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Abiotic Dechlorination in Clay to Support Natural Attenuation

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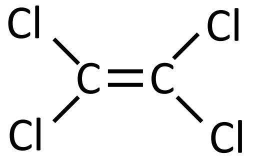
Chlorinated Solvents

Chlorinated solvents remain a significant environmental challenge:

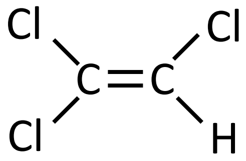
- Large dilute plumes
- Difficult geologies (back-diffusion)
  - *Back-diffusion from low permeability zones*

While even very slow rates of dechlorination can be important for natural attenuation, identifying lines of evidence for such transformations can be challenging (especially for abiotic transformations)

How should we screen for these beneficial reactions?



Tetrachloroethene (PCE)



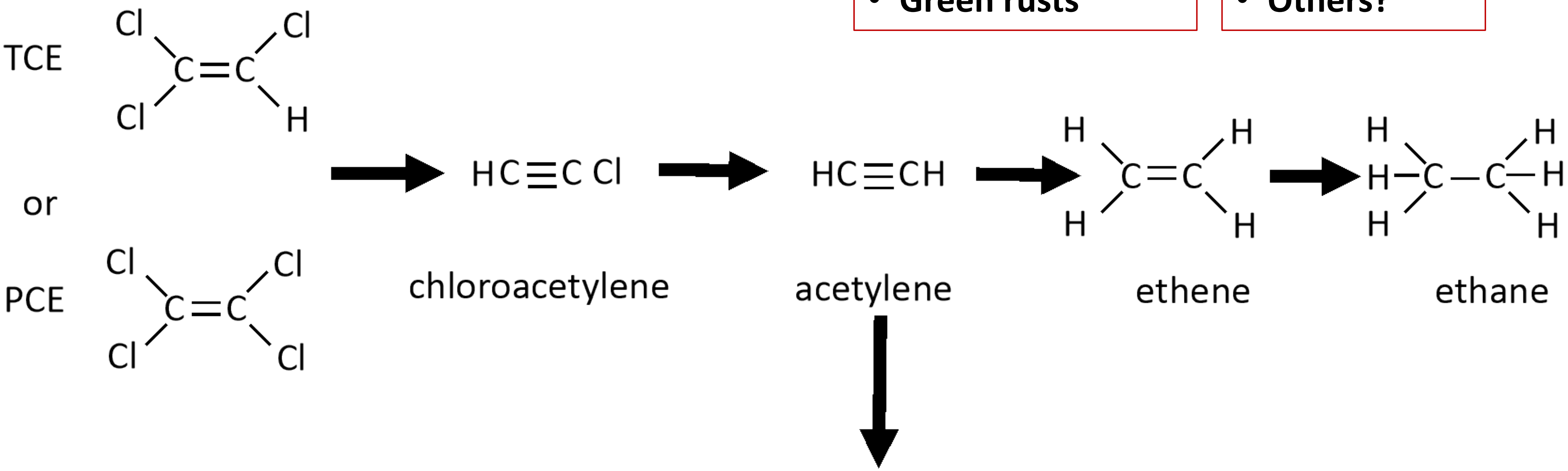
Trichloroethene (TCE)

Chlorinated Ethene Reduction via Ferrous Minerals

Anaerobic Conditions

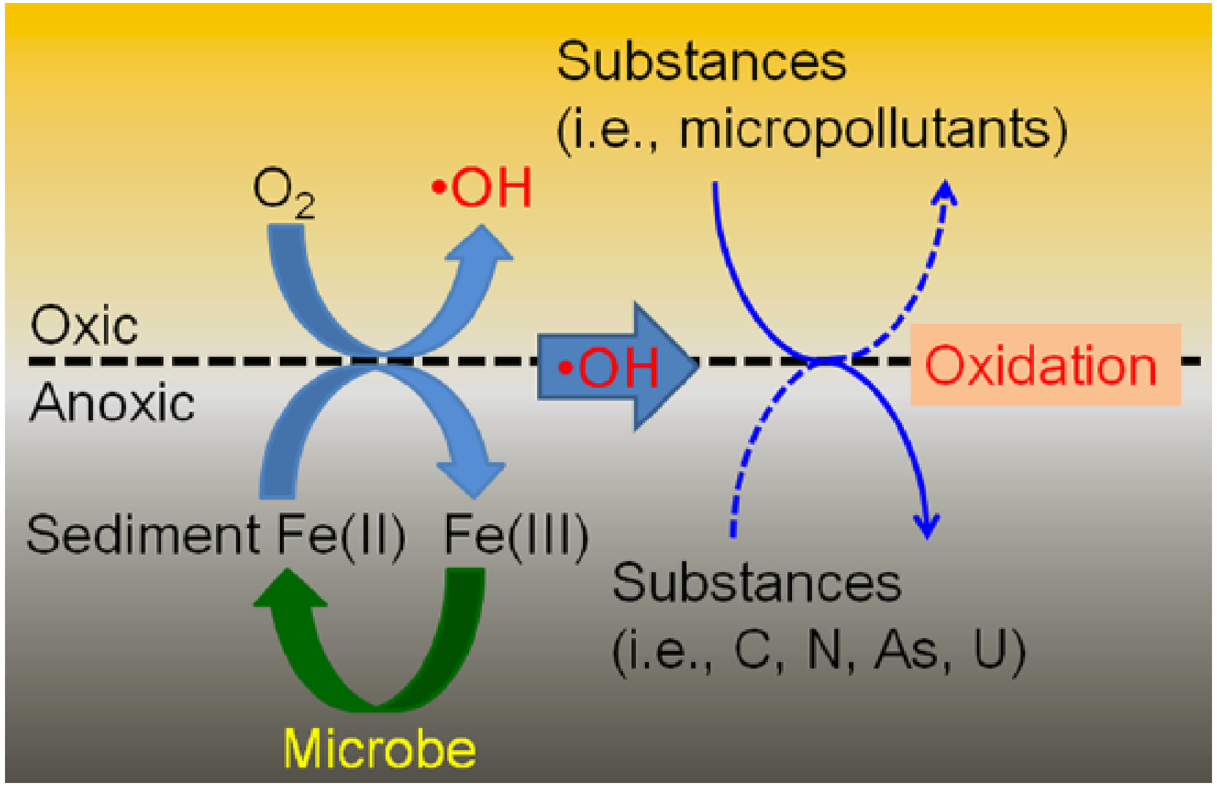
- **FeS**
- **Pyrite (FeS_2)**
- **Magnetite (Fe_3O_4)**
- **Green rusts**

