Predicting Pollutant Generation in the Subsurface to Inform Produced Wastewater Remediation and Reuse

NATIONAL ENERGY TECHNOLOGY LABORATORY

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Project Overview

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Task 27.0: Predicting Pollutant Generation in the Subsurface to Inform Produced Wastewater Remediation and Reuse

2021 $315k	2022 $450k	2023 $450k	Total Project Value (2021–2023) $1,215k

Problem

Shale well production generates large volumes of wastewater with ***unpredicted types and concentrations of pollutants*** making treatment expensive and difficult

Research Question

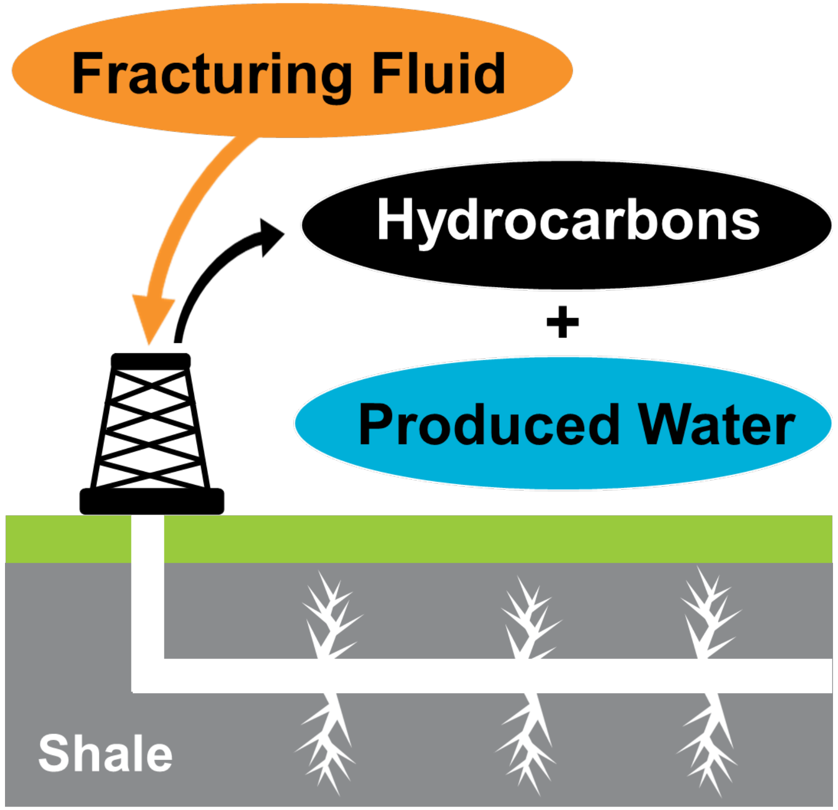
How, when, and where do reactions between **existing reservoir components** (i.e., minerals, clays, and organics) and **injected fracturing fluid additives** generate pollutants in produced wastewater?

End Products

- Report on ***where*** pollutant generation is likely to occur, which will inform ***how*** pollutants can be prevented or removed
- Develop a model to predict ***when*** during the production curve pollutant generation is expected

Oil & Gas Wastewater

Shale Oil Production Generates Large Volumes of Wastewater



Volume of water: estimated up to 14,000,000 L per well

Ratio of Water/Oil: between 3 and 20

Hazards: Vary by location and production time

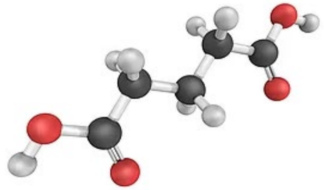
High Salinity

Up to 10 times saltier than ocean water

Radioactive

Contains Radium-226 and other radionuclides

Organic Chemicals



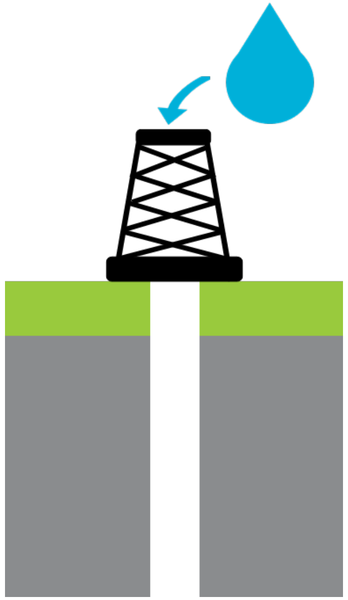
Unknown types and concentrations

Kondash, A. J.; Albright, E.; Vengosh, A., Quantity of flowback and produced waters from unconventional oil and gas exploration. *Science of The Total Environment* **2017**, *574*, 314-321. Sanchez-Rosario, R.; Hildenbrand, Z. L., Produced Water Treatment and Valorization:A Techno-Economical Review. *Energies*, **2022**, 15, 4619.

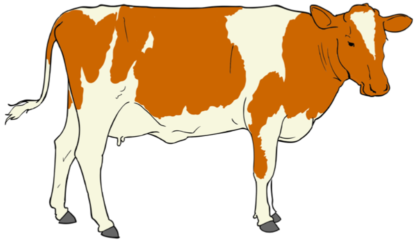
Enabling Beneficial Reuse of Produced Water

Better Solutions are Needed for Managing Produced Water

Current Management:
Disposal Wells

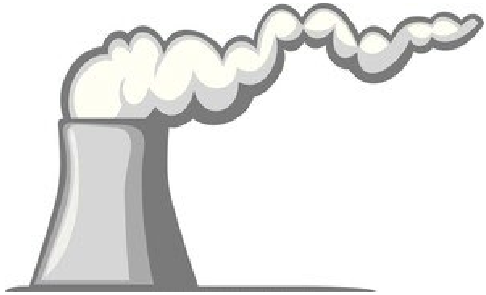


Avenues of Reuse →



Livestock Watering

Municipal Use



Industrial Cooling

Agriculture

What's in the water?

