

1 **Controls of River Dynamics on Residence Time and Biogeochemical**
2 **Reactions of Hydrological Exchange Flows in A Regulated River**
3 **Reach**

4
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13
14 **Keywords:** Residence Time Distributions, Hydrological Exchange Zone, Hydropeaking, Biogeochemical
15 reaction, Dam Operation, Surface water-groundwater interactions
16

17 **Abstract:**

18 Residence Time Distributions (RTDs) exerts an important control on biogeochemical translations in
19 watershed systems. RTDs tend to follow time-invariant exponential, lognormal, or heavy-tailed RTDs
20 that have power-law behaviors for long tails in headwater or low-order streams. However, there is
21 increasing recognition that RTDs can be more complicated and time-variable in response to dynamic
22 hydrological forcing. In this study, we use particle tracking to estimate RTDs along the Hanford Reach of
23 the Columbia River and to quantify the influences of river stage fluctuations on RTDs and
24 biogeochemical reaction potentials. Particle tracking is conducted using the velocity fields from high-
25 resolution three-dimensional groundwater flow simulations. The effects of dynamic hydrological forcing
26 on the RTDs were evaluated by applying time-varying river flow boundary conditions and continuously
27 releasing particles in different time windows. Our results revealed that dynamic stage fluctuations created
28 rapidly changing losing-gaining conditions in the river, which led to highly transient RTDs and resulted
29 in multiple modes of RTDs. Dam-induced high-frequency (sub-daily) flow variations increased the
30 fraction of short (sub-daily) residence times of the RTDs. Deviation of the reactant consumption under the
31 single-mode assumption compared to the multimodal RTDs was relatively small (~5%) and the maximum
32 deviation appeared when the Damköhler number was close to one. Dam-induced high-frequency stage
33 variations potentially increase the biogeochemical reactions by 27%. These findings suggest that current
34 large-scale hydrobiogeochemical models (reach to basin scales) could be improved by accounting for
35 dynamic hydrologic exchange flows and associated transient RTDs influenced by both short- and long-
36 term river stage fluctuations.

37 1. Introduction

38 The hydrologic exchanges between river water and groundwater play an important role in river
39 ecosystems as the groundwater-river water mixing supplies nutrients and substrates that drive
40 biogeochemical reactions (Boano et al., 2014; Cardenas, 2015; Gomez-Velez et al., 2015). Hydrologic
41 exchange flows (HEFs) are defined as the vertical and lateral exchanges of water between groundwater
42 and river water, including hyporheic exchange, bank storage, and overbank flow onto floodplains (Harvey
43 et al., 2018; Harvey & Gooseff, 2015). HEFs span a broad range of spatial scales from millimeters to
44 kilometers and time scales from seconds to tens of years (Boano et al., 2014; Wörman et al., 2007). The
45 biogeochemical consequences of the HEFs depend on the residence time of the river water in the
46 exchange zone relative to the characteristic biogeochemical time scales (BTSs), which are the intrinsic
47 time scales of given reactions (Gomez-Velez et al., 2012).

48
49 The residence time distributions (RTDs) can be measured either through stream tracer experiments or
50 from numerical simulations (Boano et al., 2014). RTD has been widely used as a master variable to
51 evaluate the biogeochemical potential of the groundwater-river water mixing (Boano et al., 2010; Briggs et
52 al., 2014; Gomez-Velez et al., 2015; Harvey et al., 2013; Zarnetske et al., 2011). RTDs tend to follow
53 time-invariant exponential, lognormal or power-law distributions under steady flow conditions or small
54 stage fluctuations in low-order streams (Aubeneau et al., 2015; Cardenas, 2008; Faulkner et al., 2012;
55 Haggerty et al., 2002; Jonsson et al., 2003; Knapp et al., 2017; Sawyer & Cardenas, 2009; Tonina &
56 Buffington, 2011; Worman et al., 2002). However, recent modeling studies demonstrated that transient
57 RTDs may result from dynamic hydrologic conditions (Gomez-Velez & Wilson, 2013; Harman et al.,
58 2016; Schmadel et al., 2017; Ward et al., 2018). Transient RTDs reflect the complex influences from one
59 or multiple discrete hydrologic events that occur at different time scales with various magnitudes
60 (McCallum & Shanafield, 2016). Even short-term perturbations (e.g., flooding) can have long-lasting
61 influences (Gomez-Velez et al., 2017).

62
63 The shapes of RTDs in real dynamic river corridors can be very complex since RTDs are influenced by
64 both subsurface physical features and hydrologic forcings (Boulton et al., 1998; Gomez & Wilson, 2013),
65 including sediment permeability and porosity (Cardenas et al., 2004; Liu & Chui, 2018; Salehin et al.,
66 2004), river morphology (e.g., riffles, bars, and dunes) (Buffington & Tonina, 2009; Cardenas, 2008;
67 Cardenas & Wilson, 2007; Stonedahl et al., 2013), naturally occurring hydrologic processes and events
68 (e.g., flooding, evapotranspiration, recharge, snowmelt and tidal cycles) (Gomez-Velez et al., 2017;
69 Gomez-Velez & Wilson, 2013; Larsen et al., 2014), and anthropogenic activities (e.g., dam-induced stage
70 fluctuations) (Shuai et al., 2019; Song et al., 2018). The dynamic hydrologic fluctuations can produce
71 equivalently complex pathways and RTDs as complex geomorphic features (Schmadel et al., 2016).

72
73 Dynamic flow variations are common in most large river systems, which exhibit multi-frequency patterns
74 that are influenced by natural processes and anthropogenic activities (Graf, 1999; Nilsson et al., 2005).
75 These stage variations cause significant pressure changes along the river shoreline and significant lateral
76 exchange flow and bank storage (Shuai et al., 2019; Zachara et al., 2016), which enhance biogeochemical
77 processes within the river corridors (Briody et al., 2016; Knapp et al., 2017; Shuai et al., 2017; Song et
78 al., 2018; Trauth & Fleckenstein, 2017). However, there have been few studies that link HEFs, RTDs and
79 their biogeochemical consequences within large river corridors due to challenges in data collection and
80 lack of modeling capability (Boano et al., 2014). The traditional tracer experiment methods [e.g., (Knapp
81 et al., 2017; Worman et al., 2002)] mainly work for low-order small streams. Numerical methods such as
82 particle tracking (Cardenas et al., 2004; Faulkner et al., 2012), time-derivative of solute breakthrough
83 curves (Cardenas, 2008), or the StorAge Selection (SAS) function (Botter et al., 2011; Rinaldo et al.,
84 2015) are often data-intensive and/or computationally expensive.

85
86 In this study, we explore three questions: (1) what are the characteristics of RTDs under dynamic river
87 flow conditions induced by dam operations? (2) how do the resulting RTDs impact biogeochemical

88 reactivity in the exchange zone? and 3) can we provide some general guidance on evaluating the impacts
89 of HEFs on biogeochemical cycling in large dynamic river systems? To resolve these questions, we
90 estimated RTDs by conducting particle tracking using multi-year velocity outputs from km-scale, 3D
91 groundwater flow and transport models. The simulated RTDs were then used to evaluate the impacts of
92 river dynamics on generalized river corridor biogeochemical reactions. We chose the Hanford Reach of
93 the Columbia River as an example in this study, which serves as an ideal testbed because of its highly
94 dynamic HEFs (Shuai et al., 2019; Song et al., 2018). In addition, extensive hydrologic and geologic data
95 collected from more than thirty monitoring wells within this site provides detailed site characteristics. The
96 general approaches of this study can be extended to other study sites. Our study improves the
97 understanding of the influences of dynamic flow conditions on RTDs, and their biogeochemical reaction
98 potential associated with groundwater-surface water exchange.
99

100 **2. Materials and Methodology**

102 We used particle tracking to evaluate the RTDs of intruded river water in the aquifer. The particle
103 tracking was conducted based on velocity fields simulated by a high-resolution 3D groundwater model
104 with in-situ groundwater monitoring data. Particles were injected at multiple locations in the river-aquifer
105 interface under various river flow conditions to account for the spatial/temporal variations of RTDs. We
106 then adopted a first-order kinetics equation to quantify the impacts of RTDs on typical biogeochemical
107 reactions expected to occur within river corridors. In addition, a second case with daily smoothed flow
108 boundaries was compared to the base case to evaluate the influence of dam-induced, high-frequency flow
109 variations.
110

111 **2.1 Site Description**

112 The study area is situated near the downstream end of the Hanford Reach of the Columbia River, located
113 within the semi-arid Pasco Basin in southeastern Washington State (Figure 1). The Hanford Reach is an
114 80 km free-flowing river segment bounded by two hydroelectric dams, including the upstream Priest
115 Rapids Dam and the downstream McNary Dam (Neitzel et al., 2001). Dam operations for power
116 generation and seasonal snow melting strongly impact the river discharge, leading to river stage
117 fluctuation up to 2 m daily and 4-5 m annually (Arntzen et al., 2006). Numerous groundwater wells were
118 installed as part of the Hanford remediation efforts for monitoring groundwater level, temperature and
119 chemistry data (Bjornstad et al., 2009). A river routing model, the Modular Aquatic Simulation System
120 in 1-Dimension (MASS1), has been well calibrated against river gauge observations with mean absolute
121 error ranging from 4 to 18 cm (Richmond & Perkins, 2009), which provided accurate river stage and
122 gradient information along the reach.

