Aqueous Sampling without NAPL-Based Impacts

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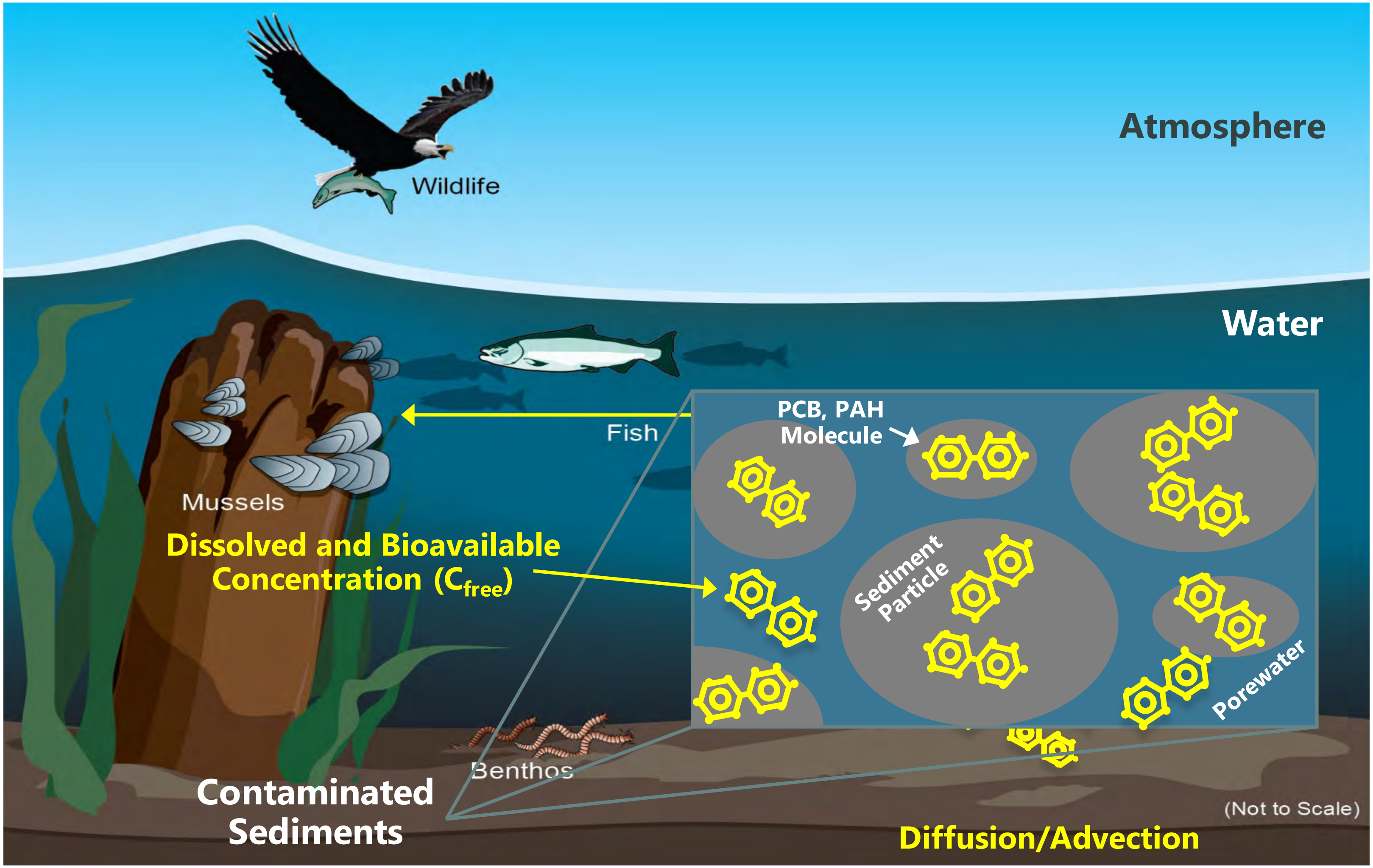
Outline

- Importance of accurate aqueous-phase samples
- Complexities due to nonaqueous phase liquid (NAPL)
- NAPL exclusion concepts and test results
- Chemical equilibration tests
- Possible applications
- Summary and conclusions

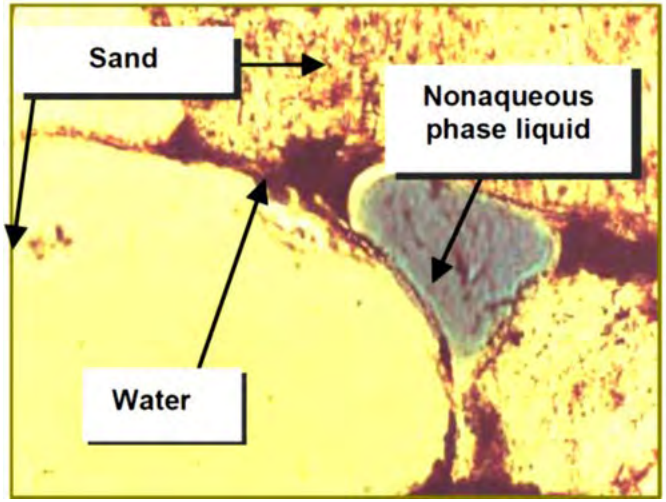
Importance of Accurate Aqueous Samples



Source: Burgess, R.M., 2013. *Passive Sampling for Measuring Freely Dissolved Contaminants in Sediments: Concepts and Principles*. Training Slides from 23rd Annual NAPRM Training. U.S. Environmental Protection Agency ORD NHEERL. Available at: https://clu-in.org/conf/tio/Porewater2_111914/resource.cfm.

