TRAINING COURSE PRESENTATION

Contaminant Flux and Fate in Fractured Rock

ESTCP Project ER-201570

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14. ABSTRACT
The objectives of this presentation are to:

•Identifying and characterizing DNAPL in bedrock
-Edwards Air Force Base (AFB)
•Abiotic Dechlorination in Rock Matrices (coupled diffusion & reaction)
•Insights at Loring AFB

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Contaminant Flux and Fate in Fractured Rock

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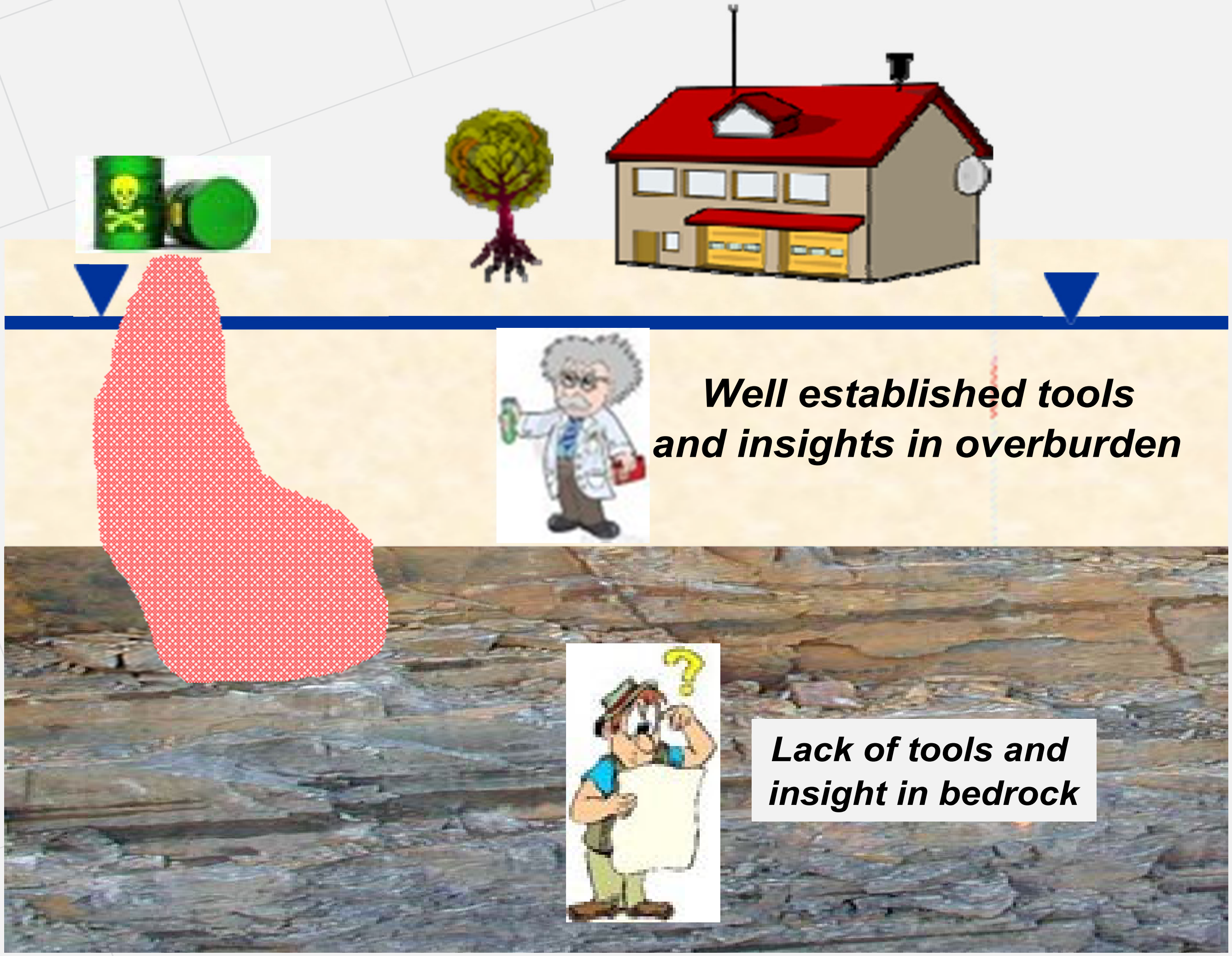
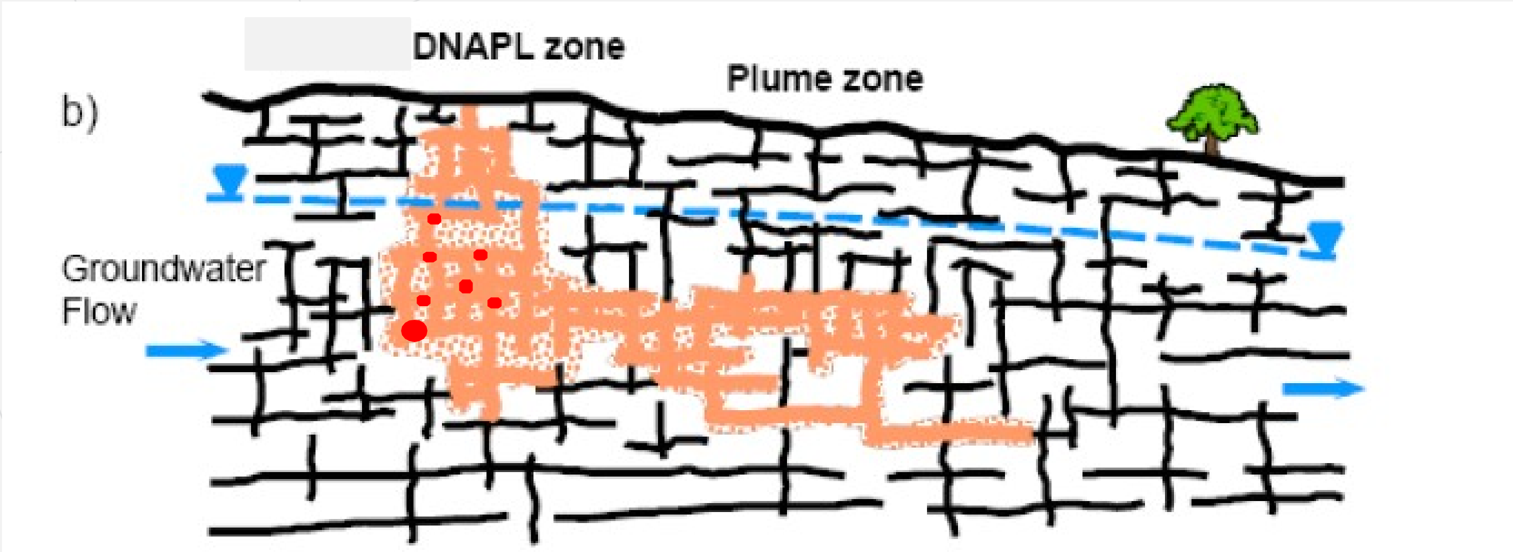
October 27, 2016


Well established tools
and insights in overburden
Lack of tools and
insight in bedrock

Chlorinated Solvents in



Modified from Parker, B.L. Fractured Rock Conference: State of the Science and Measuring Success in Remediation, September 24-26, 2007, Portland, Maine, 2007

What is sustaining Perchloroethylene (PCE)/Trichloroethylene (TCE) plumes in bedrock?

- ***Dense non-aqueous phase liquid (DNAPL)?***
- ***Matrix back-diffusion?***
- ***Low permeability fractures?***
- ***Overburden impact?***

How quickly is contaminant mass attenuating?

Objectives

- Identifying and characterizing DNAPL in bedrock
    - *Edwards Air Force Base (AFB)*

- Abiotic Dechlorination in Rock Matrices (coupled diffusion & reaction)

- Insights at Loring AFB

1. DNAPL ARCHITECTURE & DISSOLUTION

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

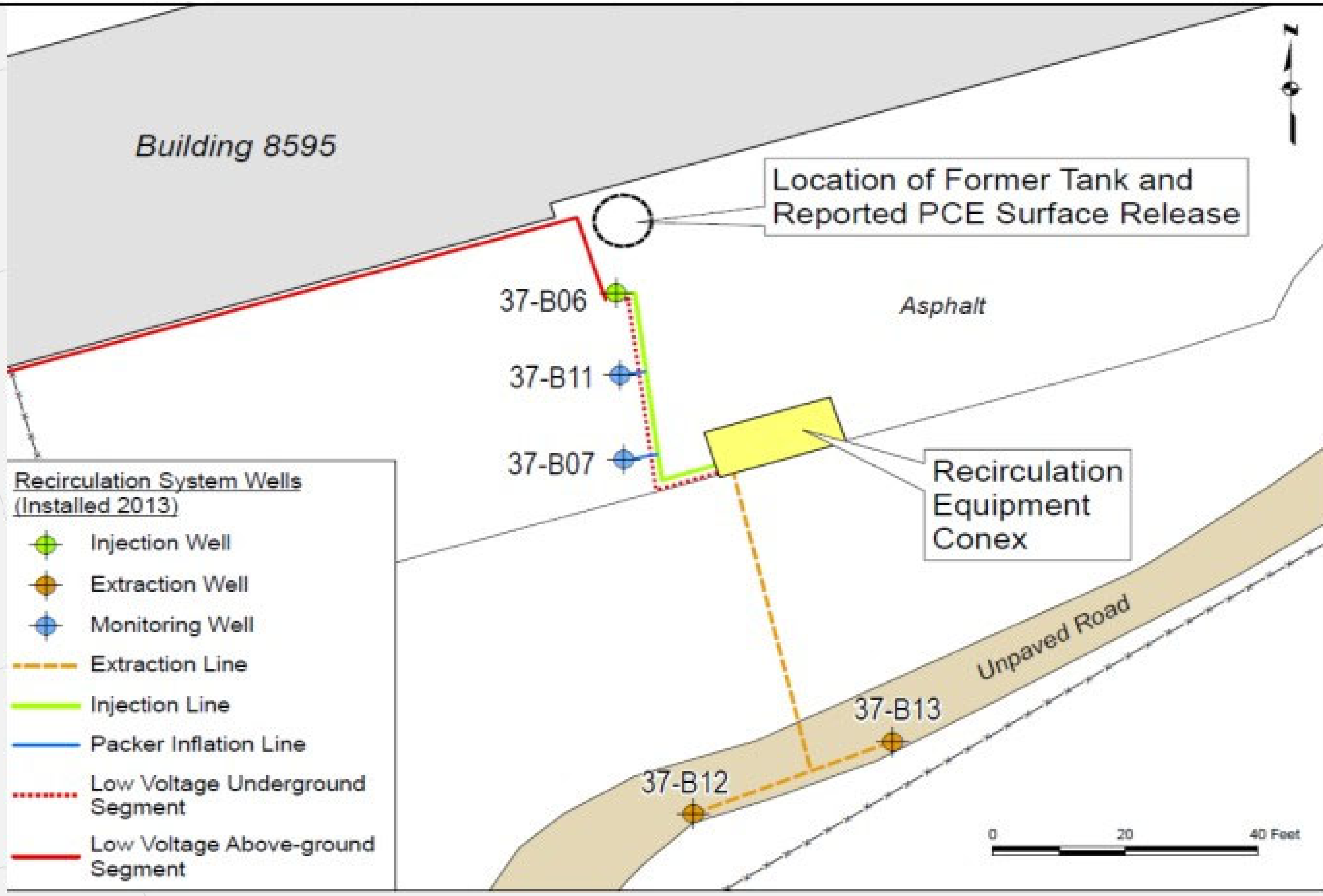
- Many of the technologies for locating and quantifying DNAPL sources are not appropriate, or have not been demonstrated, for bedrock
- DNAPL may be even more difficult to contact in fractured bedrock
- Costs

