Evaluating and Treating DNAPL in Fractured Rock

Charles Schaefer, Ph.D.

David Lippincott – APTIM
Rachael Rezez – APTIM
Graig Lavorgna - APTIM
Dr. Michael Annable – UFL
Erin White – UFL

DNAPL Architecture, Dissolution, and Treatment

The DNAPL challenge

- Most of the contaminant mass may be in the non-aqueous phase
- Dissolution rate may limit remedial effectiveness and mass discharge
- Locating and contacting DNAPL sources can be challenging

Complicating Factors in Bedrock

- Many of the technologies for locating and quantifying DNAPL sources are not appropriate, or have not been demonstrated, for bedrock
- DNAPL may be even more difficult to contact in fractured bedrock
- Costs

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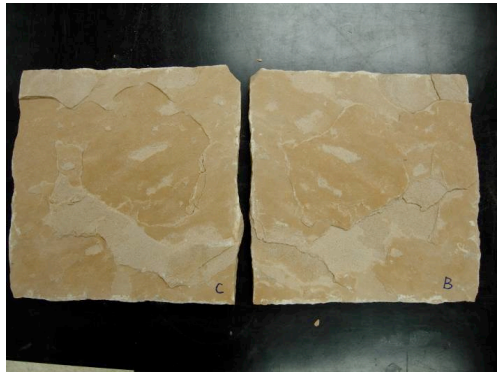
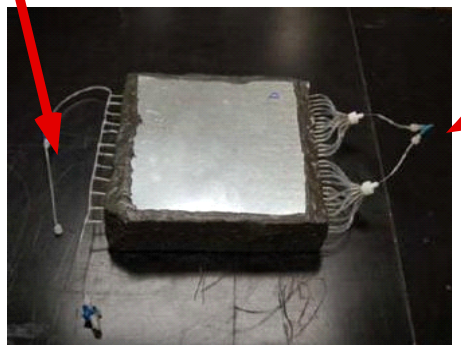
Investigating DNAPL within a Single Fracture Plane (SERDP Project ER-1554)

Construction of Discrete Fracture Systems

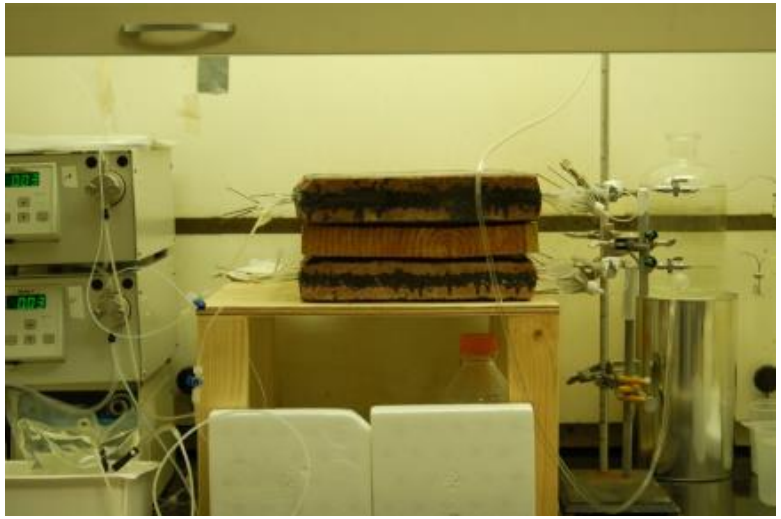
29 cm x 29cm x 5cm





Influent manifold connected to HPLC pump. Typical flow of 0.1 mL/min.

Effluent collection



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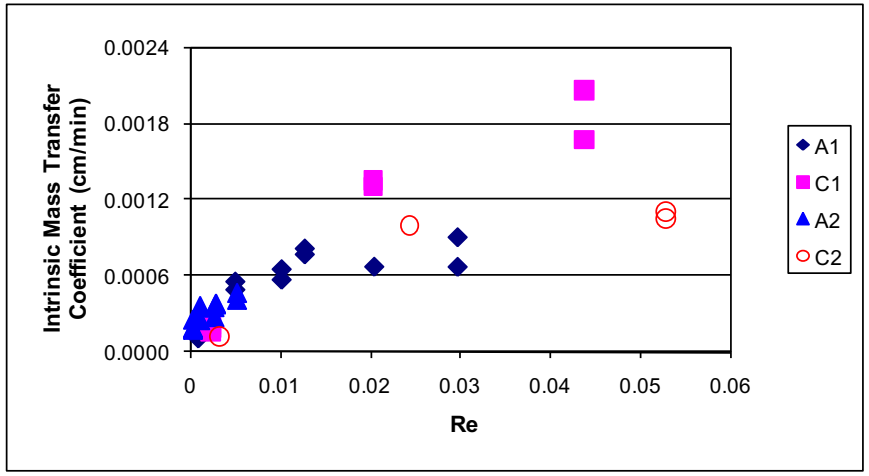
Key Findings – DNAPL Architecture

Rock	Residual Saturation (cm^3/cm^3)	Interfacial Area (cm^2/cm^3)
Colorado 1	0.24	21
Colorado 2	0.21	48
Arizona 1	0.39	56
Arizona 2	0.43	20

Area:PCE ratio ~3-times less than in sands



Mass transfer coefficient ~10-times less than in sands

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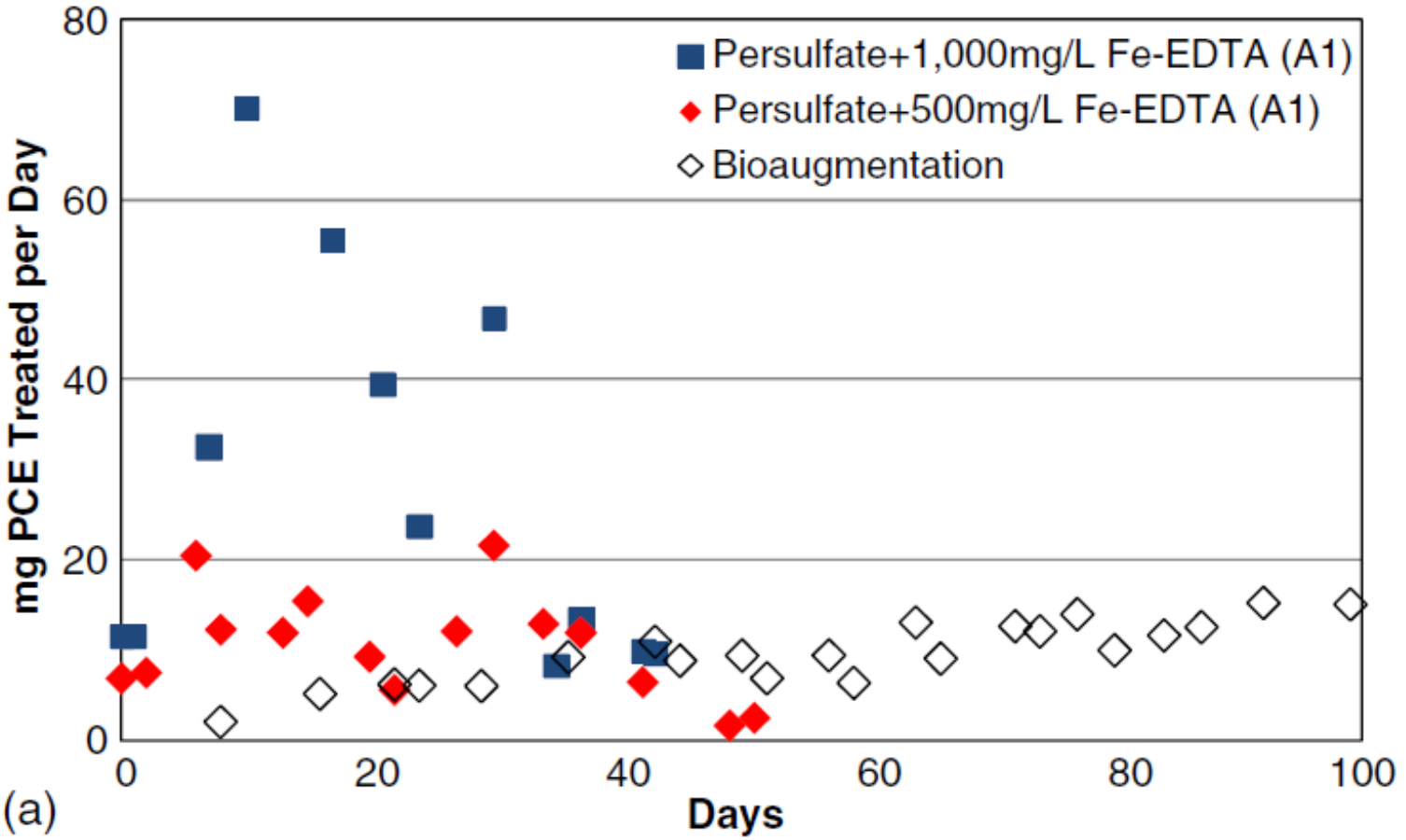
DNAPL in Fractured Rock Is Difficult to Remove Compared to Unconsolidated Materials

ISCO for TCE DNAPL in a Rock Fracture
(SERDP Project ER-1554)



