Bioaugmentation at a Fractured Rock Site

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USEPA-USGS Fractured Rock Workshop

EPA Region 10

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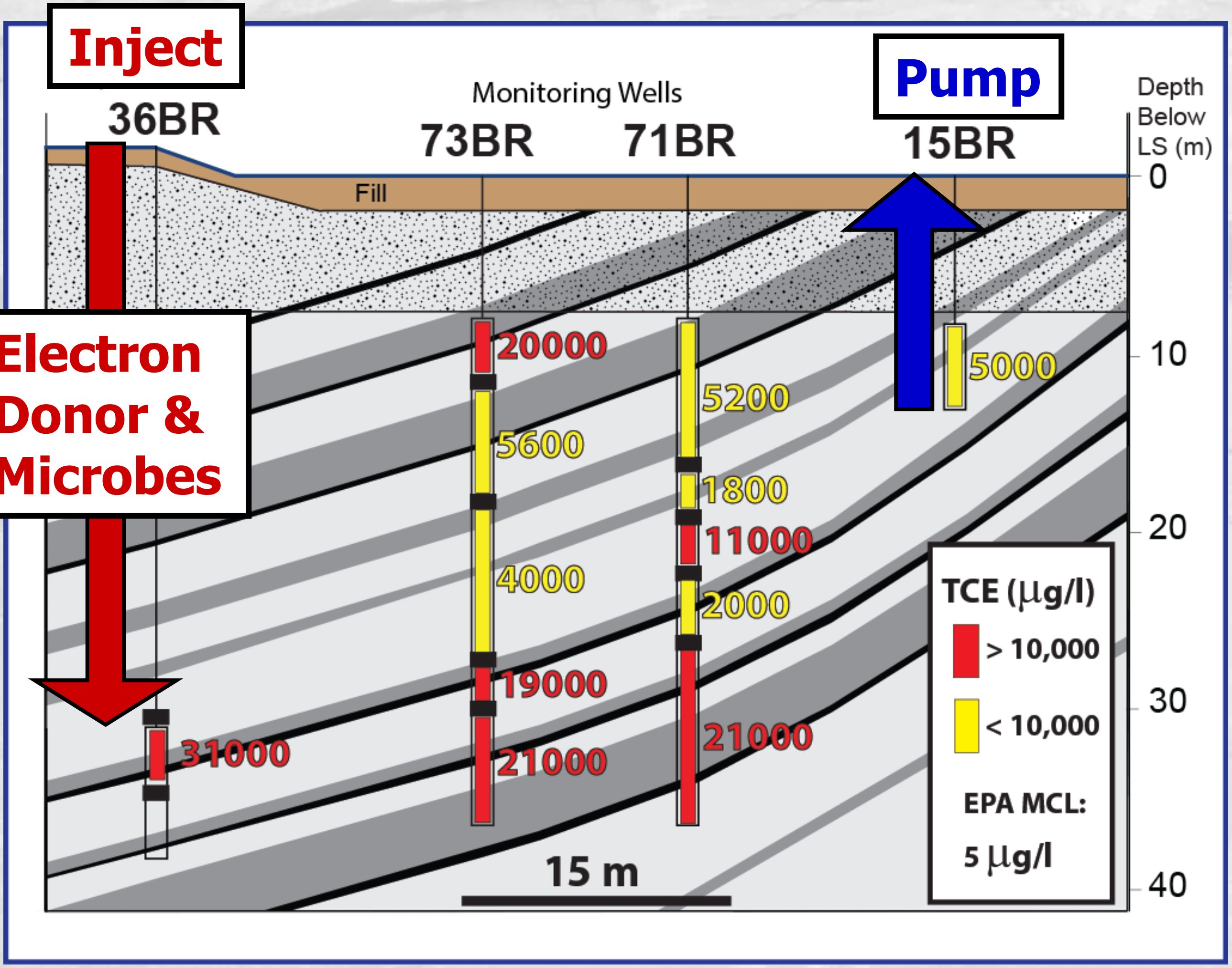
Bioaugmentation Basics

- Concept
  - Inject bacteria and food
  - Increase reductive dechlorination
- Advantages
  - Chlorinated solvents degraded in situ
  - Possible reduced need for pump & treat – lower energy and treatment costs.
- Limitations in Fractured Rocks
  - Difficult to distribute amendments over large volumes of the subsurface because of extreme geologic heterogeneity
  - Biodegradation in the matrix is limited by small pore sizes in the rock

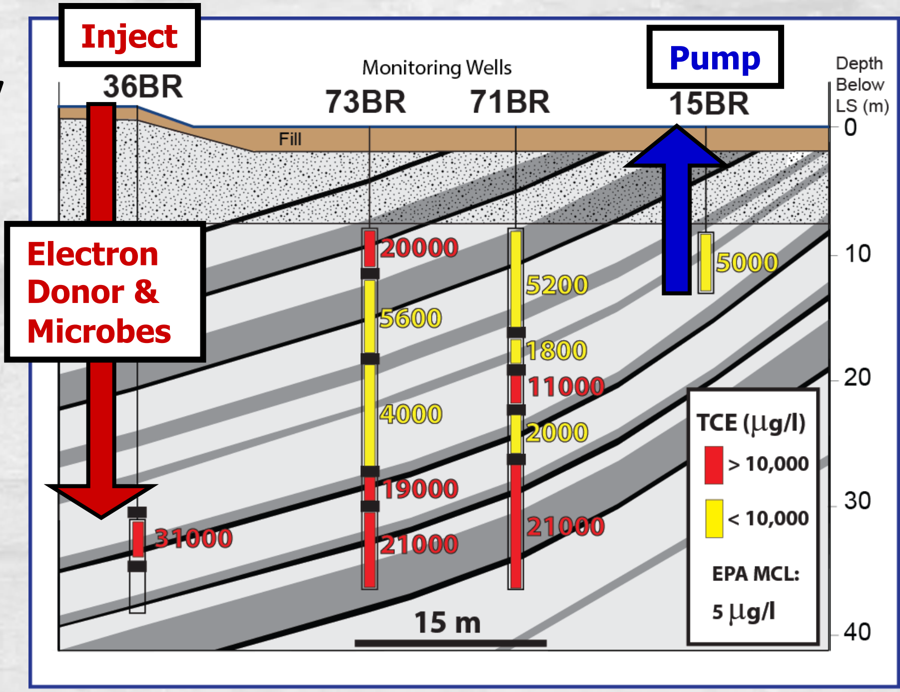
TCE → cisDCE → VC → Ethene
$+ Cl^-$ $+ Cl^-$ $+ Cl^-$

Bioaugmentation Experiment in Highly Contaminated Mudstones

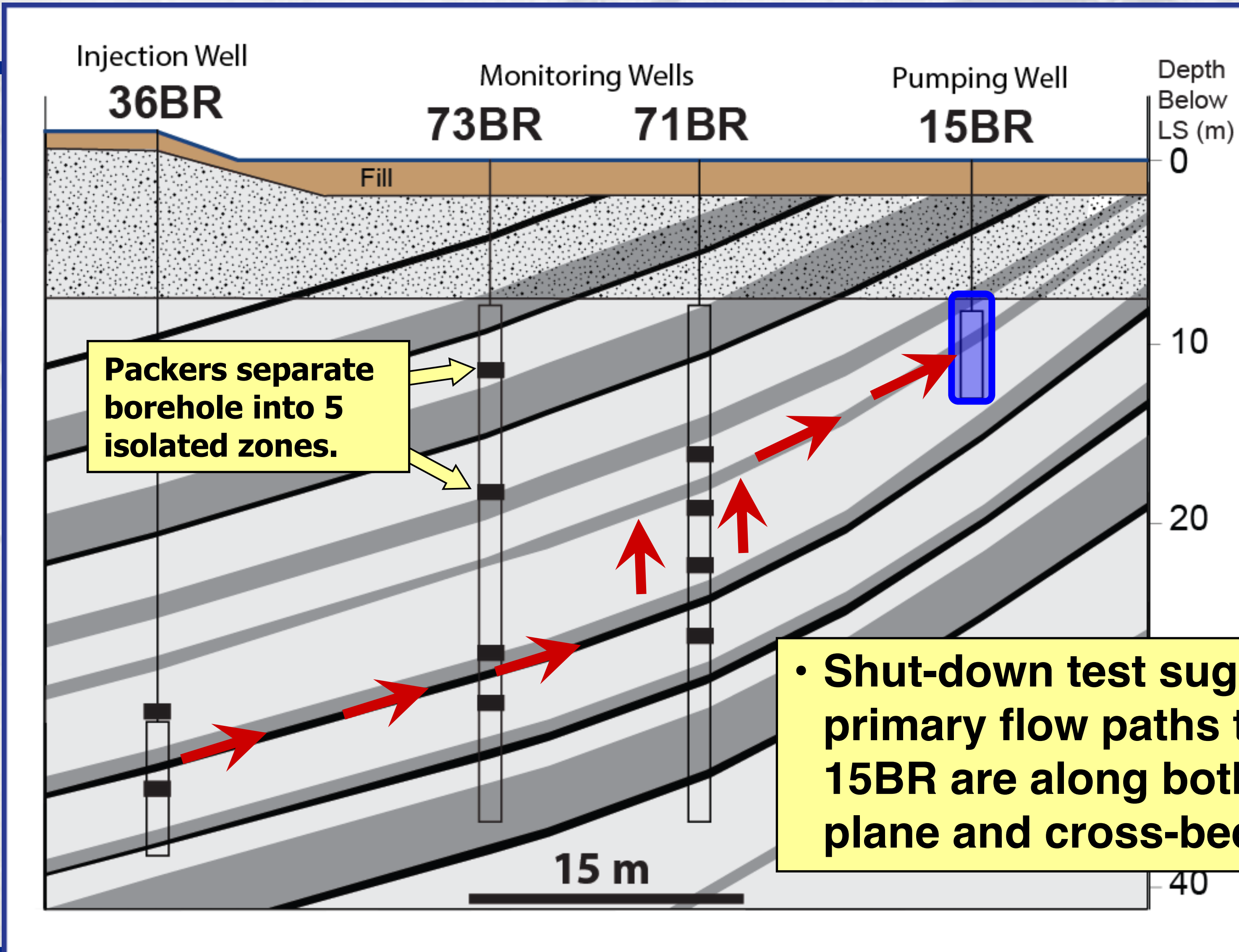


Characterization and Modeling for Bioaugmentation Design

- Questions related to hydrogeology
  - Volume of amendments to inject?
  - Expected extent of treatment zone?
  - Where to monitor?
- Characterization activities
  - Detailed stratigraphic framework
  - Single & cross-hole hydraulic testing
  - Cross-hole tracer testing
  - Flow and transport modeling
  - Push-pull tracer testing

