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# High-Resolution Delineation of Chlorinated Solvent Concentrations, Pore Water Velocity, Biogeochemical Processes, and Microbial Communities in Saturated Subsurface Environments

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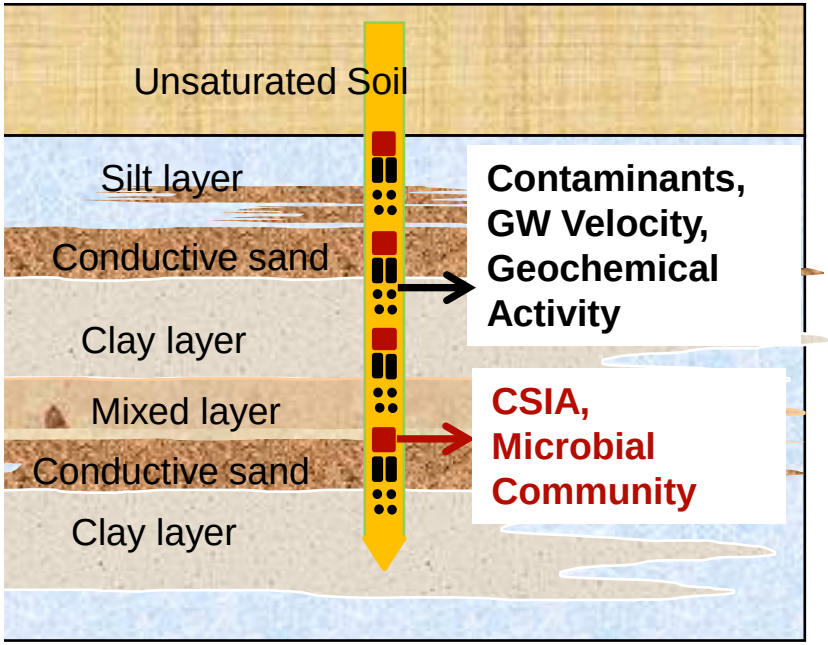
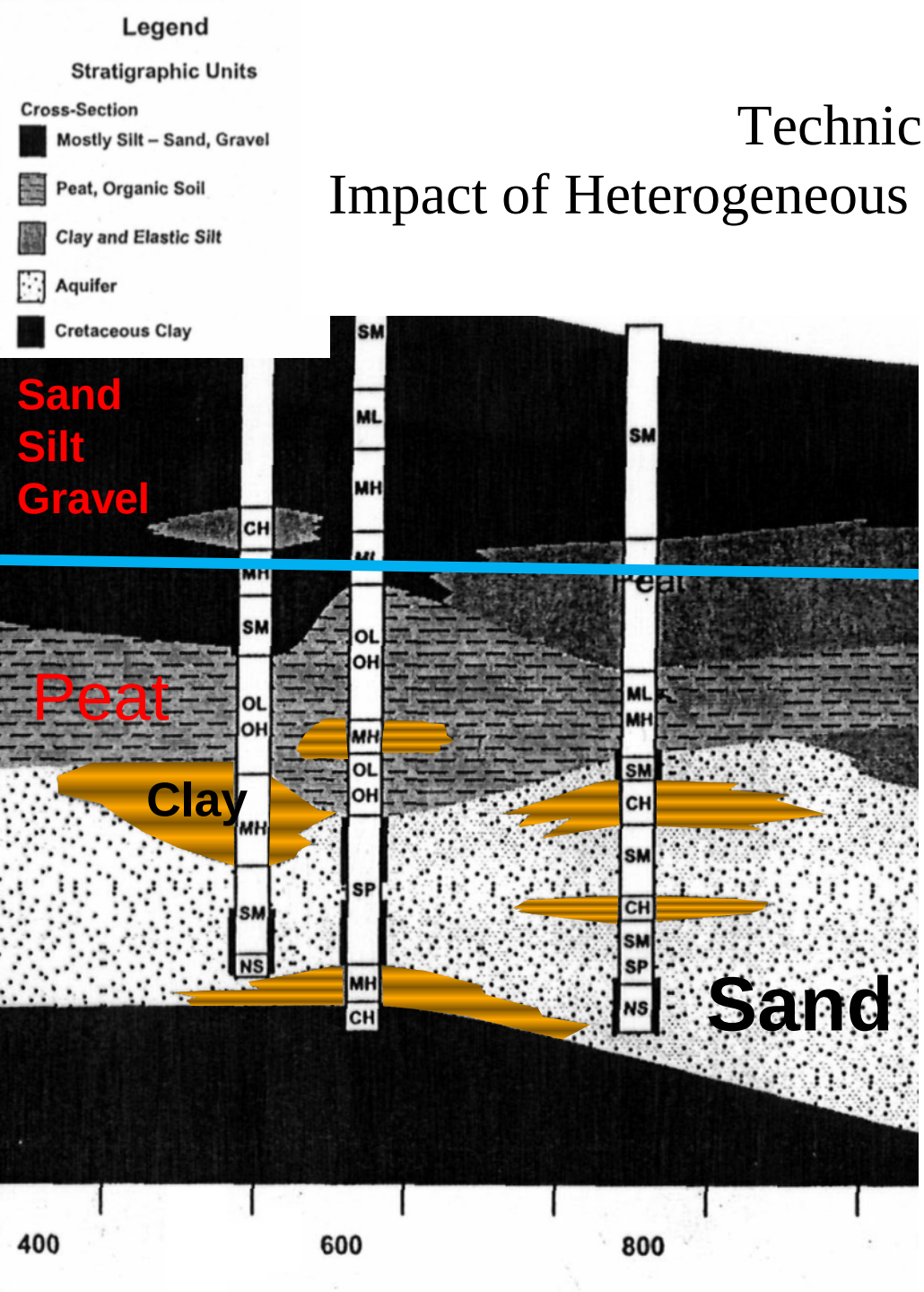
# Objectives

- **The overall goal of this research is to develop and demonstrate a High Resolution Passive Profiler (HRPP) as a fine-scale delineation tool for the saturated subsurface**
  - Directly measure groundwater and contaminant flux at the cm-scale
  - Quantify biogeochemical conditions at the cm-scale
  - Assess microbial community structure and activity at the cm-scale
  - Determine the extent to which the newly developed HRPP can be used to improve conceptual site models




Tested with laboratory experiments and a field trial

# Technical Background
# Impact of Heterogeneous Stratigraphy on Site Assessment




Oversimplified distribution of:

- Groundwater velocity
- Contaminant distribution and mass flux
- Dominant redox processes and buffers
- Abiotic and biotic degradation capacity
- Microbial activity/capacity

