Evaluation of Remedy Performance of the Uranium Plume in the 300 Area of the Hanford Site

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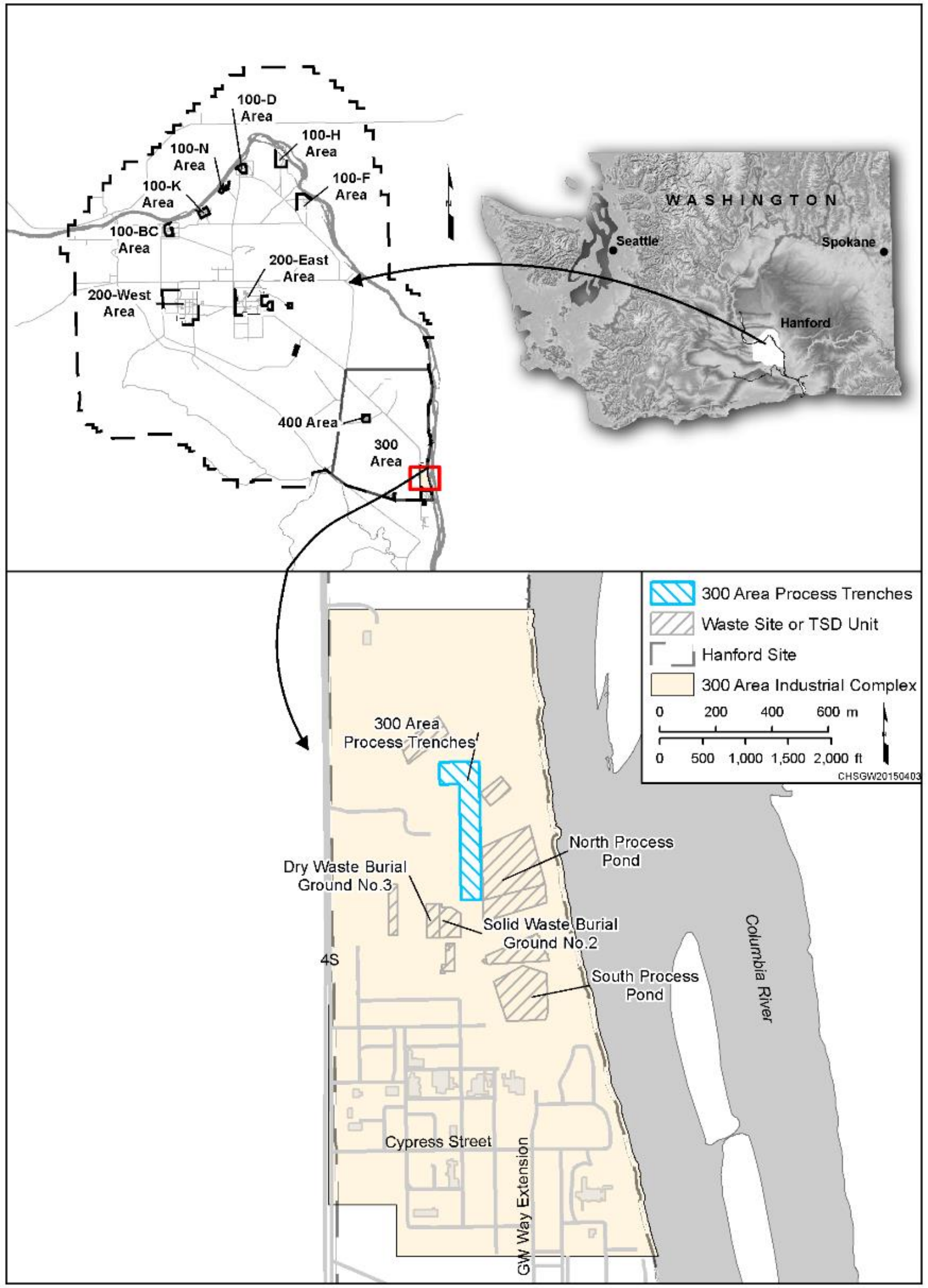
Hanford Site and 300 Area

- Hanford Site was used to produce nuclear material to support the defense mission of United States from 1943-1987
- The 300 Area
  - Uranium fuel fabrication activities generated waste was discharged to surface ponds and trenches
  - Persistent uranium groundwater plumes
- Selected remedy is monitored natural attenuation <u>with</u> enhanced attenuation in 3-acre area (12,140 m^2) of highest contamination
  - In-situ treatment with polyphosphate solutions
- Columbia River forms the Site boundary



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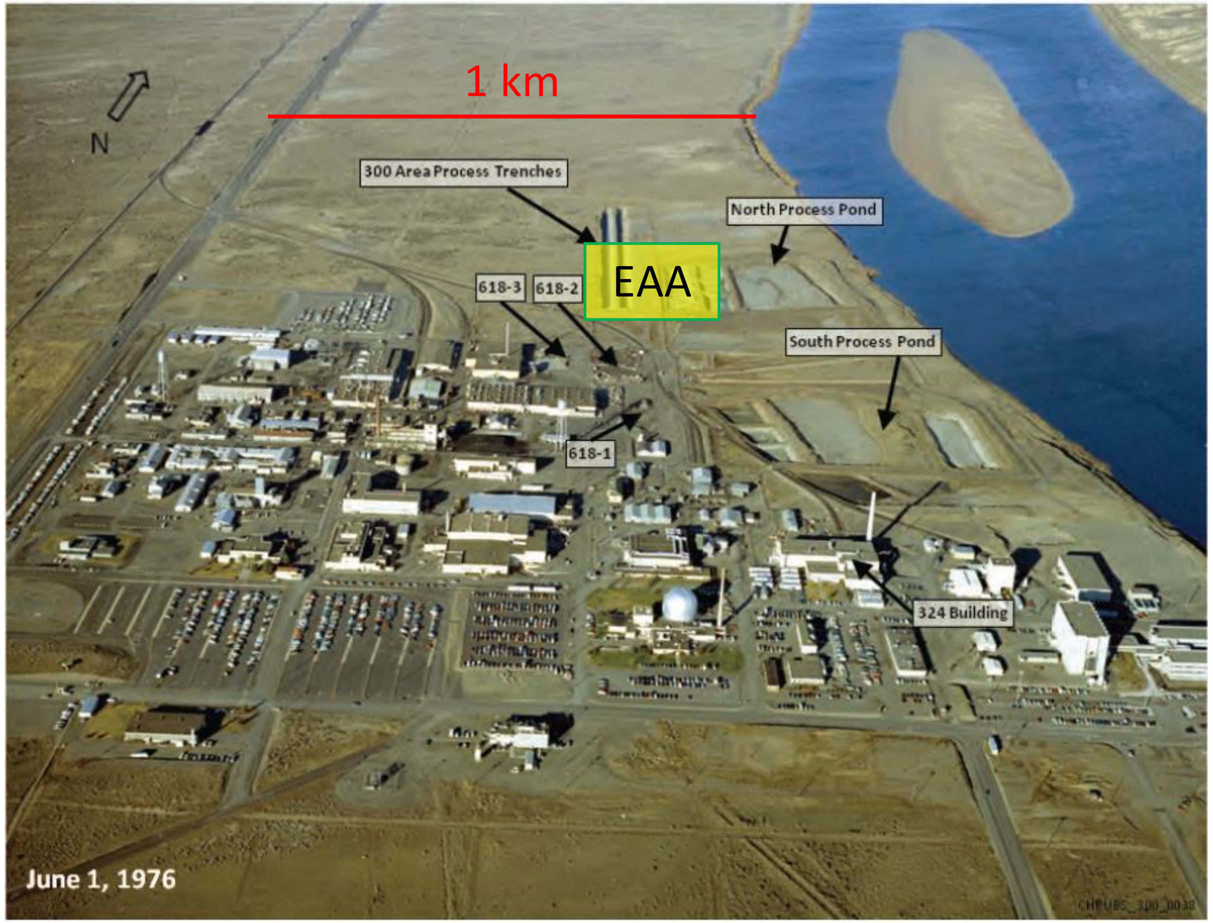
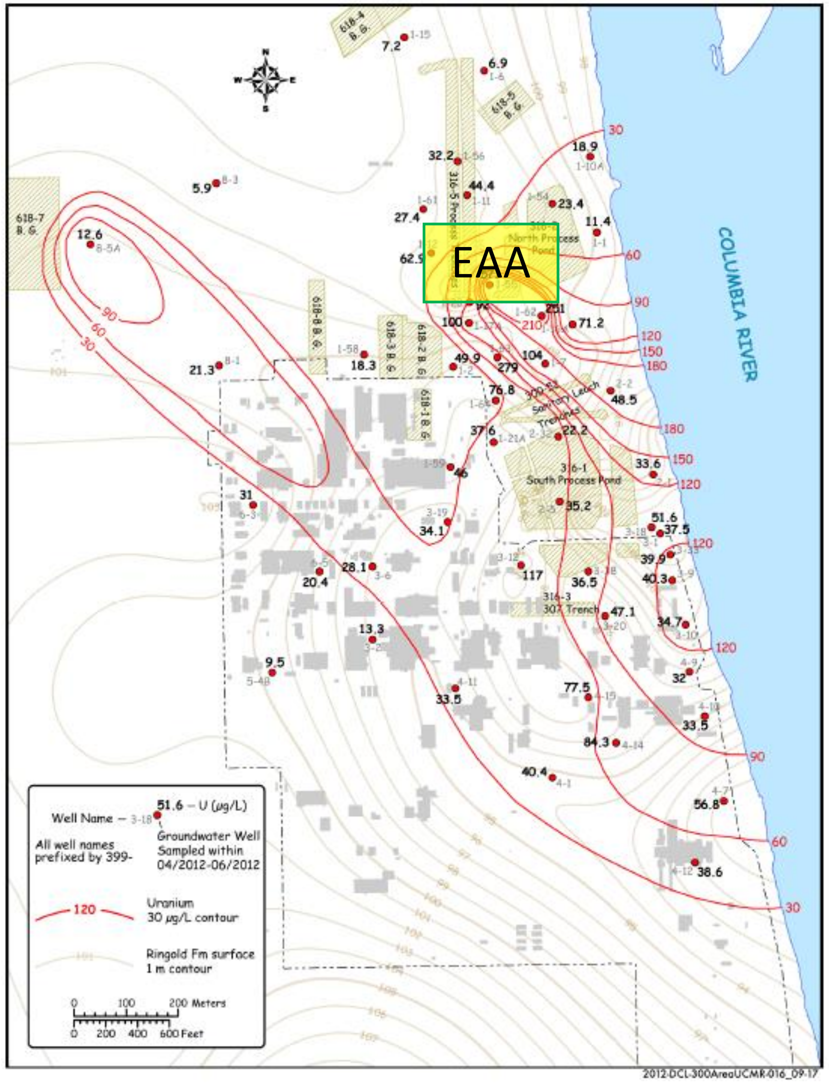
Hanford Site 300 Area



