A Framework to Incorporate Geochemical Heterogeneity into Contaminant Transport

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Richelle M Allen-King
University at Buffalo (SUNY)

Financial sponsorship from:

- US National Science Foundation
- American Chemical Society-PRF
- University Consortium Solvents-in-Groundwater, Waterloo Centre for Groundwater Research
- AWRA and NGWA student scholarships
- New project funded by DOE!

Groundwater contaminant transport

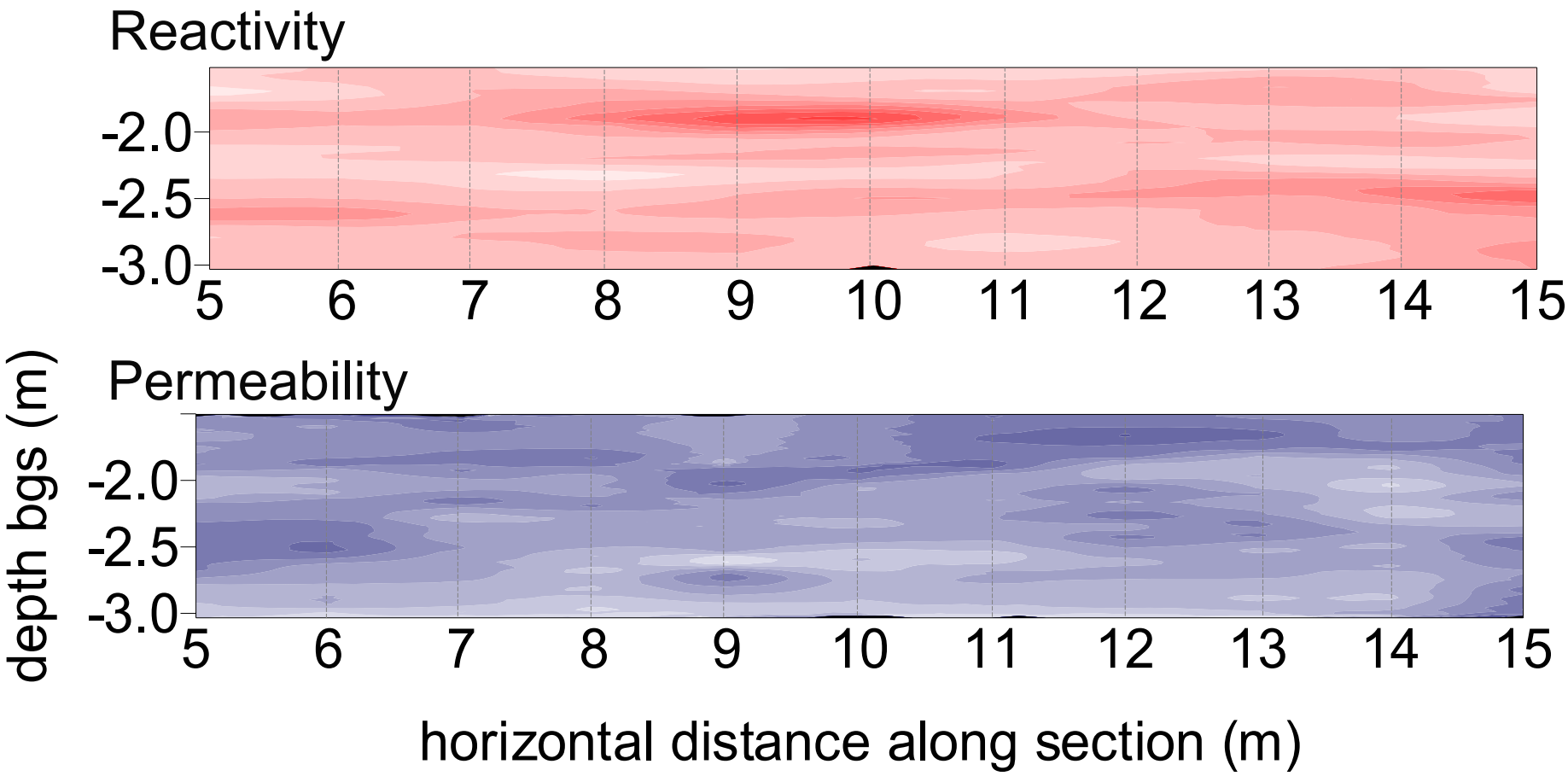
- Predictions (models) used to:
  - To estimate long term societal/ecological impacts
  - Assign risk to prioritize remediation needs
  - Plan efficient remedial design

Understanding and incorporating heterogeneous distributions of subsurface properties <u>authentically</u> will allow us to do all of these better!

Reactive transport

- Hydraulic Conductivity, K
- Parameters that describe rate-controlling reactions
  - ‘Extent’ of reaction, e.g. Kd, Ksp, or properties that control extent
  - Reaction rate, kr
- Need to know these everywhere in space and time

Reactive transport – we want the ‘complete’ picture in space&time!



