REMTEC

REMEDIATION TECHNOLOGY SUMMIT

THE FUTURE OF REMEDIATION TECHNOLOGY

FEBRUARY 26–28, 2019

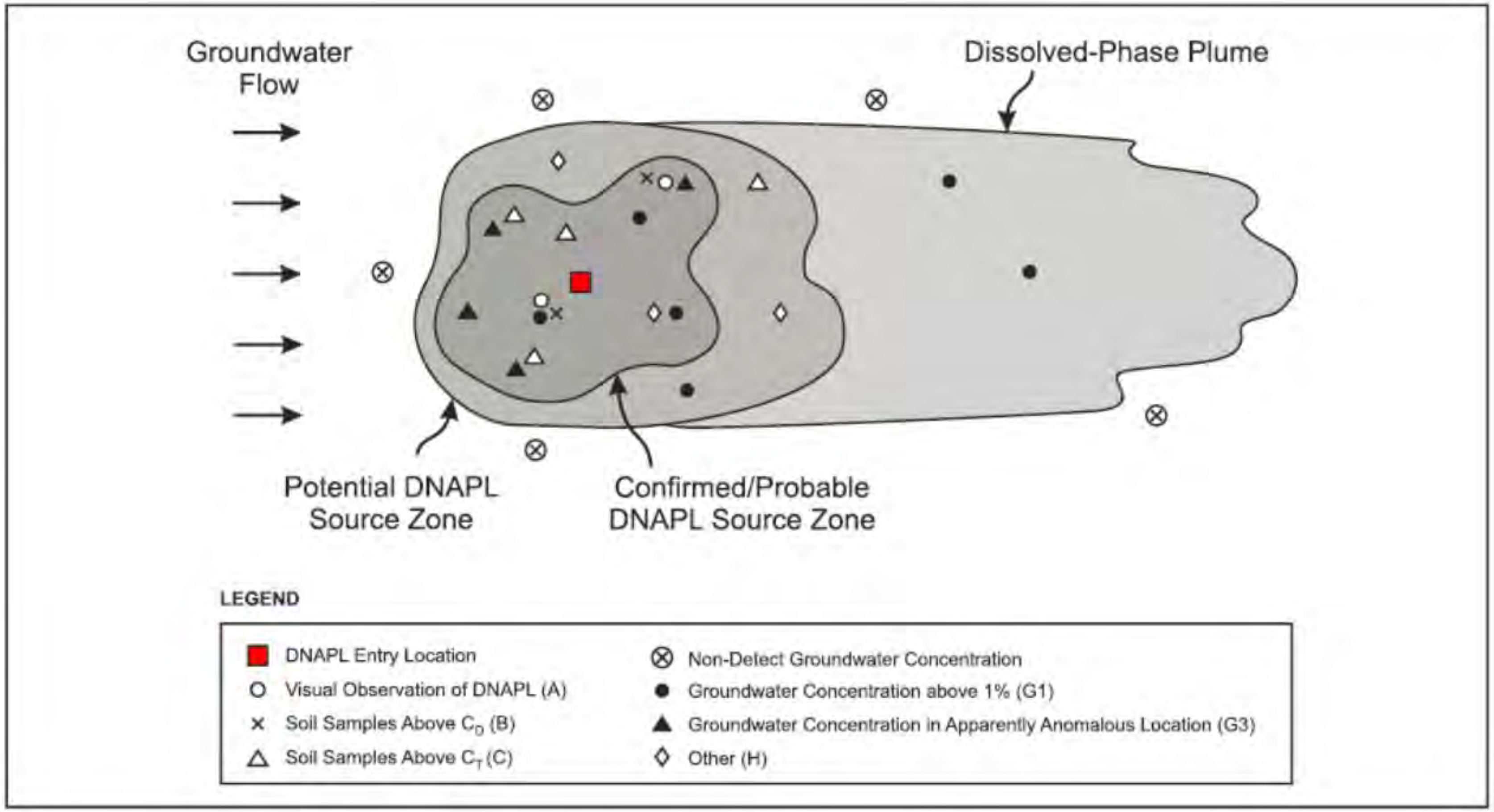
Colorado Convention Center | Denver, CO

Advancing Mobility Testing and Aqueous-Phase Sampling in NAPL Zones

Michael J. Gefell, P.G., C.P.G. (mgefell@anchorqea.com) (Anchor QEA, Lakewood, CO, USA)
Dimitri Vlassopoulos, Ph.D., and Masa Kanematsu, Ph.D. (Anchor QEA, Portland, OR, USA)
David S. Lipson, Ph.D. (HRS Water Consultants, Inc., Lakewood, CO, Lakewood, CO, USA)
Bruce Thompson (*de maximis, inc*., Windsor, CT, USA)

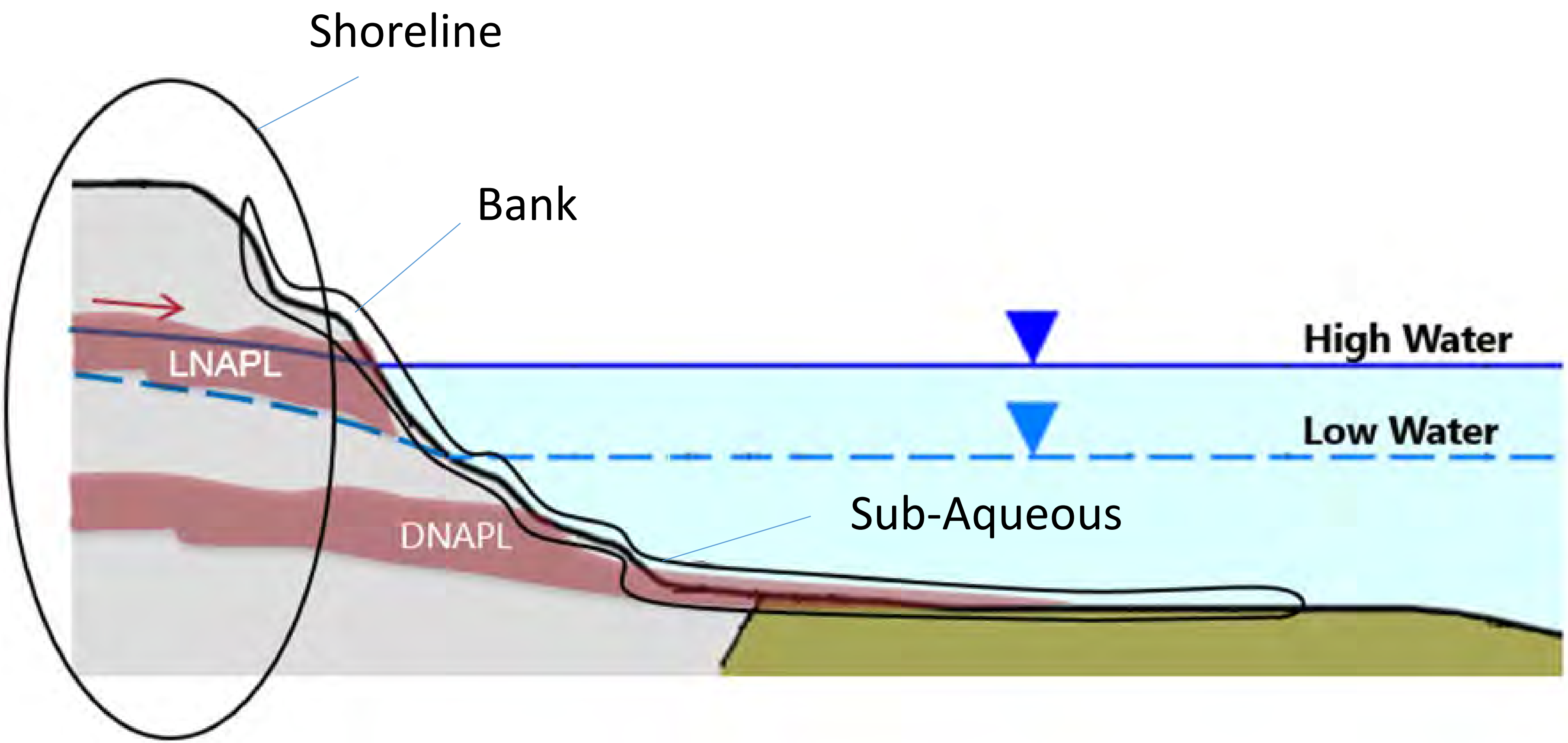
REMTEC
REMEDIATION TECHNOLOGY SUMMIT
THE FUTURE OF REMEDIATION TECHNOLOGY
FEBRUARY 26 – 28, 2019
Colorado Convention Center | Denver, CO