(a) Location map and modeling area

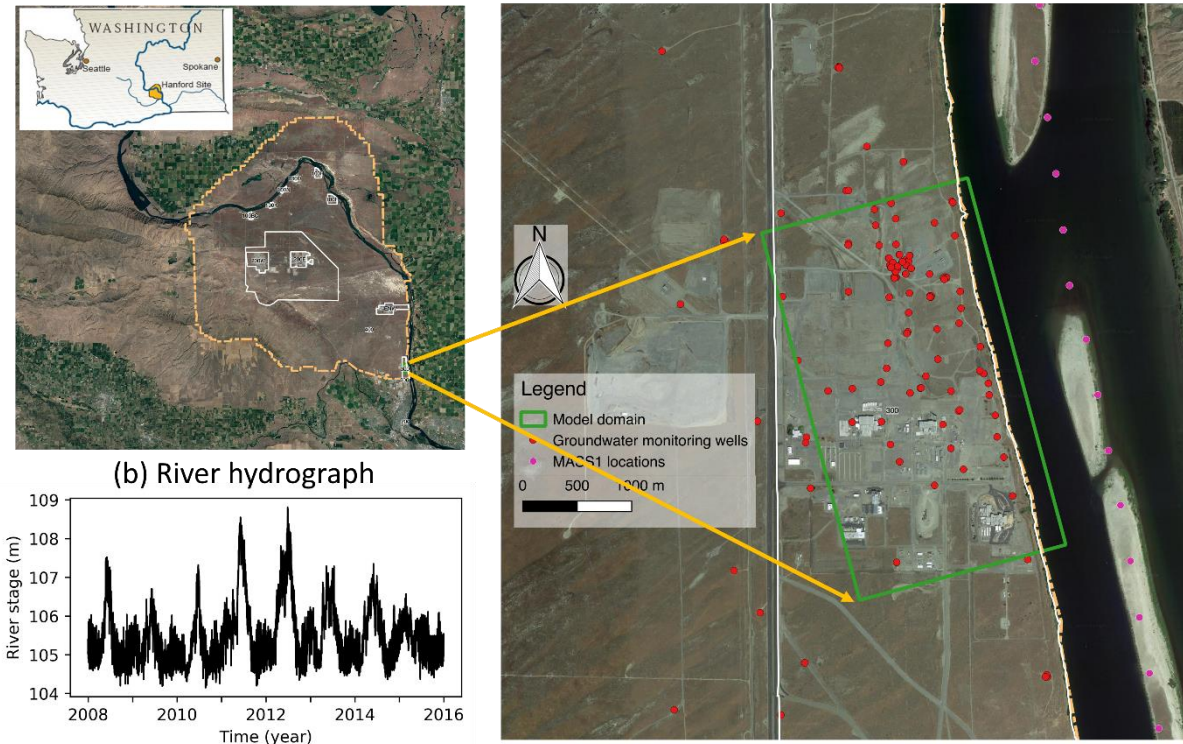


Figure 1. (a) Location map and modeling area. The red dots represent the groundwater monitoring/sampling wells, the purple dots represent MASS1 transects, and the green box shows the groundwater model domain; (b) river hydrograph between 2008 and 2015.

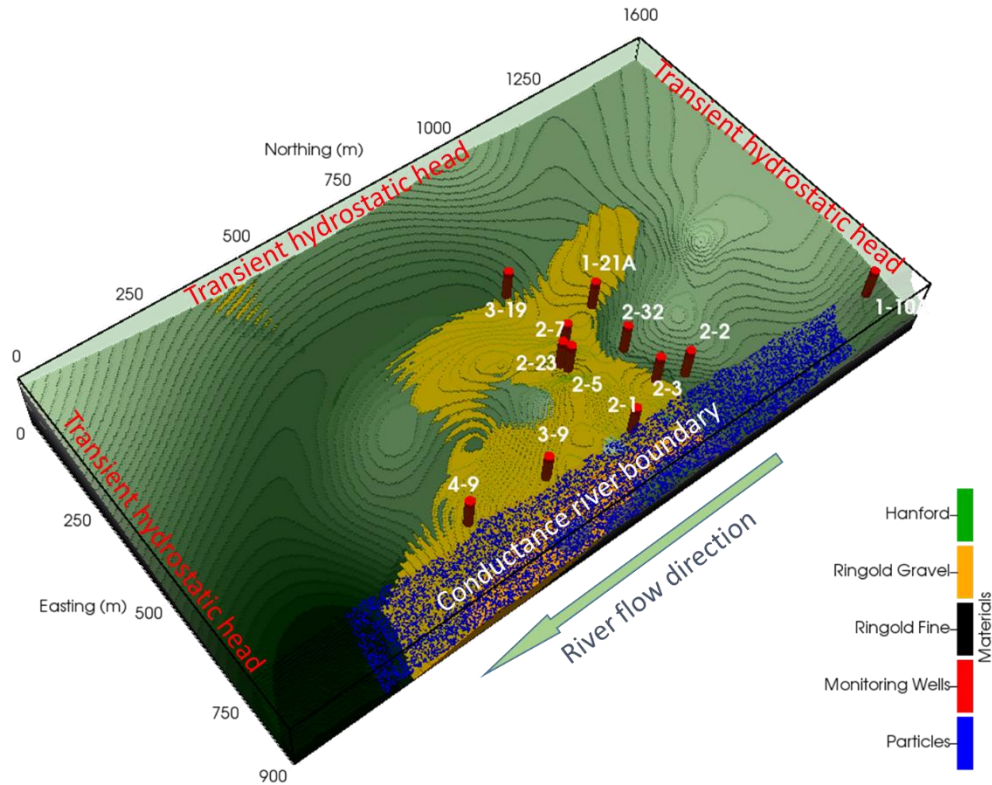
The unconfined aquifer within the river corridor consists of two major geologic formations including the upper high-permeability Hanford Formation, consisting of coarse gravelly sand and sandy gravel; and the lower, low-permeability Ringold Formation composed primarily of silt and fine sand (Bjornstad et al., 2009; Chen et al., 2012, 2013; Williams et al., 2008; Zachara et al., 2013, 2016). The aquifer-river interface is comprised of a low-permeability sandy layer of recent fluvial deposition. The thin alluvium layer (0.5m~2m) has an important influence on HEFs by dampening river fluctuation propagation into the aquifer (Hammond & Lichtner, 2010; Song et al., 2018; Zhou et al., 2018).

2.2 Flow and Transport Model

3-D groundwater flow and transport models were built to simulate the transient flow field and river intrusion using the massively parallel subsurface flow and reactive transport code PFLOTRAN (pflotran.org) (Hammond et al., 2014). The governing flow equation in PFLOTRAN is the Richards equation. The dominant solute transport mechanisms in this site are advection and macro-dispersion due to the dynamic flow conditions and the structurally heterogeneous, high-permeability aquifer, while molecular diffusion is neglected. The governing equations for flow and solute transport are included in the Supporting Information (S1).

A 1600x900x20 m model domain (the green box in Figure 1) was selected to encapsulate a known paleochannel within the Hanford 300 Area. More than 30, long-term monitoring wells exist within the domain to monitor the attenuation of a persistent uranium plume. The grid size was 4 m horizontally and 0.5 m vertically, with a total of 3.6 million grid cells. Groundwater flow and transport simulations were performed for an eight-year time window (2008-2015), with the first year used for model spin-up and the

150 other seven years used for conducting particle tracking. The maximum time step in this simulation was set
 151 to one hour, while PFLOTRAN refines the time step to achieve convergence when needed.
 152



153 Figure 2. Model domain. The upper Hanford Gravel (green) is set translucent to show the lower Ringold
 154 Fines (black to grey) and Ringold Gravel (orange). The red cylinders represent the long-term monitoring
 155 groundwater wells used for model validation. The blue dots indicate particle release locations.
 156

157
 158 Three distinct hydrogeological units were delineated from the Hanford and Ringold Formations for the
 159 3D model (Figure 2), including the Hanford Gravel (HG), Ringold Fines (RF), and Ringold Gravel (RG).
 160 The hydraulic properties were modified from earlier modeling studies performed at the site (Chen et al.,
 161 2013; Song et al., 2018) as listed in Table 1. The permeability field was assumed to be homogeneous
 162 within each unit with vertical permeability as one-tenth of horizontal permeability. Because the actual
 163 thickness of the alluvium layer is unknown (0.5m~2m) and unlikely to be accurately represented by the
 164 model resolution (4×4×0.5 m), a conductance boundary condition was applied at the river-sediment
 165 interface (Hammond & Lichtner, 2010). Four different conductance coefficient values were applied to the
 166 river boundary to find the best fit for monitored groundwater elevation and chemical data. A conductance
 167 coefficient of 2.5×10^{-13} m was chosen after comparing simulated tracer breakthrough curves with
 168 observed specific conductance in selected wells (Section 3.2). More detailed description of the
 169 conductance boundary is included in the supporting information (S1).
 170

171 **Table 1.** Hydraulic properties of Hanford Gravel/Ringold Gravel/Ringold Fine in the flow model

	Hanford Gravel	Ringold Gravel	Ringold Fine
Horizontal permeability (m ²)	7.38×10^{-9}	4.72×10^{-11}	1.18×10^{-12}

Porosity (-)	0.2	0.25	0.43
Residual saturation (-)	0.16	0.13	0.13
van Genuchten alpha parameter (Pa ⁻¹)	7.27×10 ⁻⁴	1.43×10 ⁻⁴	1.43×10 ⁻⁴
van Genuchten m parameter [-]	0.34	0.75	0.75

172

173 Hydraulic head along the river boundary was interpolated using the hourly river stage outputs from the
 174 river routing model MASS1 (Richmond & Perkins, 2009). The transient hydraulic head at the lateral
 175 inland (south/west/north) boundaries was kriged using groundwater level data of wells located inside and
 176 outside of the model domain. A constant-rate recharge of 55.4 mm/yr was applied on the upper model
 177 boundary based on monitoring results at nearby locations (Fayer & Walters, 1995). The bottom of the
 178 model domain was set as no-flow as it is underlain by the Ringold Formations with low permeability. The
 179 initial head over the model was kriged using the same set of data for the lateral inland boundaries. An in-
 180 silico conservative tracer with a unit concentration was continuously released along the river boundary to
 181 track river water penetrating in the aquifer. The simulated tracer concentration represents the fraction of
 182 river water in the aquifer. The transport conditions for the lateral inland boundaries were set as zero
 183 dispersive gradient for outflow and zero concentration tracer for inflow. The recharge of the top boundary
 184 contains no tracer while the lower boundary was zero flux due to the no flow condition.

185

186 A baseline groundwater flow model was built using the original MASS1 simulated river stage results with
 187 hourly resolution and hourly groundwater table monitoring data. An additional simulation with daily
 188 smoothed flow boundaries was used to evaluate the influence of dam-induced, high-frequency flow
 189 variations. Velocity fields of both baseline and smoothed models were used to drive particle tracking
 190 simulations to derive RTDs. The results of the smoothed case are discussed in section 3.6.

