U.S. DEPARTMENT OF ENERGY | Legacy Management

Efficient Reactive Transport Simulations of Tracer Studies at a Former Uranium Mill Site Using PHT-USG

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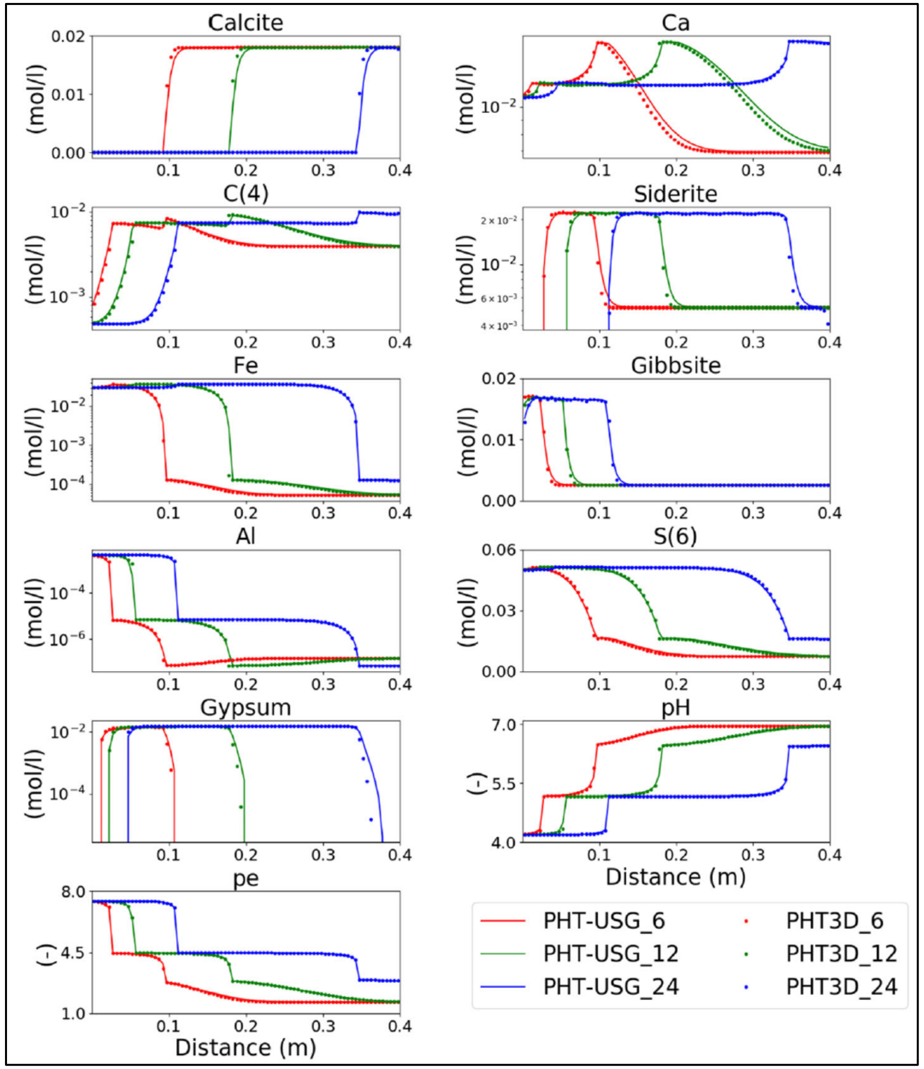
What is PHT-USG?

- PHT-USG couples USG-Transport (transport code for MODFLOW-USG) to PHREEQC
- PHT3D was used to initiate development of PHT-USG
  - PHT3D couples PHREEQC to MT3D with MODFLOW-2000
- Created by the developers of USG-Transport and PHT3D
  - GSI Environmental, CSIRO, and BGR
- Funded by the U.S. Department of Energy (DOE) Office of Legacy Management (LM)

Migration of precipitation/dissolution fronts: comparison of PHT-USG with PHT3D



Source: *PHT-USG module of the BTN Package of MODFLOW-USG Transport*, GSI Environmental, 2019

Why PHT-USG?

- Reactive transport models (RTMs) account for spatially and temporally variable geochemical conditions that affect contaminant transport
  - RTMs can simulate nonlinear sorption that varies spatially and temporally as a function of evolving geochemical conditions
  - Design simulations of remediation strategies may need to account for changing geochemical conditions (e.g., alkalinity flushing, polyphosphate injections)
- RTMs are notorious for lengthy run times
  - Run times can become unmanageable in a parameter-estimation context where hundreds or thousands of model runs are required
- Unstructured grids reduce run times by limiting the number of computational nodes outside of reactive zones

