

# **REACTIVE TRANSPORT PROCESSES IN 300 AREA HANFORD SEDIMENTS**

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# Motivating Field Observations

- ▶ **The 300 A U(VI) plume has not dissipated as rapidly as expected**
  - Erroneous sorption parameter estimates
  - Continued flux from the vadose zone
  - Non-equilibrium geochemical processes (e.g., slow desorption)
- ▶ **Groundwater U(VI) concentrations increase in irregular fashion with river stage**
  - Desorption/dissolution from capillary fringe sediments
  - Effects of contact time and water composition

# Objectives

- ▶ Evaluate desorption/dissolution rates and extent of contaminant U(VI) from vadose zone, capillary fringe, and aquifer sediments under advective conditions
- ▶ Determine sorption behavior and retardation coefficients for dissolved U(VI) in relevant groundwater matrices under *in-situ* water: rock ratios
- ▶ Identify whether U(VI) distribution reactions (sorption/desorption) exhibit equilibrium or non-equilibrium behavior and the respective conditions

# Experimental Approach

## SPP sediment

$pH_{WATER} = 8.14$

U(VI) labile fraction  
 $2.68 \mu\text{mol kg}^{-1}$

Texture  
93 % sand  
5 % silt  
2 % clay

Clay mineralogy  
montmorillonite 41 %  
muscovite 19 %  
vermiculite 19 %  
chlorite  
(Fe – clinochlore) 15%

$Fe_{AM-OX} = 48 \mu\text{mol g}^{-1}$   
 $Fe_{DCB} = 77 \mu\text{mol g}^{-1}$

## Synthetic groundwater

Carbonate concentration  
SGW1 [ $0.335 \text{ mmol L}^{-1}$ ]  
SGW2 [ $1.045 \text{ mmol L}^{-1}$ ]

$pH_{SGW1} = 7.80$   
 $pH_{SGW2} = 8.05$

Predominant aqueous species

$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$   
 $\text{UO}_2(\text{CO}_3)_2^{2-}$   
 $\text{UO}_2(\text{CO}_3)_3^{4-}$   
 $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$

$\text{HCO}_3^-$

## Column experiments

### Dimensions

$15 \times 3.2 \text{ cm}$

### Bulk Density

$1.65 - 1.69 \text{ g cm}^{-3}$

### Water content

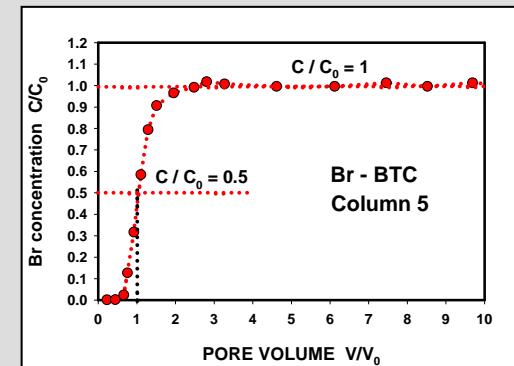
$0.4 - 0.42 \text{ cm}^3 \text{ cm}^{-3}$

