Predicting Multicomponent NAPL Dissolution Using an Equilibrium Partitioning Model, with Demonstration Using Empirical Data

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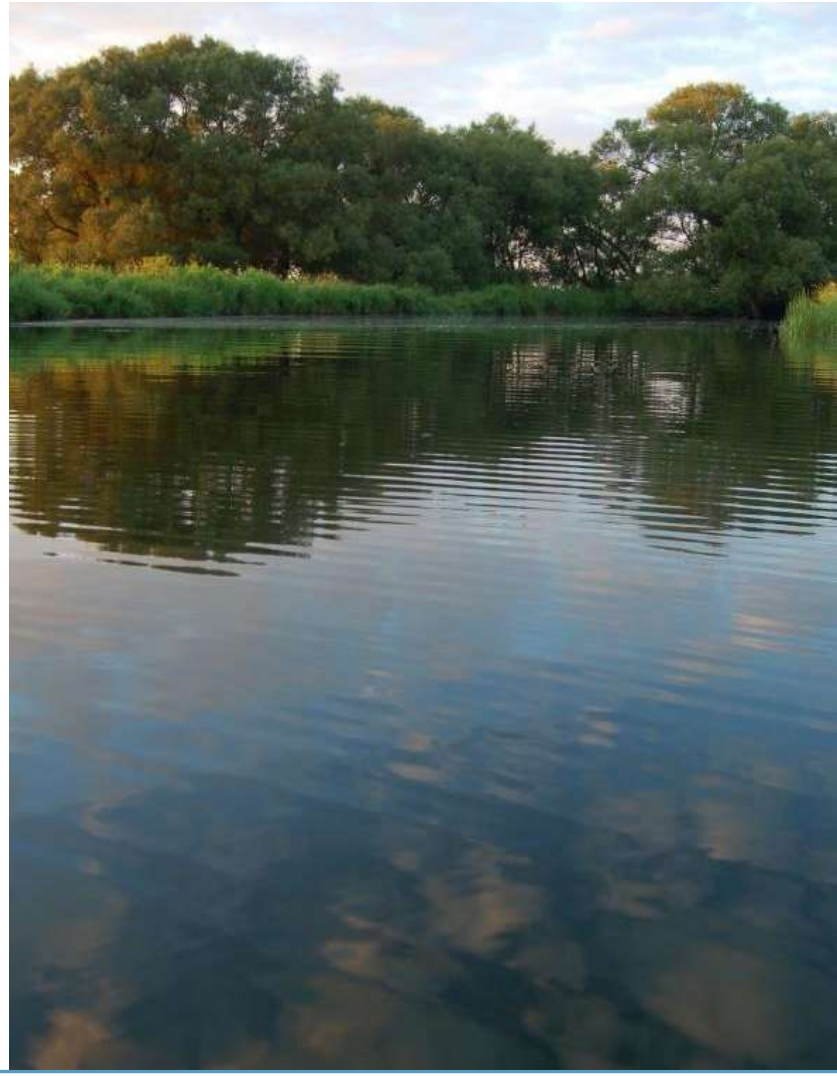
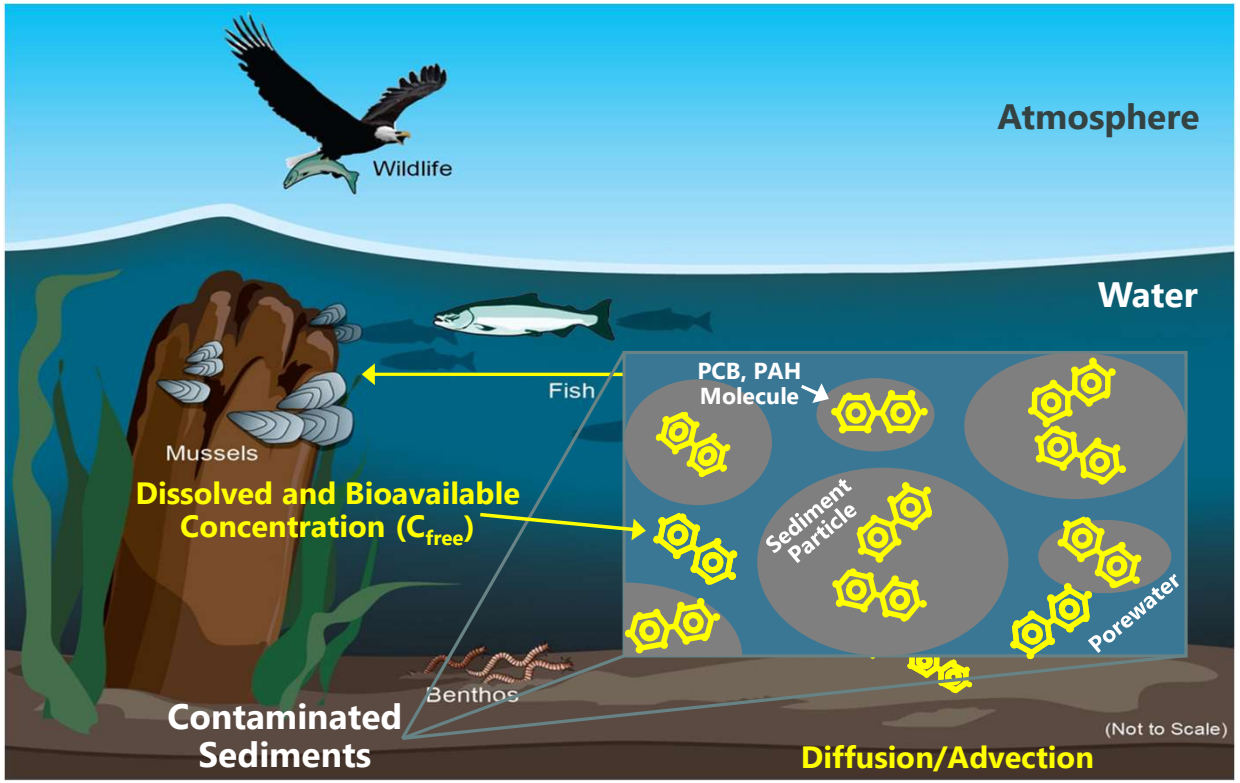
Outline

- Nonaqueous phase liquid (NAPL) in sediment—implications for remediation
- Challenge: develop method to predict long-term dissolved concentrations in NAPL zones
- Solution: innovative modeling
- Empirical verification
- Conclusions and benefits



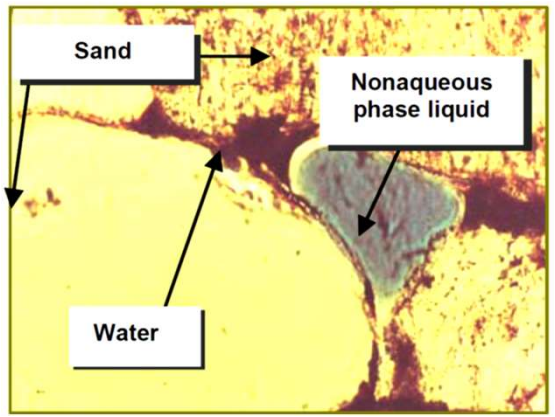
Groundwater/Surface-Water Interface Zone



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.