Stream Augmentation

- Causing induced seismicity
- Water strain in arid regions

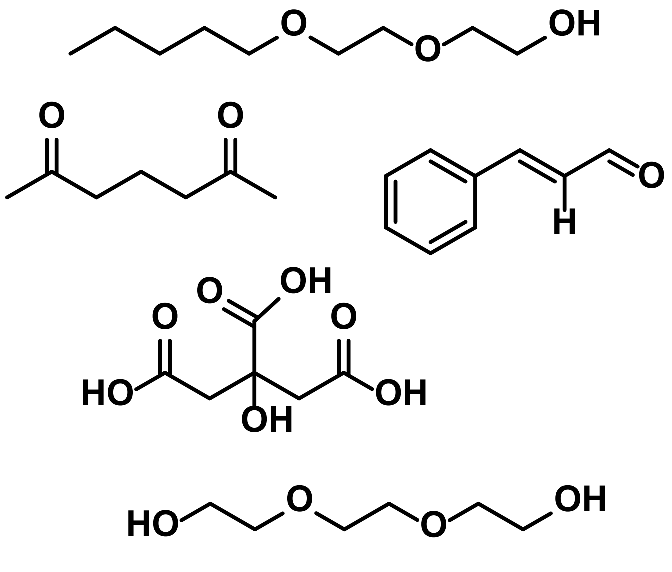
Danforth, C.; McPartland, J.; Blotevogel, J.; Coleman, N.; Devlin, D.; Olsgard, M.; Parkerton, T.; Saunders, N., Alternative Management of Oil and Gas Produced Water Requires More Research on Its Hazards and Risks. *Integrated Environmental Assessment and Management* **2019**, *15*, 677-682.

Organic Chemicals in Produced Water

Unpredicted Types and Concentrations of Organic Contaminants Make Treatment Expensive and Difficult

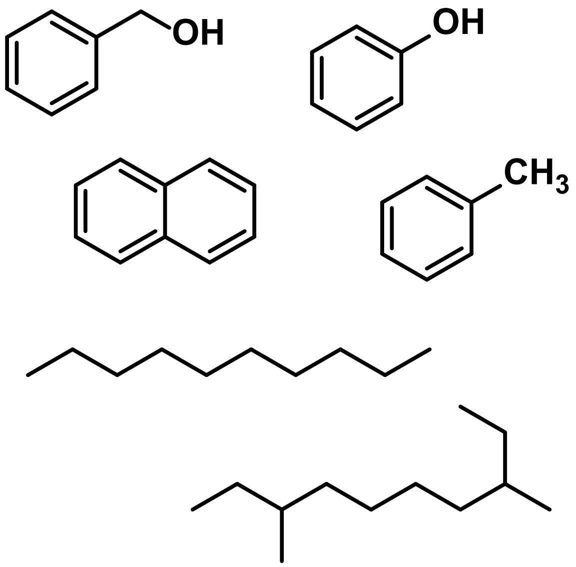
Injected Chemicals

- Surfactants, biocides, etc.
- Listed in "FracFocus"



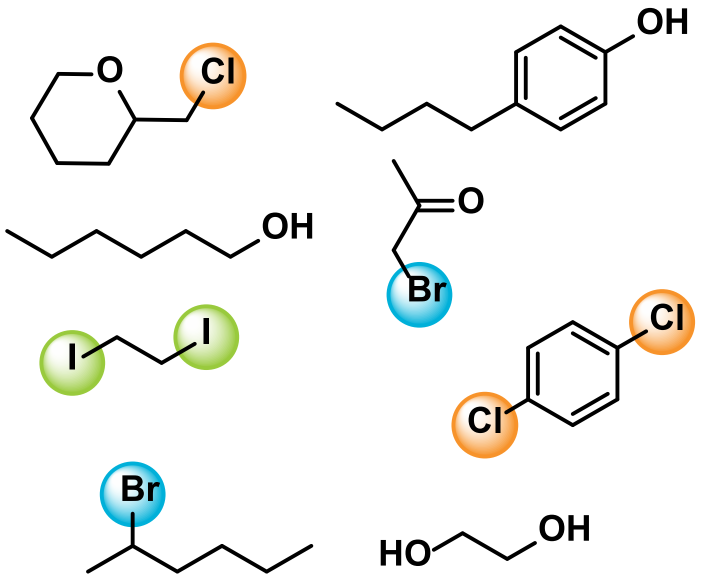
Subsurface Chemicals

- Phenols, aromatics, hydrocarbons
- Unknown concentrations



Transformation Products

- Halogenated, alcohols, PEGs
- Unknown concentrations
- High potential toxicity



Hoelzer, K.; Sumner, A. J..; Karatum, O.; Nelson, R. K.; Drollette, B. D.; O'Connor, M. P.; D'Ambrio, E. L.; Getzinger, G. J.; Ferguson, P. L.; Reddy, C. M.; Elsner, M.; Plata, D. L.; Indications of Transformation Products from Hydraulic Fracturing Additives in Shale-Gas Wastewater. *Environ. Sci. Technol*., **2016**, 50, 8036-8048.