Generic NAPL Zone and Dissolved Plume



Source: U.S. Environmental Protection Agency, 2009. *Assessment and Delineation of DNAPL Source Zones at Hazardous Waste Sites*. EPA/600/R-09/119. September 2009.

Near-Shore, Bank, and Sub-Aqueous NAPL – Little Room for Error



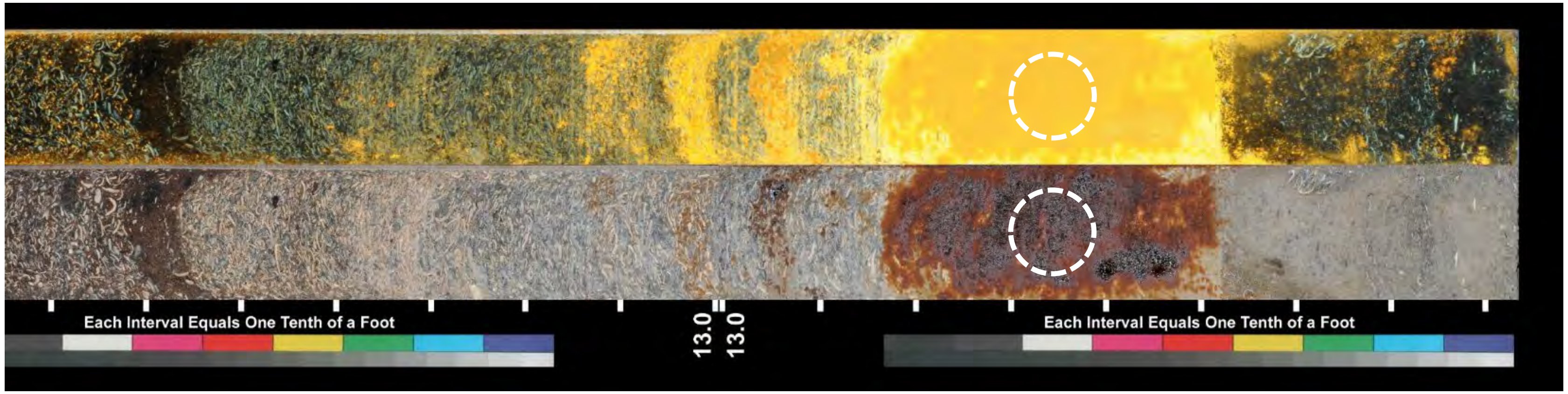
NAPL Mobility Testing

Improved Use of Laboratory Test Data

Laboratory NAPL Mobility Test Samples

- Typically 2 inches long and 1.5 inches in diameter
- Often selected based on core photography
- Usually highest apparent NAPL saturation

UV light – NAPL fluoresces



White light – NAPL has natural color

Photograph courtesy of PTS Laboratories (Houston, Texas)

Laboratory NAPL Mobility Testing

- Centrifuge
  - Relatively low cost
  - 1 “gravity” ≈ hydraulic gradient of 1
  - 1,000 “gravities” ≈ hydraulic gradient of 1,000
- Water-drive
  - Rigid wall (intermediate cost)
  - Flexible wall (higher cost)
- Tests can have multiple steps with increasing centrifuge spin rate or water injection rate

Laboratory Test Gradients Extremely High

- To complete tests in a reasonable time frame, laboratory test gradients are often **much** stronger than field conditions
- Centrifuge typically 10G to 1,000G
- Water-drive hydraulic gradients up to 100s

If no NAPL is produced from sample, NAPL is residual (immobile), but what if some NAPL **is** produced under these test conditions?

NAPL Effective Hydraulic Conductivity (K_n)

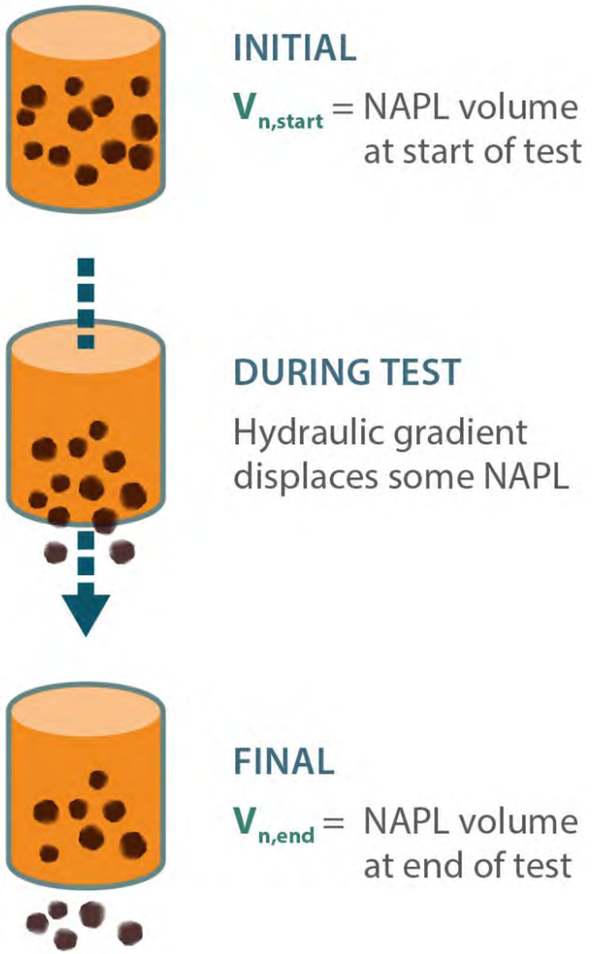
- Darcy's Law
- $K_n = Q_n/(Ai)$

  Q_n = average NAPL flow rate = $\Delta V_n/t$ [L^3/T]

  A = cross-sectional area for flow [L^2]

  i = lab test hydraulic gradient [L/L]

- K_n accounts for the following
  - Soil/sediment pore sizes
  - NAPL viscosity
  - NAPL saturation
  - NAPL relative permeability



Gefell, M.J., K. Russell, and M. Mahoney, 2018. "NAPL Hydraulic Conductivity and Velocity Estimates Based on Laboratory Test Results." *Groundwater* 56(5): 690–694.

