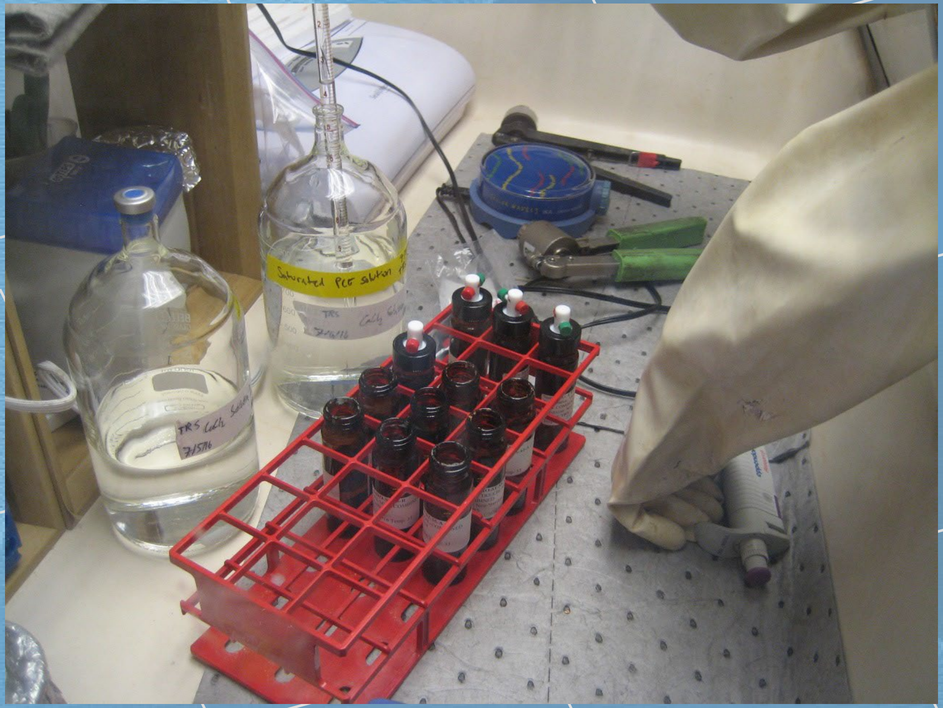
Abiotic Dechlorination of Trichloroethene by Naturally Occurring Ferrous Minerals under Aerobic and Anaerobic Conditions

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April 17, 2019

Abiotic Dechlorination via Ferrous Minerals

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

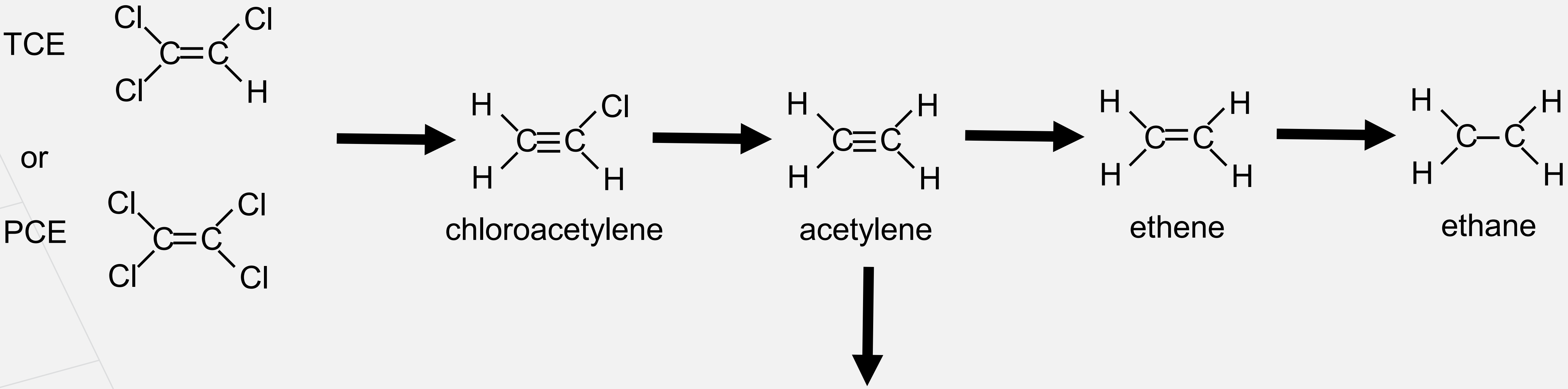
- Several studies have focused on abiotic dechlorination reactions facilitated by naturally occurring ferrous minerals
  - *Pyrite, magnetite, green rusts*
  - *Fundamental questions remain*

- Many questions remain regarding abiotic dechlorination in natural clay/rock matrices
  - *Ferrous minerals are present in many natural clays and rock*

Abiotic Dechlorination via Ferrous Minerals

Anaerobic Conditions

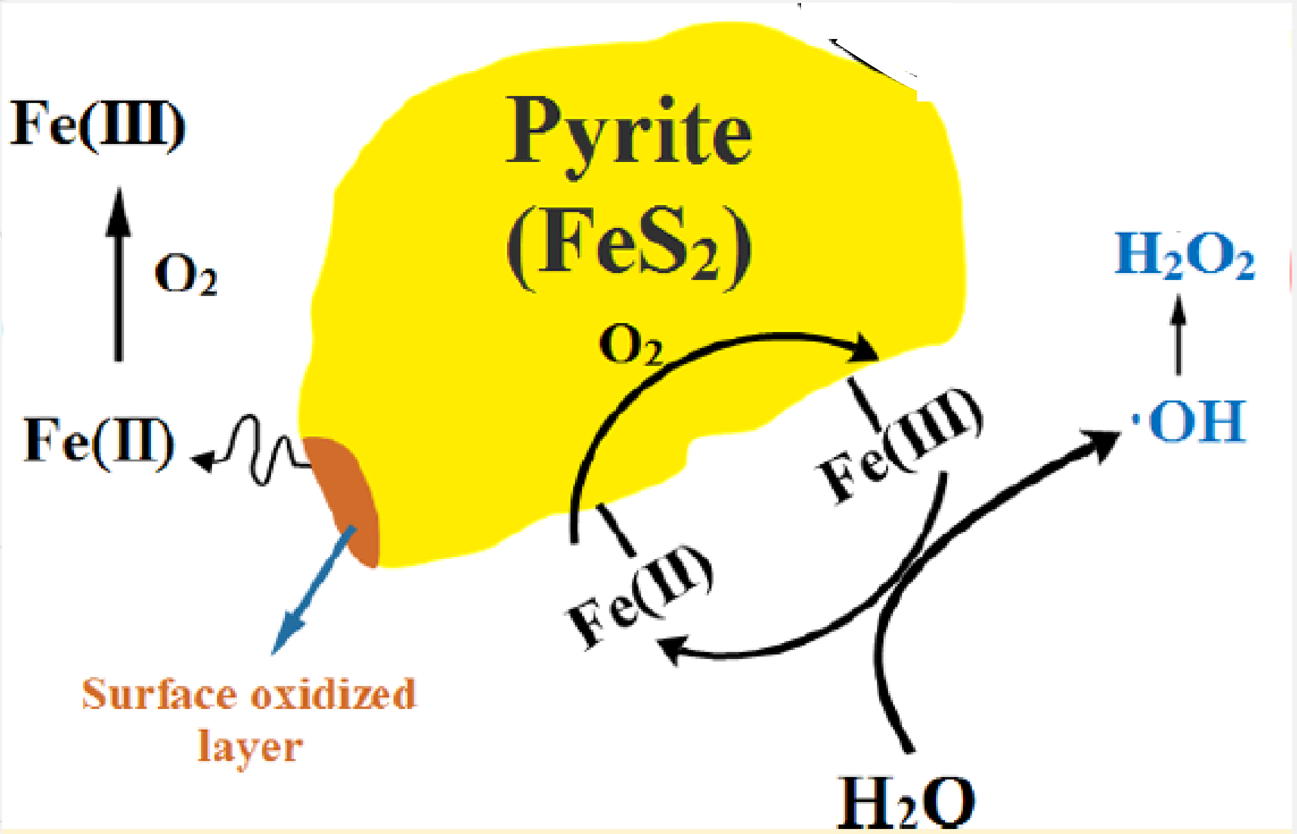
- **FeS**
- **Pyrite (FeS_2)**
- **Magnetite (Fe_3O_4)**
- **Green rusts**