Toxicity of Halogenated Compounds

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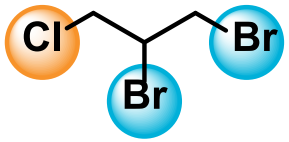
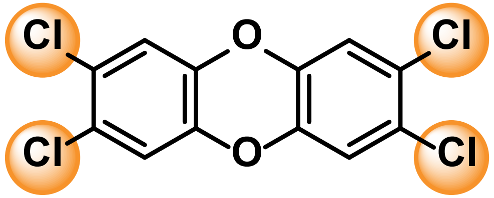
- Halogenated organic compounds are more toxic than their non-halogenated counterparts
- Fat-soluble and not broken down by the body
- Increase in toxicity from Cl < Br < I

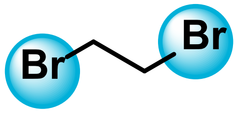
Examples:



1,2-dibromo-3-chloro propane (DBCP)
Reproductive difficulties; increased risk of cancer
Limit: 0.002 mg/L



Dioxin (2,3,7,8-TCDD)
Reproductive difficulties, increased risk of cancer,
0.00000003 mg/L



Ethylene Dibromide
Problems with liver, stomach, reproductive system, or kidneys; increased risk of cancer
Limit: 0.00005 mg/L

https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations

What subsurface conditions lead to halogenated transformation products?

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Previously studied by Sumner and Plata, 2018

High salinity + **Oxidants** + **Organic molecules** = **Halogenation Reactions**

Reservoir brine, up to 200,000 mg/L

Oxidative breakers in fracturing fluid

Naturally-occurring organics (hydrocarbons, kerogen) and fracturing fluid additives

Andrew J. Sumner; Desiree L. Plata. Halogenation Chemistry of Hydraulic Fracturing Additives under Highly Saline Simulated Subsurface Conditions. *Environ. Sci. Technol.* **2018**, *52*, 9097−9107

Mechanism of Oxidant-Initiated Halogenation Reactions

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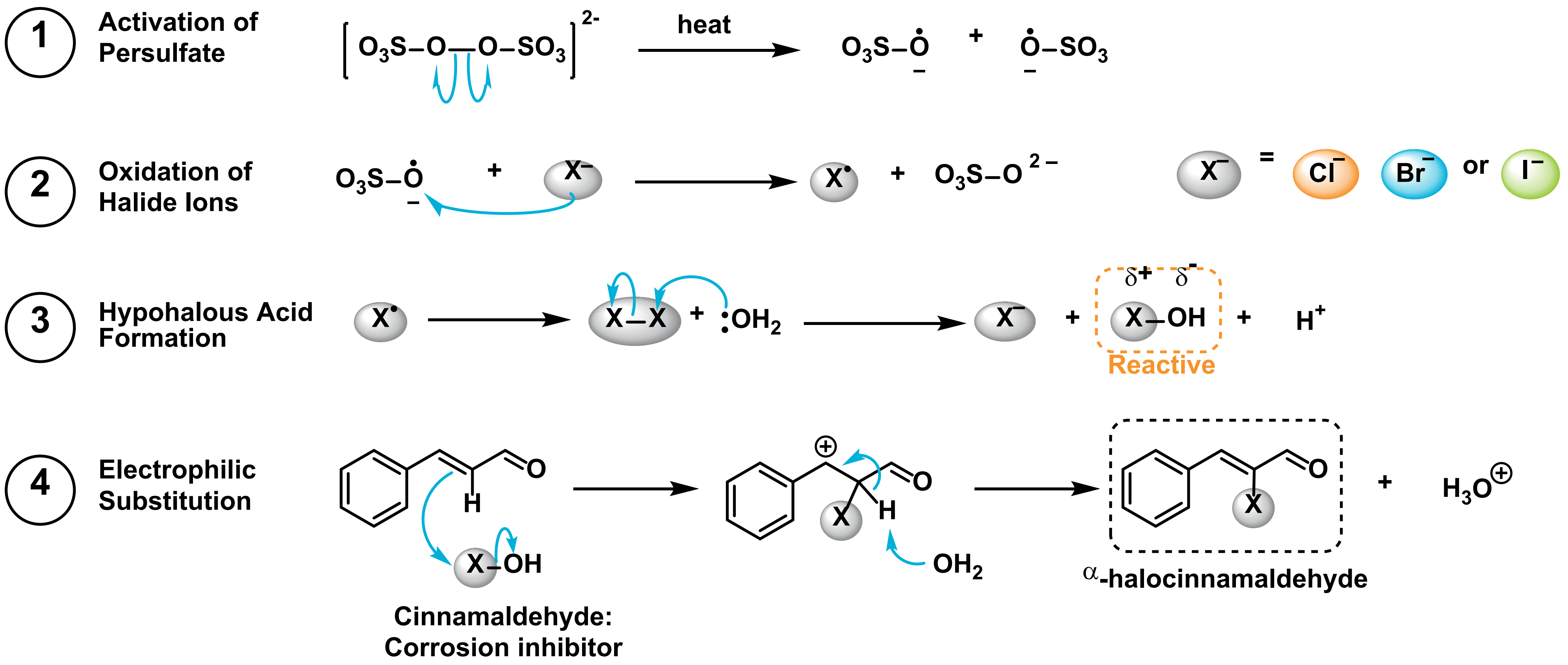
How do Oxidants, Brine, and Organics React to Give Halogenated Contaminants?