NAPL Mass Flux and Velocity

- If all NAPL mobility tests indicate NAPL is immobile, NAPL mass flux is interpreted as zero
- If some tests indicate potentially mobile NAPL, use K_n to calculate potential NAPL mass flux (dM_n/dt) and pore velocity (v_n) in the field

$$dM_n/dt = Q_n \rho_n = K_n i_n A \rho_n$$

$$v_n = K_n i_n/(nS)$$

Q_n = volumetric NAPL flow rate [L^3/T]
ρ_n = NAPL density [M/L^3]
i_n = net gradient in the field (includes hydraulic gradient and "gradient due to gravity")

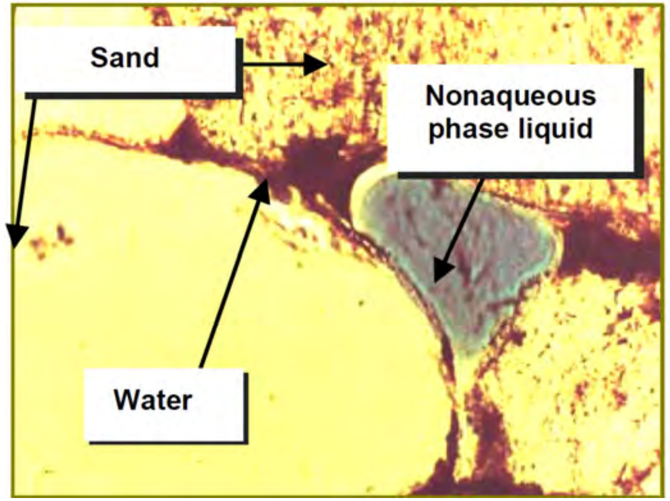
A = area of potential NAPL flow perpendicular to flow direction [L^2]
n = porosity
S = NAPL saturation

Dissolved Concentration Measurements in NAPL Zones

Avoiding False Positives

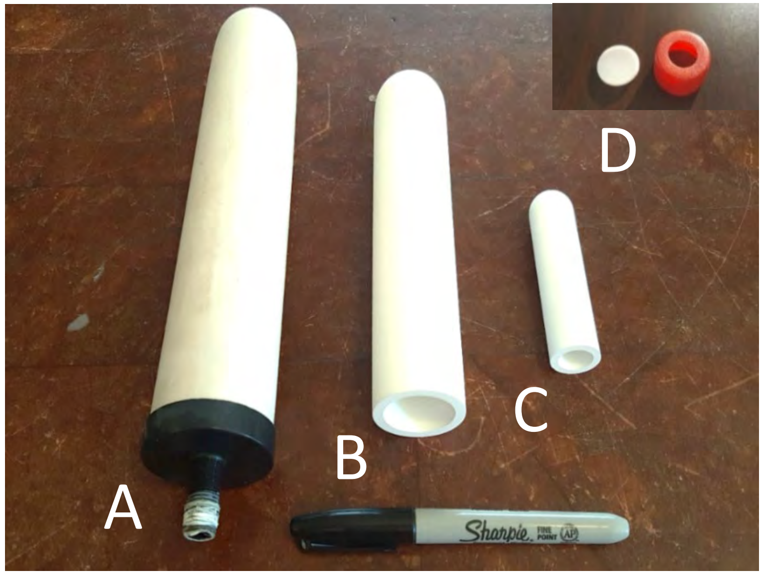
NAPL Can Exaggerate "Aqueous" Concentrations

- NAPL enters push-point samplers and wells
- NAPL coats hydrophobic passive samplers
- Aqueous concentrations calculated from soil or sediment samples can exceed effective solubility
- **NAPL can cause dissolved reported or inferred concentrations to be biased high—above true dissolved concentrations**



Source (bottom): Wilson, J.L., S.H. Conrad, W.R. Mason, W. Peplinski, and E. Hagan, 1990. *Laboratory Investigation of Residual Liquid Organics from Spills, Leaks, and the Disposal of Hazardous Wastes in Groundwater.* EPA/600/6-90/004. April 1990.

