INTRODUCTION
IFC Project Kick-Off Meeting

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Pacific Northwest National Laboratory, Richland, WA

March 21-22, 2007

(PNNL-SA-54330)

Meeting Objectives

- Introduce all to the 300 A IFC site
- Identify plans and schedule for project initiation
- Review and solicit feedback on field site location, design, and characterization
- Discuss potential field experiments and modeling
- Initiate science scope development for external participants

Hanford IFC

Science Theme ~ *Multiscale mass transfer processes influencing sorbed contaminant migration*

Associated Practical Issues

1. Accurate projection of dissipation times for groundwater plumes of sorbing contaminants
   - Sorbing solutes not equal
   - Concentrations at different scales

2. Optimal delivery of remediation reactants
   - Access
   - Kinetic formation and reaction
   - Persistence

3. Practicality and effectiveness of remediation

300 A Activities

- EM-30 (site directed research leading to ROD)*
  - RACS/Fluor
  - LFI and follow on
- EM-22 (Headquarters directed technology research leading to remedy selection)*
  - Polyphosphate treatability testing
- ERSP (Headquarters directed fundamental research ERSD/SC)*
  - Microscopic reaction and transport processes of U(VI)
  - Long term performance of phosphate barriers
  - Tc and Fe biogeochemistry in suboxic subsurface sediments
- 300 A IFC (ERSD/SC)
- ASCR (advanced computing strategies for fate and transport)
  - 300 A as a test case
- NRC-MOU (utilize unique and evolving data bases)
  - Evaluate modeling uncertainty and other issues

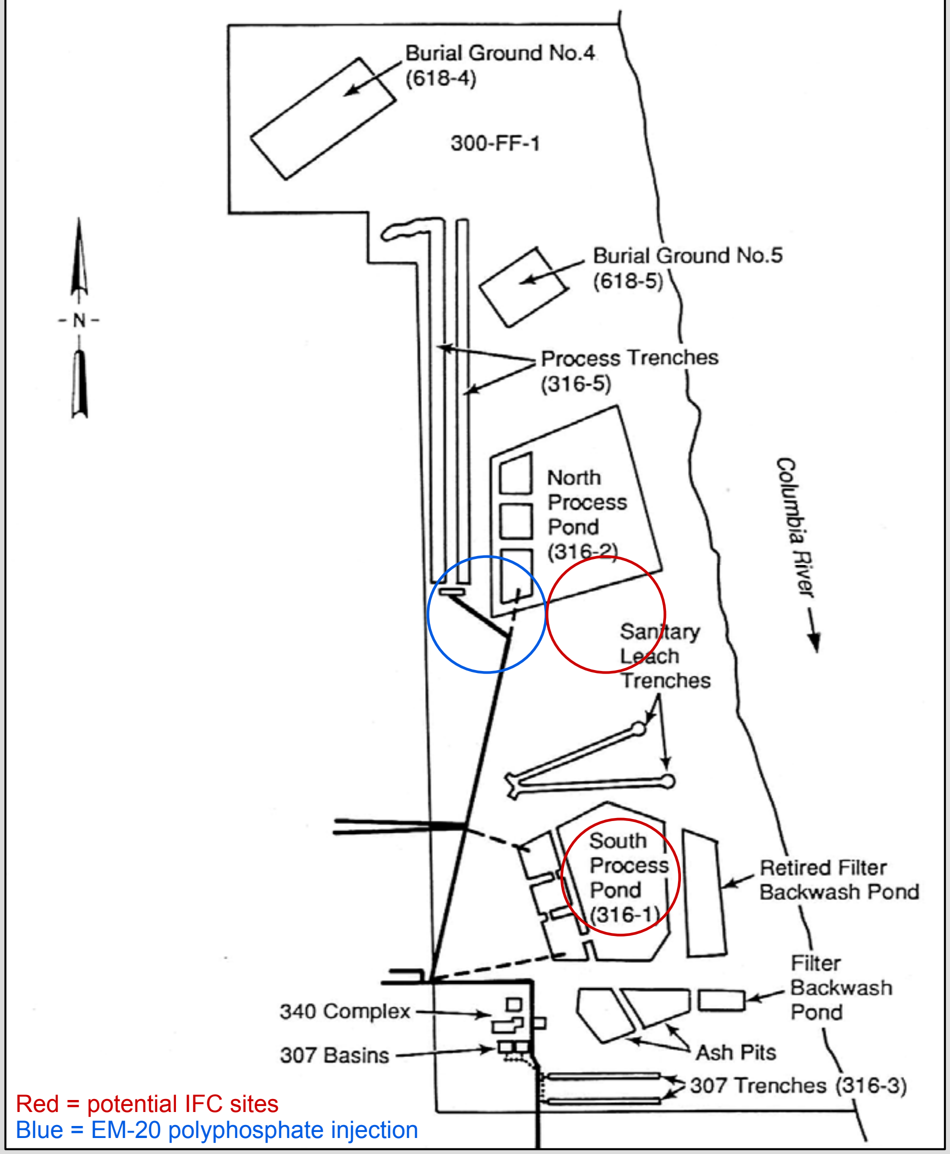
Outcomes and Legacy

- Outstanding, multidisciplinary collaborative effort that significantly advances science
  - Characterization, experiment design, interpretation
- New conceptual understanding of mass transfer processes at different scales influencing field behavior
  - Desorption, dissolution, dissipation
  - Effective reaction kinetics
  - Contaminant immobilization
- Improved linked multi-scale mass transfer/biogeochemical models for reactive contaminants
- Enduring and accessible field experiment data sets for hypothesis and model testing

Site Impacts and Linkages

- Operational model for infusion of DOE science into site remediation and closure decisions
  - Lab to field
  - Concept to application
  - Evaluation and testing of new models and measurement techniques
- 300 A site is representative of Hanford River Corridor locations
  - Applicability of conceptual and numeric models to other locations
- Scientific context for evaluation of remediation strategies and concepts
  - MNA versus active approaches
  - Optimization strategies
  - Expectations for remediation efficiency

