

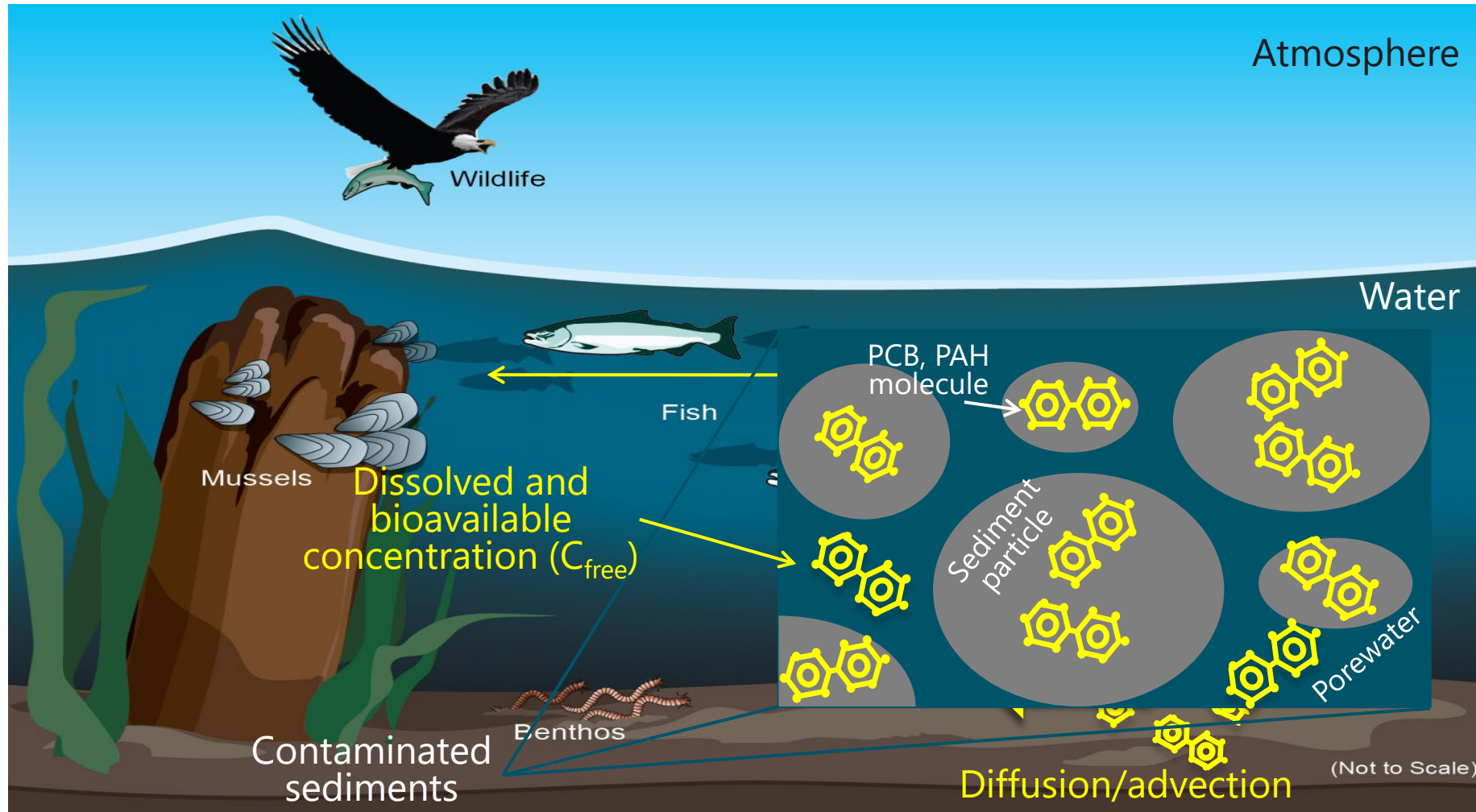
# Quantifying Aqueous Concentrations in Direct Contact with NAPL- Containing Sediment Using Porous Ceramic Samplers

Learning Lab: Tuesday and Wednesday, 2:40 to 3:05 p.m.

Presented by: Michael Gefell, PG; Dimitri Vlassopoulos, PhD; and  
Deirdre Reidy, Anchor QEA