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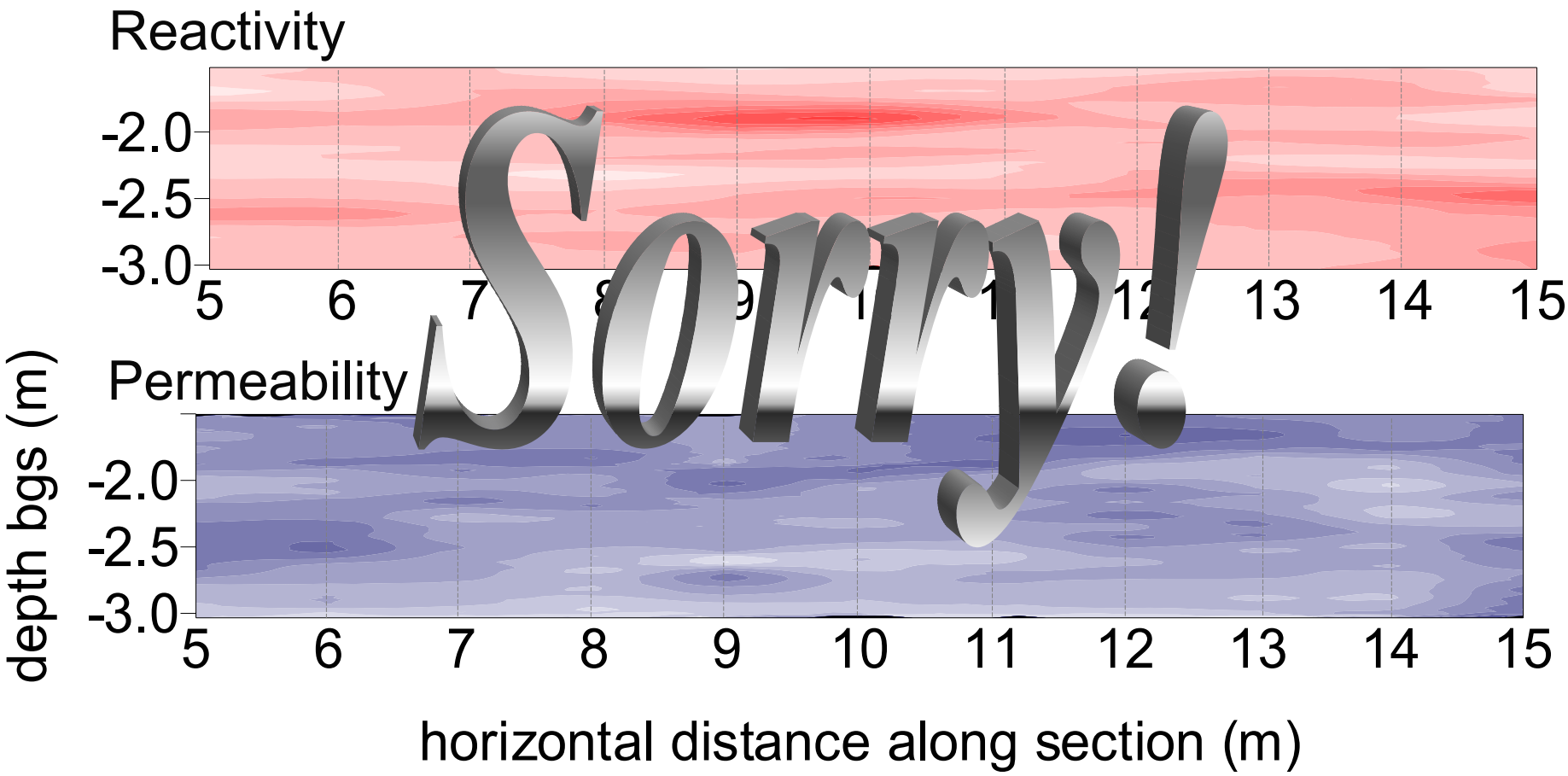
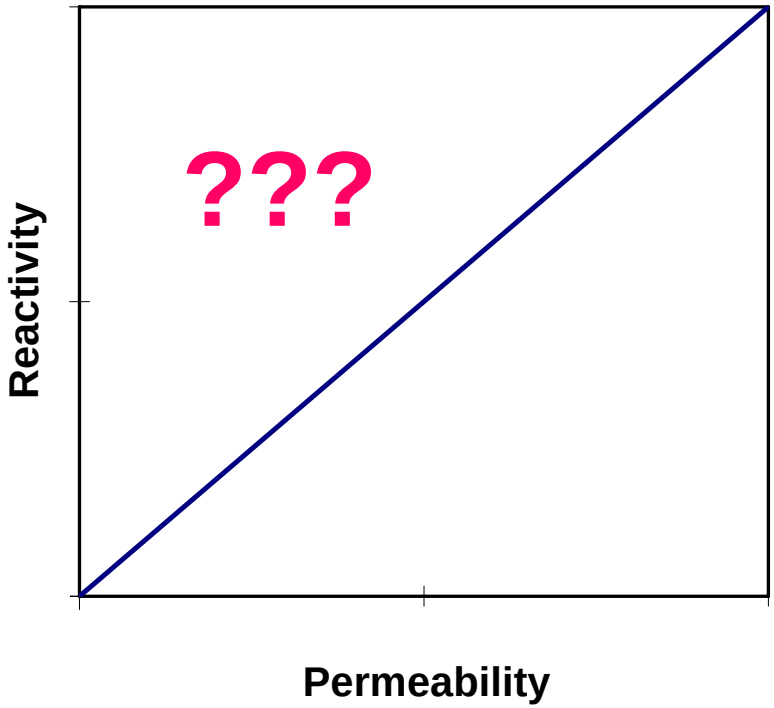
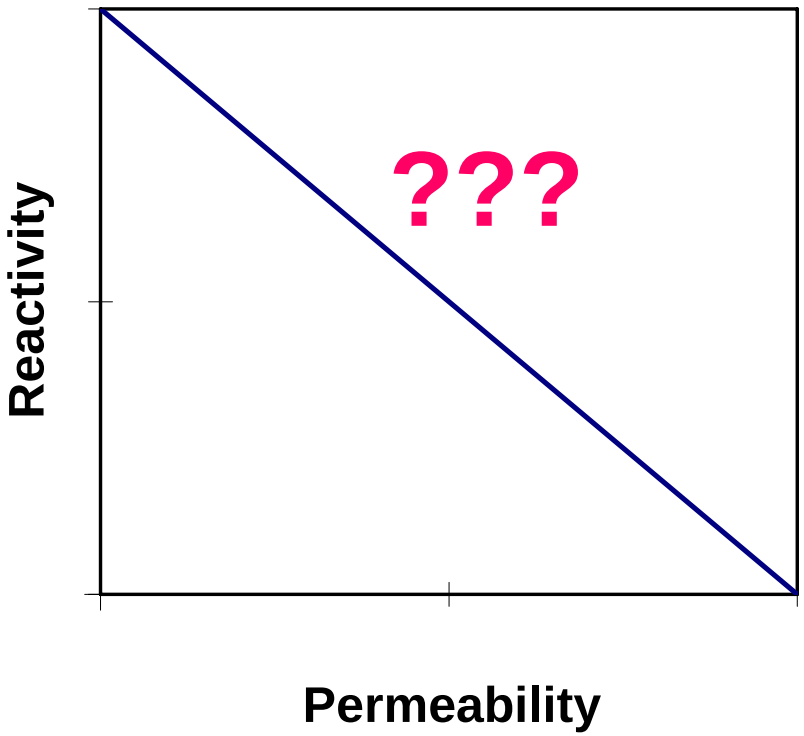


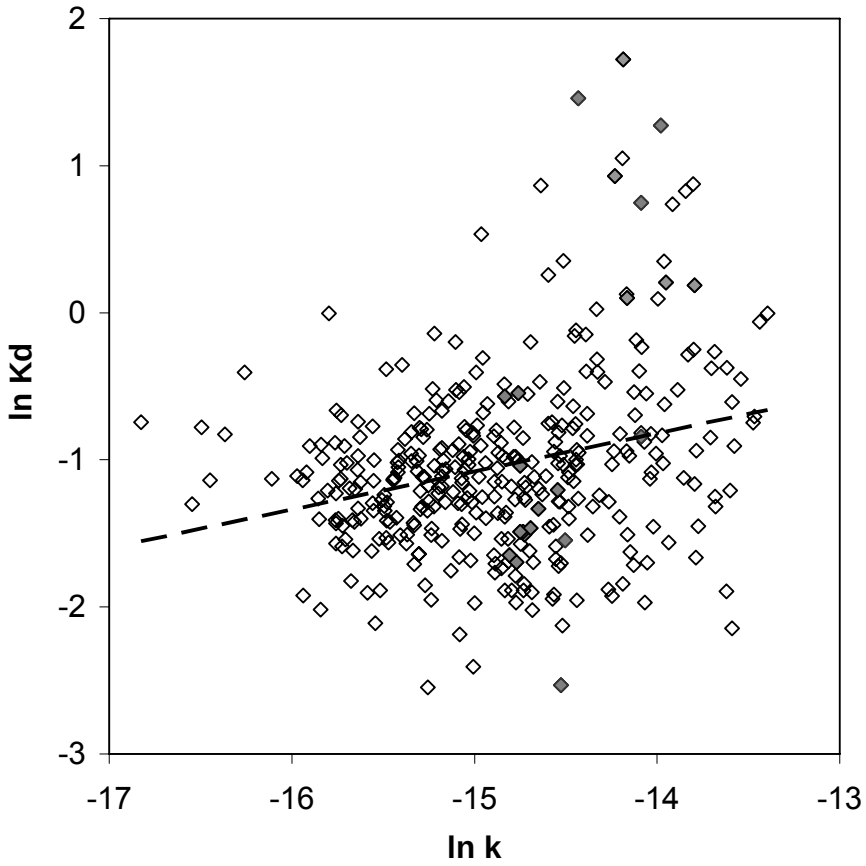
Relate reactivity to permeability?

Models have assumed





A REAL picture. . .