Higher coupling products
(e.g., butane, propane)

Abiotic Dechlorination via Ferrous Minerals

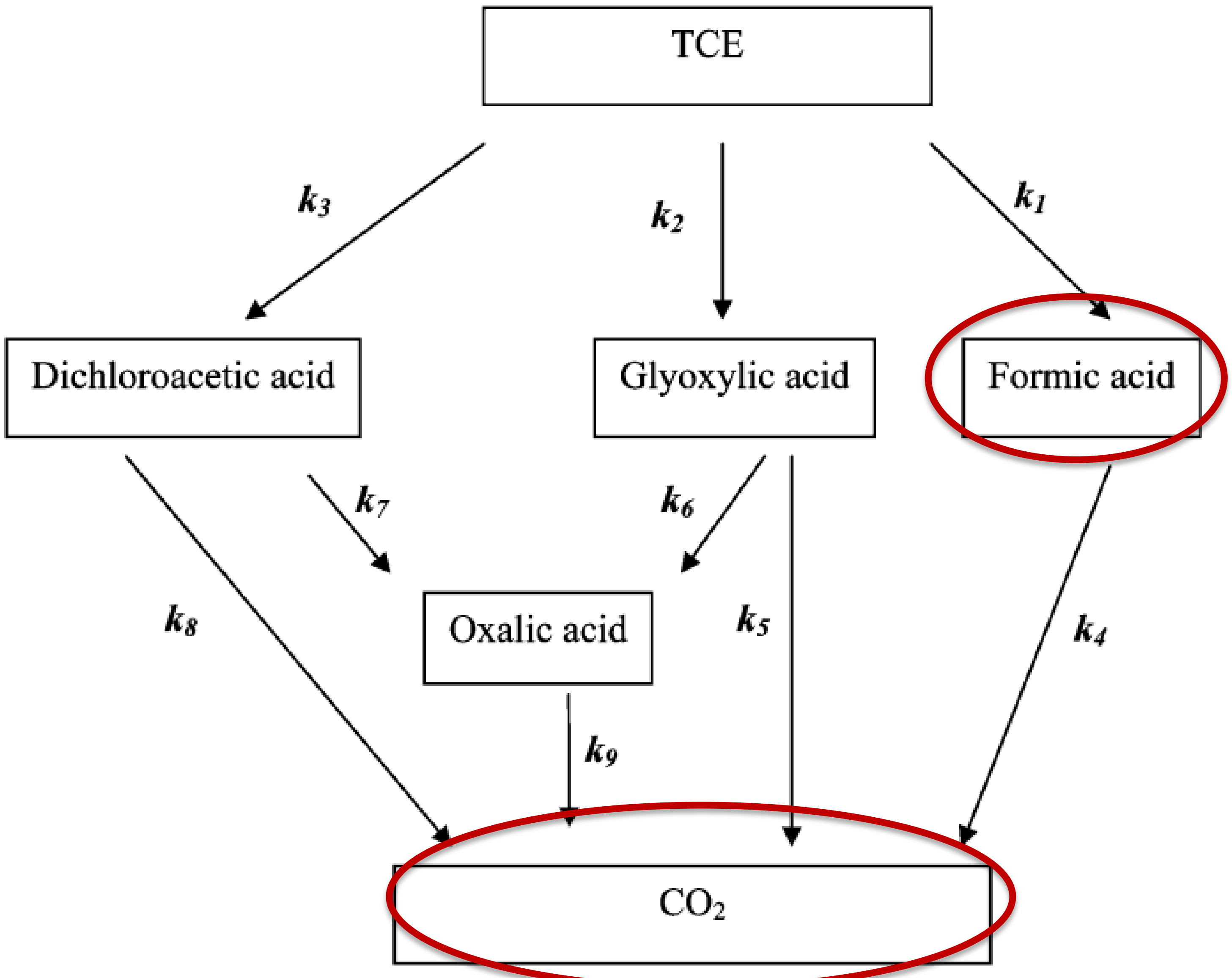
Aerobic Conditions – Hydroxyl Radical formation