NAPL Can Exaggerate "Aqueous" Concentrations

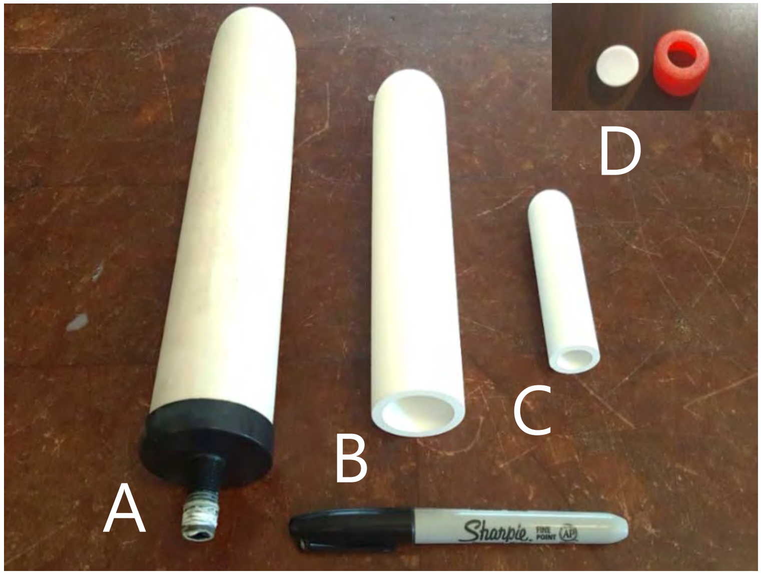
- NAPL enters pore-fluid samplers
- NAPL coats hydrophobic passive samplers
- Aqueous concentrations calculated from sediment samples can exceed effective solubility
- **Presence of NAPL can result in porewater concentrations that are biased high—above true dissolved, bioavailable concentrations**



Bottom figure from: 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, Hydrophilic Capillary Barriers

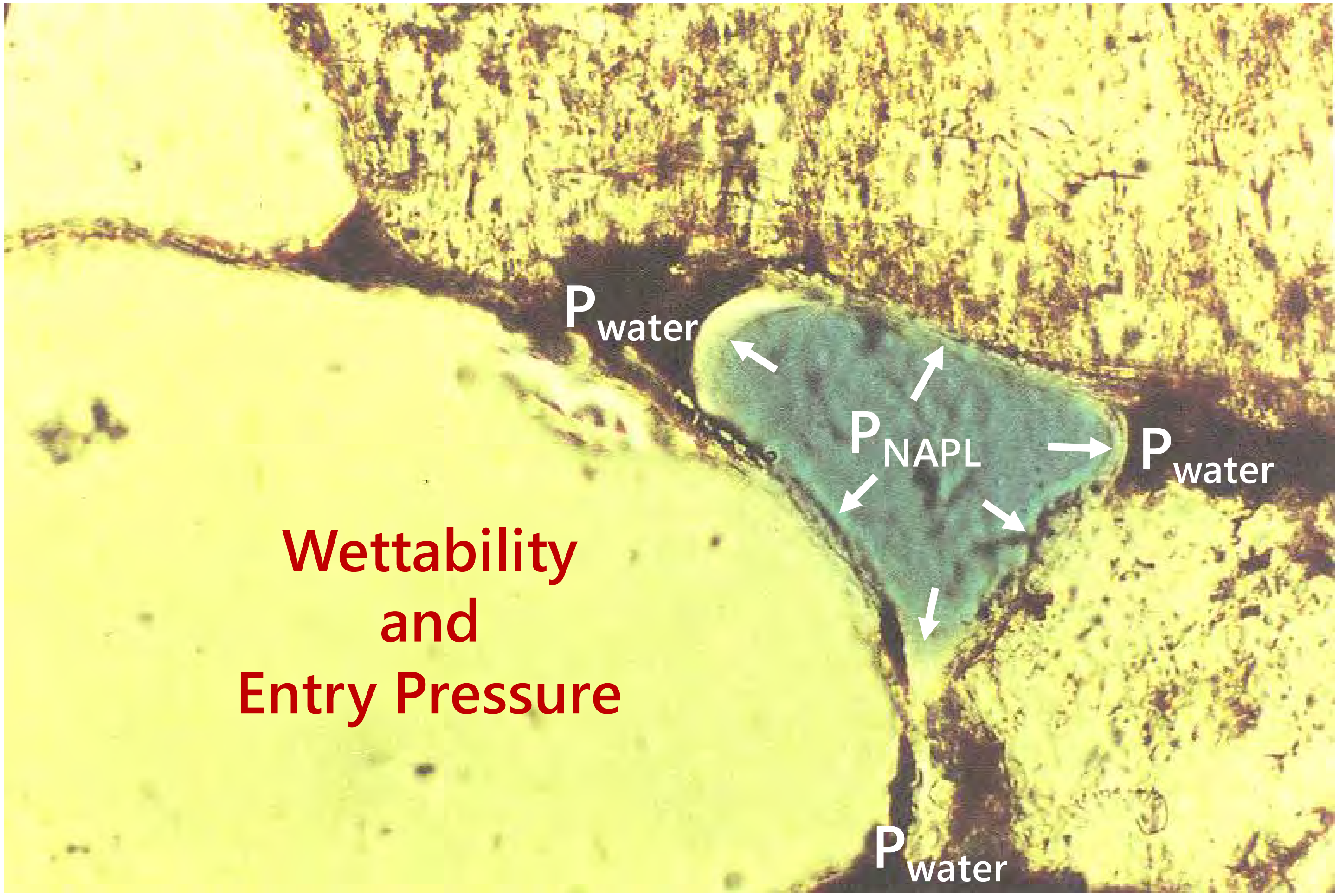
- **Ceramics**
- Bentonite
- Silica Flour
- Others?