~4% of residual DNAPL removed using activated persulfate

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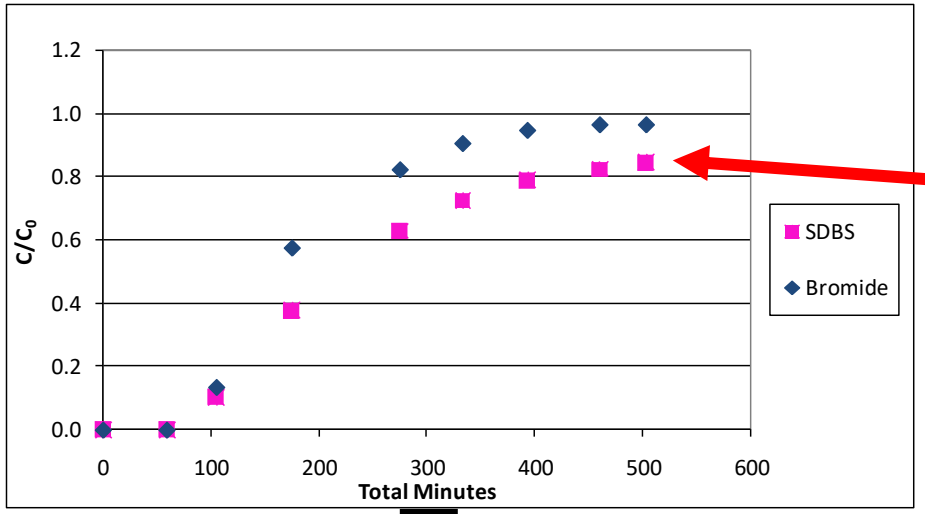
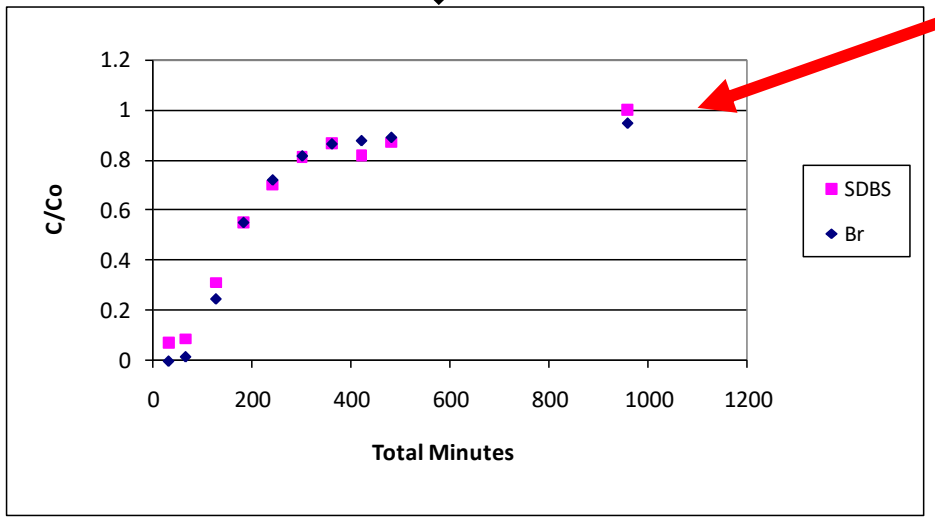
Diminished Treatment due to Blockage of DNAPL-Water Interfaces



Prior to Persulfate Oxidation

Retardation (sorption) of the interfacial tracer SDBS

No measurable retardation



Post Persulfate Oxidation

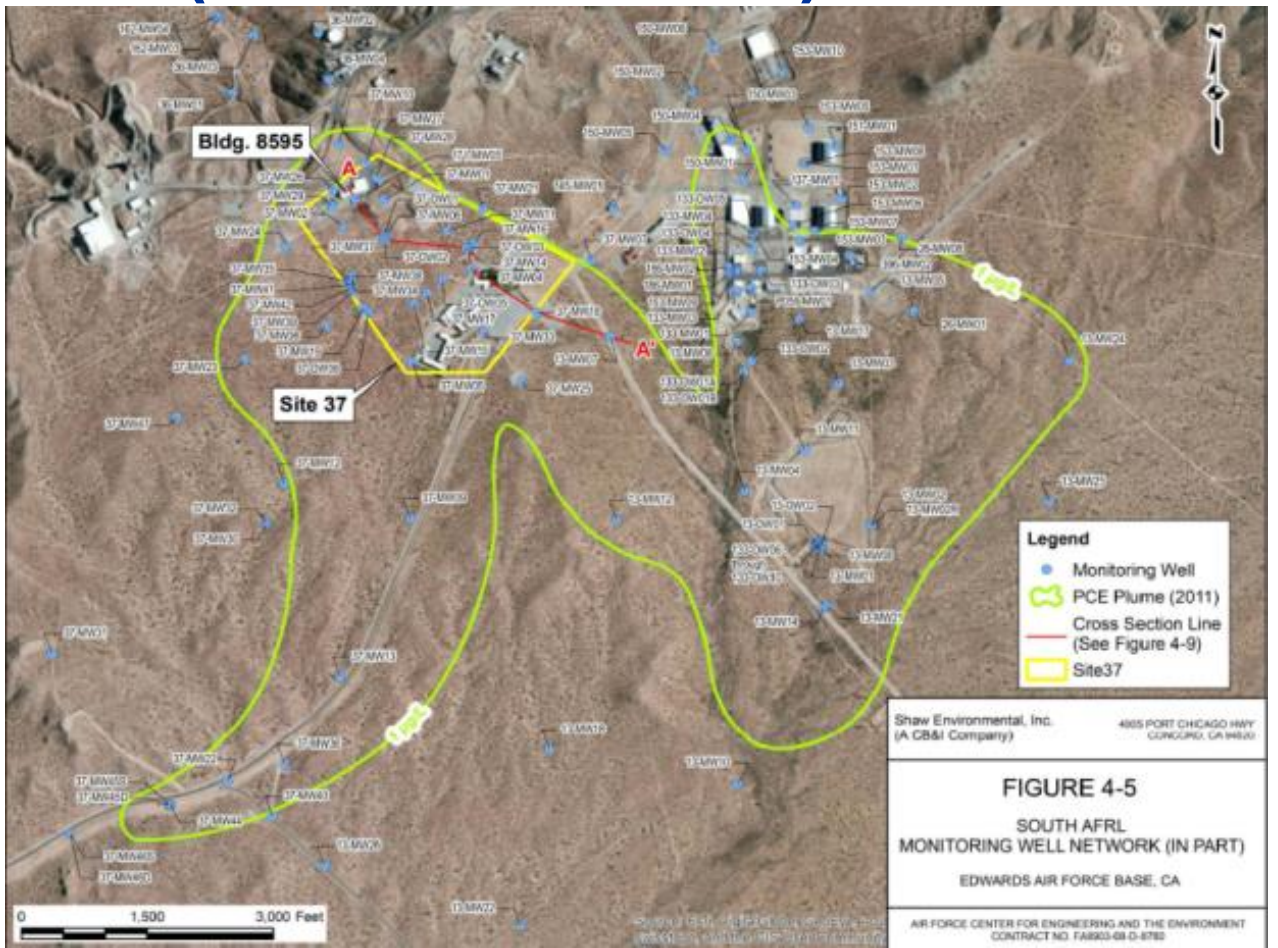
- Rate of PCE removal had decreased by approximately 7-fold
- Precipitates likely forming at DNAPL-water interfaces

Illustrative Field Example – Key Insights

Site 37 Characteristics

- Large plume (390 acres)
- Deep (>200 ft)
- Granite bedrock (quartz/feldspar)
- Low transmissivity
- Fracture flow
- PCE at >10% solubility
- No direct evidence of DNAPL

Demonstration Location - Edwards AFB (ESTCP 201210)