- **Siderite**
- **Ankerite**
- **Illite**
- **Others?**



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

Chlorinated Ethene Oxidation via Ferrous Minerals



Tong et al., ES&T, 2016

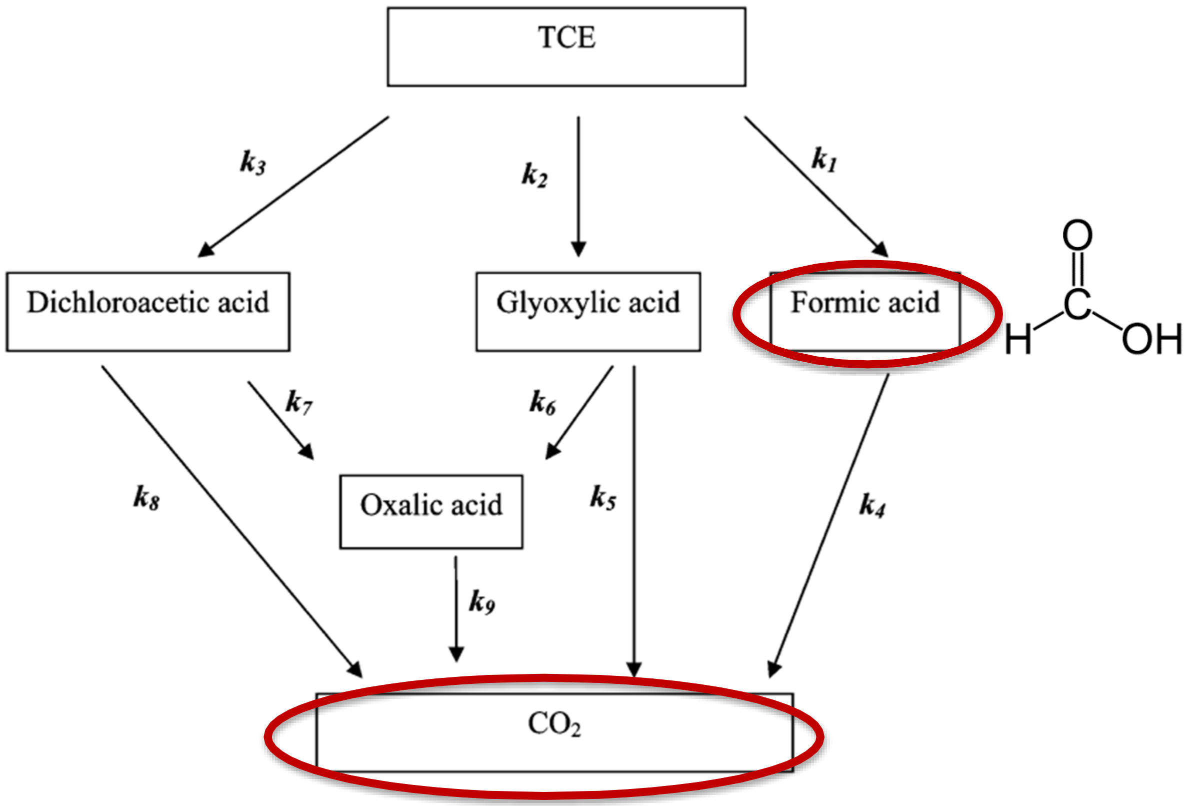
$$\mathrm{Fe^{II}_{(pyrite)}} + \mathrm{O_2} \rightarrow \mathrm{Fe^{III}_{(pyrite)}} + \mathrm{O_2^{\cdot -}}$$

$$\mathrm{Fe^{II}_{(pyrite)}} + \mathrm{O_2^{\cdot -}} + 2\mathrm{H^+} \rightarrow \mathrm{Fe^{III}_{pyrite}} + \mathrm{H_2O_2}$$

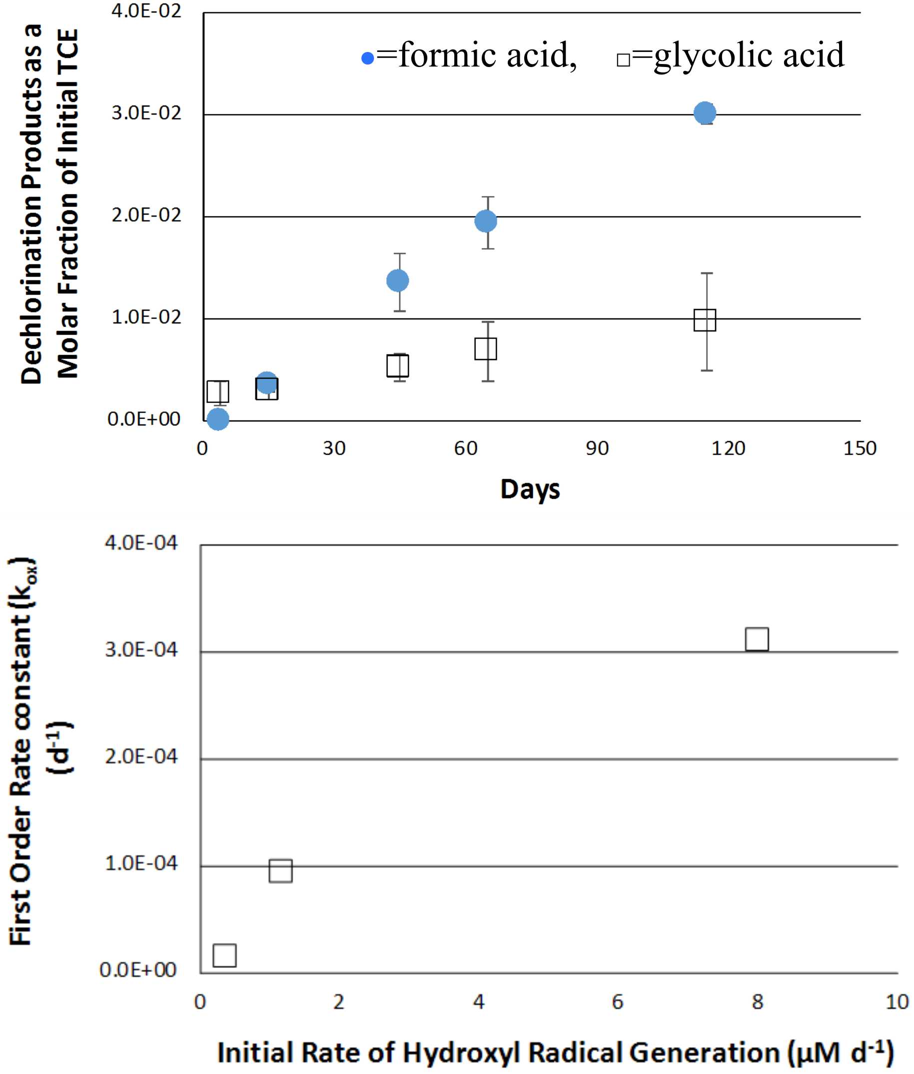
$$\mathrm{Fe^{II}_{(pyrite)}} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe^{III}_{(pyrite)}} + \cdot\mathrm{OH} + \mathrm{OH^-}$$

