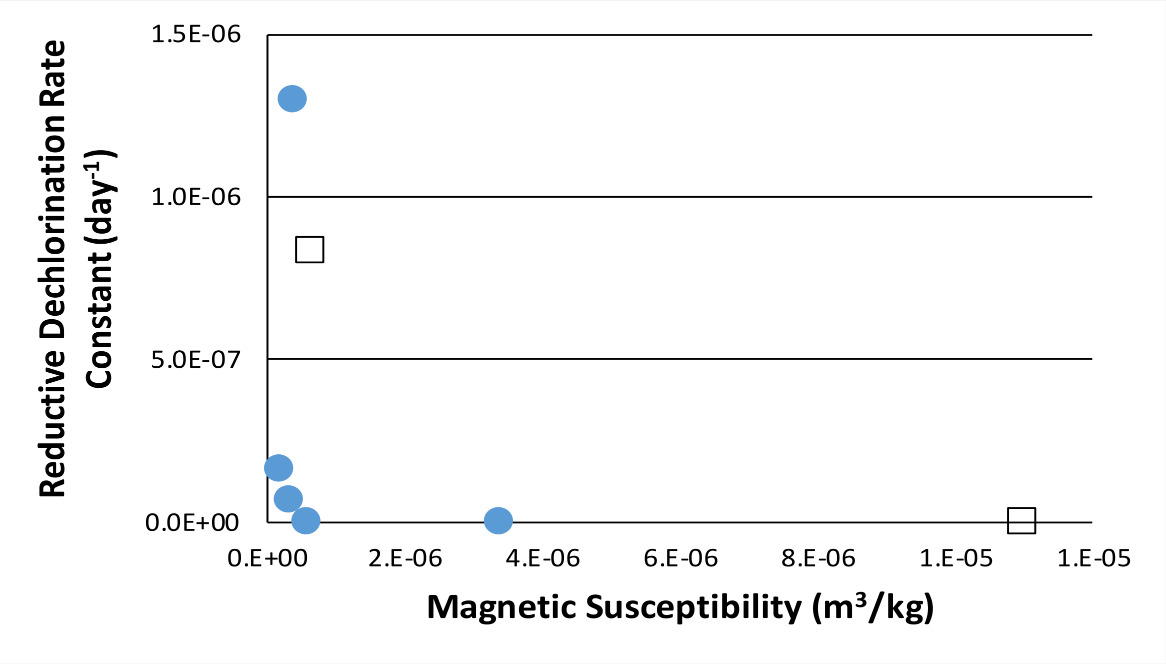
Determination of hydroxyl radicals in advanced oxidation processes with dimethyl sulfoxide trapping and liquid chromatography

Chao Tai[a], Jin-Feng Peng[a], Jing-Fu Liu[a], Gui-Bin Jiang[a,*], Hong Zou[b]