The 300-FF-1 Operable Unit



Red = potential IFC sites
Blue = EM-20 polyphosphate injection

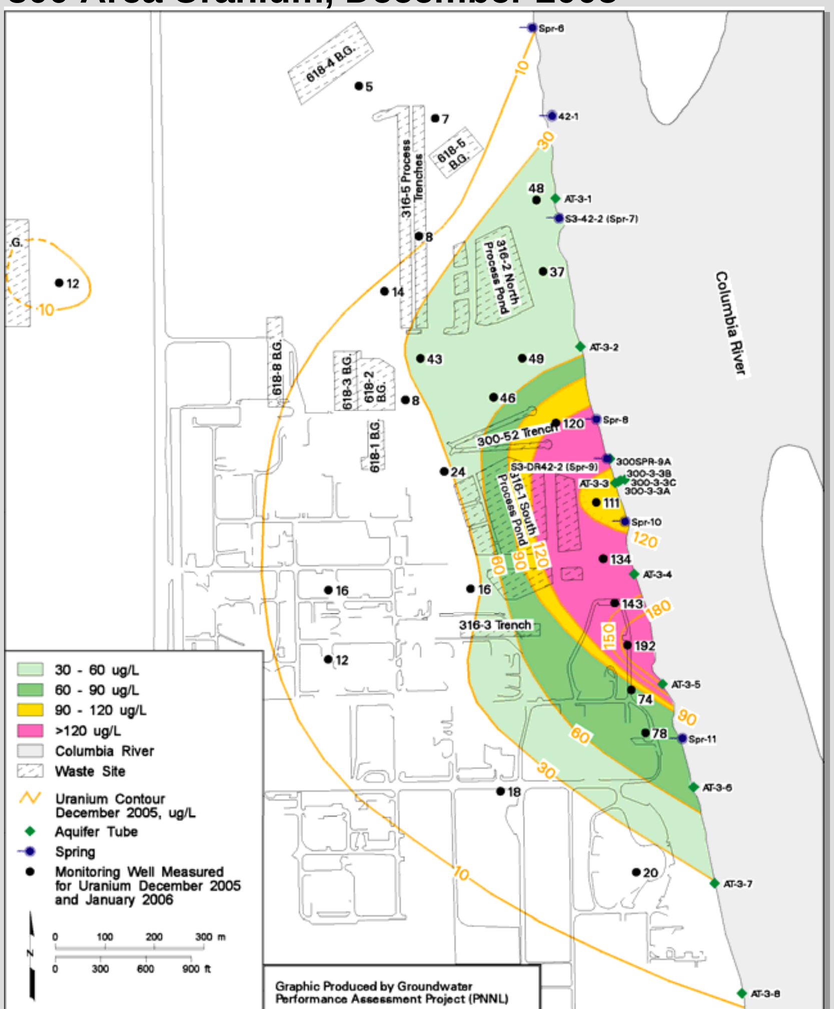
Hanford 300 Area in 1962

300 A Waste Streams

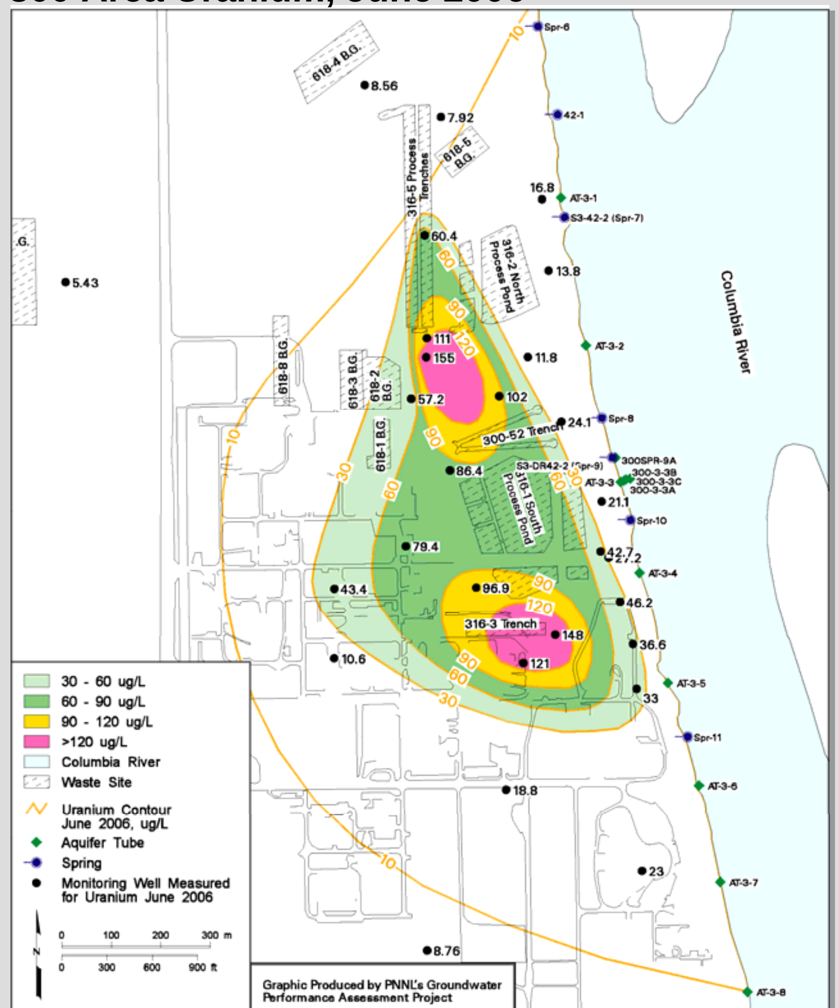
- Sodium aluminate (to ~1956)
  - Dissolved Al cladding from rejected fuel assemblies
  - 15% NaOH, Density of 1.5
- Effluents from REDOX and PUREX process development (1944 – 1954)
  - Nitric acid solutions containing uranyl nitrate
- N-reactor fuels fabrication wastes (1978 – 1986)
  - Nitric acid solutions containing U and Cu
- Different grades of enriched U as well as natural and depleted U
- Primary chemical inventory in NPP and SPP
  - 37,000 – 65,000 kg of U; 265,000 kg of Cu

Seasonal Dynamics of 300 A Uranium Plume

300 Area Uranium, December 2005



300 Area Uranium, June 2006



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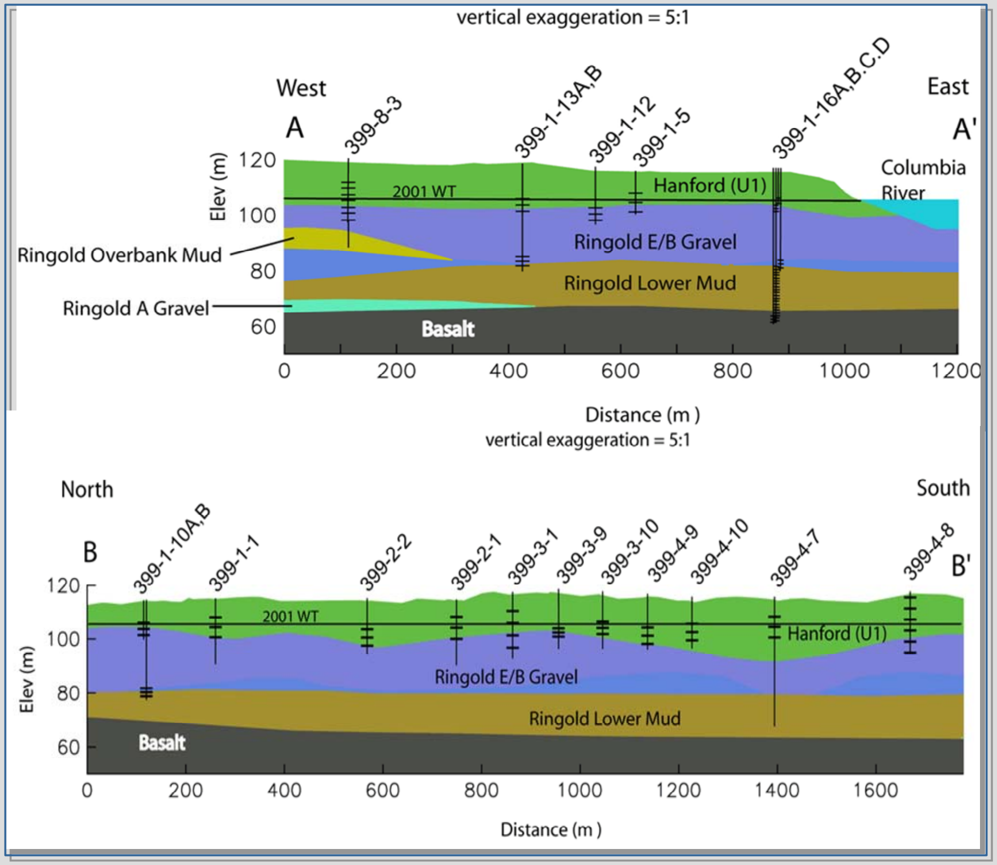
Major Geohydrologic Units and Well Placement in the 300 Area Uranium Plume