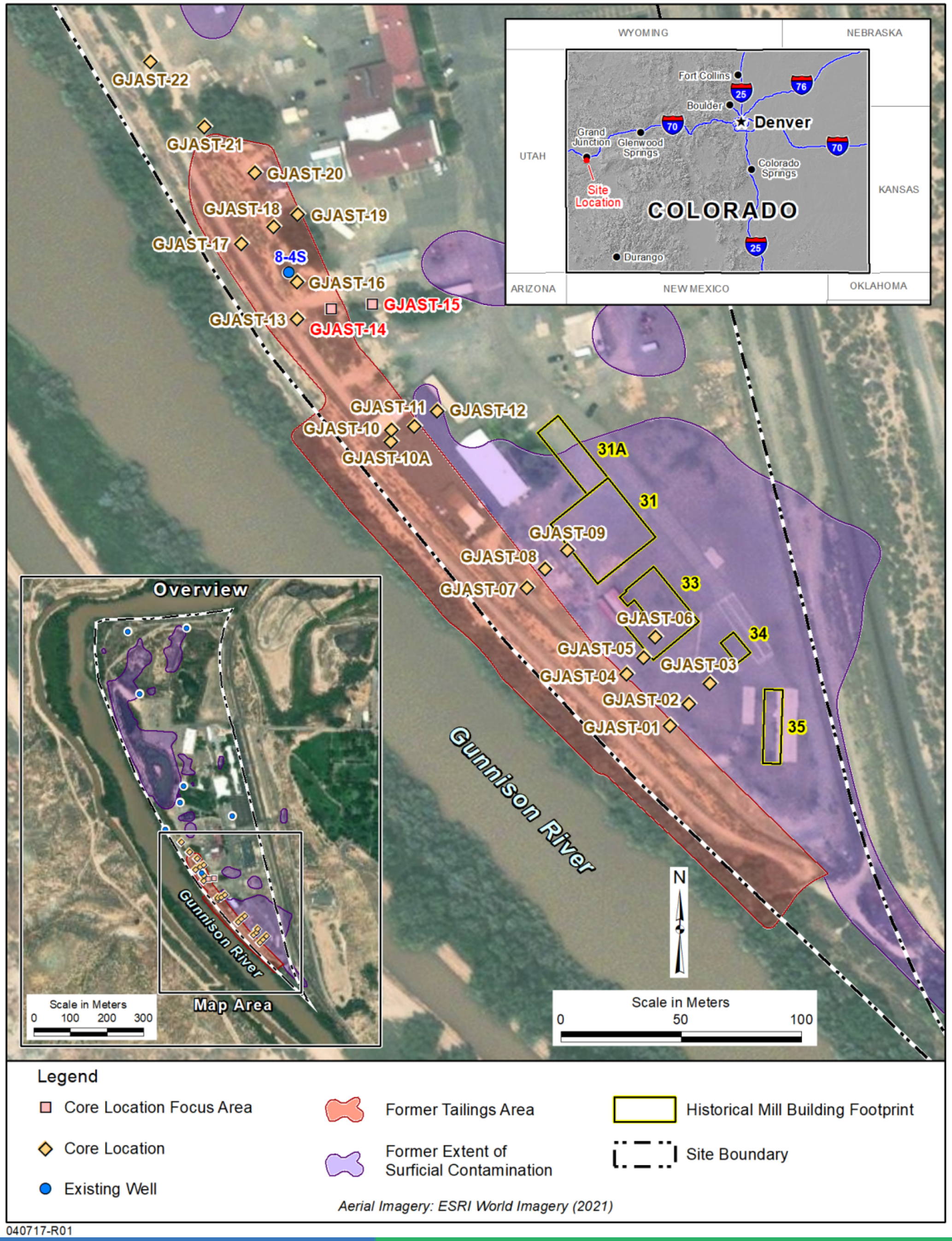
Modeling Objectives

- Simulate tracer testing in a uranium-contaminated aquifer to estimate uranium sorption parameters for use in future sitewide groundwater modeling
- Compare sorption parameter estimates from laboratory column studies, single-well tracer tests, and multi-well tracer tests
- Develop a methodology that can be used for sorption parameter estimation at other former uranium mill sites

Field tracer testing

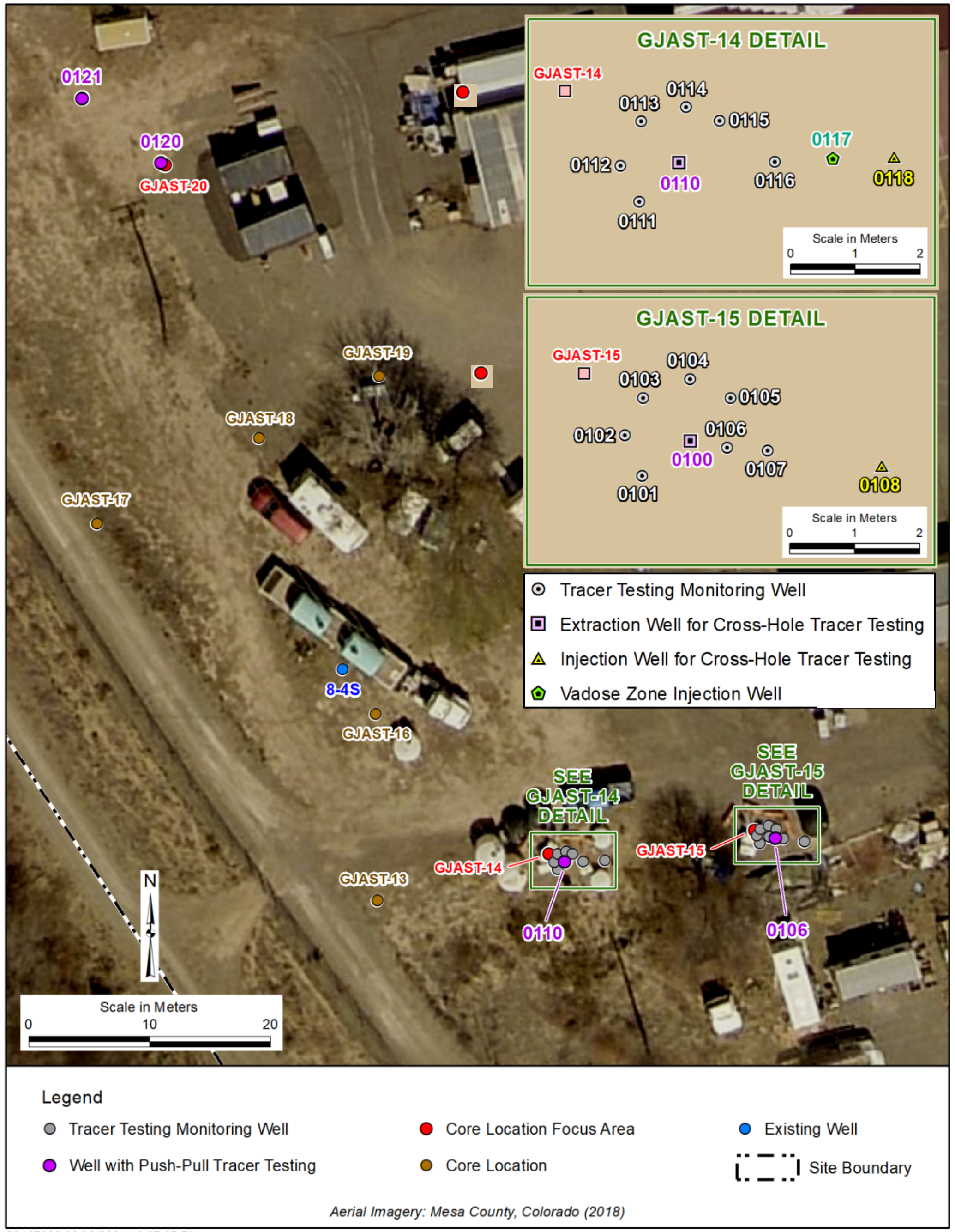
Study Site

- Grand Junction, Colorado, Site managed by LM
- Series of uranium pilot mills operated from 1943 to 1958
- Mill tailings removed by 1994 to meet radiological standards
- Zones of elevated residual uranium identified by collecting sediment samples from boreholes
- Contaminated alluvial floodplain aquifer next to the Gunnison River
- Groundwater compliance strategy:
  - Natural flushing
  - Institutional controls



Tracer Test Locations

- Organic-rich zone with elevated uranium below the water table (GJAST-15)
- Evaporites with elevated uranium in the vadose zone (GJAST-14)
- Gypsum-rich zone with elevated uranium above and below the water table (GJAST-20)
- Single well push-pull tests at wells 0106, 0110, 0120, and 0121
- Cross-hole tracer tests at wells 0108 to 0100 and 0118 to 0110
- Surface infiltration cross-hole test at wells 0117 to 0110



