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The webinar will begin promptly at
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SERDP and ESTCP Webinar Series

The webinar will begin promptly at 12:00 pm ET, 9:00 am PT

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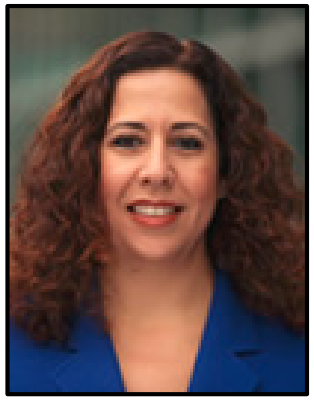
High-Resolution Site Characterization at Chlorinated Solvents Sites

May 18, 2017

SERDP DOD • EPA • DOE | ESTCP

Welcome and Introductions

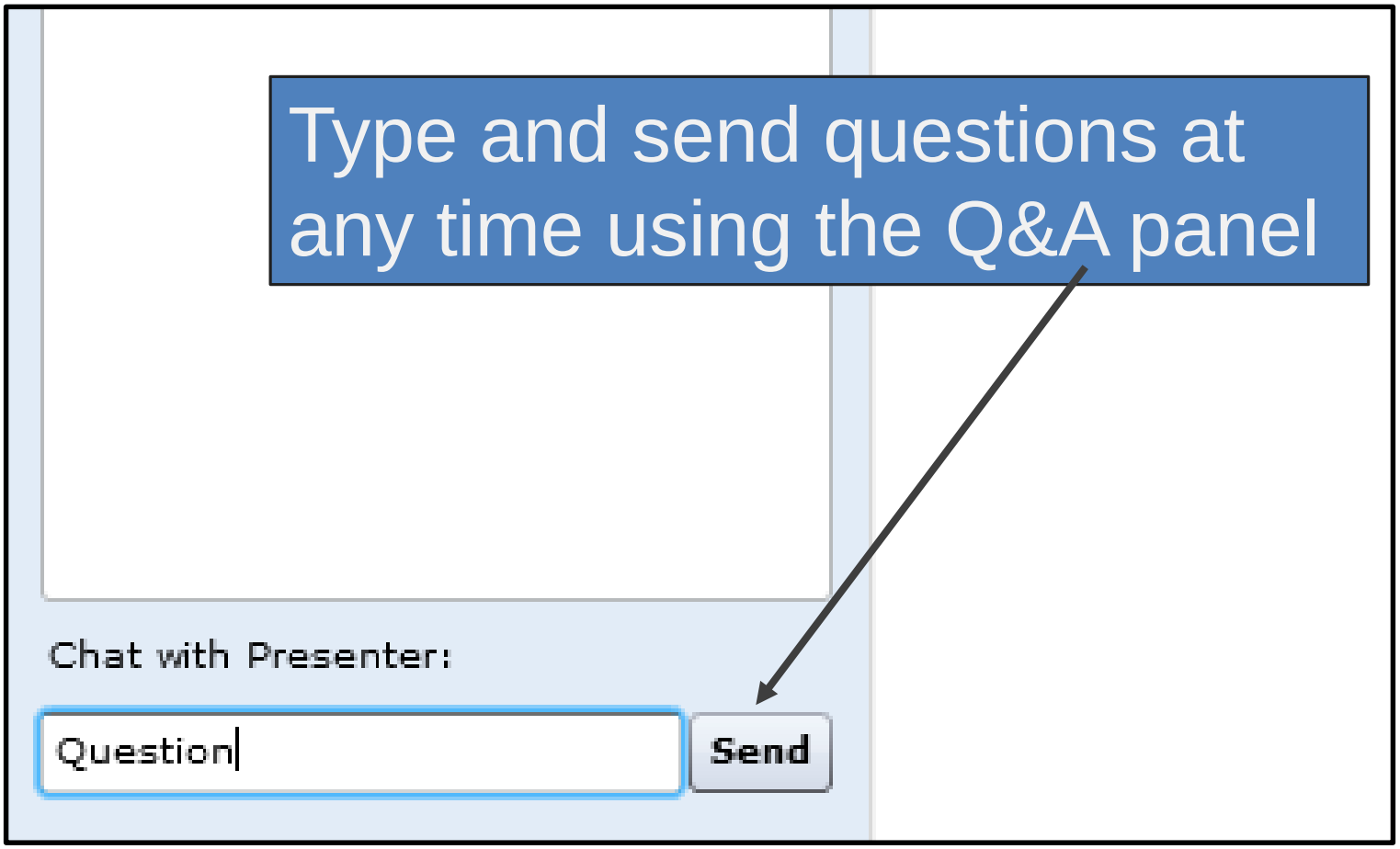


Rula A. Deeb, Ph.D.
Webinar Facilitator

Webinar Agenda

- **Webinar Logistics** (5 minutes)
  Overview of SERDP and ESTCP
  Dr. Rula A. Deeb, Geosyntec Consultants
- **Direct Push Optical Screening Tool for High-Resolution, Real-Time Mapping of Chlorinated Solvent DNAPL Architecture** (25 minutes + Q&A)
  Mr. Murray Einarson, Haley and Aldrich
- **High-Resolution Delineation of Chlorinated Solvent Concentrations, Biogeochemical Processes, and Microbial Communities in Saturated Subsurface Environments** (25 minutes + Q&A)
  Dr. Andrew Jackson, Texas Tech University
- **Final Q&A Session**

How to Ask Questions



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- Delays in the broadcast audio
  - Click the mute/connect button
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- Submit a question using the chat box

SERDP and ESTCP Overview

SERDP
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ESTCP

SERDP

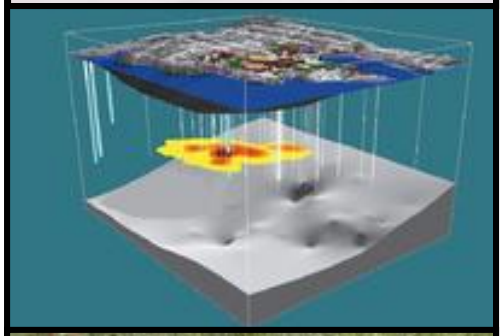
- Strategic Environmental Research and Development Program
- Established by Congress in FY 1991
  - DoD, DOE and EPA partnership
- SERDP is a requirements driven program which identifies high-priority environmental science and technology investment opportunities that address DoD requirements
  - Advanced technology development to address near term needs
  - Fundamental research to impact real world environmental management

ESTCP

- Environmental Security Technology Certification Program
- Demonstrate innovative cost-effective environmental and energy technologies
  - Capitalize on past investments
  - Transition technology out of the lab
- Promote implementation
  - Facilitate regulatory acceptance

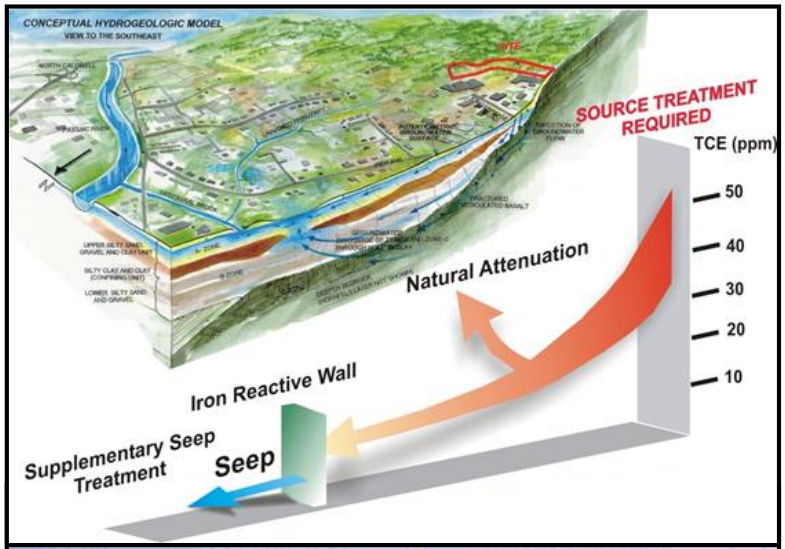
Program Areas

1. Energy and Water
2. Environmental Restoration
3. Munitions Response
4. Resource Conservation and Resiliency
5. Weapons Systems and Platforms



Environmental Restoration

- Major focus areas
  - Contaminated groundwater
  - Contaminants on ranges
  - Contaminated sediments
  - Wastewater treatment
  - Risk assessment



SERDP and ESTCP Webinar Series

Date	Topic
June 1, 2017	Tools for Risk-Based Remediation of Unexploded Ordnance
June 15, 2017	Coupling Geothermal Heat Pumps with Underground Seasonal Thermal Energy Storage
June 29, 2017	Future Vulnerabilities to Alaskan Ecosystems and Tools for Permafrost Assessment
July 20, 2017	Management of Energetic and Propellant Material Releases on Testing and Training Ranges
August 17, 2017	Zinc Nickel Dip and Brush Plating
September 7, 2017	Overview of SERDP and ESTCP Workshop on Research and Development Needs for Management of DoD's PFAS Contaminated Sites

For upcoming webinars, please visit

http://serdp-estcp.org/Tools-and-Training/Webinar-Series

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SERDP • ESTCP SYMPOSIUM

2017 | Enhancing DoD's Mission Effectiveness

A three-day symposium showcasing the latest technologies that enhance DoD's mission through improved environmental and energy performance

- November 28 - November 30, 2017
- Washington Hilton Hotel
  1919 Connecticut Avenue, NW
  Washington, DC 20009
- ***Registration is open***

Direct Push Optical Sensor for High-Resolution, Real-Time Mapping of Chlorinated Solvent DNAPL Architecture

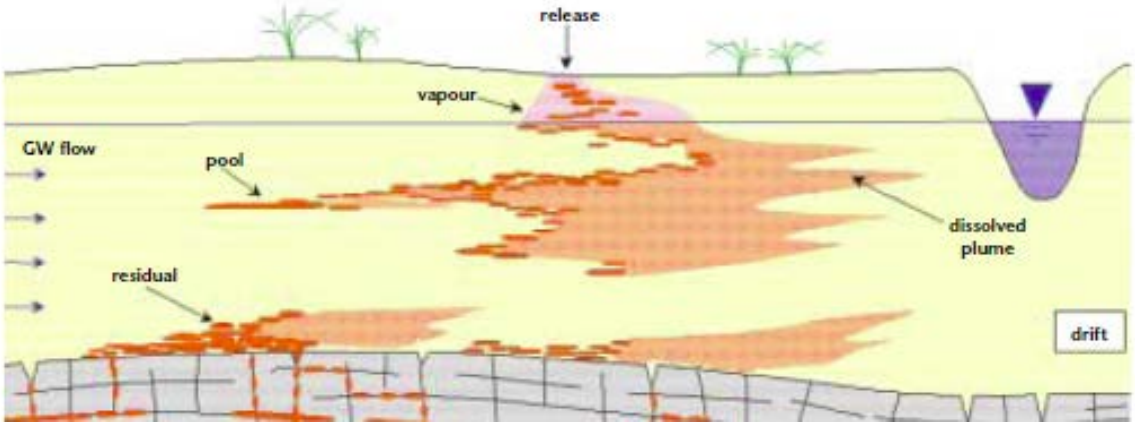
Murray Einarson
Haley & Aldrich

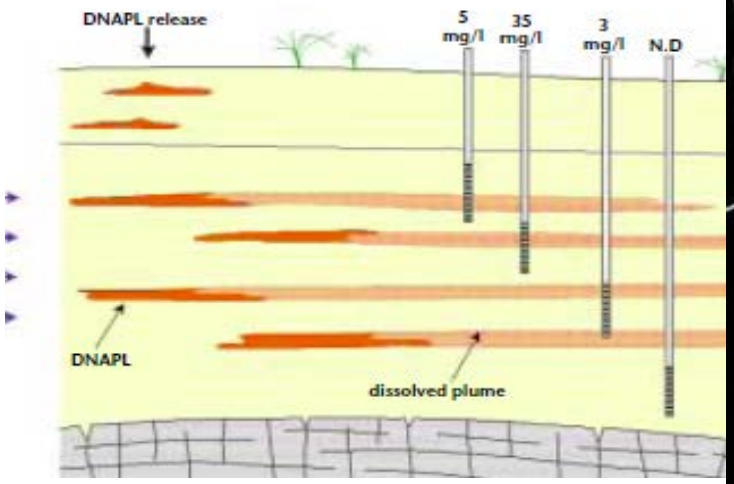
SERDP DOD • EPA • DOE | ESTCP

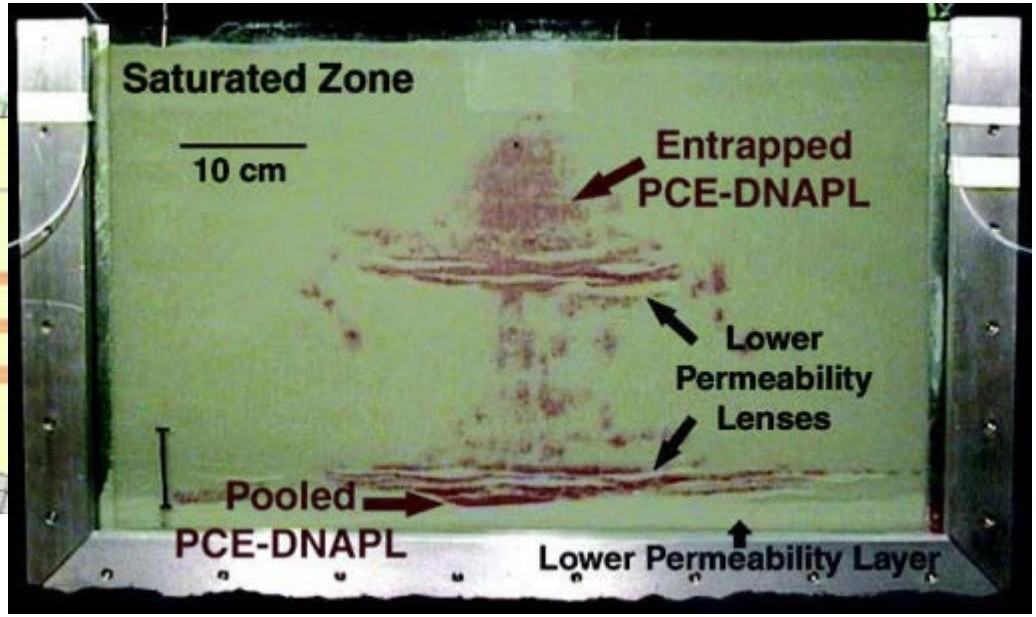
Presentation Outline

- Conventional methods of DNAPL source zone characterization
- Description of new DyeLIF technology
- Results of ESTCP field demonstration

Models of DNAPL Source Zones



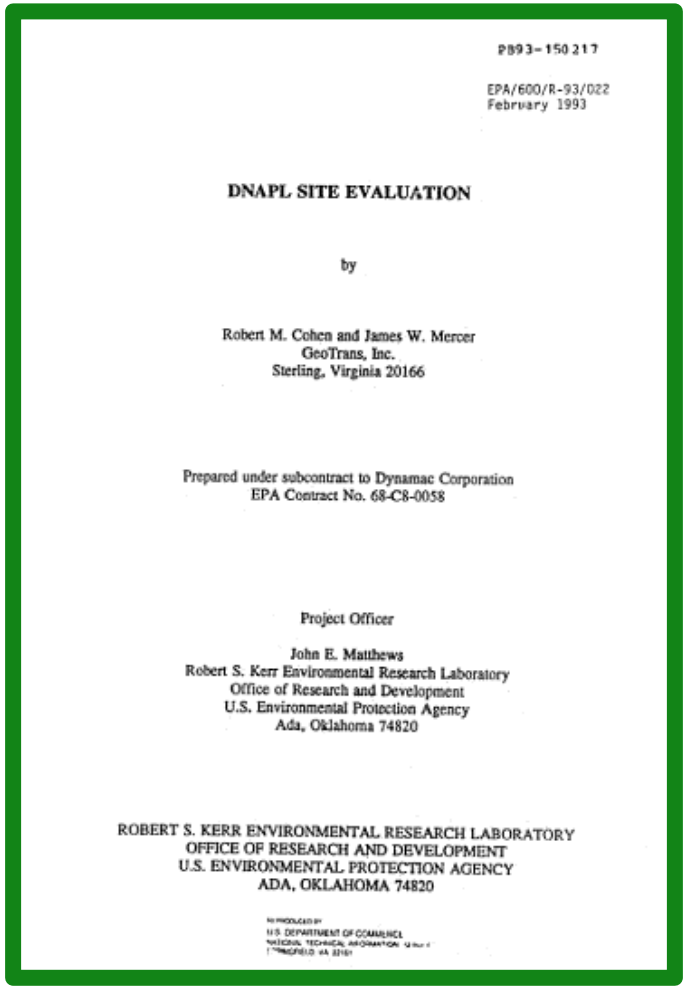




Source: Kueper et al. 2003

Traditional Methods for Delineating Subsurface DNAPL

- Direct observation
- Soil concentrations
- Dye “shake-tests”



PB93-150217

EPA/600/R-93/022
February 1993

DNAPL SITE EVALUATION

by

Robert M. Cohen and James W. Mercer
GeoTrans, Inc.
Sterling, Virginia 20166

Prepared under subcontract to Dynamac Corporation
EPA Contract No. 68-C8-0058

Project Officer

John E. Matthews
Robert S. Kerr Environmental Research Laboratory
Office of Research and Development
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Ada, Oklahoma 74820

ROBERT S. KERR ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
ADA, OKLAHOMA 74820

Dye Shake Tests

Hydrophobic Dyes Such as Sudan IV or Oil-Red-O

7.3 Screening of soil borings

Soil samples can be taken from unconsolidated deposits both above and below the water table using a variety of techniques such as hollow stem auguring, push sampling and trial pits. During drilling operations, soil samples can be taken and subjected to visual examination. If DNAPL is present at high saturations (that is, pooled DNAPL) it will be probably be readily noticeable. If the DNAPL is present at low saturations (that is, residual saturation) or if the DNAPL has the same colour as the soil matrix, it may not be visually apparent and a dye shake test may be required.

