Porewater Sampling with NAPL Exclusion

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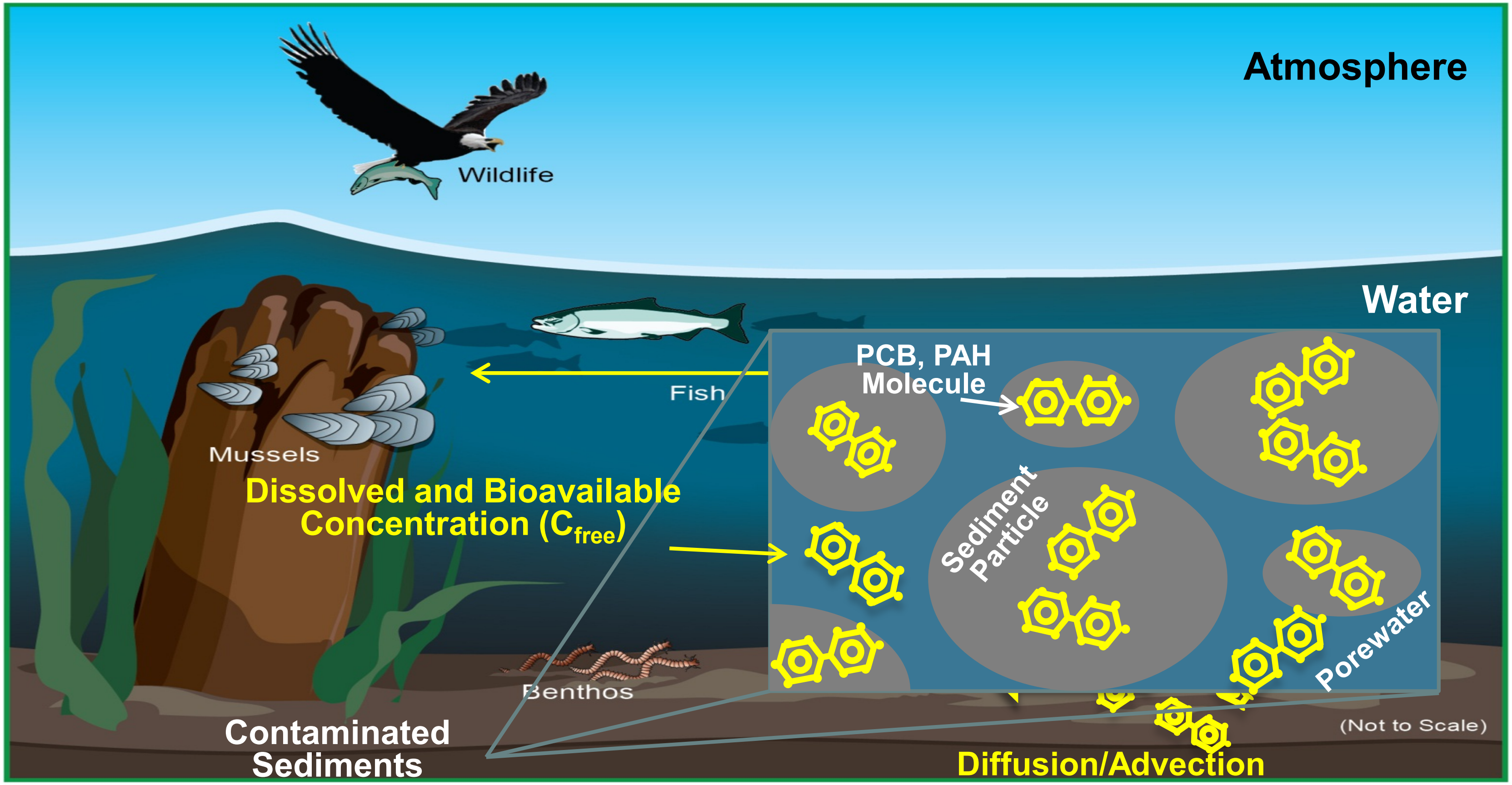
Outline

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

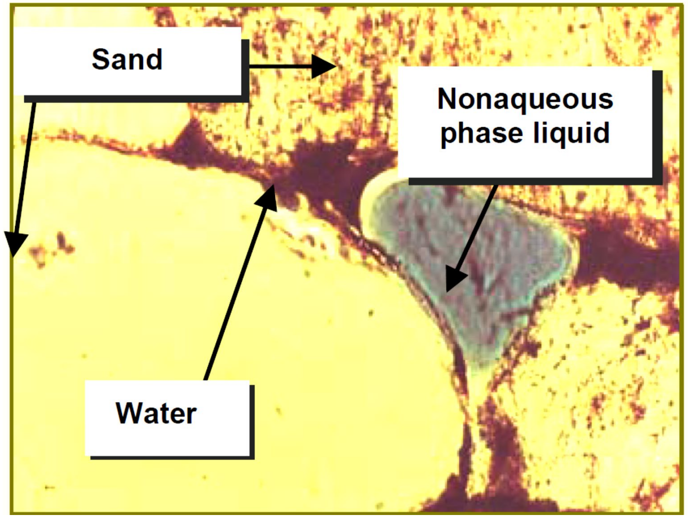
Importance of Accurate Porewater Samples



From: 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 "Porewater" Concentrations

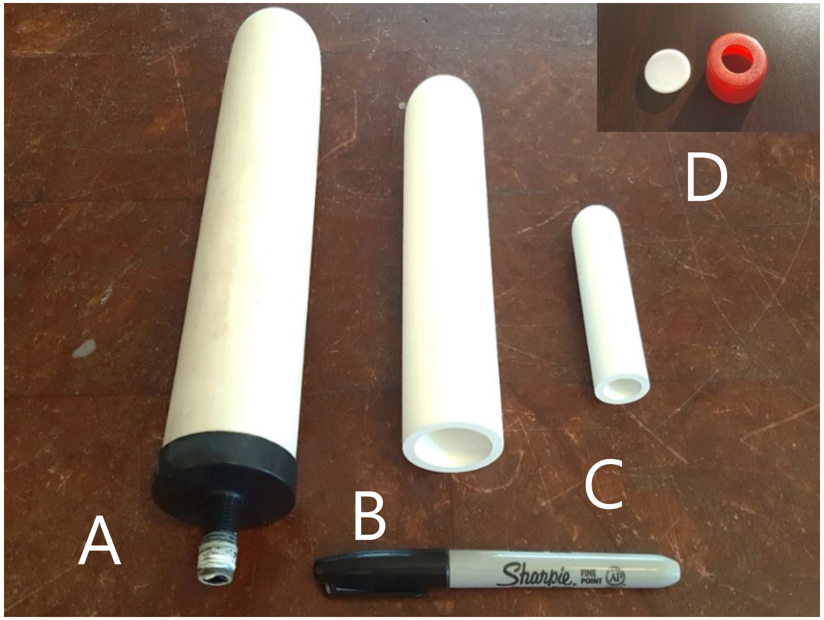
- NAPL enters pore-fluid samplers
- NAPL coats hydrophobic passive samplers
- Porewater concentrations calculated from sediment samples can exceed effective solubility
- **Presence of NAPL can result in porewater concentrations that are biased high—above true dissolved, bioavailable concentrations**



