Combined ISCR and Bioaugmentation: New Insights for Sulfidated ZVI

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COWI

REGION The Capital Region of Denmark

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Dimin Fan, PhD

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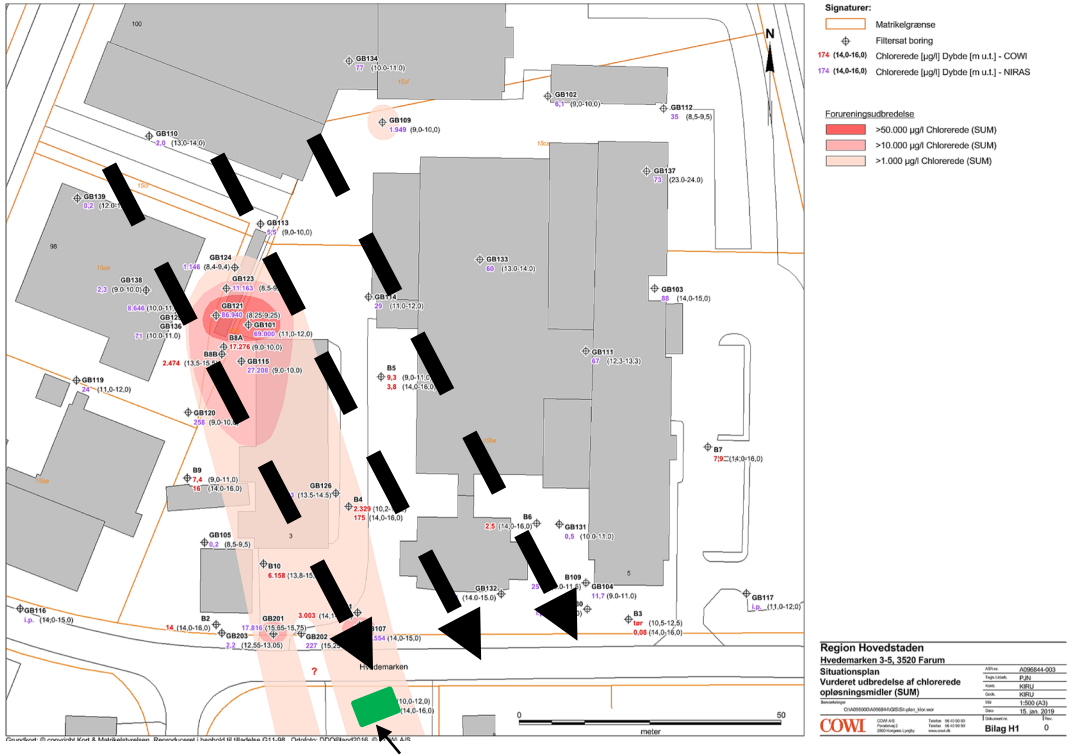
Session B1: Combined Remedy
International Symposium on Bioremediation and Sustainable Environmental Technologies
Baltimore, MD, April 15-18, 2019

Site Background



Proposed PRB location

- Former industrial site
  - A packaging and plastic factory between 1959 and 1999
  - Historical release of chlorinated ethenes and petroleum hydrocarbons (PHCs)
- Hydrogeology
  - Sandy aquifer
  - Groundwater flows to the south through two hot spots
  - 38-75 m/yr
  - Contamination Zone: 12 – 18 m bgs
- Redox
  - Mildly anaerobic – mixed TCE and cDCE up to 20 ppm

Scope of the Study

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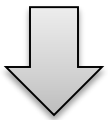
- Objective: Evaluate and select **innovative** ZVI applications for a pilot PRB to treat a mixed chlorinated solvent plume
- Two phases: Microcosm + Column
  - Microcosm: five ZVI products (two commercial **ZVI-OCs** **(organic carbon)**, three **S-ZVI** products, including two commercial ones) - Completed



  - Column: two ZVI products (one commercial ZVI-OC and one S-ZVI) to evaluate treatment longevity - Ongoing

S-ZVI: Enhanced Selectivity and Longevity

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Article

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Sulfidation of Nano Zerovalent Iron (nZVI) for Improved Selectivity During In-Situ Chemical Reduction (ISCR)

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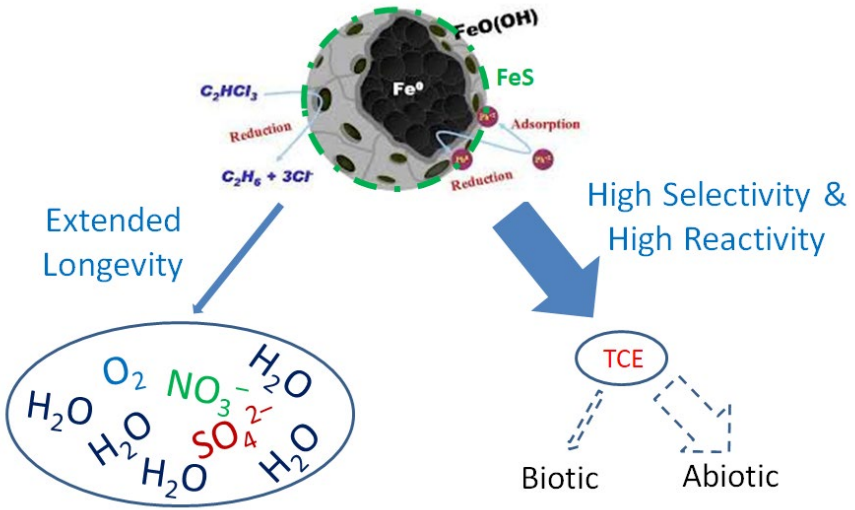