A dye shake test involves mixing a small quantity of a hydrophobic dye such as SUDAN IV with the soil sample in a sealed glass jar. In the case of SUDAN IV, the dye is red in colour and will partition only into a NAPL phase; it will not partition into water. If a NAPL is present in the soil sample, it will manifest itself as red globules interspersed within the soil matrix.

Other field screening methods for soil borings include headspace analysis using a portable vapour analyser with photoionisation detection (PID) or flame ionisation detection (FID), and the use of fluorescence analysis. Fluorescence analysis involves taking the obtained soil sample and subjecting it to a fluorescent light in a dark space. Many hydrocarbons such as aromatic and polyaromatic hydrocarbons having one or more benzene rings (for example, coal tar, creosote and PCBs) will fluoresce, along with DNAPL mixtures exposed to DNAPL. Additional screening techniques when drilling in bedrock include inspecting the drill return water for visual or olfactory evidence of hydrocarbons (for example, iridescent sheens or odours) and headspace analysis of rock core that may contain high concentrations of contaminants diffused into the matrix. Exposure to hazardous substances should, however, be controlled and sniffing cores is not appropriate unless it is clear that it is safe to do so. Prior use of calibrated PID/FID equipment may be appropriate where there is any doubt.

7.5 Laboratory analysis of soil samples

Soil characterisation programmes typically involve sending discrete soil samples to the laboratory for quantitative analysis of contaminant composition. The presence of NAPL in a soil sample can be evaluated using:

Equation 2

$$C_i^T = \frac{C_i}{P_b}\left(K_d P_b + \theta_w + H'\theta_a\right)$$

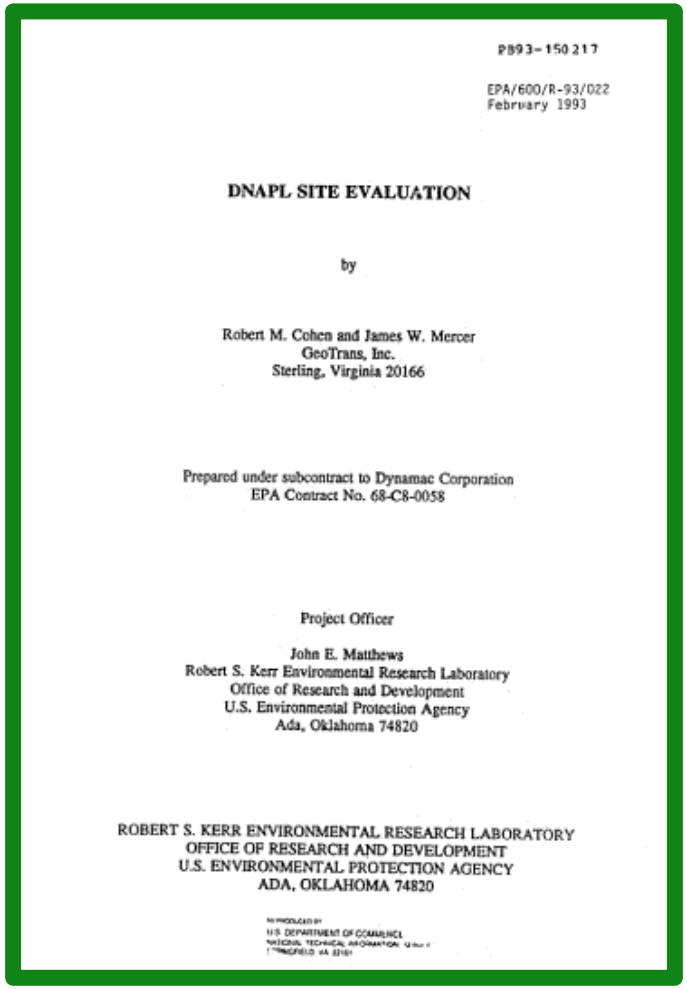
where:

C_i^T is the concentration of an organic substance at or above that which may be present in a non-aqueous phase (mg/kg);

Source: Kueper et al. 2014

Few Options for Delineating Subsurface DNAPL

- Soil concentrations
- Direct observations
- Dye “shake-tests”
- What about Membrane Interface Probe (MIP)?



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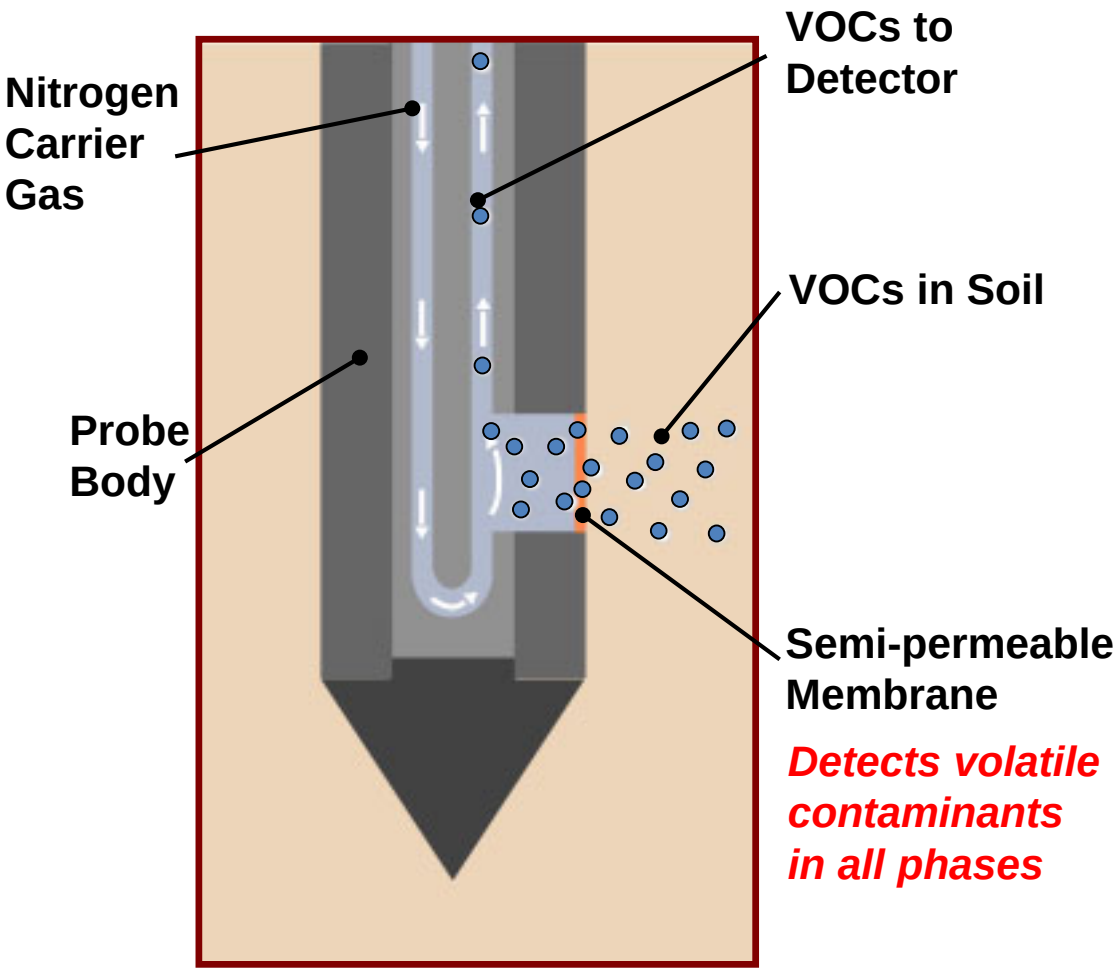
How Membrane Interface Probe Works

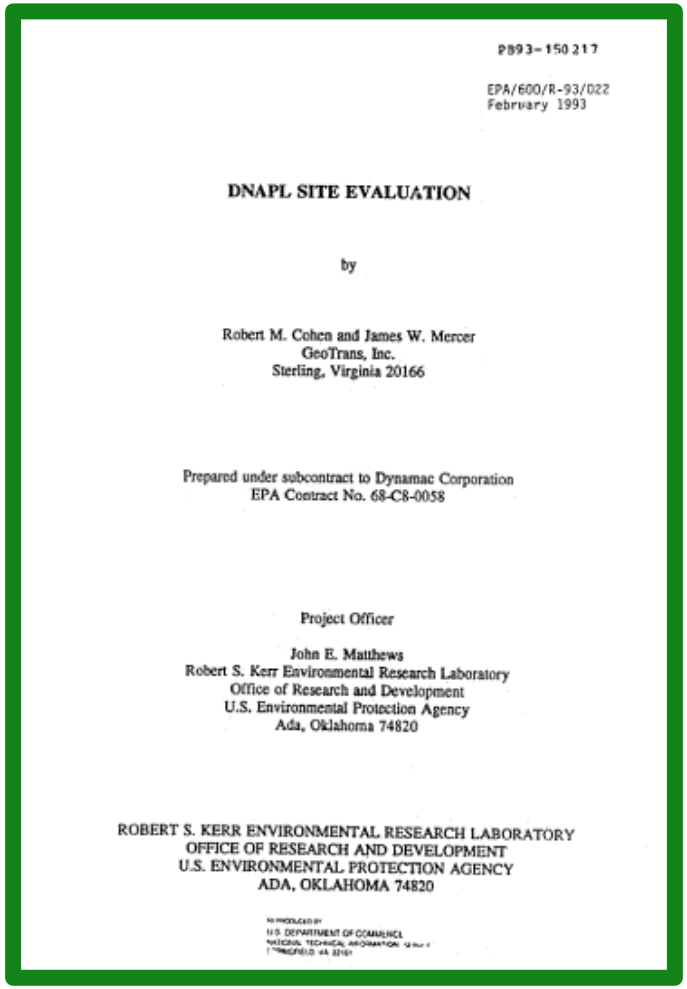


Source: Geoprobe

- Due to a concentration gradient, VOCs move across the membrane via diffusion
- VOCs are then carried to the detector at the surface in an inert carrier gas

Few Options for Delineating Subsurface DNAPL

- Soil concentrations
- Direct observations
- Dye “shake-tests”
- What about Membrane Interface Probe (MIP)?
- Laser Induced Fluorescence (LIF)?



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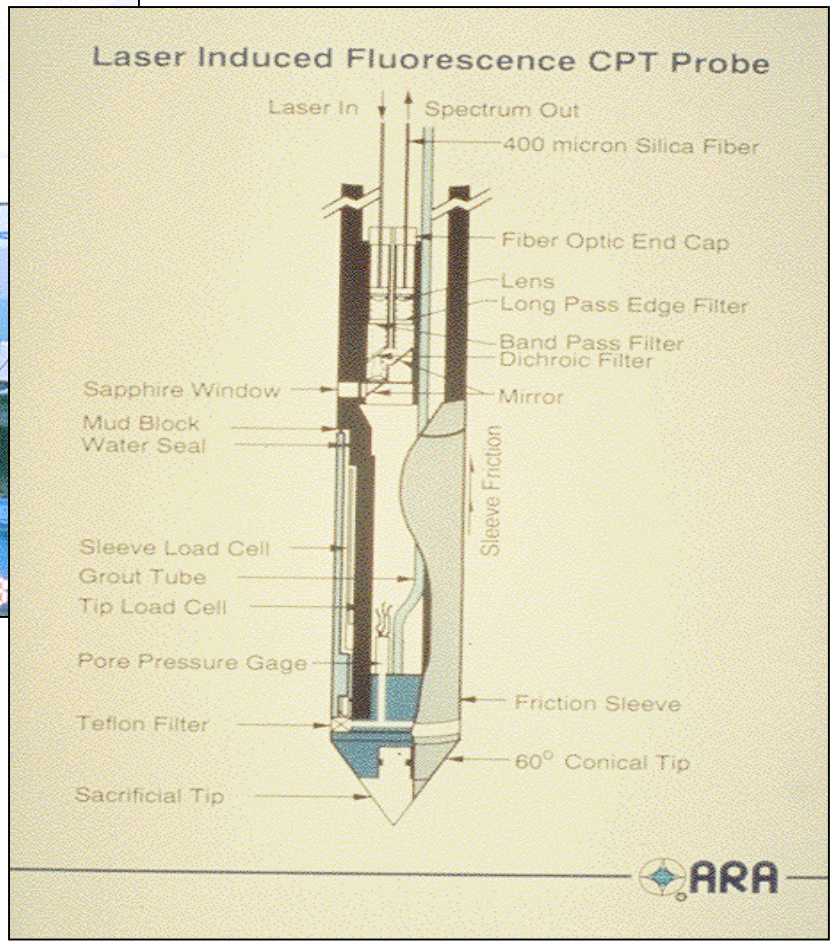
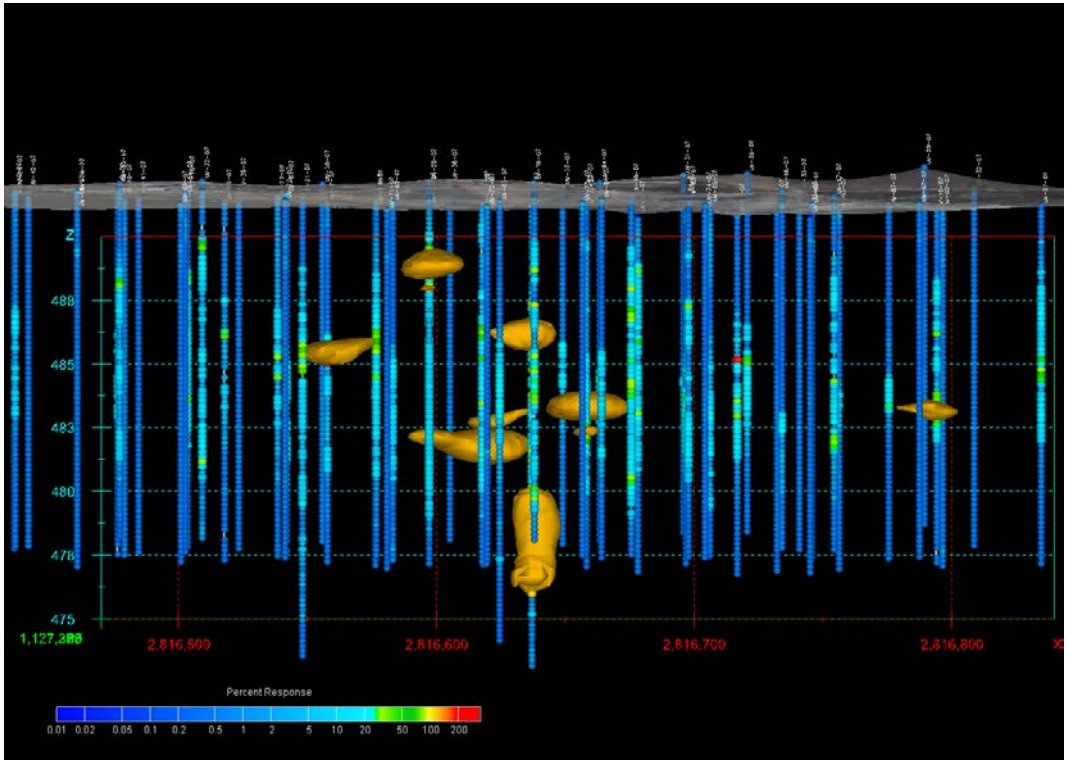
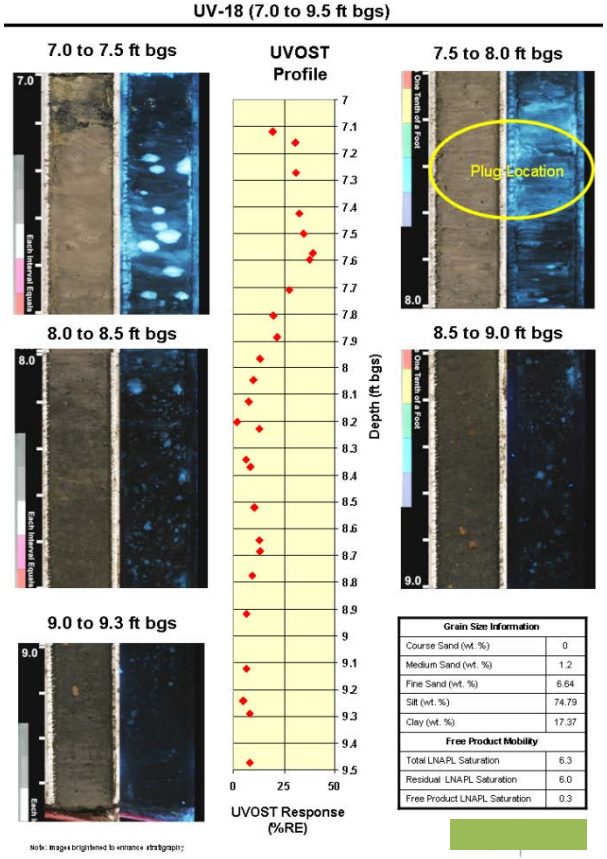
Traditional LIF Doesn't Work with Chlorinated Solvent DNAPL



