Improving Dissolved Organic Chemical Concentration Measurements at Groundwater/Surface-Water Interfaces Containing NAPL

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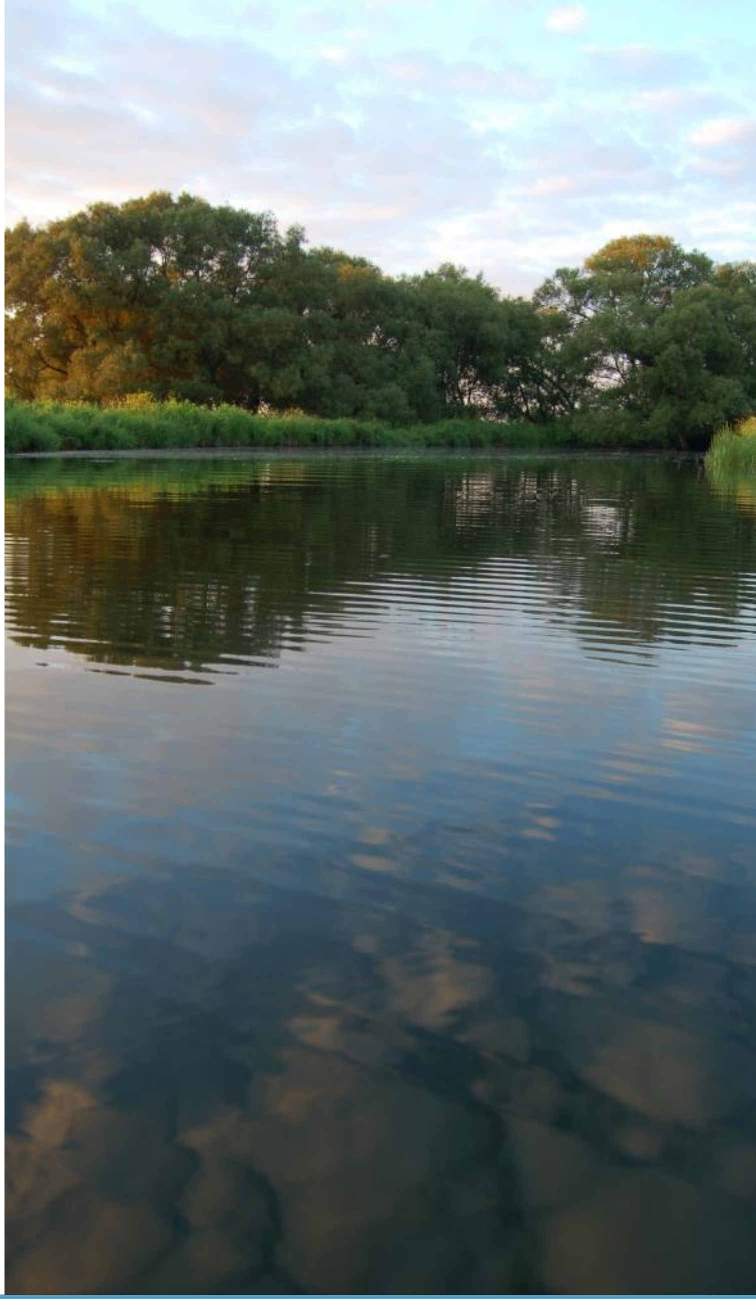
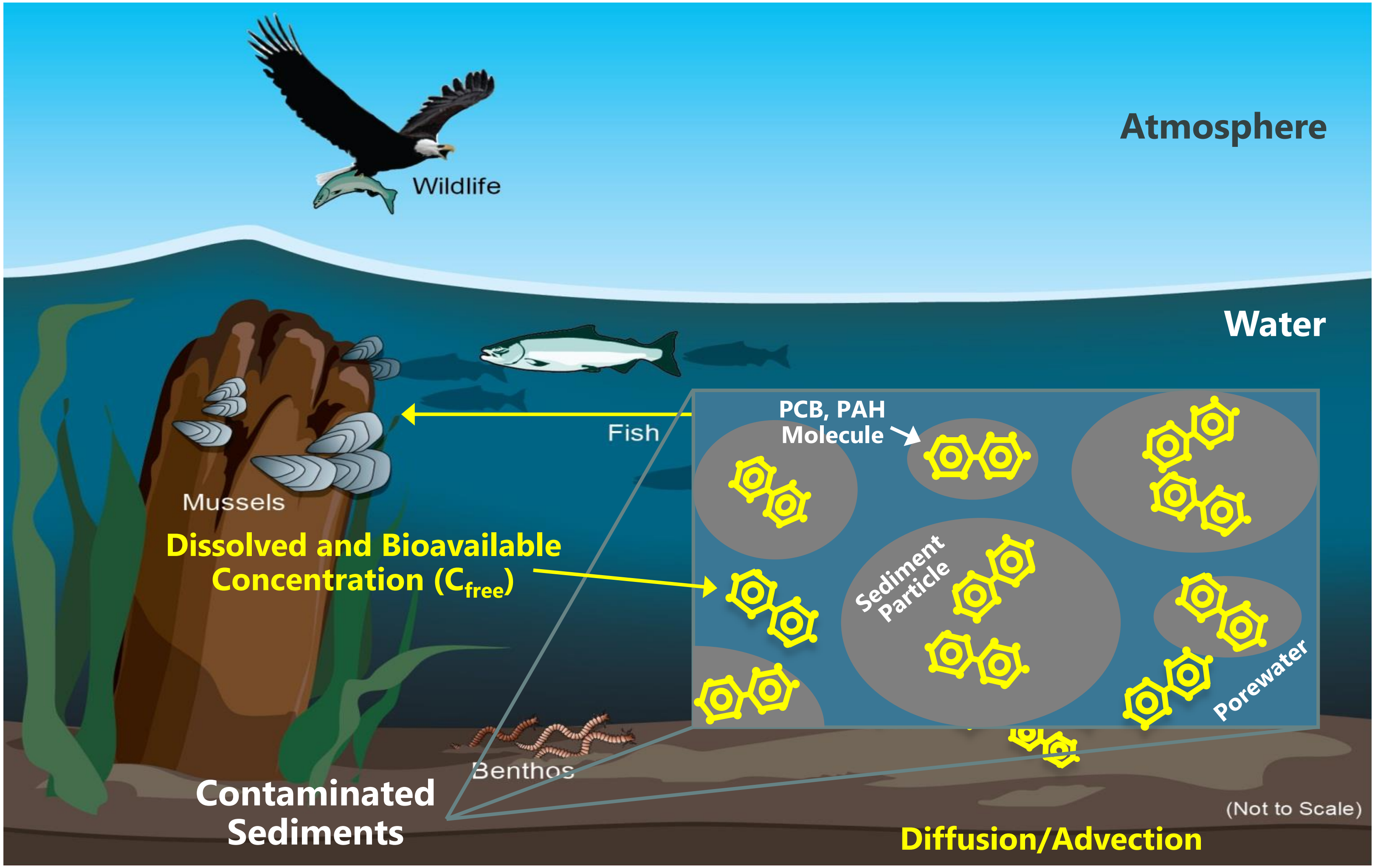
Outline