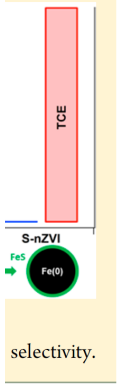

selectivity.

Abiotic vs. Biotic Reductive Dechlorination Pathways

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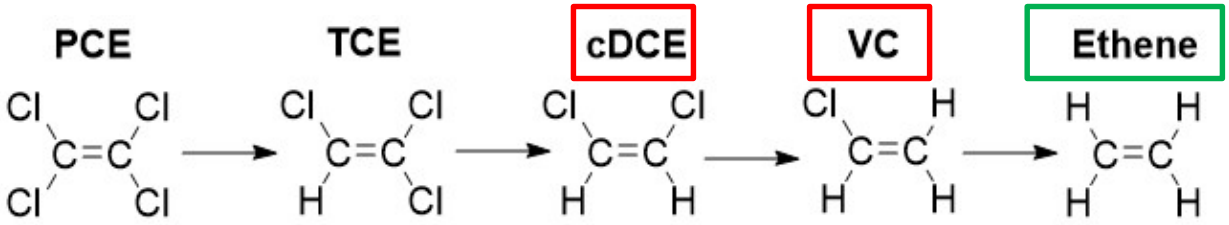
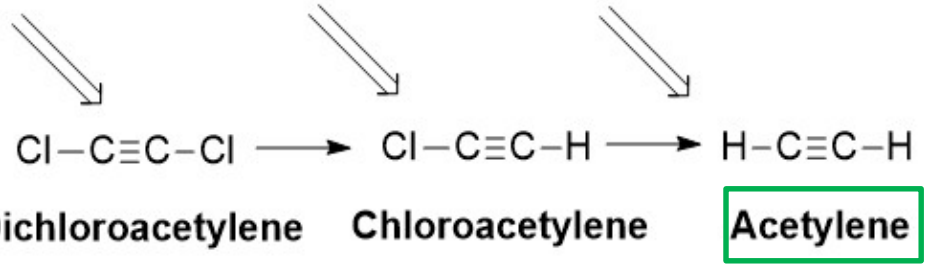
Biotic

Sequential Hydrogenolysis



Abiotic

Beta Elimination



Phase I: ZVI Products Tested

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Product	ZVI Type	Particle Size (µm)	Dosing
EHC	ZVI-OC	25–4750	30 g/L
Provect-IR	ZVI-OC (CH_4 inhibitor)	12–300	30 g/L
AquaZVI	S-ZVI	2.5–3	2 g/L
Nanofer-25DS	S-nZVI	~ 0.05	2 g/L
KU (Univ of Copenhagen)	S-nZVI	~ 0.05	2 g/L

Phase I: Microcosm

- Configuration
  - 50 g Site sediment + 200 mL Site groundwater + ZVI
  - Initial cVOCs: ~ 6 mg/L TCE, ~11 mg/L cDCE
  - Abiotic (n=2) and Biotic (n=3)
- Day 14: Bioaugmentation of DHC
  - Buffer added to ZVI-OCs
  - No added carbon for S-ZVIs
- Respike of cVOCs
  - Day 13: All treatments
  - Day 56: Three S-ZVIs only
- Monitoring: cVOCs, DHGs, anions, pH/ORP