Kong et al., ES&T, 2015; Lee et al., ES&T, 2008

TCE Oxidative Transformation via Hydroxyl Radicals Generated from Iron Minerals

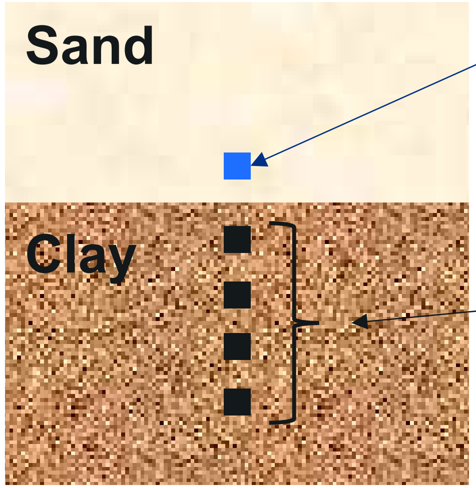


from Pham et al., *ES&T*, 2009



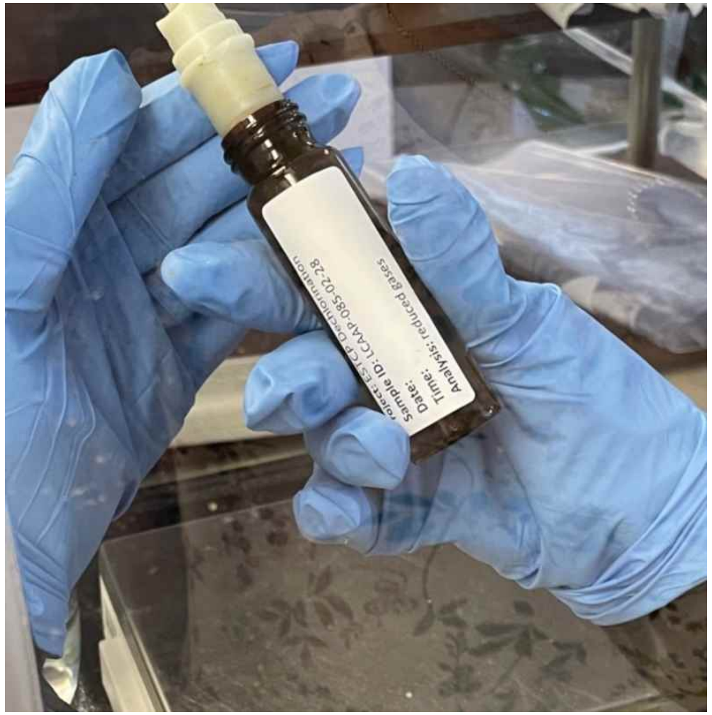
Schaefer et al., ES&T, 2018

Field Measurements (7 DoD sites impacted with PCE/TCE)



Aqueous sample for DO, ORP, turbidity, and H_2O_2

- Clay samples for VOCs & reduced gases
- Mineral analyses
  - total iron (digestion with HNO_3 and H_2O_2)
  - ferrous iron (2.5% HCl at room temp.)
  - magnetic susceptibility
  - XRD
- Additional cores for bench-scale testing



Bench-Scale Batch Experiments

- 7 TCE-impacted sites
- Mineral-water slurries (6g/35mL 5 mM $CaCl_2$)
- Gamma-irradiated soils
- Anaerobic and aerobic test systems
- Triplicates

Anaerobic Experiments

TCE spike
(3.2 mM)

No
TCE spike

Analyze headspace for:

- VOCs
- Reduced gases

Aerobic Experiments

- No TCE spike
- Monitor •OH generation using aminophenyl fluorescein method and fluorometer

Results: Clay Mineralogy

Property	LCAAP	SLOP	JAX	ALTUS	Longhorn	Minden	PV
% Mineral Content (XRD)	quartz (30); illite+mica (29); illite/smectite (22); plagioclase (7.7); kaolinite (4.5); K-feldspar (3.8); smectite (1.9); hematite (1.3)	quartz (54); smectite (16); plagioclase (7.4); illite/smectite (7.0); kaolinite (6.1); K-feldspar (4.9); illite+mica (2.6); anatase (0.7); rutile; pyrite (0.15)	quartz (63); smectite (18); kaolinite (5.0); K-feldspar (4.3); illite/smectite (4.2); plagioclase (3.5); illite+mica (3.1)	quartz (45); calcite (24); illite+mica (23); plagioclase (7.5); K-feldspar (6.2); chlorite (1.5); hematite (0.8); anatase (0.5);	quartz (55); smectite (22); plagioclase (7.0);illite+mica (7.0); K-feldspar (6.5); kaolinite (1.9)	quartz (69);smectite (14); plagioclase (6.8); K-feldspar (5.1); illite+mica (3.7); kaolinite (0.9)	illite/smectite (33); plagioclase (21); quartz (14); illite+mica (12); K-feldspar (4.5); kaolinite (4.0); chlorite (1.9); calcite (1.8)
Magnetic Suscept. (m^3/kg)	1.4×10^{-7}	9.7×10^{-8}	9.6×10^{-8}	1.1×10^{-7}	1.0×10^{-7}	5.0×10^{-8}	4.5×10^{-7}
Ferrous mineral content (mg/kg)[1]	4.8	57	2,600	1.4	2.4	0.5	930
Total iron (mg/kg)[2]	78,000	23,000	18,000	28,000	12,000	12,000	30,000

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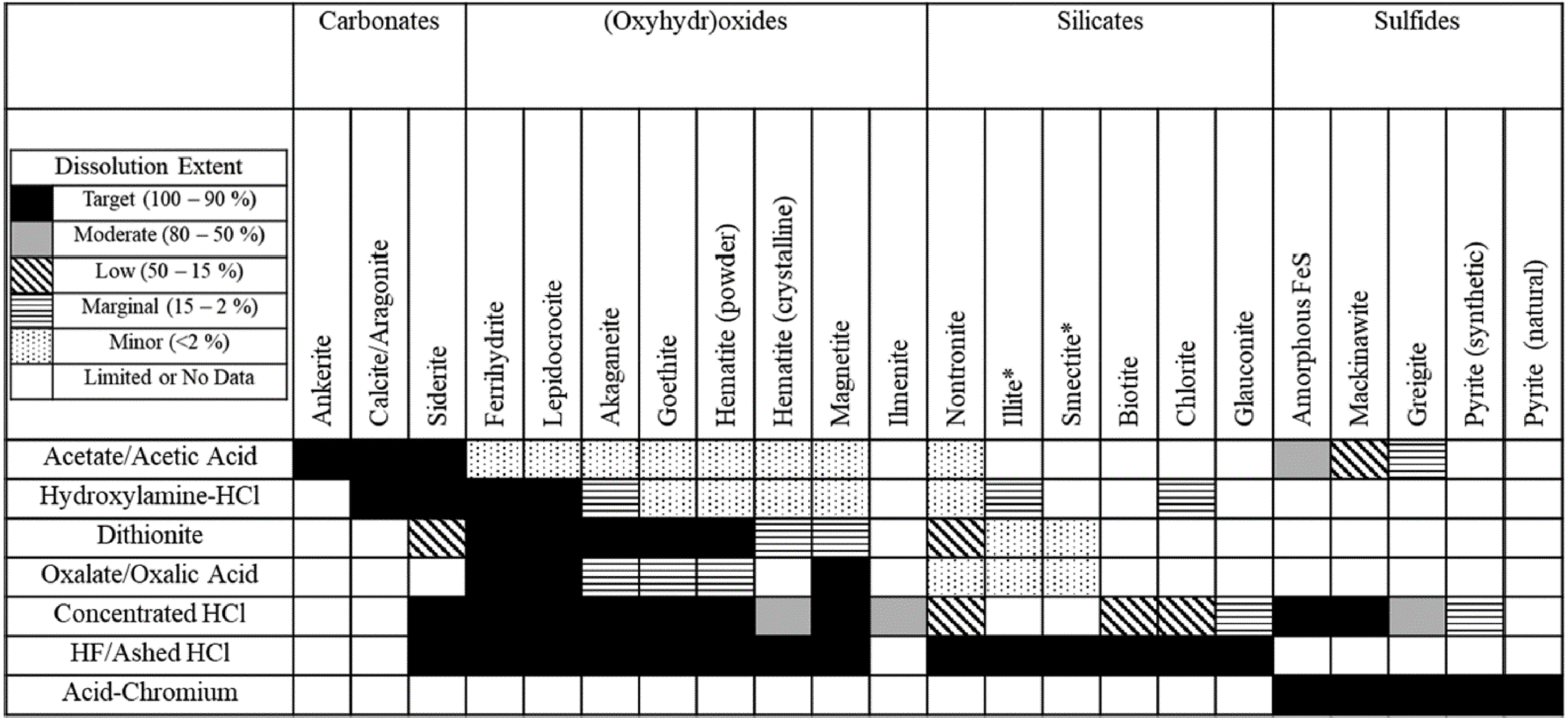
[1] 2.5% HCl at room temperature

