Case Study: Permanganate Applied to VOCs in Fractured Shale

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Research Collaborators

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  - University of Waterloo
- **Kenneth Goldstein, CGWP**
  - Malcolm Pirnie, Inc
- **Grant Anderson, P.G.**
  - U.S. Army Corps of Engineers

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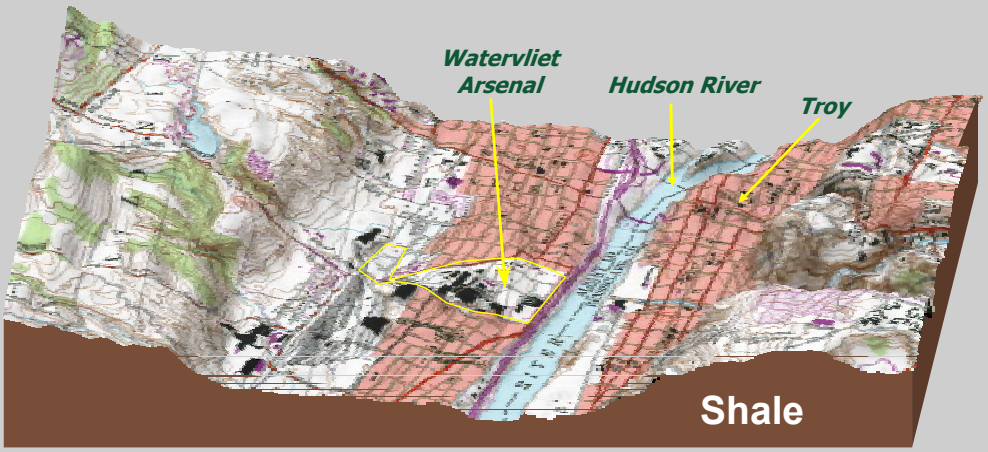
Watervliet Arsenal in New York State



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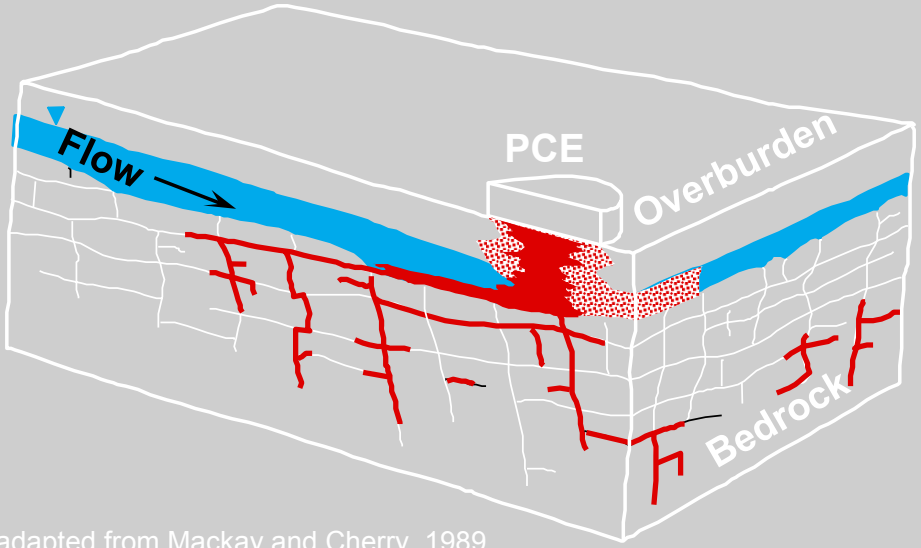
DNAPL Passed Through Overburden Into Shale



adapted from Mackay and Cherry, 1989

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The Problem

- Chlorinated ethenes – as high as 150 mg/L
- Contamination down to 150 ft. bgs
- All VOC mass in fractured shale
- AOC is 200 ft west of Hudson River

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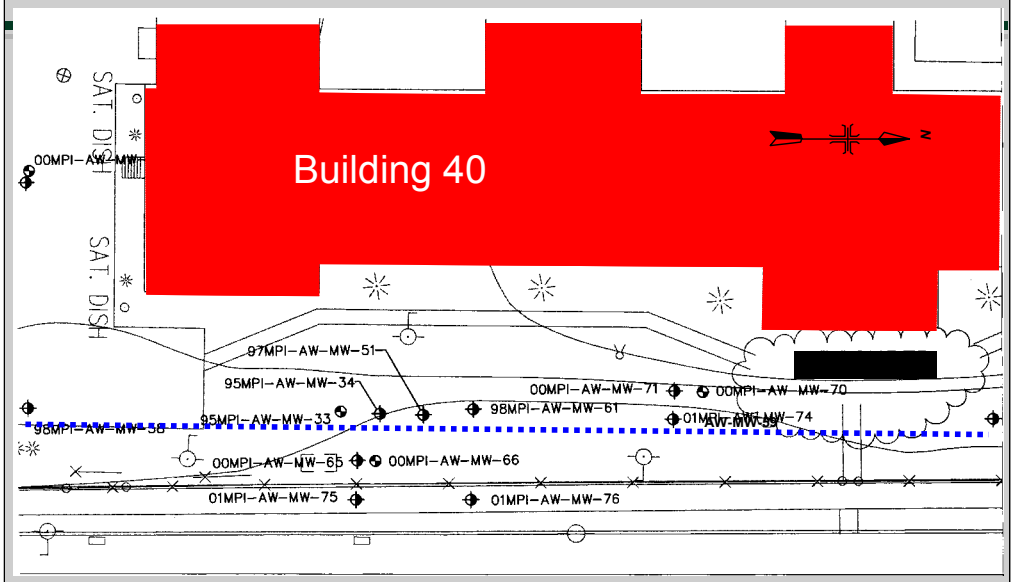
Study Area


