*Columbia River at Hanford*

# Batch Measurements of Desorption/Adsorption from Vadose Zone and Aquifer Sediments

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# Simple Conceptual Models for Geochemical Reaction of $UO_2^{2+}$

Aqueous Complexation

*Hydrolysis* $UO_{2(aq)}^{2+} + H_2O(1\text{-}4) = UO_2OH_{(aq)}^{+} + H^+$

*Carbonate complexation* $UO_{2(aq)}^{2+} + 3CO_3^{2-} = UO_2(CO_3)_{3(aq)}^{4-}$

*and many others*

Adsorption

$SOH_{(s)} + UO_2OH_{(aq)}^{+} = SO\ UO_2OH_{(s)} + H^+$

$2SOH_{(s)} + UO_2(CO_3)_{3(aq)}^{4-} + 2H^+ = (SOH_2^+)_2UO_2(CO_3)_{(s)}^{2-}$

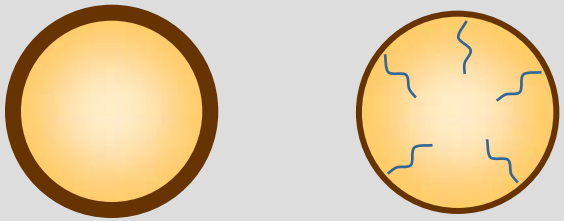
*where SOH = SiOH, FeOH, AlOH*

Precipitation

$UO_{2(aq)}^{2+} + Na_{(aq)}^{+} + H_4SiO_{4(aq)} + 1.5H_2O = Na[UO_2(SiO_3OH)](H_2O)_{1.5(s)} + 3H^+$

$UO_{2(aq)}^{2+} + Ca_{(aq)}^{2+} + 2CO_{3(aq)}^{2-} + 5H_2O = Ca[UO_2(CO_3)_2](H_2O)_{5(s)}$

Physical Considerations



The $K_d$

$$K_d = \frac{\Sigma\ [s]}{\Sigma\ [aq]}$$

# Objectives

- Objectives
  - Evaluate the sorptivity of U(VI) in contaminated groundwater on 300 A capillary fringe sediment (SPP2-18', NPP1-16')
    - Differences between groundwaters and sediments
    - Controlling physical and mineralogic properties
    - Speciation effects
  - Identify qualitative relationships between sorption-desorption
    - Time effects
    - Existence of a "common" equilibrium state
  - Determine "realistic" range for "in-situ" $K_d$ values

# Motivation

- Provide basis for improved forward and backward retardation estimates
- Determine key properties for spatial correlation and discrimination in the field for RTM
- Experimental data for generalized adsorption model calibration and testing

# Groundwater Composition and Uranium Speciation

| | 618-5 Pit 1 (26 Feb, 03) | 618-5 Pit 1 (29 May, 03) | 618-5 Pit 2 (26 Feb, 03) | SPP Pit 1 (19 Apr, 03) | SPP Pit 2 (19 Apr, 03) | NPP Pit 1 (26 Apr, 03) | NPP Pit 2 (26 Apr, 03) | Range |
|---|---|---|---|---|---|---|---|---|
| pH | 7.71 | 8.11 | 7.80 | 7.83 | 8.04 | 7.83 | 7.88 | 7.71 - 8.11 |
| Ionic Strength (mmol/L) | 7.5 | 8.2 | 7.5 | 3.5 | 4.9 | 5.2 | 6.3 | 3.5 - 8.2 |
| **Cations (mmol/L)** | | | | | | | | |
| Ca | 1.31 | 1.17 | 1.24 | 0.60 | 0.90 | 1.01 | 1.14 | 0.60 - 1.31 |
| K | 0.16 | 0.20 | 0.16 | 0.07 | 0.09 | 0.07 | 0.06 | 0.06 - 0.20 |
| Mg | 0.58 | 0.49 | 0.56 | 0.21 | 0.28 | 0.34 | 0.40 | 0.21 - 0.58 |
| Na | 1.34 | 2.65 | 1.53 | 0.77 | 0.95 | 0.84 | 1.14 | 0.77 - 2.65 |
| **Anions (mmol/L)** | | | | | | | | |
| $Cl^-$ | 0.84 | 1.21 | 0.76 | 0.14 | 0.36 | 0.36 | 0.39 | 0.14 - 1.21 |
| $NO_3^-$ | 0.42 | 0.53 | 0.40 | 0.36 | 0.40 | 0.29 | 0.43 | 0.29 - 0.53 |
| Inorg. C | 2.47 | 2.71 | 2.41 | 1.20 | 1.70 | 2.02 | 1.58 | 1.20 - 2.71 |
| $SO_4^{2-}$ | 0.69 | 0.76 | 0.85 | 0.35 | 0.43 | 0.47 | 0.88 | 0.35 - 0.88 |
| $Si_{Total}$ | 0.57 | 0.59 | 0.55 | 0.28 | 0.39 | 0.32 | 0.23 | 0.23 - 0.59 |
| **U (µmol/L)** | 4.96 | 1.39 | 1.82 | 0.30 | 0.36 | 0.30 | 1.07 | 0.30 - 4.96 |
| Species | (%) | (%) | (%) | (%) | (%) | (%) | (%) | |
| $UO_2(CO_3)_2^{2-}$ | 5.8 | 2.8 | 5.4 | 22.0 | 6.2 | 7.1 | 7.3 | |
| $UO_2(CO_3)_3^{4-}$ | 3.5 | 5.0 | 4.0 | 6.5 | 4.7 | 4.0 | 3.9 | |
| $Ca_2UO_2(CO_3)_3^0$ | 90.6 | 92.2 | 90.5 | 70.4 | 88.9 | 88.7 | 88.6 | |
| $P_{CO2}$ | -2.559 | -2.912 | -2.656 | -2.971 | -3.035 | -2.754 | -2.913 | |