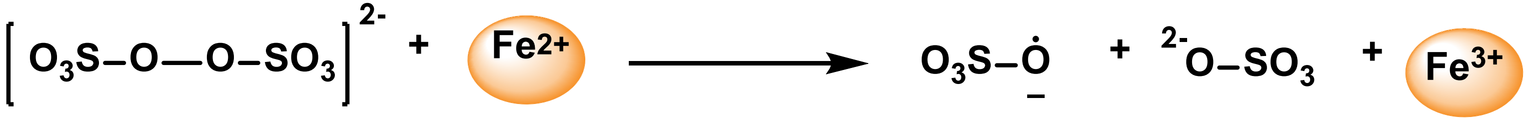


Research Question: What is the Role of Iron?

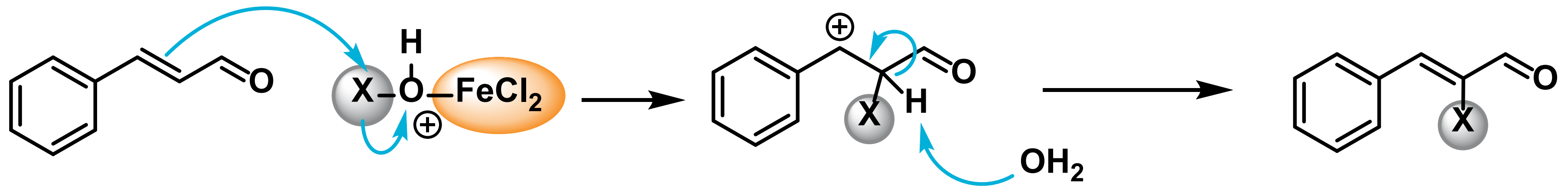
Focus of EY22 Q1 and Q2

Hypothesis: The presence of iron in subsurface shale increases the rate and scope of halogenation reactions

A Activation of Peroxydisulfate



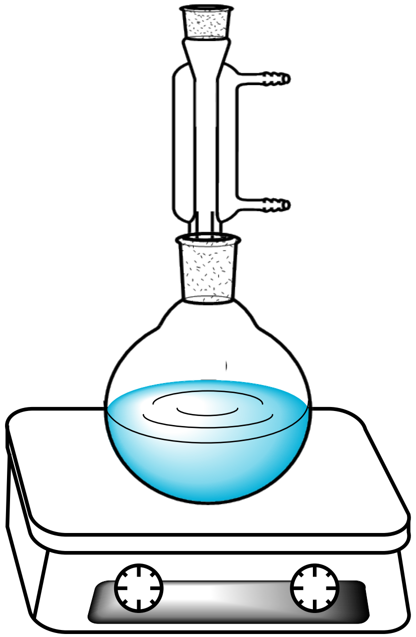
B Lewis Acid Catalyst



Goal: Develop Halogenation Rate Constants

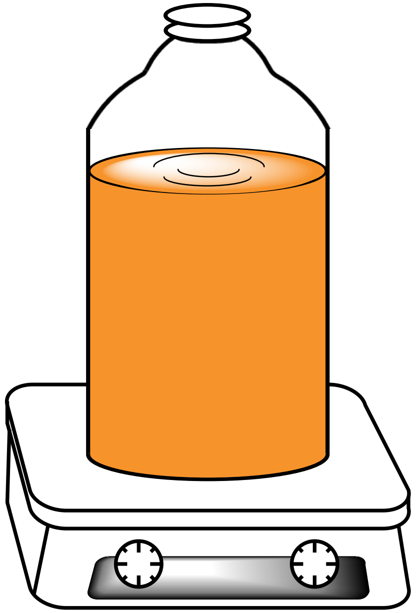
Phase 1

Model compounds & mineral standards



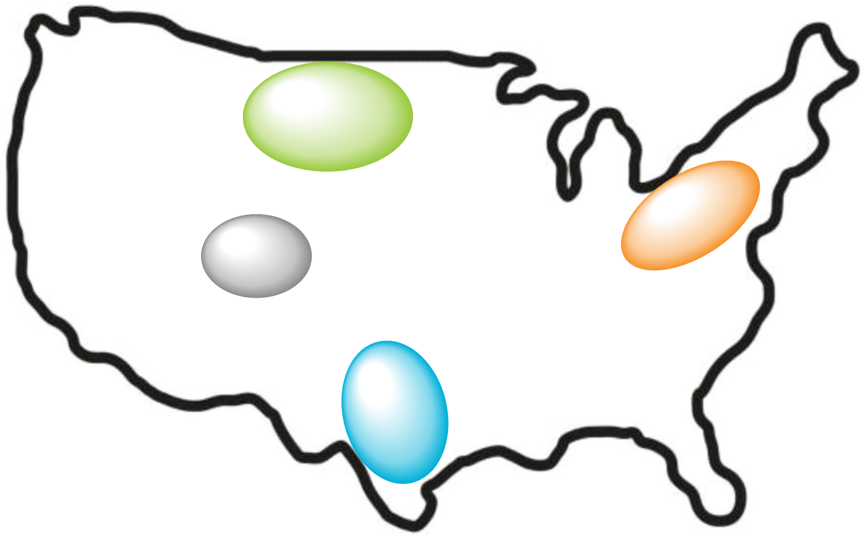
Phase 2

Geologic samples (kerogen, pyrite, shale powder)