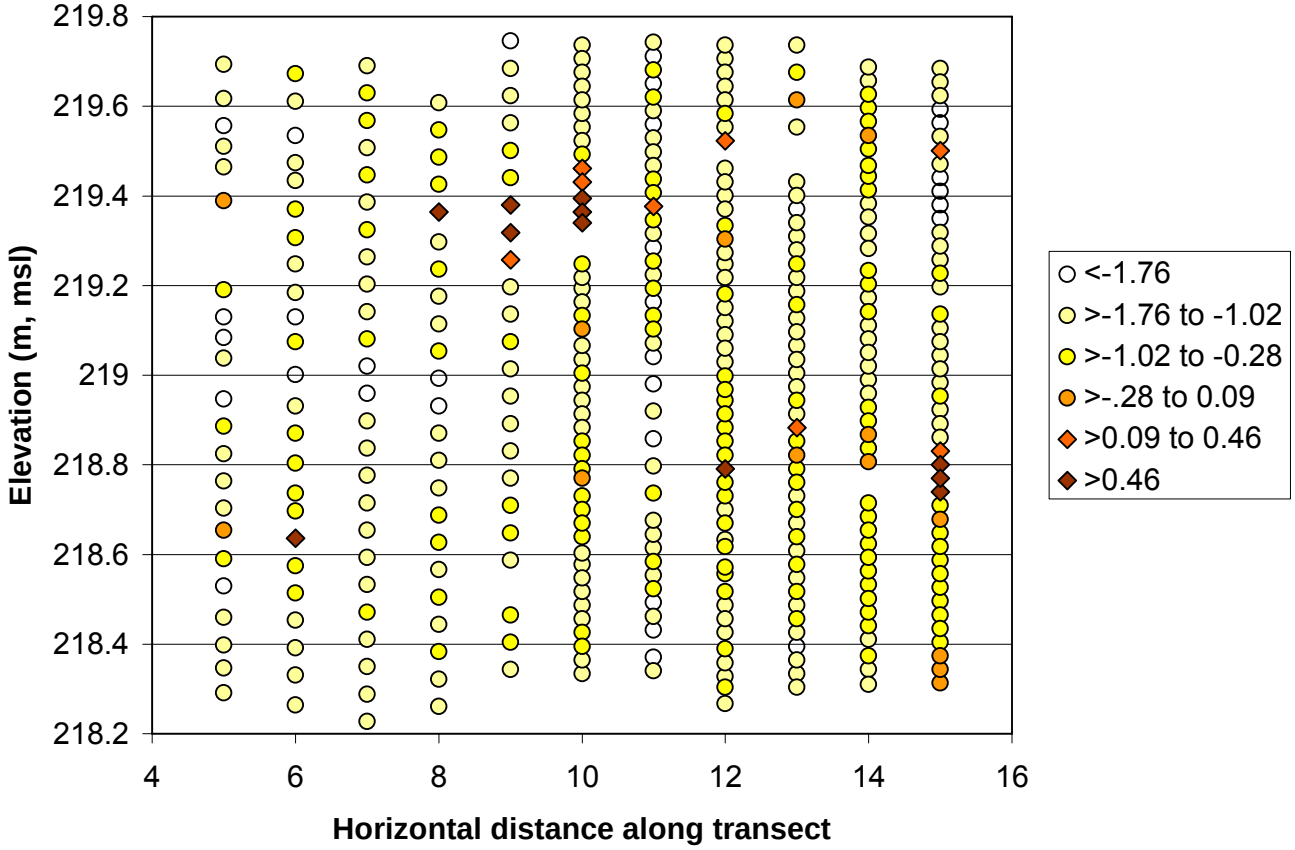


Relations between chemical/physical properties

Permeability, k ⟷ Reactivity, Kd

X

There are no complete spatial data sets



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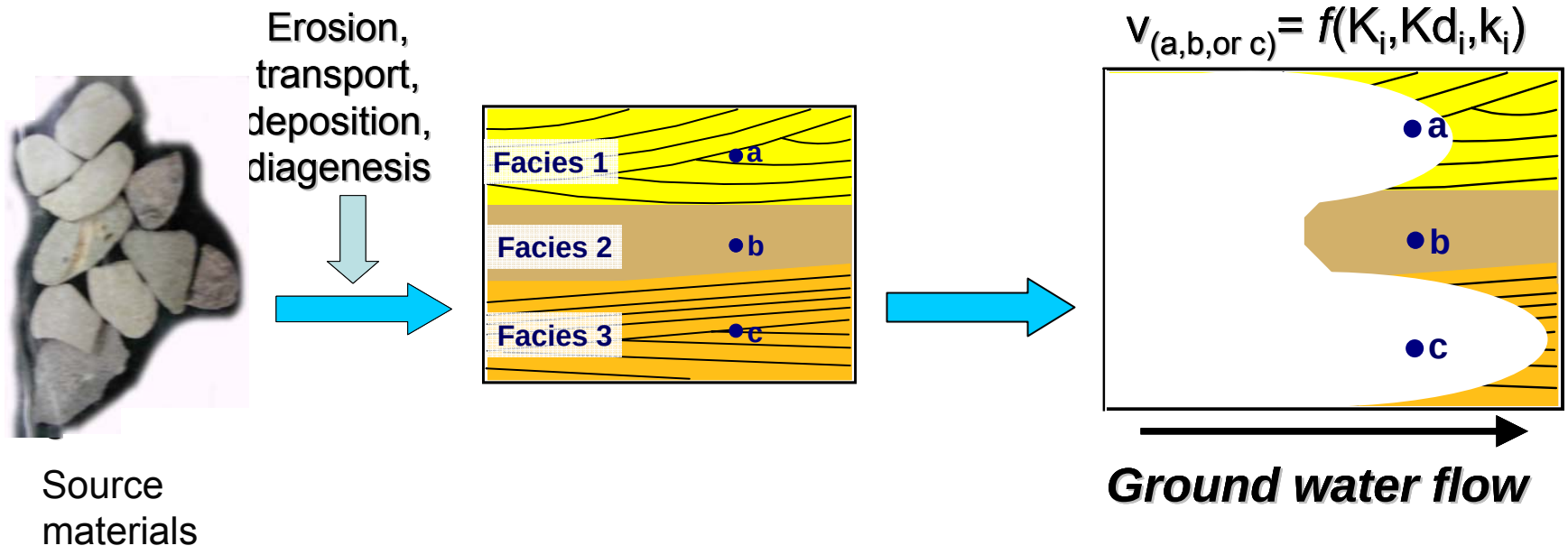
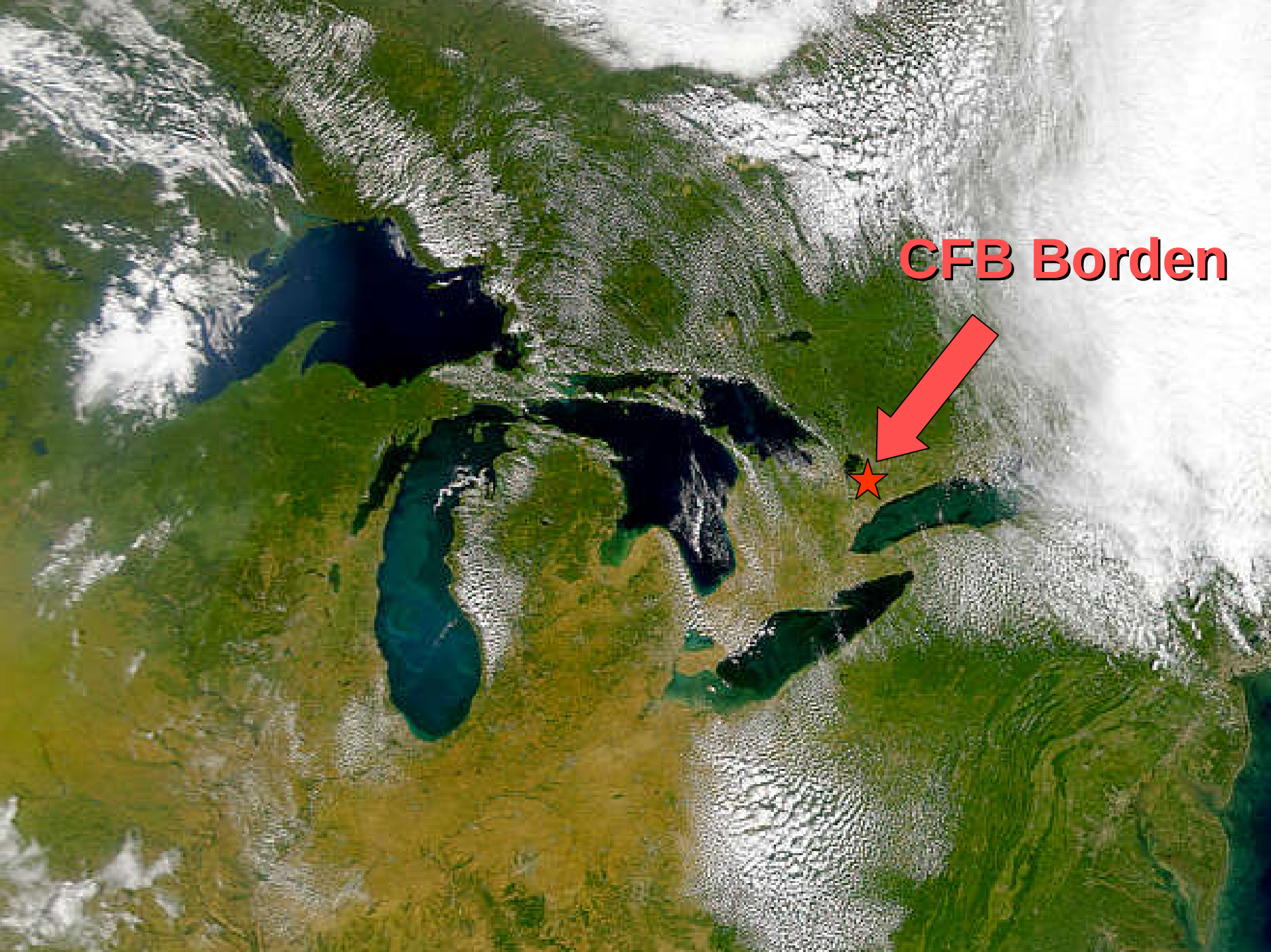
Can geochemical heterogeneity cause nonideal transport?