# U(VI) Adsorption on 300 Area Sediments from Different Groundwaters

| | | $K_d$ (mL/g) 1-Day Contact | | | | $K_d$ (mL/g) 7-Day Contact | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Inorganic C (meq/L) | SPP Pit 2 (18 ft bgs) | | NPP Pit 1 (16 ft bgs) | | SPP Pit 2 (18 ft bgs) | | NPP Pit 1 (16 ft bgs) | |
| GW 1 | 2.02 | 10.8 | (0.02) | 61.3 | (0.12) | 8.67 | (0) | 63.7 | (0.26) |
| GW 2 | 1.70 | 13.2 | (0.06) | 83.2 | (2.58) | 9.51 | (0.40) | 85.6 | (2.64) |
| GW 3 | 1.20 | 30.5 | (3.97) | 168 | (7.08) | 19.0 | (1.76) | 178 | (7.38) |
| GW 4 | 2.41 | 11.3 | (5.68) | 33.9 | (7.22) | 14.6 | (7.46) | 37.8 | (8.07) |
| GW 5 | 1.58 | 2.28 | (0) | 82.6 | (12.8) | 3.31 | (0.30) | 89.7 | (13.6) |
| GW 6 | 2.47 | 2.22 | (1.32) | 30.5 | (14.5) | 2.82 | (1.77) | 33.5 | (15.7) |
| GW 7 | 1.70 | ND | ND | 85.7 | (17.5) | 6.76 | (1.96) | 89.3 | (17.7) |

GW 1 = NPP pit 1 groundwater (58154-139); 71.4 ppb U; pH 8.29
GW 2 = SPP pit 2 groundwater (58154-132); 84.8 ppb U; pH 8.28
GW 3 = SPP pit 1 groundwater (58154-133); 70.7 ppb U; pH 8.12
GW 4 = 618-5 pit 2 groundwater; sampled 2-26-03 (58154-97-3); 433 ppb U; pH 8.43
GW 5 = NPP pit 2 groundwater (58155-17); 247.3 ppb U; pH 8.22
GW 6 = 618-5 pit 1 groundwater; sampled 2-26-03 (58154-97-4); 1181 ppb U; pH 8.30
GW 7 = SPP pit 2 groundwater spiked to ~250 ppb U; 324 or 269 ppb U; pH 8.29 or 8.08

( ) = The labile U is not considered.

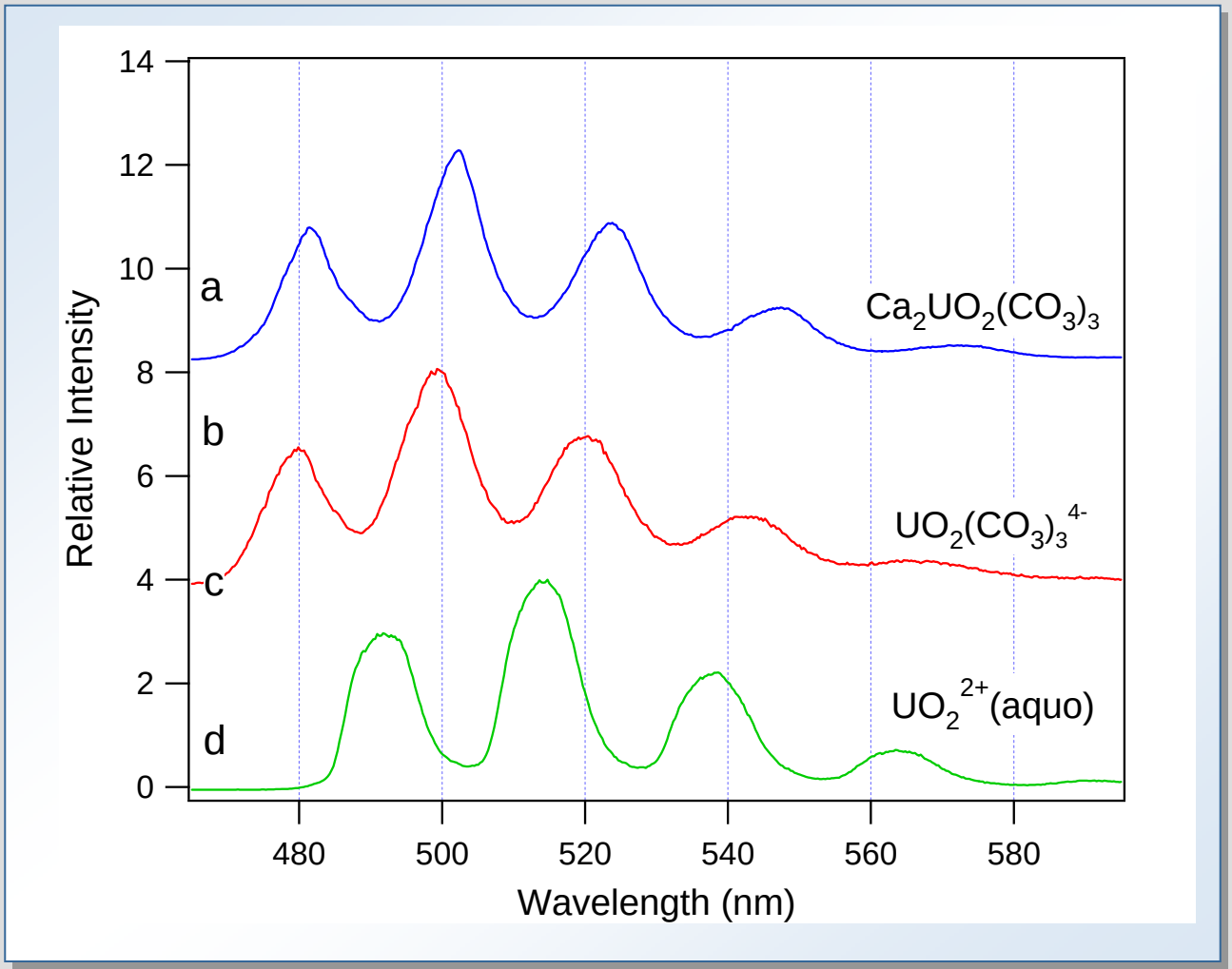
# The Distribution Ratio and Solid Phase Properties

| | | | | Extractable Fe(III) | | |
|---|---|---|---|---|---|---|
| | U(VI) $K_d$ (<2.0 mm) | Silt & Clay | SA | HAHCl | AmOx | DCB |
| | (mL/g) | (mass %) | ($m^2$/g) | (μmol/g) | | |
| | | | | | | |
| SPP2-18' bgs | 9.23±5.87 | 7 | 14.3 | 19 | 48 | 77 |
| NPP2-16' bgs | 82.5±48.3 | 30 | 23.6 | 41 | 91 | 158 |