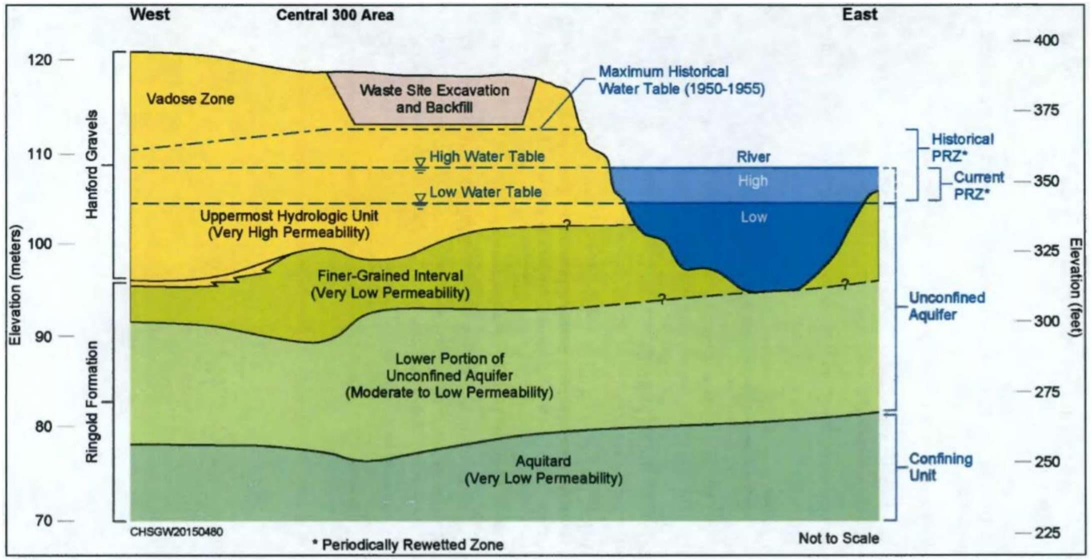
2012 Uranium Plume

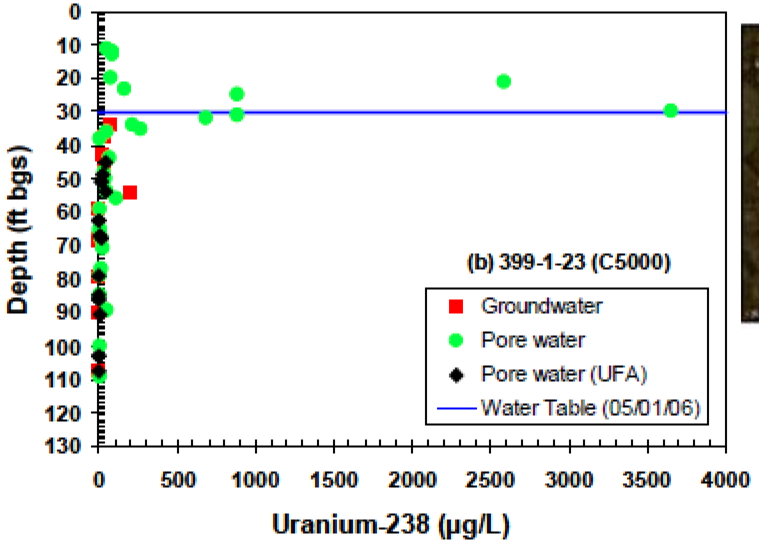


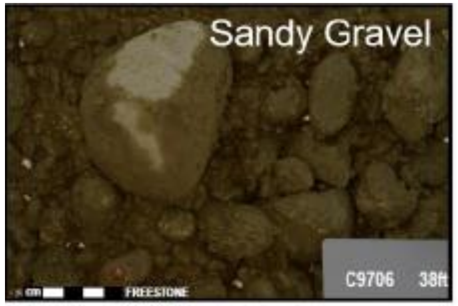
EAA = Enhanced Attenuation Area

Site Conceptual Model

- Columbia River stage fluctuations impacts water-table
  - Daily fluctuations and seasonal variations are important
- Vadose zone encompassing the historically high and low water table elevations is called the Periodically Rewetted Zone (PRZ)
- Highly variable contamination in vadose zone
- Majority of the uranium associated with <2 mm size fraction (sand, silt, and clay)
- Leachable (labile) uranium variable (up to 60% of total uranium)
- U(VI) exists primarily in form of
  - Precipitated phases (carbonates and phosphates)
  - Adsorbed surface complexes on phyllosilicates and iron oxides

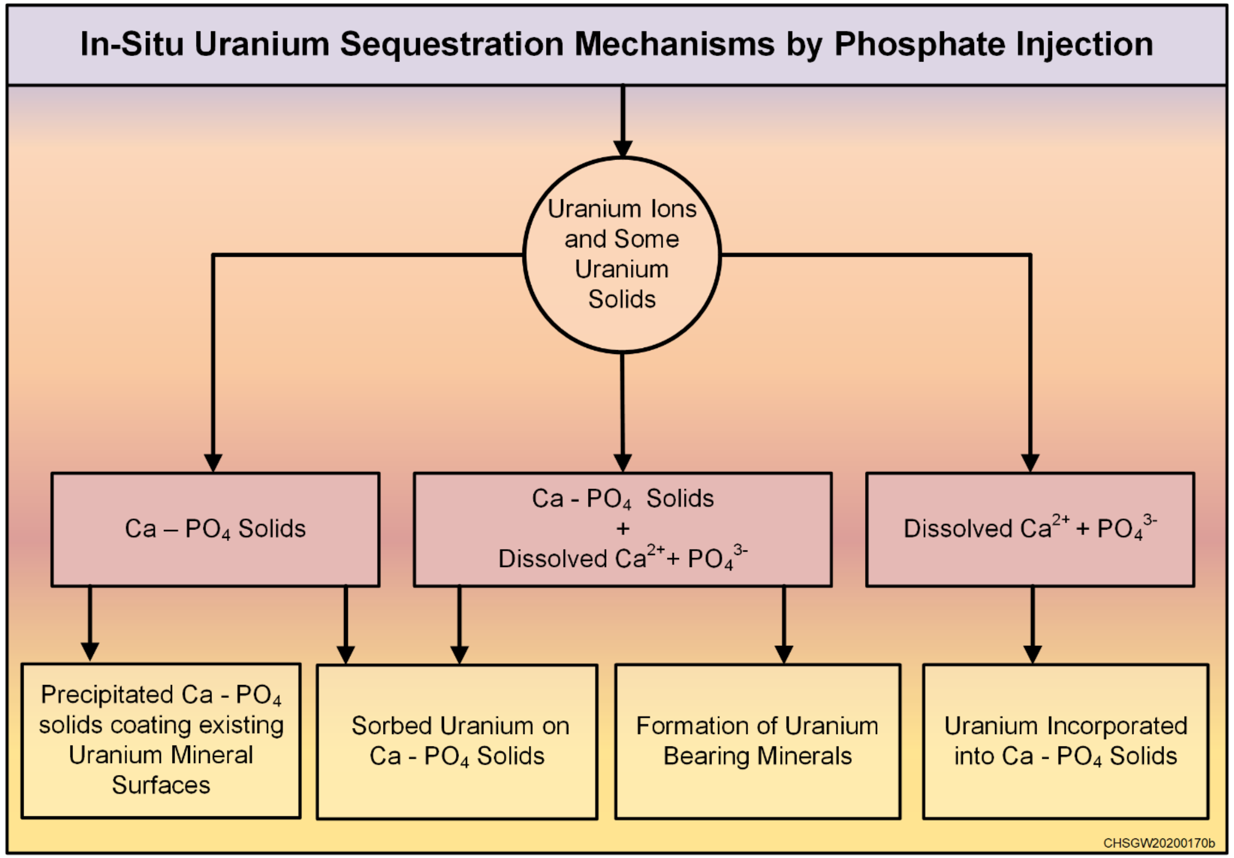




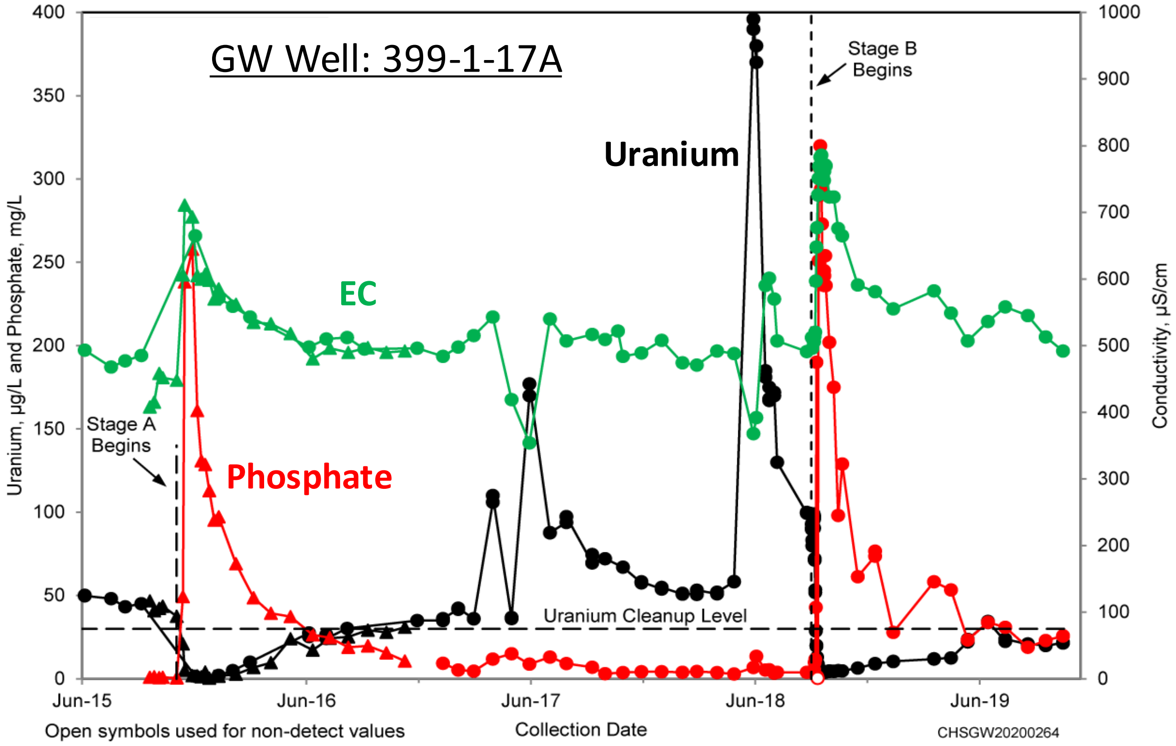


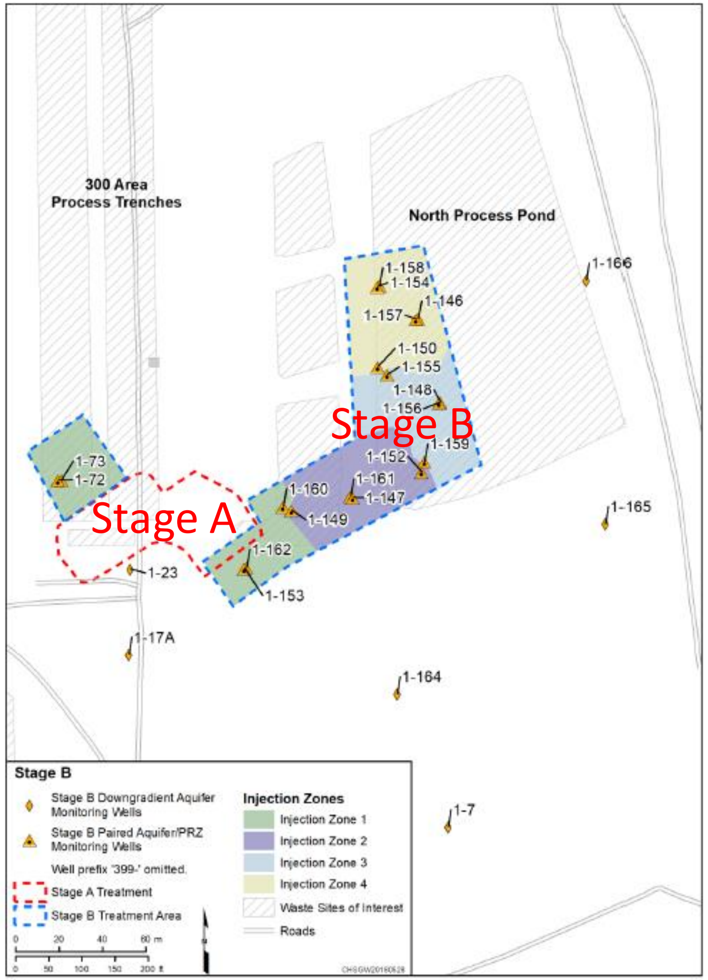
Study Approach

- Enhanced Attenuation
  - In-situ uranium sequestration by injecting polyphosphate solutions
  - Field monitoring (including ERT)
  - Laboratory analyses
  - Reactive transport modeling
  - System scale flow and transport modeling
- Monitored Natural Attenuation
  - Development of large-domain model
  - Model calibration
  - Model prediction



Enhanced Attenuation: Remedy Implementation





- Stage A: smaller area (0.75 acres); November 2015; surface infiltration and 9 injection wells
- Stage B: larger area (2.25 acres); September 2018; 48 injection wells
  - Mixture of Orthophosphate (NaH_2PO_4 and KH_2PO_4) and Pyrophosphate ($Na_4P_2O_7$)
  - Target phosphate conc: 8,250 mg/L; Injection rate: 189 L/min (50 gal/min) for 16 hours per well
  - Total volume injected: 16 x 10^6 Liters (4.2 x 10^6 gallons); Phosphate mass delivered: 133,500 kg

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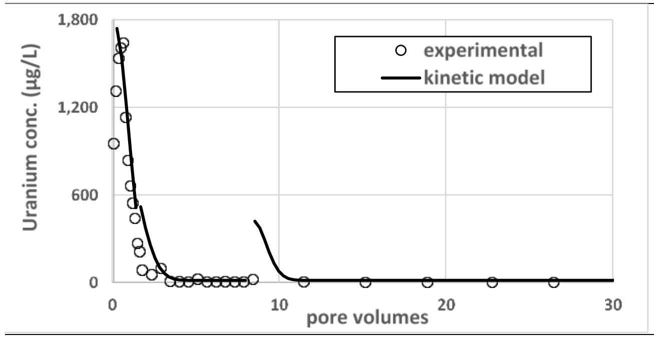
Enhanced Attenuation: Laboratory Analyses