### Dispersivity

$0.28 - 1.52 \text{ cm}$

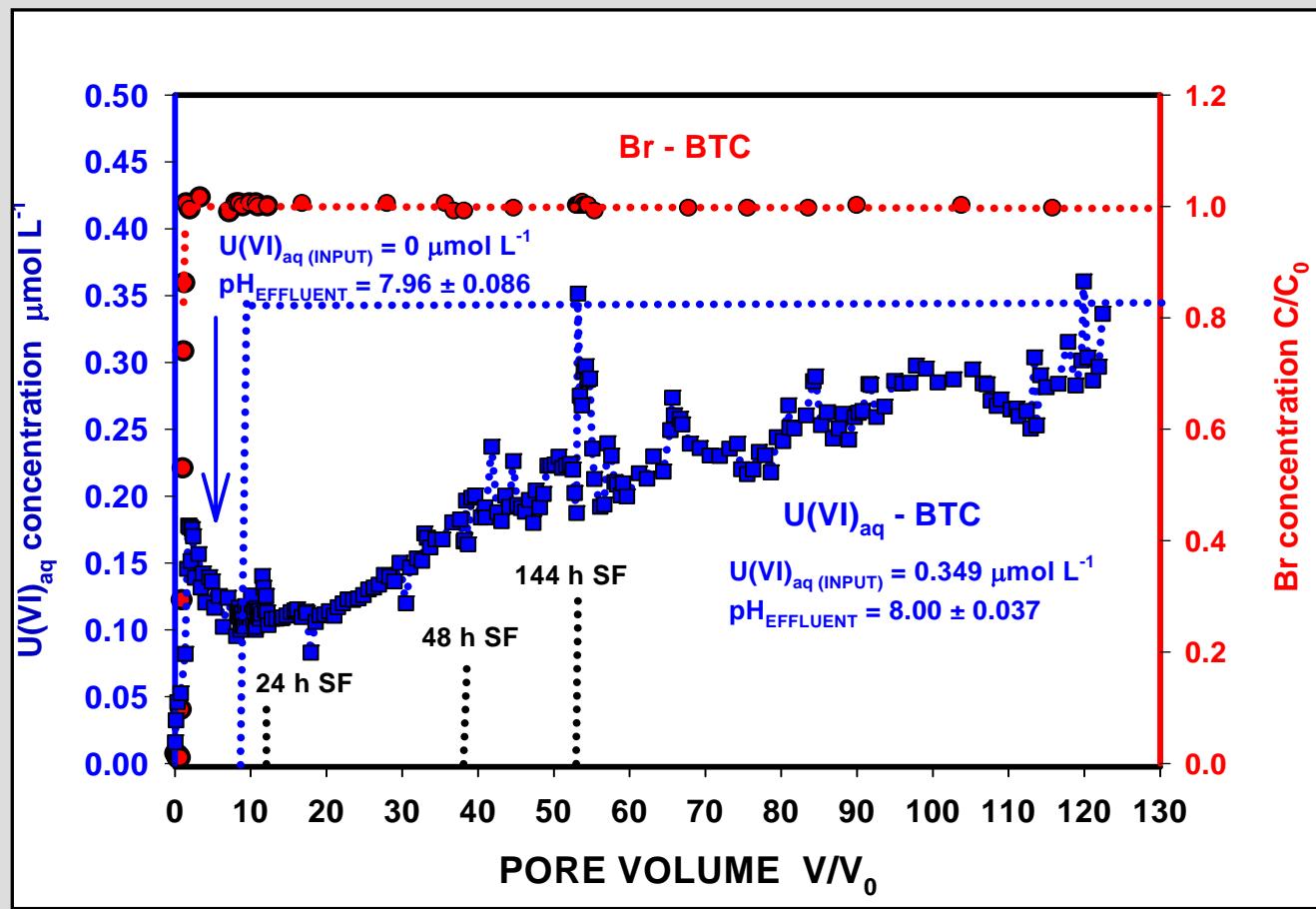
### Peclet Number

$9 - 51$



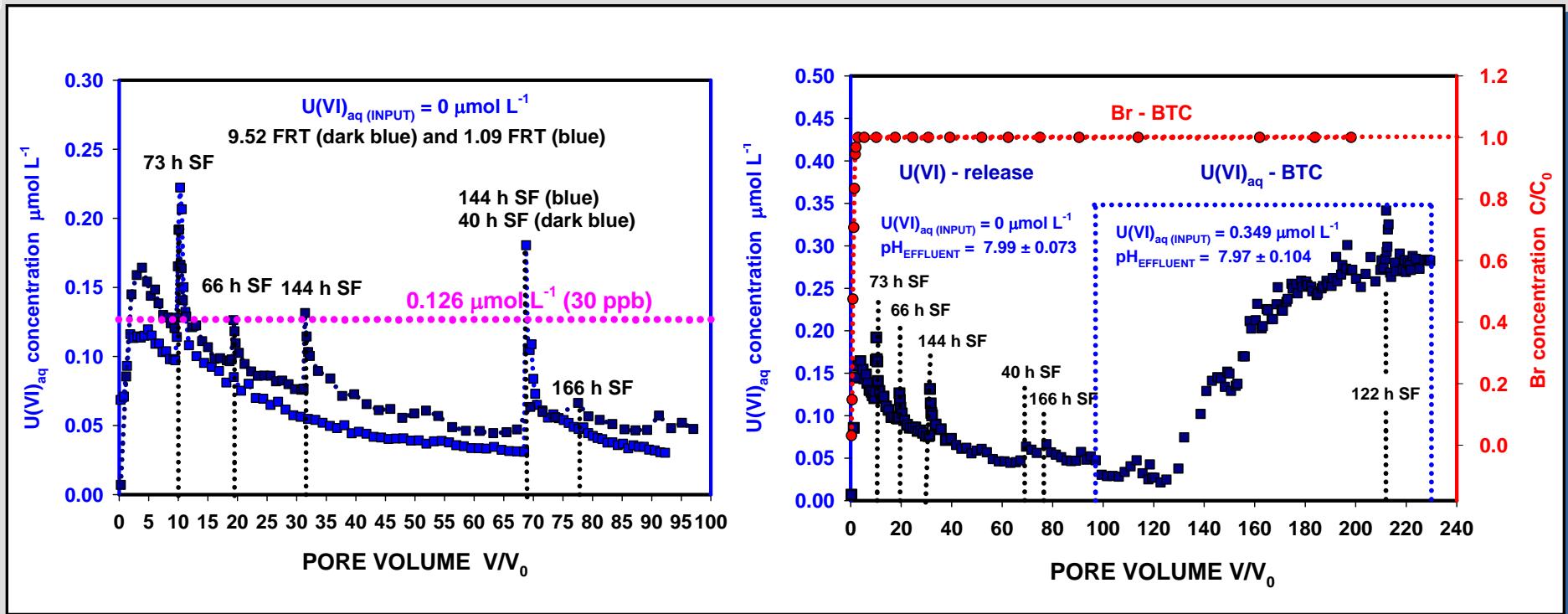
# U(VI) Breakthrough Curve (BTC)

