Developing a CSM to Inform Application of Bioremediation in Fractured Rock

Claire Tiedeman, *US Geological Survey*

Co-Authors:
Allen Shapiro, Dan Goode, Paul Hsieh,
Tom Imbrigiotta, Pierre Lacombe,
US Geological Survey

Federal Remediation Technologies Roundtable Fall 2019 Meeting
US Geological Survey, Reston, Virginia
November 13, 2019

Acknowledgements

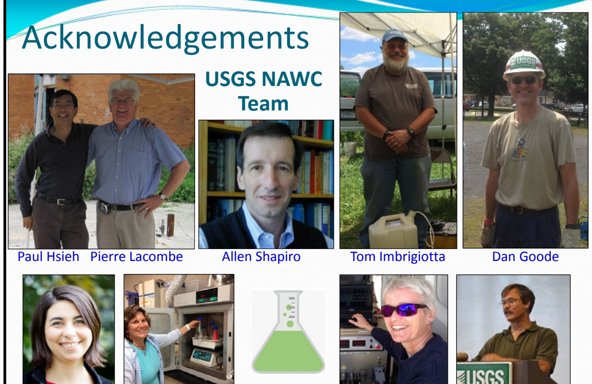
USGS science for a changing world

Toxic Substances Hydrology Program
New Jersey Water Science Center
Earth System Processes Division
National Innovation Center

DoD EPA DOE SERDP Strategic Environmental Research and Development Program

Acknowledgements

USGS NAWC Team

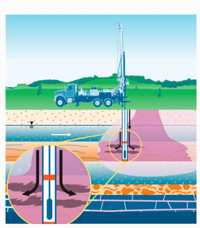


Outline

- Motivation: Importance of Hydrogeologic Conceptual Site Model to In-Situ Remediation
- Former Naval Air Warfare Center (NAWC) Site
- Development and Evolution of CSM to Inform Bioremediation Design and Expectations
- Bioremediation Results
- Summary

In-Situ Remediation of Fractured Rocks: Importance of Hydrogeologic CSM

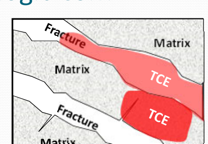
- In-situ remediation typically involves injection of amendments to stimulate biological or chemical contaminant degradation and transformation processes.
- **Distribution of hydraulic properties** controls groundwater fluxes and the spread of amendments during and after injection.



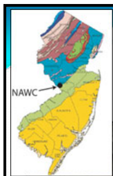
https://www.itrcweb.org/Team/Public?teamID=80

In-Situ Remediation of Fractured Rocks: Importance of Hydrogeologic CSM

- Understanding the hydrogeology is thus critical for designing injection strategies that spread amendments to locations of contamination in fractures and the rock matrix.
- While amendments might not enter the rock matrix, enhanced degradation in adjacent fractures leads to enhanced diffusion out of matrix.



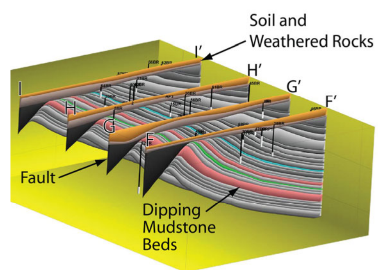
Former Naval Air Warfare Center (NAWC) West Trenton, New Jersey



- Focus site for USGS research on contaminant fate, transport, remediation under Toxic Substances Hydrology Program, 2005-2018.
- Dipping fractured sedimentary rocks.
- Groundwater highly contaminated with trichloroethene (TCE) and its degradation products DCE and vinyl chloride.

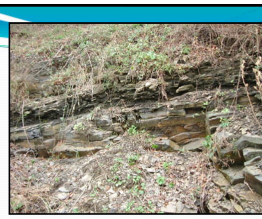
Geologic Framework

- Lockatong Formation of Newark Basin.
- Competent dipping mudstone beds overlain by weathered rocks & soil/saprolite.
- Individual mudstone beds mapped across NAWC site.
- Dominant flow paths along bedding-plane-parting fractures.