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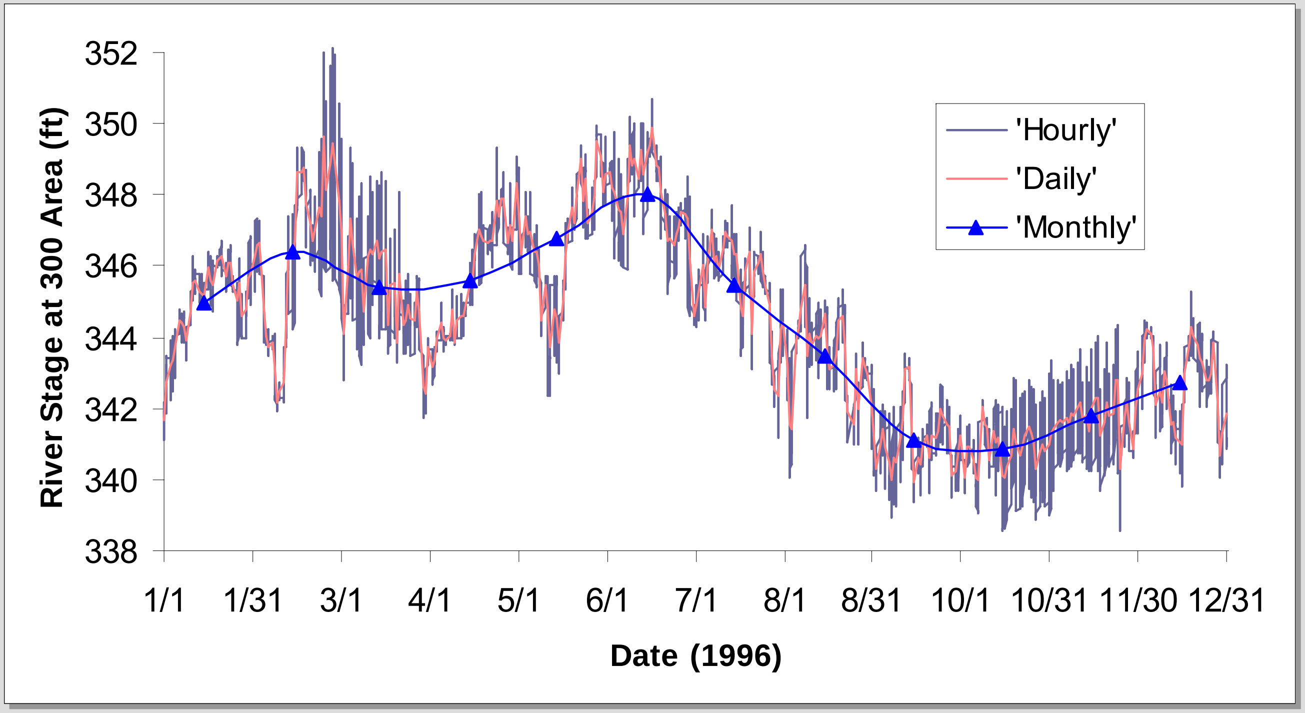
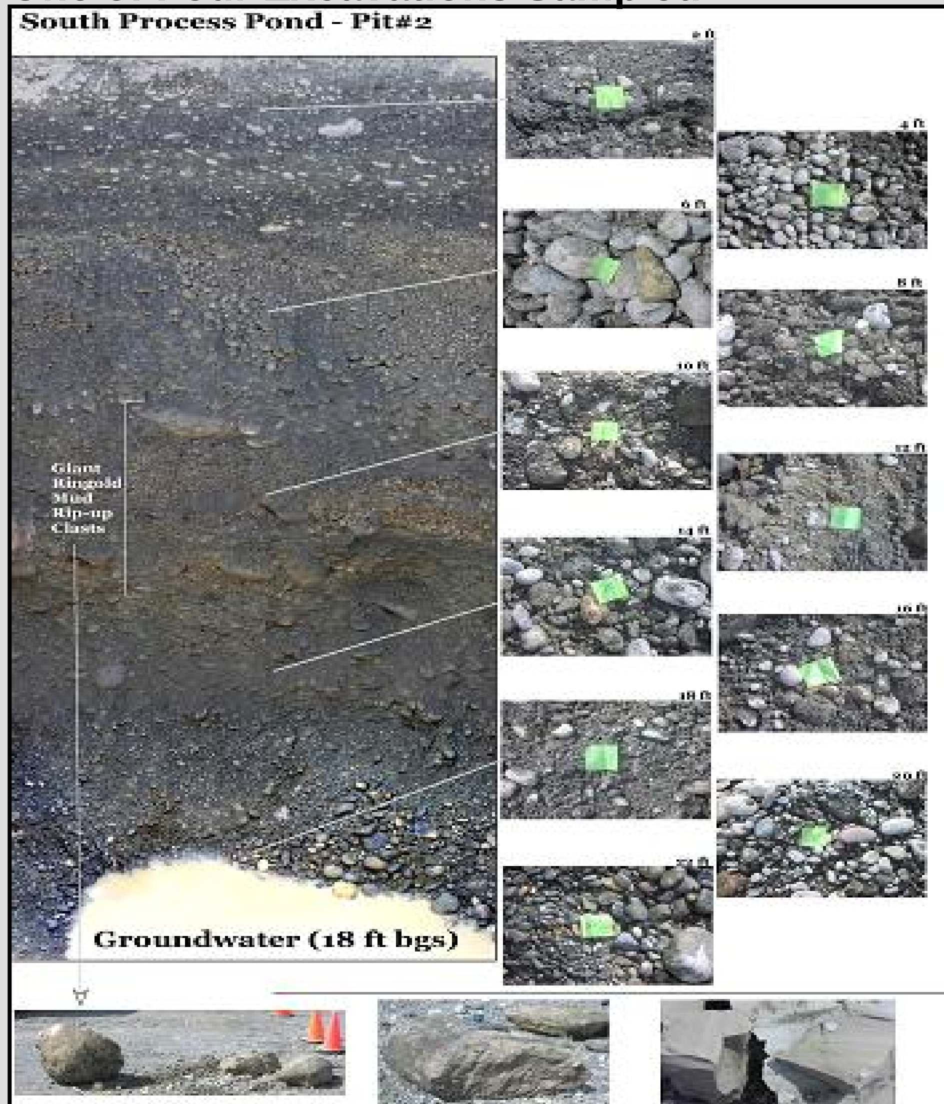
Hourly, Daily Average, and Monthly Average River Stage at the 300 Area in 1996