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



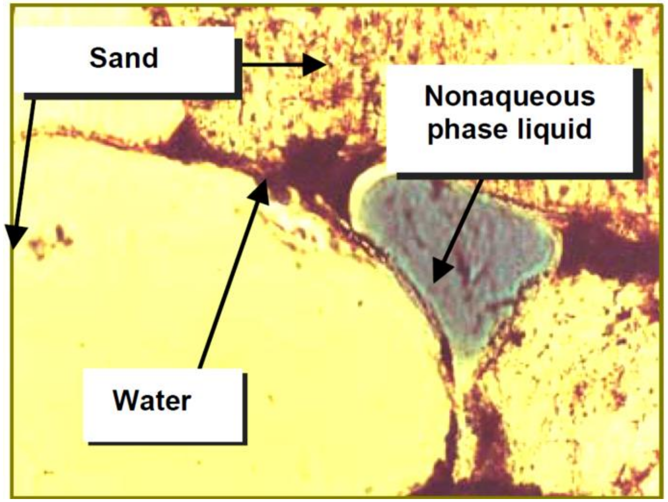
Importance of Accurate Aqueous Samples



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

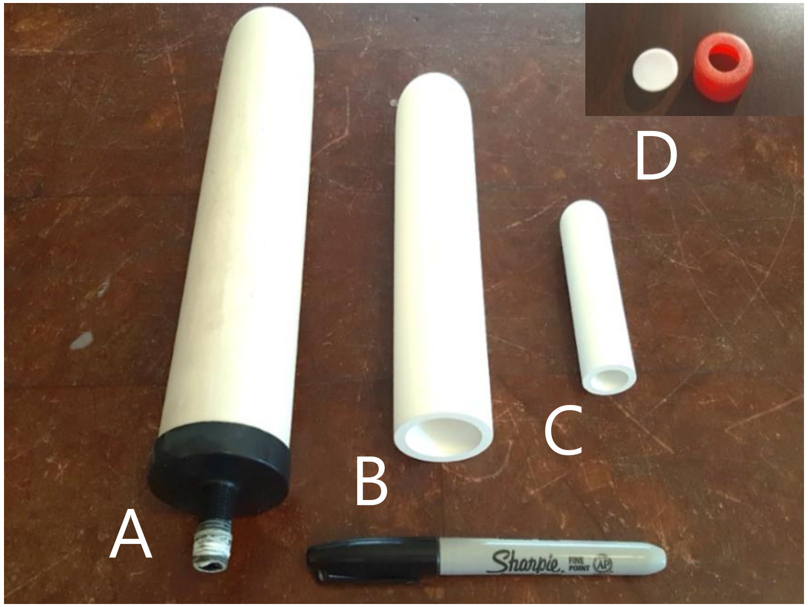
- NAPL enters pore-fluid samplers.
- NAPL coats hydrophobic passive samplers.
- Aqueous concentrations calculated from sediment samples can exceed effective solubility.
- **Presence of NAPL can result in porewater concentrations that are biased high—above true dissolved, bioavailable concentrations.**



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

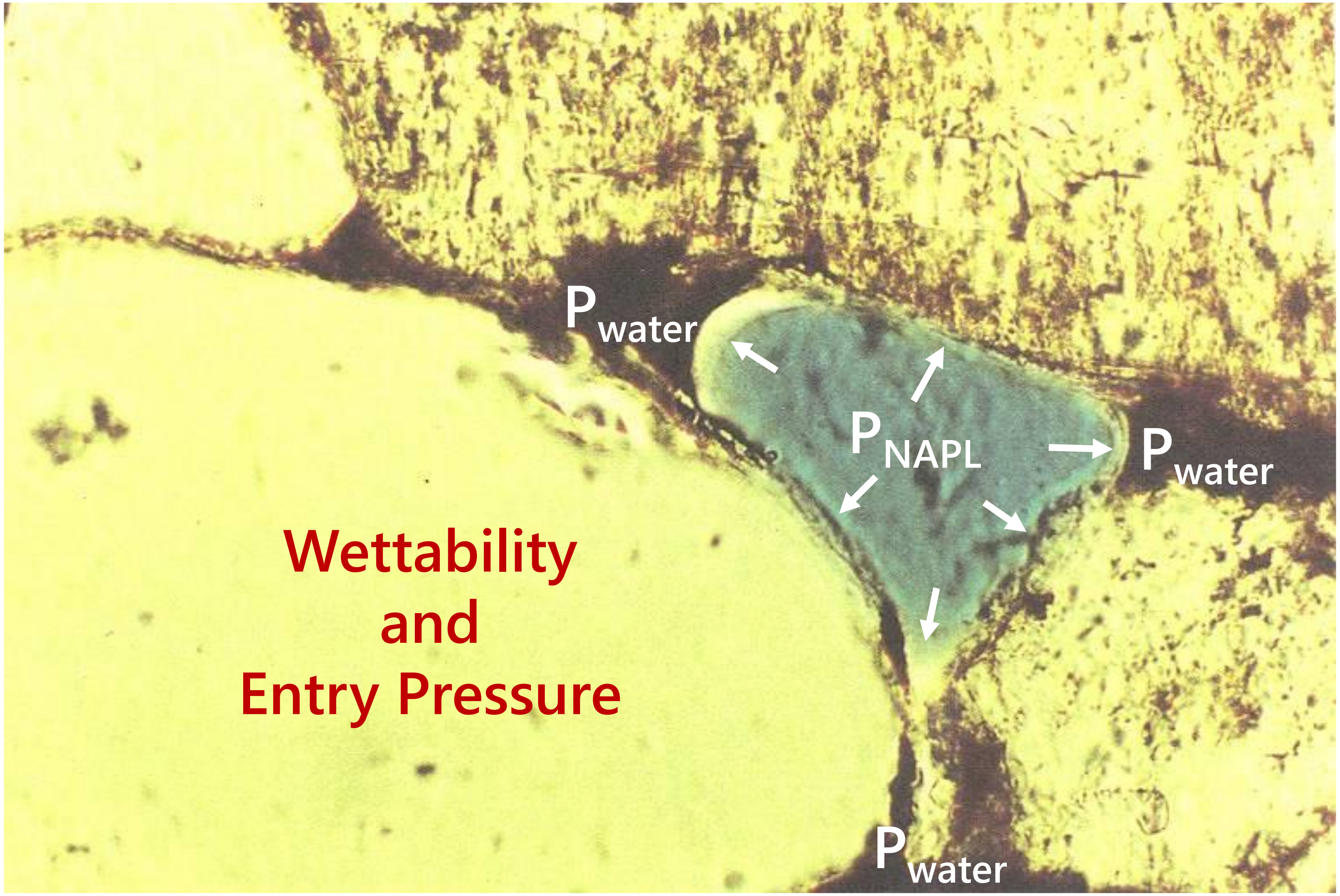
- **Ceramics**
- Bentonite
- Silica Flour
- Others?