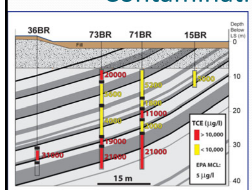


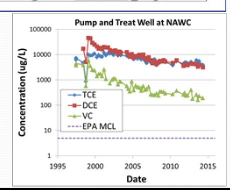
Highly weathered rock

Competent mudstones: fissile, laminated, massive



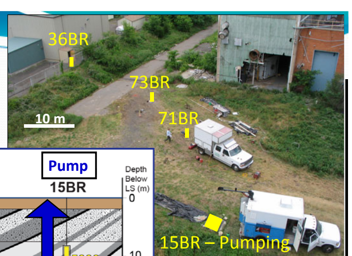
Contamination in NAWC Rocks

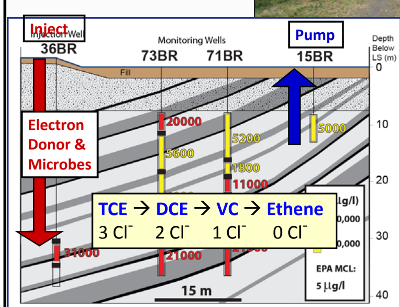




- Extremely high concentrations of TCE and DCE: Orders of magnitude above U.S. EPA standards.
- Extremely persistent: Contaminant concentrations remain high despite 20+ years of pump & treat.

Bioremediation Area





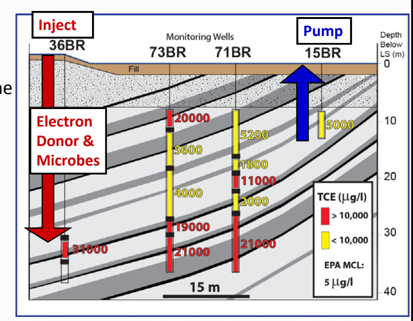
Overall objective:

Improve understanding of controls on bioremediation effectiveness in fractured rocks.

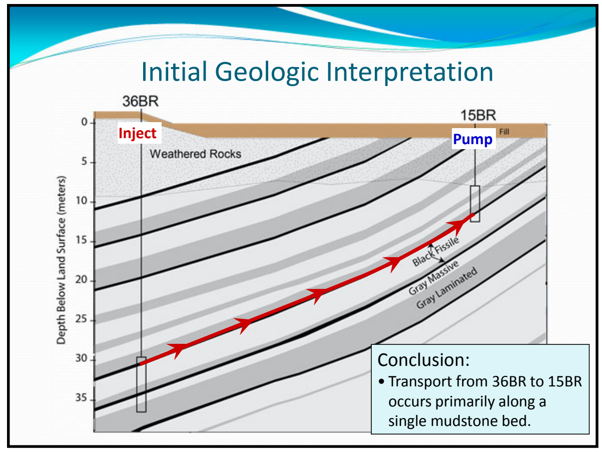
Bioremediation Design and Expectations

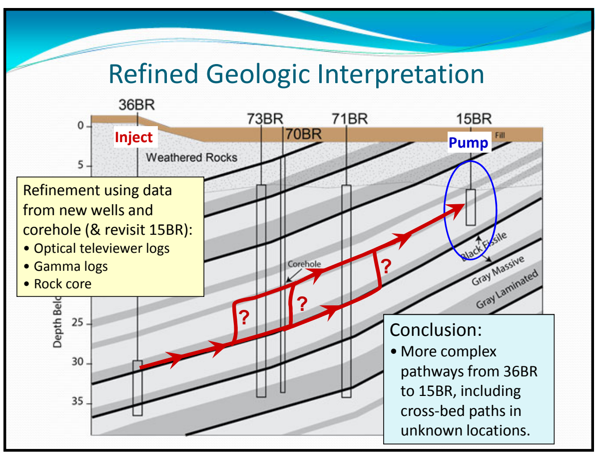
Questions related to hydrogeology:

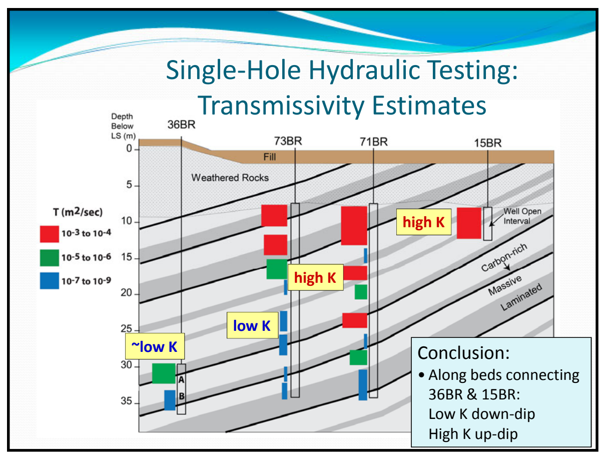
- Amendment volume to inject?
- Pumping rate at extraction well?
- Where to expect treatment?

