Developing an Acetylene Sampler for Quantitative Assessment of Long-term Abiotic Transformation Rates of Chlorinated Solvents

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06/06/2024

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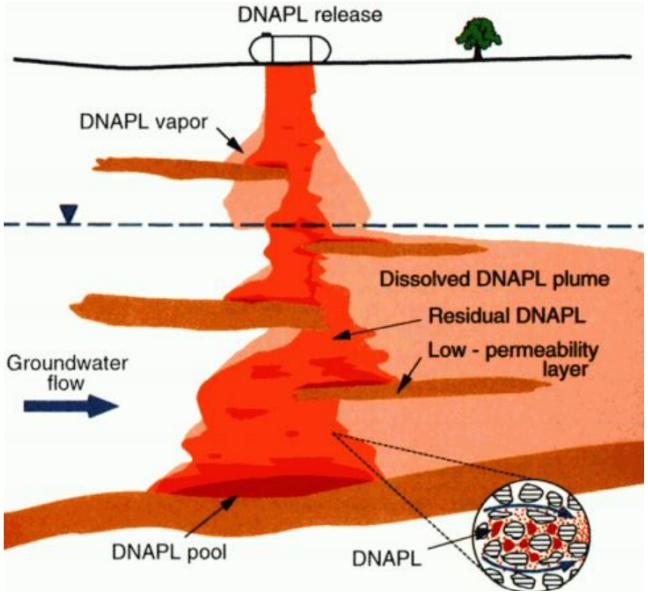
2024 Chlorinated Conference

Chlorinated Solvent Sites

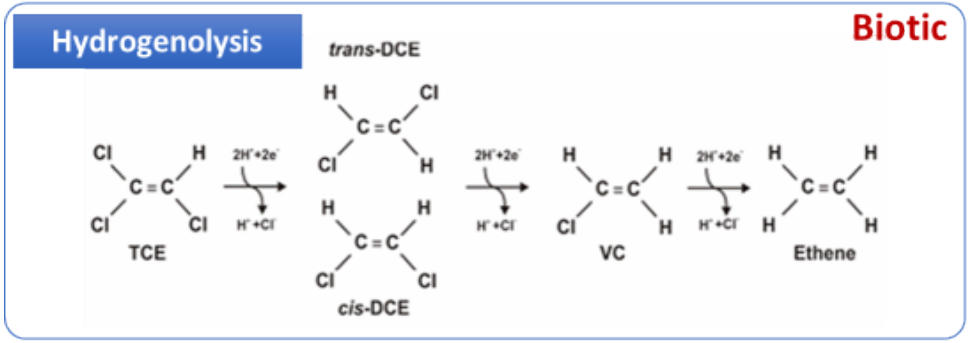
- Trichloroethene (TCE) and tetrachloroethane (PCE) are commonly detected contaminants at complex sites
- These contaminants often exist as dense non-aqueous phase liquids (DNAPL) trapped in low-permeability clay lenses or fractured bedrocks
- Evaluating the rates of natural attenuation is crucial for making long-term site management decisions