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



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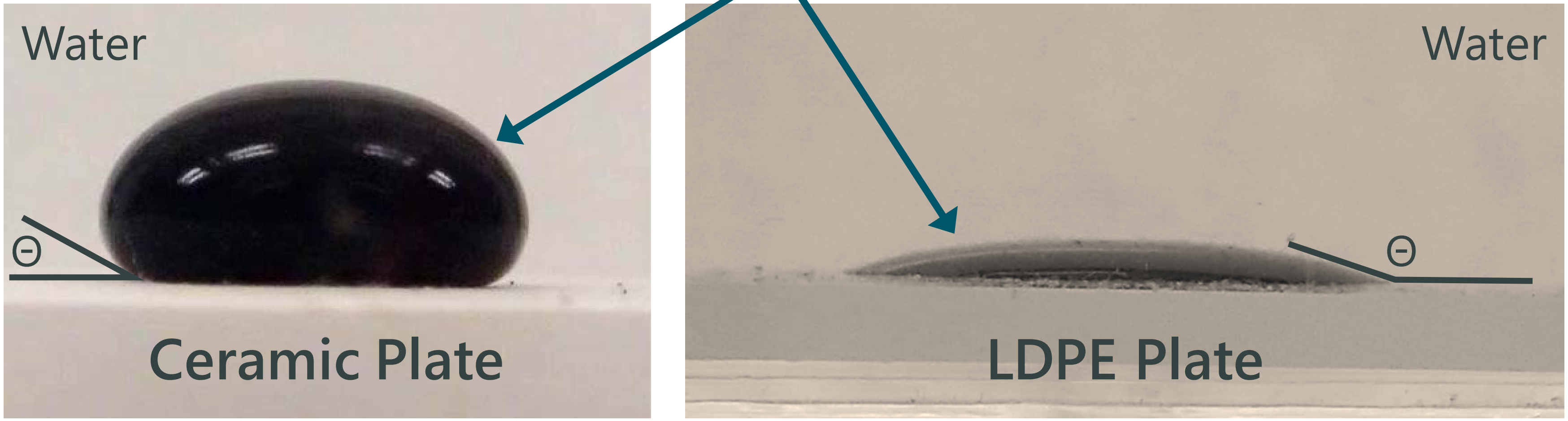
Comparative Wettability Tests—Dense NAPL on Ceramic and Low Density Polyethylene (LDPE)

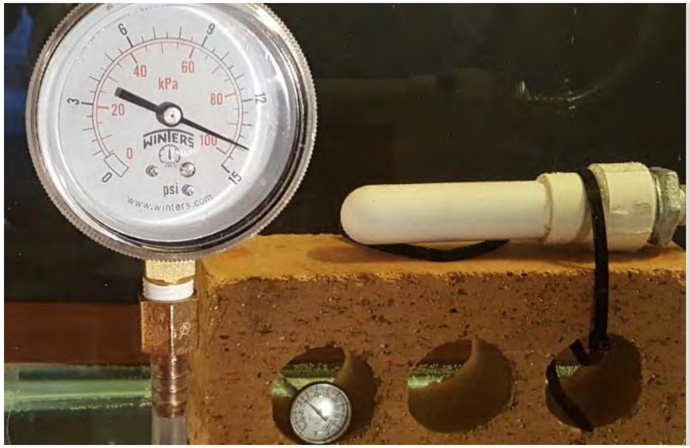
Weathered, PAH-Rich DNAPL

(23 days) | (1 day)



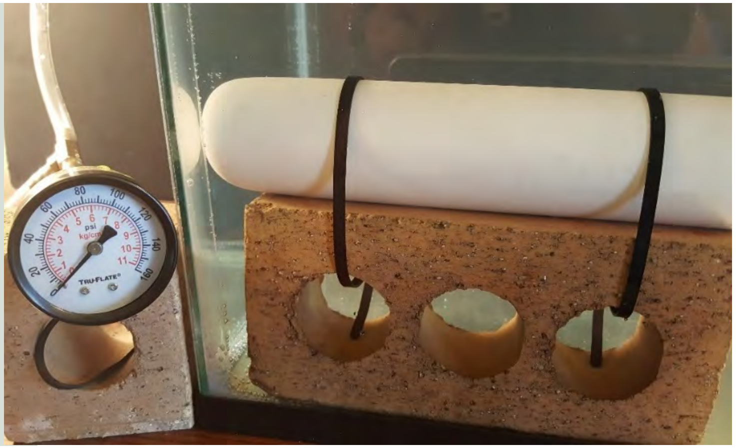
Contact angle Θ = 24°	Contact angle Θ = 162°
NAPL is non-wetting	**NAPL is wetting**

