300 A Integrated Hydrogeochemical Conceptual Model for Uranium

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Important 300 A Findings for Conceptual Model

- Process Pond Sediments (PPS, PNL-6442; PNNL-15121)
  - U(VI) present in vadose zone sediments to water table with nominal concentrations of 10-20 mg/kg. Hot spots found in NPP (100-200 mg/kg)
  - U(VI) dissolves/desorbs slowly from contaminated sediments over periods of months yielding concentrations in contacting waters > MCL. Many pore volumes (>100) needed to remove residual/sorbed U
  - U(VI) desorption and adsorption Kd's large (>5 to in excess of 10 for whole sediment)

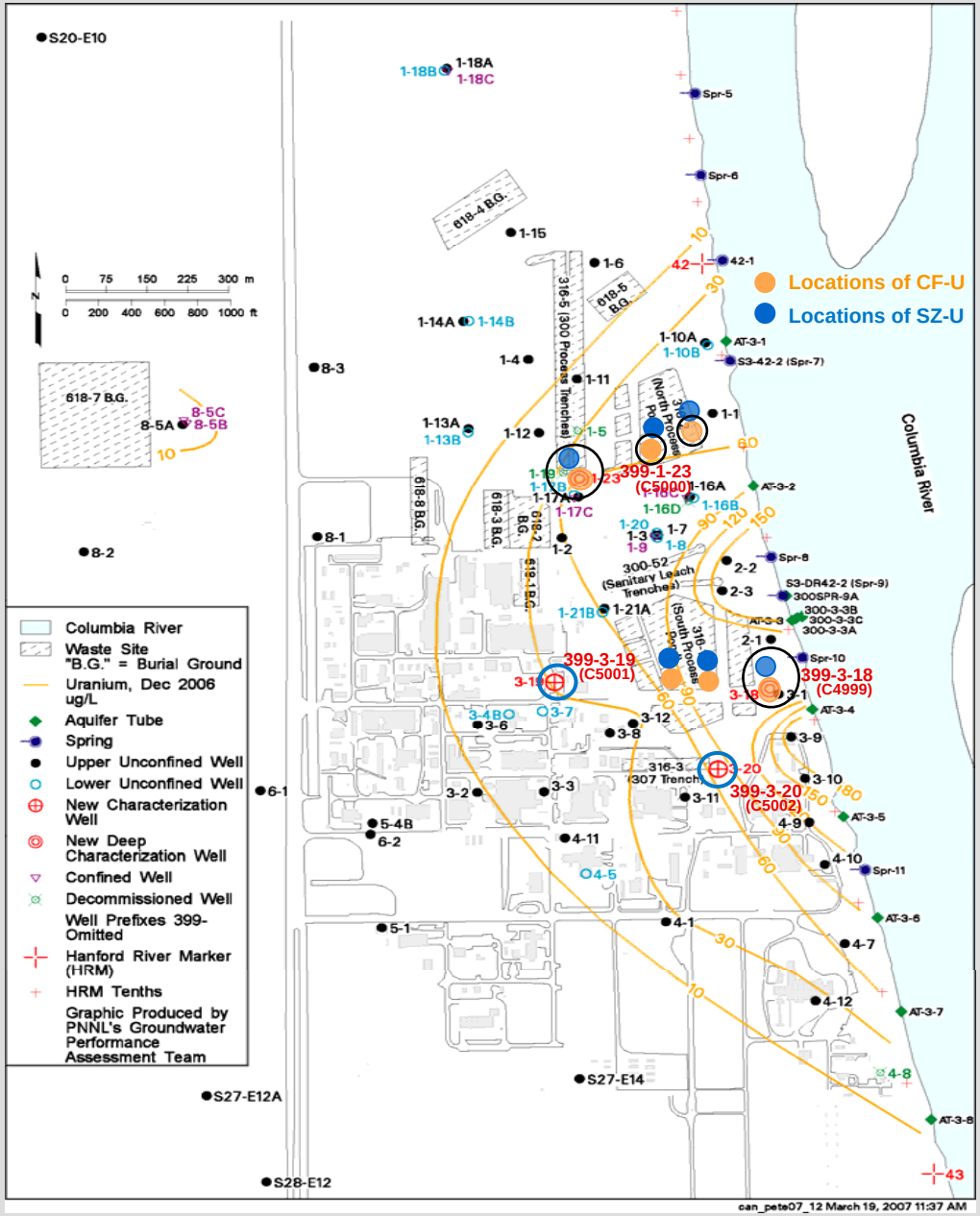
- Groundwater Monitoring (PNNL-15127)
  - Seasonal dynamics to U plume with inward and outward migration of high concentration zones
  - Lingering U concentrations near and above MCL in spite of source term removal. Slowly decreasing concentrations
  - Anecdotal evidence of fast migration

- LFI (PNNL-16435)
  - Measurable U found proximate to disposal facilities with highest concentrations in deep vadose zone
  - Groundwater concentrations variable, elevated near higher concentrations in vadose zone
  - Adsorbed concentrations in aquifer sediments low. Sorbed and total U concentrations in most sediments analytically indistinguishable from background. These contrast with PPS.

