Reactive Transport Modeling of U(VI) Migration at the Naturita Site

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Conceptual Model Development and Reactive Transport Modeling for the 300 Area Uranium Plume in 300-FF-5

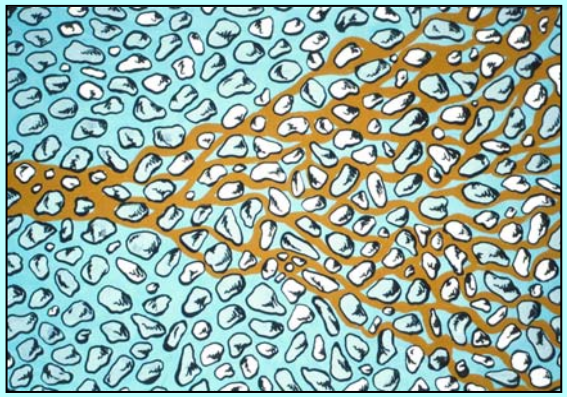
May, 2004

USGS
science for a changing world

Acknowledgements

- Field Support:
  - Dave Naftz, Geoff Freethy, Chris Wilkowske, Ryan Rowland, Walt Holmes, Charoen Sanpawanitchakit, Amaranta Marcuello, John Lenhart, Jennifer Joye, Martine van den Heuvel,Doug Kent, Chris Fuller
- US Nuclear Regulatory Commission

Groundwater Flow and Mixing



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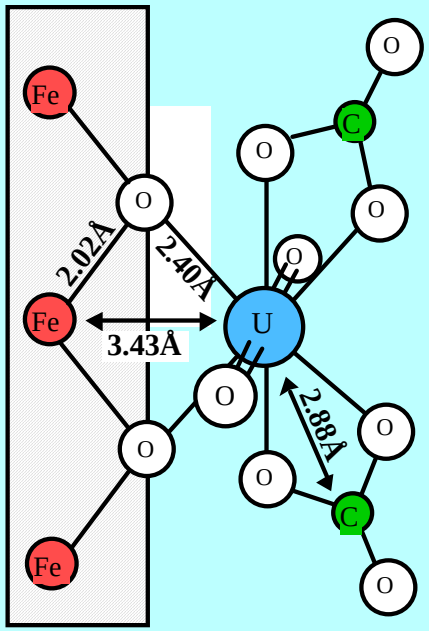
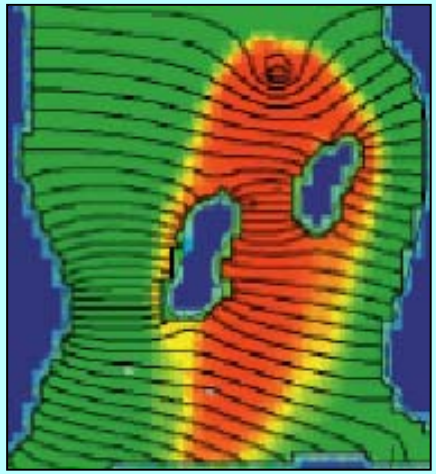
Reactive Processes

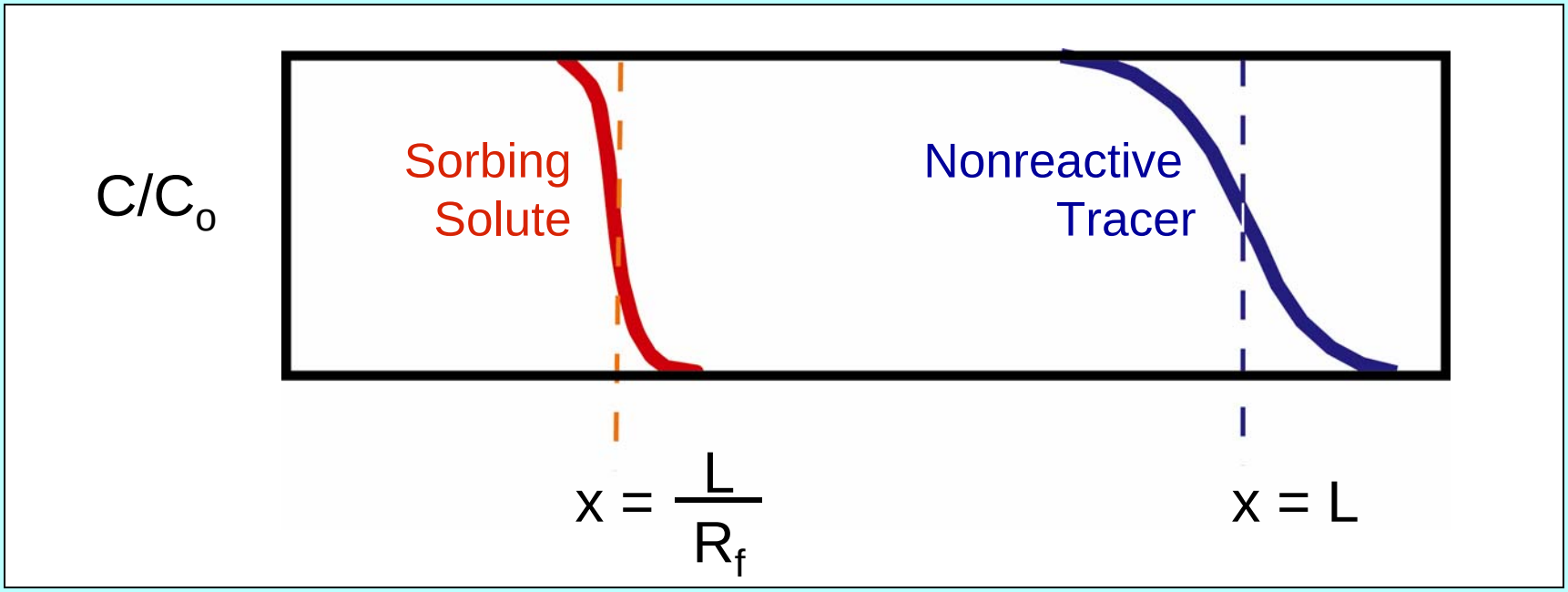


Field Scale Reactive Solute Transport



Radiological Risk Assessment

If adsorption is linear a retardation factor can be related to a distribution coefficient (K_d value) for adsorption

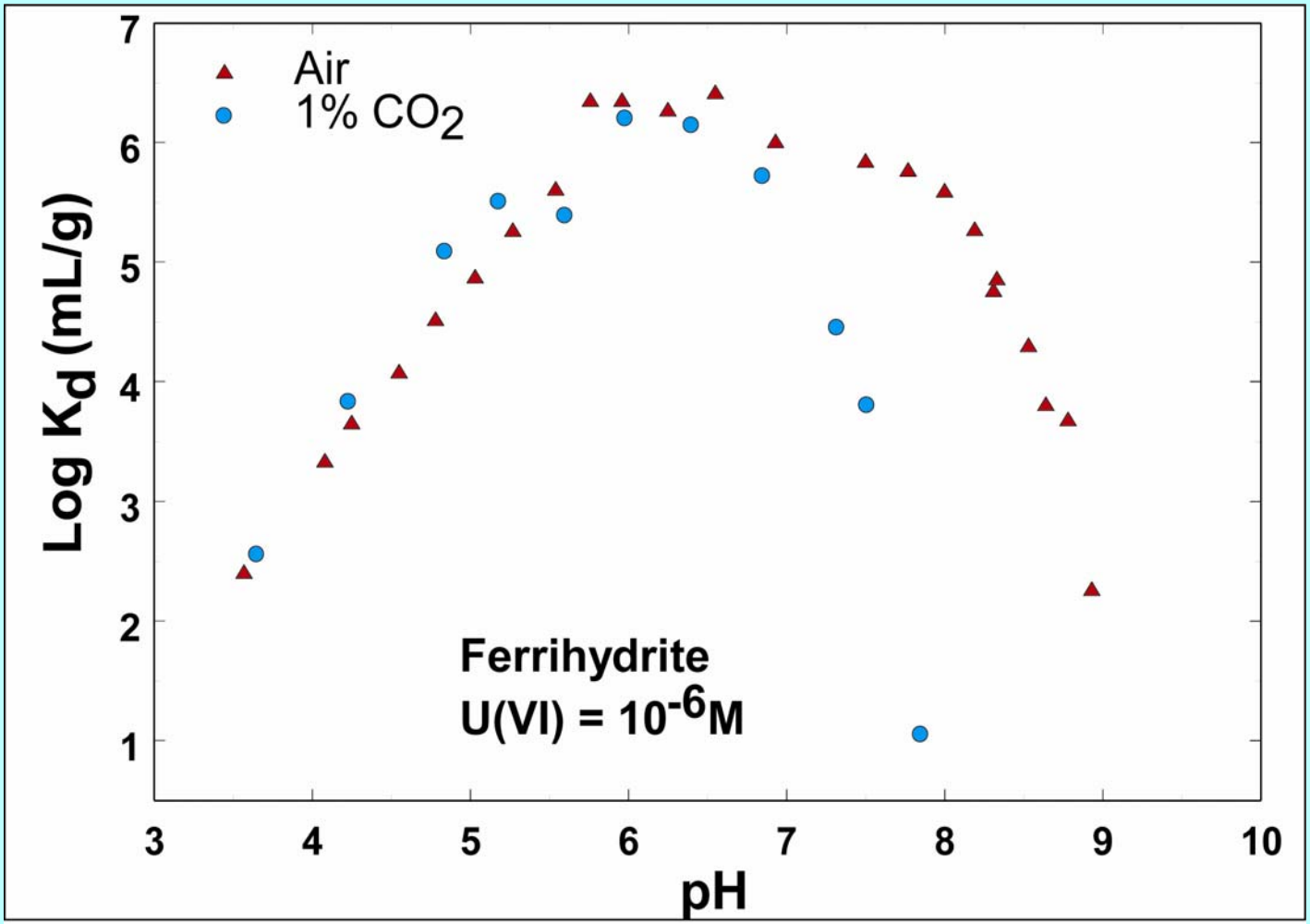


$$R_f = 1 + \frac{\rho_b}{\theta} K_d$$

$$K_d = \frac{C_{ADS}}{C_{AQU}}$$

Freeze and Cherry, Groundwater, 1979

K_d values for uranium(VI) adsorption on ferrihydrite from batch adsorption experiments



K_d values for uranium(VI) adsorption are very dependent on both pH and complexation with carbonate anions

Conceptual Models for Adsorption Reactions in Solute Transport Modeling

Constant chemistry
linear adsorption

Constant chemistry
nonlinear adsorption

Variable chemistry
aqueous speciation
reactions
nonlinear adsorption

K_d

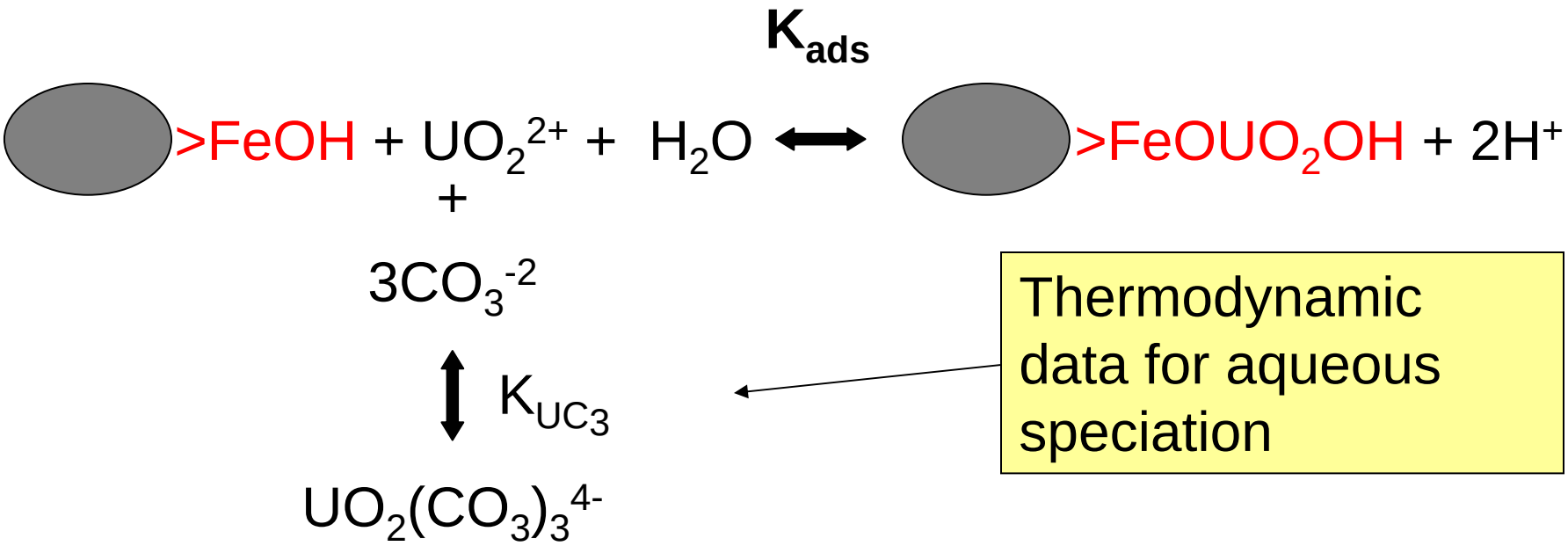
Common agency
approach

Nonlinear isotherms

(eg Freundlich)

Surface
complexation
models

Surface and Aqueous Complexation Modeling



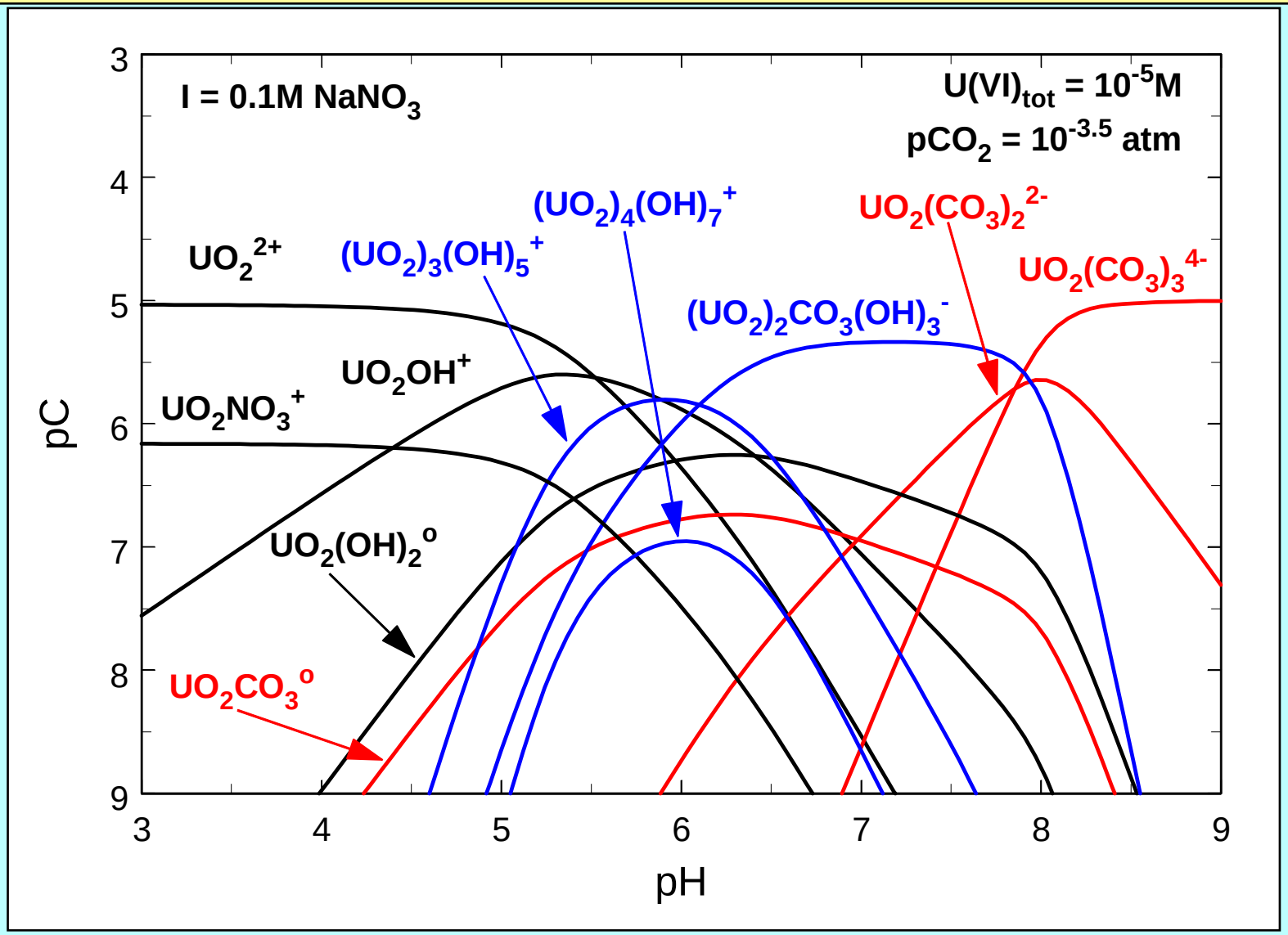
Thermodynamic data for aqueous speciation

$$K_{ads} = \frac{[FeOUO_2OH](H^+)^2}{[FeOH](UO_2^{+2})}$$

$$K_d = \frac{\text{Adsorbed}}{\text{Aqueous}} = \frac{[FeOUO_2OH]}{[U(VI)]_{AQ}} = f(K_{ads}, U(VI)_T, pH, FeOH_T, CO_3^{-2})$$