Bottom figure from: Wilson, J.L., S.H. Conrad, W.R. Mason, W. Peplinski, and E. Hafgan, 1990. *Laboratory Investigations 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

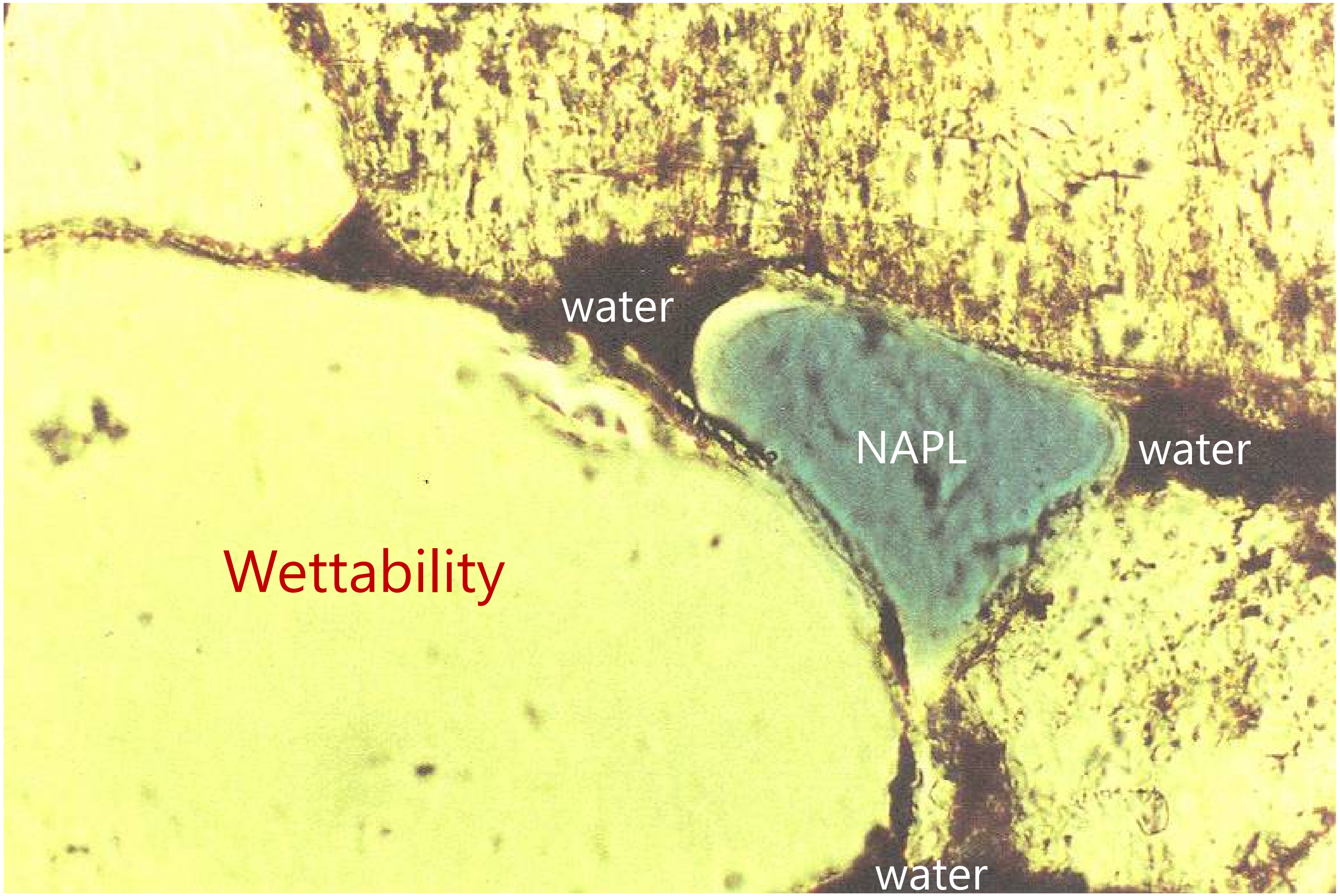
- **Ceramics**
- Bentonite
- Silica Flour
- Others?



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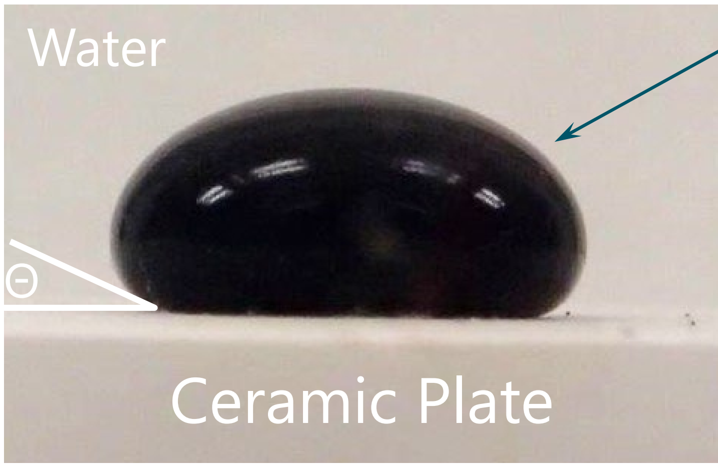
Comparative Wettability Tests – Dense NAPL on Ceramic and Low Density Polyethylene (LDPE)

Weathered, PAH-Rich DNAPL

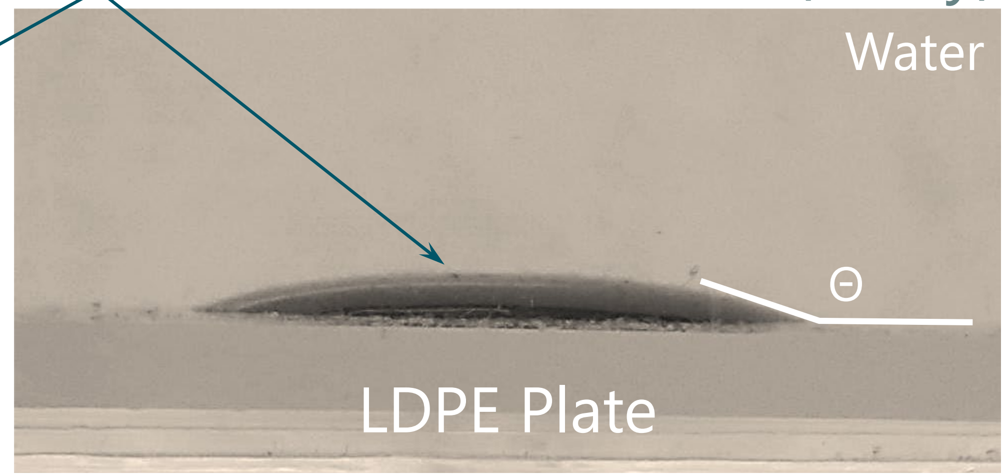
(23 days)