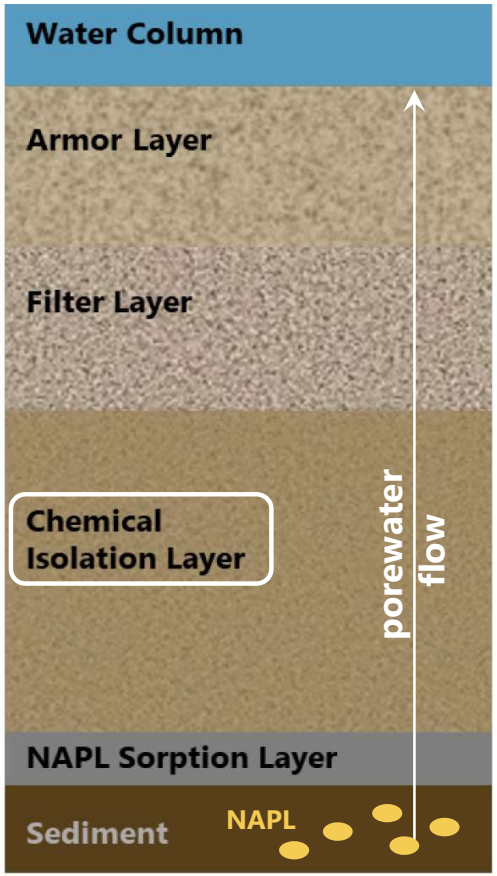
NAPL Can Pose Long-Term Risk

- Manufactured gas plants, wood-treaters, petroleum sites, urban waterways
- Ecological risk depends on dissolved concentrations in surficial porewater (bioactive zone)
  - Naphthalene, benzene, etc.
  - Most soluble, most mobile
- NAPL dissolves slowly, so dissolved concentrations remain high (solubility limit)
  - But for how long?



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.

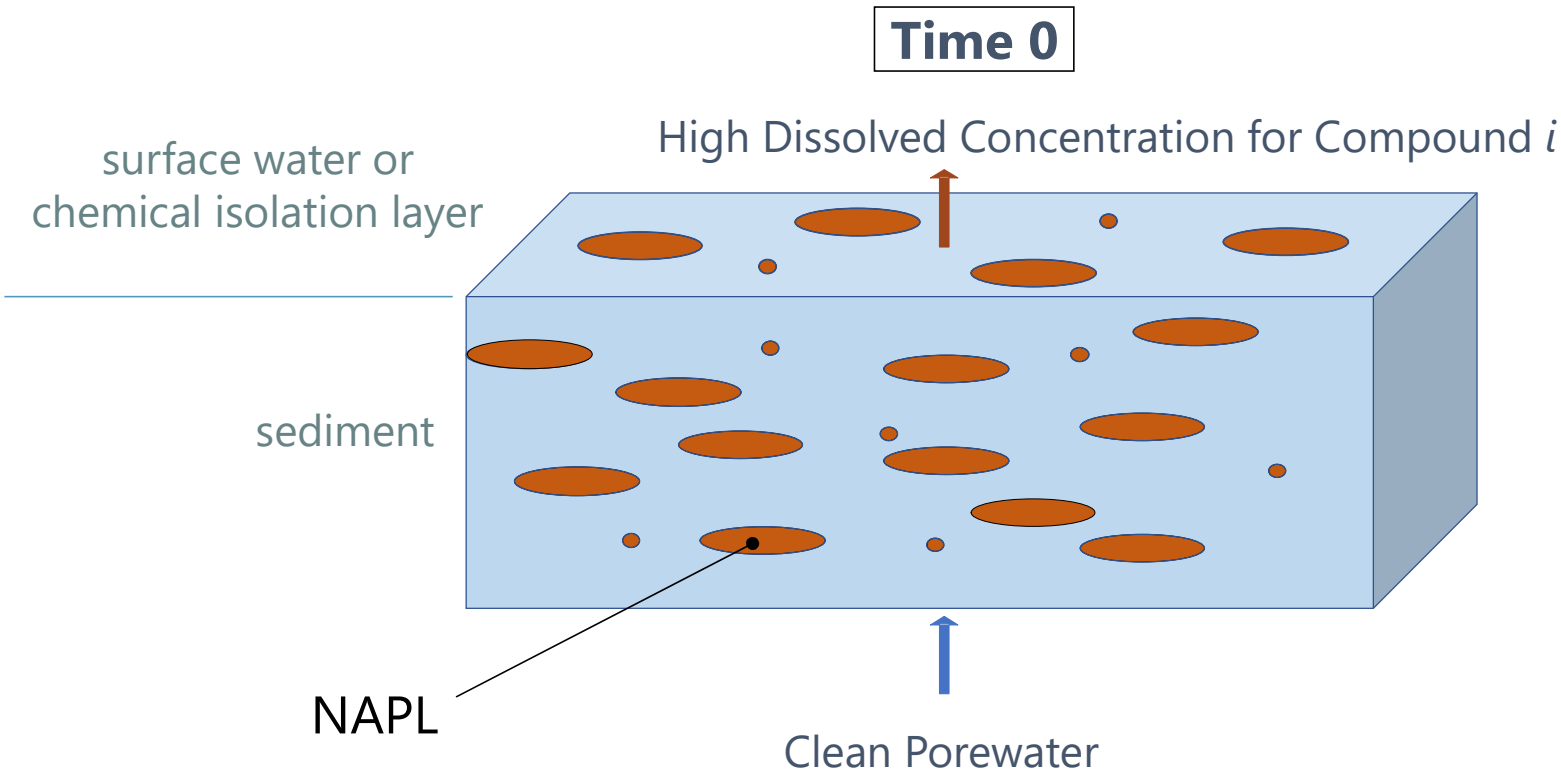
Sediment Remediation Cap (Example)