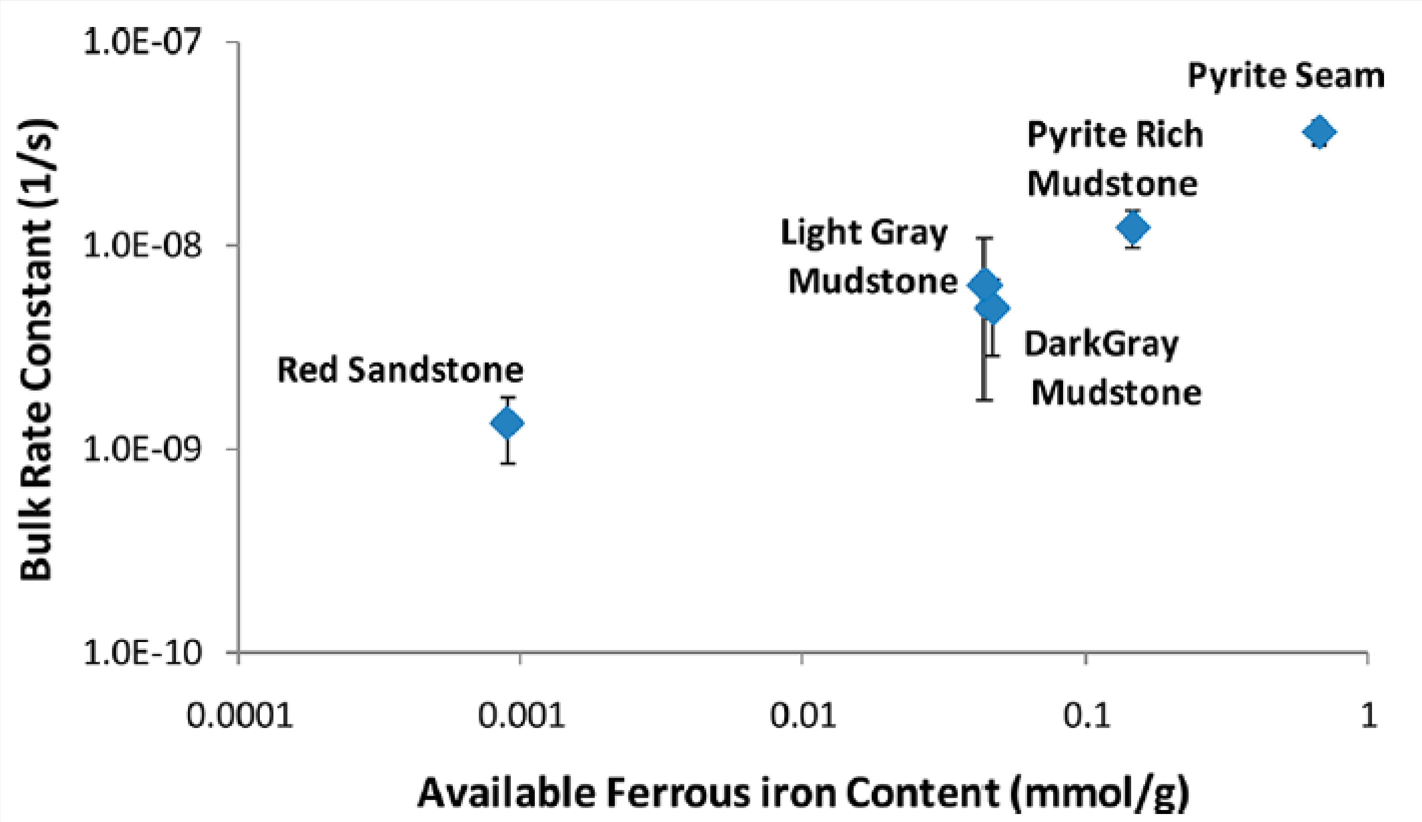


Reductive Rate Constants Related to Mineral Properties



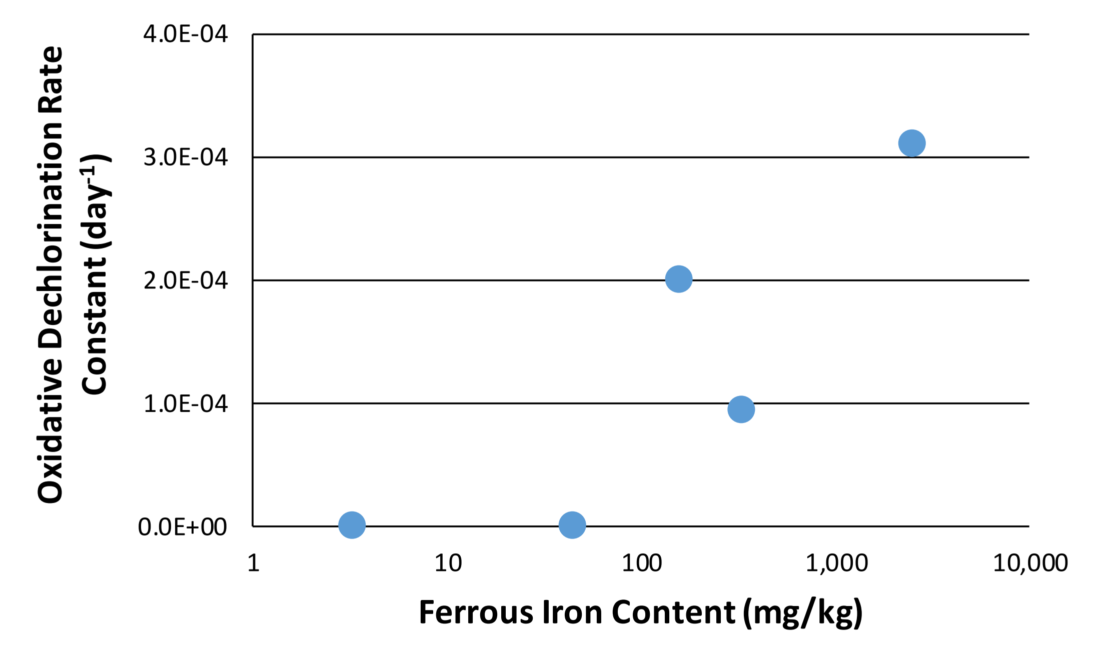