Contact angle Θ = 24°

NAPL is non-wetting

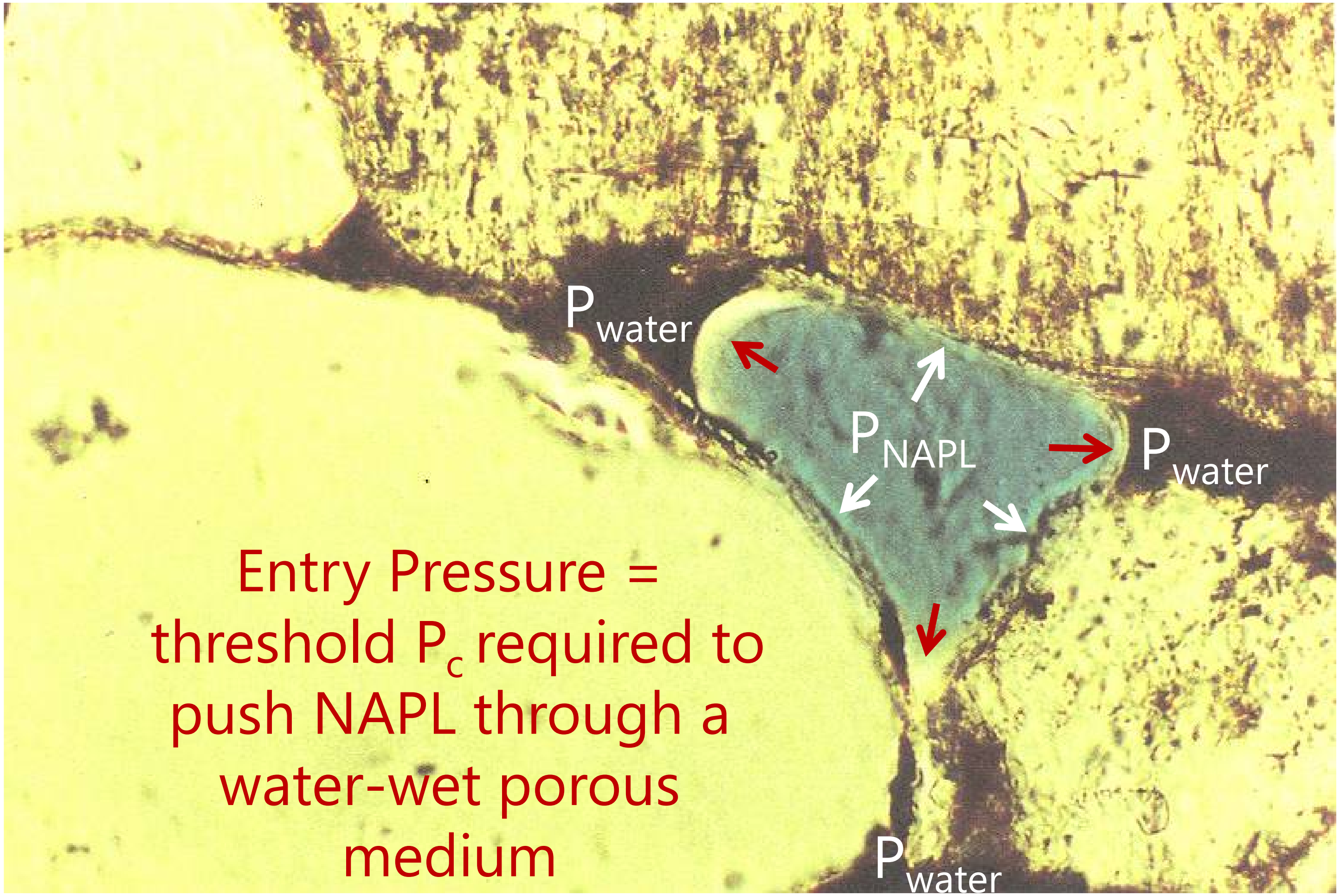
(1 day)



Contact angle Θ = 162°

NAPL is wetting

Fundamentals of NAPL Exclusion



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NAPL Entry Pressure is Proportional to Air Entry Pressure

$$P_e = 9.6\,(\sigma/\sigma_{aw})\,(K/n)^{-0.403}$$

$$P_{e,\,NAPL} = P_{e,\,air}\,(\sigma/\sigma_{aw})$$

P_e = entry pressure (cm water)

σ = non-wetting phase-water interfacial tension (dynes/cm)

σ_{aw} = air-water interfacial tension (dynes/cm)

K = hydraulic conductivity of potential capillary barrier (cm/s)

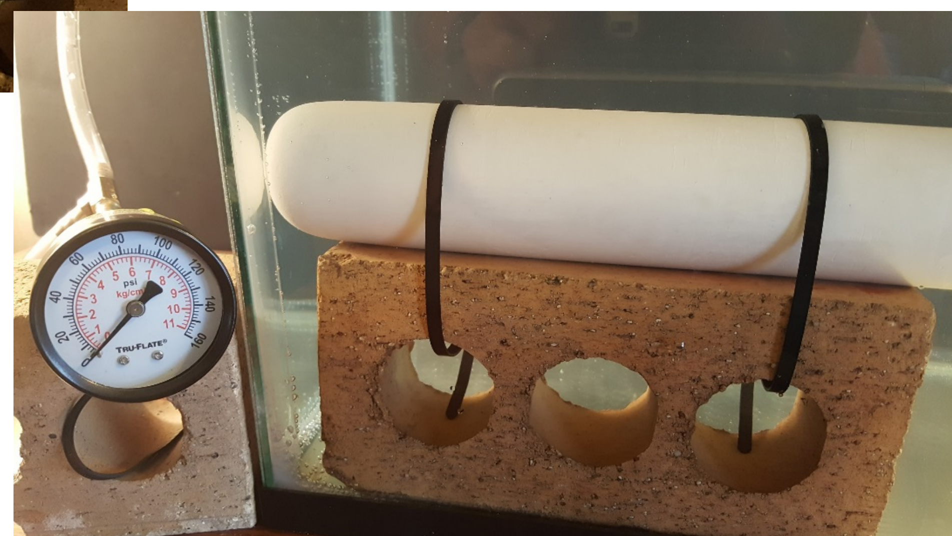
n = porosity of potential capillary barrier

From: McWhorter, D.B., and J.D. Nelson, 1996. As referenced in J.F. Pankow and J.A. Cherry (eds.), *Dense Chlorinated Solvents and other DNAPLs in Groundwater*. Waterloo Press, Portland, Oregon.