Building 40
SAT. DISH
SAT. DISH
00MPI-AW-MW-
97MPI-AW-MW-51
95MPI-AW-MW-34
95MPI-AW-MW-33
98MPI-AW-MW-58
00MPI-AW-MW-65
00MPI-AW-MW-66
01MPI-AW-MW-75
98MPI-AW-MW-61
00MPI-AW-MW-71
00MPI-AW-MW-70
01MPI-AW-MW-74
AW-MW-59
01MPI-AW-MW-76
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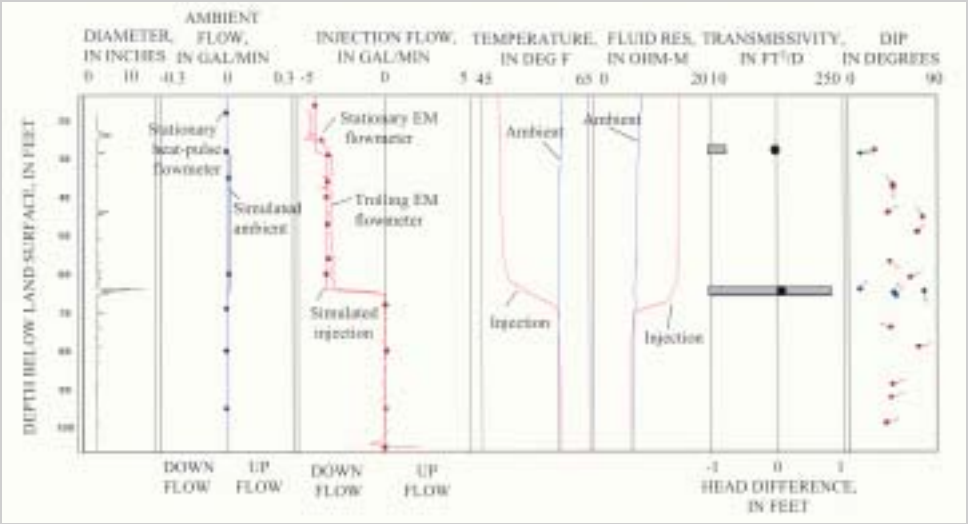
Identification of Major Transmissive Zones Using Hydro-geophysics



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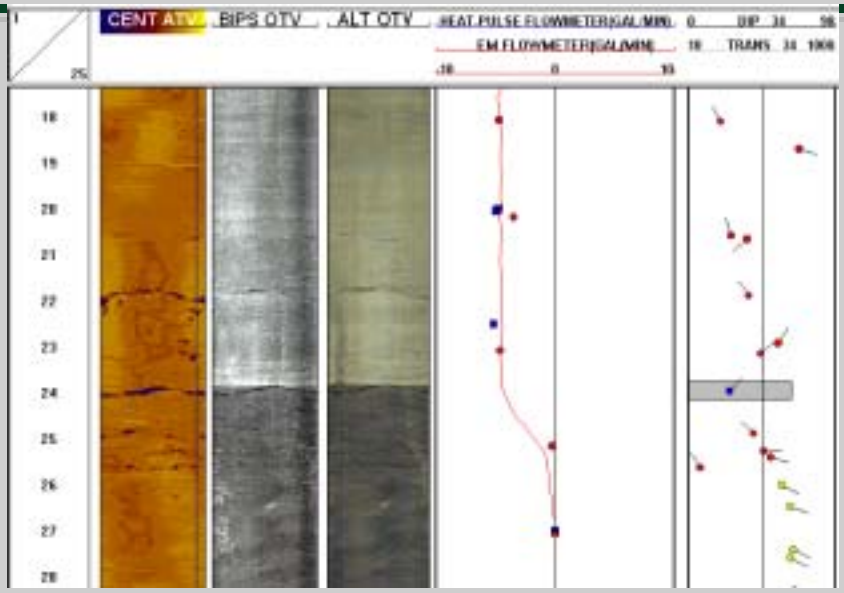
USGS, 2001

Major Transmissive Zone Identified



USGS, 2001

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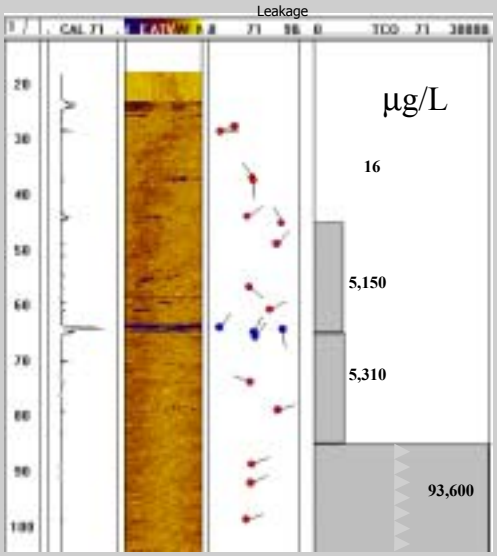
Fractures, Transmissive Zones, and Total VOCs from PACKER TESTING

MW-71



USGS, 2001

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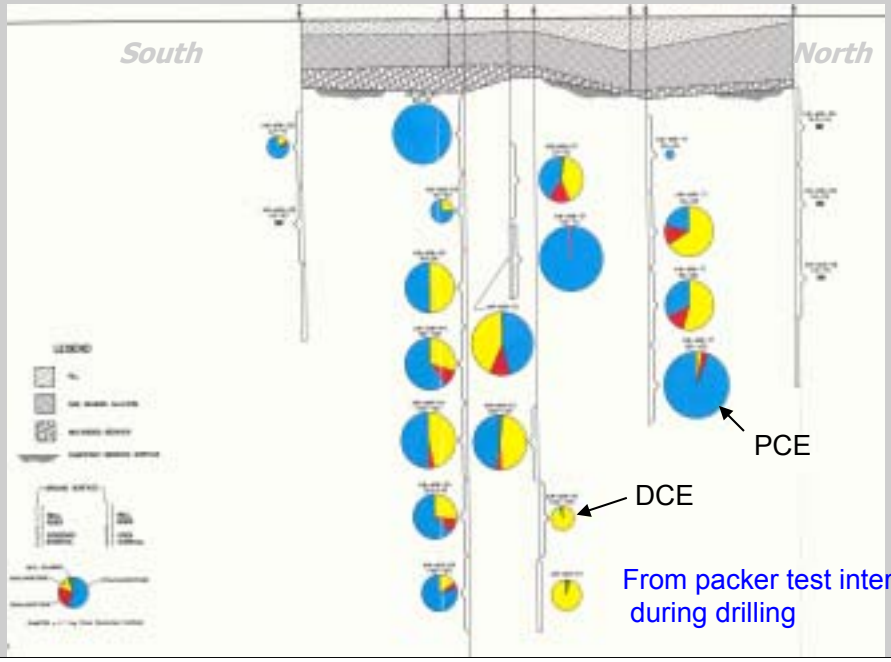
PCE and Degradation Products in Shale