Microcosm: EHC

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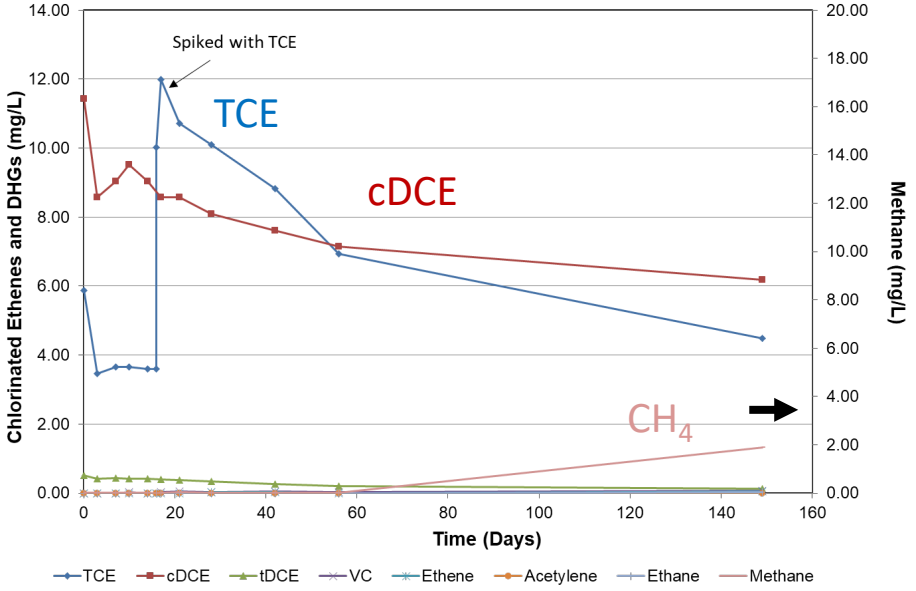
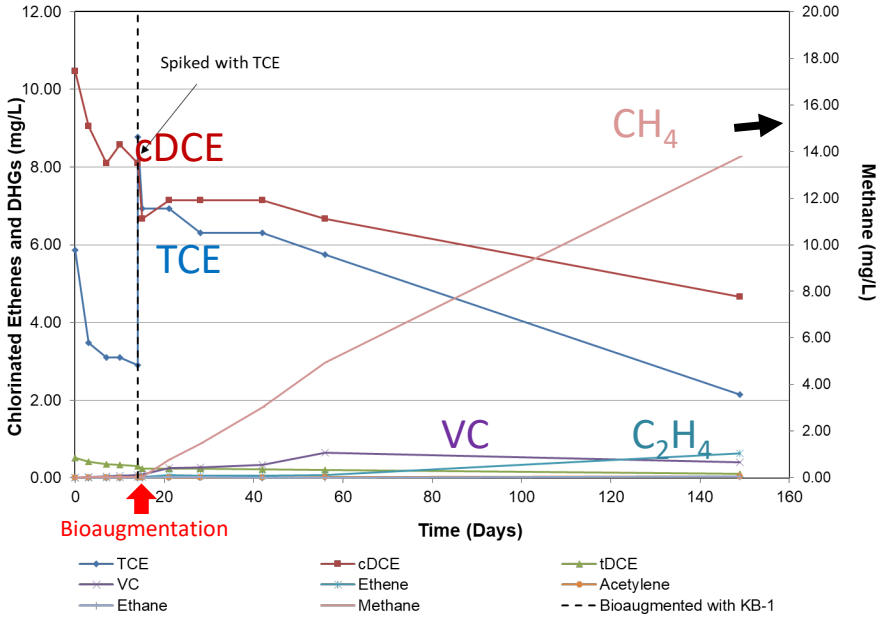
Abiotic



Biotic



Microcosm: Provect-IR

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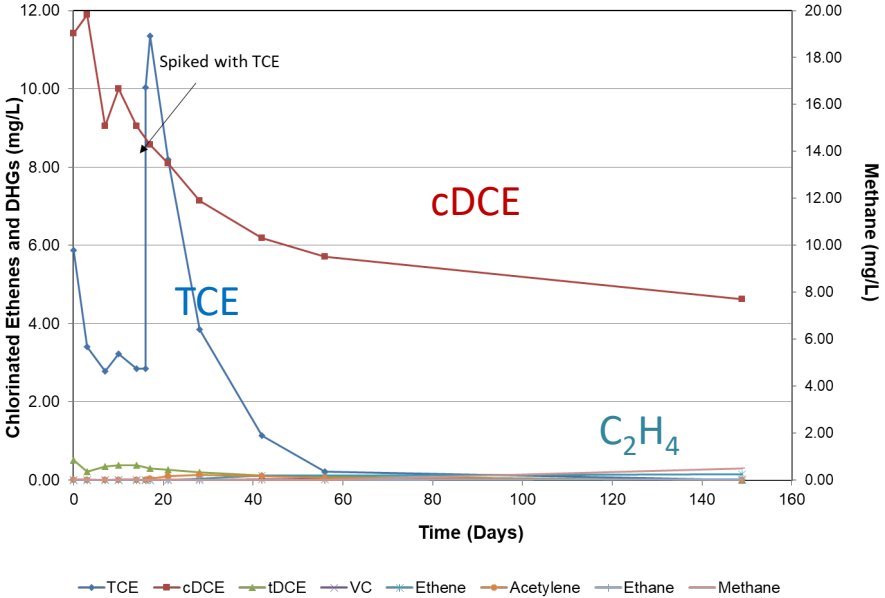
Abiotic