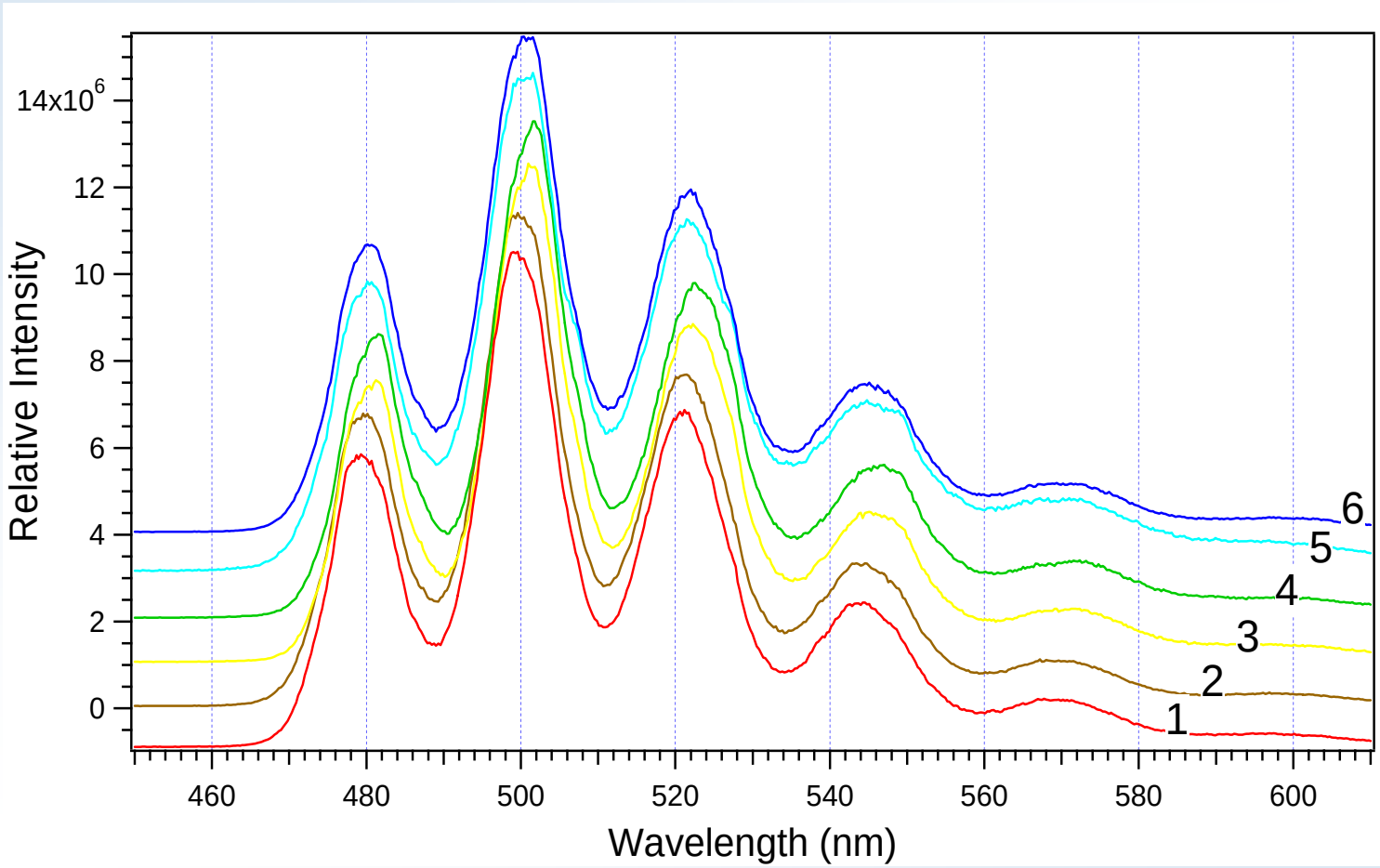
## XRD Estimated Mineral Composition of Clay Fraction

| | SPP2-18' bgs | NPP1-16' bgs |
|---|---|---|
| | (%) | (%) |
| Clinochlore | 29 | 42 |
| Muscovite | 27 | 30 |
| Montmorillonite | 34 | 20 |
| HIV | 7 | 5 |
| Feldspar & quartz | 3 | 3 |