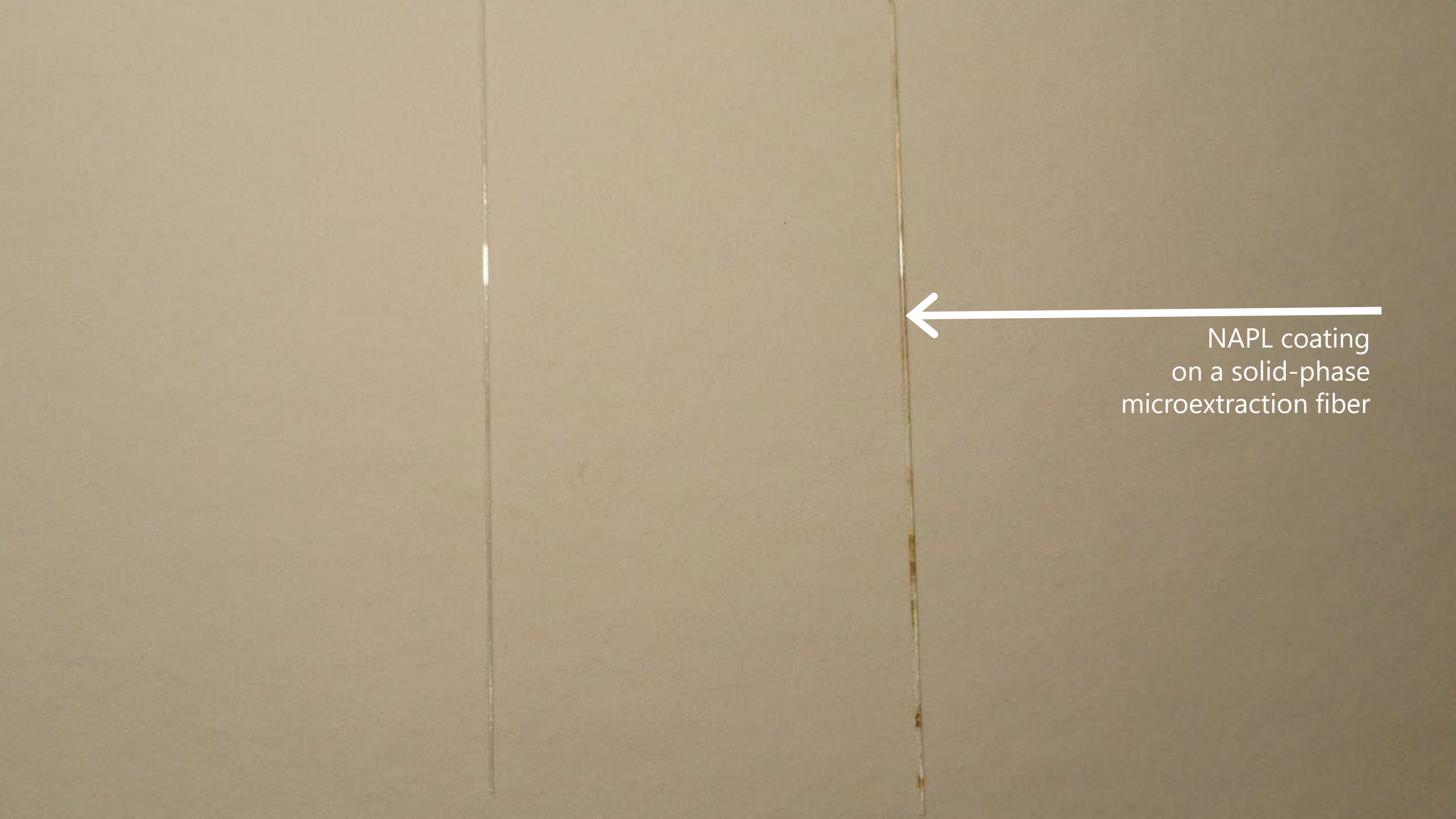


# Importance of Accurate Porewater Samples



Nonaqueous phase liquids (NAPLs) can exaggerate “aqueous” concentrations

NAPLs can enter push-point samplers and wells and coat/foul hydrophobic passive samplers

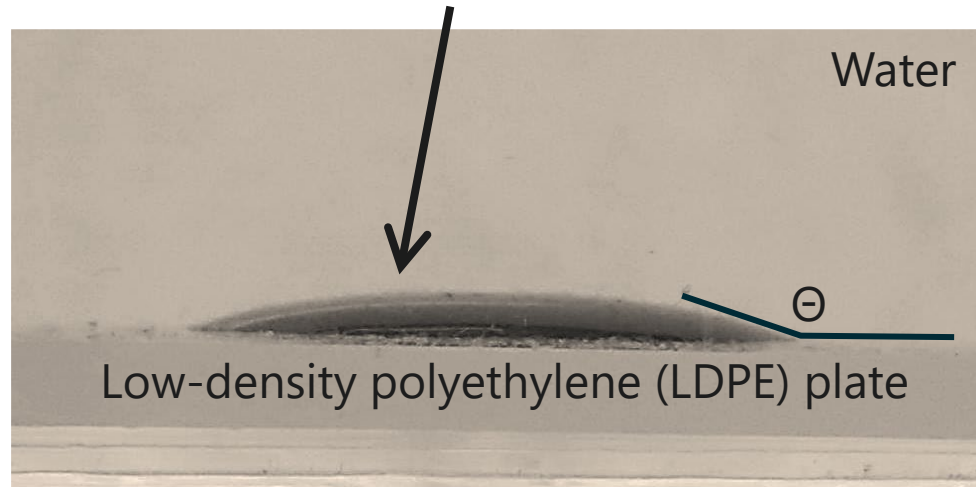


The image shows two vertical, thin fibers against a light beige background. The fiber on the right has a thin, dark, irregular coating along its length. A white arrow points from the text on the right towards this coated fiber.