- Modeling studies suggest importance heterogeneous distributions of aquifer physical and chemical properties
  - grain-scale
  - meso-scale
- Chemical property heterogeneity data for limited; little basis for exploration of the problem based on observations

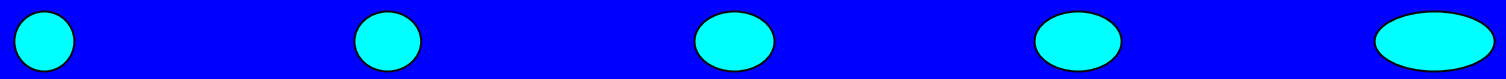
Heterogeneity at multiple scales: a *geologic* perspective



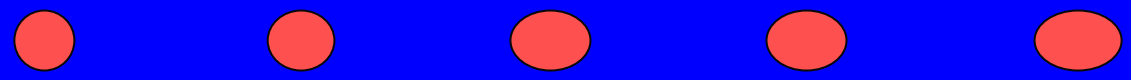

CFB Borden

“Nonideal” reactive solute transport in the S-W test

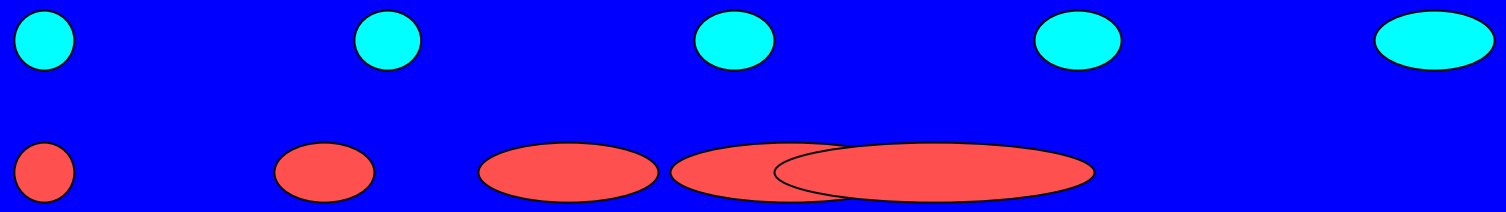
- “Ideal”, $R=v_w/v_r$=constant, α consistent
  - Nonreactive (nonsorbing) tracer



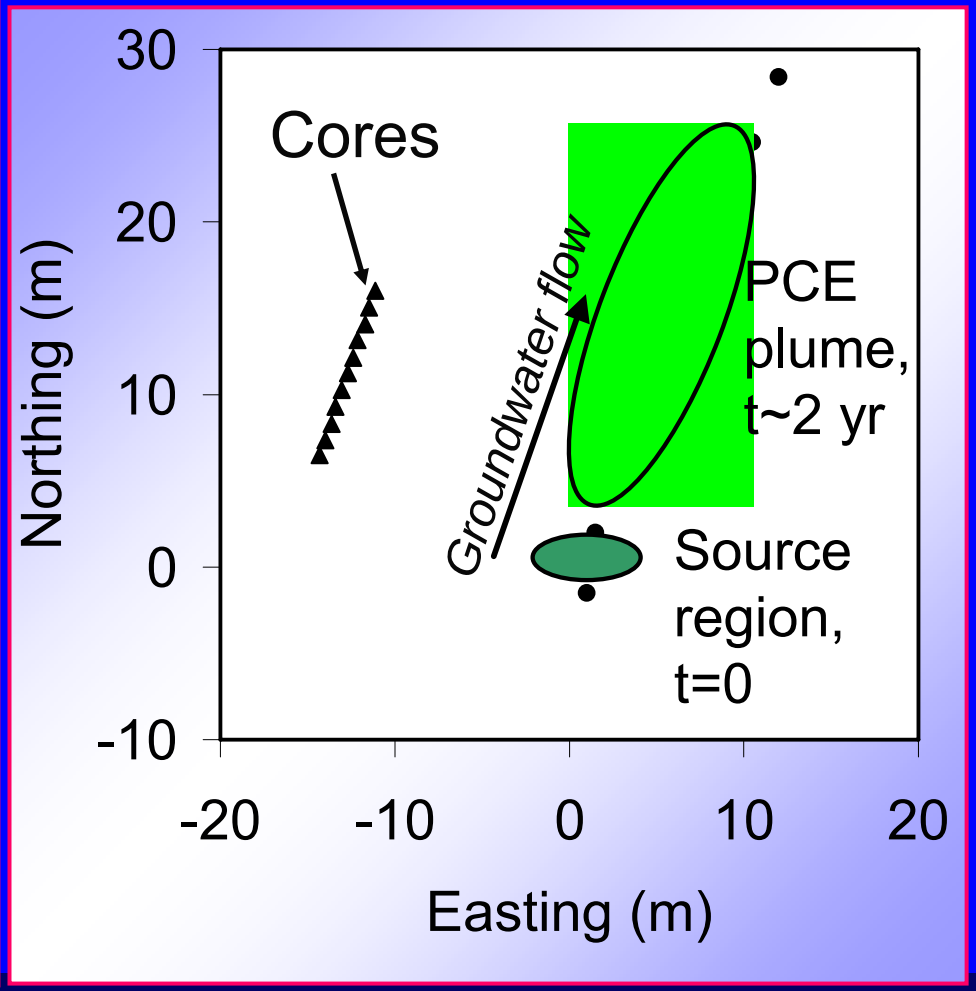
  - Reactive (sorbing) organic contaminant



- “Nonideal” R≠constant, α inconsistent



Sediment cores



How do sediment properties vary spatially?