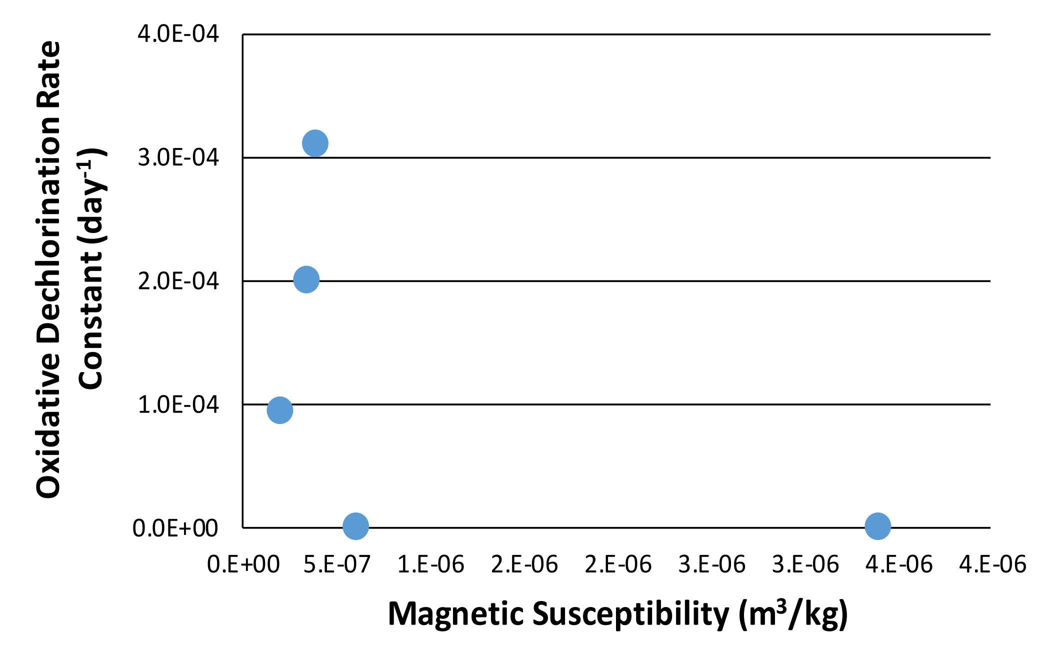
Similar Trend Observed for TCE Abiotic Dechlorination in Rock Matrices