191

192 **2.3 Particle Tracking and RTD Estimations**

193 We use forward particle tracking to simulate the hydrological exchange pathways and estimate RTDs. We
 194 adopted a classical semi-analytical particle tracking scheme (Pollock, 1994) which tracks particles from
 195 one cell to the next until the particle reaches a model boundary or satisfies a termination criterion (e.g.,
 196 particles lost in the vadose zone). Numerical particles were released from 10,000 randomly selected
 197 locations along the river shoreline at 10,000 random times during the seven-year simulation window to
 198 cover an adequate range of advection paths. Convergence tests were conducted to ensure the number of
 199 released particles were large enough to provide consistent results. Each particle was released 10⁻⁷ m
 200 below the riverbed as represented by the blue dots in Figure 2. More than half (67%) of the total 100
 201 million released particles did not enter the groundwater aquifer due to local groundwater discharge
 202 conditions when they were released. Thus they were not tracked and counted in the following RTD
 203 estimation. The parallel particle tracking scheme is described in the supporting information (S2). A
 204 parallel particle tracking software package using Python was built for this study and is publicly available
 205 on Github (https://github.com/xuehangsong/particle_tracking/).

206

207 The residence time of each particle is defined as the time elapsed from entering the riverbed to exiting
 208 through the aquifer. Then the particle residence times were weighted by the fluxes corresponding to the
 209 location and time when it was released to estimate the cumulative residence time distribution (CRTD;

210 $F_{RT}(t)$) as

$$211 \quad F_{RT}(t) \approx \hat{F}_{RT}(t) = \frac{\sum_{i=1}^N |v_i| \cdot \mathbf{1}_{T_i \leq t}}{\sum_{i=1}^N |v_i|}, \quad (1)$$

212 where $\hat{F}_{RT}(t)$ is the empirical cumulative distribution, N is the number of particles, v_i is the Darcy flux
 213 when and where the particle i is released, T_i is the particle residence time, $\mathbf{1}_{T_i \leq t}$ is the indicator of event
 214 $T_i < t$. The CRTD $F_{RT}(t)$ was then used to derive the RTD $f_{RT}(t)$ as

$$215 \quad f_{RT}(t) = \frac{d}{dt} F_{RT}(t) . \quad (2)$$

216 Three types of particles (<2.5%) were not included in our analysis: 1) particles released in the last month
 217 of the year 2015 as these particle paths failed to complete by the end of the simulation; 2) particles that
 218 flowed out the inland groundwater boundaries of the domain; 3) particles immobilized in the vadose zone.
 219 The overall RTD of all qualified particles represent lumped temporal and spatial variations of residence
 220 time along the modeled river reach during this nearly seven-year time period. We used the Bayesian
 221 Information Criterion (BIC) (Spiegelhalter et al., 2002) to find the best distribution model to describe the
 222 overall RTD. The BIC is a model selection criterion and the model with the lowest BIC has the best
 223 balance between goodness-of-fit and model parsimony. BIC usually first decreases then increases as more
 224 model parameters are included in the model fitting. To further distinguish the spatial and temporal
 225 variations of RTDs, we applied several moving temporal (one week, six months and one year) and spatial
 226 (5 m, 50 m and 500 m) windows to extract subsets of particles and estimate their temporally/spatially
 227 discrete RTDs.

228 **2.4 Impacts of RTDs on Biogeochemical Reactions**

229 We evaluated the biogeochemical impacts of the simulated RTDs by linking them to a generic
 230 biogeochemical reaction with different reaction rates. There are various formulations to describe the
 231 microbial redox kinetics in biogeochemistry literature, such as zero- and first-order kinetics, Monod, and
 232 dual-Monod kinetics depending on the number of involved reactants and the degree of mathematical
 233 complexity (Bekins et al., 1998; Boano et al., 2010). Since the solute reaction was not directly modeled in
 234 the particle tracking simulations, we adopted a simple first-order kinetics for the reactions along the
 235 exchange pathways, i.e.,

$$237 \quad \frac{dC}{dt} = -k \cdot C , \quad (3)$$

238 where C is the reactant concentration, t is time and k is the first-order decay constant and defined by

$$239 \quad k = 1 / \tau , \quad (4)$$

240 where τ refers to the characteristic biogeochemical timescale (BTS) (Gomez-Velez et al., 2015). The
 241 ratio between the median residence time $F_{RT}^{-1}(0.5)$ and τ defines the Damköhler number as

$$242 \quad D = \frac{F_{RT}^{-1}(0.5)}{\tau} . \quad (5)$$

243 The reactive transport system is regarded as mass-transfer limited and reaction rate limited when
 244 Damköhler number is larger than and smaller than one, respectively.

245
 246 By integrating Eq. (3) from time 0 to t , we get

$$247 \quad C(t) = C_0 \exp(-kt) , \quad (6)$$

248 where C_0 is the initial amount of reactant concentration entering the riverbed, $C(t)$ is the residual reactant
 249 concentration after river water resides in the riverbed for time t . Then the fraction of consumed reactant
 250 after t is

251
$$F_{solute}(t) = 1 - \frac{C(t)}{C_0} = 1 - \exp\left(-\frac{t}{\tau}\right). \quad (7)$$

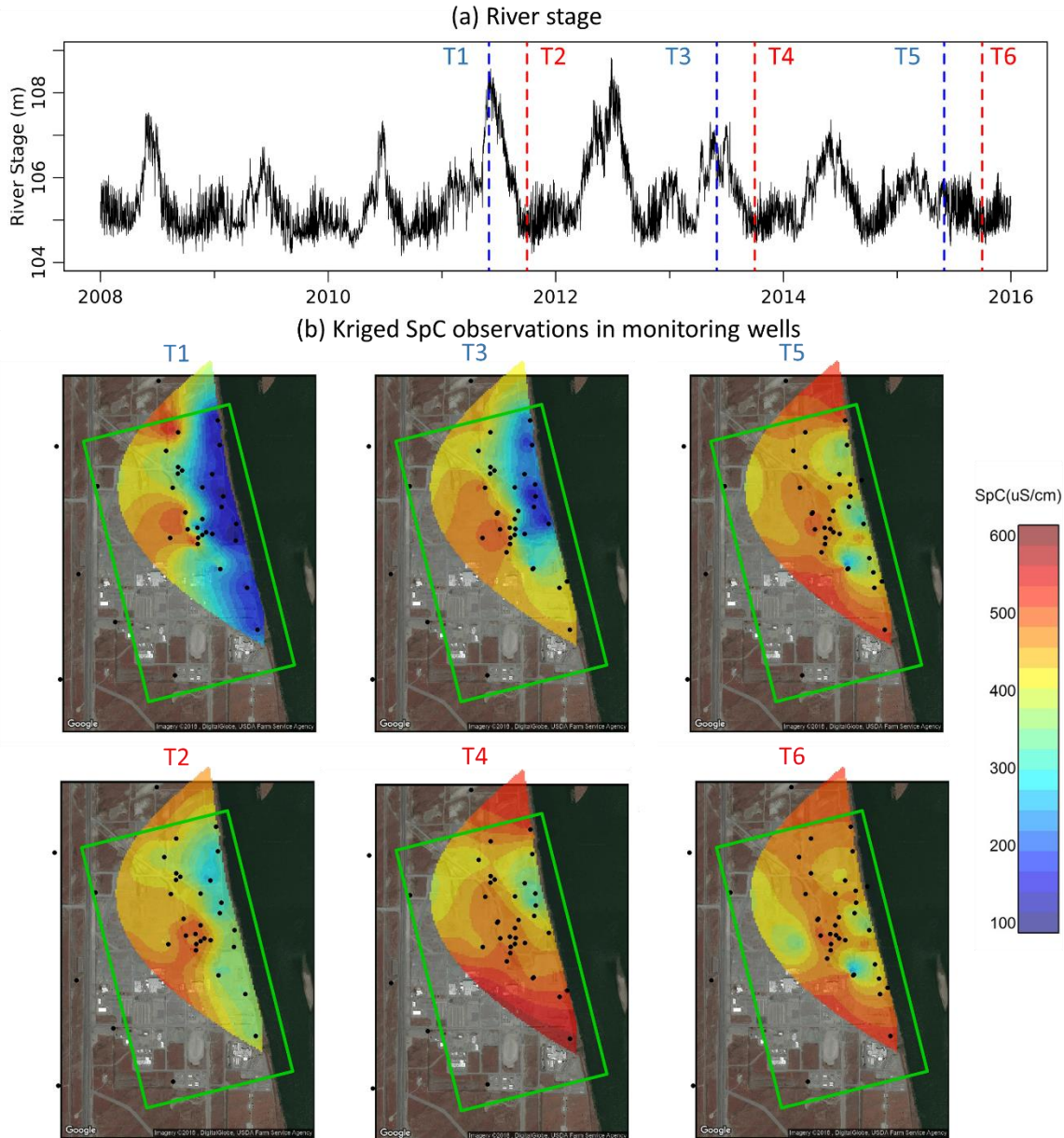
252 $F_{solute}(t)$ represents the percentage of reactive solute that can potentially be consumed in a batch reactor
 253 given a certain BTS τ within time t . The simulated RTD, $p_{rd}(t)$, represent the time distribution of
 254 reactive solute residing in the batch reactor (i.e., river bed aquifer). By integrating the product of $F_{solute}(t)$
 255 and $p_{rd}(t)$ over time window t , the percentage of total reactant consumption, P_{solute} , in the river corridor
 256 can be calculated by;

257
$$P_{solute} = \int_{-\infty}^{+\infty} [p_{rd}(t) \times F_{solute}(t)] dt. \quad (8)$$

258 **3. Results**

259 **3.1 Exchange Flow Patterns as Evidenced by Specific Conductance Measurement**

260 The distinct contrast in river water and groundwater specific conductance (SpC) at the Hanford site makes
 261 SpC a natural tracer of river water and groundwater mixing (Stegen et al., 2018). The average
 262 groundwater SpC is ~500 uS/cm, while that of the Columbia River is ~120 uS/cm. Thus, the SpC
 263 measurements in monitoring wells decreased when river water intrudes and increased when river water
 264 retreats. The annual and seasonal variations of river water exchange patterns in the near-shore region of
 265 the flood plain aquifer are illustrated in Figure 3 using SpC fields kriged from distributed well-based
 266 monitoring data. In a typical high water year (2012, T1 in Figure 3), river water intrusion (blue color) can
 267 be ~300 meters inland and occupy almost the entire shoreline. However, during a low-water drought year
 268 (2015, T5 in Figure 3), the presence of river water was limited to some preferential flow paths near the
 269 shoreline. The maximum river water intrusion for an average flow year is shown in T3 in Figure 3.
 270 Significant seasonal variations occurred in the kriged SpC field (T2, T4, and T6 in Fall compared to T1,
 271 T3, and T5 in Spring in Figure 3), river water is barely found in the aquifer, even in the near-shore areas
 272 in late fall of each year (T2, T4, and T6 in Figure 3) due to low mean river stage and groundwater outflow
 273 under a sustained period of river stage decline.
 274



275
 276 Figure 3. Observed river hydrograph (a) and snapshots of river water intrusion patterns indicted by
 277 kriged SpC maps (b). Areas with higher SpC (warm colors) have less river water presenting, while areas
 278 with lower SpC (cold colors) have more river water presenting.