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

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

Abiotic Dechlorination via Pyrite Minerals: Aerobic Pathway



TCE

k_3 k_2 k_1

Dichloroacetic acid

Glyoxylic acid

Formic acid

k_7 k_6

k_8

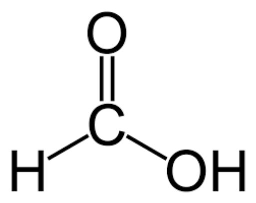
Oxalic acid

k_5

k_4

k_9

CO_2



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

Bench-Scale Testing to Determine Dechlorination Kinetics

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

TCE spike

No
TCE spike

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

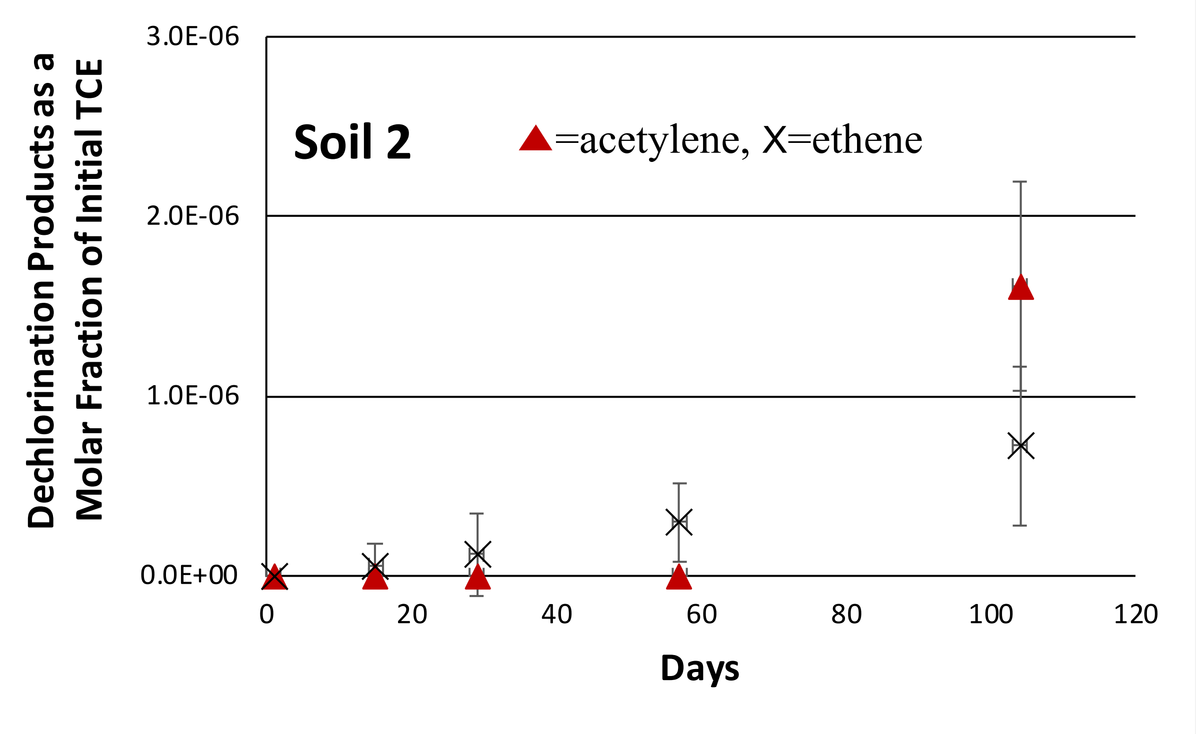
Analyze water for:
OAs
Final pH

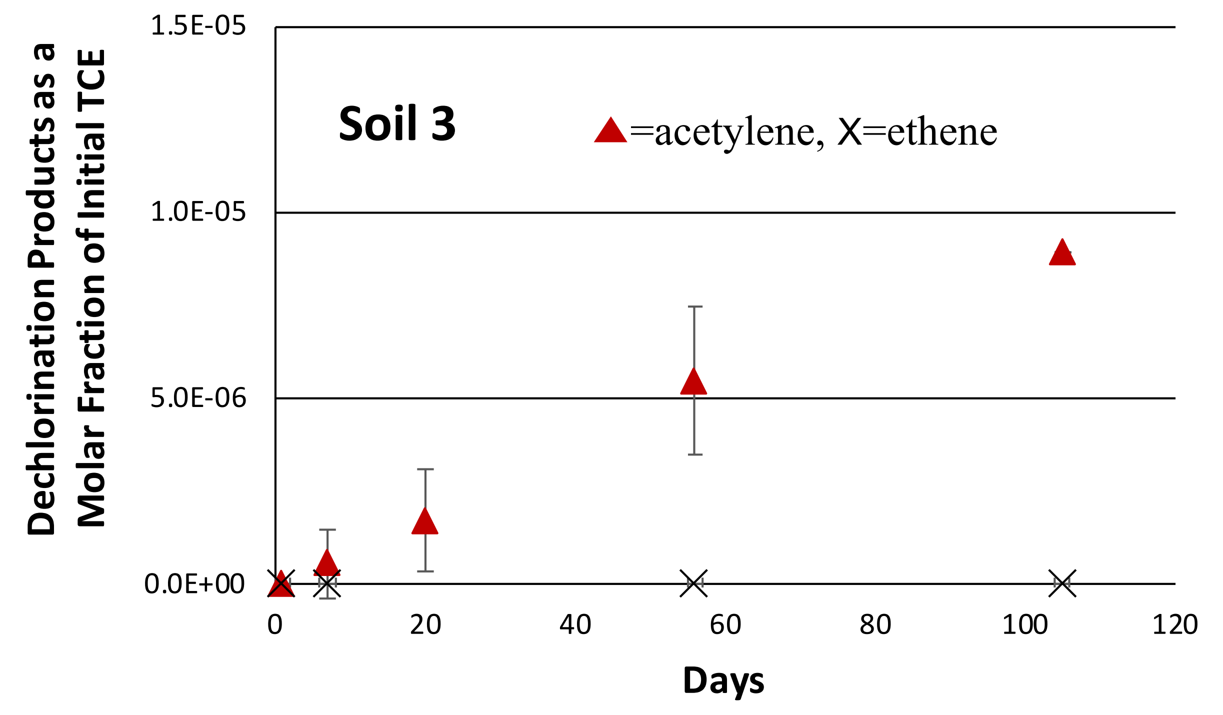
Natural Soils

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)