Important Questions for Conceptual Model

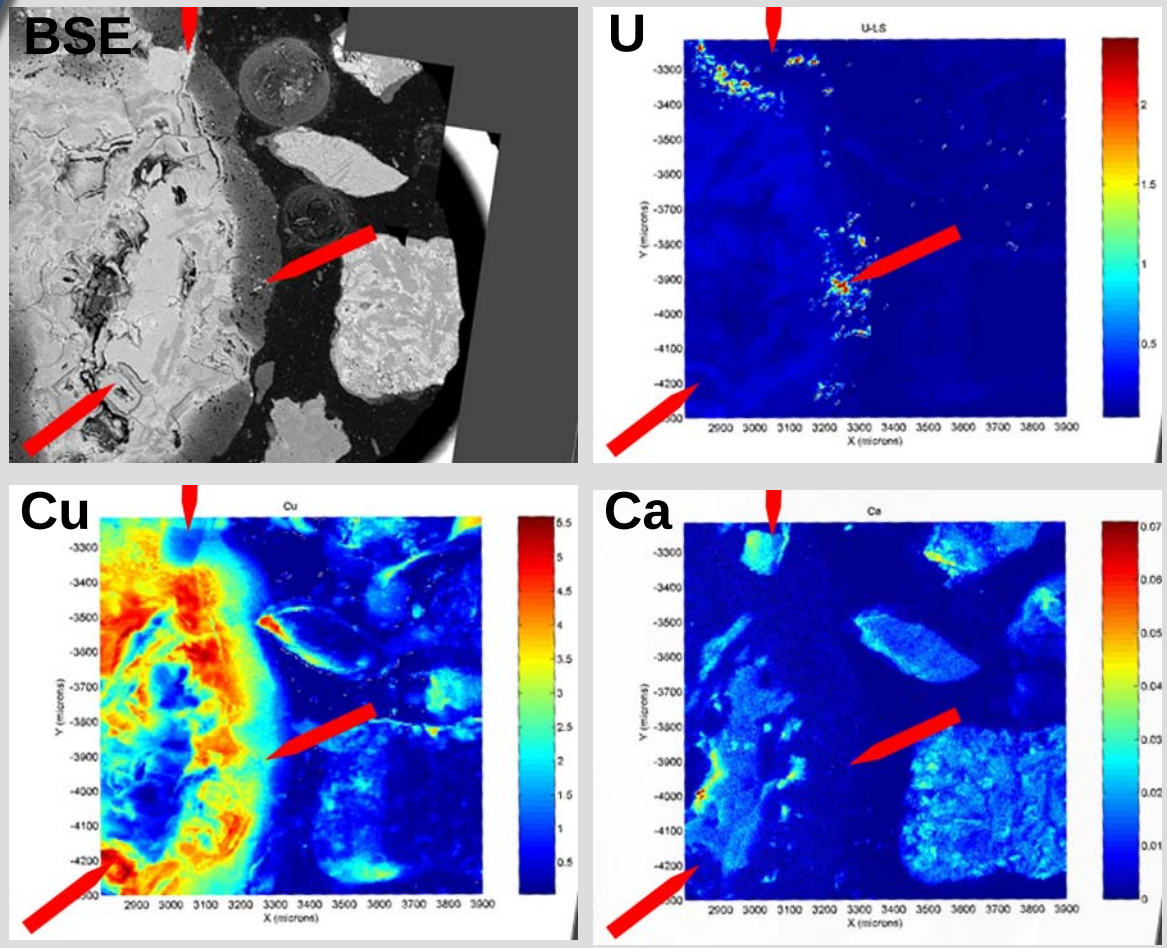
- Are Process Pond and other site sediments equivalent or different?
  - Which materials control U concentrations
  - Can behavior of materials from different sampling campaigns be reconciled
- What are potential sources for U resupply to the plume?
  - Recharge through upper vadose zone* (PNNL-15121)
  - Residual/redeposited U in lower vadose zone
  - Sorbed U on aquifer fines
  - Diffusion from the Ringold formation* (PNNL-16435)
  - Undefined "diffuse sources"
- What are causes/explanations for dramatic seasonal trends?
  - Advection versus geochemistry
  - Water composition flowpath (saturated zone) versus elevation (vadose zone) effects
- What are key processes that must be quantified for improved future projections?

Documented Locations of Solid-Associated U



Upper Vadose Zone Sediment (0.5’ bgs)

--- 238 mg/kg U ---



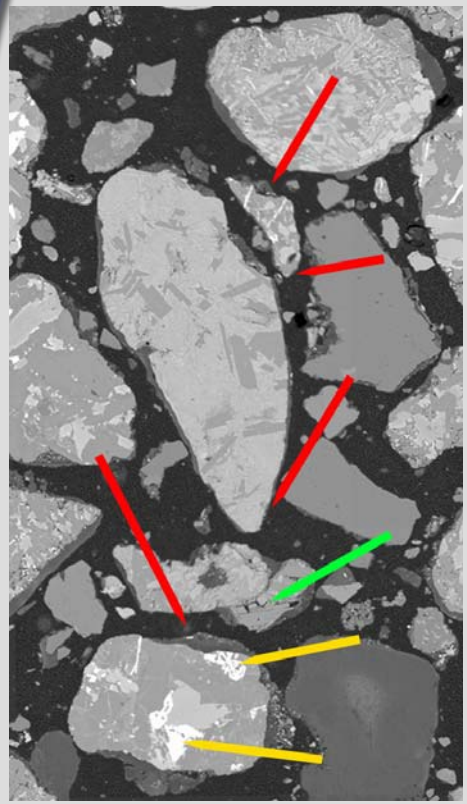
- Core includes Cu, Fe (base treatment to limit Cu mobility)
- U inclusions in aluminosilicate ‘rind’ on precipitate clast
- Multiple or varying precipitation environment
- U, Cu, and Ca do not correlate, but
- Low U associated with low Ca

NPP2 - 0.5’

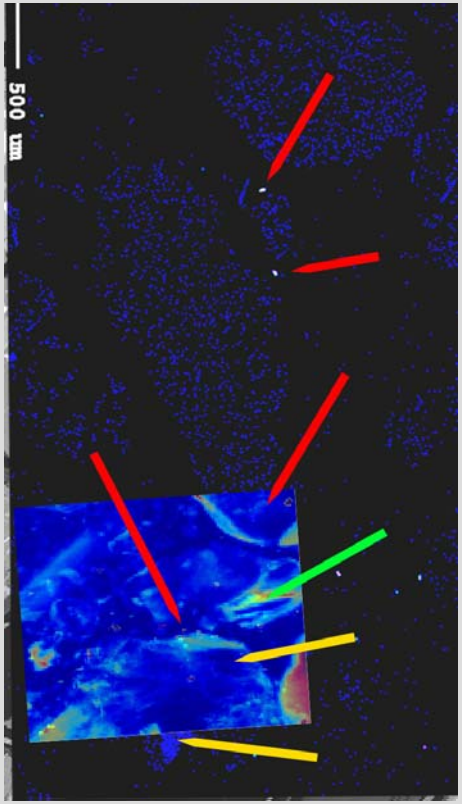
Elemental Abundances in Intermediate Depth Vadose Zone Sediment (4' bgs)