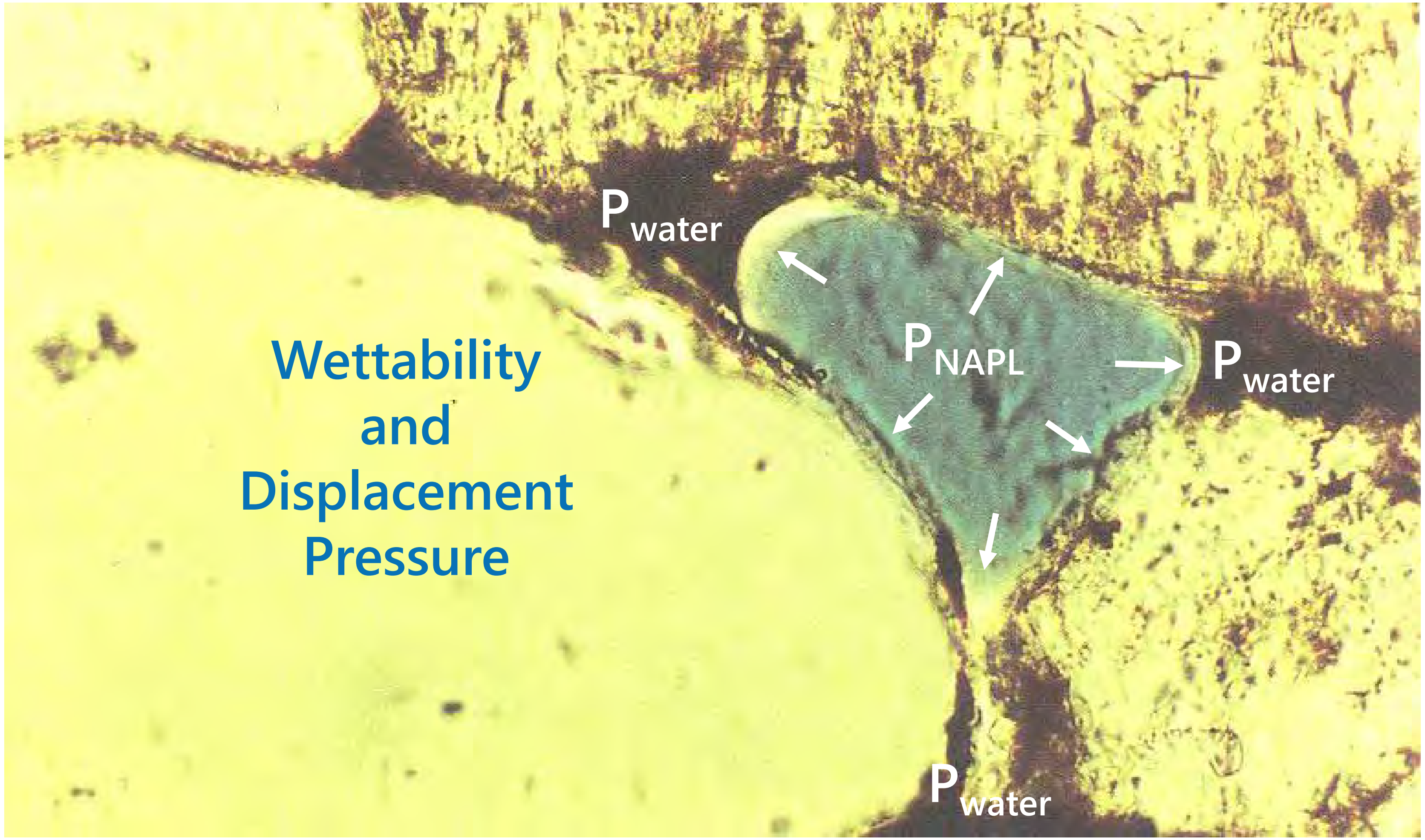
Porous Ceramics Are NAPL Barriers



ID	Shape	Pore Size (µm)	K (cm/s)	Porosity	Length (cm)	Outer Diameter (cm)	Approximate Cost (US)
A*	Tube	11.2	8×10^{-5}	0.22	24	4.9	$20
B	Tube	2.5	9×10^{-6}	0.45	17	4.0	$100
C	Tube	2.5	9×10^{-6}	0.45	8.9	2.2	$40
D	Disk	2.5	9×10^{-6}	0.45	NA	2.2	$40

Notes:
* = Physical parameters estimated based on laboratory testing by Anchor QEA. All others provided by manufacturer.
K = hydraulic conductivity

Fundamentals of NAPL Exclusion

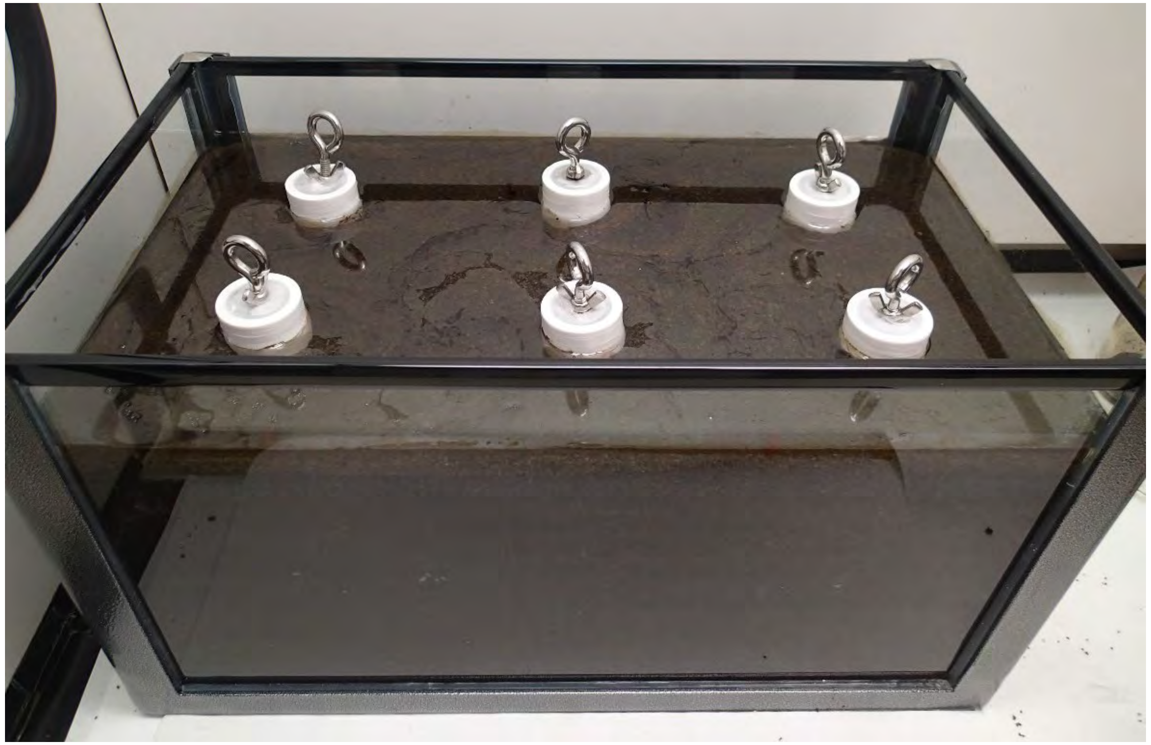


Source: Wilson, J.L., S.H. Conrad, W.R. Mason, W. Peplinski, and E. Hagan, 1990. *Laboratory Investigation of Residual Liquid Organics from Spills, Leaks, and the Disposal of Hazardous Wastes in Groundwater.* EPA/600/6-90/004. April 1990.

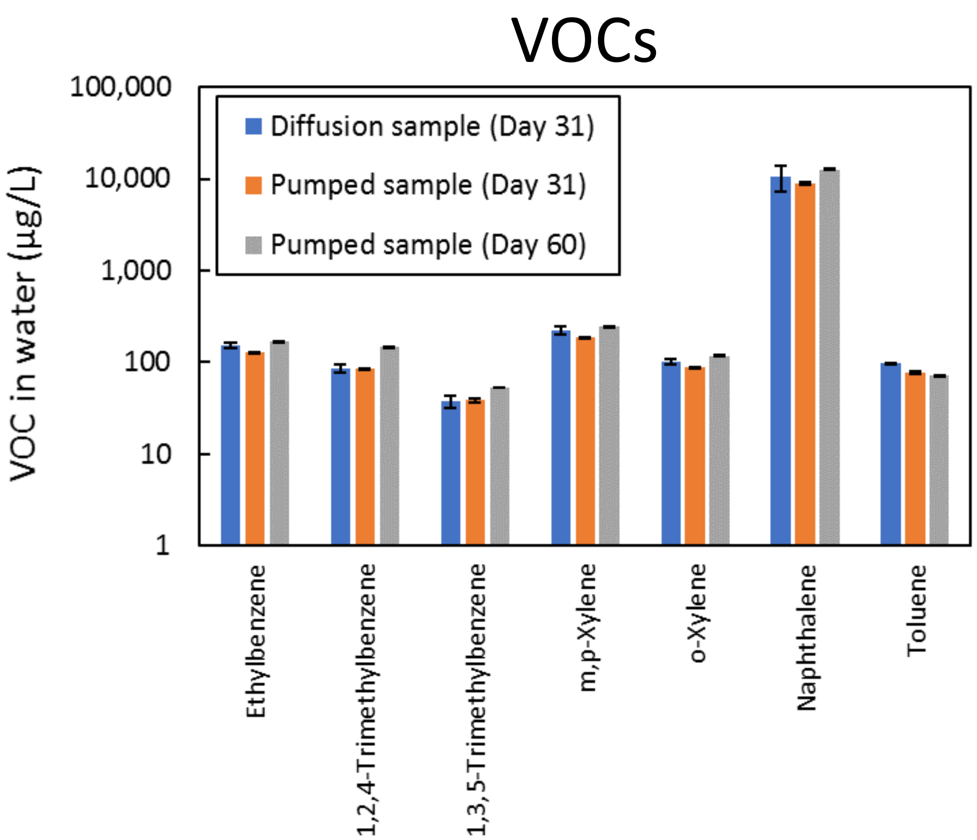
Laboratory Test of Sampling Water in Contact with NAPL