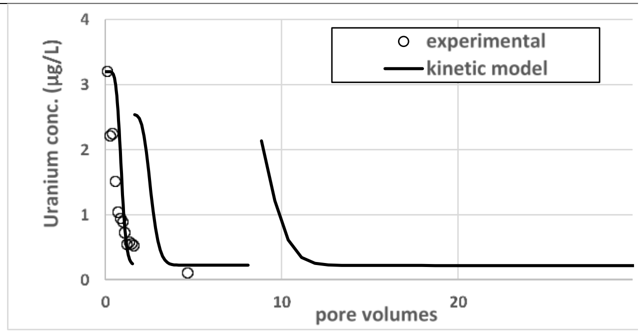
- Laboratory analyses performed on *pre*-treatment and *post*-treatment sediment samples collected from six co-located boreholes from approximately same depths
- Sequential extractions indicate dissolution of uranium carbonate and hydrous uranium silicates in post-treatment samples and reprecipitation as lower solubility uranium phosphate bearing mineral phases
- Total uranium that could be extracted from post-treatment samples was on average 33% lower compared to pre-treatment samples (based on sequential extraction)
- Labile uranium fraction was about 63% lower following treatment (based on 1000-hr carbonate extraction)

Enhanced Attenuation: Reactive Transport Modeling

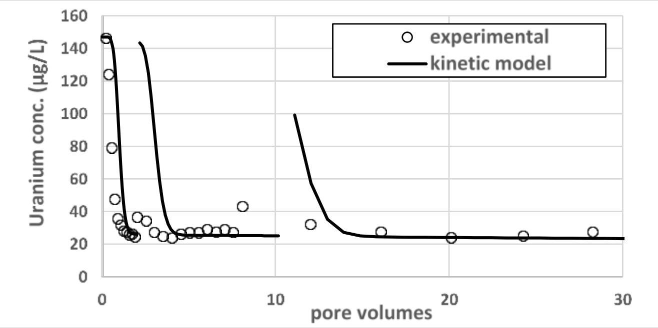
- Uranium leaching rate estimated using single-site kinetic rate constants
  - Due to complex assemblage of uranium bearing mineral phases the relative influence of each mineral phase is difficult to estimate
- 1-D finite-difference transport model used to fit and estimate the forward and reverse kinetic rate constants
  - Rate constants matched with other independent estimates



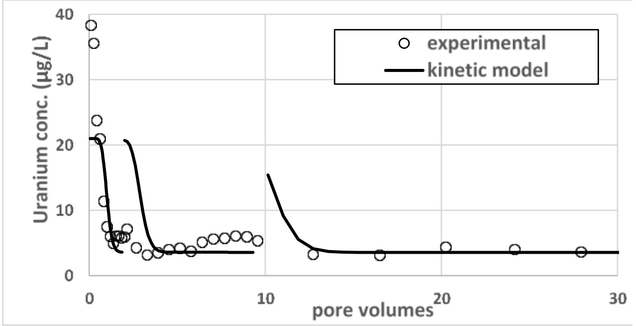
a. **Sample G-29 (pre-injection pair)**



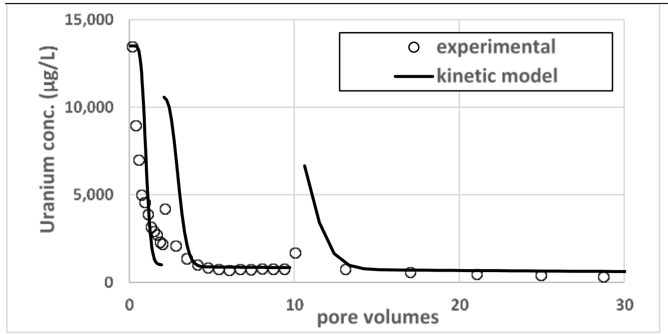
b. **Sample G-118 (post-injection pair)**



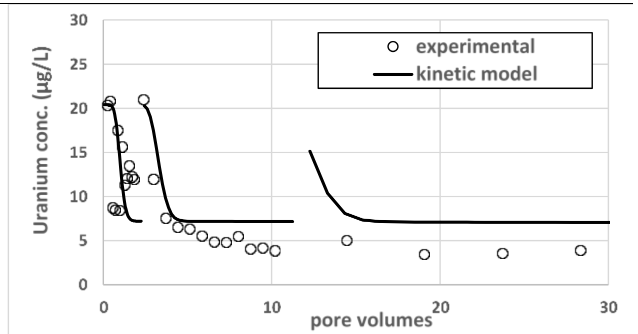
c. **Sample G-20 (pre-injection pair)**



d. **Sample G-112 (post-injection pair)**



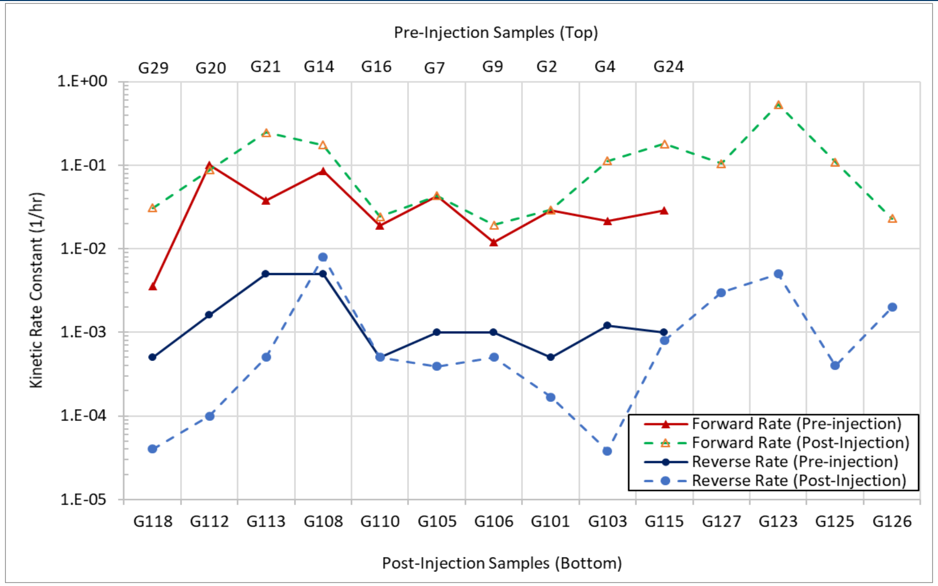
e. **Sample G-21 (pre-injection pair)**

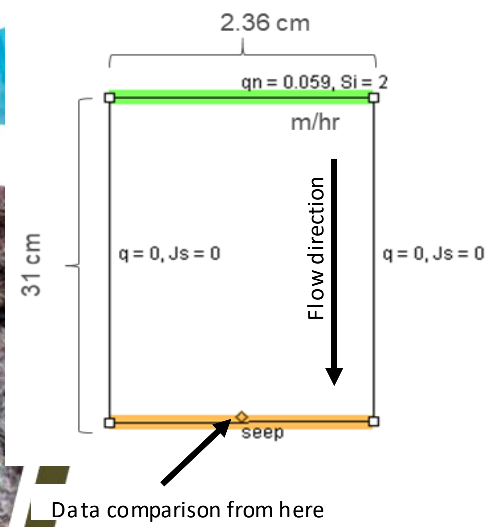


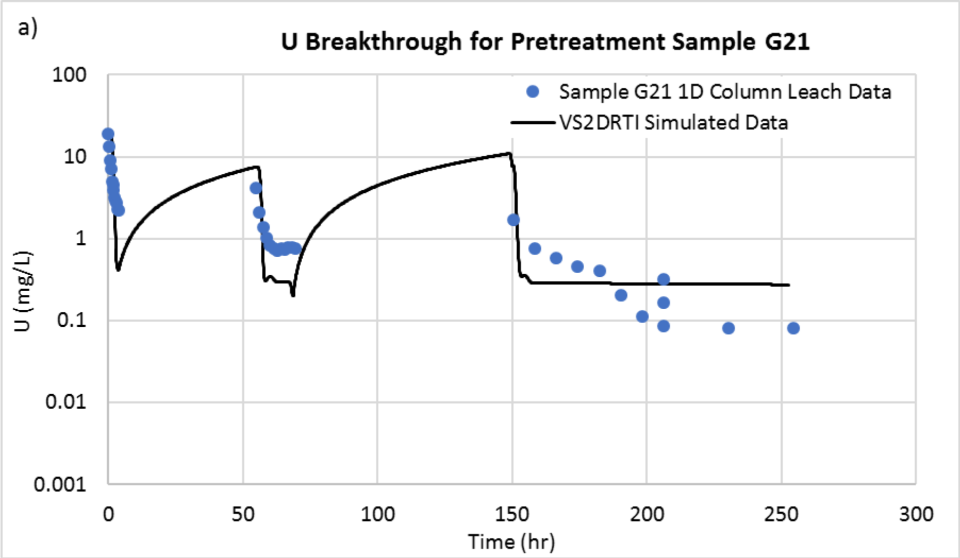
f. **Sample G-113 (post-injection pair)**

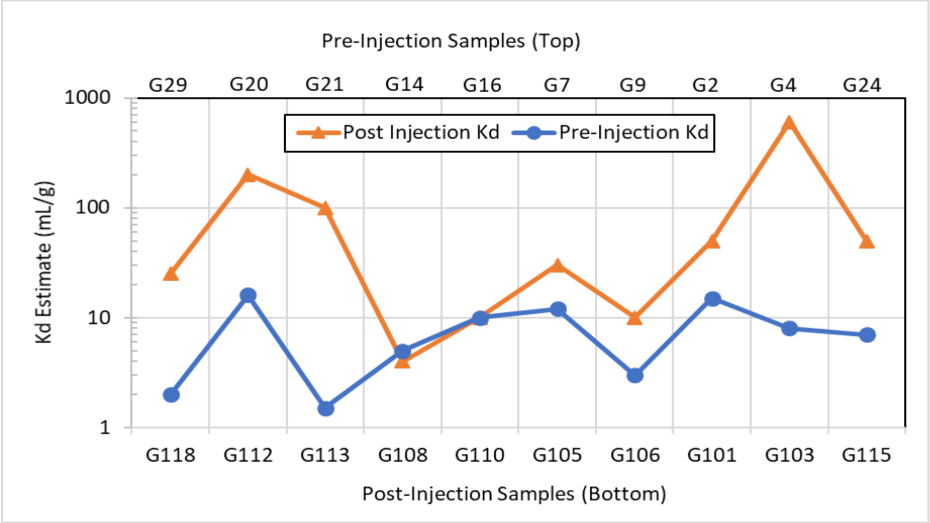
Enhanced Attenuation: Reactive Transport Modeling

- The reverse rate constants are smaller by factor 10 for the post-injection samples
  - Effectively 10x increase in “Kd value”
- Kinetically controlled release with geochemical controls modeled using VS2DRTI* coupled to PhreeqcRM and compared to Column test results (core-scale modeling)









* USGS software package for simulating water flow, heat transport, and reactive solute transport