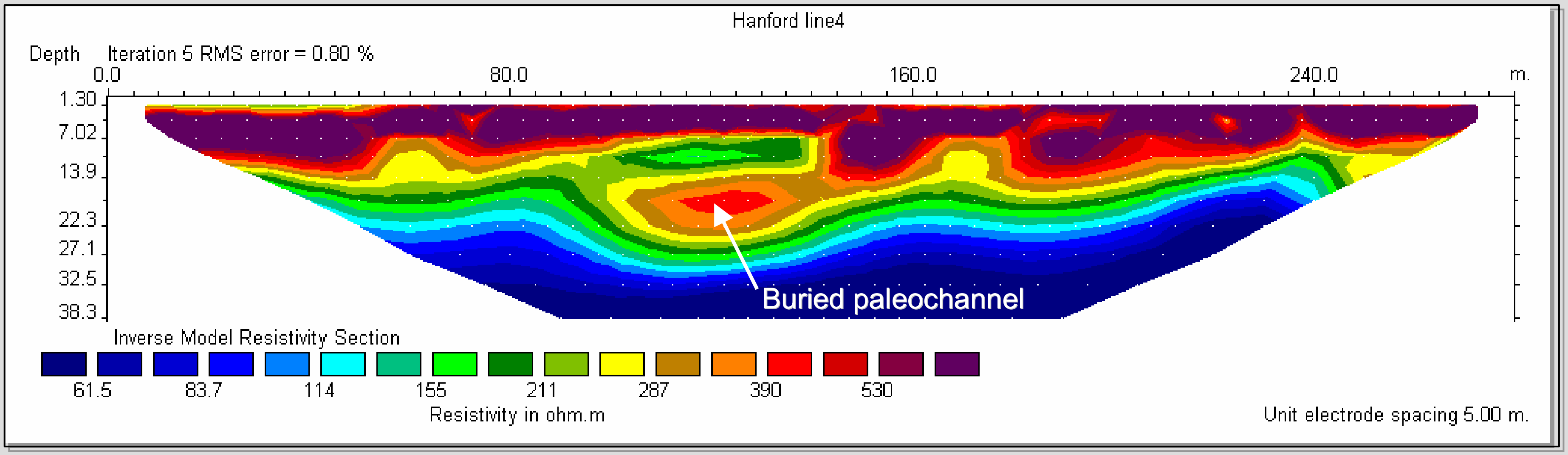
North Process Pond and Excavation

The North Process Pond

One of Four Excavations Sampled

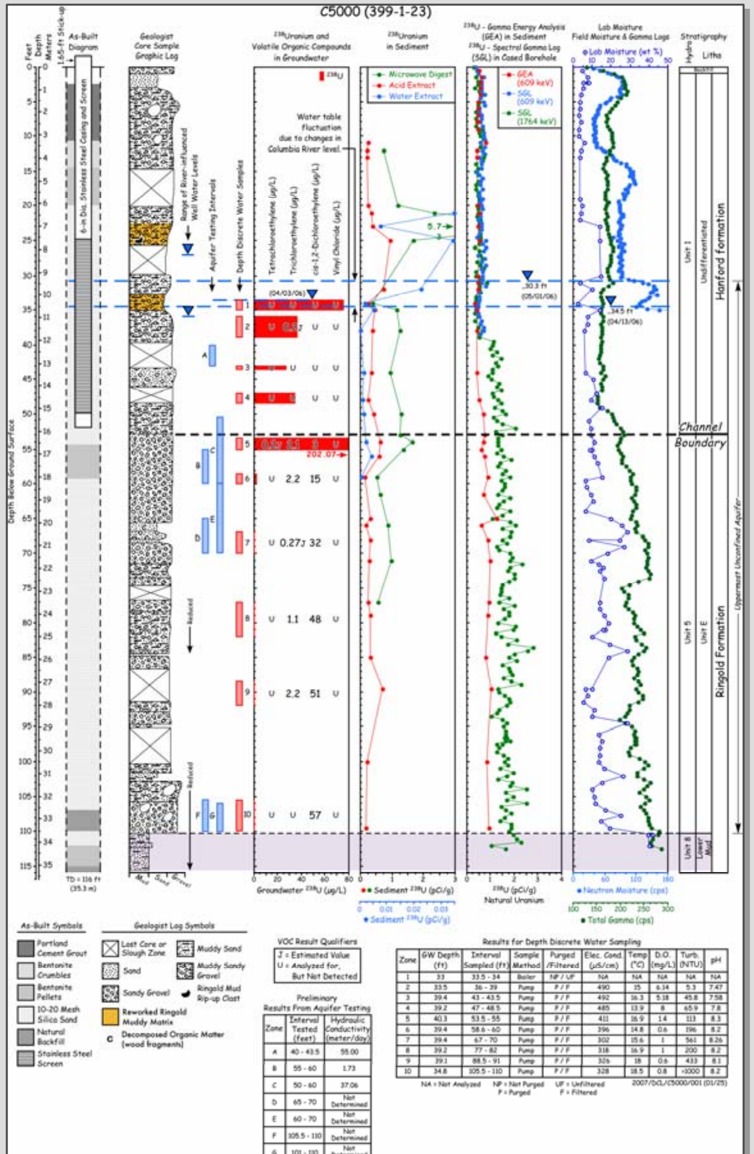


Geophysical Measurement Define Hanford-Ringold Contact and Buried Channels
(Inverse Model Resistivity Section)



RACS – Ward and Versteeg

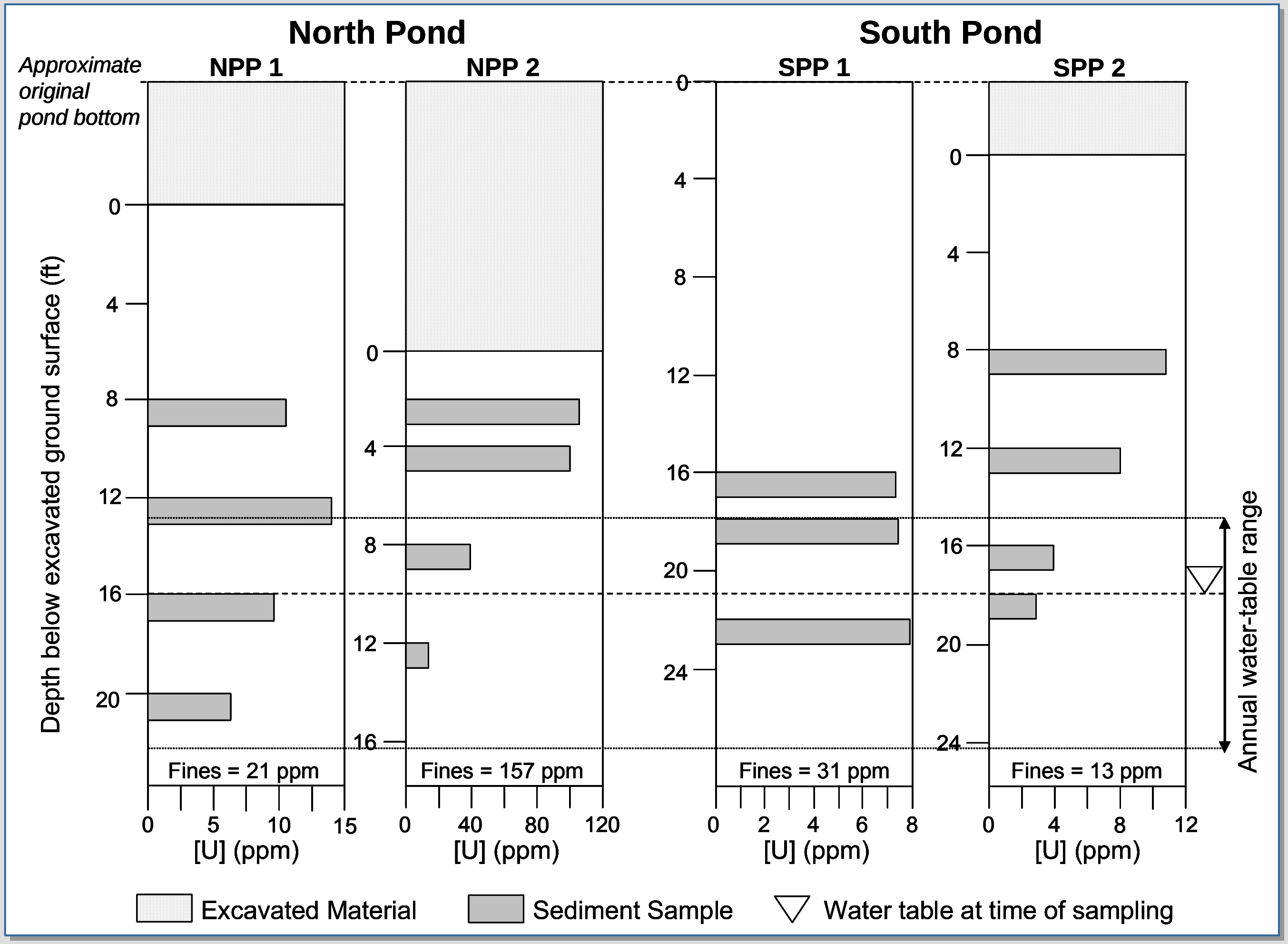
Example Results from Recent LFI Characterization