[2] Acid digestion with nitric acid and H_2O_2

Pyrite Poorly Extracted with Dilute HCl

Voelz et al., ACS Earth Space Chem., 2019, 3, 1371-1392

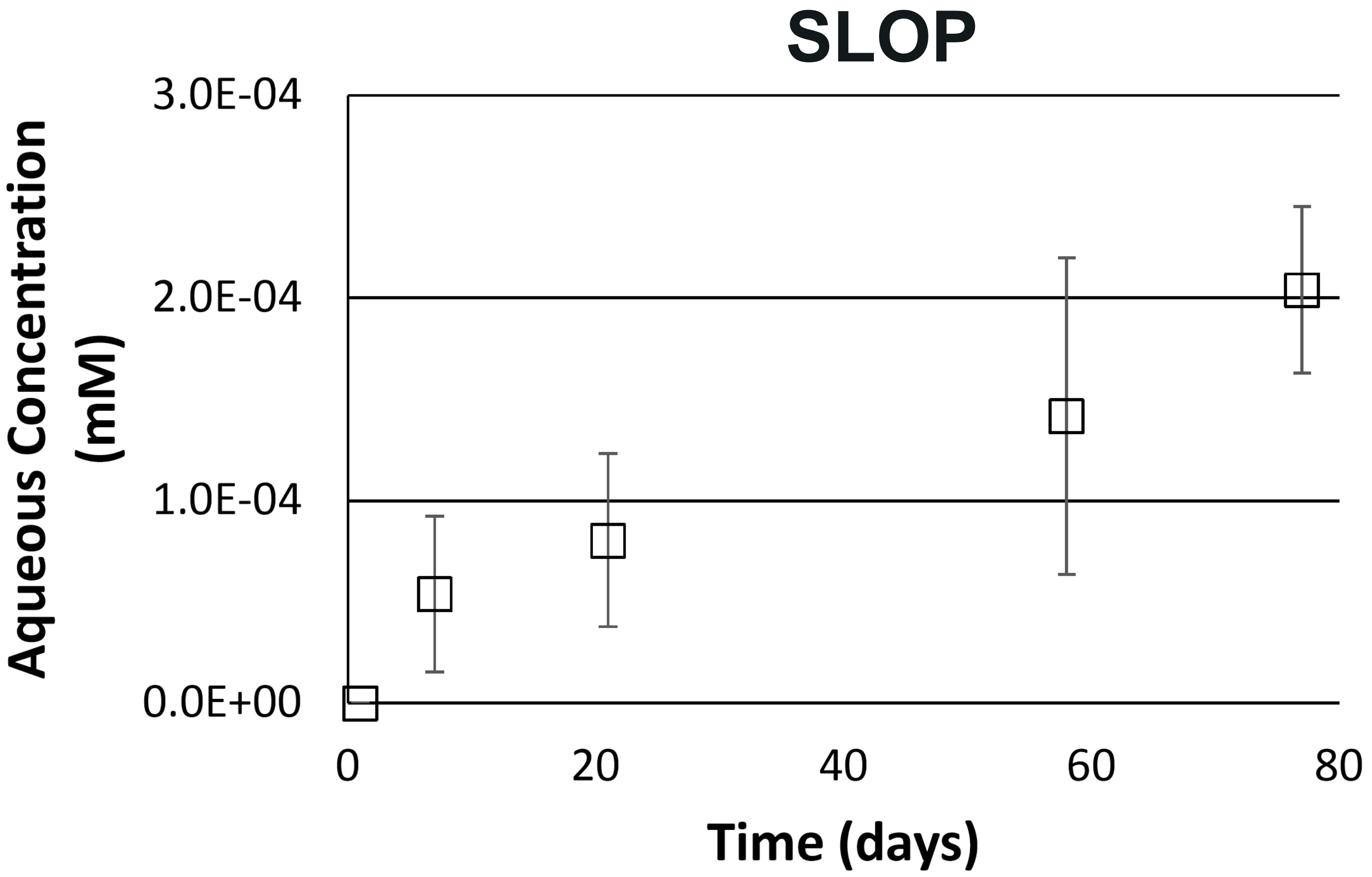


Dissolution Extent	
■	Target (100 – 90 %)
▒	Moderate (80 – 50 %)
▧	Low (50 – 15 %)
▤	Marginal (15 – 2 %)
░	Minor (<2 %)
	Limited or No Data

	Carbonates			(Oxyhydr)oxides								Silicates						Sulfides				
	Ankerite	Calcite/Aragonite	Siderite	Ferrihydrite	Lepidocrocite	Akaganeite	Goethite	Hematite (powder)	Hematite (crystalline)	Magnetite	Ilmenite	Nontronite	Illite*	Smectite*	Biotite	Chlorite	Glauconite	Amorphous FeS	Mackinawite	Greigite	Pyrite (synthetic)	Pyrite (natural)
Acetate/Acetic Acid	■	■	■	░	░	░	░	░	░	░		░						▒	▧	▤		
Hydroxylamine-HCl		■	■	■	■	▤	░	░	░	░		░	▤			▤						
Dithionite			▧	■	■	■	■	■	▤	▤		▧	░	░								
Oxalate/Oxalic Acid				■	■	▤	▤	▤		■		░	░	░								
Concentrated HCl			■	■	■	■	■	■	▒	■	▒	▧			▧	▧	▤	■	■	▒	▤	
HF/Ashed HCl			■	■	■	■	■	■	■	■		■	■	■	■	■	■					
Acid-Chromium																		■	■	■	■	■