279 **3.2 Flow Model Validation**

280 Groundwater table elevation and SpC observed in the monitoring wells were used for model validation.
 281 The simulated groundwater table elevations agreed well with the monitored water tables (supporting
 282 information S3), primarily due to the small hydraulic gradients of the highly permeable aquifer. However,
 283 the match between the simulated and observed SpC was less ideal as the local heterogeneity of flow and
 284 transport processes has more significant control on water chemistry. We link the SpC observations and
 285 simulated conservative tracer results through the concept of river water fraction, i.e., the volume fraction
 286 of river water presenting in the aquifer. The observed river water fraction ($F_{RW,obs}$) was estimated by
 287 normalizing the measured SpC data as follows:

288
$$F_{RW,obs} = \frac{SpC_{max} - SpC_{obs}}{SpC_{max} - SpC_{min}}, \quad (9)$$

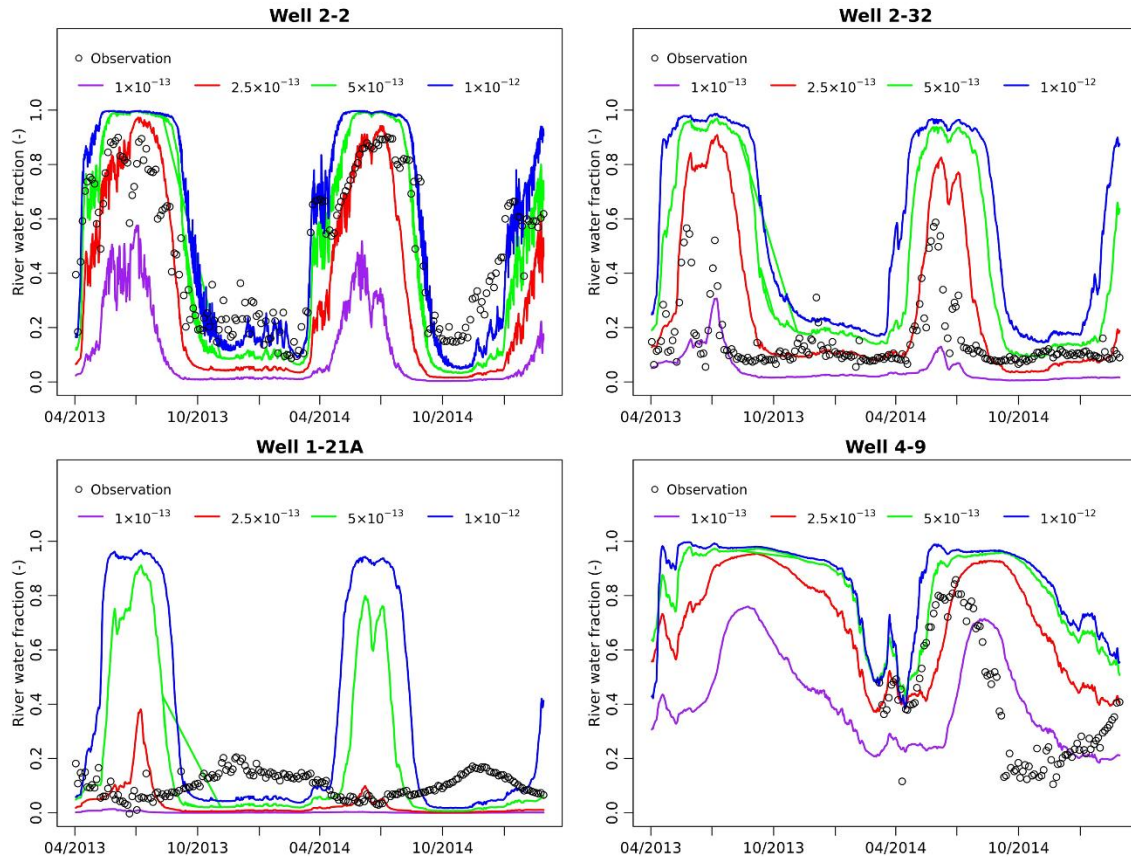
289 where SpC_{max} and SpC_{min} were the maximum and minimum SpC observations in the groundwater well
290 and river, respectively, and SpC_{obs} was the actual measured SpC value. The simulated river water fraction

291 $F_{RW,simu}$ was equal to the value of simulated tracer concentration C_{simu} as

292
$$F_{RW,simu} = \frac{C_{simu} - 0}{1 - 0} = C_{simu}, \quad (10)$$

293 since the tracer is only released at river boundary with a unit concentration.

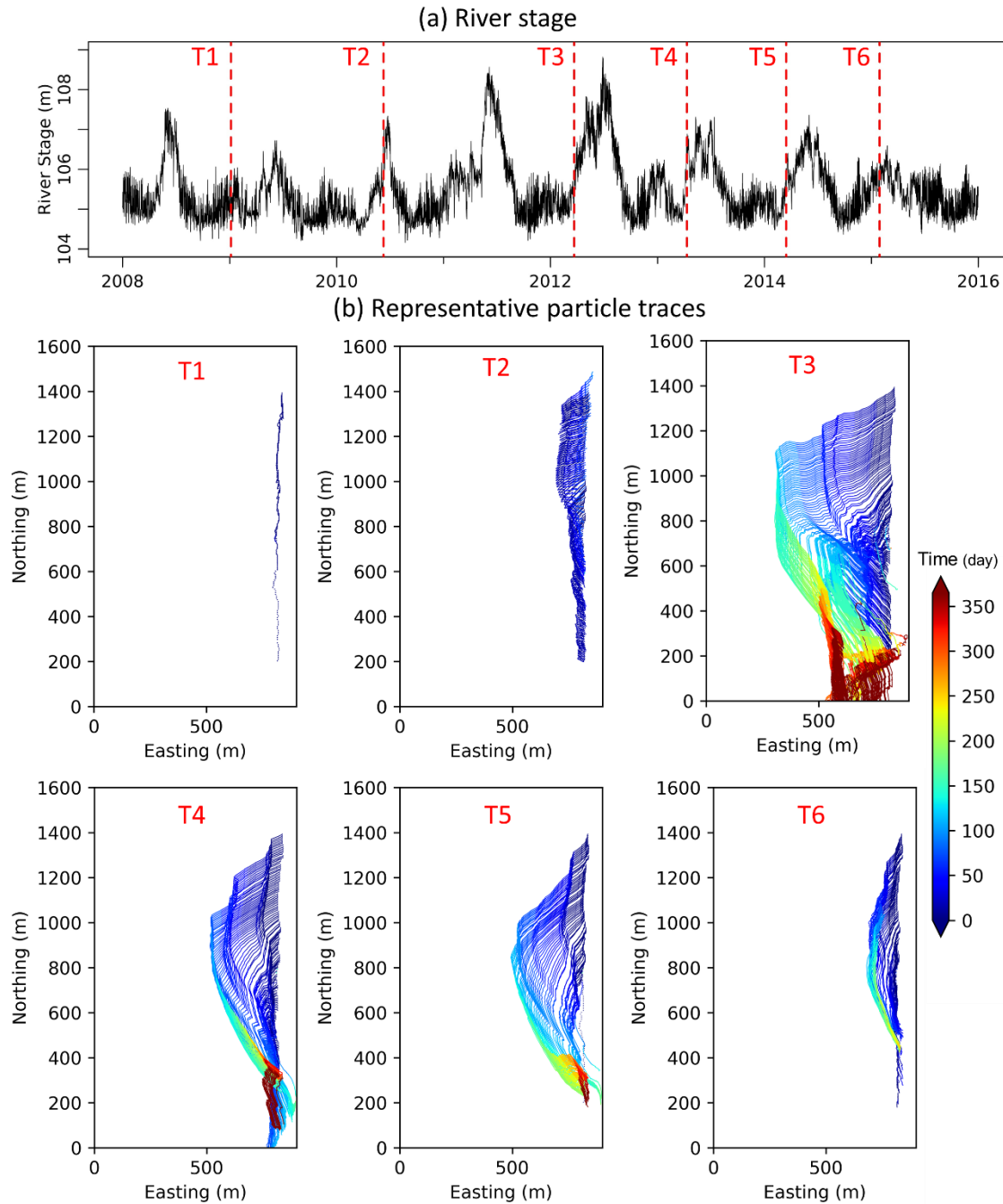
294
295 The simulated river water fractions were compared with the observed river water fractions to identify the
296 appropriate conductance coefficient (Figure 4, shown for representative wells). Well 2-2 is a
297 representative well in the upstream, near-shore locations, which usually have the highest river water
298 fraction and fastest response to river elevation changes. Well 2-32 is in the middle of the well field, which
299 is less dynamic than the near-shore wells, and experiences river water intrusion at intermediate and high
300 river stages (>106 m). Well 1-21A is relatively far inland and only experiences significant river water
301 intrusion around the peak flows of a high water year (>108 m). Well 4-9 is a downstream, shoreline well.
302 The mismatch between simulated and observed river water fractions in well 4-9, a downstream shoreline
303 well, is larger than the other wells due to the accumulated error along the upgradient flows from north to
304 south and west to east,. The match between observation and simulation was deemed quite satisfactory
305 with the conductance value of 2.5×10^{-3} m given our assumption of homogenous hydraulic properties in
306 each hydrogeological unit. The match can be further improved in the future by incorporating more field
307 surveys and characterizing local heterogeneity through data assimilation approaches. More information
308 about the flow simulation results are included in supporting information (S4).
309



310
 311 Figure 4. Comparison between modeled and observed river water fraction. The black dots are river water
 312 fractions converted based on SpC observations, the colored lines are river water fractions converted from
 313 simulated river water concentrations with different conductance values.
 314

315 3.3 Spatial and Temporal Variations of Exchange Pathways

316 The particle tracking results revealed that complex exchange pathways varying with particle release times
 317 and locations. We show in Figure 5 the seasonal and spatial variation of paths from a group of particles
 318 that were released around the elevation of 103.5m, which was chosen for illustration because it was
 319 always saturated during the 7-yr simulation window. Particles released in Jan 2009 (T1) track the
 320 exchange paths during low river stages under which the river was mainly gaining. Particles that entered
 321 the aquifer during this period were driven by short-term river fluctuations and returned to the river shortly
 322 after. Particles released in T2 exhibited dynamic, back-and-forth lateral movement that was common
 323 when there is frequent reverse of flow directions. Particles released prior to peak stage events (T3-T6)
 324 displayed the largest inland migration with longest residence time under wet (2012, T3), average (2013,
 325 T4; 2014, T5) and drought (2015, T6) conditions. The river particles released in the downstream portion
 326 were only transported tens of meters inland (T4-T6), whereas river water particles travelled hundreds of
 327 meters inland when they entered the aquifer from the upstream locations. An animation of the particle
 328 tracking results is included in the supporting information (movie S1).