New Generation Laser Induced Fluorescence (LIF)

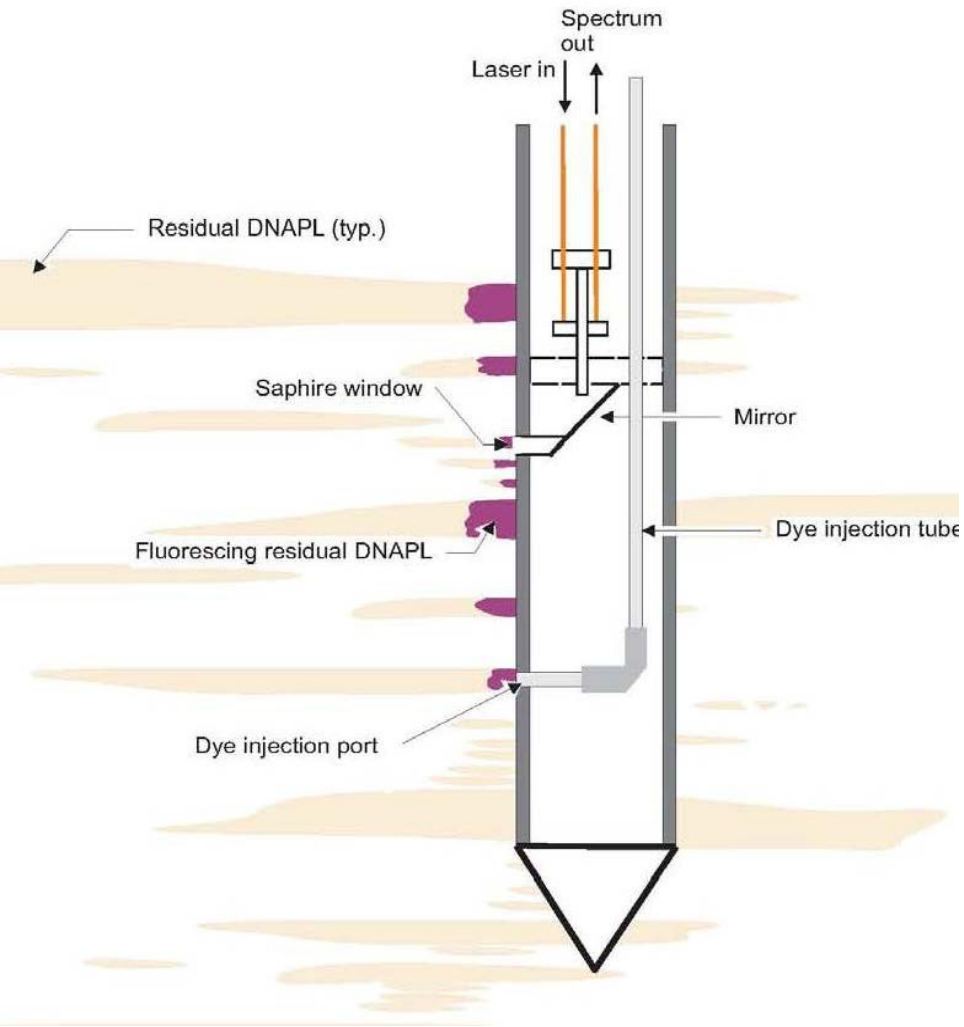
(Still Not Able to Detect Chlorinated Solvent DNAPL)





New Technology/Methodology Description

- Modification of existing LIF technology
- Adds a small port below excitation source/optics for injecting a fluorescing hydrophobic dye
- Once solvated in NAPL, the dye fluoresces, allowing for detection with conventional LIF tooling
- Referred to as “DyeLIF”



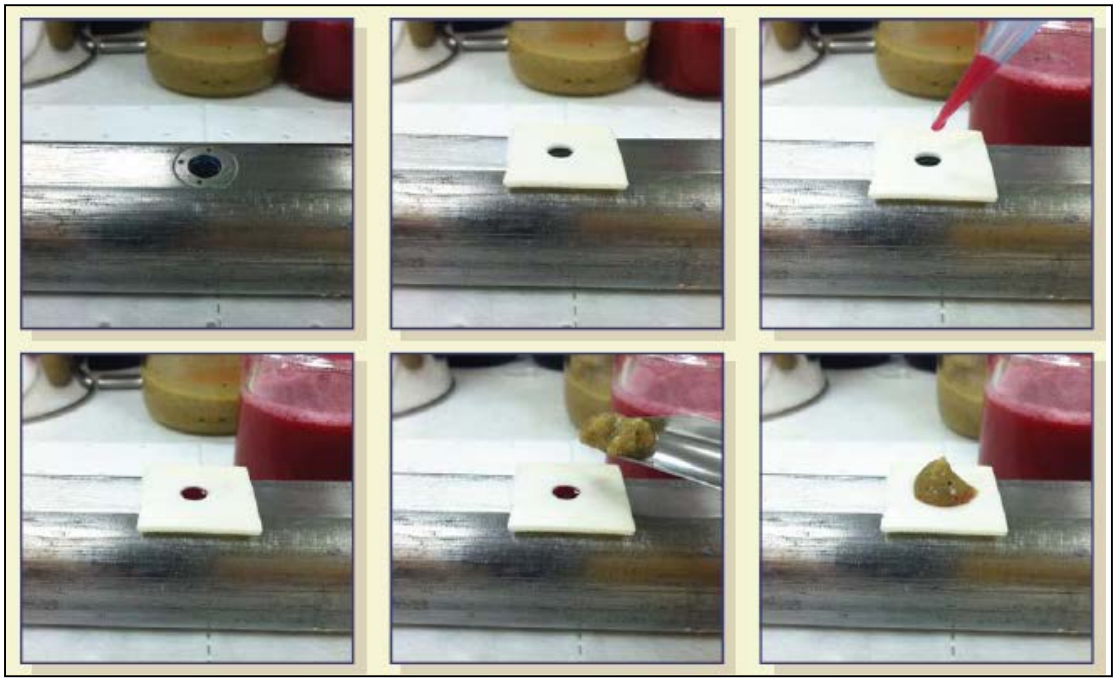
Project Scope

- Laboratory testing of DNAPL samples
  - DNAPL chemistry
  - Optical response with >40 hydrophobic dyes
- Stacked disk testing
- Field testing

Laboratory Test Design

Static Probe Tests

- Create small well around probe window (mimics dye “jacket” formed during field deployment)
- Place samples of clean sand, clean sand + dye, just DNAPL (no dye), and DNAPL + dye



Test Design

Static Probe Tests

- Developed quantitative metric for enhancement with DyeLIF
- Referred to as Enhancement Factor (EF)

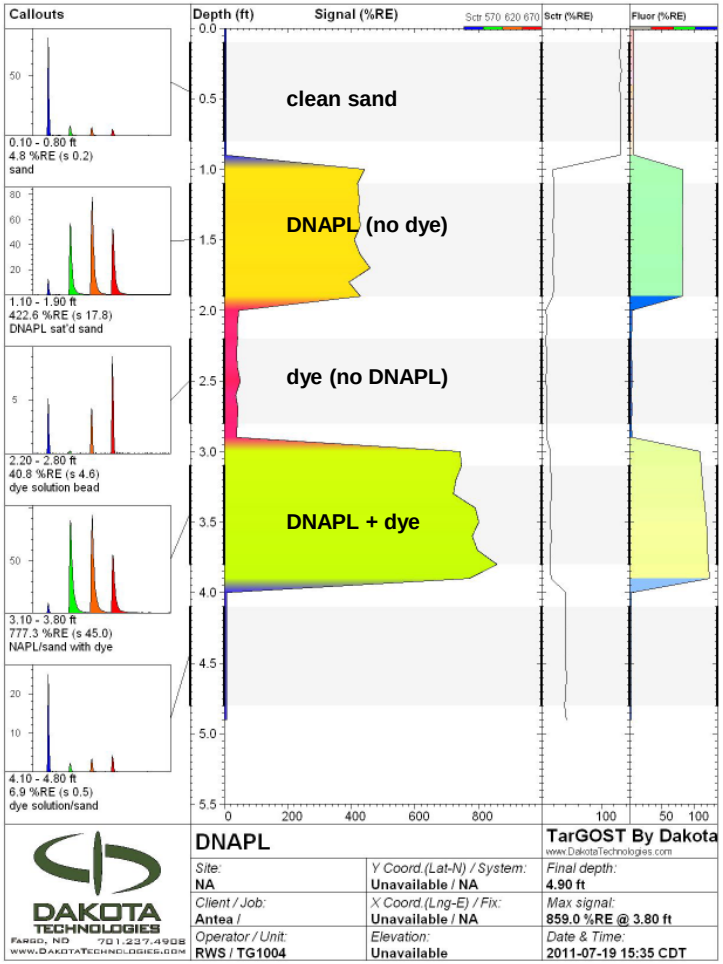
$$EF = \frac{R_D - R_{dye} - R_T}{R_T}$$

where

- RD = Response when DNAPL/sand sample placed on dye jacket (analogous to DYE-LIF moving through DNAPL zone)
- Rdye = Response when clean sand placed on dye jacket (analogous to DYE-LIF moving through clean sands)
- RT = Response when DNAPL/sand sample placed directly on TarGOST window (analogous to TarGOST moving through DNAPL zone)

Example:

- DNAPL + dye = 200%
- DNAPL (no dye) = 100%RE
- Just dye ~ 0% RE,
- EF = (200-100)/100 = 1 or 100% increase



Stacked Disk Experiments

One-inch-thick disk of clean sand with PCE (50% saturation)

Disk placed in 5-gallon bucket & encased in clean sand

Disk placed in 5-gallon bucket & encased in clean sand

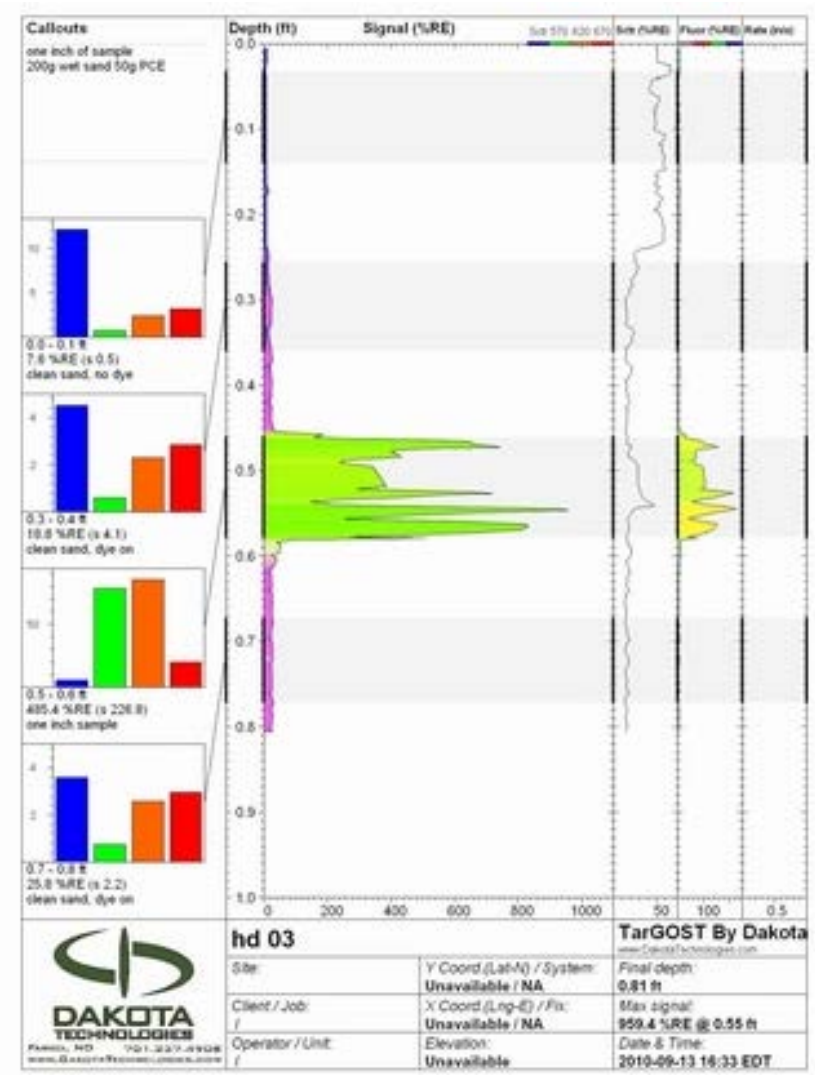
DYE-LIF probe with dye injector below sapphire window

Advancing the DYE-LIF probe through the sand bucket while injecting a hydrophobic dye

Laser visible through sapphire window

DyeLIF Detects PCE-Impacted Sand

- One-inch thick layer of PCE-impacted sand (50% saturation) perfectly detected
- No drag-down of PCE into underlying clean sand



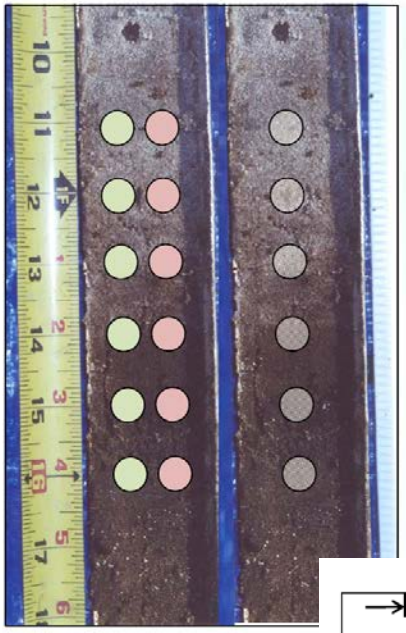
Field Testing

Site Description

- Formerly used defense site in Lowell, MA
- Site conditions ideal for field testing
  - Amenable to direct push
  - DNAPL (TCE and 1,1,1-TCA) present in site wells (could collect and perform lab testing)
  - Lots of existing high resolution site characterization data (HRSC) data – MIP, Waterloo Profiler
  - Shallow depth to DNAPL <70 ft

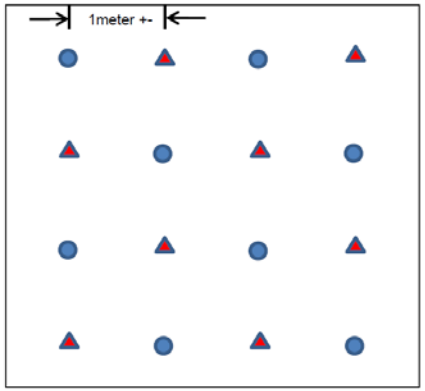
Field Test Design

- Week 1: DyeLIF probing
- Followed by 1 week of soil coring for comparison to DyeLIF responses
- Subcores collected for chemical analysis, visual testing with Oil-Red-O dye, table-top LIF window testing