U(VI) aqueous speciation as a function of pH

Total dissolved U(VI) = 10^{-5}M; equilibrium with air



Conceptual Models for Surface Complexation in Natural Systems

Science

Forward Modeling Approach

- Quantify number of quartz, goethite, feldspar, clay, etc, sites
- Use published SCMs

Produces site specific predictive adsorption model

Engineering

Inverse Modeling Approach

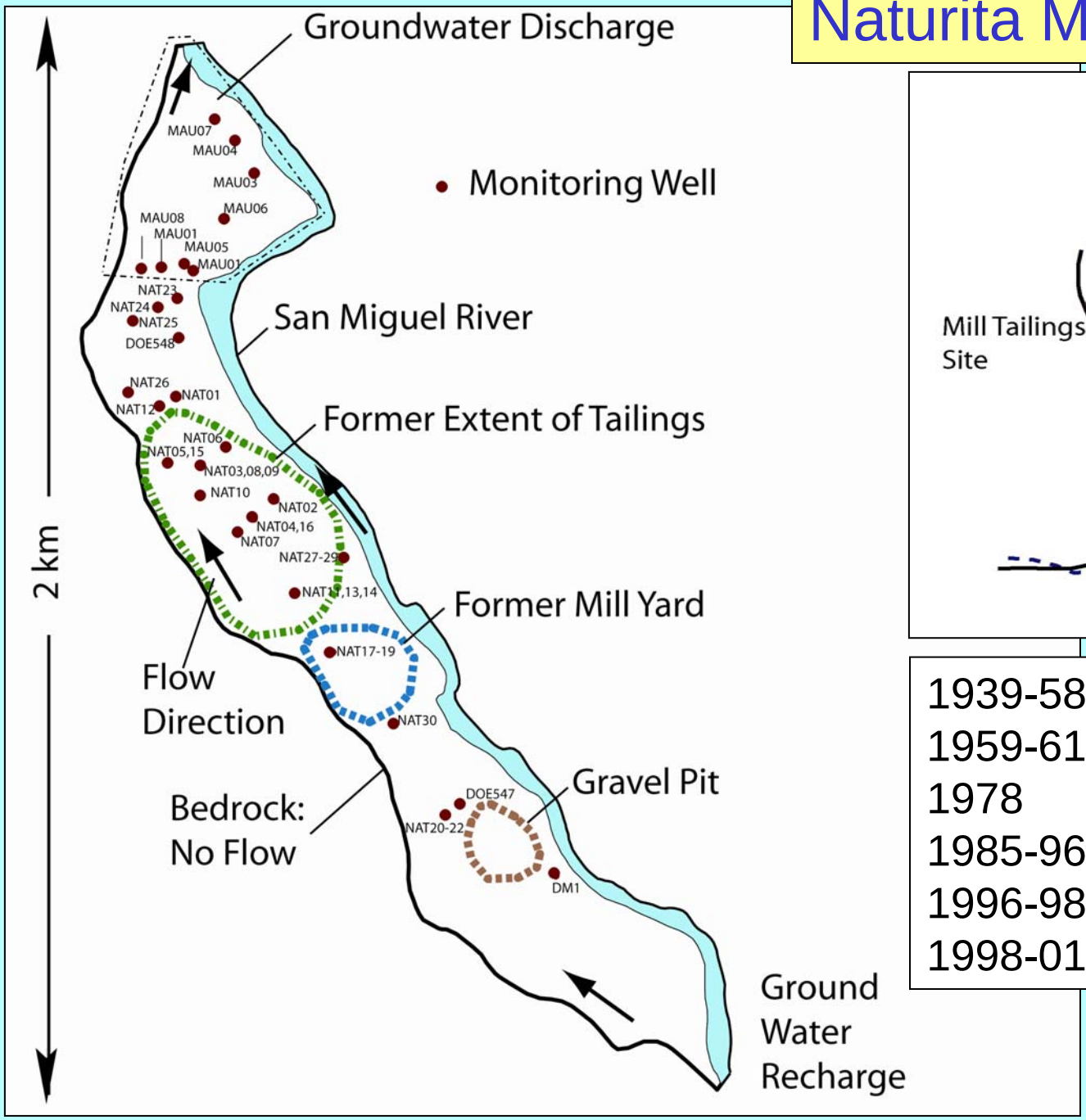
- Collect adsorption data relevant to field conditions
- Assume generic surface sites
- Use inverse models (eg FITEQL) to choose reactions and estimate parameters

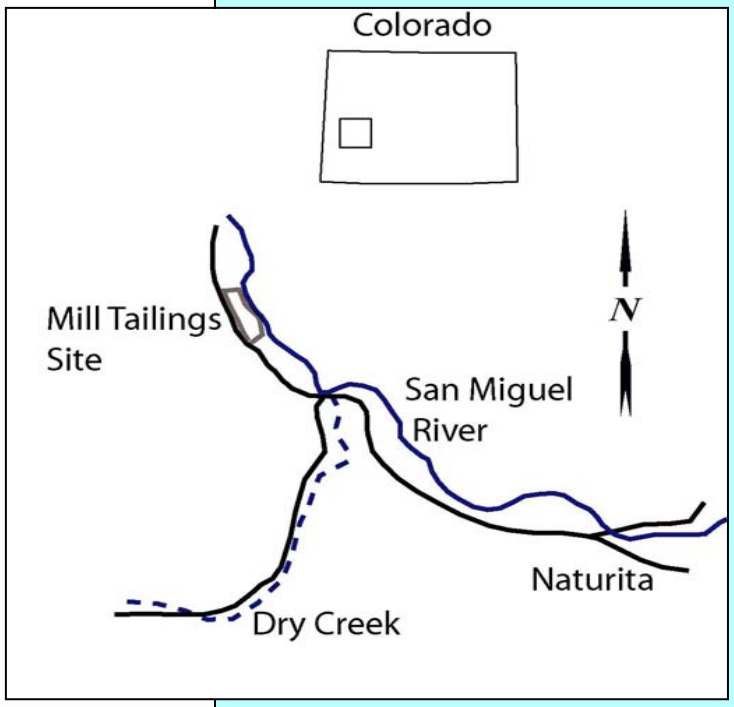
Produces site specific semi empirical adsorption model

Development and testing a surface complexation model for natural sediments

1. Characterize flow and geochemistry
2. Measure U(VI) adsorption on uncontaminated sediments
3. Fit SCM adsorption stoichiometry and log Ks
4. Field Tests of the SCM
    a.) uncontaminated sediments
    b.) contaminated sediments
5. Reactive Solute Transport Modeling
    a.) calibration
    b.) model assessment
    c.) comparison of K_D and SCM approaches

Naturita Mill Tailings Site

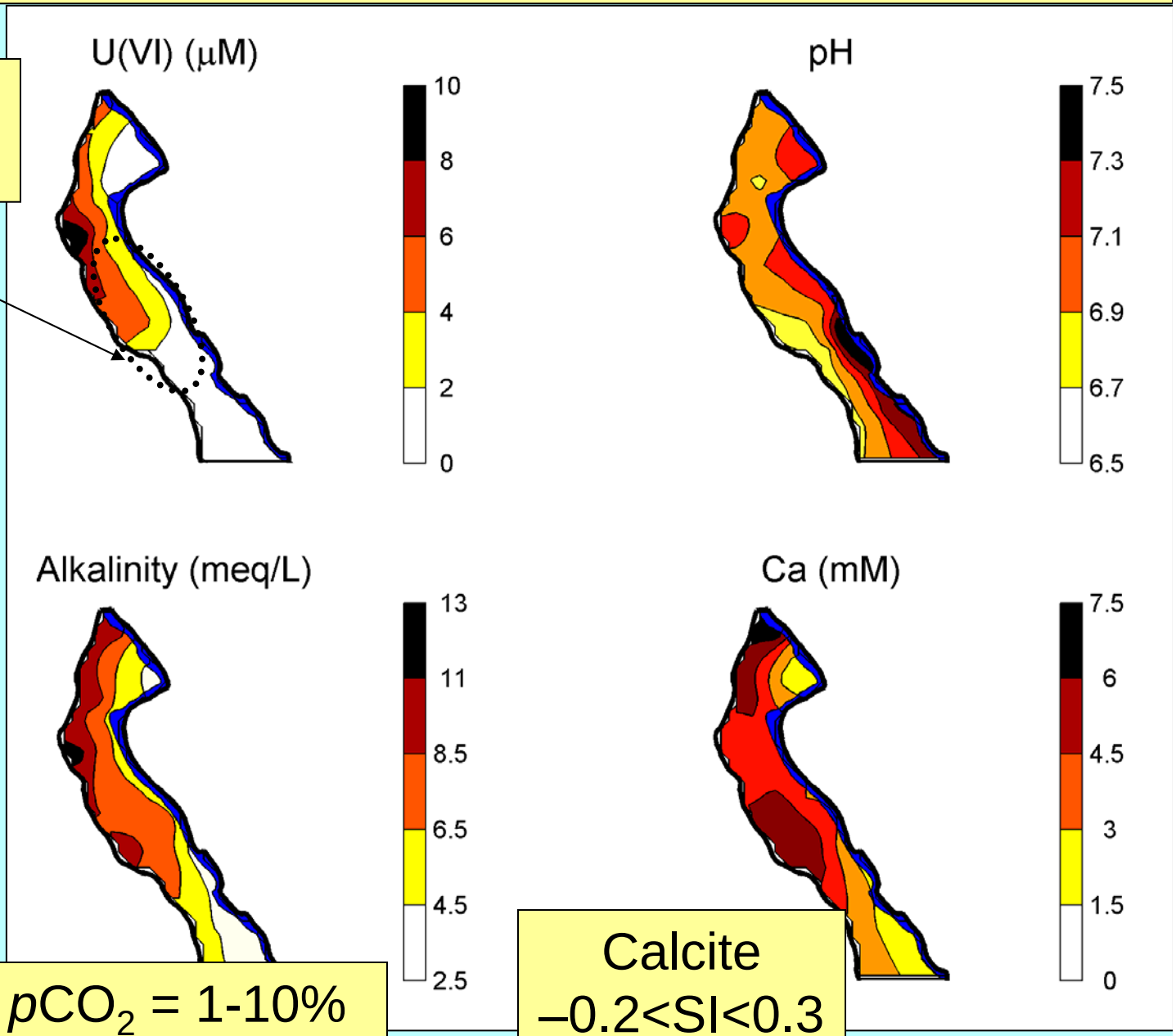




1939-58	Mill operation
1959-61	Ore buying station
1978	Tailings removed
1985-96	DOE monitoring
1996-98	Soils removed
1998-01	USGS studies

Concentration contour plots, Naturita aquifer, Sept. 1999

Location of tailings and mill



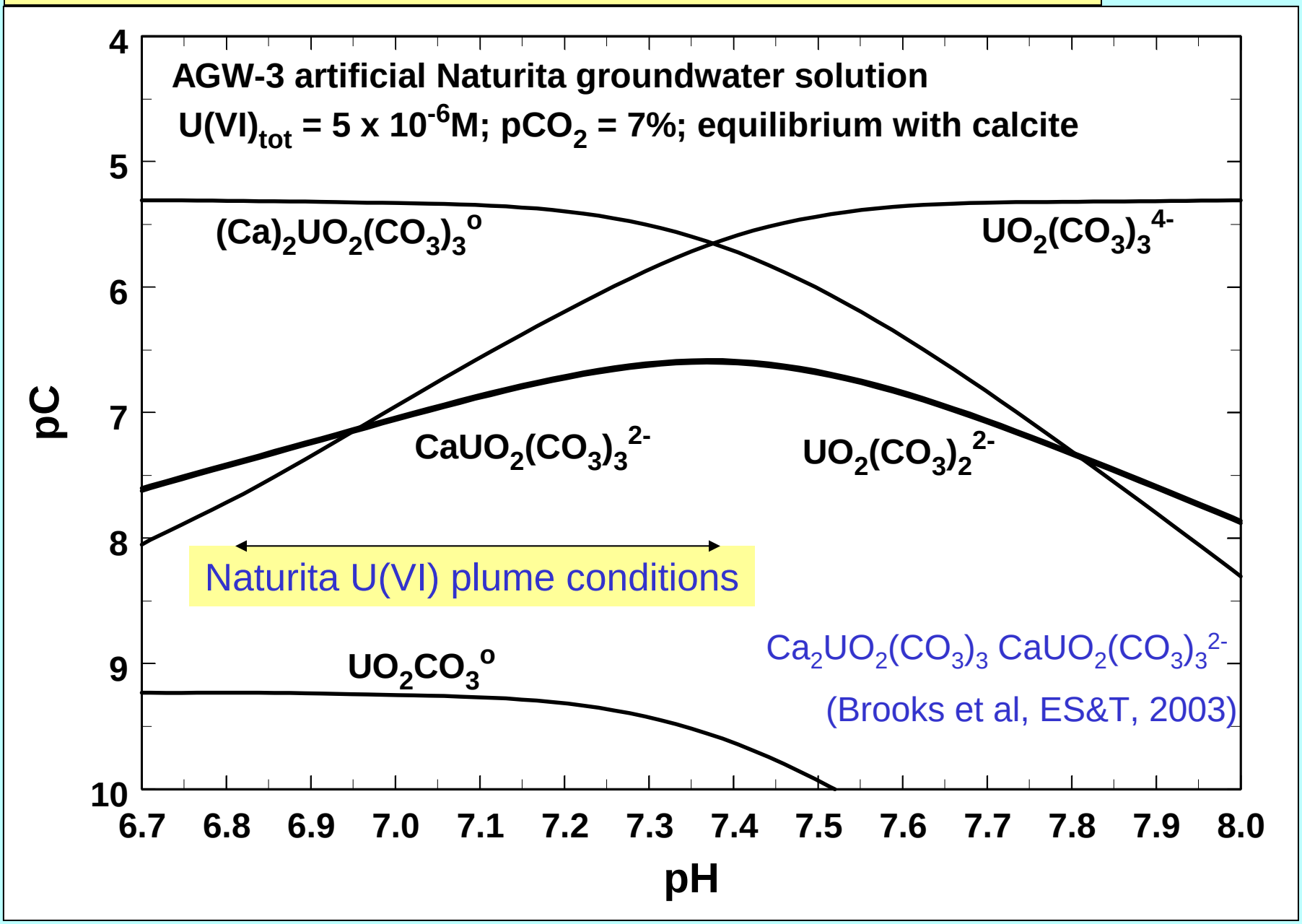
River water:

pH = 8.6
Alk = 2.3
Ca = 1.8
U(VI) = 0.01

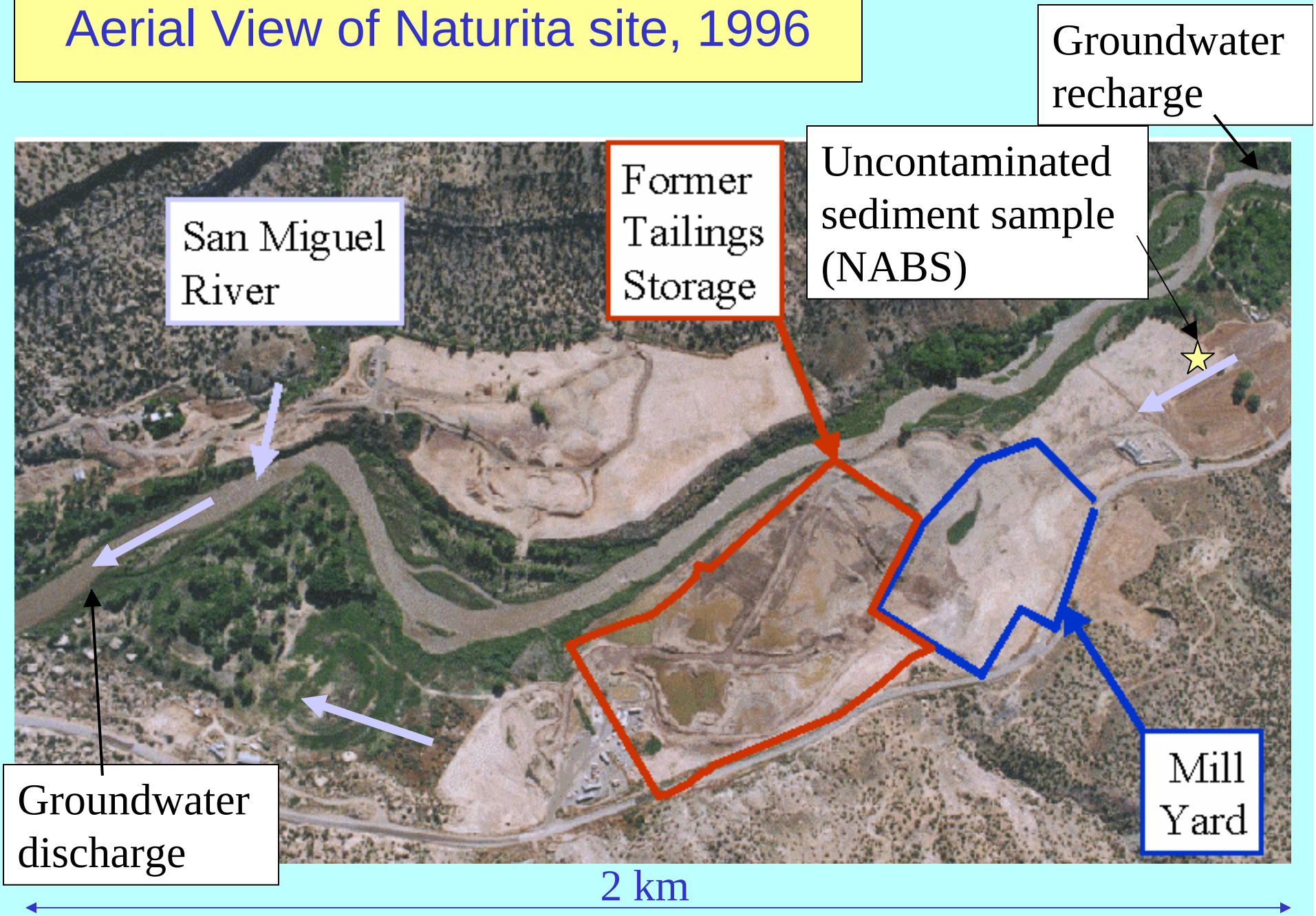
pCO_2 = 1-10%

Calcite
–0.2<SI<0.3

Aqueous speciation of Naturita groundwater



Aerial View of Naturita site, 1996



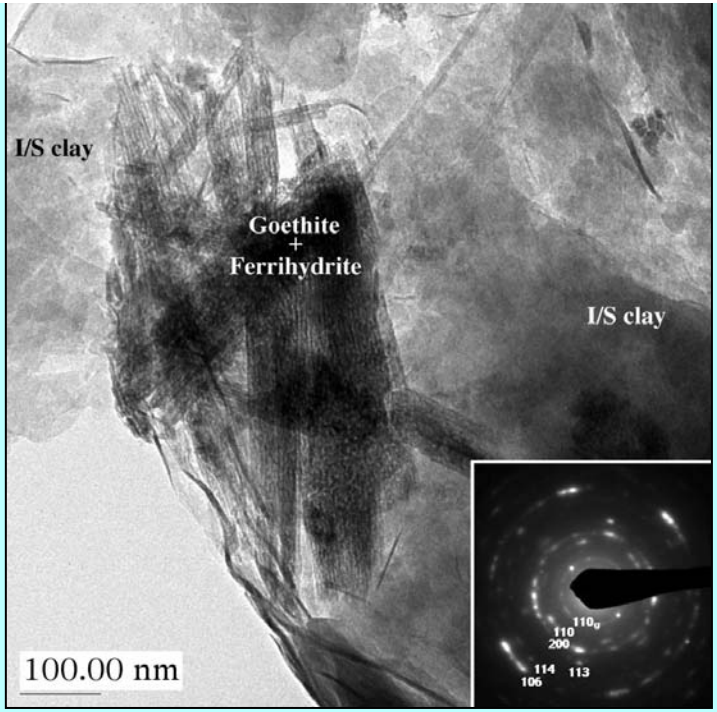
Source of Naturita Aquifer Background Sediment (NABS)

~50% of aquifer is cobbles > 6.4 cm

~ 15% of sediment <3mm and had ~85% of sorption

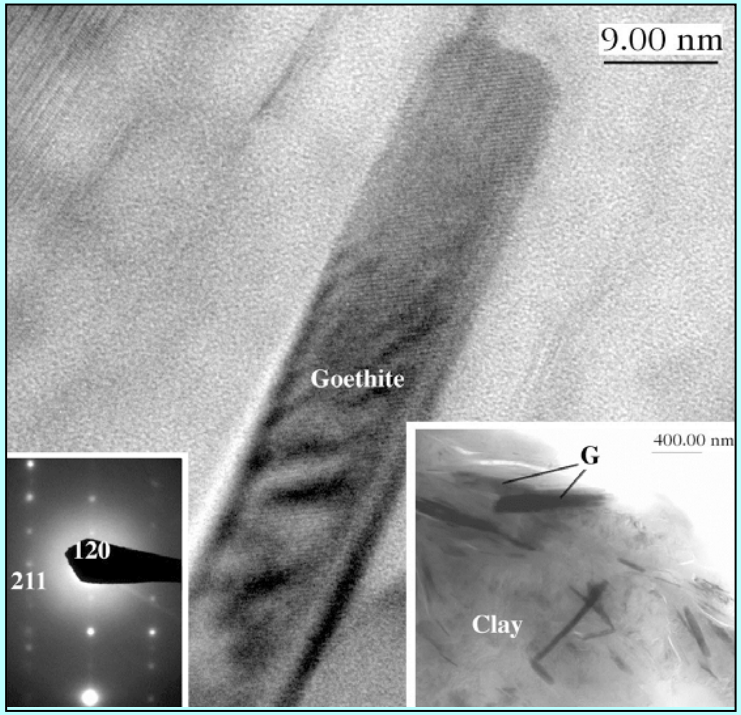
Naturita aquifer sediment: quartz, feldspars, calcite, iron oxides, illite, smectite, etc.

NABS Surface Coatings



Low-magnification TEM image of goethite immersed in surface coating of illite/smectite (I/S) clay.

Electron diffraction pattern indicative of a mixture of ferrihydrite and goethite

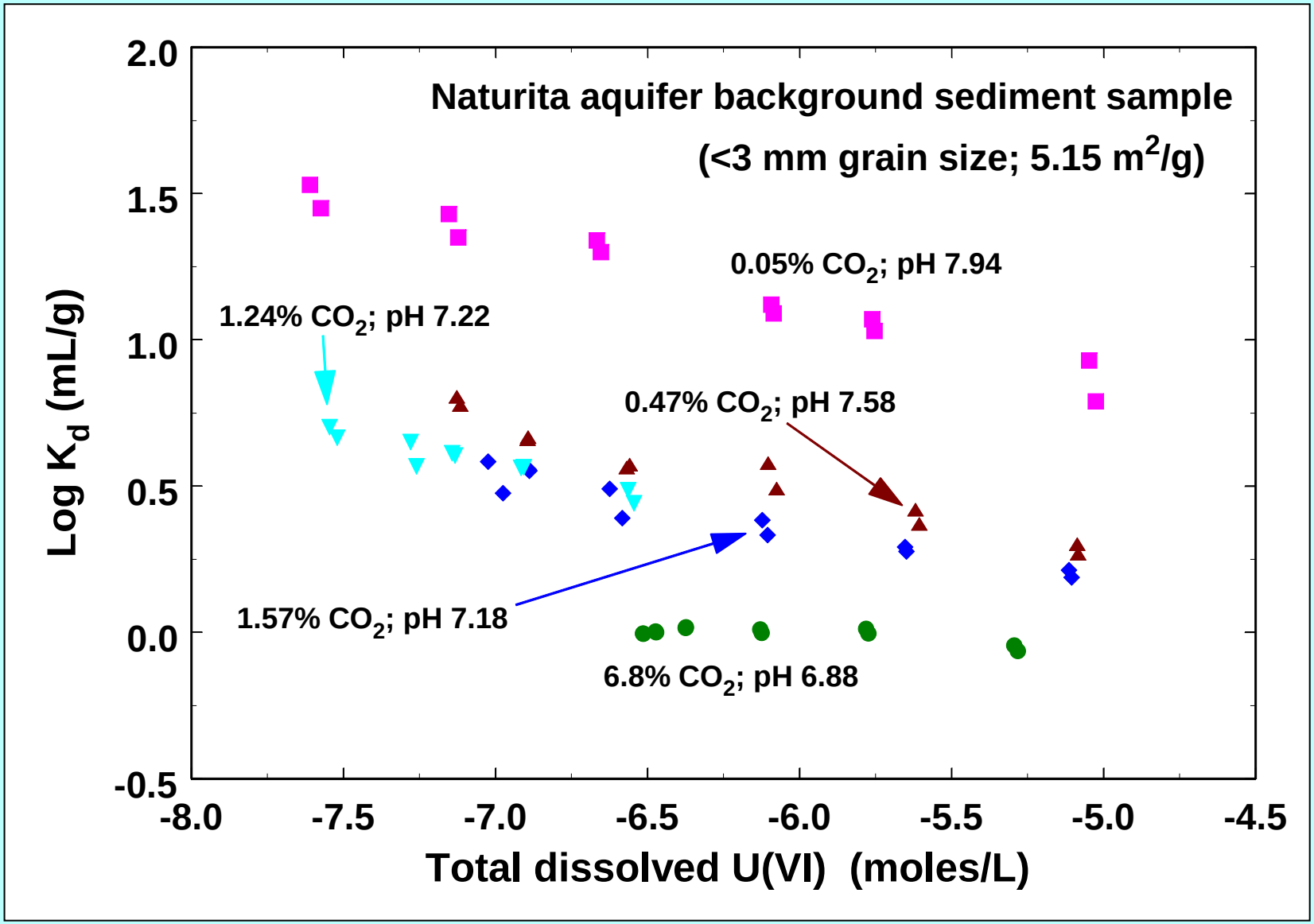


Bright-field TEM images showing needle-like goethite crystals immersed in I/S clay matrix

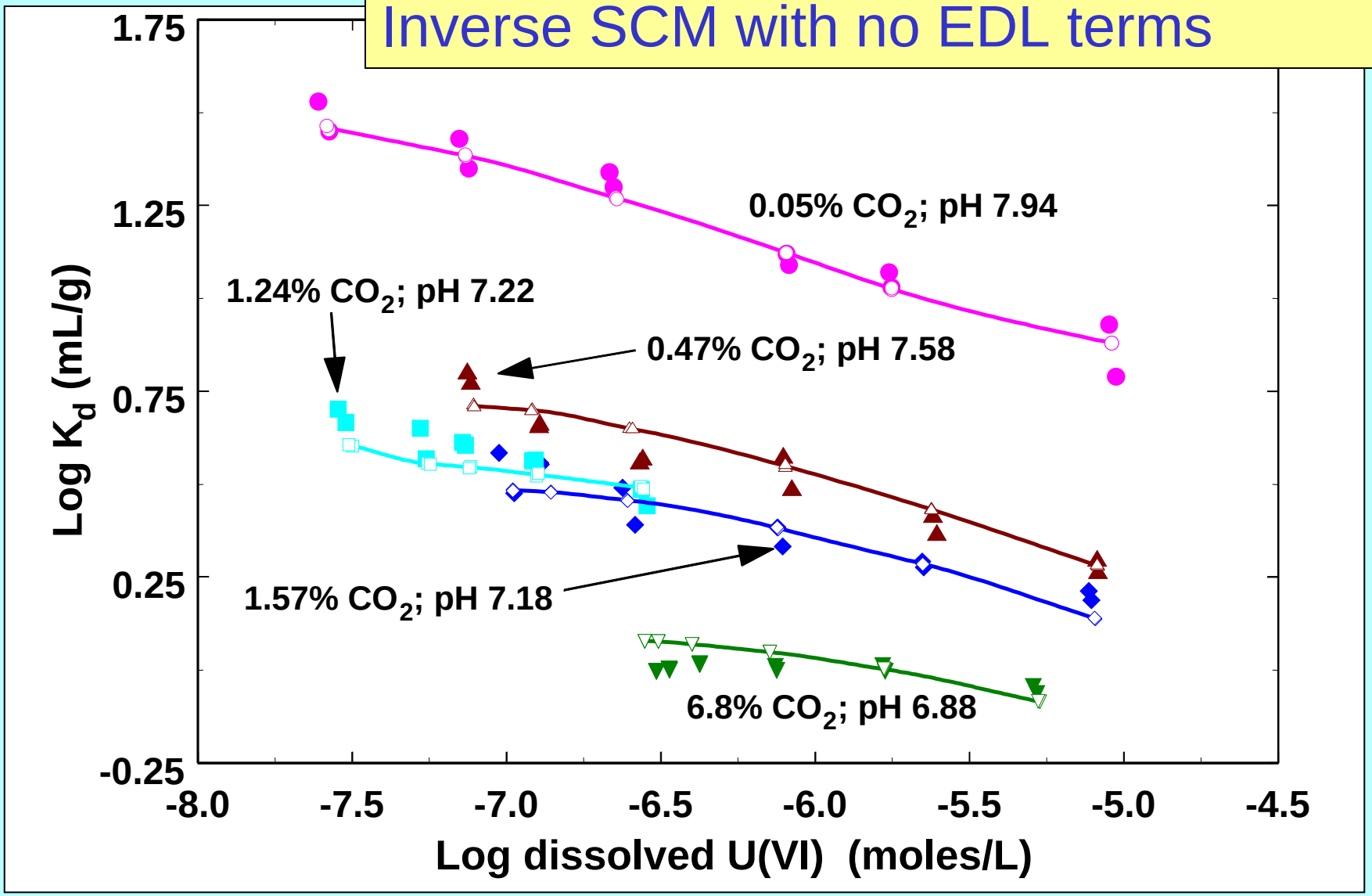
Low magnification TEM image showing many goethite (G) needles

