

# **Case Study: Permanganate Applied to VOCs in Fractured Shale**

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US Army Corps  
of Engineers  
Baltimore District

## **Research Collaborators**

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– University of New Brunswick

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– University of British Columbia

**Drs. Ramon Aravena and John Cherry**

– University of Waterloo

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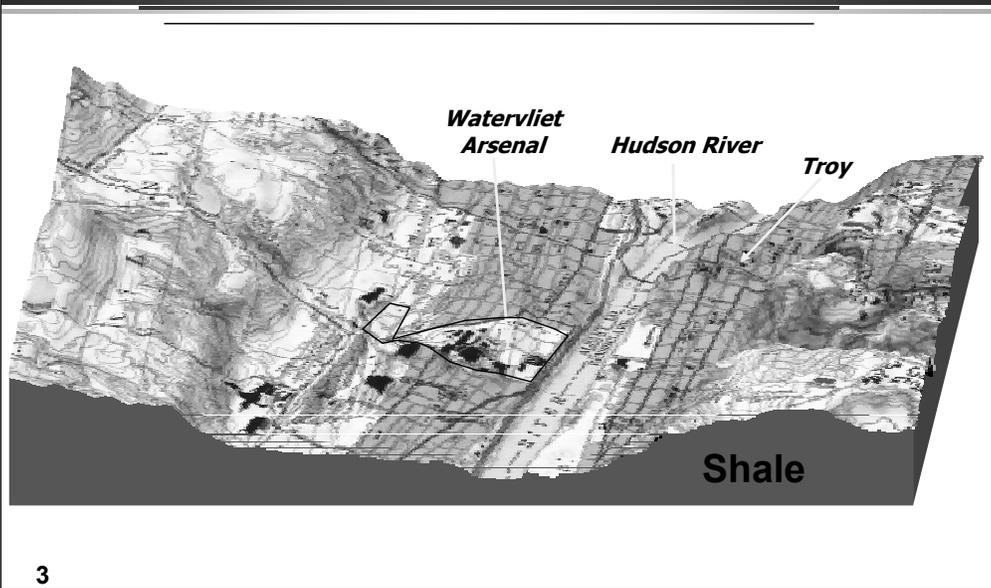
– Malcolm Pirnie, Inc

**Grant Anderson, P.G.**

– U.S. Army Corps of Engineers

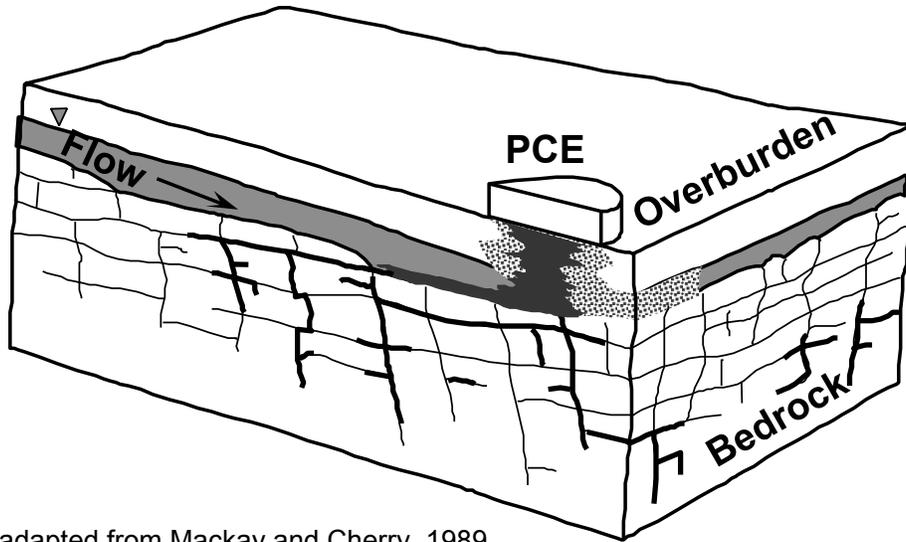
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# Watervliet Arsenal in New York State





# DNAPL Passed Through Overburden Into Shale



adapted from Mackay and Cherry, 1989

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## **The Problem**

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**Chlorinated ethenes – as high as  
150 mg/L**

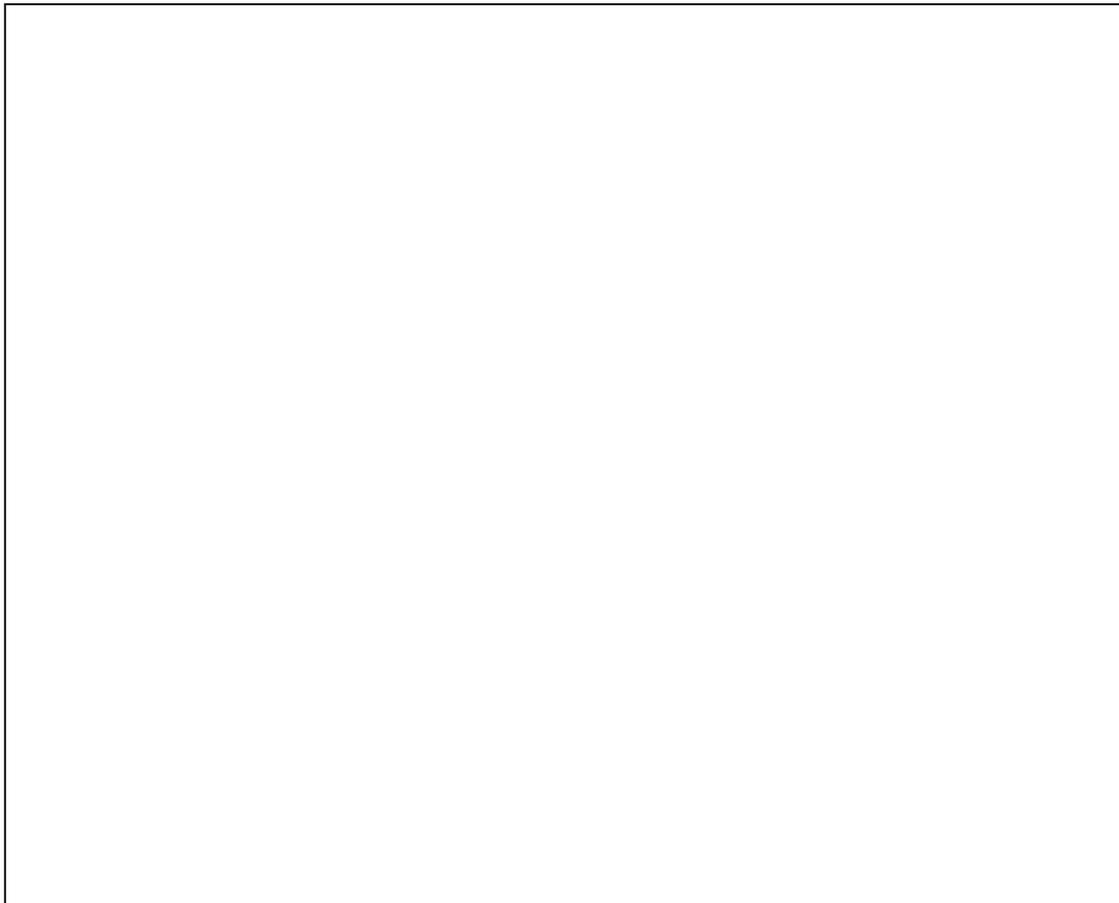
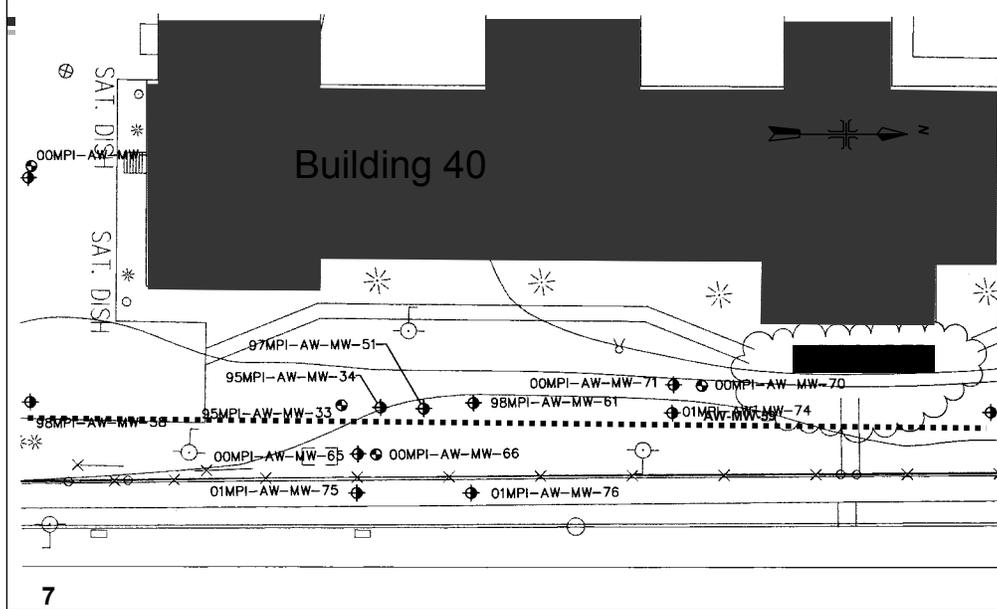
**Contamination down to 150 ft. bgs**