Explanation

- Subcore for chemical analysis
- Subcore for Sudan IV visual testing
- Subcore for DYE-LIF window testing

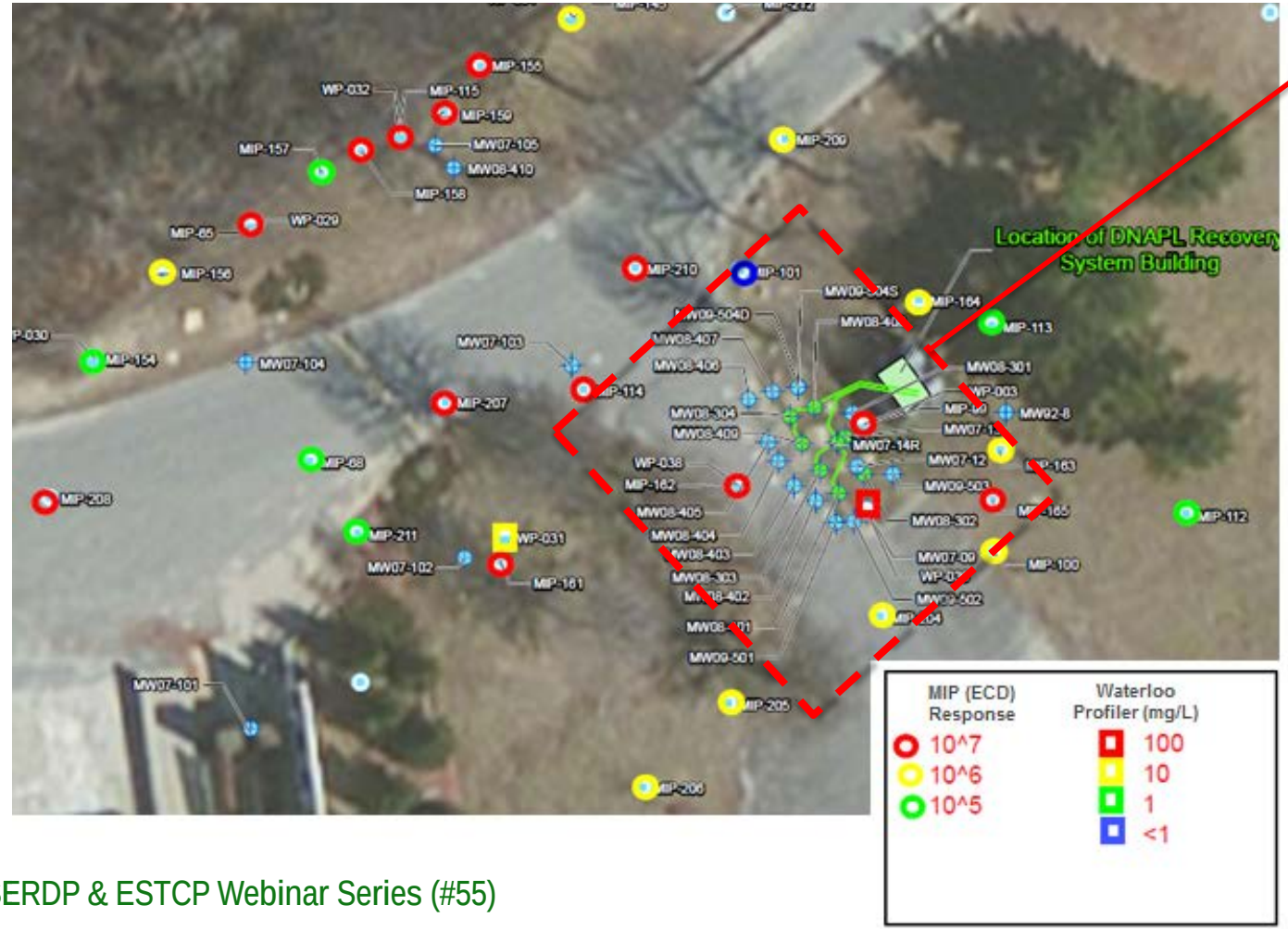


Explanation

- DYE-LIF Probe location
- Soil boring location

Field Test Design

Week 1: Focus of DyeLIF Probing



Existing HRSC data (MIP, Waterloo Profiler), DNAPL gauging data used to define area of investigation

Week 1: October 7-11

Field Test Design

Grid of DyeLIF Borings, Week 1

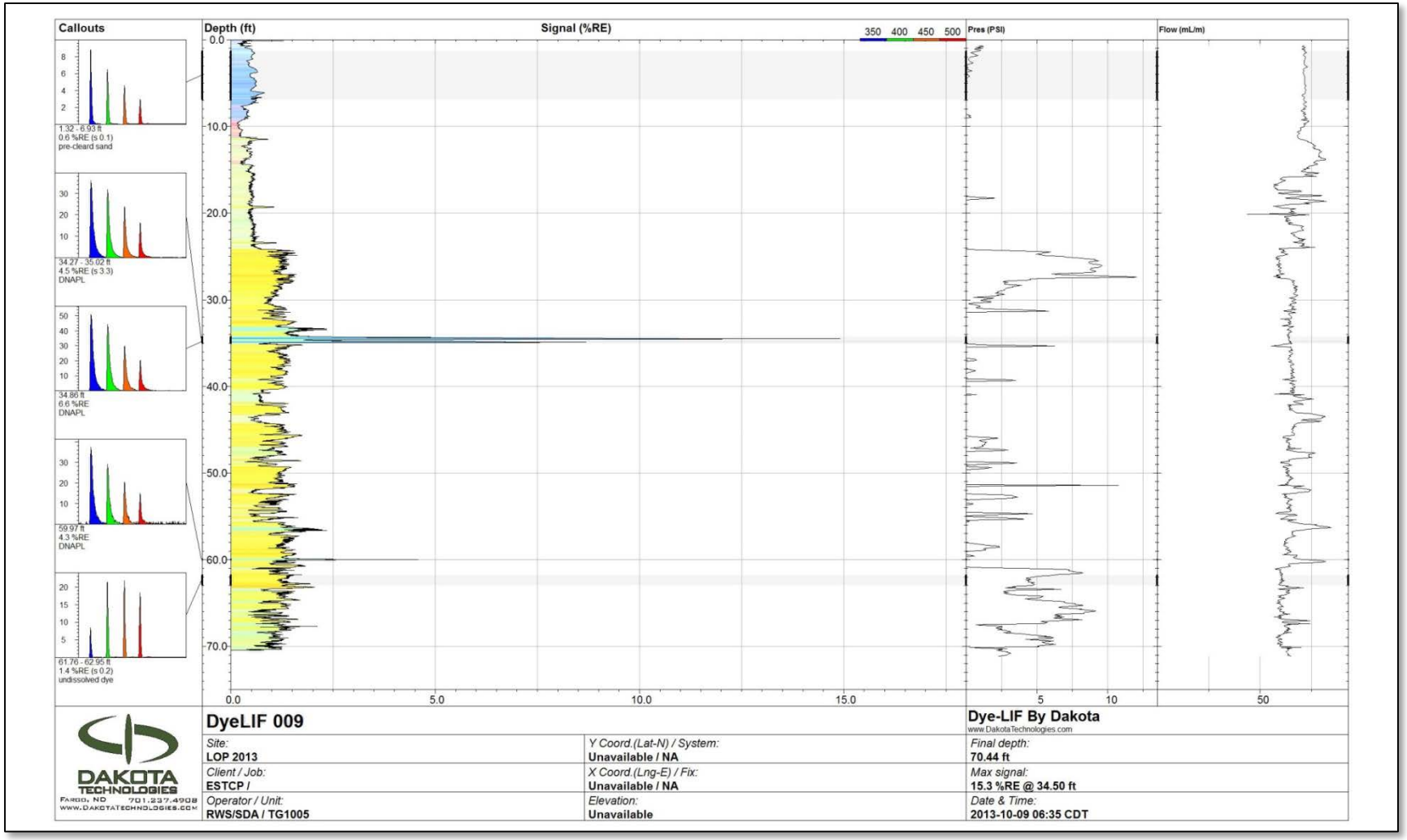
DyeLIF Logging, Week 1

Results

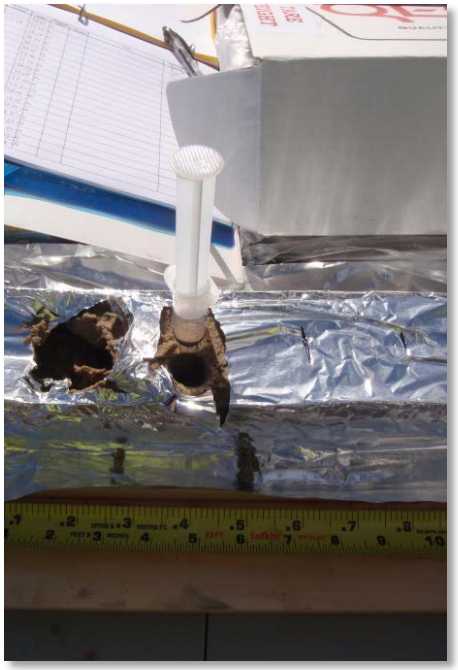
DyeLIF Logging, Week 1

- Probed 25 DyeLIF locations to an average depth of 70 ft in 4 ½ days
- Averaged 395 ft/day: 1.8 hours per 70 foot hole!
- Rate of penetration average 0.4 inch/second (1 cm/sec)
- No down time from repairs and no damaged tooling
- 0.01 g/second dye solution delivery rate (equates to ~2-3 g per hole)
- Pushed majority of locations with a Geoprobe® 5400; remainder with 7720
- DNAPL body was completely delineated in three dimensions (with exception of small building in the way)

Example DyeLIF Log



Sampling/Screening, Week 2



Results

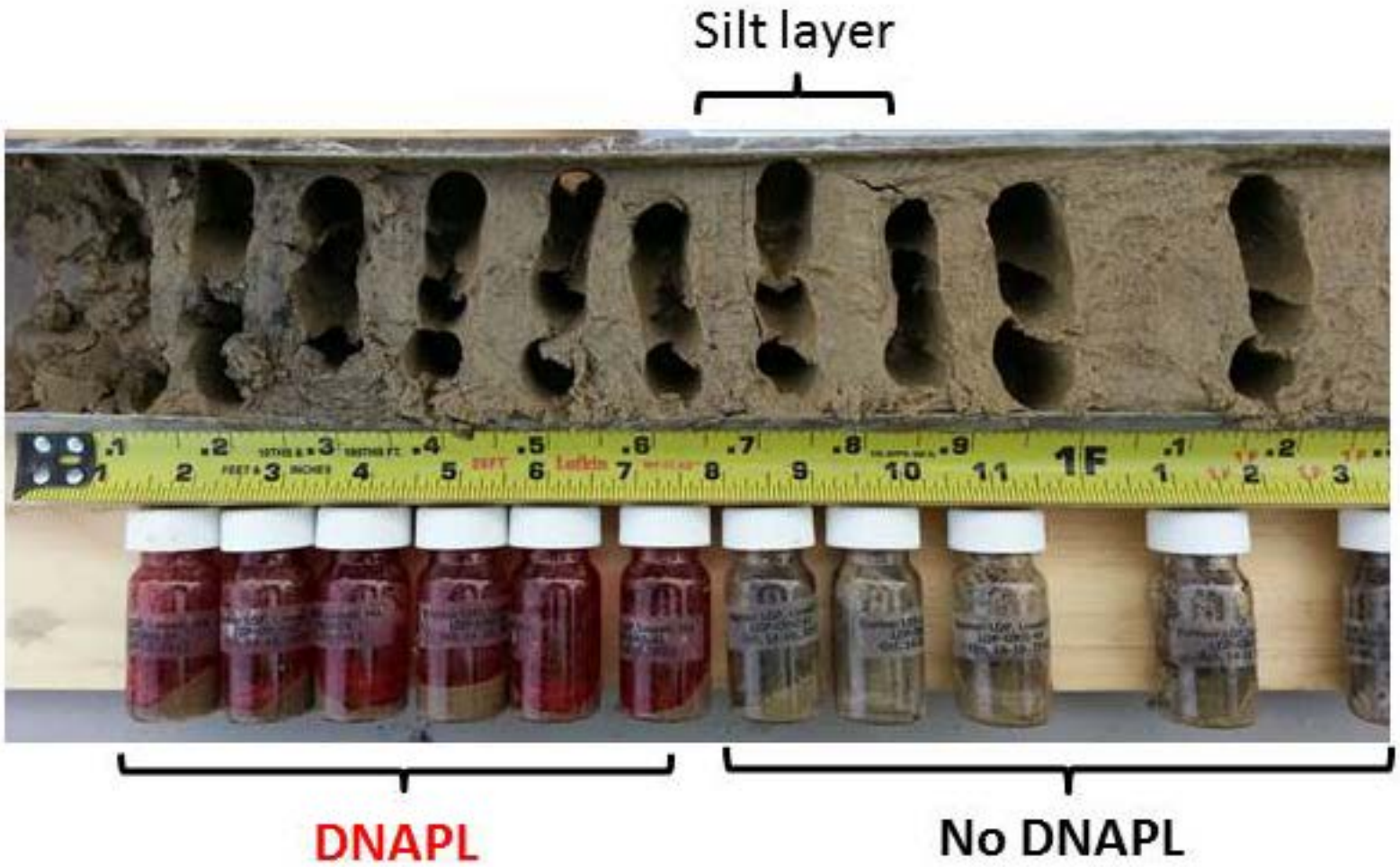
Soil Sampling/Screening, Week 2

- Extremely challenging sampling conditions – poor recovery
- After trying numerous techniques, arrived at Geoprobe MC7™ sampler with sealed piston adaptation to improve recovery
- After three days of technique refinement, average recovery climbed to (only) 65%
- 260 depth-discrete sub-samples were obtained
- PID, Oil-Red-O visual, and table-top DyeLIF were run on high-resolution sub-samples
- 50% of the sub-sampled horizons (133) sent to lab for VOC analyses

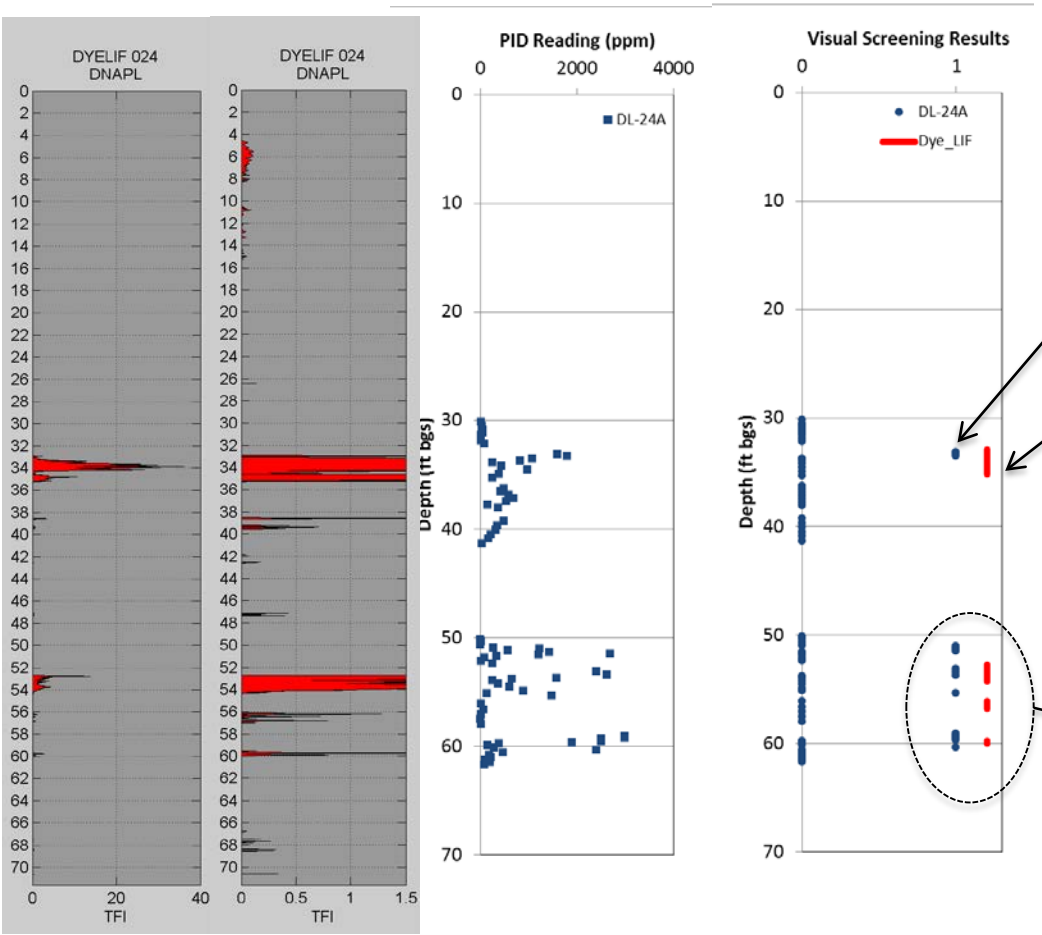
Foil Cover to Minimize Volatile Losses

PID Screening at Each Sample Interval

Positive DNAPL Results with Oil-Red-O Dye Above Silt Layer



Correlation: DyeLIF and Soil Samples



Positive ID with DYE shake test

Positive ID with table-top DyeLIF

Table-top DyeLIF is able to see thin lamina of DNAPL; consistent with dye shake test