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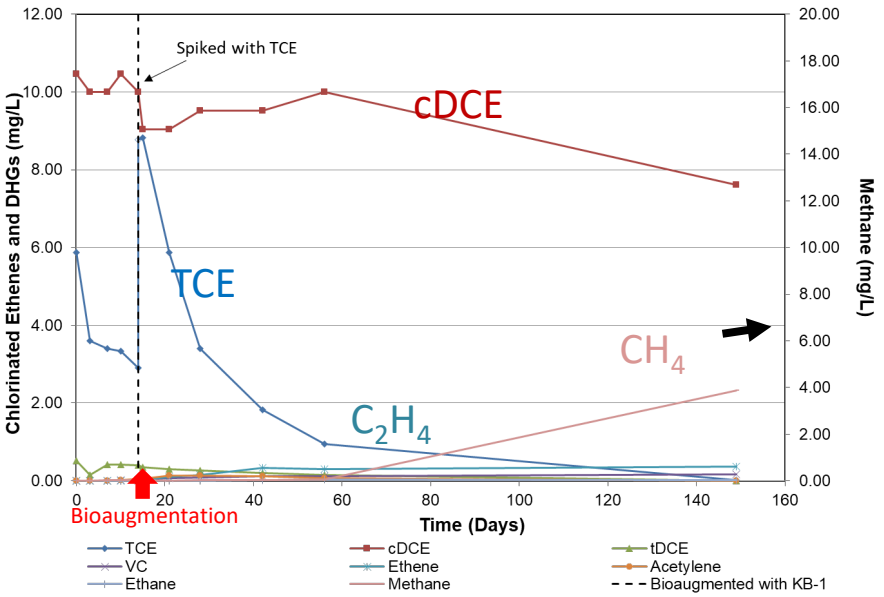

Microcosm: Nanofer 25DS

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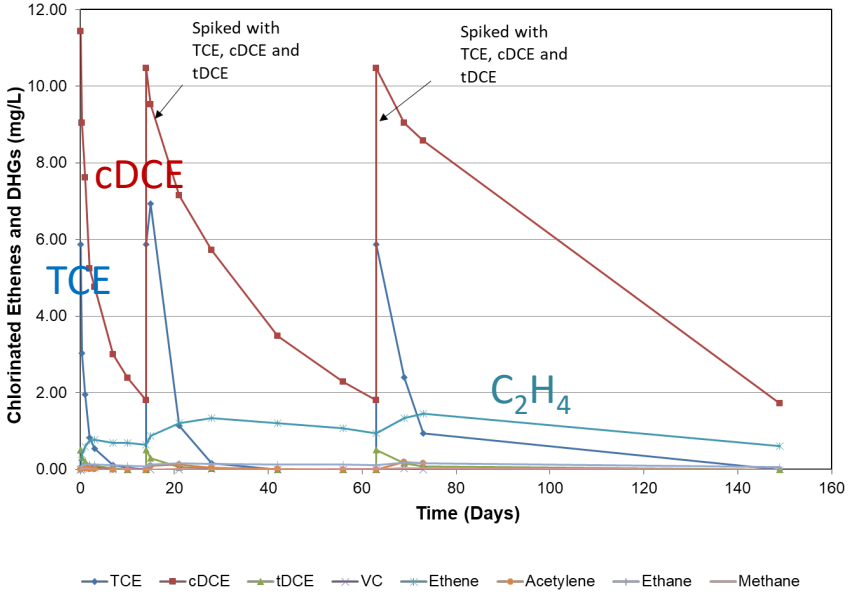
Abiotic



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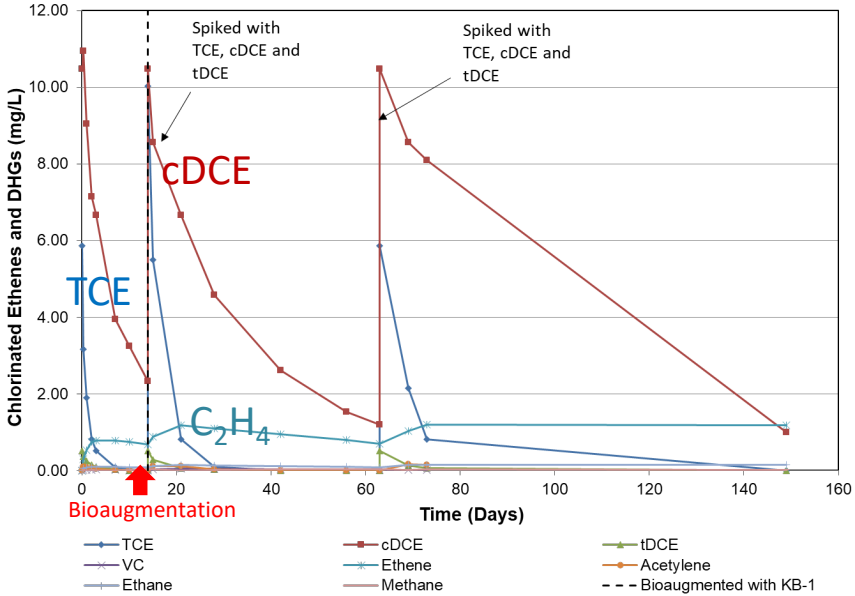