# Technical Background
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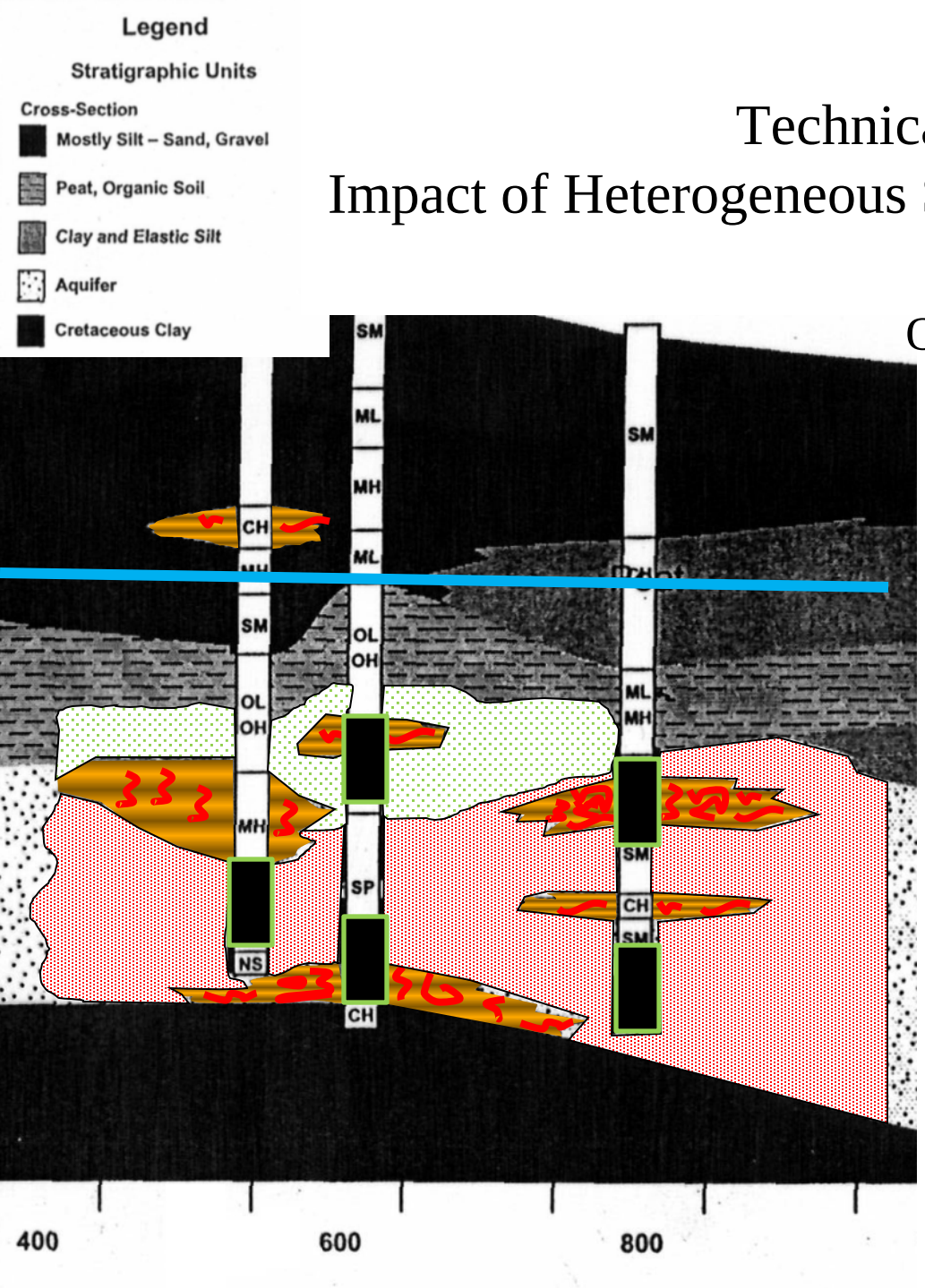


Oversimplified distribution of:

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- Contaminant distribution and mass flux
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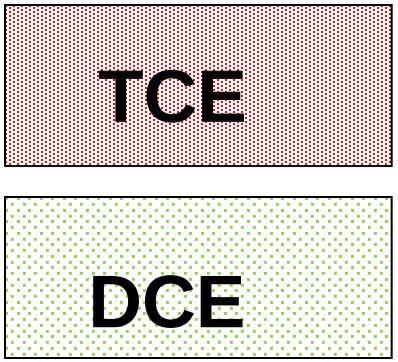
  - *Dominant redox processes and buffers*
  - *Microbial activity/capacity*




NAPL

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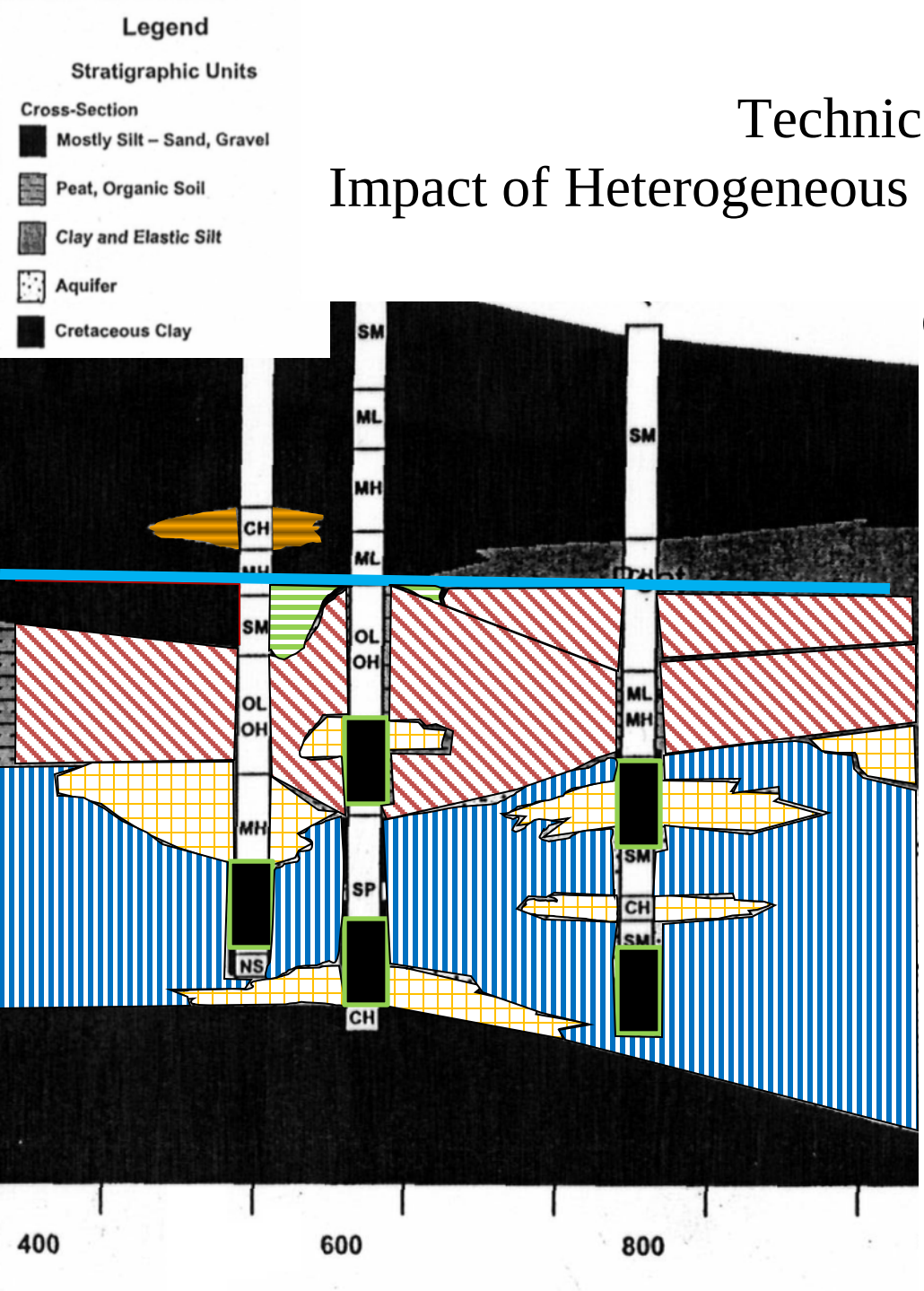


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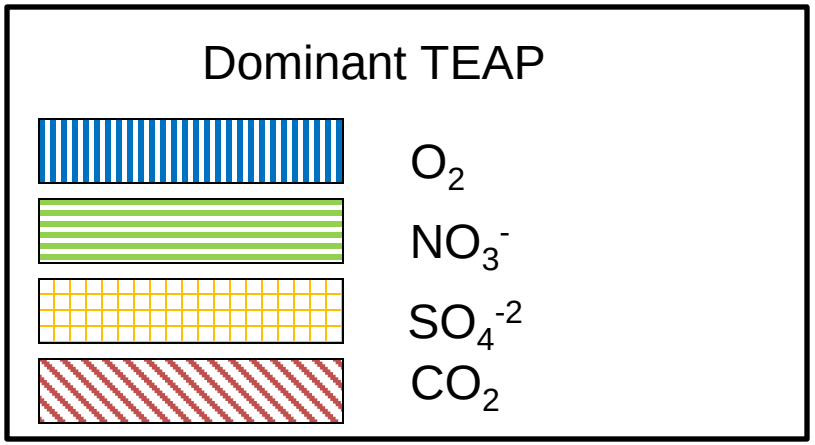
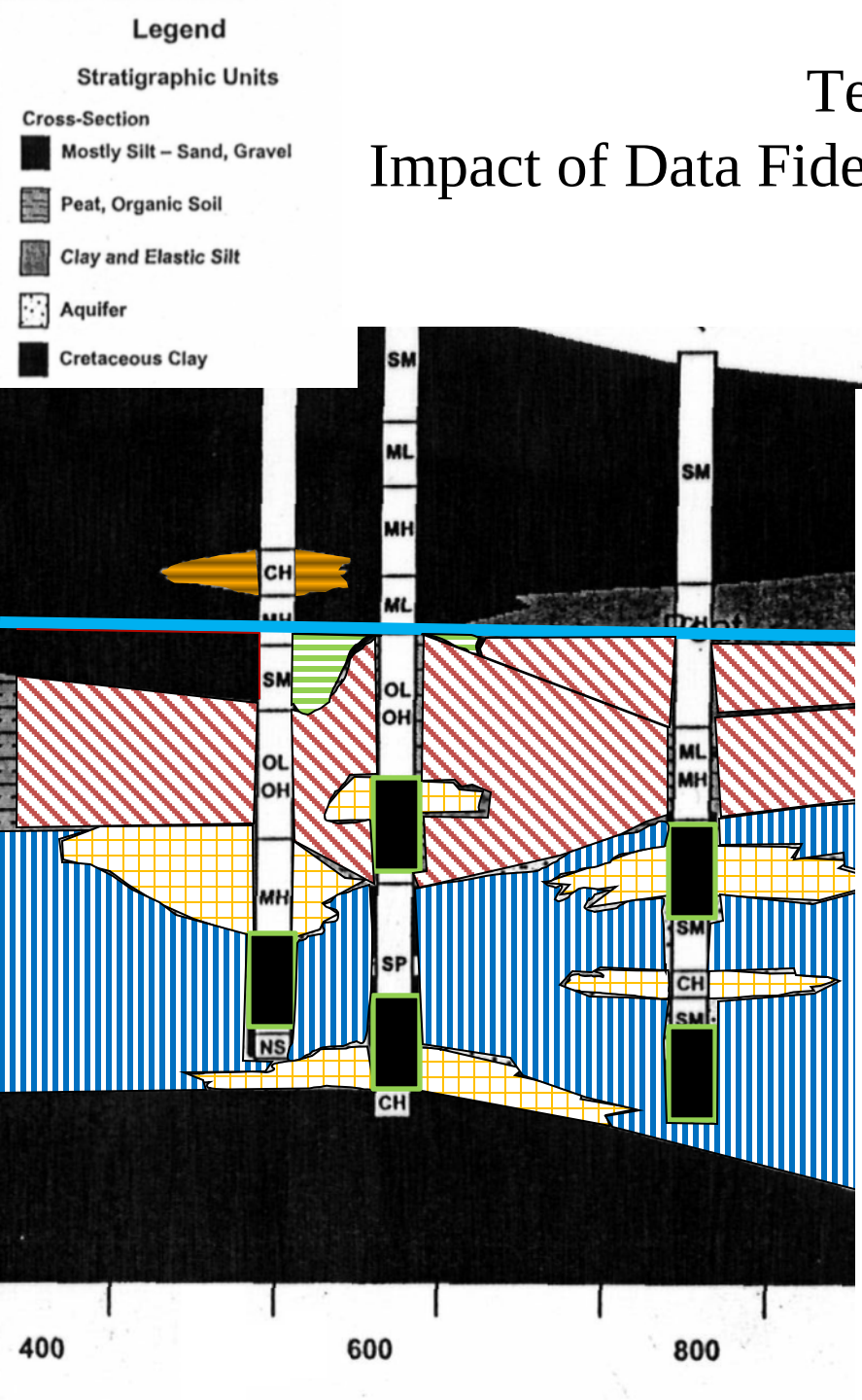