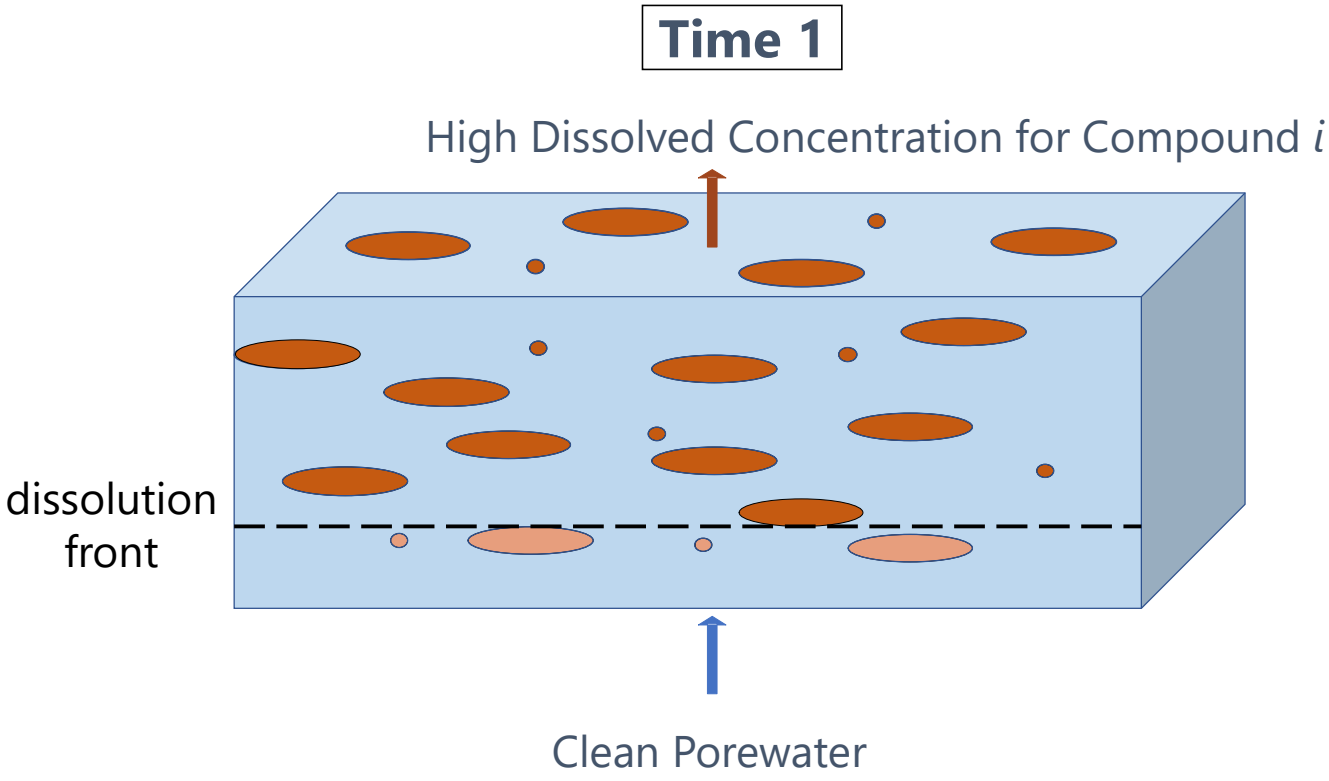
- Chemical isolation layer
  - Sorbs dissolved compounds
  - Protects surficial sediment and porewater
  - However, sorbents are expensive
- Typical cap design life is 100 years
  - Common assumption: dissolved concentrations of NAPL components will remain at current levels
  - But will they really? For that long?

Dissolution of a Select Compound from Complex NAPL in Sediment (Conceptual Illustration)

Dissolution Front Migration Through NAPL Zone



Dissolution Front Migration Through NAPL Zone



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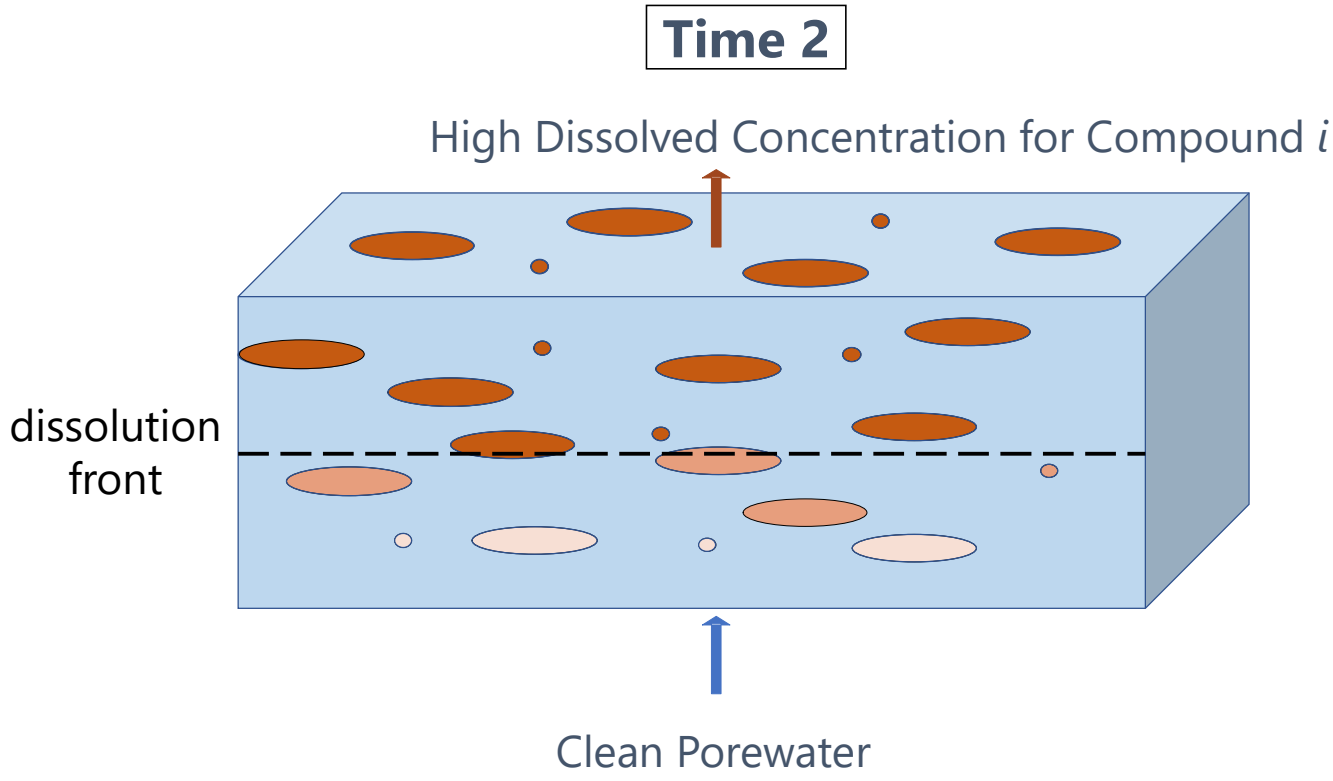