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

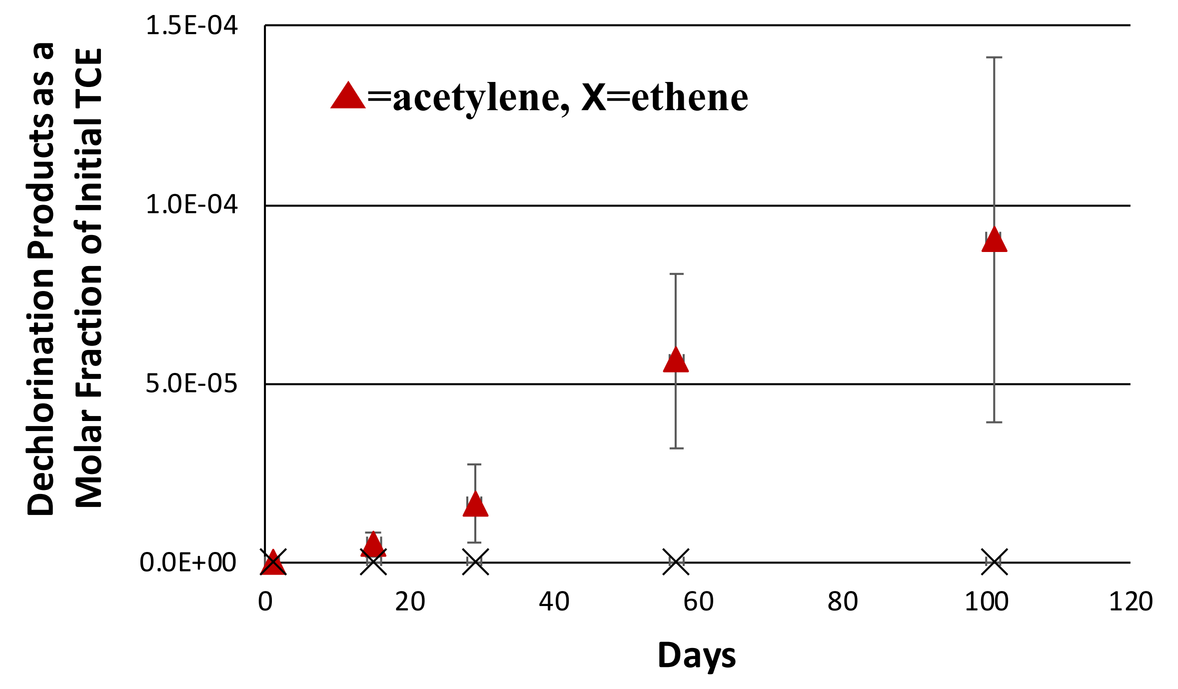




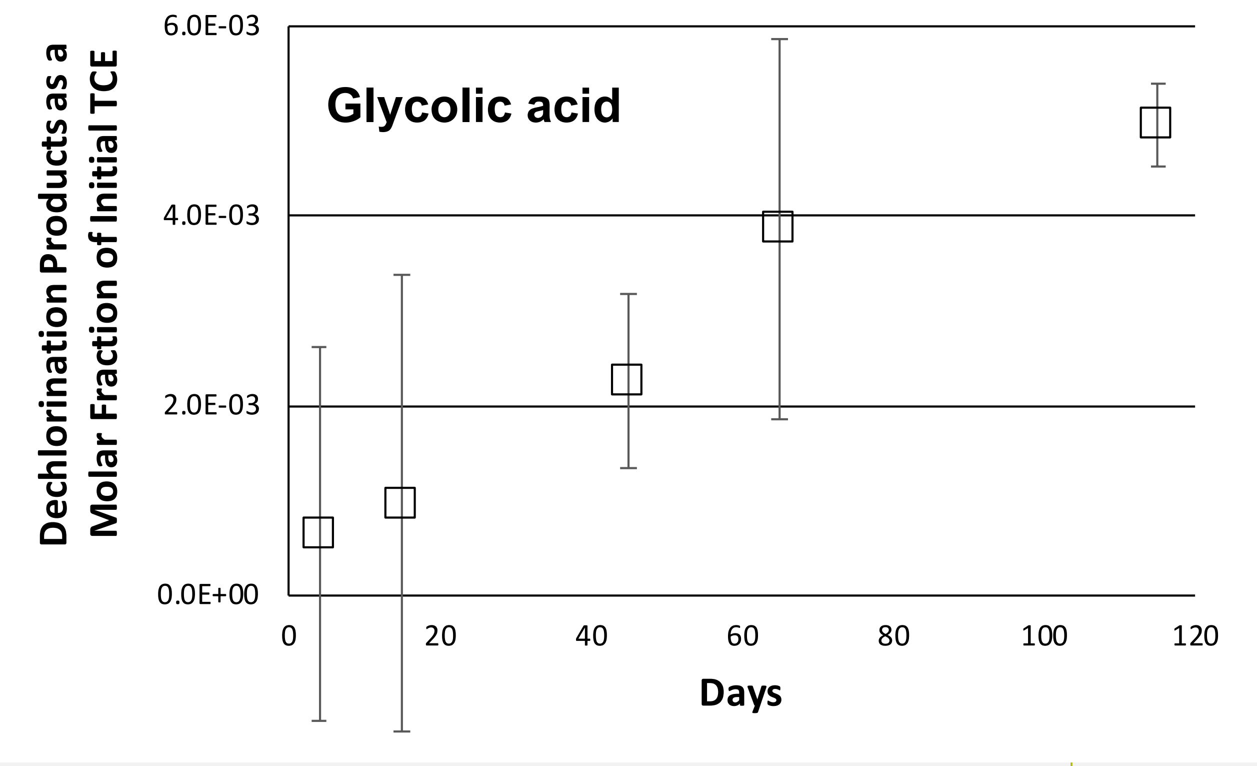
As expected, clayey soils with ferrous iron have reduced gas transformation products

Results – Anaerobic Conditions (<26μM O_2)

Soil 1



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



Results – Aerobic Conditions (>120 μM O_2)