Illustrative Example – Key Insights

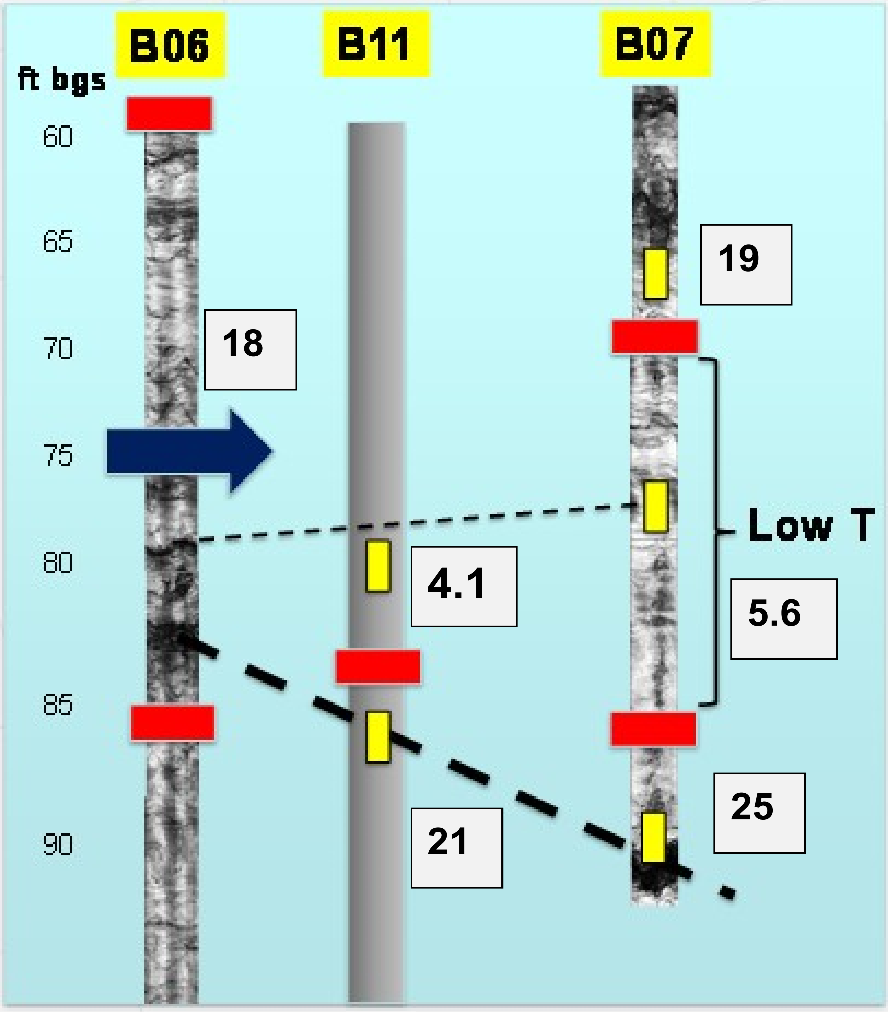
Site 37 Characteristics

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

Demonstration Location - Edwards AFB (ESTCP 201210)



~100 mL/min recirculation flow



Borehole geophysics

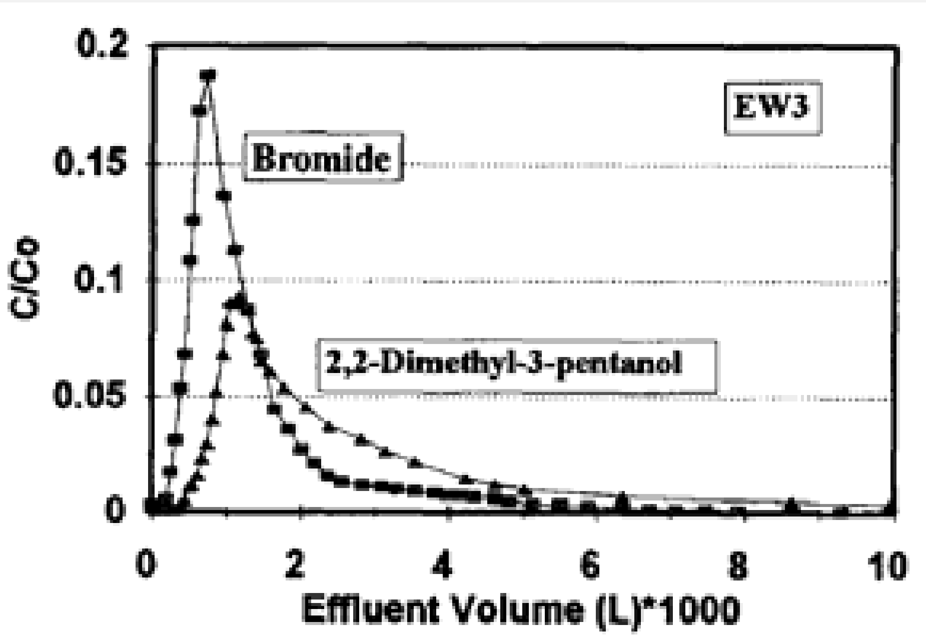
Discrete interval sampling and short-term pump testing

18 PCE concentrations

- - - - - - Low hydraulic connection
— — — High hydraulic connection
packer
Sampling pump

Partitioning Tracer Testing (PTT)

Applicable to Unconsolidated and Consolidated Materials

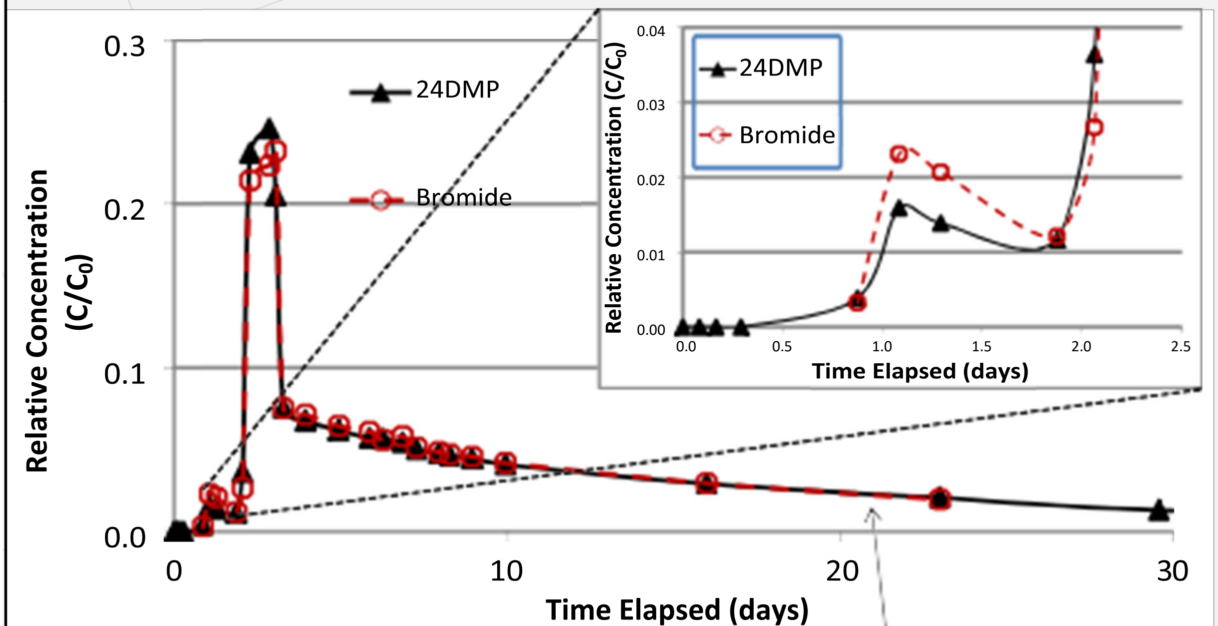


Annable et al., JEE, 1998

Compare elution of conservative and partitioning tracers (alcohols) to verify and quantify DNAPL

Tracer Results – Deep Zone

Bromide mass eluting through each zone proportional to transmissivity



Initial Peak
(low T fracture)

- 1% of flow
- Sn = 0.007

Middle Peak

- 9% of flow
- Sn = 0.0

Late Peak

- 40% of flow
- Sn = 0.0004

Mass transfer-controlled tailing

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What Else Does This Tell Us?