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Figure 5. Flow paths of particles released at elevation of 103.5m, a) river stage time series marked with six representative release times; b) representative particle traces. The colors in (b) indicate residence time of each particle in the aquifer.

Our results revealed that more than 97% of released particles returned to the river due to the gaining river conditions. Most of the rest of the 3% particles were lost through outflow across the southern groundwater boundary under significantly low river state conditions (see T3 in Figure 5b). These particles were not included in the calculation of the RTDs, although they may eventually return to the river in

339 a larger modeling domain. As a result, some particles could potentially contribute to long tails in RTDs
340 were missing in our simulation results.

341

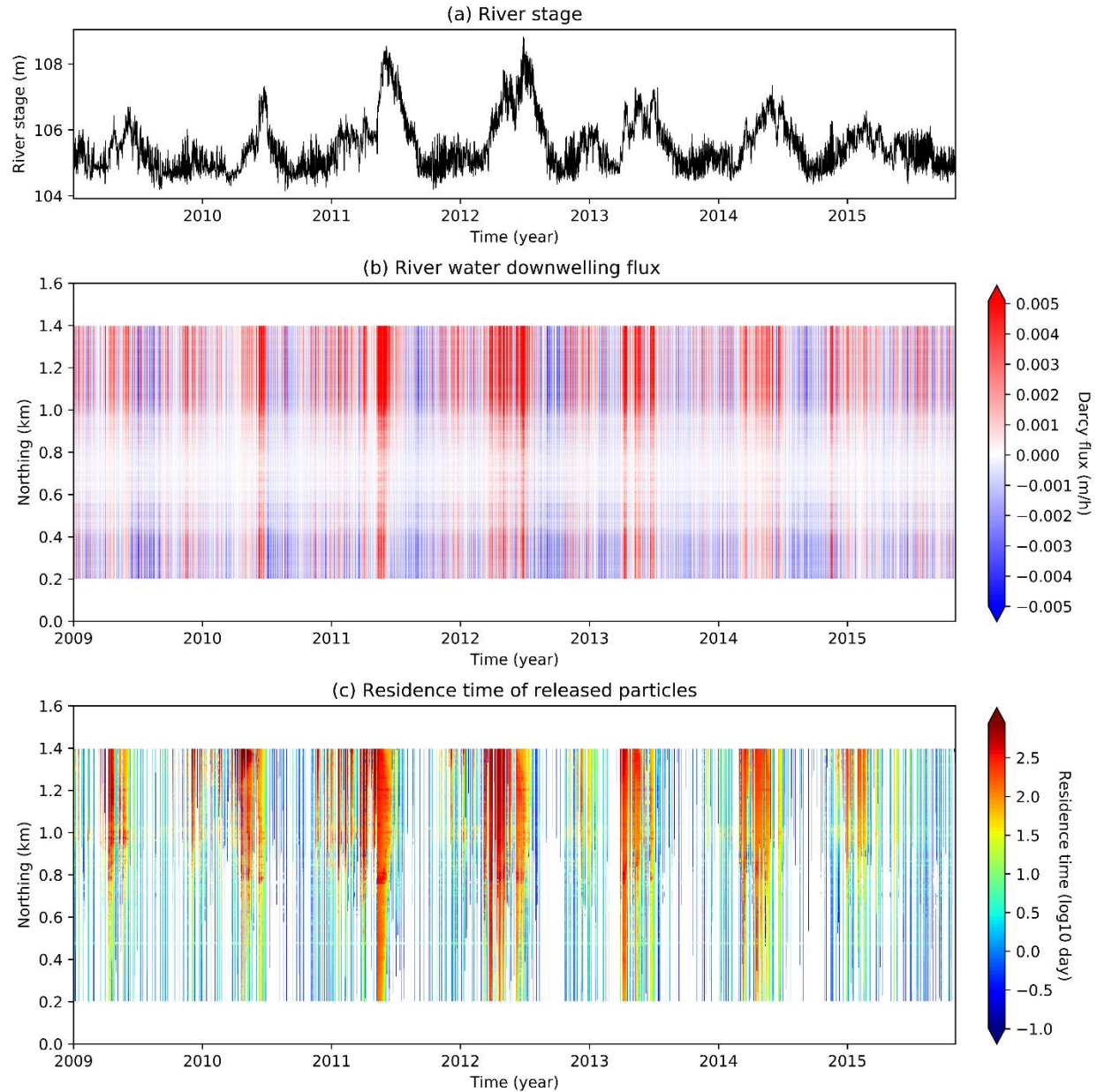
342 **3.4 Transient and Multimodal RTDs Induced by Dynamic Flow Variations**

343 The direction of the HEFs across the riverbed has a significant impact on the movement of river particles
344 in the subsurface. A particle will not enter the subsurface model domain when released under gaining
345 river conditions, hence not tracked in our algorithm. Figure 6b illustrates the distribution and direction of
346 river exchange fluxes along the river shoreline over time. The upstream segment of the riverbed
347 experienced more river water intrusion (red colors, Figure 6b), while the downstream segment was
348 dominated by groundwater discharge (blue colors, Figure 6b). The subsurface stratigraphy had a
349 significant influence on the exchange fluxes, e.g., the flux rate was 10 times lower where the less
350 permeable Ringold Formations were present within the river stage fluctuation zone (around the middle
351 part of the river shoreline shown in Figure 6b).

352

353 Residence times of the particles ranged from hours to years depending on the particle releasing time and
354 location under the baseline case (Figure 6c). The blank areas in Figure 6c correspond to locations and
355 times that groundwater discharge occurred, shown as the blue areas in Figure 6b. Particles released in the
356 northern upstream locations tended to have longer residence times, which was consistent with their long
357 exchange pathways shown in Figure 5.

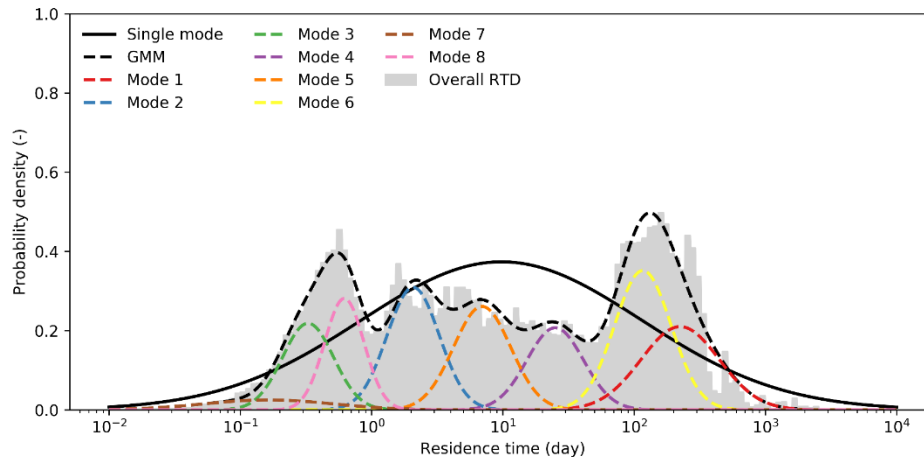
358



359
 360 Figure 6. Time series of (a) river stage, (b) spatial/temporal distribution of the exchange flux (red colors
 361 mean river water intrusion, blue colors mean groundwater discharge) on the riverbed, and (c)
 362 spatial/temporal distribution of the river particle residence time. The blank areas in (a) are time/locations
 363 where groundwater discharge happened (the blue area in (b)).
 364

365 The RTD estimated using Eq. (2) exhibited strong multimodal distributions as shown in Figure 7 (the
 366 grey shadow). Although RTDs with single-mode lognormal shapes were good representations of the
 367 advection based exchange models under steady-state flow conditions (Cardenas et al., 2004; Worman et
 368 al., 2002), our results clearly demonstrate that this assumption does not hold under highly dynamic flow
 369 conditions. The single-mode lognormal distribution (solid black line in Figure 7) could hardly fit the
 370 simulated RTD. We then used the Bayesian Information Criterion (BIC) (Spiegelhalter et al., 2002) to
 371 select an optimal number of modes that could sufficiently fit the overall RTD. However, the BIC did not
 372 converge to a minimum value even after more than 50 modes were assumed to exist in this case. Since
 373 there is negligible improvement to the BIC when the number of modes exceeds eight, we adopted an

374 eight-mode Gaussian Mixture Model (GMM) as our upper limit in Figure 7 (colored dash lines
375 representing individual modes, while the black dash line represents resulted GMM).