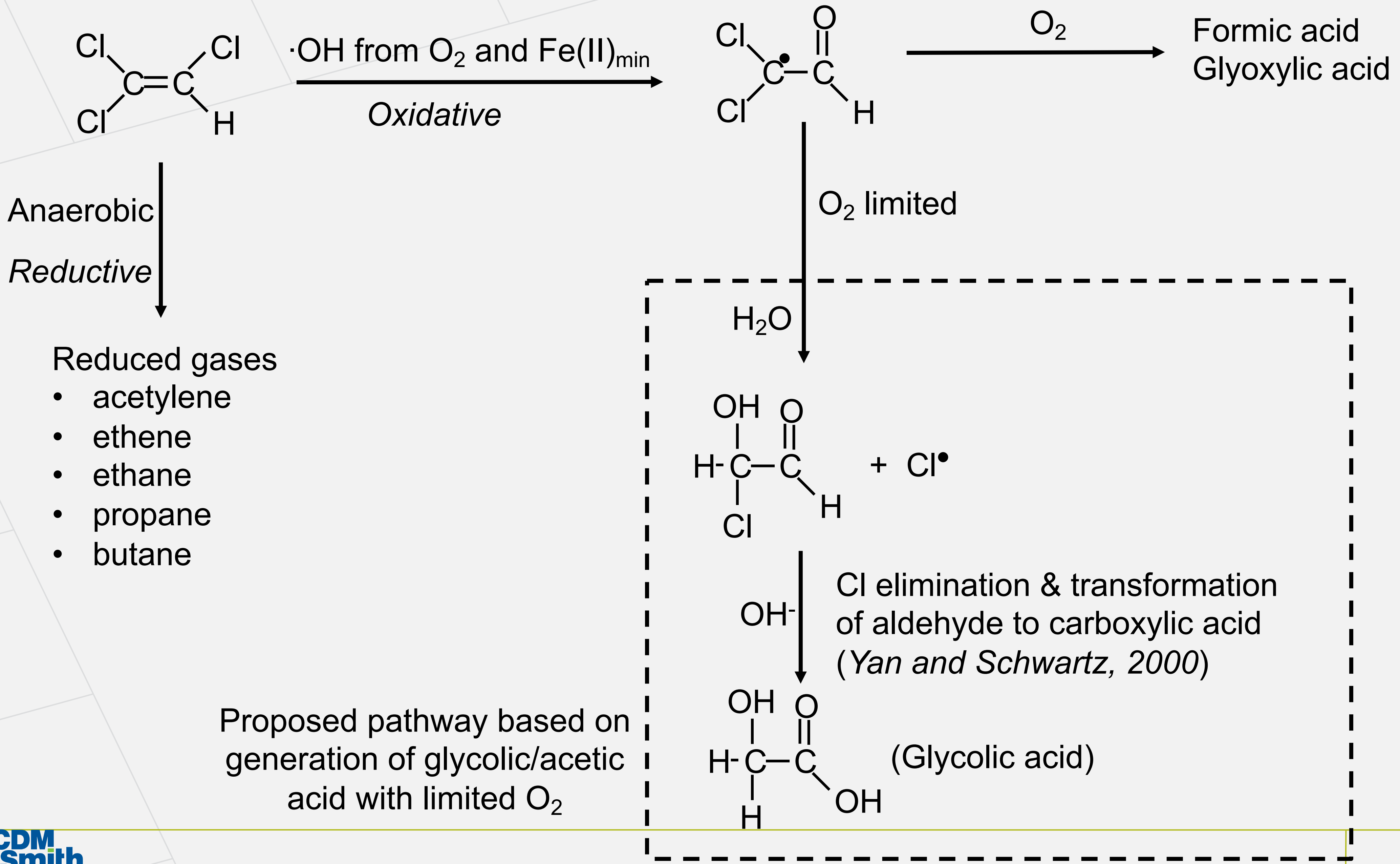


Schaefer et al., ES&T, 2013

Oxidative Aerobic Rate Constants Related to Mineral Properties






·OH from O2 and Fe(II)min
Oxidative
O2
Formic acid
Glyoxylic acid
Anaerobic
Reductive
O2 limited
Reduced gases
• acetylene
• ethene
• ethane
• propane
• butane
H2O
+ Cl•
OH-
Cl elimination & transformation of aldehyde to carboxylic acid (Yan and Schwartz, 2000)
(Glycolic acid)
Proposed pathway based on generation of glycolic/acetic acid with limited O2

CDM Smith

So How Important Are These Reactions?

Anaerobic Conditions

Half life as short as 60 years (*shorter at lower TCE concentrations*)

<0.003% of ferrous iron consumed

Aerobic Conditions

Half lives ranging from 0.25 to 0.83 years

11 to 40% ferrous mineral consumption based on hydroxyl radical generation

Field Assessment of Matrix Back-Diffusion & Abiotic Dechlorination

ESTCP Project ER-201330

D. Lippincott (APTIM), H. Klammler (UF), K. Hatfield (UF)

- While bench-scale testing is critical for demonstrating mechanisms, typically only a very small portion of the clay/rock media is interrogated (i.e., 2-inch cores)