Microcosm: Comparison among Three S-ZVIs

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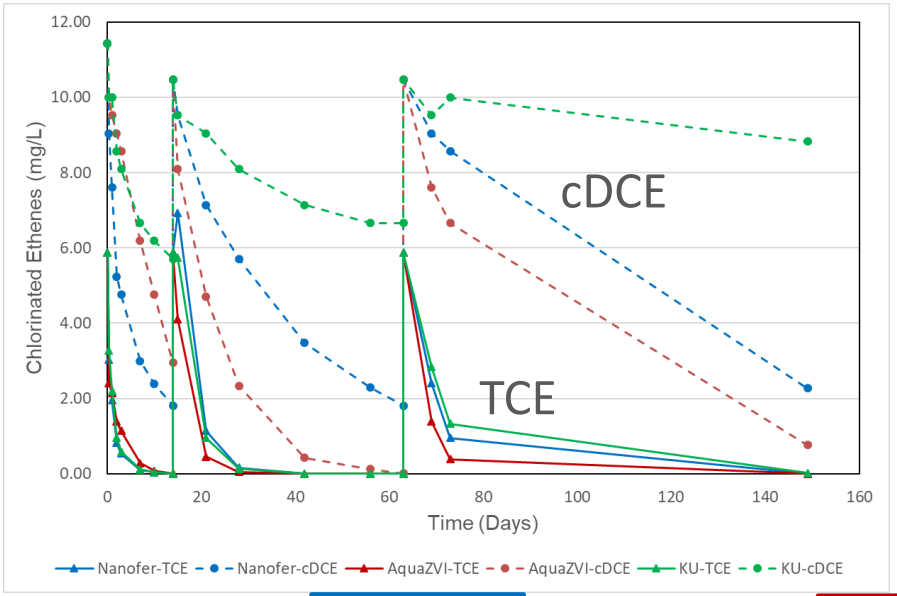
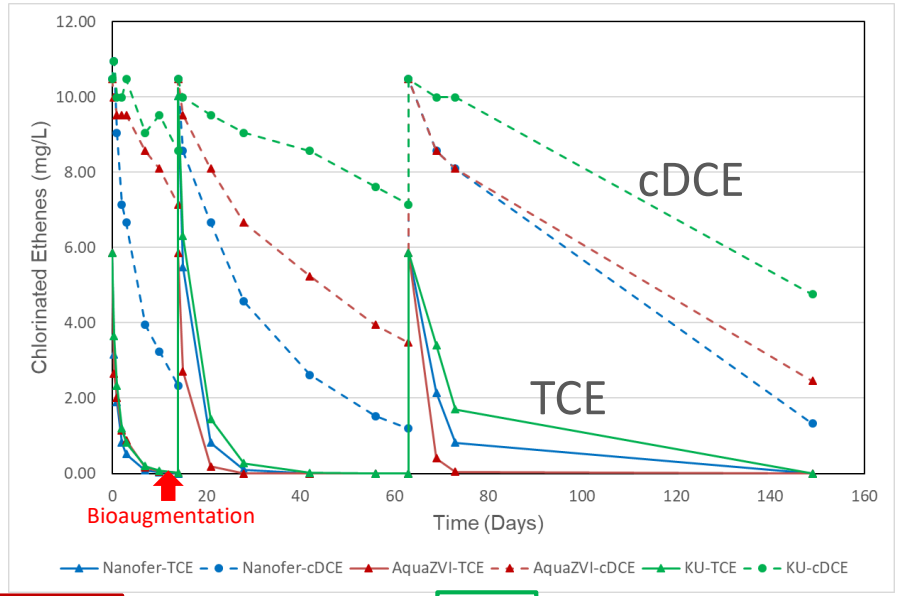
Abiotic