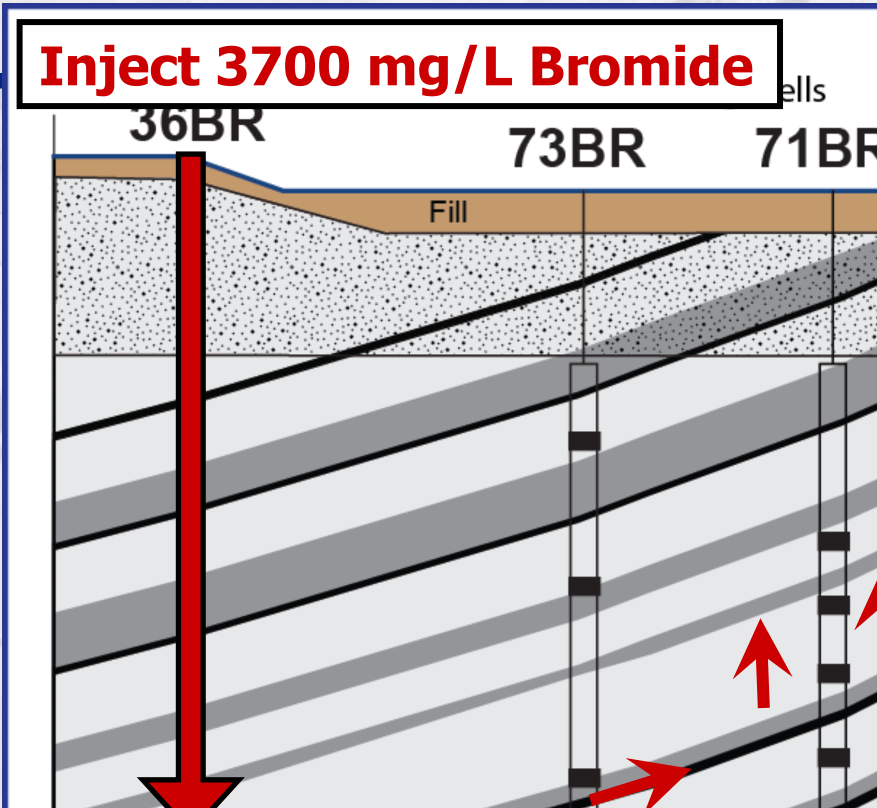


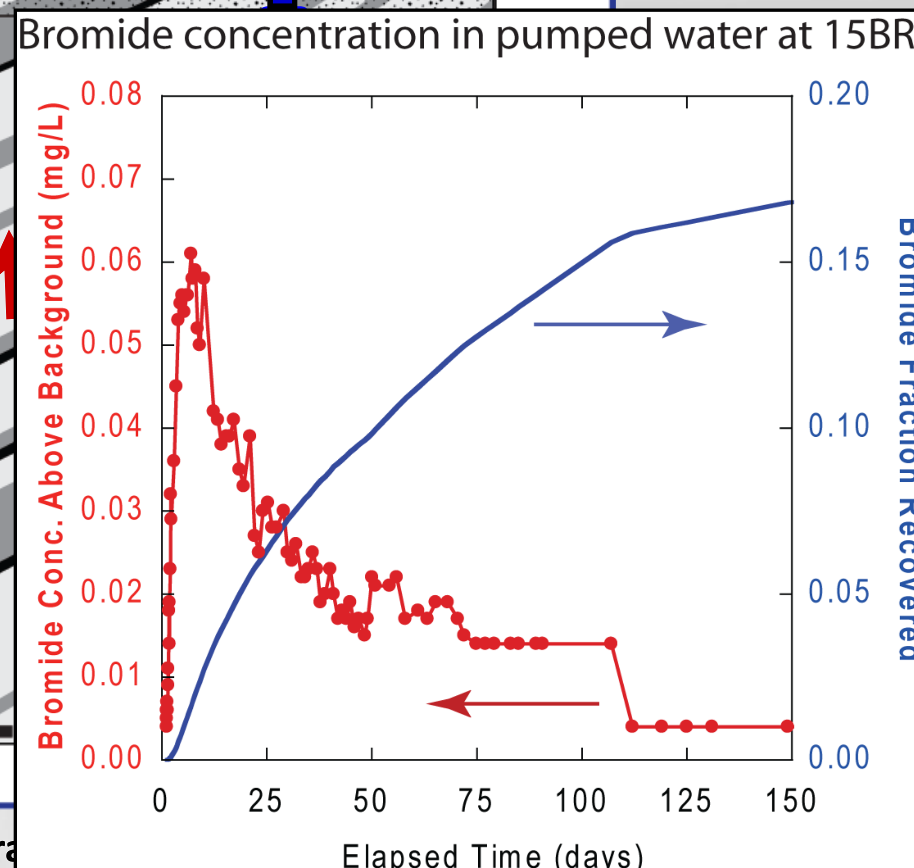
Conceptualized Flow Paths



- **Shut-down test suggests primary flow paths toward 15BR are along both bedding-plane and cross-bed fractures.**

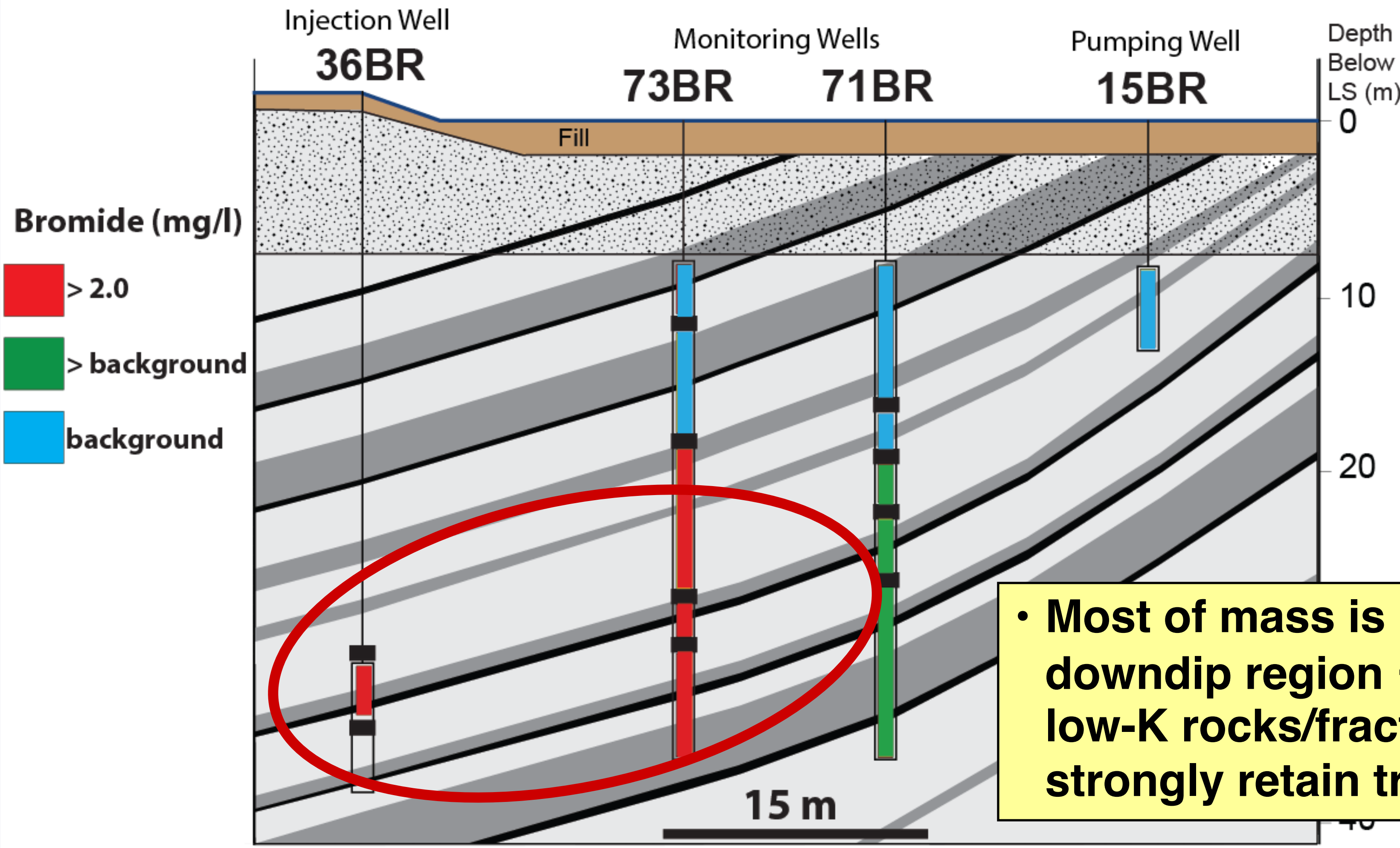
Tracer Testing





- Huge dilution at pumped well: only small amount of pumped water is coming from the region between 36BR & 15BR.
- Only 17% of bromide removed at 15BR after 5 months.

Tracer Testing: Bromide in Aquifer 6 Months after Injection



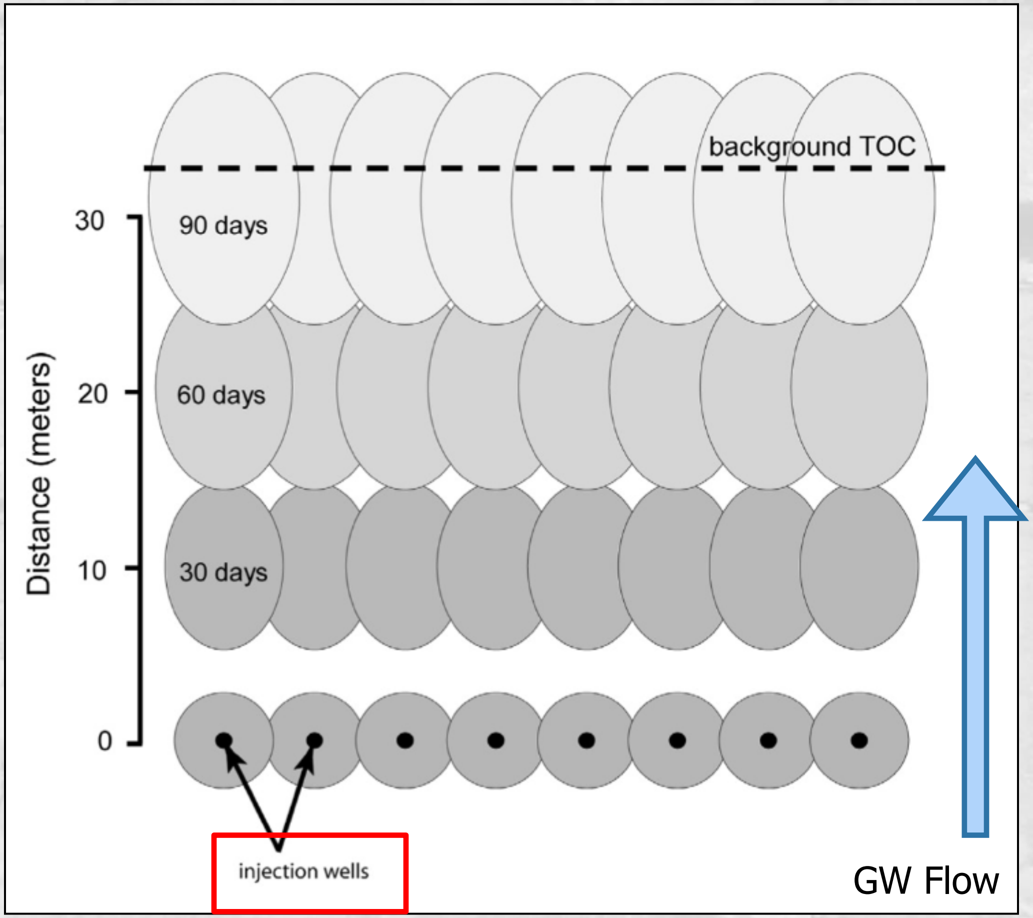
- **Most of mass is in downdip region → low-K rocks/fractures strongly retain tracer.**

Modeling Informs Bioaugmentation Design, Monitoring, Expectations

- **Motivation for Modeling**
  - Fractured rock → Highly heterogeneous permeability → Highly heterogeneous groundwater fluxes and transport paths
  - Amendment spreading and effectiveness strongly controlled by these fluxes and transport paths
  - Can't use simple homogeneous conceptualizations of groundwater flow and transport to design amendment injections in fractured rocks.