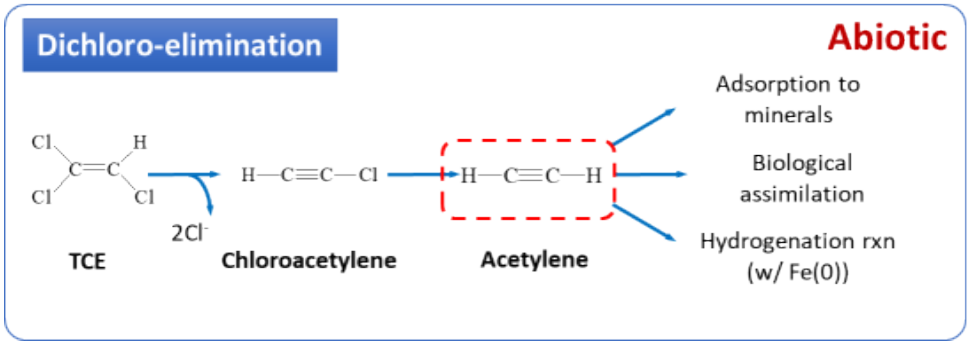


Water Resources Research Journal Volume 35, No. 3, March 1999

Abiotic Reduction of Chlorinated Ethenes

- Abiotic pathway is preferred for cleaner intermediate and final products
- **Acetylene** is a key product of abiotic reduction of chlorinated ethenes by iron minerals or ZVI metals
- A good sampling device to cumulate acetylene is desired





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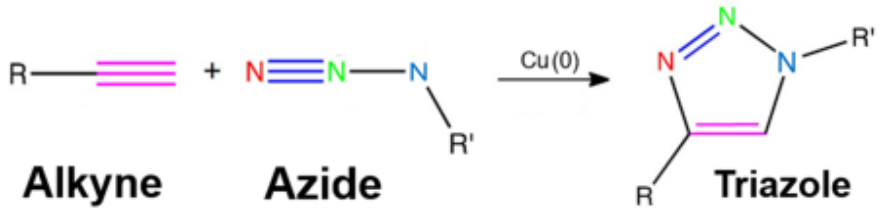
Reactive Acetylene Sampler

Cu-catalyzed Alkyne-Azide Click Reaction



Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem. Int. Ed.* 2001, 40: 2004–2021.

Click Chemistry

- Copper-catalyzed 1,3-dipolar cycloaddition between terminal alkyne and azide groups
- Product (triazole) chemically inert and biologically stable
- Widely used in organic synthesis and bioconjugation applications

Advantages

- **High specificity**: minimal interference by background solutes
- **Stable product** and **easy quantitation**

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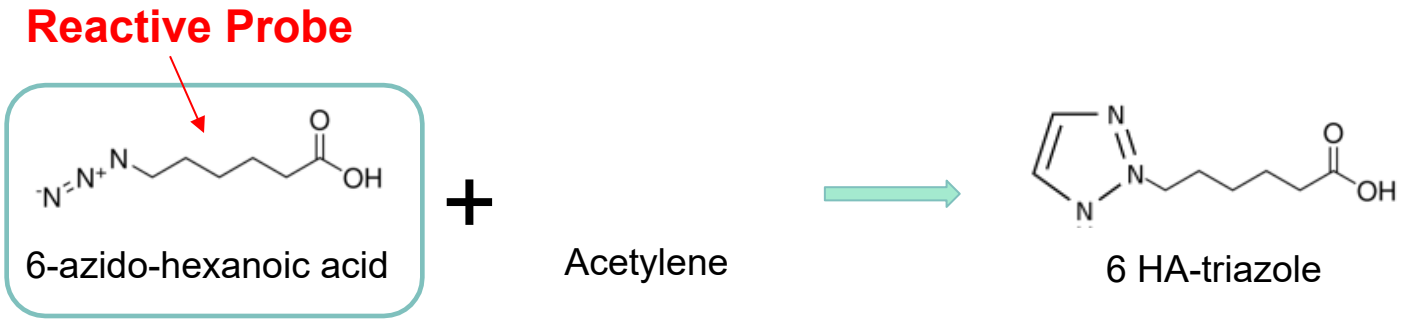
Approach to Reactive Sampler Design



- 6-azido-hexanoic acid (6AHA) a candidate probe for its aqueous stability
- Immobilizing 6AHA into polymer thin films to create reactive media for acetylene capture

Objectives

General Objective

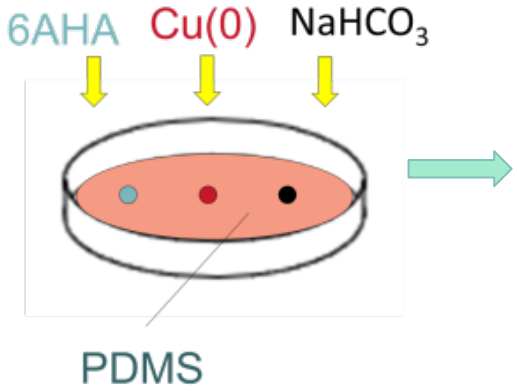
To design and evaluate a device that can be deployed *in situ* for quantitative measurement of **acetylene** at chlorinated solvent sites