Biotic



Nanofer

AquaZVI

KU

Degradation Evidence & Mechanisms

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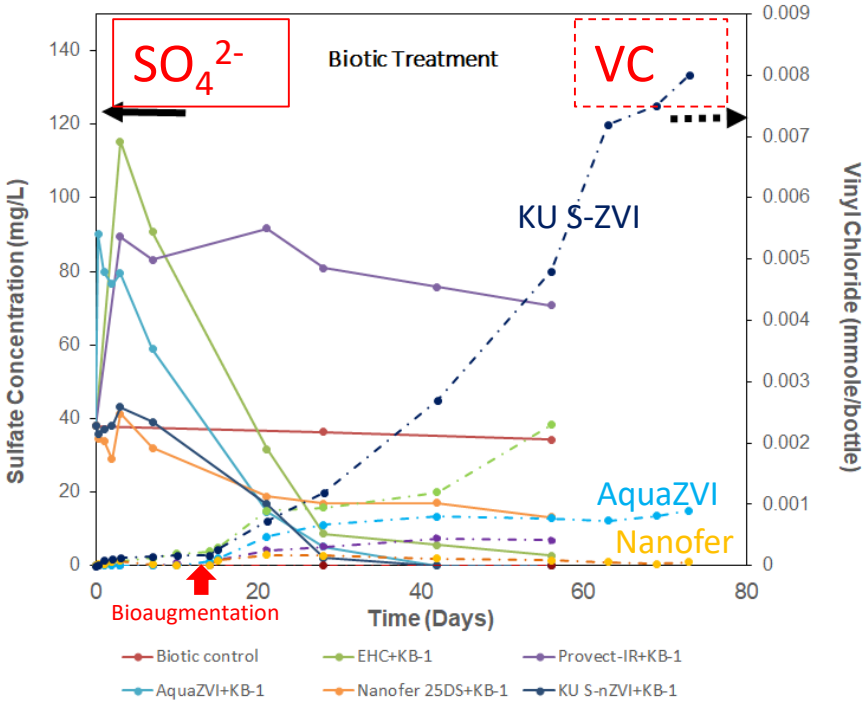
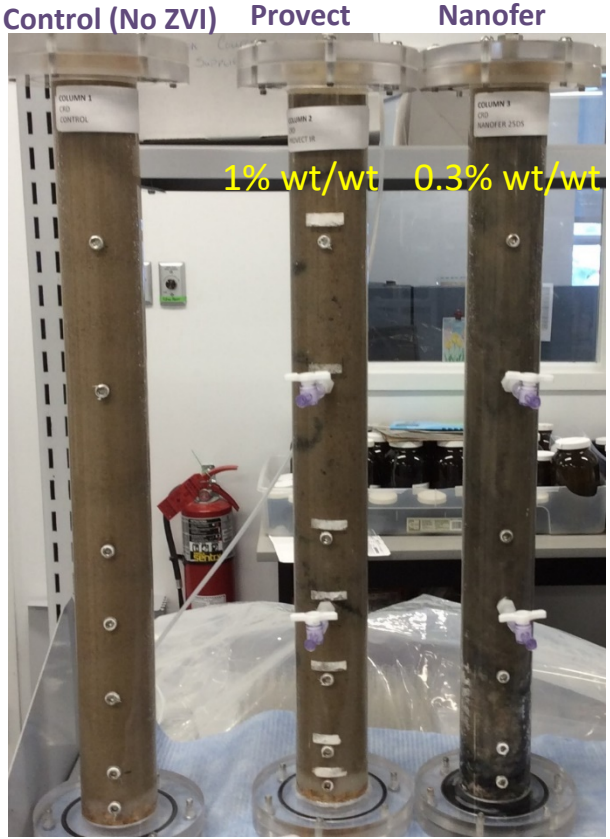
- Chloride production
  - S-ZVIs: 10–20 mg/L Cl ➔ 12–24 mg/L TCE
  - ZVI-OCs: No evident Cl increase
- Abiotic is likely dominant for S-ZVIs
  - Biotic has similar TCE kinetics to abiotic
- Biotic processes are occurring
  - Significant sulfate reduction
  - Followed by VC production
  - Variations of VC among three S-ZVIs
  - No CH_4 production with S-ZVIs



Phase II: Column

- Provect-IR and Nanofer 25DS selected
- Column preparation
  - Provect-IR: Pre-mixed with aquifer solids
  - Nanofer-25DS: Introduced as solution to approximate field injection parameters
  - No bioaugmentation but not sterilized
- Flow rate: 0.2 mL/min initially
  - ~20 hr RT vs. 350-700 h RT in the field
  - 14 weeks in column = 5 years in field
  - Lower to 0.09 mL/min (~44 hr RT) on D28
- Monitoring
  - Influent, two inner ports, and effluent
  - cVOCs, DHGs, anions, pH, and ORP



