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# **Cross-Hole and Vadose-Zone Infiltration Tracer Test Analyses to Determine Aquifer Reactive Transport Parameters at a Former Uranium Mill Site (Grand Junction, Colorado)**

Raymond H. Johnson <sup>1</sup>,\*<sup>(D)</sup>, Ronald D. Kent <sup>1</sup>, Aaron D. Tigar <sup>1</sup>, C. Doc Richardson <sup>1</sup>, Charles J. Paradis <sup>2</sup> and Paul W. Reimus <sup>3</sup>

- <sup>1</sup> RSI EnTech, LLC, Contractor to the U.S. Department of Energy Office of Legacy Management, 2597 Legacy Way, Grand Junction, CO 81503, USA
- <sup>2</sup> Department of Geosciences, University of Wisconsin-Milwaukee, P.O. Box 413, Milwaukee, WI 53201, USA
- <sup>3</sup> Los Alamos National Laboratory, P.O. Box 1663, Los Alamos, NM 87545, USA
- \* Correspondence: ray.johnson@lm.doe.gov

Abstract: The U.S. Department of Energy Office of Legacy Management is responsible for the longterm care and maintenance of former uranium mill sites in the United States. Prior predictions of site flushing times (monitored natural attenuation) are not being met due to the presence of secondary contaminant sources associated with uranium-rich sediments in the vadose zone and organic-rich sediments near the water table below and near former mill tailings (tailings have been moved to a separate disposal site). Updated sitewide modeling for future releases of contaminants (including uranium) from these secondary sources to the groundwater need appropriate input parameters. To test field techniques, two cross-hole tracer tests and one infiltration tracer test were completed at a former uranium mill site in Grand Junction, Colorado. Reactive transport modeling was completed to derive physical and geochemical parameters. The observed data from saturated zone cross-hole tracer testing was adequately simulated using PHT-USG (reactive transport model) and PEST++ (calibration routine) with reasonable estimates of hydraulic conductivity, dispersion, effective porosity, cation exchange, calcite saturation index, and uranium sorption potential. The use of multiple layering in one cross-hole model was able to capture hydraulic conductivity variations with depth, which produced a double hump in the tracer concentrations. Estimated parameter values were very similar to prior estimates from column testing and single-well push-pull testing, except for a lower uranium sorption potential in one cross-hole test. This difference is likely due to the larger scale of the cross-hole testing including pathways with a lower uranium sorption potential. The infiltration testing released constituents from the vadose zone that can contribute to ongoing groundwater contamination. Modeling simulated the immediate release of these constituents to the water table similar to downward displacement of the existing residual porewater. Delayed drainage of the infiltration water was more difficult to simulate. However, the overall contaminant release concentrations from the vadose-zone secondary sources and ongoing groundwater contamination are adequately simulated for current site purposes. Additional details on vadose-zone processes may be needed if various remedial fluids are evaluated.

Keywords: cross hole; infiltration; geochemical modeling; tracer testing; uranium; reactive transport

#### 1. Introduction

The U.S. Department of Energy Office of Legacy Management (LM) is responsible for the long-term care and maintenance of former uranium mill sites in the United States. Long-term release of uranium from secondary sources in the vadose and saturated zones at former uranium mills was often not considered in past conceptual and numerical site models, especially when tailings, the primary uranium source, were removed [1,2]. Continued weathering and dissolution of these secondary sources have resulted in ongoing



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). groundwater contamination. Thus, past predictions for the natural flushing of contaminants (monitored natural attenuation) at some LM sites has been overly optimistic by more than an order of magnitude [1,3,4].

An objective of the LM Applied Studies and Technology (AS&T) Program (https: //www.energy.gov/lm/services/applied-studies-and-technology-ast, accessed on 13 July 2023) is to evaluate various techniques for updating uranium transport controls, as conceptual and numerical models are being re-evaluated to include secondary uranium sources. While these techniques are intended for application at multiple LM sites, groundwater tracer testing was completed at a former uranium mill site in Grand Junction, Colorado, for initial testing of multiple procedures in quantifying uranium mobility controls. This testing included single-well, cross-hole, and infiltration tracer testing coupled with groundwater quality analyses. This paper describes the cross-hole and infiltration tracer testing. Prior publications discuss the single-well push–pull tracer testing results and interpretations [5,6]. In addition, laboratory column testing has been completed at the site to determine uranium release rates under controlled conditions [7].

Cross-hole testing was completed to evaluate a larger aquifer area than single-well push-pull testing in the saturated zone. Advantages and disadvantages of singe-well push-pull, cross-hole, and natural gradient tracer testing are provided by [8]. Infiltration tracer testing was completed to evaluate uranium release from secondary sources in the vadose zone at the field scale. The infiltration testing was completed directly above the saturated zone cross-hole testing.

In situ assessments can help evaluate coupled hydrogeochemical processes such as (de)sorption, mineral dissolution/precipitation, multicomponent speciation, and cation exchange that can simultaneously control the release of uranium from the solid phase to the water phase. We use the cross-hole and infiltration tracer testing data to calibrate fully coupled reactive transport models (groundwater flow, contaminant transport, and the reactions listed above) for the derivation of uranium reactive transport control parameters. Reactive transport modeling is performed using an iterative ensemble smoothing (IES) technique that allows for the efficient calibration of many parameters while directly including uncertainty analyses. Modeling the reactive transport of contaminant release from the vadose zone to the saturated zone during infiltration is a unique challenge. This paper evaluates the simplifying assumption of immediate release of infiltrating water (plus contaminants) reaching the water table. Not explicitly simulating reactive transport mechanisms in the vadose zone allows for more computationally efficient simulations.

The cross-hole tracer testing results are compared to the prior results from single-well push-pull testing [5] and column testing [7] for scale dependency. While this work uses a cross-hole approach for injection and pumping of tracers and evaluating rock-water interaction, the modeling techniques presented herein can be adapted to any injection and pumping configuration. The goal of this work is to provide the best techniques for deriving uranium reactive transport parameters that can eventually be used in sitewide reactive transport models to evaluate various site remedial options. This approach is intended for future application at multiple LM sites beyond the Grand Junction test site and these techniques can be used at any site with metal or inorganic contamination.

#### 2. Site Background

The Grand Junction, Colorado, Site (GJO) (https://www.energy.gov/lm/grand-junctioncolorado-site, accessed on 13 July 2023) is one of several legacy uranium mill sites overseen by LM for long-term surveillance and maintenance (https://www.energy.gov/lm/sites/ lm-sites, accessed on 13 July 2023). The GJO site had several uranium pilot mills operated by the U.S. Army Corps of Engineers Manhattan Engineer District from 1943 to 1958 [9]. These pilot mills were used to develop uranium extraction methods to provide uranium for the first nuclear weapons produced in the United States. Uranium tailings were deposited in low areas near the pilot mills along the Gunnison River [10] and Figure 1). These tailings were present for several decades before being removed to the Grand Junction, CO, Disposal Site [9] 28 km away, with excavation of contaminated material to depths that met radiological standards (radium levels below 5 picocuries per gram [pCi/g] above background in the top 15 cm of sediment and below 15 pCi/g above background in deeper sediment). Even though radiological standards were met, some areas still had radium measurements that were above background [11]. Solid-phase sediments collected at multiple coring locations underneath and near the former tailings area (Figure 1) identified zones with elevated uranium concentrations (especially GJAST-14, -15, and -20; [2]). Of these, two focus locations were used for cross-hole and infiltration tracer testing discussed in this study that correspond to a uranium-rich vadose zone (GJAST-14 and 110-series wells, Figures 1 and 2) and an organic-rich zone (GJAST-15 and 100-series wells, Figures 1 and 2), both of which were previously described by [5,6]. Cross-hole tracer testing targeted the GJAST-15 area as a location with potential uranium sorption/desorption reactions associated with the organic-rich sediments. Infiltration tracer testing (along with underlying cross-hole tracer testing) targeted the GJAST-14 area as a location with more solid-phase uranium in the vadose zone.



**Figure 1.** GJO site with extent of former surface contamination, former tailings area, former mill buildings, coring locations, existing wells, and two focus areas. River is flowing northward, and the side channel is an irrigation ditch.



**Figure 2.** GJO site focus areas with wells installed for tracer testing; GJAST-14 represents the 110-series wells and GJAST-15 represents the 100-series wells. The two saturated-zone injection wells are 0108 and 0118, the two extraction wells are 0100 and 0110, and the single vadose-zone injection well is 0117. All other wells were used for monitoring only (water level and water-quality sampling).