**All VOC mass in fractured shale**

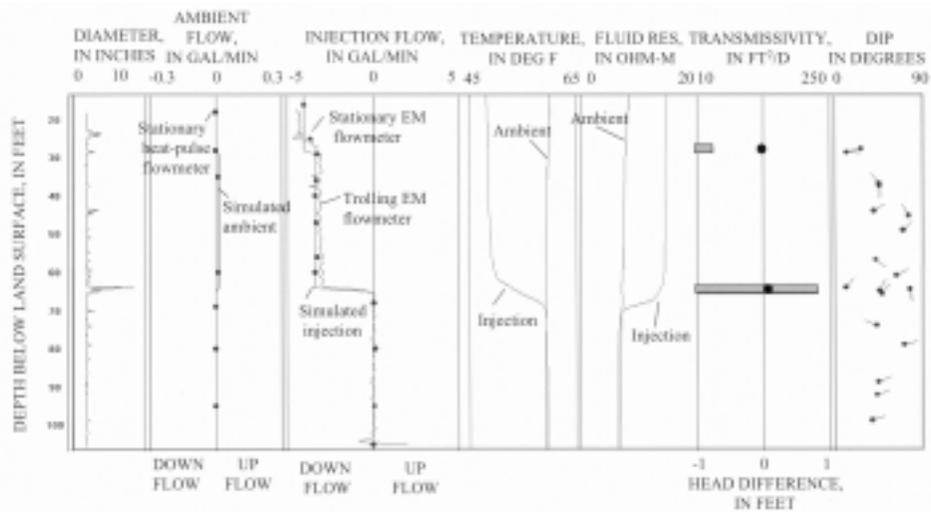
**AOC is 200 ft west of Hudson River**

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# Study Area



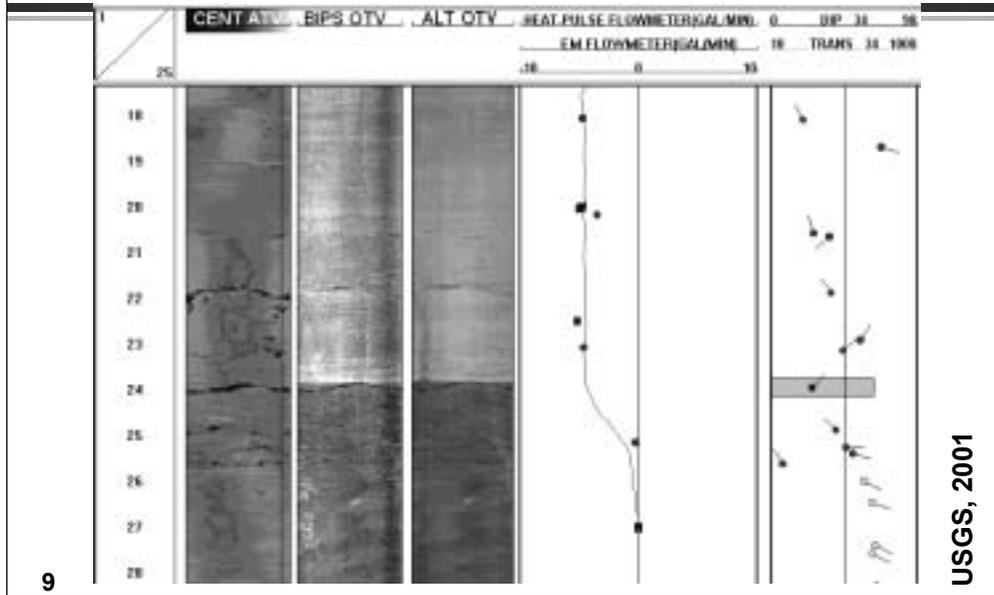
# Identification of Major Transmissive Zones Using Hydro-geophysics



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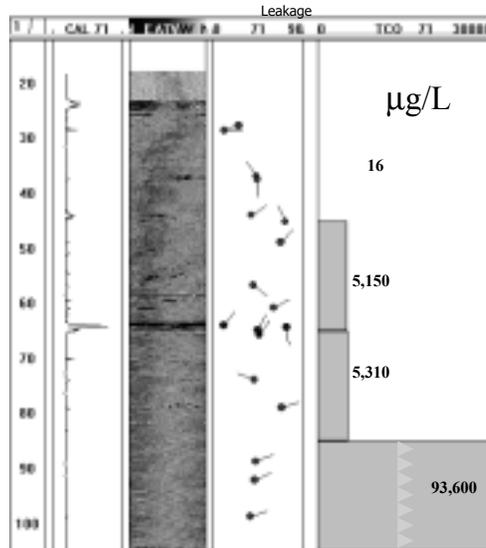
USGS, 2001