Relevance to Long-term Management of Chlorinated Solvent Sites

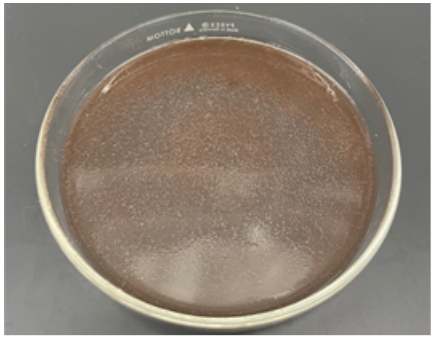
- Provide evidence to confirm the occurrence of abiotic transformation, particularly at sites with favorable biogeochemical conditions
- Enable a method to assess the rates of *in situ* abiotic transformation
- Support decision making for long-term site management

Sampler Design

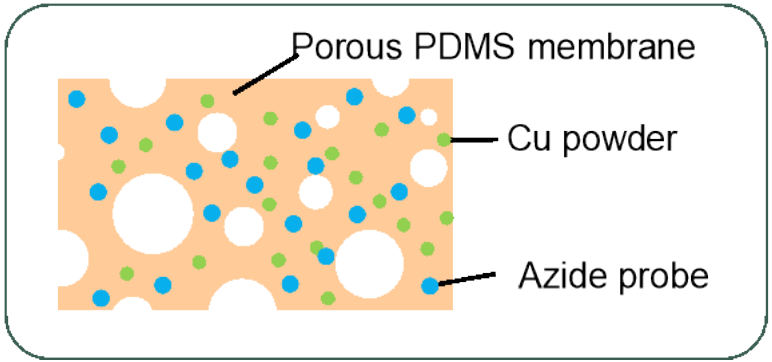
Loading Reactive Probe and Catalyst into PDMS



PDMS Film Casting (thickness < 1 mm)