- U(VI) discrete microscopic inclusions in aluminosilicate rinds (Red Arrows)
- Low-level U(VI) present in aluminosilicate rinds (Green Arrow)
- Cu associated with low-level uranium in aluminosilicate rinds
- Low-level U associated with (Ca: calcium carbonate)

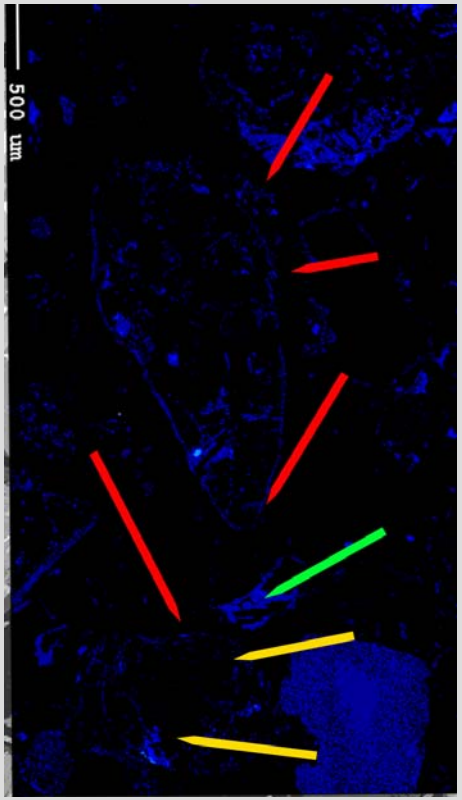
NPP2 - 4



BSE

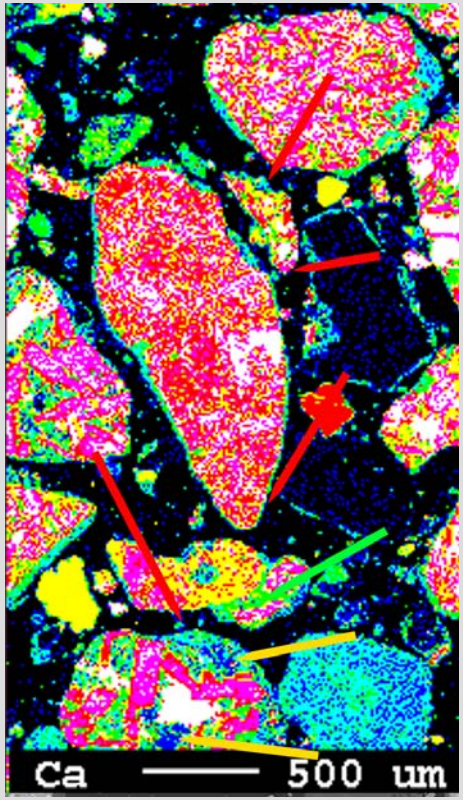


Copper



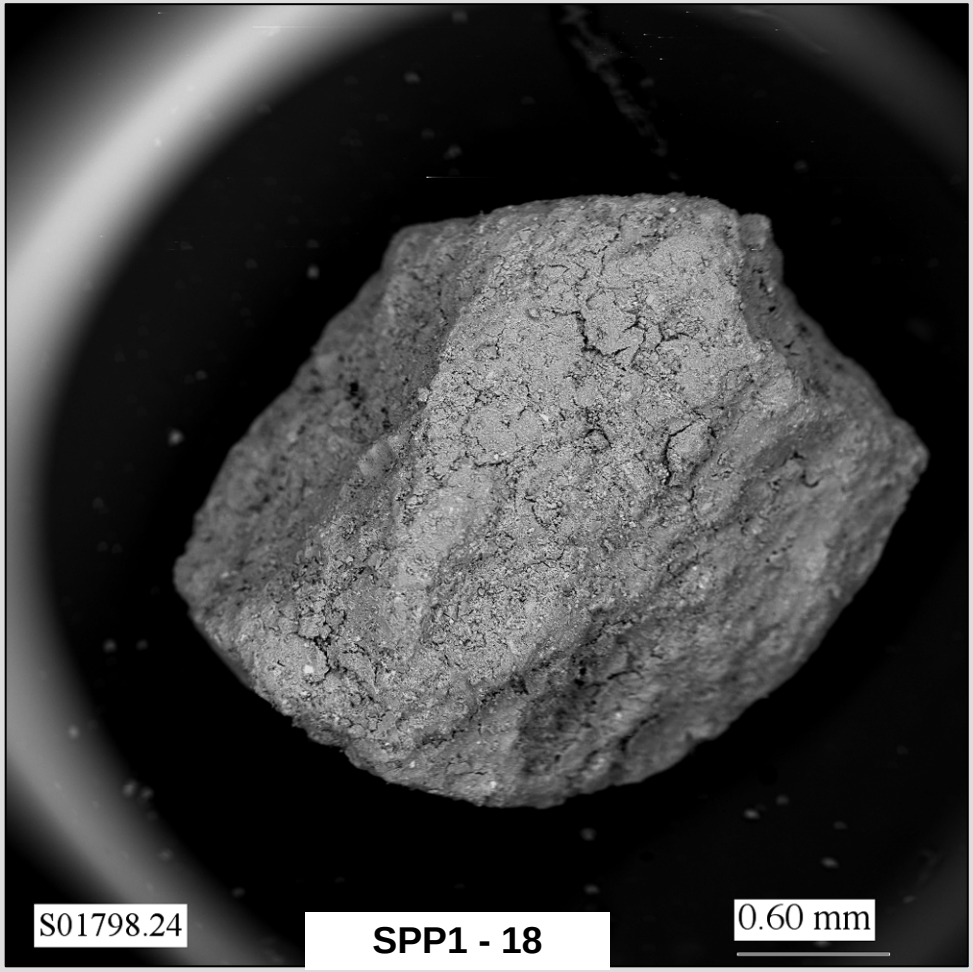
Uranium

--- 139 mg/kg ---



Calcium

Deep Vadose Zone Sediment (18' bgs)
--- 7.5 mg/kg U ---