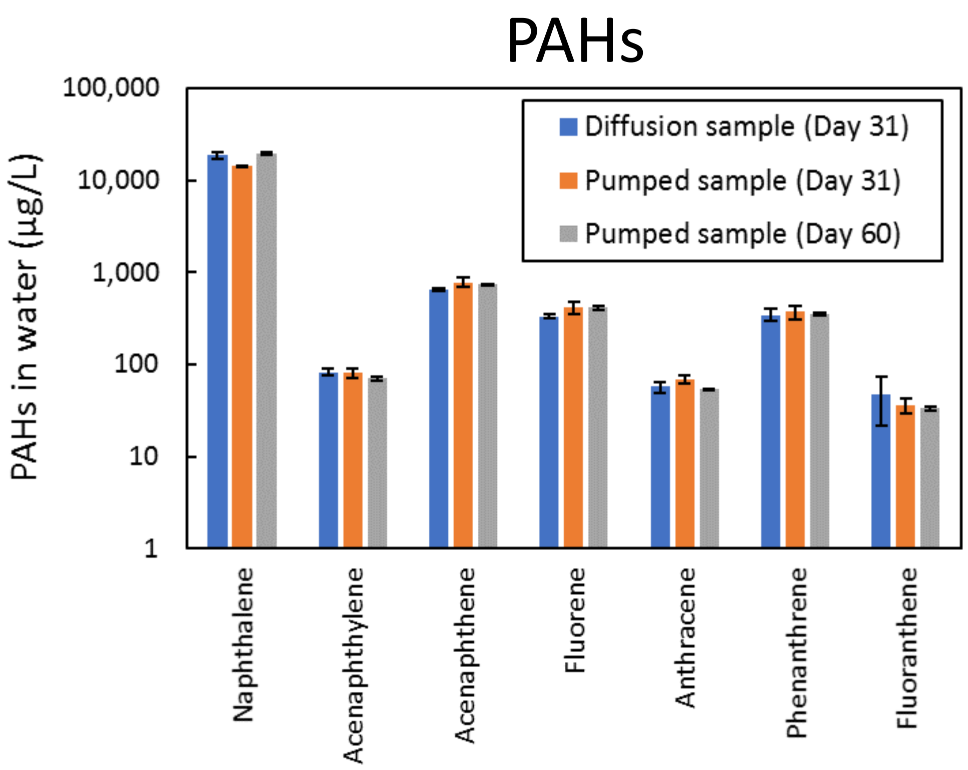
Porewater Sampling Tests with Diffusive Equilibration and Pumping (with NAPL)

- Aquarium with well-graded sand, 0.5M NaCl water, and 10% creosote NAPL saturation
- Duplicate samples
  - Diffusion-based water samples at 10, 20, and 31 days
  - Pumped water samples also collected from ceramic tubes at 31 days and 60 days



Porewater Sampling Tests with Diffusive Equilibration and Pumping (with NAPL) (cont.)





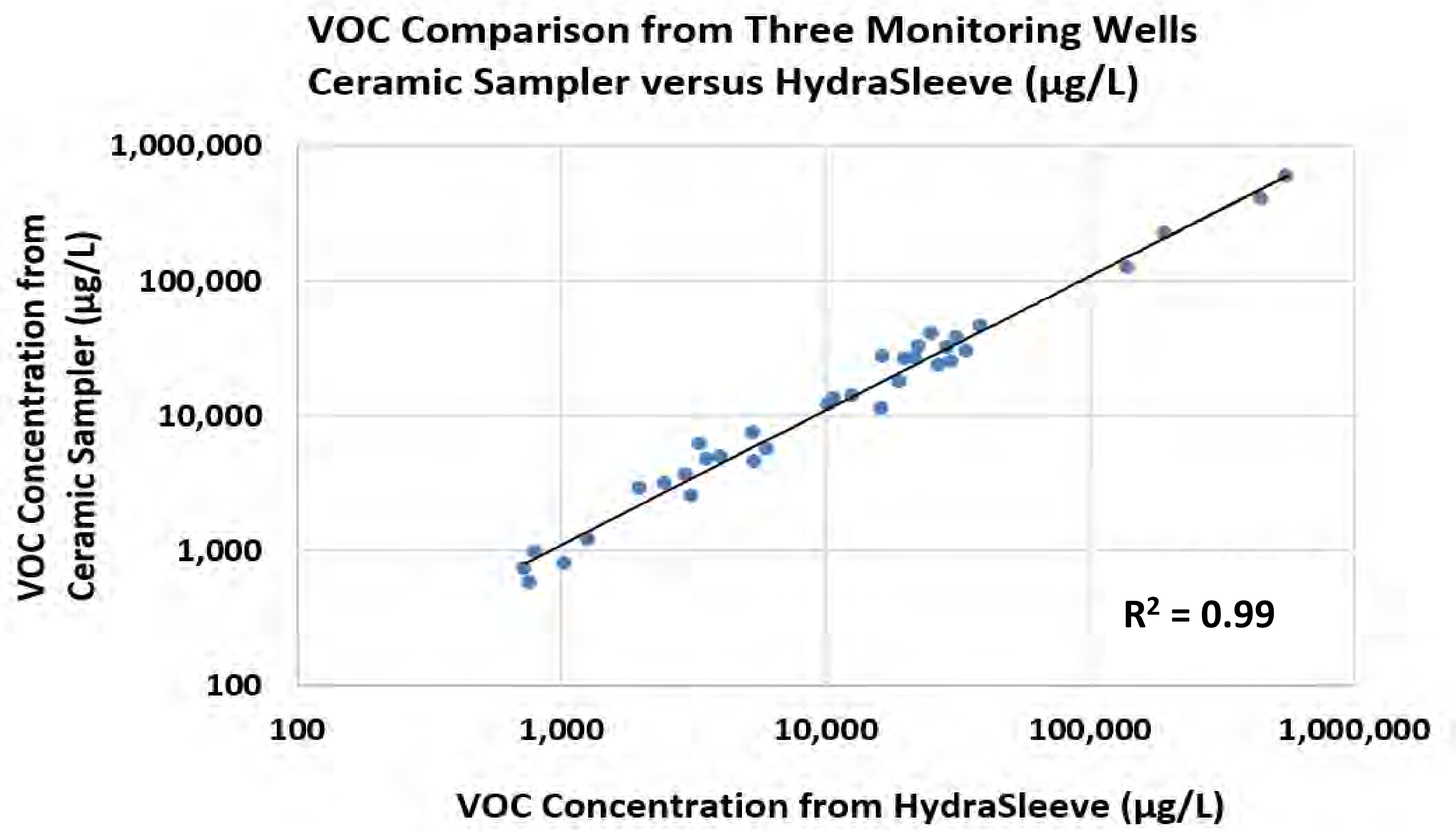
Gefell, M.J., M. Kanematsu, D. Vlassopoulos and D.S. Lipson, 2018. "Aqueous-Phase Sampling with NAPL Exclusion Using Porous Ceramic Cups." *Groundwater* 56(6): 847–851.