NAPL coating  
on a solid-phase  
microextraction fiber

# Wettability Test—DNAPL on LDPE Underwater

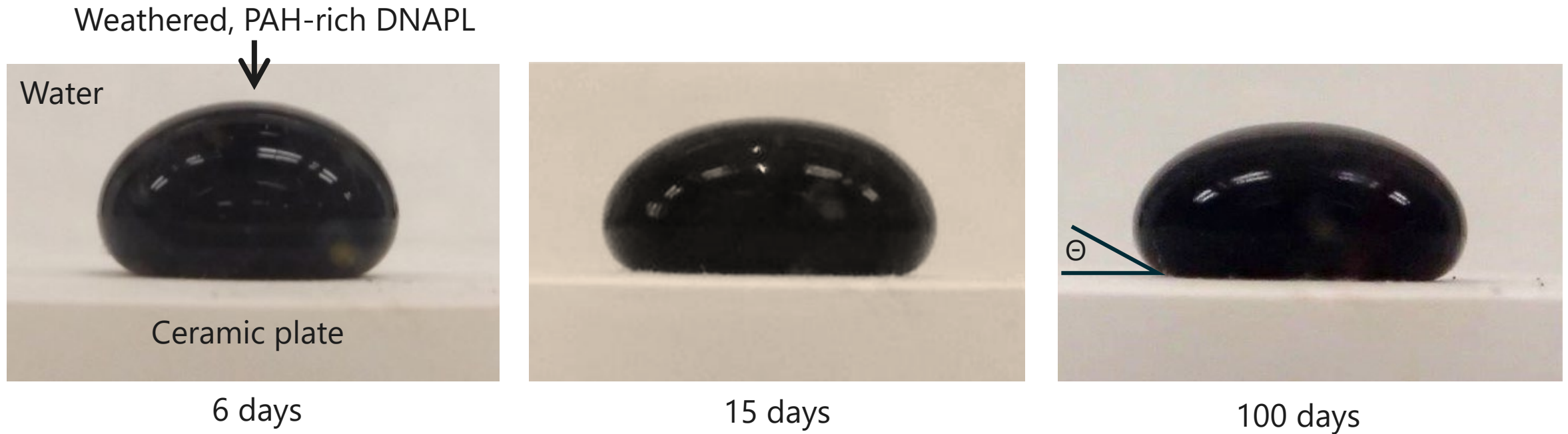
Weathered, polycyclic aromatic hydrocarbon (PAH)-rich dense nonaqueous phase liquid (DNAPL)



1 day; contact angle ( $\Theta$ ) =  $162^\circ$

NAPL is wetting phase

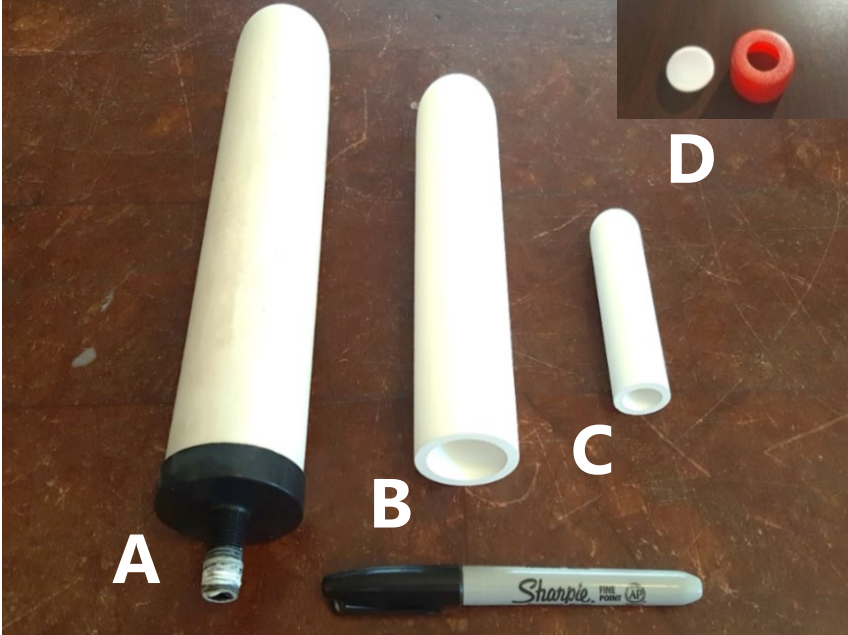
# Wettability Test—Same DNAPL on Porous Ceramic Plate Underwater



Contact angle  $\Theta = 24^\circ$   
NAPL is non-wetting phase



# Porous Ceramics are NAPL Barriers



ID	Shape	Pore Size (µm)	K (cm/s)	Porosity	Length (cm)	Outer Diameter (cm)	Approximate Cost (U.S. dollars)
A*	Tube	11.2	$8 \times 10^{-5}$	0.22	24	4.9	\$25
B	Tube	2.5	$9 \times 10^{-6}$	0.45	17	4.0	\$110
C	Tube	2.5	$9 \times 10^{-6}$	0.45	8.9	2.2	\$50
D	Disk	2.5	$9 \times 10^{-6}$	0.45	NA	2.2	\$50

Notes:

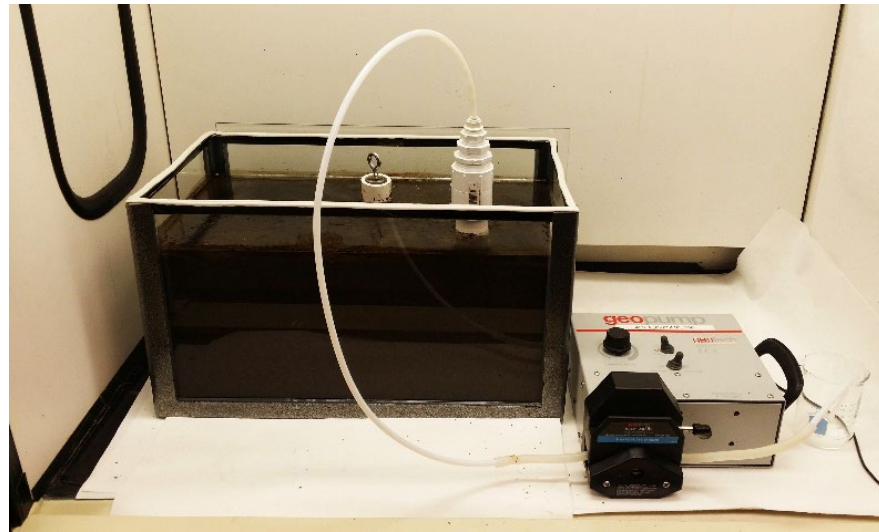
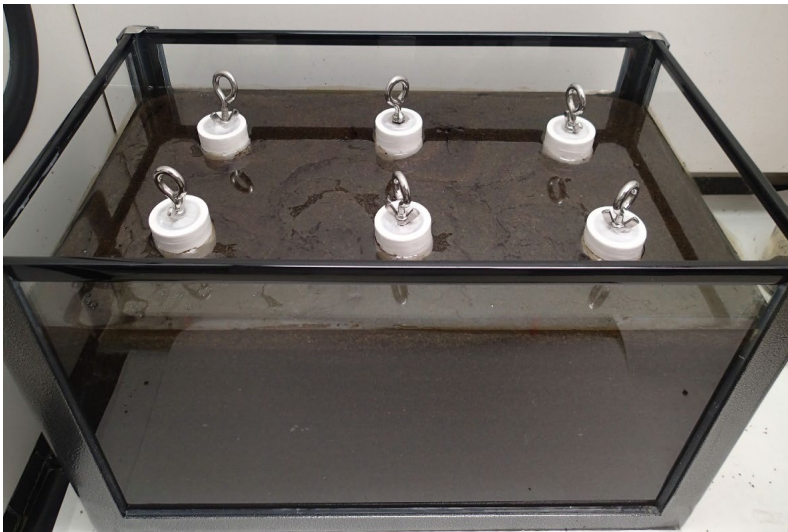
\*: Physical parameters estimated based on laboratory testing by Anchor QEA. All others provided by manufacturer.

K: hydraulic conductivity



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

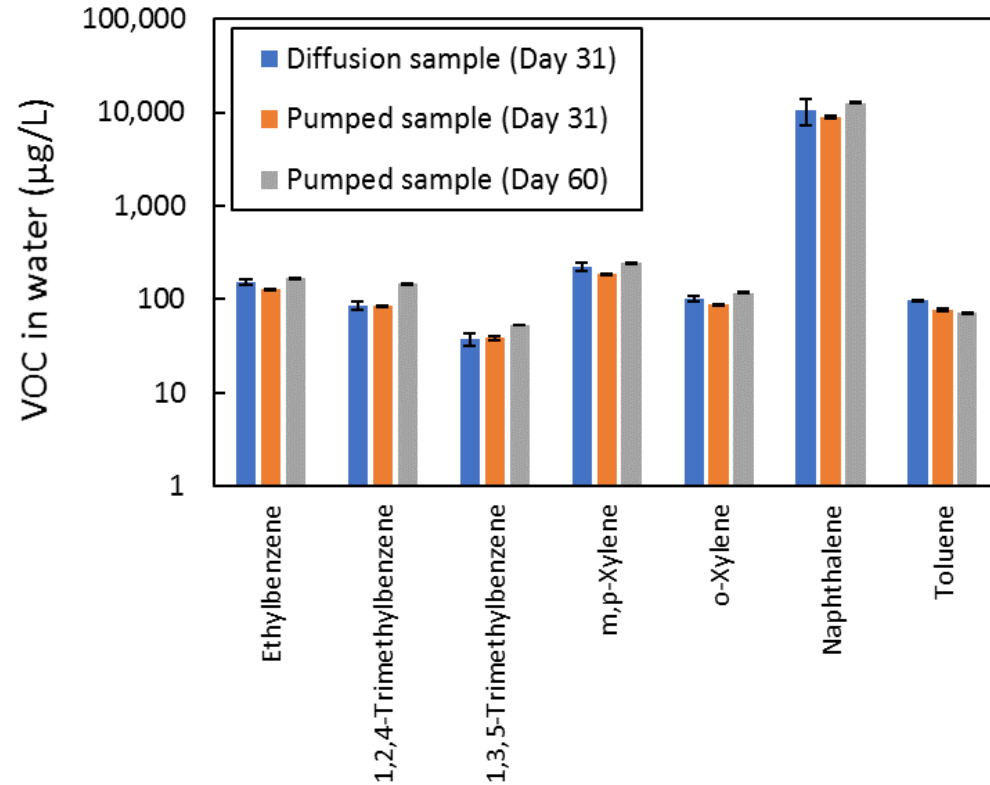
- Aquarium with well-graded sand, water, and 10% creosote NAPL saturation
- Duplicate samples
  - Diffusion-based water samples at 10, 20, and 31 days
  - Pumped-water samples also collected from ceramic tubes at 31 and 60 days