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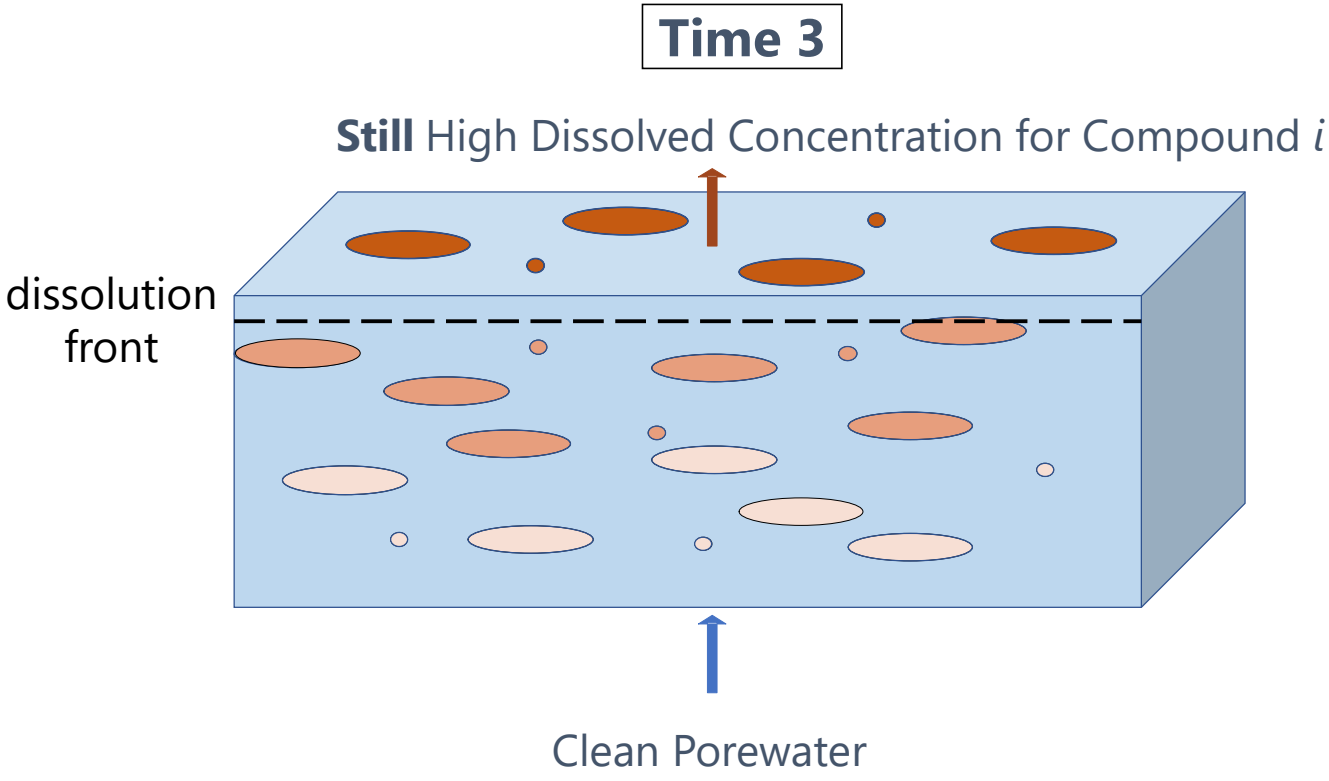
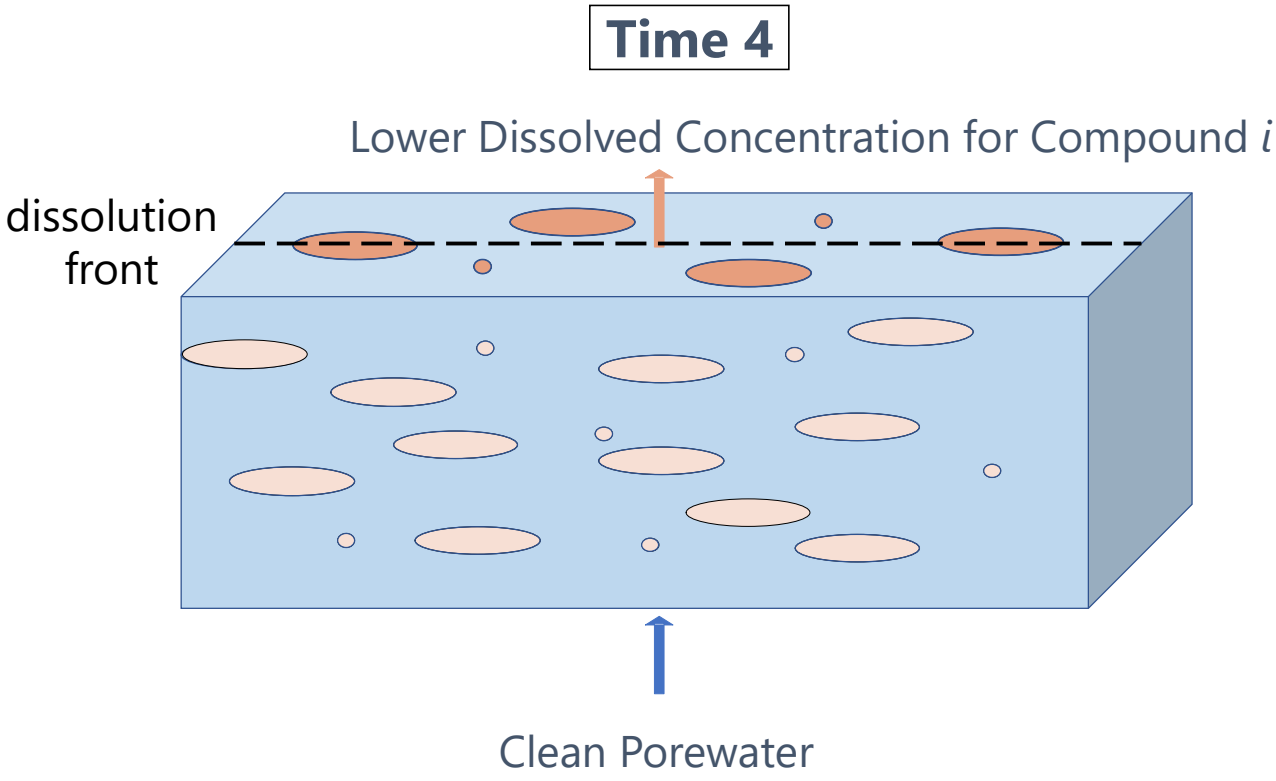


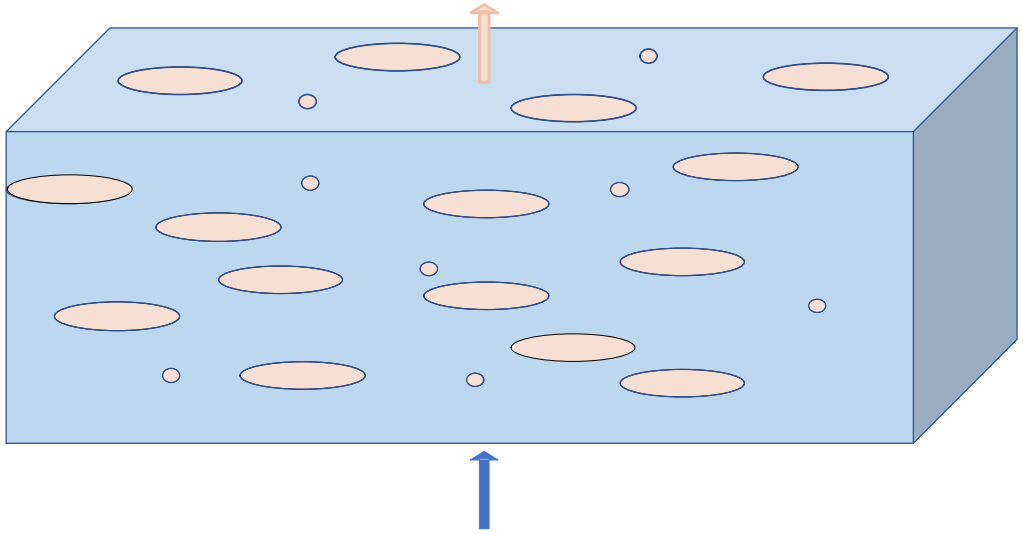
Dissolution Front Migration Through NAPL Zone