# Major Transmissive Zone Identified



# Fractures, Transmissive Zones, and Total VOCs from PACKER TESTING

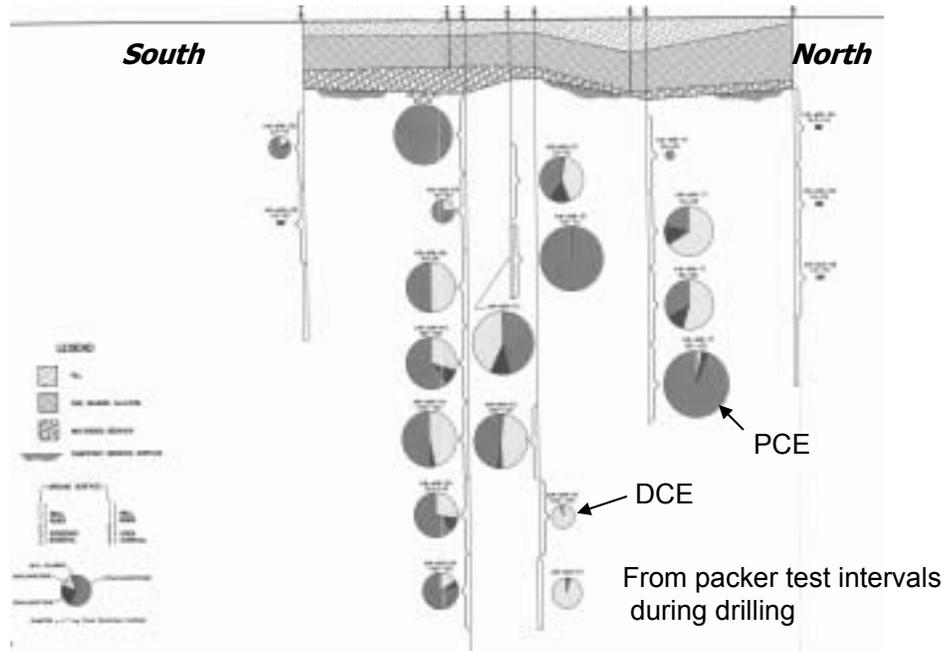
**MW-71**



USGS, 2001

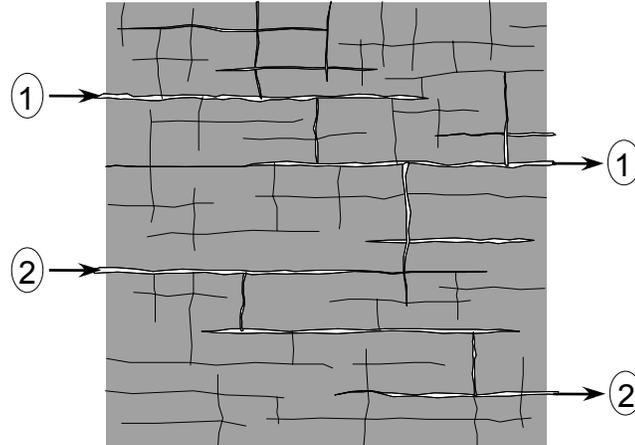
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# PCE and Degradation Products in Shale



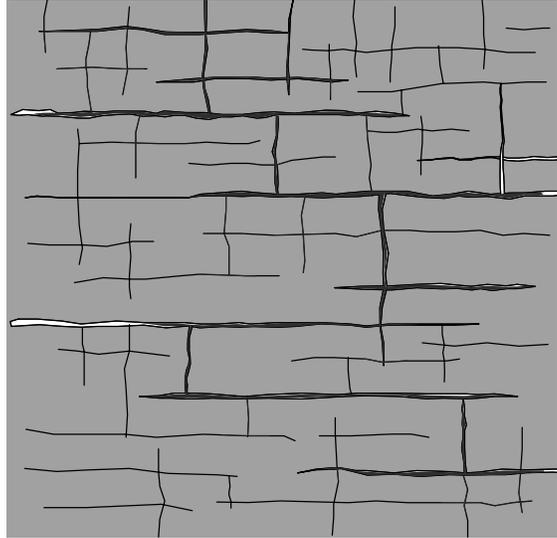
## Interconnected Fracture Network with Two Major Transmissive Zones

Cross-section view



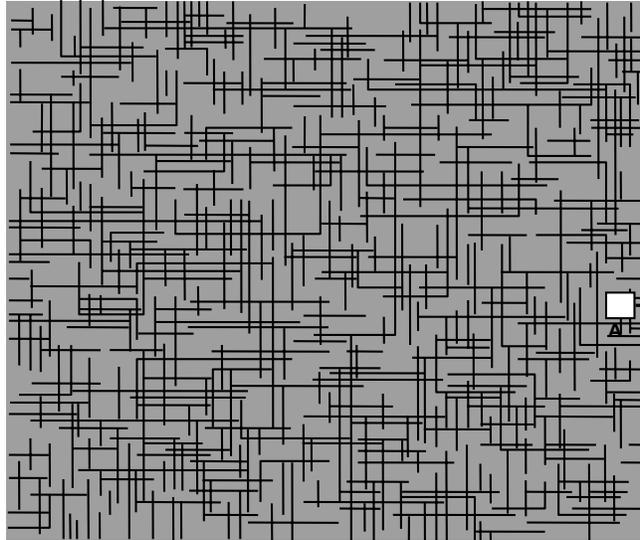
12

## DNAPL was Initially Distributed in Many Fractures

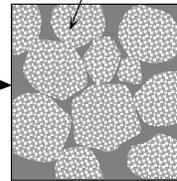


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# ILLUSTRATION OF MATRIX POROSITY