The GJO site does not have a distinct groundwater uranium plume due to the changing groundwater flow directions controlled by the Gunnison River stage and the sporadic nature of uranium tailings distributed in low spots across the site [12]. Recent uranium concentrations (1996 to 2021) in the area of interest (well 8-4S, Figure 2) have ranged from 0.097 to 0.73 mg/L. The GJO site is on a sand and gravel aquifer that is essentially a point bar deposit along the Gunnison River (Figure 1), with a depth of approximately 6.5 m to bedrock [2,10] and a typical groundwater table depth close to 3.5 m below ground surface (bgs) [5]. Groundwater flow is generally to the north-northeast and is controlled by the stage of the Gunnison River. At higher stages, groundwater flows into the point bar aquifer which reverses toward the Gunnison River at low river stages. The groundwater table can rise up to 2.5 m at high river stage and some groundwater inflow from the east is likely.

Our earlier work provides mineralogic data for uranium associations in the solid phase for some of the coring locations [13] and later work provides reactive transport parameters derived from column tests [7] and single-well push-pull tracer tests [5]. Previous studies [5–7] discuss the unique uranium geochemistry on the solid phase near GJAST-14 and -15 (Figures 1 and 2). GJAST-14 has higher solid-phase uranium concentrations in the vadose zone and GJAST-15 has higher solid-phase uranium concentrations at and just below the water table, which is associated with higher organic carbon content.

#### 3. Methods

#### 3.1. Well Installations and Flow Patterns

Wells for cross-hole tracer testing (Figure 2) were installed with a direct-push drilling rig. Core was collected at six locations (0106, 0107, 0108, 0116, 0117, and 0118) to complement the prior coring at GJAST-14 and -15. All wells were installed inside a hollow drill stem with a disposable drive point at the end. Well screens had a prepacked filter and the formation sands and gravels collapsed around this filter up to the water table as the drill stem was withdrawn. Final annulus completion included additional silica sand followed by a bentonite seal and cement at the surface. All well completion details and boring logs are provided in Supplemental Data Folder S1 (S1). Boring logs for other GJAST locations not discussed in this paper are provided in [2].

Wells were completed in two phases. The first phase installed wells 0100 through 0105 and 0110 through 0115. Subsequent borehole dilution testing and fluorescein dye tracer testing was completed in wells 0100 and 0110 and monitored in the semicircle wells (Figure 2) to confirm the groundwater flow directions and quantify aquifer properties [6]. Following evaluation, wells 0106, 0107, 0108, 0116, 0117, and 0118 (Figure 2) were installed in alignment with the groundwater flow direction for use in cross-hole and infiltration tracer testing as part of this study.

The 100-series wells, identified as having elevated solid-phase uranium near the water table associated with organic material, were screened in the saturated zone at a depth close to 3.5 to 5.0 m bgs (Figure 3). Uranium sorption to organic material, independent of sediment grain size (Figure 3), is the assumption in this area, but sediment organic carbon concentration data are not available. Visual identification of organic material and slight screen depth variations are provided in the well completion logs (S1) and shown in Figure 3. During the initial testing, it was determined that a small confining layer, possibly related to the organic-rich layer, was occurring across the completed well screen interval [6]. Thus, wells 0107 and 0106 were installed with screens above and below this confining layer, respectively. Coring and completion of well 0106 identified the higher hydraulic conductivity sandy gravel layer at depth (Figure 3), but a higher hydraulic conductivity layer within the overlying silt was not readily identifiable visually. Wells 0106 (deeper) and 0107 (shallower) were completed and screened at 4.7 to 5.0 and 3.8 to 4.1 m bgs, respectively. All wells in Figure 3 were sampled during the cross-hole testing. This included well 0105, which is not directly in-line with the cross-hole testing wells but was sampled to test the wider injection flow pattern going from well 0108 (injection) to well 0100 (pumping).

The 110-series wells, identified as having elevated solid-phase uranium in the vadose zone, were screened in the saturated zone at a depth close to 4.0 to 5.5 m bgs (Figure 4). Slight depth variations are provided in the well completion logs (S1) and shown in Figure 4. Saturated zone testing in the 110-series wells was started in the sandy gravel unit first before infiltration testing in the same well series. For infiltration testing, well 0117 was completed in the vadose zone with a well screen depth of 0.64 to 2.2 m bgs. Cross-hole conditions were established first with injection in well 0118 and pumping in well 0110 before infiltration started in well 0117 (Figure 4). All wells in Figure 4, except well 0117, were sampled during the cross-hole and infiltration testing. This included well 0115, which is not directly in-line with the cross-hole testing wells but was sampled to test the wider injection flow pattern going from well 0118 (injection) to well 0110 (pumping).



**Figure 3.** 100-series well constructions with injection and pumping pattern in relation to hydrogeology and solid-phase uranium concentrations. Red shading indicates depths with solid-phase uranium concentrations that are above background. Depths are to scale with two times horizontal exaggeration. Well 0105 is beyond the plane of the page (Figure 2). Arrows indicate flow directions.



**Figure 4.** 110-series well construction with injection and pumping pattern in relation to hydrogeology and solid-phase uranium concentrations. Red shading indicates depths with solid-phase uranium concentrations that are above background. Depths are to scale with two times horizontal exaggeration. Well 0115 is beyond the plane of the page (Figure 2). Arrows indicate flow directions.

#### 3.2. Tracer Testing Procedures

Descriptions of injection and extraction rates, extraction volumes, and testing durations for cross-hole and vadose-zone infiltration testing are presented in Table 1. Total injection volumes are very accurate based on injection of a total volume from a single tank of injection fluid. Injection and extraction rates and total extraction volumes are less accurate due to slight variations in flow rates. Detailed injection and extraction flow rates and times are provided in Supplemental Data Folder S2 (Supplemental S2). Injection and extraction were performed using high-capacity peristaltic pumps. Locations of injection and extraction wells are presented in Figure 2, with well screen depths and flow directions for the 100-series wells in Figure 3 and the 110-series wells in Figure 4. Table 1 includes a listing of the tracers used for each test (discussed below) which included two nonreactive tracers with different diffusion coefficients for use in evaluating dual porosity effects.

Test	Wells	Start Date	End Date	Total Traced Injection Volume (L)	Injection Duration and Rates	Extraction Rate/Volume	Extraction Duration	Tracers
Cross-Hole Saturated Zone	0108 (injection) and 0100	21 March 2018	5 April 2018	1140	21.3 h for traced water (~0.90 L/min) followed by chase water (~0.80 L/min)	~1.0 L/min	21 March 2018 to 29 March 2018 and 3 April 2018 to 5	LiBr, DFB, 2-NS
100-series	(extraction)				ending on 27 March 2018	14,800 L	April 2018	
Cross-Hole Saturated Zone	0118 (injection) and 0110	27 March 2018	7 April 2018	1140	15.6 h for traced water (~1.2 L/min) followed by chase water (~1.0 L/min) through the end of	~2.0 L/min	Continuous	PFB, NaI
110-series	(extraction)				extraction	30,500 L		
Vadose Zone110-series	0117 (infiltration)	29 March 2018	7 April 2018	1140	4.5 d for traced water (~0.20 L/min) then 4 d for chase water (~0.25 L/min)	~2.0 L/min	Continuous for 110-series cross-hole	DFB, LiBr

Table 1. Cross-Hole Testing Summary.

Abbreviations: LiBr = lithium bromide, DFB = sodium 2,6-difluorobenzoate, 2-NS = sodium 2-naphthalene sulfonate, PFB = sodium pentafluorobenzoate, NaI = sodium iodide.

#### 3.2.1. 100-Series Wells

The saturated-zone cross-hole tracer testing in the 100-series wells was completed by injecting into well 0108 and pumping from well 0100. The injection fluid was traced Gunnison River water, which was injected at approximately 0.90 L/min for 21.3 h for a total of 1140 L (300 gallons). Chase water injection (untraced Gunnison River water) continued at a rate of approximately 0.80 L/min for an additional 5 days after the traced injection was completed and was temporarily stopped before the final extraction period. No injection or extraction occurred for a period of 4.5 days to test rebound affects. Pumping without injection resumed for the final 2.5 days. The total extracted volume for well 0100 was 14,400 L (3800 gallons) at a pumping rate of approximately 1.0 L/min (Table 1).