Dissolution Front Migration Through NAPL Zone

Time 5

Low Dissolved Concentration for Compound *i*



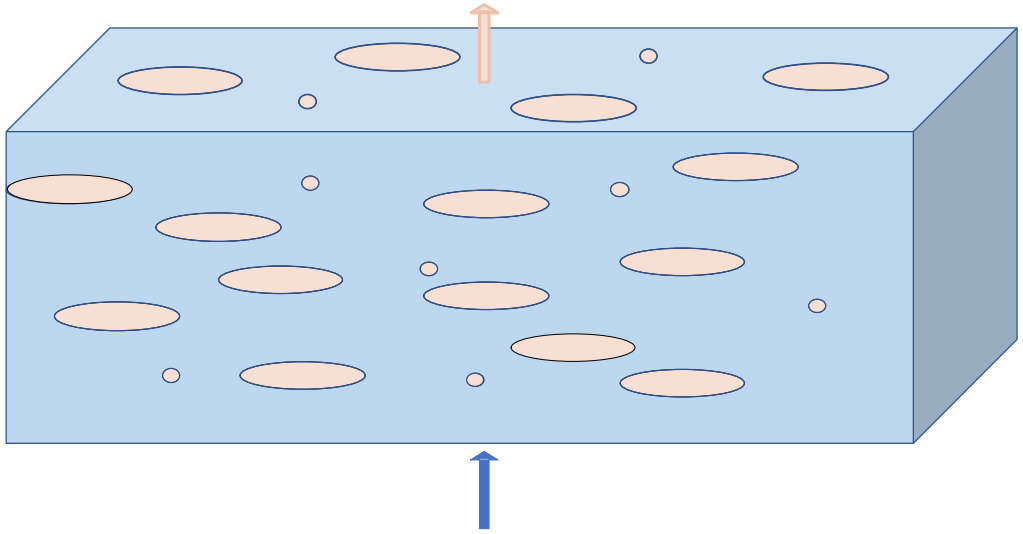
Clean Porewater

Dissolution Front Migration Through NAPL Zone

Time 5

Low Dissolved Concentration for Compound *i*

This process may take many pore volumes exchanges!



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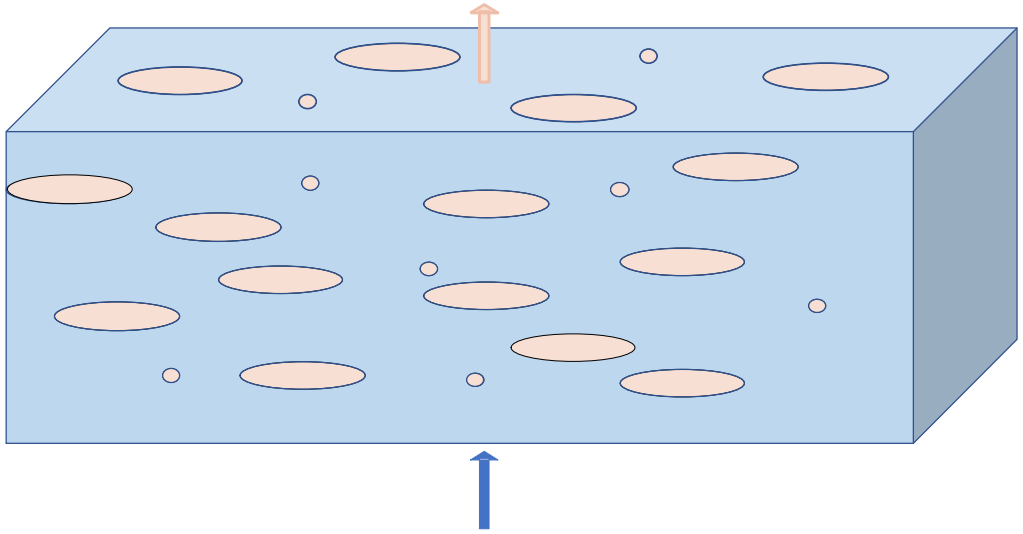

But it's a finite number.

Clean Porewater

Dissolution of a Select Compound from Complex NAPL (Empirical Demonstration)

ELSEVIER

Journal of Contaminant Hydrology 59 (2002) 45–66

JOURNAL OF Contaminant Hydrology

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Time scales of organic contaminant dissolution from complex source zones: coal tar pools vs. blobs

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Abstract

Groundwater contamination due to complex organic mixtures such as coal tar, creosote and fuels is a widespread problem in industrialized regions. Although most compounds in these mixtures are biodegradable, the contaminant sources are very persistent for many decades after the contamination occurred (e.g., more than 100 years ago at gasworks sites). This limited bioavailability is due to slow dissolution processes. This study presents results from a large scale tank experiment (8 m long) on the long-term (354 days) dissolution kinetics of BTEX and PAHs from a 2.5 m long coal tar pool and 0.5 m long (smear) zone containing coal tar blobs distributed in a coarse sand. The results indicate (1) that Raoult's law holds for estimation of the saturation aqueous concentrations of the coal tar constituents, (2) that for the dissolution of smear zones longer than approximately 0.1 m and with more than 3–5% residual saturation, the local equilibrium assumption is valid and (3) that although very small (<0.1 mm), the transverse vertical dispersivity dominates the pool dissolution processes. Typical time scales for removal of the pollutants from the blob zone and the pool are in the order of a few weeks to more than 10,000 years, respectively.