From packer test intervals during drilling

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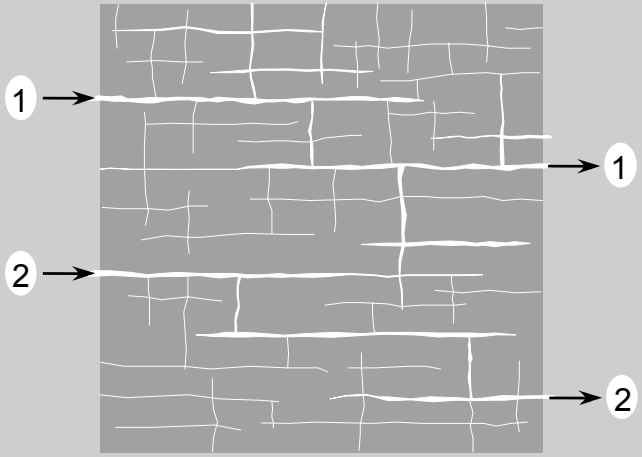
Interconnected Fracture Network with Two Major Transmissive Zones

Cross-section view



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DNAPL was Initially Distributed in Many Fractures

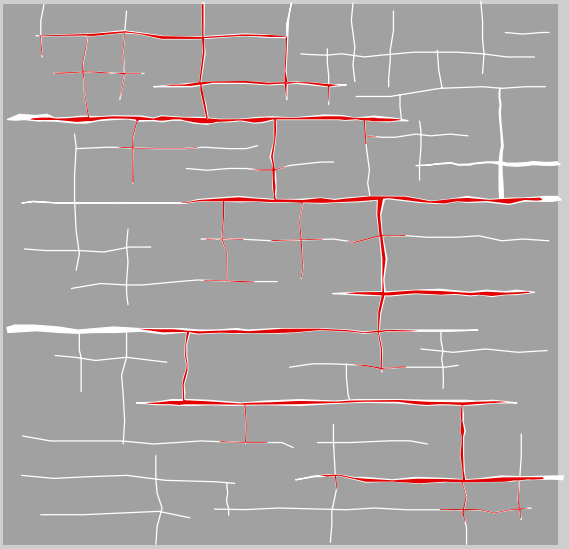

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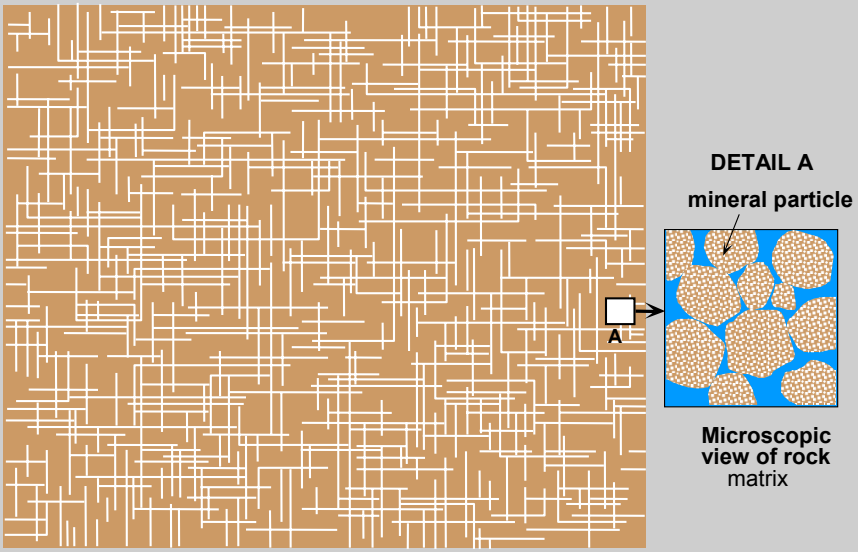
ILLUSTRATION OF MATRIX POROSITY



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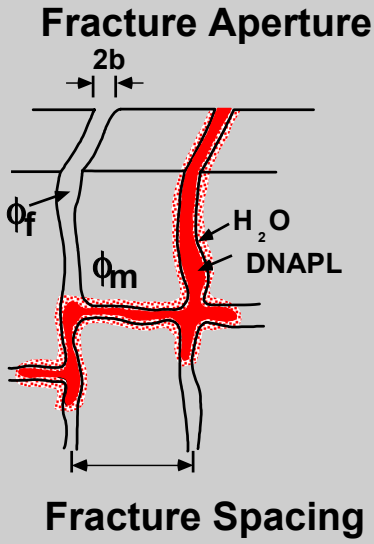
DNAPL Phase Initially Resides within Fractures



Matrix porosity is 1000 times greater than fracture porosity

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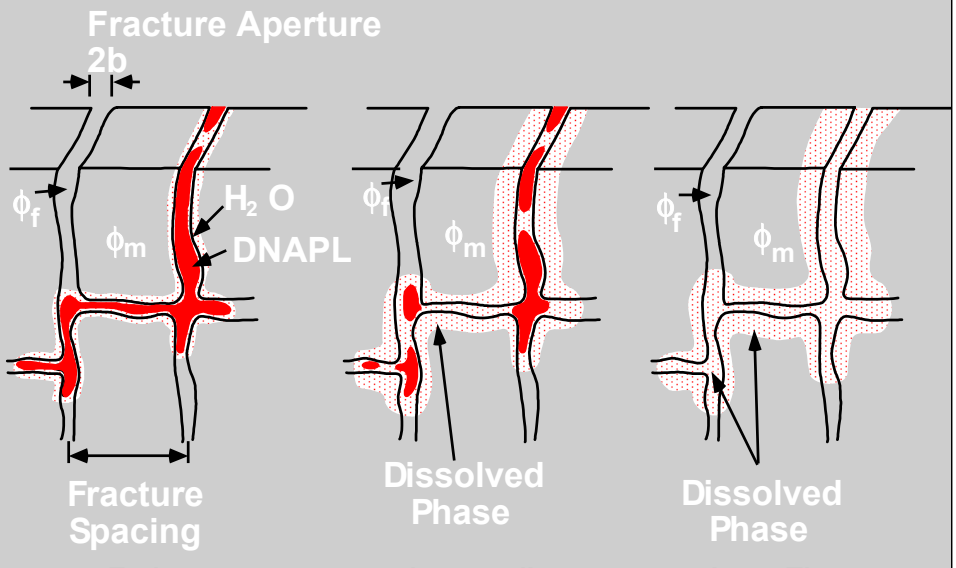
DNAPL Disappearance by Diffusion
Parker *et al.* (1994)