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

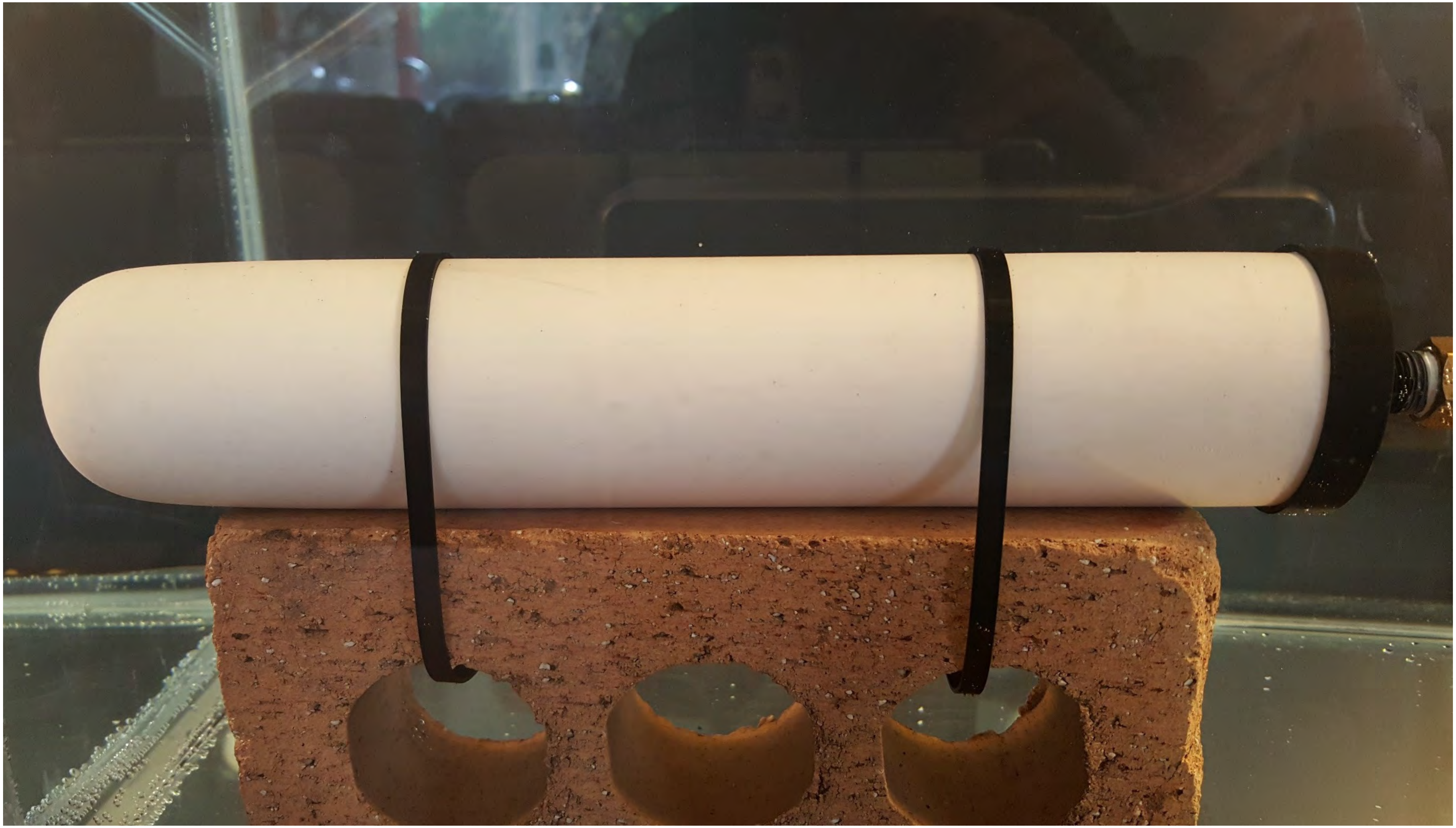


- 2.5-micron pore diameter (reported by manufacturer)
- Measured air entry pressure = 16 psi

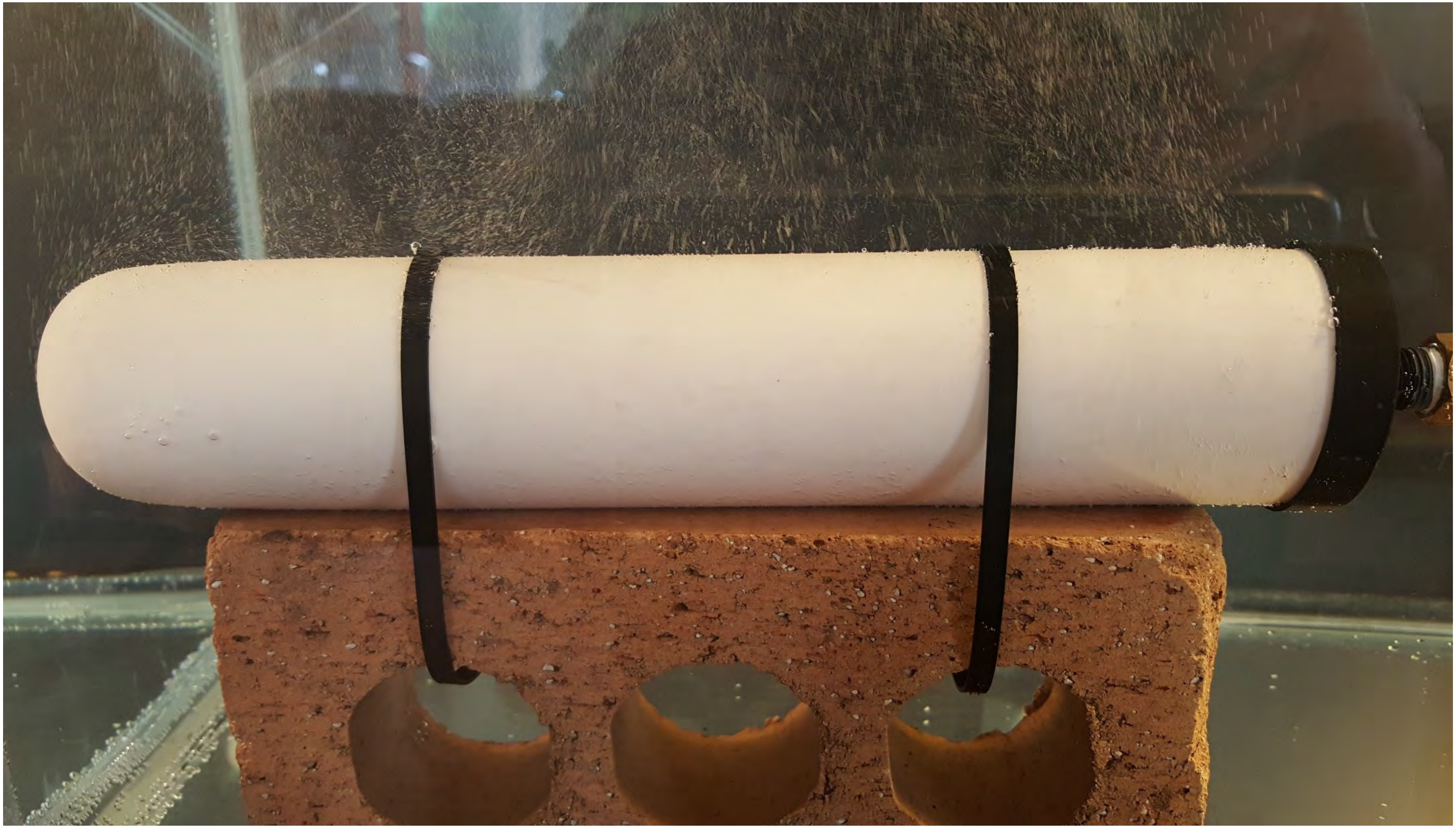
- Measured air entry pressure = 4 psi
- Pore diameter = 11 microns (calculated)