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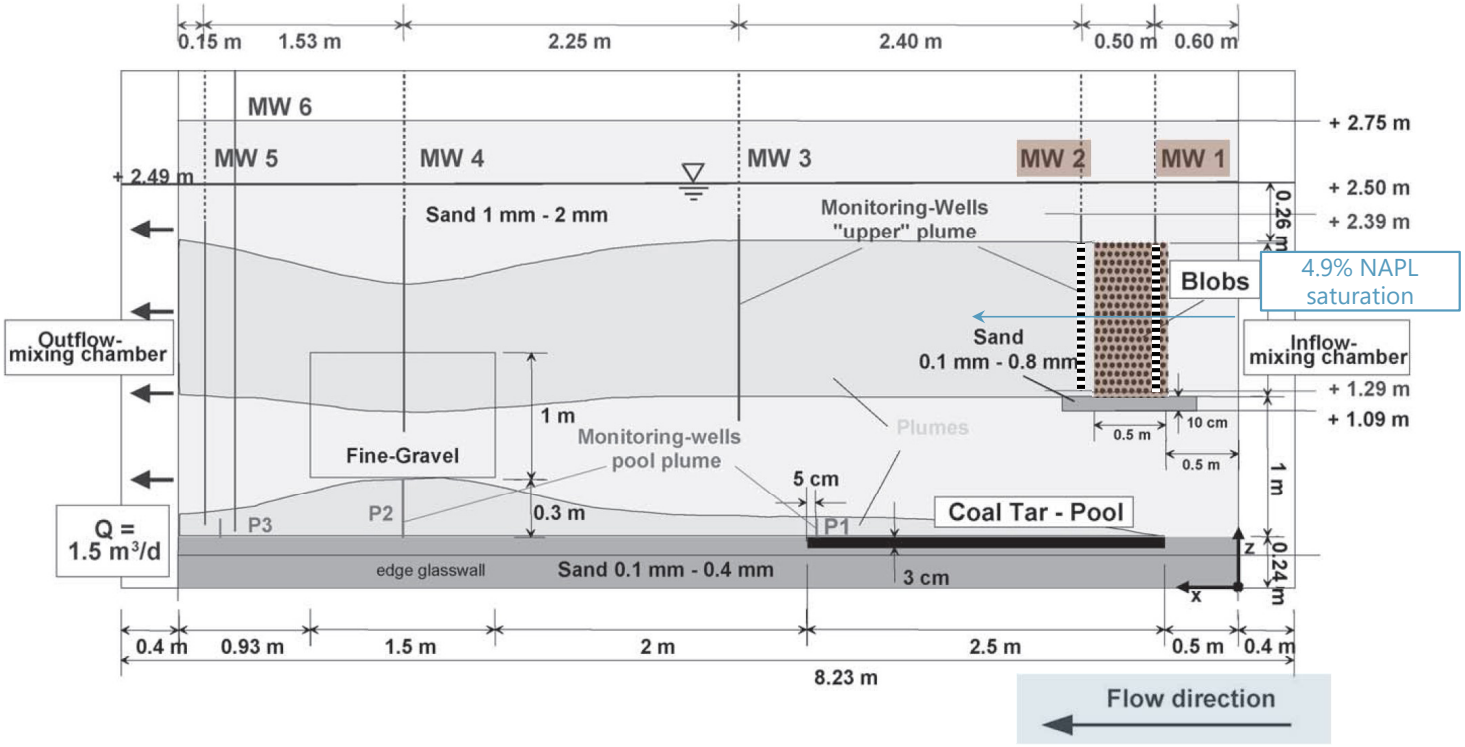
Empirical Sand Tank Experiment with Coal Tar

(Eberhardt and Grathwohl 2002)

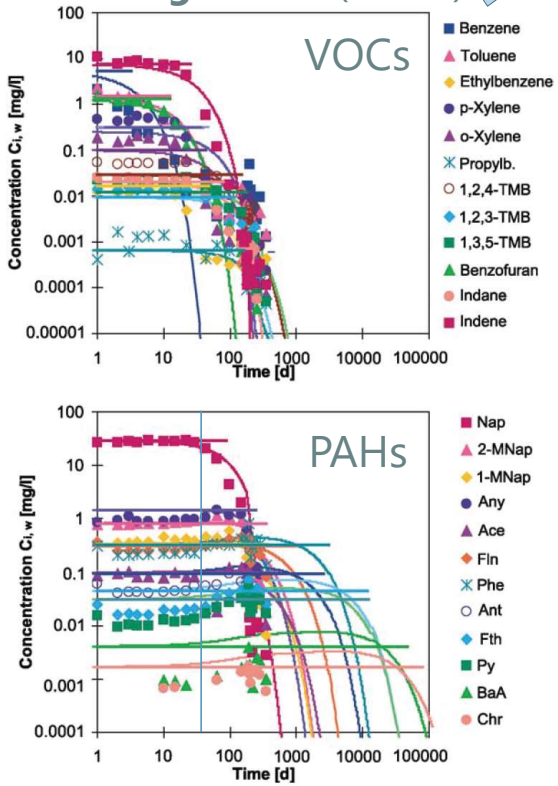


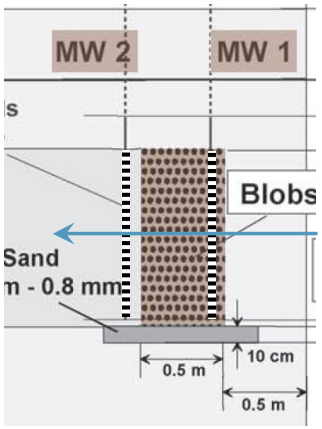
Source: Eberhardt, C., and P. Grathwohl, 2002. "Time Scales of Organic Contaminant Dissolution from Complex Source Zones: Coal Tar Pools vs. Blobs." *Journal of Contaminant Hydrology* 59:45–66.

Dissolved Concentrations Versus Time

(Eberhardt and Grathwohl 2002)

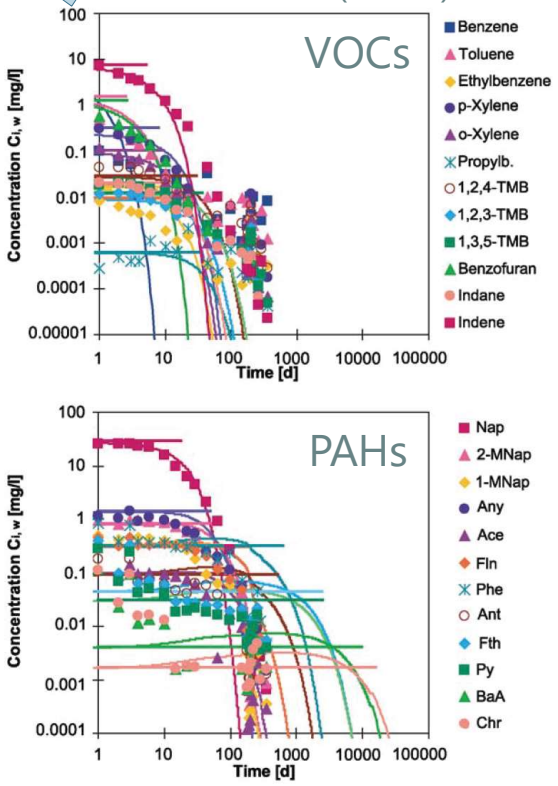
Downgradient (MW 2)





water travel time through NAPL zone **≤8 hours**

In NAPL Zone (MW 1)



Dissolution Front Retardation

- **90 pore volume exchanges** before naphthalene concentration decreased downgradient of NAPL zone
- Retardation of dissolution front relative to porewater flow (Eberhardt and Grathwohl 2002)

Equation 1: $R = 1 + (\rho_0 f_{i,o} n S^0) / (C_{i,sat} n_c)$

where:

ρ_0	=	NAPL density
$f_{i,o}$	=	mass fraction of compound *i* in NAPL
n	=	total porosity in NAPL zone
S^0	=	NAPL saturation
$C_{i,sat}$	=	effective solubility for compound *i*
n_c	=	effective (water-filled) porosity in the NAPL zone