# Technical Background
# Impact of Data Fidelity on Site Assessment and Remedial Activities




Modeling of contaminant transport

Determination of realistic clean up goals and duration

- Rebound due to dissolution of trapped NAPL
- Transport out of low permeability zones

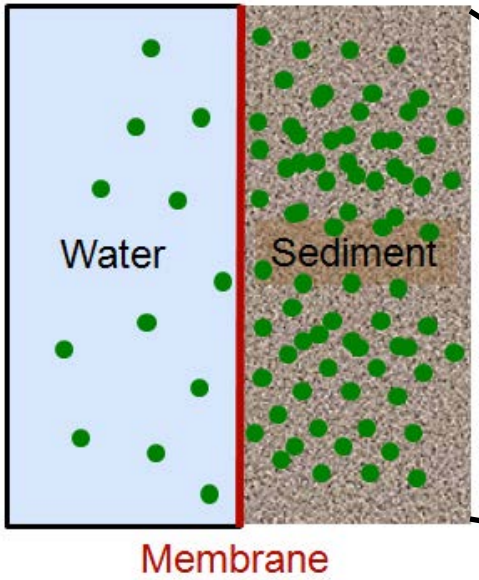
Selection of optimal remedial processes

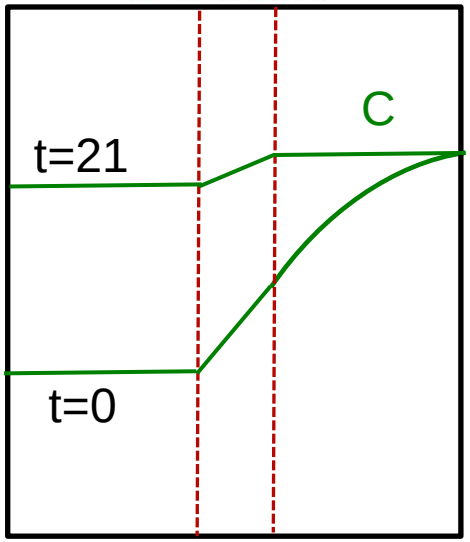
- Biological
- Chemical
- Physical

Location and frequency of application of remedial activities

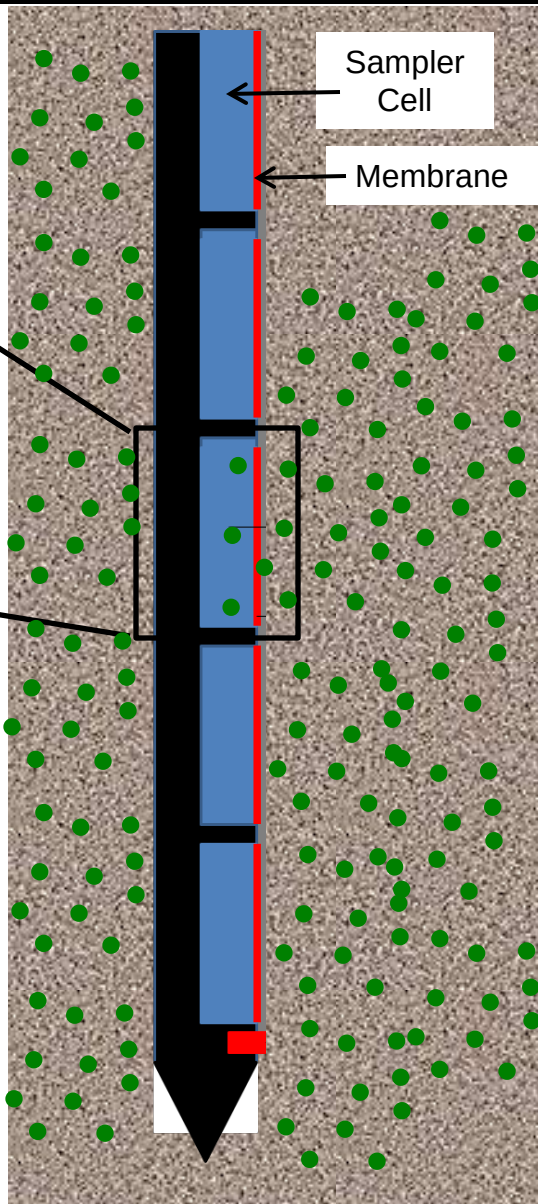
- Injection well locations (vertical and aerial)
- Number of applications and at what interval?

# Equilibrium Pore Water Sampling




$$C = C_0(1 - e^{-k_m \frac{A}{V}})$$



# Equilibrium Porewater Sampling

## Applications

- Species
  - Cl, Br, $NO_3$, $NH_4$, DOC, $SO_4$
  - RDX, $ClO_4$, BTEX
  - Chlorinated Solvents (e.g. TCE, PCE, TeCA)
  - Metals (Sr, Pb, Hg, Cd, Cu)
- Environments
  - Wetlands
  - River/Lake Sediments
  - Shallow Aquifers

## Advantages

- Least Sediment Disturbance
- Simple to use
- High Spatial Resolution
- Low Cost
- No Well Installation
- Concentrations not Fluxes

## Processes

- Fate of Contaminants
- Bioavailabity
- Monitoring of Remediation
- Plant Contaminant Interactions