Column: Nanofer 25DS

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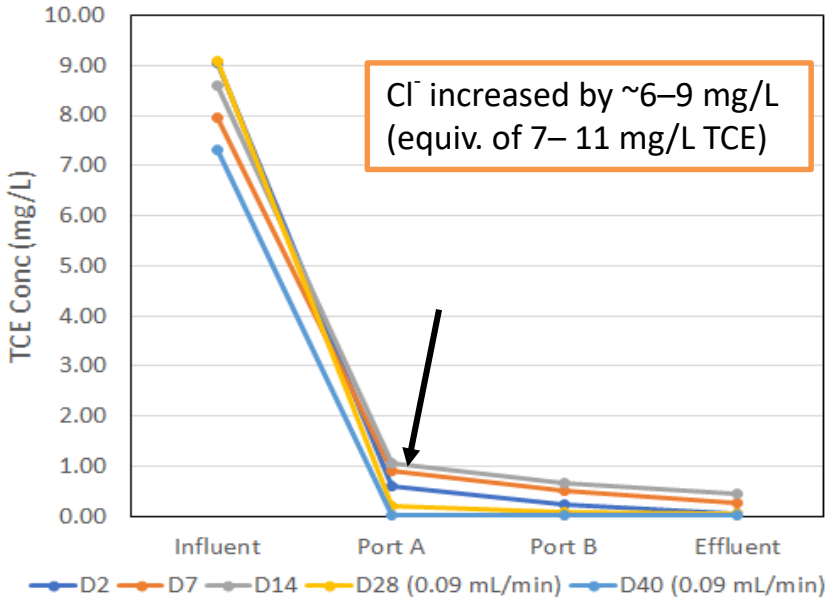
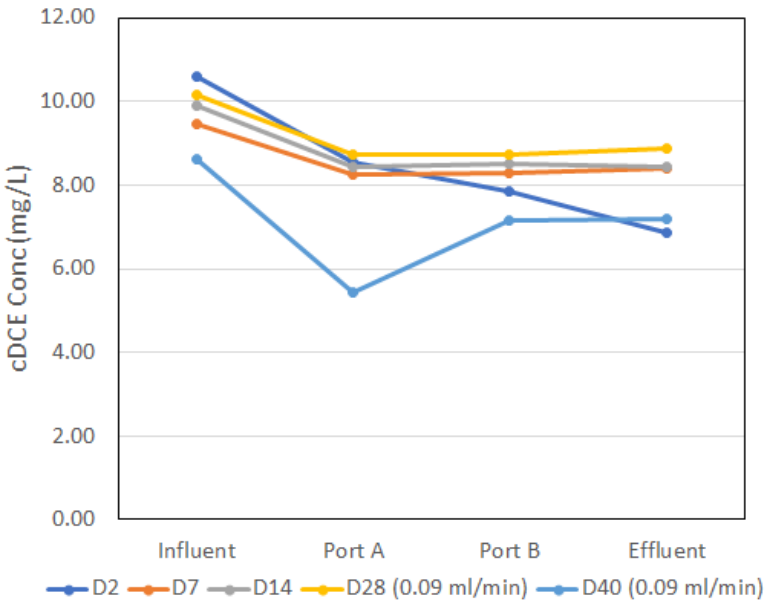
TCE



cDCE



~ 550 field days equiv.

Column: Provect-IR

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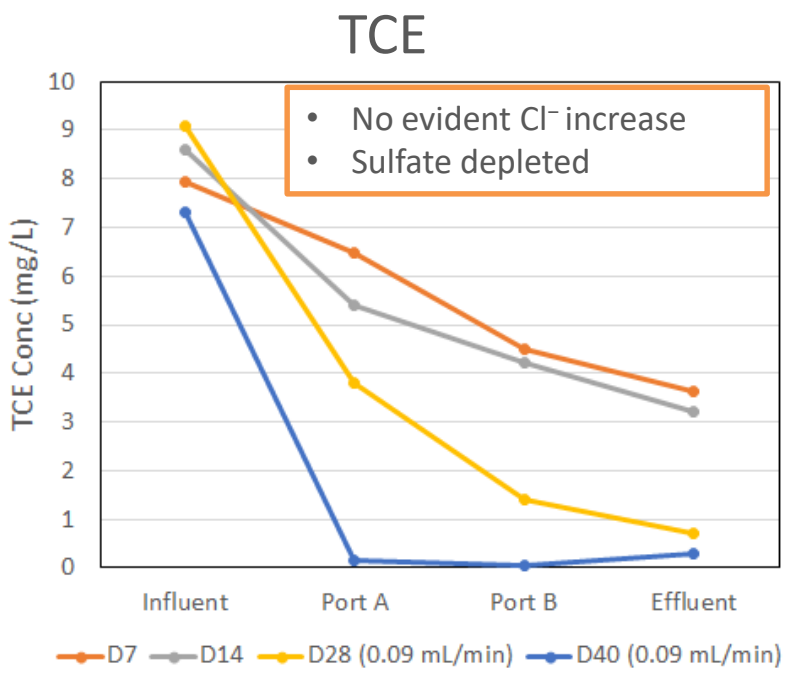

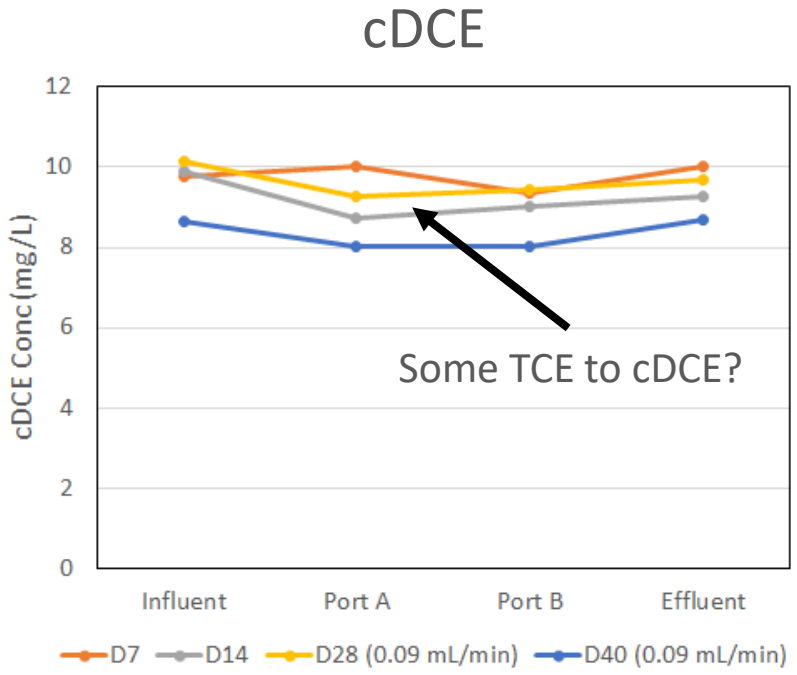

~ 550 field days equiv.