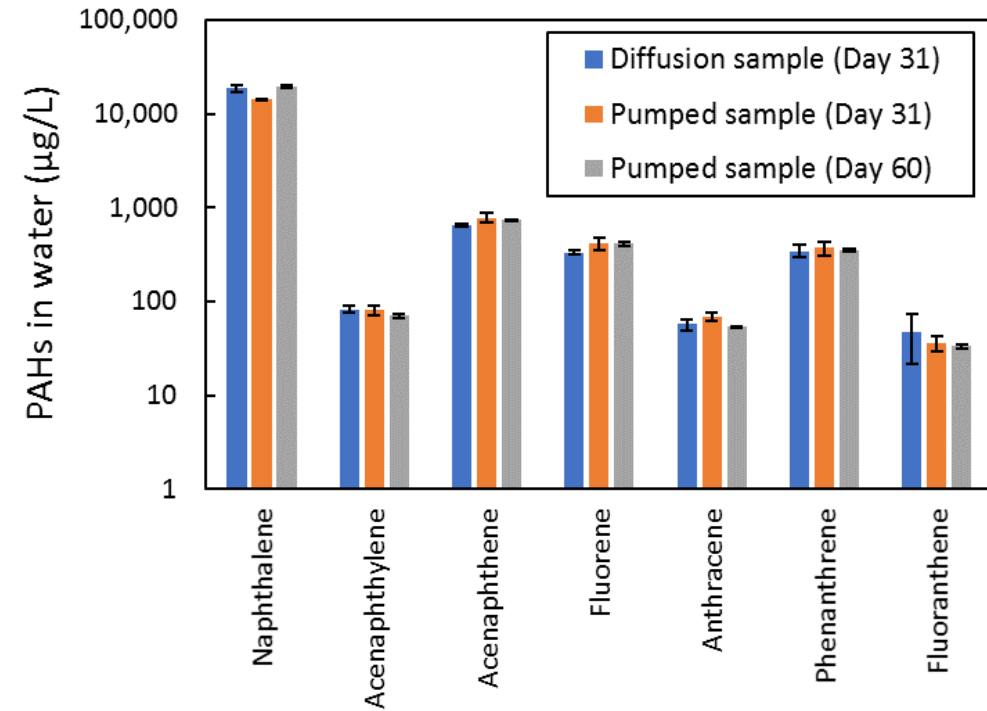


# Porewater Sampling Tests with Diffusive Equilibration and Pumping (with NAPL)

Volatile organic carbons



PAHs



# Experience at 11 Sites Across United States and Canada

## Groundwater

Technology Spotlight/

---

## Aqueous-Phase Sampling with NAPL Exclusion Using Ceramic Porous Cups

by Michael J. Gefell<sup>1</sup>, Masa Kanematsu<sup>2</sup>, Dimitri Vlassopoulos<sup>2</sup>, and David S. Lipson<sup>3</sup>

Source: Gefell et al. (2018)



# Pumping from Push-Point, Well, Piezometer, or Drill Casing



Intake mode (after sampling  
groundwater below light  
nonaqueous phase liquid in well)