## Disadvantages

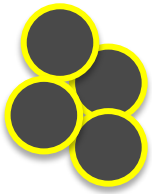
- Detection limit

# Microbial Community Analysis

Bio-sep beads

HRPP microbial cell

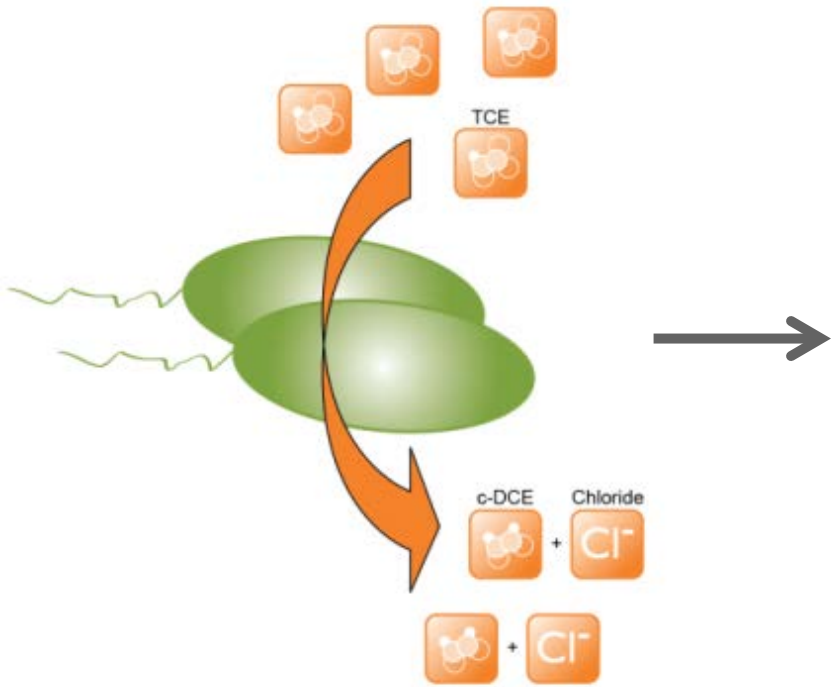
Microbes colonize beads

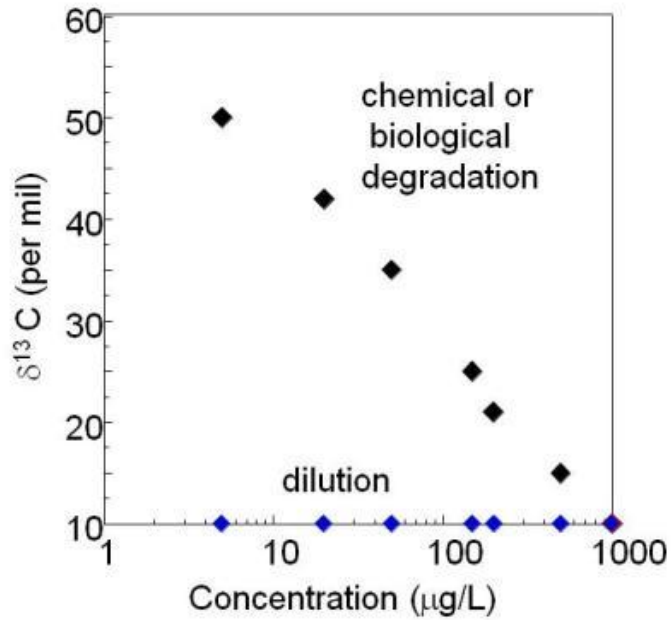


Extract DNA and Analyze for:

- Bacterial Species Metabolic Capability
- CSIA

# Compound Specific Isotope Analysis (CSIA)

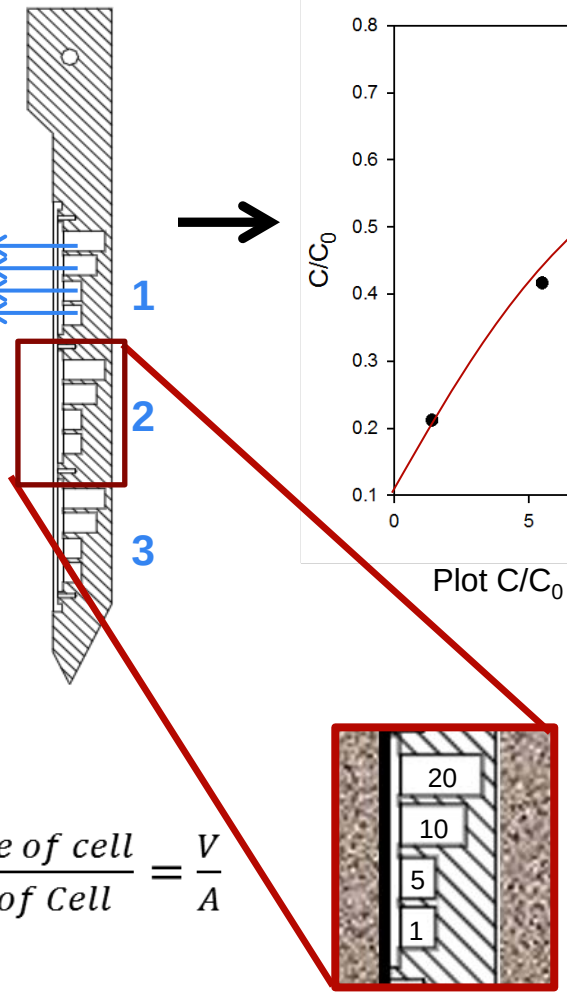


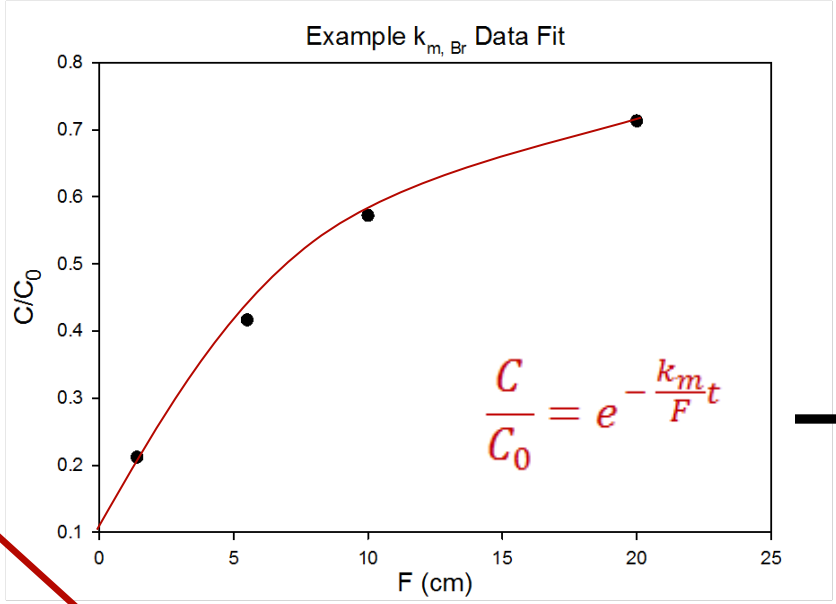




- Bacteria enrich stable isotopes of C and Cl in parent VOCs during reductive dechlorination
- Enrichment also occurs during abiotic reduction
- Strong indication of VOC degradation *in situ*

# Measuring Pore Water Velocity Using Mass Transfer Coefficient, $k_m$

Measure Br- concentration after HRPP is retrieved



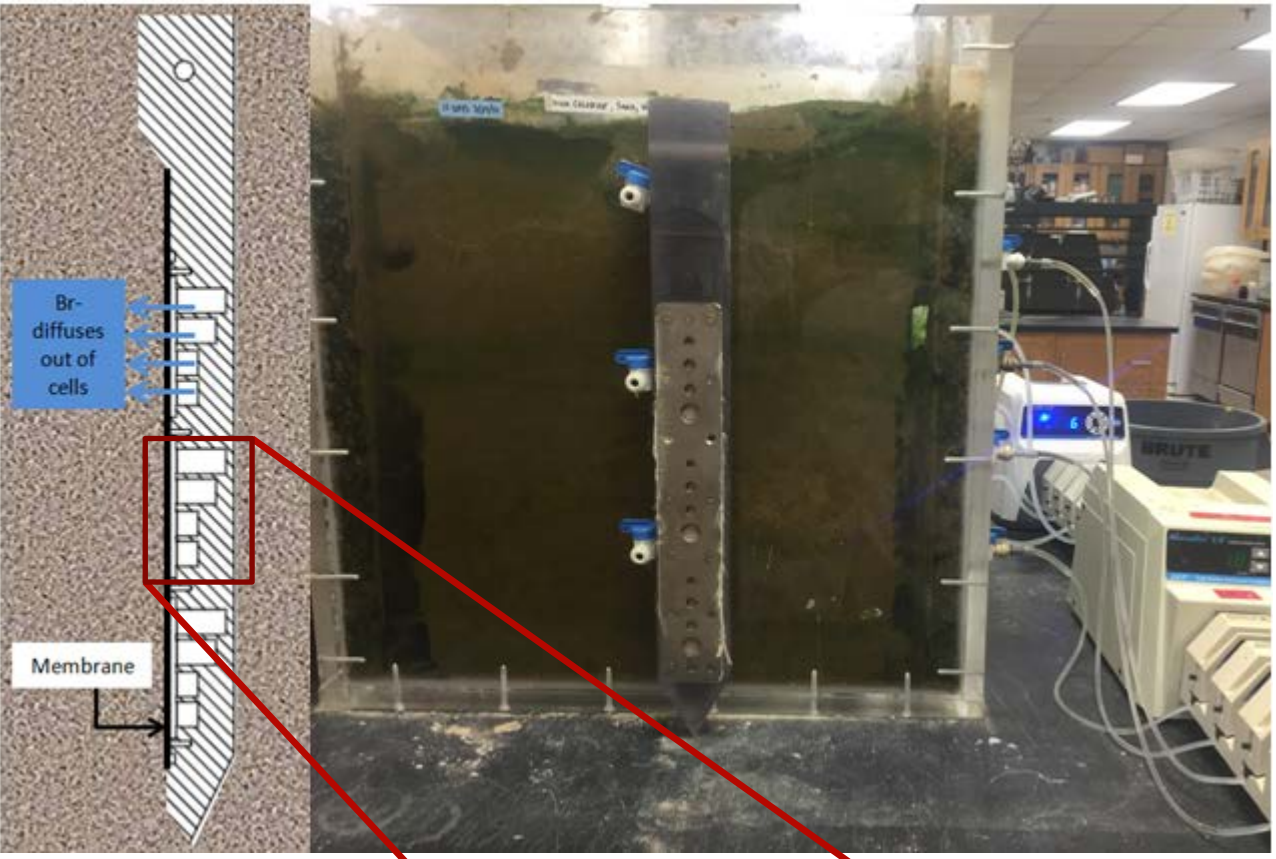

Plot $C/C_0$ vs. F (use the average of 3 sets)