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

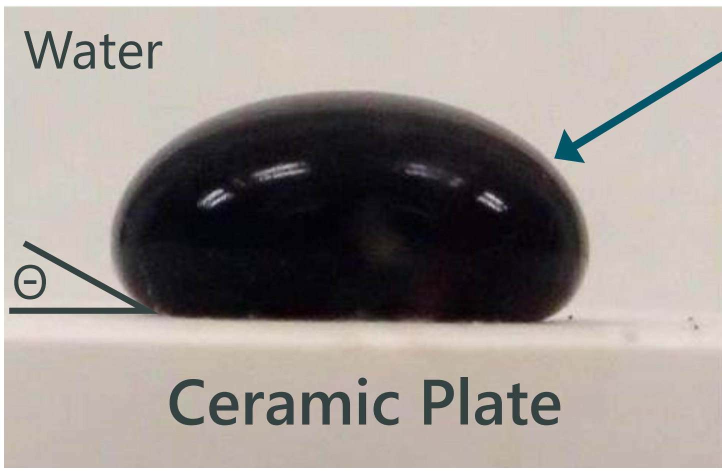


Source: Wilson, J.L., S.H. Conrad, W.R. Mason, W. Peplinski, and E. Hagan, 1990. *Laboratory Investigation of Residual Liquid Organics from Spills, Leaks, and the Disposal of Hazardous Wastes in Groundwater.* EPA/600/6-90/004. April 1990.

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

Weathered, PAH-Rich DNAPL

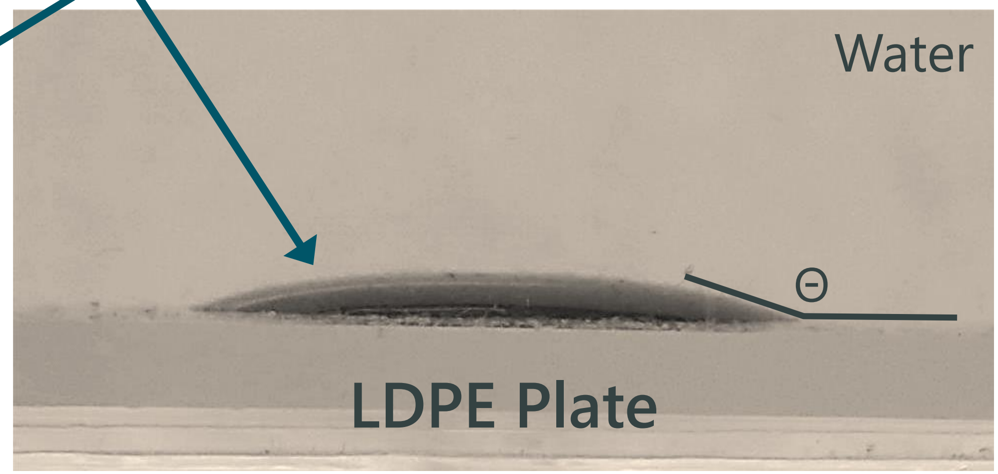
(23 days)



Contact angle Θ = 24°

NAPL is non-wetting

(1 day)