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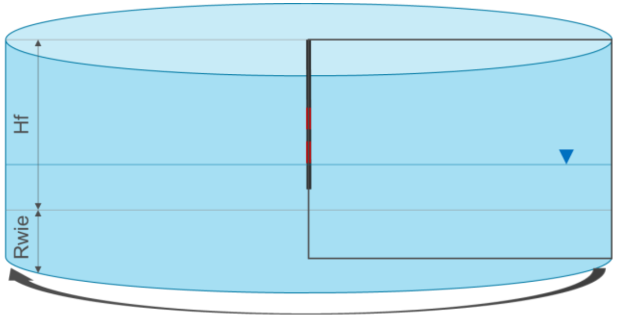
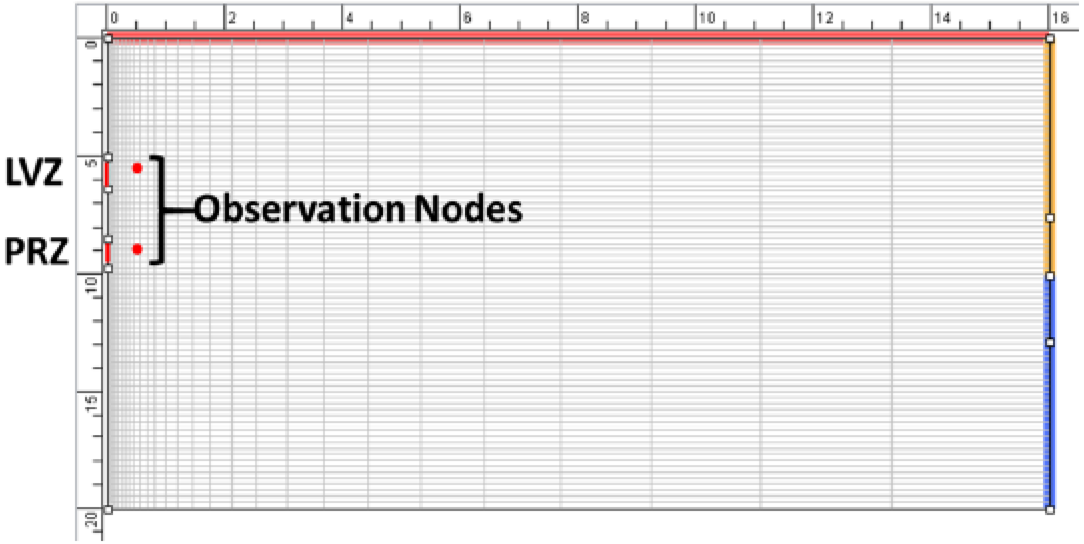
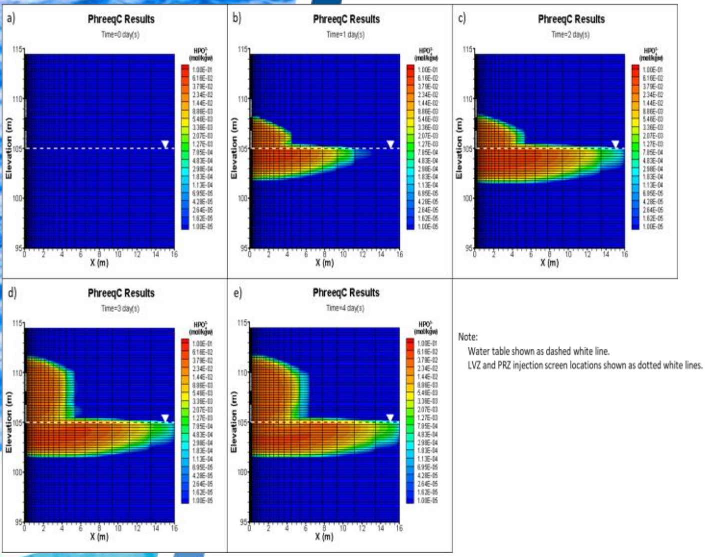
3-D Reactive Transport Model Using VS2DRTI

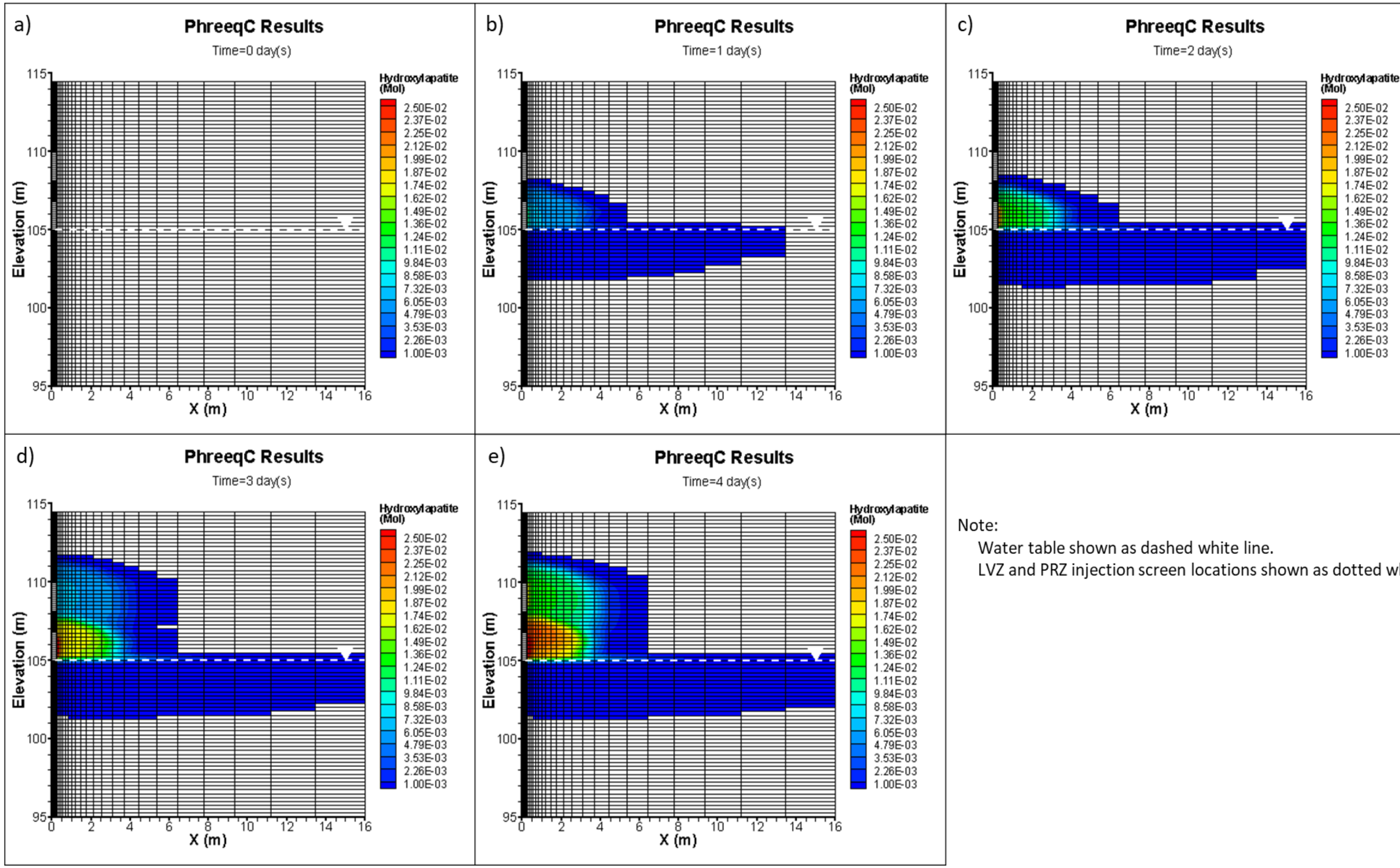
- Simulate 3-D injections at a single well in radial coordinates (near-field modeling)
- Incorporate unsaturated and saturated zones
- Include local geologic model
- Model flow and reactive transport
  - Aqueous chemistry
  - Cation exchange
  - Simplified single site surface complexation
  - Mineral precipitation/dissolution
  - Kinetically mediated dissolution/precipitation of calcite and uranium





Reactive Transport Model : HPO_4^{2-} injection and formation of Hydroxylapatite





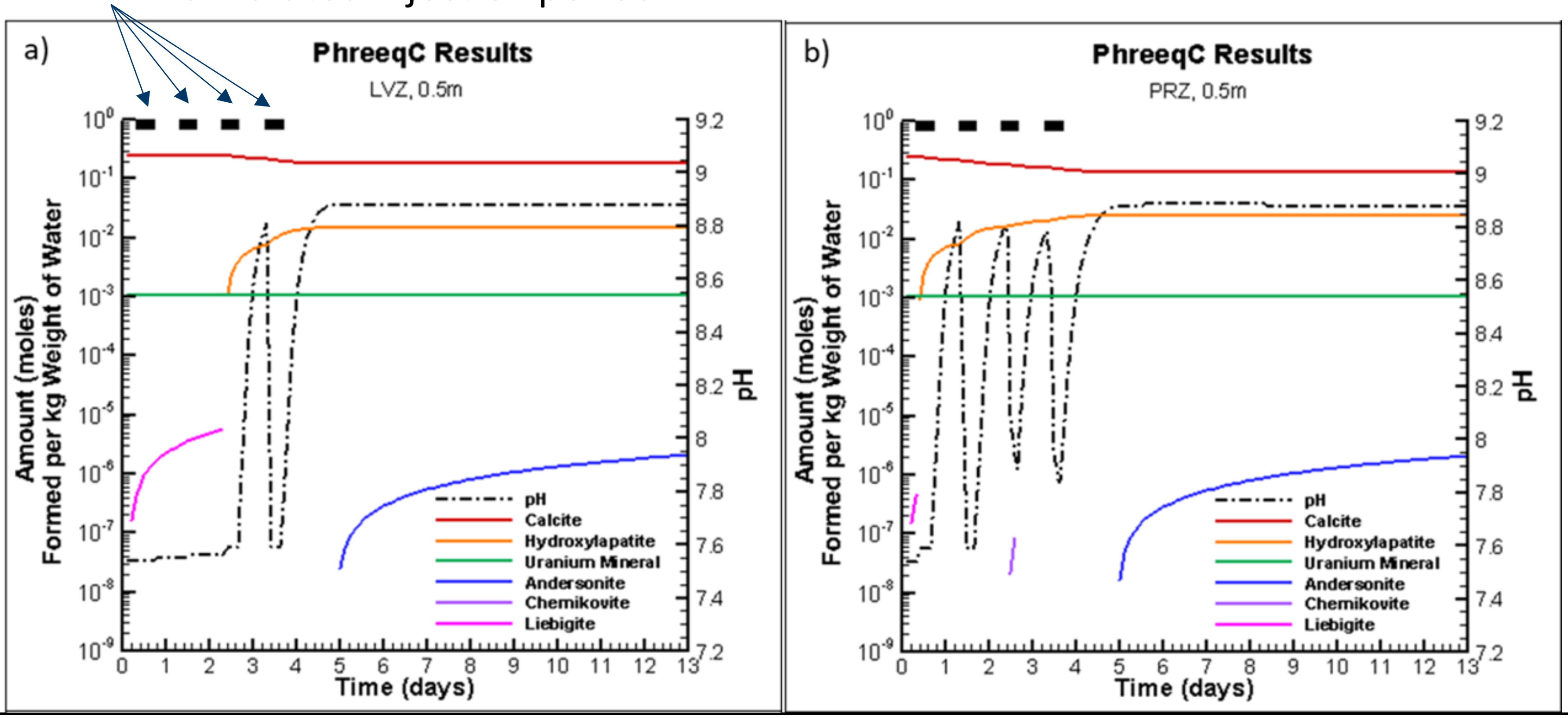
Note:

Water table shown as dashed white line.

LVZ and PRZ injection screen locations shown as dotted white lines.

3-D Reactive Transport Model: Observation Pts

▬ = simulated injection period



Mineral	Equation	log K
Hydroxylapatite	$Ca_5(OH)(PO_4)_3 + 4H^+ = H2O + 3\ HPO_4^{2-} + 5\ Ca^{2+}$	-3.0746
Andersonite	$Na_2CaUO_2(CO_3)_3(H_2O)_6 = 2Na^+ + Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} + 6H_2O$	-37.5
Chernikovite	$(UO_2)HPO_4(H_2O)_4 = UO_2^{2+} + HPO_4^{2-} + 4H_2O$	-22.73
Liebigite	$Ca_2UO_2(CO_3)_3(H_2O)_{10} = 2Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} + 10H_2O$	-36.9