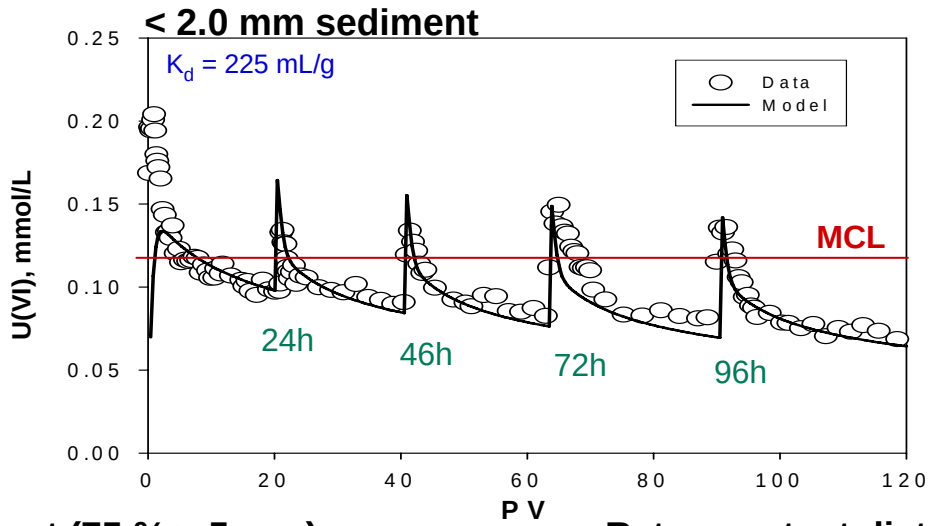
- Secondary surface precipitates even at this depth
- U(VI) around 2X background is invisible to most microscopies and spectroscopies

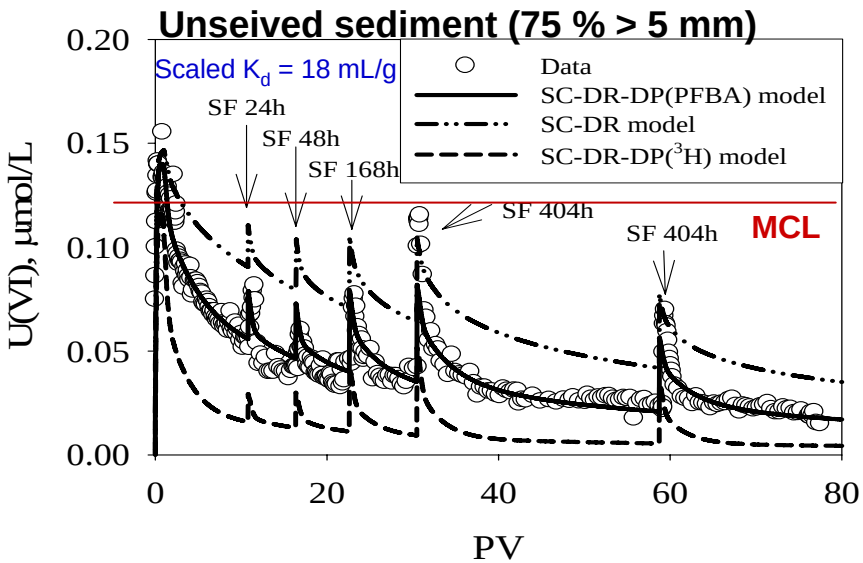
Large Column Experiment with NPP1-14 to Investigate Scaling of Reaction and Mass Transfer Parameters

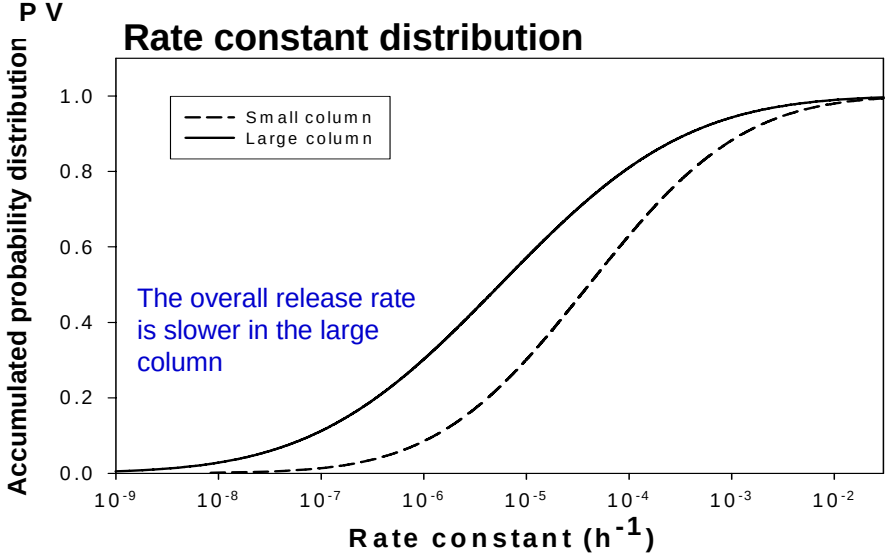
Unseived Sediment with River Cobble and Mud

The 80 kg Column

Small and Large Column Results and Rate Constant Distribution from the Distributed Rate Model (DRM)