LFI Team

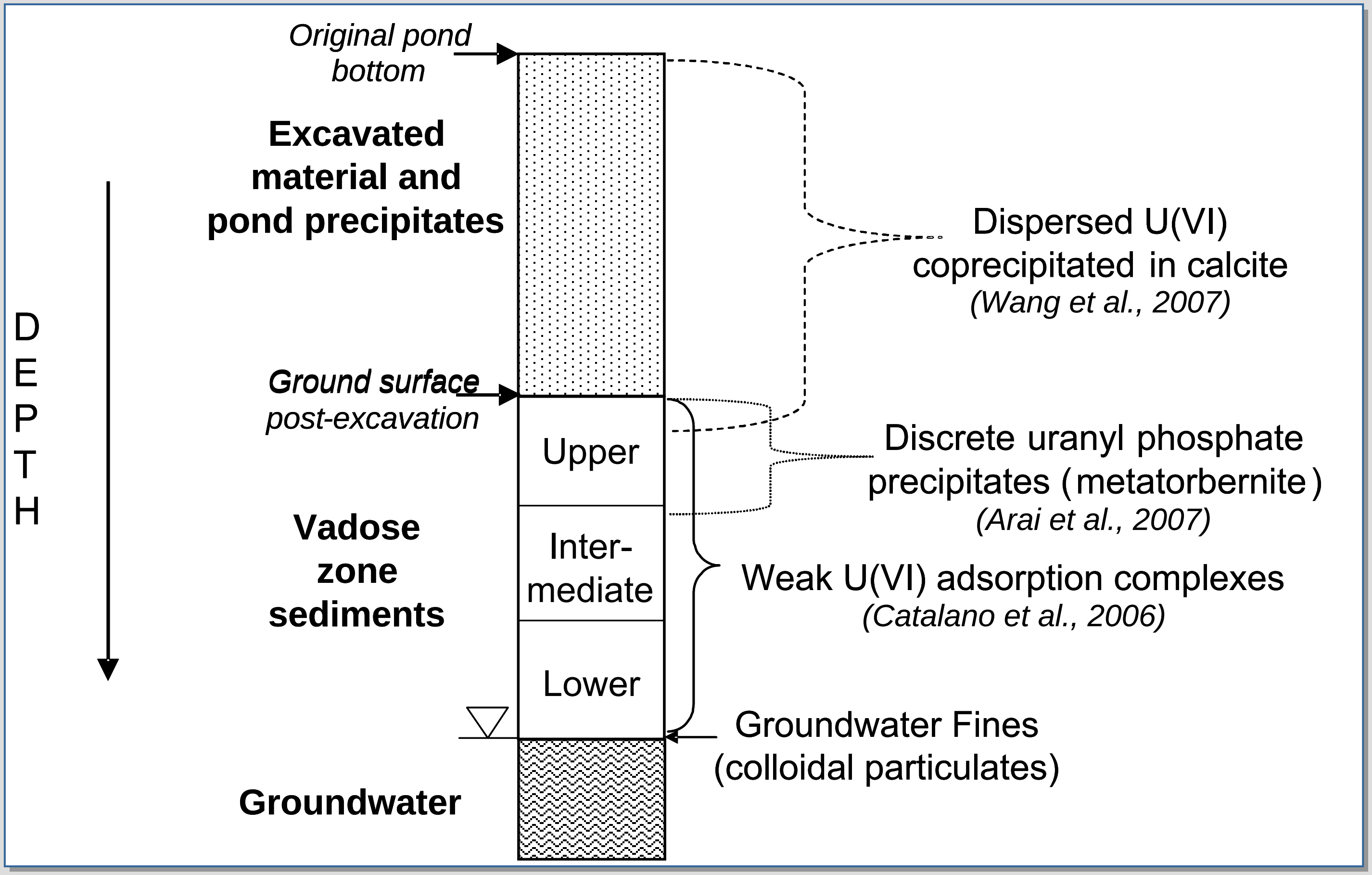
Smith, Williams, Brown, Um, and collaborators

U(VI) Depth Distribution Beneath North and South Process Ponds

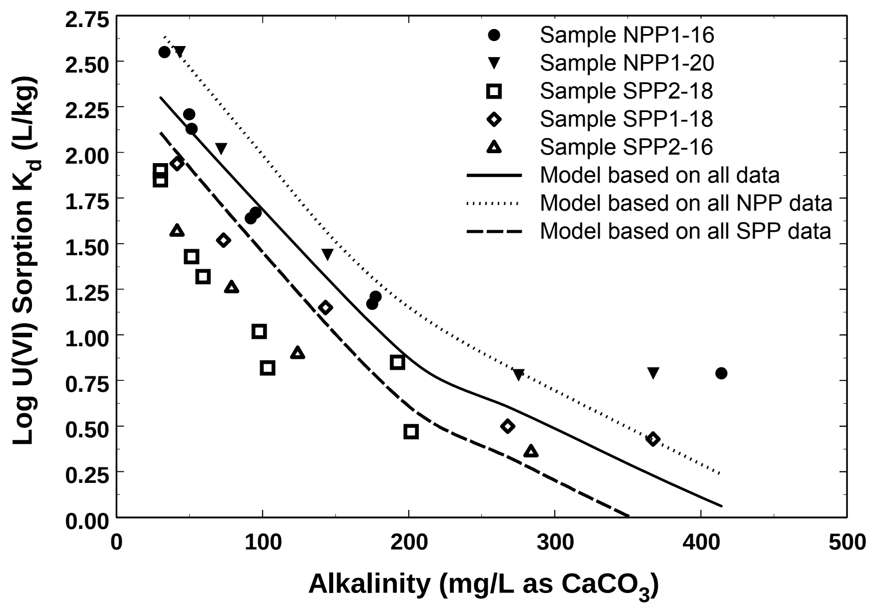


(Bond et al., 2007)

U(VI) Speciation Through the Vadose Zone



Alkalinity Dependence of Log Kd Values for U(VI) Sorption to 300 Area Sediments



$$SOH + UO_2^{2+} + H_2O = SOUO2OH + 2H^+$$
$$SOH + UO_2^{2+} + H_2CO_3 = SOUO_2CO_3 + 2H^+$$

(Bond et al., 2007)