Two conservative, non-reactive compounds (2,6-difluorobenzoate [DFB] and lithium bromide [LiBr]) were added to Gunnison River water as tracers with approximate concentrations of 340 mg/L for DFB and 710 mg/L for Br. These two tracers have different diffusion coefficients and were used to determine the existence of any dual porosity effects resulting from diffusive mass transfer between flowing and non-flowing water, with Br having a higher diffusivity than DFB. Li has the potential to be involved in cation exchange reactions and Br is considered conservative [6]. A similar cross-hole testing approach with multiple tracers was used by [14,15] to evaluate dual porosity effects in fractured media. Sodium 2-naphthalene sulfonate (2-NS) strongly sorbs to organic material [16] and was added at a concentration of 70 mg/L (for the 2-NS) to test for the presence of organics. Chloride was used as a naturally occurring conservative tracer because concentrations in groundwater are greater than in the Gunnison River water. Further discussion of tracer properties is presented by [6].

### 3.2.2. 110-Series Wells

The saturated-zone cross-hole tracer testing in the 110-series wells was completed by injecting into well 0118 and pumping from well 0110. The injection fluid was traced Gunnison River water, which was injected at approximately 1.2 L/min for 15.6 h with a total injected volume of 1140 L (300 gallons). Traced water injection in well 0108 was followed by continuous injection of chase water (untraced Gunnison River water) at a flow rate near 1.0 L/min. Vadose-zone infiltration of traced Gunnison River water started 2 days after the start of the saturated-zone injection. The vadose-zone infiltration rate was approximately 0.20 L/min over 4.5 days followed by chase water for another 4 days. This slower injection rate than the saturated zone testing was needed to avoid excessive head rise in the infiltration well due to the lower permeability of the vadose zone with the presence of unsaturated conditions as well as to avoid "air locking" the vadose zone. Extraction from well 0110 was continuous during the saturated-zone injection and vadosezone infiltration at approximately 2.0 mL/min for a total extraction volume of 30,300 L (8000 gallons) (Table 1).

Saturated-zone tracers added to Gunnison River water were sodium iodide (NaI) and sodium pentafluorobenzoate (PFB) at concentrations of 680 mg/L for iodide and 340 mg/L for PFB. Iodide has a higher diffusivity than PFB to again test for dual porosity.

The vadose-zone infiltration used DFB and LiBr tracers added to Gunnison River water with Br having a higher diffusion rate than DFB. As with the 100-series, differences in chloride concentrations between river water and groundwater were significant enough to allow for the use of chloride as an additional naturally occurring conservative tracer.

#### 3.3. Sampling and Analyses

All water samples were collected using a peristaltic pump with plastic sample tubing that was dedicated to each well or injection water tank. Pre-tracer testing and post-tracer testing groundwater samples were collected at injection wells 0108 and 0118; monitoring wells 0102, 0105, 0106, 0107, 0115, and 0116; and extraction wells 0110 and 0100. Vadose-zone infiltration at well 0117 did not have any available water for sampling before or after the tracer testing. During the tracer testing, sampling included: (1) injection/infiltration water, (2) the monitoring wells, and (3) the extraction wells. Extraction well samples included 60 mL samples that were continuously collected via a split pumping line and an autosampler for composited hourly samples. Periodic sampling of the outflow from the extraction wells allowed collection of water quality parameters in the field. For the monitoring wells, the sample tubing was set at the center of the screen, unless otherwise noted.

Field analyses of temperature, specific conductance, pH, oxidation–reduction potential (ORP), and dissolved oxygen (DO) were taken from the monitoring well or extraction well peristaltic pump line with a field multimeter and probe (YSI 556MPS) connected to a flow-through cell. Alkalinity analyses were completed via titration. Fe<sup>2+</sup> analyses (select nonpumping samples only) were completed via colorimetry following Hach method 8146. Two wells in each well gallery (106 and 107 in the 100-series area; 110 and 116 in the 110-series area) had down well electrical conductivity probes (CS547A-L, Campbell Scientific) measuring specific conductance and temperature in these wells every hour after all pumping ceased (Supplemental Data Folder S3, Supplemental S3).

All samples were passed through a 0.45  $\mu$ m filter and then split into two aliquots. One aliquot was kept at 4 °C for subsequent analyses of anions (Cl, Br, NO<sub>3</sub>, and SO<sub>4</sub>) by ion chromatography (ThermoFisher Aquion) and dissolved organic carbon (DOC) (Shimadzu TOC-L), I, DFB, and PFB by high-performance liquid chromatography (ThermoFisher Ultimate 3000). The other aliquot was acidified to pH < 2 with trace-metal grade nitric acid and subsequently analyzed for cations and metals via inductively coupled plasma–optical emission spectroscopy (ICP-OES) (Perkin Elmer DV7000) and uranium via kinetic phosphorescence (KPA) (Chemchek KPA-11). Uranium results from the KPA are considered more accurate than uranium results from the ICP-OES analyses. ICP-OES results for uranium below 0.1 mg/L were not used in any interpretations, albeit still considered above method detection limits. Analytical procedures followed the LM Grand Junction Environmental Sciences Laboratory (ESL) procedure manual ([17]).

Selected acidified samples were split for analyses at the Los Alamos National Laboratory (LANL) on an inductively couple plasma–mass spectrometer (ICP-MS) (Perkin-Elmer NexION) with analyses for trace metals (Mo, Mn, U, Se, Sr, Li, and V). The final full analyte list includes pH, temperature, specific conductance, ORP, DO, alkalinity, DOC, Cl, NO<sub>3</sub>, SO<sub>4</sub>, I, Br, DFB, PFB, Ca, Mg, Na, K, Fe<sup>2+</sup>, Fe, Mn, Se, U, Mo, SiO<sub>2</sub>, Sr, Li, and V.

All final water geochemistry data are provided in Supplemental Data Folder S4 (Supplemental S4) along with associated graphs for all analytes. Data from multiple analysis techniques and multiple laboratories are included in the final data files for completeness. Wells 0106 and 0110 have groundwater geochemistry data from prior single-well push–pull tracer testing [5]. These data are included in Supplemental S4 for reference and are clearly

indicated in the associated files. Supplemental S4 also has a master data file that includes data from other monitoring wells (0101, 0103, 0104, 0111, 0112, 0113, and 0114), mainly with data before and after the cross-hole and infiltration tracer testing. Data from those wells are not discussed in this paper, because the data from the other monitoring wells (0102, 0105, 0106, 0107, 0115, and 0116) are adequate for cross-hole and infiltration tracer testing interpretations.

#### 3.4. Geochemical Modeling

Geochemical modeling was completed using PHREEQC [18] when pH, alkalinity, and all major cation and anion data were available. During auto sampling, given the 60 mL samples being collected every hour, field parameters were not collected with every sample. Using these data along with trace metal data from the ESL or LANL, mineral saturation indices (SIs) were calculated for an extensive mineral list using the minteq.v4.dat database (available with the PHREEQC program download). PHREEQC input files are provided in Supplemental Data Folder S5 (Supplemental S5). Tabular and graphical results for CO<sub>2</sub> concentrations, likely controlling minerals (calcite, gypsum, dolomite, rhodochrosite, and magnesite) and possible minerals that could control Mo, U, and V (powellite, uraninite, carnotite, tyuyamunite, and Fe(VO<sub>3</sub>)<sub>2</sub>) are included in Supplemental S4 with the water quality results. SIs less than zero indicate possible mineral dissolution if that mineral exists and SIs greater than zero indicate possible mineral precipitation. SIs near zero are considered an indicator of mineral equilibrium between the water and solid phase, within an error bound of approximately  $\pm 0.3$  to account for possible analytical variability.

All other PHREEQC modeling was completed to set up files for use in reactive transport modeling. These PHREEQC files used an updated database (Supplemental Data Folder S6) that includes the most recent uranium thermodynamics [19] and uranium complexation species [20]. Prior work [21] has indicated that the use of this updated database decreases the SIs of carnotite and tyuyamunite (less likely to precipitate) due to the addition of calcium and magnesium uranyl carbonate complexes that keep uranium in solution. Carnotite, tyuyamunite, and powellite are in the mineral evaluation lists but always have negative SIs because the concentrations of Mo and V are generally near or below detection limits.