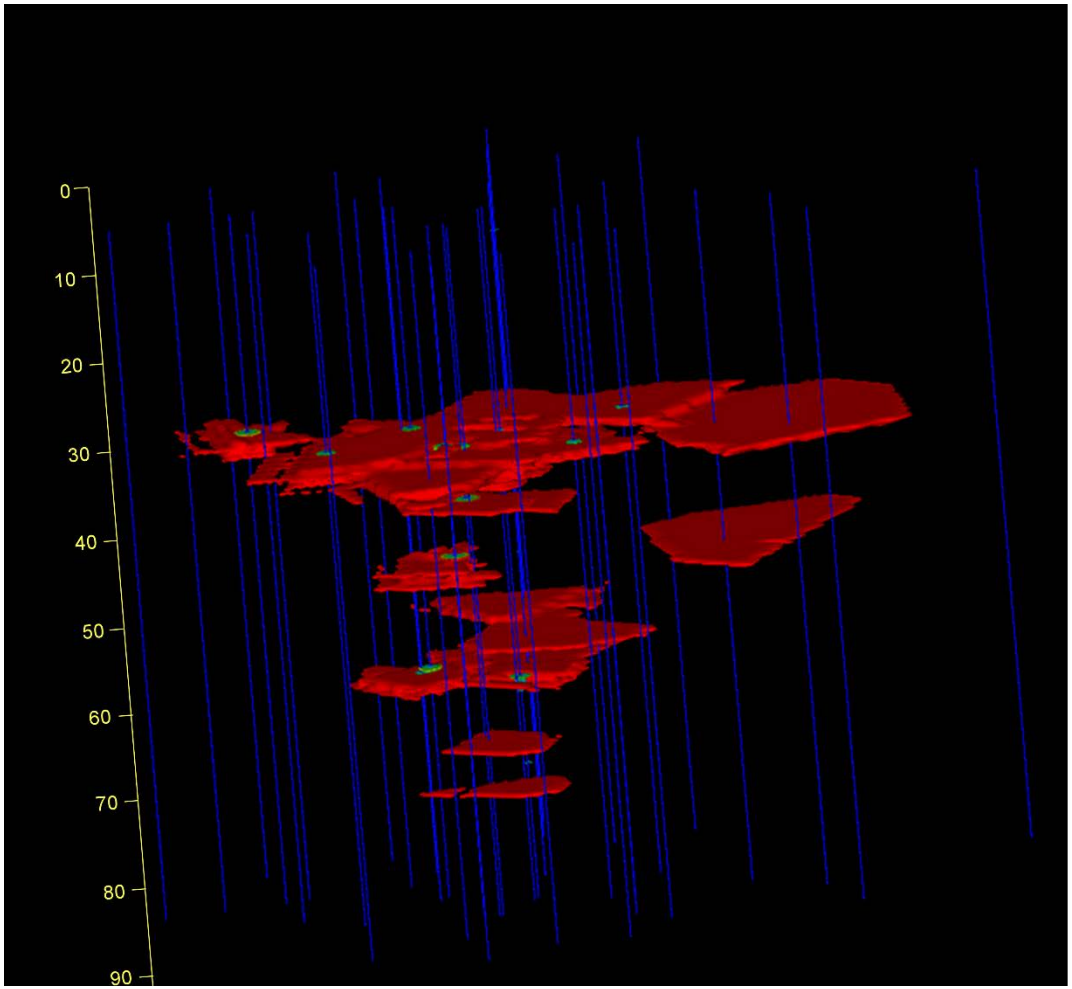
Correlation: DyeLIF and Soil Samples

- Excellent agreement between data from cores and adjacent DyeLIF logs
- DyeLIF achieved excellent correlation with Oil-Red-O visual shake test
  - 100% match for samples of > 2.5% pore saturation DNAPL
  - 98% match for samples of > 0.7% pore saturation DNAPL
- Field detection limit of between 1.0% and 0.1% pore saturation, but will vary from site to site

Conclusions

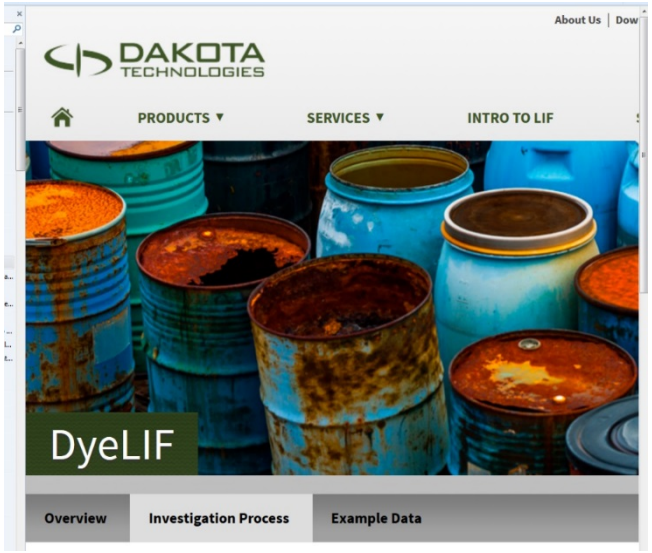
- 1,750 feet of soil continuously characterized using DyeLIF in 4½ days
- DyeLIF detected chlorinated solvent DNAPL layers as thin as 1 mm
- No response to dissolved phase VOCs (as expected)
- Limit of detection of ~1.0%-0.1% DNAPL pore saturation
- DyeLIF produced the equivalent of an Oil-Red-O shake test at 0.5 cm spacing - with average daily production of 395 ft
- In other words, DyeLIF generated the equivalent of 12,039 individual Oil-Red-O shake tests per day - with 100% “recovery”
- Tracking the indicator dye solution’s flow and pressure reveals details of hydraulic conductivity with depth
- DyeLIF probe technology is compatible with both percussion and CPT direct push platforms. Is being combined with other DP tooling

Three-Dimensional Rendering of DNAPL Source Zone, Lowell MA Site



Technology Status

- ESTCP Final report available online
- DyeLIF is commercially available from Dakota Technologies
- New dyes are being tested



http://www.dakotatechnologies.com/services/dyelif

Acknowledgments

- Adrian Fure, Haley & Aldrich
- Randy St. Germain, Dakota Technologies
- Beth Parker and Steve Chapman, University of Guelph

For additional information, please visit

https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Monitoring/ER-201121

Speaker Contact Information

MEinarson@haleyaldrich.com; 650-400-0248

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Q&A Session 1

SERDP DOD • EPA • DOE | ESTCP

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

Dr. W. Andrew Jackson
Texas Tech University

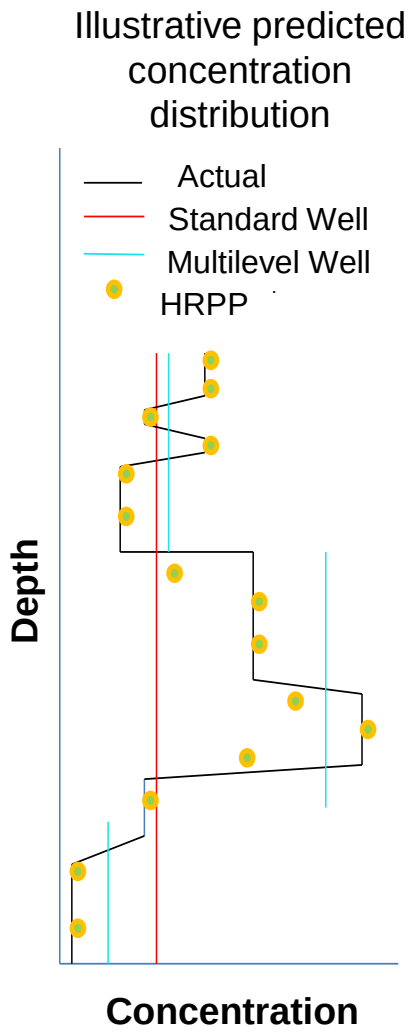
SERDP DOD • EPA • DOE | ESTCP

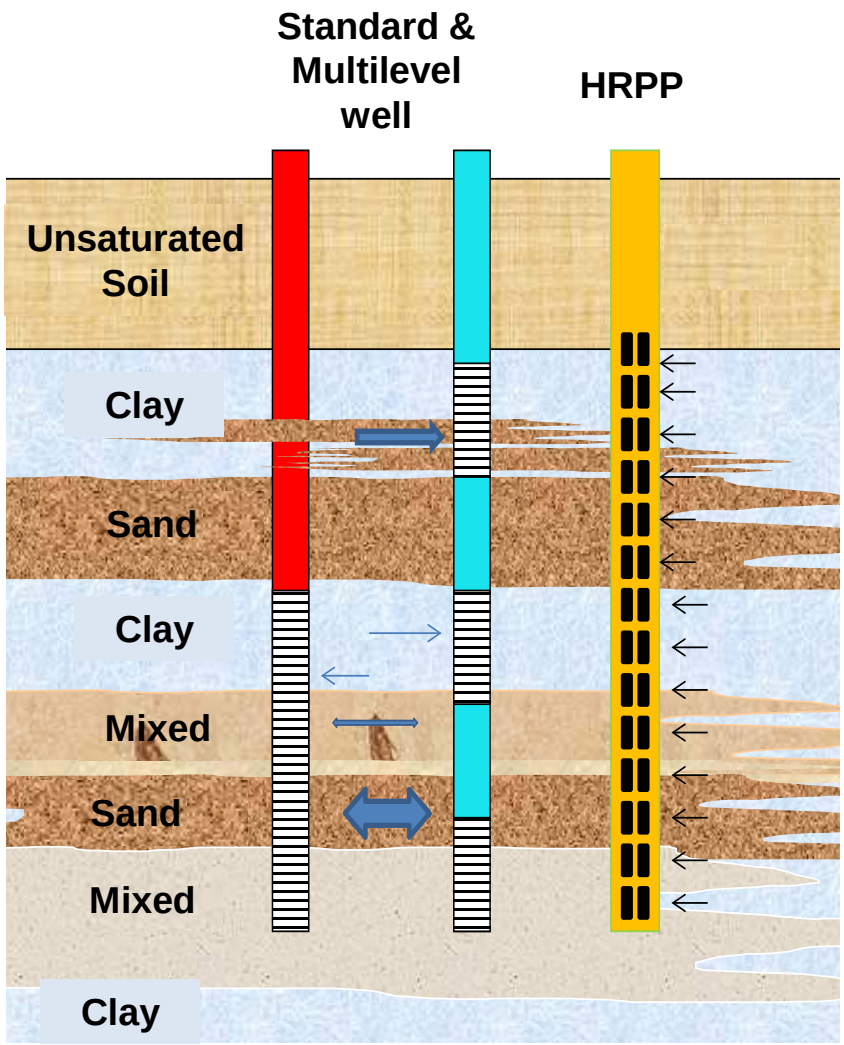
Agenda

- Need for High Resolution Site Sampling
- Function and Use of High Resolution Passive Profiler (HRPP)
- Field Demonstration of HRPP
  - Deployment
  - Retrieval
  - Data comparison to exiting technologies
- Conclusion

Problem Statement

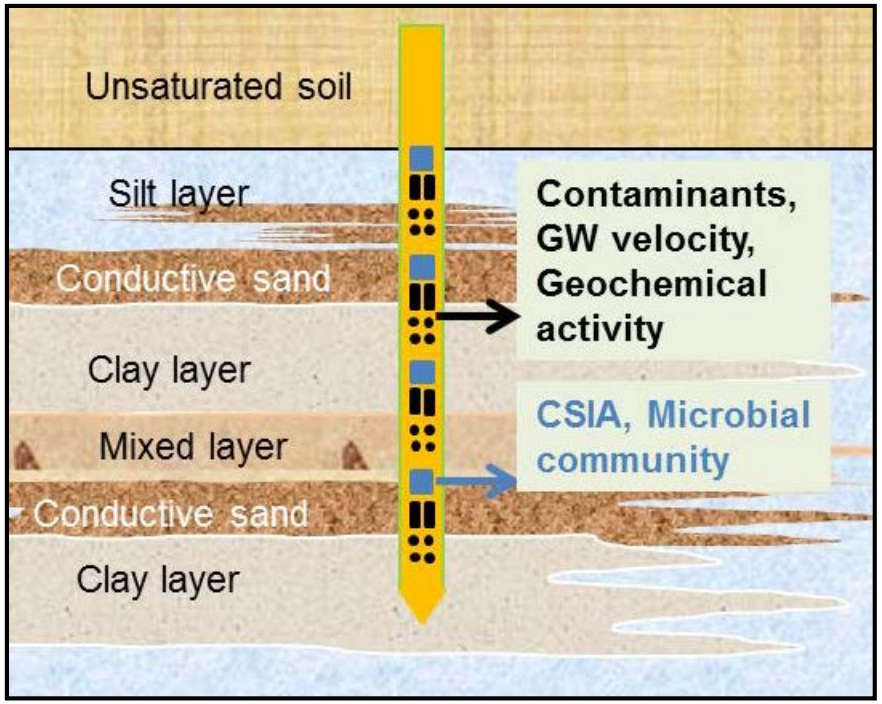
- Contaminant fate and transport prediction limited by intrinsic heterogeneity
- Low permeability zones sustain groundwater plumes





Research Objectives

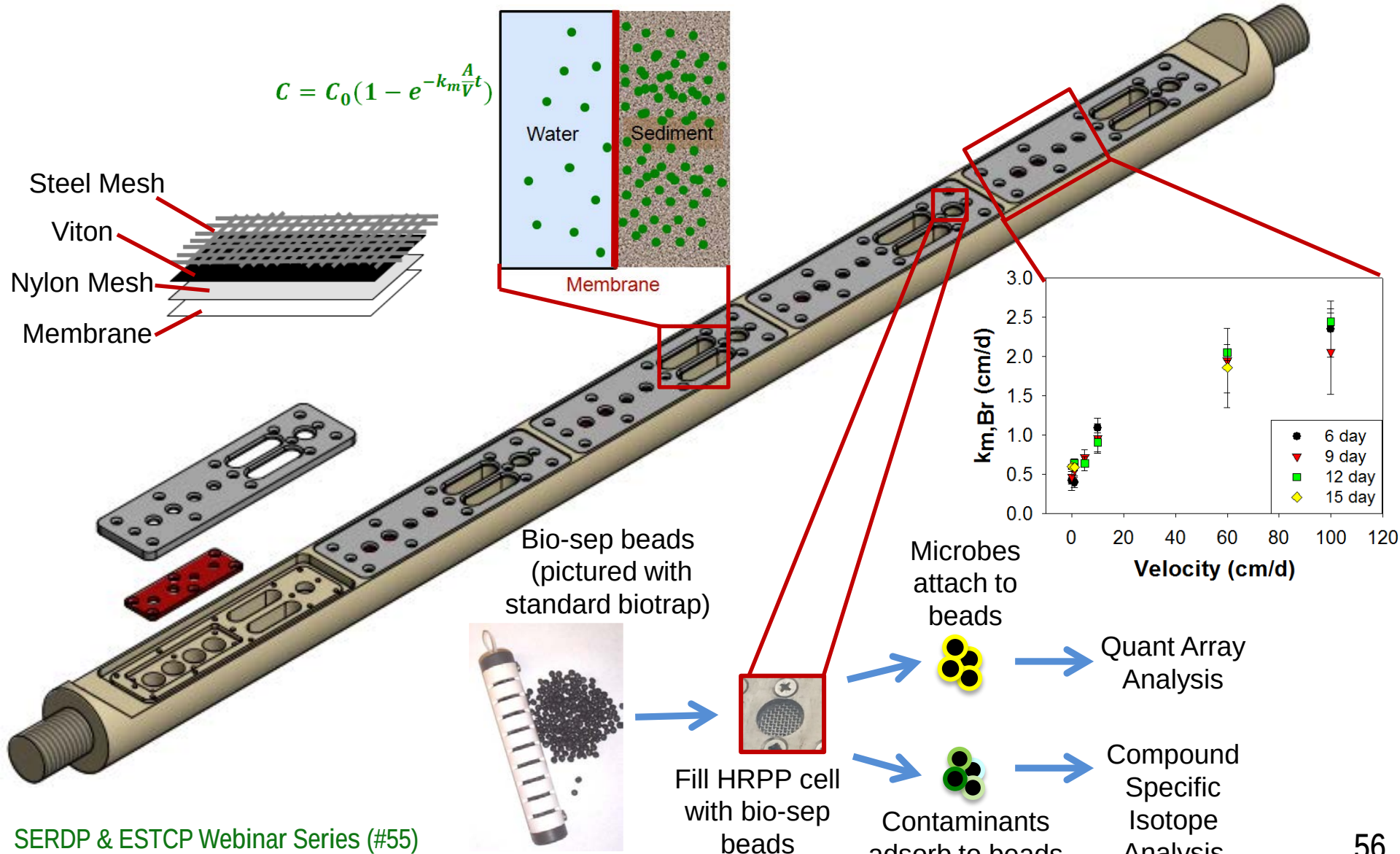
- Overall goal
  - Develop and demonstrate a High Resolution Passive Profiler (HRPP) as a fine-scale delineation tool for the saturated subsurface
- Specific objectives
  - Directly measure groundwater and contaminant flux at the cm scale
  - Quantify biogeochemical conditions at the cm-scale
  - Assess microbial community structure and activity at the cm scale