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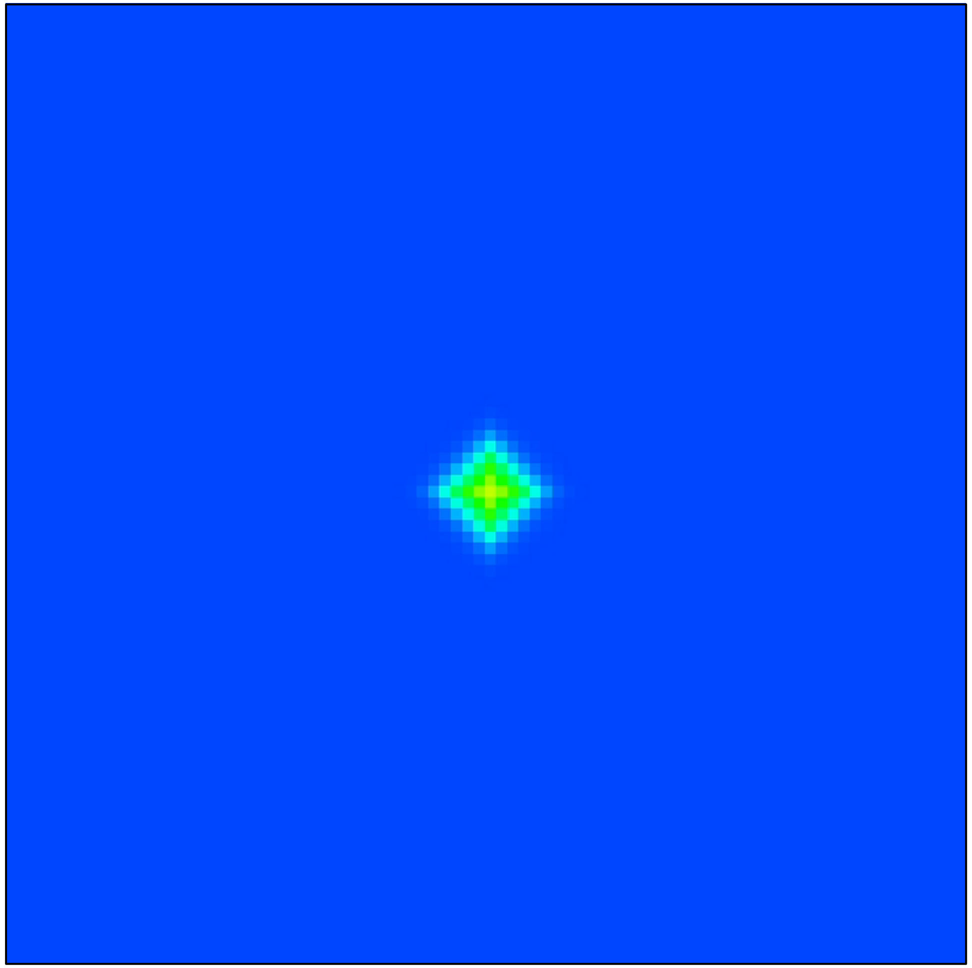
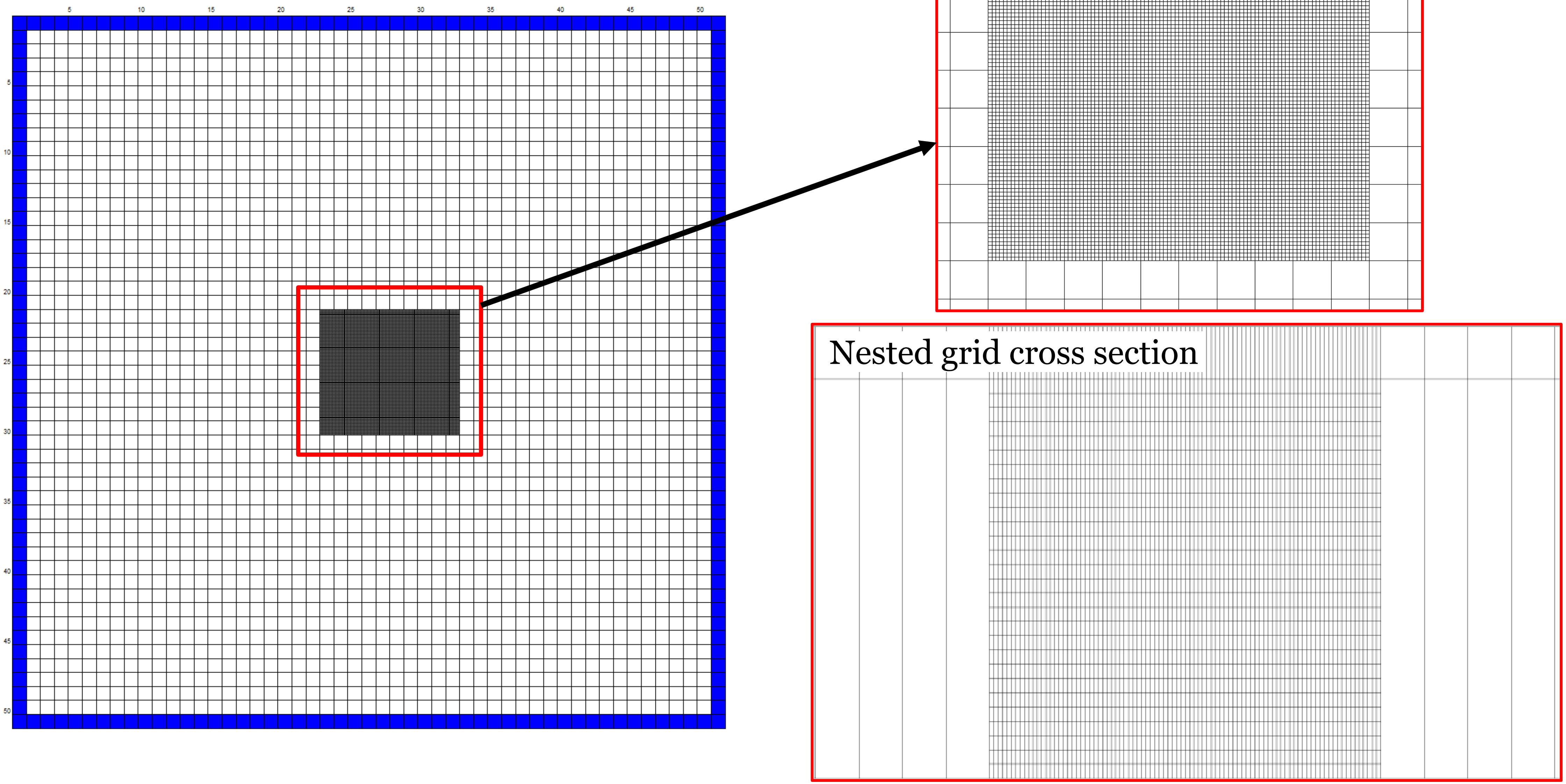
Tracer Test Methods