376
377 Figure 7. Overall RTD of particles released in 6-year simulation period and fitted GMM modes.
378

379 We decomposed the overall particle tracking results to smaller subsets based on their releasing times and
380 locations to evaluate the temporal and spatial variations of RTDs. Temporally, moving windows of one
381 week, six month and one year were chosen and their CRTDs were calculated based on Eq. (1) and plotted
382 against the overall CRTD in Figure 8a. Longer time windows tended to yield smaller variations in their
383 CRTDs and were closer to that of the overall CRTD as they captured river dynamics over a bigger time
384 window. However, the variation in CRTDs using time windows of one year is still considerably large
385 (light blue lines in Figure 8a). Similarly, spatial moving windows of 5m, 50m, and 500m were chosen to
386 generate spatially discrete CRTDs (Figure 8b). The comparison between Figure 8a and Figure 8b show
387 that dynamic river stage variation is the major contributor to the complex RTDs pattern, as the spatial
388 variations in CRTDs are much smaller compared to their temporal variations, e.g. the spread of the
389 CRTDs in 5m spatial window (dark green lines in Figure 8b) is even smaller than the spread of the
390 CRTDs in one year time windows (light blue lines in Figure 8a). We adopted the Kolmogorov–Smirnov
391 (K-S) tests to compare the temporal/spatial discrete RTDs with the overall RTD. All the tests were
392 rejected with significance levels below 1%, indicating that the temporal/spatial discrete RTDs and the
393 overall RTD did not follow the same distribution. These results suggest that it may not be possible to
394 determine a precise shape of RTDs for a river reach with complex aquifer hydrogeological features that
395 experiences dynamic flow conditions.

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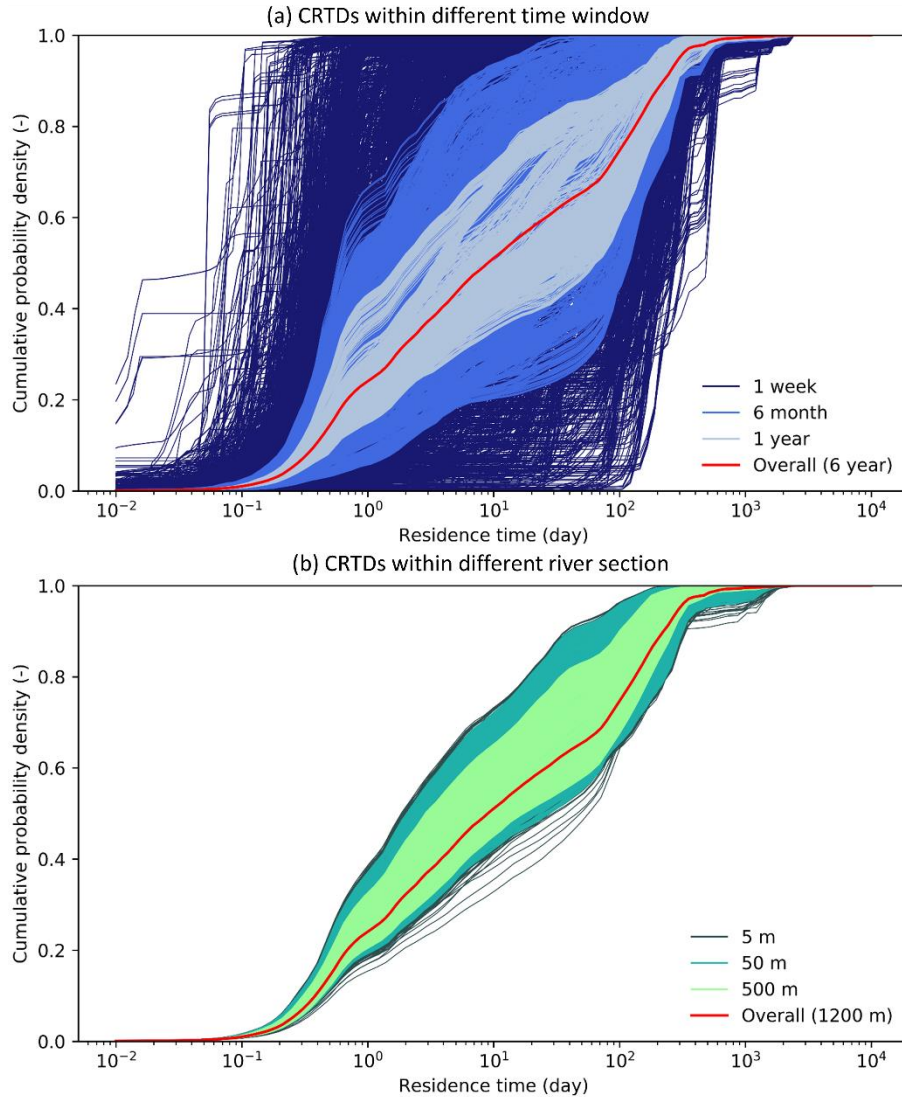
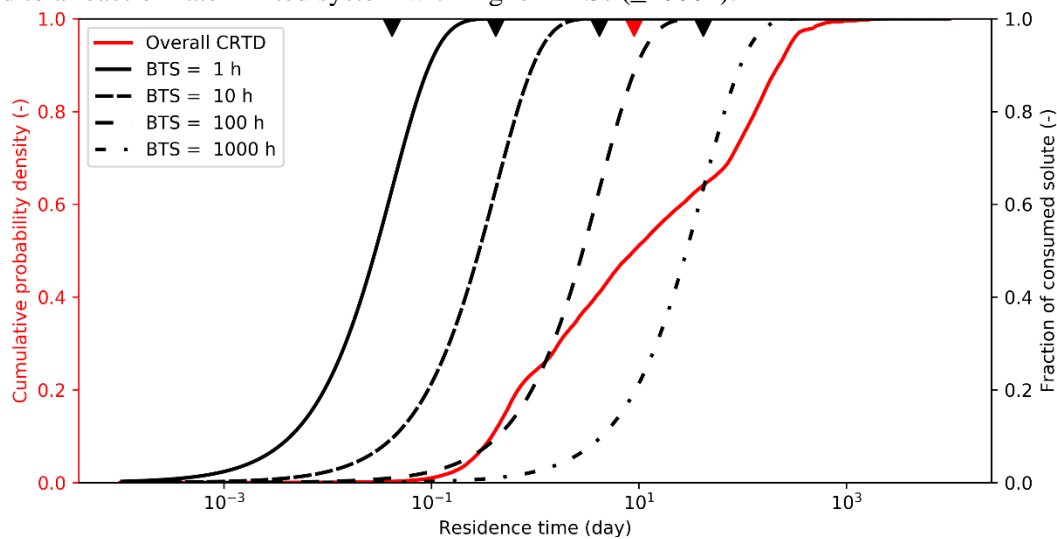


Figure 8. Estimated CRTDs of temporal (a) and spatial (b) subsets of particles. The red line is the overall CRTDs for all the eligible particles

3.5 Biogeochemical Implication of the Transient Multimodal RTDs

The consumption fractions of reactants were used to evaluate the potential biogeochemical implications of transient multimodal RTDs. The BTS (biogeochemical time scale) τ has a wide range in value depending on the microbial, geochemical, and hydrologic of sediment properties. We chose four representative BTSs at 1, 10, 100 and 1000 hours to explore its uncertainty. As a reference, the BTSs of two typical biogeochemical reactions common to river corridors, denitrification and aerobic respiration, range from 0.5 h to 1000 h with a median of 10 h and 0.5 to 10 h with a median of 1 h, respectively (Boano et al., 2010; Gomez-Velez et al., 2015; Gomez et al., 2012; Pinay et al., 2009; Zarnetske et al., 2011). The lower bound of our representative BTSs was set to 1 h since reactions with BTS below 1 h are all very fast relative to the RTD, for which the form of distribution will make little difference. On the other hand, BTS larger than 1000 h was not explored because the exceeding probably of residence times beyond 1000 h is negligible. The fractions of consumed reactant with time $F_{solute}(t)$ of the four representative BTSs were compared with the overall CRTD in Figure 9. The values of BTSs and mean residence time were marked with black and red triangles, respectively. Based on the definition of

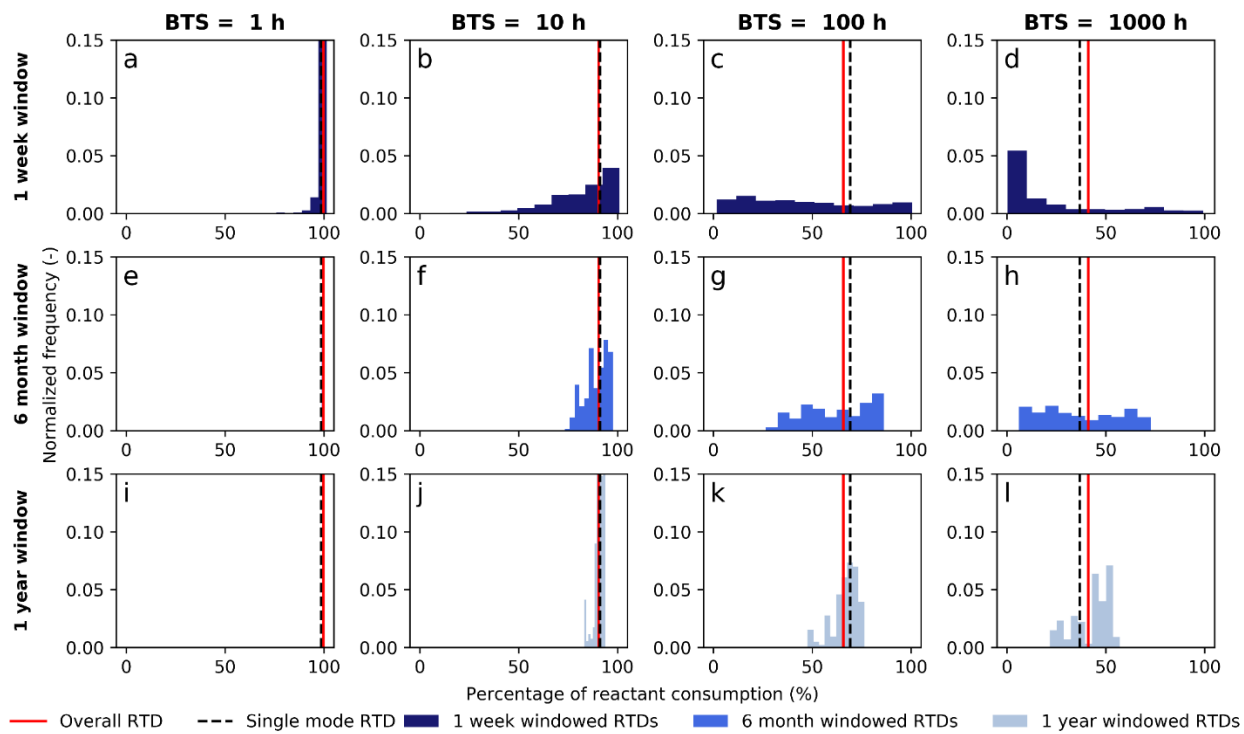
417 Damköhler number, our simulated HEFs were mass-transfer limited with lower BTSs ($\leq 100\text{h}$), then
418 switched to a reaction rate limited system with higher BTSs ($\geq 1000\text{h}$).