MCG
massive coarse grained

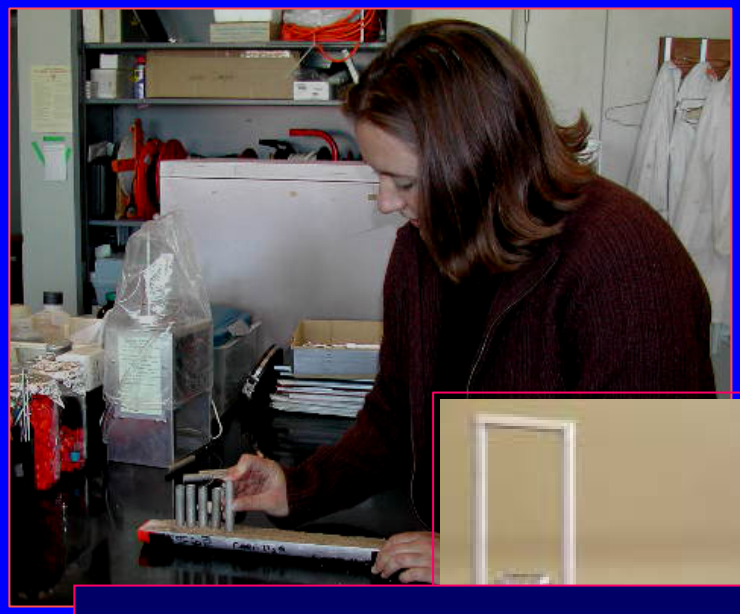
DPL
distinct plane laminated

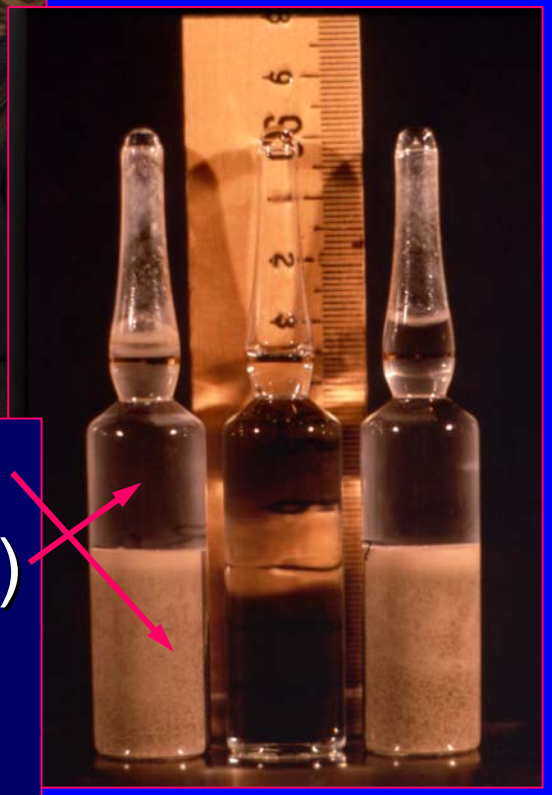
MFG
massive fine grained

CPXS
complex
cross stratified

DPL

Map lithofacies, measure permeability and sorption

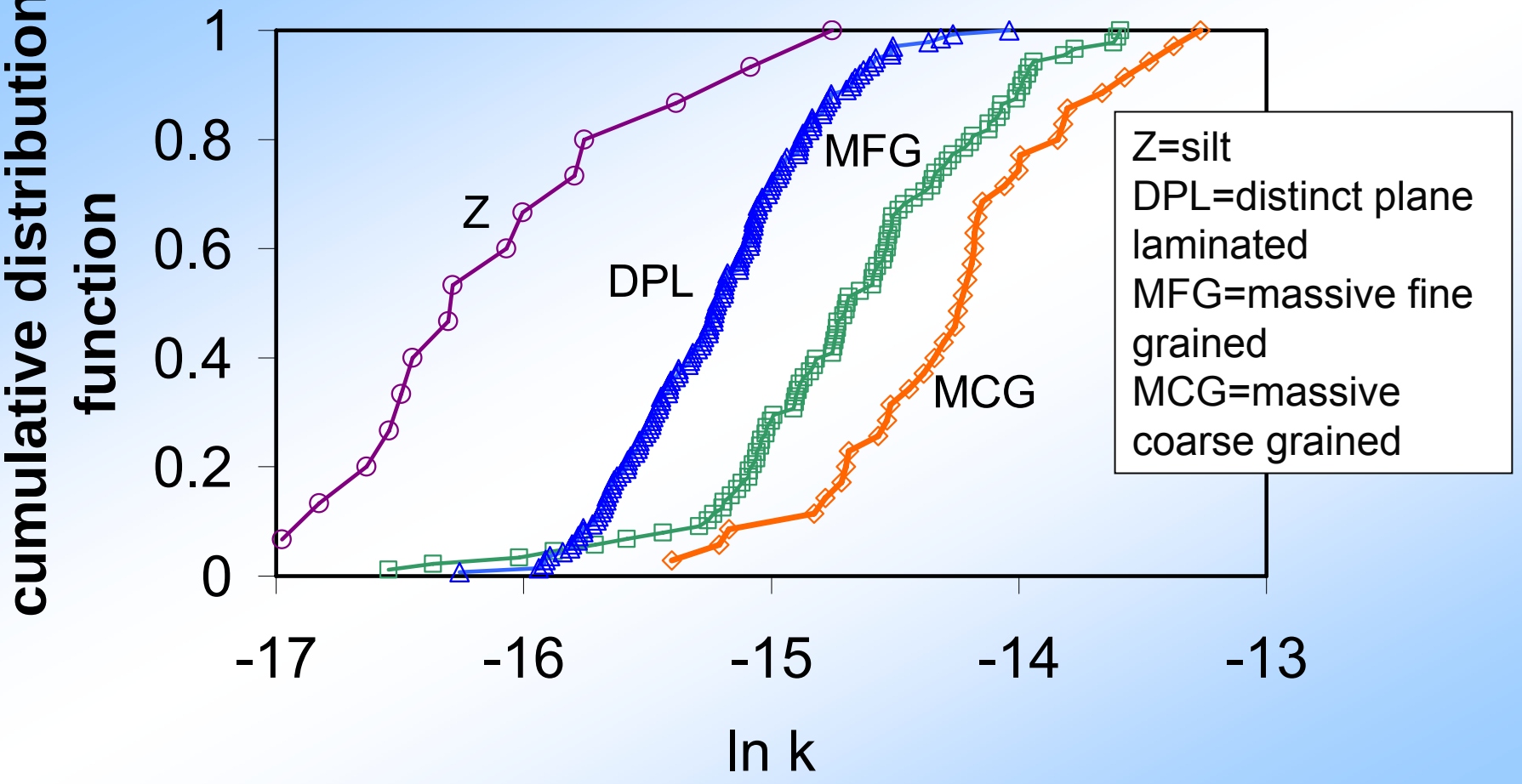




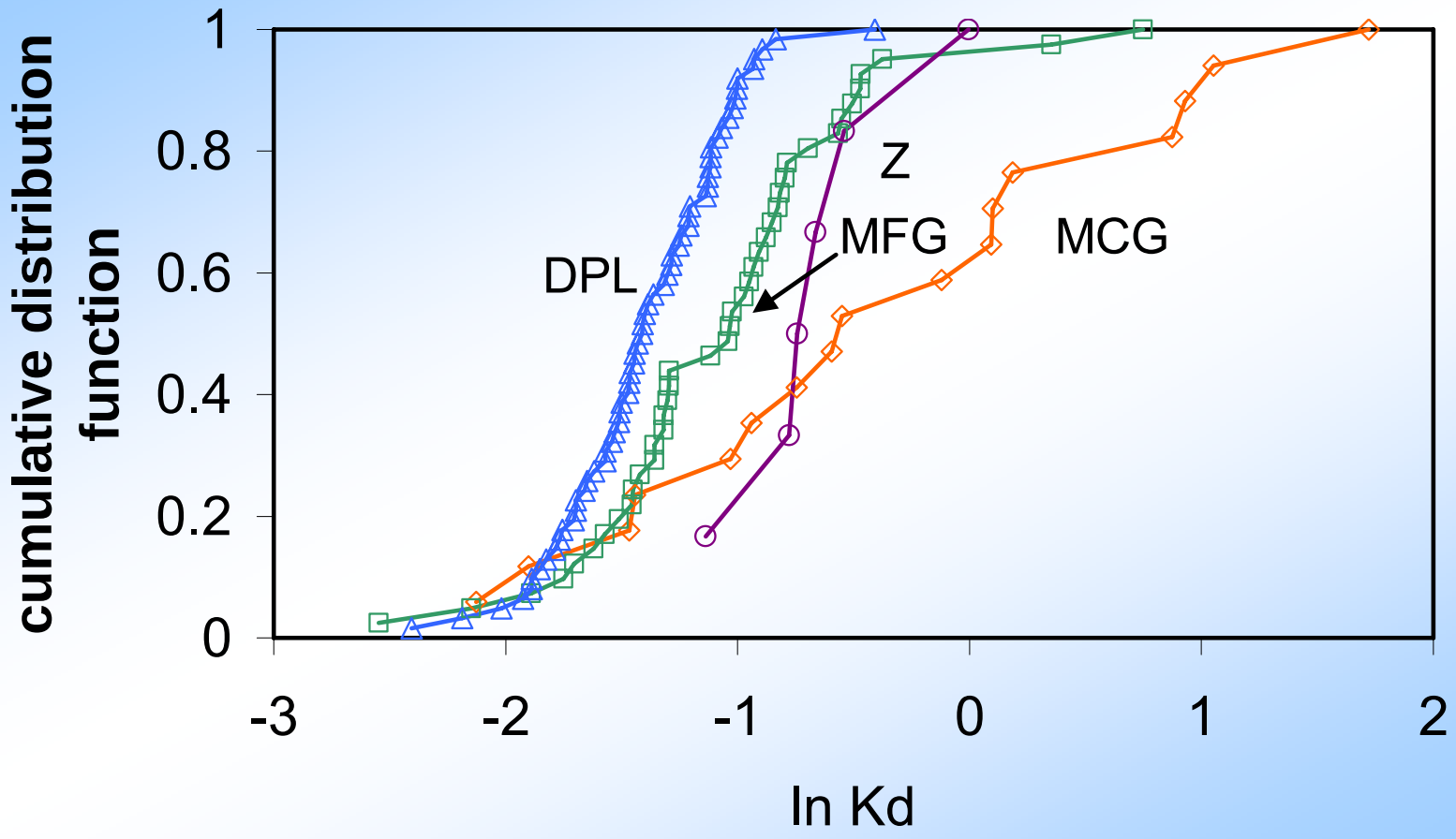
$$Kd = \frac{\text{sorbed PCE concentration (q)}}{\text{dissolved PCE concentration (C)}}$$

