# Economical Innovations for Improved Chemical Mass Flux Quantitation in Sediment

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Source: Boano et al. (2013)



# What sorts of economical innovations can improve chemical mass flux measurements in sediment?

## Chemical Mass Flux

- $J = C \times q$ 
  - where: J = chemical mass flux per unit area per unit time, C = concentration in fluid phase, and q = seepage rate (aka Darcy flux or specific discharge)
    - q = K × i
    - K = hydraulic conductivity
    - i = hydraulic gradient
- Two fluid phases: dissolved phase (porewater) and NAPL

### $\mathcal{O}$ APPROACH + METHODS

## Economical Innovations

Develop innovative solutions

Use in the field Adapt to site-specific conditions



# Dissolved-Phase Mass Flux— Porewater Seepage and Concentrations

## Porewater Seepage—Spatial Variability

- Hyporheic flow, heterogenous sediment
  - Multiple data collection locations
  - Stratigraphy, geomorphology, and known areas with chemicals of interest



## Porewater Seepage—Temporal Variability

- Tides, storms, and seasons
  - Multiple measurement "snapshots" or long periods (typically months)



4-month data collection period

## **Potential Pitfalls**

- Seepage meters
  - Fouling by biota or gas
  - Possible instability in soft sediment
  - Difficult to install in hard sediment
  - Hyporheic flow complexities
  - Impractical to deploy for long periods
- Piezometers
  - Destruction by flood, ice, and debris
  - Colocated vertical permeability measurement required—standard methods have significant costs





## Hydraulic Gradient

- Vertical hydraulic gradient (VHG) device with transducers
  - Dr. Donald Rosenberry, USGS
- Subaqueous piezometers with transducers
- Big picture: avoid hyporheic zone and collect continuous data



*Q* ECONOMICAL INNOVATION

## Hydraulic Conductivity

- Measure vertical hydraulic conductivity ( $K_v$ ) of whole sediment core by gravity drainage
- Avoid: sample cutting, packing, shipping to lab, transferring to lab test cell, over-consolidation, and use of multiple small samples



### ECONOMICAL INNOVATION



Figure 1. Schematic equipment setup and parameters used to calculate  $K_{\nu}$  from gravity drainage tests.

## Intertidal Zone Seepage





---Flow Rate ---Darcy Flux ---Temperature ---Spec Cond

Calculate  $K_v$  and combine with full gradient dataset for comprehensive seepage evaluation

## Intertidal Zone Gradient

• Vertical gradient from piezometer pair or VHG rod





datalogger

ECONOMICAL INNOVATION

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### Intertidal Piezometers

## Porewater Concentrations

- Spatially variable (3D)
  - Multiple sampling locations
  - Target anticipated future dredge depth (if known)
- Common data collection methods
  - Calculation: sediment–porewater partitioning
  - Pumped sampling: push point, drill casing
  - Passive sampling: solid-phase microextraction (SPME), polyethylene samplers





## **Potential Pitfalls**

- Hard, gravelly, cobbly sediment difficult to deploy porewater samplers at depth
- NAPL in sediment complicates partitioning calculations
- Big risk: NAPL inclusion in porewater samples (pumped or passive)— unrealistically high concentrations



 Weathered,

 PAH-Rich DNAPL

 Water

 Polyethylene

## Porewater Sampling at Depth in Dense, Coarse-Grained Sediment



### $\ensuremath{\mathbb{G}}$ ECONOMICAL INNOVATION

# Exclude NAPL from Porewater Samples

- Porous ceramics
- Water goes through; NAPL doesn't
- Economical, versatile, and effective
  - Diffusion-based equilibration
  - By direct porewater pumping or after sediment centrifuging or gravity drainage





# Learning Lab

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

Tuesday and Wednesday, 2:40 p.m.