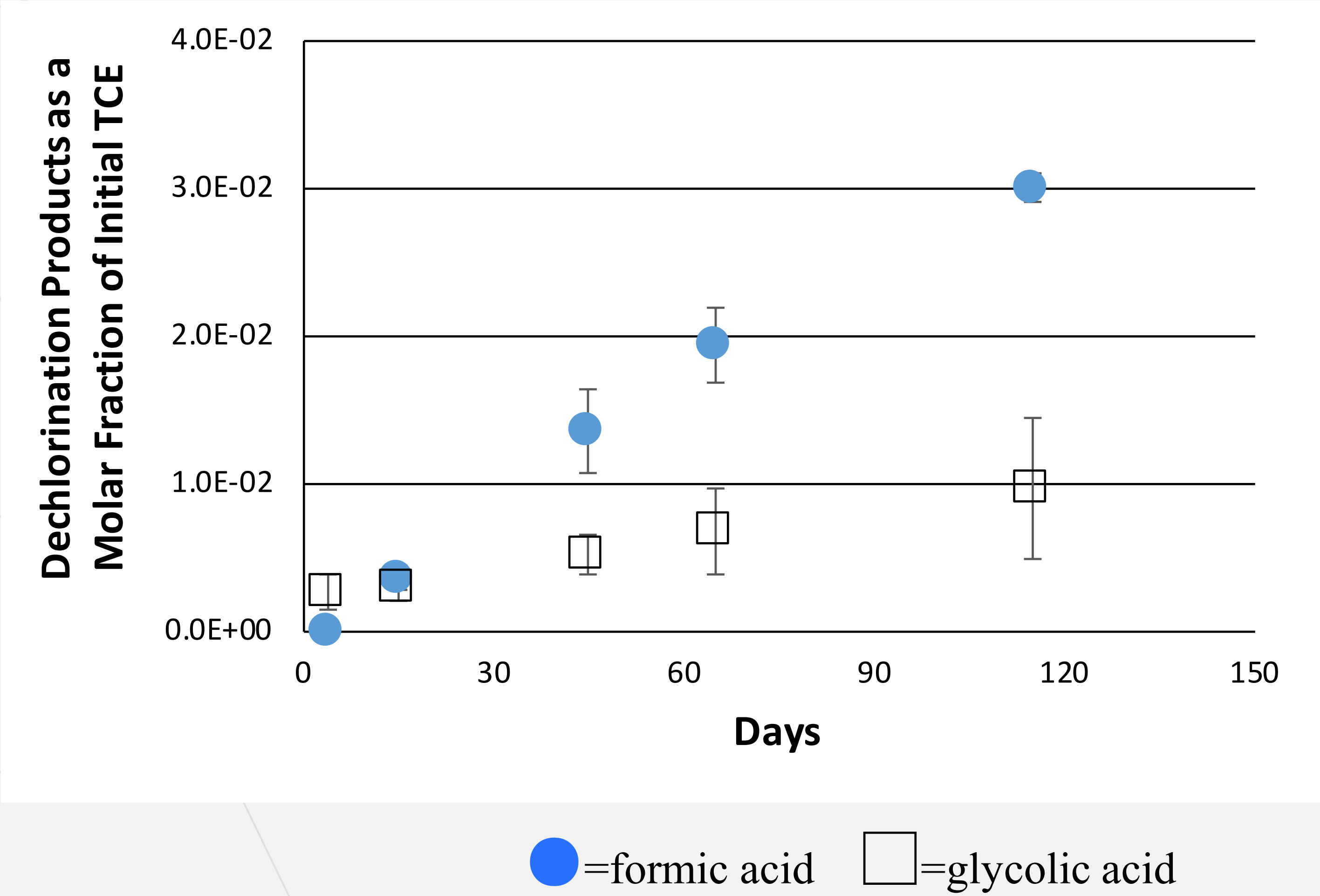
Soils 4 & 5: No transformation products detected (reduced gases, CO_2, OAs)

Reduced gases: none observed for any soil

OAs: observed in Soils 1 through 3

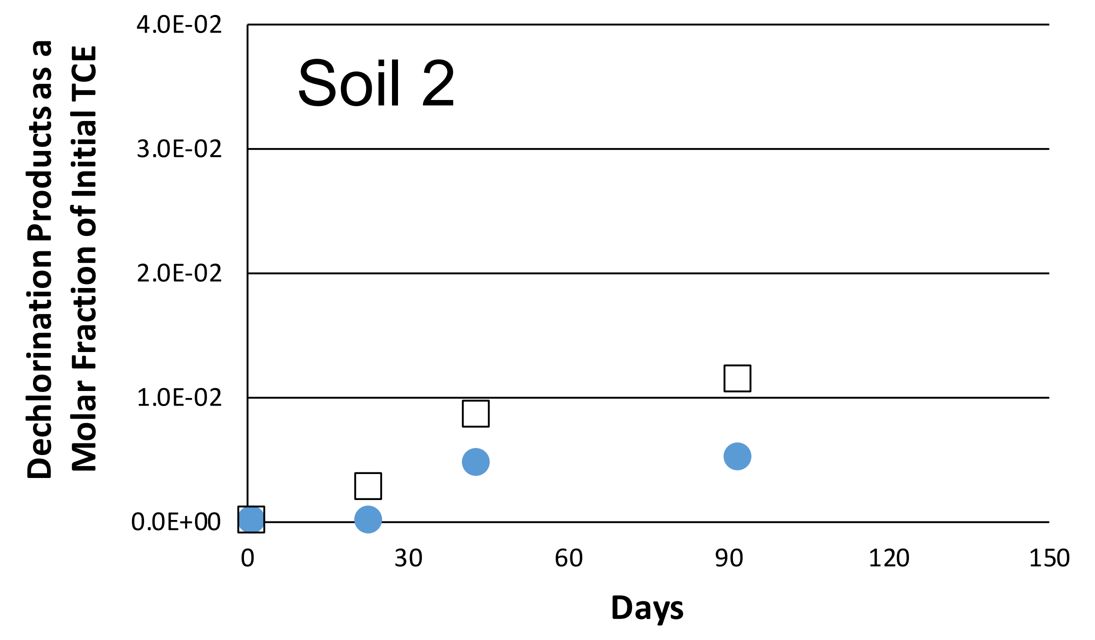
Results – Aerobic Conditions (>120 µM O_2)