Contact angle Θ = 162°

NAPL is wetting

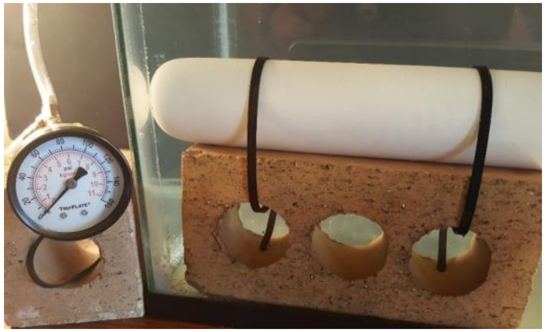
Entry Pressure and NAPL Exclusion Tests

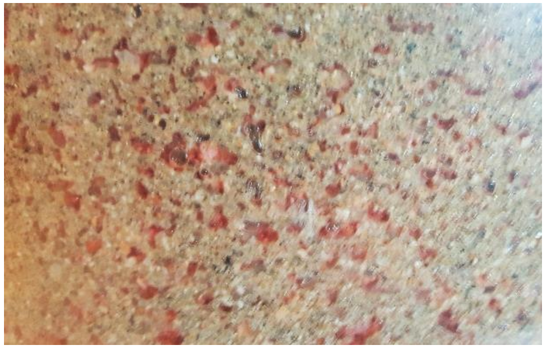
- Measured entry pressure using air pressure bubbling tests

- Tested water pumping in well-graded, fine-to-course sand and 25% to 50% NAPL saturation (S_n)

  - **S_n = 0.25:** pumped **25 mL/min** water flow with no sheen or NAPL in effluent—**potentially useful**

  - **S_n = 0.50:** Sheen in effluent with only 1.5 mL/min water flow—**impractical**





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

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

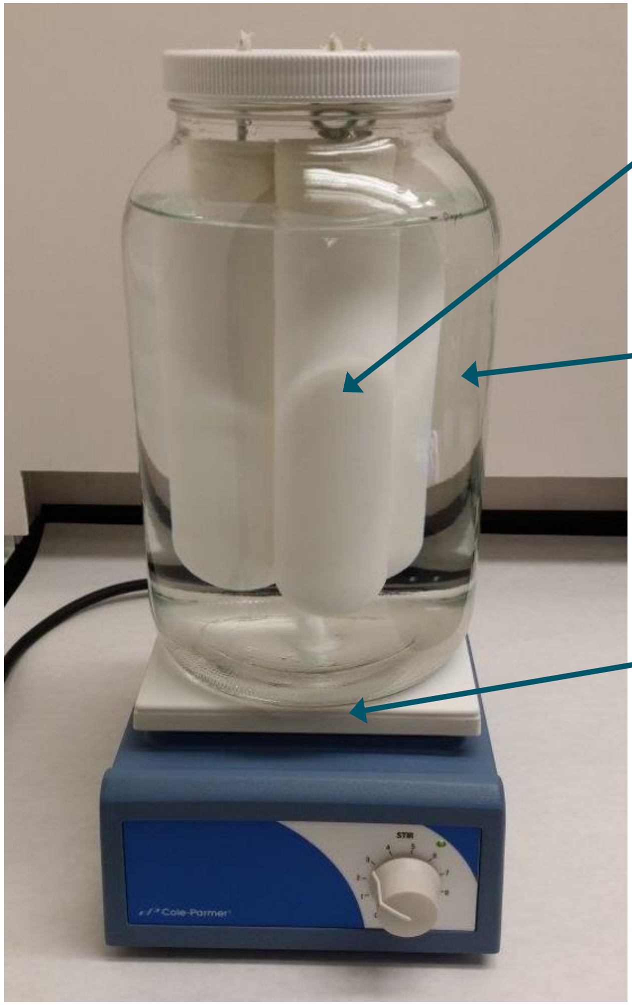
Z_n = critical DNAPL height above ceramic sampler (cm)
σ = NAPL-water interfacial tension (20 dynes/cm = 20 g/s^2)
φ = contact angle (24°)
r = pore radius (1.25 to 5.6 microns = 0.000125 to 0.00056 cm)
g = gravitational constant (980 cm/s^2)
ρ_n = non-wetting phase (NAPL) density (1.07 g/cm^3)
ρ_w =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