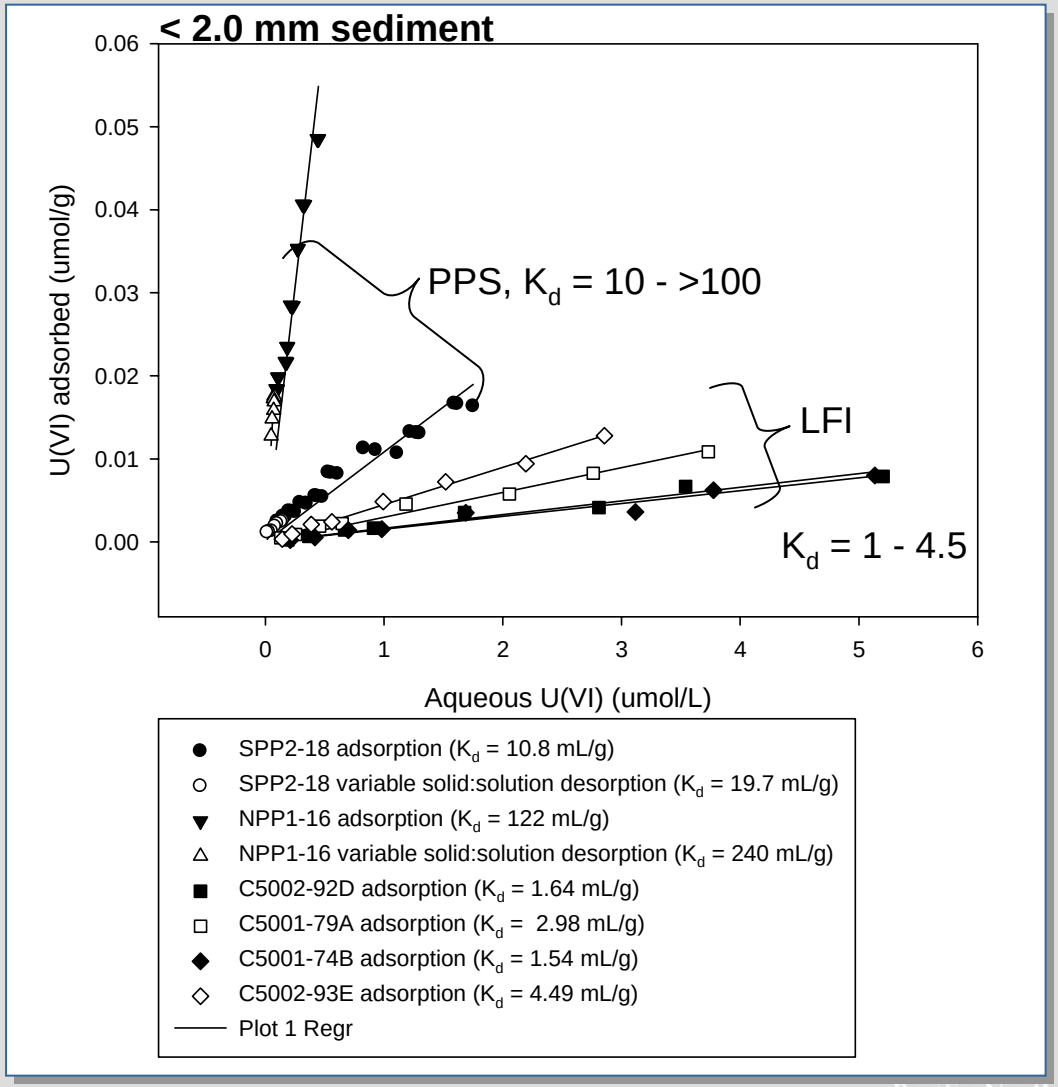




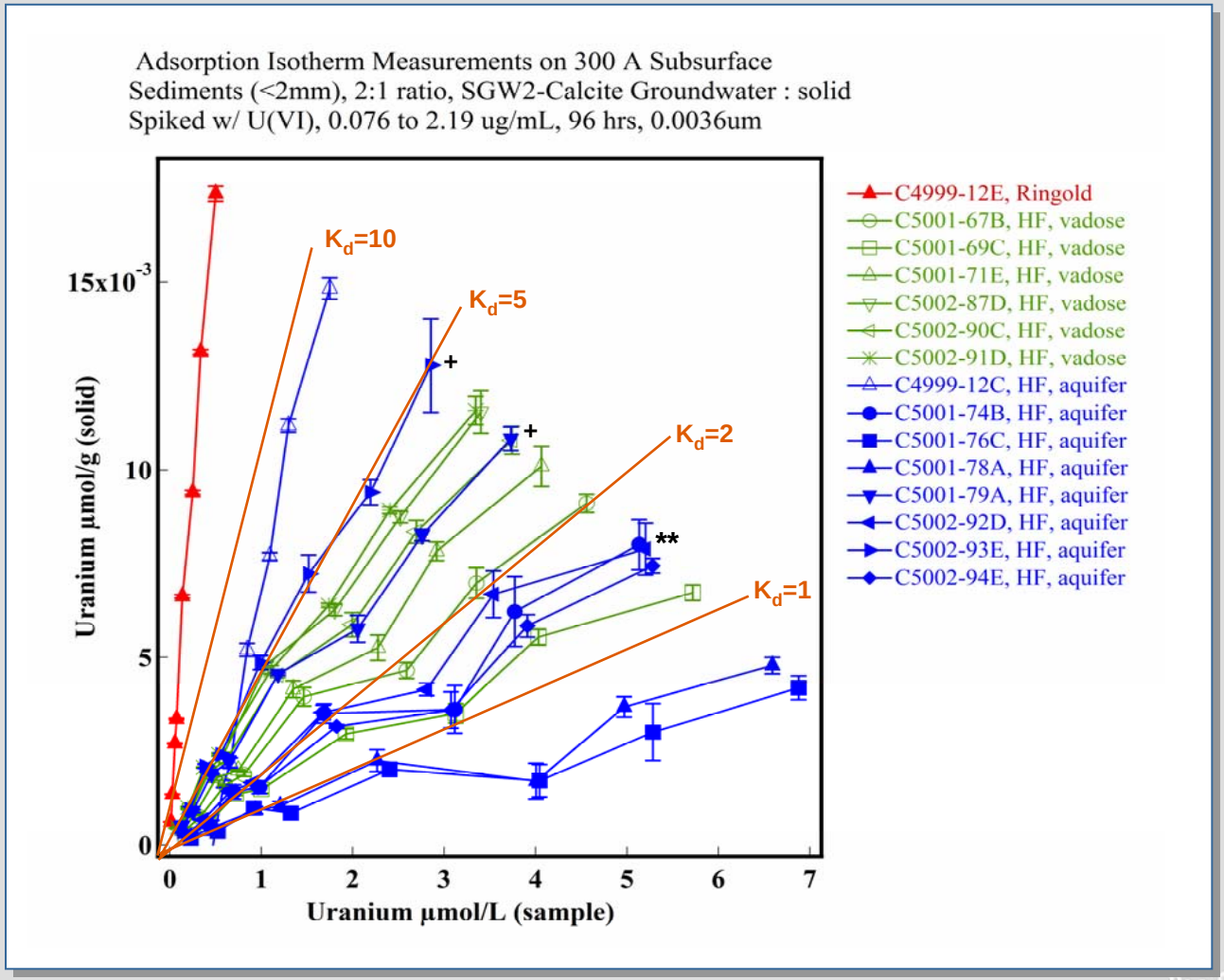


Adsorption Isotherms of U(VI) on Process Pond and LFI Sediments (pH ≈ 8.2)