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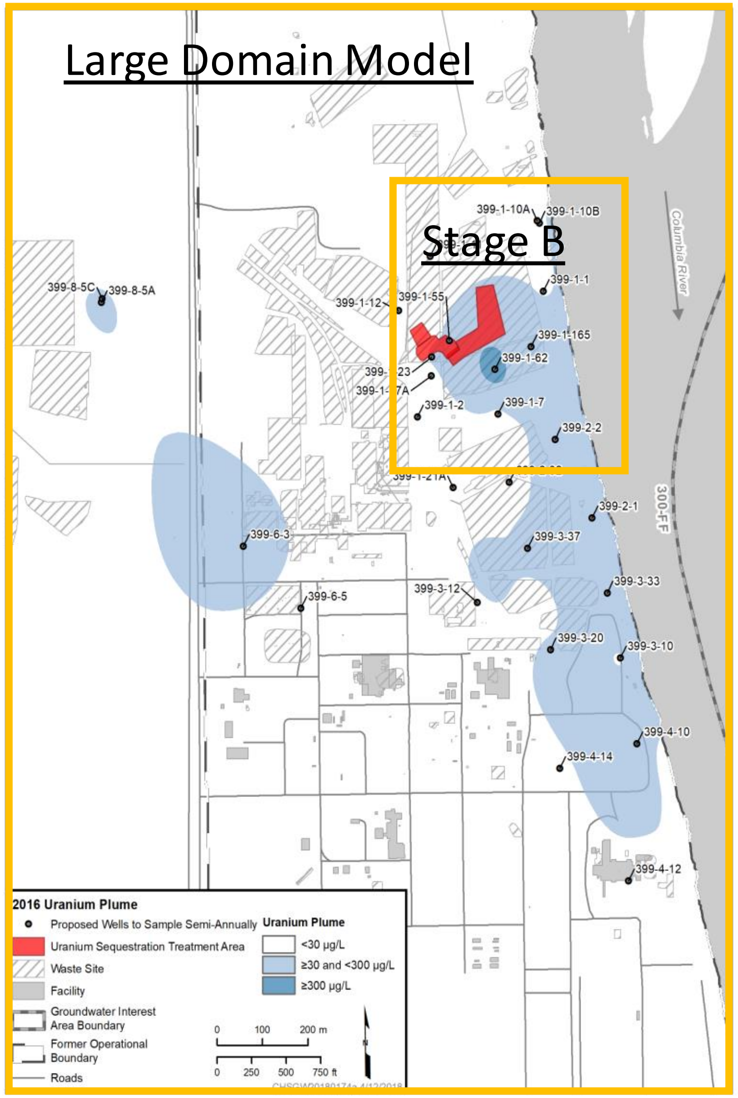
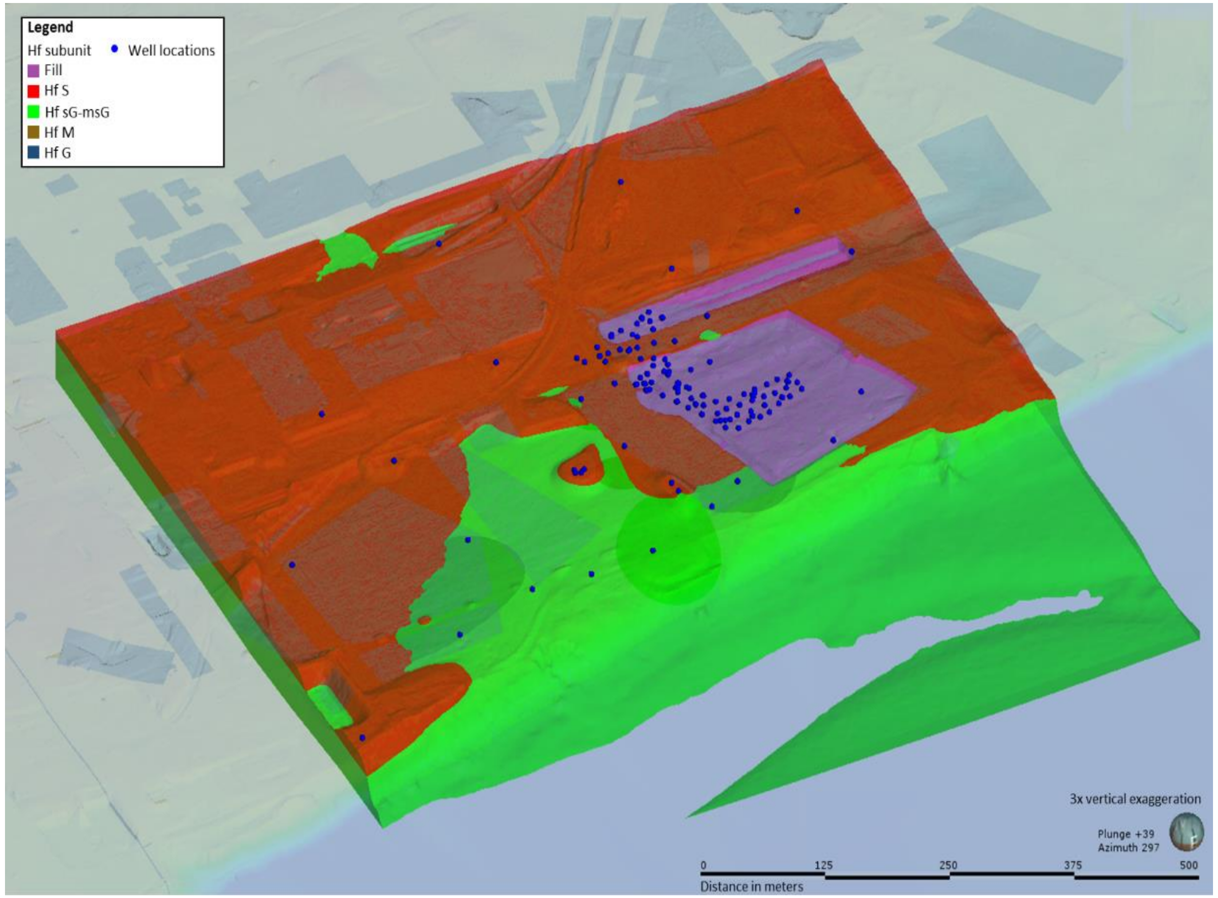
System Scale Flow and Transport Models

Large Domain Model

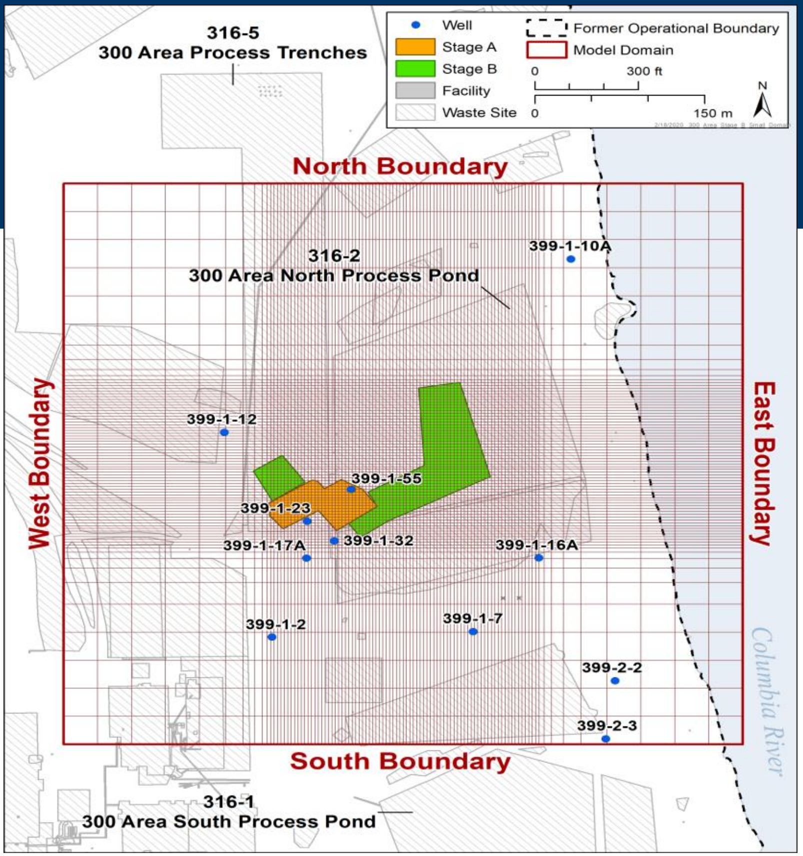


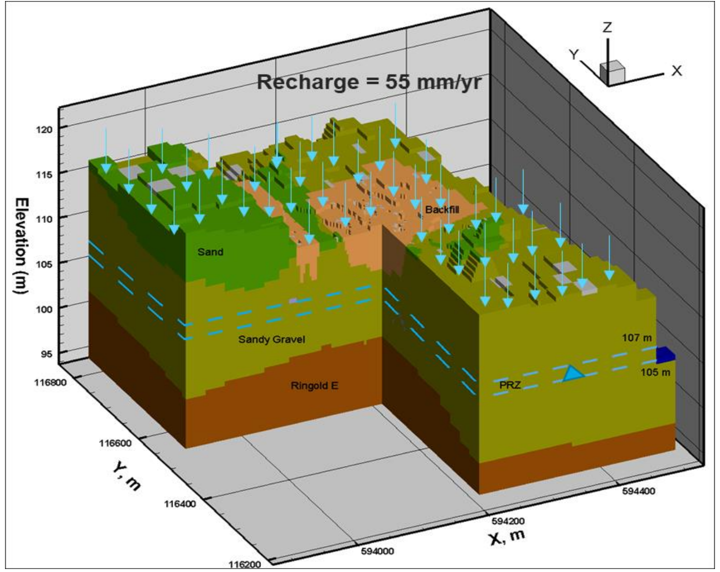
300 Area Geoframework Model



System Scale: Stage B Model

- 3-D model built using eSTOMP code
  - To handle variably saturated conditions
  - 600 m x 600 m x 20 m domain
- Vadose zone and saturated zone comprised of multiple Equivalent Homogeneous Media (EHM)
  - Each heterogeneous hydrostratigraphic unit is treated as an anisotropic EHM having upscaled (effective) flow and transport properties
- Daily averaged hydrostatic pressure boundary conditions based on hourly record of Columbia River stage and water levels in monitoring wells
  - Complete record from 2008 - 2018
- Kinetic model implemented for uranium transport calculations + injections simulated
- Hydraulic conductivity field based on model calibration to hydraulic heads and river water-groundwater mixing based on EC measurements





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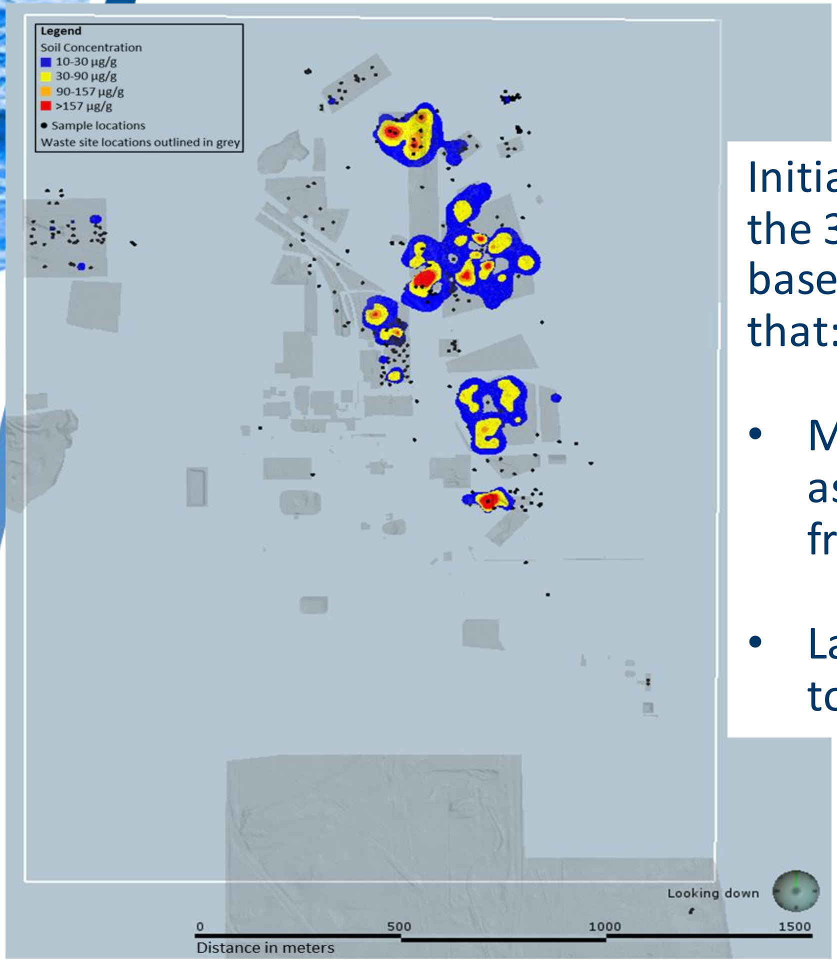
System Scale: Stage B Model

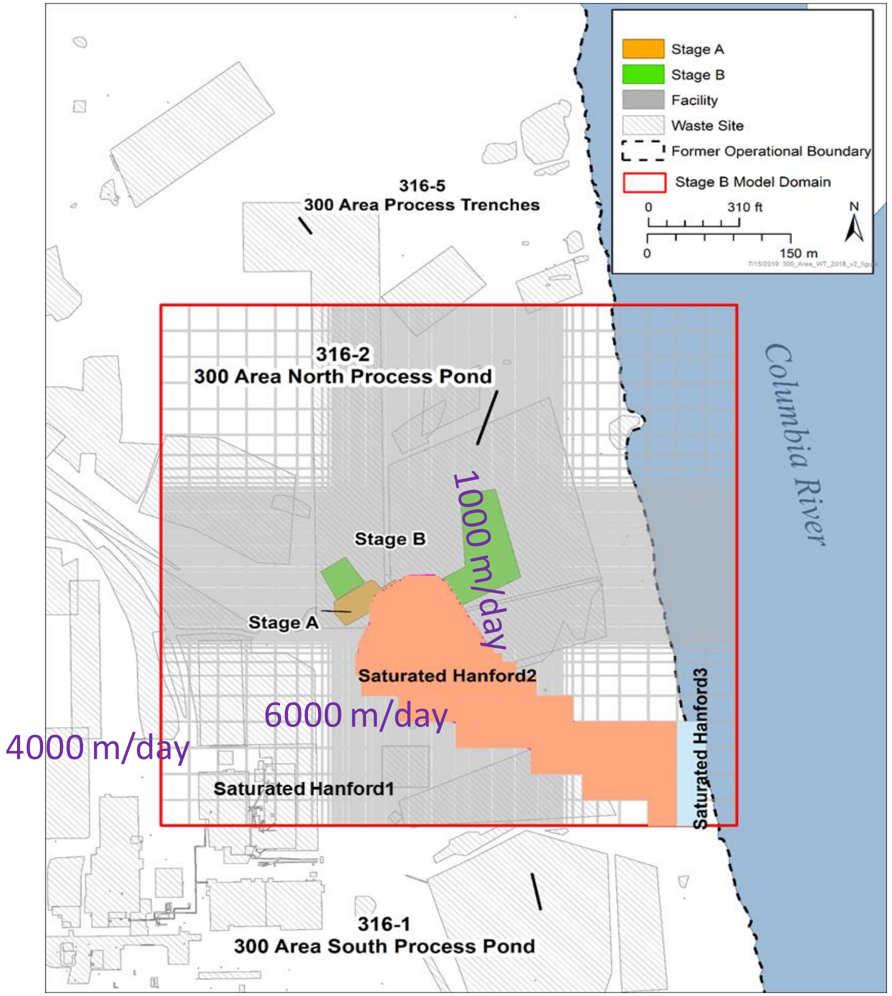
Uranium Soil Distribution



Initial labile uranium mass in the 3-D Model was introduced based on the understanding that:

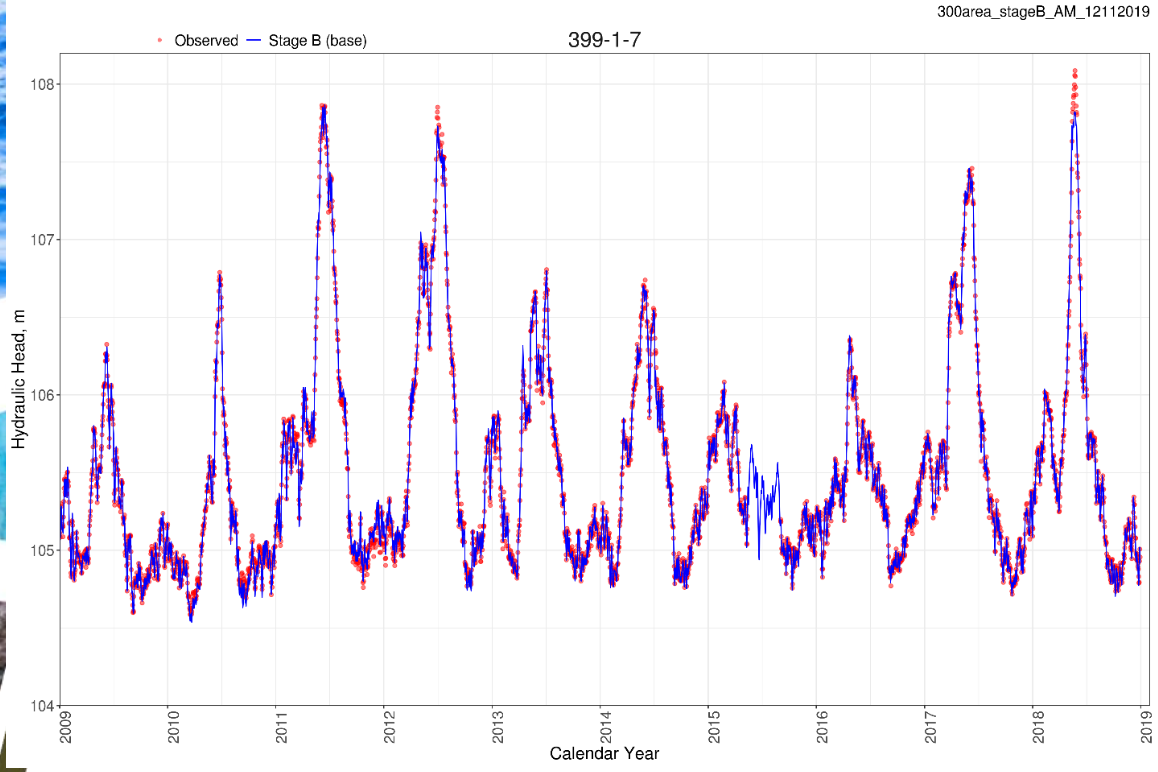
- Majority of the uranium is associated with <2 mm size fraction (sand, silt, and clay)
- Labile uranium variable (up to 60% of total uranium)

Zones of Variable Hydraulic Conductivity

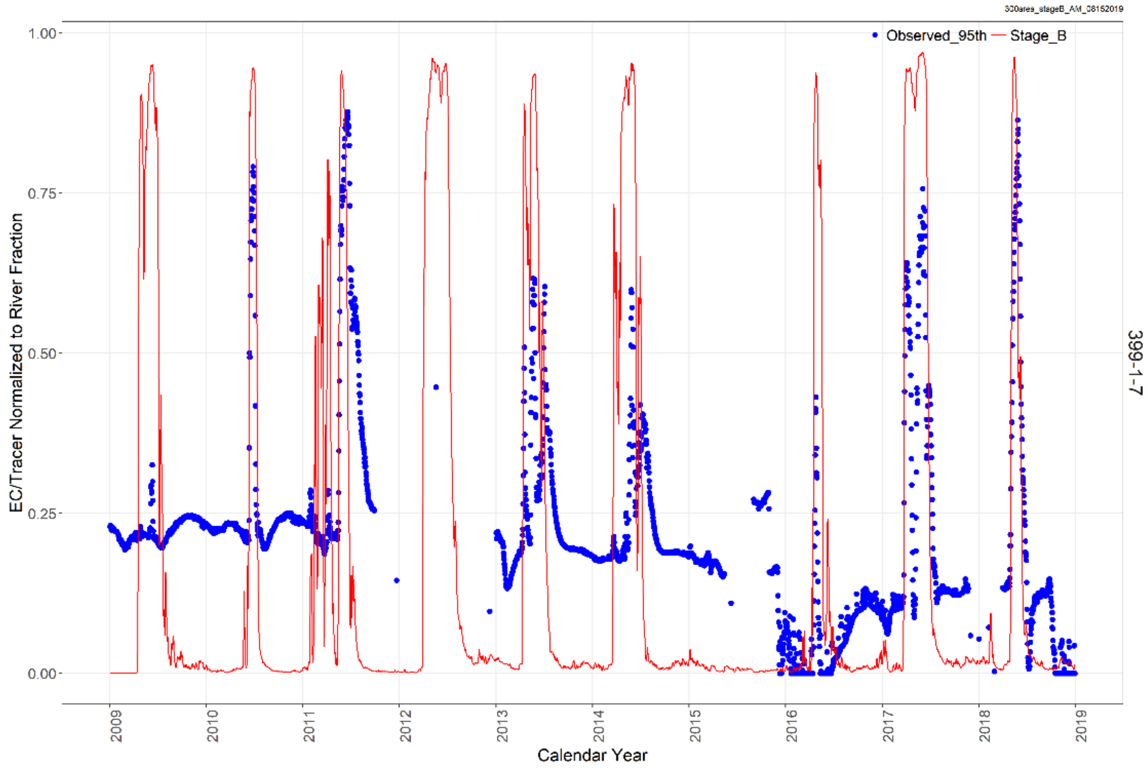


System Scale: Stage B Model

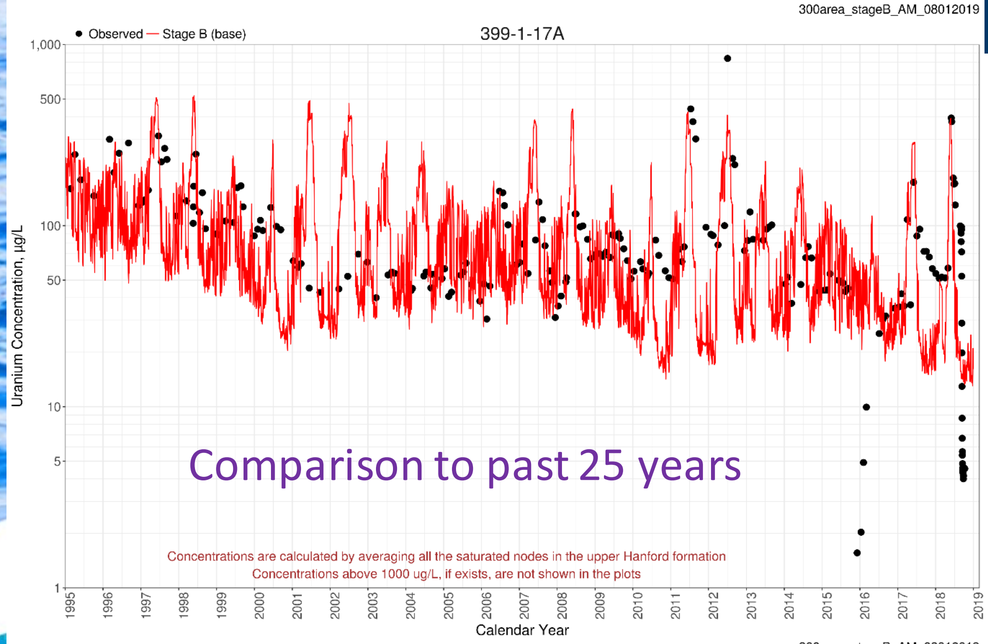
Calibrated Flow Model

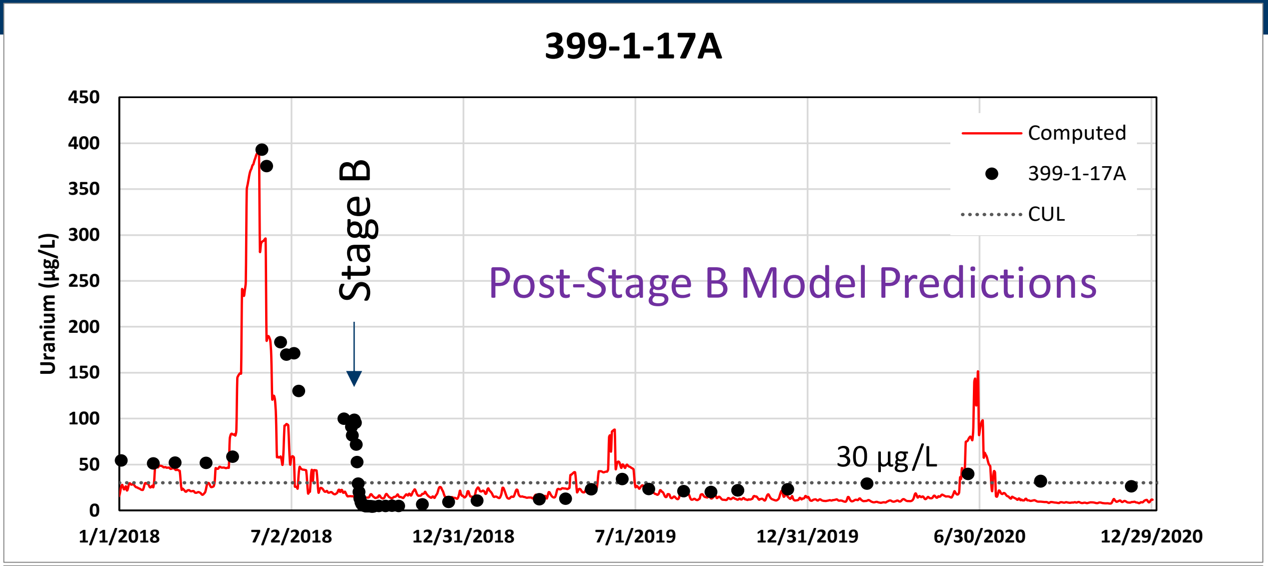


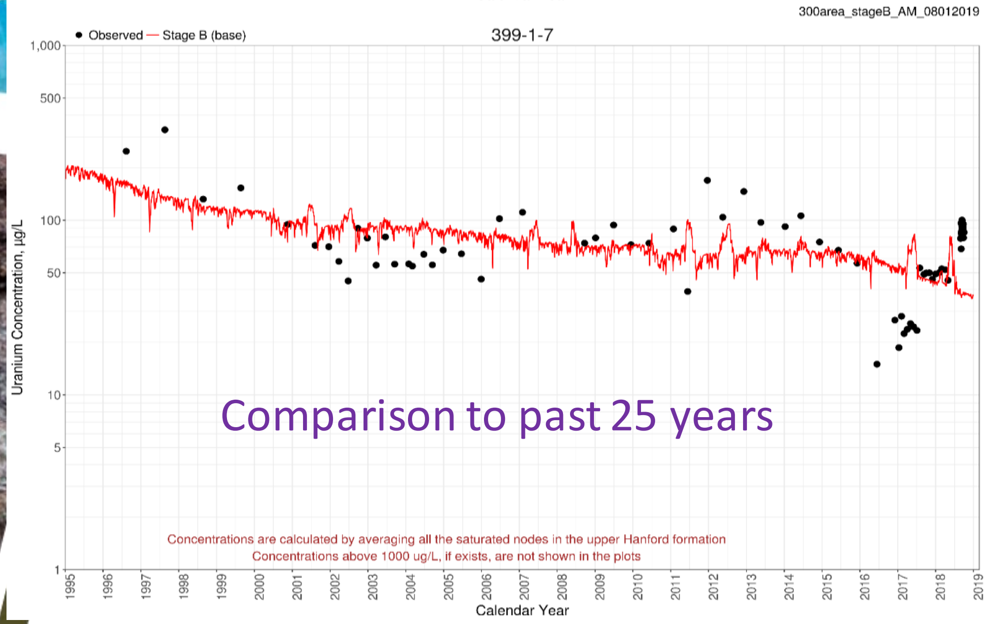
Calibrated Tracer Model: Riverwater-GW mixing