Images from Jove-Colon et al. (2004)

Experiments with artificial groundwater



Inverse SCM with no EDL terms



Model has 2 reactions:

$$\equiv S(OH)_2 + UO_2^{2+} = \equiv SO_2HUO_2^{+} + H^{+}$$

$$\equiv S(OH)_2 + UO_2^{2+} = \equiv SO_2UO_2 + 2H^{+}$$

Model has 3 site types

Independent tests of the semi-empirical SCM

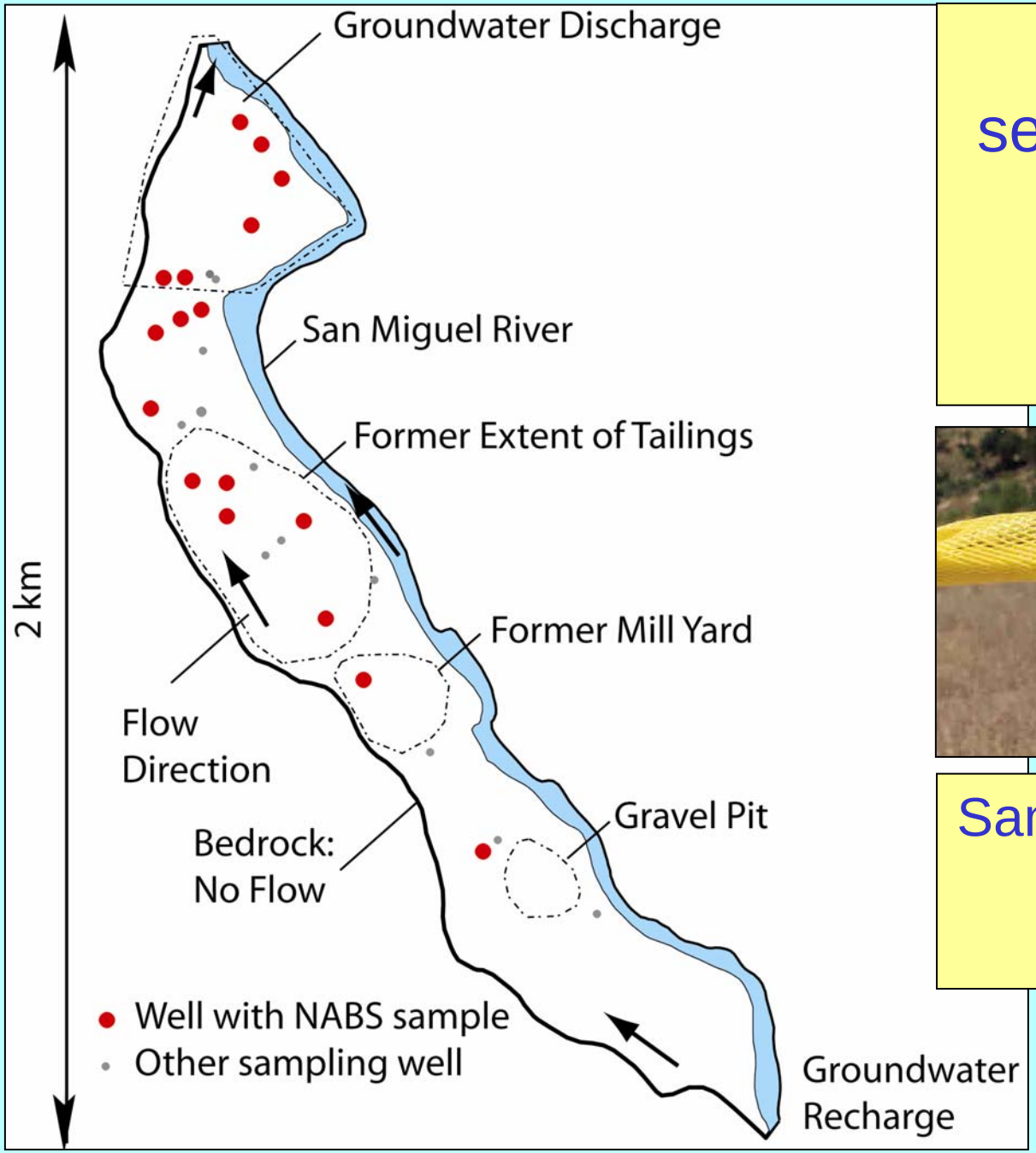
Variable chemical conditions --

uncontaminated sediment

contaminated sediments

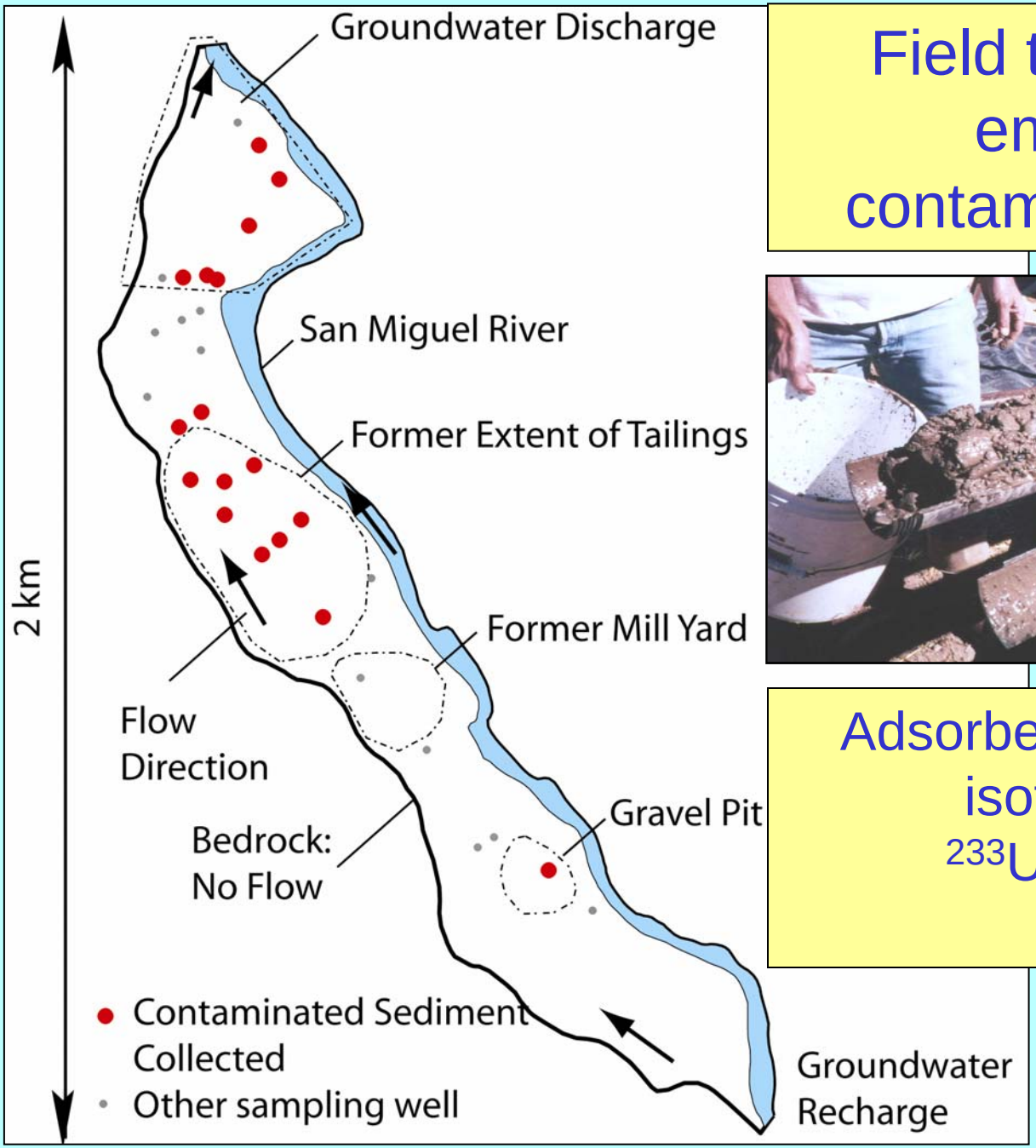
Nearly constant chemical conditions --

contaminated sediments



Field tests of the semi-empirical SCM: Mesh bags with uncontaminated sediments

Samples were suspended in wells for 3 to 15 months

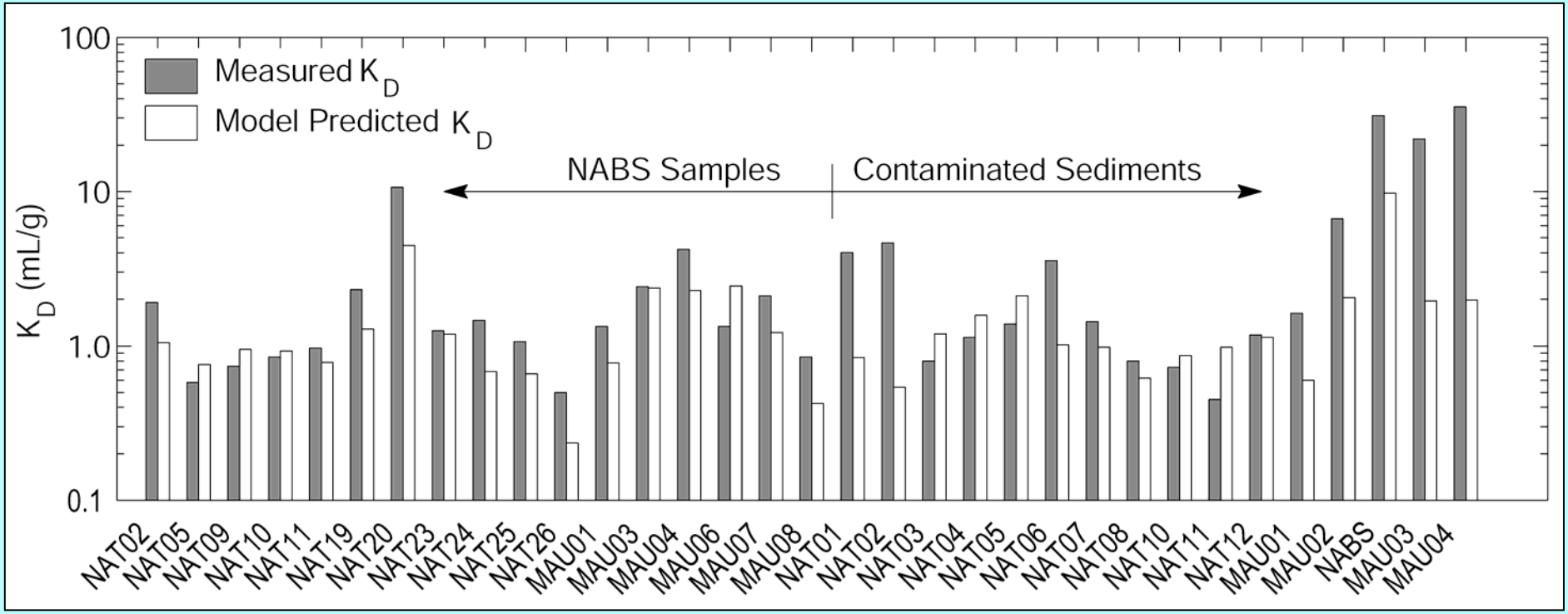


Field tests of the semi-empirical SCM: contaminated sediments

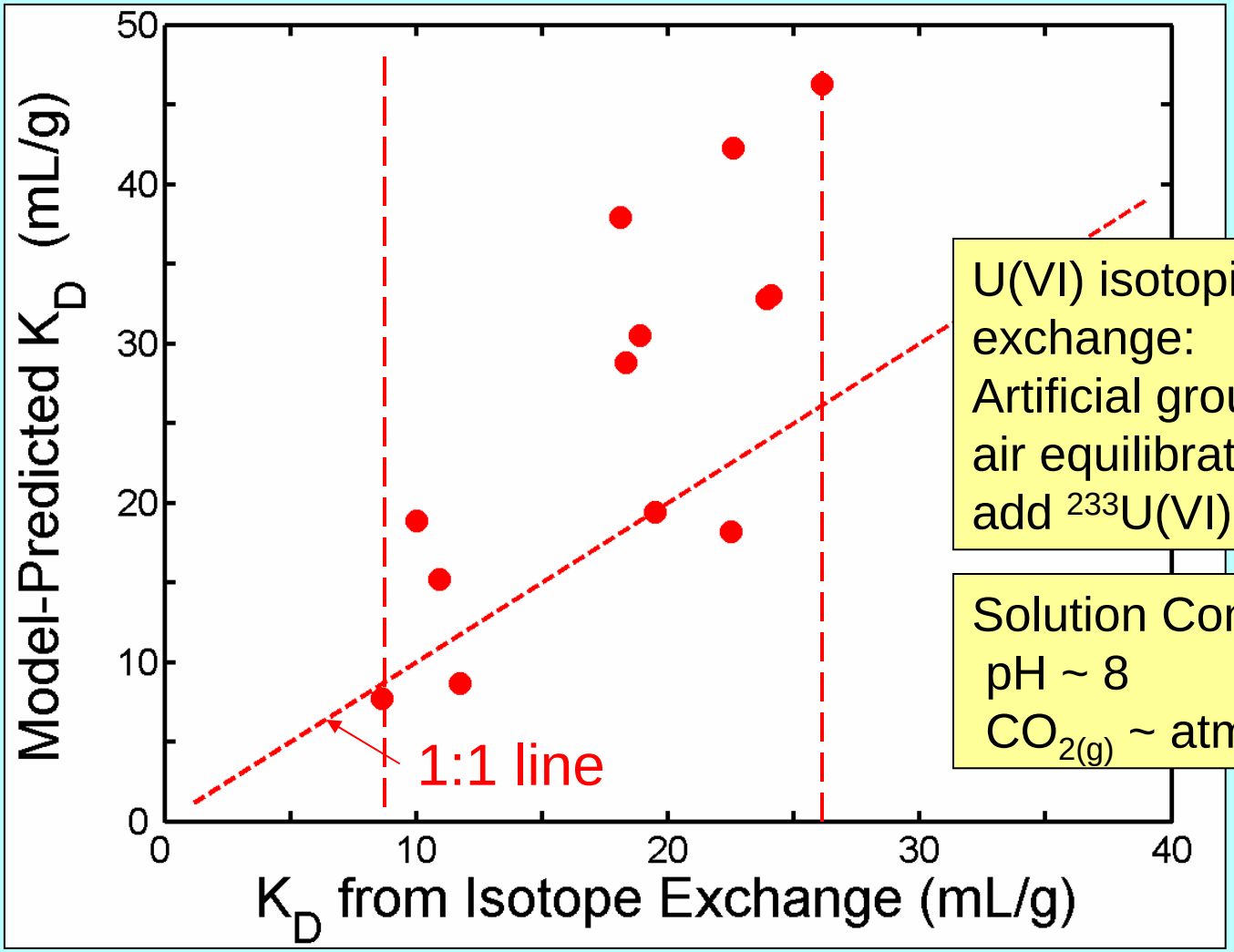
Adsorbed U(VI) evaluated by isotopic exchange:

$^{233}U(VI)_{sed}/^{233}U(VI)_{aq}$

Comparison of K_d values measured for field samples with model-predicted values



K_D values from isotopic exchange with contaminated Naturita sediment samples and predicted by semi-empirical U(VI) SCM