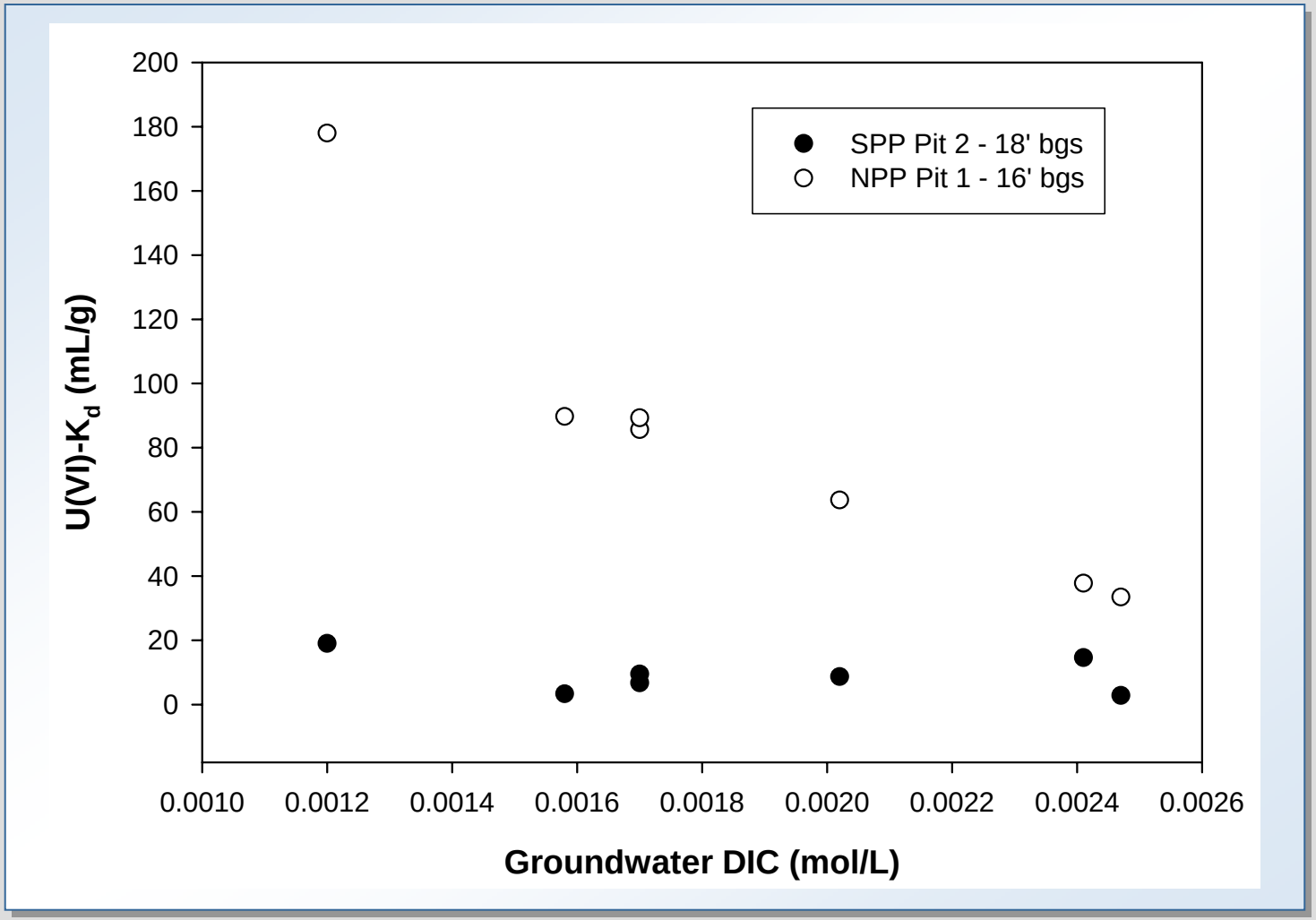
# Normalized U(VI) Fluorescence Spectra of Three Known Aqueous Uranyl Carbonates Species at Liquid Helium Temperature