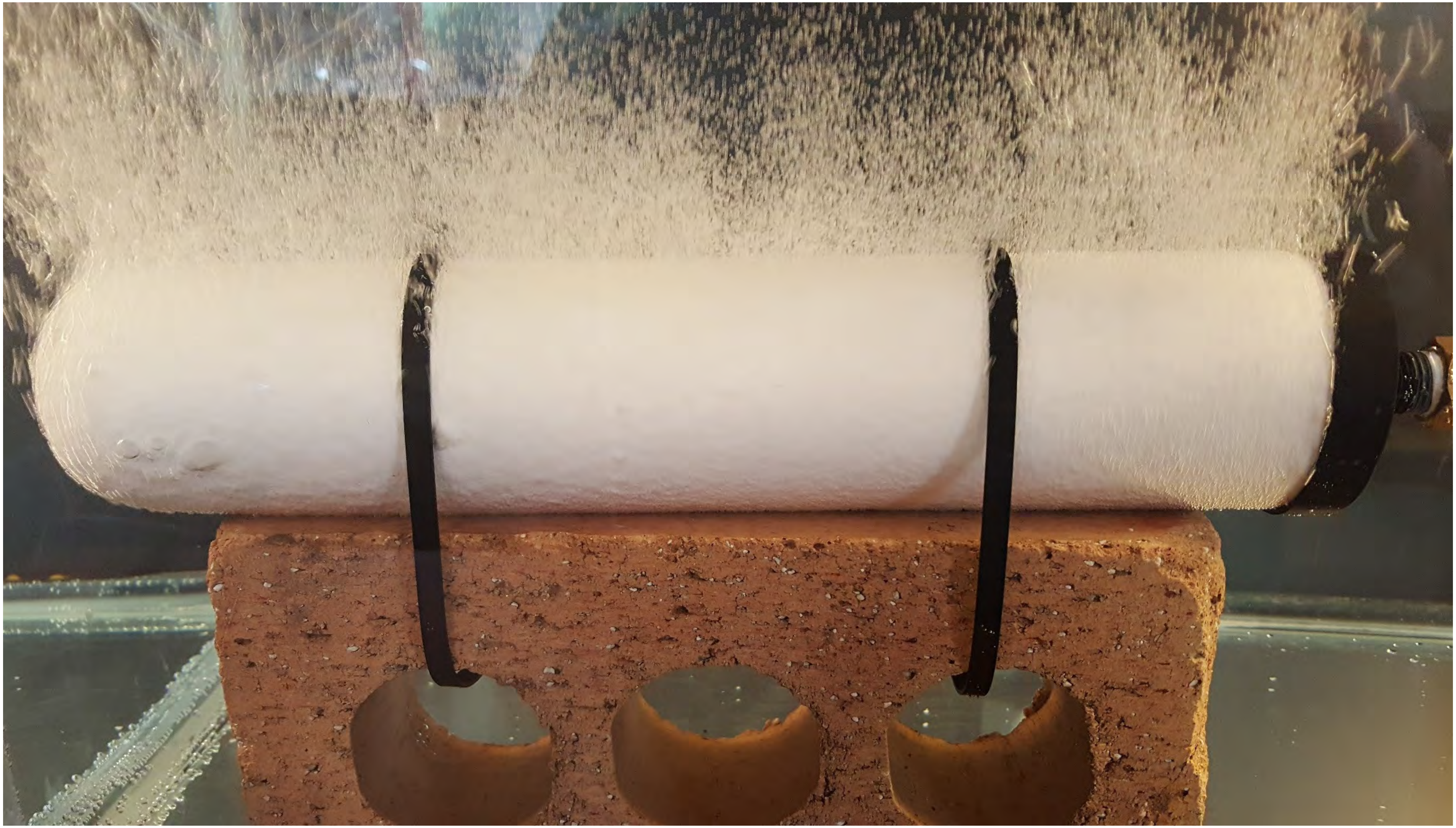
Entry Pressure Testing



Entry Pressure Testing



Entry Pressure Testing



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

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

Z_n = critical DNAPL height above ceramic sampler (cm)