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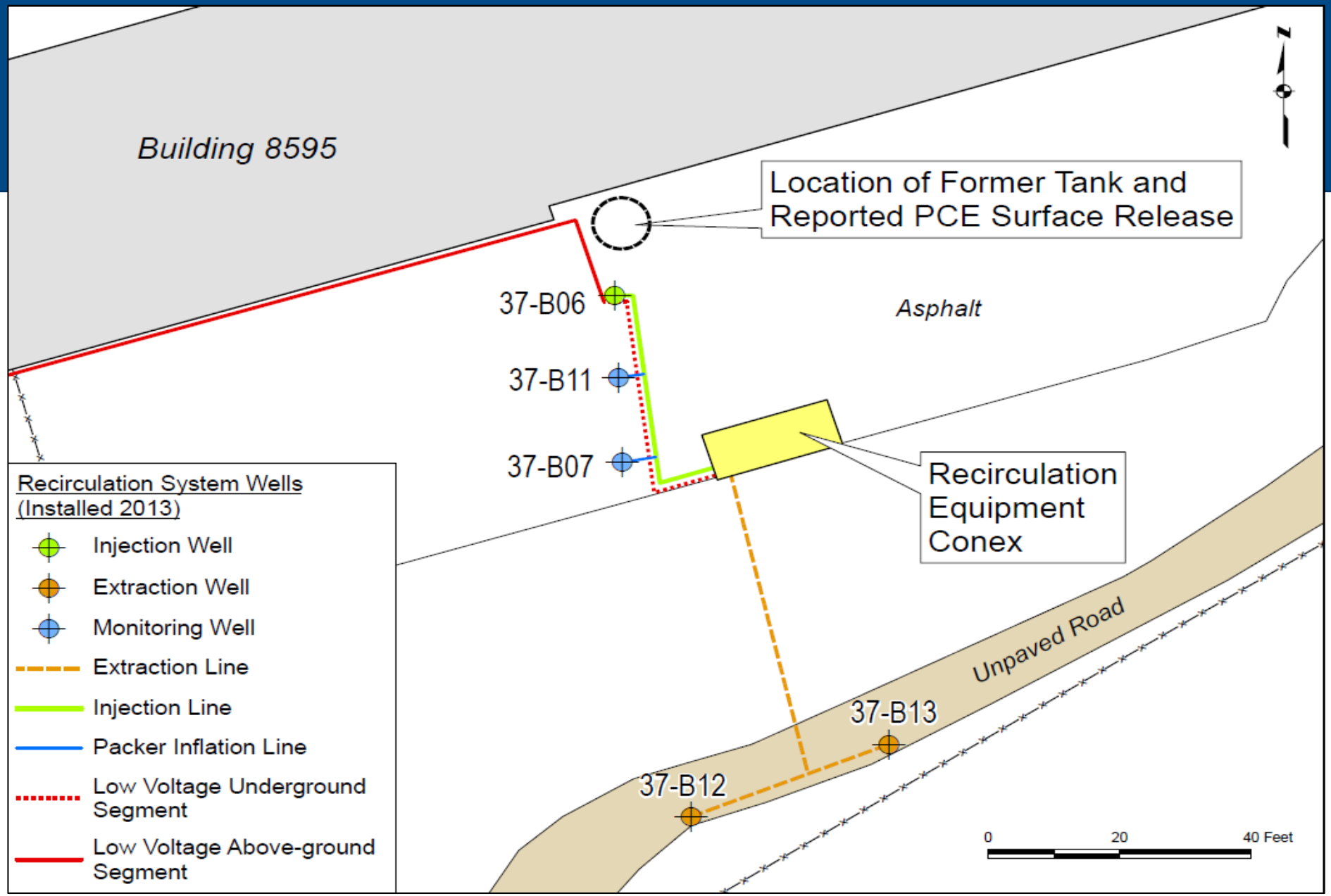
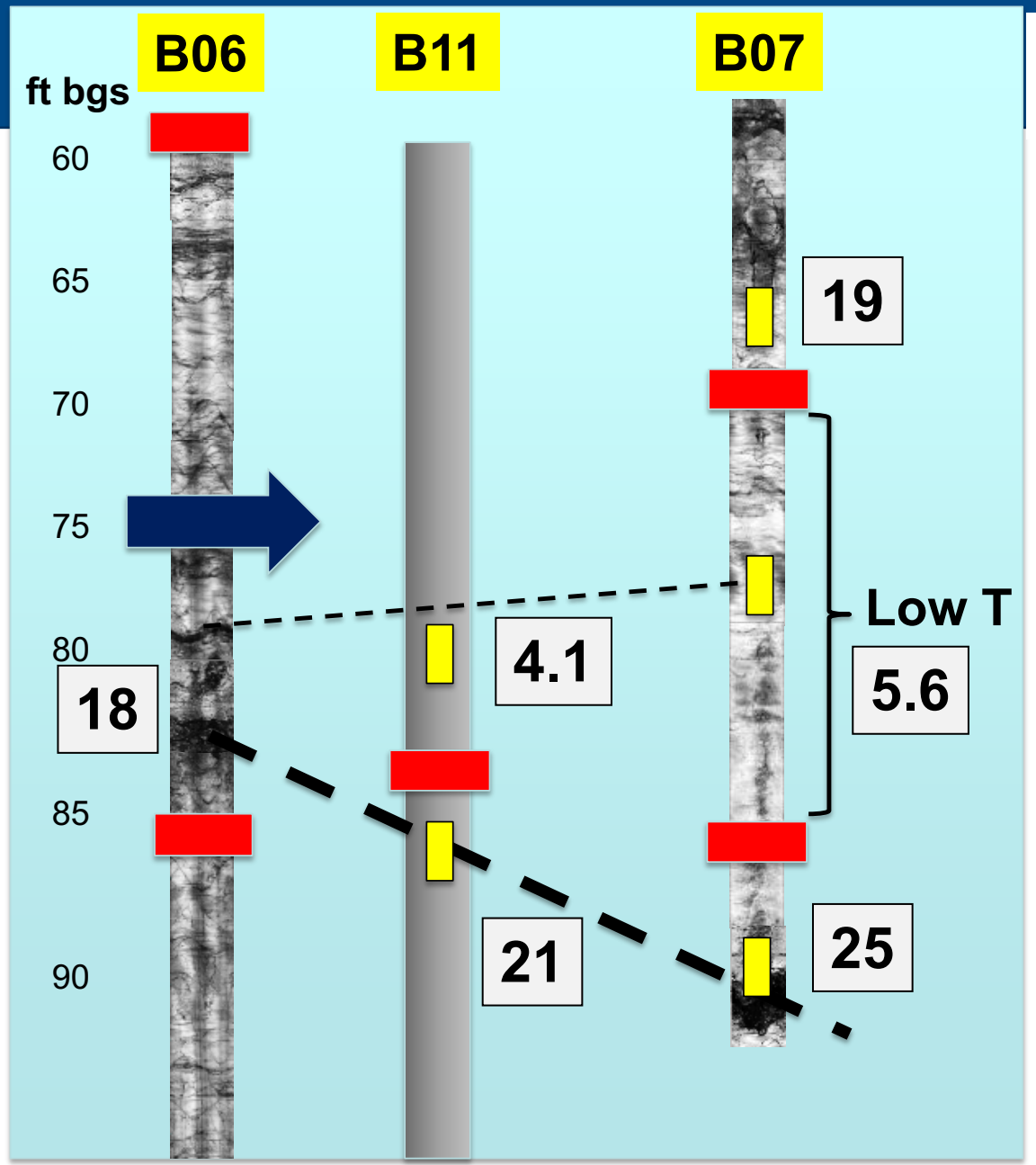


~100 mL/min recirculation flow

Initial Source Investigation

- Borehole geophysics
- Rock core analysis
- Discrete interval groundwater sampling & drawdown testing
- Short term pump tests
- Push-pull tracer tests

PCE (mg/L)



Two Phases of Testing Using the Recirculation System

- Partitioning Tracer Test (PTT) to assess flow field and DNAPL architecture
- Bioaugmentation

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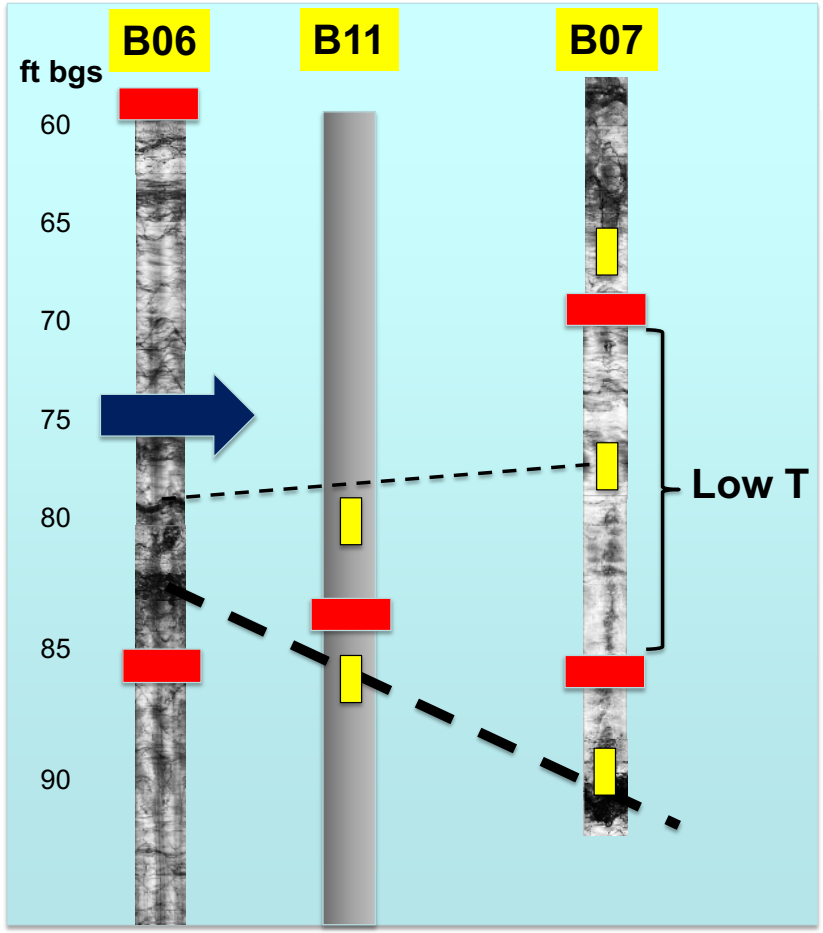
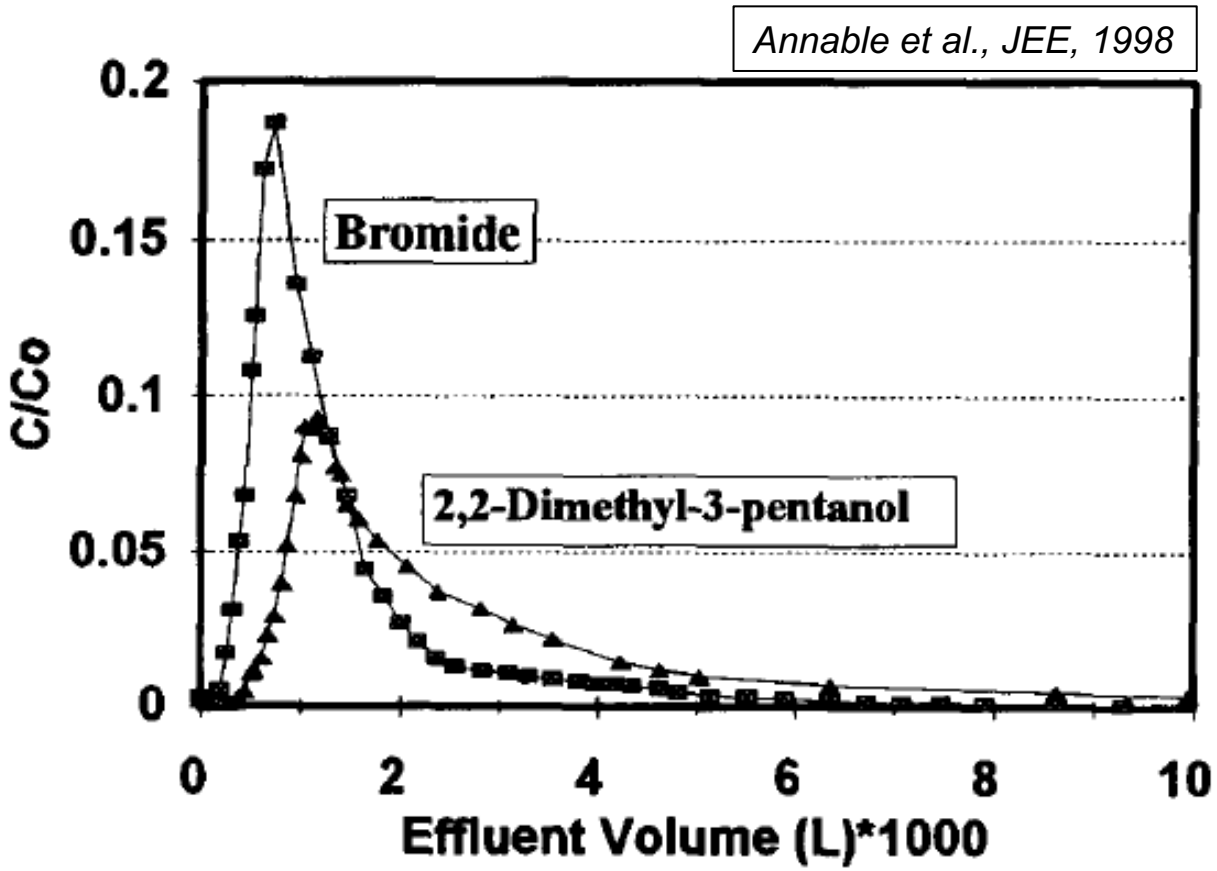
Partitioning Tracer Testing