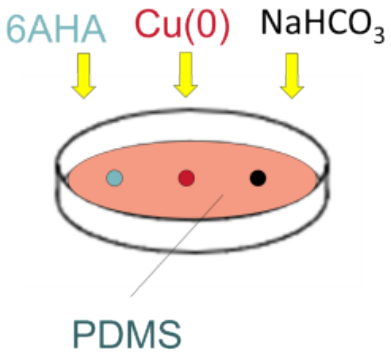


Schematics of Azide-loaded PDMS Membrane

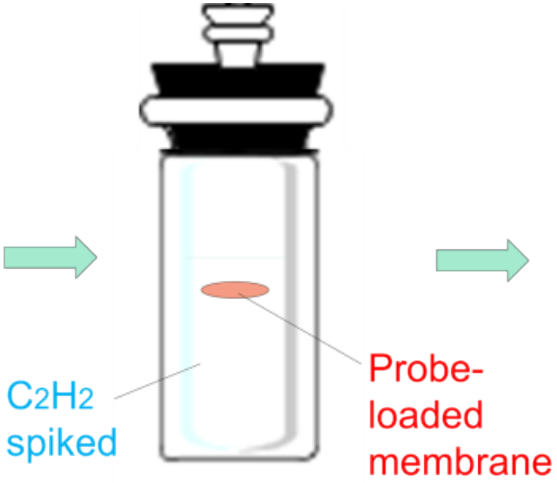


Sampler Evaluation in Acetylene-spiked Solution

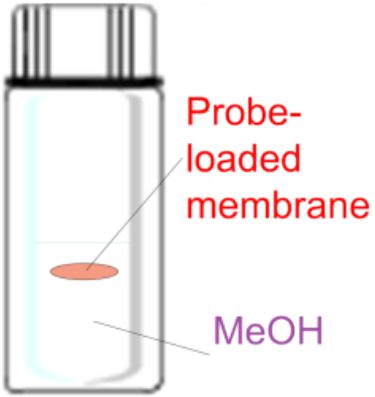
Preparation of Sampler



Batch Reactor

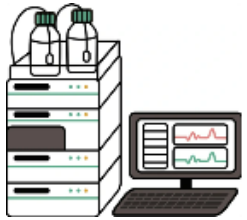


Extraction of Product



Product Analysis

Liquid chromatography–mass spectrometry (LC-MS)



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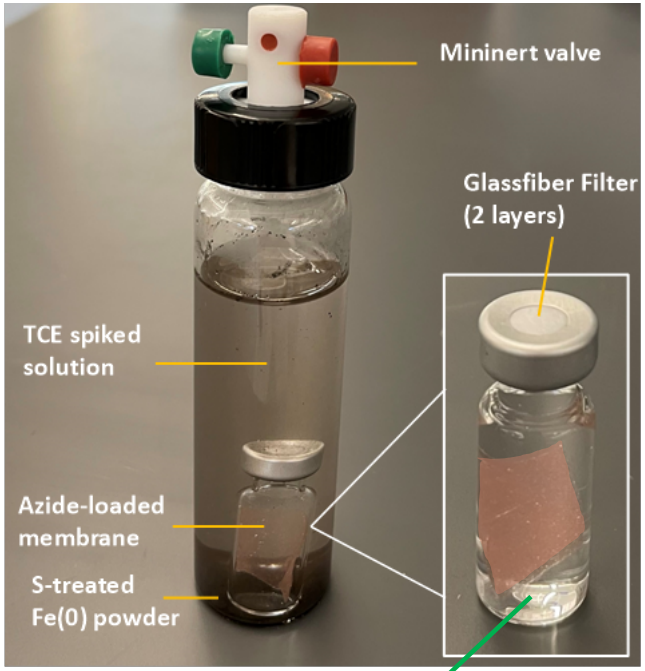
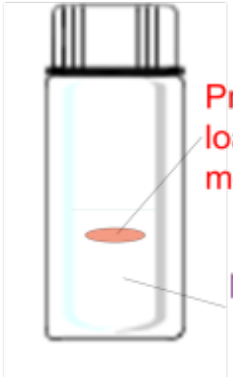
Sampler Validation in TCE-ZVI Microcosm

Abiotic Dechlorination Microcosm



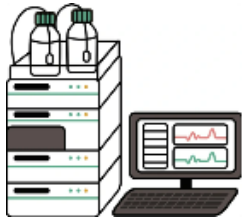
Acetylene Passive Sampler

Extraction of Product



Product Analysis

Liquid chromatography–mass spectrometry (LC-MS)