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Snake Hill Shale Formation

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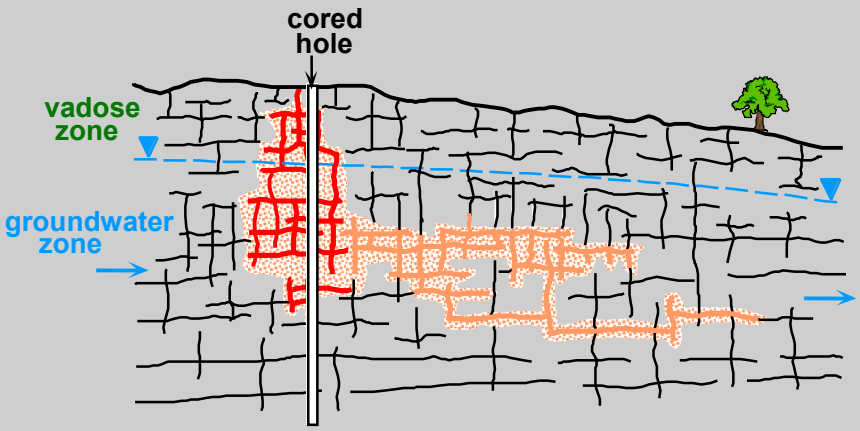
Core Hole In Source Zone



B.L. Parker, 2000

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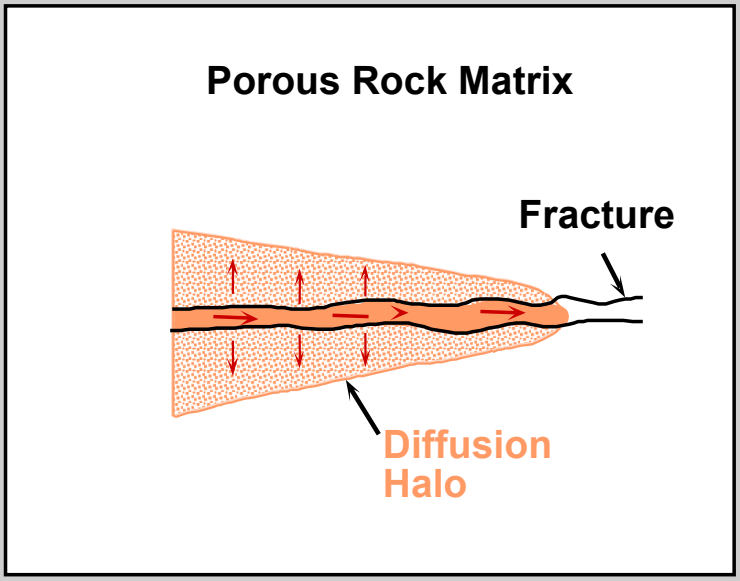
Diffusion Into Rock Matrix



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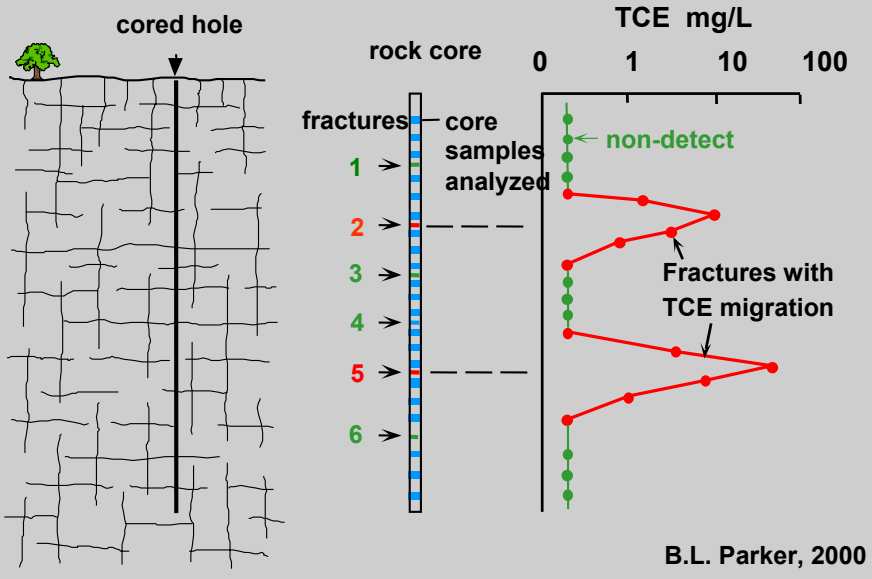
Core Sampling for Migration Pathway Identification



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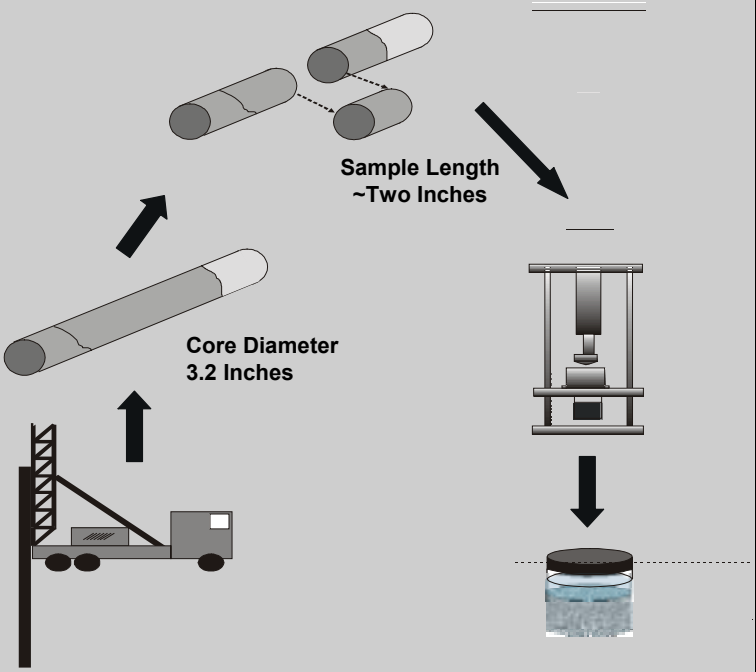
Overview of the Rock Core Method