Environmental Science & Technology

Dense Nonaqueous-Phase Liquid Architecture in Fractured Bedrock: Implications for Treatment and Plume Longevity

Charles E. Schaefer, Erin B. White, Graig M. Lavorgna, and Michael D. Annable

<u>DNAPL distribution</u>
DNAPL present in high transmissivity fractures, but also in low transmissivity zones

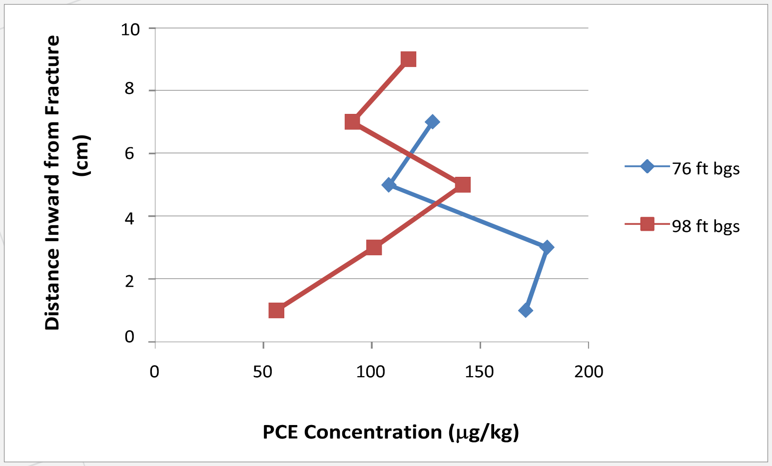
<u>Average fracture porosity</u>
0.004

<u>DNAPL mass</u>
2.4 kg in 15 ft radius around injection well interval

<u>DNAPL persistence under ambient conditions (dissolution only)</u>
B11s (high T) – 65 years B11d (tail) – 13 years
B11d (low T) – 194 years

PCE Mass Distribution and Flux

Rock Matrix vs Fractures



Based on PTT DNAPL

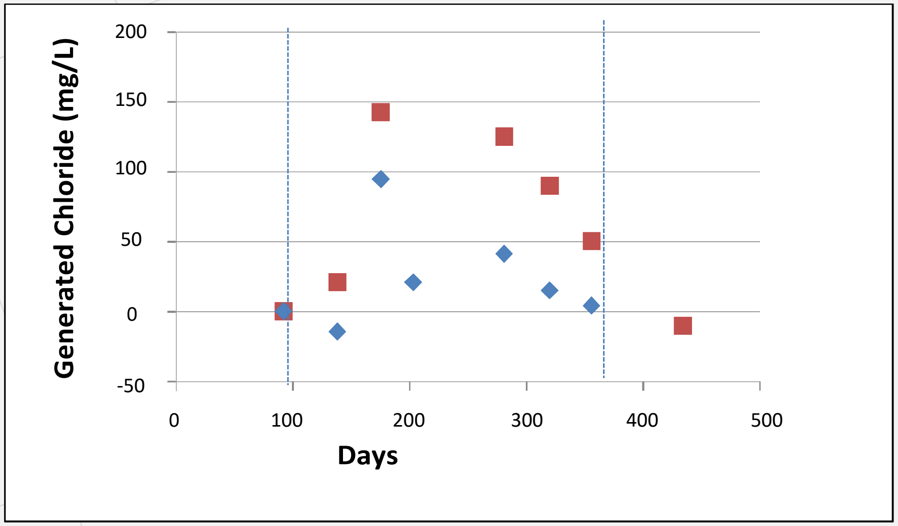
149 g PCE in rock matrix

PCE concentration profile suggests back-diffusion not occurring

2,400 g PCE as DNAPL in fractures

Treating to remove DNAPL might make sense

Bioaugmentation Results



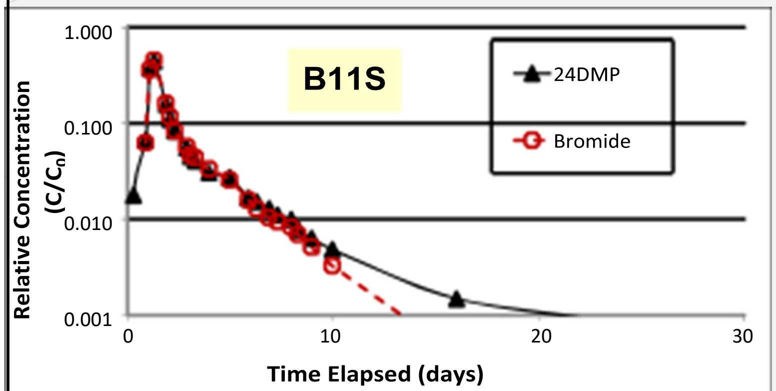
Shallow zone

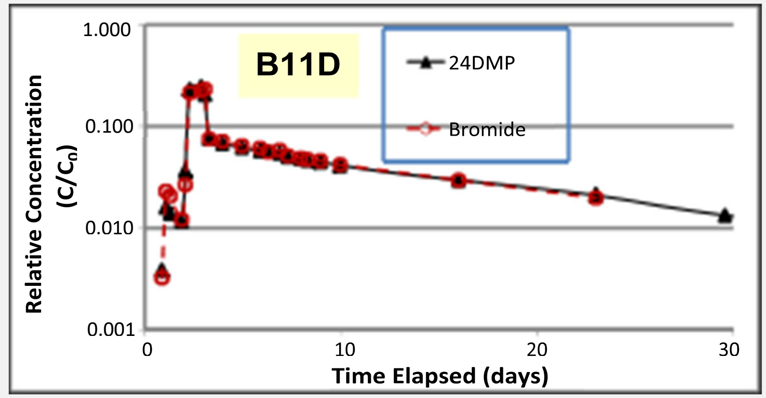
Deep Sone

Substantial chloride generation indicated DNAPL dissolution (2.1 mM of PCE to Dichloroethylene [DCE])

Chlorinated volatile organic compounds (CVOC) & ethene are not the best indicator of DNAPL removal (Schaefer et al. ES&T, 2010)

Impacts of DNAPL Architecture on Treatment During Bioaugmentation





~100% DNAPL removal
Limited rebound (97% CVOC decrease)
High DNAPL diss. enhancement

Only 45% DNAPL removal
Rebound
Low DNAPL diss. enhancement

But a small fraction of DNAPL mass removal may result in a large improvement in groundwater

2. Rock Matrix Dechlorination Reactions

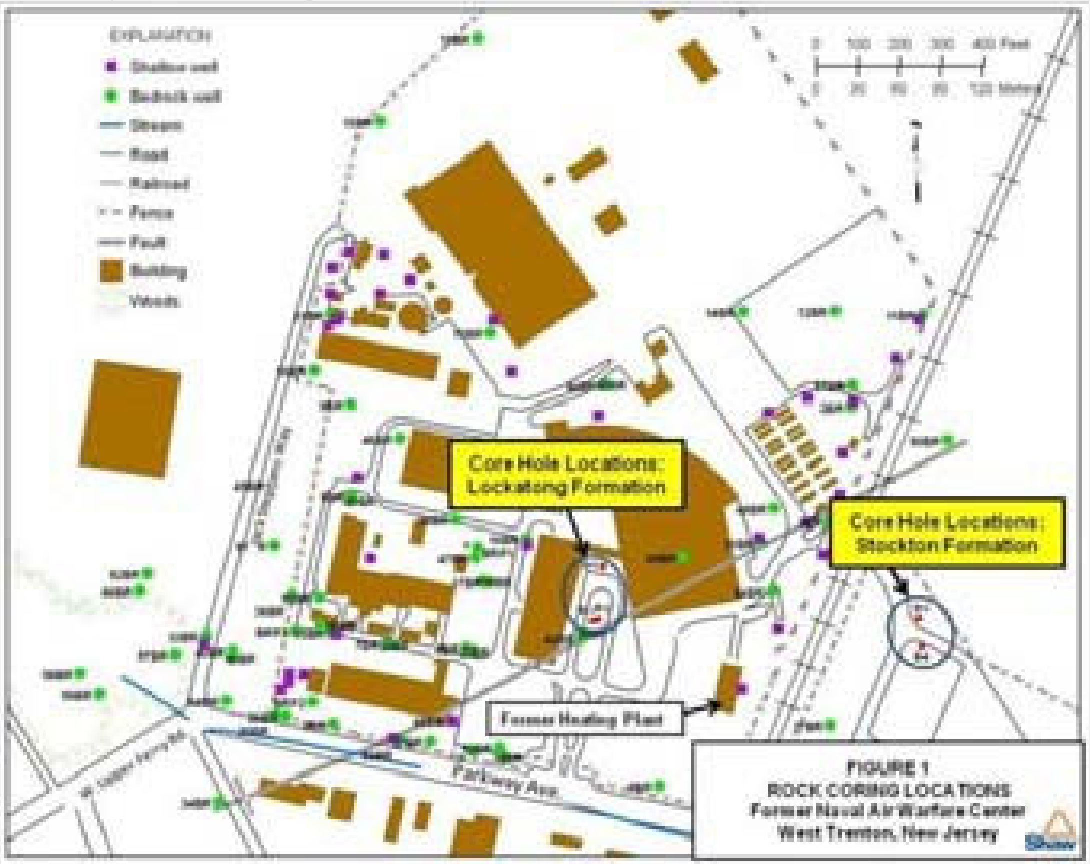
- Matrix diffusion is a SLOW process, so even a slow dechlorination reaction can be significant

- Several studies have focused on abiotic dechlorination reactions facilitated by naturally occurring ferrous minerals
  - *Bedrock matrices have received little attention*
  - *Ferrous minerals are present in many bedrock aquifers*

- **Are such reactions occurring, can they be measured, and are they important for my site?**

Rock Core Collection (SERDP Project ER-1685)

former Naval Air Warfare Center, Trenton, NJ



Lockatong Formation:

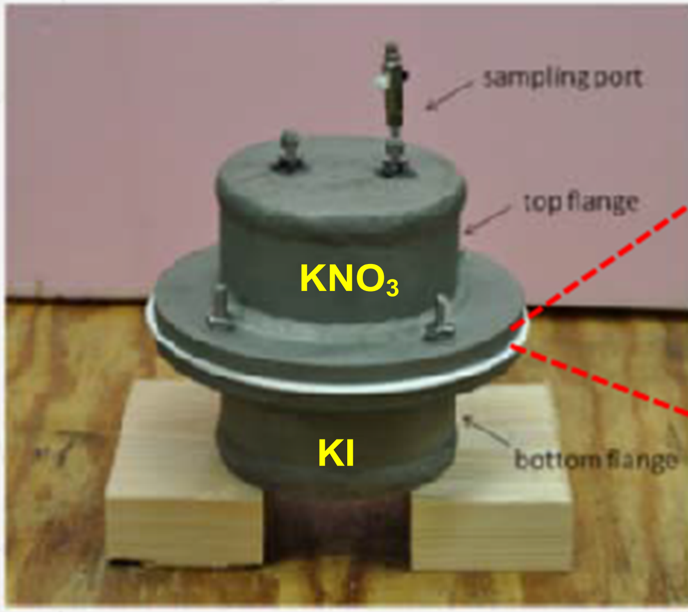
- Multiple types of mudstones and shale
- Multiple water bearing fractures
- Ferrous iron minerals

Stockton Formation

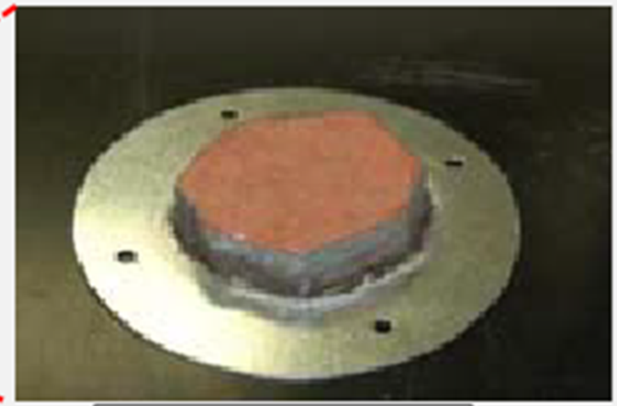
- Multiple water bearing fractures
- Red and white sandstones/siltstones

Cores collected outside of the TCE plume

Diffusion Cell Experiments



7 inches



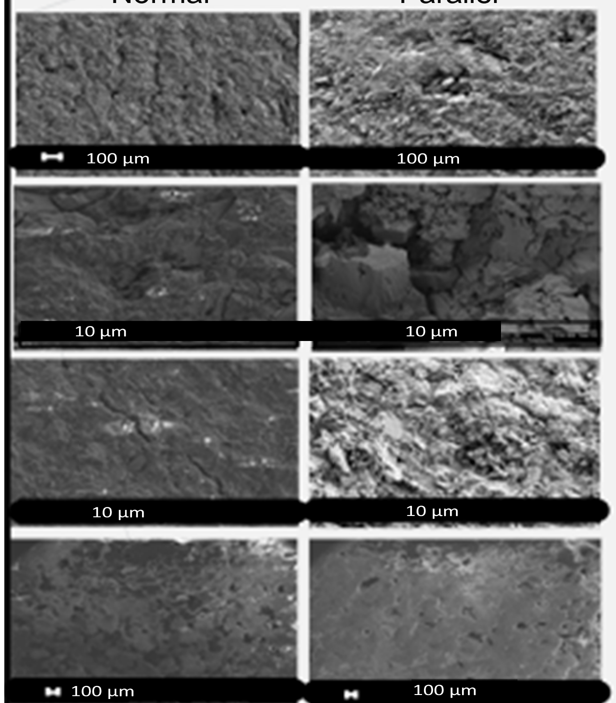
Mounted Rock Disc
(0.5 to 2 cm thick)

Iodide tracer experiments to assess diffusion parallel and normal to bedding
- four rock types

Iodide Diffusion Results: Impact of Mineral Bedding

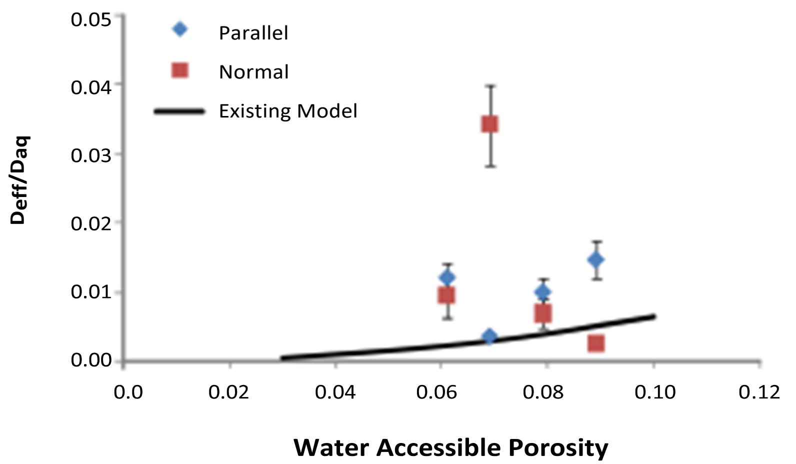
Scanning Electron Microscope (SEM) Images

Normal | Parallel



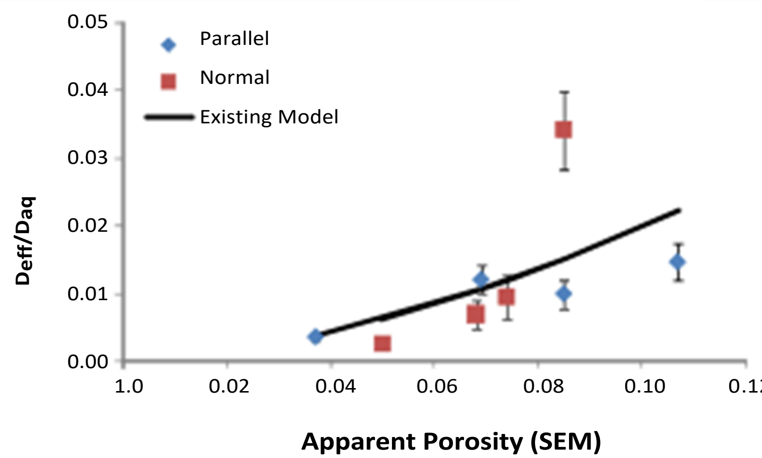
		SEM Porosity	Effective Diffusion Coefficient (cm^2/s)
Red Sandstone	Normal:	0.074	1.8×10^{-7}
	Parallel:	0.069	2.3×10^{-7}
Tan Sandstone	Normal:	0.068	1.3×10^{-7}
	Parallel:	0.085	1.9×10^{-7}
D.G. Mudstone	Normal:	0.050	0.49×10^{-7}
	Parallel:	0.11	2.8×10^{-7}
Quarry Sandstone	Normal:	0.085	6.5×10^{-7}
	Parallel:	0.037	0.68×10^{-7}

Predicting Diffusion Based on Apparent Porosity

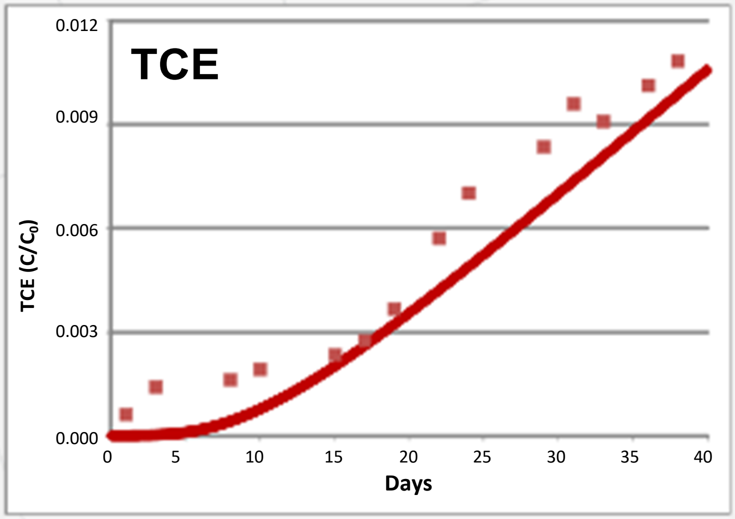


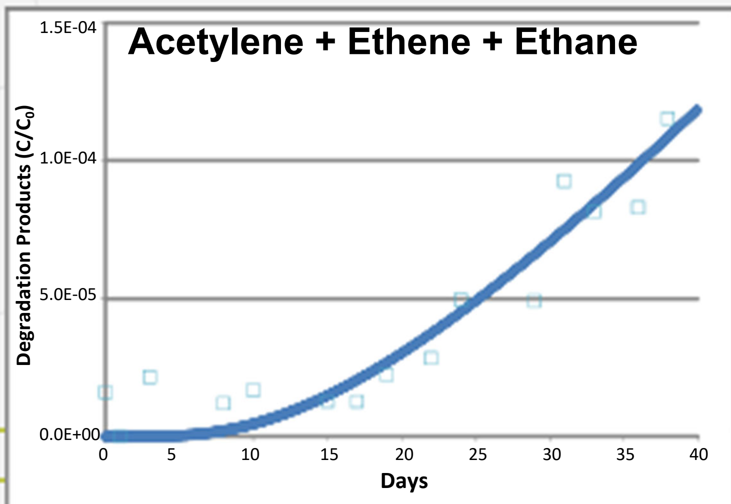
$$\frac{D_{eff}}{D_{aq}} = \varepsilon^{2.2}$$ *(Boving and Grathwohl, 2001)*