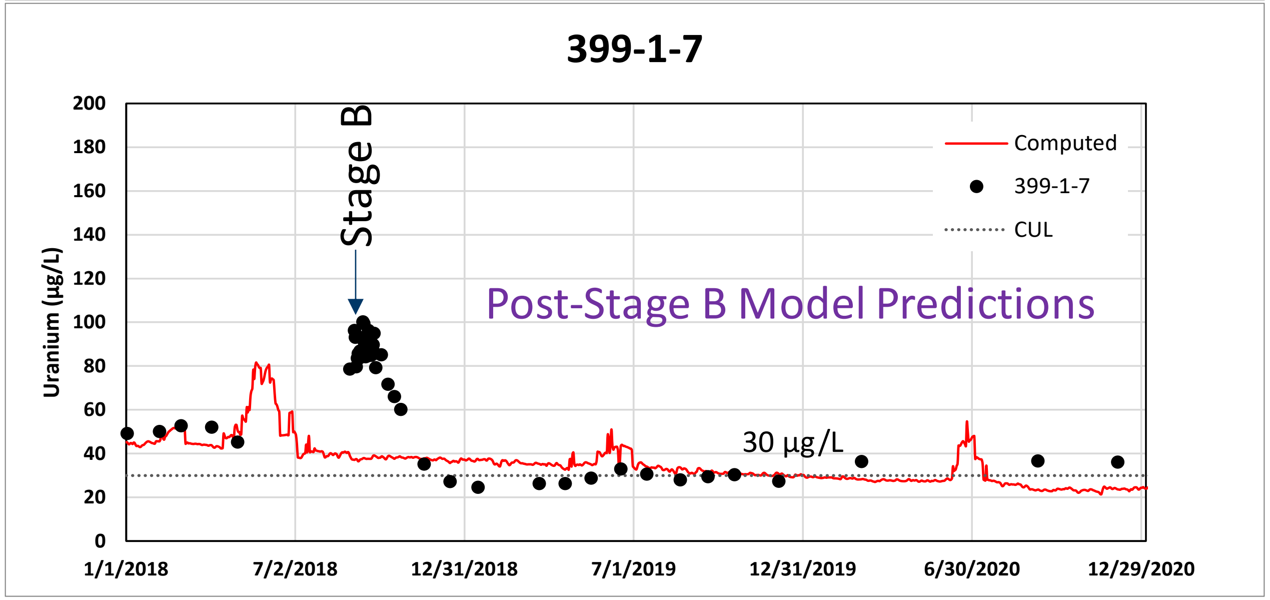


System Scale: Stage B Model









System Scale: Stage B Model

Model Prediction: Enhanced Attenuation Remedy

Model Prediction: Under No Action Scenario

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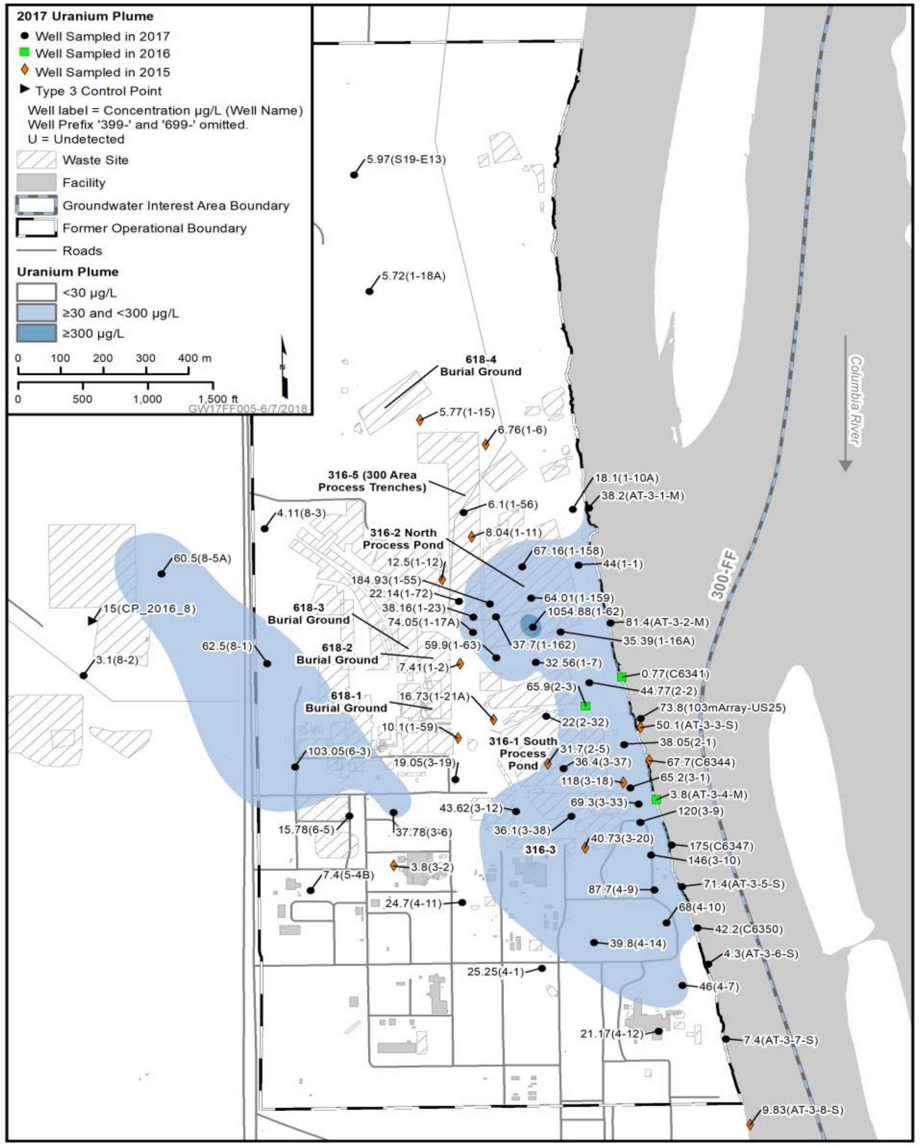
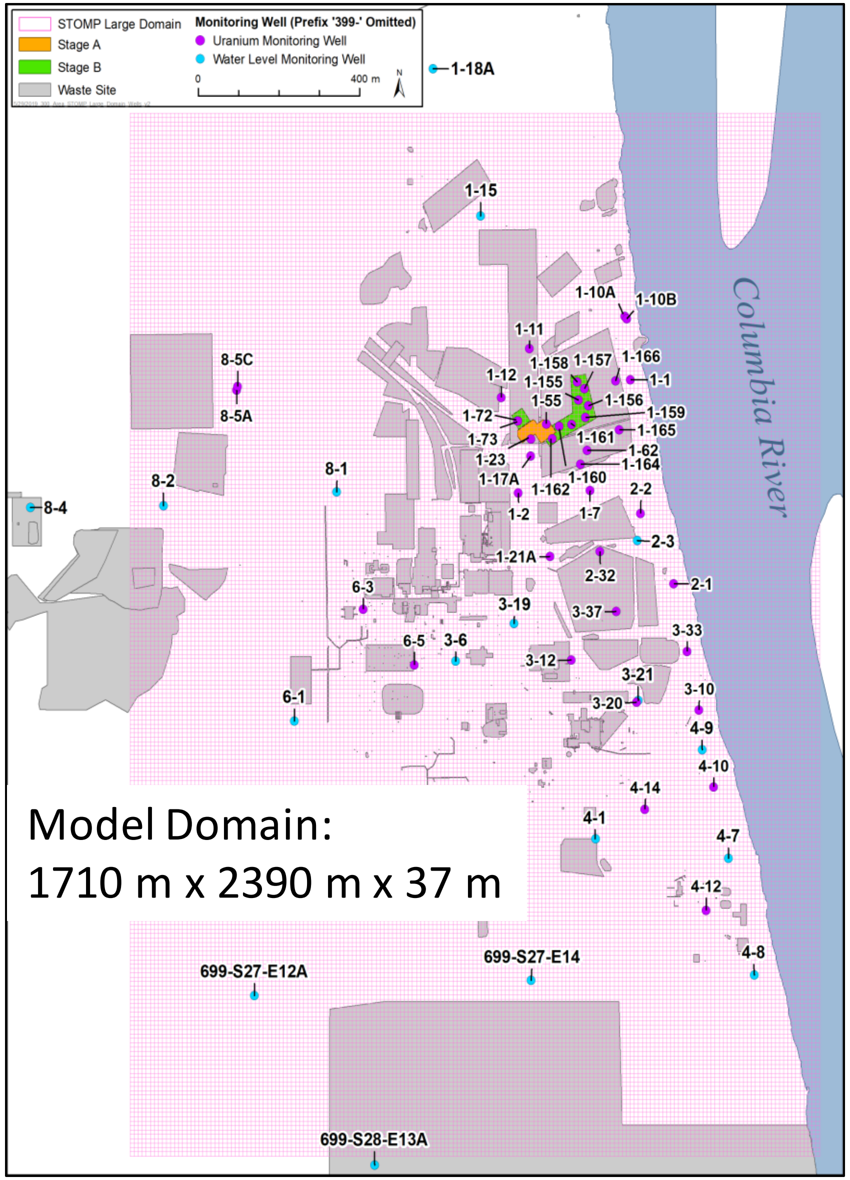
Large Domain Model