- Push-pull tests
  - Push: inject river water with tracers
  - Chase: inject river water
  - Drift: natural gradient flow
  - Pull: extract the injected water
- Cross-hole tests
  - Push and chase phases at the injection well
  - Continuous pumping at the extraction well during and after injection phases
  - Drift phase (no injection or extraction) in the well 0108 to 0100 test between two pumping-only phases



Plan view of simulated tracer in Well 0121 push-pull test

Model Grid Setup



Geochemical Model Setup

- Generalized surface complexation model
  - Two-site equilibrium sorption model
  - Strong (S) sorption sites
  - Super strong (SS) sorption sites
  - Two equilibrium constants and two sorption site densities

$$SOH + UO_2^{2+} = SOUO_2^{+} + H^{+}$$

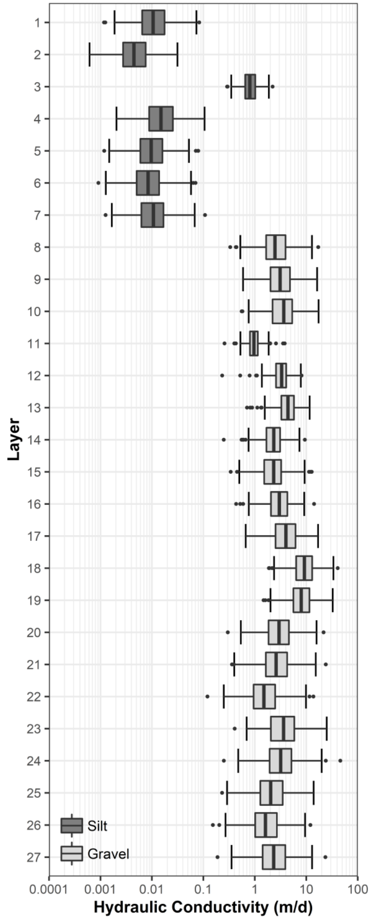
$$SSOH + UO_2^{2+} = SSOUO_2^{+} + H^{+}$$

- Minerals
  - Calcite
  - Gypsum (0120 and 0121 push-pull tests only)
- Cation exchange
- Tracers: Li, Br, I, pentafluorobenzoate (PFB), 2,6-difluorobenzoate (DFB)
- Other dissolved species: U, pH, pe, Ca, Mg, Sr, Na, K, Cl, S(6), C(4)
- Used PHREEQC database updated with recent uranium complexation species information and thermodynamics

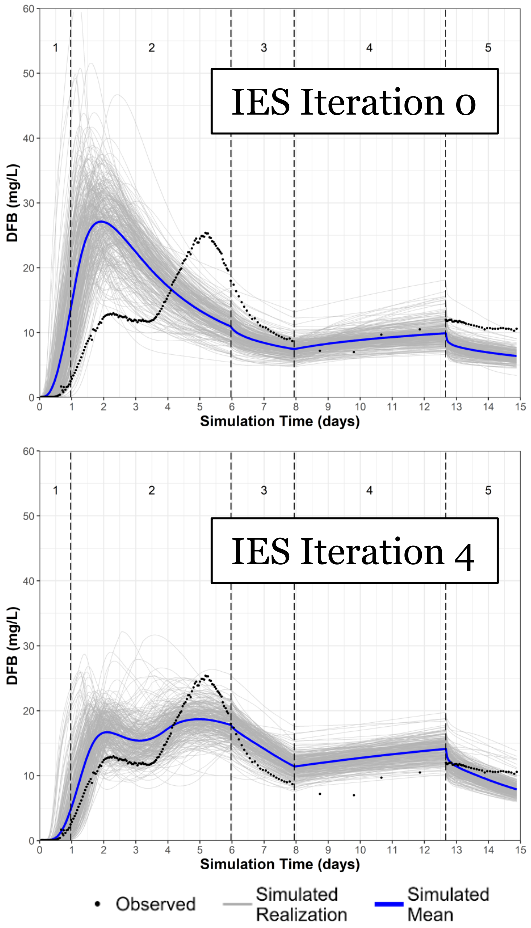
Calibration Approach

- Physical calibration parameters
  - Horizontal and vertical hydraulic conductivity
  - Longitudinal and transverse dispersivity
  - Effective porosity (cross-hole tests only)
- Geochemical calibration parameters
  - Uranium sorption site densities
  - Ion exchange site density
  - Calcite saturation index (SI)
  - Gypsum SI (well 0120 and 0121 tests only)
  - Equilibrium constants held fixed
- Traditional PEST for push-pull simulations
  - Uniform parameter distributions limit the number of calibration parameters
- Stochastic calibration using PESTPP-IES for cross-hole simulations
  - Parameter values vary by layer to account for heterogeneity

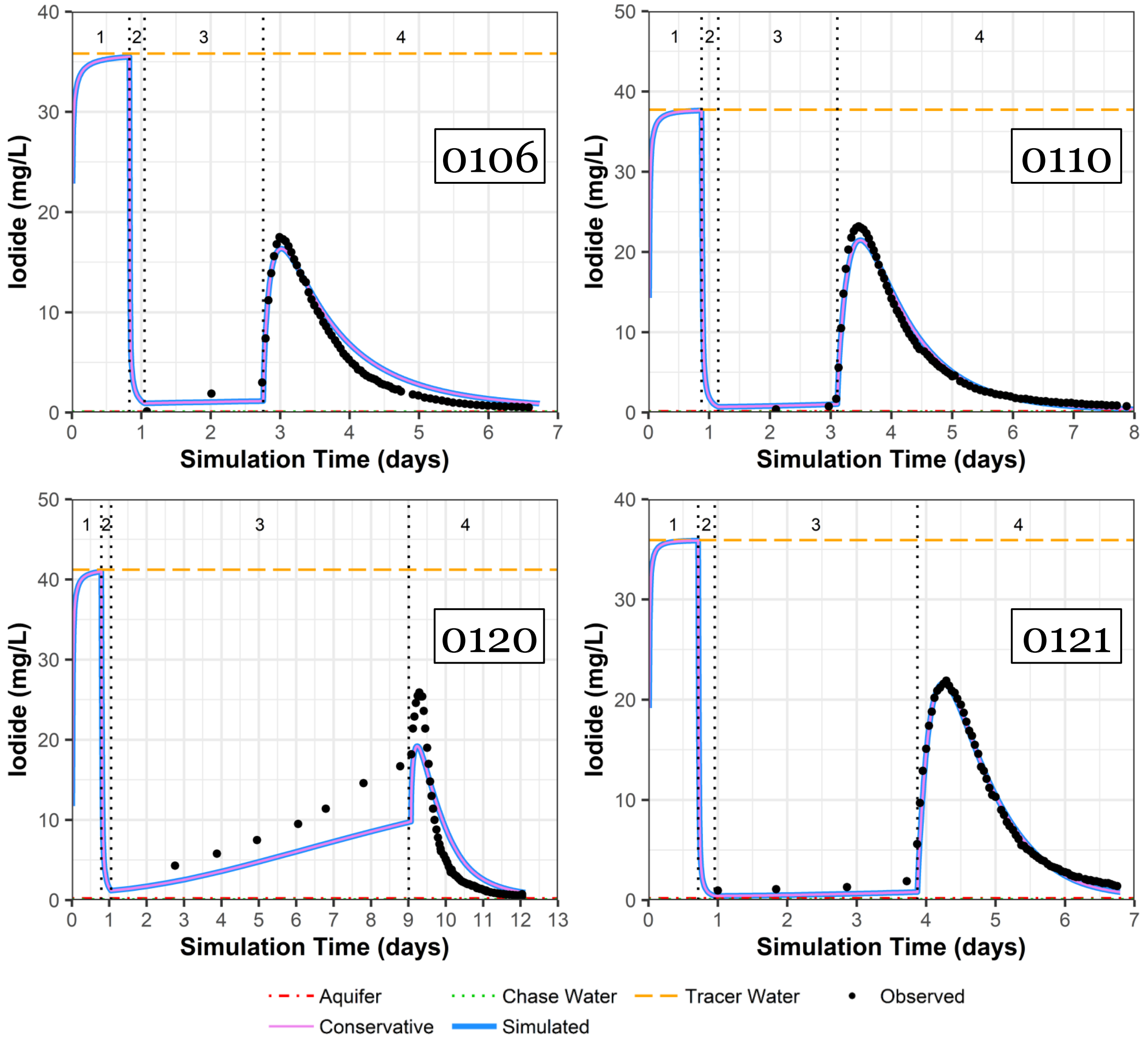
Calibrated hydraulic conductivity distribution