Uranium sorption-desorption was evaluated using the generalized surface complexation modeling (GSCM) approach of [22]. For simplicity, the GSCM used only two adjustable uranium sorption parameters to match the observations, (1) GC\_ss: super strong sorption site density in moles/kg-water and (2) GC\_s: strong sorption site density in moles/kgwater, following the approach discussed in our previous work [23]. The equilibrium constants for the super strong and strong sorption equations were not adjusted [23]. This same approach using the GSCM with two uranium sorption parameters was used for the single-well push-pull tracer testing, along with an additional evaluation of using just one uranium sorption parameter [5].

The PHREEQC program includes a 1D reactive transport mode [18]; however, flow velocities cannot be changed along a simulated 1D "column". With the cross-hole wells, flow velocities can change along multiple flow paths from the injection to the extraction wells. Thus, additional evaluations of geochemical parameters were completed using the 3D capable reactive transport modeling approach discussed in the following section (Section 3.5).

#### 3.5. Reactive Transport Modeling

The reactive transport code PHT-USG [24] was used to simulate each cross-hole test (100-series and 110-series) plus a simulation with the inclusion of infiltration to the 110-series cross-hole test. PHT-USG couples MODFLOW-USG [25] for groundwater flow and USG-Transport [26] for contaminant transport with PHREEQC, which provides geochemical reaction modeling capabilities. Calibration of the simulation output to the observed data used the PEST suite of software [27,28]. The graphical input/output software, Groundwater Vistas Version 8, was used for efficient model set up, simulations, calibration, and output

visualization for PHT-USG and PEST. The PHREEQC-related PHT-USG input files were created using the updated database and GSCM approach discussed in Section 3.4.

The version of PEST selected for this modeling effort was PEST++-IES [29,30], which implements an IES to accomplish parameter estimation and uncertainty analysis. This method uses a stochastic ensemble of models that are generated by probability distributions of the model input parameters. An ensemble of 300 realizations was used for each simulation in this study. Unlike previous versions of PEST that calculate parameter sensitivities by adjusting parameters one by one, PEST++-IES estimates parameter sensitivities empirically from the ensemble. This innovation decouples the number of model runs from the number of parameters to be estimated; thus, many more parameters can be included in the calibration process than was previously possible [29].

Initial groundwater flow gradients were computed using monitoring wells in the area from the time just before testing. During simulations, the groundwater flow gradients outside of the area of influence from the cross-hole and infiltration tracer testing were held at a constant head to produce the same consistent gradient across the testing areas. All geochemical reactions were assumed to go to equilibrium and no kinetic rates were included. For infiltration testing, water was initially simulated as immediately reaching the water table with estimated constituent concentrations based on the dimensions of one model cell. Documentation of the model cell sizes, injection/infiltration rates, and input parameters are provided in Supplemental Data Folder S7 along with all modeling files created for PHT-USG, PEST, and PHREEQC.

The calibration was performed in two steps. The first step used added nonreactive tracer data (i.e., PFB, DFB, iodide, and bromide) to estimate hydraulic conductivity, porosity, and dispersivity. The second calibration step used U, pH, alkalinity, Ca, Cl, Mg, and Na data to estimate the uranium GC\_s, GC\_ss, calcite SI, and cation exchange capacity. A calcite SI near zero was expected but was included as a calibration parameter for added confirmation. In addition, the input concentrations of infiltrating water were used as calibration parameters for the vadose zone injection in the 110-series cross-hole test. PHT-USG required the use of sulfate to charge-balance the water data in PHREEQC, so sulfate data were not used as calibration targets. Sorption sites and cation exchange sites were initialized at equilibrium with the initial groundwater chemistry, and alkalinity was entered into PHT-USG as an equivalent carbon species ( $C^{4+}$ ).

#### 4. Results and Discussion

#### 4.1. Initial Groundwater and Surface Water Geochemistry

Groundwater quality for monitoring wells in both the 100-series and 110-series were measured just before starting the cross-hole testing (Table 2). Table 2 includes data for the traced injection waters and the untraced chase water (Gunnison River). The untraced Gunnison River water contains less dissolved constituents, no detectable uranium, a higher pH, and more DO than the groundwater (Table 2), thus creating a good measurable contrast in geochemistry between the Gunnison River water and the native groundwater. The traced river water has greater sodium concentrations and a greater specific conductance due to the tracer additions. While ORP differences between the groundwater and the river water are minimal, the DO concentrations in the groundwater are at or near detection limits. The groundwater can be considered slightly suboxic because it contains low to no concentration of oxygen, but it is not reducing enough to have significant amounts of dissolved iron or manganese. Differences in geochemistry between the 100-series area and the 110-series area are subtle, but the 110-series area has greater amounts of dissolved constituents overall, which is reflected in the larger specific conductance values observed.

N Location o	Number of Sam-	Sample Date(s)	pН	Specific Conduc- tance	ORP	DO	Alkalinity	U	Cl	NO <sub>3</sub>	$SO_4$	Mg	Ca	Na	K	SiO <sub>2</sub>	Fe	Mn	Sr	
	ples		L · · ·	1	1		μS/cm	mV	mg/L	mg/L as CaCO <sub>3</sub>	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
								100-Seri	es											
100	1	21 March 2018	7.2	1700	190	0.6	280	0.26	41	16	570	56	140	220	6.0	24	0.020	0.020	1.3	
105	1	21 March 2018	7.3	1700	200	0.3	270	0.23	37	20	530	52	140	210	6.0	24	0.020	0.020	1.3	
106	1	21 March 2018	7.3	1700	180	0.2	280	0.21	37	17	530	52	140	210	6.2	24	0.020	0.057	1.4	
107	1	21 March 2018	7.2	1700	170	0.4	300	0.21	37	18	540	54	130	210	6.0	24	0.020	0.034	1.3	
108	1	21 March 2018	7.2	1600	120	0.4	270	0.22	35	21	530	49	130	210	6.5	24	0.020	0.020	1.4	
Traced Water	3	21 March 2018	8.7	1800	140	7	120	0.050	9.6	1.0	230	29	72	110	3.0	7.9	0.020	0.020	0.73	
Gunnison River	5	23–26 March 2018	8.4	630	190	10	120	na	6.2	2.3	190	24	70	38	2.8	10	0.020	0.030	0.66	
								110-Seri	es											
110	4	26 & 27 March 2018	7.3	1900	186	0.6	350	0.33	46	15	620	63	160	220	6.9	23	0.020	0.032	1.5	
115	1	26 March 2018	7.2	2100	191	0.4	350	0.33	50	14	680	67	170	240	7.0	23	0.020	0.065	1.6	
116	1	26 March 2018	7.3	2100	194	0.6	370	0.29	50	12	730	70	190	240	7.6	22	0.020	0.59	1.7	
118	1	26 March 2018	7.3	2000	208	0.5	370	0.35	50	13	680	67	170	230	7.4	23	0.020	0.45	1.6	
Traced Water Saturated Injection	3	27 March 2018	8.5	1400	147	9	na	0.050	6.8	2.1	180	24	72	210	2.9	11	0.020	0.031	0.65	
Traced Water Vadose Infiltration	3	29 March 2018	8.5	1400	145	na	na	0.050	8.6	na	200	21	62	86	2.7	9.2	0.020	0.020	0.62	
Gunnison River	6	28 March–6 April 2018	8.4	640	140	10	120	0.050	6.8	2.9	190	23	68	53	2.8	10	0.022	0.022	0.67	

Table 2. Preinjection Groundwater, Traced and Chase (Gunnison River) Water Chemistry.

Note: Detection limits are represented by bold italics; na = not available; all values are rounded to 2 significant figures, except for DO, which is rounded to 1 significant figure.

Geochemical modeling (Supplemental S4 and S5) indicates larger groundwater concentrations of carbon dioxide than the river water  $(-1.7 \text{ to } -1.9 \log$  atm for groundwater and near  $-3.4 \log$  atm for the river water). For the 100-series, calcite SIs are typically between -0.036 and +0.20, and for the 110-series calcite SIs are typically between 0.12 and 0.25. Gunnison River water (traced and untraced) is supersaturated with respect to calcite and dolomite, with average SI values near 0.6 and 0.3, respectively, indicating the potential importance of carbonate system controls during injection and infiltration testing with the possibility of calcite and dolomite precipitation. No other major cation–anion mineral controls are indicated besides calcite and dolomite. No uranium mineral controls are indicated, and thus, dissolved uranium is anticipated to be controlled mainly by sorptiondesorption from the solid phase. For both areas, dissolved vanadium concentrations are below detection limits and molybdenum concentrations are near or below detection limits.