419
420 Figure 9. Fraction of consumed reactant under various BTSs (black lines) with the overall CRTD (red
421 line). The red triangle maker indicates the mean residence time value, the black triangle markers indicate
422 the BTS values.
423

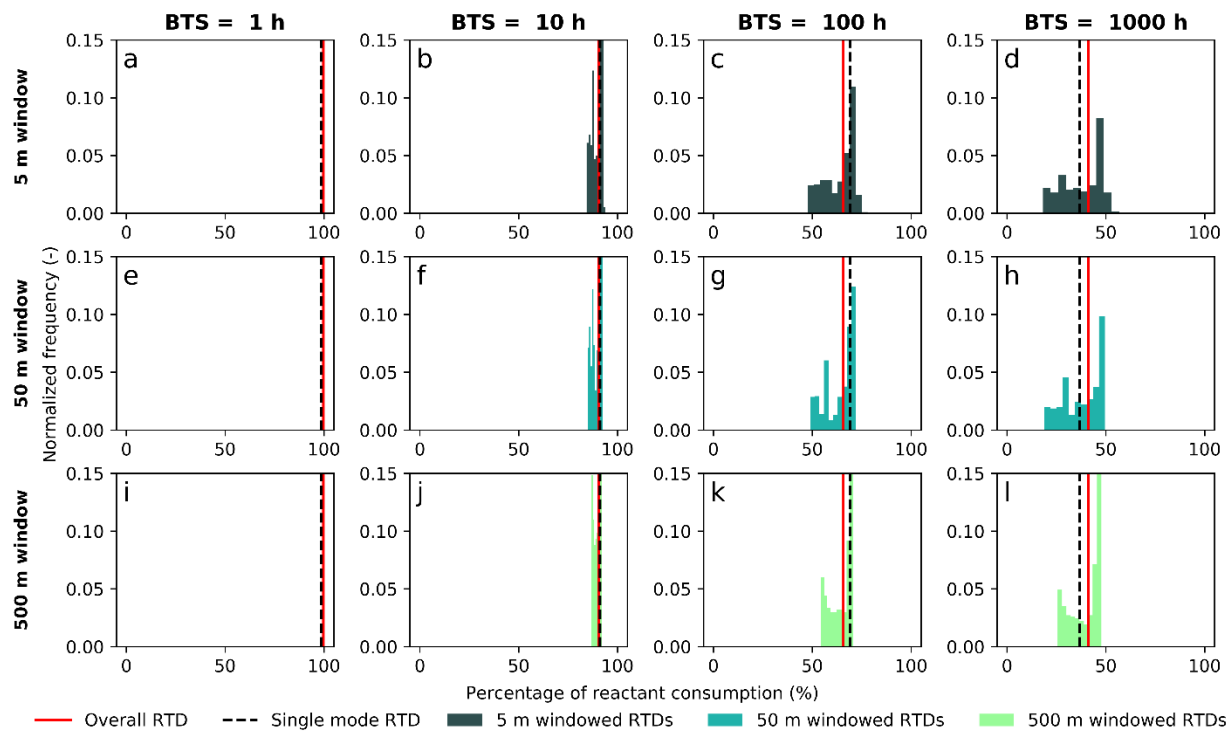
424 The biogeochemical reaction potentials under different combination of RTDs and BTSs are illustrated by
425 the predicted reactant consumptions (Figures 10-11). The simulated overall RTD (red solid lines) and the
426 single-mode RTD (black dash lines) produced almost identical reactant consumption in a strongly mass-
427 transfer limited ($\text{BTS} \leq 10\text{h}$, $D \gg 10$) system (e.g., Figure 10 a, b). The differences between the simulated
428 RTD and the single-mode RTD became large when the Damköhler numbers were closer to one
429 ($\text{BTS} = 100\text{h}$, 1000h), but they were still less than 5% (e.g., Figures 10 c, d). It would be expected that
430 their differences become smaller with a even smaller Damköhler number ($D \ll 0.1$) and the associated
431 minimum reaction rates.
432

433 The biogeochemical impacts of RTD's temporal and spatial variations are revealed by the uncertain
434 ranges of discrete RTDs (colored shadows in Figures 10-11). RTDs estimated from the smaller time
435 windows produced markedly different reactant consumption profiles (the dark blue histograms in Figure
436 10 a-d). The uncertainty range of predicted reactant consumption reduced to less than $\pm 20\%$ when a full-
437 year window of particles were included for the RTD estimations (the light blue histogram in Figure 10 i-
438 l). The largest uncertainty of reactant consumptions appeared when the Damköhler numbers were close to
439 one (Figures 10c, d, g, h, k, l). Our results also showed that the spatial uncertainty of the reactant
440 consumption (Figure 11) was relatively small compared to its temporal counterpart (Figure 10), which is
441 consistent with the smaller spatial variations of RTDs observed in section 3.4. It should be noted that we
442 underestimated the spatial heterogeneity of reaction rates by applying universal BTSs to the entire reach.
443 We did not account for large differences in microbial communities and associated reactions in two
444 locations that were only 150 m apart as revealed in a previous study at the same site (Graham et al.,
445 2018).



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Figure 10. Prediction of reactant consumption with various BTSs and temporally discrete RTDs. Each column represent different BTS and each row represent RTDs from different temporal subsets of particals. The red solid lines are results from reactant consumption of the simulated overall RTDs, the black dash lines are results from fitted single mode RTDs.



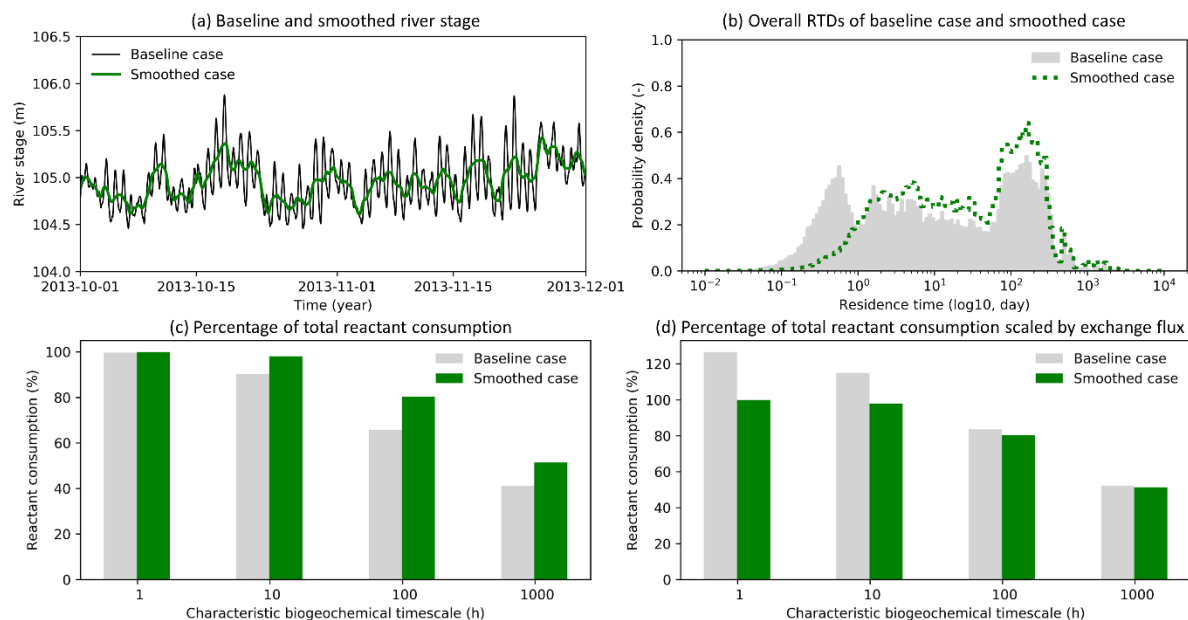
453

454 Figure 11. Prediction of reactant consumption with various BTSs and spatially discrete RTDs. Each
 455 column represent different BTS and each row represent RTDs from different spatial subsets of particles.
 456 The red solid lines are results from reactant consumption of the simulated RTDs, the black dash lines are
 457 results from fitted single mode RTDs.

458 3.6 Impacts of Dam-Induced High-Frequency Flow Variations on RTDs

459 One common characteristic of regulated river corridors is dam-induced, high-frequency flow variations.
 460 In a previous study (Song et al., 2018), it is found that upstream dam operations of the Hanford site for
 461 power production cause additional strong daily and weak weekly signals in river discharge and
 462 hydrograph. Here, we use moving average as a low pass filter to remove the sub-daily signal of river stage
 463 and groundwater data to create a new flow model with the smoothed flow boundaries (Figure 12a). This
 464 smoothed model was used to evaluate the effects of short-term river flow variations on the RTDs.
 465

466 Comparison of the RTDs under the baseline case and smoothed case revealed an inherent correlation
 467 between the modes of RTDs and river stage variations. The fraction of short resident time components
 468 was dramatically reduced due to the removal of high-frequency river fluctuation in the smoothed case
 469 (Figure 12b). As a result, the high residence time components in the overall RTD of the smoothed case
 470 increased. Since the overall residence time increased in the smoothed case, the reactant had more time to
 471 react and the HEFs leaned towards a more reaction rate limited system. The smoothed case consumed
 472 more reactant than the baseline case among all BTSs, especially for the reactions with longer BTSs
 473 (Figure 12c). Since the total exchange flux of the baseline case is 127% of the smoothed case with the
 474 high-frequency flow variations, we further scaled the percentage of reactant consumption of the baseline
 475 case in Figure 12c by 1.27 to reflect the difference of hydrologic exchange. The results (Figure 12d)
 476 revealed that daily high-frequency flow variations could potentially induce 16%~27% more reactant
 477 consumption over the smoothed case with dam operations removed for BTSs lower than 10h. It is
 478 interesting to note that the impacts of increased exchange volume were almost offset by the decrease of
 479 the overall RTD in the baseline case compared to the smoothed case for BTSs larger than 100h. This
 480 means the dam operation has the larger impacts on the reactions with shorter BTSs such as aerobic
 481 respiration and has fewer impacts on the reactions with longer BTSs.
 482



483
 484
 485 Figure 12. Impact of high-frequency flow variation on RTDs and biogeochemical reactions: a) baseline
 486 and smoothed river stage, b) simulated overall RTDs of baseline case and smoothed case, c) percentage of

487 total reactant consumption, and d) percentage of total reactant consumption scaled by exchange flux
488 volume.

