Determining in-channel (dead zone) transient storage by comparing solute transport in a bedrock channel–alluvial channel sequence, Oregon

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Received 21 July 2004; revised 10 March 2005; accepted 24 March 2005; published 21 June 2005.

[1] Current stream tracer techniques do not allow separation of in-channel dead zone (e.g., eddies) and out-of-channel (hyporheic) transient storage, yet this separation is important to understanding stream biogeochemical processes. We characterize in-channel transient storage with a rhodamine WT solute tracer experiment in a 304 m cascade-pool-type bedrock reach with no hyporheic zone. We compare the solute breakthrough curve (BTC) from this reach to that of an adjacent 367 m alluvial reach with significant hyporheic exchange. In the bedrock reach, transient storage has an exponential residence time distribution with a mean residence time of 3.0 hours and a ratio of transient storage to stream volume of 0.14, demonstrating that at moderate discharge, bedrock in-channel storage zones provide a small volume of transient storage with substantial residence time. In the alluvial reach, though pools are similar in size to those in the bedrock reach, transient storage has a power law residence time distribution with a mean residence time of >100 hours (estimated at nearly 1200 hours) and a ratio of storage to stream volume of 105. Because the in-channel hydraulics of bedrock reaches are simpler than alluvial step-pool reaches, the bedrock results are probably a lower end-member with respect to volume and residence time, though they demonstrate that in-channel storage may be appreciable in some reaches. These results suggest that in-stream dead zone transient storage may be accurately simulated by exponential RTDs but that hyporheic exchange is better simulated with a power law RTD as a consequence of more complicated flow path and exchange dynamics.

Citation: Gooseff, M. N., J. LaNier, R. Haggerty, and K. Kokkeler (2005), Determining in-channel (dead zone) transient storage by comparing solute transport in a bedrock channel–alluvial channel sequence, Oregon, *Water Resour. Res.*, *41*, W06014, doi:10.1029/2004WR003513.

1. Introduction

[2] Study of transient storage in stream channels is important to understanding biogeochemical transport and fate within stream ecosystems, particularly in nutrient cycling [e.g., *Mulholland et al.*, 1997; *Thomas et al.*, 2003; *Gooseff et al.*, 2004]. Transient storage occurs as a result of two mechanisms: (1) in-channel storage, the exchange of stream water between the relatively fast moving water in the stream channel and in-channel dead zones (i.e., side pools or eddies) [*Thackston and Schnelle*, 1970; *Valentine and Wood*, 1977], and (2) hyporheic exchange, the exchange of stream water between the channel and streambed sediments, the hyporheic zone [*Bencala and Walters*, 1983; *Savant et al.*, 1987]. The most widely used technique to characterize reach-integrated transport dynamics is the stream tracer experiment, in which a dissolved tracer is introduced to the stream and solute samples are obtained downstream to define breakthrough curves (BTCs). Subsequent simulation of a solute transport model to BTC data provides estimates of reach-integrated velocity, dispersion, and transient storage parameters.

[3] The stream tracer technique does not allow for the separation of the two transient storage mechanisms, because in most reaches, solute transport is subject to both in-channel and hyporheic storage. *Harvey and Bencala* [1993] detailed differences between stream solute BTC (indicative of reach-scale transient storage residence times) and hyporheic well solute breakthrough dynamics, suggesting that reach-scale responses are sensitive to both transient storage mechanisms. *Choi et al.* [2000] evaluated a multiple exponential residence time distribution (RTD) storage zone transient storage model and found that unless the transient storage mechanisms are drastically different, a multiple storage zone model is not appropriate to discriminate in-channel from hyporheic transient storage in most stream tracer experiments, because it is difficult to discern one storage zone from another.

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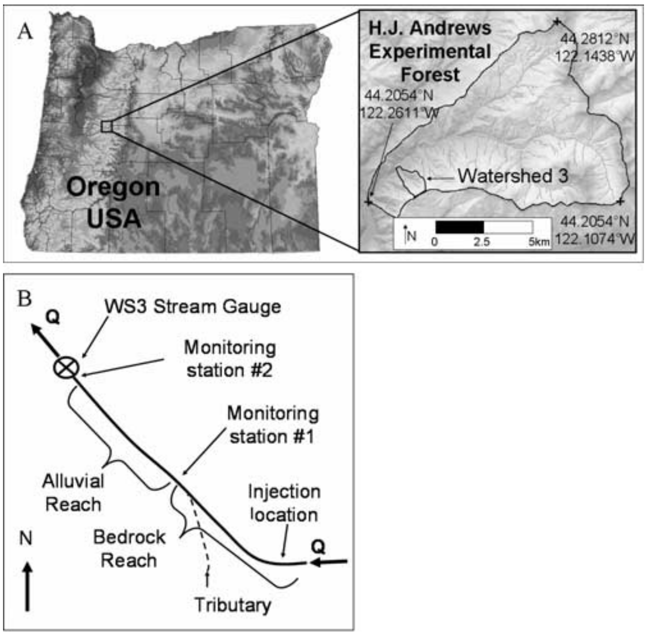