Stop-Go Cycle to Increase Residence Time

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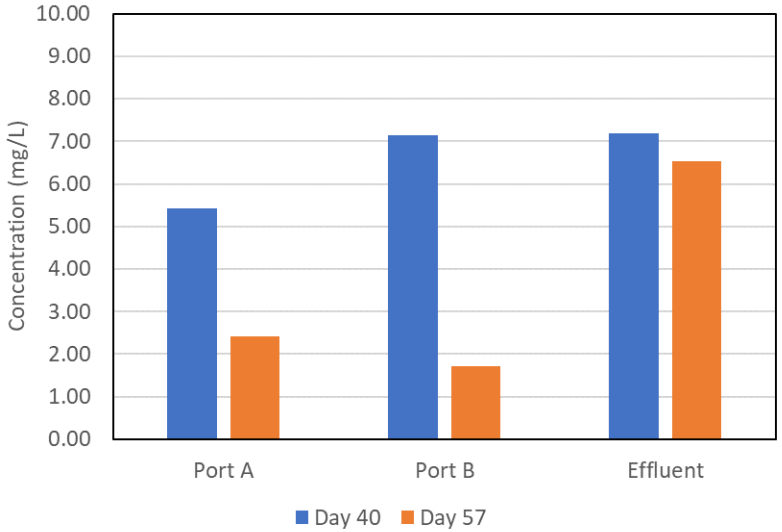
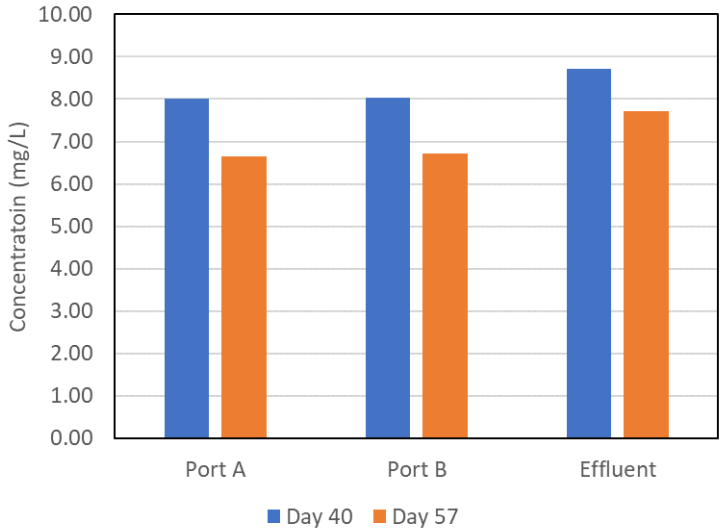
cDCE concentrations at the time of shutdown (Day 40) vs. after 17-day incubation (Day 57)

Nanofer Column



Significant cDCE degradation in Ports A & B

Provect Column



Less cDCE degradation in all ports

Column: Summary

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- TCE: Fast degradation is sustained over ~550 simulated field days
  - Nanofer 25DS: Complete abiotic dechlorination achieved
  - Provect-IR: Partial dechlorination, likely mixed abiotic and biotic
- cDCE: Less degradation observed
  - Consistent with microcosm data
  - Stop-Go results confirmed that short RT in the flow-through column explains the lack of cDCE degradation
  - Competitive sorption of TCE to ZVI over cDCE (Schafer, 2003, Journal of Contaminant Hydrology)
- Ongoing work
  - Provect-IR: Bioaugmentation
  - Nanofer-25DS: Two more Stop-Go cycles to evaluate cDCE degradation

Lessons Learned

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- S-ZVIs achieved *rapid*, *sustained* and *complete* TCE dechlorination, primarily via abiotic dechlorination.
- Abiotic degradation of cDCE by S-ZVIs is slower than TCE ($t_{1/2}$: 21 vs. 2 days in microcosm) – Design for a mixed plume likely driven by cDCE.
- Biological activities observed in S-ZVI microcosms despite no added carbon sources.
- Different S-ZVIs could have different effects on biological dechlorination.

↓

Optimal design for specific site conditions (e.g., with Bio for cDCE)?

- Complete dechlorination has occurred to a very small extent in microcosm with ZVI-OCs within 5 months.

Q&A

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