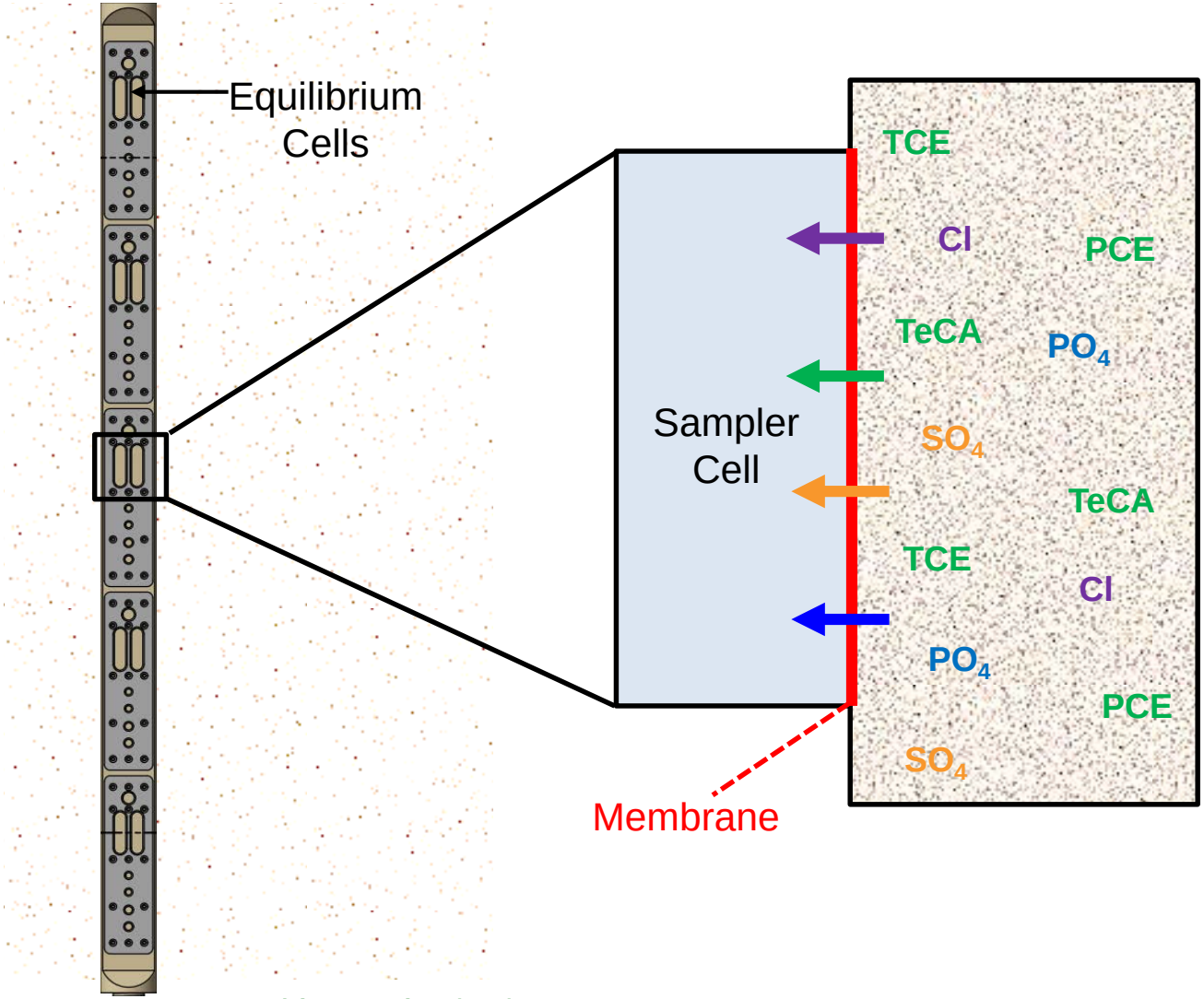
Tested with laboratory experiments and 2 field trials

HRPP Functionality

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

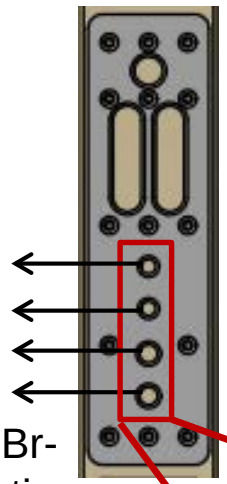


Equilibrium Porewater Sampling

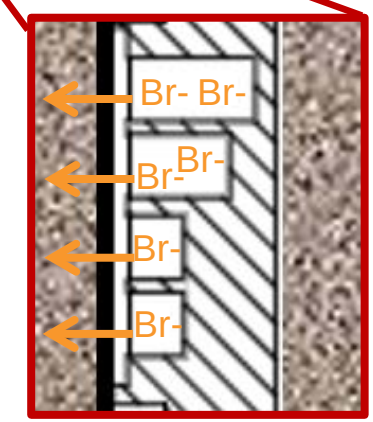


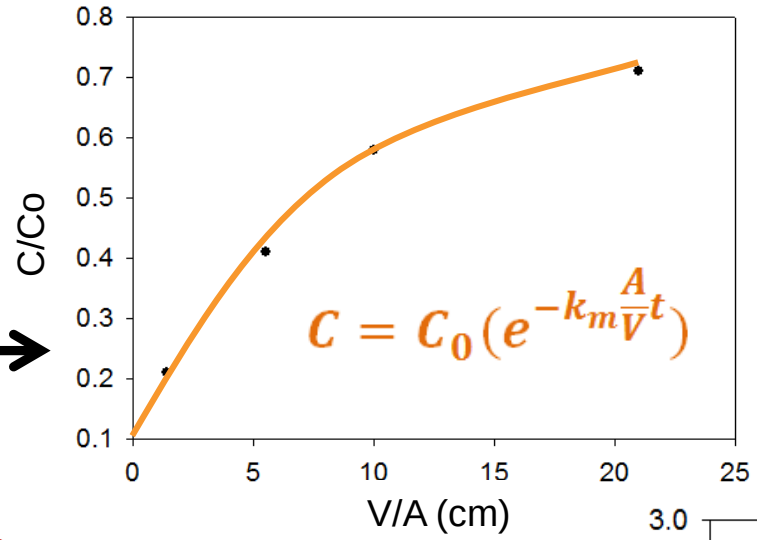
- ~3 weeks (tunable)
- Any soluble species

Estimating Groundwater Velocity

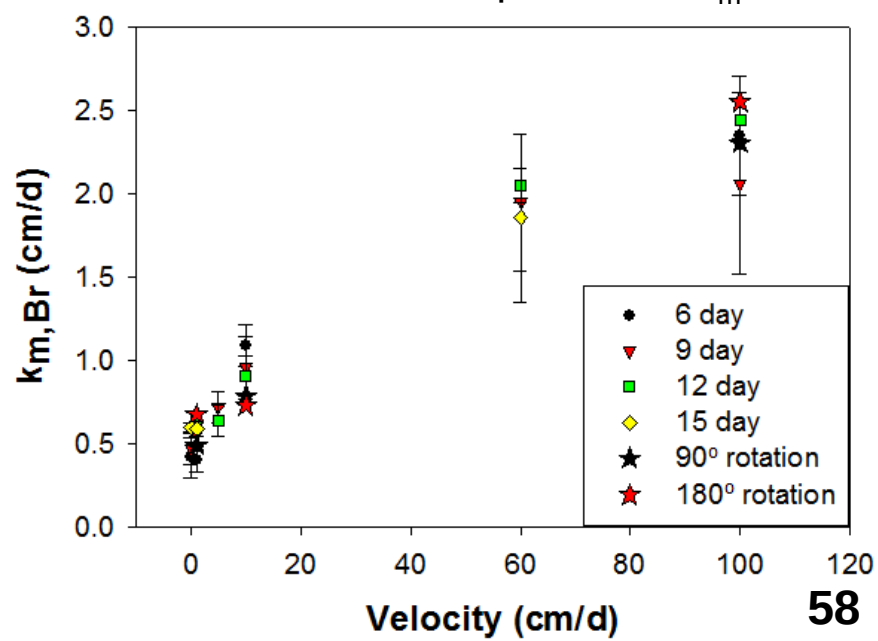


Measure Br- concentration after HRPP is extracted





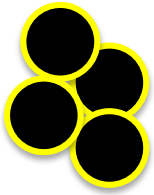
Plot C/Co vs. V/A and fit equation for k_m



Microbial Community and Compound Specific Isotope Analysis

Bio-sep beads (pictured with standard biotrap)

Microbes attach to beads



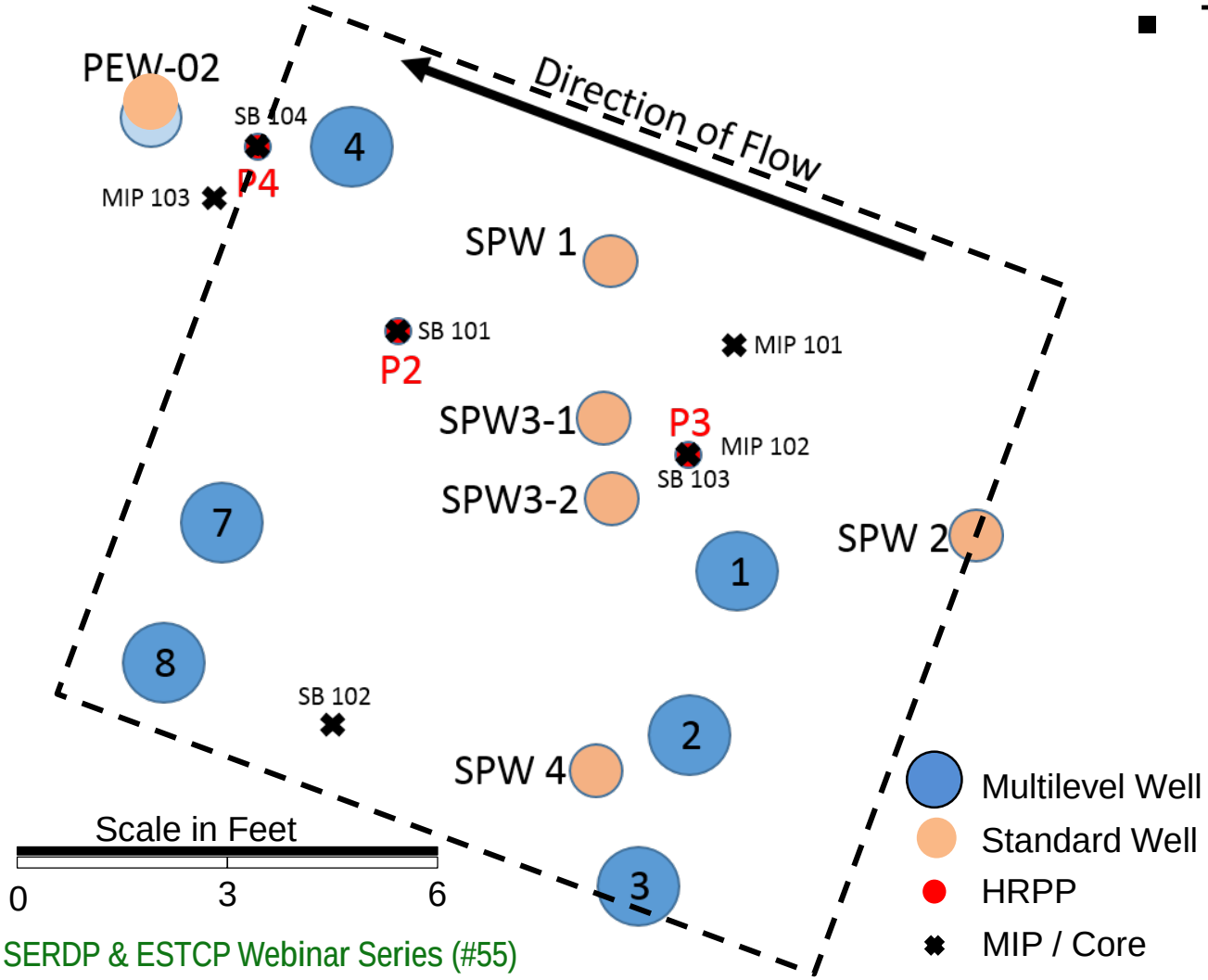
Quant Array Analysis:
Detection of microbial communities and degradative genes

Contaminants adsorb to beads

Compound Specific Isotope Analysis:
Contaminant source, potential for degradation, extent of current degradation

Naval Air Station Alameda

Field Deployment of HRPP



- Test HRPP for
  - Direct push insertion into shallow aquifer (~20 ft BGS)
  - Delineation of groundwater velocity, volatile organic compounds (VOCs), microbial communities, and compound specific isotope analysis (CSIA) compared to monitoring wells, soil cores, and membrane interface probe (MIP) data