Phase 3

Geochemical modeling: Basin-specific reaction predictions



Phase 1 Experimental Plan

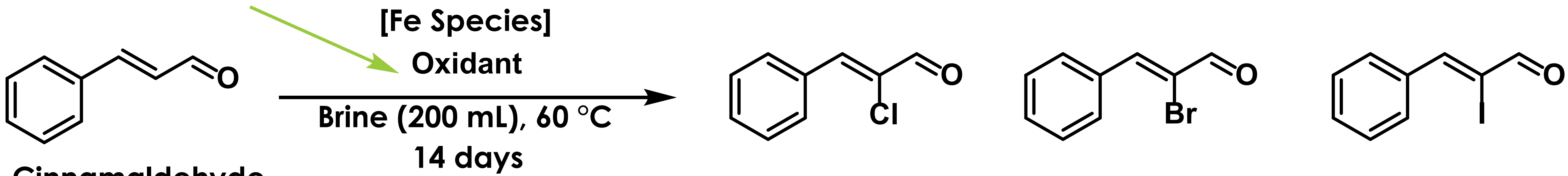
Set Up Reactions in Flasks, Meant to Mimic Subsurface Condition

Oxidative Breakers in frac fluid

- Tested $(NH_4)_2S_2O_8$, NaOCl

Naturally occurring in shale

- Tested No Fe, $FeCl_2$, $FeCl_2$ with citric acid, $FeCl_3$



Cinnamaldehyde

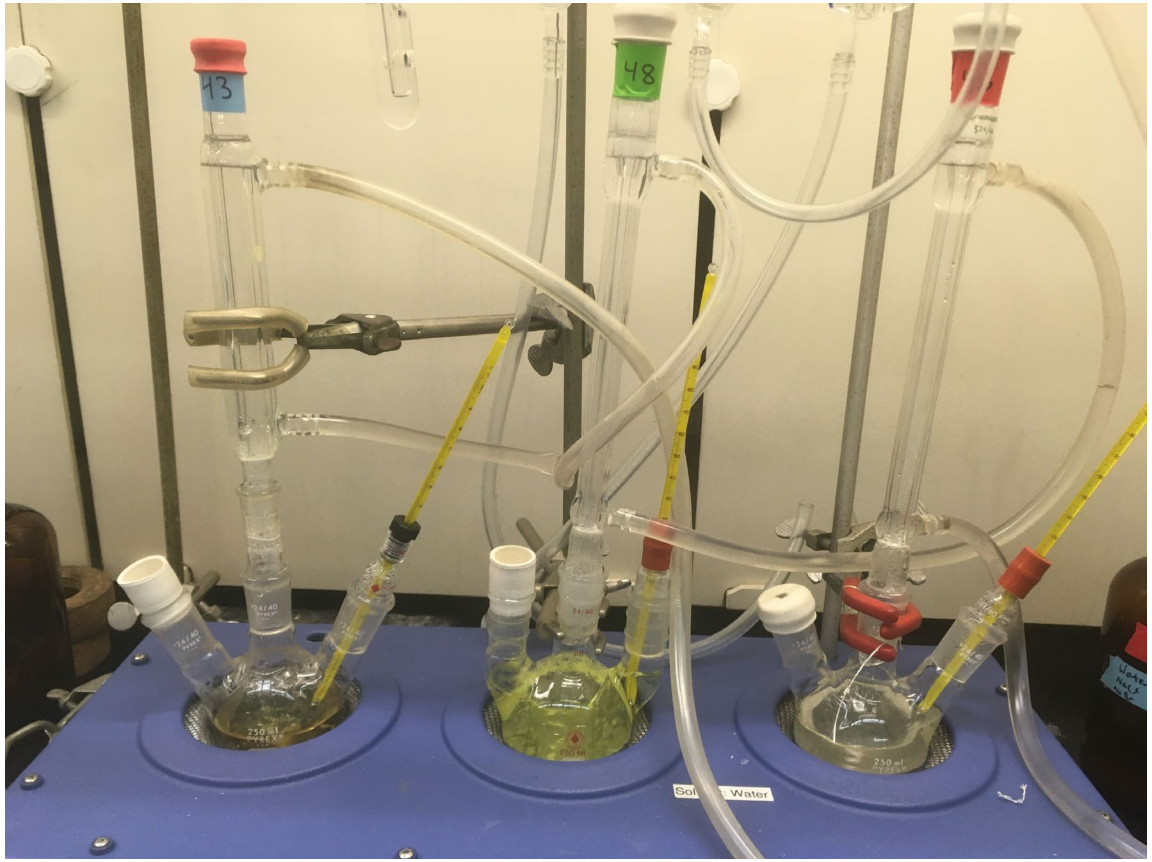
Corrosion Inhibitor

Halide Ions

Brine Recipe			
Cl^-	50,000 mg/L	$CaCO_3$	40 mg/L
Br^-	500 mg/L	HCl	pH = 3
I^-	25 mg/L		