Z_n = 10 to 40 meters

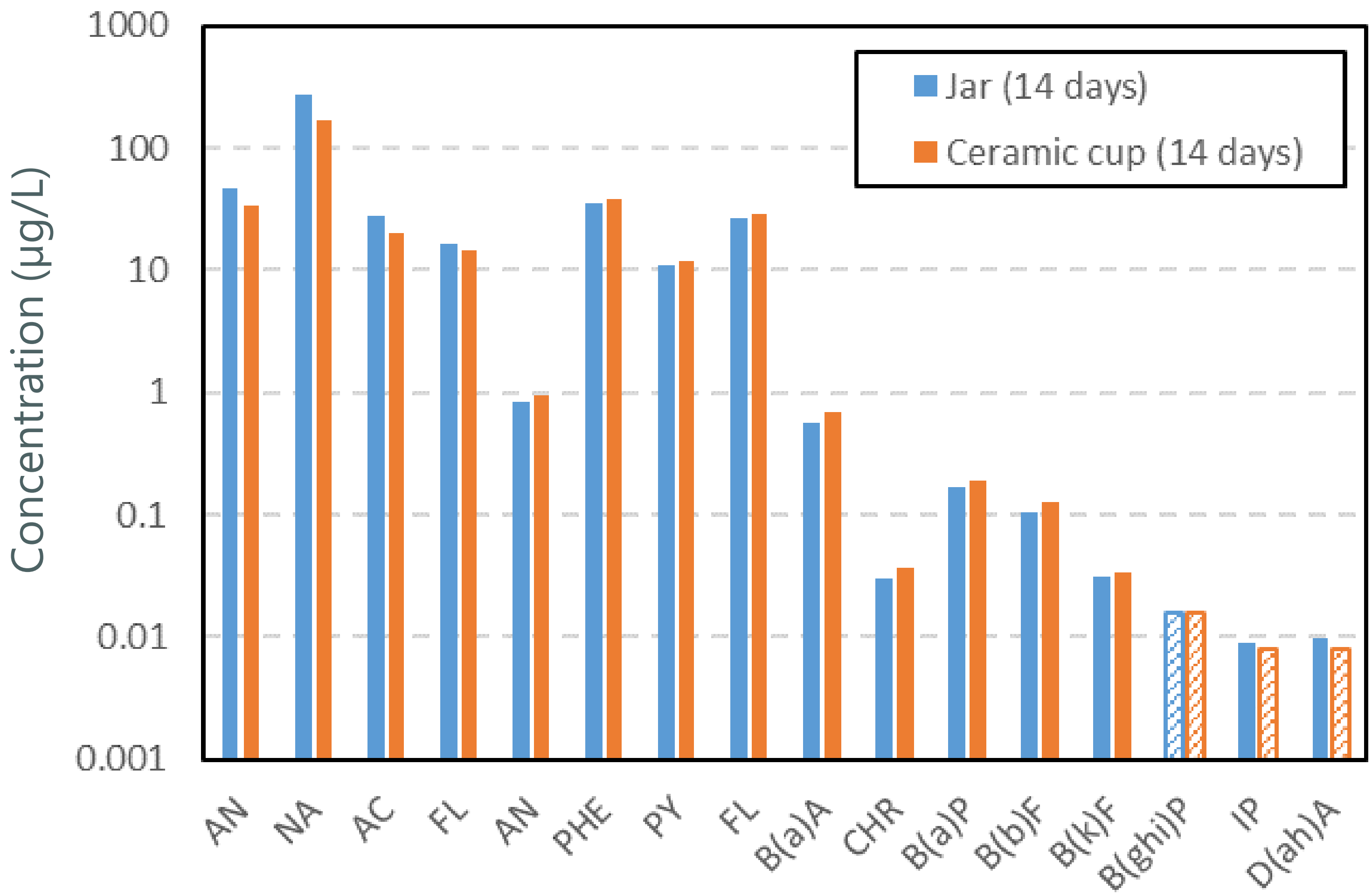
Source: Cohen, R.M., and J.W. Mercer, 1993. *DNAPL Site Evaluation*. C.K. Smoley, Boca Raton, Florida.

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



PAH Equilibration, 14-Day Results (No NAPL)