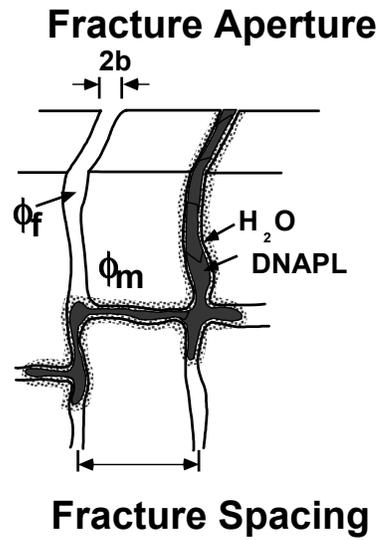
**DETAIL A**  
mineral particle



**Microscopic  
view of rock  
matrix**

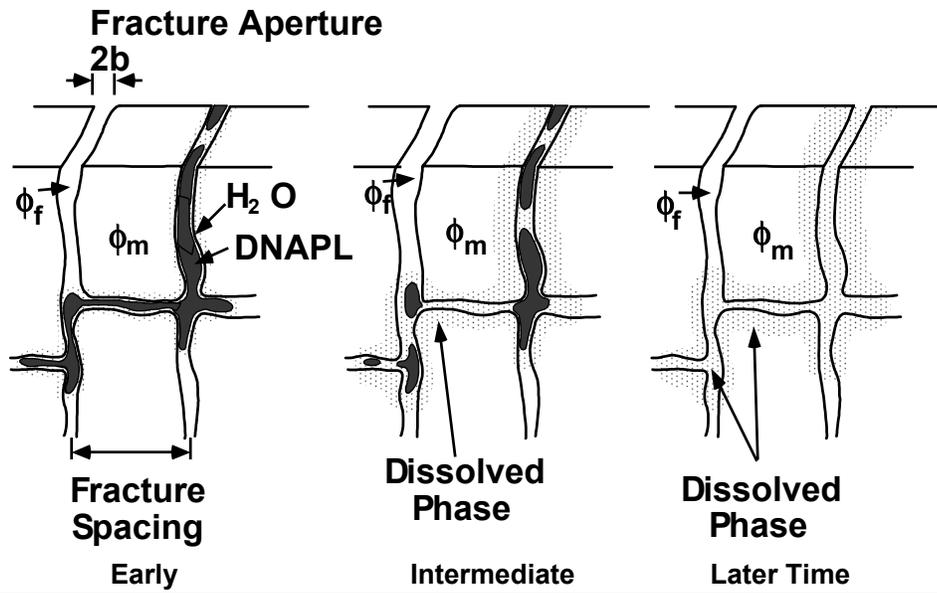
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## DNAPL Phase Initially Resides within Fractures



Matrix porosity is  
1000 times greater than  
fracture porosity

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

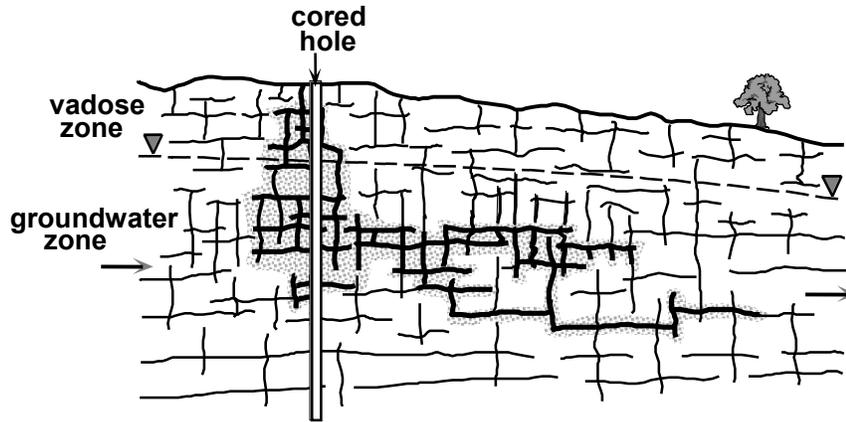


## Snake Hill Shale Formation



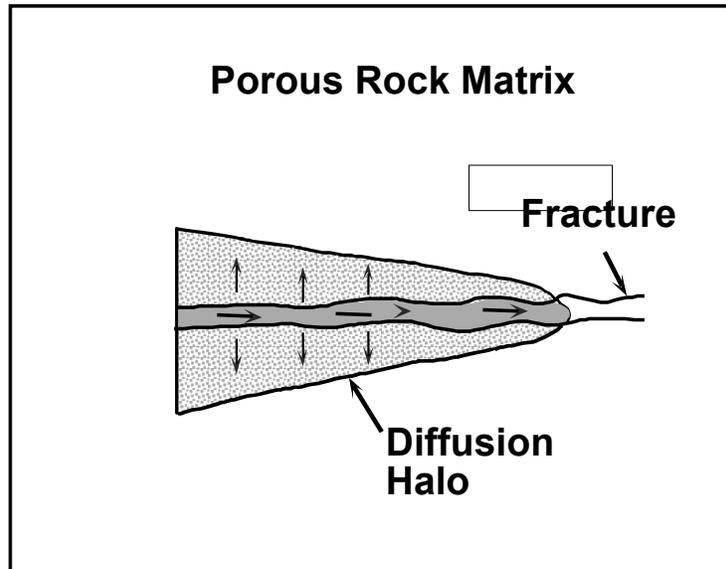
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# Core Hole In Source Zone



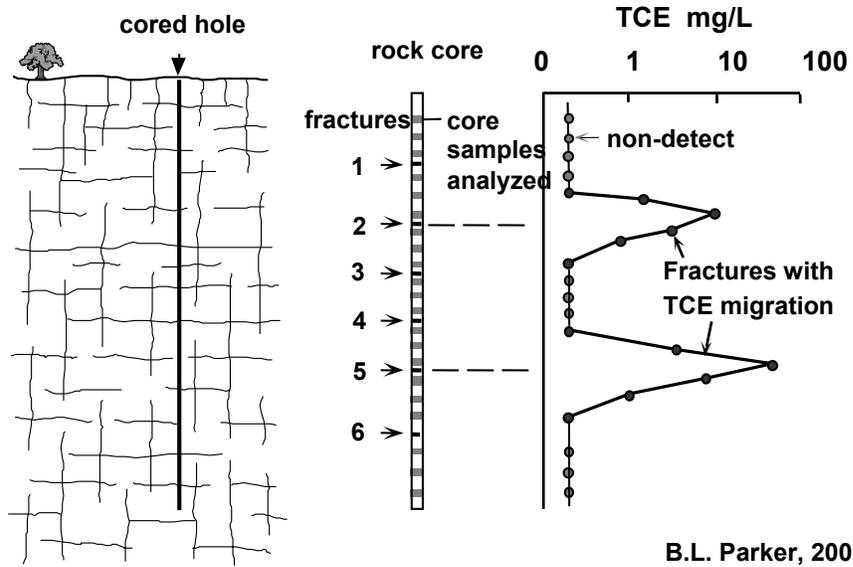
B.L. Parker, 2000

## Diffusion Into Rock Matrix



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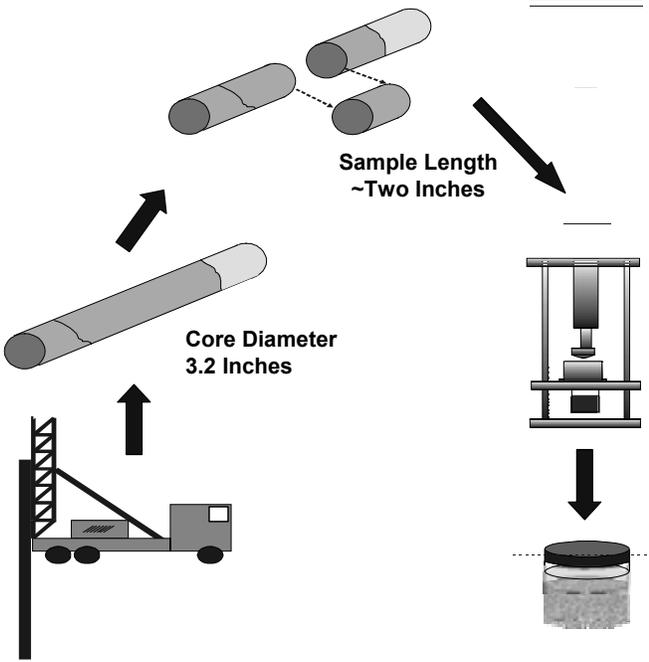
# Core Sampling for Migration Pathway Identification