Field Deployment of HRPP

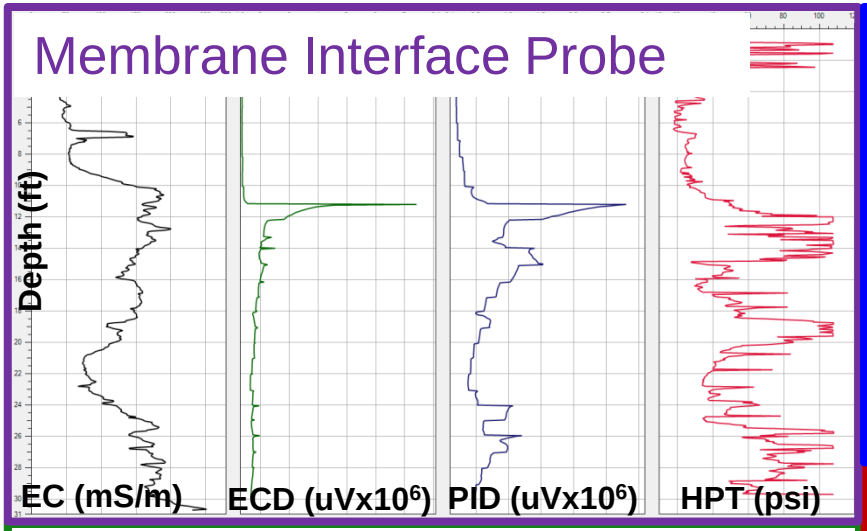
Preparation

Insertion

Sampling

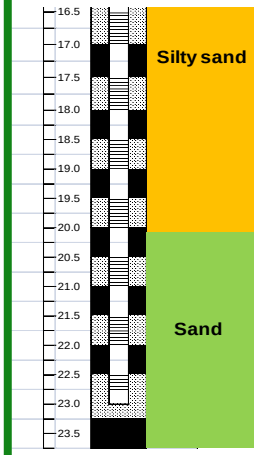
Comparative Data Sets

Membrane Interface Probe

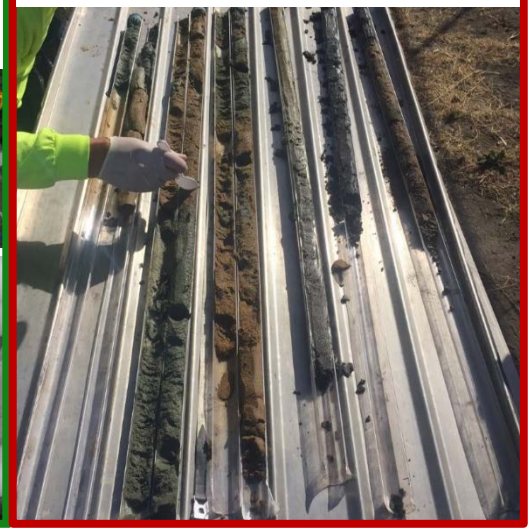


Passive Flux Meter

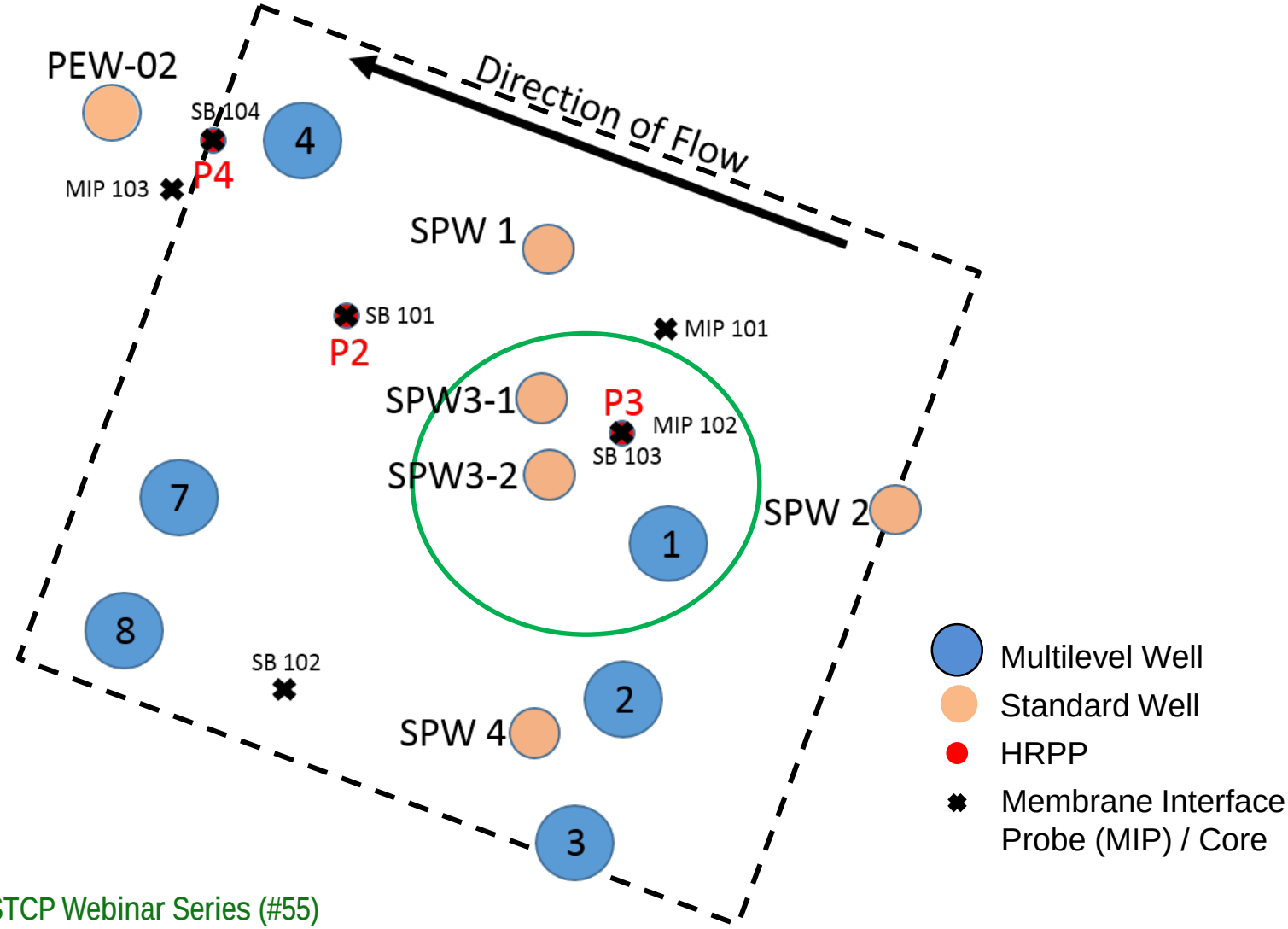
Multilevel Wells



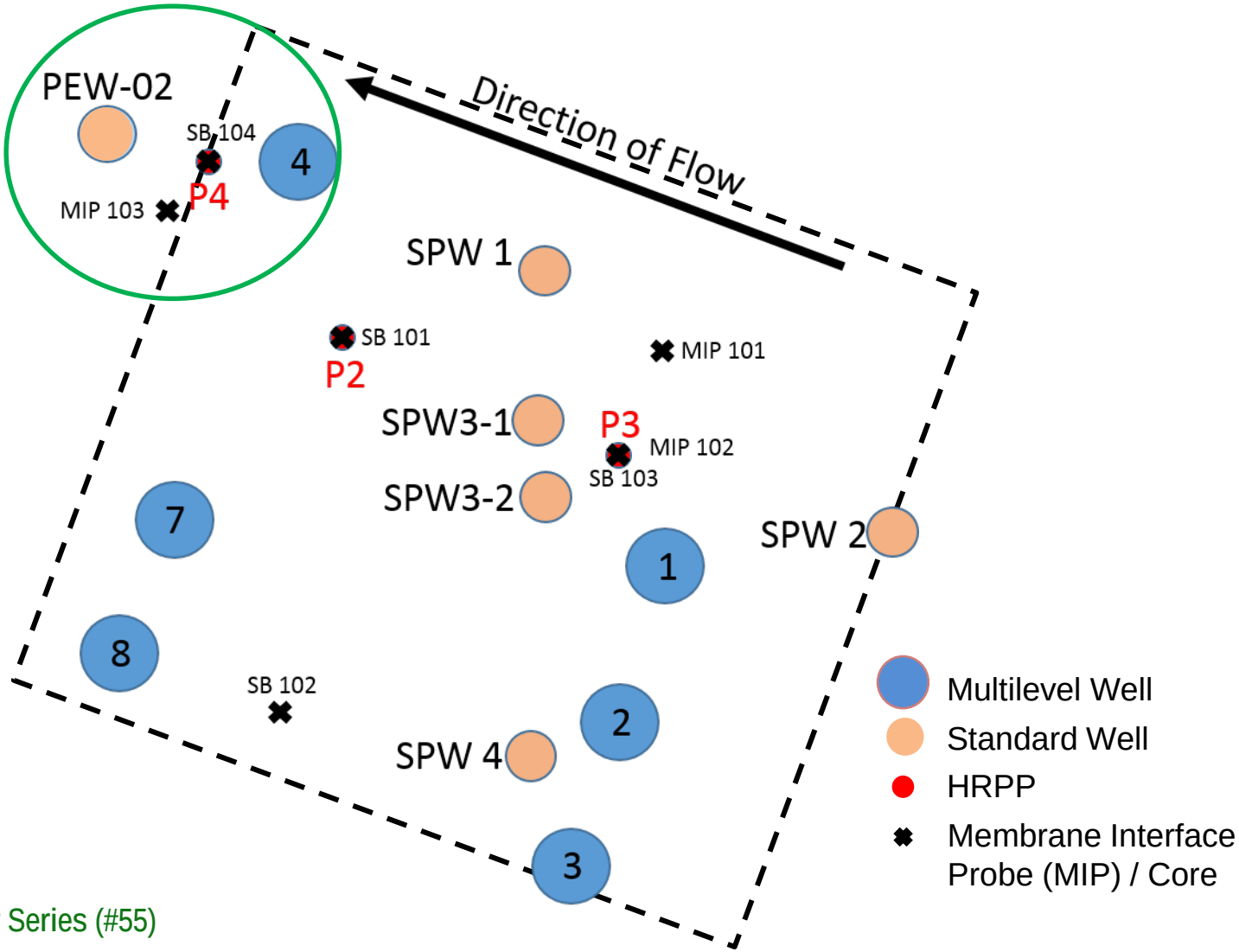
Soil Cores



P3 and Surrounding Area

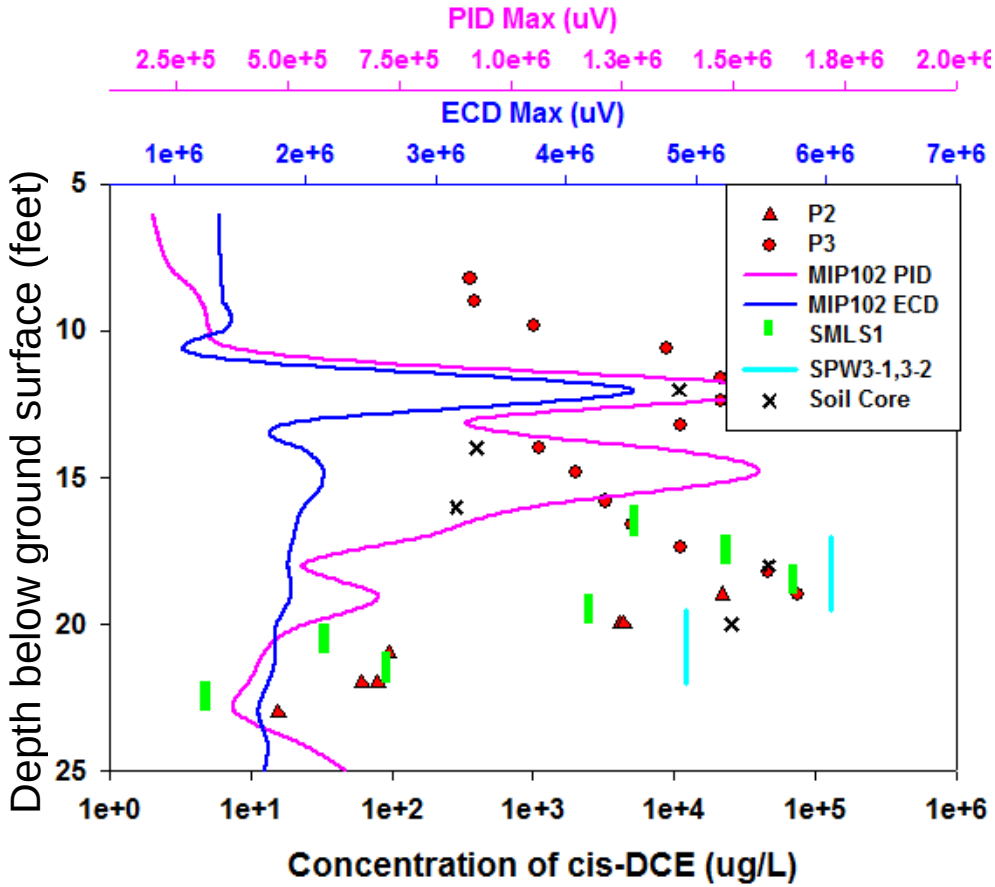


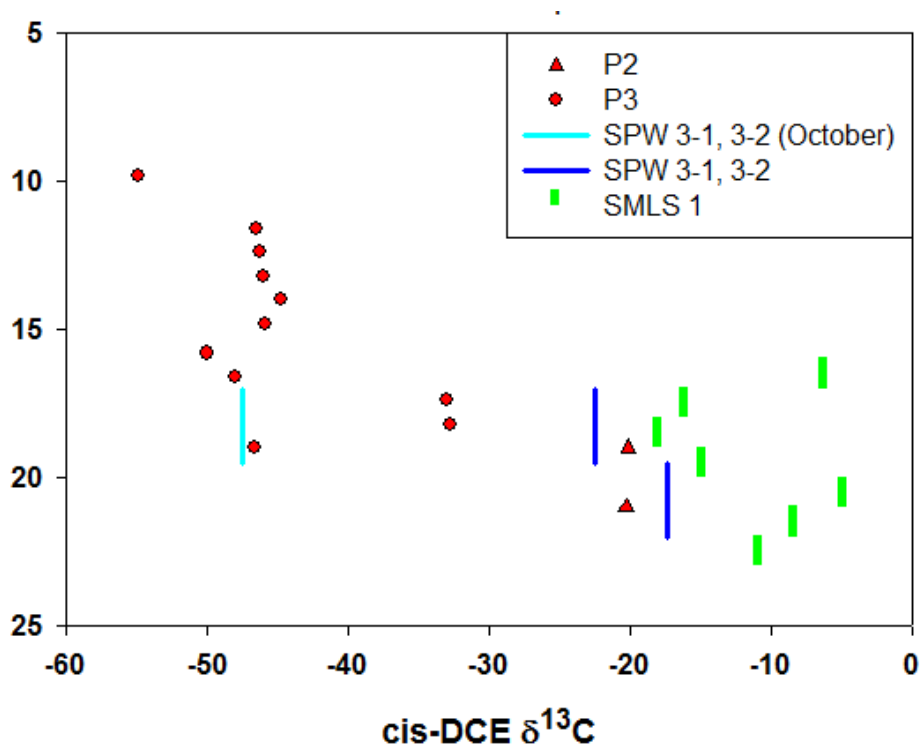
P4 and Surrounding Area



cis-1,2-Dichloroethylene

Concentrations and Compound Specific Isotope Analysis

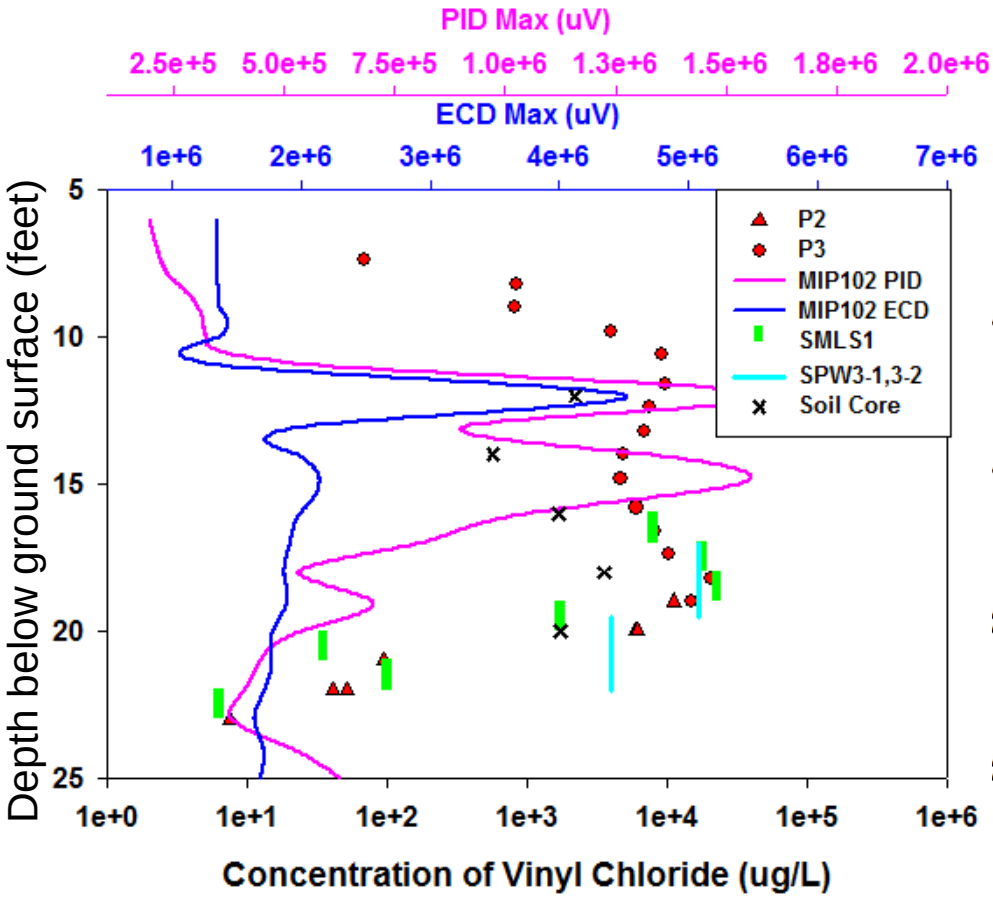


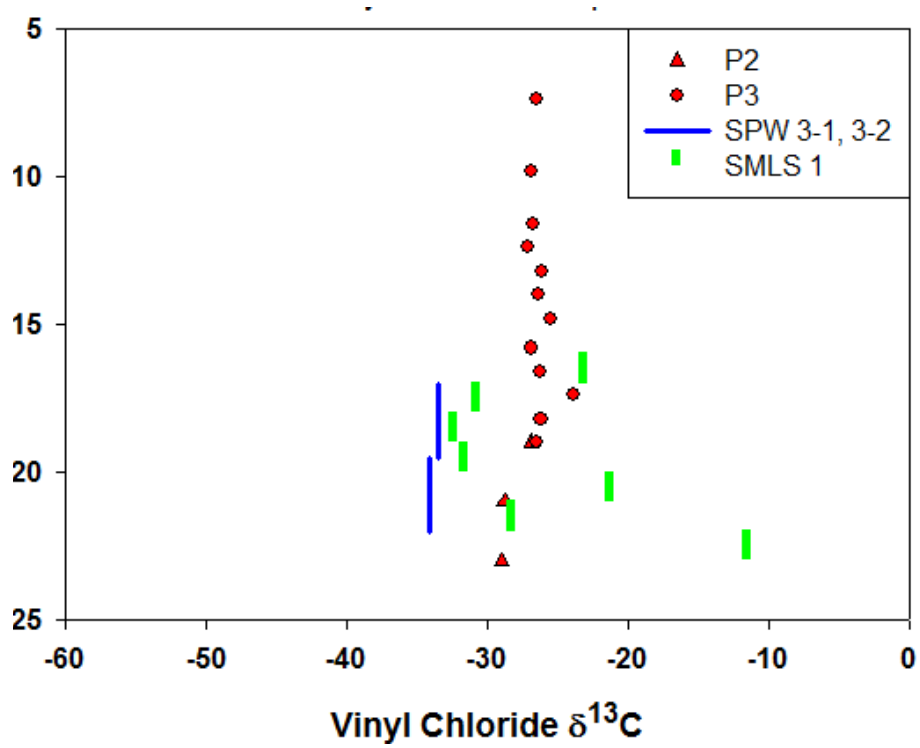


PID: Photoionization detector
ECD: Electron capture detector

Vinyl Chloride

Concentrations and Compound Specific Istotope Analysis





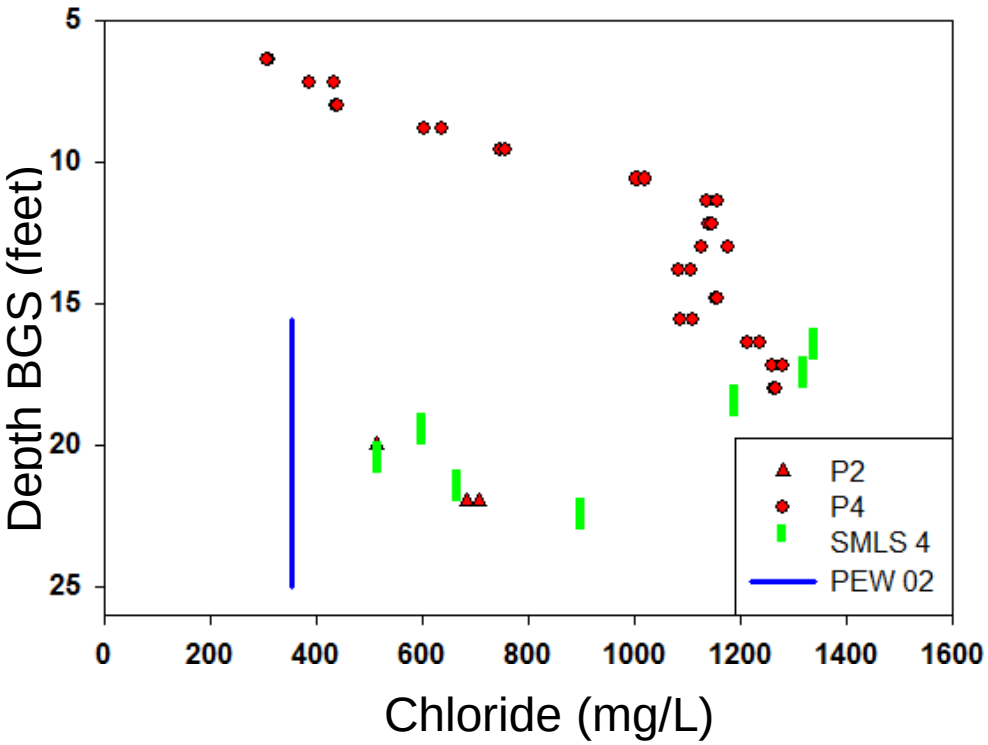
PID: Photoionization detector

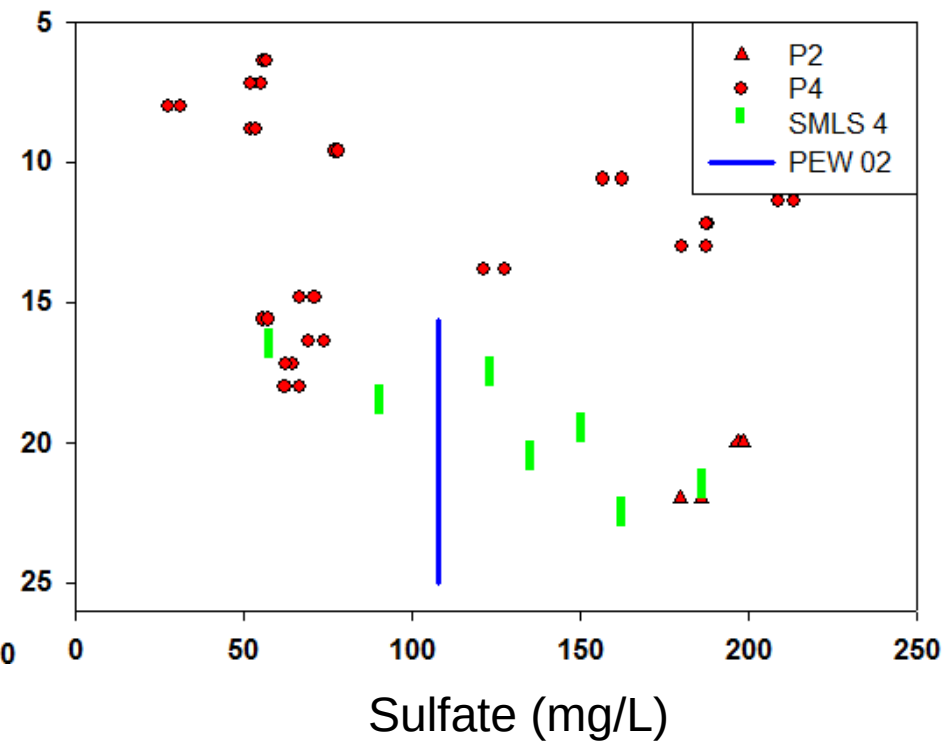
ECD: Electron capture detector

Geochemistry

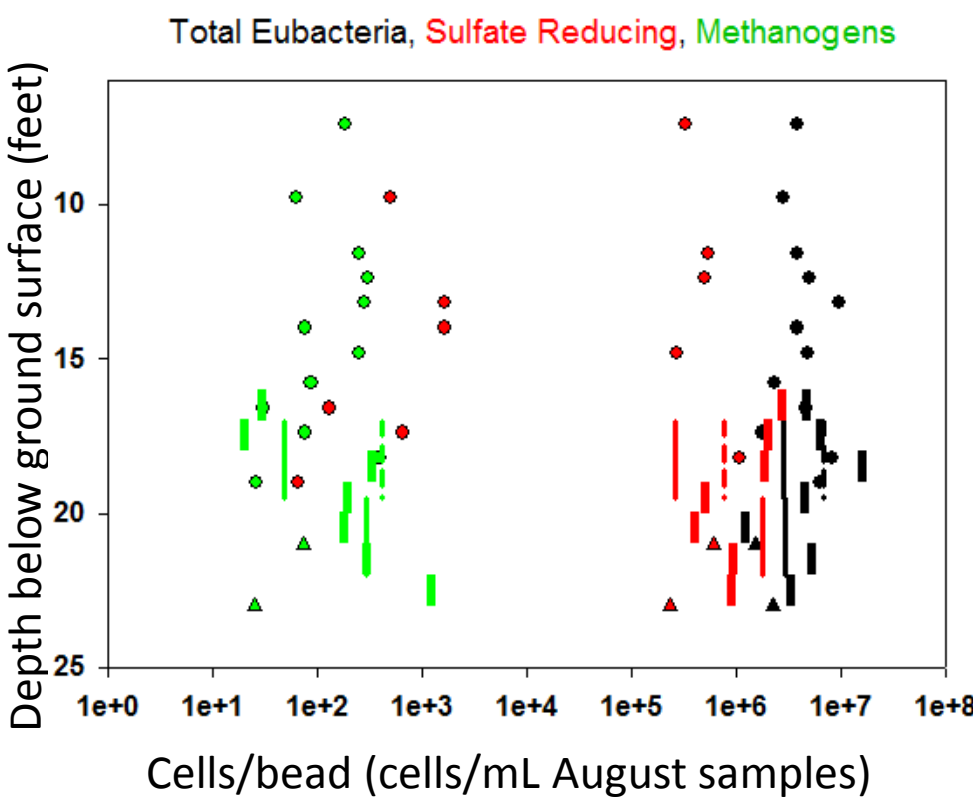
Chloride, Sulfate

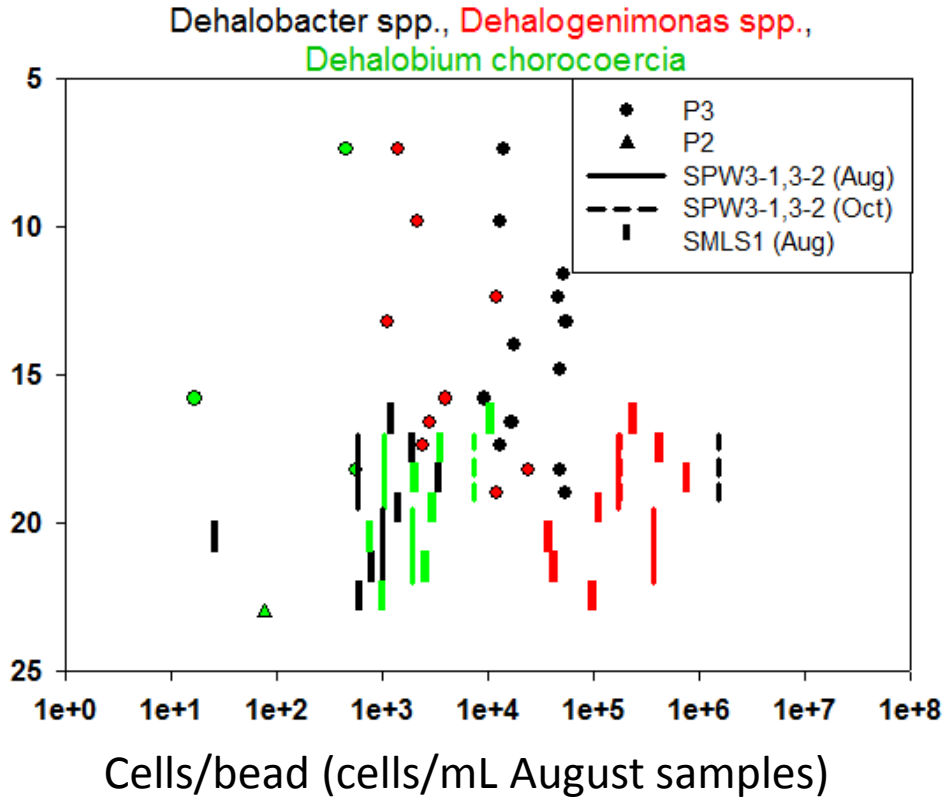
- Other possible groundwater constituents: NO_3^-, NO_2^-, FeT, Fe^{+2}, DOC





Microbial Communities

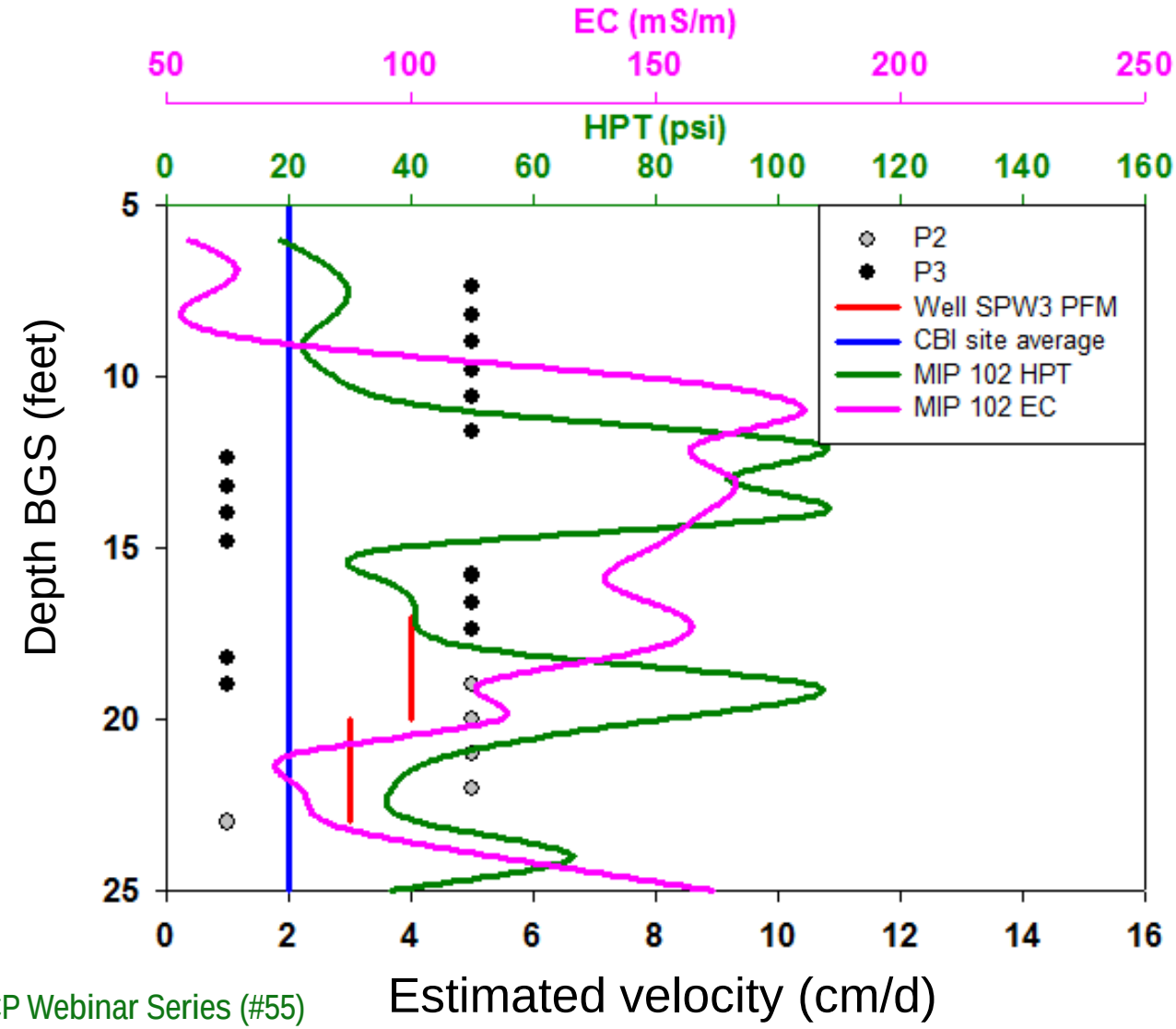




<u>Other Possible Data</u>

DHC	DSM	RDEG	VCR	TOD	EtnE	DCM	PHE	DCMA
DSB	TCBO	TCE	SMMO	RMO	BVC	PMMO	EtnC	

Groundwater Velocity Estimates



EC – electrical conductivity

HPT – hydraulic profiling tool

Conclusions

- Groundwater velocity can be estimated (~1-100 cm/d)
- HRPP yields
  - Higher resolution contaminant profiles
  - Independent of formation hydraulic conductivity
- HRPP capabilities
  - Microbial community analysis
  - Compound Specific Isotope Analysis
- HRPP is structurally adequate for direct-push insertion

Importance of Work

- High resolution data can independent from well production rates
  - Enable better site modeling
  - Remediation design
    - Natural attenuation potential
    - Need for bioaugmentation
  - Impact of remedial activities
    - Distribution of amendments
    - Bacterial community/capacity
  - Determine impact of low permeability zones
    - Potential for rebound
    - Well placement

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Danny Reible
Henry Yew

For additional information, please visit

https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Persistent-Contamination/ER-2419

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