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PTT Limitations

- Must contact DNAPL
- Not appropriate for mobile DNAPL
- High TOC solids may limit sensitivity
- Matrix diffusion

$$F_{frac}/F_{matrix} = \frac{A_{cs}V}{A_{fs}\sqrt{\frac{D_{eff}}{\pi t}}}$$

Based on conceptual model by Parker et al., 1994

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Partitioning Tracer Test

Groundwater recirculation (~120 mL/min

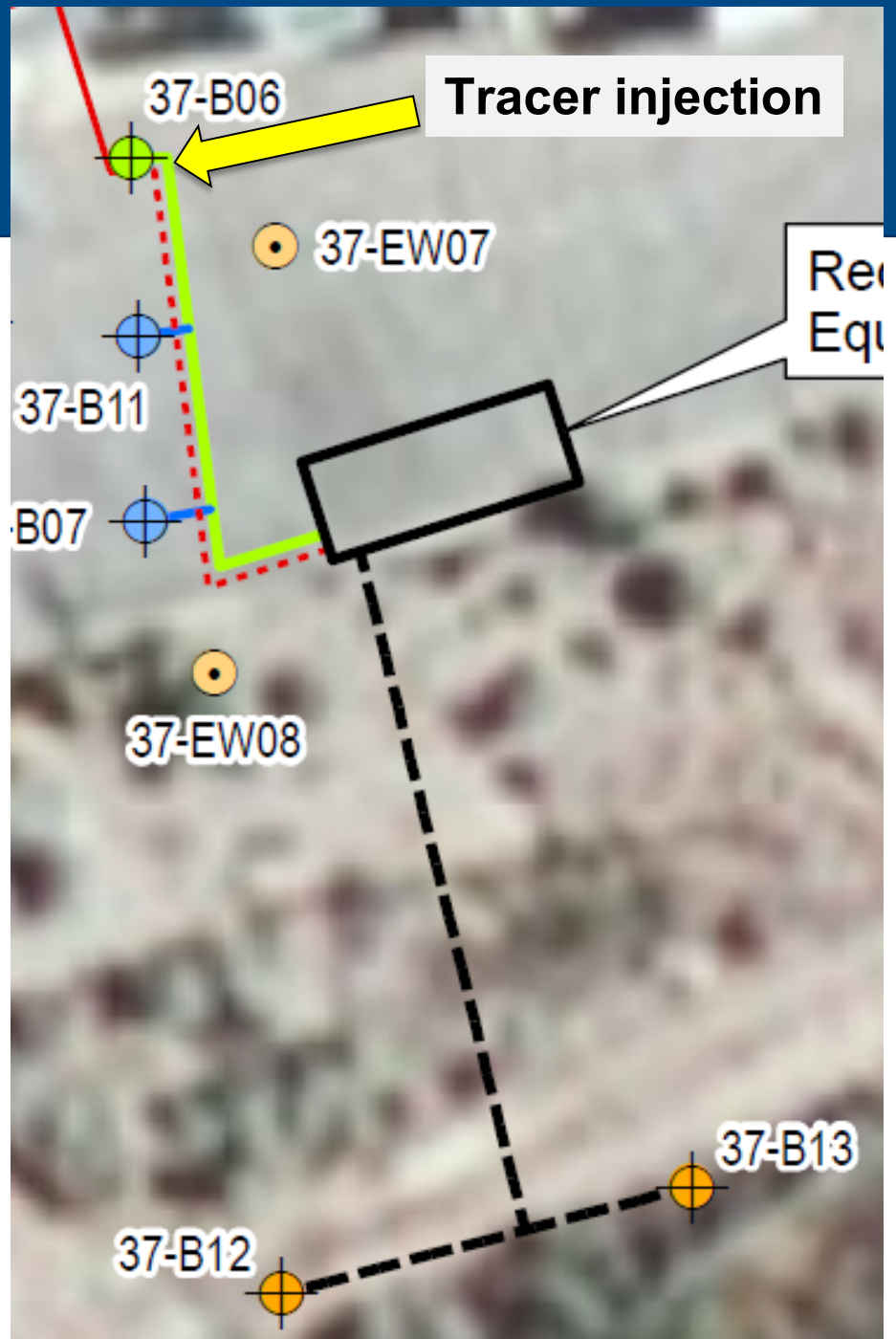
Inject 50 gal tracer slug (no PCE)
- *bromide*
- *alcohols*

Collect extracted water & treat with GAC during tracer injection

Continue GW recirculation

Monitor tracers and VOCs at monitoring and extraction wells over a 6 week period

- No impacts at extraction wells
- Primary response at B11(S,D)



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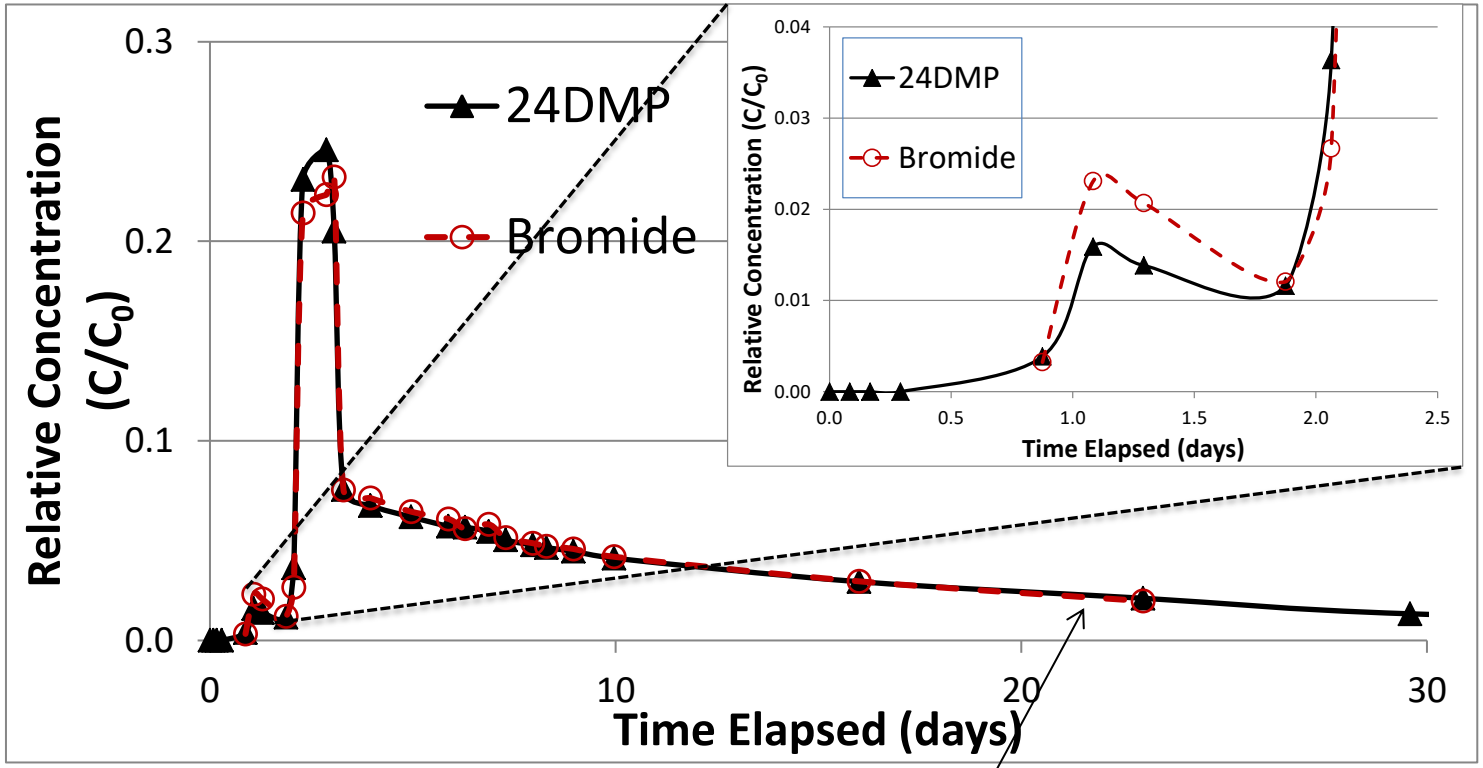
Tracer Results – Deep Zone