# Normalized U(VI) Fluorescence Intensities of 300 A Groundwater Samples

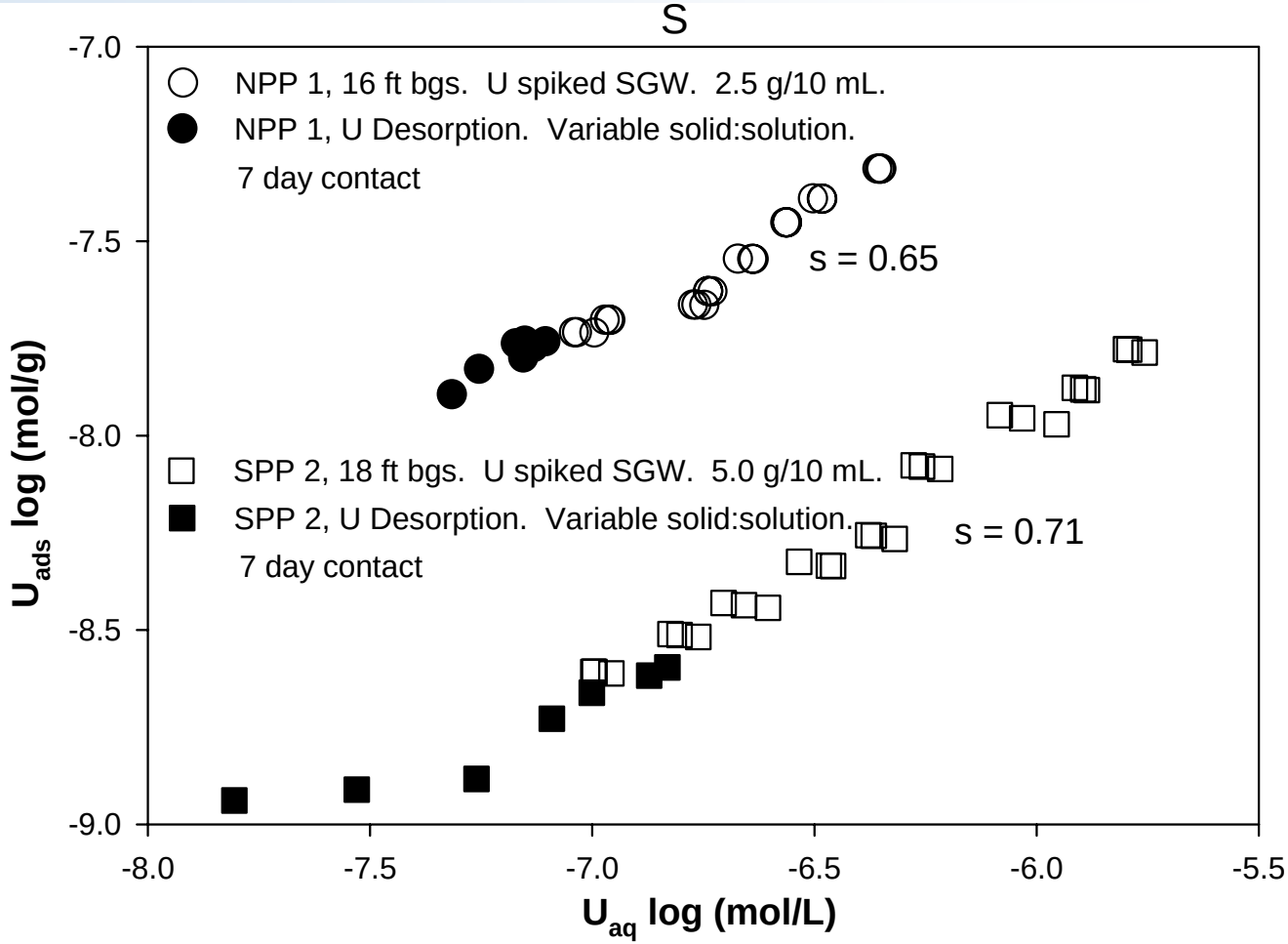


# Dependence of U(VI)-$K_d$ (<2 mm sediment) on Groundwater Dissolved Inorganic Carbon ($HCO_3^-$)



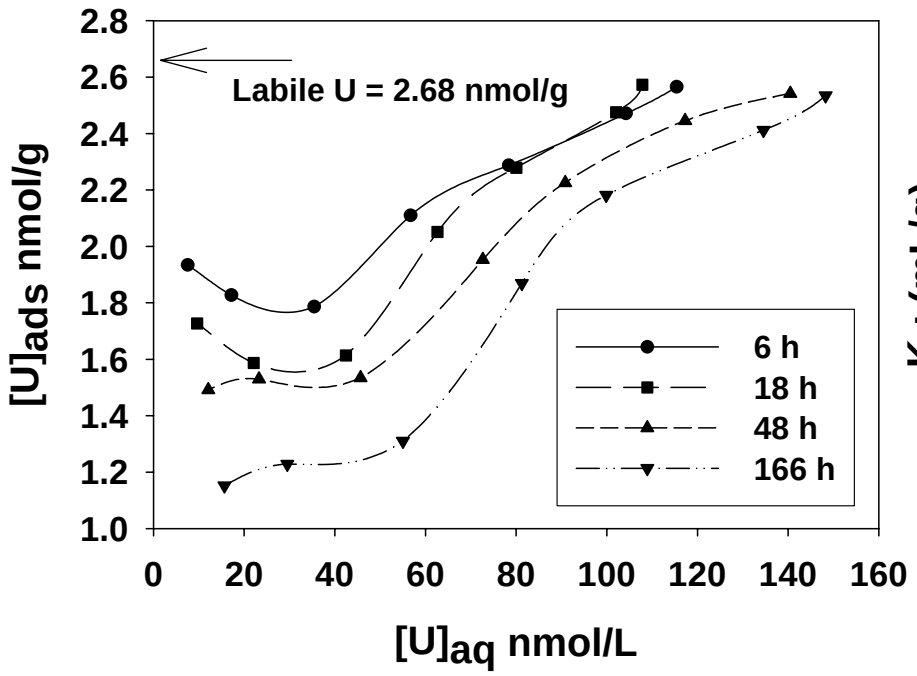
# Uranium Sorption on SPP and NPP Capillary Fringe Sediments

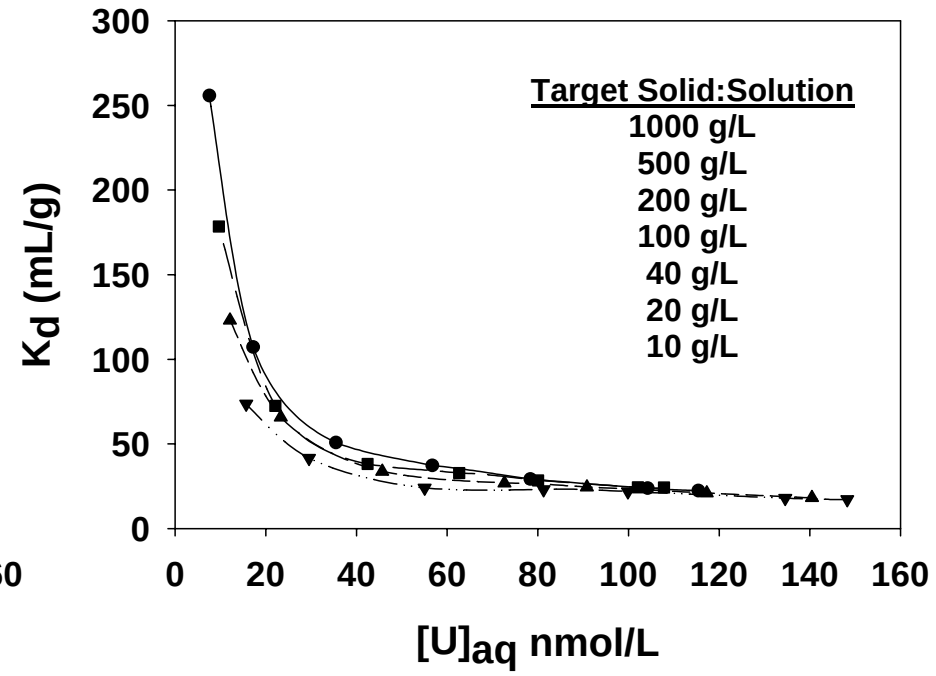
$$\Gamma_i = \frac{\Delta m_i M_{Tw}}{S}$$




$$[U(VI)]_{TOT} = [U(VI)]_{lab} + [U(VI)]_{spike}$$

# Uranium Desorption from SPP2, 18 ft bgs Sediment in Synthetic Groundwater



# $K_d$ Estimation for "*In-Situ*" 300 Area Sediments

Basic Data

SPP2-18', $K_d$ (< 2.0 mm) = 9.24 ± 5.87 mL/g

NPP1-16', $K_d$ (< 2.0 mm) = 82.5 ± 48.3 mL/g

F = .917 (> 2.0 mm)