#### 4.2. 100-Series Cross-Hole Saturated Zone

# 4.2.1. Tracer Results

The tracers used for the 100-series cross-hole saturated zone test were DFB, Li, Br, and 2-NS. As summarized by [6], Br is nonreactive with a higher diffusion rate, DFB is nonreactive with a lower diffusion rate, Li can sorb due to cation exchange processes, and 2-NS can sorb to organic carbon. Normalized concentrations for these four tracers (Figure 5) demonstrate the conclusions from [6] that (1) the similar normalized concentrations of DFB and Br do not indicate any dual porosity; (2) the reactive tracer, 2-NS, does indicate sorption during the drift phase (phase 4, with 2-NS concentrations below detection limits); and (3) Li does show significant sorption with much lower normalized concentrations than DFB. The slight differences between DFB and 2-NS (except for the drift phase) are likely due to slight analytical error in injection concentrations, as desorption rebound is not seen in phase 5 (return to natural gradient conditions) for 2-NS like that seen for Li (Figure 5). Mass recovery for DFB, Br, and 2-NS are 45, 41, and 38 percent, respectively [6].



Figure 5. Cont.



**Figure 5.** Tracer concentrations (measured concentration divided by injection concentration  $[C/C_0]$  at well 0100) for DFB and Br, DFB and 2-NS, and DFB and Li. Injection is in well 0108 and pumping is from well 0100. Phases specified in plots are: (1) traced river water injection with pumping; (2) untraced river water injection (chase) with pumping; (3) no injection, pumping only; (4) no injection or pumping (drift); (5) no injection, only pumping.

The double humps in the DFB, Br, and 2-NS concentrations are likely a result of tracer flowing through at least two layers with different hydraulic conductivities. At the time of the test, the water table was slightly lower than typical at 3.6 m bgs (Supplemental S2), but still had injection water flowing through both the silt and sandy gravel layers (Figure 3). DFB is detected in the upper silt unit (well 0107) sooner, at higher concentrations, and with a much narrower concentration curve (less time) than the lower sandy gravel (well 0106) (Figure 6). However, well 0107 is closer to the injection well (Figure 3). While it is not readily apparent in the tracer concentration data (Figure 6), modeling results indicate that the double hump is created by heterogeneity within the sandy gravel (next section) with tracer in the conductive silt unit arriving at well 0100 (pumping well) corresponding

with an addition to the second concentration hump. The broader concentration curve for well 0106 along with continued detection of DFB at 20 mg/L in phases 4 and 5 (Figure 6) is a key indicator of the heterogeneity in the sandy gravel layer. This creates multiple tracer arrival times in well 0100 due to hydraulic conductivity variations along with additional dispersion.



**Figure 6.** Tracer concentrations in wells 0106 (deeper), 0107 (shallower), and 0100 (fully screened interval) (left) and chloride concentrations in 0106, 0107, and 0108 (fully screened interval) (right). Injection is in well 0108 and pumping is from well 0100. Phases are: (1) traced river water injection with pumping; (2) untraced river water injection (chase) with pumping; (3) no injection, pumping only; (4) no injection or pumping (drift); (5) no injection, only pumping.

In well 0106, higher chloride concentrations (Figure 6) indicate about 70% river water and 30% native groundwater during the cross-hole test compared to 100% river water in well 0107 (river water chloride concentrations are 6.2 mg/L and preinjection aquifer chloride concentrations are about 37 mg/L, Table 2). After injection into well 0108 is discontinued, chloride concentrations start to increase and later return to aquifer concentrations (Figure 6). Wells 0106 and 0107 also return to aquifer chloride concentrations, albeit later than that of 0108 (Figure 6), which is the more upgradient well. The difference in water quality between wells 0106 and 0107 is also seen in the specific conductance data (Supplemental S3).

#### 4.2.2. Modeling Results

Overall model-simulated versus observed DFB concentrations in all wells show a good model fit (Figure 7). For the pumping well (0100) plotted on a larger scale (Figure 8), the model fits the overall DFB concentration trends with some differences in exact concentrations, albeit the multiple realizations do incorporate most of the observations. The silt is simulated as layer 1 through 7, with layer 3 simulating the greater hydraulic conductivity layer within the silt (well 0107 interval). Model layers 8 through 27 simulate the sandy gravel (includes well 0106 interval) (Figure 9). As discussed above, the double hump in the DFB concentrations (Figure 8) is due to subtle hydraulic conductivity variations (Figure 9) that result in different DFB arrival times and concentrations (Figure 8). With detailed examination of the model output, the model simulates DFB arrival at the pumping well (0100) sooner and for a longer time from the deeper sandy gravel unit than from the silt unit. DFB occurs in multiple layers in the sandy gravel compared to DFB occurring only in layer 3 within the silt.

The earliest arrival of DFB at well 0100 in the simulations is from greater hydraulic conductivity layers (layers 18 and 19) that are below the 0106 well screen (Figure 9). The model indicates DFB arrival from layer 3 contributing to the second concentration hump. In comparing Figure 8 with model flow velocities, the model simulates the linear velocities in the various model layers that produce the DFB arrival times at well 0100. The sandy gravel layers 18 and 19 (greater hydraulic conductivity) have velocities near 1.4 m/day to produce the first DFB concentration hump, and the other sandy gravel layers and layer 3 in the silt all have velocities near 0.61 m/day, which produce the second concentration hump (Figure 8). However, the simulated volumetric flow in the greater hydraulic conductivity layers is too large (model concentration is too high in the first peak in well 0100) and is too low in the lower hydraulic conductivity layers (model concentration is too low in the second peak at well 0100). Having hydraulic conductivity estimates for each model layer with associated confidence intervals is a major advantage of using the IES routine provided by PEST++. This provides for the added heterogeneity that helps match the double hump tracer concentration results, with multiple realizations that cover a range of heterogeneities which can incorporate the majority of the measured data (Figure 8). Calibrated results for the other estimated parameters are provided in Supplemental Data Folder S8 (Supplemental S8).

Simulated versus observed chloride concentrations show a reasonable model fit through the end of phase 3, with simulated chloride concentrations in well 0100 being slightly lower than observed values (Figure 7). In phases 4 and 5 (drift followed by pumping only), observed chloride concentrations in wells 0106 and 0108 are significantly greater than the simulated concentrations. The same is true for well 0100 during phase 4. The reverse is true for wells 0105 and 0107, albeit with smaller concentration differences. These trends occur in other constituents such as alkalinity, calcium, magnesium, sodium, and sulfate to varying degrees (Supplemental S8). The likely explanation for these results is heterogeneity in the sandy gravel near or below the well screens (Figure 9) that brings in native groundwater faster than what is simulated when injection is not occurring. This is captured somewhat by a few model realizations showing greater simulated concentrations of chloride for phases 4 and 5 in well 0106 and at the end of phase 5 for well 0108 (Figure 7 and Supplemental S8).



**Figure 7.** Model-simulated versus observed DFB and chloride concentrations. Injection is in well 0108 and pumping is from well 0100. Phases are: (1) traced river water injection with pumping; (2) untraced river water injection (chase) with pumping; (3) no injection, pumping only; (4) no injection or pumping (drift); (5) no injection, only pumping.



**Figure 8.** Model-simulated versus observed DFB for well 0100 (pumping well). Phases are: (1) traced river water injection with pumping; (2) untraced river water injection (chase) with pumping; (3) no injection, pumping only; (4) no injection or pumping (drift); (5) no injection, only pumping.



**Figure 9.** Calibrated hydraulic conductivity values. Data are plotted in the style of [31]. Well screen completions corresponding to model layers are provided for the extraction well (0100) and the two upgradient monitoring wells (0106 and 0107) with shorter screens.

Simulated uranium concentrations show a relatively good fit compared to observed concentrations for extraction well 0100, but they rebound in phase 4 when there is no pumping (Figure 10). Because these same results are seen for chloride (not reactive, Figure 7) and other constituents (reactive, Supplemental S8), this rebound is likely due to heterogeneity in the sandy gravel as previously discussed and is not a geochemical reaction. Given this, it is initially unclear why the simulated uranium concentrations for well 0106 in phases 3, 4, and 5 are greater than observed (Figure 10) compared to the reverse for chloride (Figure 7). The explanation appears to be the large difference in pH values because simulated pH values are much greater than observed (Figure 10). This in turn can greatly influence the simulated uranium desorption from the solid phase [23]. This pH difference is due to the simulation having more river water in well 0106 than observed, given the heterogeneity in the sandy gravel that is not captured in the model. By comparison, in well 0107, the model fits for chloride, uranium, and pH are very good (Figures 7 and 10).