Modified Correlation: $$\frac{D_{eff}}{D_{aq}} = \varepsilon_o^{1.7}$$

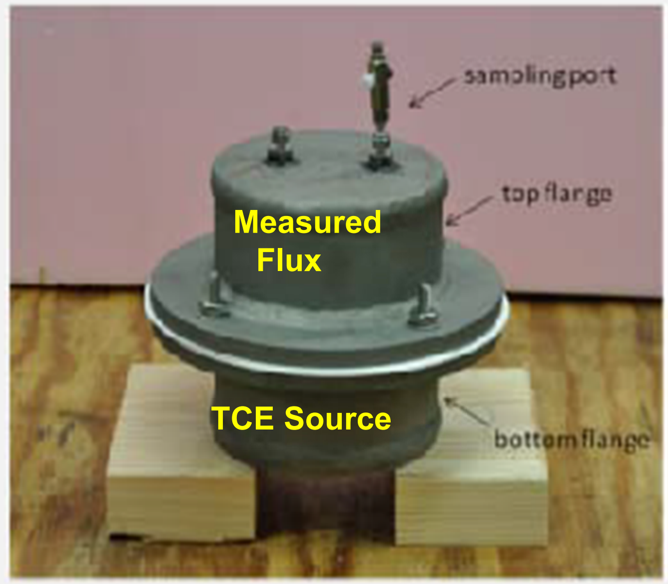


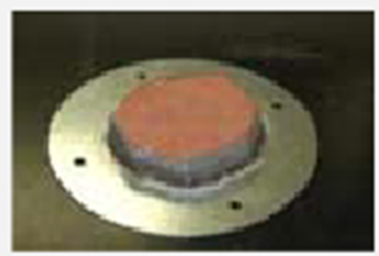
Coupled TCE Diffusion and Reaction





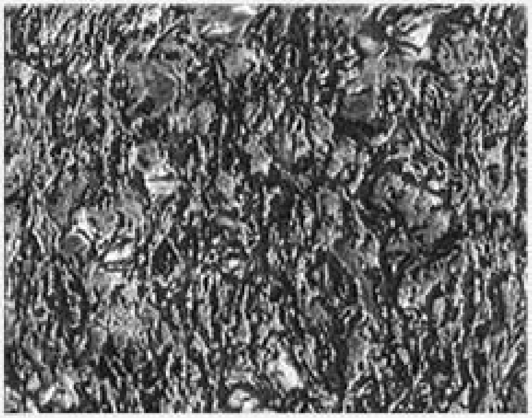
Light Gray Mudstone



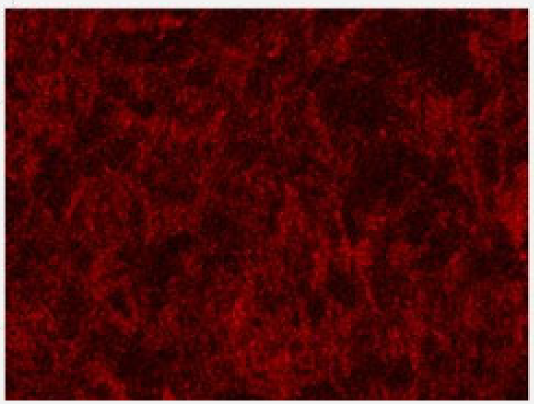


$HgCl_2$ added to inhibit microbial activity

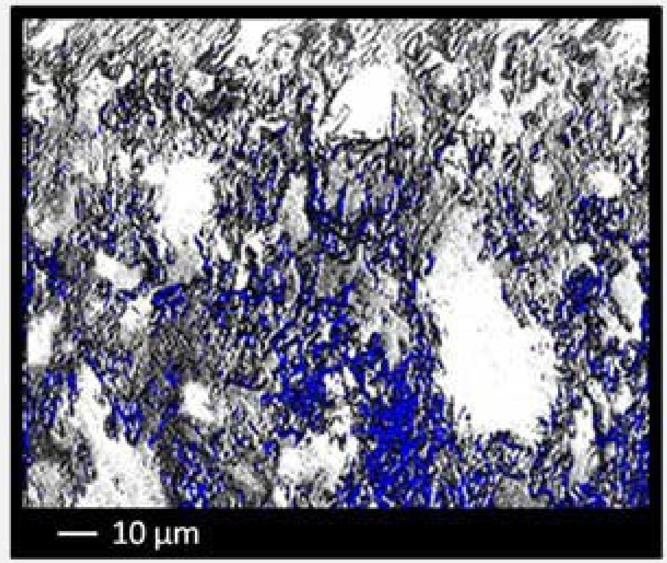
Available Ferrous Iron



SEM for porosity distribution



Electron Dispersive Spectroscopy for Fe^{2+} distribution

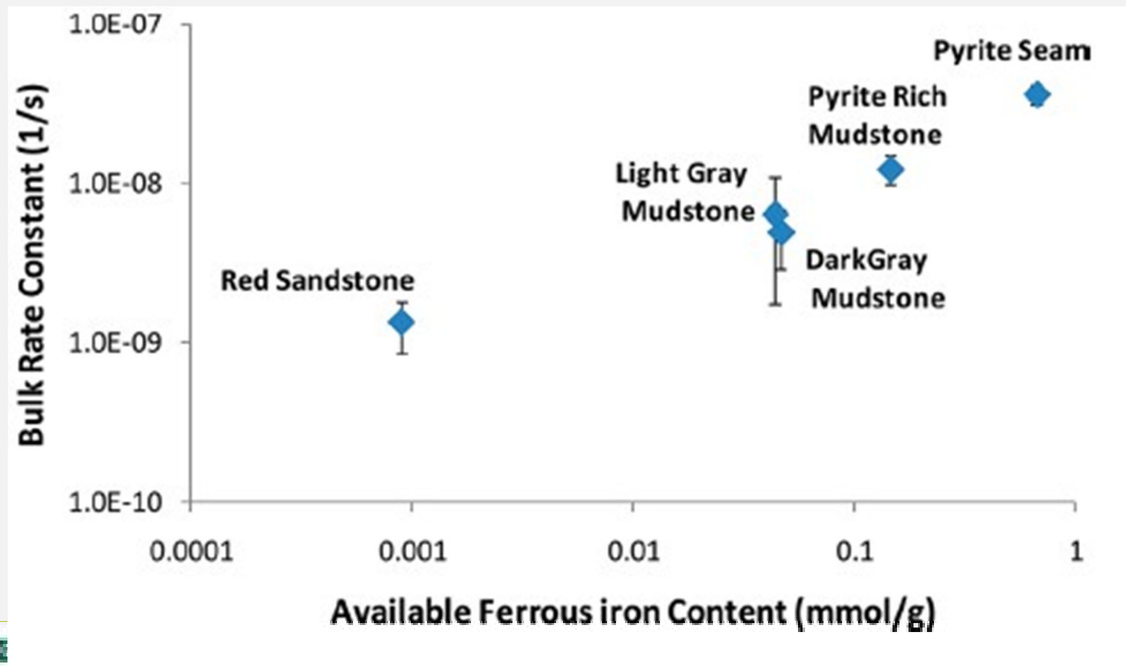


"Available" Fe^{2+} indicated by blue

Coupled Diffusion and Reaction of TCE through Rock


Environmental Science & Technology

Coupled Diffusion and Abiotic Reaction of Trichlorethene in Minimally Disturbed Rock Matrices



- Up to 10 months exposure at elevated TCE concentrations (200 mg/L) did not result in any decrease in the observed dechlorination rate constant
- Low stoichiometric Fe^{2+} consumption (<2%)

But are these reactions really occurring in historically contaminated bedrock aquifers?

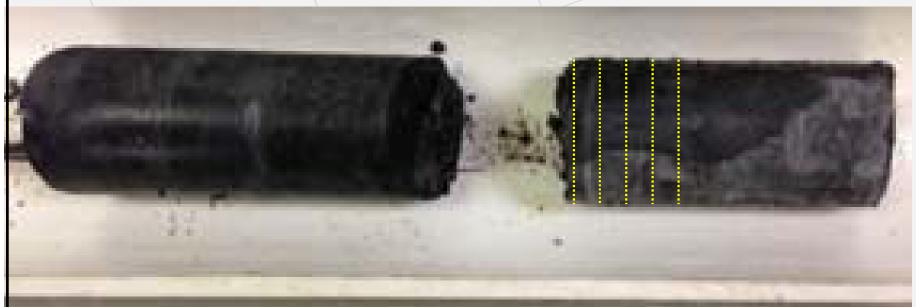
Collect Core from within the TCE Plume

- Collection at the former Naval Air Warfare Center, Trenton, NJ, USA
- Core collected adjacent to fractures at three depth intervals

Groundwater Data as Screening for Potential Abiotic Dechlorination Reactions

<u>Groundwater Packer Sampling (µg/L)</u>

Compound	49′	53′	83′
TCE	203	463	24,800
cis-DCE	59	410	260
vinyl chloride	2	31	6.2
methane	28	31	4.8
ethane	3.2	2.0	0.48
ethene	-	3.6	-
propane	2.4	2.4	0.3
acetylene	-	-	4.8



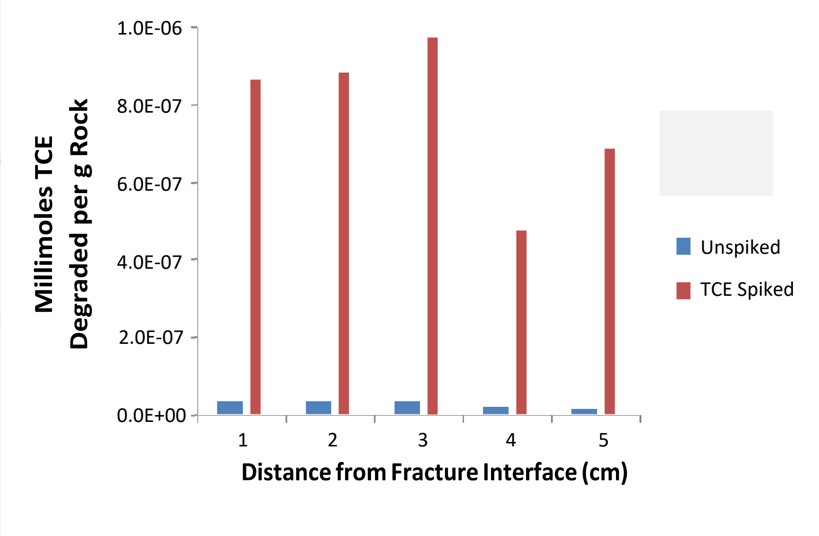
Chemosphere

Short Communication

Abiotic dechlorination in rock matrices impacted by long-term exposure to TCE

Charles E. Schaefer, Richard M. Towne, David R. Lippincott, Pierre J. Lacombe, Michael E. Bishop, Hailiang Dong