Field Testing in Monitoring Wells at NAPL Sites

Field Test 1 – Diffusion Groundwater Sampling September 2018

- USEPA Region 1 Superfund Site
- Chlorinated solvents and petroleum-based aromatics
- Tested in three wells with historical DNAPL
- 30-day ceramic sampler equilibration
- Comparative HydraSleeve samples

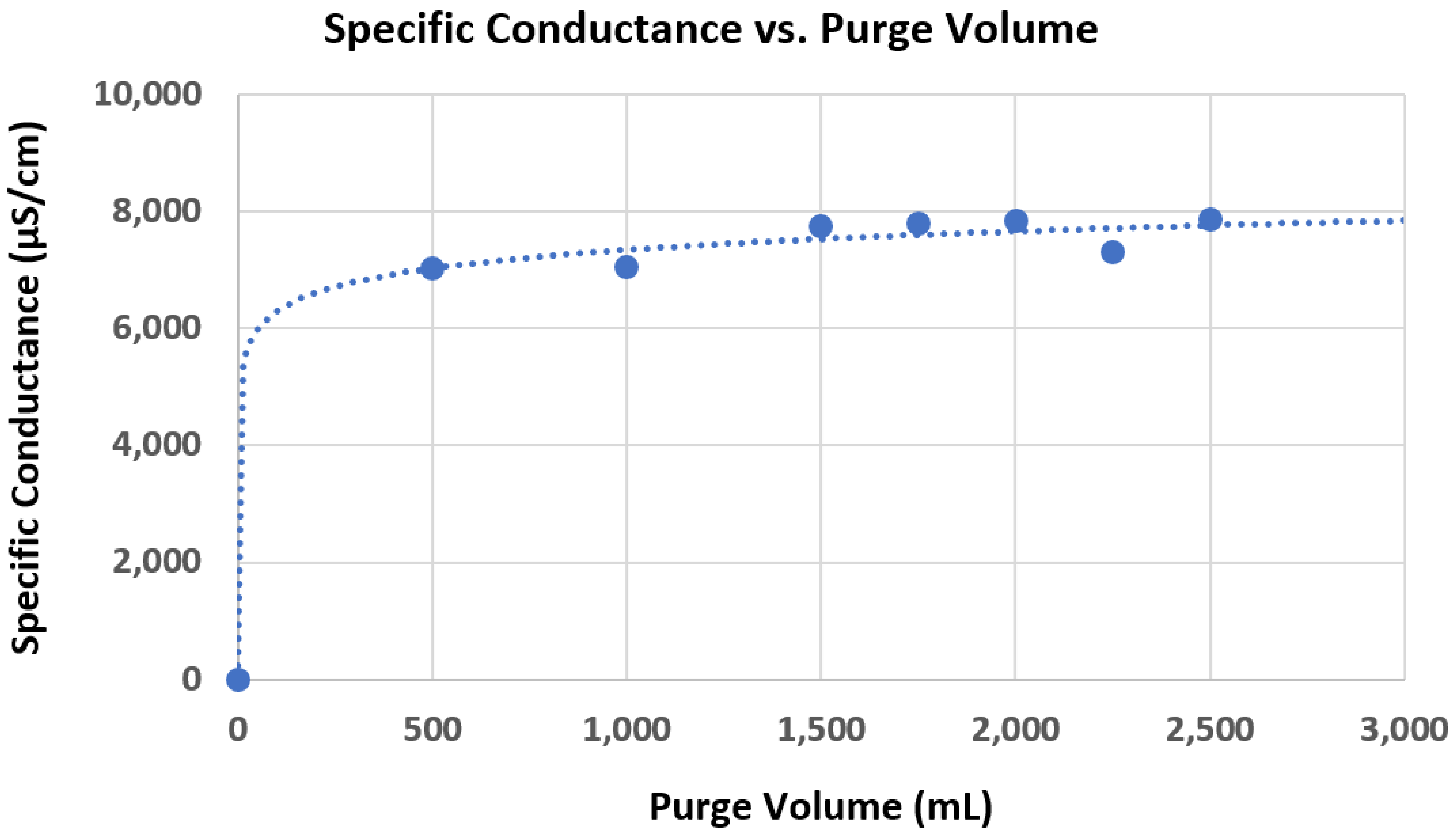
Field Test 1 – Results



Field Test 2 – Pumped Groundwater Sampling September 2018

- Petroleum LNAPL site in Colorado
- BTEX compounds
- Tested below LNAPL layer in two wells and in other wells without LNAPL
- Purged five ceramic sampler volumes before sampling
- Comparative low-flow samples at wells without LNAPL

Field Test 2 – Results



Field Test 2 – Results (cont.)
Groundwater Concentrations in Wells with LNAPL (from Ceramic Samplers)

Compound (mg/L)	Well 1	Well 2
Benzene	7.54	16.4
Toluene	22.1	23.0
Ethylbenzene	2.39	1.60
Xylenes	28.5	15.3
Total BTEX	**60.5**	**56.3**

- 17% of total LNAPL mass detected in VOC analysis (Method 8015)
- BTEX was 11% of total mass
- Calculation of effective solubility challenging and unreliable based on available data

Field Test 2 – Results (cont.) Groundwater Concentrations in Wells without LNAPL

Compound (µg/L)	Well 3 Ceramic	Well 3 Low-Flow
Benzene	63.0	71.8
Toluene	3.14	3.89
Ethylbenzene	26.0	29.6
Xylenes	15.7	20.2
Total BTEX	**108**	**125**

- 13% to 25% relative percent difference, within typical acceptability range for laboratory MS/MSDs

Potential Uses of Capillary Barrier Materials for Water Sampling Without NAPL Impacts

- Sample porewater by diffusion-based equilibration
- Pump water samples through capillary barrier in situ (intake end of sampler) or ex situ (water filter) to exclude NAPL
- Use capillary barrier devices in wells with NAPL

Summary and Conclusions

- Concentrations and flow rates drive risk and remediation
- Laboratory-based NAPL mobility tests provide an opportunity to quantify the NAPL effective hydraulic conductivity
- Any NAPL in samples can severely bias interpreted aqueous concentrations
- Capillary barrier materials such as porous ceramics can be used to sample aqueous phase and avoid impacts due to NAPL

Thanks for Your Attention – Any Questions?