Bromide mass eluting through each zone proportional to transmissivity



Mass transfer controlled tailing

Initial Peak
(low T fracture)

- 1% of flow
- 0.7% DNAPL

Middle Peak

- 9% of flow
- No DNAPL

Late Peak

- 40% of flow
- 0.04% DNAPL

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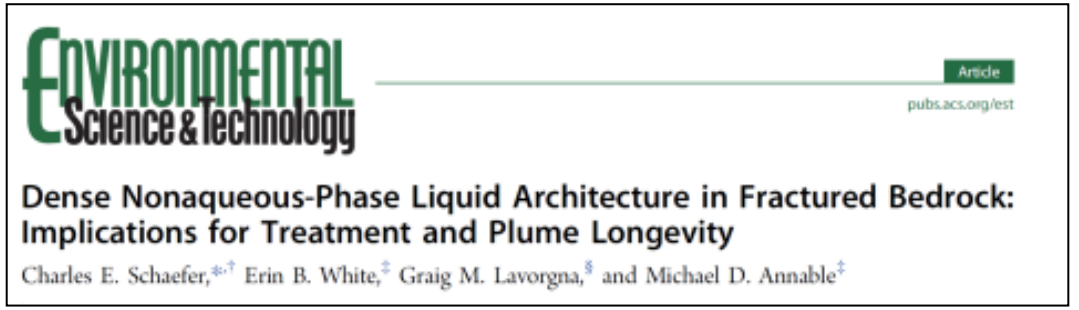
What Else Did We Learn from the PTT?

DNAPL distribution
DNAPL present in high transmissivity fractures, but also in low transmissivity zones

Average fracture porosity
0.004

DNAPL mass
2.4 kg in 15 ft radius around injection well interval



DNAPL persistence under ambient conditions (dissolution only)
DNAPL in moderate to high T zones – 65 years
DNAPL in low T zone – 194 years

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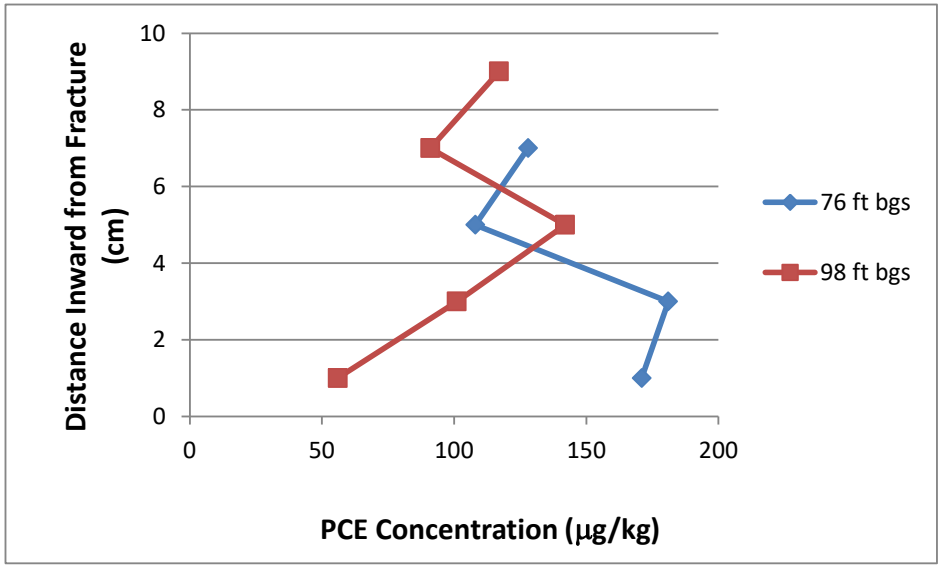
PCE Distribution

Rock Matrix vs Fractures



Based on PTT DNAPL estimate

149 g PCE in rock matrix

2,400 g PCE as DNAPL in fractures

PCE concentration profile suggests back-diffusion not occurring

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So treating to remove DNAPL might make sense

Bioaugmentation
(August 29, 2014)

- Initial electron donor delivery
  - 59L lactate (2,000 mg/L) in injection interval
  - GW recirculation overnight
- 19 L SDC-9 culture + 38 L lactate chaser (500 mL/min)
- $5x10^{11}$cells DHC
- 9 months of active treatment (gw recirc.)
- 10 months rebound (no recirc.)

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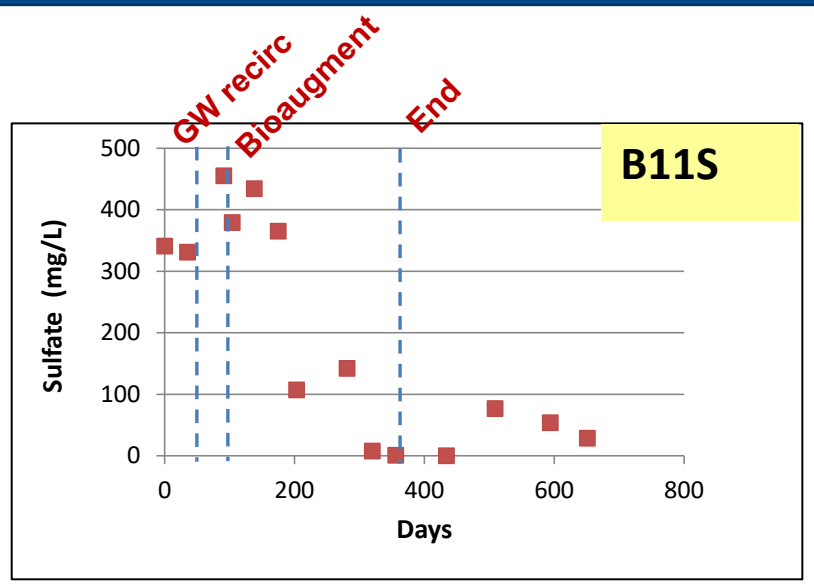
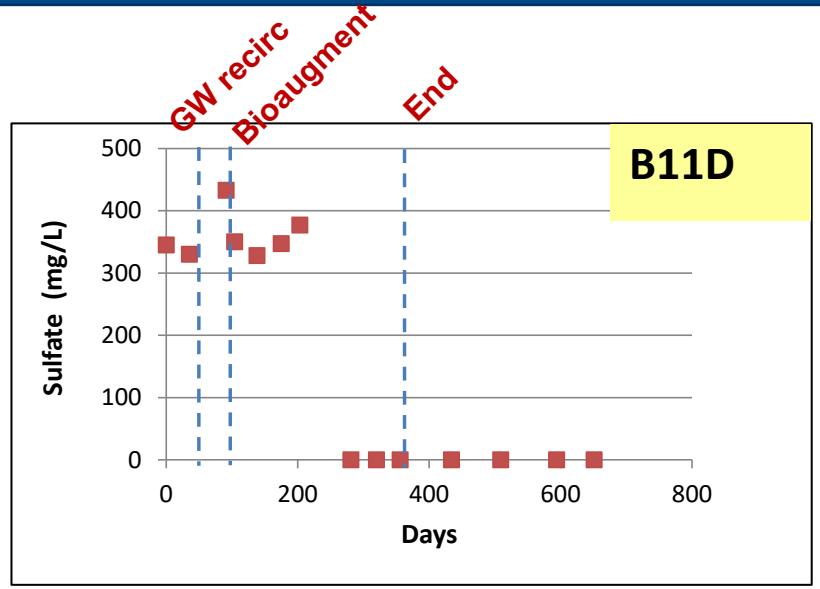
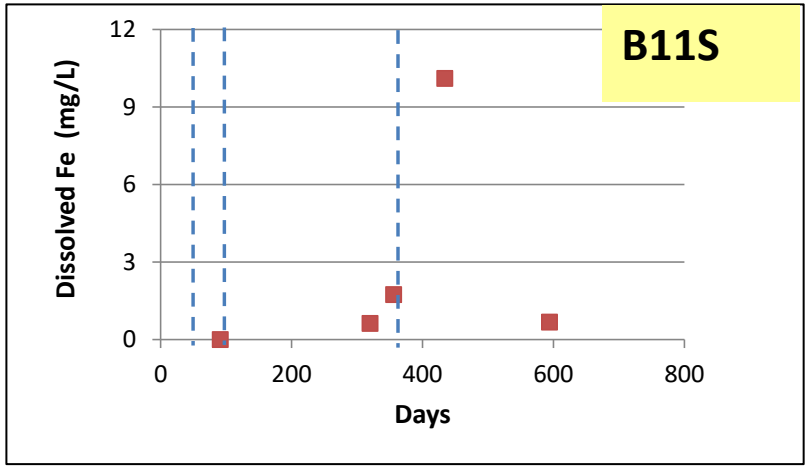
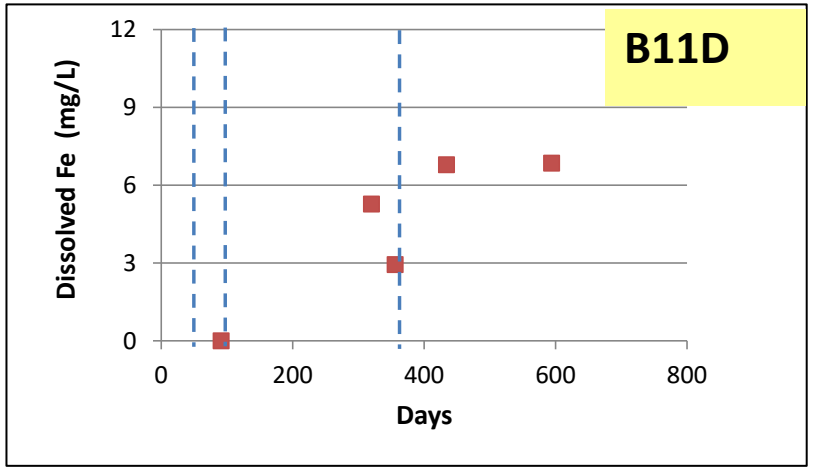
Geochemical Changes During Treatment