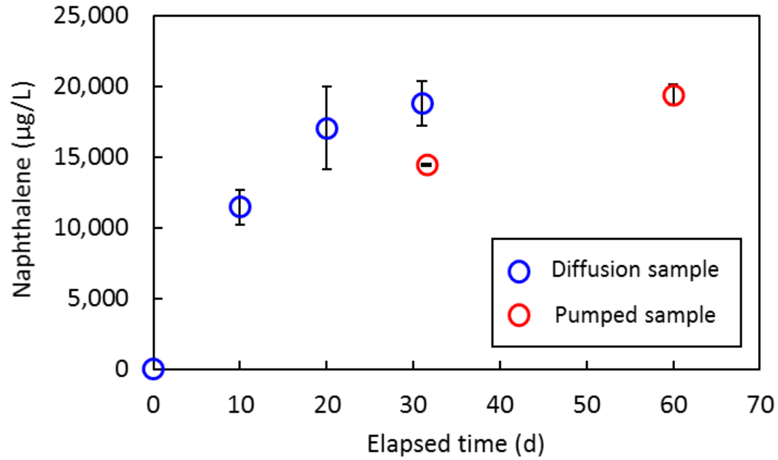


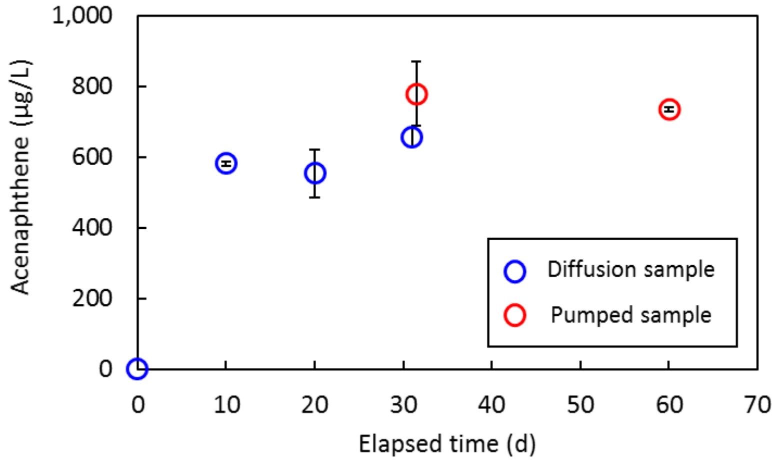
Note: Striped pattern bars indicate method detection level.

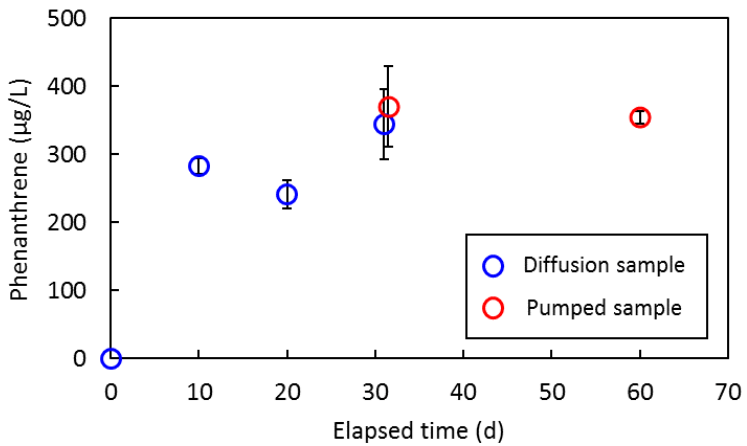
Porewater Sampling Tests With Diffusive Equilibration and Pumping (With NAPL)

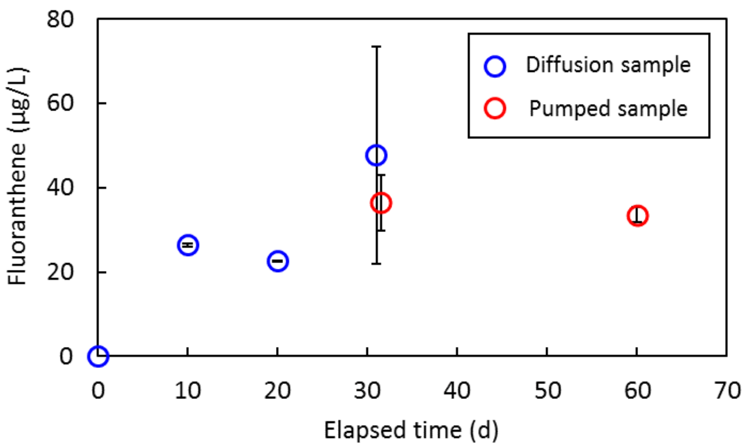
- Aquarium with well-graded sand, 0.5M NaCl water, and 9% creosote NAPL saturation
- Duplicate samples:
  - NAPL-coated sand at 0 and 31 days
  - Diffusion-based water samples at 10, 20, and 31 days
  - Pumped water samples also collected from ceramic tubes at 31 days and 60 days