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

2.5-micron pore diameter (reported by manufacturer)

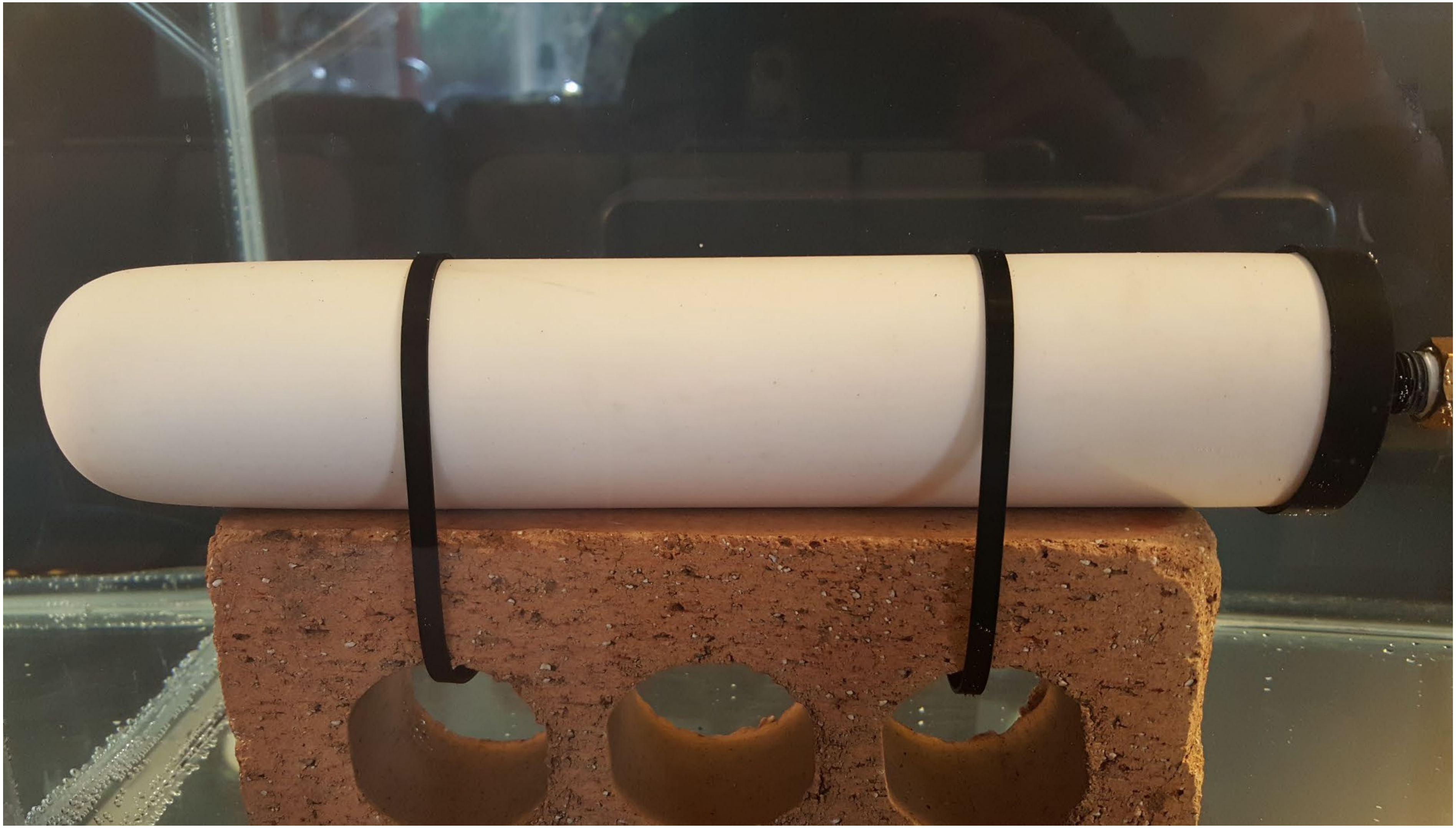
Measured air entry pressure = 16 psi



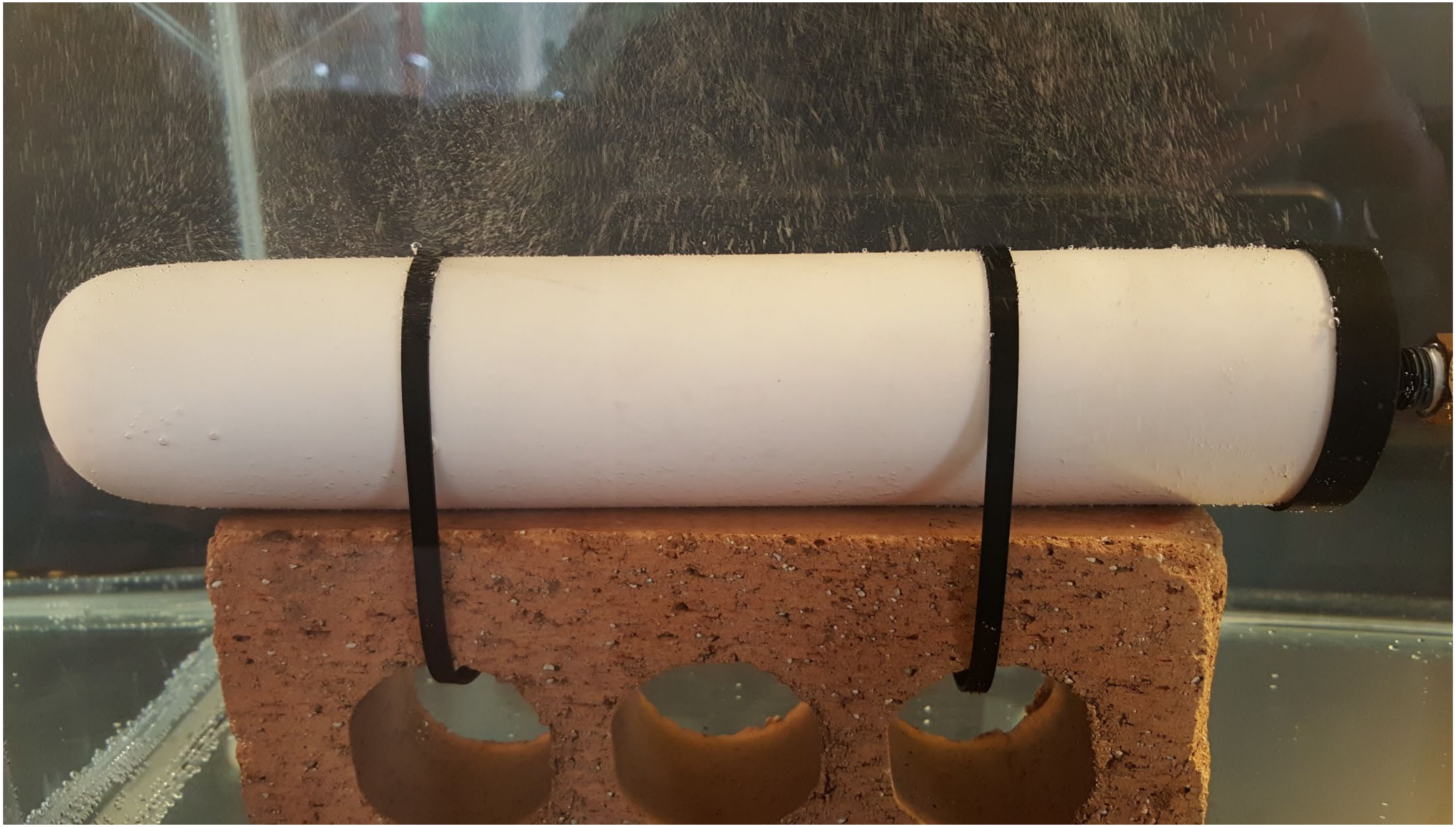
Measured air entry pressure = 4 psi

Pore diameter = 11 microns (calculated)