Figure 1. (a) Location map of watershed 3 (WS03) in the H.J. Andrews Experimental Forest and (b) schematic of experimental reaches. See color version of this figure at back of this issue.

[4] Transient storage increases contact time between stream solutes and biofilms, microbial communities that interact with these solutes. However, because current stream solute transport approaches do not allow investigators to partition dead zone from hyporheic exchange, assuming that all storage and all biogeochemical cycling is hyporheic may lead to difficulties in the interpretation of biogeochemical activity, particularly for photoactive or redox-sensitive solutes. In a study of Hubbard Brook stream N cycling and fate, *Hall et al.* [2002] found that conservative tracer concentrations in a side-pool (in-channel storage) behaved similar to in-storage solute concentrations predicted by transient storage modeling, which, they conclude suggests that hyporheic exchange is not an important process in those streams (and so neither is hyporheic N retention). However, *Mulholland et al.* [1997] and *Thomas et al.* [2003] have shown that hyporheic transient storage is important to P and N retention, respectively. *McKnight et al.* [2002] corroborated stream tracer data and downstream patterns in aromticity of injected fulvic acid, and found strong sorption of fulvic acid to streambed and hyporheic sediments in an acidic stream in Colorado. Their transient storage simulations suggest appreciable storage and exchange, though without the ability to discriminate between hyporheic and in-channel storage, they could not determine whether photoreduction of metals in surface storage locations or hyporheic reaction surfaces dominate fulvic acid sorption.

[5] The goal of this paper is to compare the difference in solute dynamics in two very different stream reaches: one bedrock reach with no alluvium, in which any transient storage behavior is a result of in-channel processes, and an adjacent (downstream) alluvial reach that should store water and solute in-channel and in-hyporheic, in the context of discriminating between in el and hyporheic transient storage processes. We use a stream tracer technique that is sensitive to late time tracer behavior, and simulate the observed BTCs with a general residence time distribution solute transport model. We also present the results of a pool survey in both reaches, to compare in-channel storage zone features. We propose that the bedrock reach BTC reflects only in-channel transient storage and that the alluvial reach reflects both in-stream and hyporheic transient storage processes, thus in addition to simulating the observed data in both reaches, we also simulate solute transport in the alluvial reach with in-channel storage parameters derived from the bedrock reach solute simulation.

[6] The only other published tracer experiment in a bedrock channel we could find was from a large experiment performed on the Colorado River through the Grand Canyon [*Graf*, 1995], which had the purpose of estimating experimental flood wave velocity, rather than river transient storage processes. Flume experiments have been conducted with artificial dead zones [*Valentine and Wood*, 1977; *Uijttewaal et al.*, 2001, *Weitbrecht*, 2004]. These experiments show that eddies and dead zones in model streams have exponential residence distributions with mean transient storage residence times of 35–100 times the ratio of the width of the eddy to the stream velocity. The research reported here directly compares the storage characteristics of adjacent bedrock and alluvial reaches with the objective of determining in-channel storage in a field setting.

2. Site Description and Methods

[7] We investigated transient storage dynamics in first- and second-order reaches of Watershed 3 (WS03) in the H.J. Andrews Experimental Forest in central Oregon, USA (Figure 1). WS03 experienced a large debris flow during a rain-on-snow flood event in February 1996, and the main first-order stream channel was scoured to bedrock. This channel now has a cascade-pool morphology, free of alluvium. Thus it represents a natural channel with in-channel storage potential, but no hyporheic zone. The second-order reach experienced some scour and deposition from the debris flow, resulting in a streambed with extensive colluvial and entrained alluvial fill (hereafter simply referred to as alluvium) and a step-pool morphology. From a 10 m digital elevation model of the watershed, we estimate the slope of the bedrock reach to be 0.28, and the slope of the alluvial reach to be 0.15. *Wondzell* [2005] performed NaCl tracer experiments in both of these reaches, showing that the storage zone in the bedrock reach is small compared to that of the alluvial reach. *Wondzell* [2005] also reports NaCl tracer arrival times to hyporheic wells within the alluvial reach, indicating that transient storage in the alluvial reach is largely due to hyporheic exchange. Other work by *Haggerty et al.* [2002] documented a power law residence time distribution in the second-order alluvial reach of WS03 with a rhodamine WT dye transport experiment.