U(VI) isotopic exchange:
Artificial groundwater, air equilibration, then add $^{233}U(VI)$ isotope

Solution Conditions:
pH ~ 8
$CO_{2(g)}$ ~ atmospheric

Variability of Uranium K_d values at Naturita

Uncontaminated sediments (NABS):

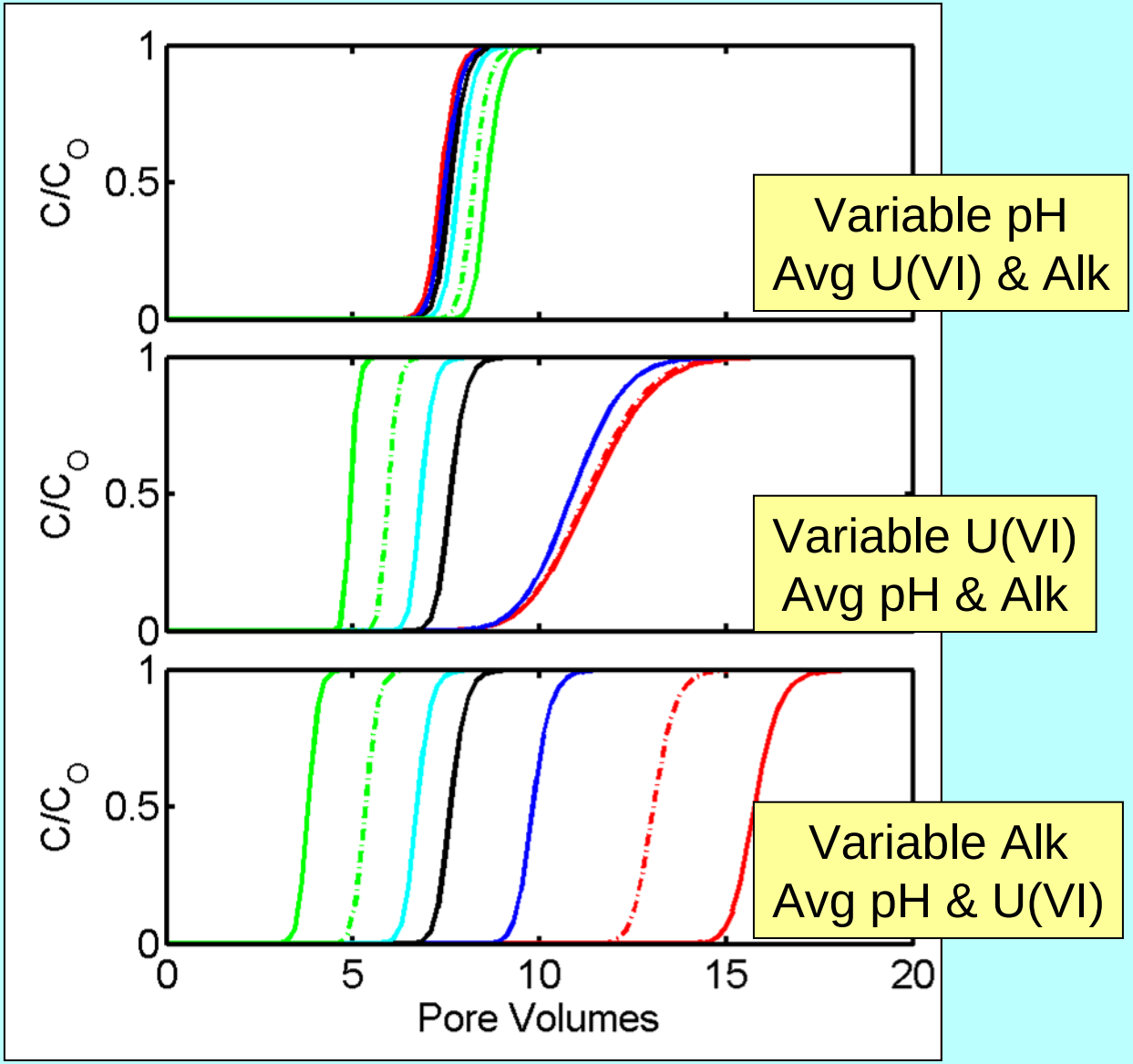
1 Sediment + 17 Wells ➔ Factor of 22

Contaminated sediments

16 Sediments + 1 Water ➔ Factor of 2.6

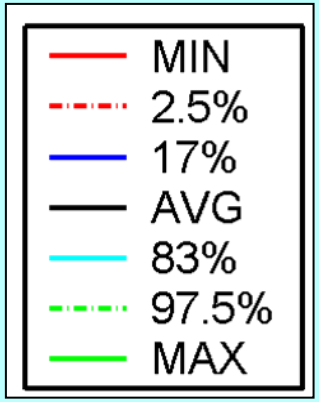
Conclusion: At this site, spatially variable groundwater chemistry is more important than variable sediment composition in determining uranium K_d values. Davis et al. (1998) made a similar observation for zinc K_d value variation in a Cape Cod sand and gravel aquifer.

1-D Naturita U(VI) transport modeling with the semi-empirical U(VI) adsorption model

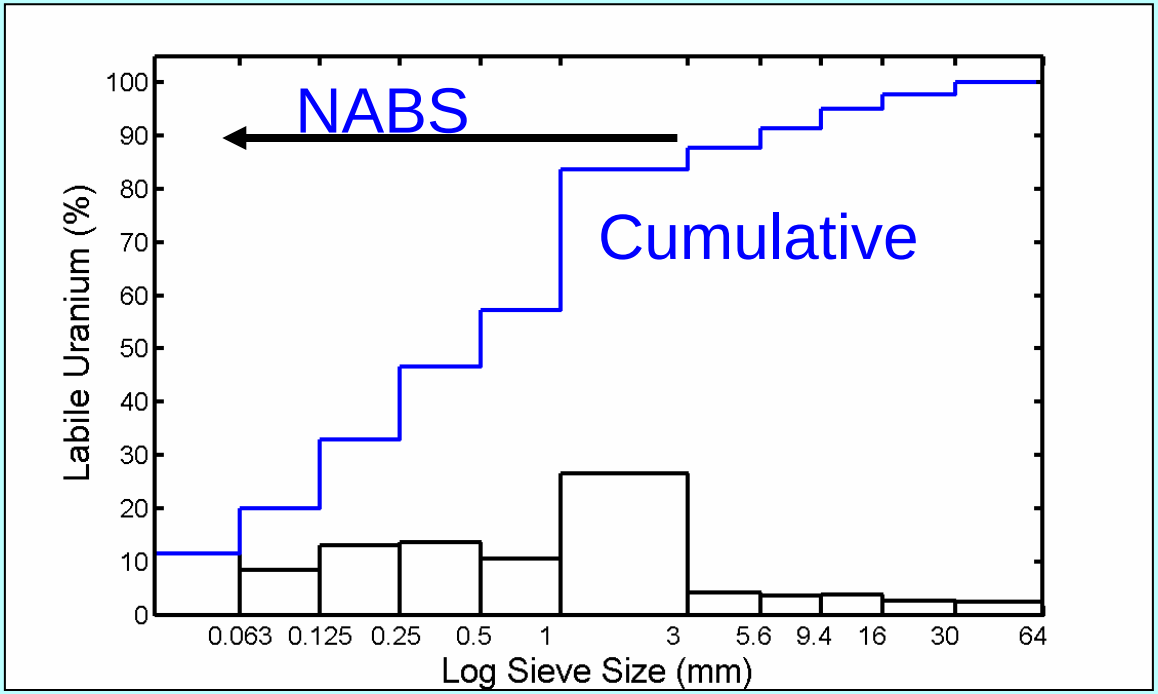


Simulation conditions:
step change in inlet boundary

observed ranges of pH, alkalinity, and U(VI) (n=459)



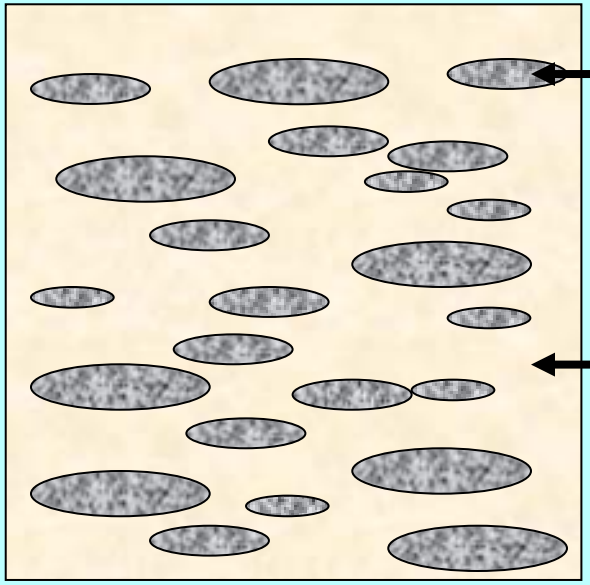
Effect of Cobbles 1: Size Distribution



~50% of aquifer is cobbles > 6.4 cm

The remaining ~50% was size fractionated and examined for labile U(VI)

Effect of Cobbles 2: Porosity



Cobbles:
Volume ~50 %
Porosity 0.0

Gravels,sand,silts:
Volume ~50 %
Porosity 0.4

Average Porosity = 0.2

Effect of Cobbles 3: K_D corrections

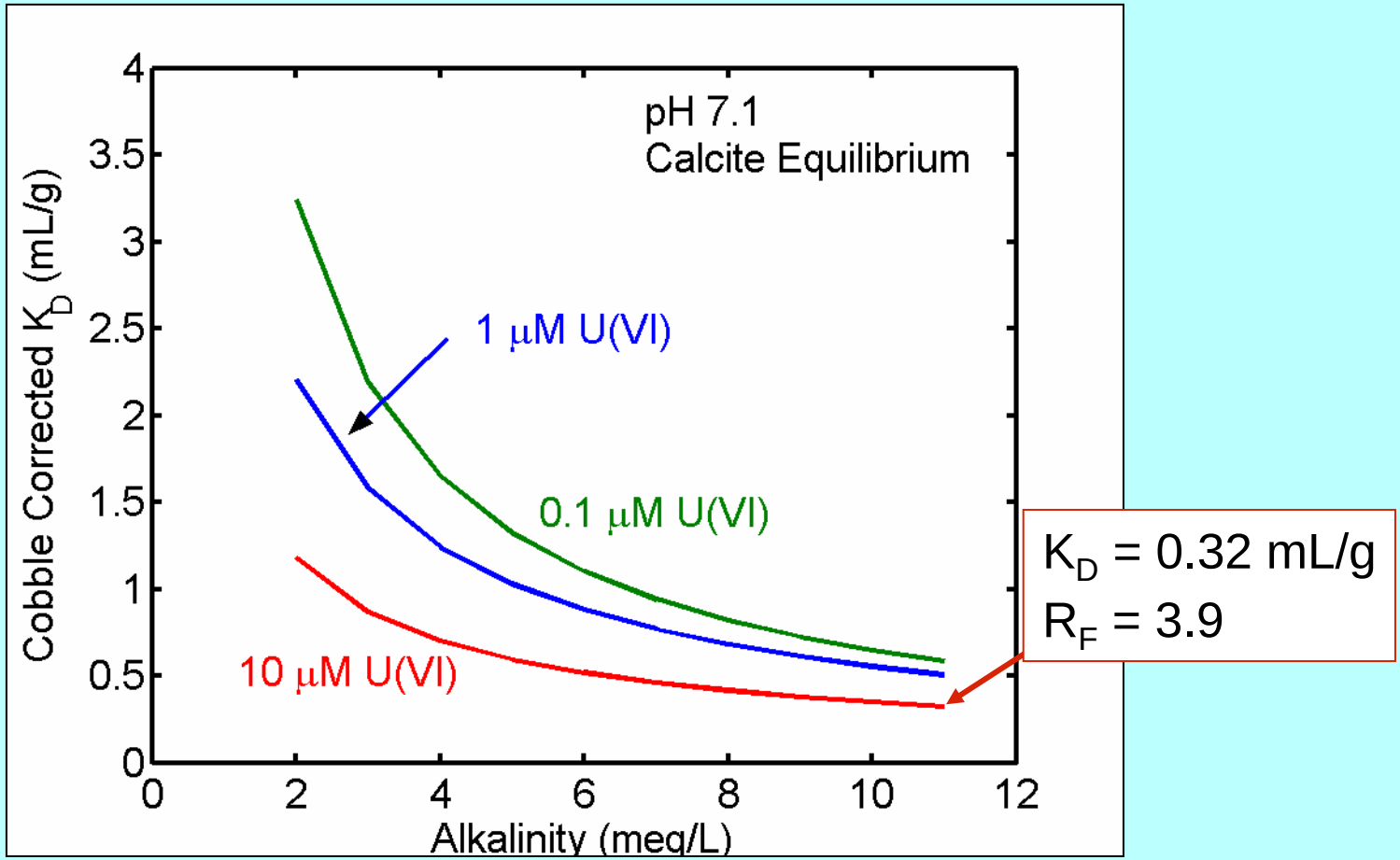
Adsorption sites:

$$\text{Sites/L} = \text{Sites/m}^2 \times \text{Avg m}^2\text{/g} \times \text{g(<3mm Sed)/ g(Aquifer sed)}$$

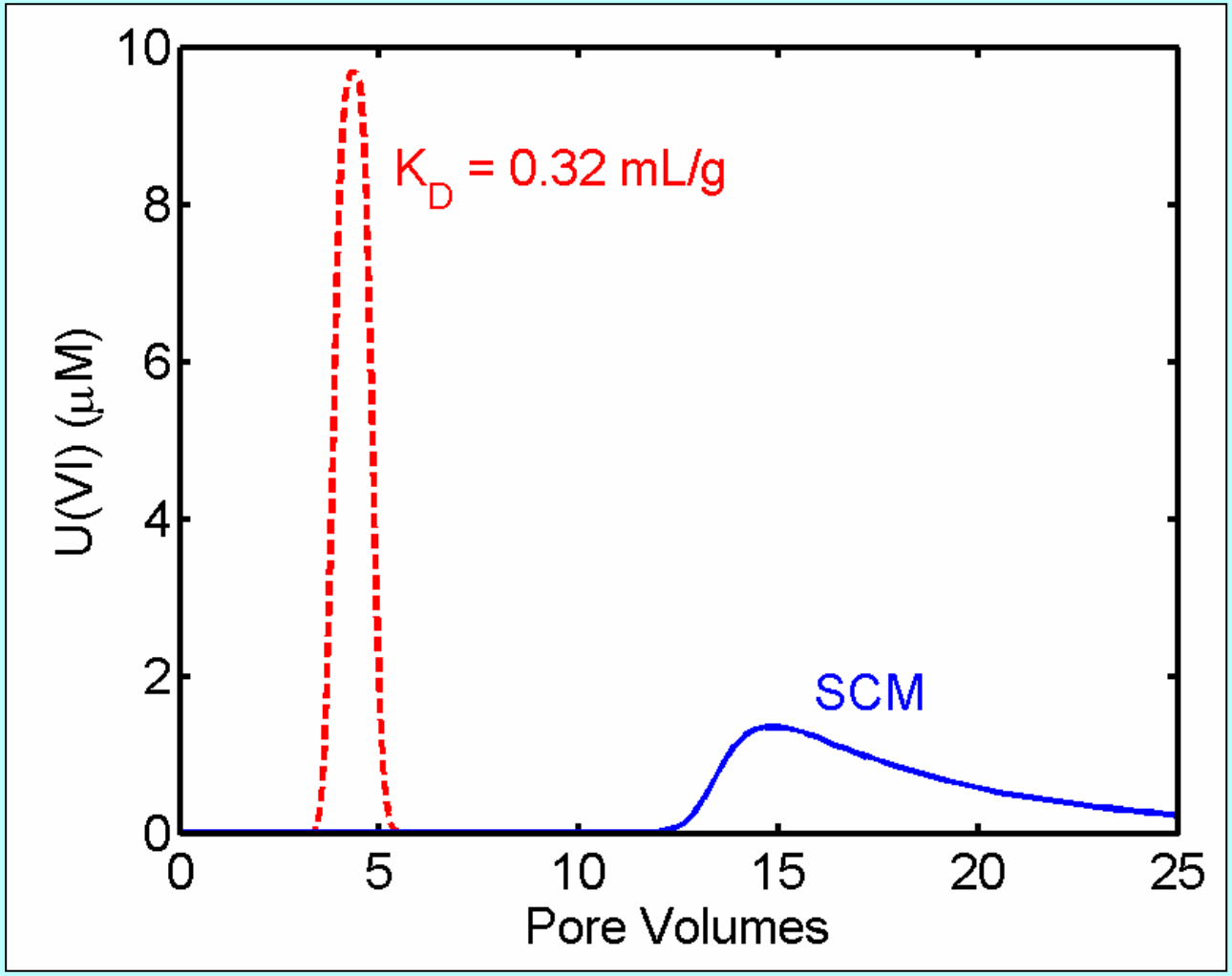
Gravel Corrected K_Ds:

$$K_D = \text{fraction}_{<3mm} \times K_{D\text{-}NABS}$$

Effect of Alkalinity on Model-Predicted K_D



Simulated U(VI) Breakthrough

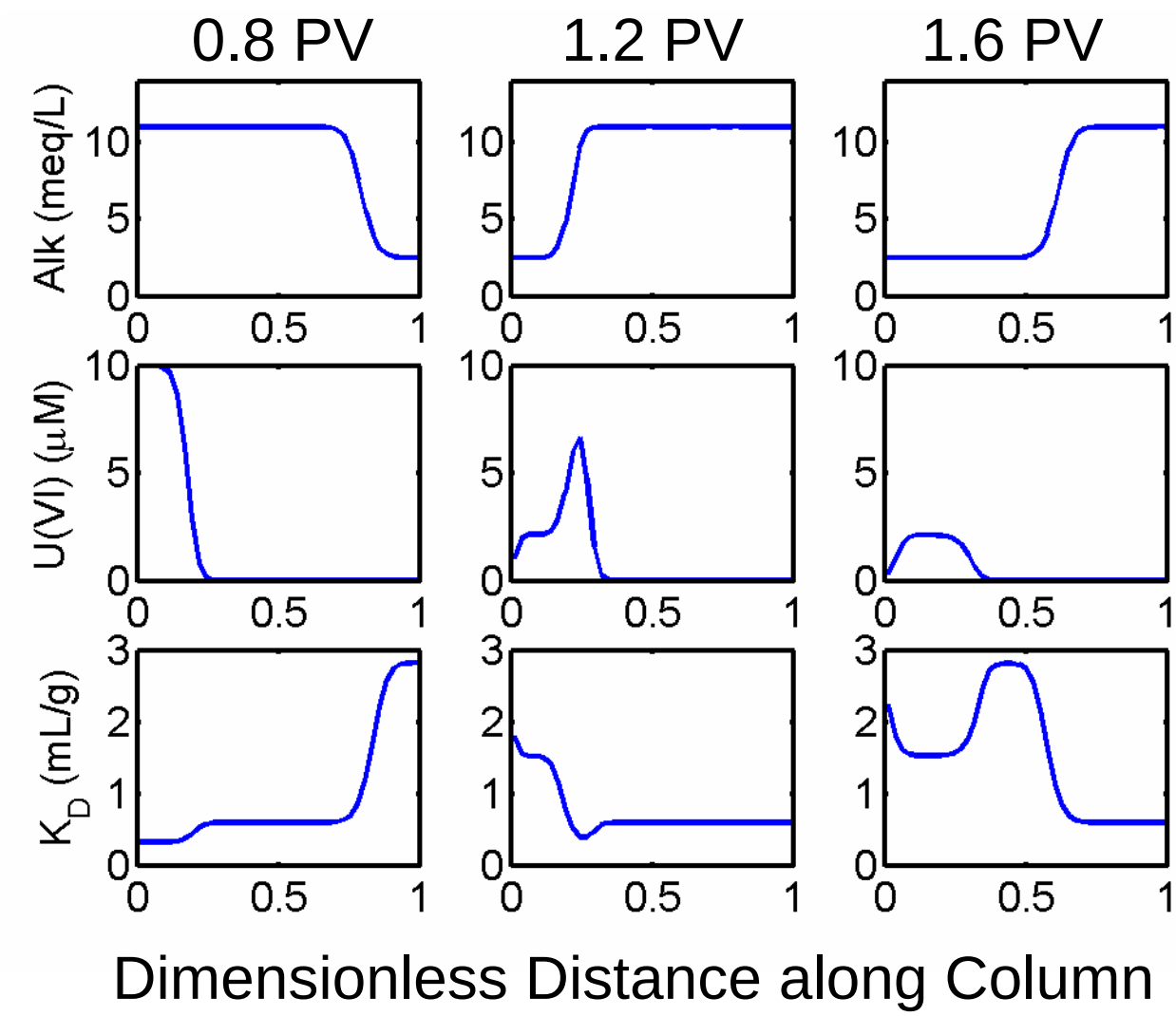


SCM simulation conditions:

1 Pore Volume injection of
pH 7.1,
10 μM U(VI), &
11 meq/L Alk

into
pH 7.1,
0.01 μM U(VI), &
2.5 meq/L Alk

Simulated Profiles



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pH 7.1,
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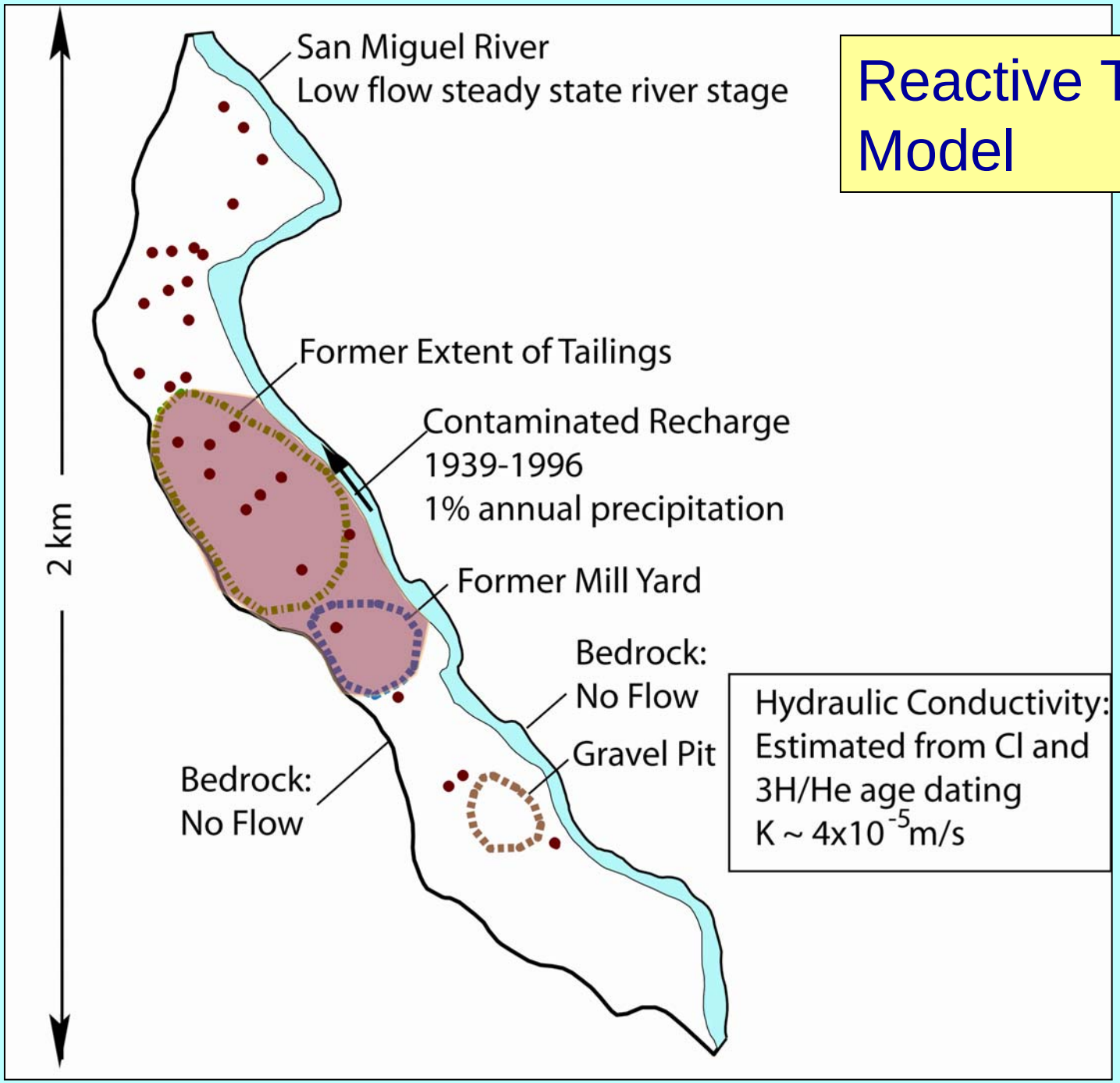
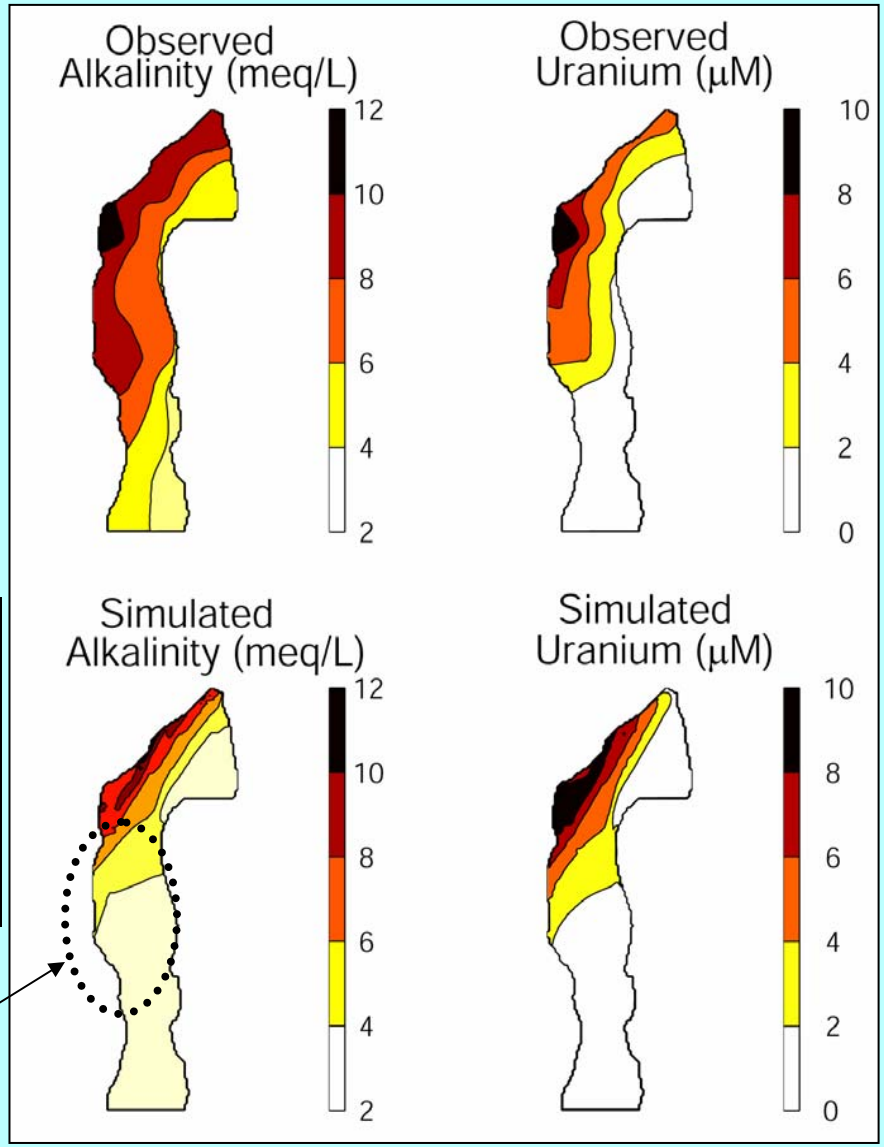
pH 7.1,
0.01 μM U(VI), &
2.5 meq/L Alk

Reactive Transport Model



2-D Reactive Transport Modeling of Uranium(VI) at the Naturita UMTRA site



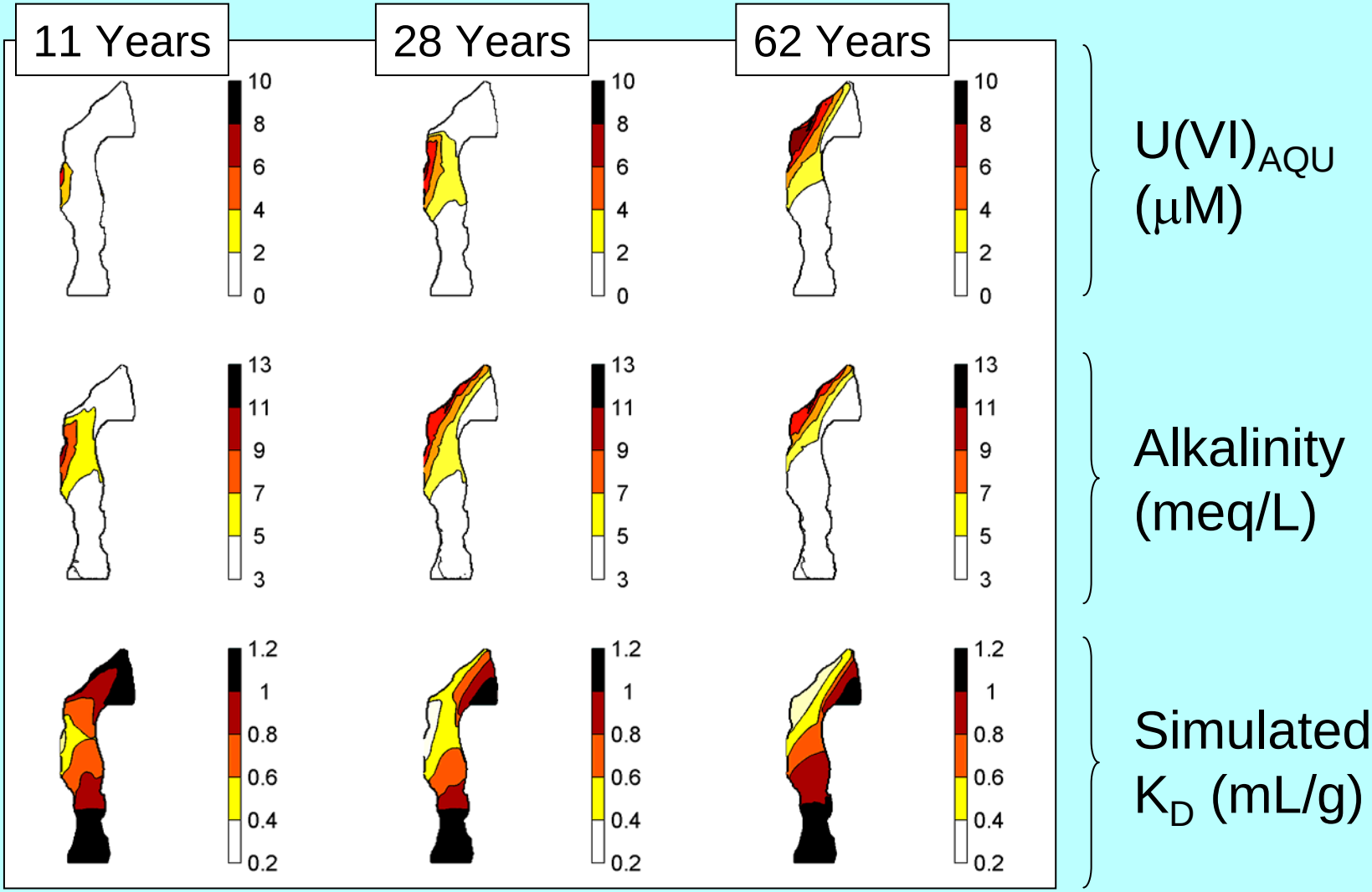
Observed

Simulated

62 years of transport simulated

Source term at t = 0

Spatial and Temporal Evolution



$$\text{Simulated } K_D = \frac{\text{Total Simulated Adsorbed U(VI)}}{\text{Total Simulated Aqueous U(VI)}}$$