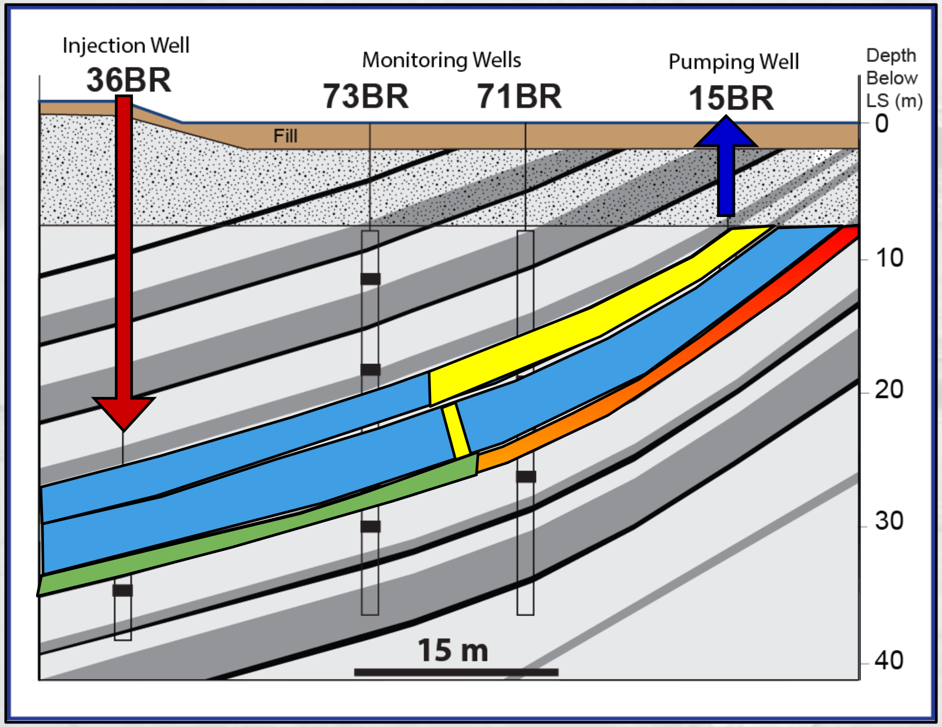
Assumption of Homogeneity

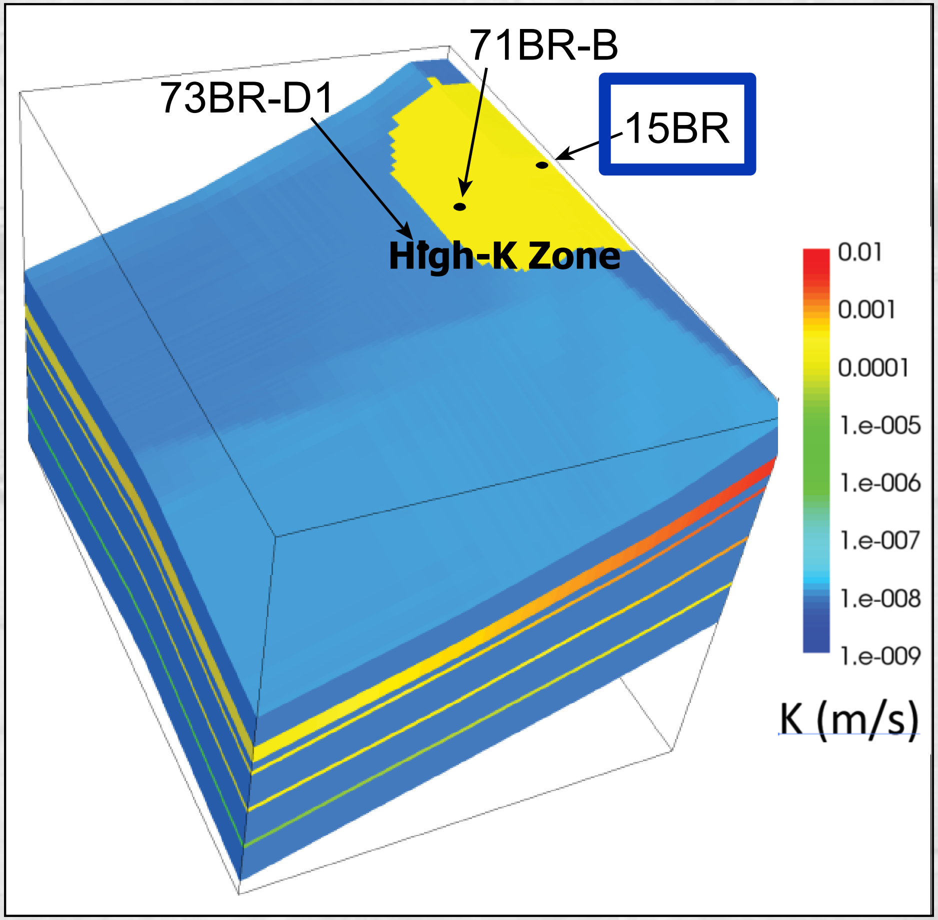
- Amendment spreading will never look like this in fractured rocks!



Payne et al., Remediation Hydraulics, 2009

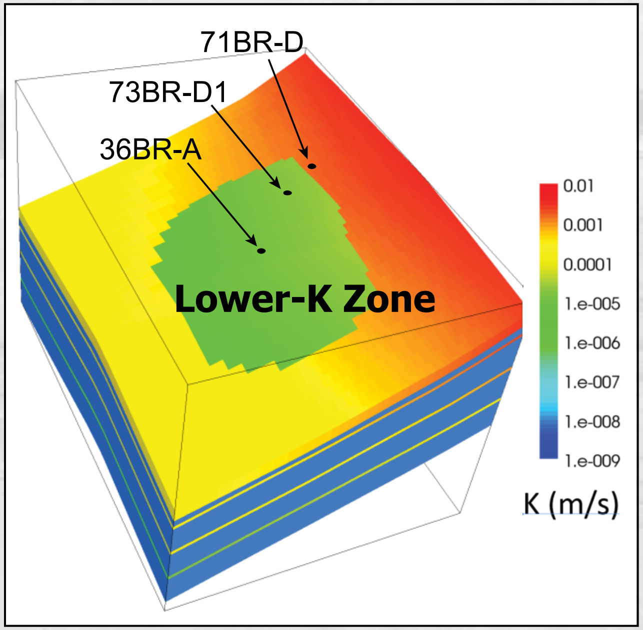
Model Synthesizes Field Data and Incorporates Heterogeneity

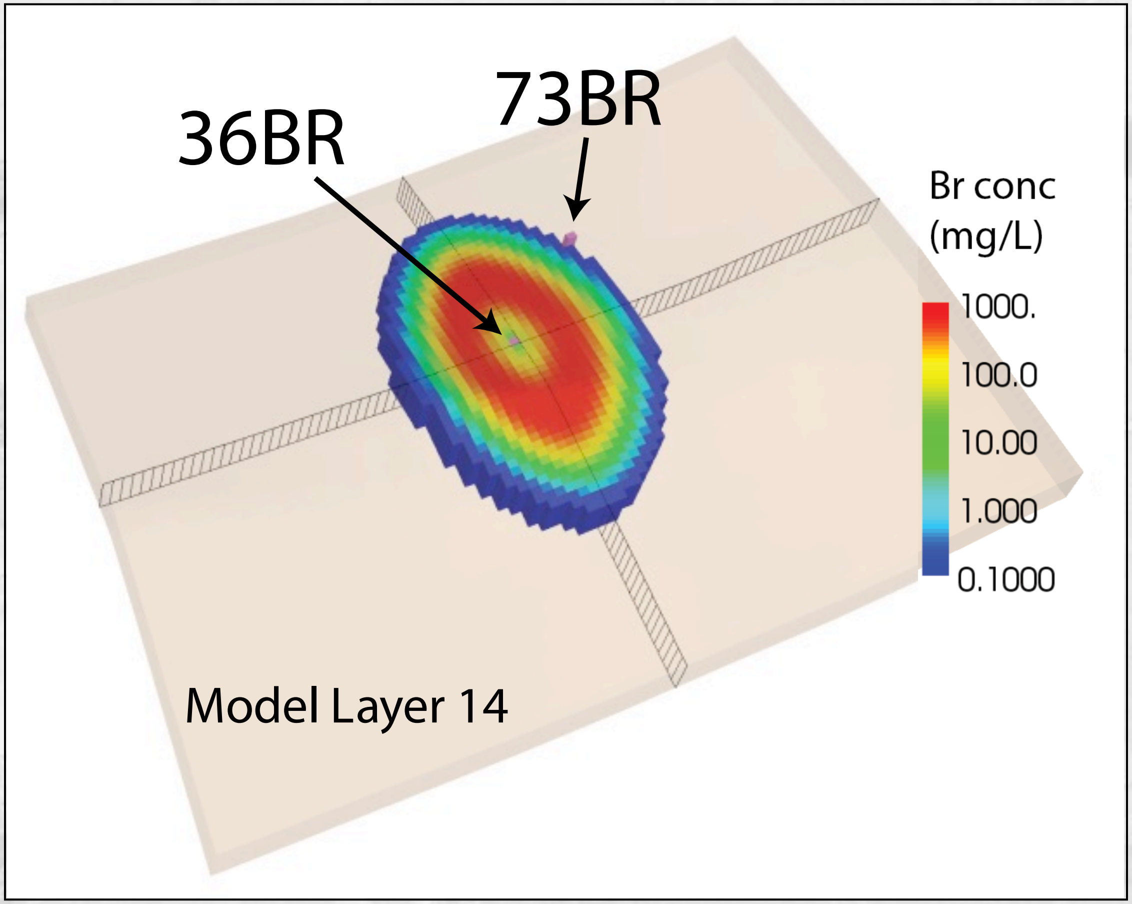




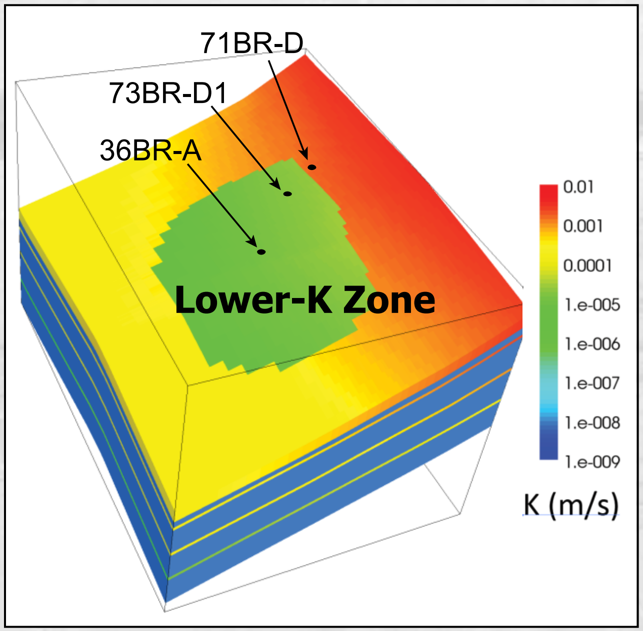
Simulate Bromide: Insight into Amendment Advective Transport