$$R = f\,(Kd)$$

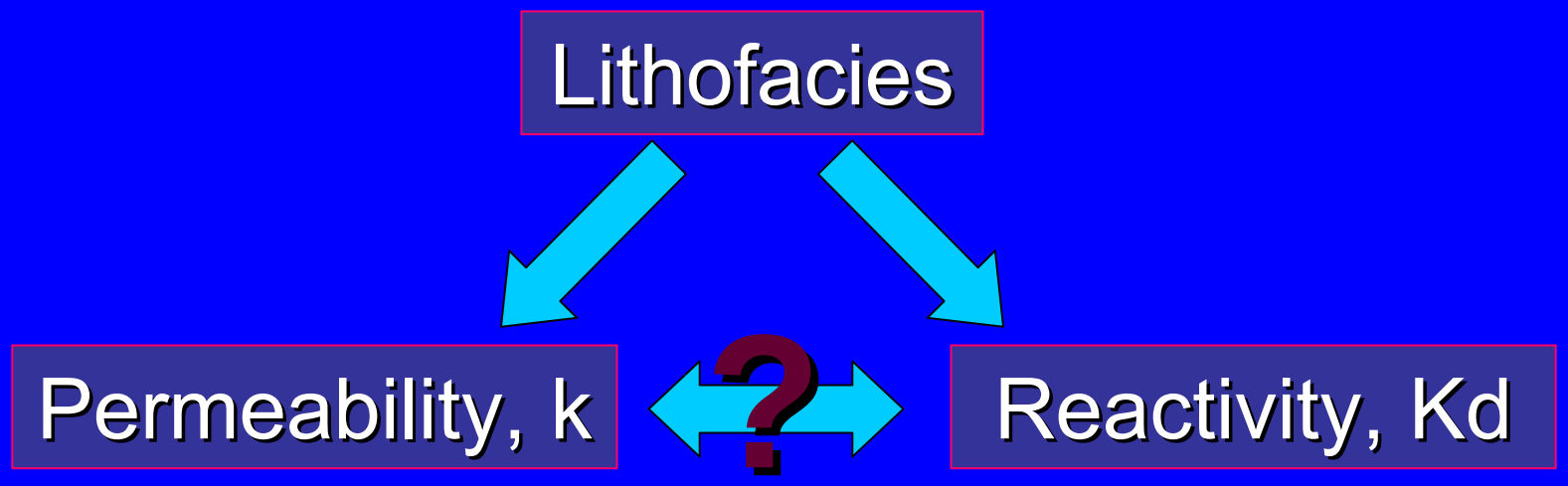
Permeability (k) distribution differs by lithofacies



Some lithofacies have distinct sorption signatures

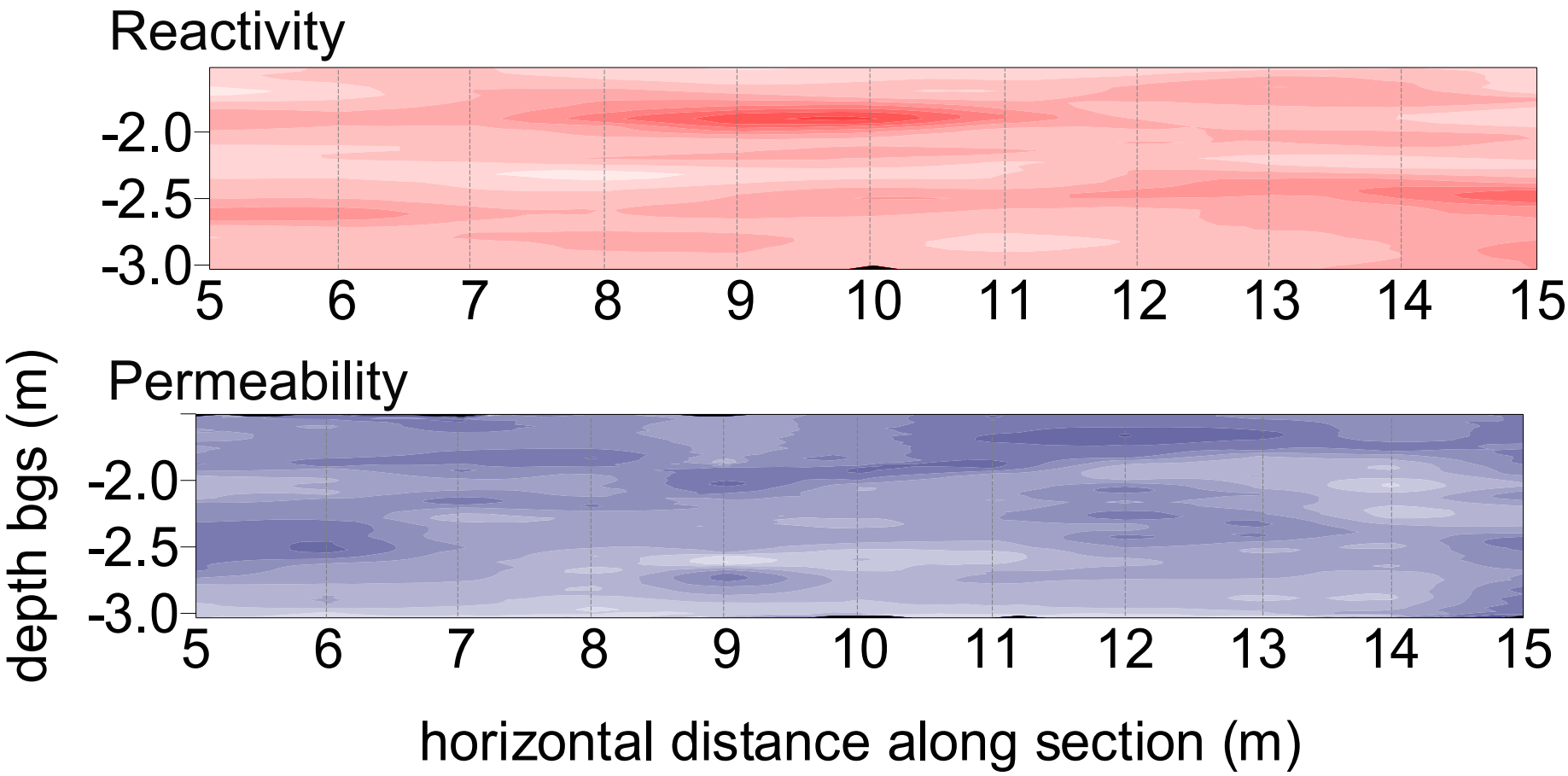


Relations between chemical/physical properties



- We suggest that trends can be explained by differential “averaging” for each property combined with lithologic differences

Variance Kd= Variance k!



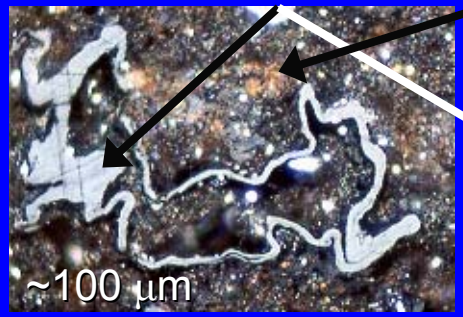
Heterogeneous Borden carbonaceous matter extract

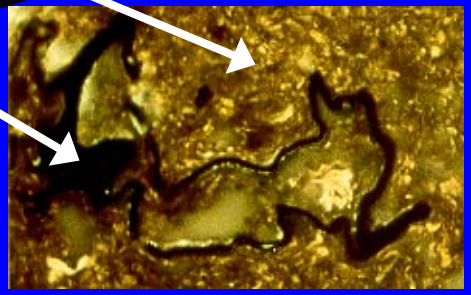
Incident white light

Fluorescence mode

•Amorphous organic matter in network

•Vitrinite in amorphous groundmass





•Fusinite
•Vitrinite (aV) w/ small inertinite (i)

Petrography by Bertrand Louigi, University of Tübingen

Conclusions-combined interpretation of field& lab exps

Nonideal 1st-order transport dynamics are (or may be…) geochemical!