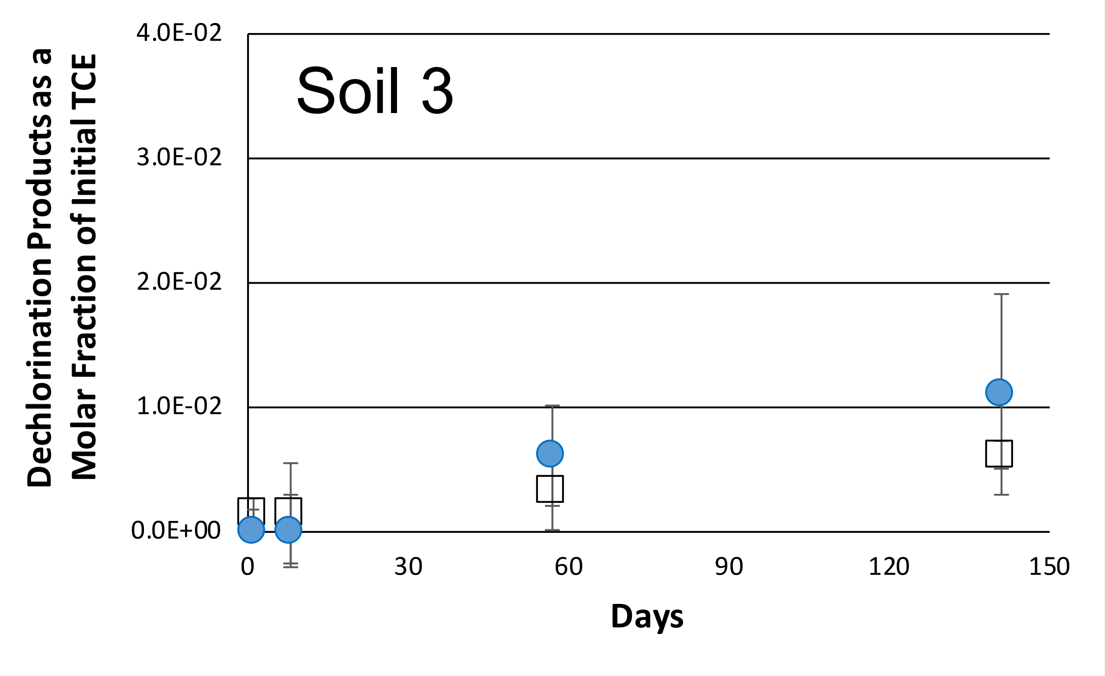
Soil 1



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

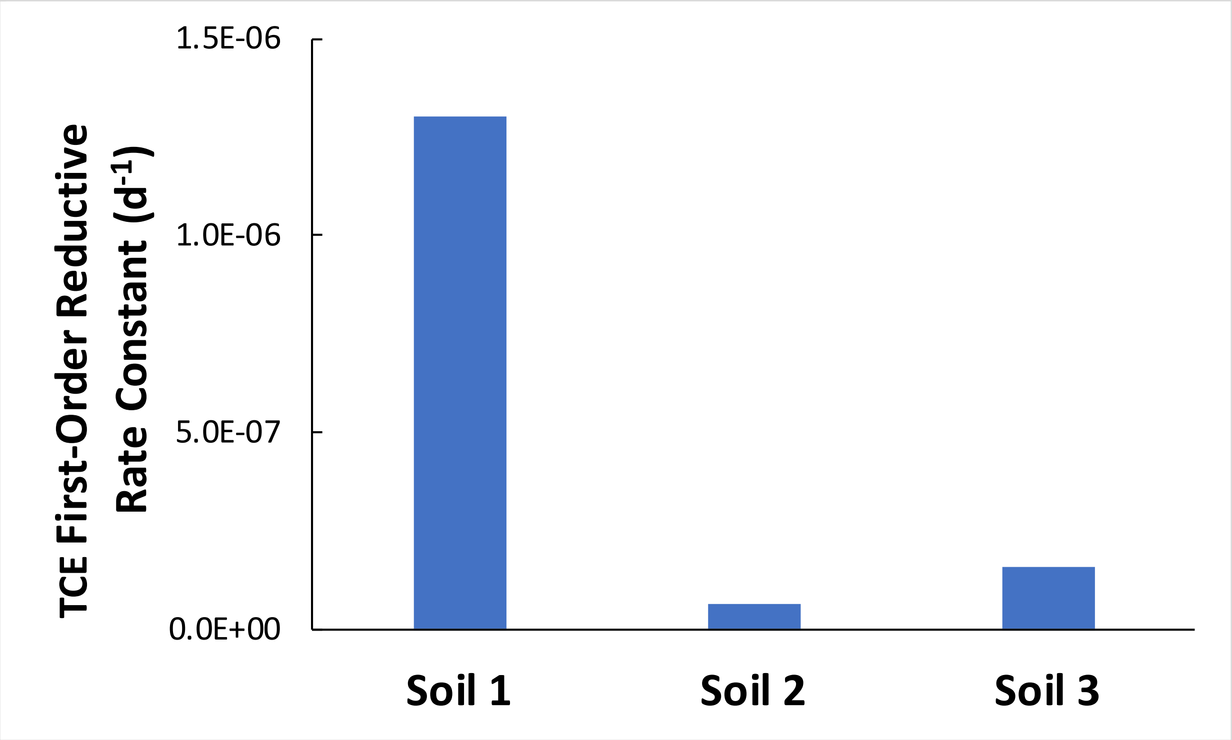
Results – Aerobic Conditions (>120 μM O_2)