Model Evaluation

- Parameter Sensitivity

  Total SCM parameter sensitivity is ~40% that of hydraulic conductivity

- Effect of surface charge development

  The total surface charge resulting from $\equiv SO_2HUO_2^+$ has a negligible effect on transport

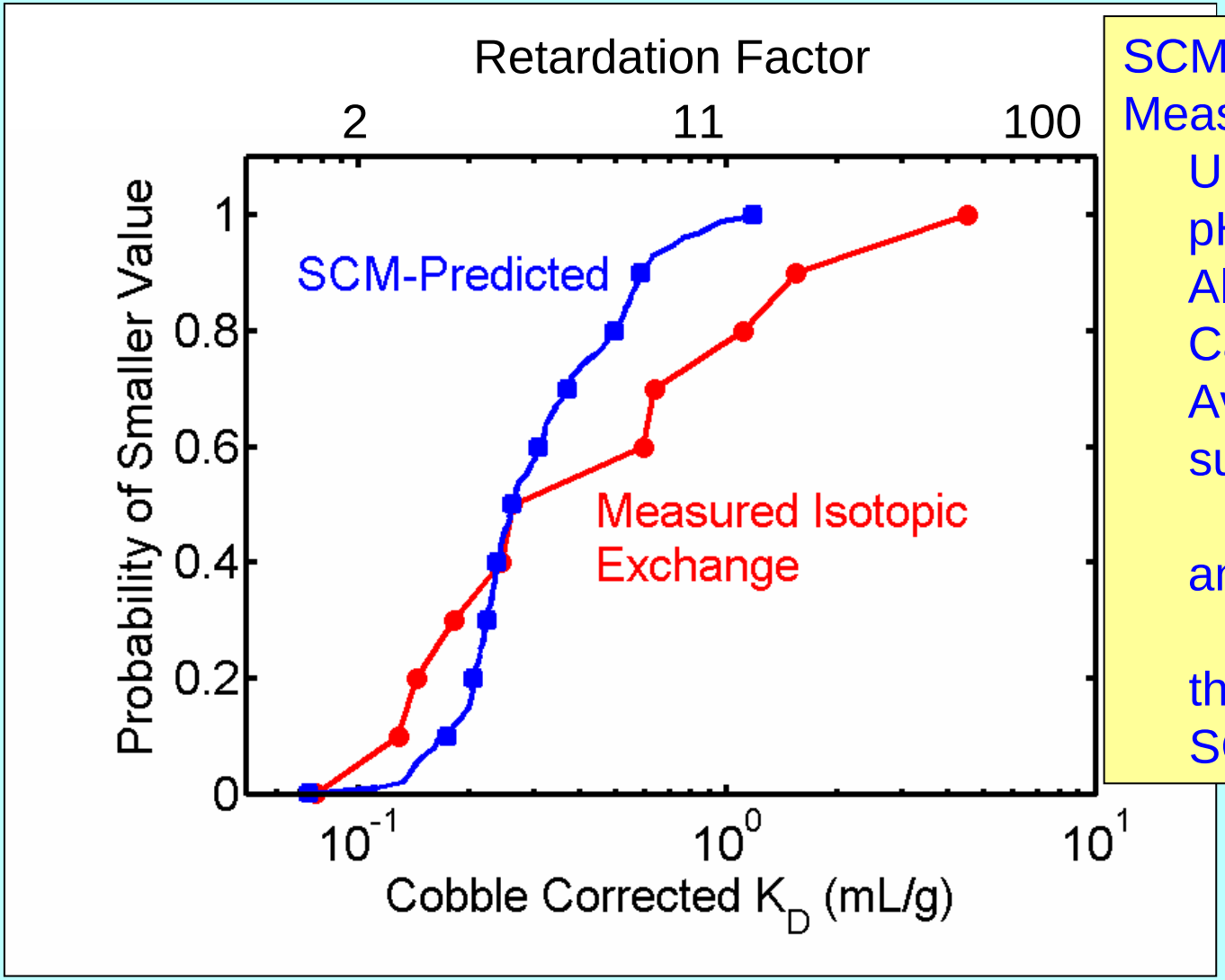
- Is local equilibrium valid?

  using a rate law fit to batch data in the transport model gave results essentially identical to that observed assuming local equilibrium.

Comparison of K_D and SCM Transport Simulations of Future U(VI) Migration

- Start from observed conditions in the field
- Simulate transport for 500 years
- Simulate U(VI) adsorption using –
    1. semi empirical SCM
    2. K_D distribution observed from studies with contaminated sediments
    3. K_D distribution computed from semi empirical SCM
- Compare peak concentrations, flux to river, and cleanup time

K_D Distributions



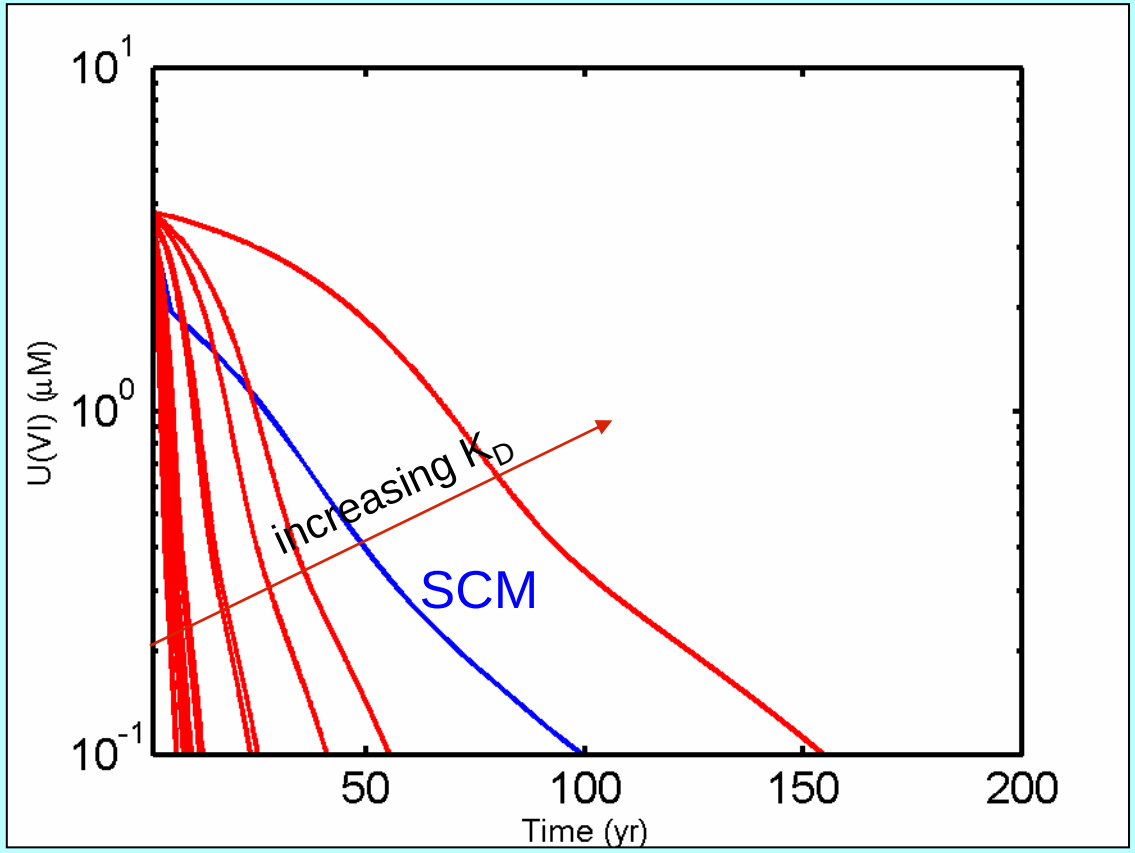
SCM-Predictions Use Measured:

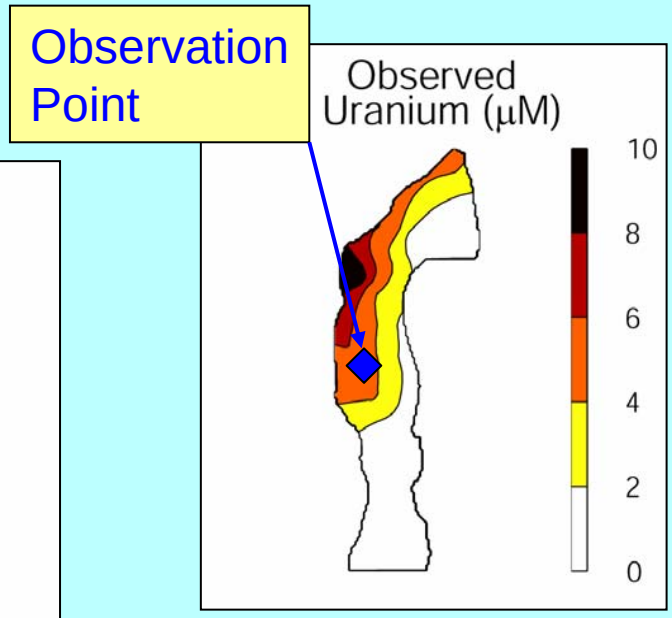
- $U(VI)_{aq}$
- pH
- Alkalinity
- Ca^{+2}
- Average surface area