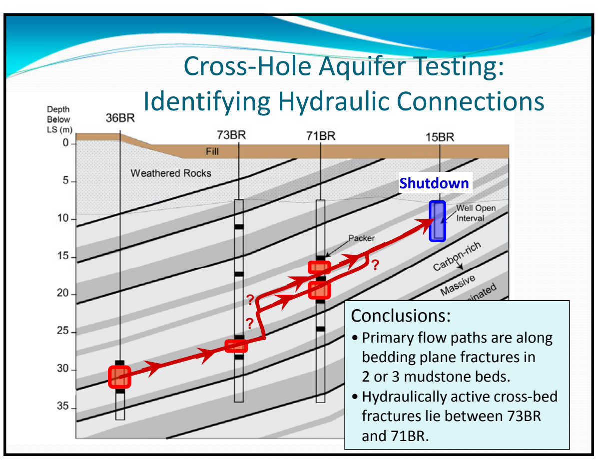


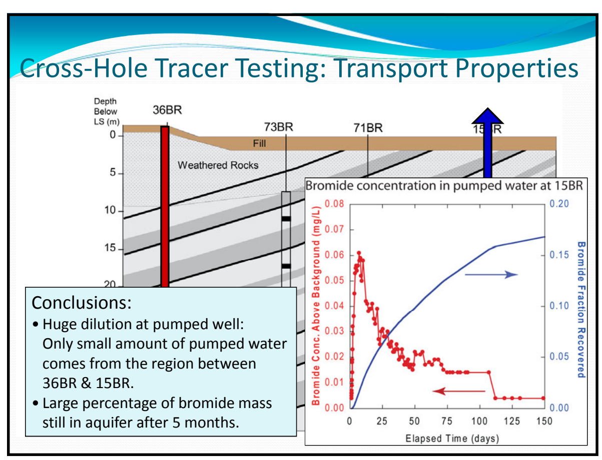

Hydrogeologic Investigation to Guide Bioremediation Design
Geologic interpretation
Single- & cross-hole hydraulic tests
Cross-hole tracer test
Flow & transport modeling
36BR - Injection
73BR
71BR
10 m
15BR – Pumping
Results will be shown along transect between 36BR and 15BR. In reality, flow and transport are 3D.


Initial Geologic Interpretation
36BR
15BR
Inject
Pump
Fill
Weathered Rocks
Depth Below Land Surface (meters)
0
5
10
15
20
25
30
35
Black Fissile
Gray Massive
Gray Laminated
Conclusion:
• Transport from 36BR to 15BR occurs primarily along a single mudstone bed.

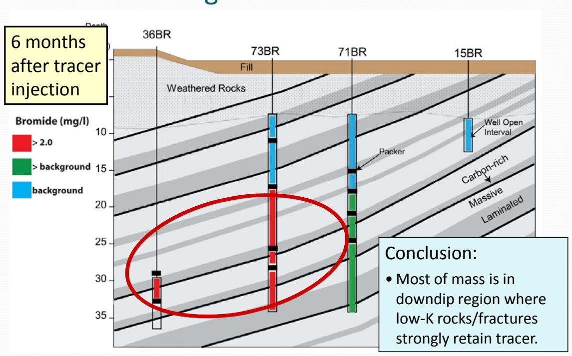

Refined Geologic Interpretation
36BR
73BR
70BR
71BR
15BR
Inject
Pump
Fill
Weathered Rocks
Refinement using data from new wells and corehole (& revisit 15BR):
• Optical televiewer logs
• Gamma logs
• Rock core
Corehole
Black Fissile
Gray Massive
Gray Laminated
Conclusion:
• More complex pathways from 36BR to 15BR, including cross-bed paths in unknown locations.


Single-Hole Hydraulic Testing: Transmissivity Estimates
Depth Below LS (m)
36BR
73BR
71BR
15BR
Fill
Weathered Rocks
T (m2/sec)
10-3 to 10-4
10-5 to 10-6
10-7 to 10-9
high K
Well Open Interval
high K
low K
~low K
Carbon-rich
Massive
Laminated
Conclusion:
• Along beds connecting 36BR & 15BR:
Low K down-dip
High K up-dip


Cross-Hole Aquifer Testing: Identifying Hydraulic Connections
Depth Below LS (m)
36BR
73BR
71BR
15BR
Fill
Weathered Rocks
Shutdown
Well Open Interval
Packer
Carbon-rich
Massive
Conclusions:
• Primary flow paths are along bedding plane fractures in 2 or 3 mudstone beds.
• Hydraulically active cross-bed fractures lie between 73BR and 71BR.