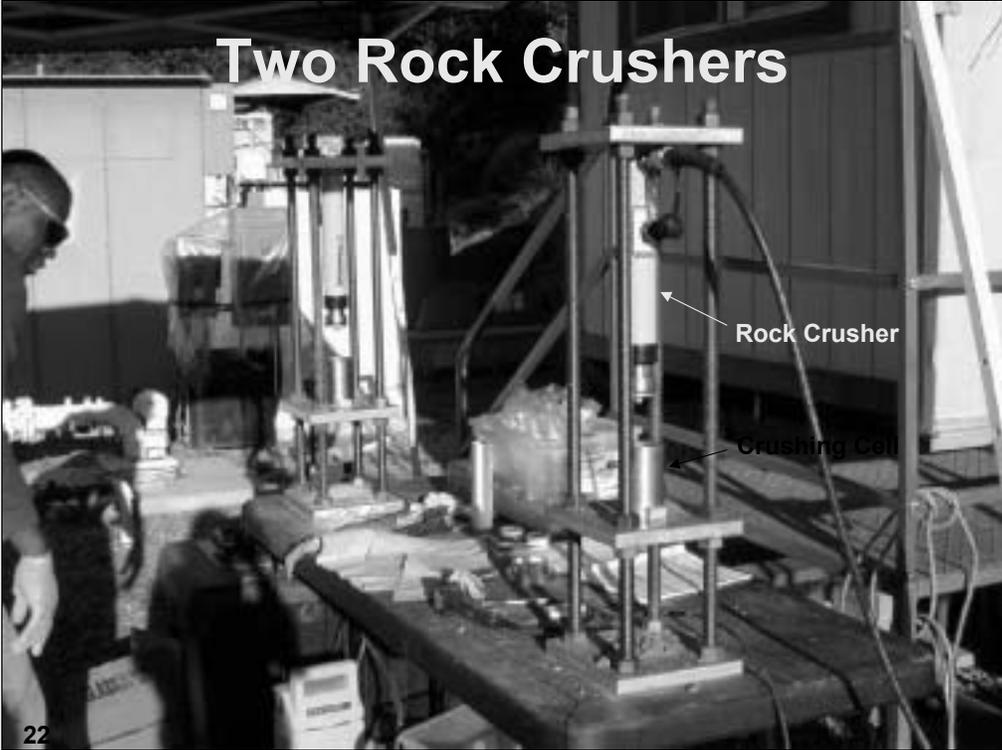
B.L. Parker, 2000

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# Overview of the Rock Core Method



# Two Rock Crushers

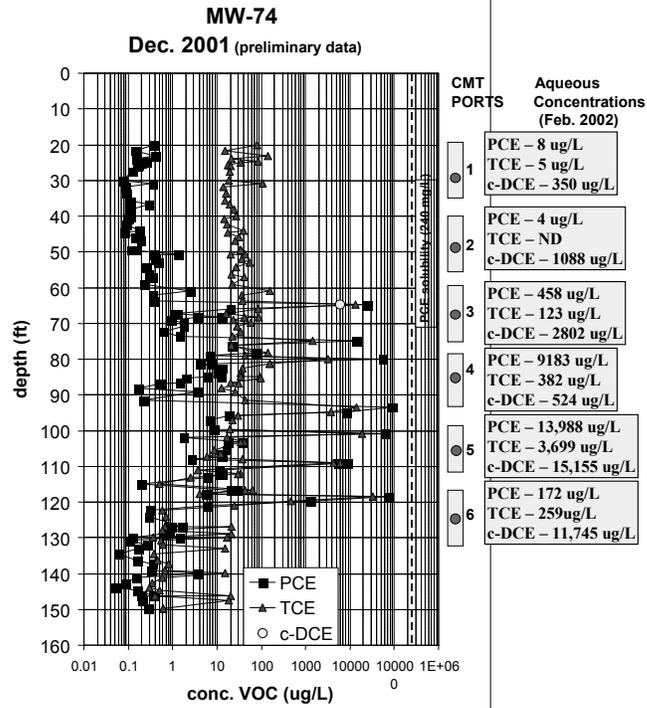


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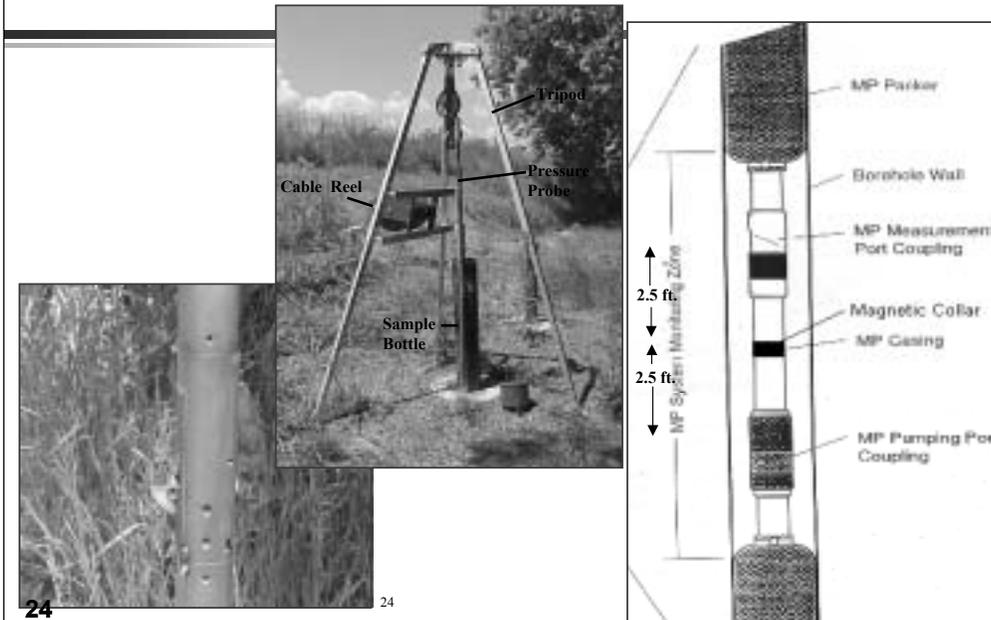
# Rock Core Profile Dec 2001