I-F = .083 (< 2.0 mm)

$K_d$ Estimation [*Cantrell, Serne, and Last (2002)*]

$K_{dgc}$ = (I-F) $K_d$ < 2.0 mm + (F) 0.23 $K_d$ < 2.0 mm

SPP2-18', $K_{d(gc)}$ = 1.94 (0.73 – 4.43)

NPP1-16', $K_{d(gc)}$ = 24.2 (10.1 – 38.4)

$K_{dgc}$ = (I-F) $K_d$ < 2.0 mm

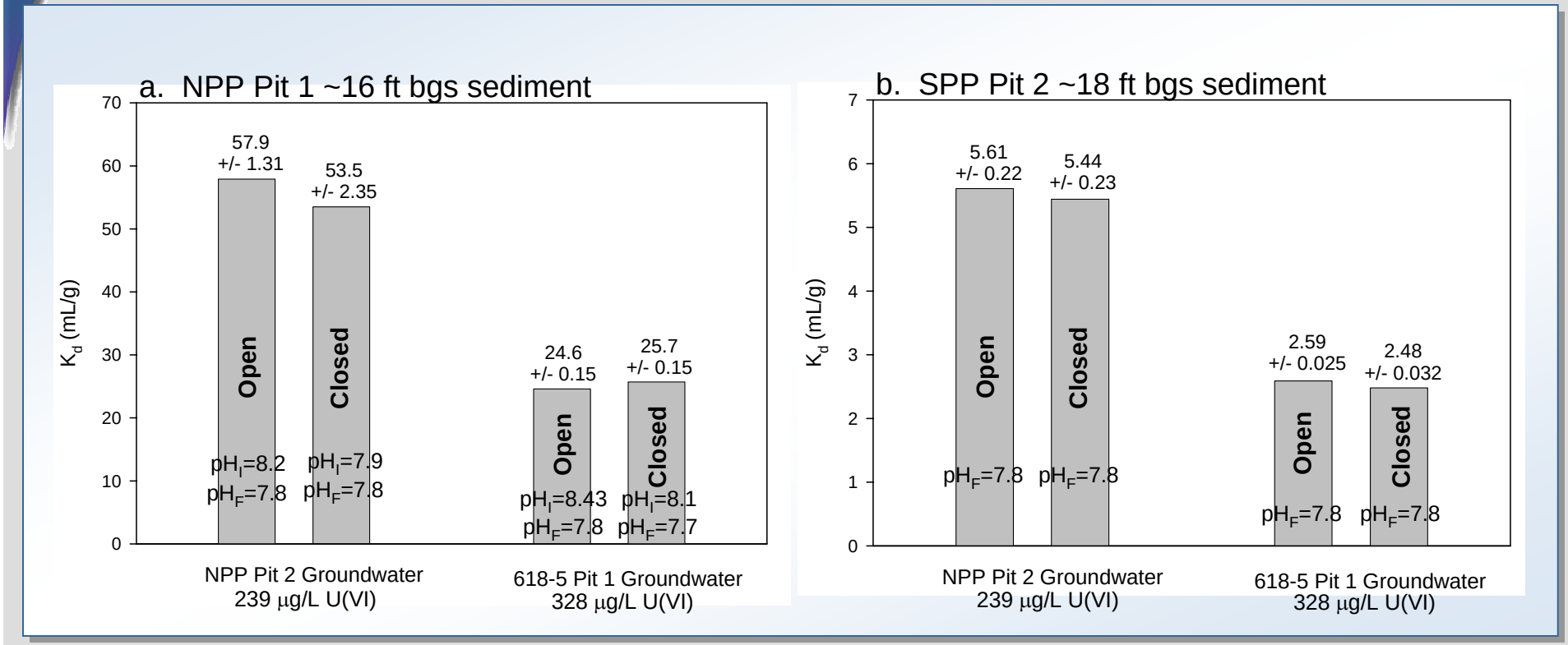
SPP2-18', $K_{d(gc)}$ = 0.76 (0.27 – 1.25)

NPP1-16', $K_{d(gc)}$ = 6.84 (2.84 – 10.85)