Parker and Colleagues 1997

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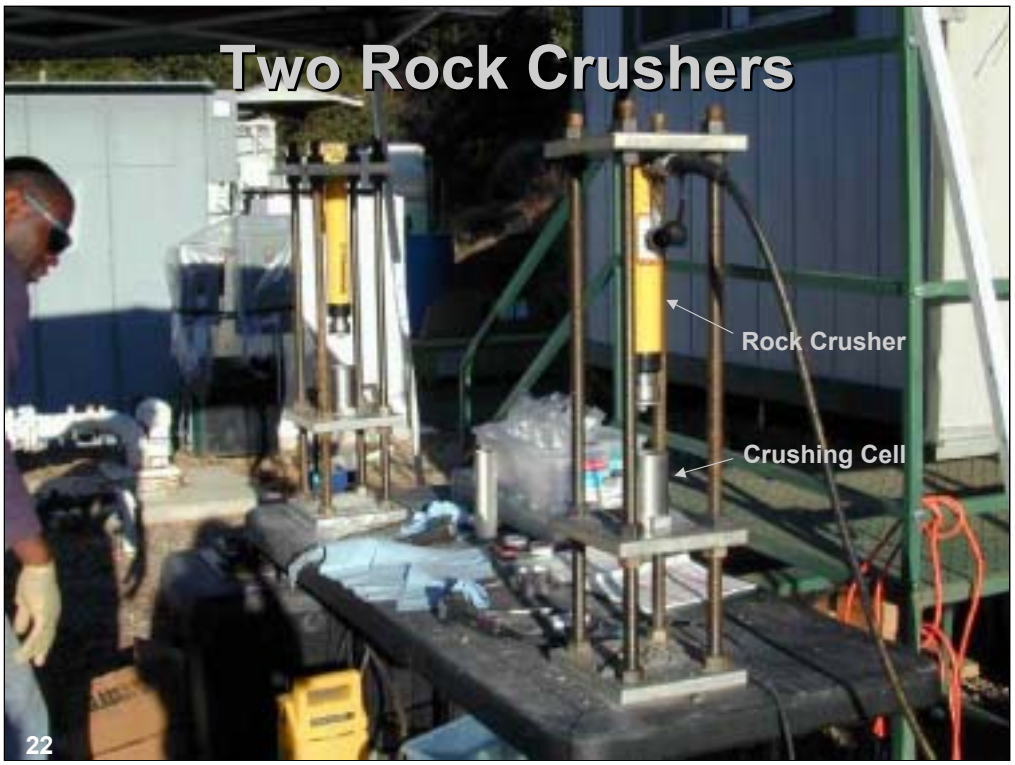
Two Rock Crushers
Rock Crusher
Crushing Cell
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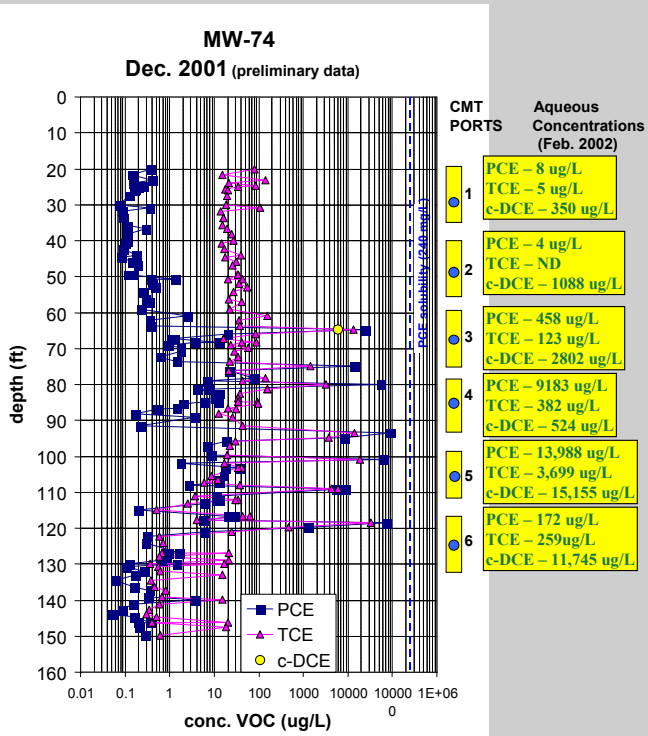
Rock Core Profile Dec 2001

Pre-$KMnO_4$ Injection



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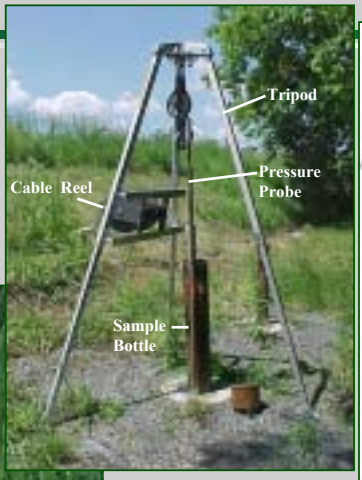
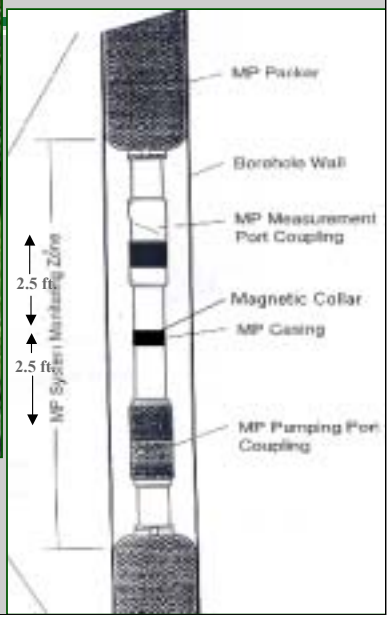
WESTBAY ® MP SYSTEM





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SOLINST CMT ® SYSTEM

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Site Conceptual Model

VOC migration occurs in a large number of interconnected fractures

Nearly all VOC mass resides in the rock matrix rather than in the fractures

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It is well established that permanganate completely destroys chlorinated ethenes

However, to do so,

it must be delivered to the contaminant mass

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Can permanganate be effective for remediating chlorinated ethenes in fractured sedimentary rock?

Important factors:

- **Delivery throughout fracture network**
- **Diffusion rates into rock matrix**
- **Oxidant Demand of Shale**

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$KMnO_4$ Injections at Watervliet