489 **4. Discussions**

490 **4.1 Implication to Other Large River Corridors under Dynamic Flow Conditions**

491 Our results demonstrate the significant contributions of lateral exchange flows in the HEFs of a gravel-
492 bedded river system. The typical approach to evaluate HEFs at the large scale (reach to basin) is to
493 develop surrogate models with modest requirements for 1) hydrologic and hydrogeologic data and 2)
494 computational resources, such as the Networks with EXchange and Subsurface Storage (NEXSS)
495 (Gomez-Velez & Harvey, 2014). These analytical or semi-analytical models often rely on steady-state
496 flow conditions by assuming riverbed hyporheic exchange as the dominant exchange form in large river
497 corridors. Using this approach, (Gomez-Velez et al., 2015) concluded that vertical hyporheic exchange is
498 at least five times larger than the lateral hyporheic exchange in the Mississippi River network. Our
499 simulations and observations revealed that highly dynamic river fluctuations could create significant
500 lateral bank storage with a broader range of RTDs than previously reported (Kiel & Cardenas, 2014)
501 because of the gravel-bedded nature of the Columbia River and corridor. The lateral exchange flows
502 should be accounted for in the future development of river basin scale models for gravel-bedded systems.
503

504 Our simulated RTDs inherit the dynamic nature of river fluctuations. The impact of multi-frequency flow
505 variations interacting with the complex subsurface stratigraphy led to temporally and spatially varied
506 exchange patterns and RTDs. On one hand, the estimated RTDs from particle tracking had more long-
507 term components in flood years and more short-time components in drought years. Thus the overall shape
508 of the simulated RTDs depended strongly on the hydrological characteristics of the years being evaluated.
509 On the other hand, the frequency of river fluctuations has a profound influence on the shape of RTDs.
510 After removing the high-frequency fluctuations, the short-term components were significantly reduced
511 with resulted increasing mean RTDs. For future studies in a regulated river, we suggest 1) including the
512 river dynamic as one contributing factor in reduced-order models (e.g., NEXSS) and 2) using the
513 dominated frequencies of river fluctuations as one guidance for in-situ experiment designs (e.g.,
514 determining the sampling frequency of tracer tests).
515

516 The single mode RTDs and associated mean RTDs are still valuable overall statistics for quantifying the
517 biogeochemical impacts of RTDs in dynamic river systems. It is challenging to generate a universal
518 multimodal RTD for different locations and periods in a given river reach, and even more so for different
519 riverine systems. Despite that, we note that not all the modes of the multimodal RTDs have equal
520 contributions to biogeochemical transformation. The number of long-term modes (e.g., more than one
521 year) in the RTDs may be less critical since the transport scale will be long enough for most
522 biogeochemical reactions to reach completion (Harvey et al., 2018). For the reactions with fast reaction
523 rate (e.g., aerobic respiration), only first one or two modes impact reactant consumption. Thus, the impact
524 of RTD multimodality at any given site will depend on the BTSs of its dominant reactions. We found that
525 multimodality had the largest impact on biogeochemical reactions when the Damköhler number was close
526 to one. The single mode approximation to the multimodal RTD yields equivalent predictions (<5%
527 difference) of reactant consumption over the wide range of BTSs evaluated in this study. It seems a
528 single-mode RTD assumption can be generally applied to a multimodal system without inducing
529 excessive reactivity bias (e.g., 10%). However, it should be noted that uncertainty in the temperature
530 dependence of reactions, rate constants, and associated functional microbial populations, and local
531 vegetation (Graham et al., 2018) may produce even more significant uncertainty which is not accounted
532 for in this study. Expanded investigations leveraging more field survey data to evaluate the rate variation
533 in the same river reach and across many rivers would be valuable in future studies.
534

535 Dam-induced high-frequency stage fluctuations shorten the RTDs, which has significant impacts on
536 biogeochemical processes in the HEFs. The influences of the high-frequency stage fluctuation on HEFs
537 has been evaluated in several studies. High-frequency flow variations induce more flow reversals, higher

538 mass exchange, and deeper penetration depth of river thermal signals into the aquifer (Sawyer et al.,
539 2009; Shuai et al., 2019; Song et al., 2018). The increased mass exchange might accelerate the subsurface
540 reactions by providing more reactants (Song et al., 2018; Trauth & Fleckenstein, 2017) or decrease
541 specific reactions by inducing strong inhibition (Knights et al., 2017). The response of biogeochemical
542 reactions to stage fluctuation can be even more complicated if coupled with heterogeneous aquifer
543 properties and thermal-dependent reactions (Song et al., 2018). By comparing the overall RTD of the
544 baseline case and smoothed case, our results showed the high-frequency flow variation reduced the
545 reaction rates by shortening the residence time, while the overall reactant consumption rose due to
546 increased exchange volume. For reactions with longer reaction time scales (BTS>100h), the impacts of
547 increased mass exchange was offset by the residence time reduction. It should be noted that the
548 biogeochemical impacts of dam operation on arbitrary river systems can vary a lot according to distinct
549 sediment properties, flow dynamics, and microbial community, etc. These results of dam-induced stage
550 fluctuations have important implications for river management strategies that strive to optimize river
551 biogeochemical function for maximum ecological services, riverine health, and water quality.

552

553 **4.2 Limitations of this Study**

554 There are limitations to our modeling approach that should be acknowledged. First, water flow through
555 the alluvium was not directly modeled due to insufficient field measurements and the limitation of model
556 resolution. Whereas the conductance boundary condition adopted in this study is an adequate approach to
557 dampen river pulse propagation into the aquifer, it cannot represent the higher porosity (~0.4) of alluvium
558 layer as compared to the Hanford Formation (~0.2). Pore velocity in the near-shore area was
559 consequently overestimated by a factor of 2~3, artificially accelerating particle movements in the near-
560 shore area. In addition, a uniform conductance value for the flow model was fit to capture the
561 rising/falling trends of SpC measurements in the monitoring wells, but this was not a rigorous model
562 calibration. The actual exchange flow pattern was undoubtedly more complicated with a heterogeneous
563 riverbed permeability field that would lead to longer tailings of the RTDs.

564

565 Second, a simple first-order decay rate assumption was applied for the biogeochemical reactions. The
566 actual transformations are far more complex, which usually involve various electron donors (e.g., carbon)
567 and acceptors (e.g., oxygen and nitrate). Additionally, nonlinear interactions among reactions such as
568 inhibition of aerobic respiration to denitrification may be significant. These sophisticated biogeochemical
569 processes are not captured in the decay model used in our study.

570

571 Third, the smoothed case with a moving average was an estimation of the flow without dam operation, the
572 impacts of dam operation might be overestimated since moving average removed all sub-daily frequency
573 induced by both natural processes and anthropogenic activities.

574

575 Finally, the river channel geomorphology and hydrogeology also have strong controls on the locations of
576 exchange hot spots and potentially RTDs (Shuai et al., 2019), which were not fully accounted in this
577 study with the 1.6km river reach model. The influence of larger scale (10~100km scale) channel
578 geomorphology, hydrogeology and also riverbed sediment heterogeneity (Hou et al., 2019) on RTDs will
579 be addressed in our future work.

580

581 **5. Conclusion**

582 Dynamic flow variation is a common phenomenon in most large regulated rivers. Here, we used particle
583 tracking to evaluate influences of river stage variations on RTDs, and their biogeochemical reaction
584 potentials in the Hanford Reach under dam operations. Our results showed that river fluctuations created
585 rapidly changing losing-gaining conditions between river and groundwater, which interacted with
586 complex aquifer hydrogeological structure and led to complex exchange flow paths in the aquifer. This

587 study also demonstrated that RTDs of hydrological exchange flows can exhibit transient multimodal
588 distributions as compared to the time-invariant RTDs commonly observed under steady flow conditions.
589

590 Analysis of RTDs from temporal and spatial subsets of particles showed that temporal river flow variation
591 was the major contributor to multimodal RTDs. Statistical tests suggested that it may not be possible to
592 determine a precise shape of RTDs in an aquifer with complex hydrogeological features under dynamic
593 flow conditions. Thus it is needed to include river dynamics as one contributing factor in the assessment
594 of RTDs in similar managed river corridors and development of reduced-order models in large scale
595 (basin to watershed scale) studies. The simulations conducted under different flow conditions indicated
596 that the frequency components of flow variation also had substantial impacts on the multimodal
597 distribution of RTDs.
598

599 Our results also revealed that the multimodal characteristic of RTDs had a relatively small impact (<5%)
600 on the computed extent of reactant consumption of representative biogeochemical reactions. Although the
601 impacts of RTD multimodality at any given site will depend on the BTSs of its dominant reactions, our
602 results suggested the largest deviation of the conventional single-mode assumption from the simulated
603 multimodal RTDs appeared when the Damköhler number was close to one.
604

605 We found that high-frequency flow variations significantly altered the shape of RTDs and had a strong
606 influence on river corridor biogeochemistry compared to that under the case without high-frequency
607 flows. High-frequency flow variations created more short-time turnovers of exchange flow, which
608 induced more exchange volume with shorter residence time. The impact of high-frequency flow variation
609 on hyporheic biogeochemical reactions was found to be two-sided. The increased exchange volume
610 brought more biogeochemical reactants to the hydrologic exchange zone, but the short residence time
611 might not be sufficient for complete reaction. Our results indicated that the high-frequency flow
612 variations generally increased biogeochemical transformations within HEFs, especially for reactions with
613 higher rates. These findings have important ecological implications on how to maximize the potential
614 benefits, or minimize the drawbacks, of river regulation to river ecosystems.

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629

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