- Sediment suspensions spiked with increasing U(VI) concentrations [c], with [c]<MCL>[c]
- Solid-liquid distribution measured and final aqueous and sorbed concentrations plotted to yield "isotherm"
- Linear relationships indicate the K_d concept is valid for the experimental conditions
- Isotherm slope = K_d

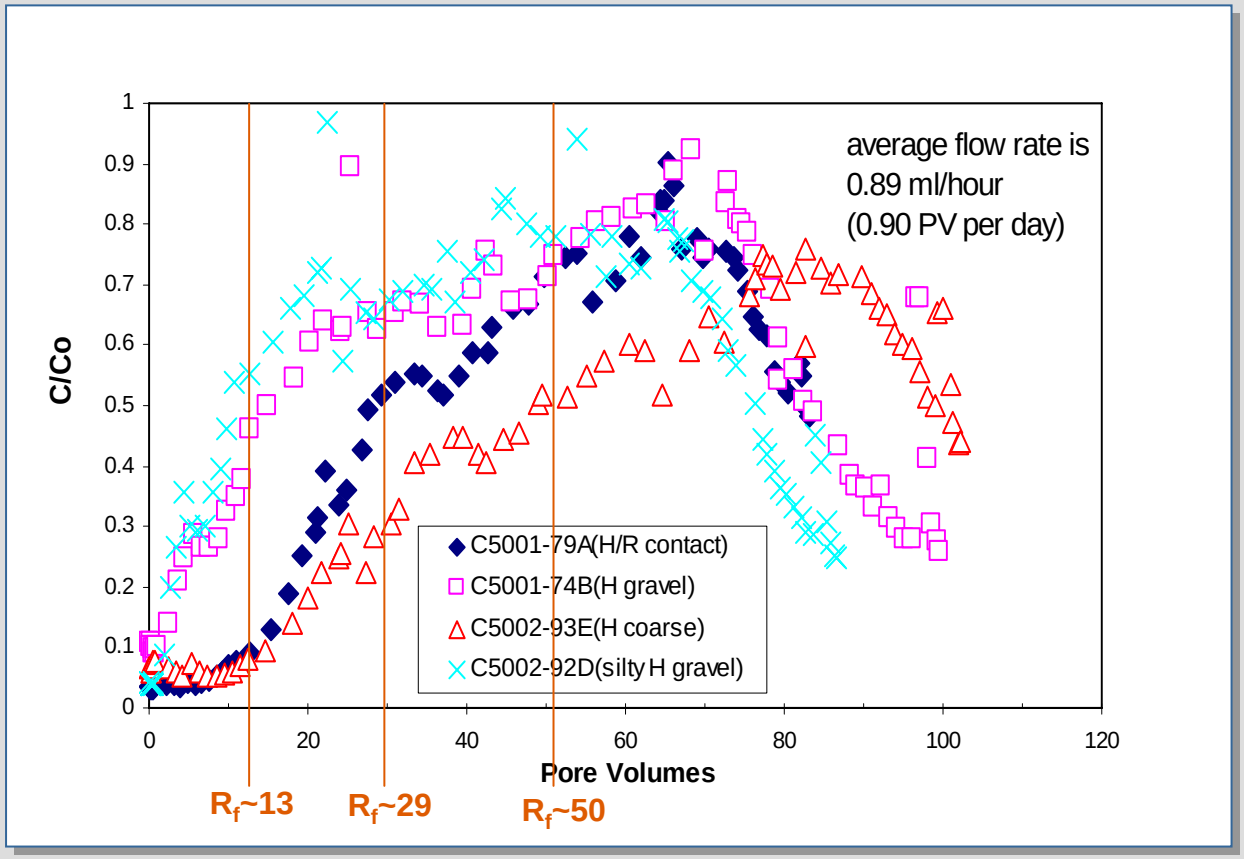


U(VI) Adsorption Isotherms on Uncontaminated 300 A Vadose Zone and Aquifer Materials from LFI Cores



* K_d for whole sediment ≈ K_d (2 mm)/10

Advective Transport of U(VI) through Hanford Formation Saturated Zone Sediments from LFI Cores (pH ≈ 8.0)

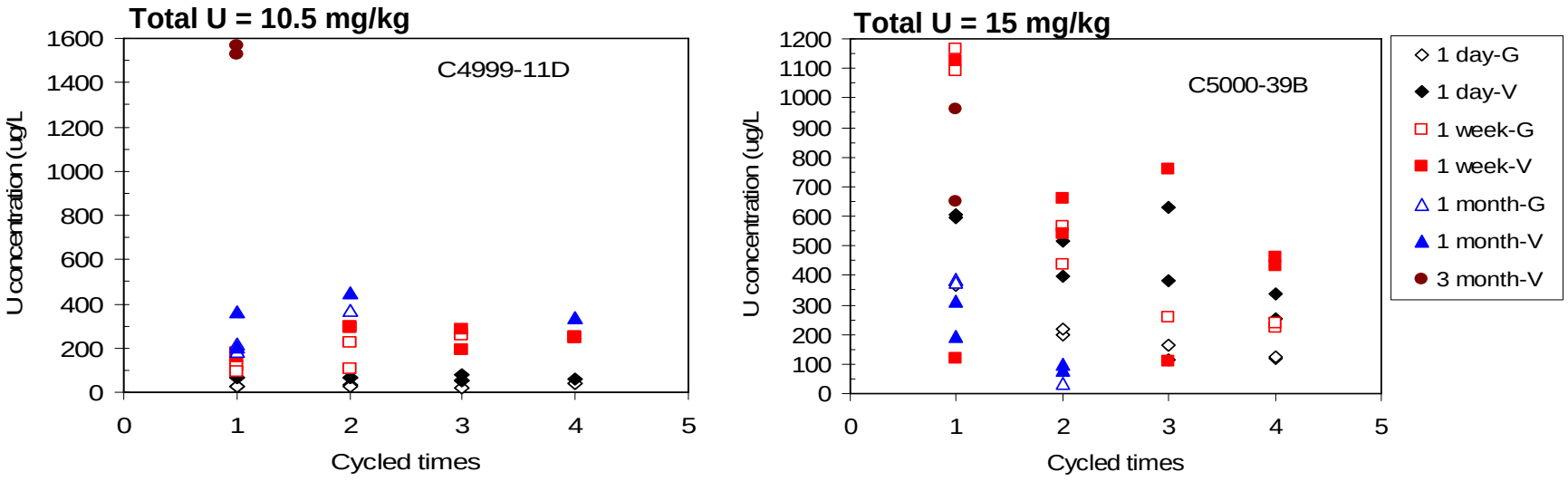


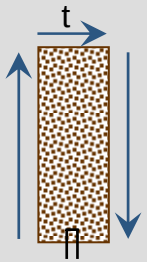
R_f for SPP ≈ 60
R_f for NPP ≈ 700

- R_f range from 13 to 29 to 50
- Processes in addition to adsorption implied

Simulated Effects of Water Table Rise and Fall in U(VI) Desorption from LFI Capillary Fringe Sediments