Journal of Contaminant Hydrology 209 (2018) 33–41

Contents lists available at ScienceDirect

Journal of Contaminant Hydrology

journal homepage: www.elsevier.com/locate/jconhyd

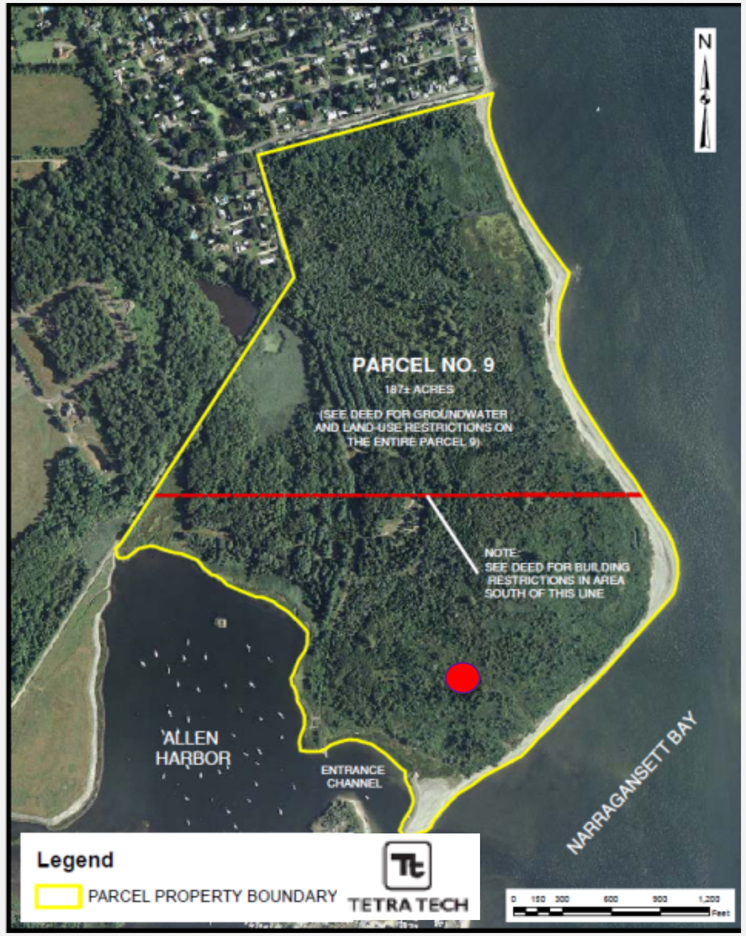
ELSEVIER

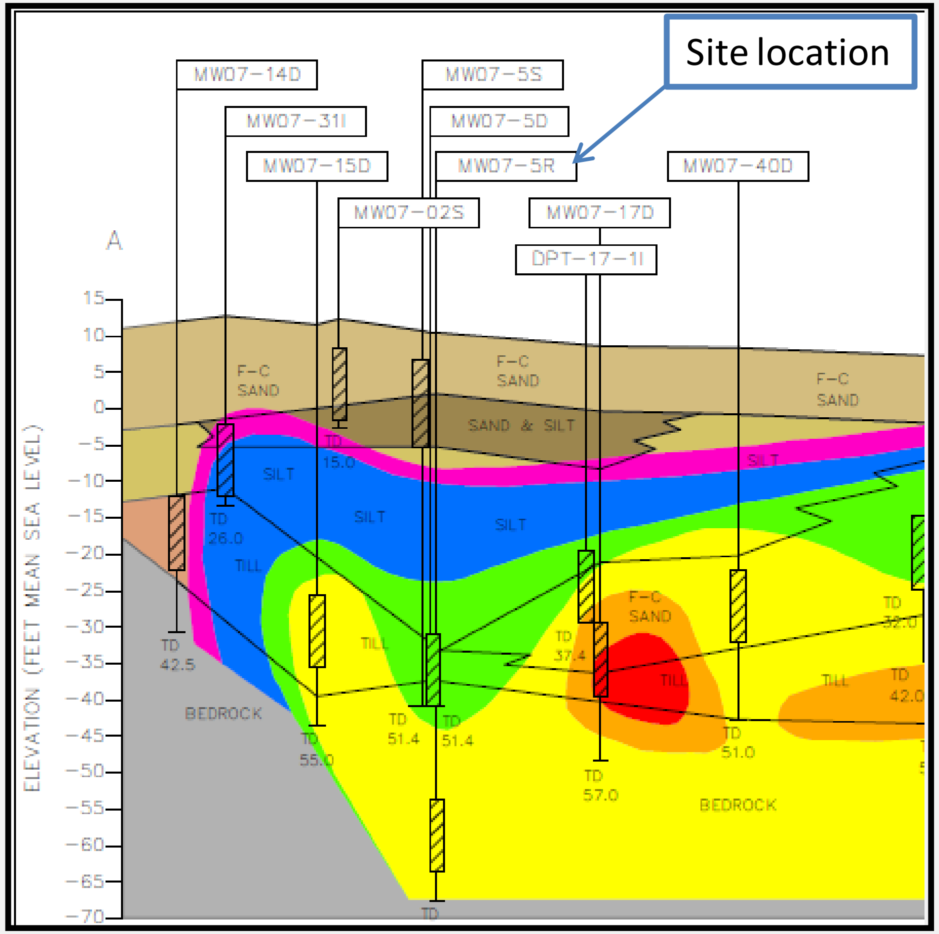
Evidence of rock matrix back-diffusion and abiotic dechlorination using a field testing approach