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



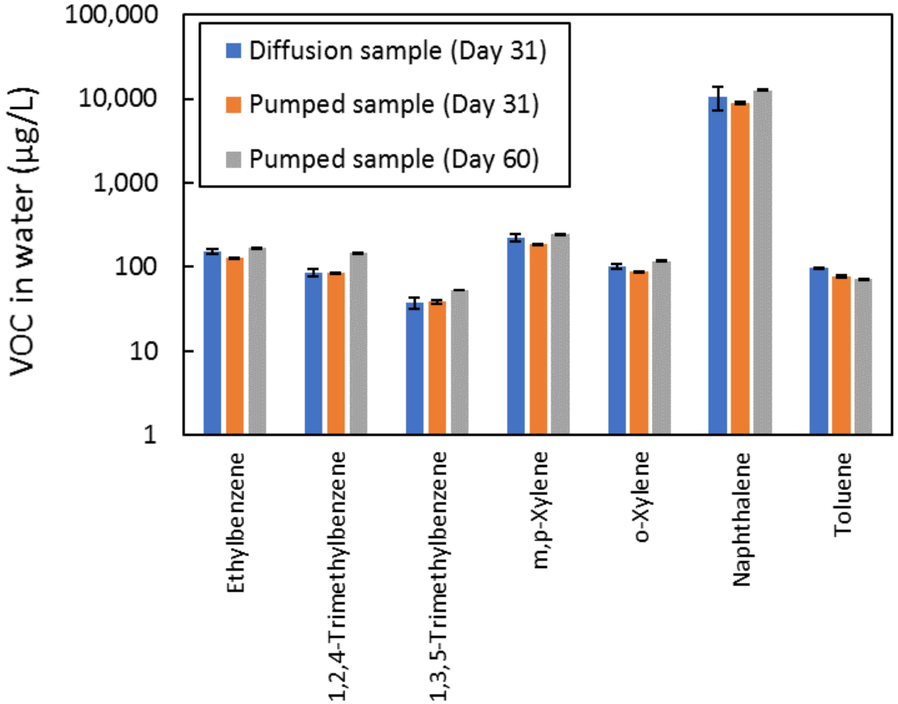




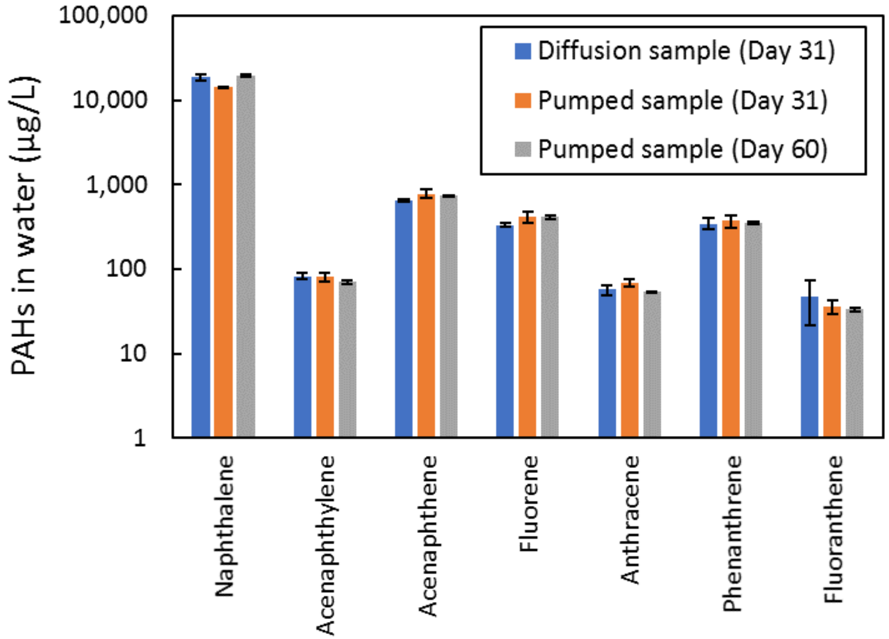


Porewater Sampling Tests With Diffusive Equilibration and Pumping (With NAPL)

VOCs



PAHs



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

- Sample porewater by diffusion-based equilibration.
- Protect hydrophobic, sorption-based samplers.
- 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, even when directly contacting NAPL.
- Wettability and entry pressure of porous ceramics appear favorable—also readily available and economical.
- Sampling by PAH diffusive equilibration and pumping through ceramic has been demonstrated.

Next Step

- Field application!

Acknowledgements

- Anchor QEA Innovation Program
- HRS Water Consultants

Questions/Discussion