Discharge mode

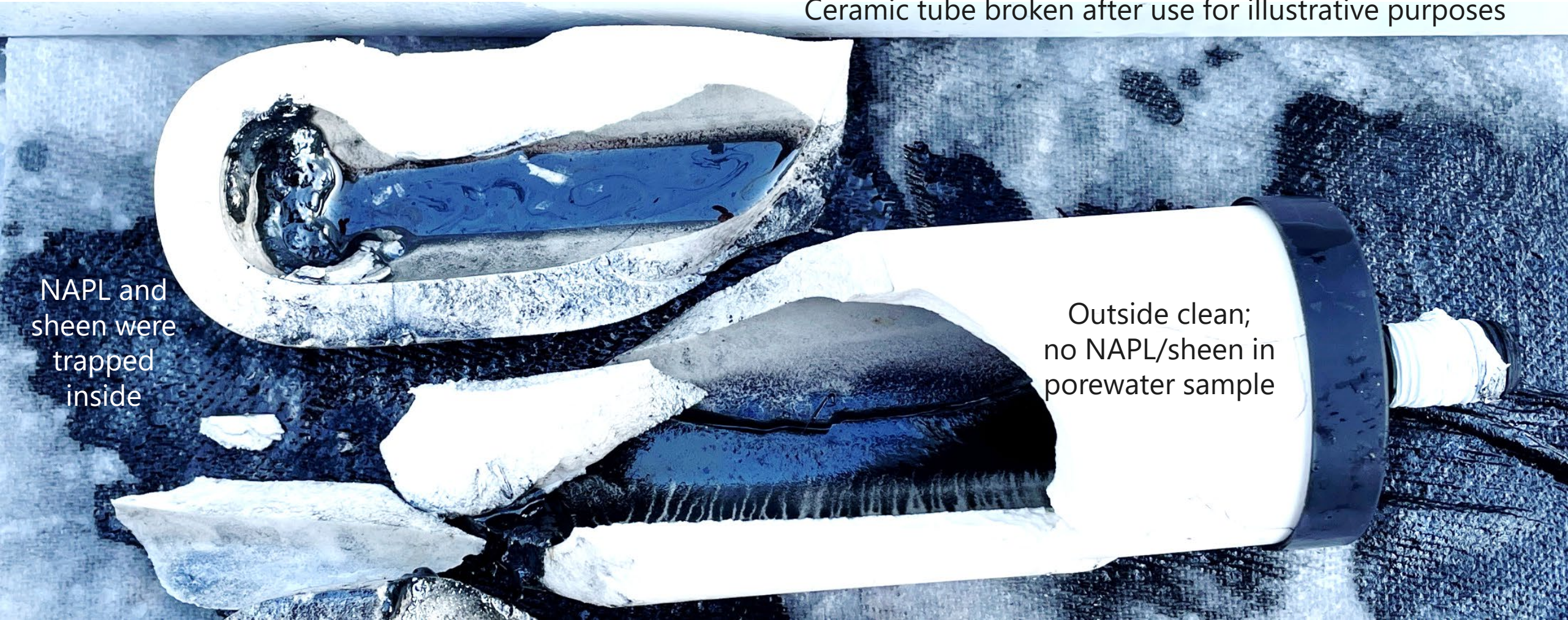


# After Porewater Sampling at Coal Tar Site (Discharge Mode)

Ceramic tube broken after use for illustrative purposes

NAPL and  
sheen were  
trapped  
inside

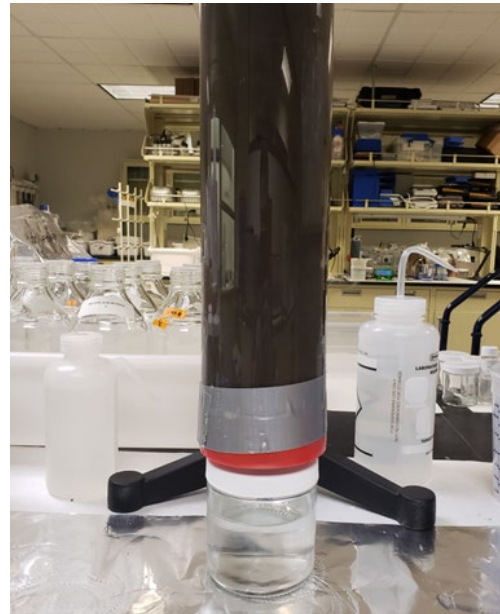
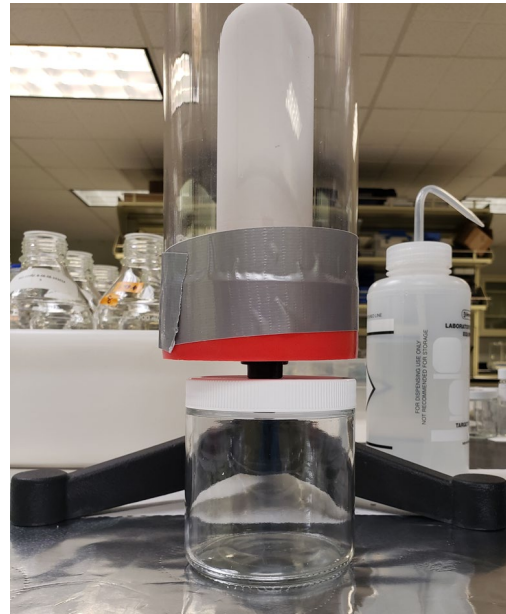
Outside clean;  
no NAPL/sheen in  
porewater sample





# Other Sampling Methods

- In situ, diffusion-based equilibration ( $\geq 30$  days)
- Ex situ porewater: gravity drainage from sediment through filter
- Ex situ porewater: centrifuge from sediment, then pump through filter