## Pre-KMnO<sub>4</sub> Injection



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# WESTBAY<sup>®</sup> MP SYSTEM



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# SOLINST CMT<sup>®</sup> SYSTEM



## **Site Conceptual Model**

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**VOC migration occurs in a large number of interconnected fractures**

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

**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**

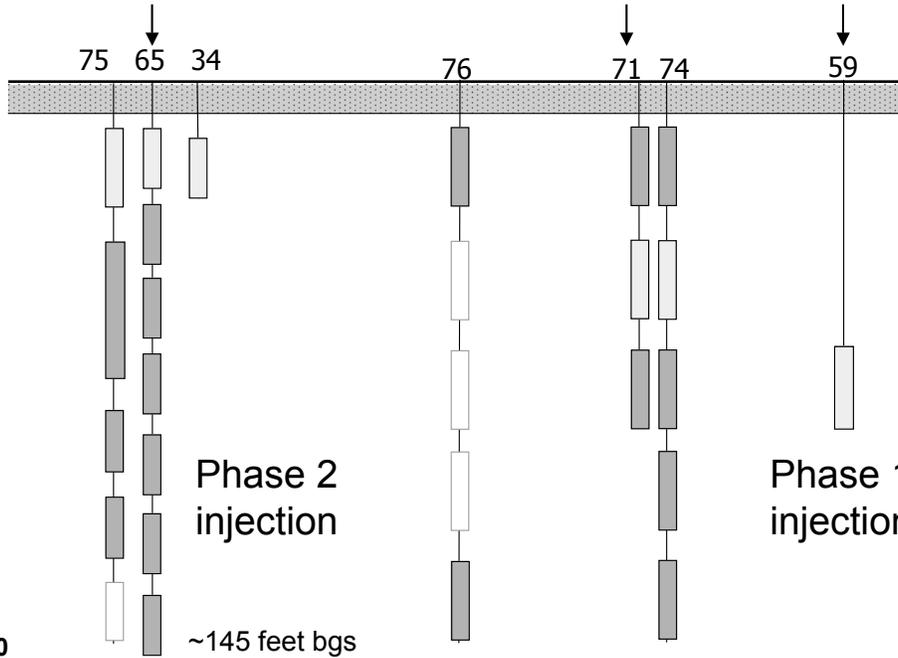
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## $\text{KMnO}_4$ Injections at Watervliet

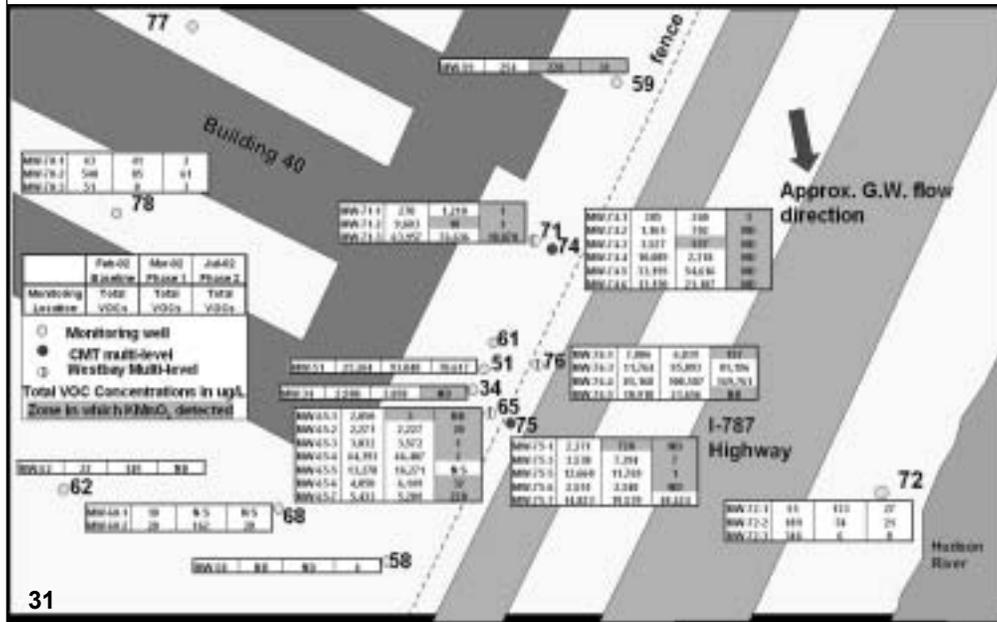


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# Potassium Permanganate Injection



# PILOT STUDY RESULTS in 2002



# Treatment Approach

## Permanganate

- Permanganate oxidizes chlorinated ethenes

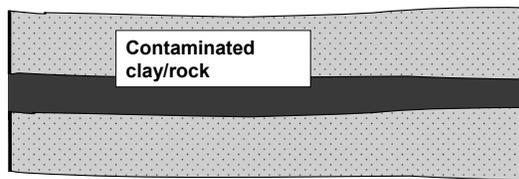


- $^{13}\text{C}$  /  $^{12}\text{C}$  and Chloride used to confirm destruction
- Stable chemistry in subsurface allows time for diffusion into matrix

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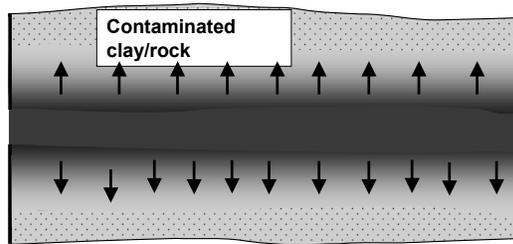
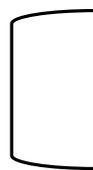
# Remediation in Fractured Porous Media

KMnO<sub>4</sub> in fracture



Early Time

Treatment zone



Later Time

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B.L. Parker, 1993

## **In Situ Oxidation in Fractured Porous Media**

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- **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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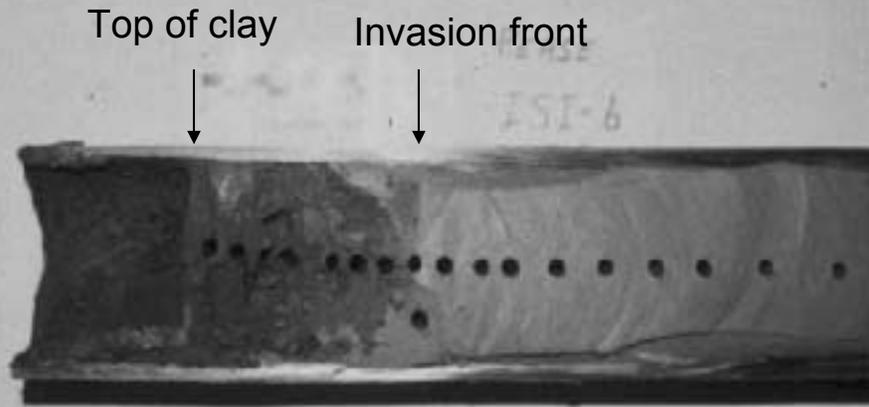
# **Analogy to Fractured Shale**