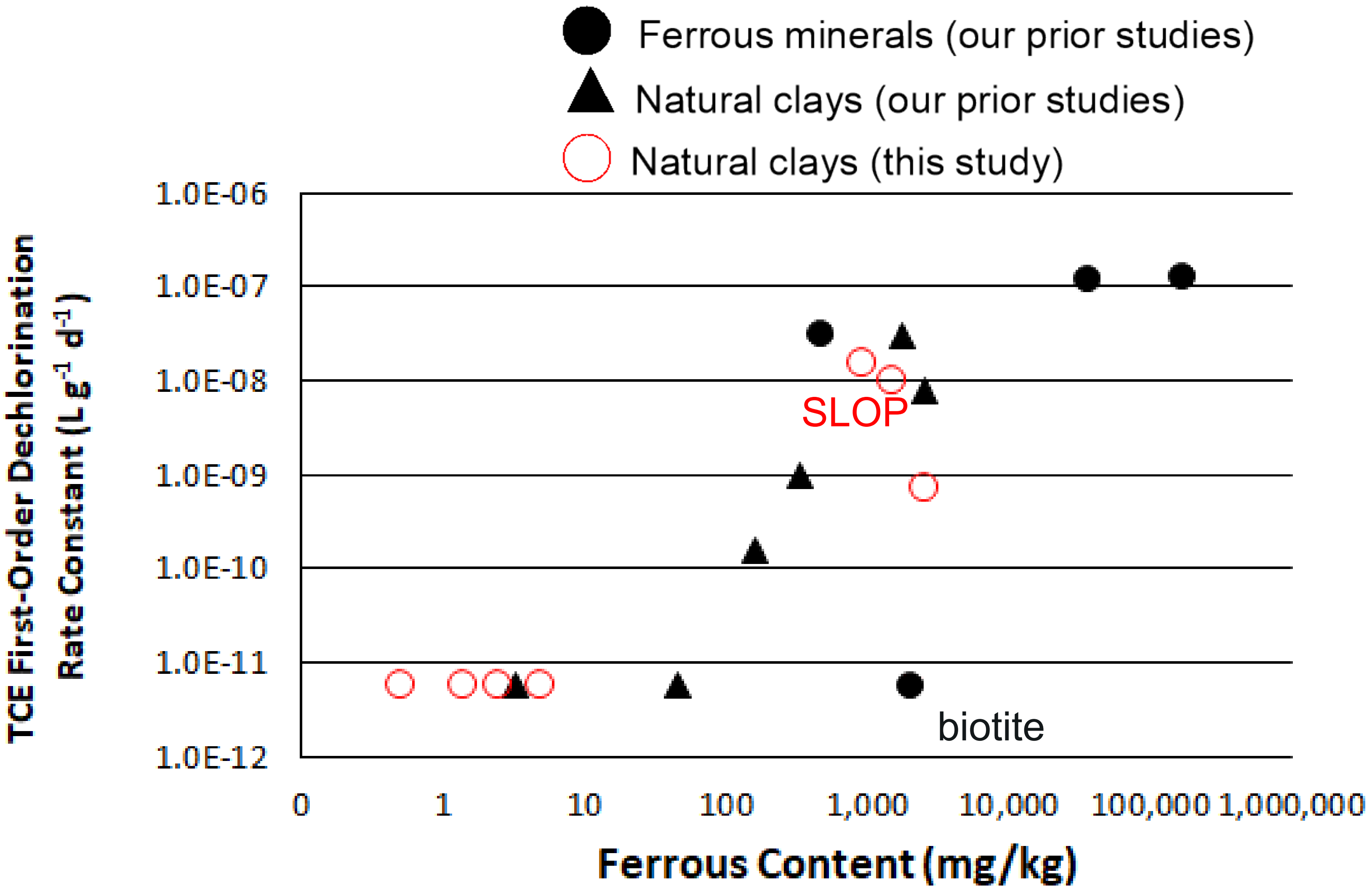
Thus, for clays containing pyrite, Fe(II) is better estimated based on pyrite content

Results: TCE Reductive Dechlorination under Anaerobic Conditions



Acetylene was the primary dechlorination product

Results: TCE Reductive Dechlorination under Anaerobic Conditions



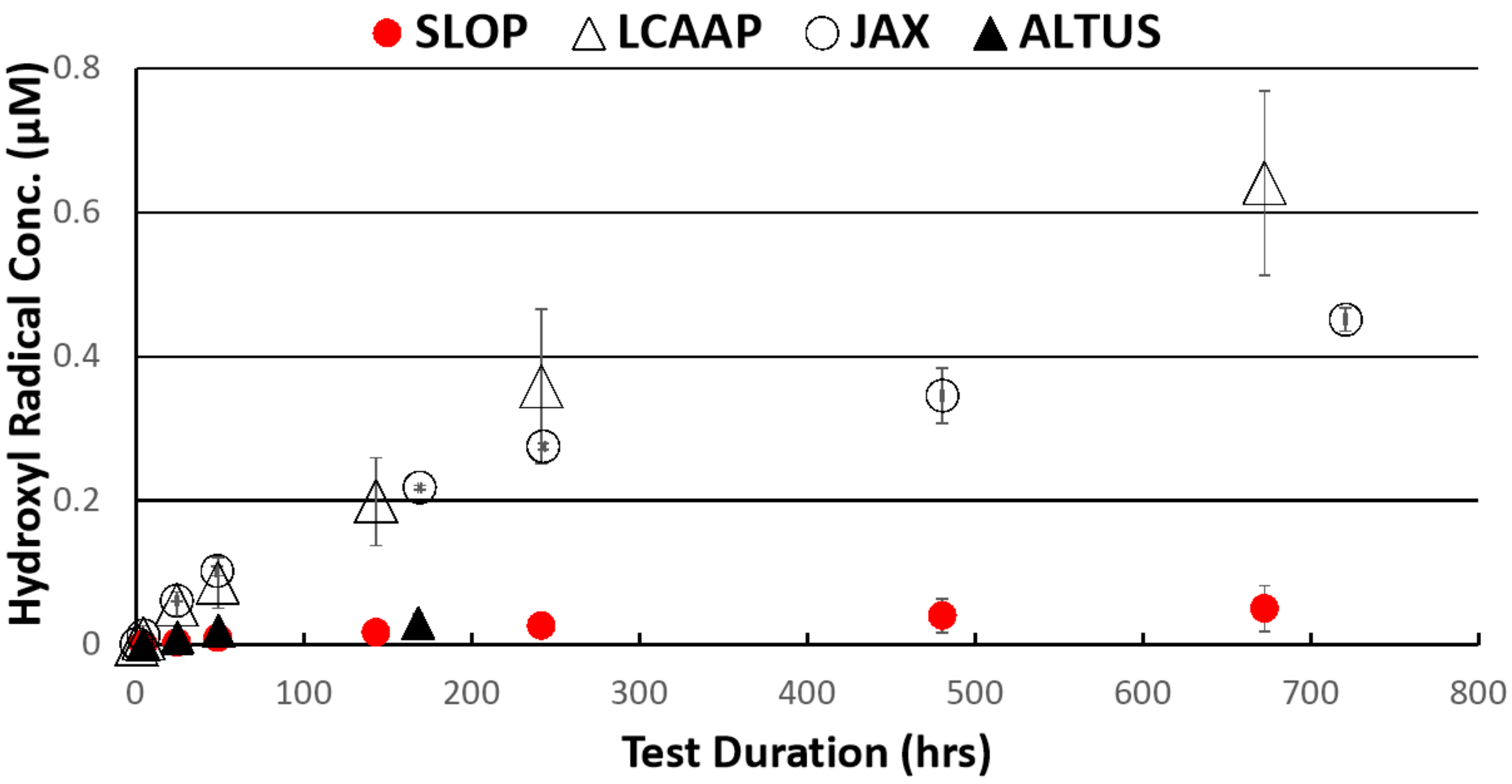
No trend observed with total iron or magnetic susceptibility