**Figure 10.** Model-simulated versus observed uranium concentrations and pH values. Injection is in well 0108 and pumping is from well 0100. Phases are: (1) traced river water injection with pumping; (2) untraced river water injection (chase) with pumping; (3) no injection, pumping only; (4) no injection or pumping (drift); (5) no injection, only pumping.

## 4.3. 110-Series Cross-Hole Saturated Zone and Infiltration

#### 4.3.1. Tracer and Chloride Results

For the 110-series area, cross-hole testing in the saturated zone was started first and continued during vadose-zone infiltration. Injection of river water with PFB and NaI tracers into the saturated zone was used to assess hydrogeologic conditions, with injection in well 0118 and pumping in well 0110 (Figures 2 and 4). While well 0118 injection and well 0110 pumping continued (chase water only, no tracer, see Table 1), river water traced with DFB and LiBr was infiltrated into vadose-zone well 0117 (Figures 2 and 4) with the presumption that most of the infiltrating traced river water would be captured by the 0110 pumping well. As discussed by [6], the I and Br tracers had similar normalized concentrations to the PFB and DFB tracers, indicating no dual porosity issues. For the saturated zone injection, the mass recovery for PFB and iodide was 35 percent for both, compared to a much lower mass recovery of DFB and Br (7.9 and 6.3 percent, respectively) from the vadose-zone infiltration [6].

A relatively homogenous, yet dispersive, property of the sandy gravel unit is evident by the smooth PFB concentrations with a long tail (Figure 11), especially compared to the double hump tracer breakthrough curve for DFB in the 100-series cross-hole test (Figure 8). The model fit for PFB in well 0110 for the cross-hole test is very good, with observed and simulated delays of approximately 2 days from the start of tracer injection (day 0) to a peak concentration (Figure 11). This original modeling effort uses the full 10.5 days of observation data for parameter calibration, which includes cross-hole and infiltration tracer testing.



**Figure 11.** Model-simulated versus observed PFB, DFB, and chloride concentrations for well 0110 (pumping well). Phases include: (1) traced river water injection in well 0118, (2) untraced river water injection (chase) in well 0118, (3) traced river water infiltration into vadose-zone well 0117, (4) untraced river water infiltration (chase) into vadose-zone well 0117. Well 0110 is pumping the whole time.

Phase 3 (just before day 2) marks the start of vadose-zone infiltration, and DFB is not observed at well 0110 until day 6.6 (approximately 5 days after the infiltration starts). The simulated DFB concentrations begin to increase just before day 5 (approximately 3 days after the start of the infiltrations) (Figure 11). The peak observed PFB concentration corresponding with the start of phase 3 and the detection of DFB corresponding with the start of phase 4 are unplanned consequences of the groundwater flow rates and the timing of the next testing phase.

While the traced infiltrating river water is low in chloride, this fluid removes chloride from the vadose zone, which is seen at well 0110 just before day 6 (or about 4 days after infiltration started). Chloride and other constituents (e.g., uranium, magnesium, calcium, and sulfate) all start to increase in concentration at day 5.7 (Supplemental S8). The difference in arrival timing between DFB and chloride at well 0110 is likely due to the traced infiltration water pushing out preexisting chloride-rich pore water in the vadose zone. No other explanation is plausible for an arrival of chloride without tracer because the cross-hole testing saturated zone chloride concentrations were stable by day 4.5. The simulated chloride trend generally matches the observed trend but has significant concentration differences after day 3 (Figure 11).

The following two questions arise from the above discussion and the results shown in Figure 11:

- Would calibrating to the cross-hole data only (days 0 to 5.7 before chloride concentrations increase from infiltration) improve simulated chloride concentrations from days 3 to 5.7 and result in any estimated parameter changes?
- Would a 2-day delay in infiltration timing create better simulated results for DFB?

#### 4.3.2. Additional Modeling

Two additional models were completed after the original model was calibrated to the full cross-hole and infiltration pumping period. These additional models (1) used only the cross-hole data for calibration and (2) delayed the infiltration by 2 days while using the parameters from the original model. Simulated versus observed concentrations for the three wells with measurement data for DFB, chloride, and uranium are shown in Figure 12, Figure 13, and Figure 14, respectively. For the calibrated cross-hole data model, the phase 3 and 4 observed and simulated results during infiltration are shown, but infiltration is not included as part of the simulation. The earliest infiltration influence is approximately 5.7 days for chloride for all three wells (Figure 13).



**Figure 12.** Model-simulated versus observed DFB concentrations for wells 0115, 0116, and 0110 (pumping well). Phases include: (1) traced river water injection in well 0118, (2) untraced river water injection (chase) in well 0118, (3) traced river water infiltration into vadose-zone well 0117, (4) untraced river water infiltration (chase) into vadose-zone well 0117. Well 0110 is pumping the whole time.



**Figure 13.** Model-simulated versus observed chloride concentrations for wells 0115, 0116, and 0110 (pumping well). Phases include: (1) traced river water injection in well 0118, (2) untraced river water injection (chase) in well 0118, (3) traced river water infiltration into vadose-zone well 0117, (4) untraced river water infiltration (chase) into vadose-zone well 0117. Well 0110 is pumping the whole time.

The model calibrated to cross-hole data shows only subtle differences in simulated versus observed concentrations for all constituents through day 5.7 (Figures 13 and 14 and Supplemental S8). Simulated concentrations for chloride (Figure 13) and uranium (Figure 14) are slightly lower than the original model, creating a slightly better visual fit for chloride during days 3.5 to 6 for wells 0115 and 0116. Estimated parameters had minimal differences (discussed more in Section 4.4).

The second additional model with the infiltration delay has a better starting time for DFB detection, but simulated concentrations are lower afterward (Figure 12). Simulated chloride and uranium concentration increases occur too late at about 8.5 days compared to about 5.7 to 6 days for the original model, which is best seen in well 0116 (Figures 13 and 14). This also occurs for calcium, magnesium, sodium, and sulfate (Supplemental S8). These results likely reflect vadose zone pore water release (high in dissolved constituents) being pushed out of the vadose ahead of the infiltrating tracer river water. Thus, the original model better reflects the pore water release as a nearly immediate transfer of that water

to the saturated zone. The traced river water with the DFB must move through a greater portion of the vadose zone. Thus, more complex vadose-zone modeling would be required to improve the simulated tracer transport. This added complexity is beyond the scope of this paper, and a decision on whether to include vadose zone flow and transport would depend on site modeling needs. In any case, simulating both flow and reactive transport in the vadose and saturated zones would greatly increase computational time.



**Figure 14.** Model-simulated versus observed uranium concentrations for wells 0115, 0116, and 0110 (pumping well). Phases include: (1) traced river water injection in well 0118, (2) untraced river water injection (chase) in well 0118, (3) traced river water infiltration into vadose-zone well 0117, (4) untraced river water infiltration (chase) into vadose-zone well 0117. Well 0110 is pumping the whole time.

Regardless of the exact timing for vadose-zone pore water or traced river water reaching the saturated zone, dissolved constituent concentrations (e.g., chloride and uranium) continue to increase or become relatively stable through phase 4 (Figures 13 and 14 and Supplemental S8). Thus, the river water infiltration is removing constituents from the vadose zone to the underlying groundwater, including contaminants like uranium. This is an important implication for the site because vadose-zone contaminants will only be removed during recharge events. Likewise, remedial strategies to remove contaminants from the saturated zone will not be effective at removing the residual contaminant mass.

#### 4.3.3. Final Drift Phase

Groundwater sampling continued at the 110-series wells after pumping and infiltration was stopped, albeit, in hindsight, more sampling would have been beneficial. The model was not recalibrated, and the simulation used the original calibrated model discussed in Section 4.3.2. The variable increases in observed DFB, chloride, and uranium during the drift phase (Figure 15) represent delayed vadose-zone drainage that is not accounted for in the model. Given the configuration with well 0110 being downgradient from well 0116 (Figures 2 and 4), it is difficult to explain why DFB concentrations in well 0110 from days 11 to 22 are greater than in well 0116 (Figure 15). The most likely explanation is a large amount of physical heterogeneity in the vadose zone where delayed drainage occurred in a location between wells 0110 and 0116. Heterogeneity in the saturated zone is also a possibility, but such heterogeneity was not seen an any other data. Similarly, observed chloride and uranium concentrations do not necessarily correspond to DFB concentrations and likely represent geochemical heterogeneity in the vadose zone with delayed drainage of both traced and untraced infiltrated river water occurring in a complex manner. While simulating the vadose zone is beyond the scope of this paper, it is likely that more data on the physical and chemical heterogeneity of the vadose zone would be required to improve the simulations.