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## **Results from Permanganate Field Tests in Marine Clay**

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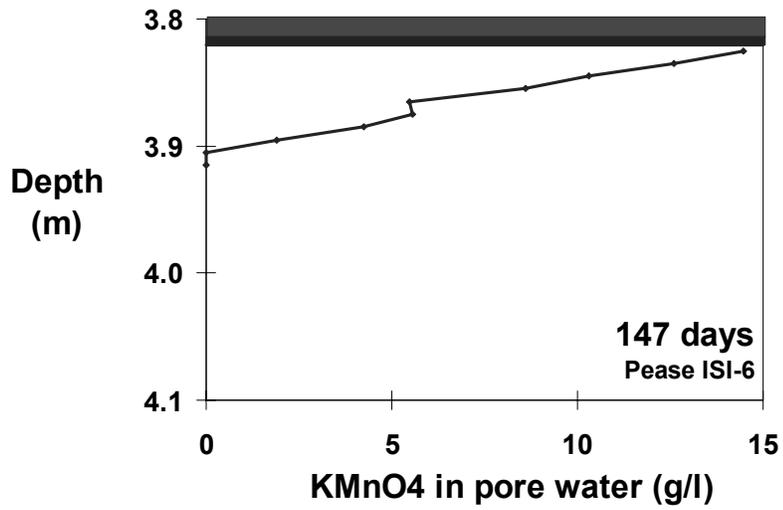
Oxidized zone shows extent of diffusion invasion and treatment by  $\text{KMnO}_4$



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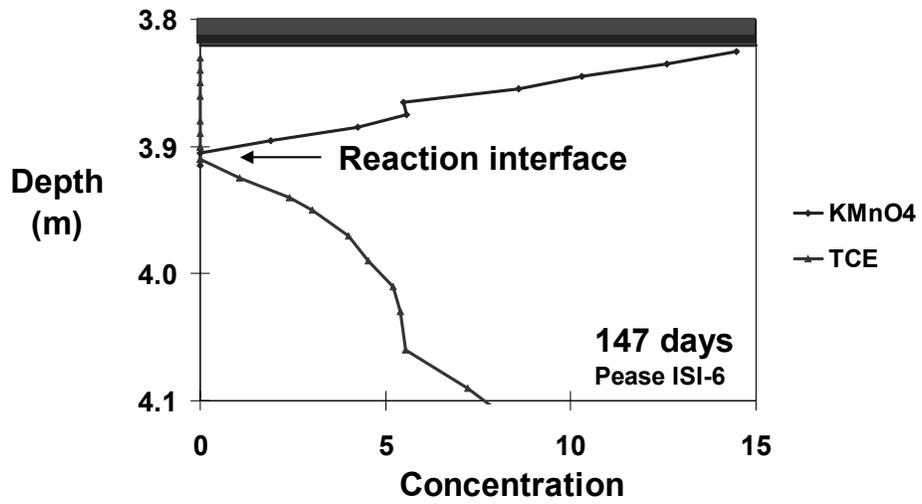
B.L. Parker, 1996

# KMnO<sub>4</sub> Profile in Clay



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# Combined Profiles in Clay



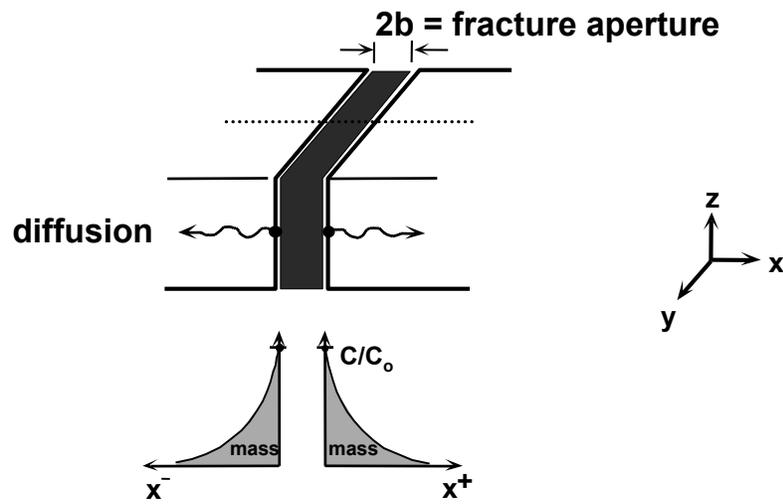
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## Snake Hill Shale Formation



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# Permanganate Diffusion into Matrix from Fracture

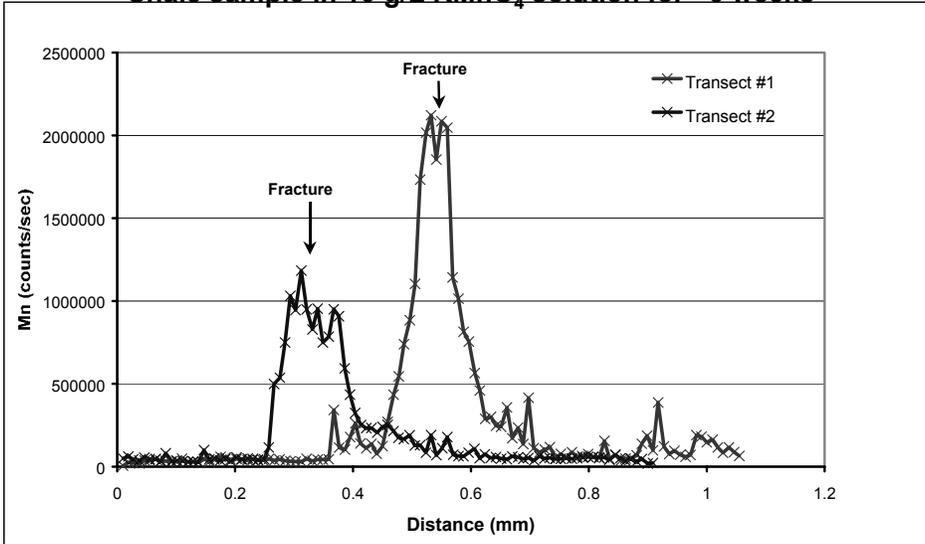


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# Elemental Manganese Profiles in Shale

## Transects Normal to Fractures Propagating in from Surface of Rock Sample

Shale sample in 10 g/L  $\text{KMnO}_4$  solution for ~6 weeks



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## How long will $\text{MnO}_4$ take to remediate the source zone?