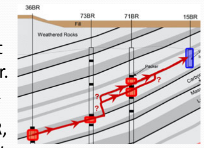

Cross-Hole Tracer Testing: Transport Properties
Depth Below LS (m)
36BR
73BR
71BR
15BR
Fill
Weathered Rocks
Bromide concentration in pumped water at 15BR
Bromide Conc. Above Background (mg/L)
Bromide Fraction Recovered
Elapsed Time (days)
Conclusions:
• Huge dilution at pumped well: Only small amount of pumped water comes from the region between 36BR & 15BR.
• Large percentage of bromide mass still in aquifer after 5 months.

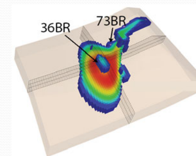
Strong Tracer Retention



Further Advancing the CSM: Flow and Transport Modeling

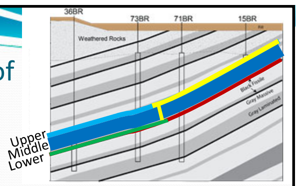
- Field characterization: *Qualitative* info about flow and transport paths and tracer behavior.
- No info about distribution and magnitude of groundwater fluxes between 36BR and 15BR, which *strongly control amendment transport*.
- Flow modeling provides fluxes.
- Bromide transport modeling uses these fluxes and simulates temporally varying distribution of the tracer.
- Simulated tracer transport informs expected advective transport of amendments.

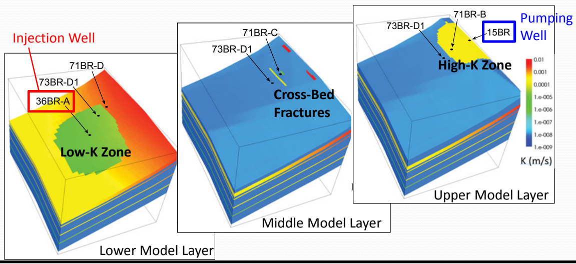




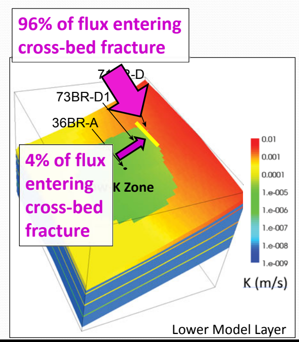
Model Representation of Hydraulic Conductivity

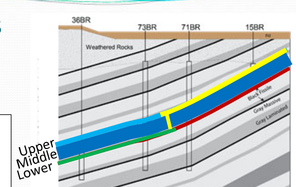
Informed by geology and hydraulic & tracer testing





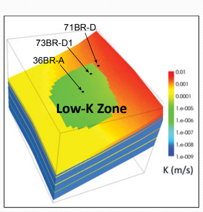
Groundwater Fluxes





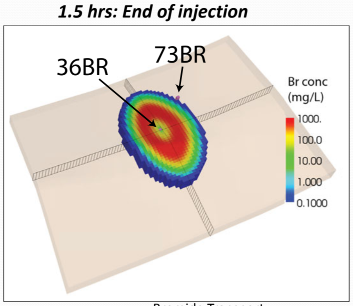
Conclusion:
- Most of gw flux entering cross-bed fracture is from the high-K region