DFB tracer at extraction well 0100 (cross-hole test)

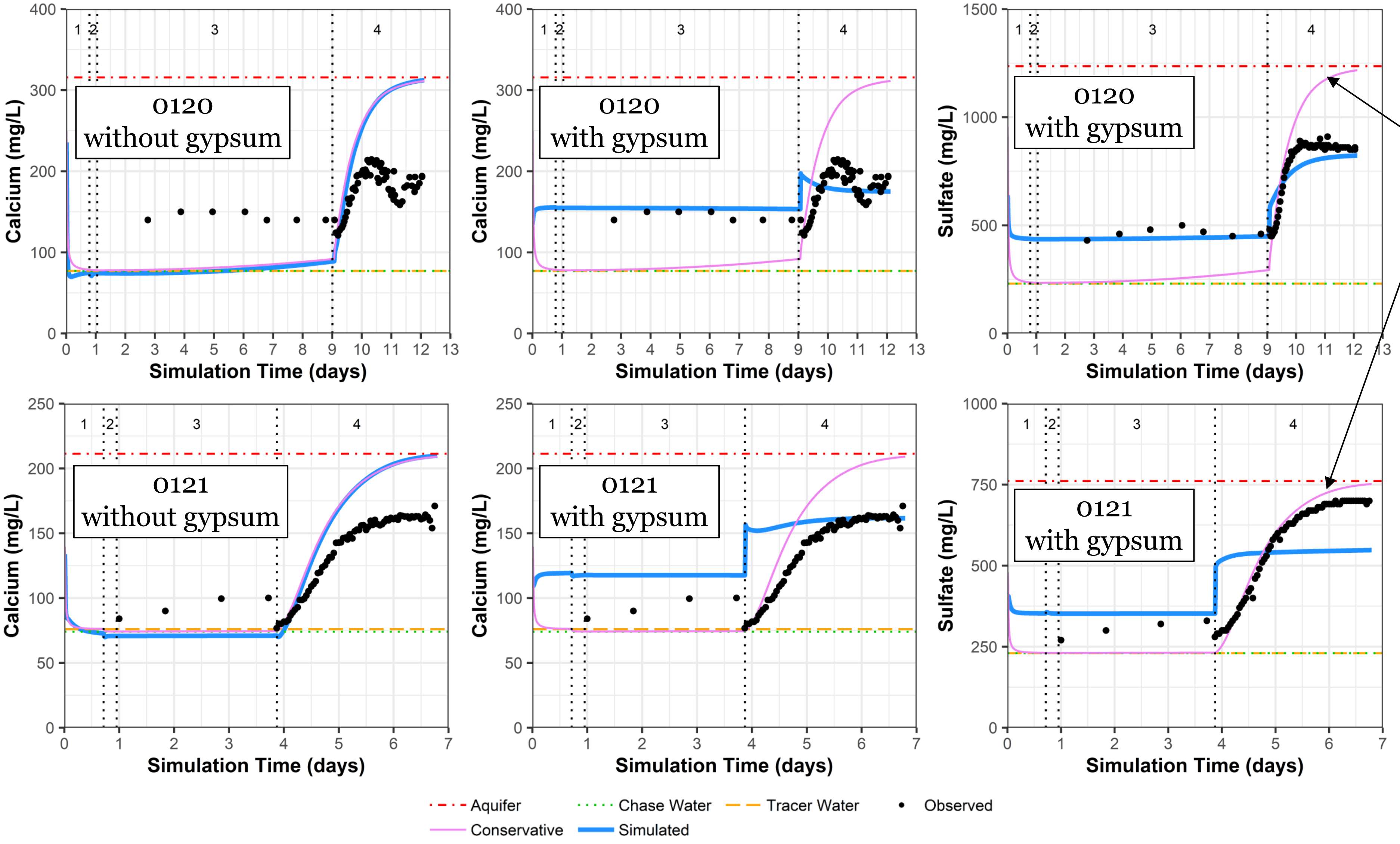


Push-Pull Test Conservative Tracers



Phases:
1: Tracer injection
2: Chase injection
3: Drift
4: Extraction

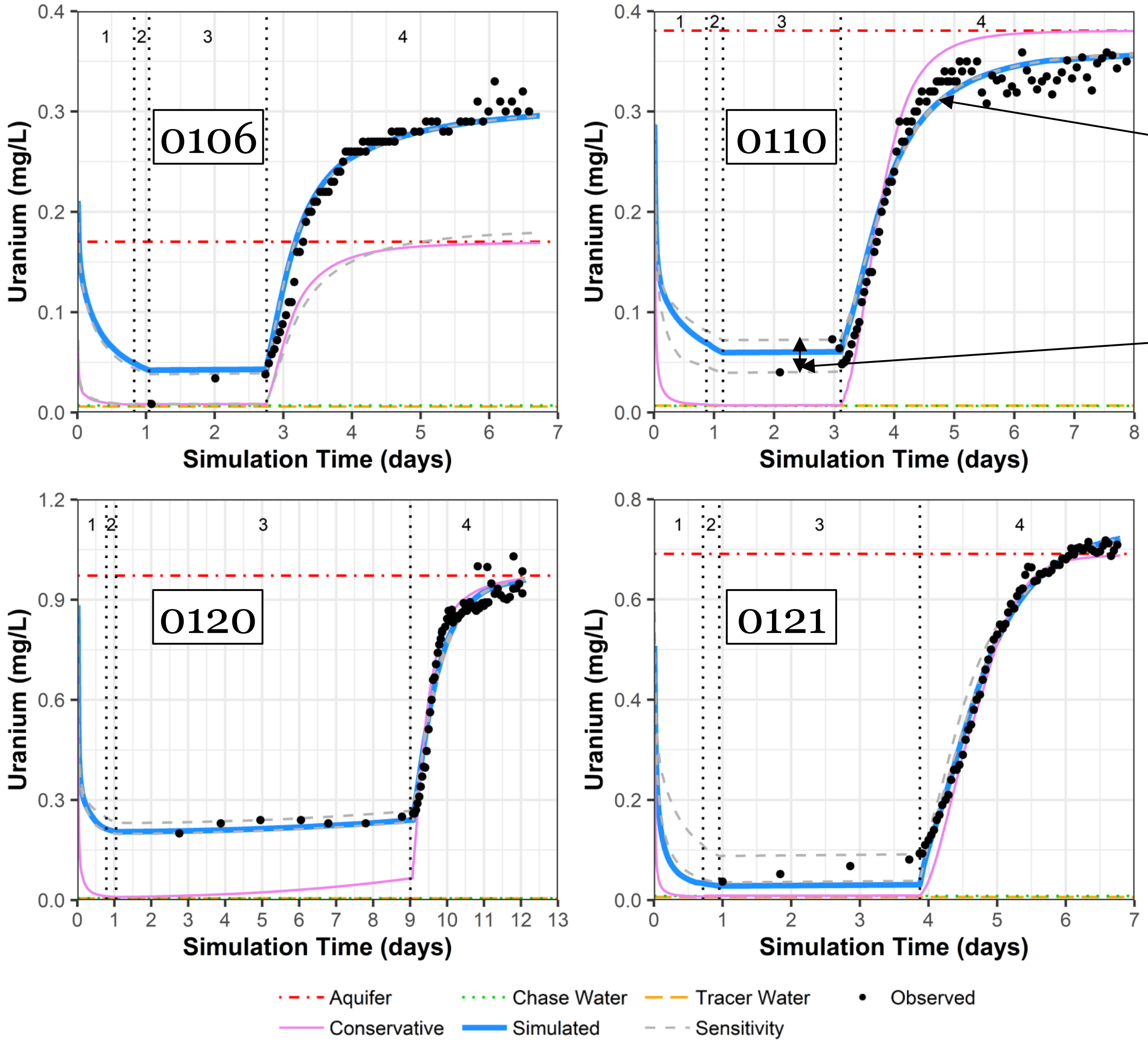
Effects of Gypsum in Wells 0120 and 0121