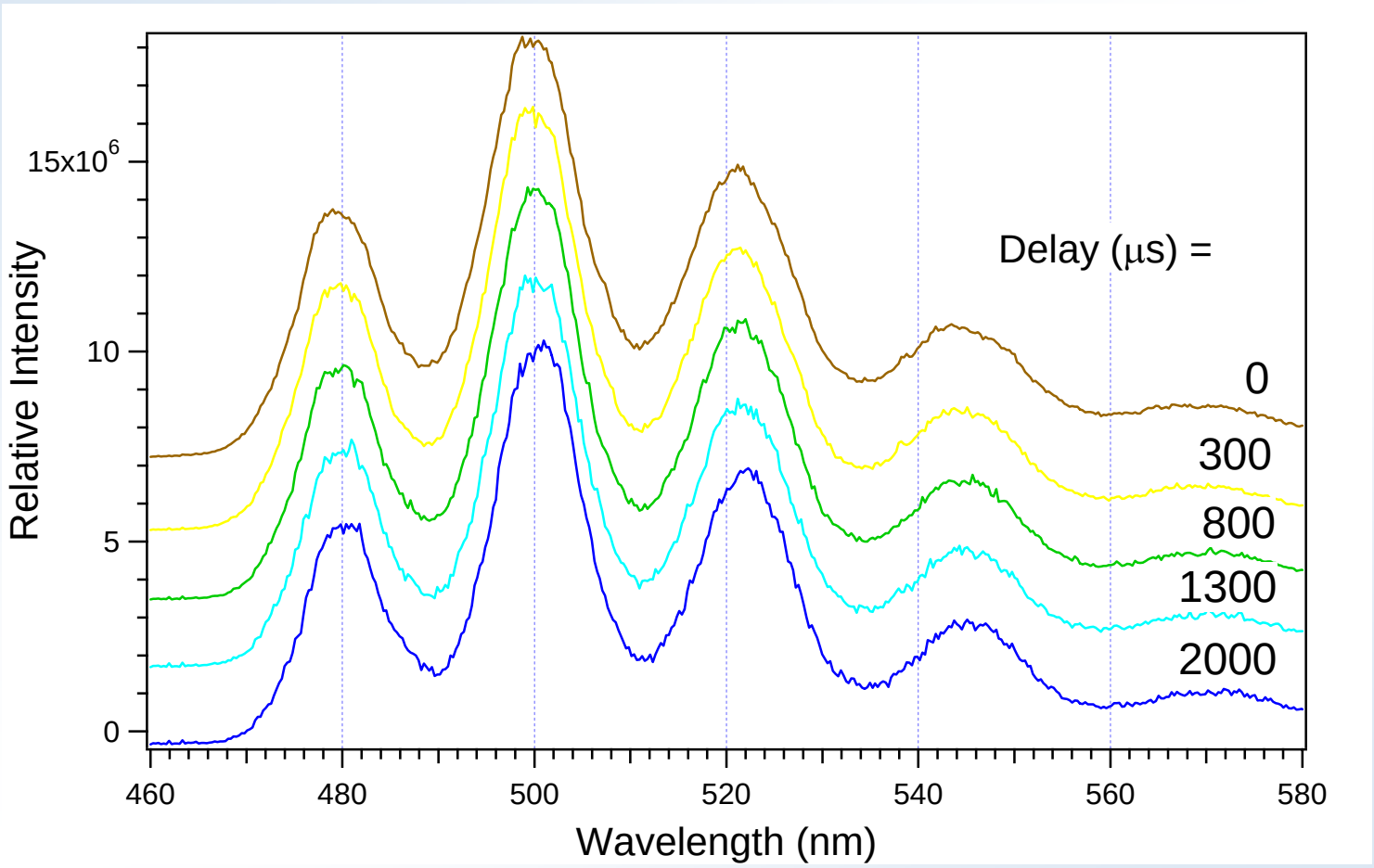
# Conclusions

- Sorption degree dependent in groundwater composition and materials properties
  - DIC
  - Silt and clay
  - Extractable Fe(III) ?
  - Clinochlore ?
- $K_{d(gc)}$ may range between 0.27-38.4 mL/g
  - $F_g$ and $F_{s+c}$ are critical
  - Spatial variance across 300 A
- Sorption and desorption reach a common equilibrium state
  - Significant times are required

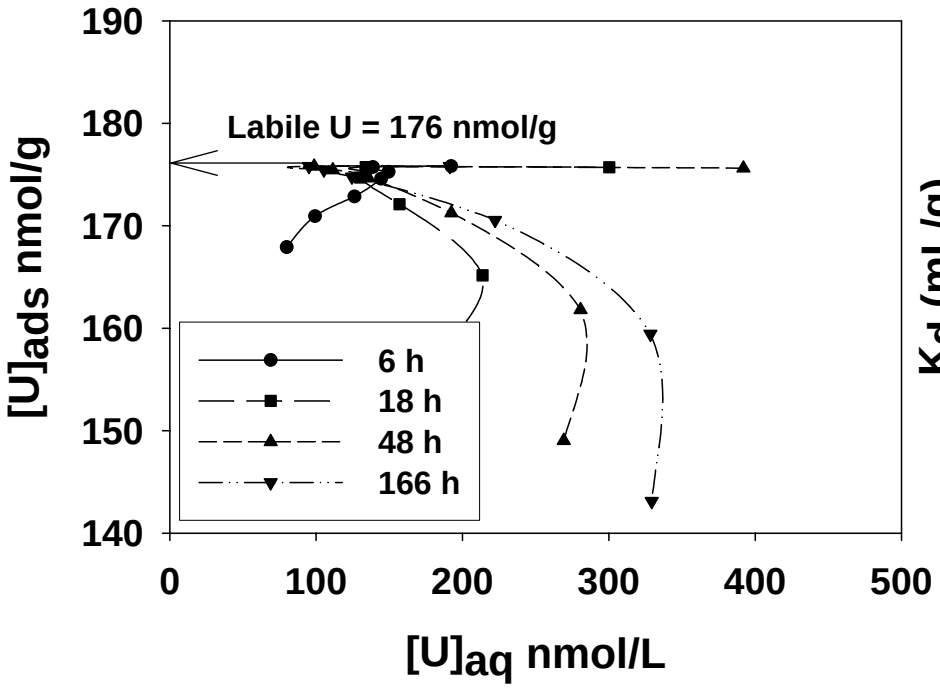
# Effect of Groundwater Degassing on U(VI) Distribution Ratio