Simulated Bromide Tracer Test: Insight Into Expected Amendment Transport



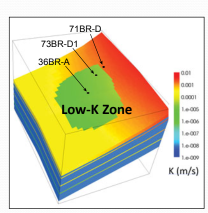
K Distribution

1.5 hrs: End of injection



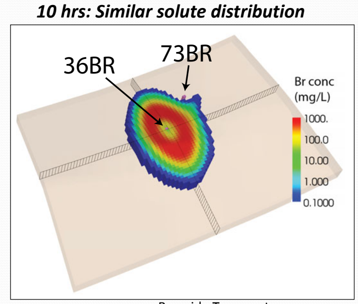
Bromide Transport

Simulated Bromide Tracer Test: Insight Into Expected Amendment Transport



K Distribution

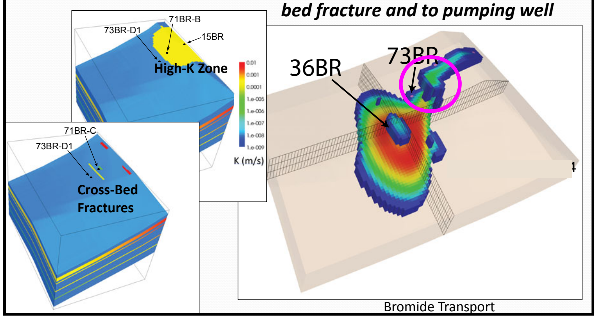
10 hrs: Similar solute distribution



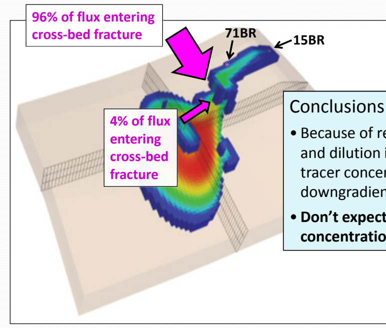
Bromide Transport

Simulated Bromide Tracer Test: Insight Into Expected Amendment Transport

100 hrs: Solute migrates thru cross-bed fracture and to pumping well



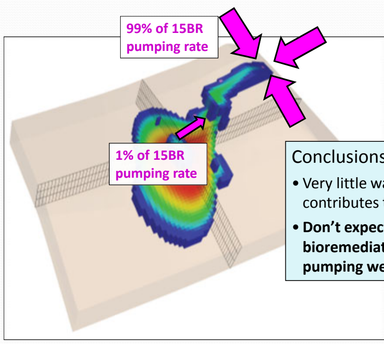
Role of GW Fluxes



Conclusions:

- Because of retention in low-K zone and dilution in cross-bed fracture, tracer concentrations are lower downgradient of this fracture.
- **Don't expect high amendment concentrations at well 71BR.**

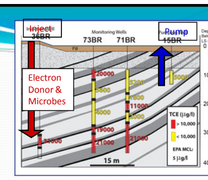
Role of GW Fluxes



Conclusions:

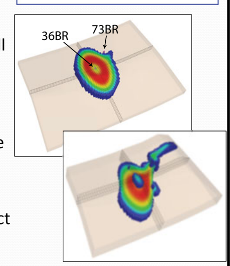
- Very little water from low-K zone contributes to pumped volume.
- **Don't expect to observe bioremediation effects at pumping well.**

Bioremediation Design and Expectations



Answers from conceptual site model:

- **Amendment volume to inject?**
  Inject enough volume to spread amendments widely over low-K zone. Ambient flow field will not produce much spreading in this zone.
- **Pumping rate at extraction well?**
  No need to reduce rate. Large quantities of amendments will not be pumped out, because of strong retention in low-K zone.
- **Where to expect treatment?**
  In low-K zone. Because of dilution, don't expect substantial bioaugmentation effectiveness at 71BR and 15BR.

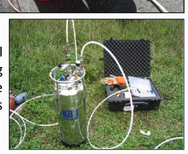


Bioremediation

- Final pre-bioremediation characterization activity: Push-pull tracer test in 36BR that showed 650 liters injectate volume is needed to spread amendments to 73BR (near edge of low-K zone).
- October 2008:
  Injected 670 liters amendments plus borehole flush water into 36BR:
  - 470 liters EOS™ solution
  - 20 liters KB-1™
  - 180 liters borehole flush water

Injection bladders

EOS™ – Emulsified soybean oil

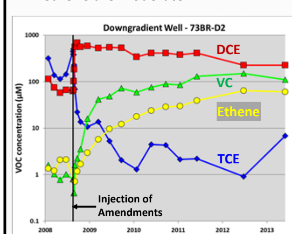


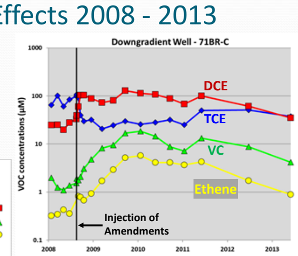
KB-1™ – Microbial consortia containing complete dechlorinators

Bioremediation Effects 2008 - 2013

In low-K zone:

- TCE quickly degraded
- DCE produced and remains high
- Rates of degradation to VC & ethene are moderate