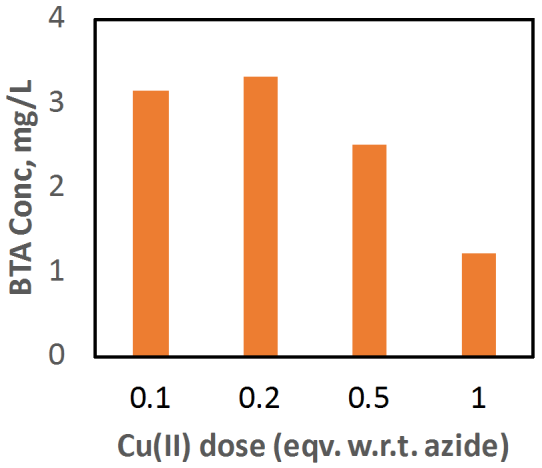


CEs and Acetylene Quantification

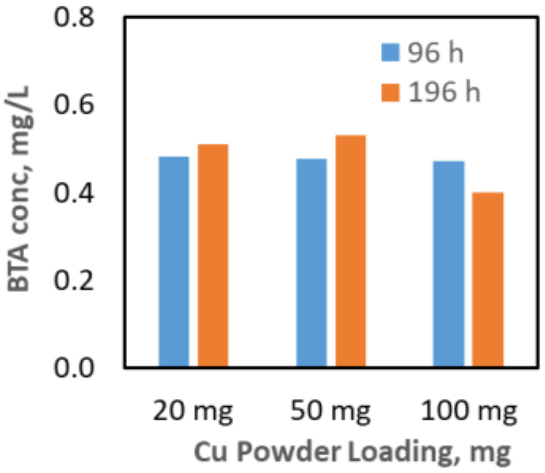
Gas chromatography with flame ionization detector (GC-FID)

Results – Choice of Catalyst

a) Dissolved Cu(II)



b) Cu(0) Powder (< 45 µm)



Cu(0) powder optimal catalyst

- Stable catalyst performance
- Slow-release source of Cu(I) ion (active form of catalyst)
- Antimicrobial protection

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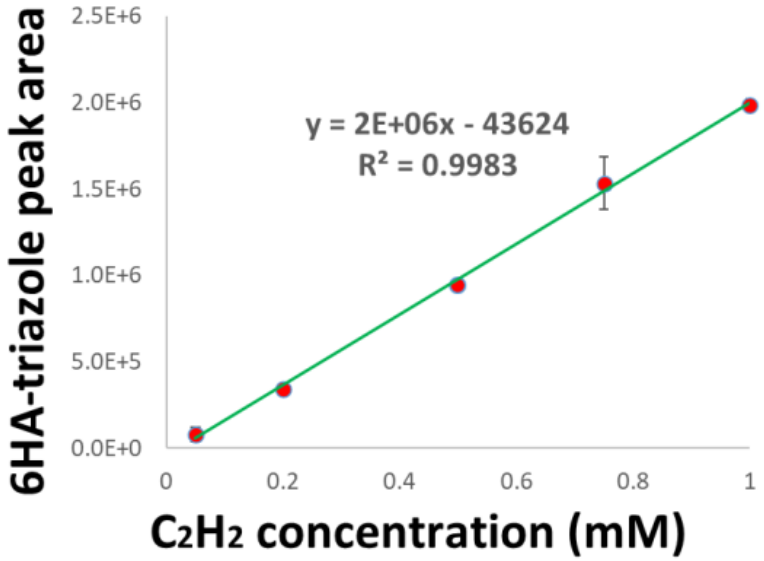
Calibration Curve



Validation

Product (6HA-triazole) yield is ***proportional*** to acetylene concentration

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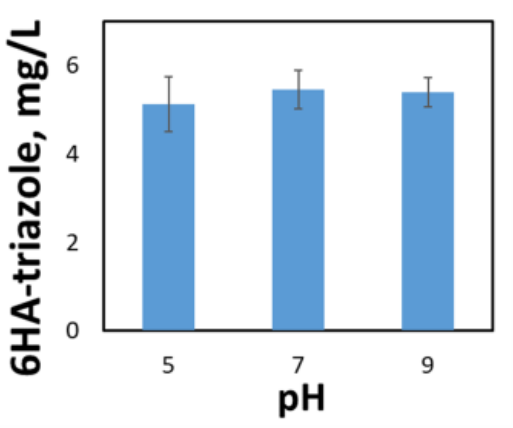
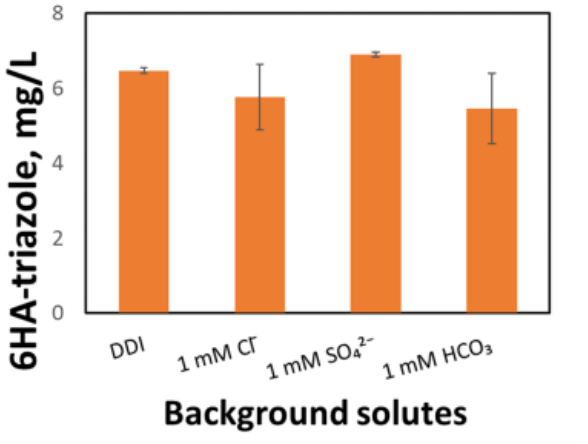
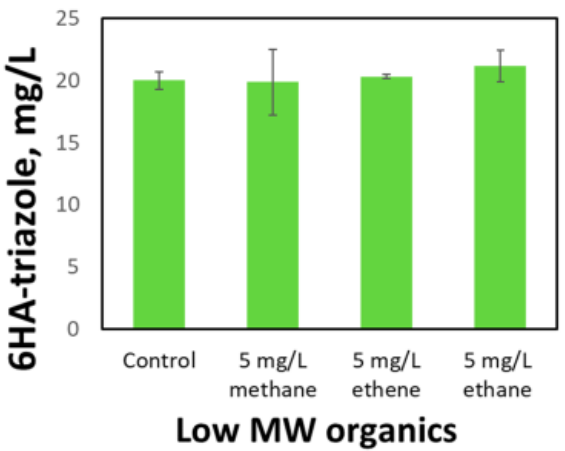
Effect of Groundwater Chemistry on Product Yield