-Heterogeneity at multiple scales may be important in plume scale behavior

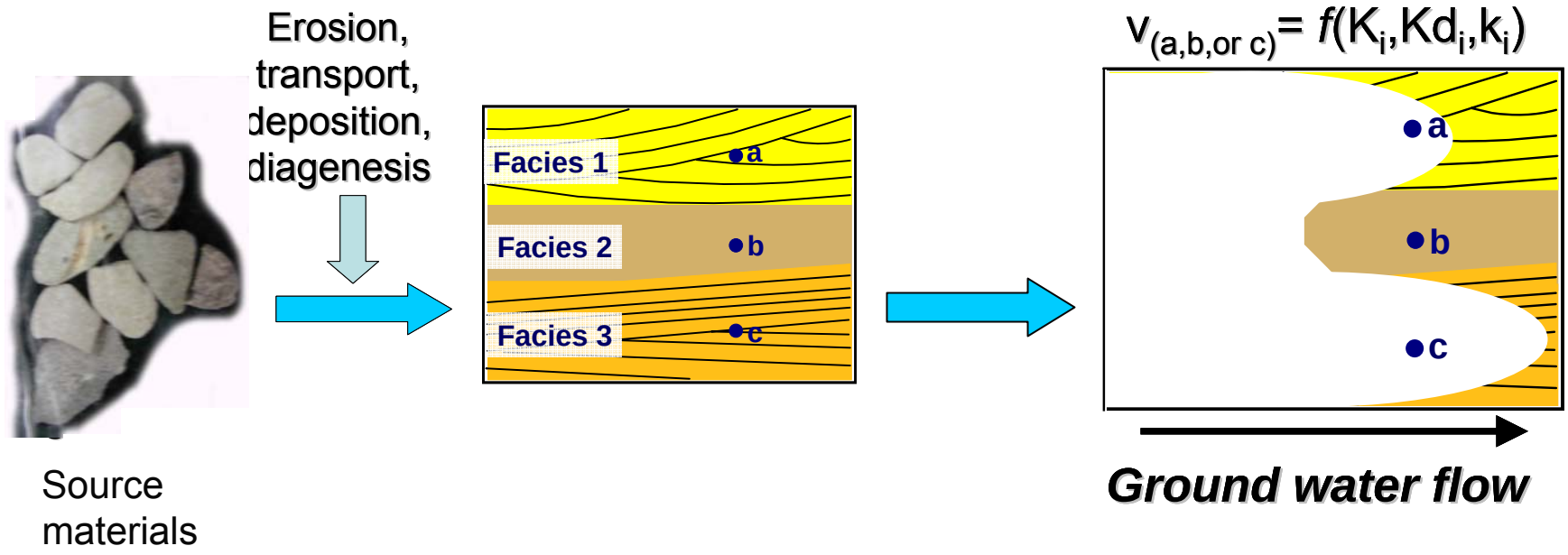
-Extremely small proportion of the total aquifer may exert a control on transport.

Spatial information and underlying geochemical (and physical) sedimentary aquifer properties can be obtained through lithofacies mapping and correlation

Two Central Issues to Start Discussion

- Rational methods to connect point geochemical measurement information within a realistic geologic context
  - What are the relations between what we image and the hydrogeochemical/hydrogeophysical properties that we need to know?
  - How can we develop means to evalulate the correlation between reactivity and permeability within a fmn or unit? Between fmns/units?
- Identification of ‘rate controlling processes’ pertinent to a spatial/temporal scale of interest? (including reaction rates, grain-scale, ‘layer-scale’ processes)

Heterogeneity at multiple scales: a *geologic* perspective



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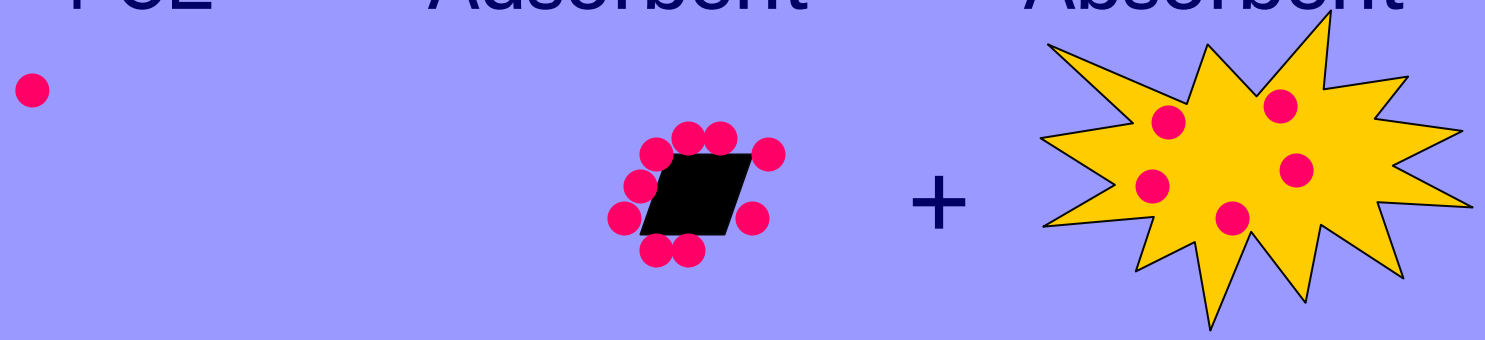
www.geology.buffalo.edu
www.groundwater.buffalo.edu

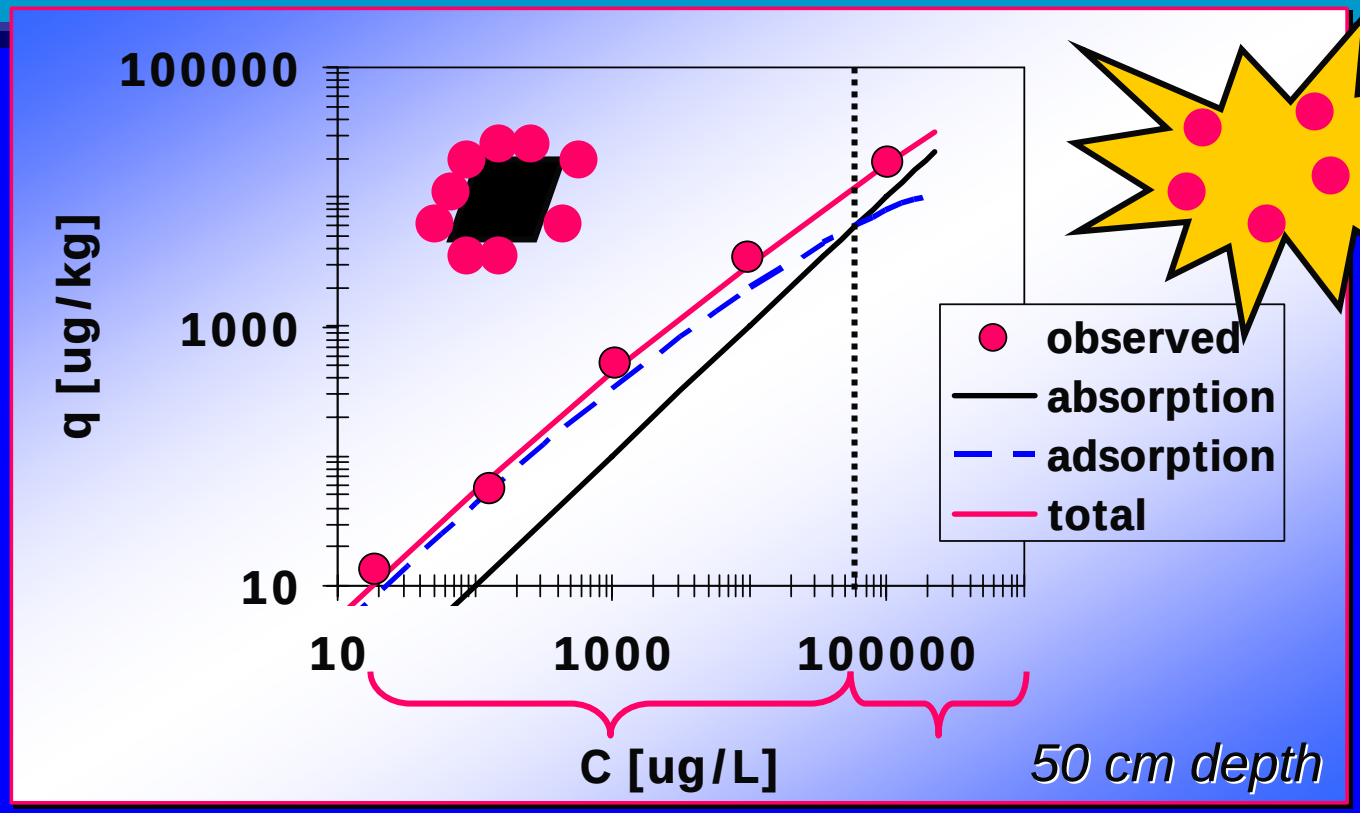
Two carbonaceous phases causing sorption&retardation?