and

the semi-empirical SCM

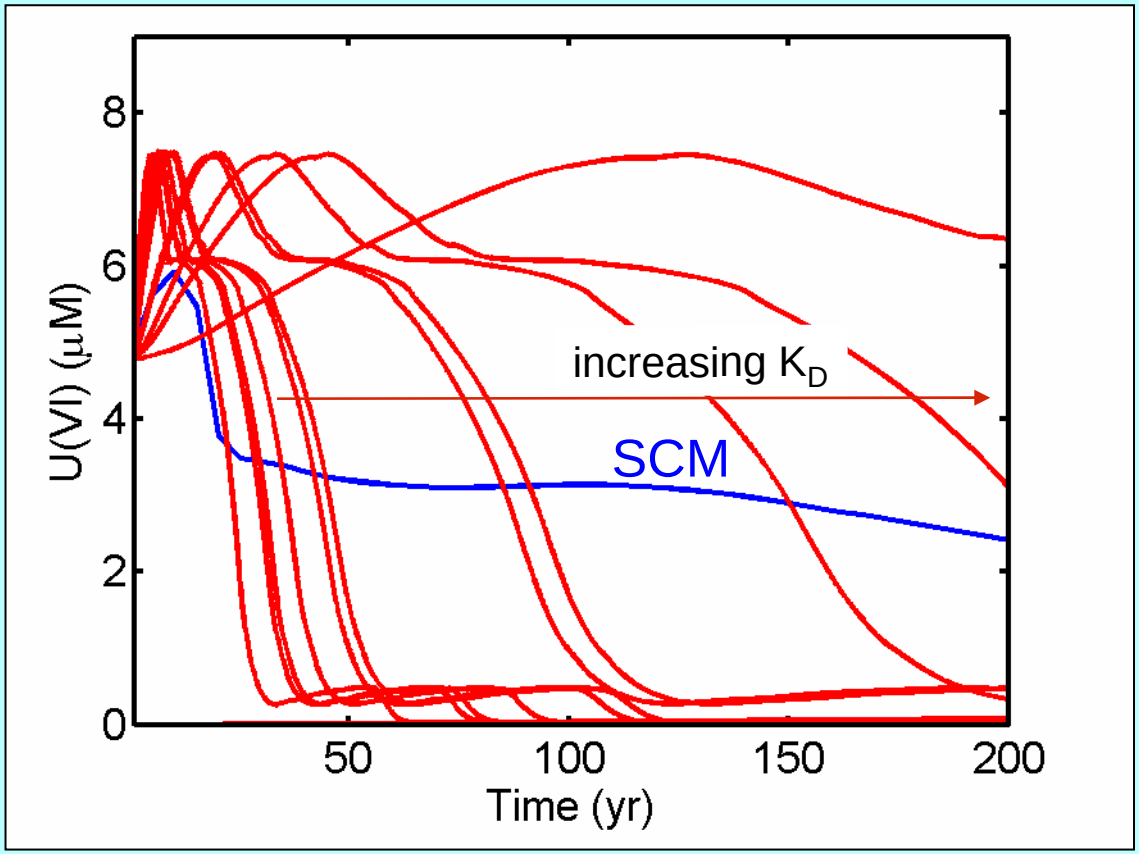
Simulated Clean Up Times

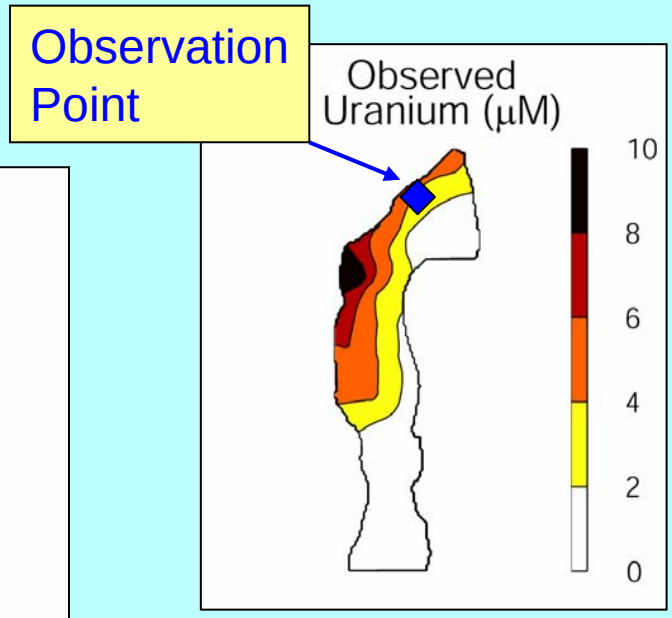




Initial Condition

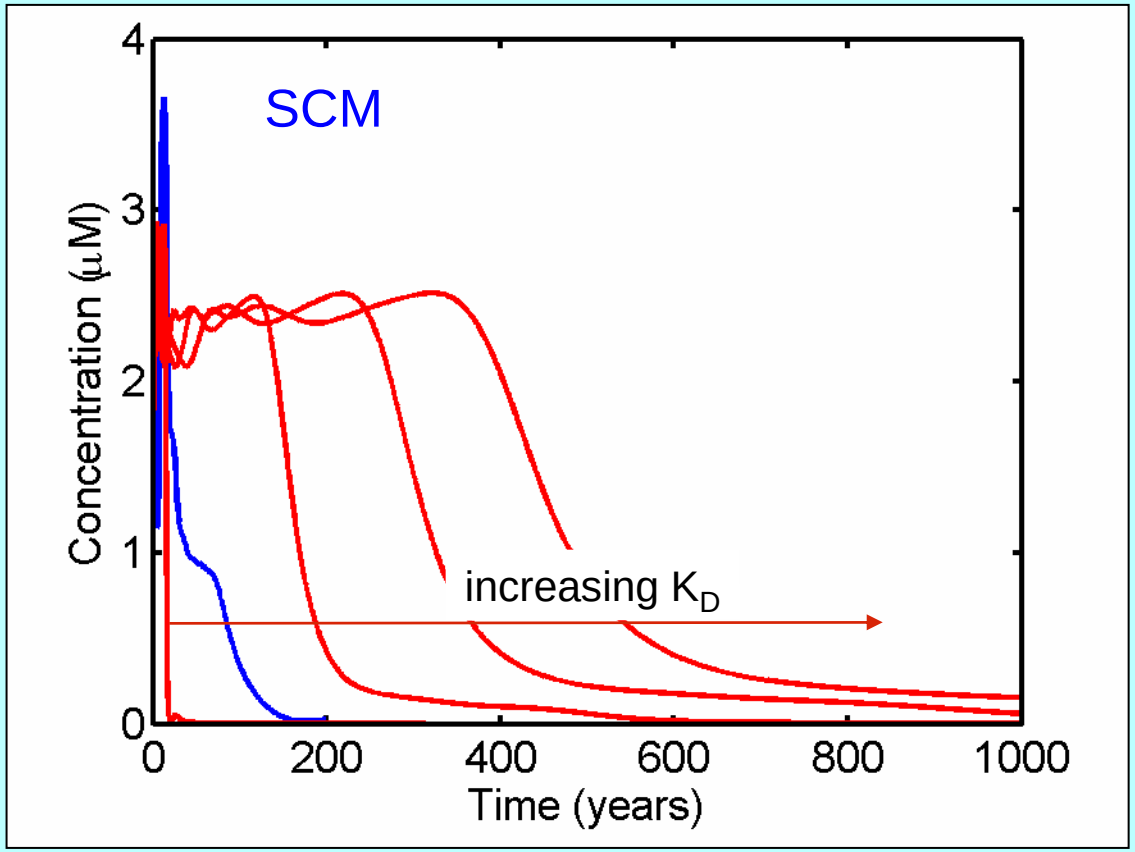
Simulated Peak Concentrations



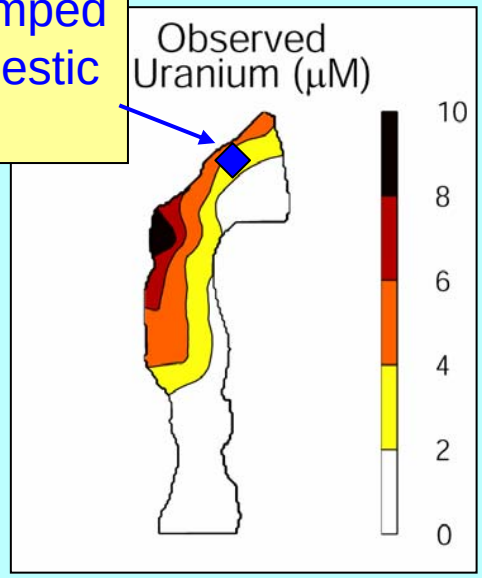


Initial Condition

Concentration in Pumped Well



Well Pumped For domestic Use

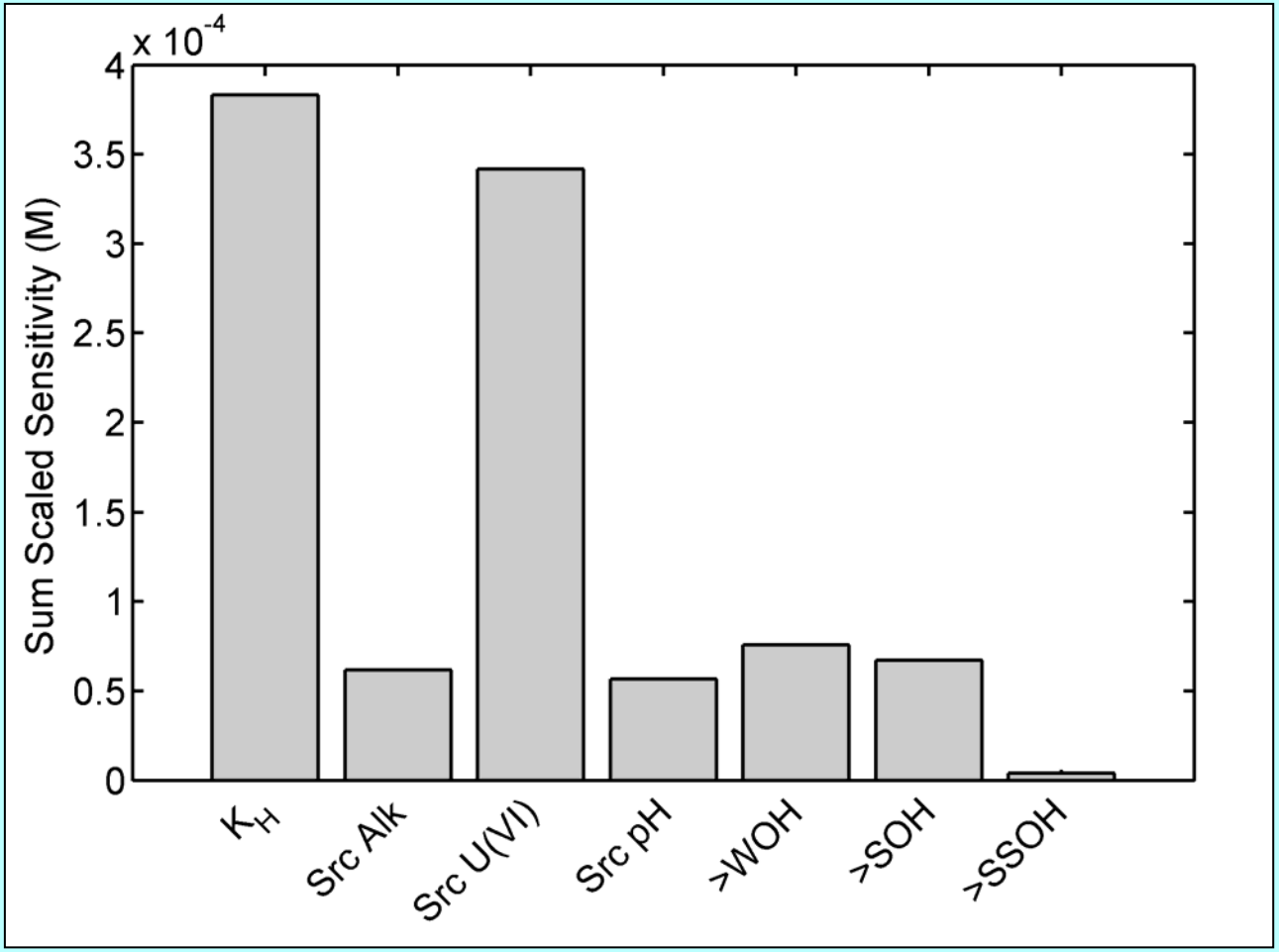


Initial Condition

Conclusions

- Current reactive transport models can accommodate the surface complexation concept to describe retardation of inorganic contaminants during transport. Use of the K_D concept is no longer required.
- Semi-empirical surface complexation modeling can reduce transport modeling uncertainty with respect to sorption under conditions of temporal or spatial variable chemical conditions in groundwater
- Spatial variability in groundwater chemical conditions may be more important in influencing the retardation of strongly adsorbing species than is the variability in the surface properties of aquifer materials (at the km scale)
- Predictions based on a range of site specific K_D values do not always bracket simulation results obtained using the semi empirical surface complexation model.

Transport Model Sensitivity



Effect of Surface Charge

For the reaction:

$$\equiv S(OH)_2 + Ca_2UO_2(CO_3)_3^o \leftrightarrow \equiv SO_2HUO_2^+ + 2CaCO_3^o + HCO_3^-$$

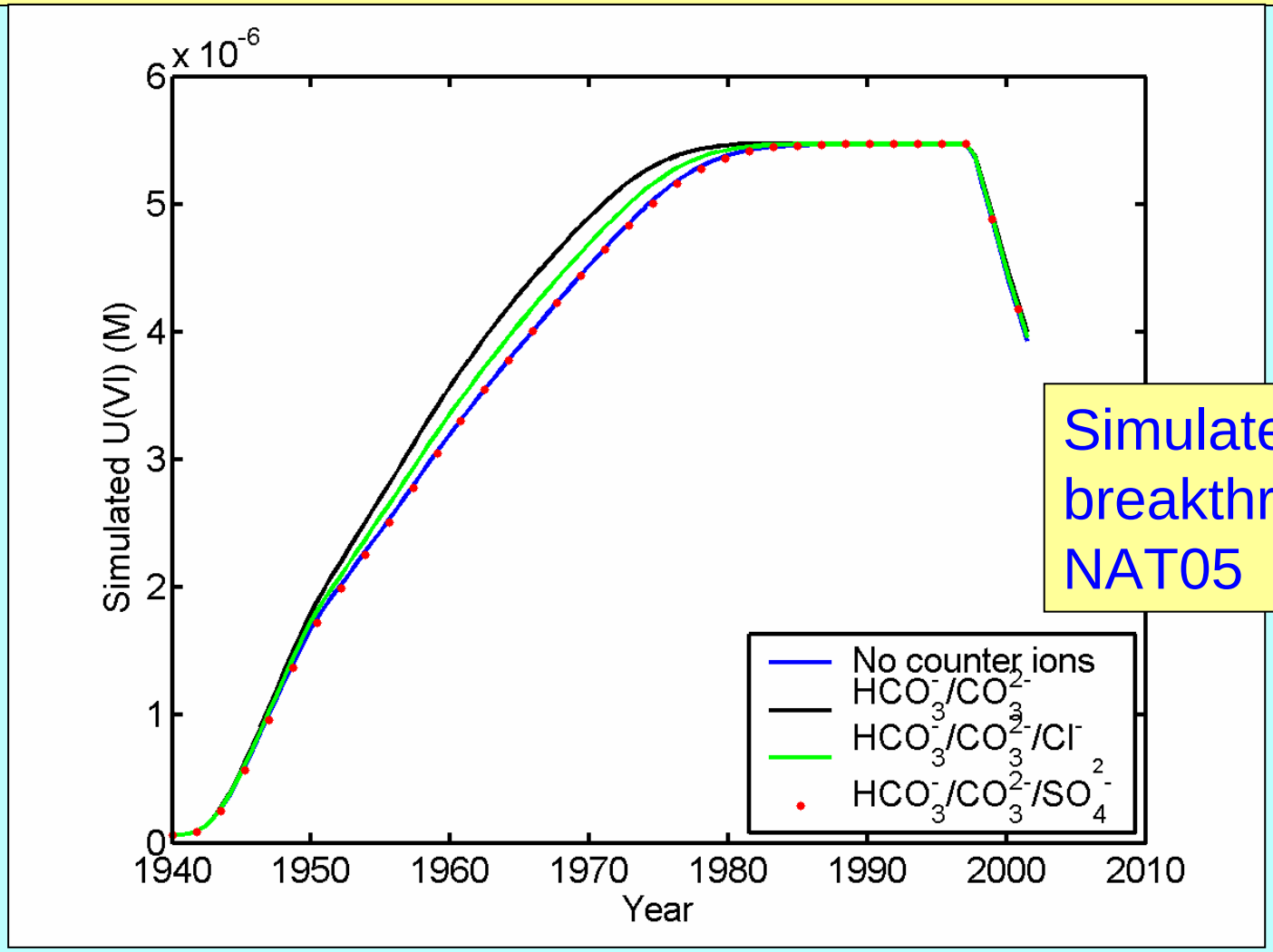
charge is separated
calcite equilibrium shifts

Approach

Balance the positive surface charge with an immobile anion

Anion concentration is proportional to
bulk aqueous concentration
anion charge

Effect of Surface Charge

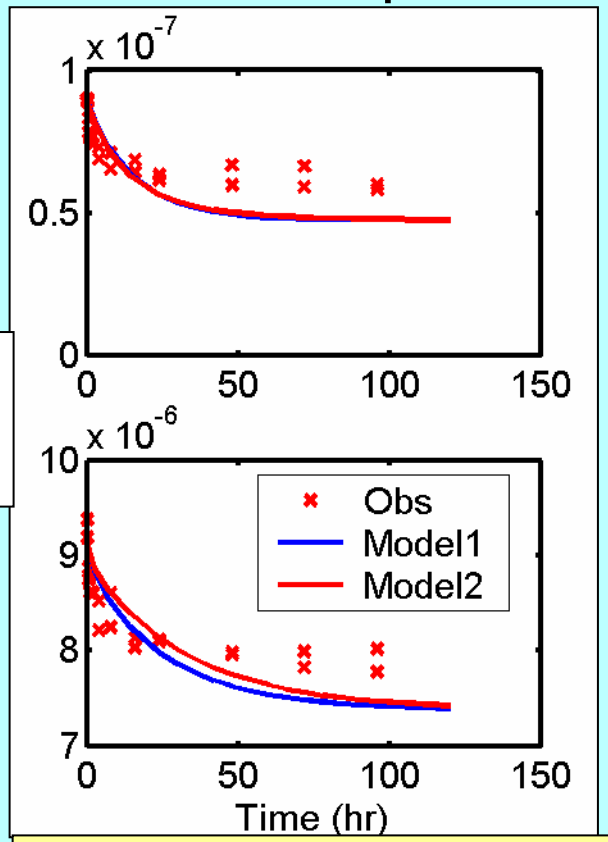


Simulated U(VI) breakthrough at NAT05

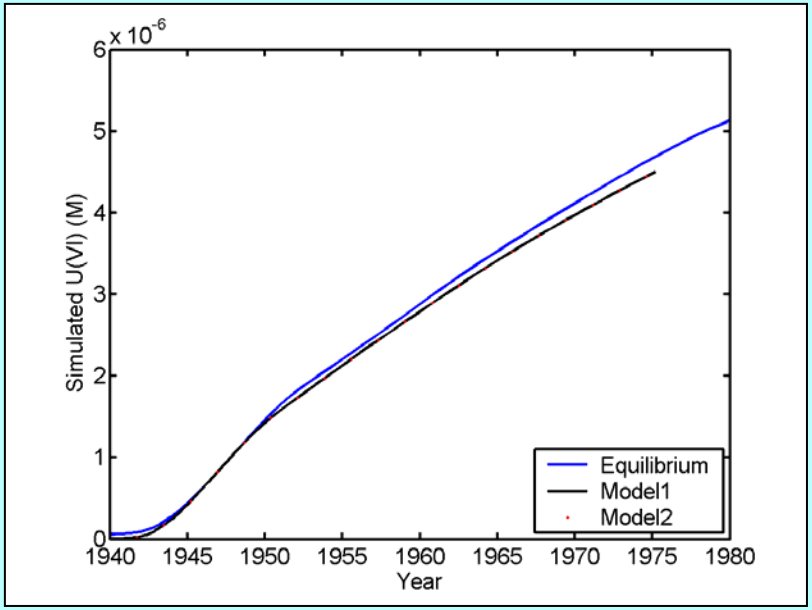
Comparison of Rate and Equilibrium Controlled Transport

Batch Adsorption Rates

U(VI) (M)



Simulated U(VI) Breakthrough



Model 1: UO_2^{+2}

Model 2: $Ca_2UO_2(CO_3)_3^o$

Species used in empirical rate law

Variable inorganic carbon in groundwater

Naturita site:

0.002 – 0.014 moles/L

Factor of 7

Yucca Mountain hydrologic system:

0.0005 – 0.08 moles/L

Turner et al. (2002)

Factor of 160