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**Answer being sought using**

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

***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  $\text{MnO}_4^-$  invasion into shale matrix where PCE has been diffusing in for 40 years to examine rates of matrix clean-up
- Parameters:
  - Site-specific  $\phi$ ,  $D_e$ ,  $f_{oc}$
  - $\text{MnO}_4^-$   $R = 1$
  - PCE  $R = 220$  (estimated using  $f_{oc}=0.5\%$ )
  - Source [ PCE ] = 150 mg/L for 40 years
  - Injection [  $\text{KMnO}_4$  ] = 5 g/L

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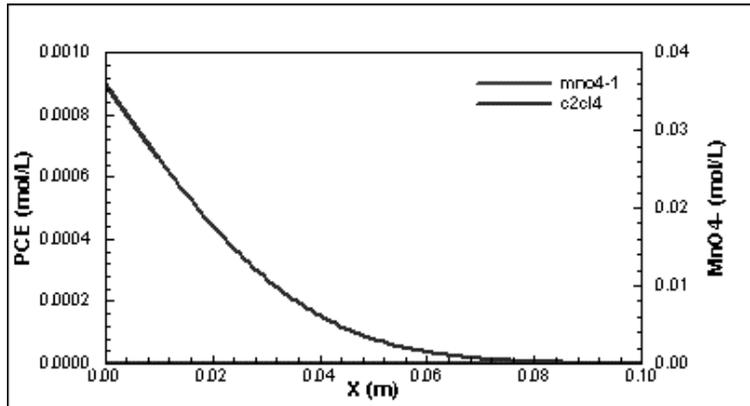
## Chloride Diffusion Test Cell for Rock



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# Initial Condition 40 years PCE Diffusion-In

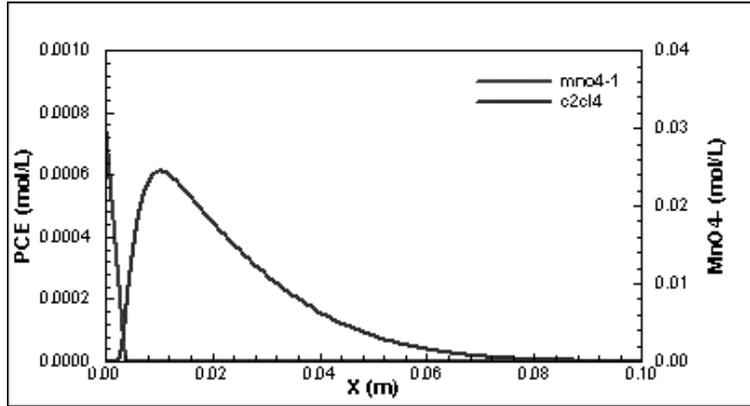
MIN3P Model – Snake Hill Shale



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# Matrix Profiles after 1 year $\text{MnO}_4^-$ Injection

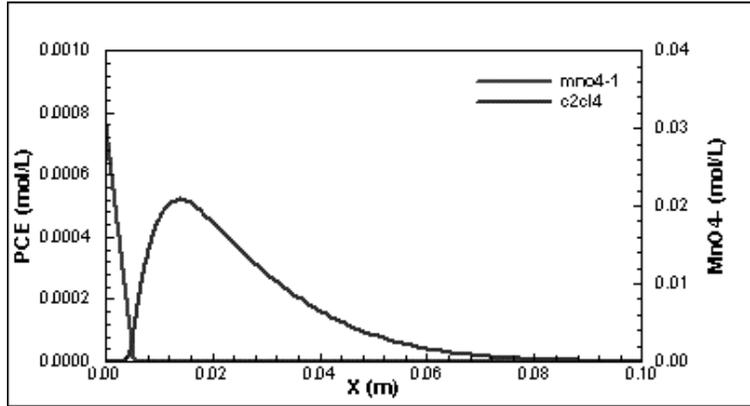
MIN3P Model – Snake Hill Shale



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# Matrix Profiles after 2 years $\text{MnO}_4^-$ Injection

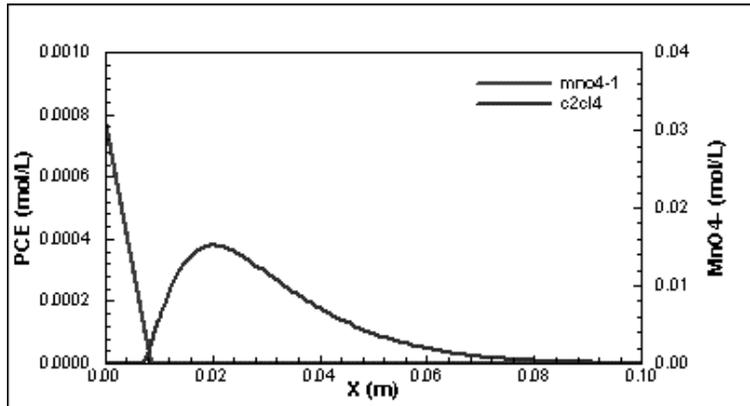
MIN3P Model – Snake Hill Shale



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# Matrix Profiles after 5 years $\text{MnO}_4^-$ Injection

MIN3P Model – Snake Hill Shale



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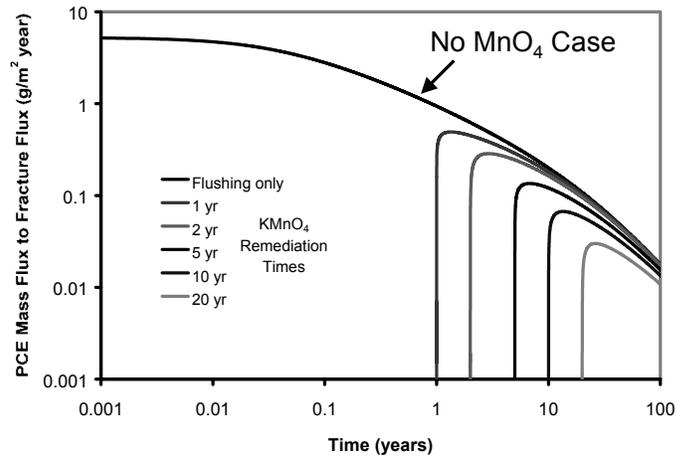
## **Partial Mass Destruction**

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

# PCE flux to fracture after partial permanganate treatment

Frac3DVS Modeling Log - Log Scale



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## **Preliminary Conclusions**

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### **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 ?**

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**Chloride increases at many locations**

**Change in carbon isotope ratio of PCE**

# **ON-GOING WORK**

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**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

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## **Project Contributors:**

- ~ Steven Chapman and Martin Guilbeault (UWaterloo)
- ~ Daria Navon and Andrew Vitolins (Malcolm Pirnie)
- ~ Stephen Wood (U.S. Army Corps of Engineers)
- ~ JoAnn Kellogg (Watervliet Arsenal)
- ~ John Williams and Fred Paillet (U.S.G.S)

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- ~ U.S. Army Corps of Engineers
- ~ Solvents-In-Groundwater Research Program

**The End**