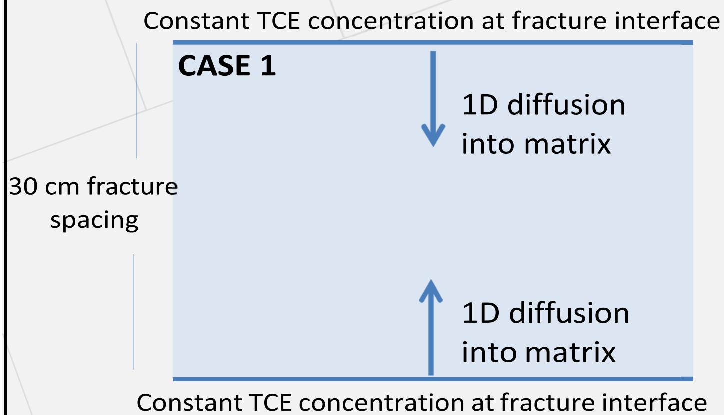
Abiotic TCE Dechlorination in Rock Collected within the TCE Plume



Comparison of TCE spiked vs. non TCE spiked samples in laboratory system

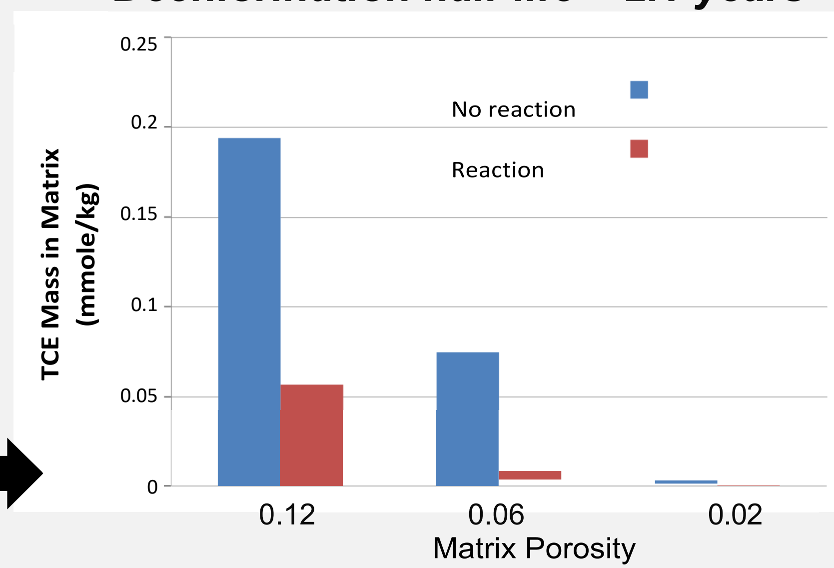
Rock minerals still able to dechlorinate TCE (similar rate constant)

How Important are These Reactions?



Simulated 30 years of uptake

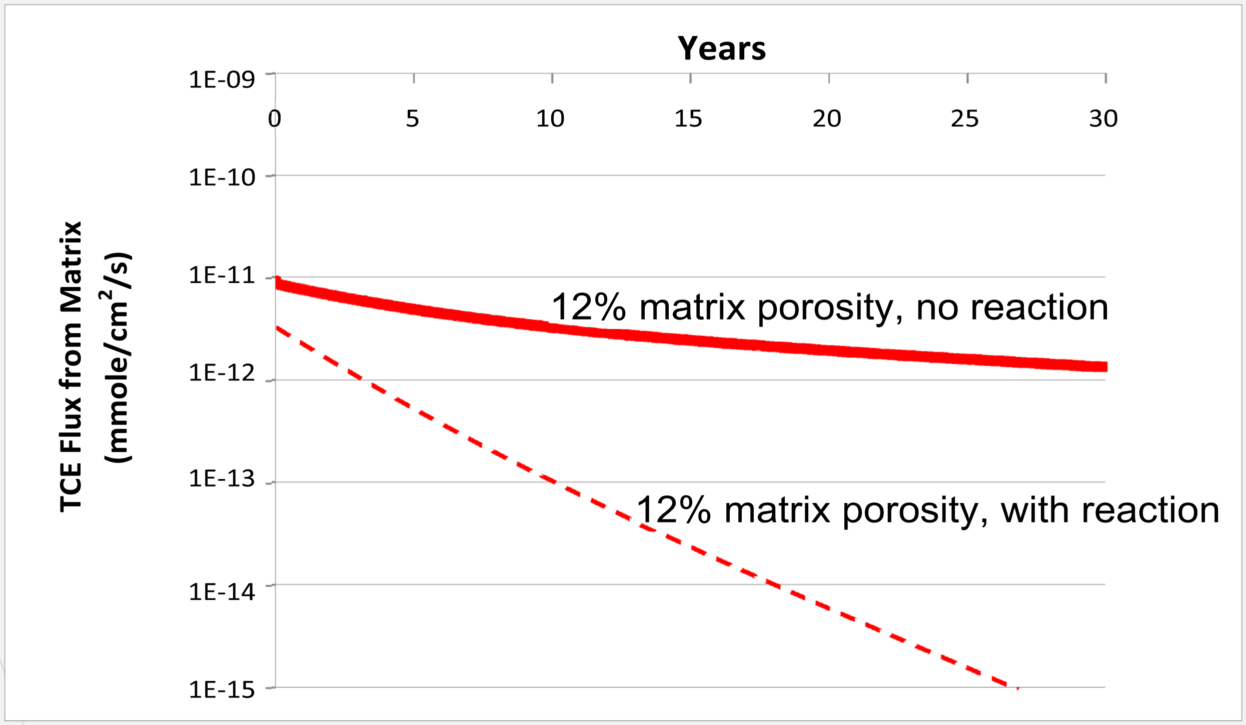
Dechlorination half-life = 2.1 years



How Important are the Reactions?

Diffusion Simulations

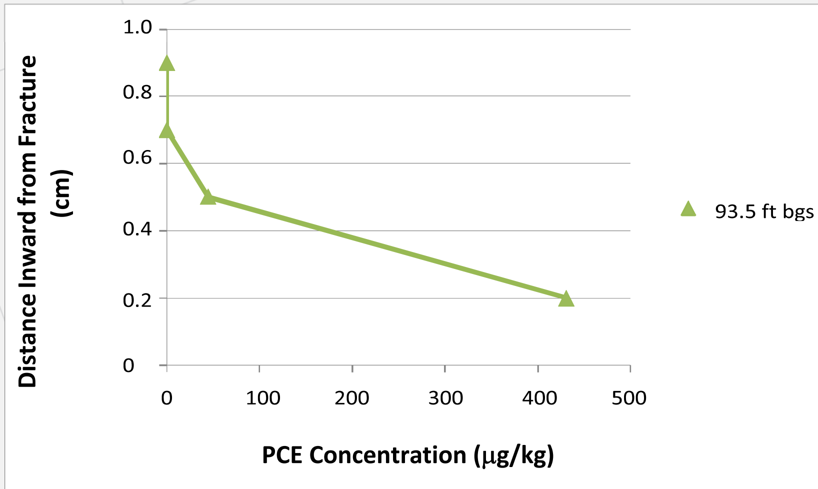
- After 30 years constant TCE exposure, 30 years of back-diffusion (maximum gradient: no TCE in fractures)



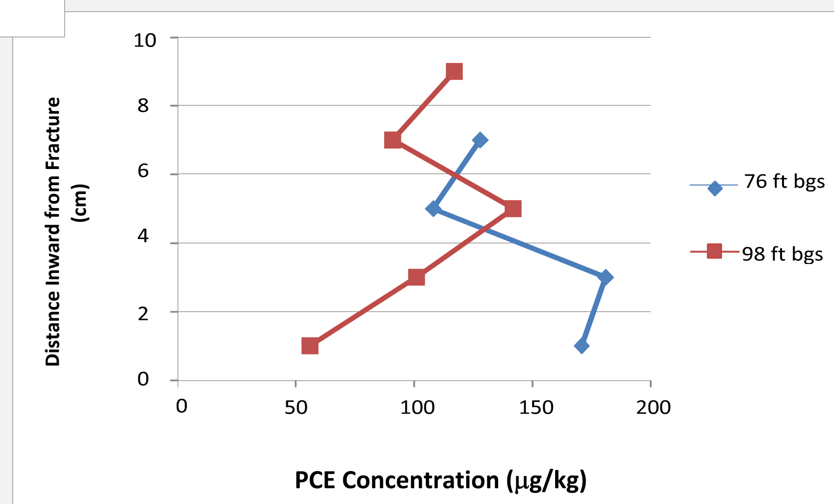
Can help determine if matrix back-diffusion is sustaining the plume

More Evidence

PCE/TCE concentrations profiles in the rock matrix moving inward from the fracture interface (cm-scale):



- **Loring AFB Limestone**
- **Batch testing showed substantial abiotic reactivity**



- **Edwards AFB Granite**
- **Batch testing showed negligible abiotic reactivity**

How Readily Can This Information Be Attained?