Experimental Procedure

Redox Geochemistry Lab

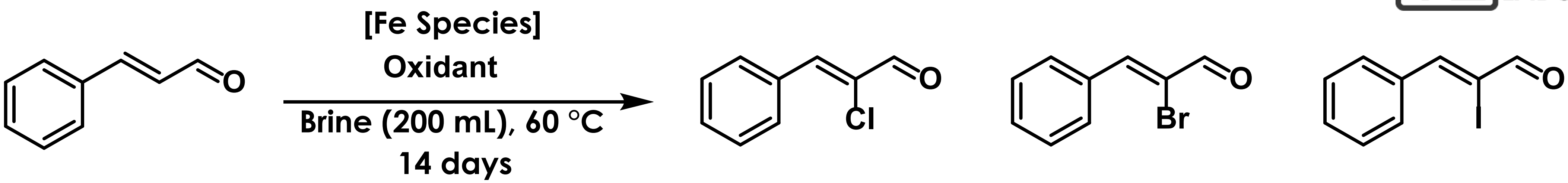


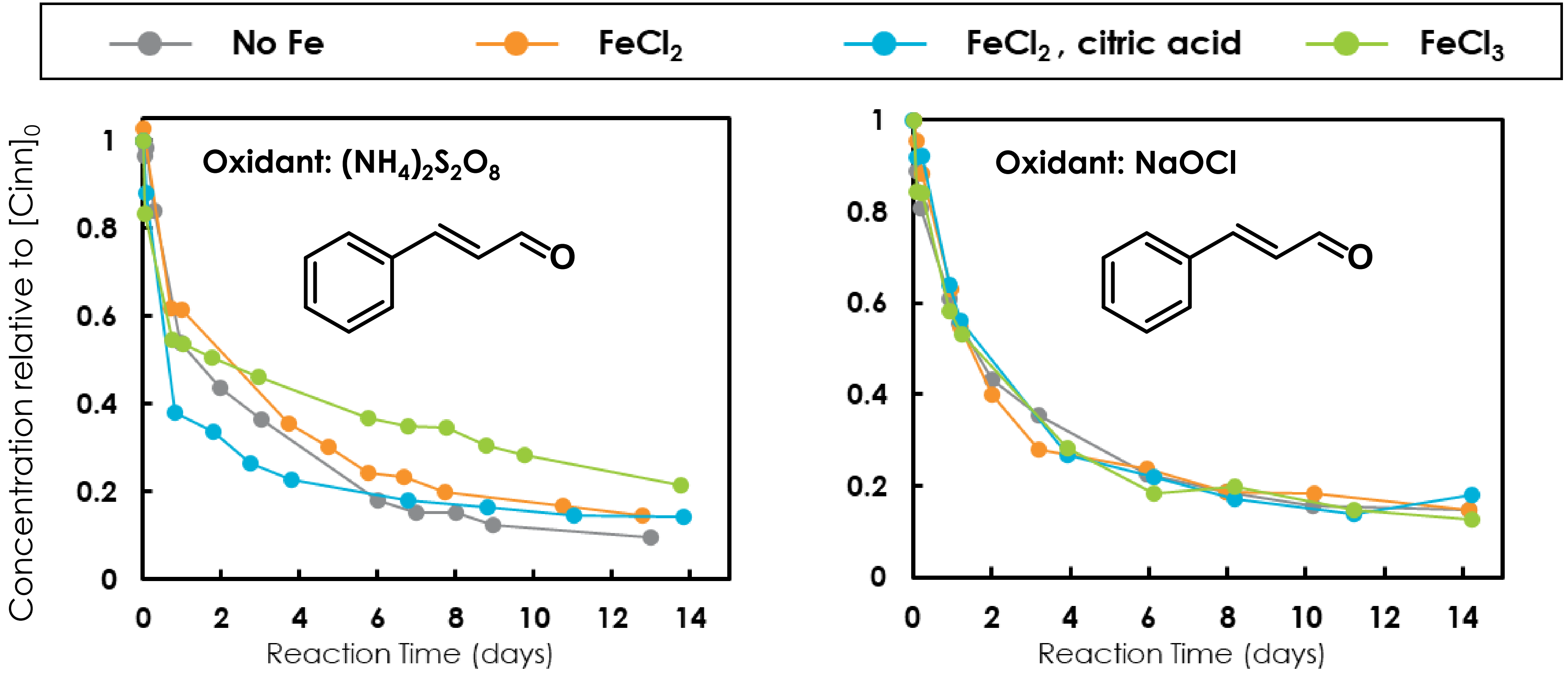
Reaction Setup

Agilent 7890A GC
Agilent 5975C MSD

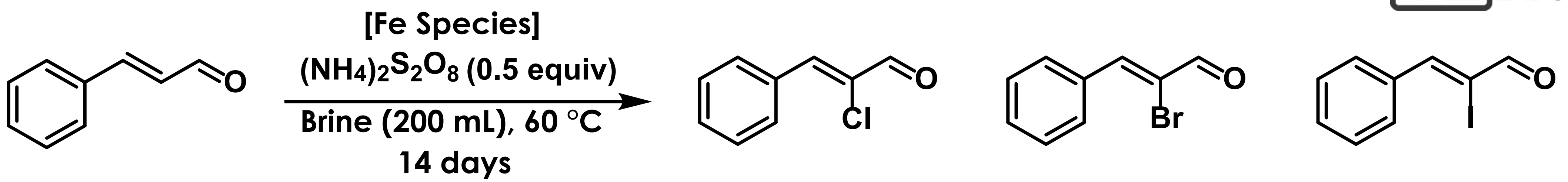
Measured concentrations using gas chromatography-mass spectrometry