**SGW2 [U(VI)] = 0.349  $\mu\text{mol L}^{-1}$ ;  $\text{CO}_3$  = 1.045 mmol  $\text{L}^{-1}$**   
**Fluid Residence Time (FRT) = 9.90 h**



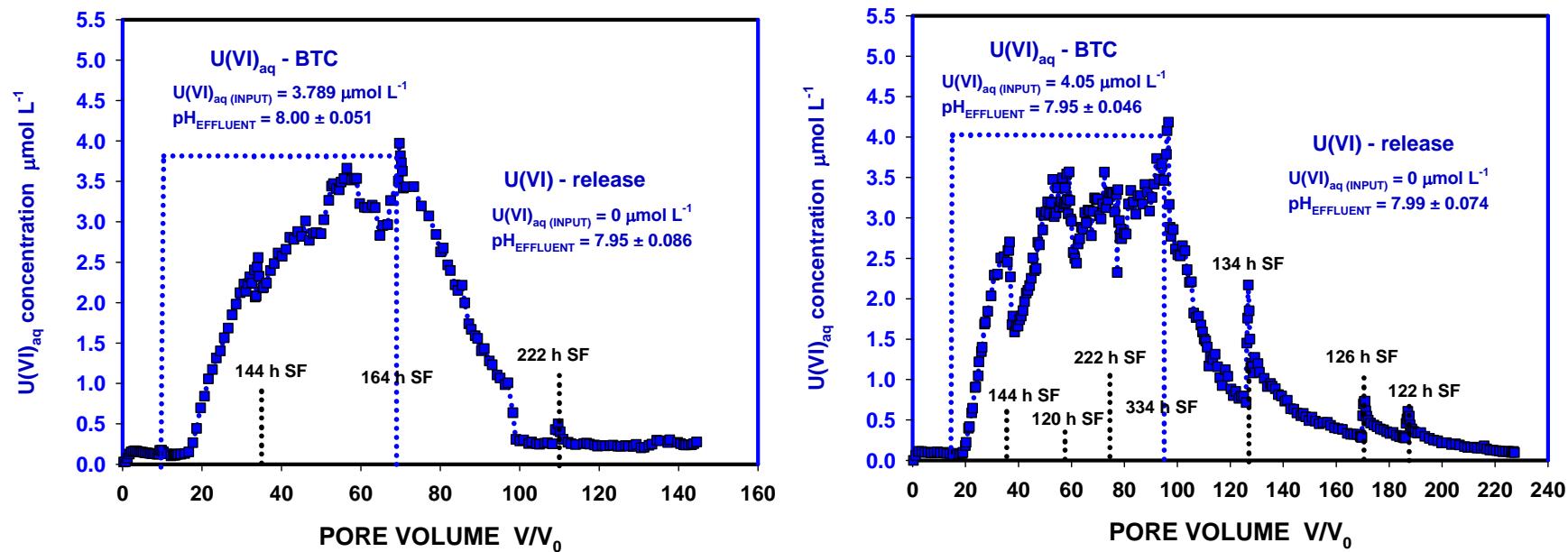
# U(VI) Release from the Sediment

**SGW2 [CO<sub>3</sub> = 1.045 mmol L<sup>-1</sup>]  
FRT = 1.09 and 9.52 h**



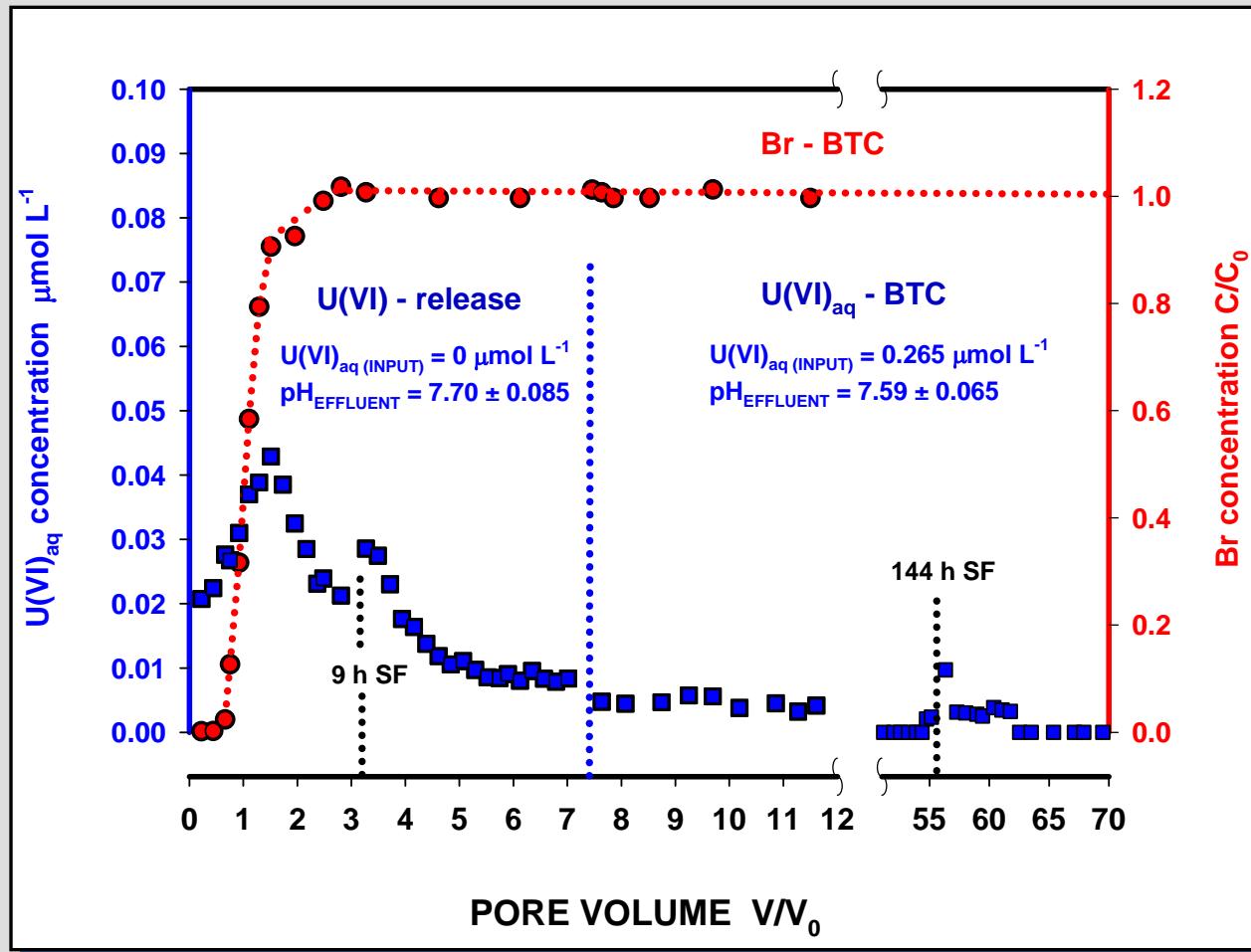
# U(VI) Sorption and Desorption

**SGW2 [U(VI)] = 3.7 and 4.0  $\mu\text{mol L}^{-1}$ ;  $\text{CO}_3 = 1.045 \text{ mmol L}^{-1}$   
FRT = 10.21 h (left) and 1.10 h (right)**



# Carbonate Effect on U(VI) Sorption

**SGW1 [U(VI) = 0.265  $\mu\text{mol L}^{-1}$ ;  $\text{CO}_3 = 0.335 \text{ mmol L}^{-1}$ ]  
FRT = 8.89 h**



# Overall Findings and Implications

- ▶ U(VI) sorption and dissolution/desorption show strong time dependence in < 2 mm sediment
  - Non-equilibrium conditions may persist in the field
- ▶ Considerable variation in qualitative rates of uptake and release
  - Contact time, physicochemical state, sediment properties, and  $[HCO_3]$
  - U(VI) reaction vector
- ▶ Residual U(VI) in the vadose zone below SPP and NPP has potential to influence groundwater quality
  - Recharge amount and porewater velocity are key

# Additional Research

- ▶ Saturated column studies with other contaminated 300 A sediments to parameterize a kinetic U(VI) dissolution/desorption transport model
- ▶ Unsaturated flow experiments to determine the influence of water content and large pore desaturation on vadose zone release, transport, and U(VI) flux
- ▶ A larger, flow-cell experiment to test model scale-up to 300 A materials with significant gravel content