1.5 hrs: End of injection

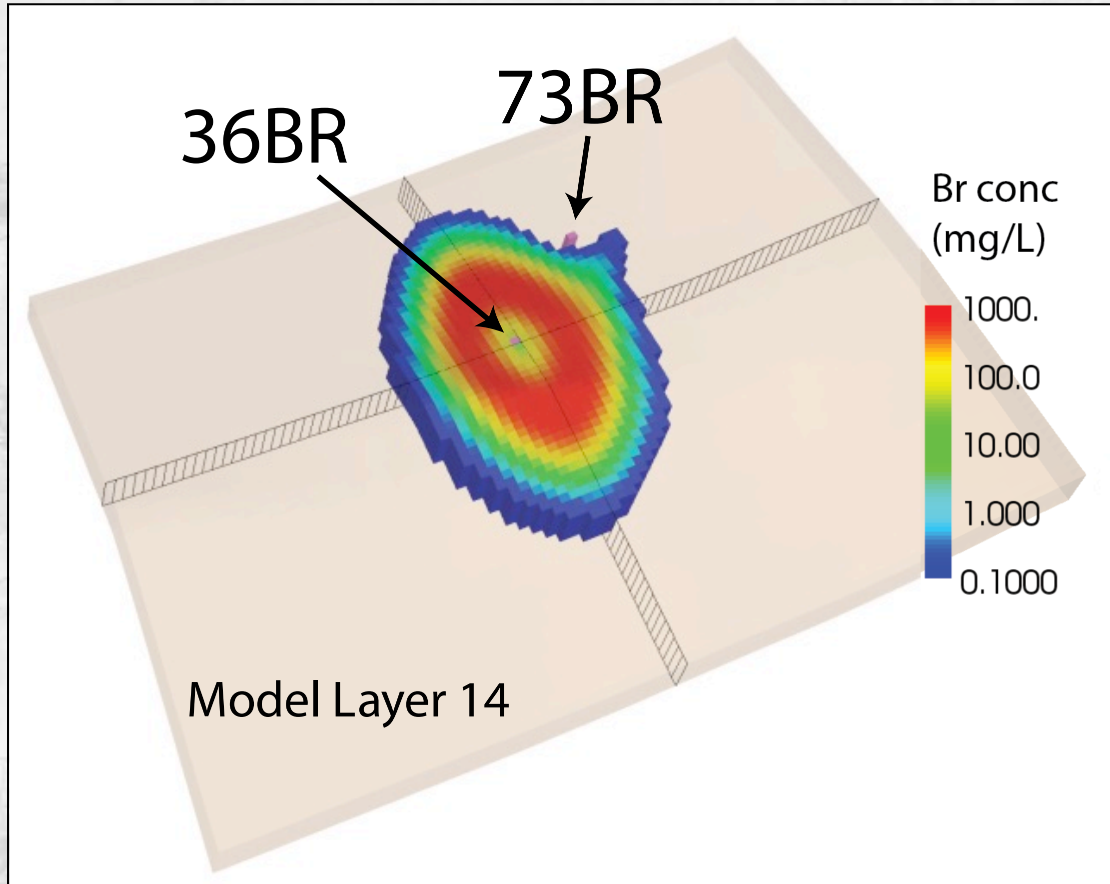




Simulate Bromide: Insight into Amendment Advective Transport

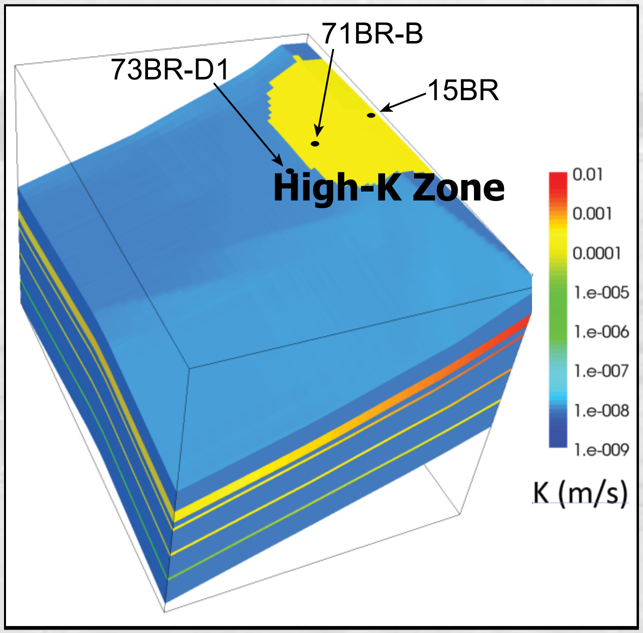


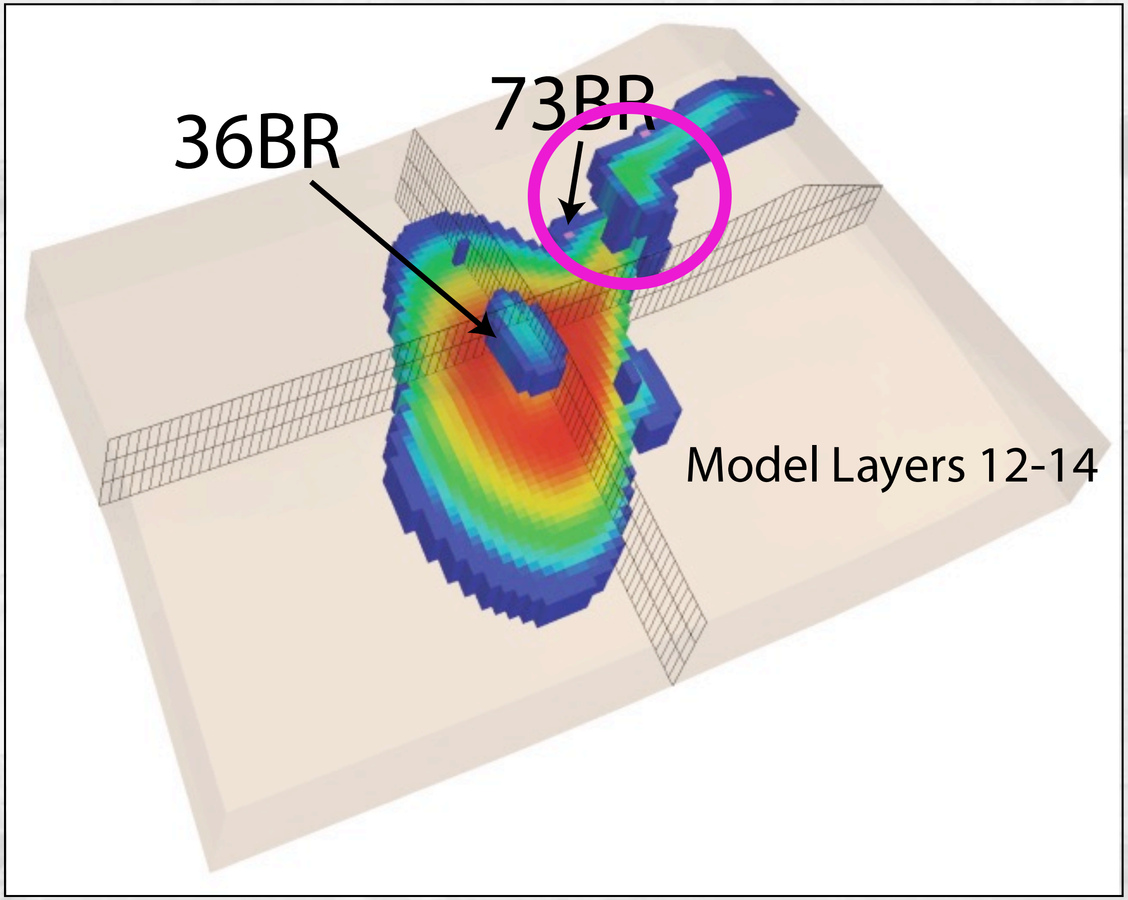
10 hrs: Similar solute distribution



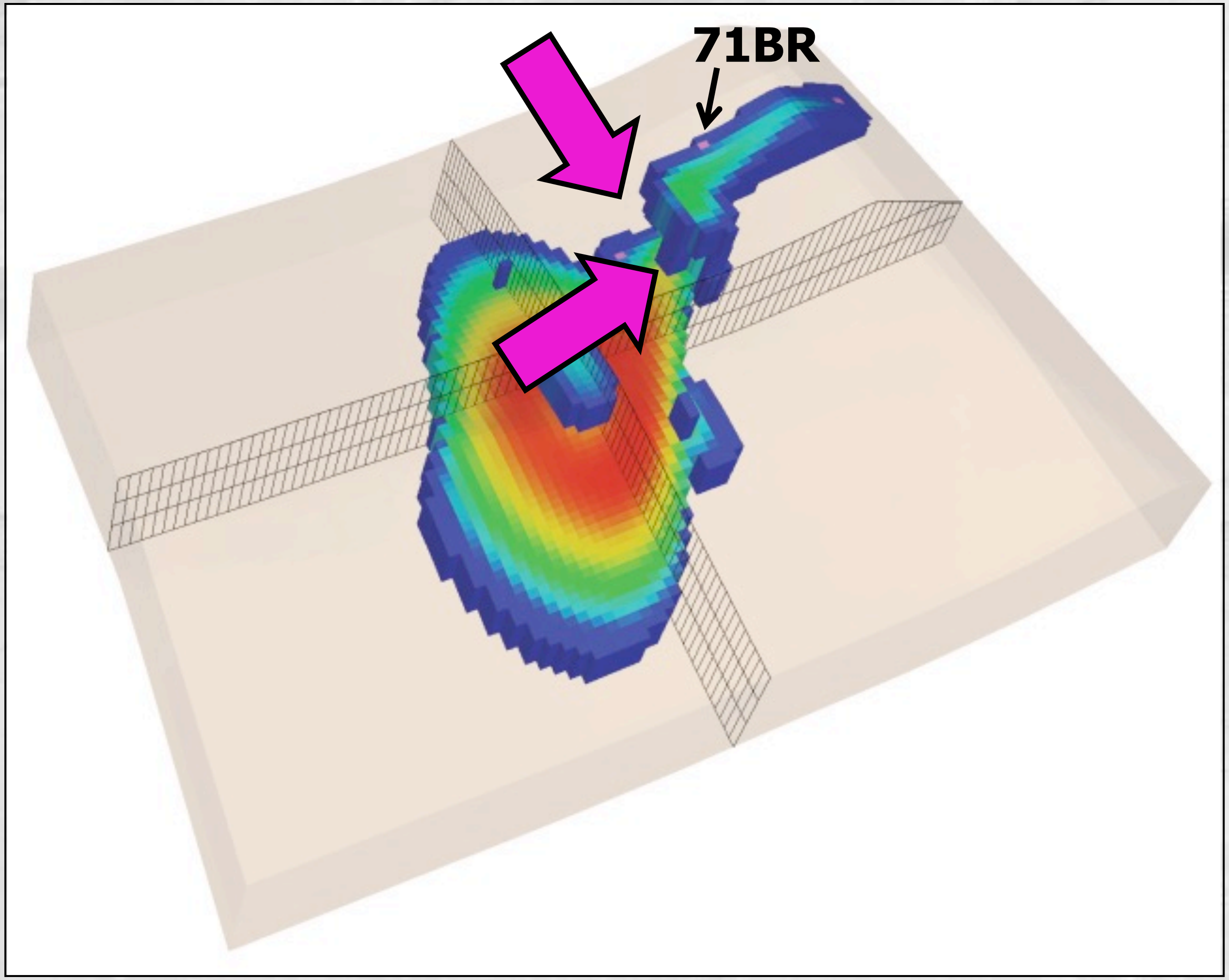
Simulate Bromide: Insight into Amendment Advective Transport

100 hrs: Solute migrating thru cross-bed fracture





GW Fluxes Along Solute Paths



Total GW Flux Entering Cross-Bed Fracture:

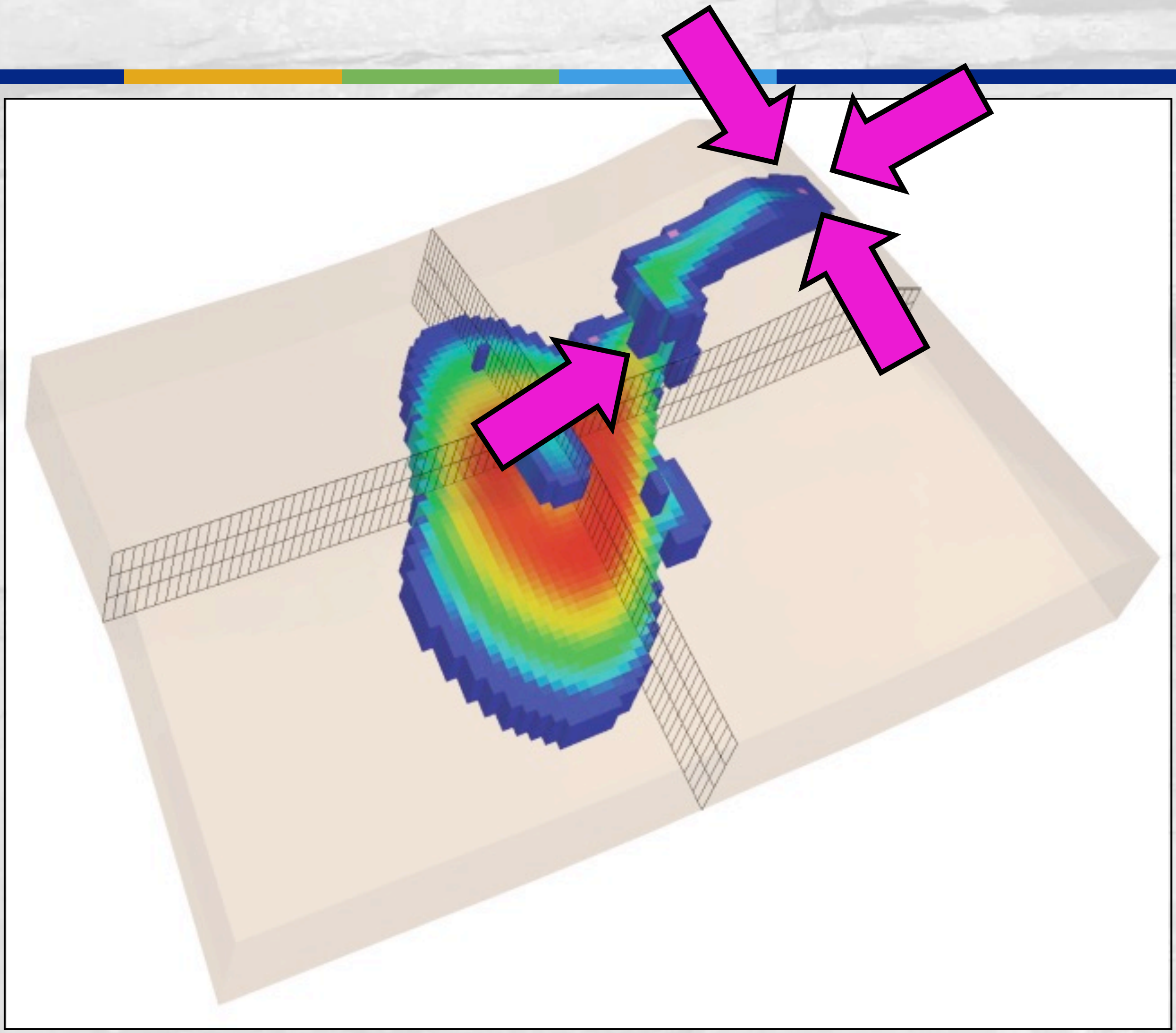
4% From Lower-K zone

96% From along strike

→ Dilution.

Don't expect high amendment concentrations at downgradient monitoring well

GW Fluxes Along Solute Paths



Total GW Flux Entering Cross-Bed Fracture:

4% From Lower-K zone

96% From along strike

→ Dilution.

Don't expect high amendment concentrations at downgradient monitoring well

Total Pumping Rate at 15BR:

1% From Lower-K zone

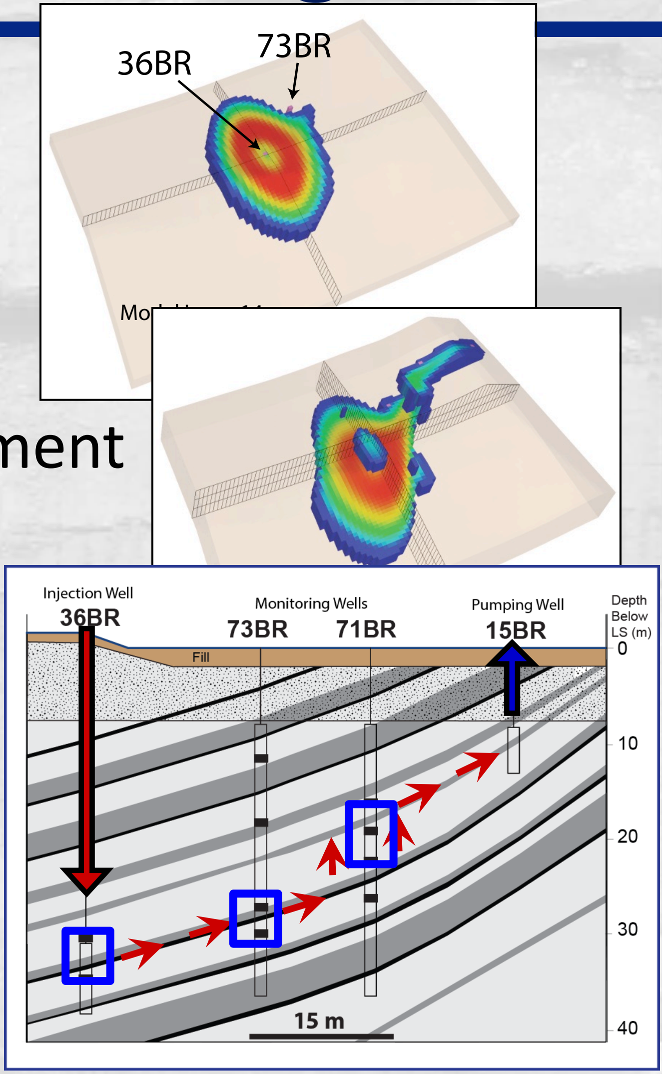
99% From other directions

→ Even Greater Dilution.

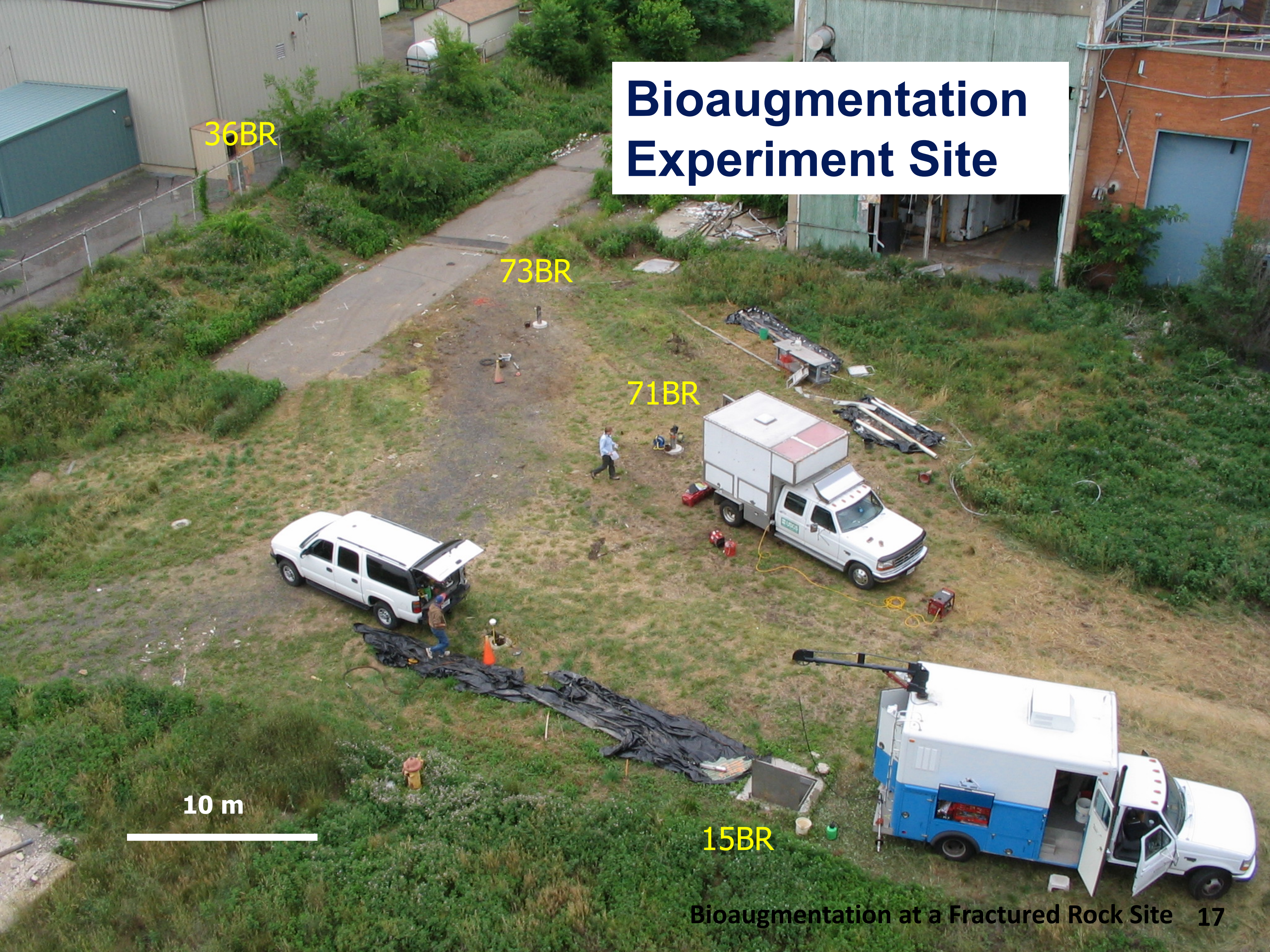
Don't expect to observe bioaugmentation effects at pumping well.

Modeling Informed Bioaugmentation Design, Expectations, Monitoring

- **Design:** Inject enough volume to spread amendments widely over lower-K zone. Ambient flow field will not contribute much to spreading in this zone.
- **Expectations:** Region of greatest amendment effectiveness will be in lower-K zone. Amendment concentrations will be diluted further downgradient.
- **Monitoring:** Field data and model reveal well intervals where bioaugmentation effects are likely to be observed.