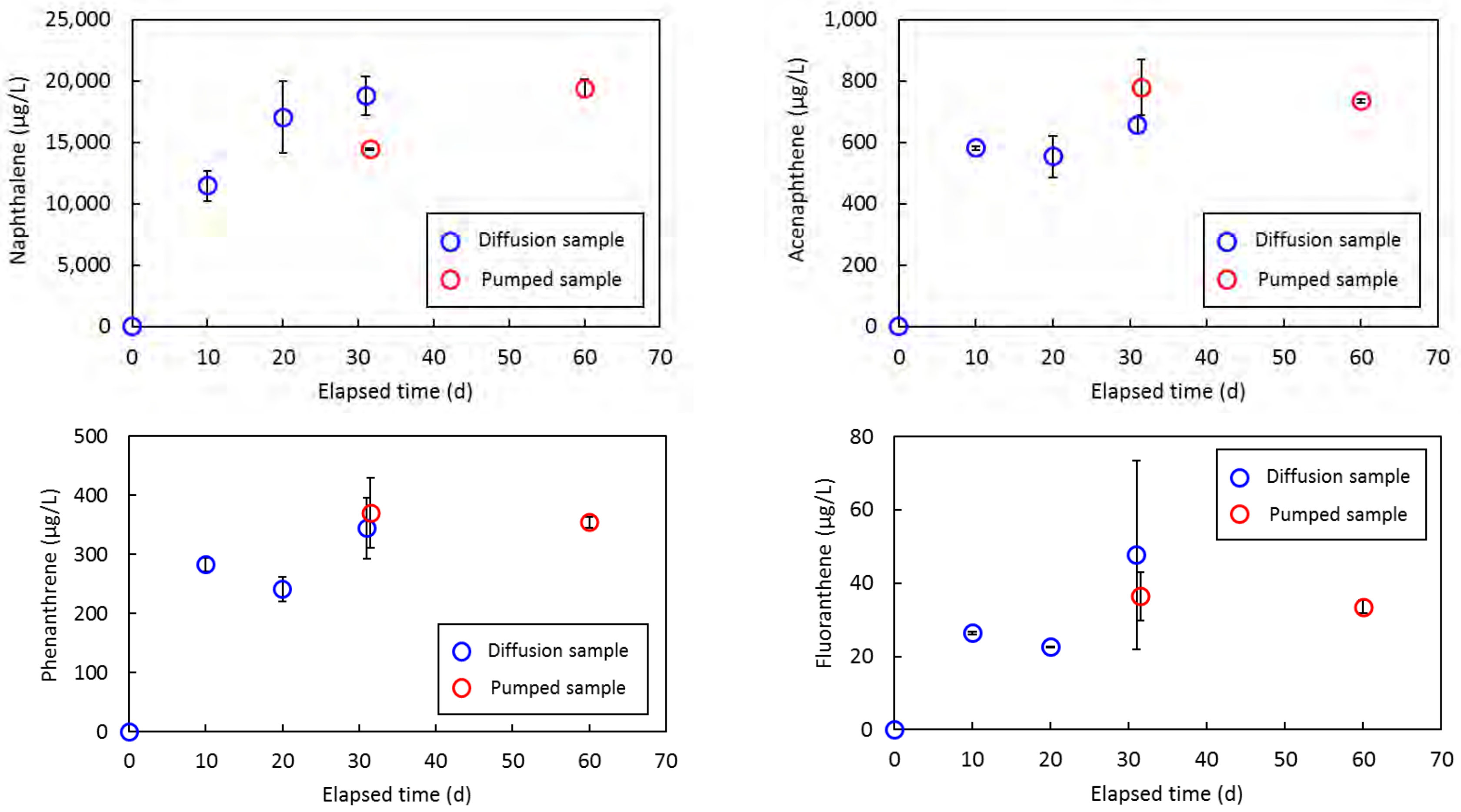
Michael J. Gefell
Anchor QEA, LLC
Lakewood, Colorado
303-984-6250
mgefell@anchorqea.com

Examples of Very Low *Initial* NAPL Saturations (Likely Residual NAPL) Mobilized By Lab Tests –

- 7.0% with test gradient of 10
- 3.7% with test gradient of 100
- 2.5% with test gradient of 1,000

Significant risk of mobilizing even residual NAPL during laboratory tests!

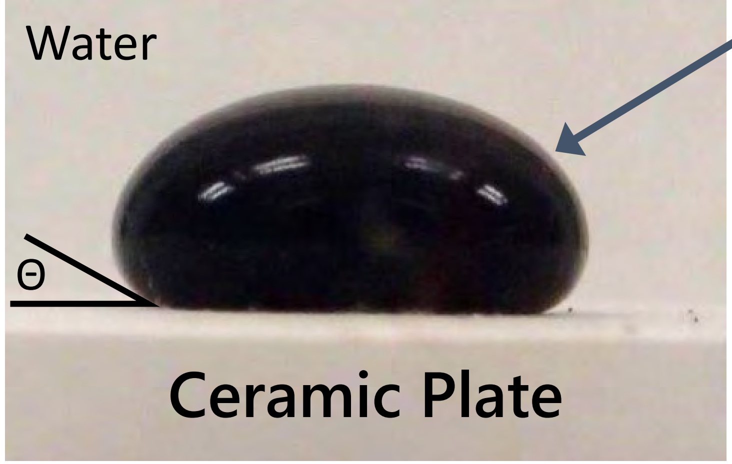
Porewater Sampling Tests With Diffusive Equilibration and Pumping



Wettability Tests—Dense NAPL on Ceramic and Low Density Polyethylene (LDPE)

Weathered, PAH-Rich DNAPL

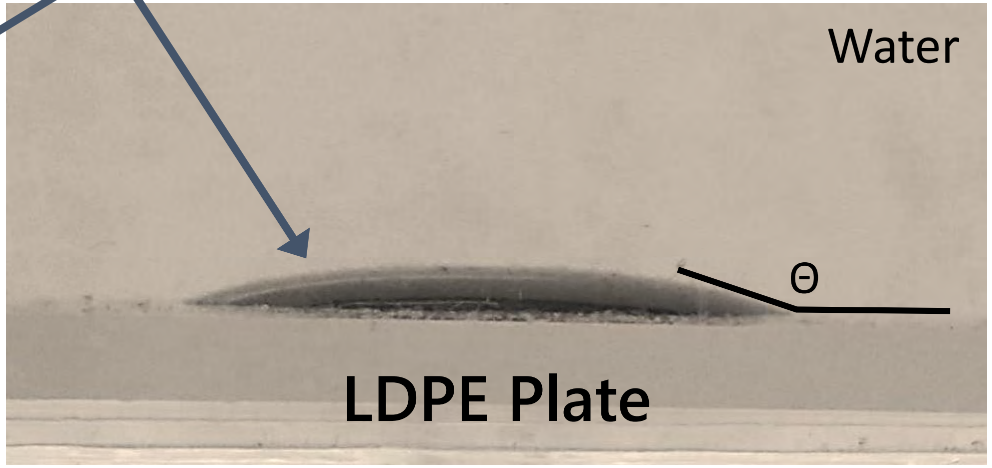
(23 days)