**Figure 15.** Model simulated versus observed DFB, chloride, and uranium concentrations for wells 0115, 0116, and 0110 (pumping well). Graphs highlight the post pumping drift phase data. Data during cross-hole pumping and infiltration are included in Figures 12–14.

# 4.4. Summary of Estimated Parameters

# 4.4.1. Physical Parameters

Estimated parameters for the 100-series cross hole and 110-series cross hole and infiltration testing are provided in Table 3. For the 100-series cross-hole tracer testing, a separate summary is provided for the greater hydraulic conductivity layer within the silt (layer 3). The parameter summary for the 110-series cross hole and infiltration testing includes the estimated values for the infiltration fluid that reaches the water table (river water plus solid-phase interactions within the vadose zone). Table 3 also includes the 110-series parameters derived by calibrating to just the cross-hole data (data after day 5.7 are not used in the calibration).

Parameter	Minimum	25th Percentile	Median	75th Percentile	Maximum						
0100 Series Cross-Hole Test Parameter Summary											
$\alpha_{\rm L}$ (m)	0.014	0.035	0.042	0.048	0.079						
$\alpha_L: \alpha_{th}$	7.0	11	13	15	91						
$\alpha_L$ : $\alpha_{tv}$	69	118	137	160	732						
Calcite SI	0.012	0.020	0.022	0.024	0.030						
Silt Layers Parameter Summary (Excluding Layer 3)											
$K_{h}$ (m/d)	0.0006	0.0054	0.0094	0.016	0.11						
K <sub>h</sub> :K <sub>z</sub>	1.1	7.3	9.2	11	23						
Effective Porosity	0.010	0.10	0.17	0.23	0.39						
GC_s	$9.5  imes 10^{-5}$	$8.0 imes10^{-4}$	$1.4  imes 10^{-3}$	$2.4 imes10^{-3}$	$2.2  imes 10^{-2}$						
GC_ss	$4.9 imes10^{-6}$	$7.1  imes 10^{-5}$	$1.3  imes 10^{-4}$	$2.3 imes10^{-4}$	$2.0  imes 10^{-3}$						
X	0.0008	0.27	0.38	0.48	2.8						
Silt Layer 3 Parameter Summary											
$K_{h}$ (m/d)	0.29	0.65	0.80	1.0	2.2						
K <sub>h</sub> :K <sub>z</sub>	3.1	8.7	11	13	18						
Effective Porosity	0.044	0.10	0.12	0.15	0.25						
GC_s	$1.2  imes 10^{-7}$	$9.1  imes 10^{-7}$	$1.4  imes 10^{-6}$	$2.3 imes10^{-6}$	$9.9 imes10^{-6}$						
GC_ss	$1.1  imes 10^{-8}$	$7.9 imes10^{-8}$	$1.4  imes 10^{-7}$	$2.2  imes 10^{-7}$	$1.1  imes 10^{-6}$						
X	0.064	0.10	0.11	0.11	0.30						
Grave	el Layers Paramet	er Summary									
$K_{h}$ (m/d)	0.12	1.6	2.9	4.8	46						
K <sub>h</sub> :K <sub>z</sub>	1.2	7.7	10	12	25						
Effective Porosity	0.17	0.25	0.28	0.32	0.39						
GC_s	$1.1  imes 10^{-4}$	$9.2  imes 10^{-4}$	$1.5  imes 10^{-3}$	$2.5  imes 10^{-3}$	$2.4  imes 10^{-2}$						
GC_ss	$5.3  imes 10^{-6}$	$8.0 imes10^{-5}$	$1.4  imes 10^{-4}$	$2.5  imes 10^{-4}$	$2.3 imes10^{-3}$						
X	0.0003	0.27	0.36	0.44	0.86						
0110 Series Cross-Hole Test Parameter Summary											
$\alpha_{\rm L}$ (m)	0.065	0.10	0.11	0.11	0.13						
$\alpha_{\rm L}$ : $\alpha_{\rm th}$	8.4	11	13	15	40						

Table 3. Parameter Estimates using PHT-USG for 100- and 110-Series.

Parameter	Minimum 25th Percentile		Median	75th Percentile	Maximum	
$\alpha_L: \alpha_{tv}$	31	48	54	60	105	
Calcite SI	0.20	0.22	0.23	0.23	0.28	
K <sub>h</sub> (m/d)	0.034	2.8	5.8	13	207	
K <sub>h</sub> :Kz	1.0	7.8	10	12	22	
Effective Porosity	0.076	0.24	0.28 0.33		0.57	
GC_s	$1.4 \times 10^{-6}$ $1.9 \times 10^{-5}$ $3.3 \times 10^{-5}$		$3.3 imes10^{-5}$	$5.5  imes 10^{-5}$	$5.1  imes 10^{-4}$	
GC_ss	$3.8  imes 10^{-8}$	$1.8  imes 10^{-6}$	$3.1  imes 10^{-6}$	$5.5 imes10^{-6}$	$6.7 imes10^{-5}$	
Х	0.0003	0.086	0.11	0.14	0.24	
Vadose Zone Injection pH	6.9	6.9 7.5 7.7			8.4	
Vadose Zone Injection Alkalinity (mg/L as CaCO <sub>3</sub> )	136	283	326	374	514	
Vadose Zone Injection Ca (mg/L)	170 471 564		666	930		
Vadose Zone Injection Cl (mg/L)	68	145	167	188	264	
Vadose Zone Injection Mg (mg/L)	65	174	211	245	370	
Vadose Zone Injection Na (mg/L)	284	669	776	906	1326	
Vadose Zone Injection U (mg/L)	2.5	4.4	5.0	5.7	8.0	
0110 Series Cross-Hole Test Para	ameter Summar	y (Without Vad	ose Zone Inject	ion)		
α <sub>L</sub> (m)	0.016	0.12	0.14	0.15	0.22	
$\alpha_L: \alpha_{th}$	9.2	13	16	19	77	
$\alpha_L: \alpha_{tv}$	42	60	72	85	268	
Calcite SI	0.15	0.19	0.20	0.21	0.26	
K <sub>h</sub> (m/d)	0.190	2.7	5.0	9	118	
K <sub>h</sub> :Kz	1.0	8.4	10	12	21	
Effective Porosity	0.149	0.23	0.27	0.30	0.38	
GC_s	$1.5  imes 10^{-6}$	$2.2  imes 10^{-5}$	$3.7  imes 10^{-5}$	$6.3 imes10^{-5}$	$6.4 imes10^{-4}$	
GC_ss	$8.3  imes 10^{-8}$	$2.0  imes 10^{-6}$	$2.0 \times 10^{-6}$ $3.6 \times 10^{-6}$ $6.4 >$		$8.3 imes10^{-5}$	
Х	0.0003	0.085	0.11	0.15	0.49	

Table 3. Cont.

Abbreviations:  $\alpha_L$  = longitudinal dispersivity,  $\alpha_{th}$  = transverse horizontal dispersivity,  $\alpha_{tv}$  = transverse vertical dispersivity,  $K_h$  = horizontal hydraulic conductivity,  $K_z$  = vertical hydraulic conductivity,  $GC_s$  = strong sorptionsite density parameter (moles/L-water),  $GC_s$  = super-strong sorption-site density parameter (moles/L-water), X = cation exchange parameter (moles of exchange sites/L-water), SI = saturation index.

The hydraulic conductivity of the sandy gravel from past bail tests at well 8-4S (Figures 1 and 2) was 3.3 m/d [10]. Prior hydraulic conductivity estimates for wells 0106 and 0110 (Figure 2) from single-well push–pull tracer testing were 3.0 and 4.7 m/d, respectively [5]. For this study, the median hydraulic conductivity estimates for the 100-series and 110-series sandy gravel compare very favorably at 2.9 and 5.8 m/d, respectively (Table 3). The median hydraulic conductivity estimates for the 110-series sandy gravel excluding the infiltration data is 5.0 m/d, which is even closer to the push–pull testing estimate. As expected, the silt layer in the 100-series area is lower in hydraulic conductivity (0.0094 m/d) except for layer 3 at 0.80 m/d, which is the more transmissive layer in the silt. The effective porosity is lower in all silt layers (Table 3).