Charles E. Schaefer[a,*], David R. Lippincott[b], Harald Klammler[c], Kirk Hatfield[c]

Site Location – Calf Pasture Point (RI)

- Navy construction battalion center (1951-1994)
- meta-sandstone/schist/gneiss
- TCE+DCE





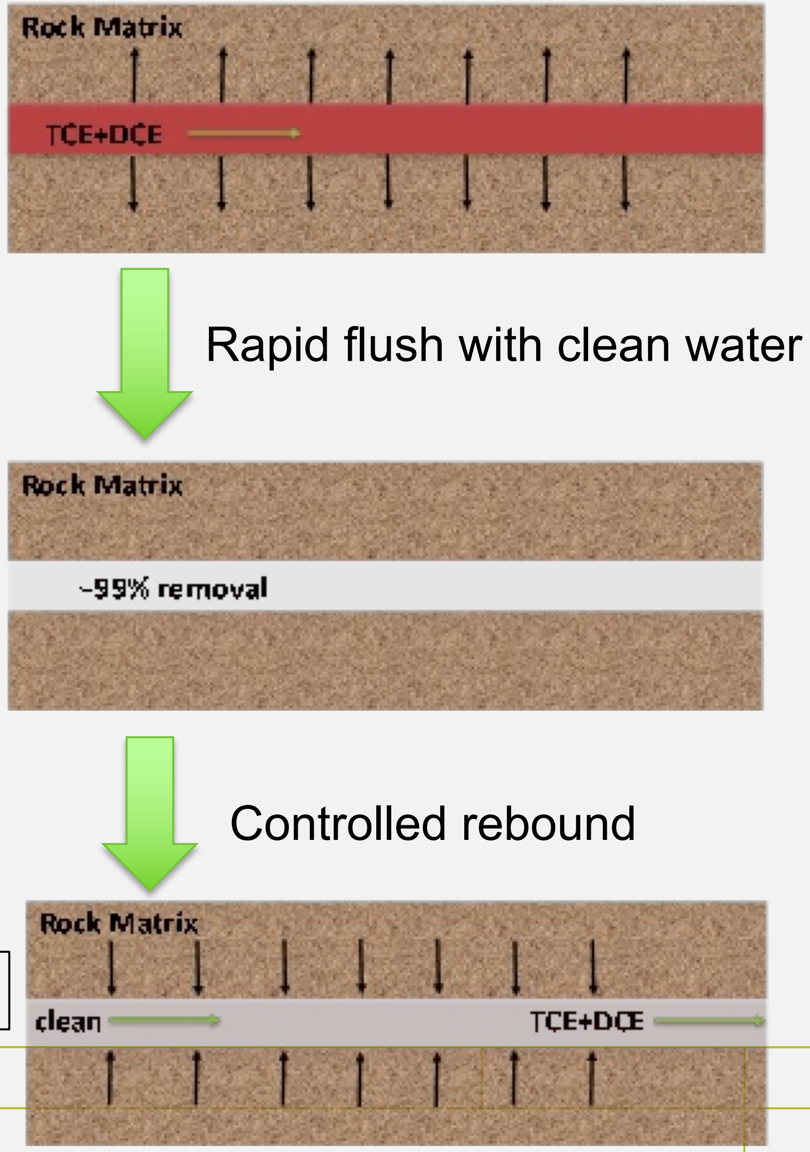
Evidence of Abiotic Dechlorination Using Compound Specific Isotopic Analysis (CSIA)

Enrichment observed (TCE+DCE), without generation of VC. Consistent with abiotic reaction.

<u>Baseline CSIA</u>

$$x_{TCE}\delta^{13}C_{TCE} + x_{DCE}\delta^{13}C_{DCE}$$

-24.2 ‰



<u>CSIA After Rebound</u>

$$x_{TCE}\delta^{13}C_{TCE} + x_{DCE}\delta^{13}C_{DCE}$$

-19.0 ‰

Conclusions

- Abiotic dechlorination reaction can occur in natural aquifer solids due to the presence of ferrous minerals
- The presence of oxygen impacts reaction pathways and kinetics
- These reactions can be important when considering long-term contaminant fate and transport
- Field-assessment techniques using CSIA can provide additional insight and verification

Becoming an increasingly important approach for addressing our clients needs: mineral screening & treatability testing

Research Funding

SERDP
DOD ▪ EPA ▪ DOE

ESTCP

Contact Information

Charles Schaefer, Ph.D.
732-590-4633
schaeferce@cdmsmith.com