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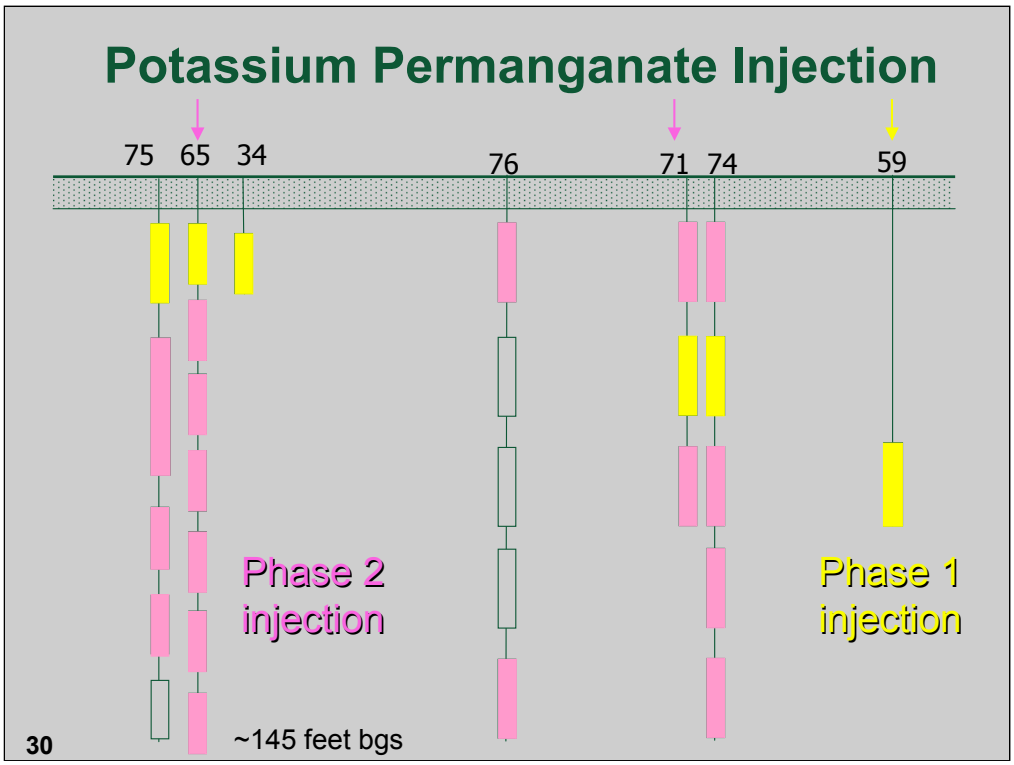
Potassium Permanganate Injection
75
65
34
76
71
74
59
Phase 2
injection
Phase 1
injection
~145 feet bgs
30

PILOT STUDY RESULTS in 2002

Treatment Approach
Permanganate

- Permanganate oxidizes chlorinated ethenes

$$\text{Solvent} + MnO_4^- \longrightarrow MnO_2(s) + Cl^- + \text{Acid}$$

- ^{13}C / ^{12}C and Chloride used to confirm destruction
- Stable chemistry in subsurface allows time for diffusion into matrix

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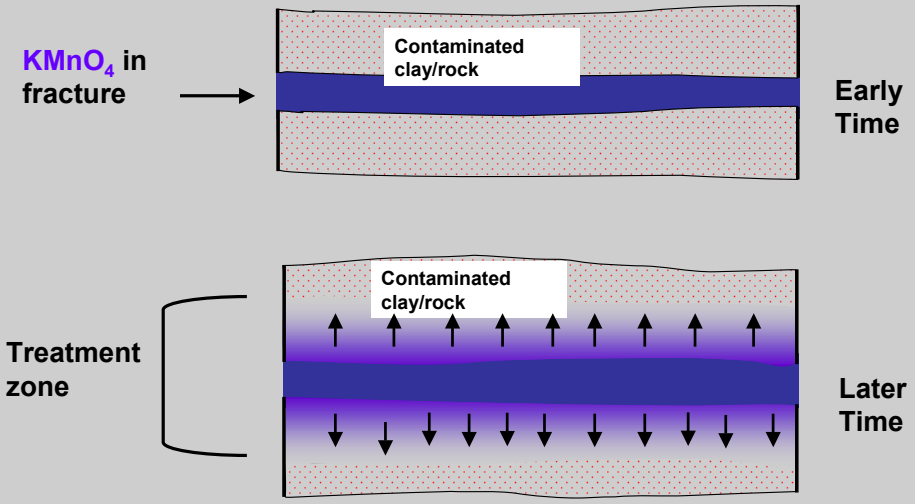
Remediation in Fractured Porous Media



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B.L. Parker, 1993

In Situ Oxidation in Fractured Porous Media

- Diffusion of both reactants occurs in opposite directions
- Readily destroys sorbed phase contaminants

Greatly reduces time scale for remediation

B.L. Parker, 1993

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Analogy to Fractured Shale

Results from Permanganate Field Tests in Marine Clay

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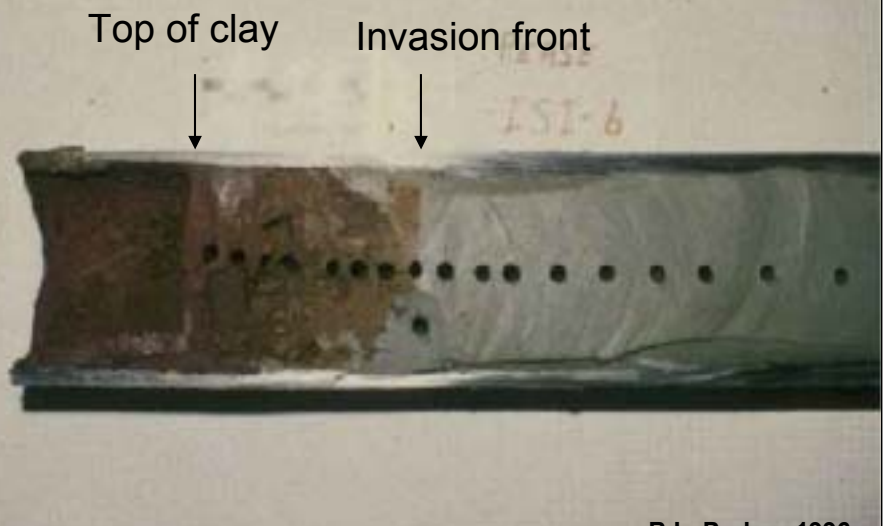
Oxidized zone shows extent of diffusion invasion and treatment by $KMnO_4$



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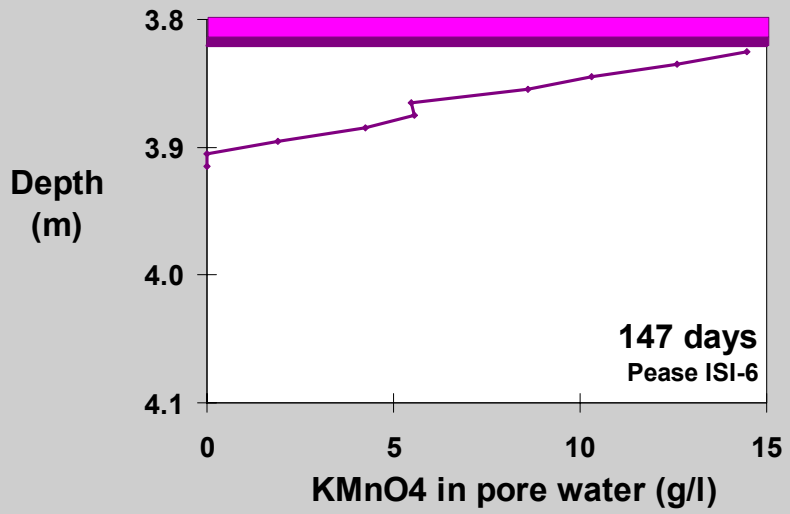
B.L. Parker, 1996