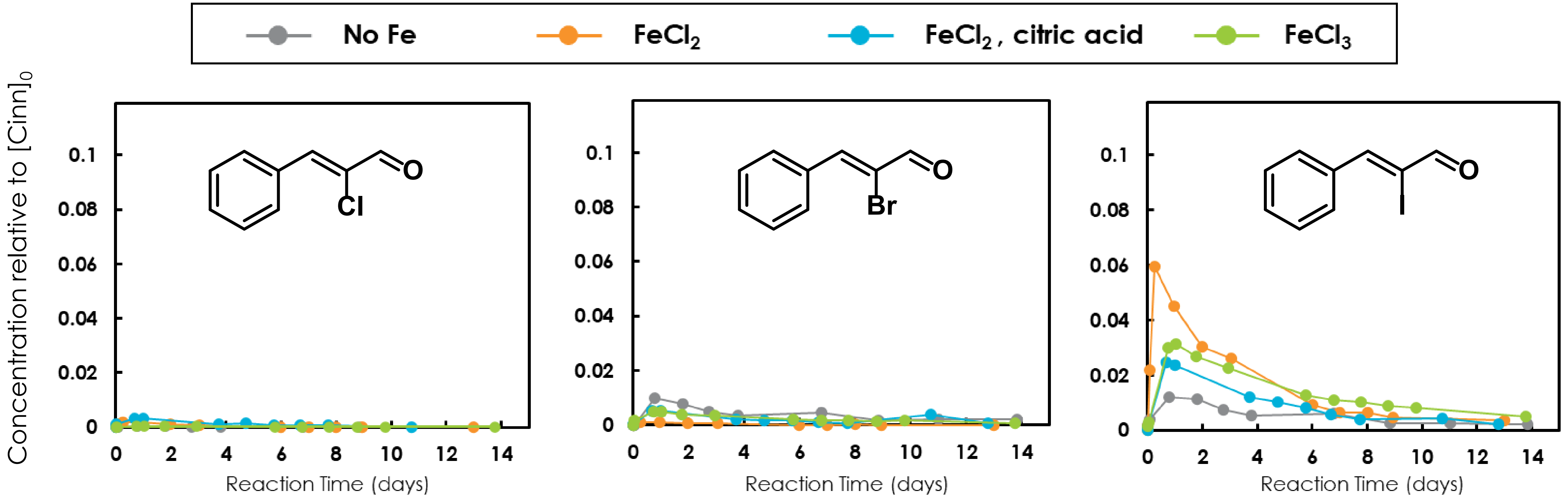
Results: Degradation of Cinnamaldehyde



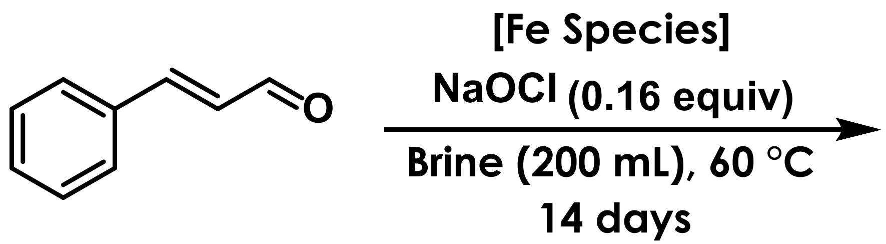


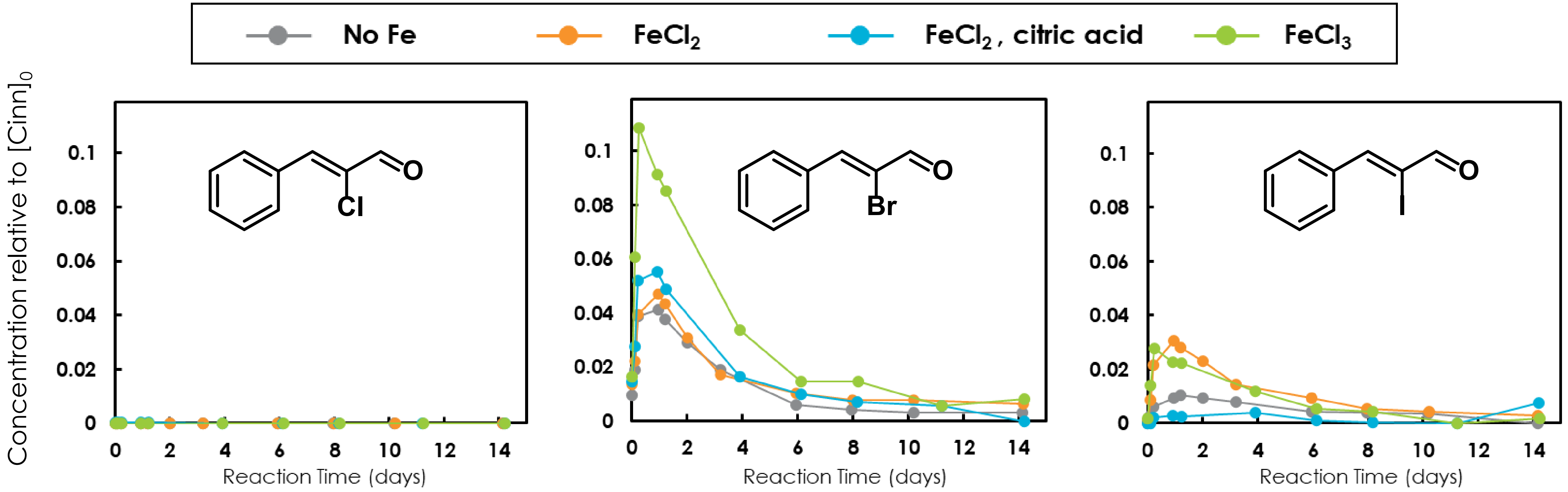
Results: Halogenation Products, $(NH_4)_2S_2O_8$