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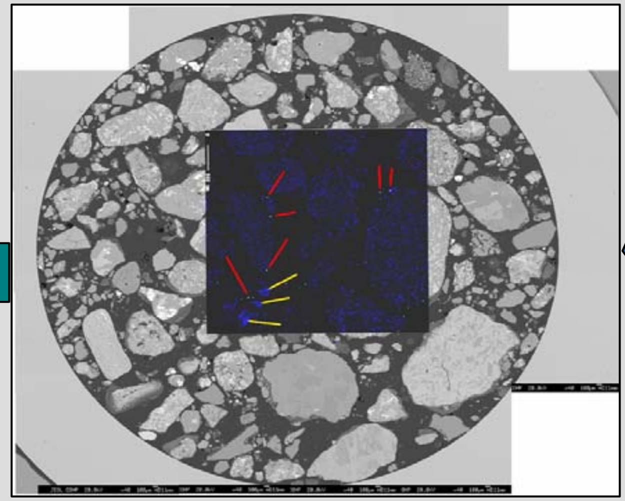
Transport Behavior (Desorption/Sorption) in < 2 mm Sediment is Kinetically Controlled

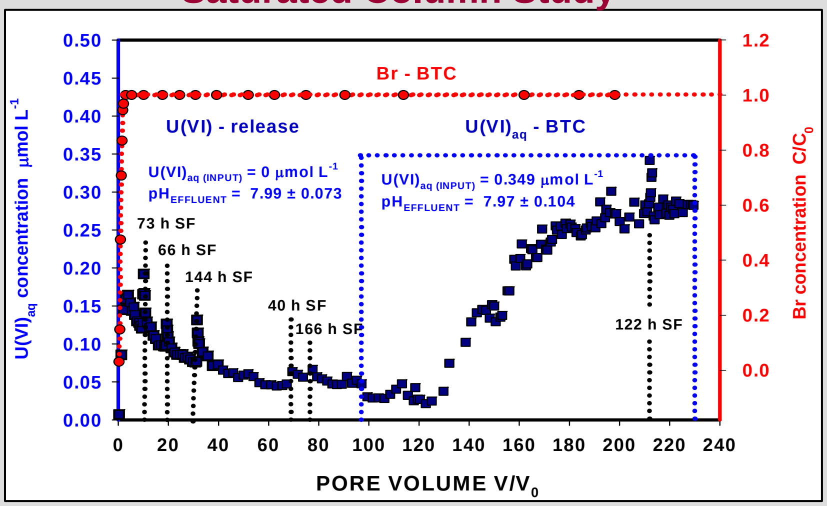
North Process Pond Pit 1 – 14 ft

	Size Range (mm)	Mass Distribution (%)	U_{Total} (nmol/g)
Cobbles			
	> 12.5	74.5	< 22
	2.0 - 12.5	17.2	< 19
Sand			
	1.0 - 2.0	2.64	26
	0.5 - 1.0	2.34	< 18
	0.25 - 0.5	0.78	< 21
	0.149 - 0.25	0.33	37
	0.106 - 0.149	0.19	< 23
	0.053 - 0.149	0.20	< 23
Silt + Clay			
	< 0.053	1.78	125

Electron Microprobe U Abundance Map on Backscattered Electron Image



Saturated Column Study



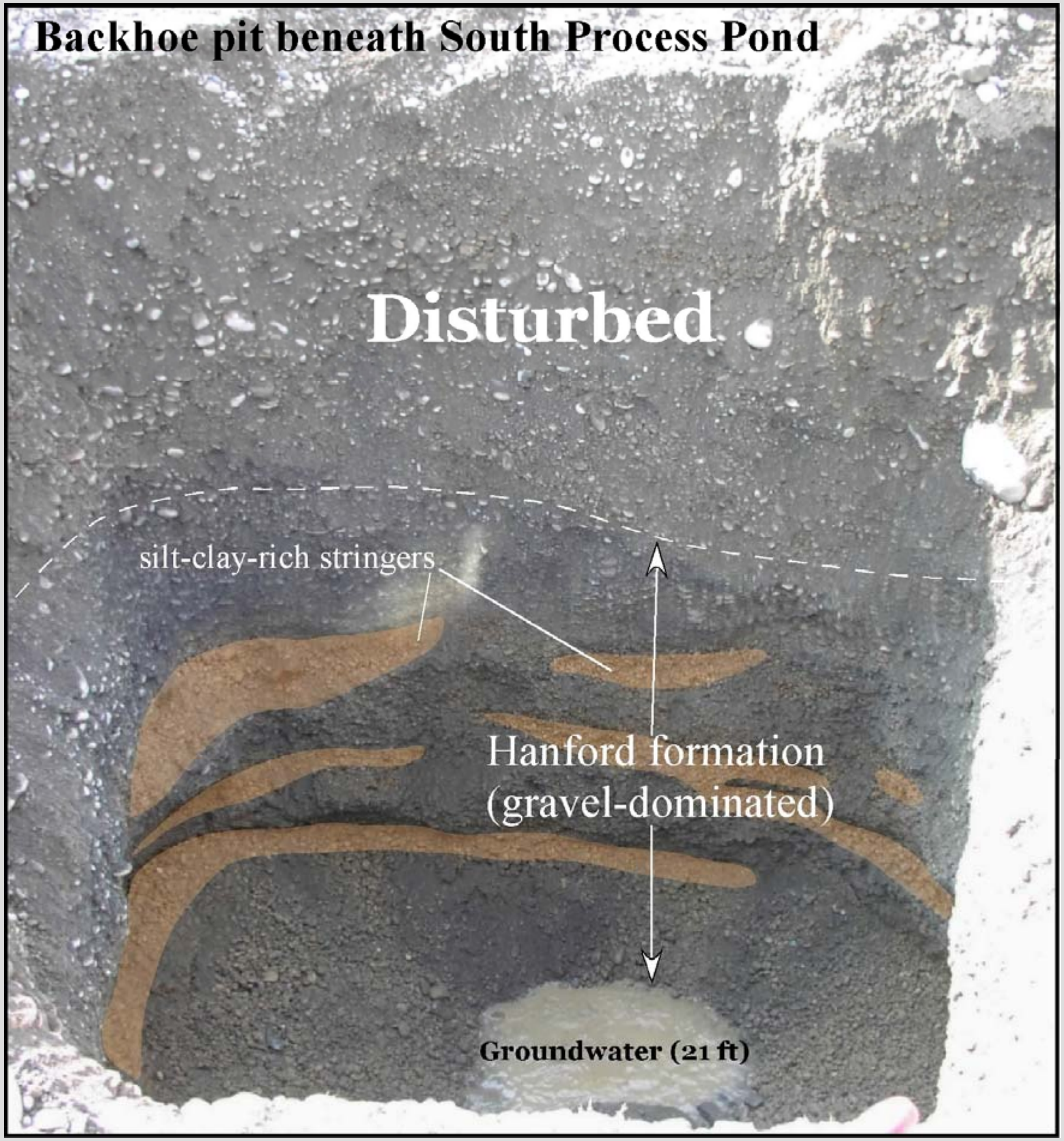
The release of sorbed contaminant U(VI) and the adsorption of U(VI) from contaminated groundwater both show strong kinetic behavior

(Qafoku et al., 2005; Liu et al., 2007)

IFC Science Questions

- Can the field experimental domains be sufficiently characterized to unravel the effects of spatially variable sorbent, sorbate, and microbe concentrations; rate processes; and hydraulic conductivity on U water concentrations?
- What is the dominant mass transfer scale or process controlling vadose zone porewater or groundwater U concentrations?
- What is the relationship between laboratory mass transfer rates and those measured in the field? Can differences be reconciled and sufficiently understood to allow field scale projections?