σ = NAPL-water interfacial tension (20 dynes/cm = 20 g/s^2)

φ = contact angle (24°)

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

g = gravitational constant (980 cm/s^2)

ρ_n = non-wetting phase (NAPL) density (1.07 g/cm^3)

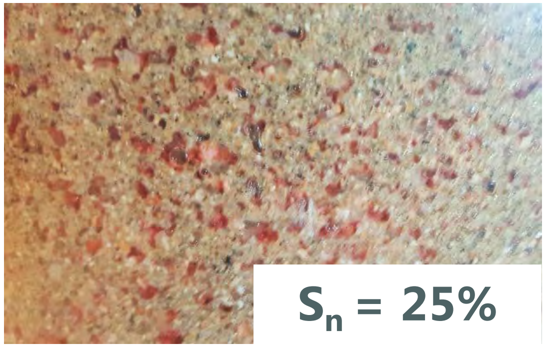
ρ_w = wetting phase (water) density (1.0 g/cm^3)

Z_n = 10 to 40 meters

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

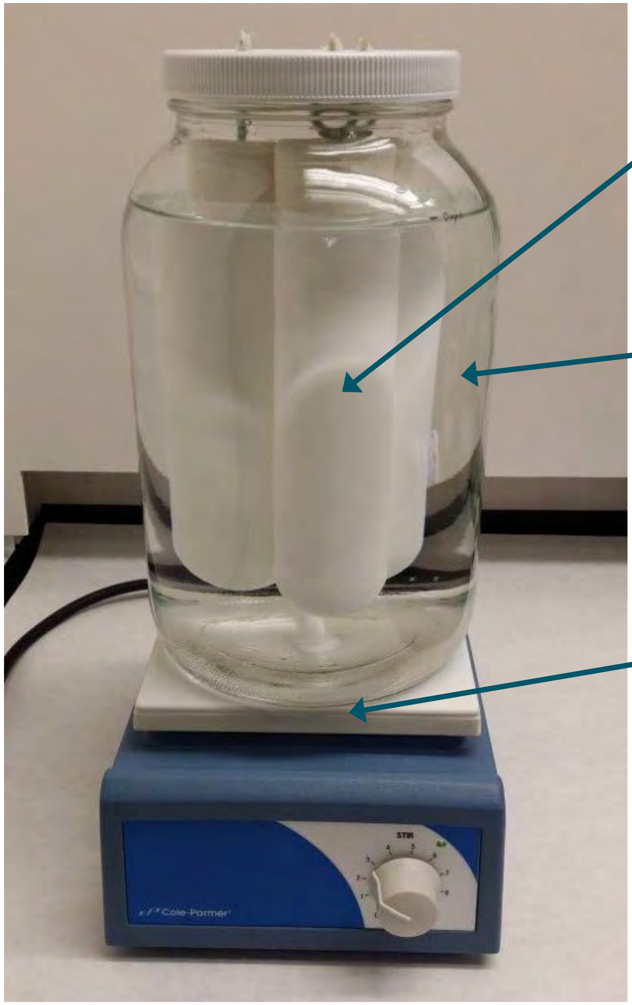
Water-Pumping NAPL Exclusion Tests