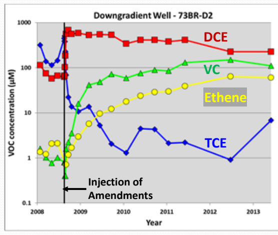
Downgradient of low-K zone at 71BR:

- TCE degradation & DCE production to a lesser degree
- Minor VC & ethene production

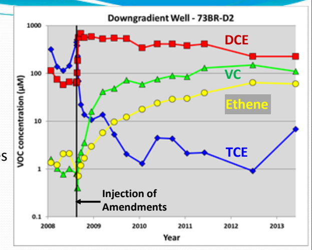
At 15BR: No concentration changes post-injection.

Expectations Vs Reality

- Expected more complete treatment of VOCs in low-K zone.
- Amendments were spread into this zone, and included microbes capable of completely degrading TCE to ethene.
- However, degradation of DCE and vinyl chloride is incomplete.



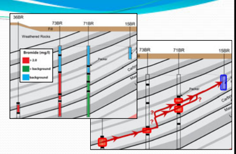
Cause of High DCE

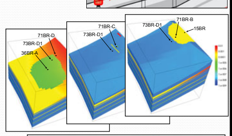


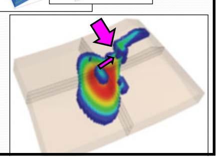
- High DCE Production Rate:
  - Bioremediation rapidly degrades TCE in fractures, producing DCE.
  - Reduced TCE in fractures increases TCE diffusion out of rock matrix.
  - New TCE in fractures also rapidly degrades to DCE.
- Moderate DCE Degradation Rate:
  (work by J. Underwood, D. Akob, M. Lorah)
  - Microbial community analyses show that partial dechorinators and other microbes dominate the post-injection population, rather than native and injected microbes capable of transforming DCE to VC to ethene.
  - Analyses suggest that the population of complete dechlorinators remained suppressed because of competition and toxicity effects.

Summary

- Hydrogeologic characterization and modeling to understand controls on amendment transport is one key component of a CSM for designing in-situ bioremediation, by providing information about:
  - Transport pathways
  - Injection volume
  - Expected spatial variability of amendment effectiveness

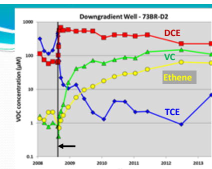


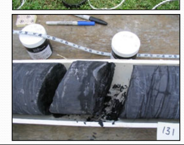




Summary

- Additional important components of CSM for designing bioremediation and setting expectations about treatment:
  - Biogeochemical conditions and processes that will affect evolution of microbial community after introduction of electron donor and microbial culture.
  - Effect of potentially large contaminant mass in rock matrix (or sediments where diffusion processes dominate) on biodegradation processes.





References: Bioremediation at NAWC

Goode, D.J., Imbrigiotta, T.E., and Lacombe, P.J., 2014, **High-resolution delineation of chlorinated volatile organic compounds in a dipping, fractured mudstone--Depth- and strata-dependent spatial variability from rock-core sampling**: Journal of Contaminant Hydrology, v. 171, p. 1-11, doi:10.1016/j.jconhyd.2014.10.005.

Révész, K.M., Sherwood Lollar, B., Kirshtein, J.D., Tiedeman, C.R., Imbrigiotta, T.E., Goode, D.J., Shapiro, A.M., Voytek, M.A., Lacombe, P.J., and Busenberg, E., 2014, **Integration of stable carbon isotope, microbial community, dissolved hydrogen gas, and $^2H_{H2O}$ tracer data to assess bioaugmentation for chlorinated ethene degradation in fractured rocks**: Journal of Contaminant Hydrology, v. 156, p. 62-77, doi:10.1016/j.jconhyd.2013.10.004.

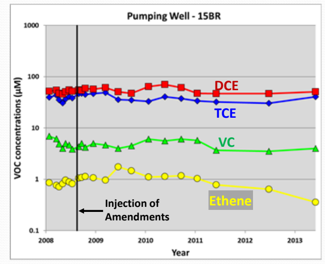
Shapiro, A.M., Tiedeman, C.R., Imbrigiotta, T.E., Goode, D.J., Hsieh, P.A., Lacombe, P.J., DeFlaun, M.F., Drew, S.R., and Curtis, G.P., 2018, **Bioremediation in fractured rock--2. mobilization of chloroethene compounds from the rock matrix**: Groundwater, v. 56, no. 2, p. 317-336, doi:10.1111/gwat.12586.