PCE Adsorbent Absorbent



Description:	"hard"	"soft"
Composition:	aromatic	polar groups
HOC Sorption:	"high", n<1	*K*oc*f*oc, n~1
e.g.:	soot, char, hard coal	humic acid

Adsorption dominates when [PCE]<~10,000 mg/L



- Absorption (empirical) dominates when [PCE]>~10,000 mg/L
- 'Hard C' α $CaCO_3$ content

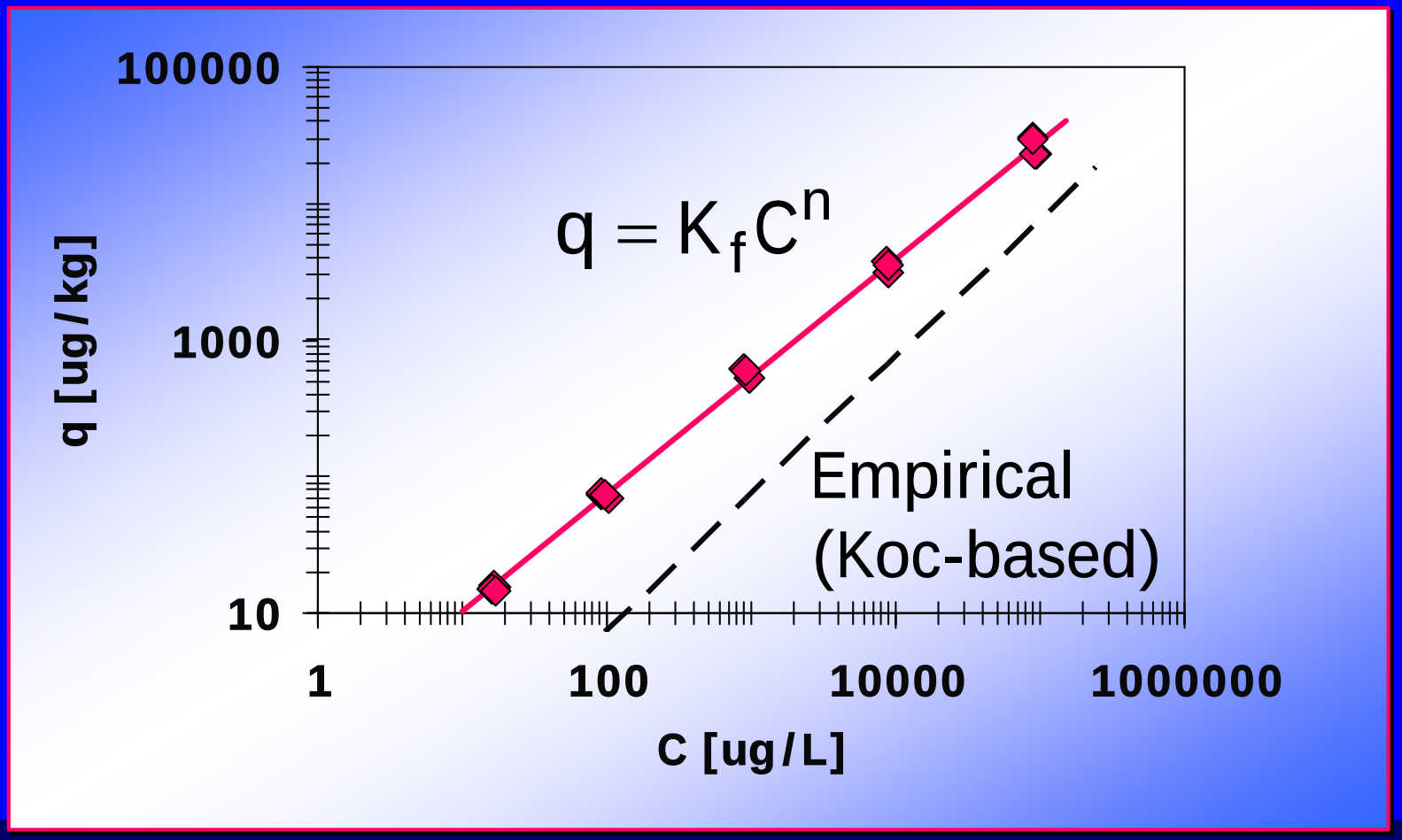
Transport implications

- "Lenses" of high sorption will result in enhanced plume-scale dispersivity for reactive solutes
- Geochemical control of plume dynamics consistent with this distribution!

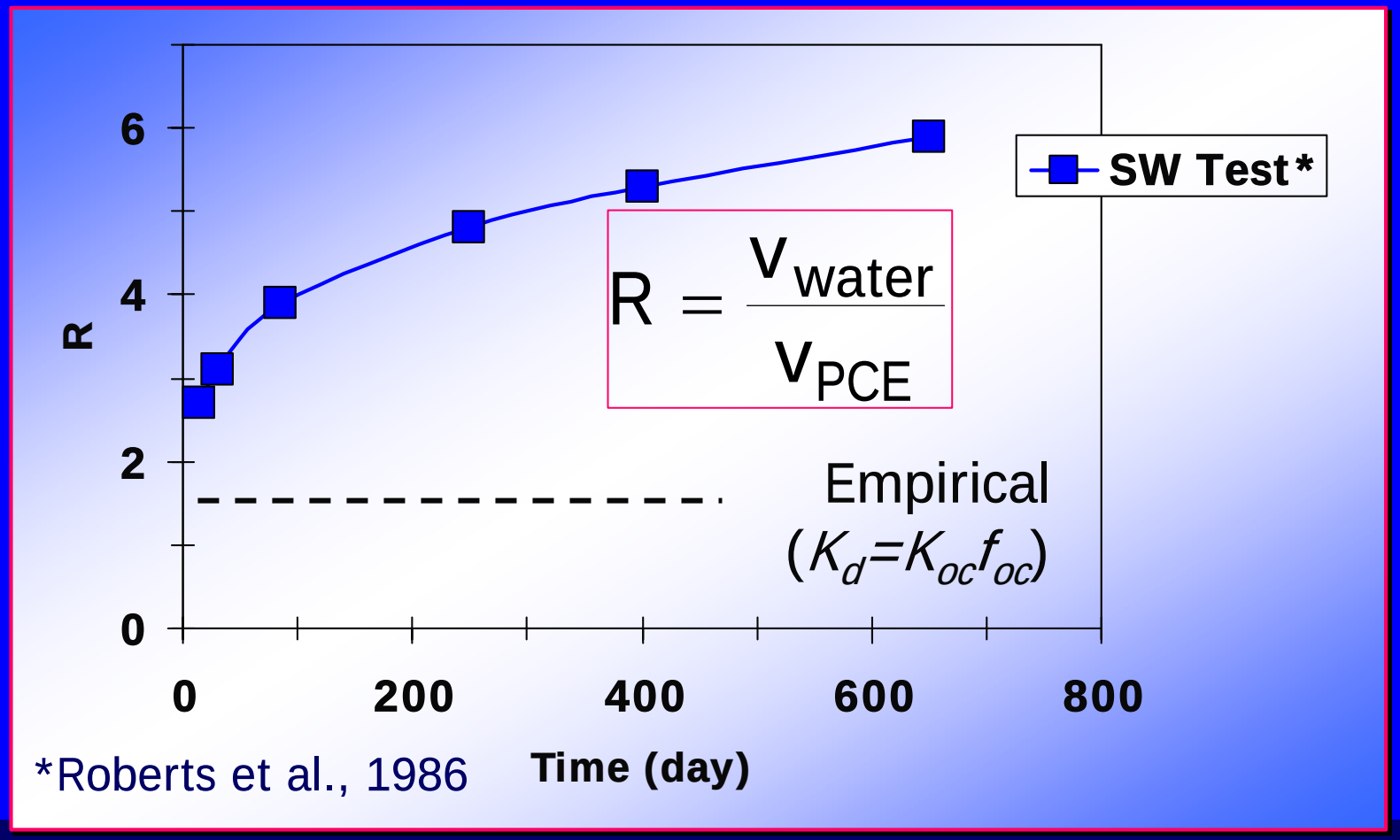
Is micro-scale chemical heterogeneity important to R prediction?

- What is the sorbent causing contaminant retardation?
- Where is the sorbent?
- What are the characteristics of sorbent interactions with PCE?

Sorption depends nonlinearly on concentration (n<1)



“Nonideal” organic contaminant plume deceleration



*Roberts et al., 1986