Field Measurements: Reduced Gases

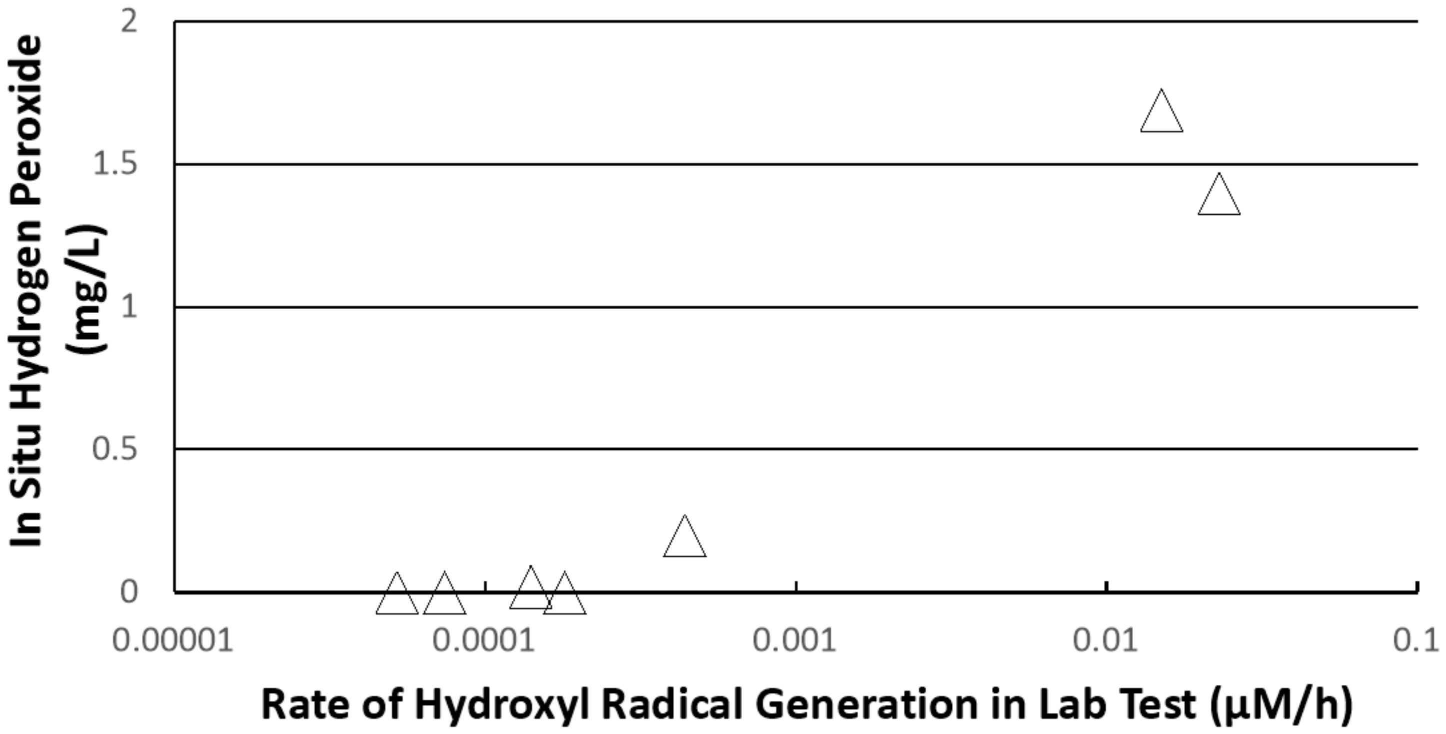
- No acetylene quantified in any field sample, despite acetylene being the predominant reductive dechlorination product
- 5 to 10 µg/L ethane at most reactive (SLOP) site

Looking for reduced gases in collected field samples may not always be a useful tool for identifying the occurrence of abiotic dechlorination reactions

Hydroxyl Radical Generation: Oxic Conditions



Is this reaction really occurring in situ?