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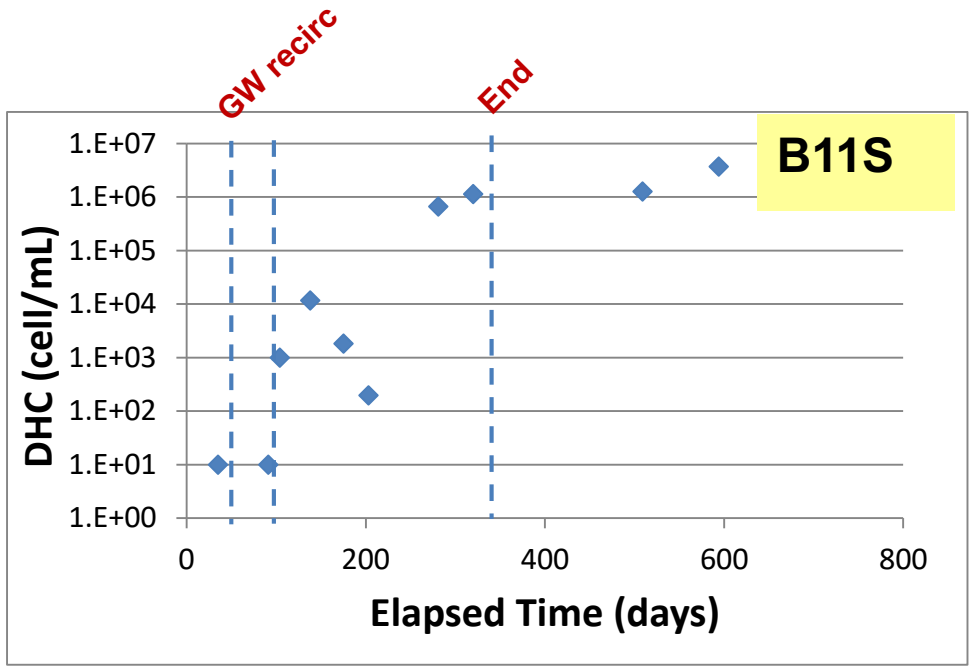
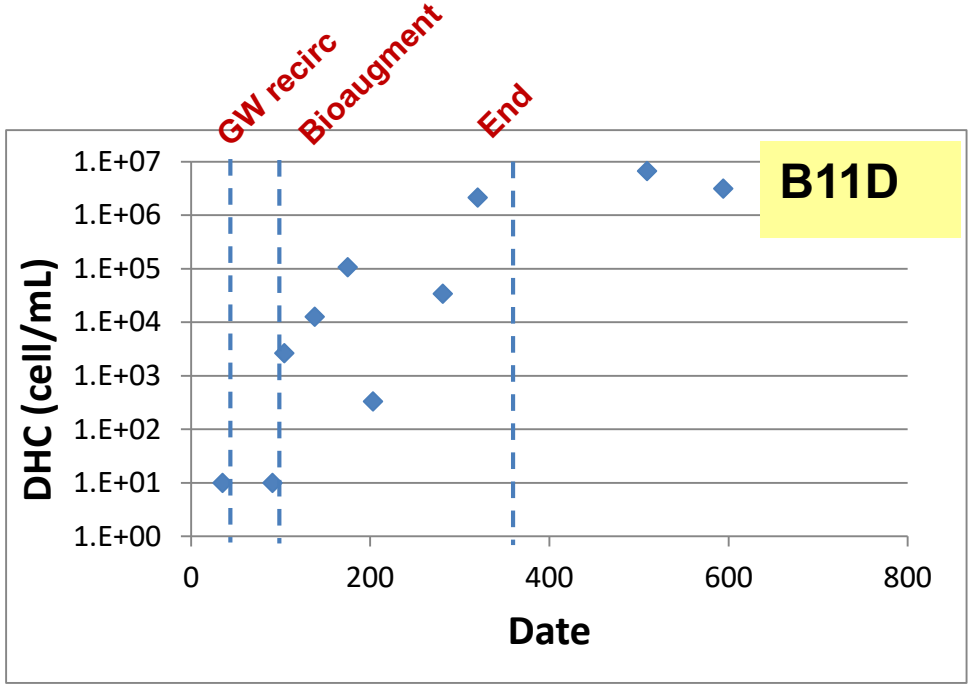
Dehalococcoides sp. (DHC)

Dehalococcoides sp.