Product yield ***not*** affected by:

- pH
- Groundwater solutes
- Presence of other low MW hydrocarbons

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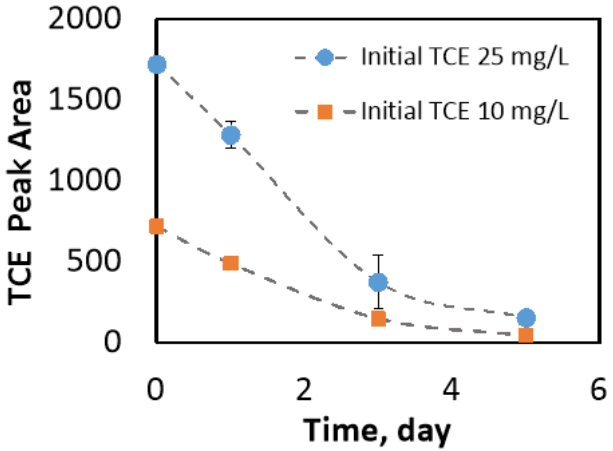
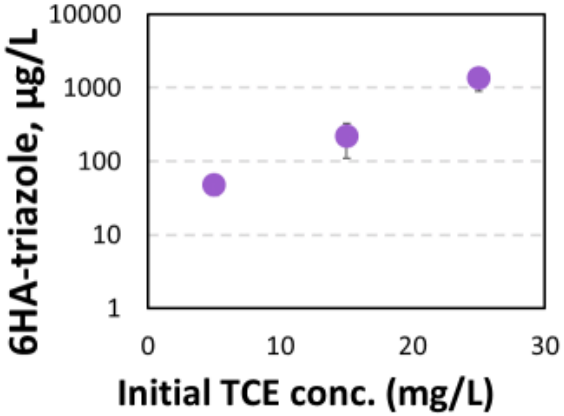
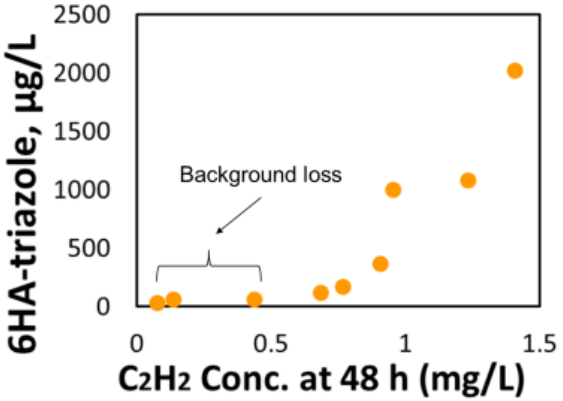
Sampler Validation in TCE-ZVI Microcosm