Entry Pressure Testing



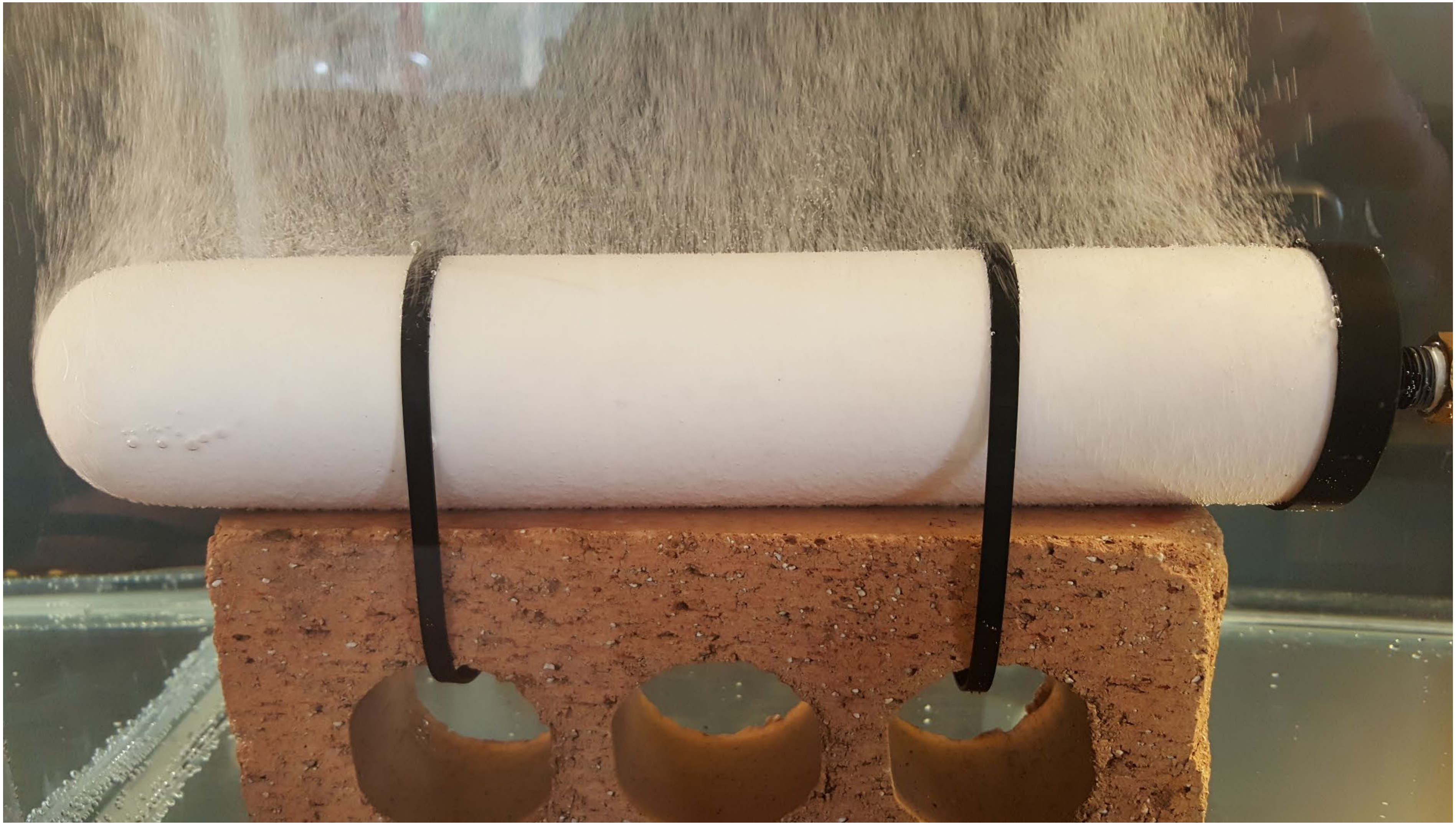
Entry Pressure Testing



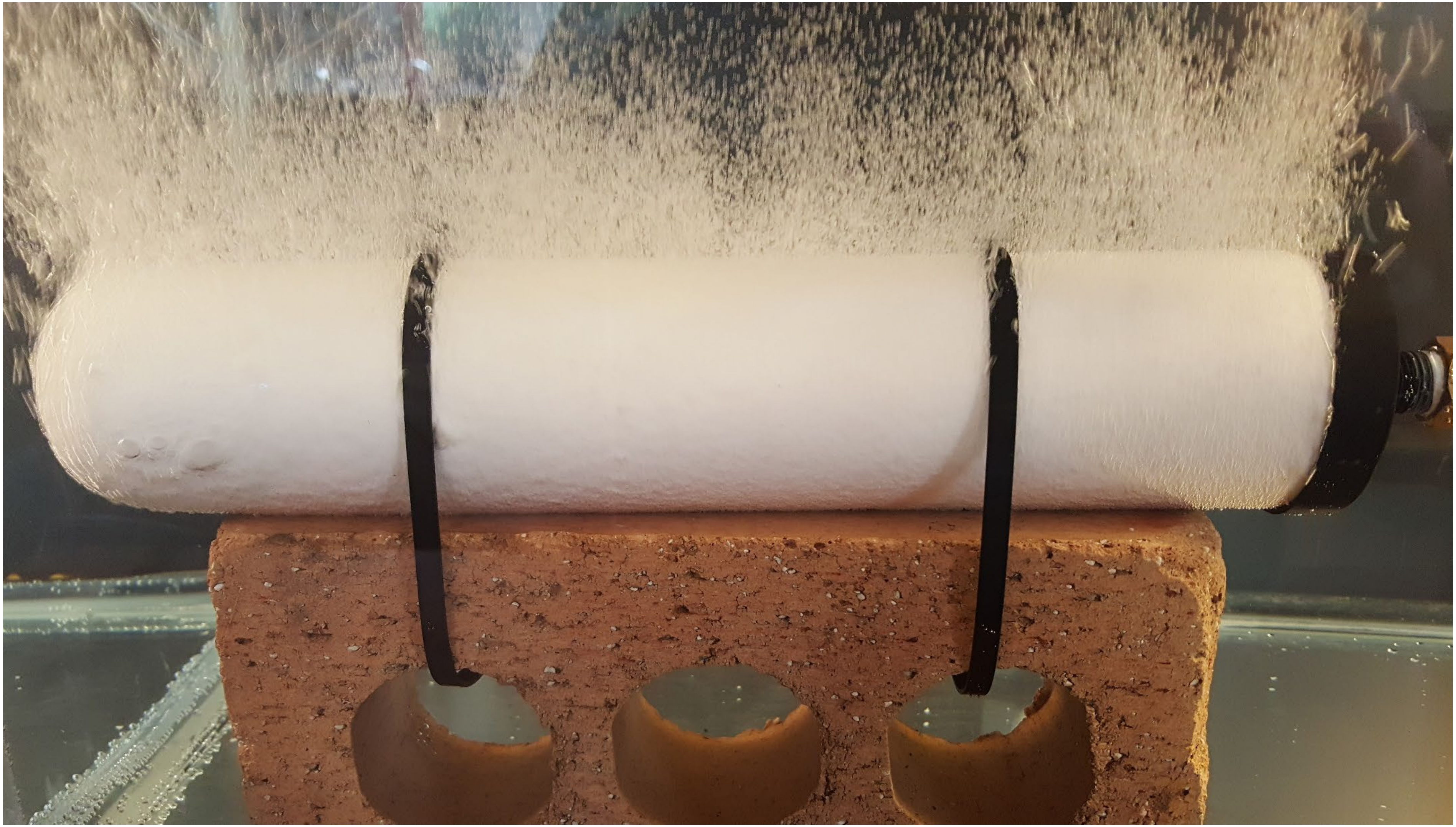
Entry Pressure Testing

Entry Pressure Testing

Entry Pressure Testing



Entry Pressure Testing