Contact angle Θ = 24°

NAPL is non-wetting

(1 day)

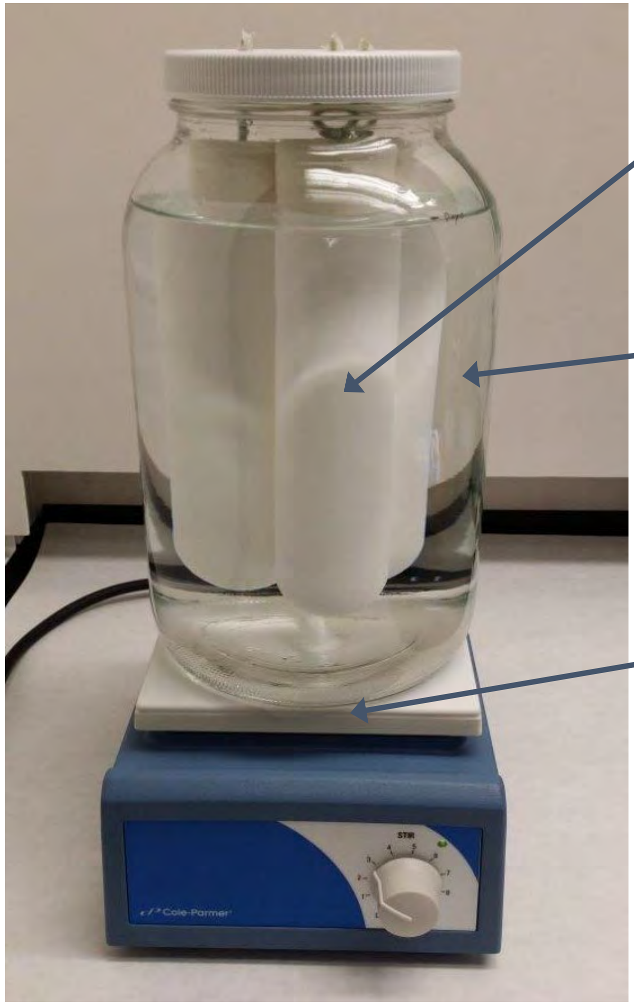


Contact angle Θ = 162°

NAPL is wetting

PAH Equilibration Test (No NAPL)

- 16 priority PAHs spiked in water in a 2-L jar
- Porous ceramic cups each containing 120 mL deionized water submerged in jar
- Water in the jar was slowly stirred by a magnetic stir bar and stored in the dark at 20 °C
- Diffusion-based equilibration

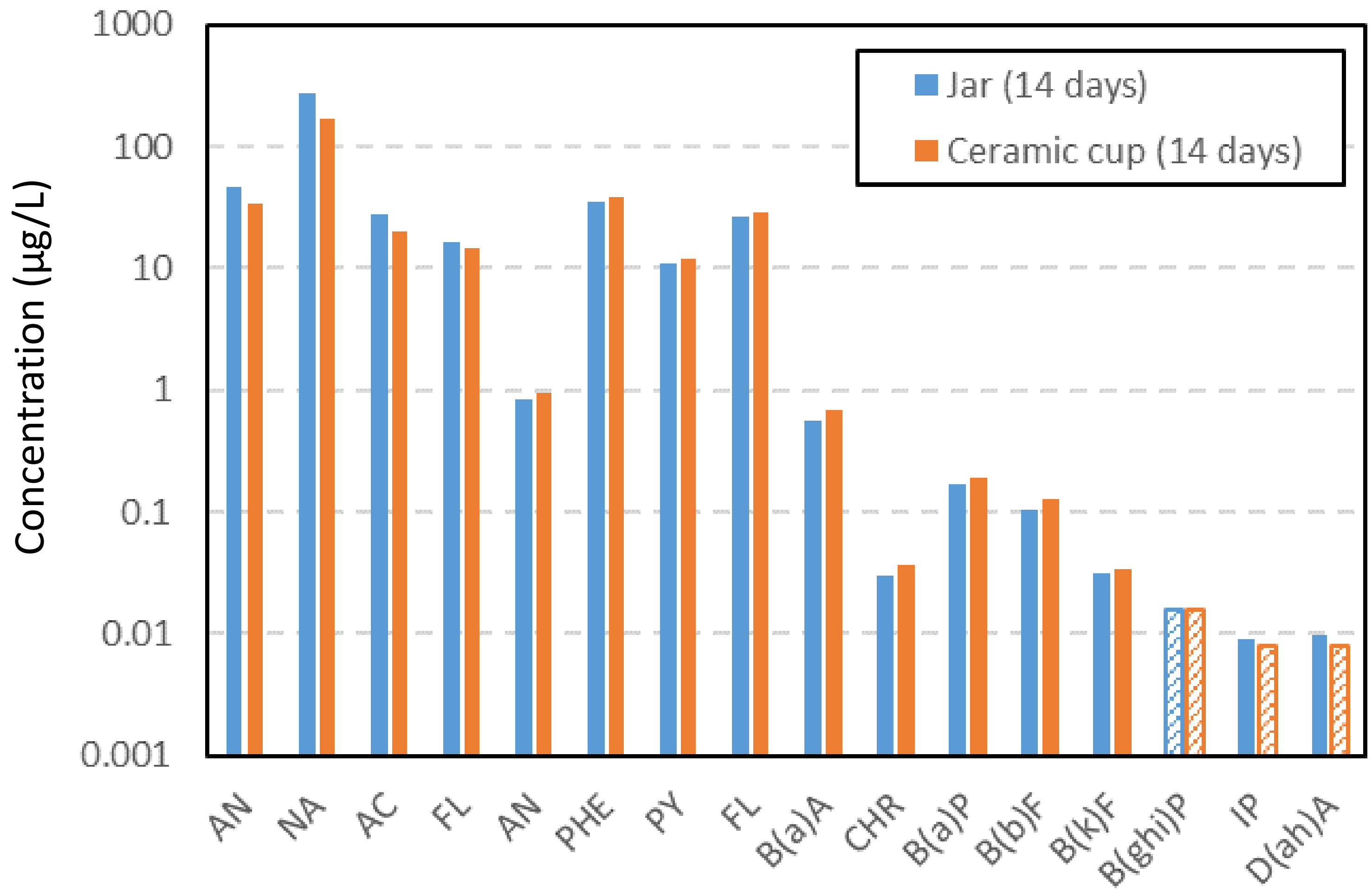


Capped ceramic tubes

PAH-spiked water

Magnetic stirrer

PAH Equilibration, 14-Day Results (No NAPL)



Note: Striped pattern bars indicate method detection level.