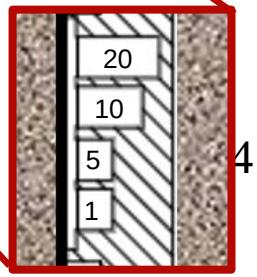
= $k_m$ for one time point

$$F = \frac{Volume\ of\ cell}{Area\ of\ Cell} = \frac{V}{A}$$

4 different F values for each set

# Experimental Approach – Determining Velocity



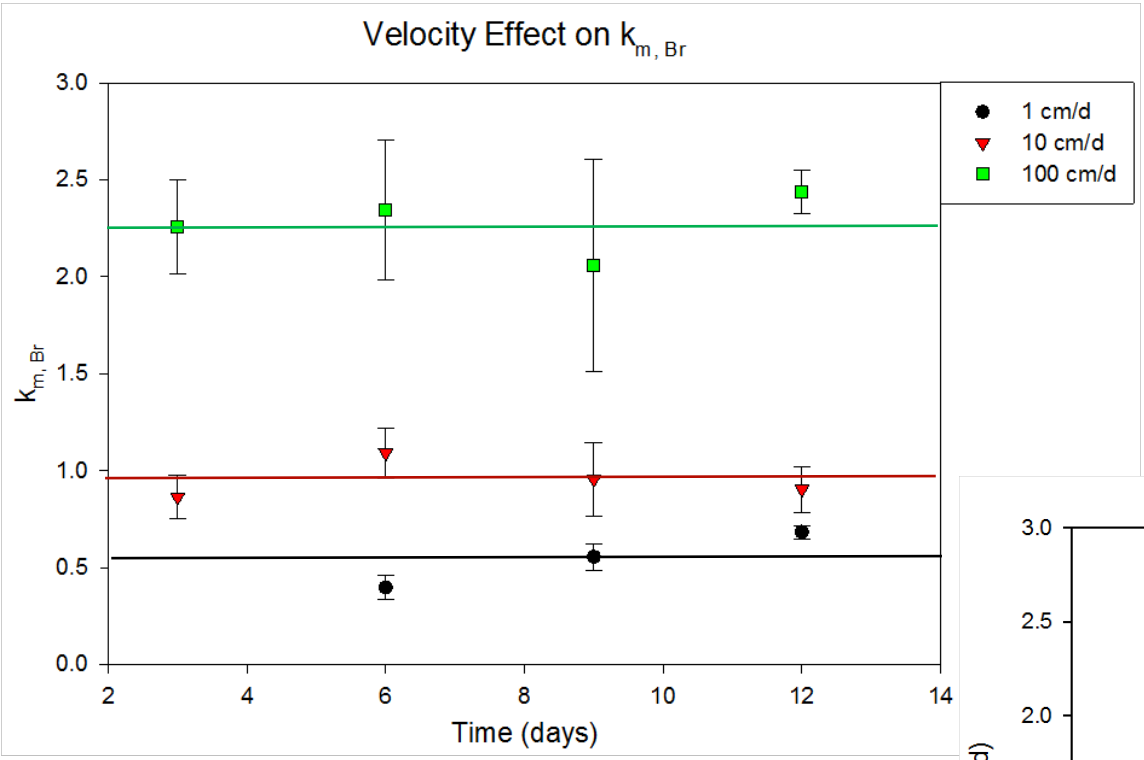

$$F = \frac{Volume\ of\ cell}{Area\ of\ Cell} = \frac{V}{A}$$

4 different F values for each velocity set

## Specialized HRPP's with only velocity cell sets

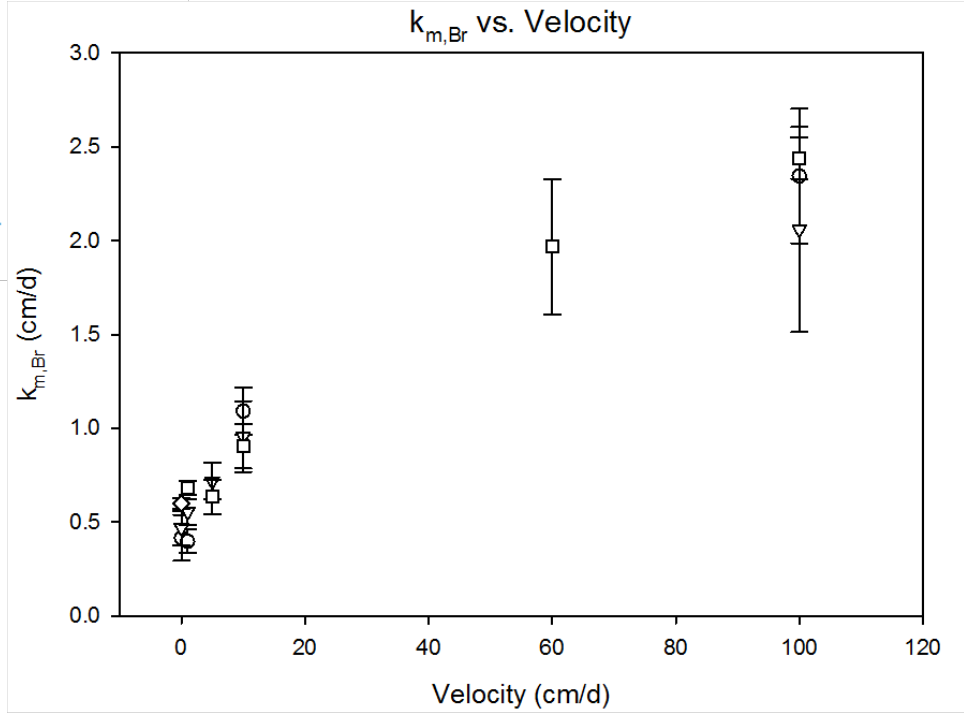
1. Equilibrate laboratory flow box with 100 mg/L $Cl^-$ solution
2. Fill HRPP cells with 100 mg/L $Br^-$ solution
3. Insert HRPP into flow box
4. Remove HRPP after prescribed number of days and measure $Br^-$
5. Change velocity through flow box and repeat 1-4

# Results – Effect of Velocity on $k_m$

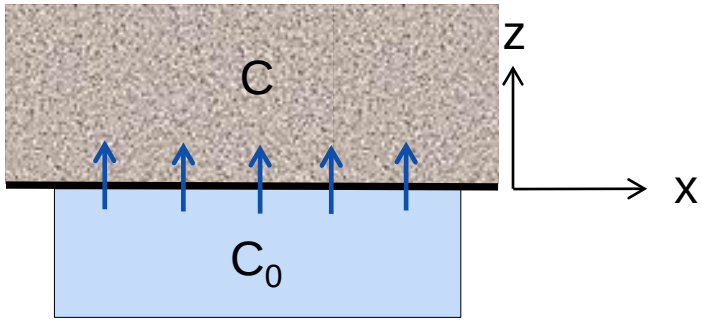



Key points:

1. $k_m$ increases with velocity
2. $k_m$ is independent of time



# Analytical Model – Effect of Velocity on $k_m$




$C_0$ = concentration in cell

C = concentration in porous media

δ = membrane thickness

U = groundwater velocity

x = ½ cell length in x direction

$D_m$ = membrane diffusivity

$D_z$ = diffusivity in z direction

$D_w$ = free water diffusivity

Θ = porosity

τ = tortuosity

α = transverse dispersion

$d_p$ = particle diameter

2D Quasi Steady State

$$U\frac{dC}{dz} = D_z\frac{d^2C}{dz^2}$$

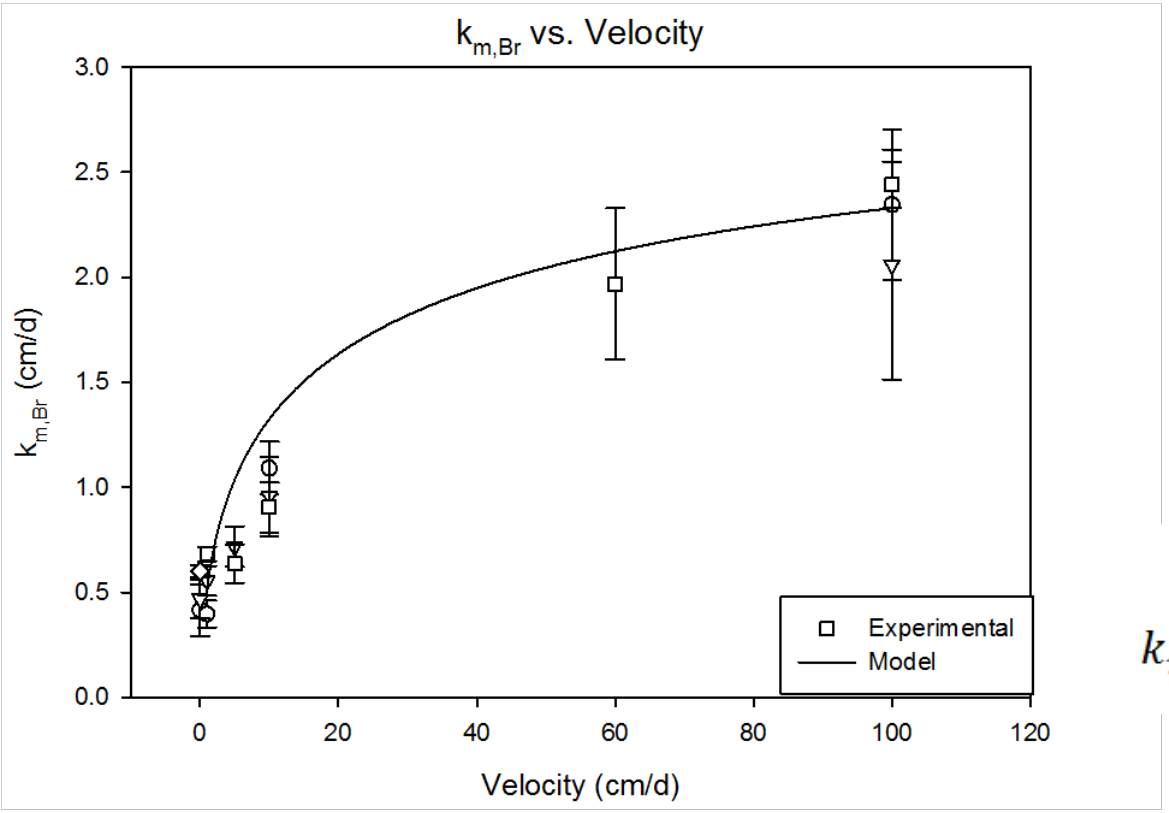
$$C_0 - C = C_0 \qquad z = 0 \rightarrow \infty,\ x = 0$$

$$D_z\frac{dC}{dz} = \frac{D_m}{\delta}(C_0 - C) \qquad z = 0 \rightarrow \infty,\ x > 0$$

$$\boxed{k_m = \frac{D_m}{\delta}e^{\left(\frac{\left(\frac{D_m}{\delta}\right)^2 x}{UD_z}\right)} erfc\left(\frac{D_m}{\delta}\sqrt{\frac{x}{UD_z}}\right)}$$

$$D_z = \frac{D_w\theta}{\tau} + \alpha U \qquad \frac{\theta}{\tau} = \theta^{4/3} \qquad \alpha = \frac{d_p}{10}$$

# Results – Model vs. Experimental




Key points:

1. Model seems representative of general $k_m$ correlation to velocity
2. Current experiments to determine intermediate data points (V~50 cm/d)

$$k_m = \frac{D_m}{\delta} e^{\left(\frac{\left(\frac{D_m}{\delta}\right)^2 x}{UD_z}\right)} erfc\left(\frac{D_m}{\delta}\sqrt{\frac{x}{UD_z}}\right)$$