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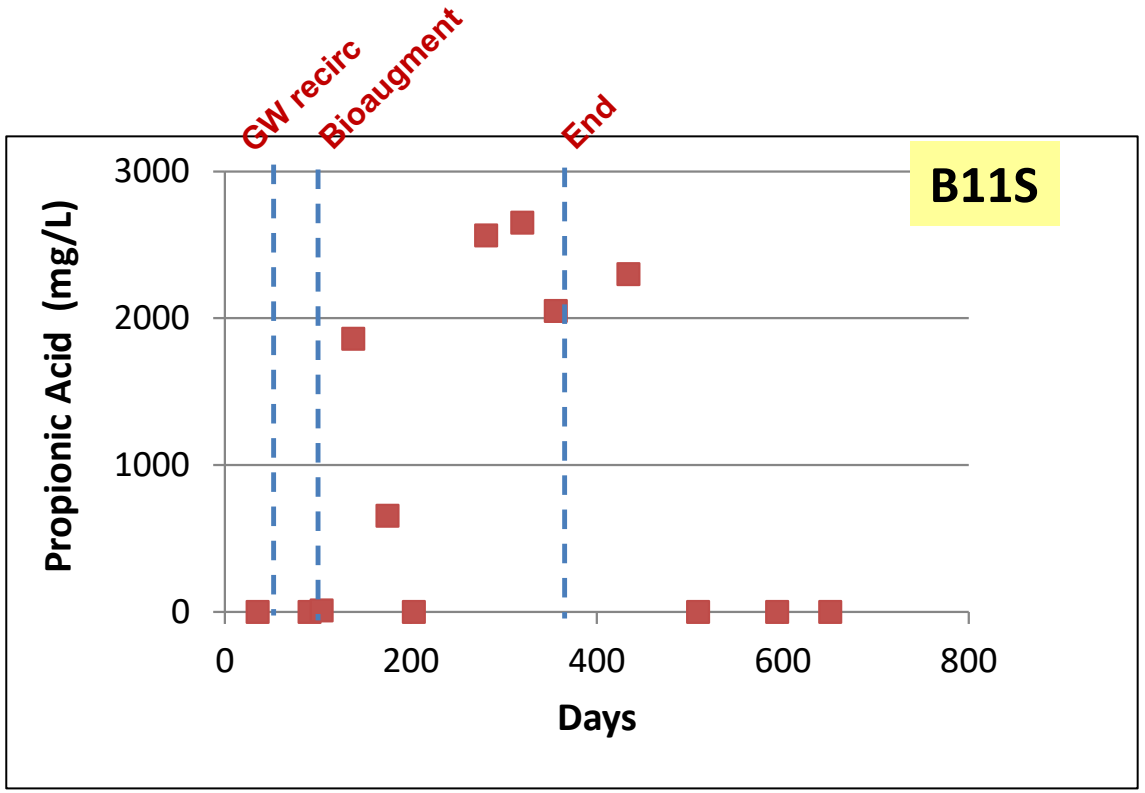
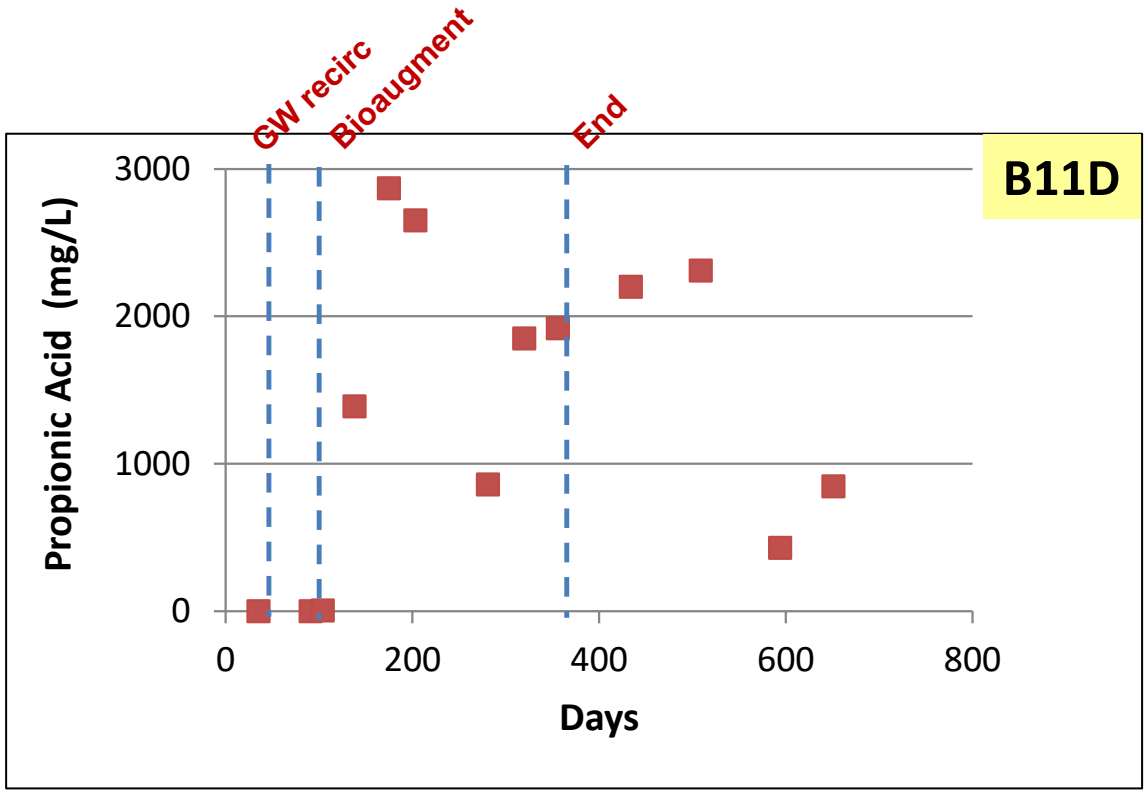
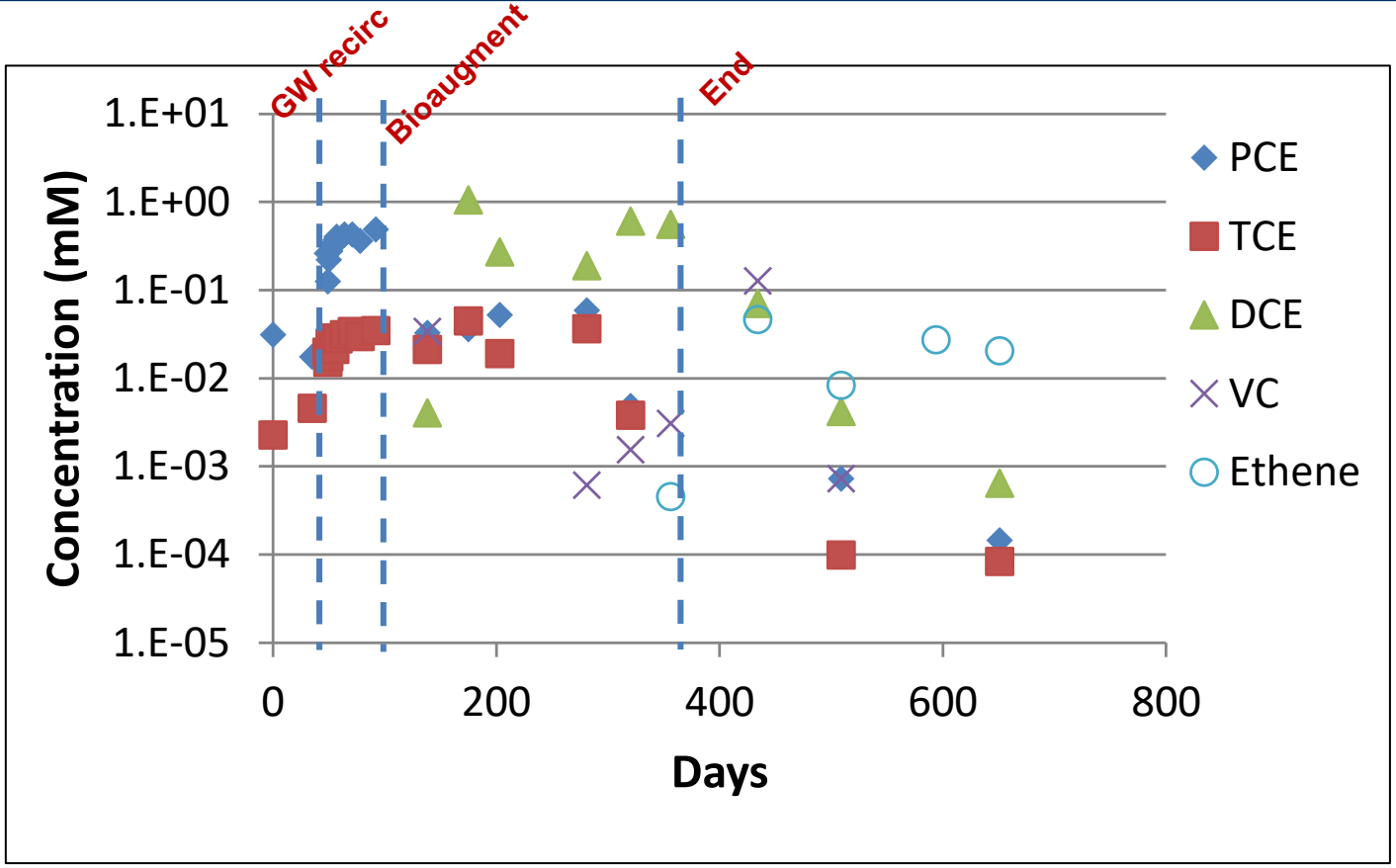
Electron Donor





VOC and Ethene Results - Shallow



- Ethene primary product at end of rebound, and only trace CVOCs
- Total molar concentrations decrease ~20x during rebound
- *Data suggest minimal on-going impacts from PCE sources*

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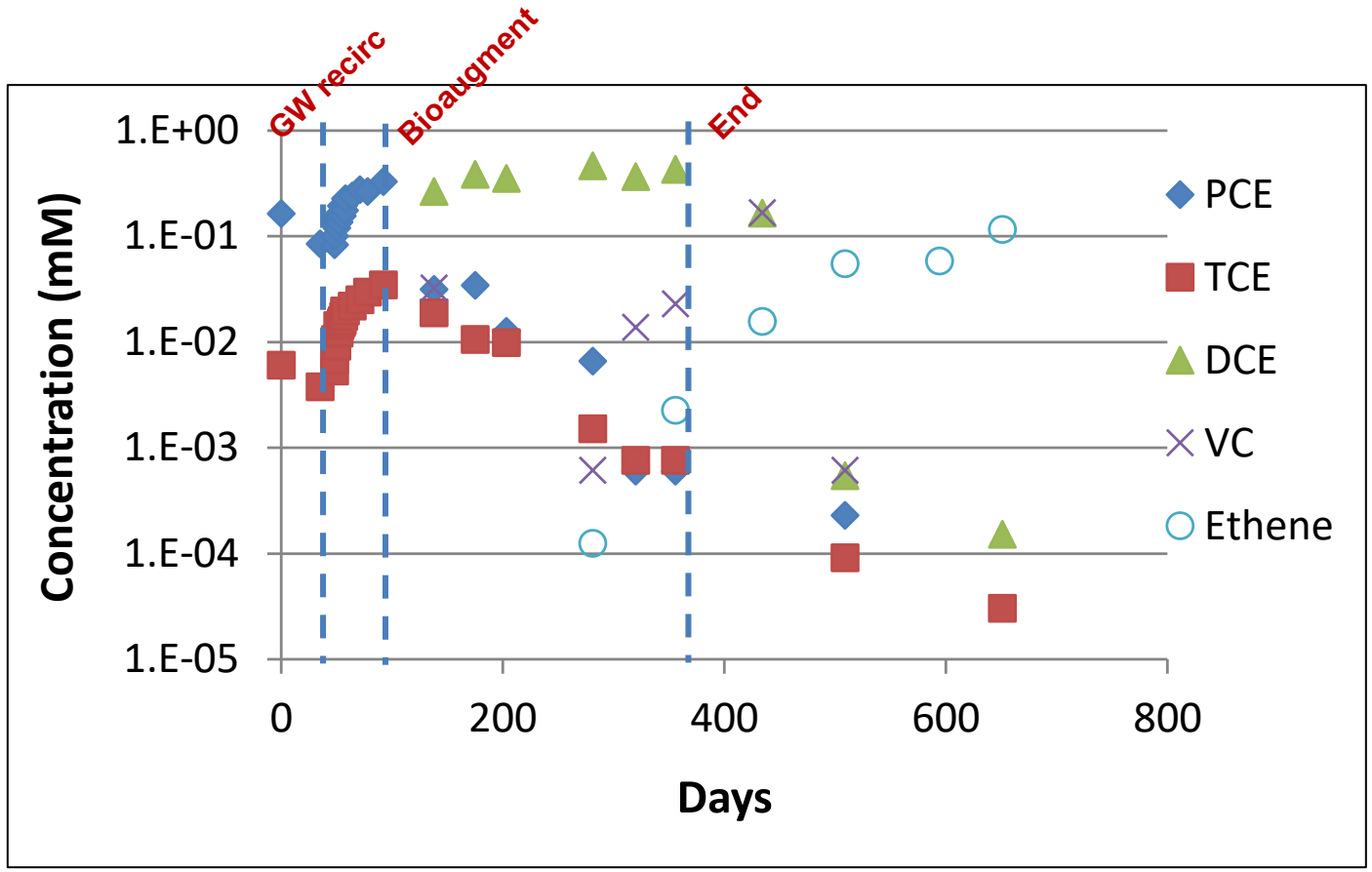
VOC and Ethene Results - Deep