Initial Screening

- Porosity analysis
  - <$400/sample ***Several commercial labs***
- Reduced gases in groundwater (acetylene, propane, ethane, ethene)
  - <$100/sample ***Several commercial labs (ask for gases)***
- Ferrous iron in crushed rock (EPA Method SM3500-Fe B.4.c)
  - ~$75/sample ***ALS Environmental & McCampbell Analytical***

Next Steps - Using Intact Rock Core:

- Field crushing and methanol extraction of rock "slices"
  - $10K (***not including drilling***) ***Several labs***
- Batch reactivity and sorption testing
  - ~$25K lab cost (assuming core available) ***Published methods***

3. Impacts of Matrix Diffusion and Reaction on the Dissolved Plume: Loring AFB – Groundwater Management Zone (GMZ) 4

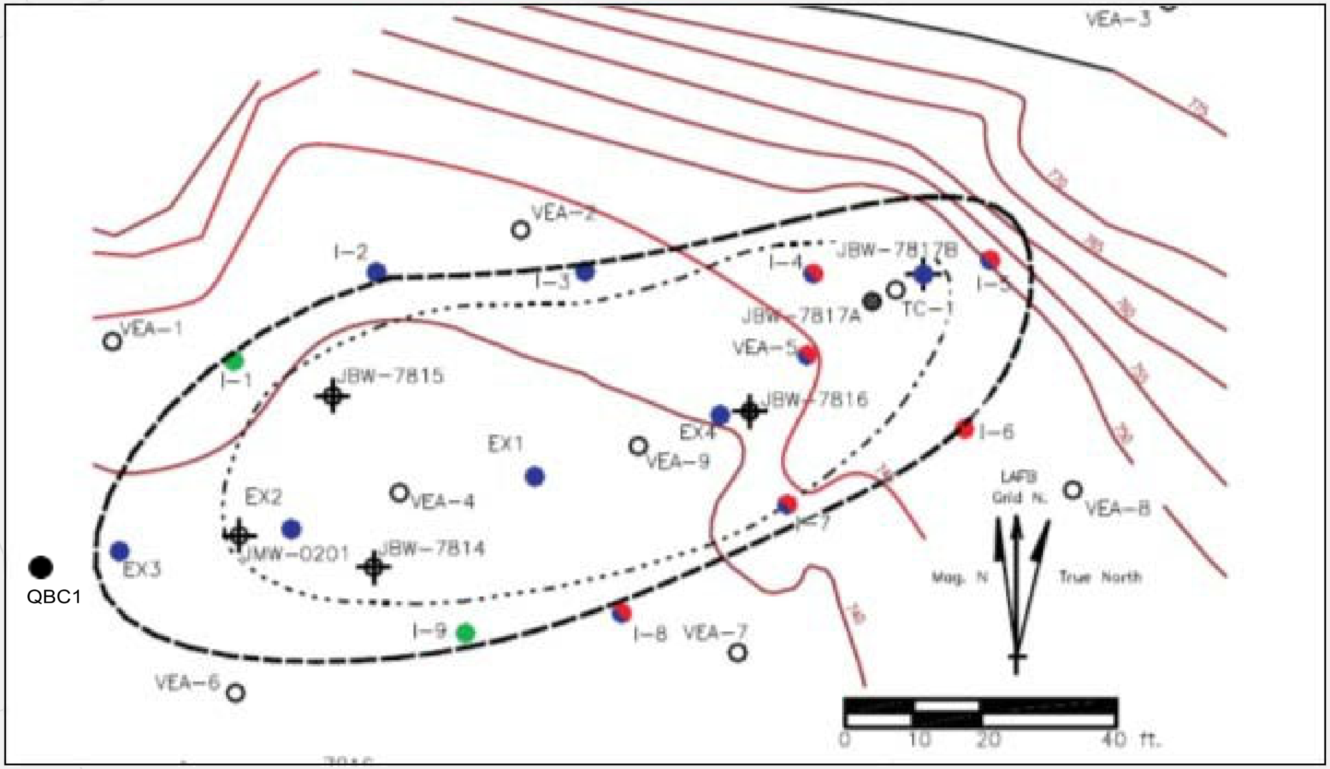
Remedial efforts as part of sitewide performance based contract (CB&I)

USAF, Maine DEP and USEPA very involved

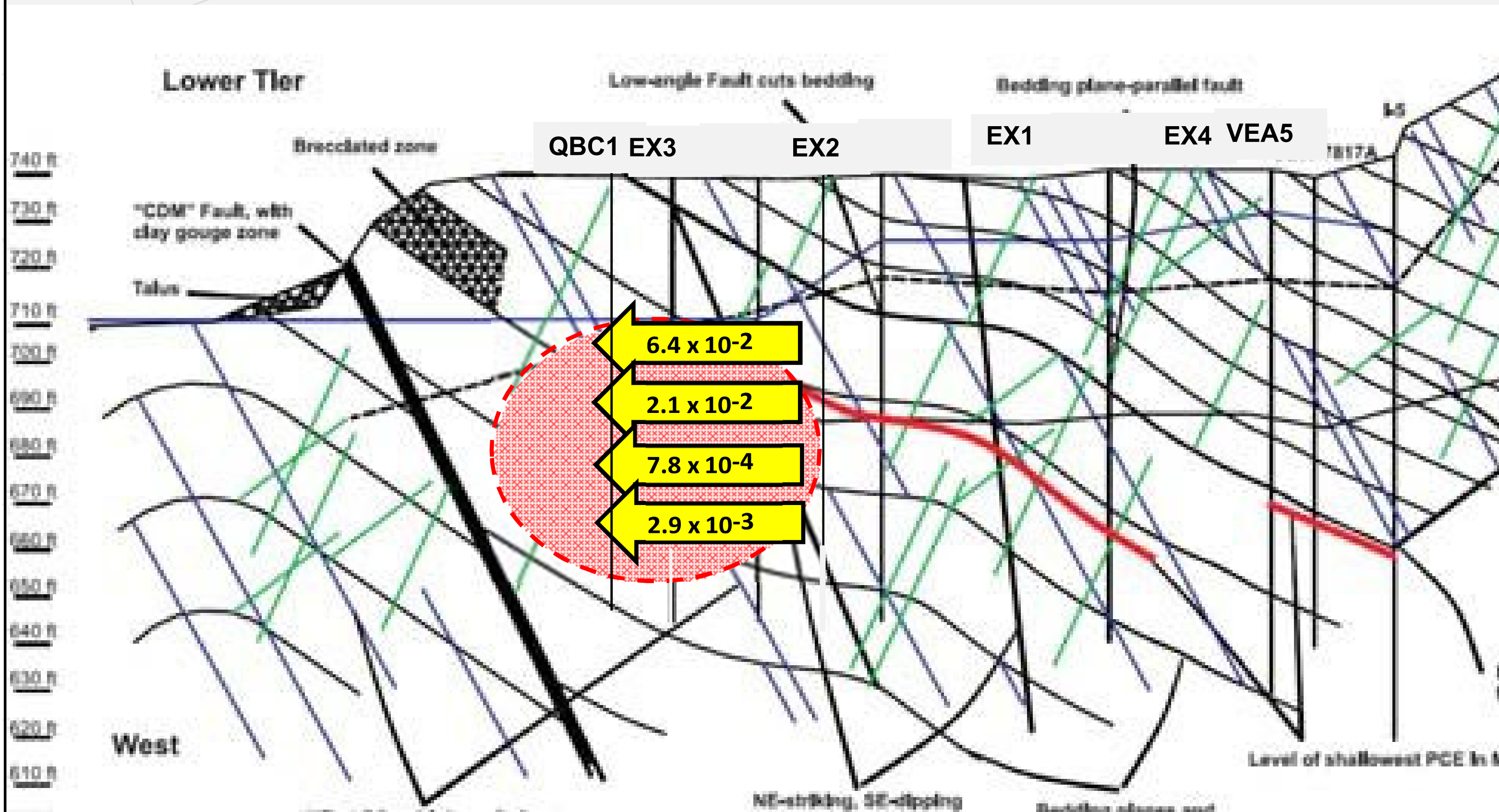
<u>GMZ 4</u>

- **fractured limestone**
- **complex fracture flow**
- **former drum disposal**
- **PCE (DNAPL likely)**
- **prior steam injection**
- **no groundwater data for ~10 years**