Innovative Solution

- Standard retardation equation for clean-water front during desorption (standard solute-transport modeling)

  Equation 2: $R = 1 + (\rho_b/n)\ \boldsymbol{K_d}$

  where:

ρ_b	=	bulk density
n	=	total porosity
$\boldsymbol{K_d}$	=	distribution coefficient

- Equating (1) and (2)

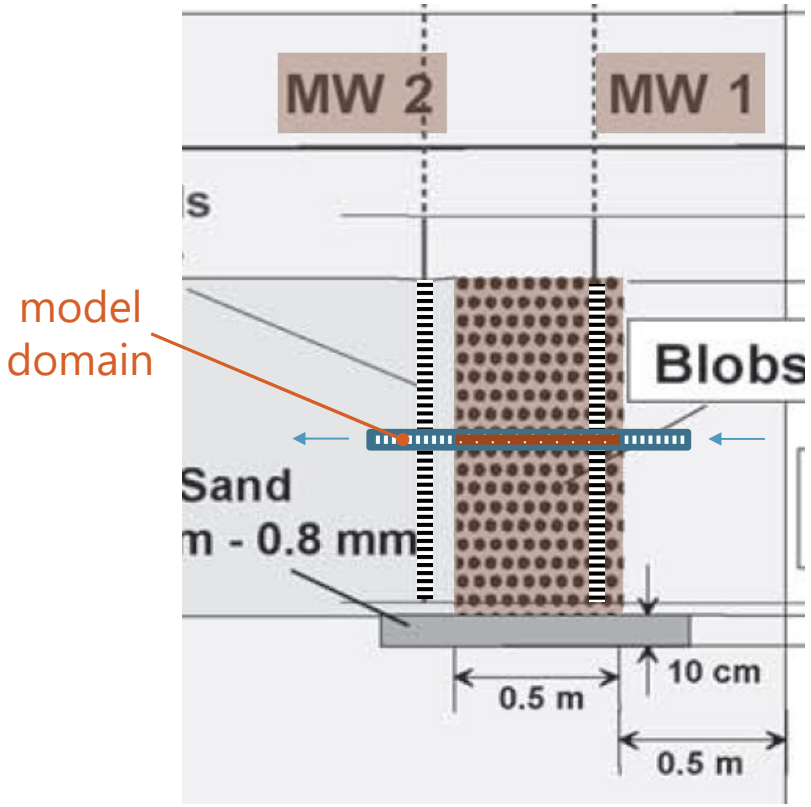
  Equation 3: $\boldsymbol{K_d} = (\rho_0\ f_{i,o}\ n^2\ S^0) / (\rho_b\ C_{i,sat}\ n_c)$

- Hypothesis: Dissolution of a select compound from multicomponent NAPL (e.g., MGP NAPL, creosote, etc.) can be approximated as desorption, with an effective $\boldsymbol{K_d}$ value that can be readily calculated

Verification: Numerical Modeling

Numerical Model Setup

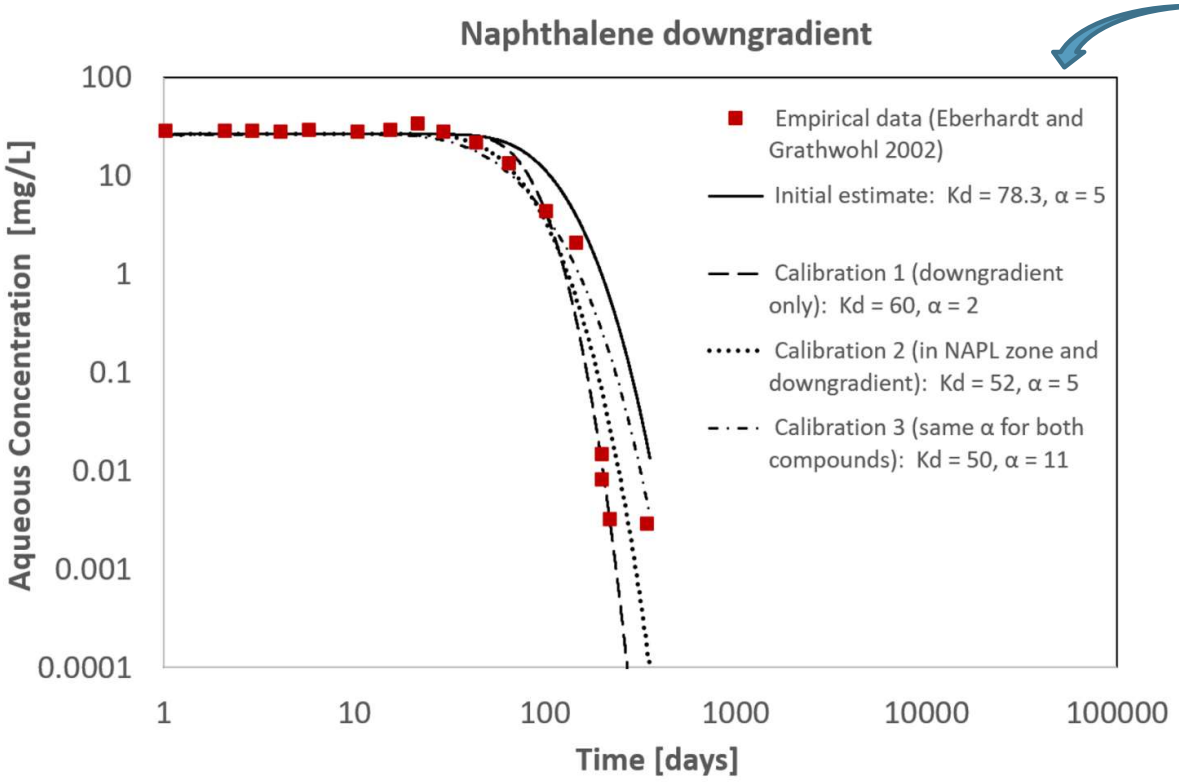
- 1D MT3D model through NAPL zone (1 m long)
- 100 cells parallel to flow
- Initial dissolved concentration in NAPL zone = $C_{i,sat}$
- K_d value used in NAPL zone, zero elsewhere (equilibrium partitioning)
- Initial sorbed concentration calculated by model
- Other parameters from Eberhardt and Grathwohl (2002)