Heterogeneity and Mass Transfer Domains in 300 A Vadose Zone Sediments



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Representative Facies from LFI Cores

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Mass Transfer Scales

intragrain ⟶ coating ⟶ pore fluid $10^{-6} – 10^{-3}$ m

fine textured ⟶ coarse textured sediments $10^{-2} – 10^{-.5}$ m

fine textured ⟶ coarse textured facies 1.0 – 10 m

groundwater (high HCO^{3-}) promotes desorption (⟶)

river water (low HCO^{3-}) promotes adsorption (⟵)

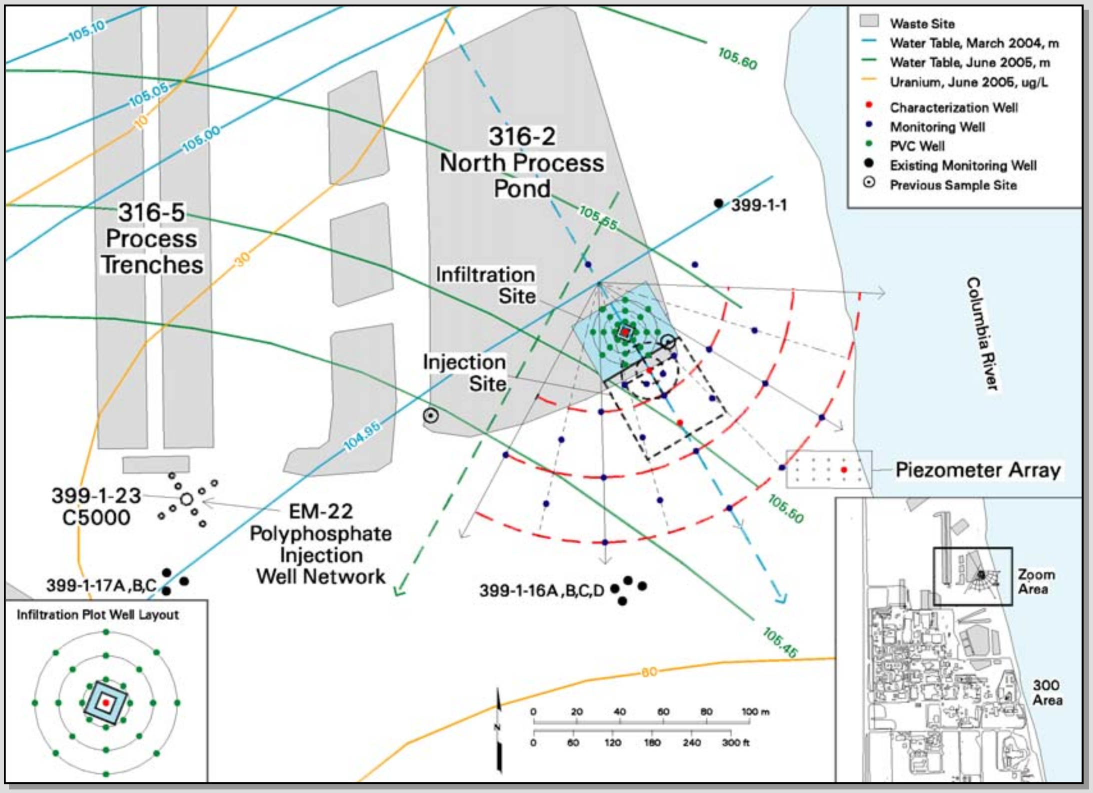
Comments from Formal Proposal Review
Scientific Concept

- Scientific concept is good
- A management plan is needed that illustrate how the team of collaborators will integrate individual pieces of research
- Will field experiments generate data over sufficient time frames and concentration ranges to follow rigorous study of multi-rate processes (e.g., slow rate processes)? How will long term rates be observed that are most significant to 300 A contamination?
- Proposal could be strengthened by stronger links between personnel working on data interpretation (modeling), characterization, and experiment. How will stochastic analyses be used in interpretation?
- Enhance the use of geophysics to bridge scales of investigation
- Microbiology associated with EM-22 collaboration experiments can be strengthened

Project Structure

- Management & Reporting
- Field site development and characterization
- Field experimental program
  - Hypothesis 1 ~ Vadose zone/capillary fringe
  - Hypothesis 2 ~ Saturated zone
  - Hypothesis 3 ~ Remediation science
- Data management
- Interpretation and modeling

Proposed Design of the Field Experimental Plot in the North End of the 300 Area



- Characterization wells are drilled to 10” and finished at 4”
- Monitoring wells are drilled to 4-6” and finished at 2”
- Exploit seasonal changes in groundwater flows directions
- Optimal location and design are TBD based on new EM-30 and EM-20 results and meeting

Comments from Formal Proposal Review
Field Site Design

- Adequacy of the field design to handle heterogeneity”
  - Source term
  - Geohydrology
- Unclear that the final # of wells is sufficient. What criteria will be used to decide?*
- Control site not well described
- How will spatially localized macropore type flow channeling and associated connected structures be characterized in the vadose zone?
- Rigorous and detailed site characterization is essential to unravel the influence of complex heterogeneities (contaminant, physical, chemical, and microbiologic) on processes and rates*

Hypothesis 1 ~ Vadose Zone/Capillary Fringe

Vadose zone porewaters will show large variations in dissolved U because of spatial heterogeneity in i.) sorbed U(VI), ii.) pore scale desorption/ mass transfer rate, and iii.) unsaturated water flow field. Mass transfer limited desorption is a critical U(VI) resupply mechanism to groundwater as the water table fluctuates.

Vadose zone experiment site

1. 30m x 30m x 5m
2. Instrumented to measure water and solute flux
3. Variable speciation

Infiltration experiments

1. Application rate and volume
2. Water composition (HCO_3/pH; Na/Ca, PO_4)

Hypothesis 2 ~ Saturated Zone

Waste sediment reaction and mineral weathering in mud domains between river cobble have created sorbent aggregates that undergo slow mass transfer-controlled adsorption/desorption. Downgradient U(VI) concentrations will be resupplied by diffusive flux from finer textured domains. Groundwater U(VI) will be strongly dependent on residence time, transport proximity to fine facies, and water composition.

Saturated zone injection site and well array

1. Radial well array that links with infiltration plot
2. Continuous monitoring of key variables
3. Interrogate multiple flowpaths/directions

Experiments

1. Vary HCO_3 to promote desorption
2. Vary $[U(VI)]_T$ to evaluate adsorption
3. $^{233}U(VI)$ to evaluate mass transfer w/o reaction

Hypothesis 3 ~ Remediation

The effectiveness of remedial polyphosphate (P) additions for U(VI) immobilization will be limited by its preferential transport through permeable domains that bypass zones of U(VI) sorption in finer textured materials. Hydrolyzed P will stimulate microbial growth and activity by providing a limiting nutrient that changes carbonate chemistry, pH, and U(VI) distribution. Kinetic effects related to polyphosphate hydrolysis, mass transfer controlled adsorption/desorption (of U and P), and diffusive transport into less permeable zones will control microbial activity and U(VI) precipitation.