$KMnO_4$ Profile in Clay



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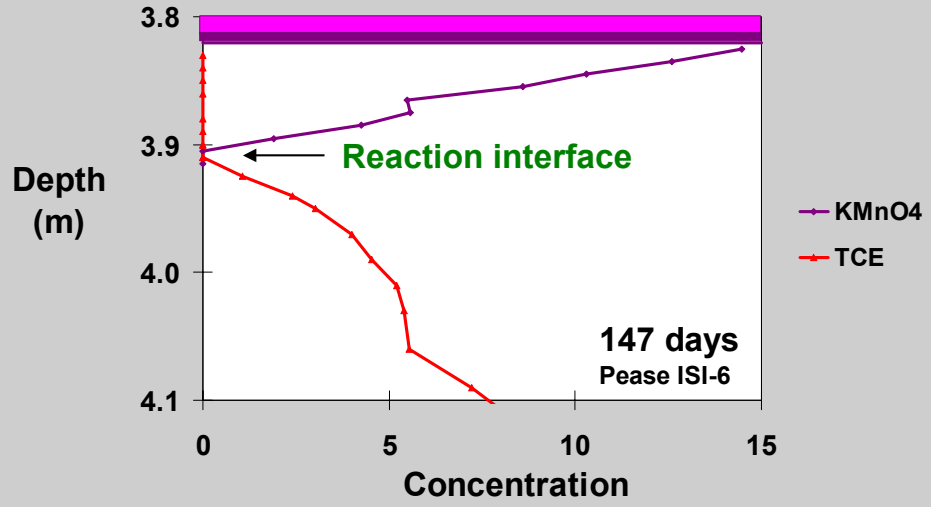
Combined Profiles in Clay



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Snake Hill Shale Formation

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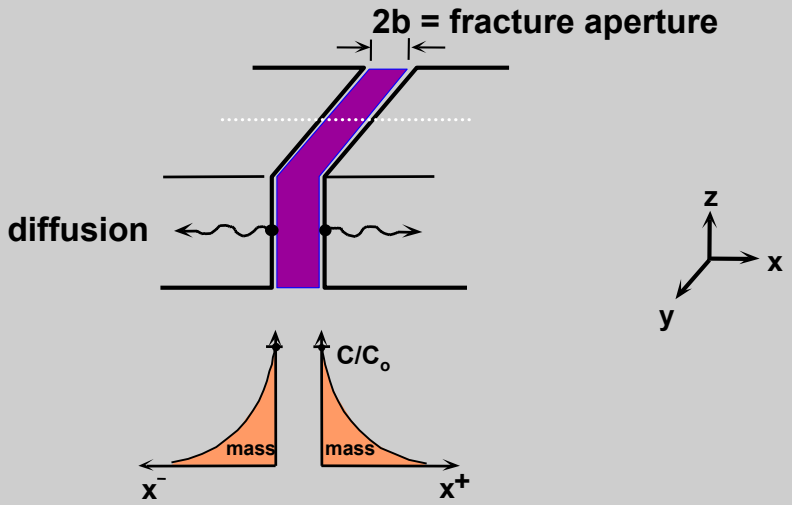
Permanganate Diffusion into Matrix from Fracture



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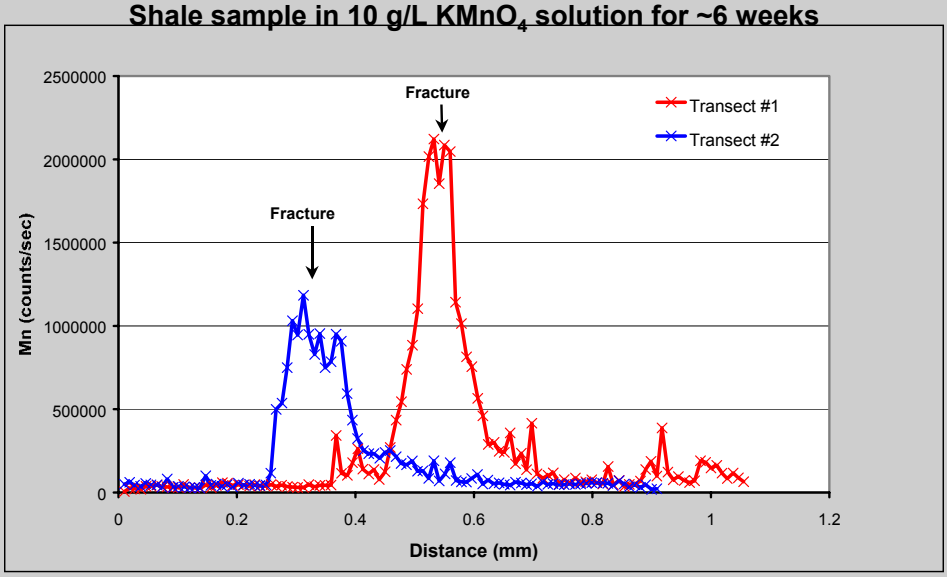
Elemental Manganese Profiles in Shale

Transects Normal to Fractures Propagating in from Surface of Rock Sample

Shale sample in 10 g/L $KMnO_4$ solution for ~6 weeks



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How long will MnO_4 take to remediate the source zone?

Answer being sought using

- ~ field data
- ~ laboratory tests
- ~ numerical models

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Preliminary MIN3P Simulations
Watervliet Arsenal

Model developed by
Dr. Ulrich Mayer (1999)

3D multicomponent reactive transport model

Now being modified for permanganate oxidation

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MIN3P Simulation

- Simulate 1D MnO_4^- invasion into shale matrix where PCE has been diffusing in for 40 years to examine rates of matrix clean-up
- <u>Parameters</u>:
  - Site-specific ϕ, D_e, f_{oc}
  - MnO_4^- R = 1
  - PCE R = 220 (estimated using f_{oc}=0.5%)
  - Source [PCE] = 150 mg/L for 40 years
  - Injection [$KMnO_4$] = 5 g/L

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Chloride Diffusion Test Cell for Rock