$D_m$ = membrane diffusivity

δ = membrane thickness

U = groundwater velocity

$D_z$ = diffusivity in z direction

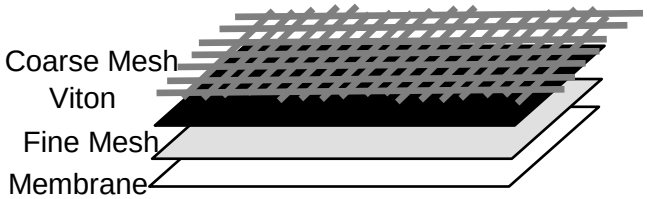
x = ½ length of cell in x direction

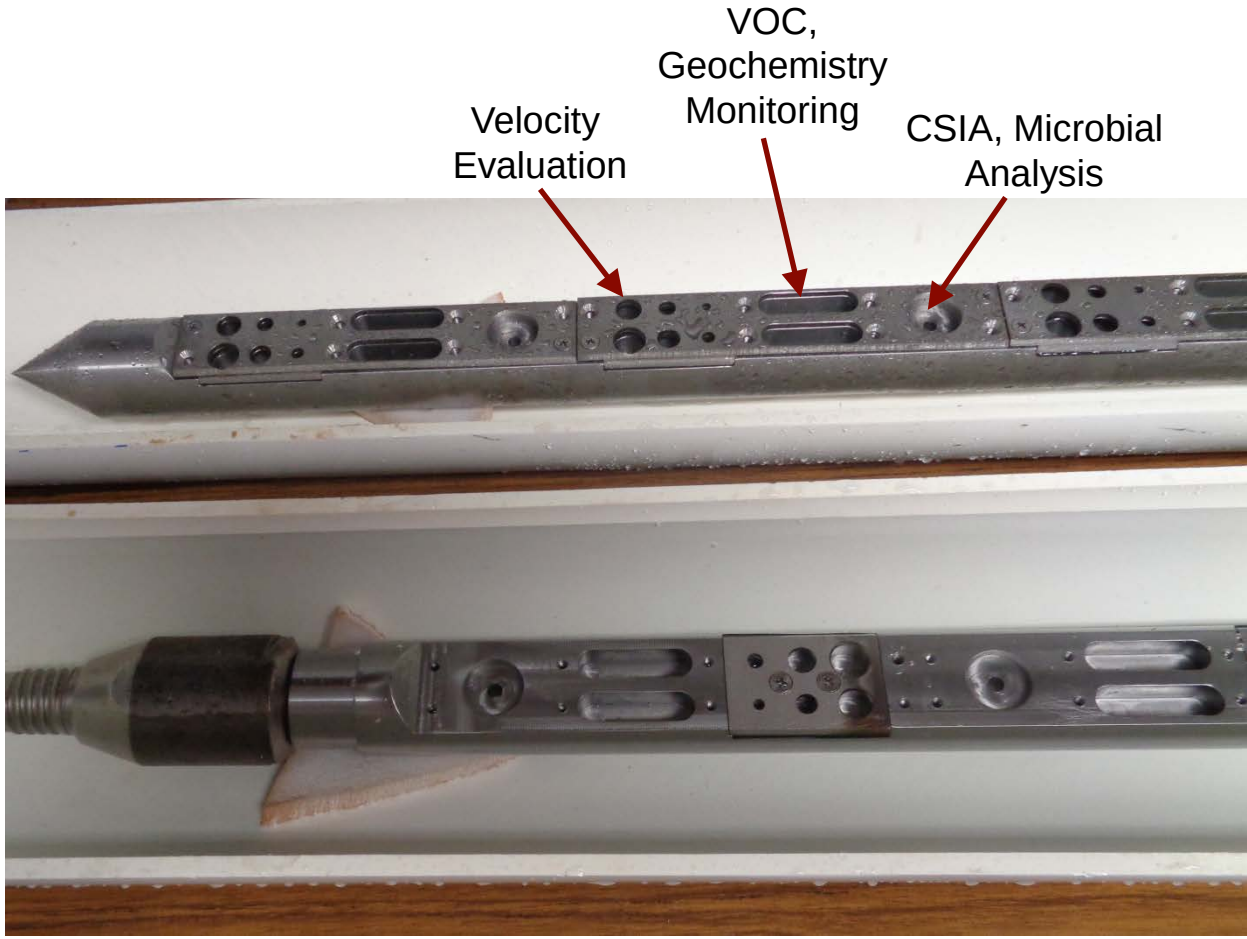
# HRPP Design – Prototype #1

## Prototype #1 used for field trial

- 5cm diameter
- 316 steel

## Material Layers:

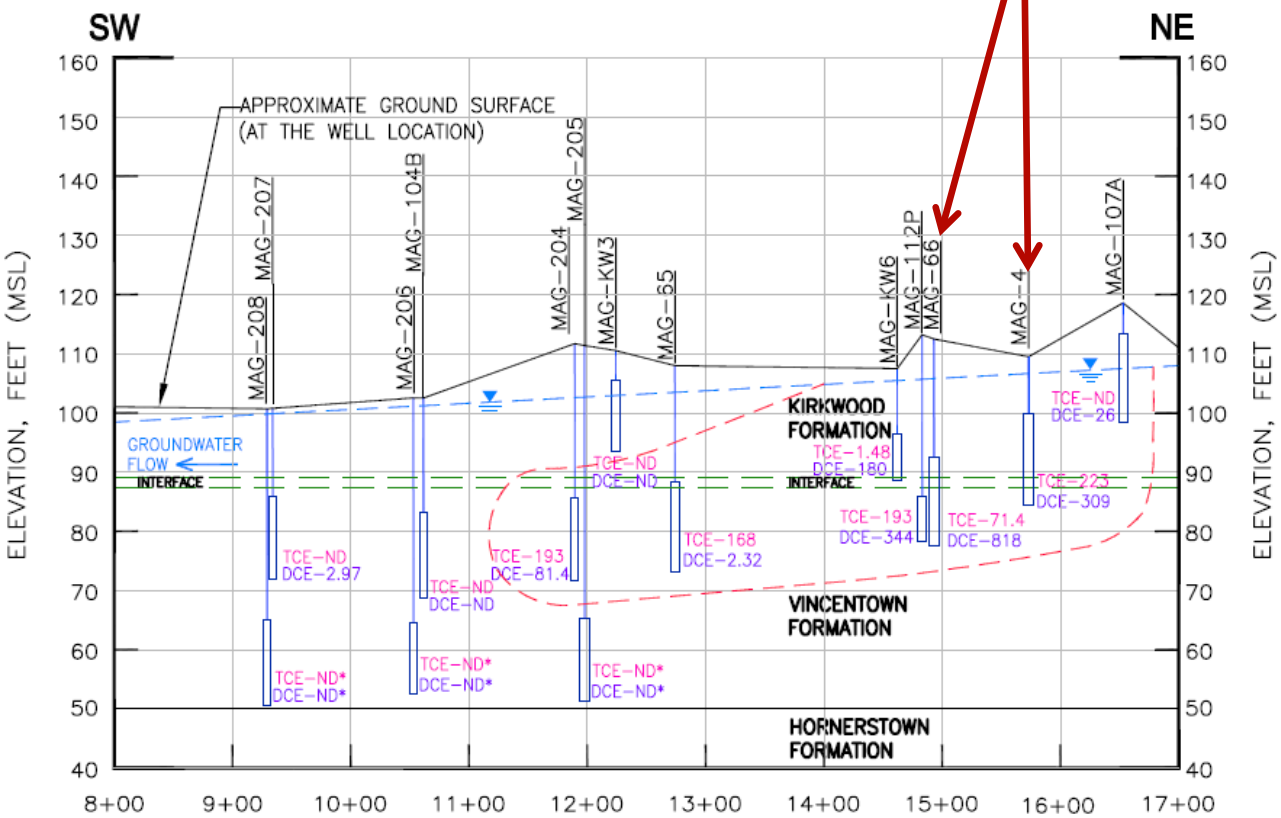



5 full data sets over 4 feet

# Field Trial – Fort Dix Site Profile

Testing locations,
MAG 66 and MAG 4




PROFILE SW-NE

LEGEND:

TCE-223 TCE CONCENTRATION (ug/L) – MAY 2015

DCE-309 DCE CONCENTRATION (ug/L) – MAY 2015

* ND IN MOST RECENT SAMPLING (DECEMBER 2013)

TCE/DCE ABOVE GWQS PLUME BOUNDARY

**GROUNDWATER QUALITY STANDARDS (ug/L)**

| FORMATION | TCE | DCE |
|---|---|---|
| KIRKWOOD | 1 | 1 |
| VINCENTOWN | 1 | 70 |

HORIZONTAL SCALE
0 100 200 FEET

VERTICAL SCALE
0 20 40 FEET

CB&I
200 Horizon Center
Trenton, New Jersey 08691-1904

# Field Trial – Insertion & Sampling

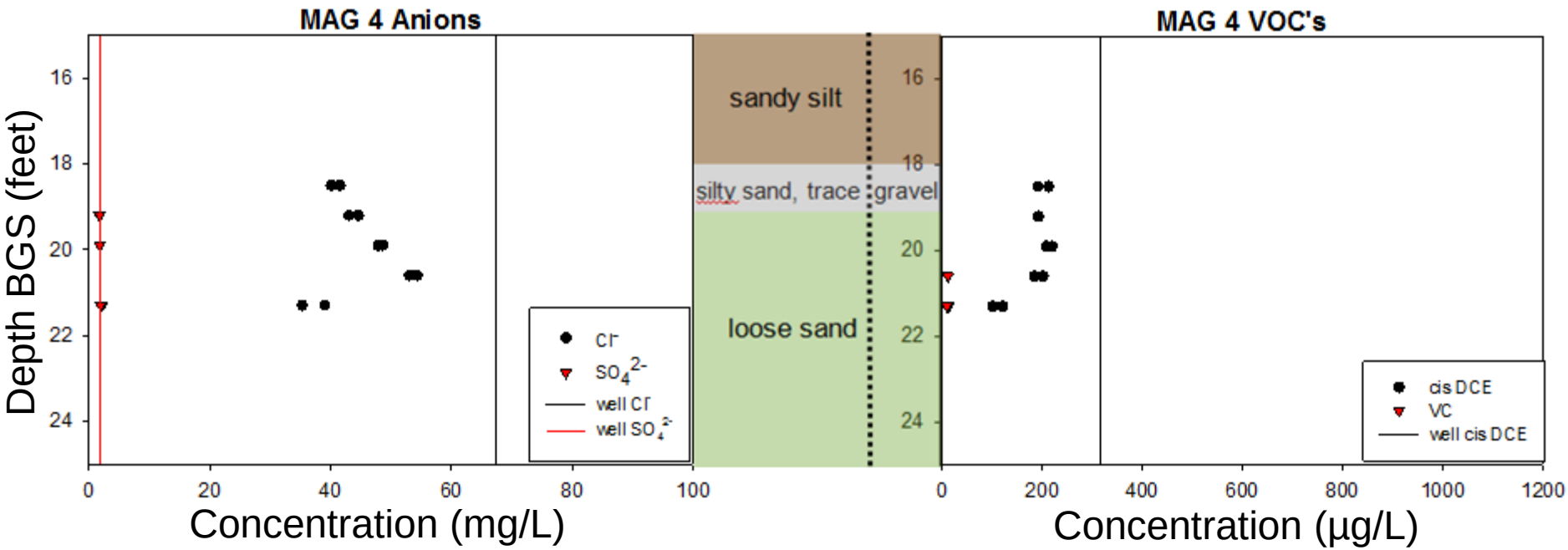
Two Prototype Samplers Installed for 3 weeks at Fort Dix (18 to 26ft BGS)