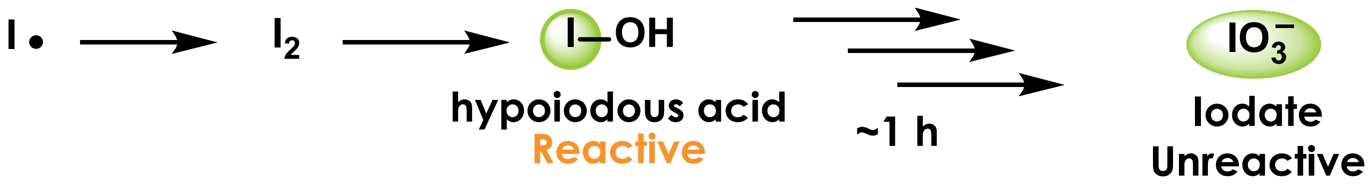
Results: Halogenation Products, NaOCl





Why Do a-Halocinnamaldehydes Decrease Over Time?

- Hypoiodous acid forms and oxidizes quickly



- a-halocinnamaldehydes undergo oxidative degradation

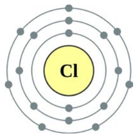
Supported by decrease in TOC over the reaction (540 mg/L to 200-300 mg/L)

Li, J.; Jiang, J.; Pang, S. Y.; Cao, Y.; Zhou, Y.; Guan, C., Oxidation of iodide and hypoiodous acid by non-chlorinated water treatment oxidants and formation of iodinated organic compounds: A review. *Chemical Engineering Journal* **2020**, *386*, 123822.

Why are iodo- and bromo-cinnamaldehyde formed instead of chloro?

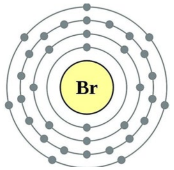
Iodine Radical (I•) is Formed ~100x Faster than Br• and ~1000x Faster than Cl•

$Cl^- + SO_4^{-}\bullet \longrightarrow Cl\bullet + SO_4^-$ 3.0 × 10^8 M^{-1}s^{-1}



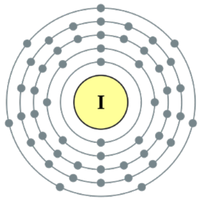
(Peyton 1993)

$Br^- + SO_4^{-}\bullet \longrightarrow Br\bullet + SO_4^-$ 3.5 × 10^9 M^{-1}s^{-1}



(Das 2001)

$I^- + SO_4^{-}\bullet \longrightarrow I\bullet + SO_4^-$ 3.2 × 10^{11} M^{-1}s^{-1}



(Chen 2012)

Chen, L.; Peng, X.; Liu, J.; Li, J.; Wu, F., Decolorization of Orange II in Aqueous Solution by an Fe(II)/sulfite System: Replacement of Persulfate. *Industrial & Engineering Chemistry Research* **2012**, *51*, 13632-13638.
Das, T. N., Reactivity and role of SO5•- radical in aqueous medium chain oxidation of sulfite to sulfate and atmospheric sulfuric acid generation. *Journal of Physical Chemistry A* **2001**, *105*, 9142-9155.
Peyton, G. R., The free-radical chemistry of persulfate-based total organic carbon analyzers. *Marine Chemistry* **1993**, *41*, 91-103.

Phase 2: Reactions of Extracted Kerogen

West Virginia University

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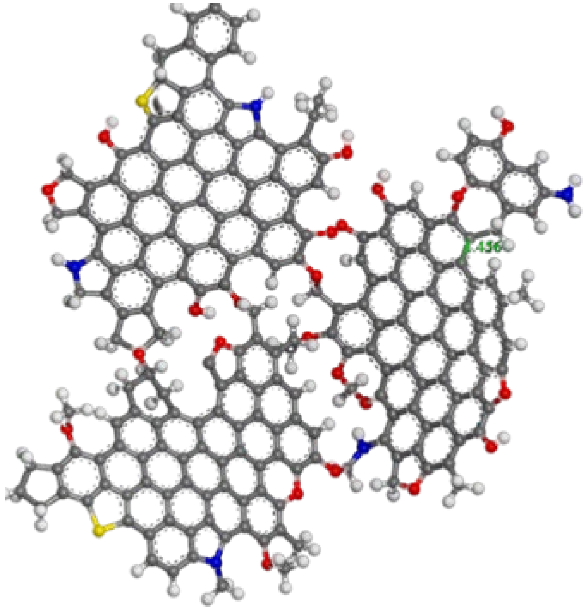
Extracted Kerogen



$(NH_4)_2S_2O_6$, $NaBrO_4$, or NaOCl

→

Brine Recipe			
Cl^-	50,000 mg/L	$CaCO_3$	40 mg/L
Br^-	500 mg/L	HCl	pH = 3
I^-	25 mg/L		

Elemental Analysis: Extent of kerogen oxidation

GC-MS: Types and amount of halogenated compounds

^{13}C Solid State NMR: Mechanism of kerogen oxidation

ICP-MS: Inorganic contaminants and critical minerals

Summary and Implications for Produced Water Treatment

- Iodinated and brominated contaminants may be formed in higher amounts in produced water than previously expected.
- High-salinity brine that contains I^- and Br^-, in the presence of oxidants, is susceptible to generation of toxic contaminants.
- The results so far with cinnamaldehyde show that the halogenated compounds form and then degrade.
- Rates of formation and degradation are important for understanding water toxicity.
- Water treatment using Fe should be avoided (or carefully timed).

Thank you!

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