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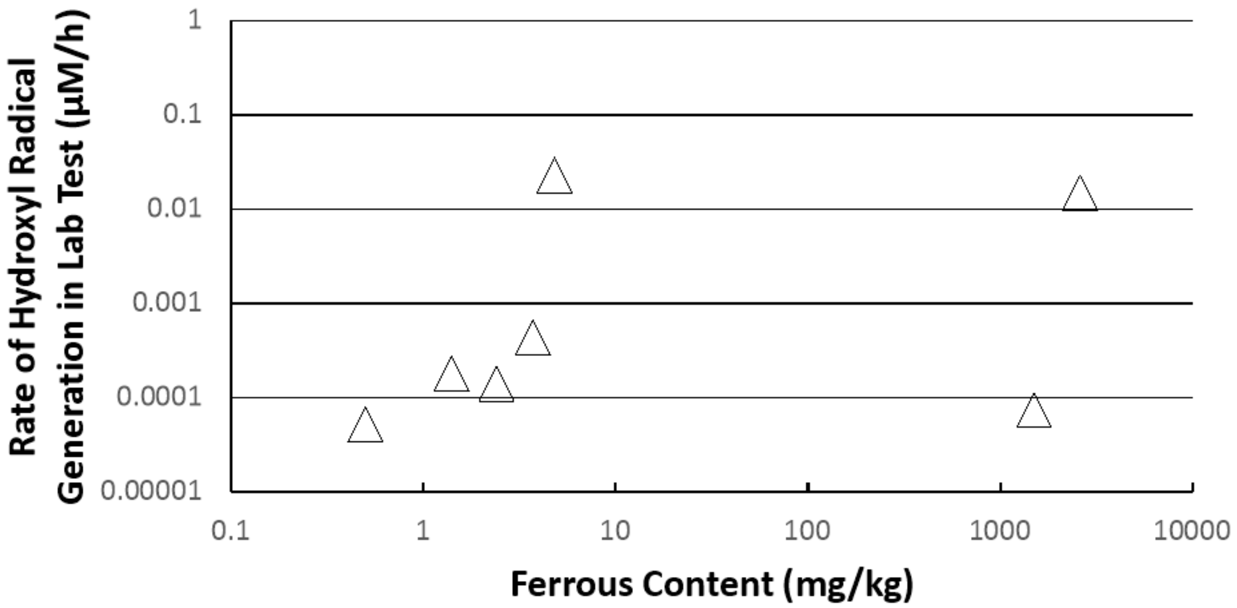
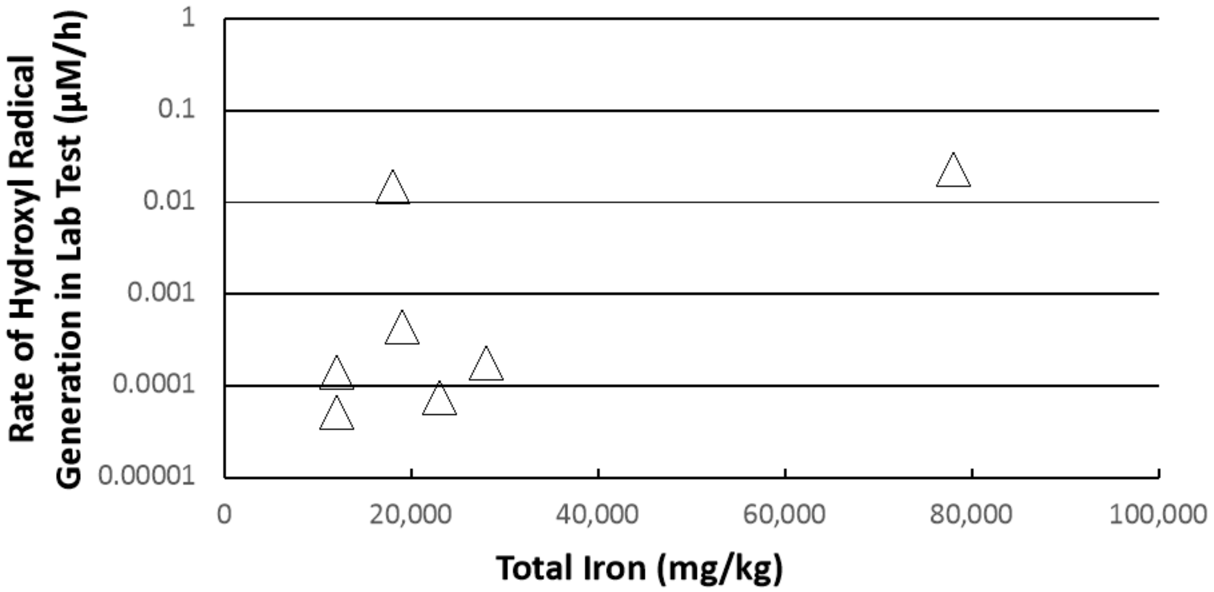
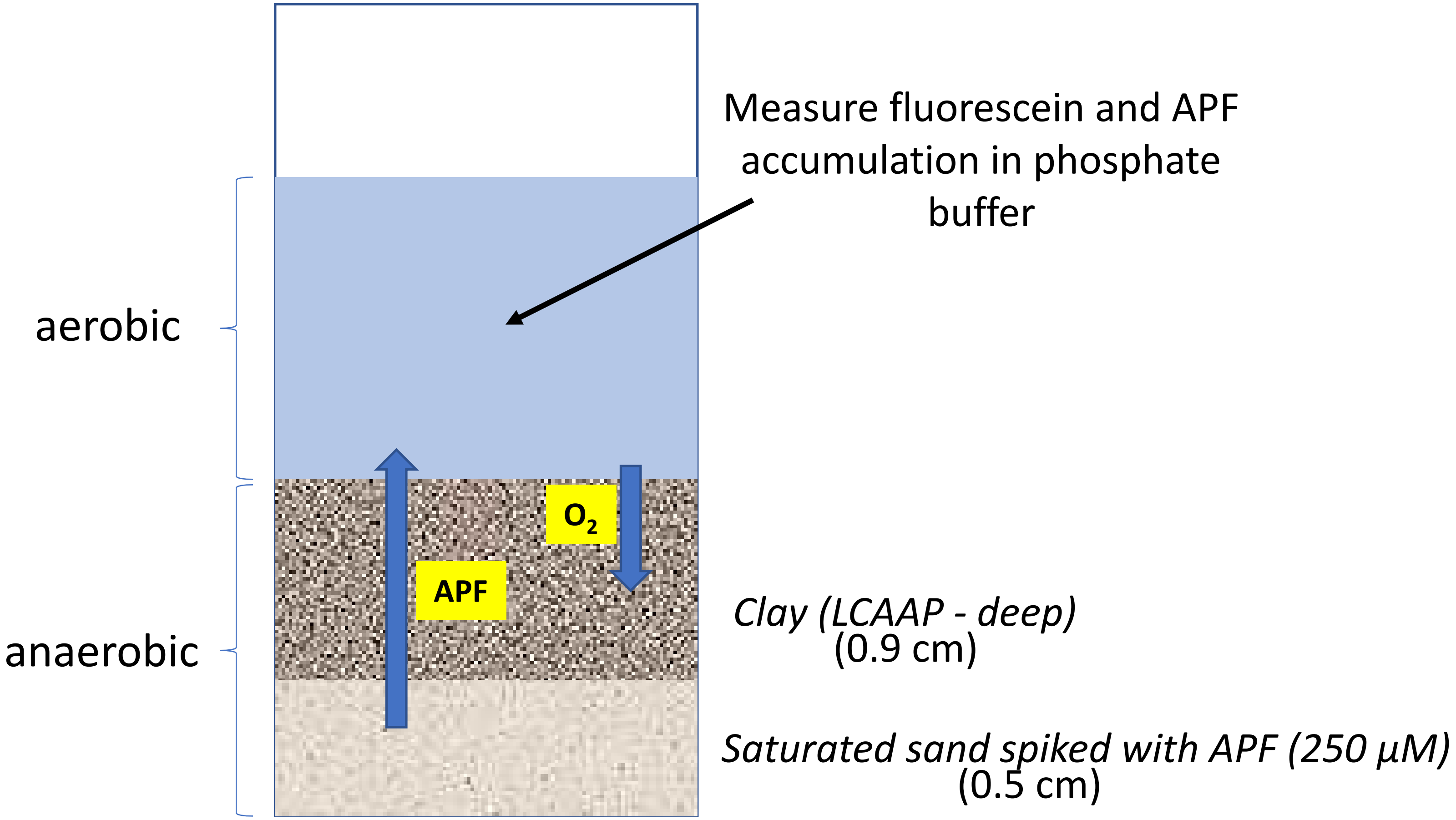
Kong et al., ES&T, 2015; Lee et al., ES&T, 2008