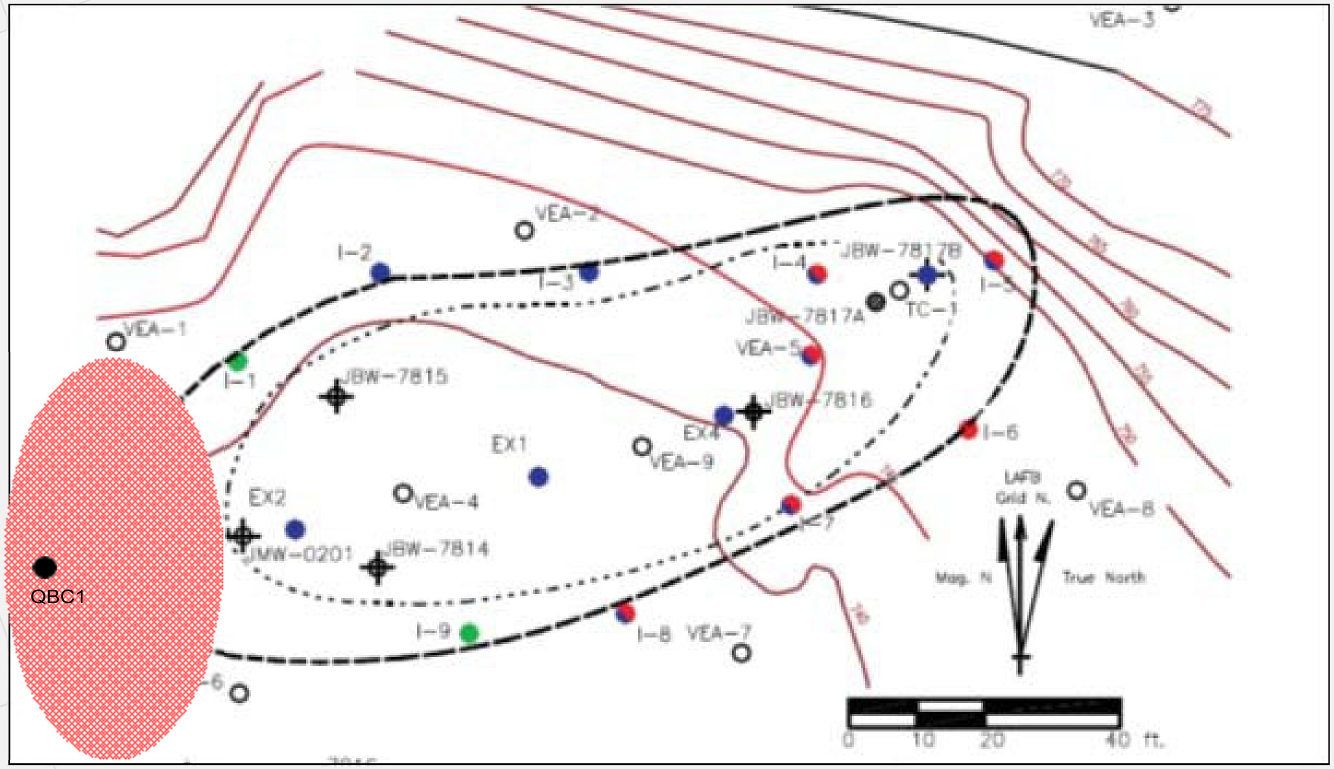
PCE Source Area in Fractured Limestone



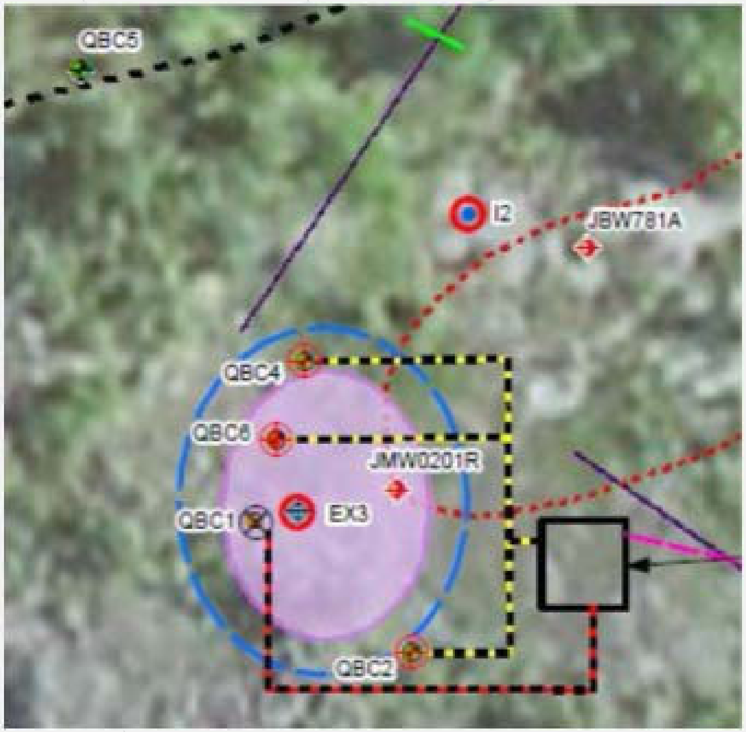
Identify High Contaminant Flux Zones

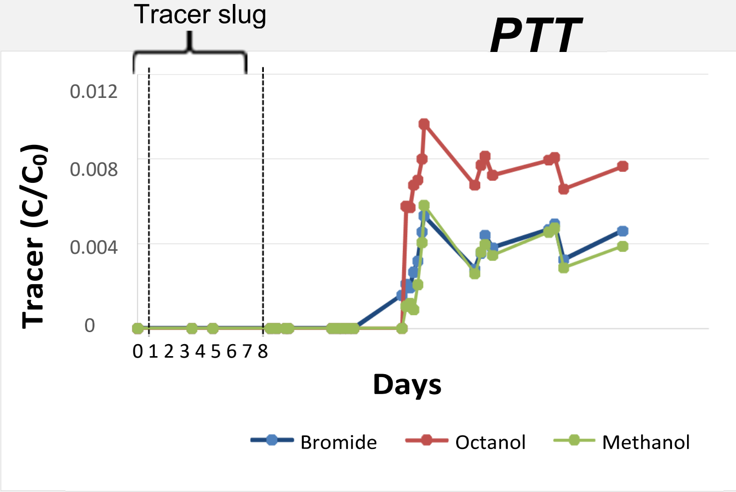


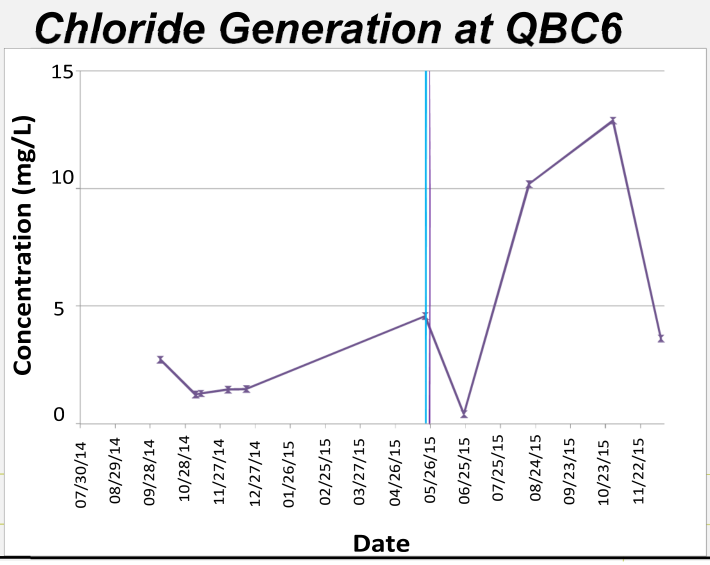
Target Treatment Area



Bioaugmentation to Target High PCE Flux Zone







Treatment is on-going

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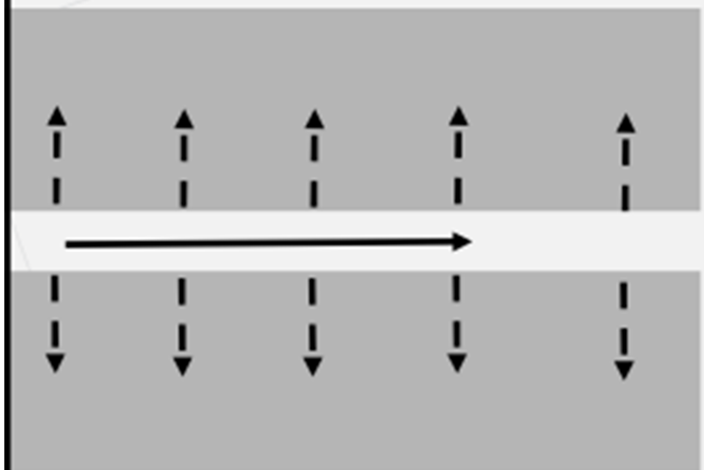
Preliminary Assessment – Role of Matrix Dechlorination Reactions

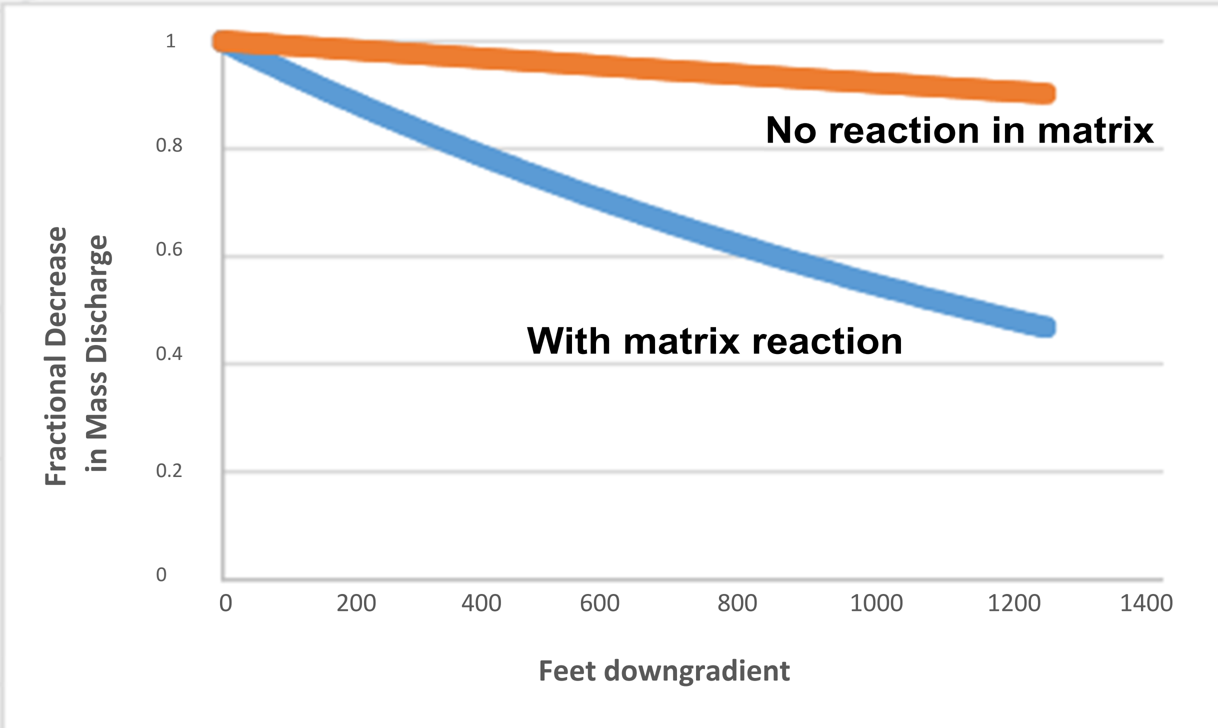


Determine:

- Fracture aperture (cubic law and transmissivity) [0.021 cm]
- Superficial velocity (Darcy's Law and fracture porosity) [400 cm/day]
- Rock matrix effective diffusion coefficient estimated from rock matrix porosity
  [3.6×10^{-9} cm^2/s]
- First order dechlorination rate constant
  [6.6×10^{-7} s^{-1}]

Flux at fracture surface = *2* erf (Crank, 1995)

Role of the Rock Matrix for Natural Attenuation of the Downgradient Dissolved Plume



Model assumes no dilution due to dispersion

Conclusions

- Residual DNAPL can be identified and quantified in fractured rock
- DNAPL in low transmissivity fracture zones may be sustaining bedrock plumes
- In DNAPL source areas, most of the contaminant mass and flux might be due to DNAPL
  - *thus, treatment may be worthwhile*
- Abiotic dechlorination reactions in rock matrices may be mitigating back-diffusion and contaminant migration at many sites
- Identifying and quantifying these dechlorination reactions can be readily performed

Contact Information

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