Tiedeman, C.R., Shapiro, A.M., Hsieh, P.A., Imbrigiotta, T.E., Goode, D.J., Lacombe, P.J., DeFlaun, M.F., Drew, S.R., Johnson, C.D., Williams, J.H., and Curtis, G.P., 2018, **Bioremediation in fractured rock--1. modeling to inform design, monitoring, and expectations**: Groundwater, v. 56, no. 2, p. 300-316, doi:10.1111/gwat.12585.

Extra Slides

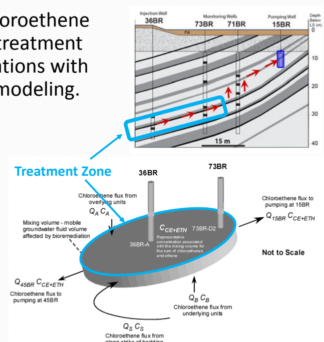
Treatment at Pumped Well 2008 - 2013

VOC concentrations at 15BR show no effect of bioremediation



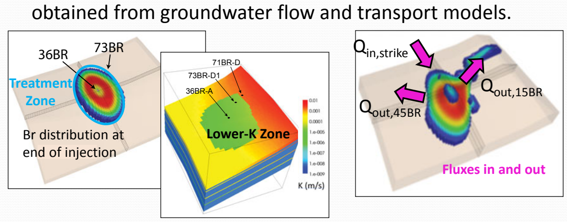
Mass Balance Analysis Approach

- Perform a rudimentary chloroethene (CE) mass balance for the treatment zone, using scoping calculations with inputs from groundwater modeling.
- Goal: Estimate CE mobilization rate out of the rock matrix.
- Mobilized CE can be from variety of sources in the matrix: DNAPL dissolution, desorption, diffusion of aqueous CE



Scoping Calculations Inputs

- Size of treatment zone and fluxes in and out of treatment zone obtained from groundwater flow and transport models.



- CE concentrations in treatment zone obtained from samples collected in 36BR and 73BR.

Scoping Calculations

- Chloroethene + Ethene (CE+Eth) mass balance for treatment zone (TZ):

Change of CE+Eth flux in TZ fractures	=	CE+Eth flux into TZ	-	CE+Eth flux out of TZ	+	CE+Eth mobilization rate (from rock matrix)

- Calculation is for molar sum of all CE species + Ethene.
- Assume:
  - Steady flow: GW flux into TZ = GW flux out of TZ
  - Mobilization rate is net rate of all processes affecting CE transport in rock matrix: e.g., diffusion, sorption, abiotic degradation
  - CE+Eth spatially constant within TZ; calculation done using two possible values

Results: CE Mobilization Rate

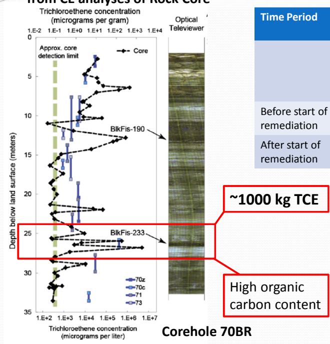
Estimates of CE Mobilization Rate Before and After Bioremediation

Time Period	CE Mobilization Rate (kg TCE/yr)	
	C_{CE+ETH} defined from 36BR-A	C_{CE+ETH} defined from 73BR-D2
Before start of remediation	7.3	4.2
After start of remediation	44.6	34.0

Bioaugmentation causes rate to increase by a factor of 6 to 8, due to increased concentration gradients between rock matrix and fractures

Developing a CSM to Inform Application of Bioremediation in Fractured Rock

Estimate of CE in Rock Matrix (BlkFis-233) from CE analyses of Rock Core



Corehole 70BR

Estimates of CE Mobilization Rate Before and After Bioremediation

Time Period	CE Mobilization Rate $V_F F_{CE+ETH}$ (kg TCE/yr)	
	C_{CE+ETH} defined from 36BR-A	C_{CE+ETH} defined from 73BR-D2
Before start of remediation	7.3	4.2
After start of remediation	44.6	34.0

Prior to remediation, 100’s of years to mobilize CE mass in rock matrix. . .

After remediation, likely decades to mobilize CE mass, but multiple remediation treatments would be required. . .

The economics of each alternative would need to be evaluated