Capillary Pressure Within DNAPL Body and Porewater Sampling Depth

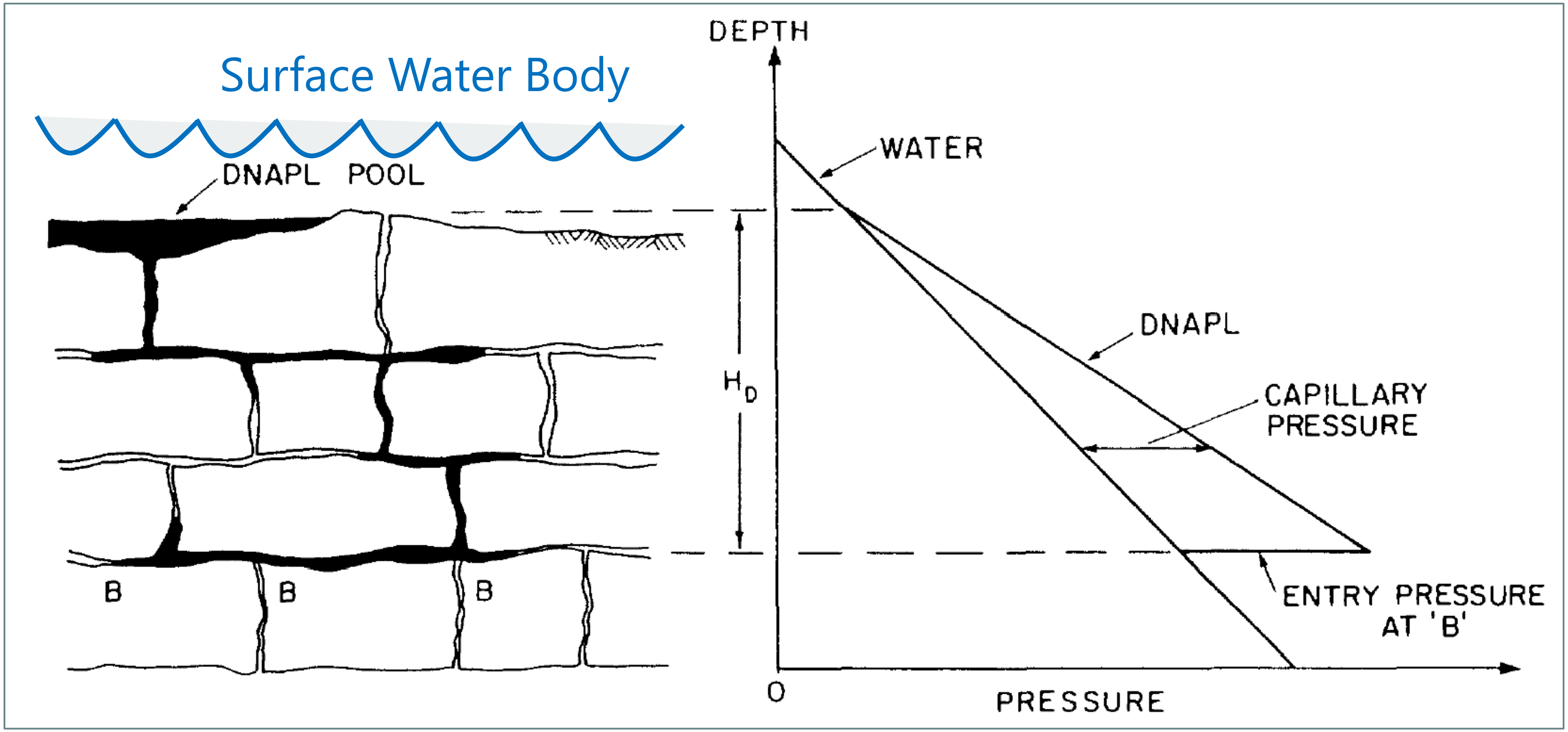


Figure from: Kueper, B.H. and McWhorter, D.B., 1991. The behavior of dense, non-aqueous phase liquids in fractured clay and rock. Journal of Ground Water, Vol. 29, No. 5, pp. 716-728.