- Ethene primary product at end of rebound, and only trace CVOCs
- Total molar concentrations decrease ~3x during rebound
- *Data suggest on-going reducing conditions are masking VOC rebound, and DNAPL source is still present*

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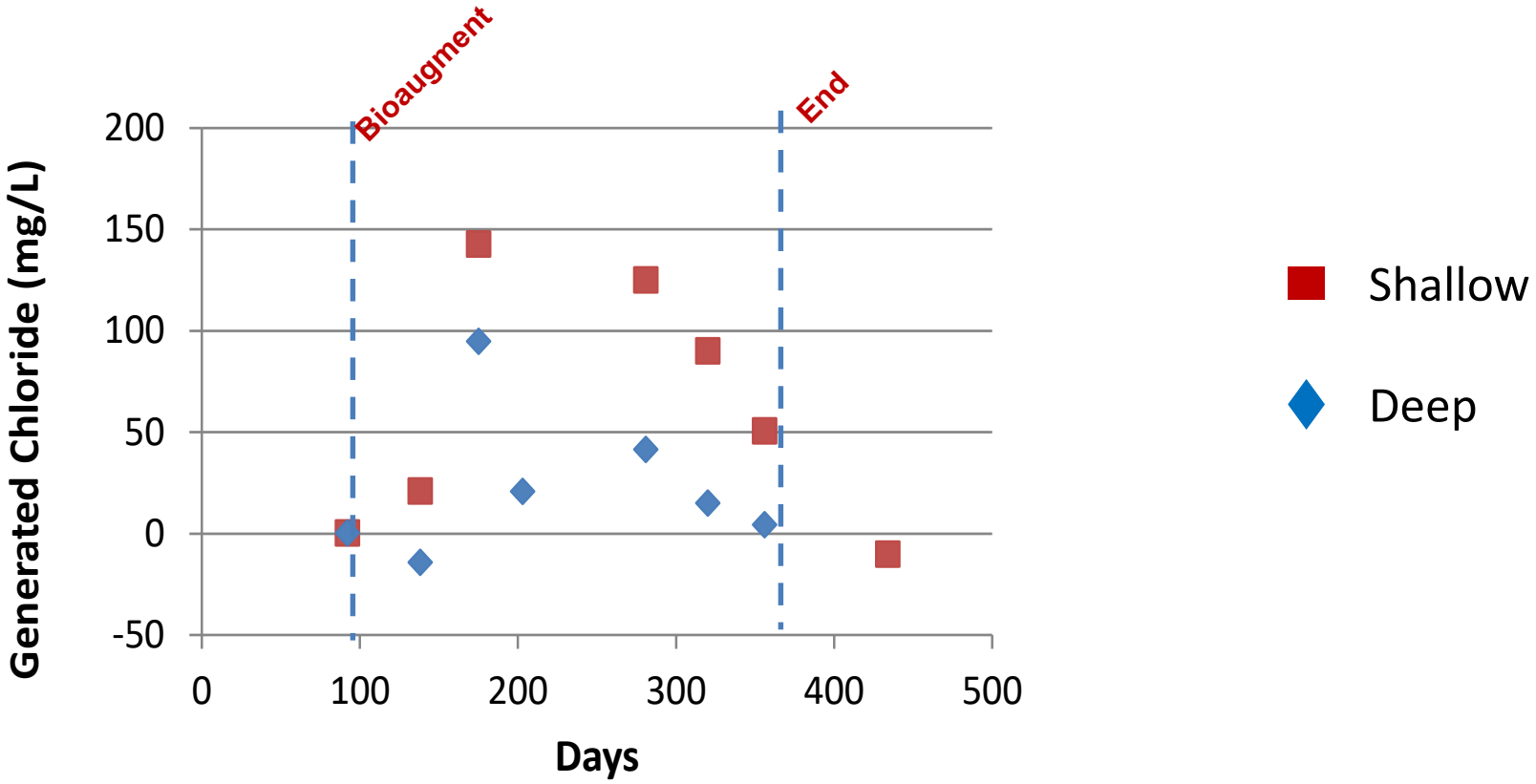
Chloride Generation



DNAPL mass removal based on chloride generation

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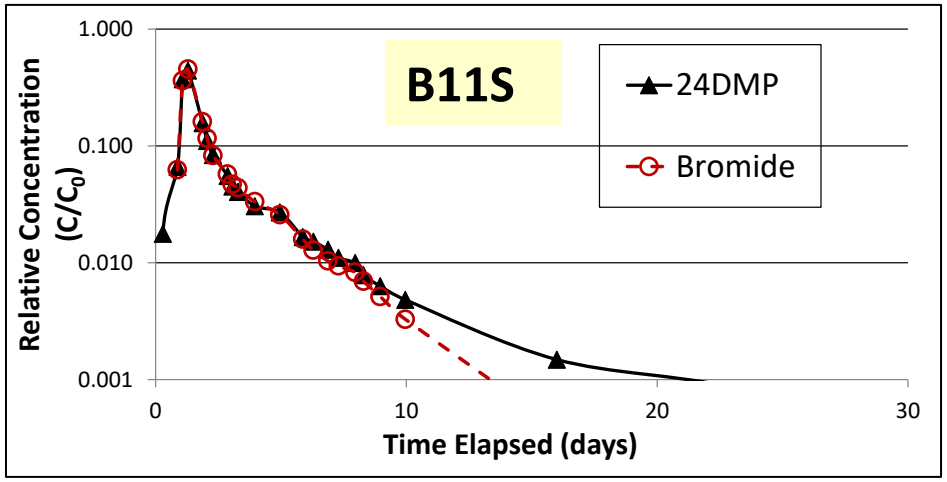
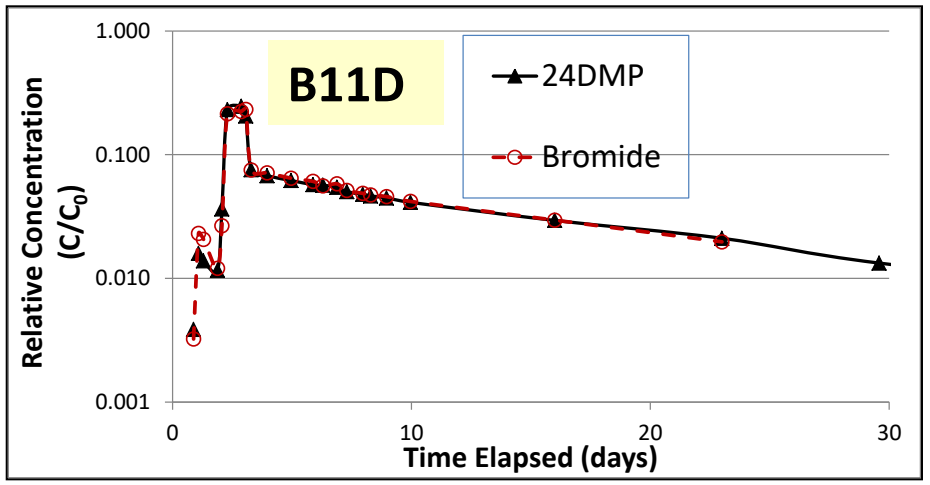
Impact of DNAPL Architecture n Treatment





~100% DNAPL removal

Large molar decrease post treatment

Only 45% DNAPL removal

Limited molar decrease post treatment

DNAPL Architecture Matters!
(a tool to manage treatment)

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Summary – DNAPL Architecture, Dissolution, and Treatment

- DNAPL in fractures more problematic than in unconsolidated media
- ISCO may be ineffective for relatively high levels of residual DNAPL
- DNAPL can be identified and quantified in fractured rock
- DNAPL in low transmissivity fractures can sustain plumes (not just matrix back diffusion)
- DNAPL architecture and flow field can determine the efficacy of DNAPL source treatment
- Bioaugmentation can be effective for treating DNAPL sources and reducing mass discharge

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