Insertion

Sampling

After Retrieval

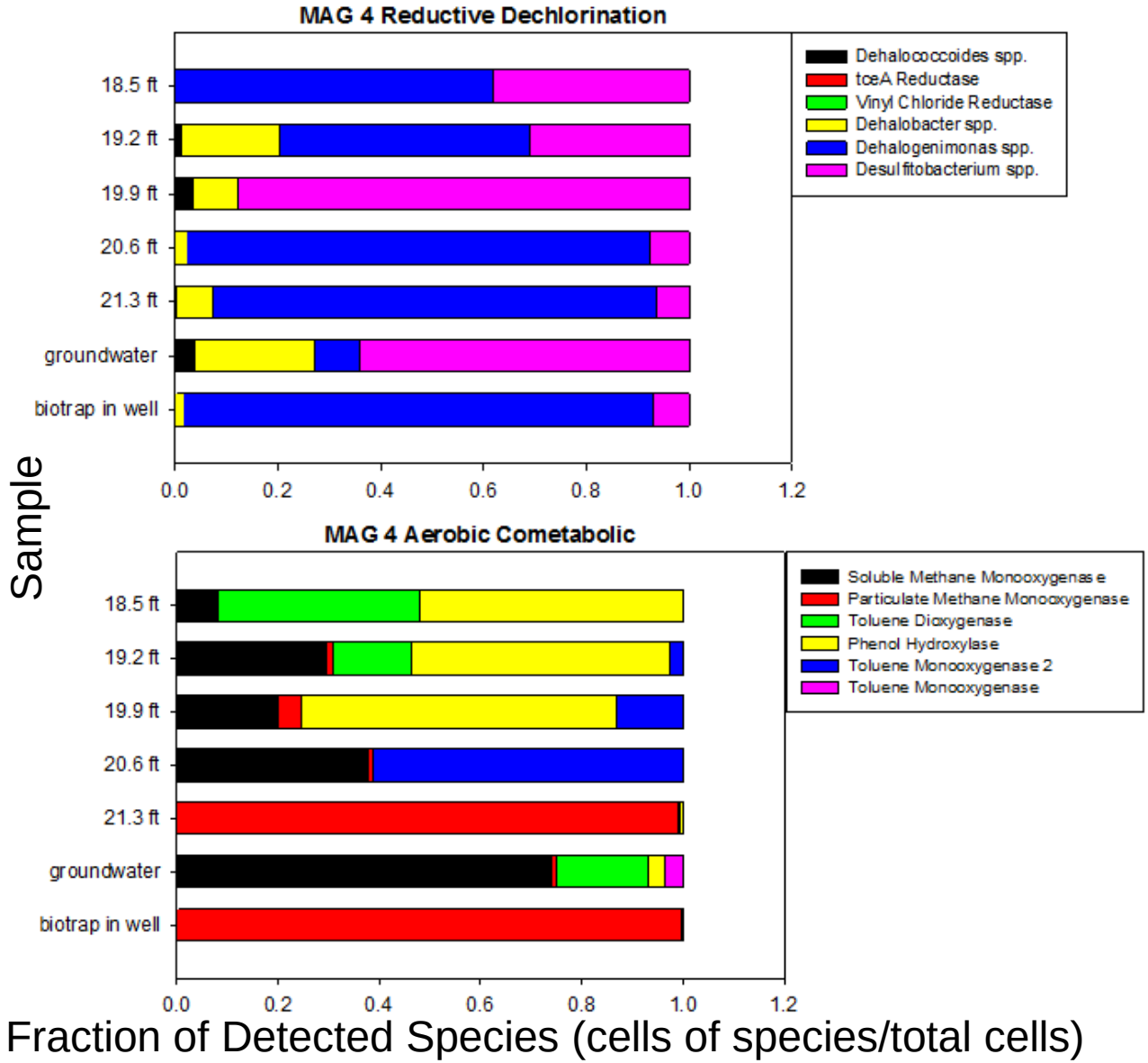
# Field Trial Results – Anions and VOC's

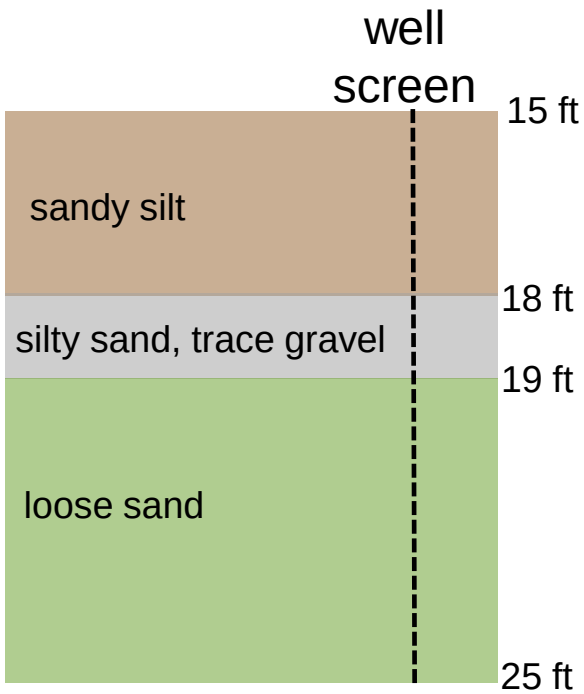



CSIA for Cis-1,2,Dichloroethene

| MAG 4 $\delta^{13}C$‰ | | |
|---|---|---|
| **Well Water** | **18 feet BGS** | **22 feet BGS** |
| -25.70 | -23.34 | -21.36 |

# Field Trial Results – MAG 4 Microbial Data

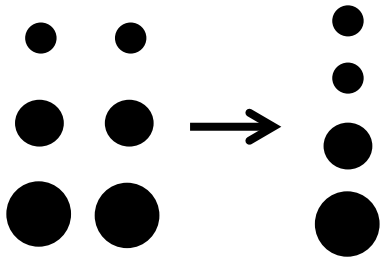


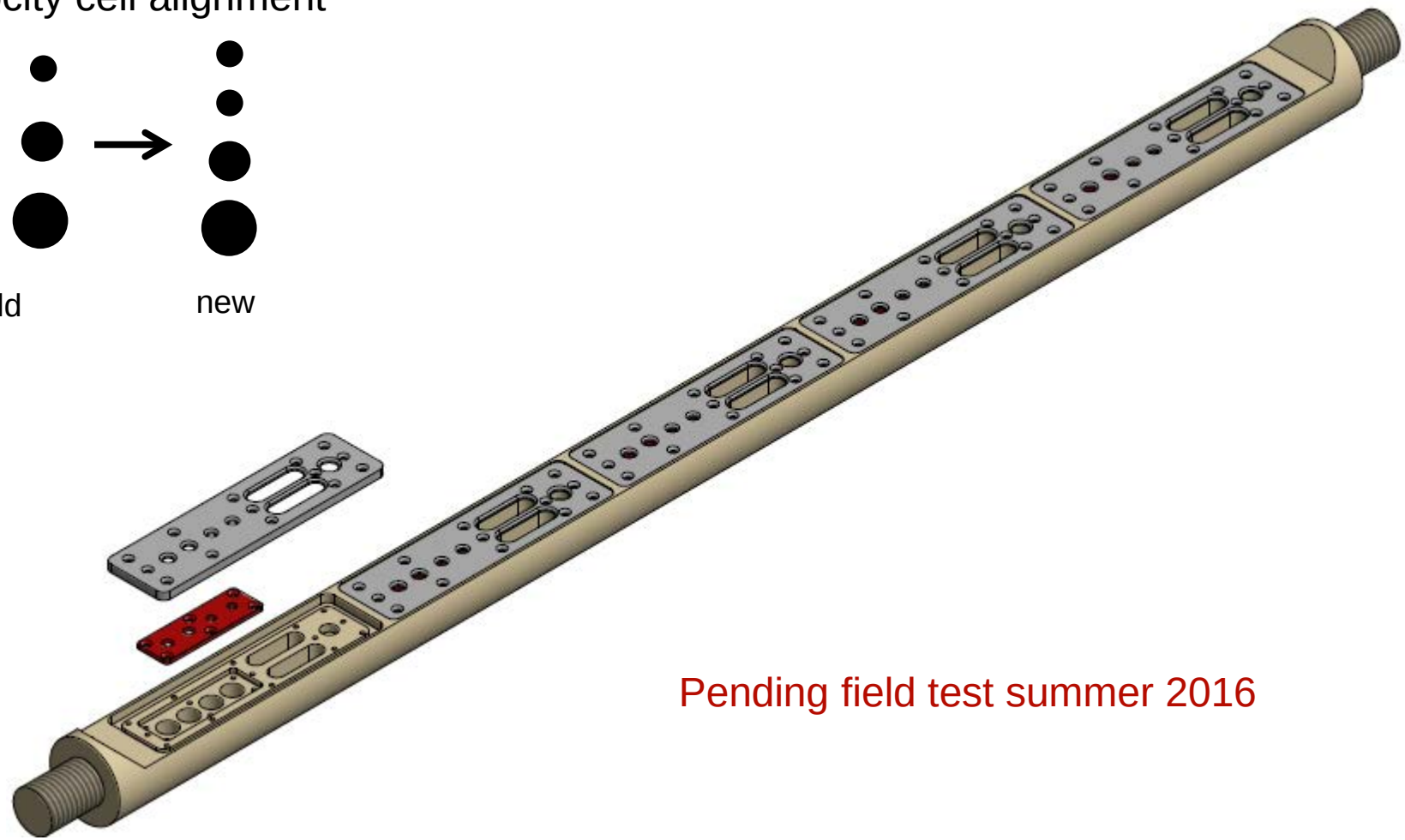
# Current HRPP Prototype

Changes:

- Increased diameter (5cm → 6.4cm)
- Smaller bio-sep bead cell
- Velocity cell alignment



old new



Pending field test summer 2016

# Conclusions

- Direct Insertion to depths >30ft
- Sample interval 4’ to 30’
- Deployment time of 2-3 weeks
- Chlorinated VOC concentrations at 20~cm resolution (DL ~20ppb)
- Biogeochemical indicator concentrations at 20cm intervals ($NO_3^-$, $NO_2^-$, $SO_4^{-2}$, $Fe_T$, DOC)
- Ground Water Velocity
- Microbial community analysis and abundance
- Fate of cVOCs (CSIA)

# Acknowledgements

Funding

SERDP ER-2419