Sulfate is a conservative species when gypsum is not simulated

Phases:
1: Tracer injection
2: Chase injection
3: Drift
4: Extraction

Push-Pull Test Uranium

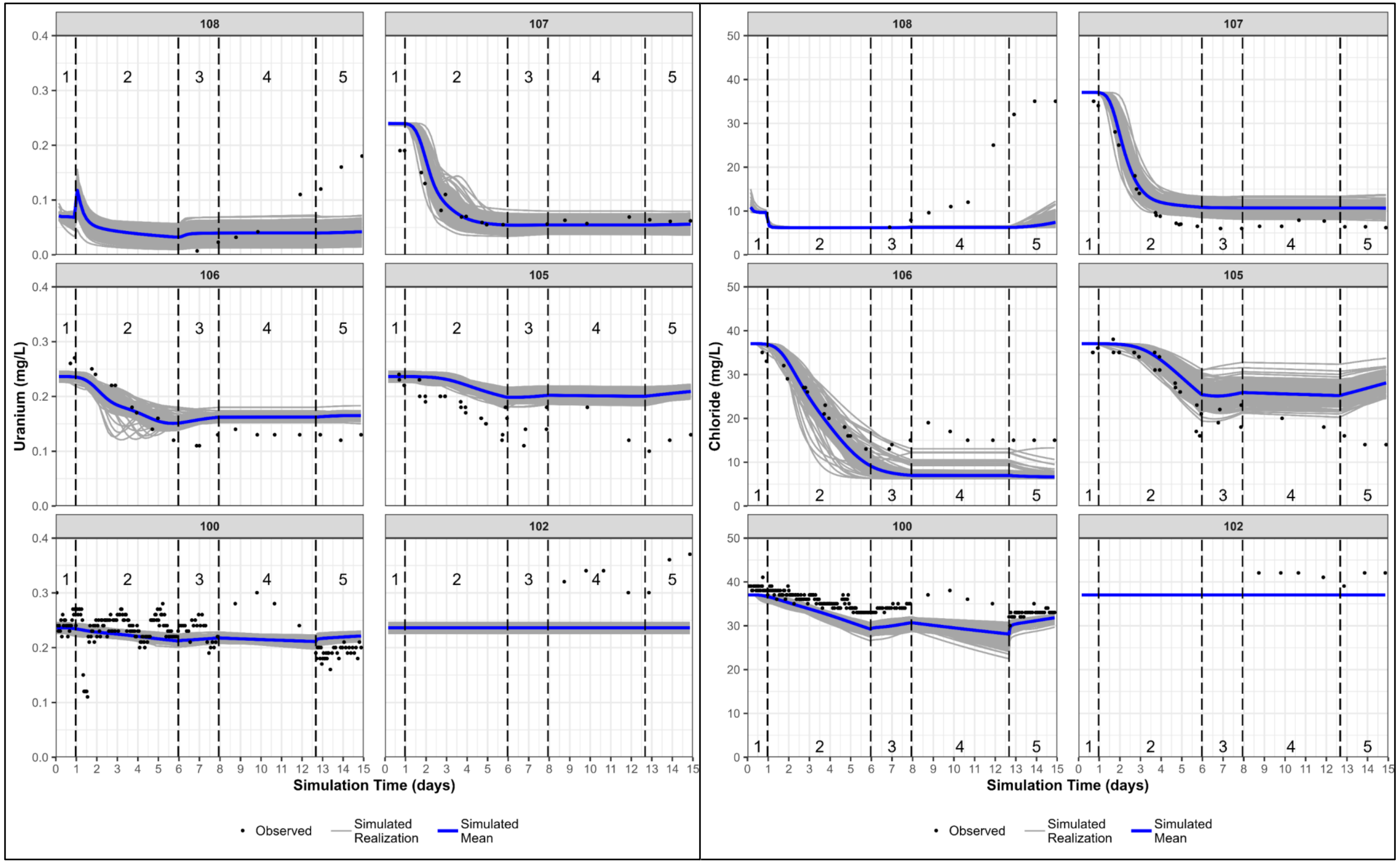


Limited sensitivity to sorption parameters in extraction phase

Increased sensitivity to sorption parameters in drift phase