Bioaugmentation Experiment Site



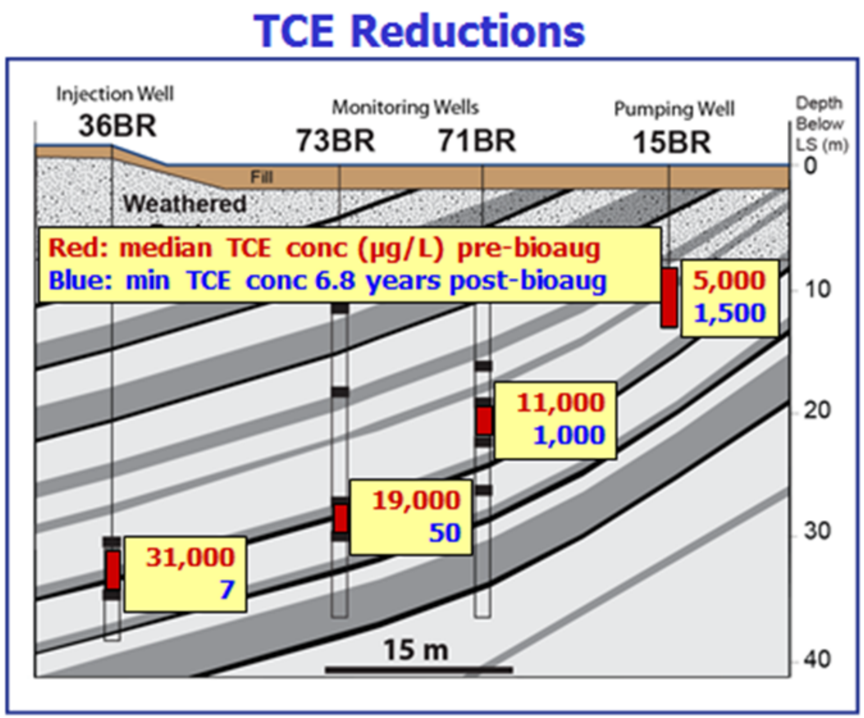
Bioaugmentation Implementation

Water-quality monitoring

Injection bladders

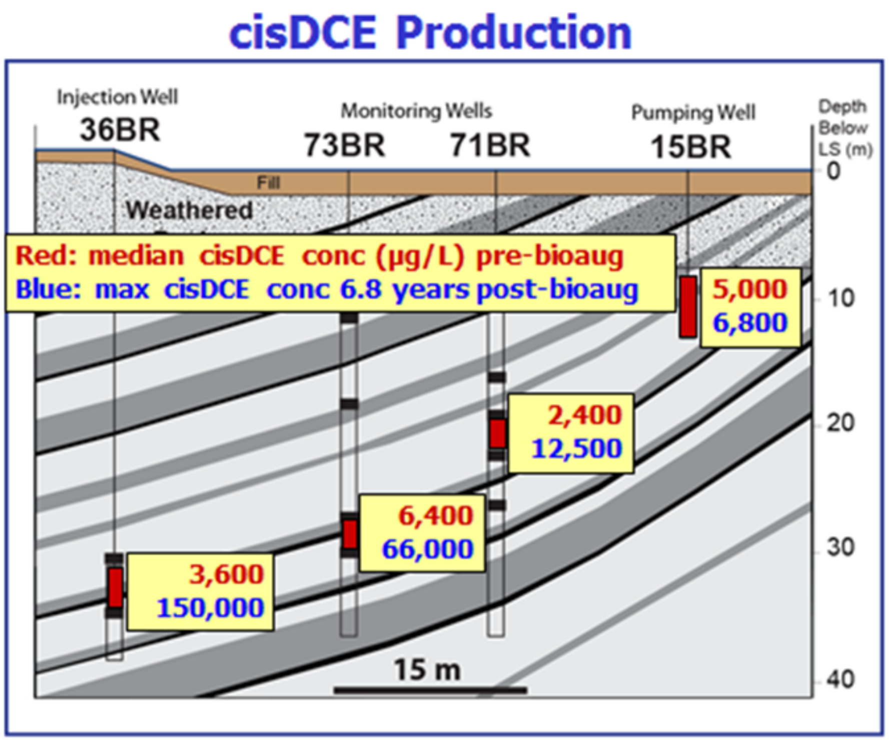
EOS

Observed changes in organic contaminants during monitoring

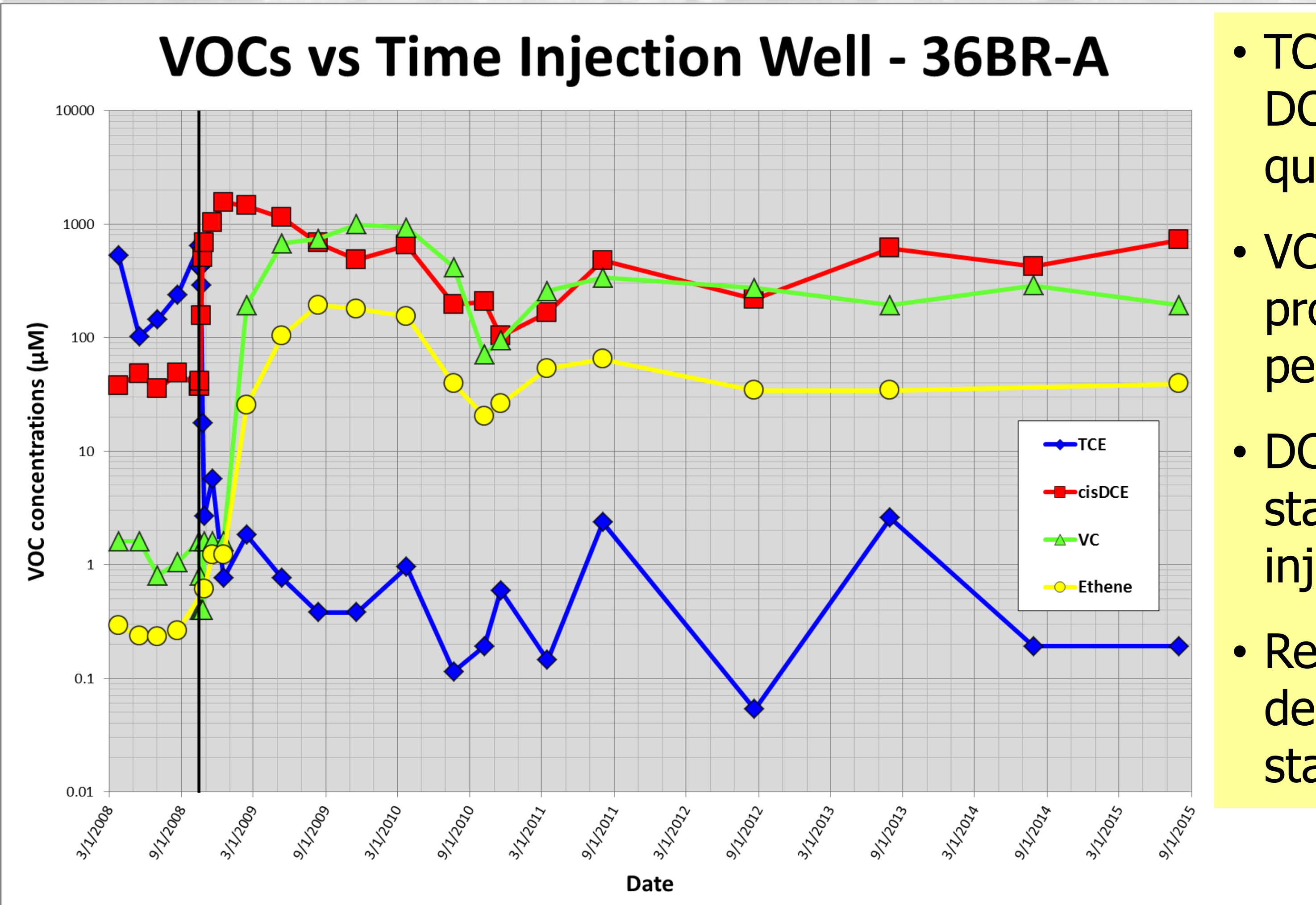


- Significant TCE decreases seen in wells 18 m and 30 m down the flow path

- Significant cisDCE increases seen in these same wells



Is the bioaugmentation effective?

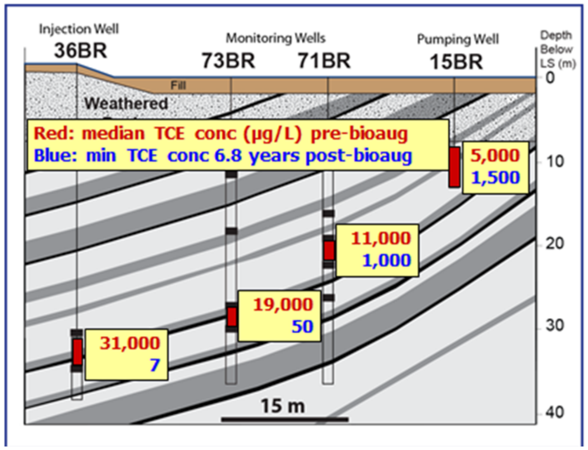


- TCE degraded & DCE produced quickly.
- VC & ethene produced after lag period.
- DCE & VC plateau starting ~1 yr post-injection.
- Reductive dechlorination is stalled.

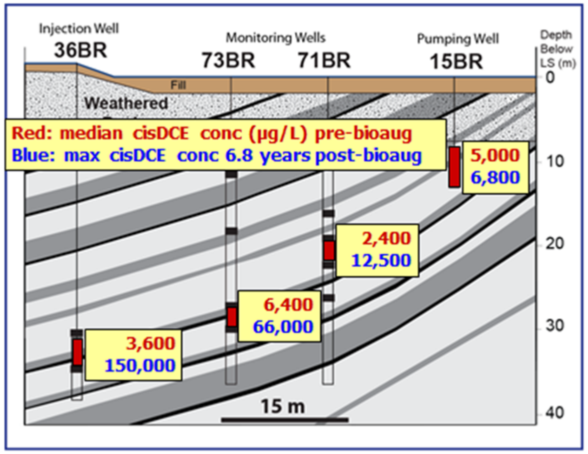
Cause of Sustained High DCE

- Bioaugmentation dramatically reduces TCE in fractures.
- Increased TCE gradient from rock matrix to fractures mobilizes TCE from matrix to fractures.
- New TCE in fractures rapidly degrades to DCE.
- → High TCE concentrations in matrix sustain high DCE concentrations in fractures.
- These conditions symptomatic of in-situ remediation in fractured rocks, where effectiveness depends on contact between amendments and contaminated groundwater

TCE Reductions



cisDCE Production

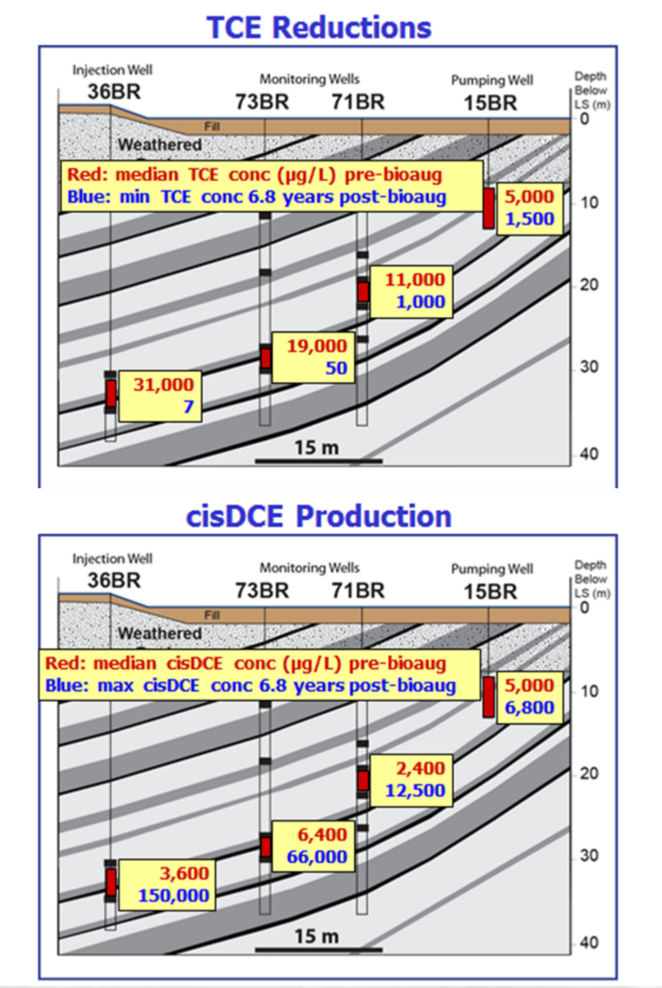


Decisions Regarding Further Treatment

- Chloroethene (CE) concentrations do not meet remedial objectives.
- Additional remedial treatments ?
- Or, just continue with hydraulic containment?

Decision Support Analysis:

- Evaluate CE mass mobilized from remedial treatments.
- Compare CE mass mobilized with CE mass in the formation.