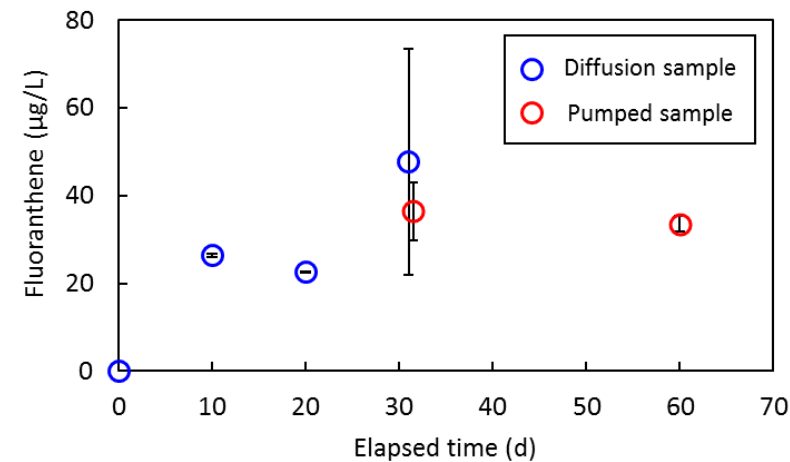
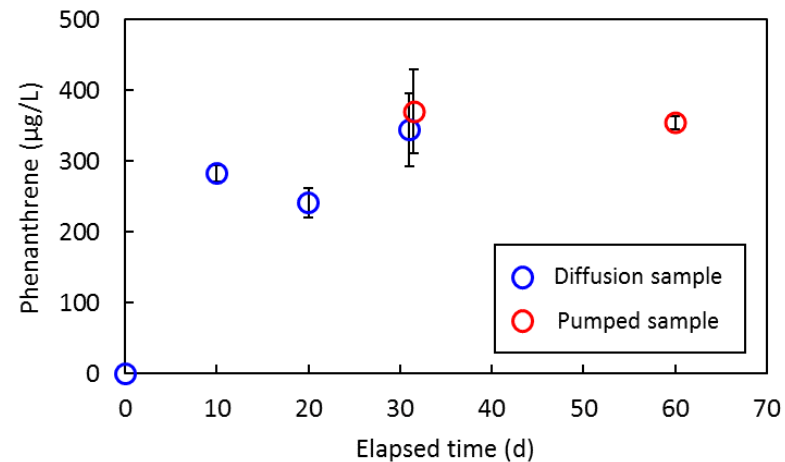
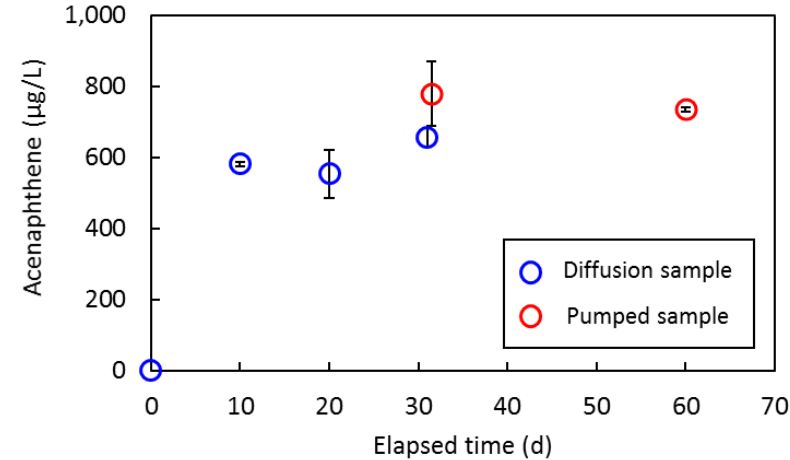
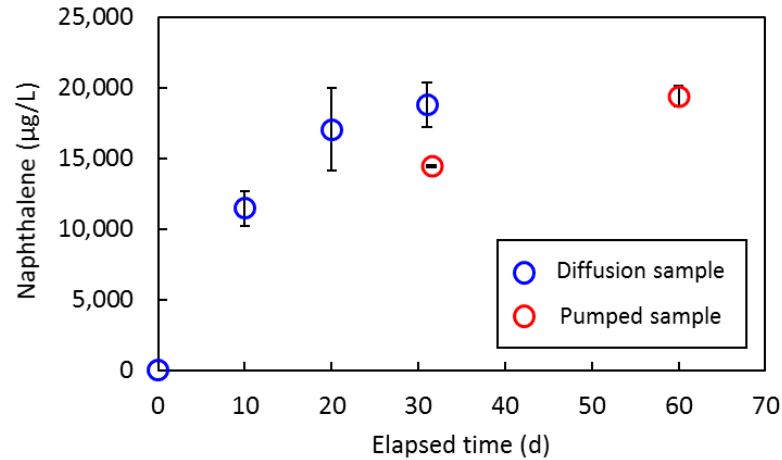




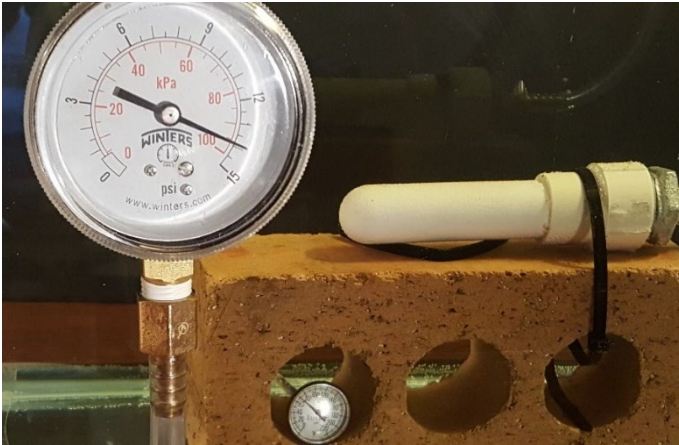
## LESSONS LEARNED

- Pumped discharge mode
  - Clogging/breaking due to excess turbidity or trapped air
- In situ diffusion-based equilibration
  - Detection levels can be affected by limited sample volume
  - Tubes may be washed away during long deployment (several months) in fast-moving river