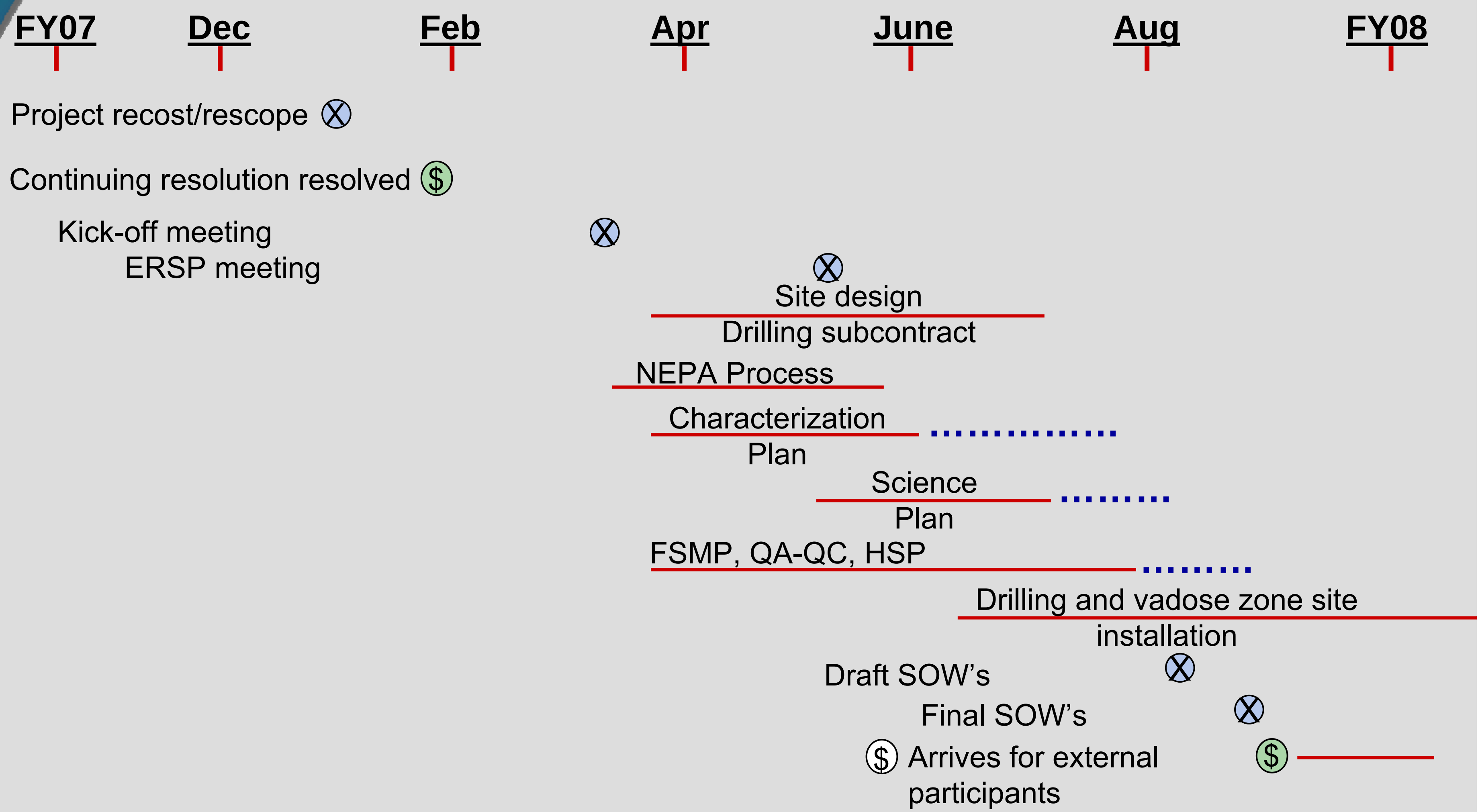
Experimental site

TBD – Reactive PO_4 may cause significant changes to system chemistry (use IFC or EM-22 site)

Injection experiments

1. Injections of different P forms with different reaction kinetics and sorptivity (polyphosphate, Ca-citrate/PO_4, organic P)
2. Injections of P + HCO_3 (desorb and precipitate), and cycling

Schedule for IFC Project Initiation



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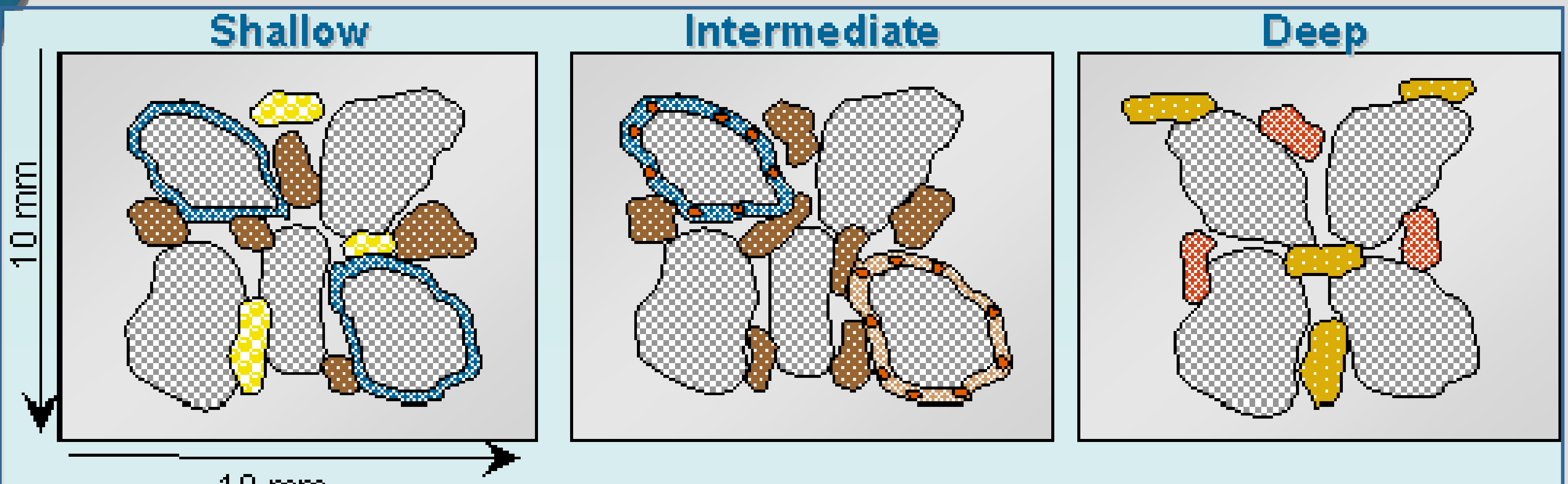
Conceptual Speciation Model Based on EXAFS, CLIFS, and Synchrotron XRD



Speciation #1

1.) Dispersed U(VI) coprecipitated in calcite
2.) Major copper grain coatings ( )

Speciation #2

Discrete uranyl phosphate precipitates (metatorbermite, autunite) in grain coatings of:
1.) Malachite( ) and
2.) Aluminosilicates ( )

Speciation #3

1.) Adsorbed U(VI) in aggregates of clay sized phyllosilicates with variable Fe(III) oxide resulting from chlorite weathering