Prior estimates of longitudinal dispersivity from single-well push-pull testing for wells 0106 and 0110 were 0.20 and 0.10 m, respectively, with a fixed ratio of 10 times less for transverse dispersivity [5]. Median cross-hole testing longitudinal dispersivity estimates for the 100-series, 110-series cross-hole calibration only, and 110-series cross-hole

plus infiltration test were 0.042, 0.14, and 0.11 m, respectively. The smaller longitudinal dispersity for the cross-hole 100-series test compared to the single-well (0106) testing is likely due to the more detailed incorporation of heterogeneity with depth. The transverse horizontal and vertical dispersivities (Table 3) are close to the typical 10 and 100 times less than the longitudinal dispersivities, respectively. Because the IES calibration approach allows for a greater number of estimated parameters, these additional dispersivity values can be estimated directly, rather than using a fixed ratio to reduce the number of parameters, which was performed for single-well push-pull testing [5].

#### 4.4.2. Geochemical Parameters

Calcite SIs were estimated as one value for all layers (a current limitation of PHT-USG) for each testing scenario and ranged from 0.012 to 0.28 (Table 3). PHREEQC results for calcite SI on the observed groundwater geochemistry after injection and infiltration typically indicate equilibrium conditions (calcite SI near zero  $\pm$  0.15) even though the river water prior to injection had a calcite SI mean of 0.72. Thus, the injected river water equilibrates to the subsurface conditions during the cross-hole injection and pumping and the infiltration testing by equilibrating with calcite. This evolution results in a new groundwater derived from the river water that has a lower pH, larger alkalinity, and larger carbon dioxide concentrations than the original river water, albeit with values that are not the same as the original groundwater (see data and graphs for individual wells in Supplemental S4). These geochemical changes are also simulated by the reactive transport modeling (Supplemental S8).

The median cation exchange parameter (X in moles of exchange sites per liter of pore water) in the 100-series cross-hole test, excluding silt layer 3, is 0.38 and 0.36 for the silt and sandy gravel layer, respectively (Table 3). The silt layer 3 had a value of 0.11 consistent with more permeable material. For the 110-series cross-hole test the median cation exchange parameter was 0.11. These values match the single-well push-pull test results from well 0106 and 0110 exactly. Apparently, the sandy gravel in the 100-series area has a greater cation exchange capacity, which is reasonable given the overlying and possibly interbedded silt material at the top of the saturated zone. Column-derived values for the cation exchange parameter are very similar, with a value of 0.20 for 100-series and 0.15 for 110-series sandy gravels [7].

For the 100-series, uranium sorption site, density parameter estimates are nearly identical in the silt (excluding layer 3) as the sandy gravel layer, with a strong sorption value (GC\_s in moles/kg-water) of  $1.5 \times 10^{-3}$  and a super strong sorption value (GC\_ss in moles/kg-water) of  $1.4 \times 10^{-4}$  (Table 3). Sorption capacity in silt layer 3 is nearly trivial in retardation control, with three orders of magnitude reduction in sorption values from adjacent layers (Table 3). This seems counterintuitive for a silt layer, which suggests that this layer may be a find sand layer with minimal sorption capacity. Excluding model layer 3, sorption values for the 100-series test are essentially the same as sorption parameters from previous multilayer modeling for single-well push-pull tests at well 0106 ( $1.5 \times 10^{-3}$  for GC\_s and  $1.4 \times 10^{-4}$  for GC\_ss) ([5]).

For well 0110, prior single-well sorption parameter estimates were  $3.5 \times 10^{-3}$  for GC\_s and  $3.5 \times 10^{-4}$  for GC\_ss [5]. However, the cross-hole median uranium sorption parameters for the 110-series are two orders of magnitude less with values of  $3.7 \times 10^{-5}$  for GC\_s and  $3.6 \times 10^{-4}$  for GC\_ss for the cross-hole only calibration, and  $3.3 \times 10^{-5}$  for GC\_s and  $3.1 \times 10^{-6}$  for GC\_ss with the infiltration data (Table 3). These data indicate that the lower sorption estimates at the 110-series area are not related to the use of the infiltration data for calibration. A more likely explanation is the possibility of high hydraulic conductivity pathways with lower uranium sorption that are encountered in the cross-hole testing. Thus, the scale of the column testing and single-well push-pull testing may not be large enough to capture this additional heterogeneity.

For the 110-series vadose-zone infiltration, the water reaching the saturated zone was not sampled and is represented in the model as an estimated parameter (Table 3).

These estimated values demonstrate an increase in constituent concentrations as the river water removes these constituents from the vadose zone. More significantly, the infiltrating water concentrations at the water table are 3.5 to 4.2 times greater than the preexisting groundwater concentrations for Na, Ca, Cl, and Mg and approximately 20 times higher for uranium. These results indicate a secondary source of dissolved constituents that can be released from the vadose zone to the saturated zone after recharge events.

#### 5. Conclusions

Reactive transport modeling using PHT-USG and PEST++ with IES provides an efficient method for estimating a variety of physical and chemical parameters. This technique is especially powerful for estimating many parameters without losing computational efficiency. These parameters will be the initial input for any future sitewide reactive transport modeling, albeit the model scale will need to be considered carefully in relation to the available data. In addition, the IES approach provides information on simulation uncertainty using multiple realizations.

For this cross-hole tracer testing, model calibration uses all available data (i.e., data from pumping and monitoring wells). However, when interpreting the visual results, having data from monitoring wells besides the pumping well is extremely valuable. Because the pumping well is pulling in a large quantity of surrounding groundwater besides the cross-hole injection water, smaller geochemical differences are seen in the pumping well than other monitoring wells. In hindsight, more sampling in nonpumping monitoring wells would have been valuable. As an added practical implication, cross-hole testing produces a large volume of contaminated water that needs to be treated. Thus, we recommend an injection or infiltration test with groundwater drift (no pumping) whenever possible. This was not considered feasible for the GJO site based on the groundwater flow rates and the time available for the completion of testing.

Parameters derived from the cross-hole tracer testing were compared to results from single-well push-pull tracer testing and column testing. Overall, the final parameters were quite similar regardless of technique. The main exception was the uranium sorption parameters for the 110-series testing. We hypothesize that this test exceeded the scale of aquifer homogeneity and included some heterogeneous pathways with low sorption potential. Such heterogeneity did not impact the physical parameter estimates or the other geochemical parameter estimates, but did dramatically lower the uranium sorption parameter value. As a practical implication on a large site scale, uranium may move more conservatively (with less sorption) than expected based on column or single-well testing that analyzes smaller aquifer areas, depending on the scale being considered.

For the release of constituents from the vadose zone in the 110-series testing, a direct addition of these constituents to the saturated zone in the model created a reasonable match for the timing. Such a simulation likely reproduced the quick movement of existing pore water being pushed downward into the saturated zone. However, the slower movement of tracer from the infiltration well to the saturated zone could not be simulated without a delayed release. Additional delayed drainage of tracer, uranium, and chloride after pumping ended is indicated and was not adequately simulated. Thus, the modeling approach in this paper does not fully capture the complexities of the vadose zone. However, our simplified approach does provide for a reasonable estimate of constituent release concentrations from the vadose zone during a recharge event (Table 3). These estimates have concentrations that are greater than the underlying groundwater and explain the increases in groundwater uranium concentrations after recharge events when secondary sources are present in the vadose zone. Added complexities of flow and transport in the vadose zone are not necessarily needed for initial modeling of general reactive transport controls and site understanding. For simulations of possible remedial actions to remove uranium from the vadose zone (i.e., addition of specific remedial fluids beside river water), the addition of more detailed vadose-zone flow and geochemistry may be needed. The actual implementation of a remedial action can be hampered by field complexities that

would likely require field pilot testing. While such efforts are beyond the scope of this paper, vadose-zone column testing [7] could be used to test contaminant release rates with various remedial fluids as an initial step.

**Supplementary Materials:** The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/min13070947/s1, Folder S1: Boring Logs; Folder S2: Injection Extraction Details and Water Levels; Folder S3: Specific Conductance Probe Data; Folder S4: Geochemistry Data; Folder S5: PHREEQC Files; Folder S6: PHREEQC Database; Folder S7: PHT-USG Model Files; Folder S8: Graphical Model Results.

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