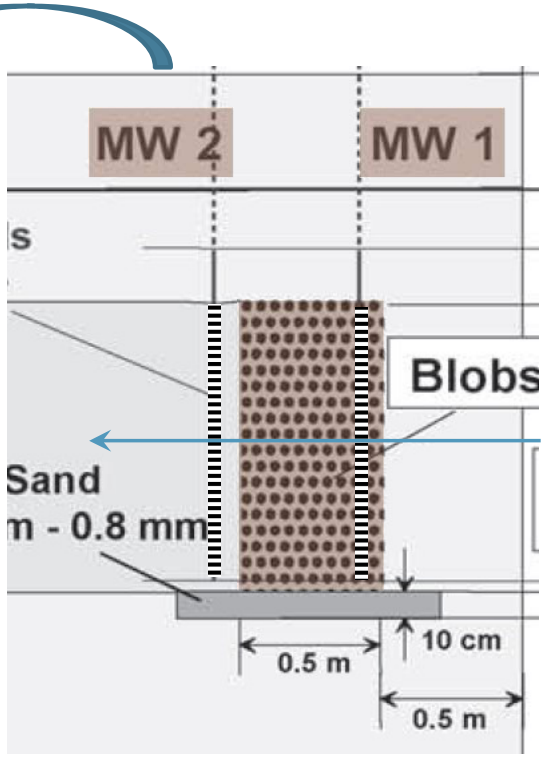


Simulation Summary

- Focused on naphthalene and indene (PAH and VOC, respectively, with highest effective solubility):
  - **Initial estimate:** K_d calculated using Equation 3
  - **Calibration 1:** adjusted K_d and longitudinal dispersivity (α) to achieve best match for each location and compound
  - **Calibration 2:** used the midpoint values of K_d and α from Calibration 1 for both locations
  - **Calibration 3:** used the midpoint α value for both compounds for each location, adjusted K_d values

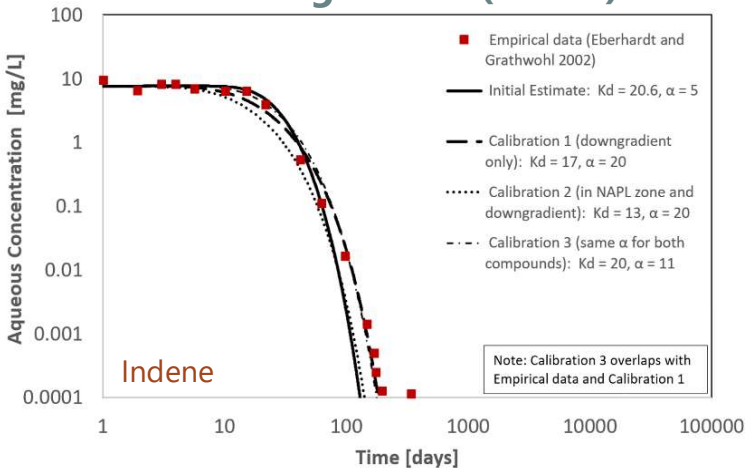
Example of Modeling Results: Naphthalene at MW 2



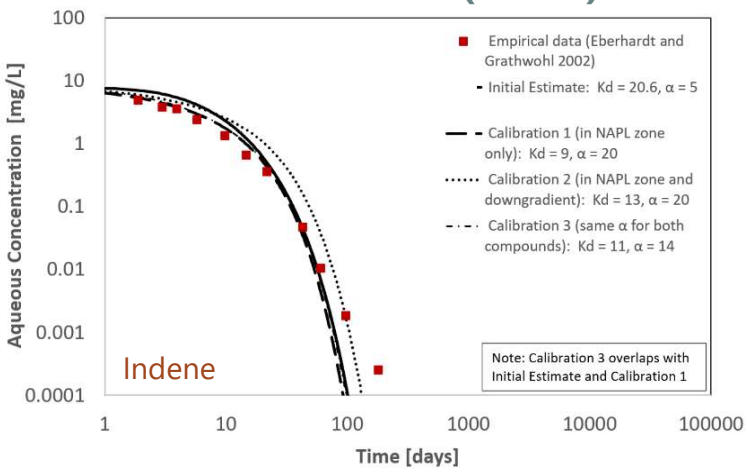


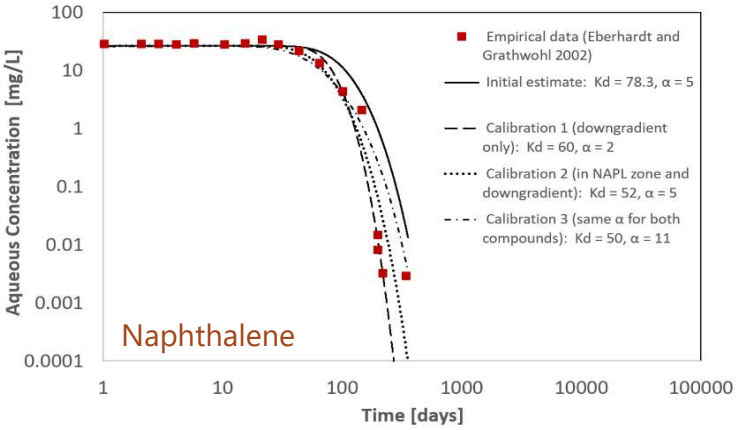
All Modeling Results

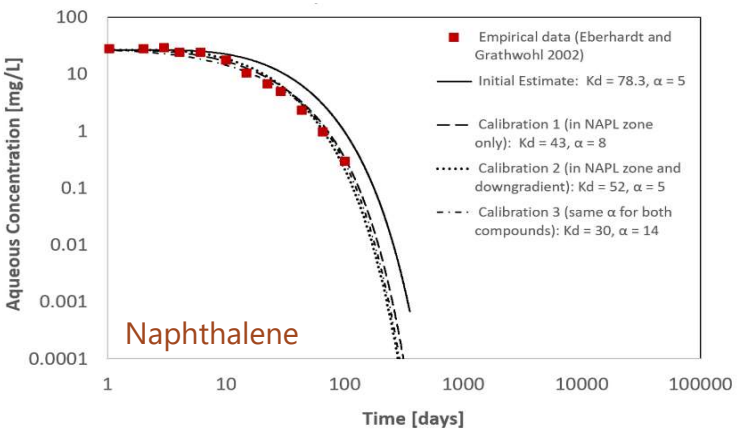
Downgradient (MW 2)



In NAPL Zone (MW 1)







Model Results (Summary)

- All simulations closely matched timing of dissolution front observed in empirical model (Eberhardt and Grathwohl 2022)
- Predicted times to achieve a three-order-of-magnitude concentration decrease downgradient of NAPL zone matched within a factor of approximately 2
- Calibrated K_d values were within a factor of approximately 2 of the initial K_d estimates calculated using Equation 3
- Minor differences between model results and empirical data may relate to non-uniform NAPL composition and saturation in the empirical sand tank model

Conclusions

- Dissolution of a relatively soluble compound from a complex NAPL can be simulated equivalent to desorption using a calculated K_d value
  - Timing of dissolution front
  - Concentration decrease over time
- The effective K_d value for a given compound can be calculated based on the properties of the NAPL and soil or sediment

Benefits of Numerical Modeling Approach

- Equilibrium partitioning numerical models widely available and versatile
  - Heterogeneous porous medium properties
  - Various NAPL properties (composition, saturation, etc.)
  - Hydraulic gradient changes (tides, pump and treat, etc.)
  - Degradation in aqueous phase
- Can compare cleanup time frames for various remedial alternatives
- Potentially use less sorbent mass in chemical isolation layer of sediment remedy

Questions/Discussion

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