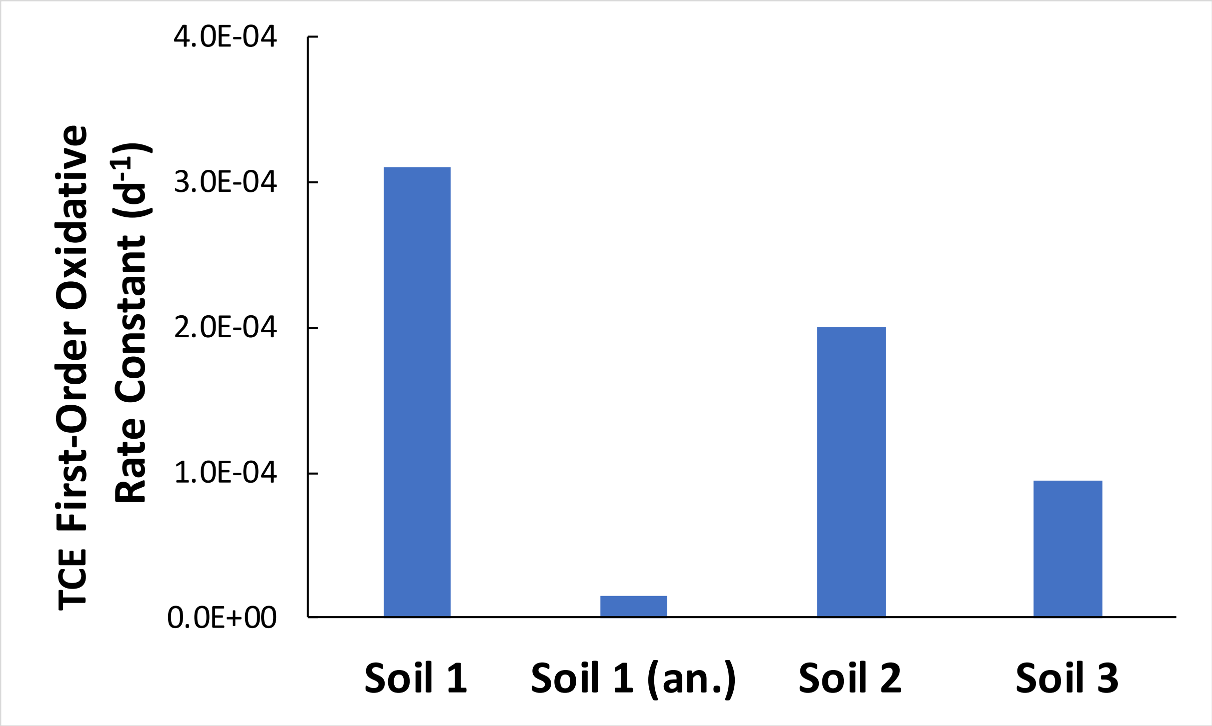




● =formic acid ☐ =glycolic acid

Reductive and Oxidative First-Order Rate Constants





Anaerobic conditions only

Oxidative Rate Constant vs. Hydroxyl Radical Generation Rate

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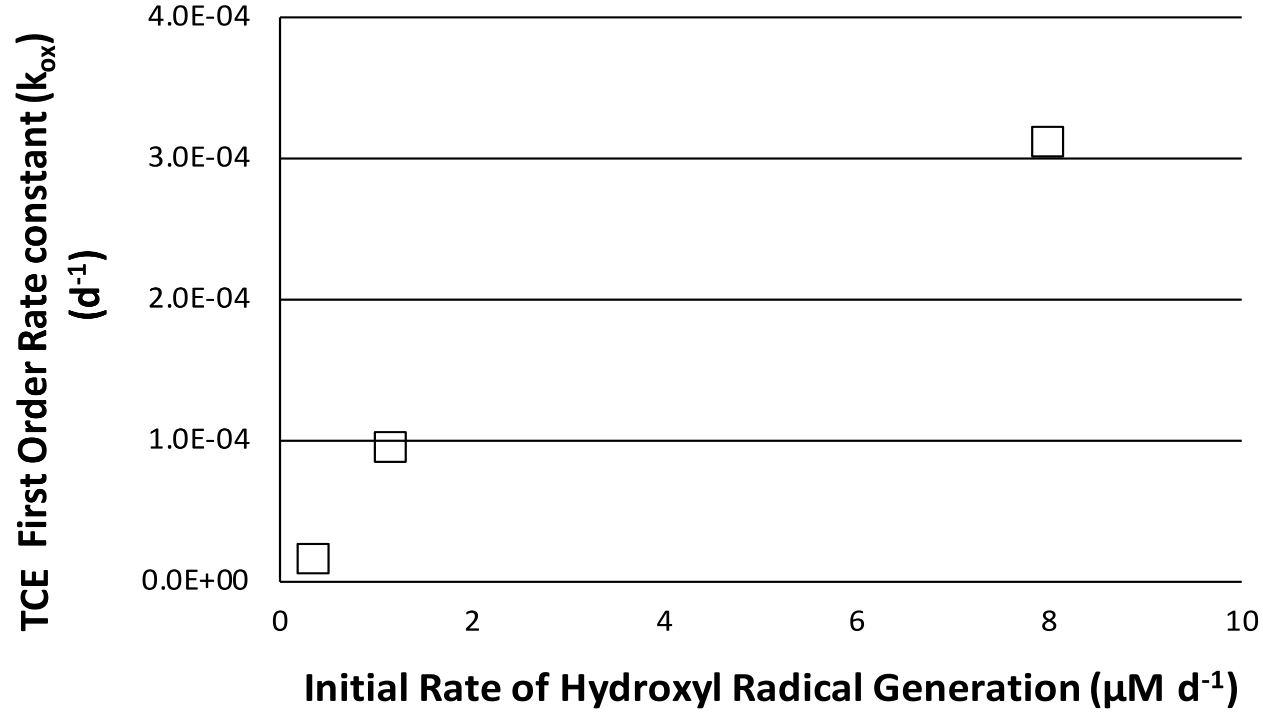
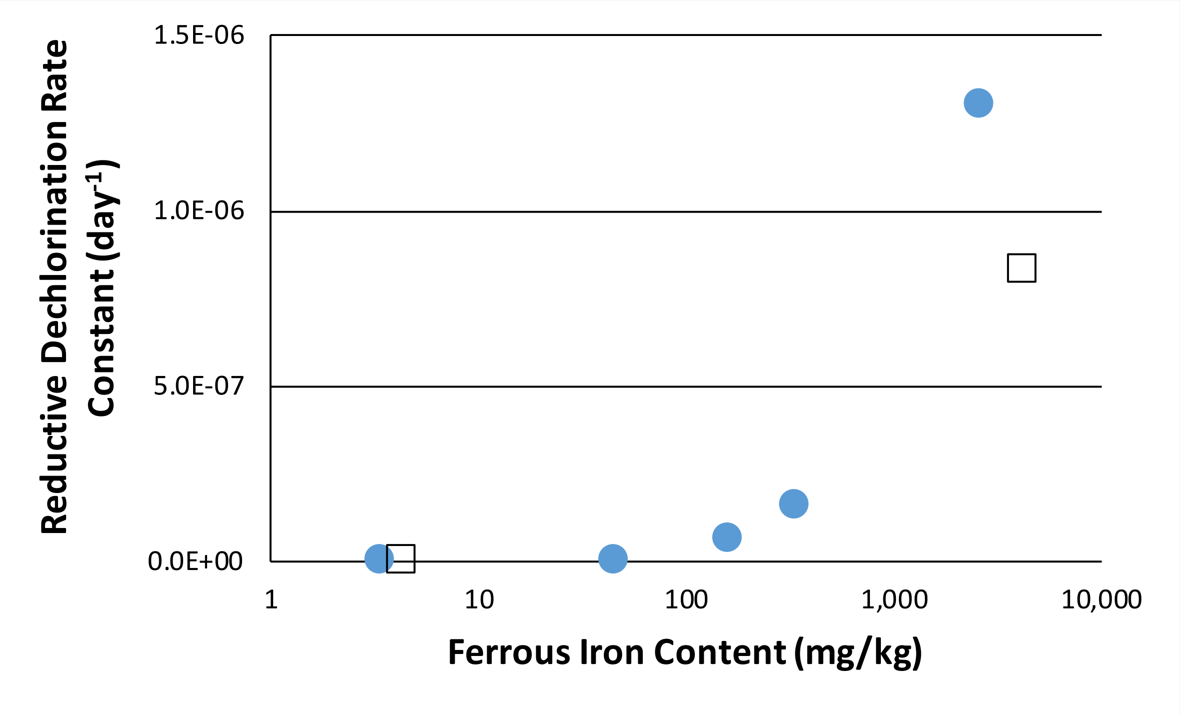
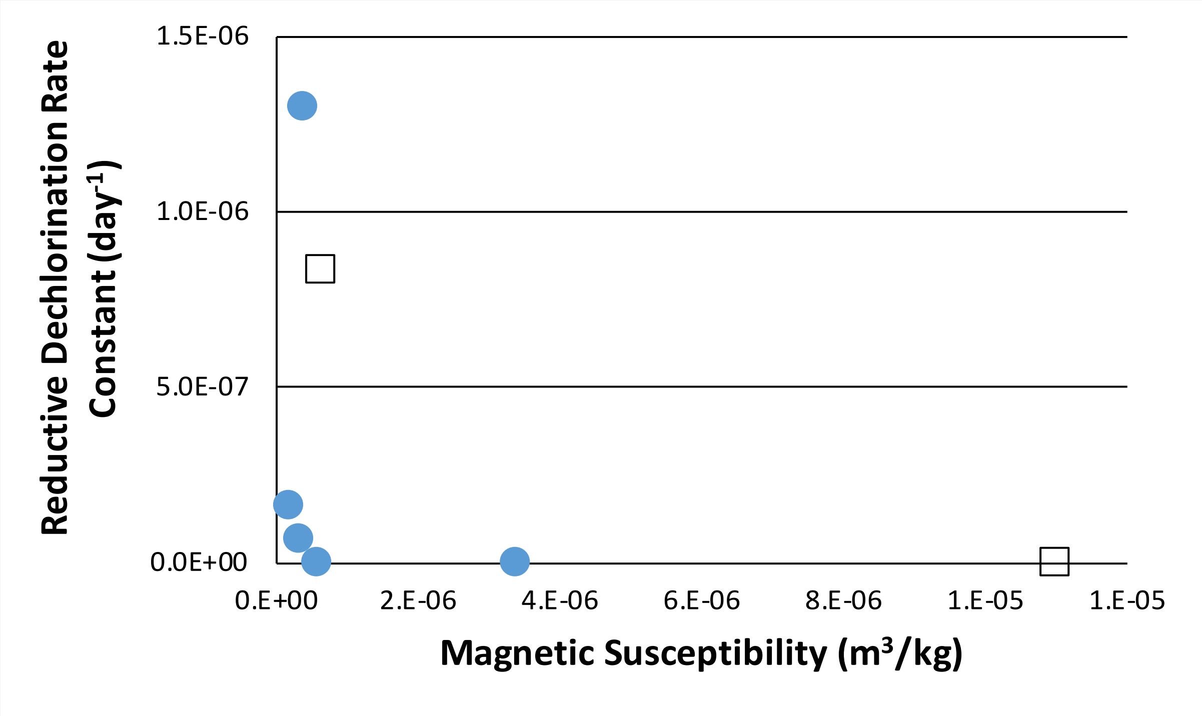
Determination of hydroxyl radicals in advanced oxidation processes with dimethyl sulfoxide trapping and liquid chromatography