- 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**

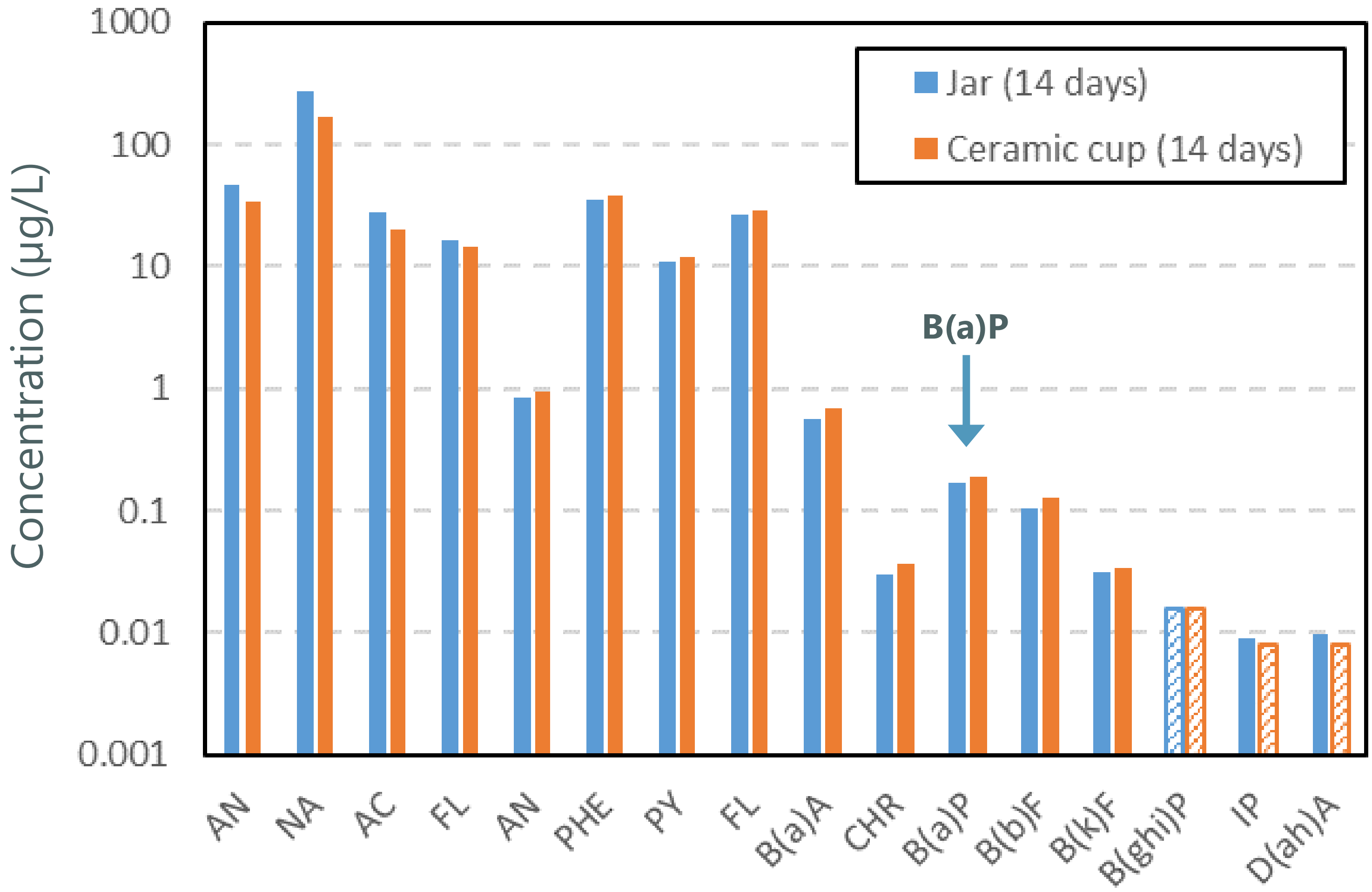


PAH Equilibration Test without SPMEs

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



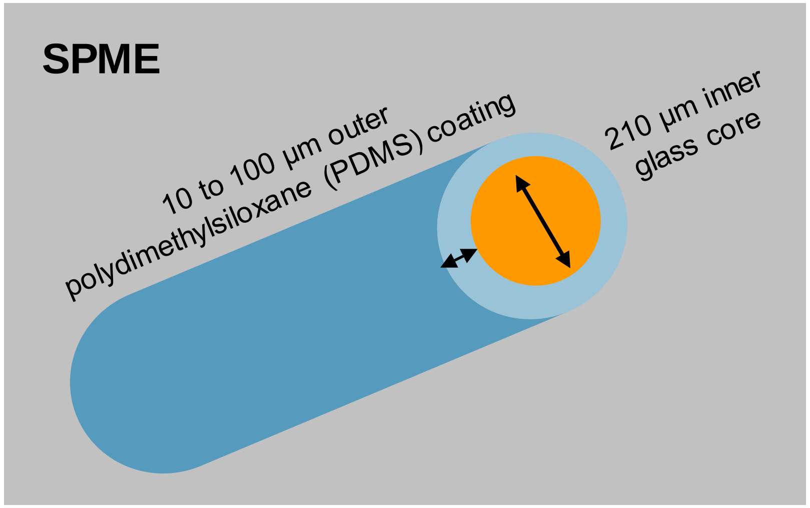
PAH Equilibration, 14-Day Results without SPMEs



Note: Striped pattern bars indicate MDL

PAH Equilibration Test with SPMEs

- SPMEs in ceramic tube and metal mesh sleeve
- Sampled after 7, 14, 30, and 60 days of diffusion-based equilibration