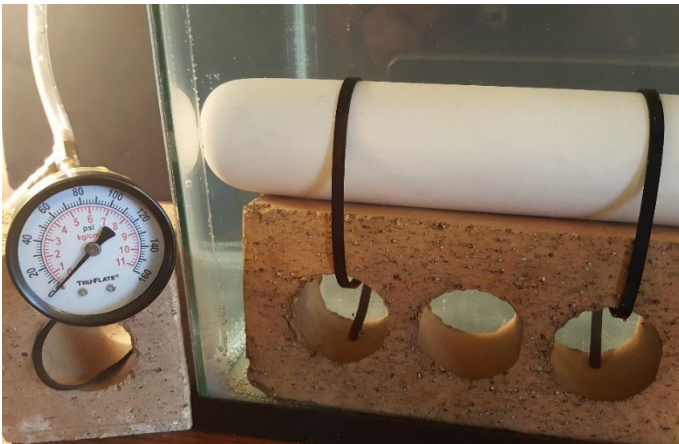
# Porewater Sampling Test Results



# Entry Pressure Test of Ceramics Using Air in Water-Filled Tank



- 2.5-micron pore diameter (reported by manufacturer)
- Measured air entry pressure: 16 psi



- Measured air entry pressure: 4 psi
- Pore diameter: 11 microns (calculated)





Entry pressure testing

# Depth Below Top of DNAPL Pool Required for Coal Tar/Creosote to Enter Ceramic Pores Without Water Pumping

$$Z_n = (2\sigma \cos \varphi) / [r g (\rho_n - \rho_w)]$$

where:

$Z_n$  = critical DNAPL height above ceramic sampler (cm)

$\sigma$  = NAPL-water interfacial tension (20 dynes/cm = 20 g/s<sup>2</sup>)

$\varphi$  = contact angle (24°)

$r$  = pore radius (1.25 to 5.6 microns = 0.000125 to 0.00056 cm)

$g$  = gravitational constant (980 cm/s<sup>2</sup>)

$\rho_n$  = non-wetting phase (NAPL) density (1.07 g/cm<sup>3</sup>)

$\rho_w$  = wetting phase (water) density (1.0 g/cm<sup>3</sup>)

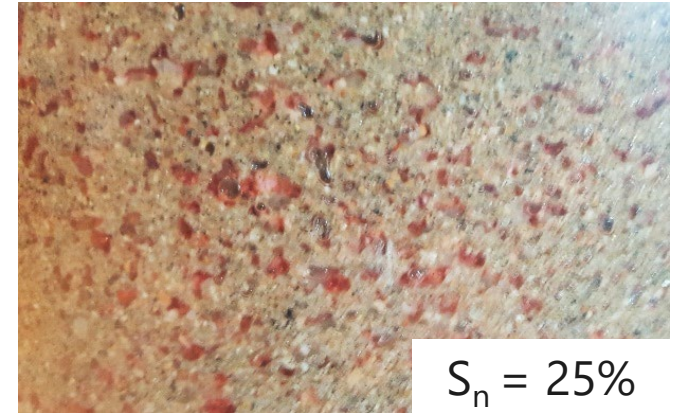
$$Z_n = 10 \text{ to } 40 \text{ meters}$$

Source: Cohen and Mercer (1993)



# Water-Pumping NAPL Exclusion Tests

- Well-graded, fine to course sand
- 25% to 50% NAPL saturation ( $S_n$ ), red paraffin oil (46 dynes/cm, 3 centistokes)
- Peristaltic pump, water recirculated, monitored vacuum (drawdown), pumping rate, and effluent for visible NAPL/sheen
- Results: converted for typical coal tar interfacial tension (20 dynes/cm)
  - $S_n = 0.25$ : Up to 12 feet drawdown and **25 mL/min** water flow with no sheen or NAPL in effluent—**potentially useful**
  - $S_n = 0.50$ : Sheen in effluent with 5 feet water drawdown and only 1.5 mL/min water flow—**impractical**



THANK YOU

---



Michael  
Gefell, PG

Principal Scientist  
Anchor QEA  
[mgefell@anchorqea.com](mailto:mgefell@anchorqea.com)



THANK YOU

---



# Dimitri Vlassopoulos, PhD

Principal

Anchor QEA LLC

[dvllassopoulos@anchorqea.com](mailto:dvllassopoulos@anchorqea.com)



THANK YOU

---



Deirdre  
Reidy

Manager

Anchor QEA

[dreidy@anchorqea.com](mailto:dreidy@anchorqea.com)



## REFERENCES

---

Burgess, R.M., 2013. *Passive Sampling for Measuring Freely Dissolved Contaminants in Sediments: Concepts and Principles*. Training slides from 23rd Annual National Association of Residential Property Manager Training. (Slide 2)

Cohen, R.M., and J.W. Mercer, 1993. *DNAPL Site Evaluation*. Boca Raton, Florida: C.K. Smoley. (Slide 19)

Gefell, M., M. Kanematsu, D. Vlassopoulos, and D. Lipson, 2018. "Aqueous-Phase Sampling with NAPL Exclusion Using Ceramic Porous Cups," *Groundwater* 56(6): 847–851. (Slide 10)