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

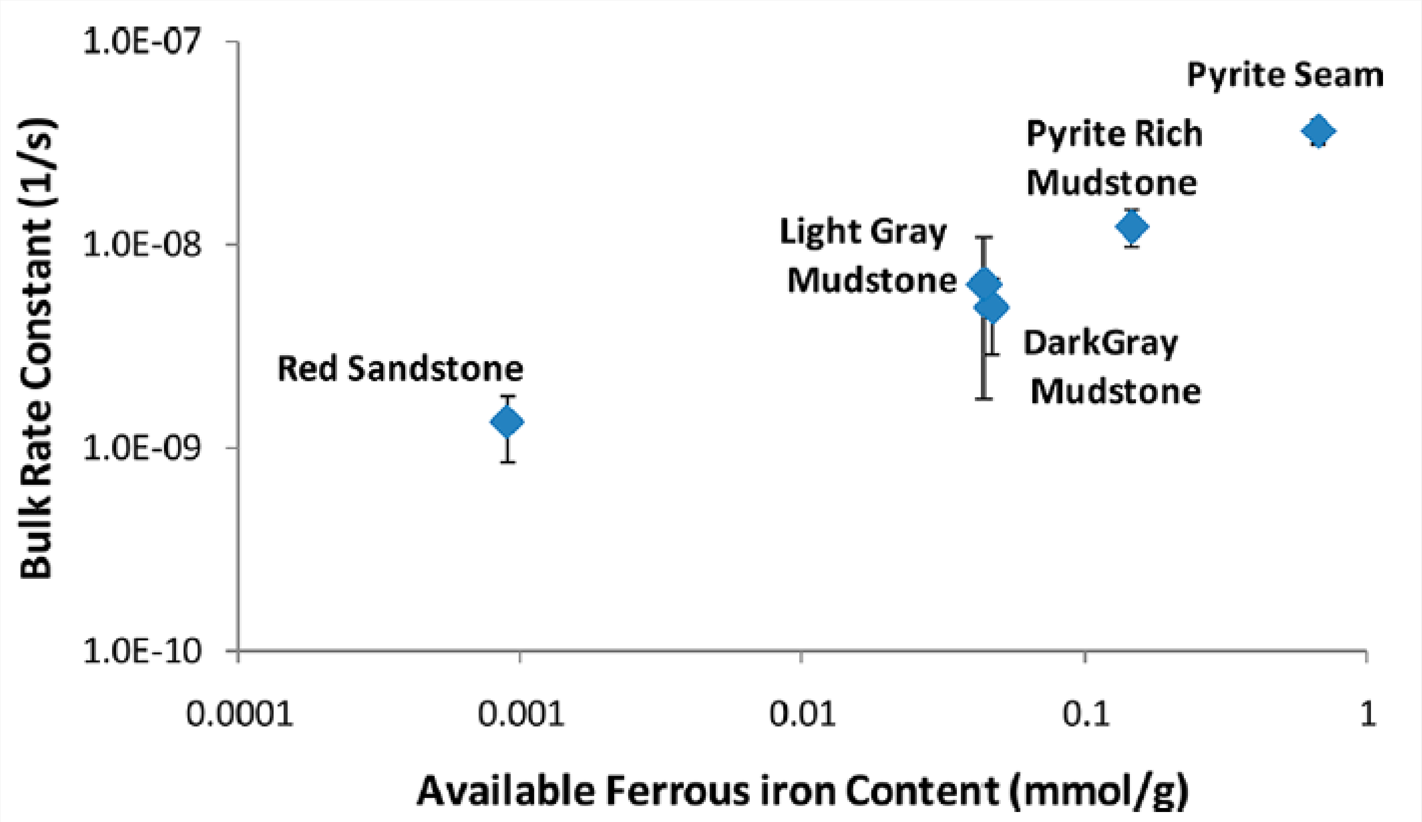


Reductive Rate Constants Related to Mineral Properties





Similar Trend Observed for TCE Abiotic Dechlorination in Rock Matrices



Schaefer et al., ES&T, 2013

Mineral Tests (preliminary results - anoxic)

Mineral	Ferrous Content (mg/kg)	Surface Area (m^2/g)	Rate Constant (d^{-1})
Illite	36	64	3.7×10^{-6}
Siderite	4400	9.7	1.2×10^{-5}
Ankerite	23000	0.64	1.6×10^{-5}
Biotite	1000	2.0	~0

So How Important Are These Reactions in Natural Clays?

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

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

Research Funding

SERDP

DOD ▪ EPA ▪ DOE