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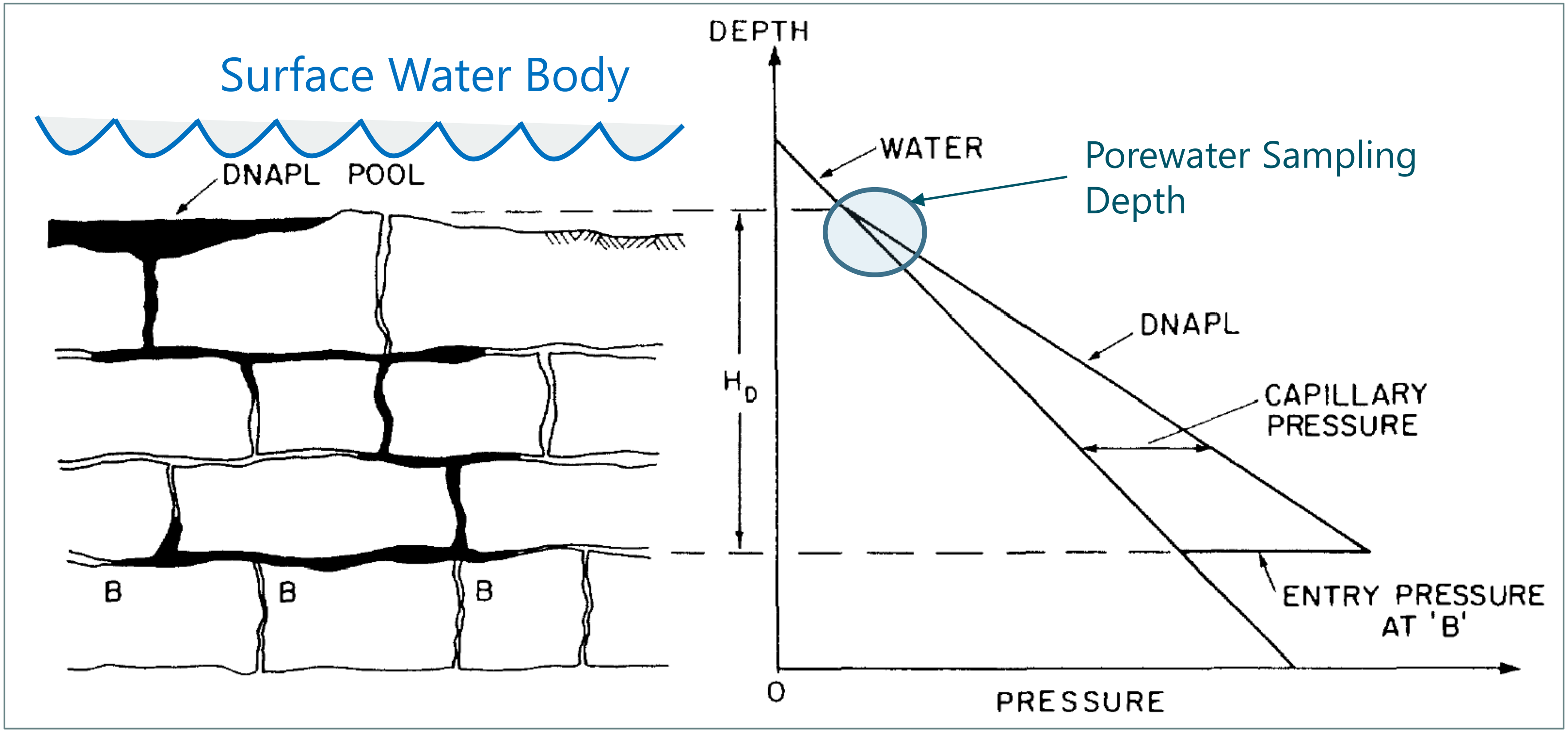

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Depth Below Top of DNAPL Pool Required for Coal Tar/Creosote to Enter Ceramic Pores

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

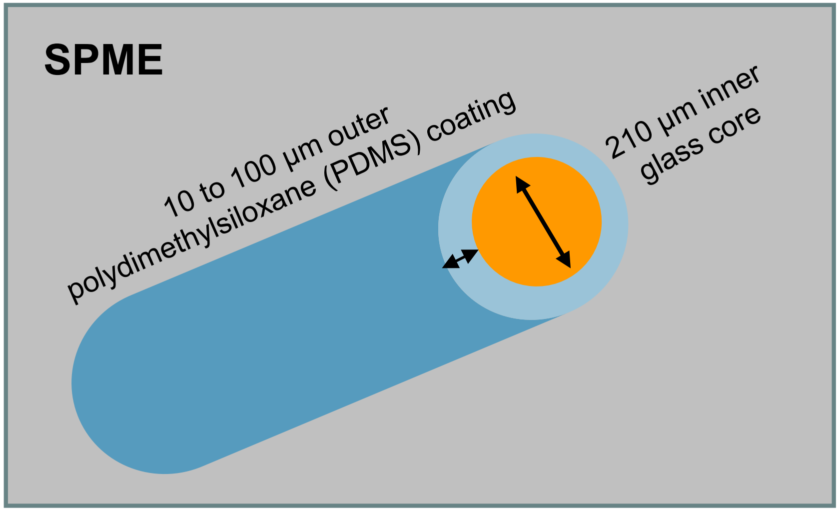
Z_n = critical DNAPL height above ceramic sampler (cm)
σ = NAPL-water interfacial tension (20 dynes/cm = 20 g/s^2)
φ = contact angle (24°)
r = pore radius (1.25 to 5.6 microns = 0.000125 to 0.00056 cm)
g = gravitational constant (980 cm/s^2)
ρ_n = non-wetting phase (NAPL) density (1.07 g/cm^3)
ρ_w = wetting phase (water) density (1.0 g/cm^3)

Z_n = 10 to 40 meters

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

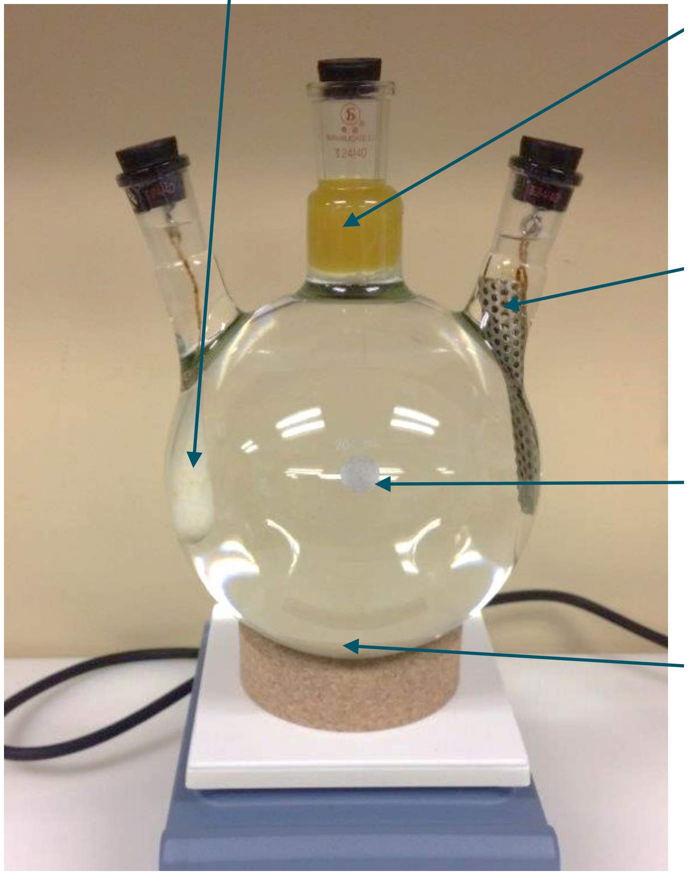
Chemical Equilibration Test

- SPMEs in ceramic tube and metal mesh sleeve
- Sampled after 7, 14, and 30 days



SPME figure from: 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.