Near River | **Distant from River**



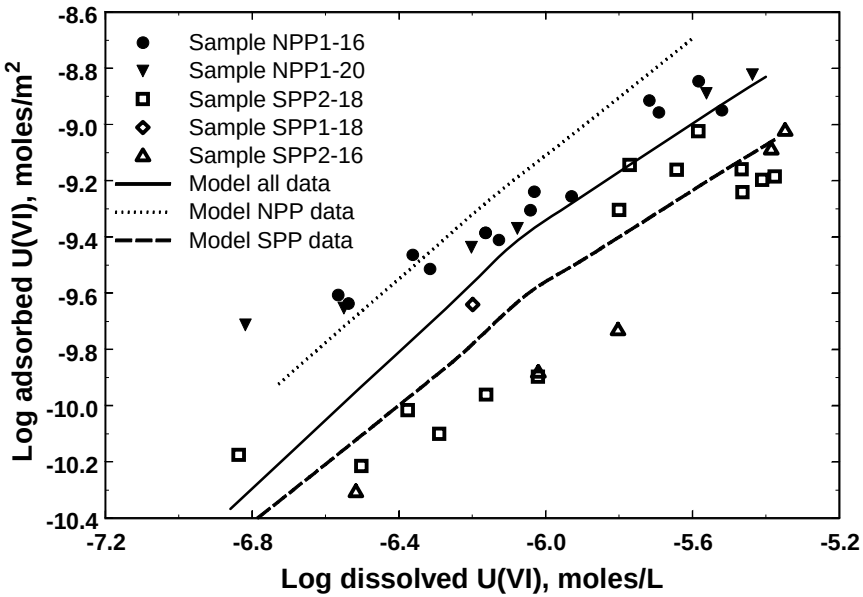


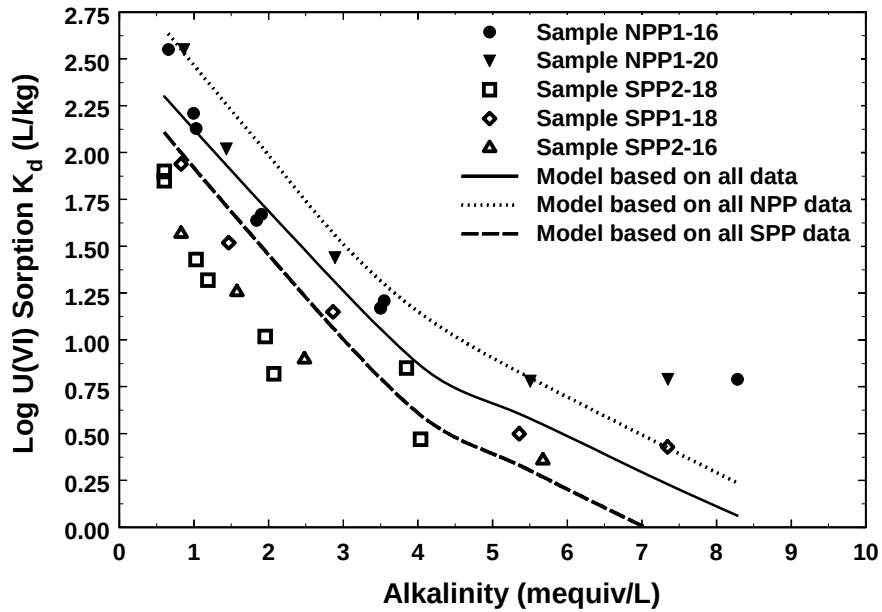
= 1 cycle
t = 24, 168, 720, 2160 h

Cycles
24h – 4
168h – 4
720h – 2
2160 - 1

Water Composition Strongly Effects Solid-Liquid Distribution

Adsorption extent from riverwater > groundwater



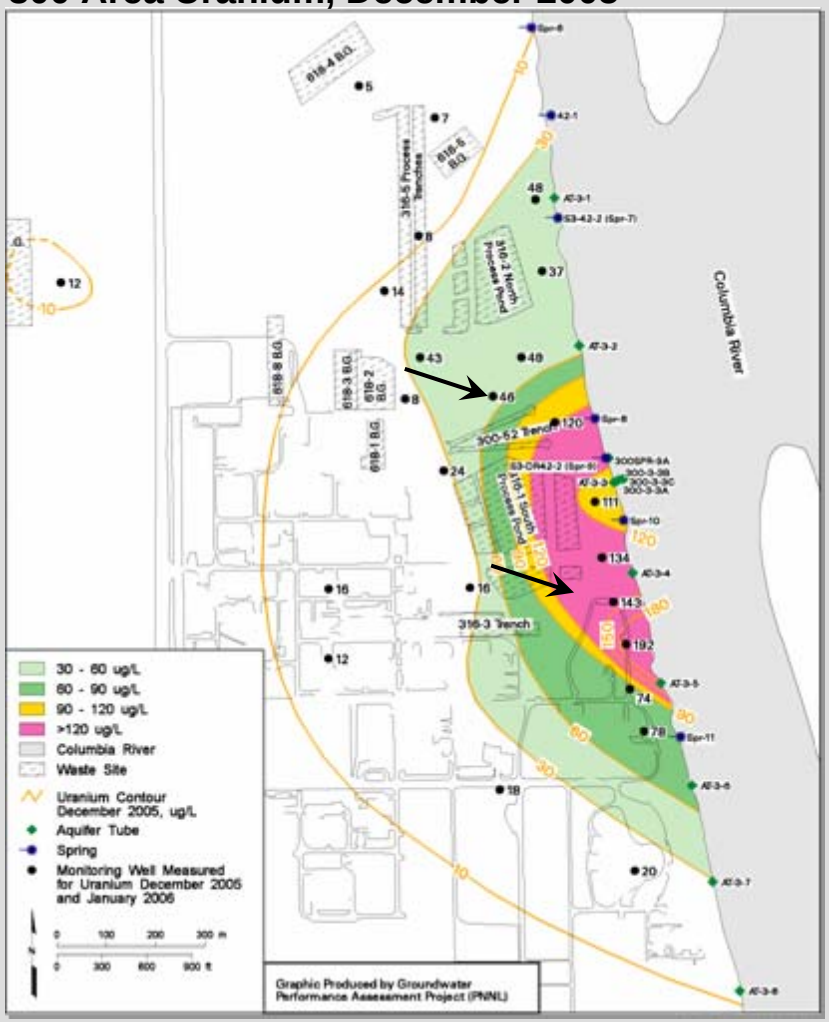


Qualitative Inventory Projections of Waste Sites and Plume Based on Recent Sampling and Analysis

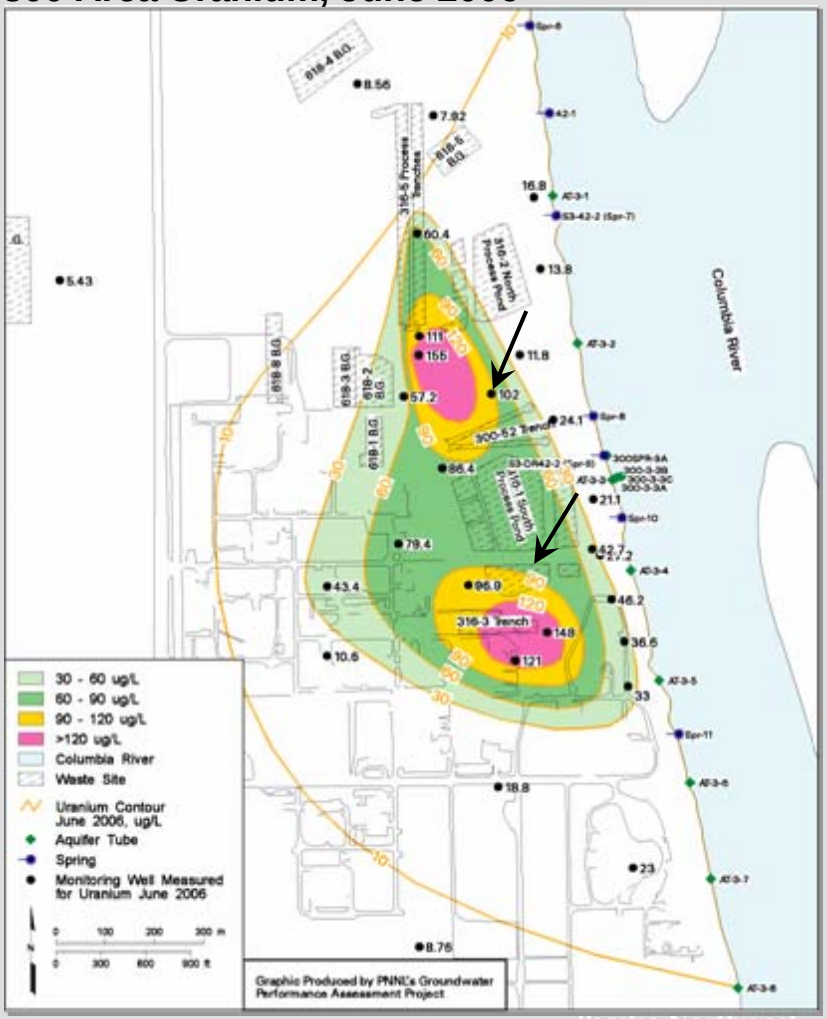
	(U in kg)	
316-1		
• remaining in vadose zone (~4.88m)	289	(based on 10 mg/kg in <2mm)
• lower 2m	118	
316-2		
• remaining in vadose zone (~4.58m)	659	(based on 20 mg/kg in <2mm)
• lower 2m	287	
316-5	?	
Other	?	
Groundwater U plume – water	29	(assumed 50 μg/L over 0.4 km^2)
Groundwater U plume – solids	76	(solids with ρ =1.9 and K_d=0.25)
Estimated annual discharge to CR	40-80	

Seasonal Dynamics of 300 A Uranium Plume

300 Area Uranium, December 2005



300 Area Uranium, June 2006



Primary Elements of the Conceptual Model

- Contributing U Sources
  - Adsorbed U in the lower vadose zone near disposal facilities accessed during periods of high river stage
  - Potentially large areas beneath NPP and SPP exhibiting slow, sustained release of waters with U near MCL
  - Other, isolated hot spots with higher U lability
- Seasonal U groundwater dynamics
  - Advectively dominated system with changes paralleling complex and changing flowpaths and gradients
  - Low retardation and small adsorbed concentrations, but integrated sorbed inventory dominates the aqueous inventory by a factor of 3
  - Remobilization/redistribution of sorbed inventory in response to seasonal, near-river water composition changes
- Slow plume dissipation
  - Mass transfer from lower lower vadose zone sediments, aquifer fines, and less permeable zones
  - Continued fluxes from lower vadose zone, that will asymptotically decrease
  - Unresolved contributions from Ringold formation and undefined "diffuse sources"

Key Uncertainties

- Inventory and spatial distribution
  - Disposal sites
  - Areas of seasonal high concentration in groundwater
  - Others, such as Ringold formation beneath PP
- Shorter term temporal dynamics linked to hydrology
  - U concentrations during evolving stages to test conceptual and numeric model predictions
- In-situ aquifer properties and their variation
  - Texture, porosity, and fines
  - Adsorption/desorption and mass transfer behavior
  - U aqueous and solid concentration distribution
- Fluxes within and from the system
  - Vadose zone to groundwater
  - Between saturated facies with variable hydraulic conductivity
  - Groundwater to river