Golder Associates, Toronto

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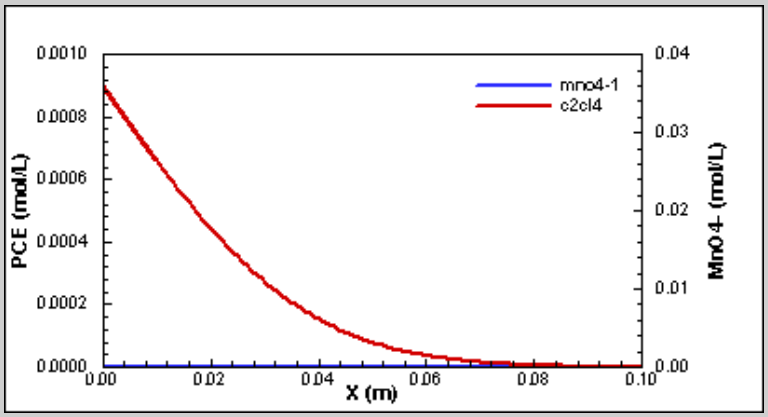
Initial Condition
40 years PCE Diffusion-In

MIN3P Model – Snake Hill Shale



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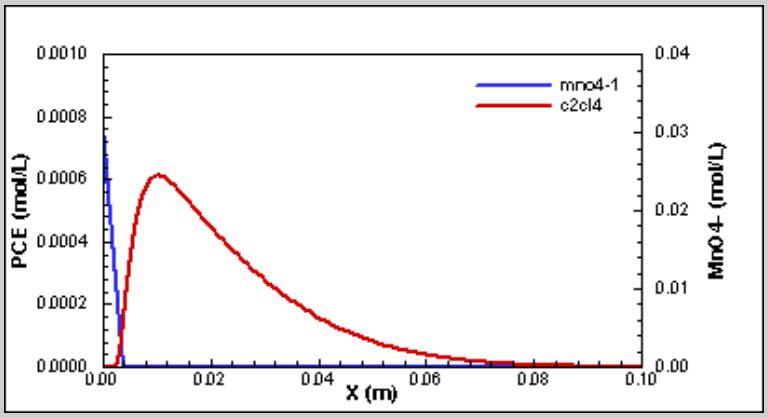
Matrix Profiles after 1 year MnO_4^- Injection

MIN3P Model – Snake Hill Shale



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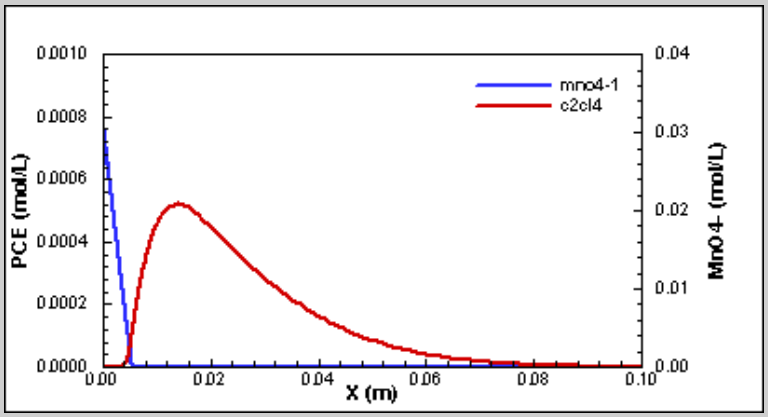
Matrix Profiles after 2 years
MnO_4^- Injection

MIN3P Model – Snake Hill Shale



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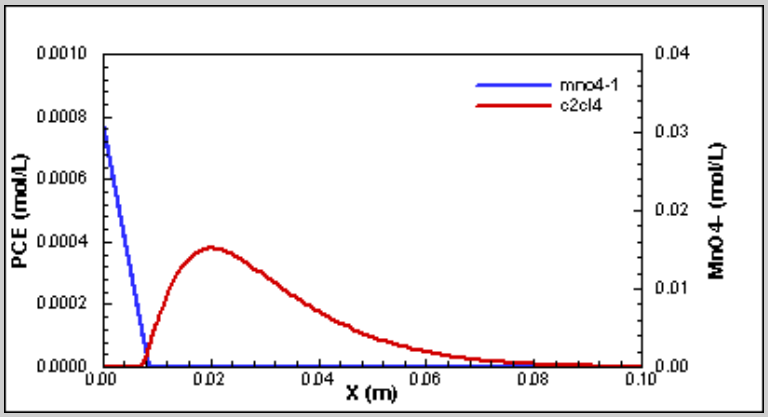
Matrix Profiles after 5 years MnO_4^- Injection

MIN3P Model – Snake Hill Shale



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Partial Mass Destruction

Greatly diminishes VOC mass flux into fracture network after permanganate is gone

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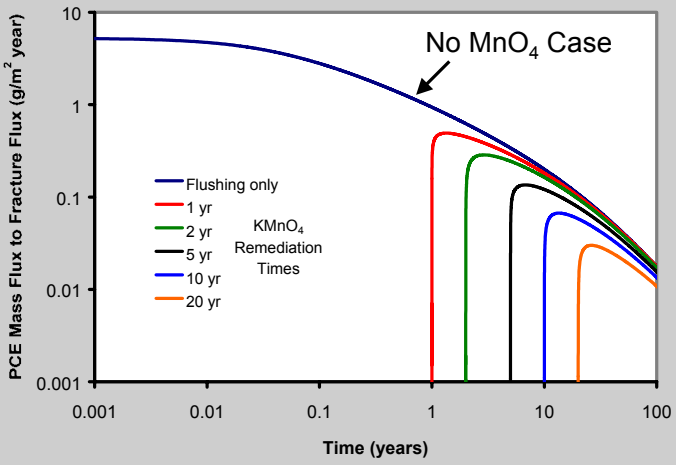
PCE flux to fracture after partial permanganate treatment

Frac3DVS Modeling Log - Log Scale



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Preliminary Conclusions

Permanganate…

- Diffuses and reacts in low K matrix
- Prevents release of mass from matrix to flowing groundwater while present in fractures
- Greatly reduces magnitude of flux from matrix even after partial treatment

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How do we know that VOCs are being destroyed ?

Chloride increases at many locations

Change in carbon isotope ratio of PCE

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ON-GOING WORK

- Rebound monitoring after pilot injections
- Permanganate invasion tests
  - Laboratory samples
  - Field cores
- Reactive transport modeling
  - Single fractures and fracture networks
- Design of full-scale system and monitoring

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Acknowledgements

Project Contributors:

- ~ Steven Chapman and Martin Guilbeault (UWaterloo)
- ~ Daria Navon and Andrew Vitolins (Malcolm Pirnie)
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- ~ JoAnn Kellogg (Watervliet Arsenal)
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The End