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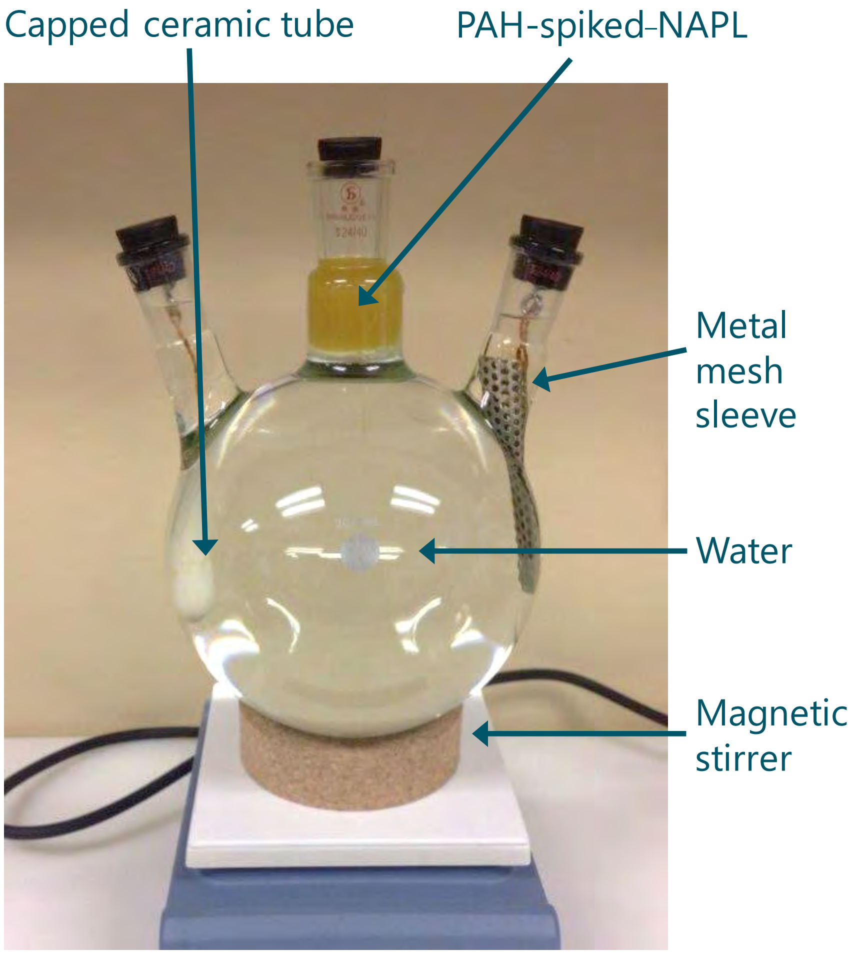
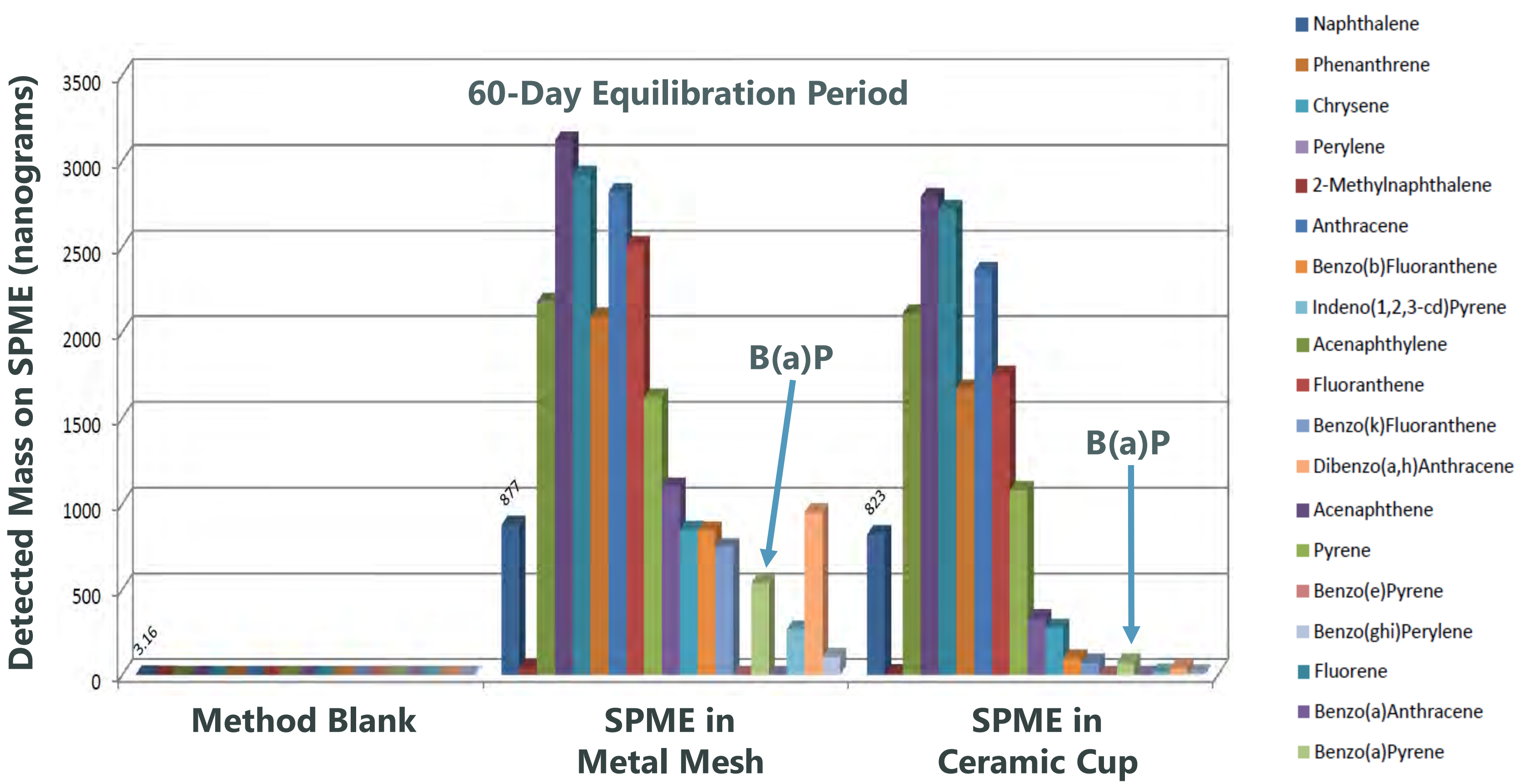


PAH Equilibration, 60-Day Results with SPMEs



Note: SPME analysis performed and reported by SGS North America, Wilmington, North Carolina.

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

- Equilibration-based water sampling
- Protect hydrophobic, sorption-based equilibrium samplers
- Replace Teflon septum on VOA vial with porous capillary barrier, use for in situ passive sampling
- Pump water samples through capillary barrier in situ (push-point sampler) or ex situ (water filter) to exclude NAPL
- Use capillary barrier devices in wells with NAPL

Summary and Conclusions

- Aqueous concentrations drive risk and remediation
- Any NAPL in samples can severely bias interpreted aqueous concentrations
- Capillary barrier materials can be used to sample aqueous phase and avoid impacts due to NAPL
- Wettability and entry pressure of porous ceramics appear favorable—also readily available and economical
- PAH diffusive equilibration through ceramic has been demonstrated

Acknowledgements

- Anchor QEA Innovation Program
- Hydro Science + Engineering

Questions/Discussion