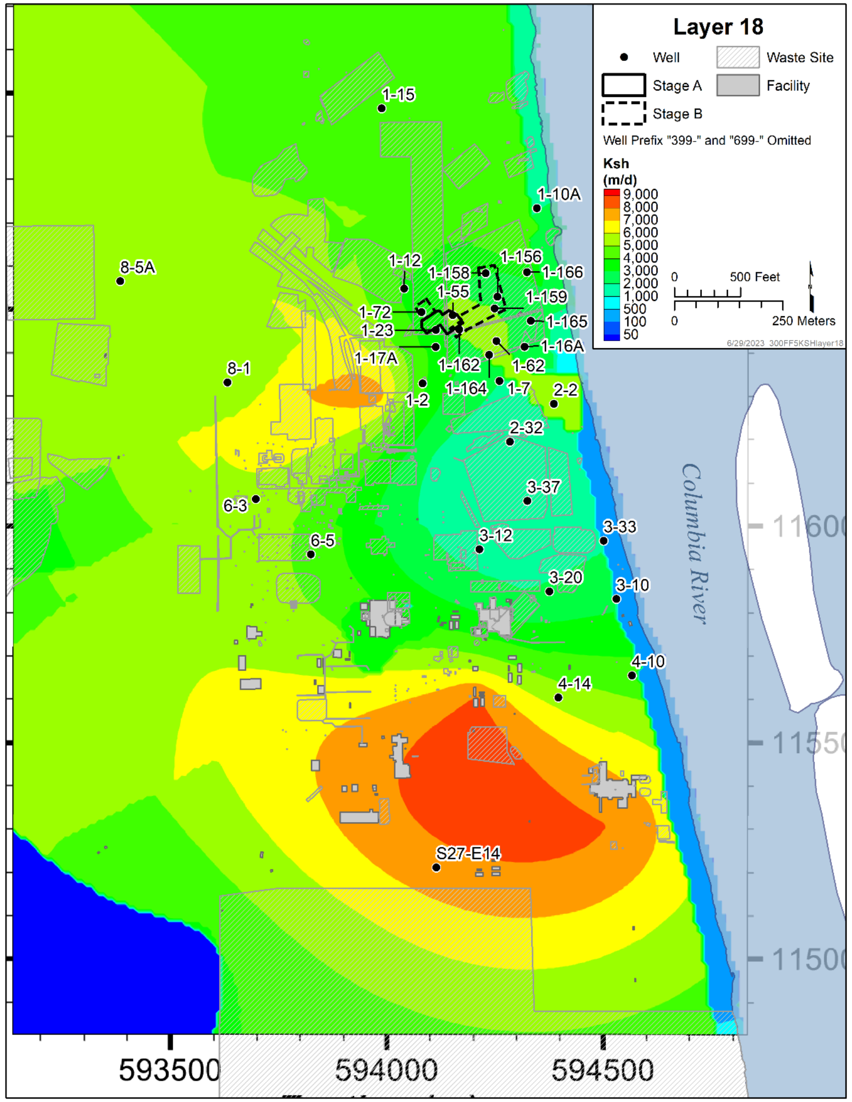


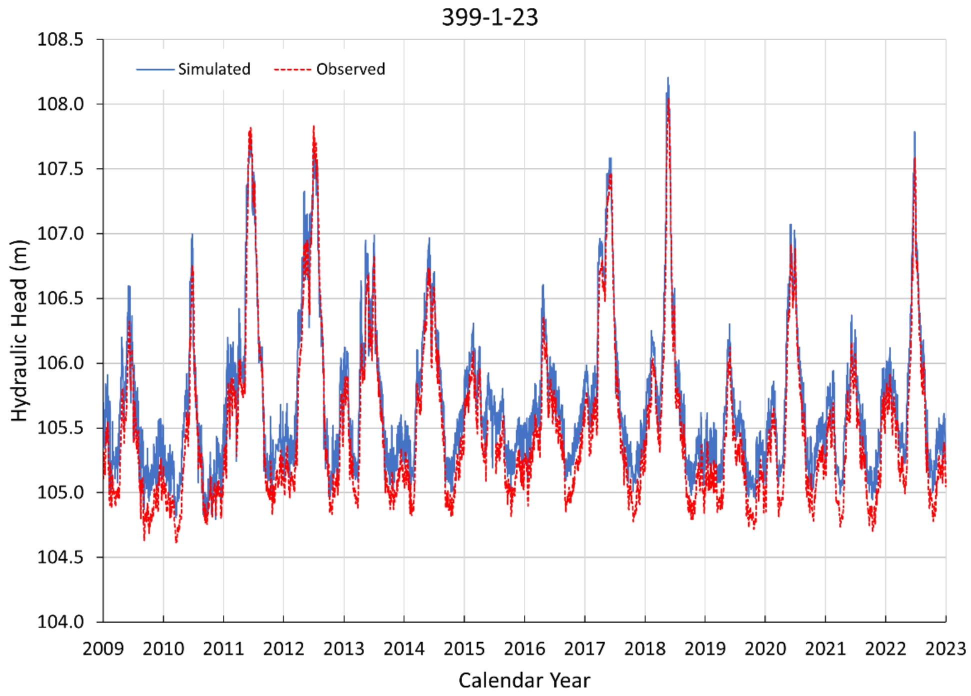


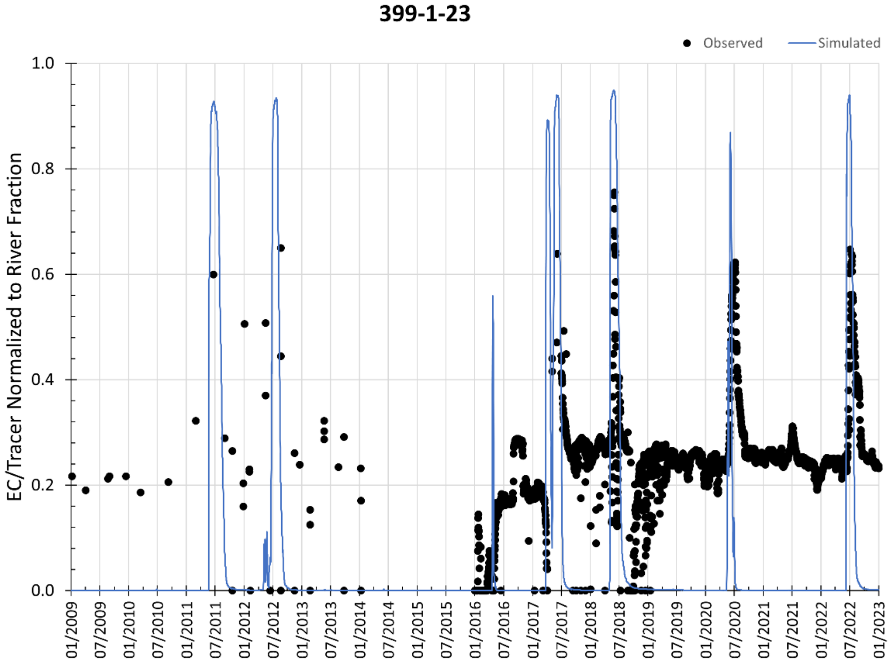
Model Domain:
1710 m x 2390 m x 37 m

Large Domain Model

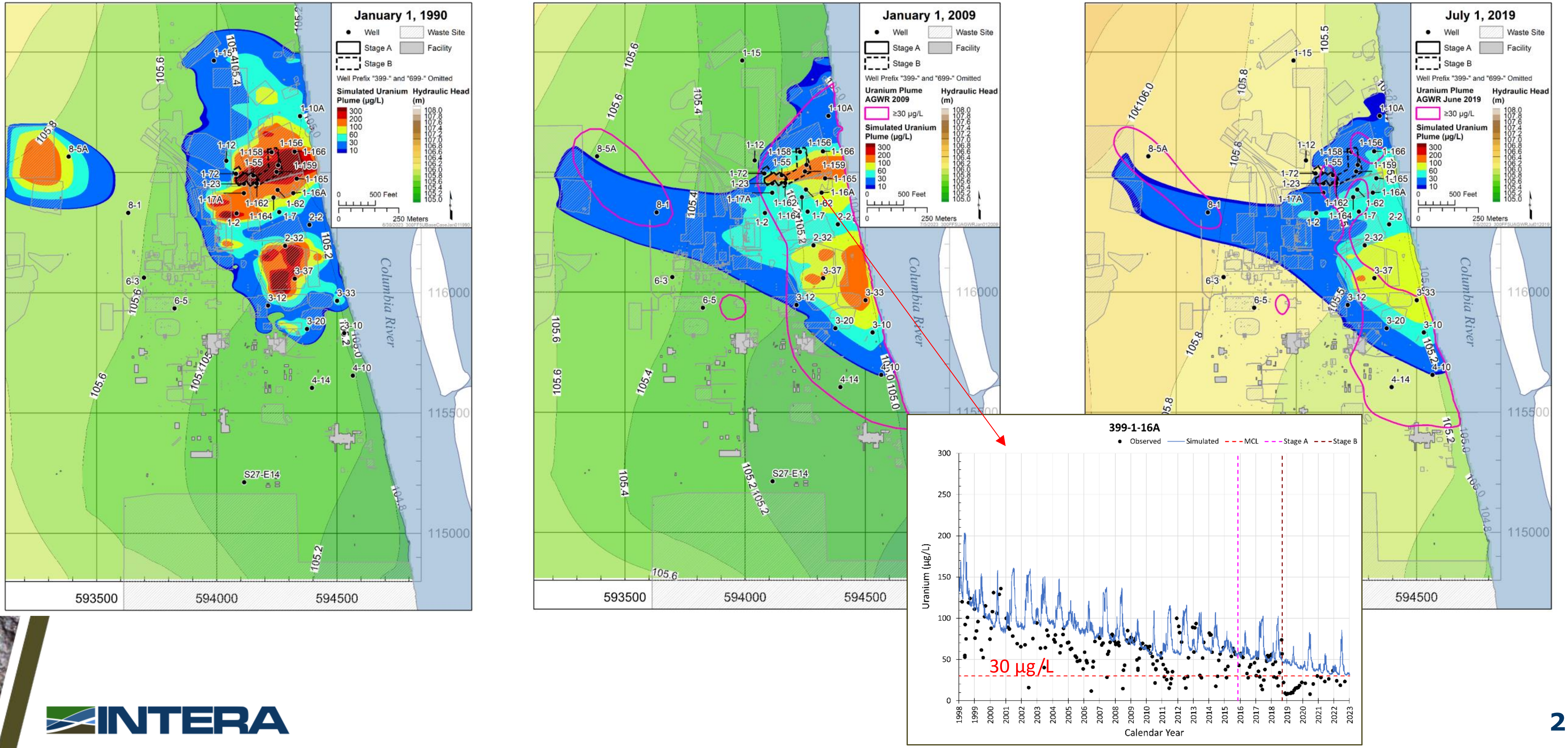
Calibrated Hydraulic Conductivity Field (using PEST)



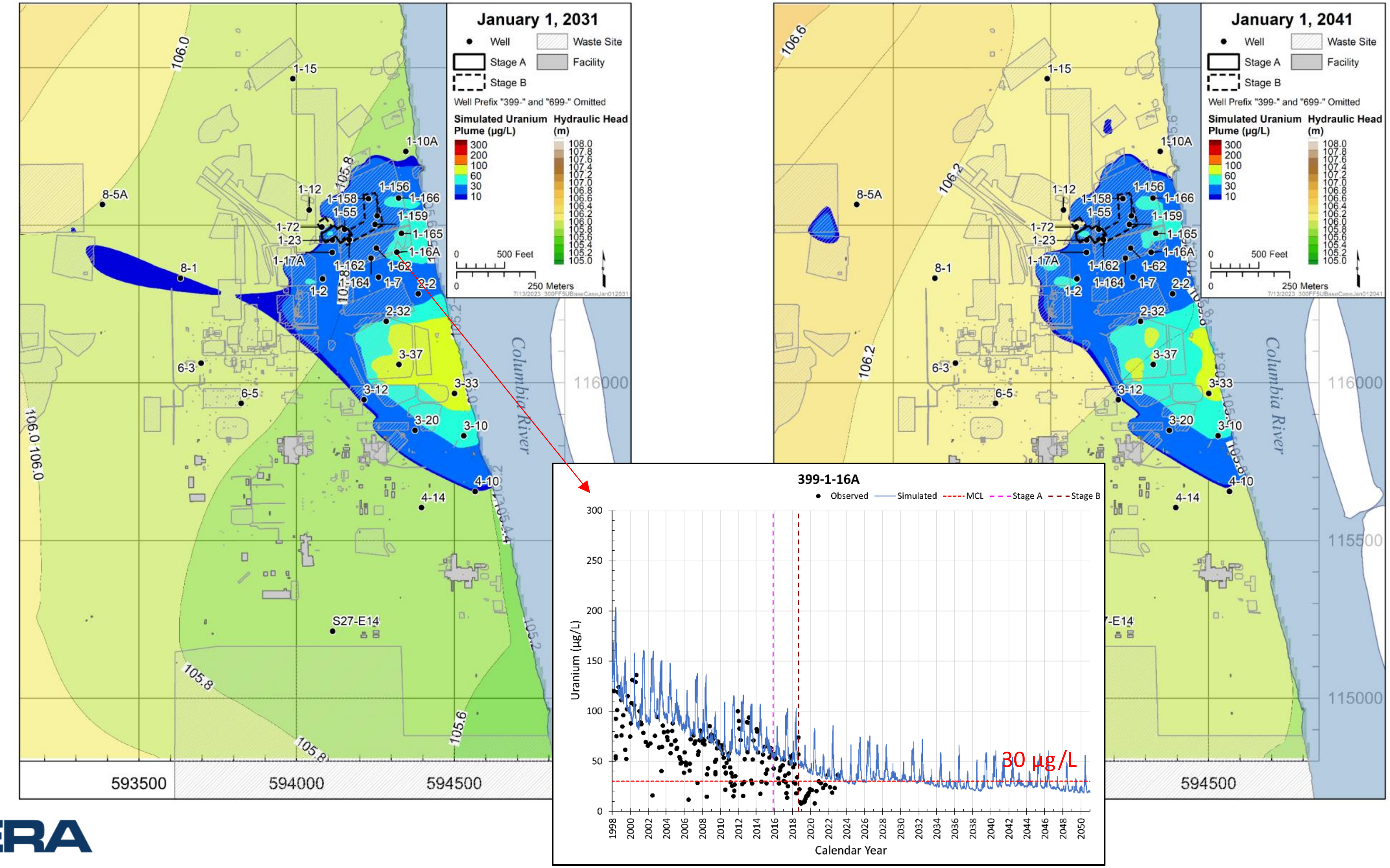




Large Domain Model: Comparison to Observations



Large Domain Model: Predictions



Conclusions

- Evaluation of remedy performance of uranium plume in the 300 Area of the Hanford Site was performed using multiscale modeling
  - Kinetic sorption/desorption parameters based on flow-through column tests (core scale)
  - Effect of polyphosphate solution injections evaluated using a detailed reactive transport model near an injection well
  - Focused system-scale modeling performed to evaluate Stage A & B injection impact in the subsurface (for evaluation of enhanced attenuation)
  - Larger scale modeling performed to evaluate overall remedy performance over next two decades
- Enhanced attenuation through polyphosphate injection appears to be effective in reducing the mobilization of uranium (sequestration)
- Uranium concentrations continue to decline and by 2050 the plume area is predicted to be significantly reduced