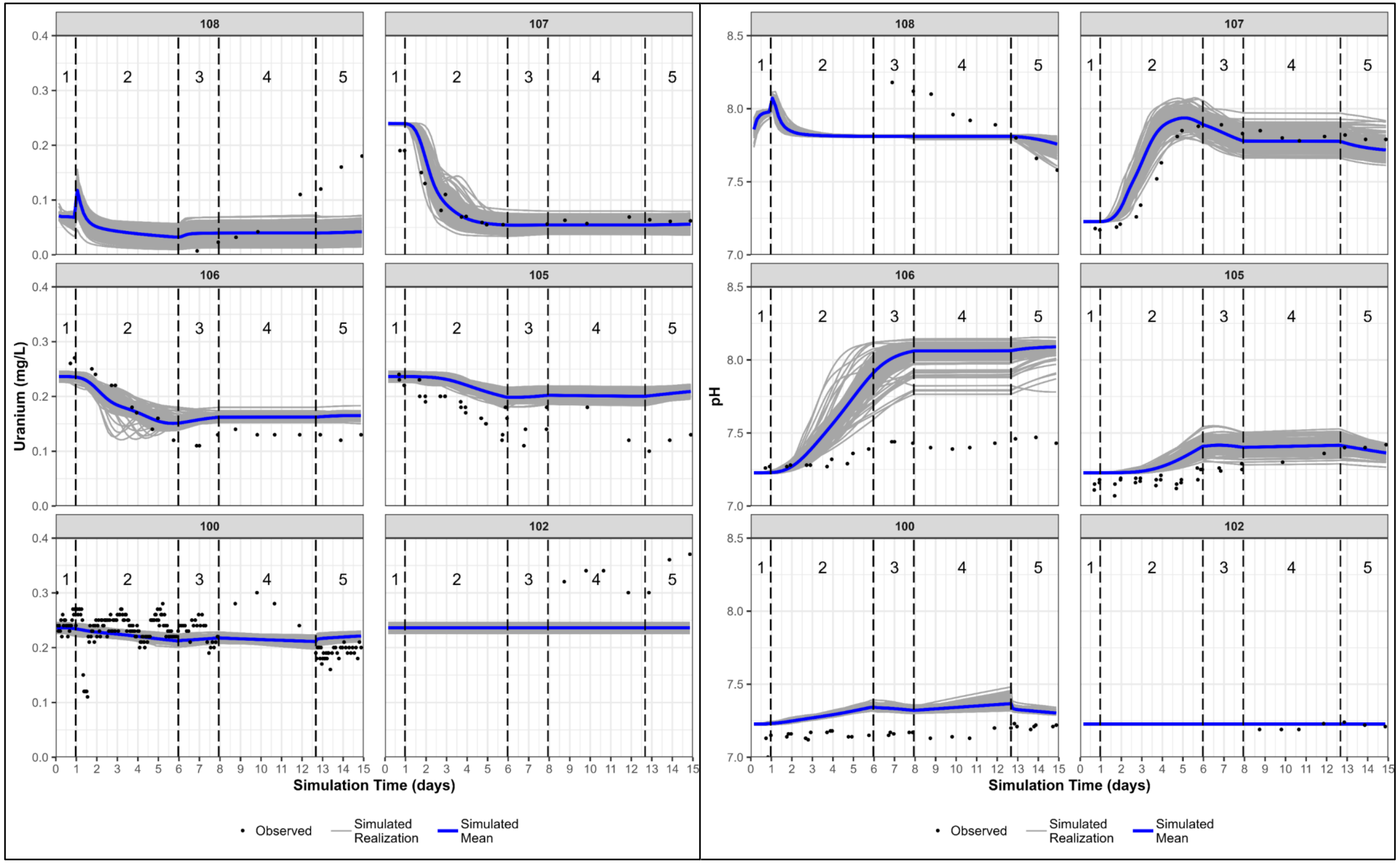
Phases:
1: Tracer injection
2: Chase injection
3: Drift
4: Extraction

Cross-Hole Test Results: 0108 to 0100



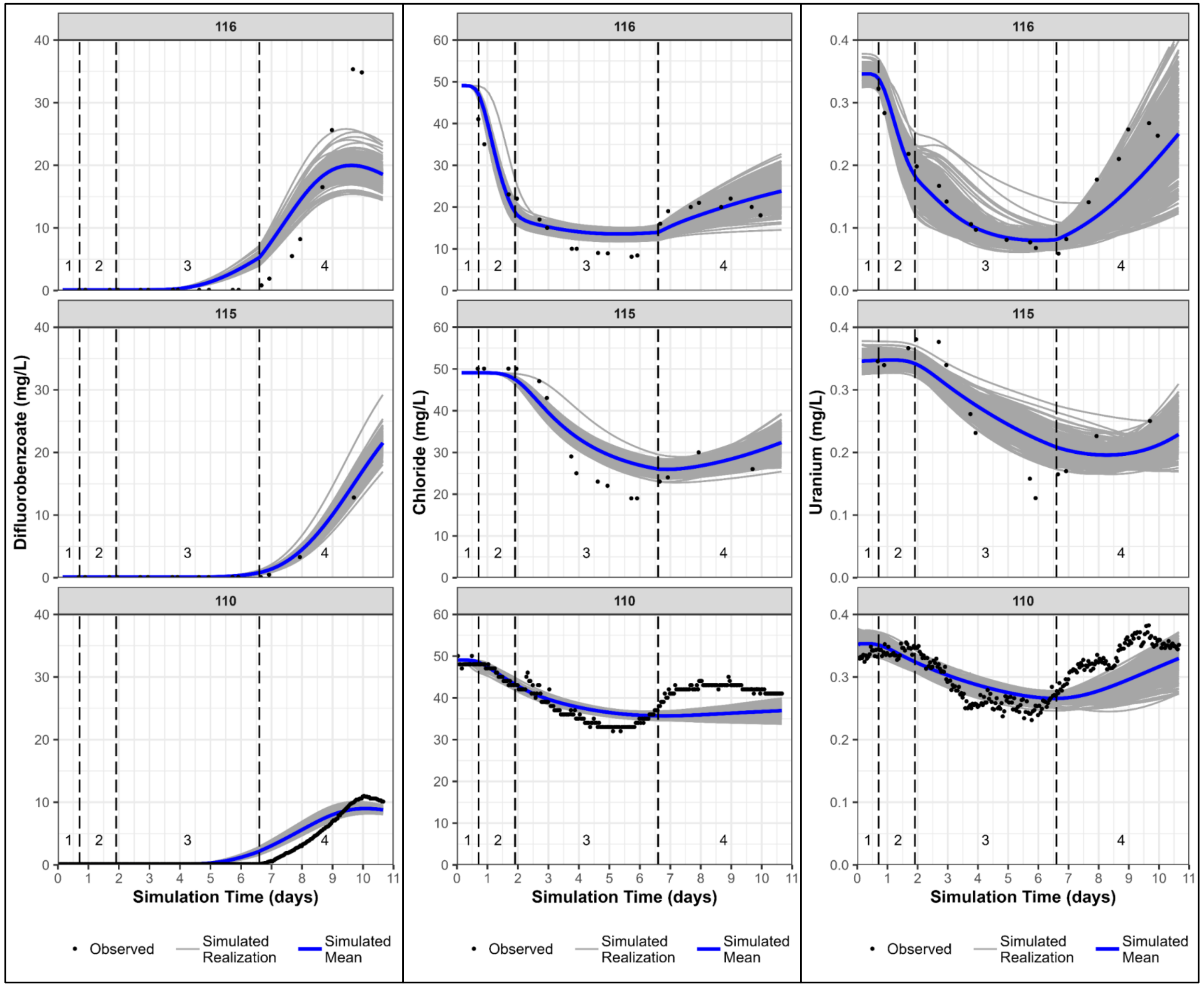
Phases:
1: Tracer injection and pumping
2: Chase injection and pumping
3: Pumping only
4: Drift
5: Pumping only