Hydroxyl Radical Generation as a Function of Fe(II) or Total Fe





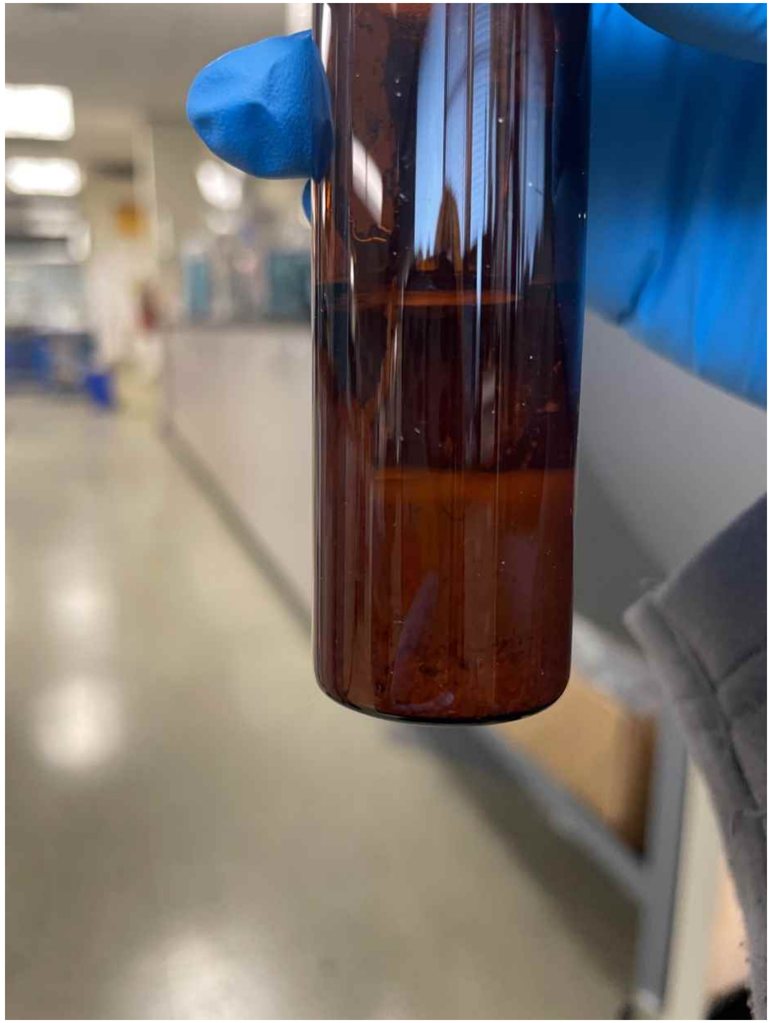
Back-Diffusion Experiment: Long-term oxidation



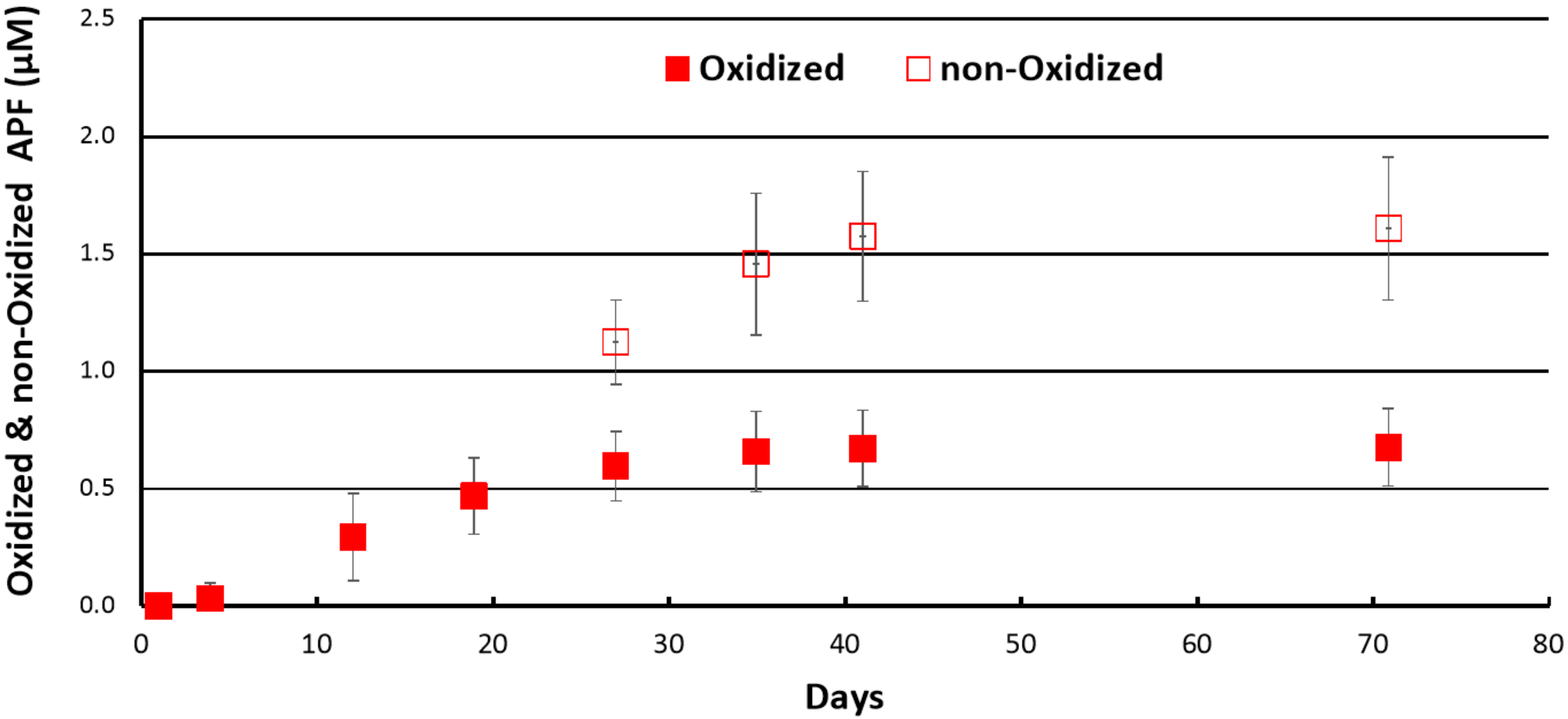
Measure fluorescein and APF accumulation in phosphate buffer

Clay (LCAAP - deep) (0.9 cm)

Saturated sand spiked with APF (250 µM) (0.5 cm)



Diffusion Experiment Results (preliminary)



- Only 1 – 3% of the ferrous iron consumed for hydroxyl radical generation

Monitoring on-going

Summary

- **Abiotic dechlorination reactions can be facilitated by ferrous minerals**
  - These reactions can occur under aerobic or anaerobic conditions

- **Ferrous mineral content, determined by dilute acid extraction, serves as a reasonable predictor for the abiotic reductive dechlorination rate constant**
  - Exceptions: pyrite and biotite

- **H_2O_2 may be a good indicator for oxidative abiotic reactions**
  - Research needed to develop methods to quantify and predict in situ abiotic dechlorination rates

Acknowledgement

ESTCP

Project ER20-5031

Thank You

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