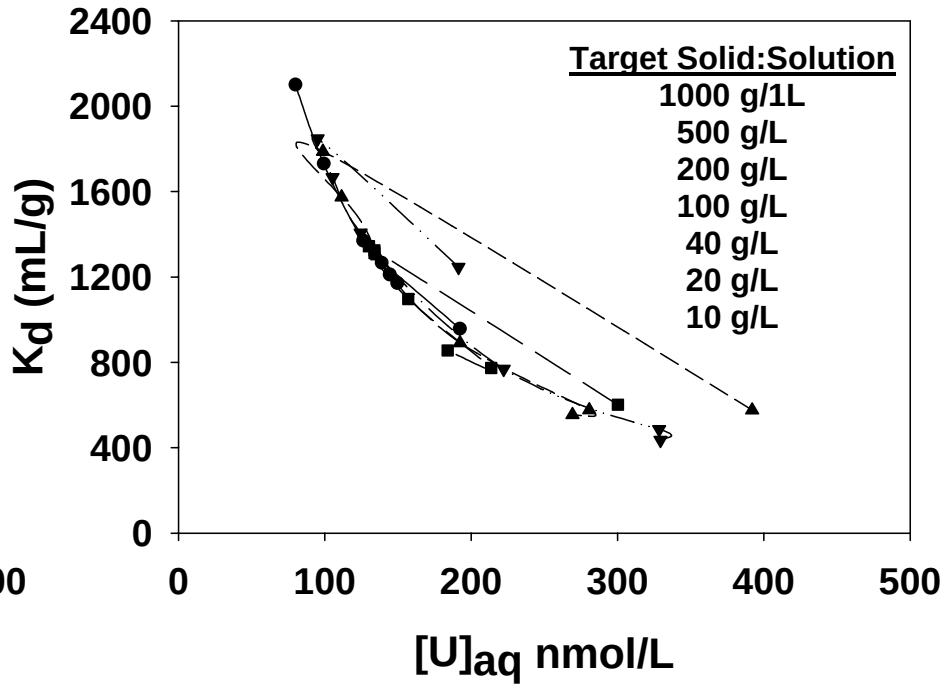


# Normalized Time-Resolved U(VI) Fluorescence Intensities of JOOHM2 Groundwater Sample

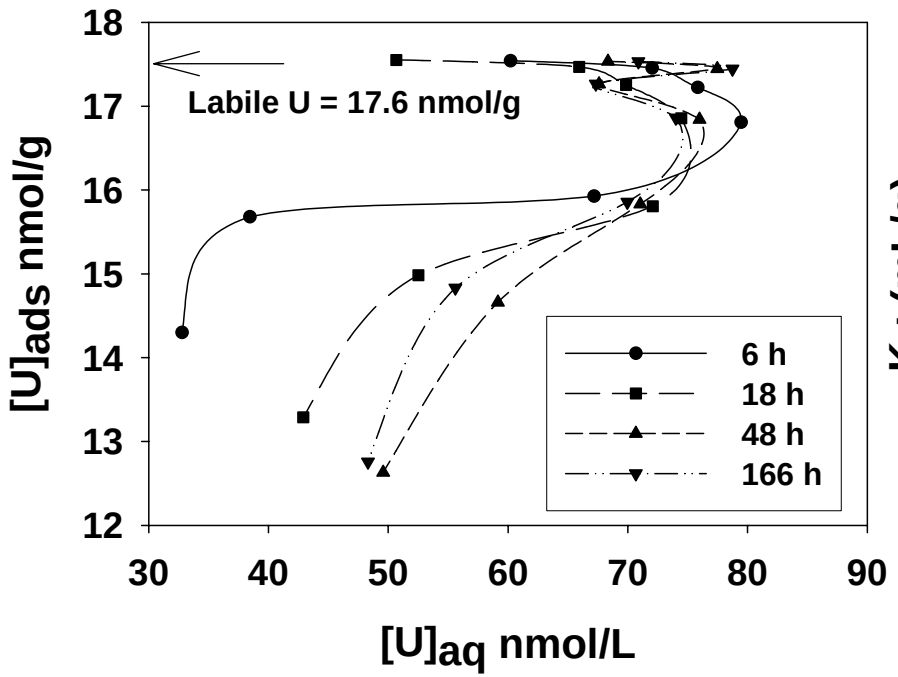


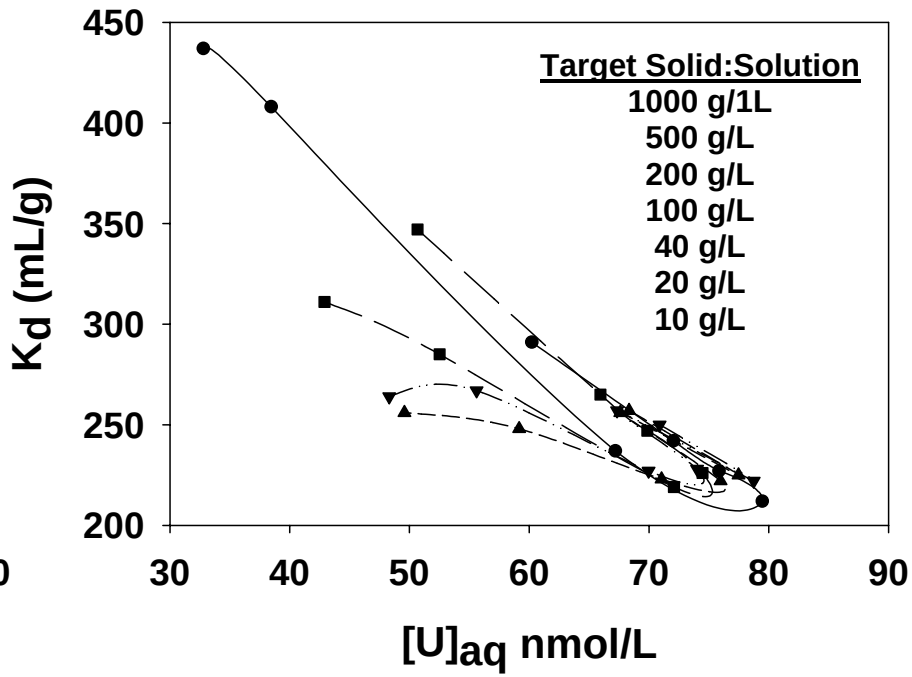
# Uranium Desorption from NPP2, 2 ft bgs Sediment in Synthetic Groundwater



# Uranium Desorption from NPP1, 16 ft bgs Sediment in Synthetic Groundwater



# U(VI) Distribution in NPP1-16' Sediments Equilibrated in Simulated Groundwater at Different Solids Concentrations