Decision Support Analysis: Modeling Reductive Dechlorination

Analytical models:

- Biochlor
- RemChlor
- ART3D
- Natural Attenuation Software (NAS)
- MNA Toolbox
- BioBalance ToolKit

Numerical models:

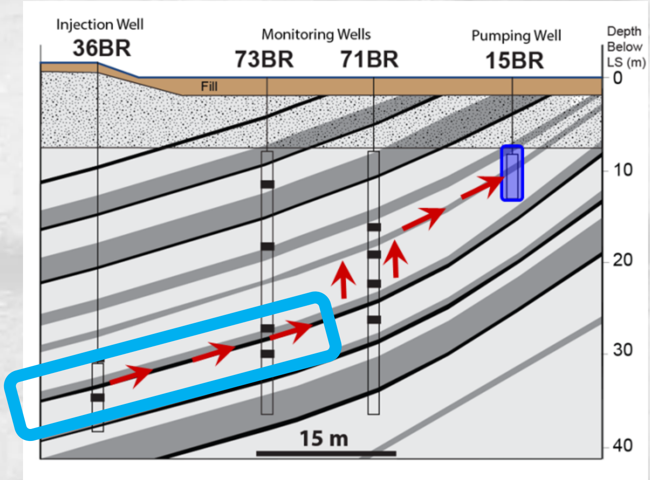
- SEAM3D
- Bio-Redox–MT3D-MS
- RT3D
- PHT3D
- BioBalance ToolKit

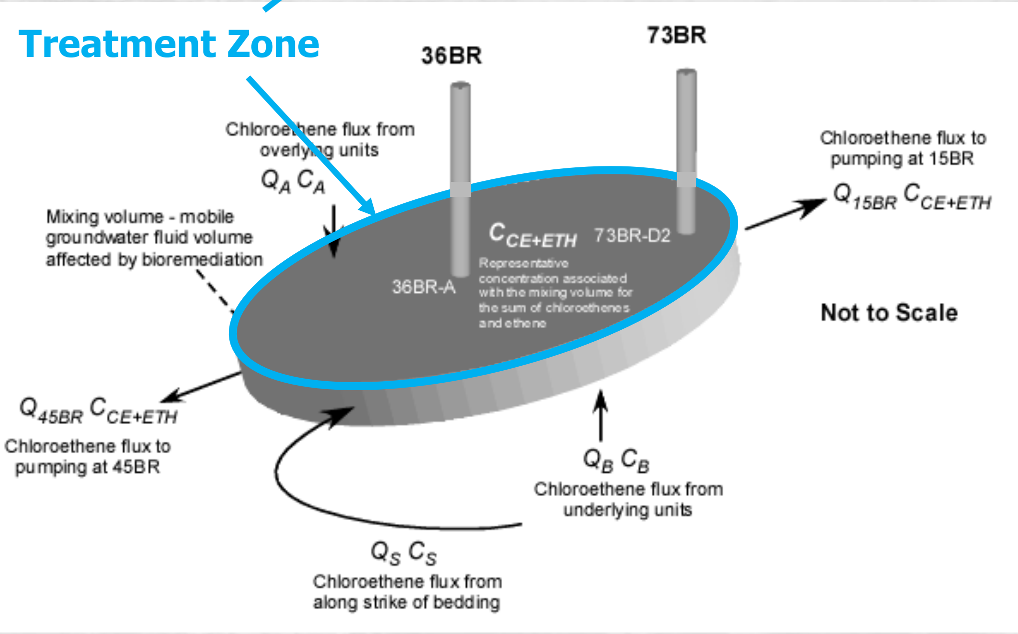
- Analytical solutions may not be able to address the complexity of the flow regime in fractured rock

- Numerical solutions: Computationally demanding, uncertainty in identifying properties governing chemical transport, sorption/desorption, chemical transformations, and biological processes

Alternative 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





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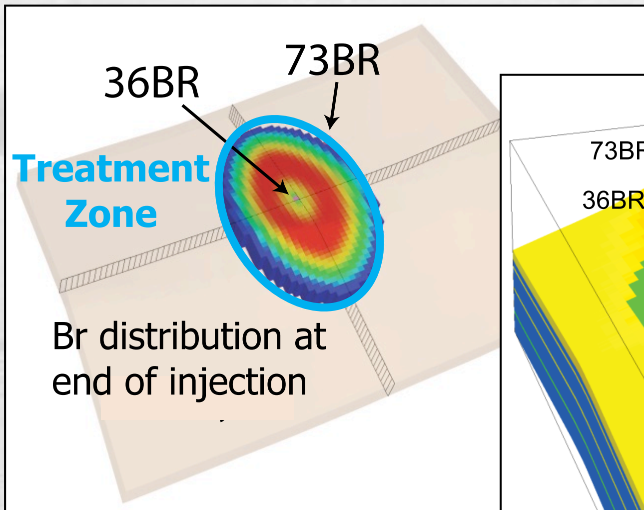
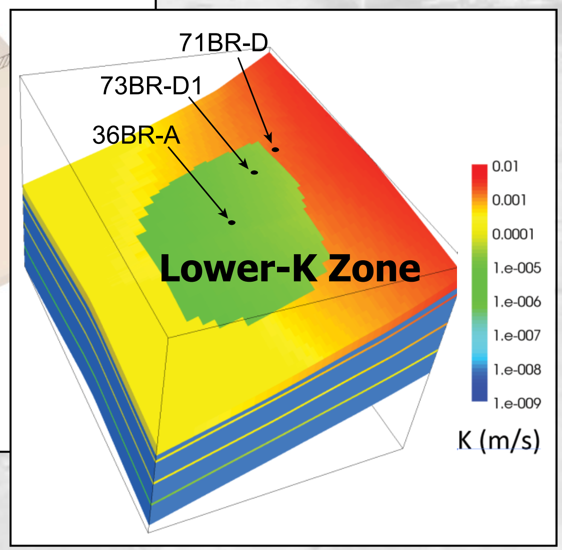
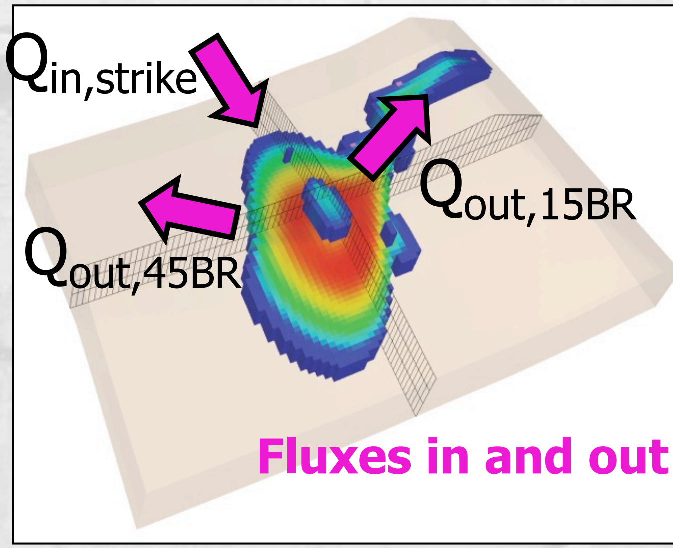
Scoping Calculations Inputs

- 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**

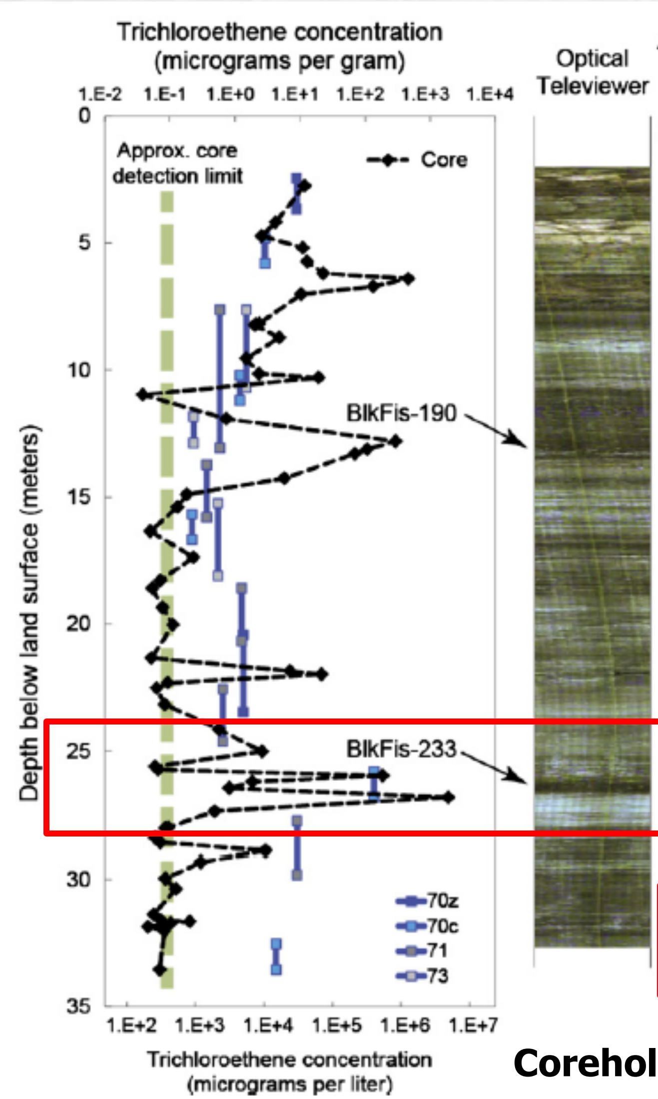
Results: CE Mobilization Rate

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

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



Corehole 70BR

~1000 kg TCE

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

Summary

- Synthesis of site characterization through groundwater flow and transport modeling is critical in designing remediation amendment injections and identifying monitoring locations
- Bioaugmentation resulted in increased reductive dechlorination, more reducing conditions, breakdown of electron donor, and presence of increased bacterial concentrations.
- Chloroethene (CE) compounds remain in the treatment zone (TCE concentrations decrease, DCE & VC concentrations increase)

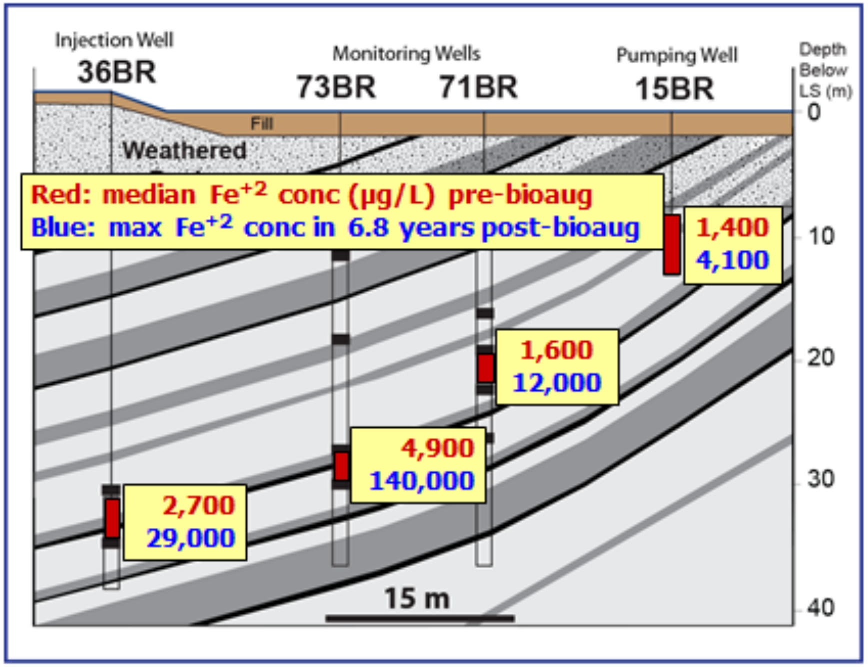
Summary

- Degradation rates in fractures are not sufficient to overcome TCE mobilized from rock matrix
- Groundwater fluxes are used to formulate CE mass balance and CE mobilized from the treatment zone
- Comparing CE mobilization rate with estimate of CE in treatment zone provides information for evaluating next steps in achieving remedial objectives.

Extra Slides

Inorganic geochemistry. . .