- The quantity of product recovered correlates strongly to TCE transformed
- Acetylene detection limit (~ 0.5 mg/L) controlled by background loss of acetylene

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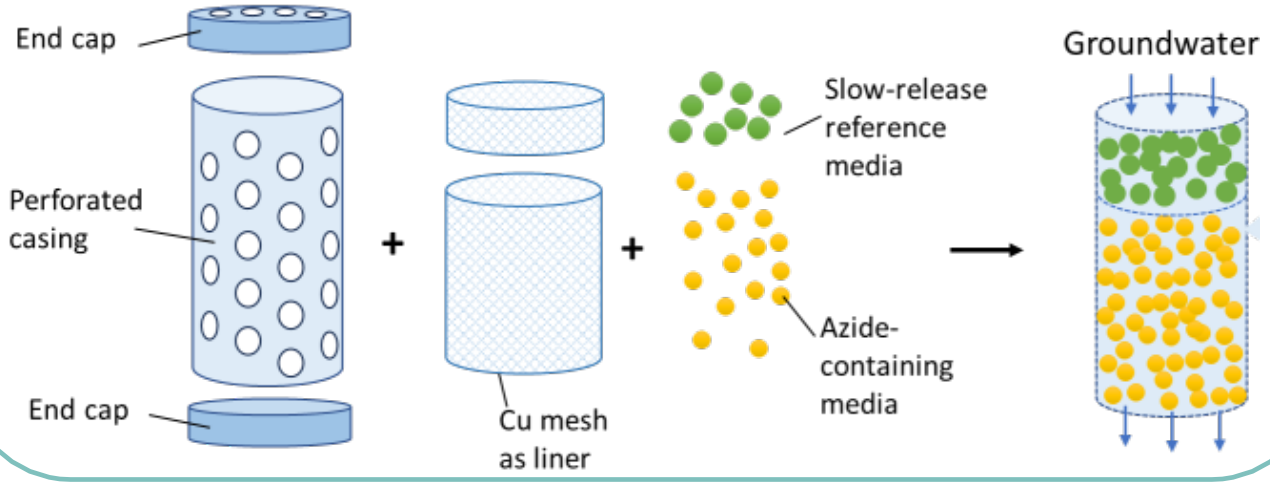
Conclusions

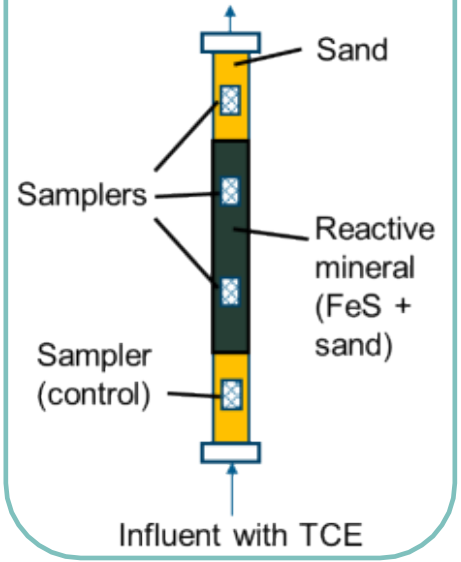
- A reactive sampler based on click chemistry was demonstrated for detecting low levels of acetylene in water.
- Product (triazole) yield is proportional to aqueous acetylene concentration.
- Sampler response is not affected by pH, common groundwater solutes, NOM, and other small MW hydrocarbons.
- TCE-ZVI microcosm study showed strong correlation between product quantity and the amount of TCE degradation, confirming the sensitivity and quantitation mechanism of the sampler.

Future Work

Improvements in Sampler Design



Evaluation in 1-D Column



- **Sampler deployment** and **field validation** at contamination sites

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Questions

Do you have any questions?

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Thank you!

Acknowledgements: the authors acknowledge funding support from DOD SERDP/ESTCP Program (Project # ER19-1411).