Cross-Hole Test Results: 0108 to 0100 (continued)



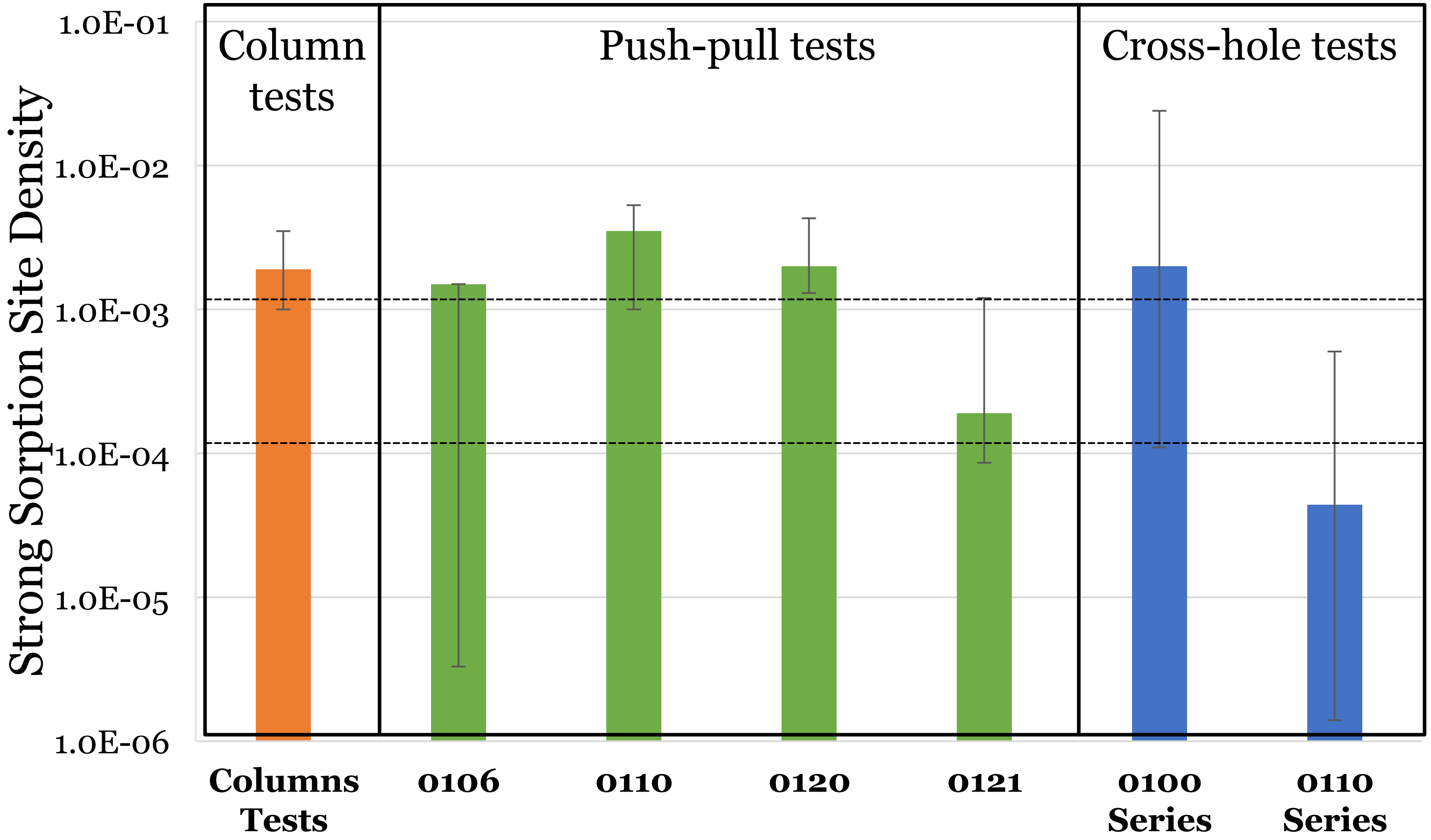
Phases:
1: Tracer injection and pumping
2: Chase injection and pumping
3: Pumping only
4: Drift
5: Pumping only

Surface Infiltration Test Results



Phases:
1: Saturated zone tracer injection
2: Saturated zone chase injection
3: Vadose zone tracer injection
4: Vadose zone chase injection
(Continuous pumping during all four phases)

Sorption Parameter Estimates



	Bar Height	Error Bars
Column tests	Mean	Range
Push-pull tests	Calibrated value	Sensitivity analysis range
Cross-hole tests	Ensemble mean	Ensemble range

Conclusions

- Using PHT-USG, unstructured grids reduced RTM run times, enabling more efficient parameter estimation with RTMs of tracer studies
- Estimated uranium sorption parameters from field tracer tests were generally similar to those estimated from laboratory column tests
  - The exception to the above was likely caused by differences in scale
  - At the larger volume test scale (multi-well), more permeable pathways with lower sorption potential can be accessible to the injected solution
  - At the smaller volume test scale (lab and single-well), fluids must move through local lower permeability material with higher sorption potential
- Uranium sorption parameters were sensitive to drift phase uranium concentrations in push-pull tests
- Parameters estimated through this modeling effort will be used in future sitewide reactive transport modeling