# NAPL Mass Flux— *Quantifying Potential Advection Rate*

## NAPL Advection (Flow Through Pores)

- $J_N = \rho_N \ge q_N$  (NAPL mass flux per unit area per unit time)
  - where:  $\rho_N$  = NAPL density and  $q_N$  = NAPL seepage rate
- $q_N = K_N \times i_n$ 
  - where:  $K_N$  = NAPL effective hydraulic conductivity and  $i_n$  = net gradient
  - only applies if NAPL is capable of moving



## K<sub>N</sub> Estimation Methods

- Common methods
  - Calculate from NAPL accumulation in wells (via NAPL transmissivity)
  - Calculate based on:  $K_N = k_{r,n} K v_w / v_n$
- Potential pitfalls
  - NAPL rarely seen in wells/piezometers in sediment
  - Accumulation rates unknown
  - Calculation requires several assumptions



# K<sub>N</sub> from Laboratory Tests

- Get the full value from NAPL mobility laboratory tests
  - Use ASTM E3282-21 weight-of-evidence methods
  - $K_N$  in sediments often extremely low
- In most cases, NAPL has little or no potential to migrate via advection in sediments

### *Q* ECONOMICAL INNOVATION



V<sub>n,start</sub> = NAPL volume at start of test



**DURING TEST** 

Hydraulic gradient displaces some NAPL



FINAL V<sub>n,end</sub> = NAPL volume at end of test

## NAPL Hydraulic Conductivity in Sediment at 10 Sites



- Chemical mass flux is crucial for successful sediment remediation
- Beware of pitfalls in data collection
- Economical innovations can improve versatility in the field, data quality, mass flux quantification, and remedial outcomes







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#### $\mathsf{R}\mathsf{E}\mathsf{F}\mathsf{E}\mathsf{R}\mathsf{E}\mathsf{N}\mathsf{C}\mathsf{E}\mathsf{S}$

Best S., M. Gefell, D. Keith, M. Zhang, and D. Rosenberry, 2019. *Characterizing Groundwater Seepage in an Urban, Tidal Estuary Using Multiple Lines of Evidence*. Presented at: NGWA 2019 National Expo and Annual Meeting (Las Vegas); December 3–5, 2019. (Slides 9 and 10)

Boano, F., J.W. Harvey, A. Marion, A.I. Packman, R. Revelli, L. Ridolfi, and A. Wörman, 2013. "Hyporheic Flow and Transport Processes: Mechanisms, Models, and Biogeochemical Implications." *Rev. Geophys.* 52:603–679. DOI: 10.1002/2012RG000417. (Slide 2) Broecker, T., V.S. Gollo, A. Fox, J. Lewandowski, G. Nutzmann, S. Arnon, and R. Hinkelmann, 2021. "High-Resolution Integrated Transport Model for Studying Surface Water– Groundwater Interaction." *Groundwater* 59(4):488–502. (Slide 7)

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: <u>https://cluin.org/conf/tio/Porewater2\_111914/resource.c</u> <u>fm</u>. (Slide 14)

#### REFERENCES

Gefell, M.J., K. Russell, and M. Mahoney, 2018a. "NAPL hydraulic conductivity and velocity estimates based on laboratory test results." *Groundwater* 56(5):690–694. (Slide 21)

Gefell, M.J., M. Kanematsu, D. Vlassopoulos, and D. Lipson, 2018b. "Aqueous-phase sampling with NAPL exclusion using ceramic porous cups." *Groundwater* 56(6):847–851. (Slides 15 and 17)

Gefell, M.J., M. LaRue, and K. Russell, 2019. "Vertical Hydraulic Conductivity Measurement by Gravity Drainage." *Groundwater* 57(4):511– 516. (Slide 11) Gefell, M.J. and B. Gauley, 2022. *If It's Immobile, How Did It Get There? Debunking NAPL Presence as Evidence of NAPL Mobility in Sediments*. Presented at: MGP Conference 2022 (Chicago, Illinois); September 28-30, 2022. (Slide 22)

Kueper, B.H., G.P. Wealthall, J.W.N. Smith, S.A. Leharne, and D.N. Lerner, 2003. *An Illustrated Handbook of DNAPL Transport and Fate in the Subsurface*. UK Environment Agency R&D Publication 133. (Slide 4)

### REFERENCES

Zimmerman, M.J., D.A. Vroblesky, K.W. Campo, A.J. Massey, and W. Scheible, 2013. *Field Tests of Nylon-Screen Diffusion Samplers and Pushpoint Samplers for Detection of Metals in Sediment Pore Water, Ashland and Clinton, Massachusetts, 2003.* Training Slides from 23rd Annual NAPRM Training. U.S. Environmental Protection Agency ORD NHEERL. Available at: <u>https://clu-</u>

<u>in.org/conf/tio/Porewater2\_111914/resource.c</u> <u>fm</u>. (Slide 14)