capped ceramic tube



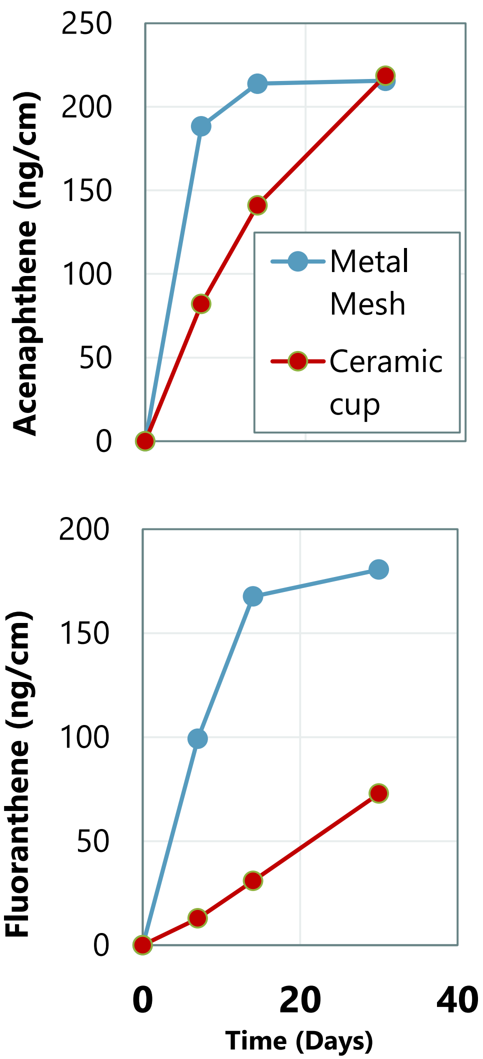
PAH-spiked NAPL

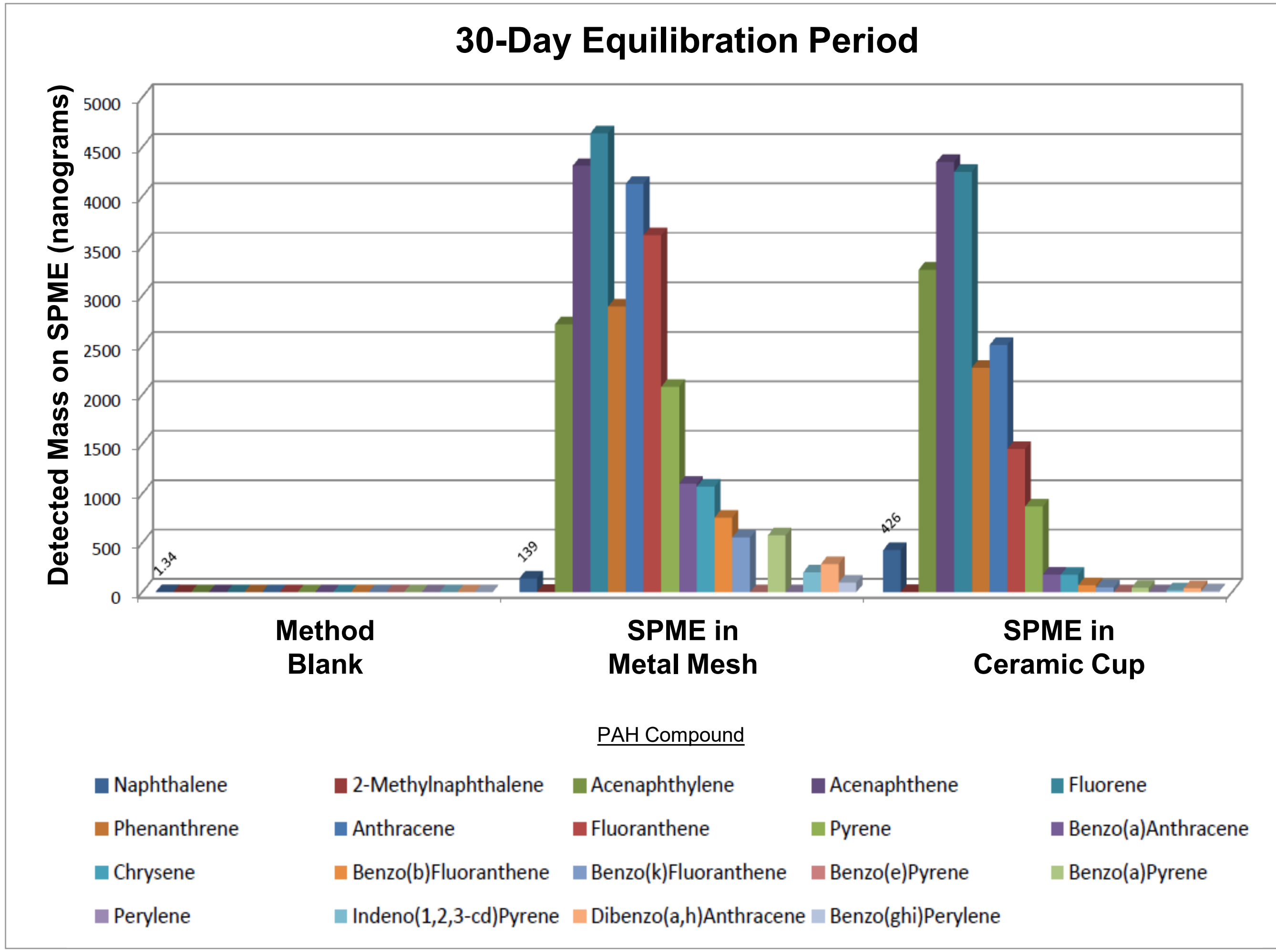
metal mesh sleeve

water

magnetic stirrer

Equilibration Test Results – PAHs





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

Potential Uses of Capillary Barrier Materials for Water Sampling with NAPL Exclusion

- Protect hydrophobic, sorption-based equilibrium samplers
- Collect water sample by diffusive equilibration across capillary barrier
- 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

- Porewater concentrations drive risk and remediation
- Any NAPL in sediments can severely bias porewater sampling results
- Capillary barrier materials can be used to sample porewater and avoid artifacts 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

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- Special thanks to David S. Lipson, Hydro Science and Engineering (Arvada, Colorado)