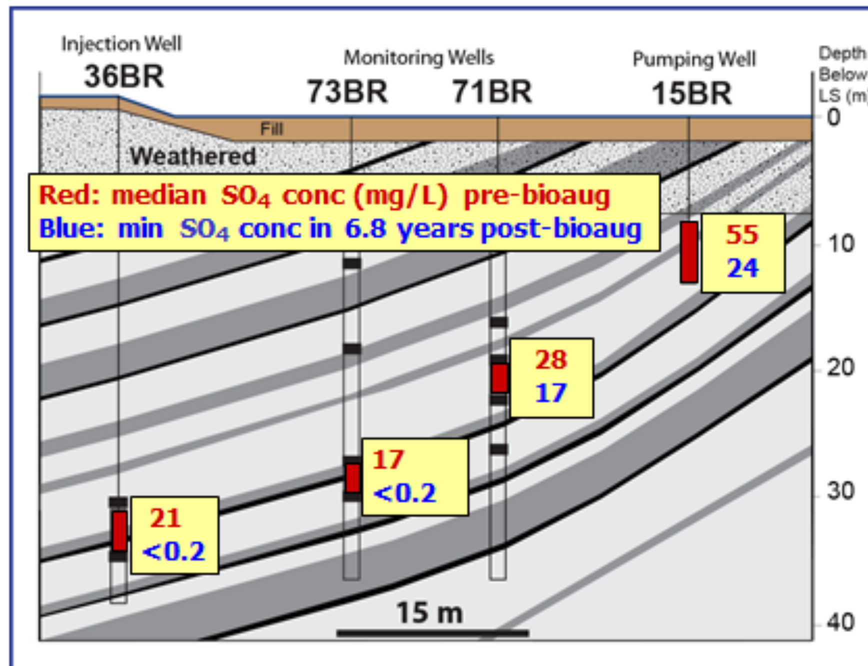
Ferrous Iron Production



- Fe^{+2} increases seen in wells 18 m and 30 m down the flow path

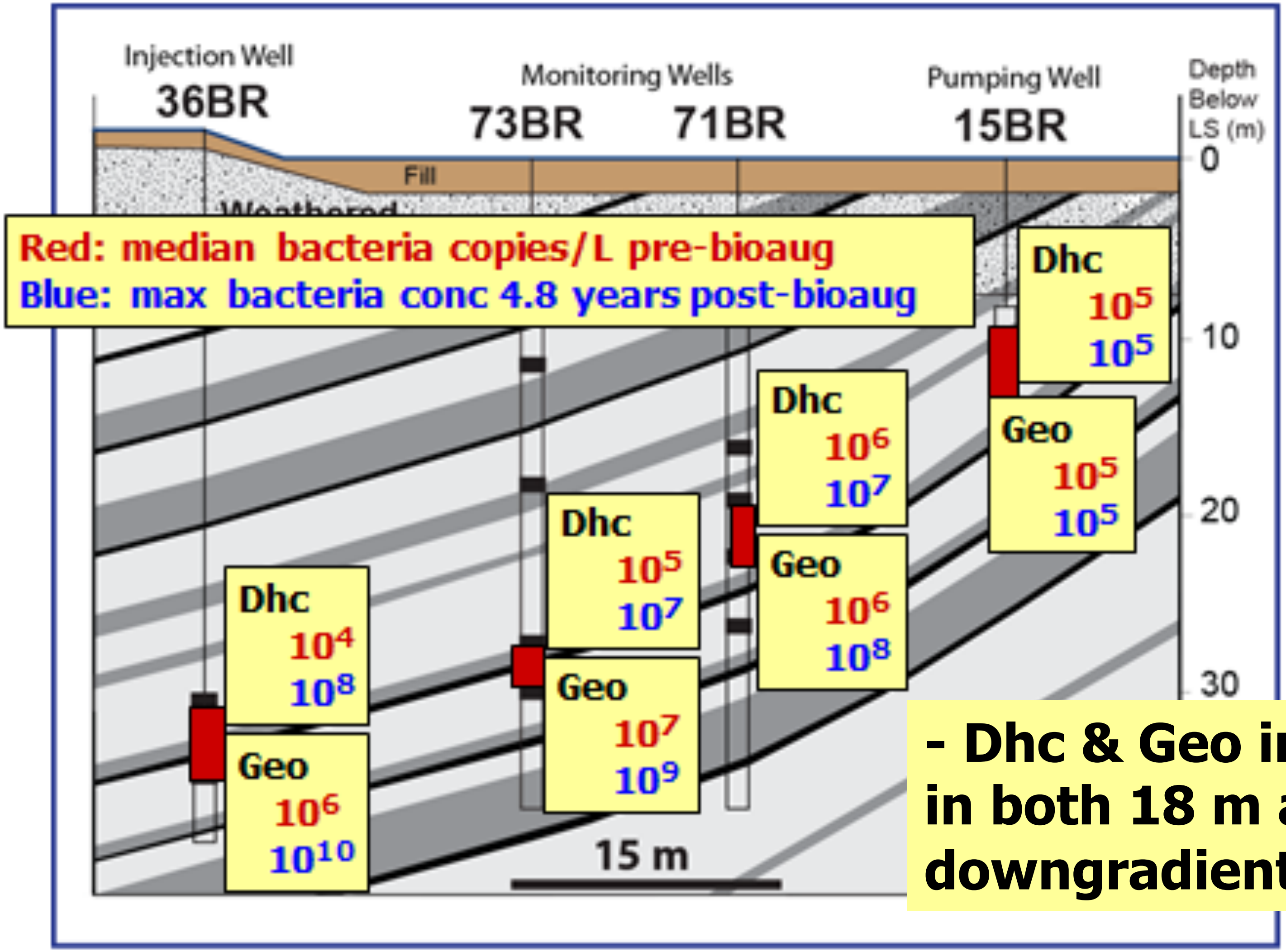
- SO_4 decreases seen in well 18 m down the flow path

Sulfate Reduction



Microbial abundances. . .

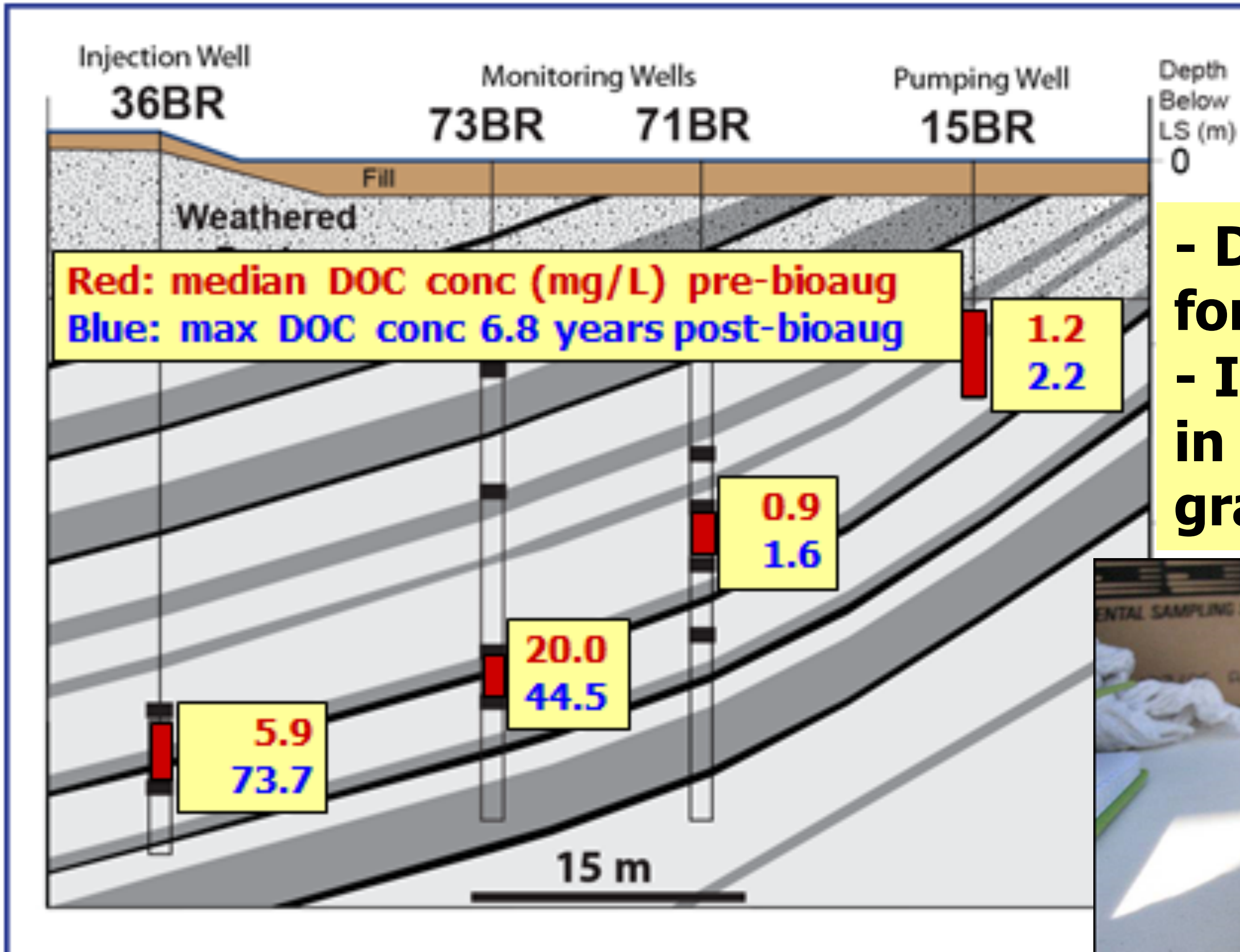
Dehalococcoides and Geobacter Increases



- Dhc & Geo increases seen in both 18 m and 30 m downgradient wells.

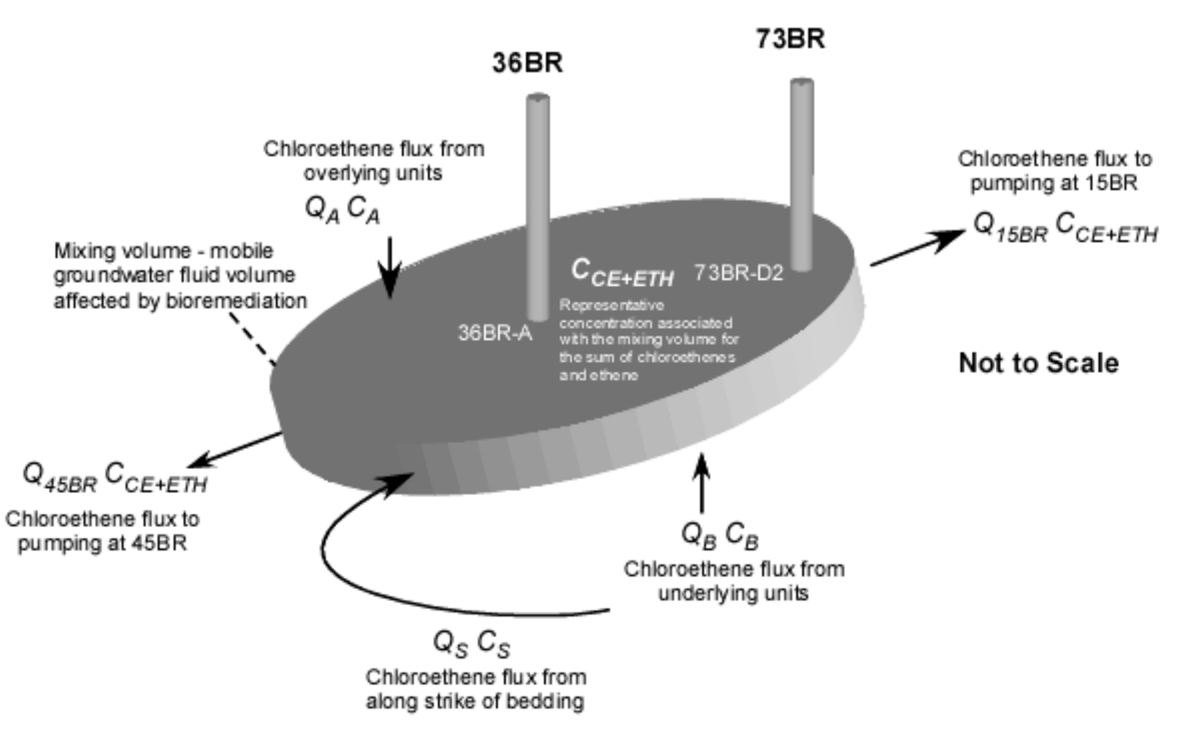
Electron donor. . .

DOC Concentrations



- DOC surrogate for EOS.
- Increases seen in 18 m down-gradient well.

Scoping calculations – a rudimentary chloroethene mass balance. . .



CE mobilization in treatment zone

$$Q_S + Q_A + Q_B - Q_{15BR} - Q_{45BR} = 0$$

$$V_F \frac{dC_{CE+ETH}}{dt} = -(Q_{15BR} + Q_{45BR})C_{CE+ETH} + Q_A C_A + Q_B C_B + Q_S C_S + V_F F_{CE+ETH}$$

$$F_{CE+ETH} = F_{DIS} + F_{DIF} + F_{SORP} - F_{alt}$$