2.1. Stream Tracer Experiment

[8] A continuous-addition stream tracer experiment was performed using rhodamine WT (RWT) dye (Bright Dyes, Miamisburg, OH), for 4 hours on 6 April 2002. A Mariotte bottle was used to control the RWT addition rate (~2.2 mg-RWT s^{-1}). Stream water RWT concentrations were analyzed in the field with two Turner Designs Model 10-AU

fluorometers (Turner Designs, Inc., Sunnyvale, CA) fitted with flow-through cells, one located 304 m downstream of the drip site (the end of the bedrock reach), the other located 667 m downstream of the drip site (the end of the alluvial reach) at the WS03 stream gauge (Figure 1). A small tributary to the WS03 stream joins the first-order channel just below the bedrock reach sampling site. Stream RWT concentrations were recorded at a 5 s interval for 16.5 hours below the bedrock reach, and for 21 hours below the alluvial reach. An ISCO (ISCO Inc., Lincoln, NE) automated water sampler continued to sample at the WS03 gauge house for 3 more days on a 2 hour interval.

[9] Stream discharge at the head and end of the bedrock reach was measured with a Marsh-McBirney model 200 velocity meter (Marsh-McBirney, Inc., Fredrick, MD) periodically throughout the experiment. Stream discharge was also recorded on a 15 min interval at the end of the alluvial reach (where we collected stream RWT data), at the WS03 stream gauge, operated by the H.J. Andrews Experimental Forest.

2.2. Solute Transport Simulation

[10] RWT tracer transport was simulated using the STAMMT-L general residence time distribution (RTD) solute transport model [*Haggerty and Reeves*, 2002]. Previous RWT solute transport studies in this and other alluvial stream reaches within the H.J. Andrews Experimental Forest by *Haggerty et al.* [2002] and *Gooseff et al.* [2003] revealed only power law RTDs for transient storage. We present three simulations of RWT transport utilizing STAMMT-L. In simulation 1 we simulate the bedrock reach BTC to determine in-channel exchange characteristics. In simulation 2 we present the simulation of the combined in-channel and hyporheic transient storage in the alluvial reach. In simulation 3 we use the bedrock simulation parameters (from simulation 1), combined with the appropriate length and velocity from simulation 2 to estimate in-channel transient storage in the alluvial reach.

[11] The STAMMT-L model applies a user-specified RTD to a general one-dimensional advection-dispersion transport equation. For an initially tracer-free system with no longitudinal inputs the transport equation is

$$\frac{\partial C}{\partial t} = -v\frac{\partial C}{\partial x} + D_L\frac{\partial^2 C}{\partial x^2} - \beta_{tot}\frac{\partial}{\partial t}\int_0^t C(\tau)g^*(t-\tau)d\tau \qquad (1)$$

where v is the mean advection velocity (m s^{-1}), D_L is the longitudinal dispersion (m^2 s^{-1}), β_{tot} is the ratio of storage to stream volumes (dimensionless), C is the solute concentration in the stream (μg L^{-1}), and τ is a lag time (s). In the last term of (1), $g^*(t)$ is convolved with the stream concentration to represent exchange with the transient storage zone following an appropriate RTD. This would be formulated as

$$g^*(t) = \alpha e^{-\alpha t} \qquad (2)$$

for an exponential RTD where α is the first-order rate coefficient (s^{-1}). This is similar to the standard first-order model [e.g., *Thackston and Schnelle*, 1970; *Bencala and Walters*, 1983]. The $g^*(t)$ for a power law RTD in the storage zone is expressed as

$$g^*(t) = \frac{(k-2)}{\left(\alpha_{\max}^{k-2} - \alpha_{\min}^{k-2}\right)}\int_{\alpha_{\min}}^{\alpha_{\max}} \alpha^{k-2}e^{-\alpha t}d\alpha \qquad (3)$$

where α is a rate coefficient (s^{-1}), k is the power law exponent, which corresponds to the slope of late time concentration tail after a pulse injection [*Haggerty et al.*, 2000]. Equation (3) defines a power law function with cutoffs at $\alpha_{\max}$ and $\alpha_{\min}$, with behavior $g^*(t) \sim t^{1-k}$ between the inverse of those limits. The governing equations of the STAMMT-L model do not include a direct mass loss term for nonconservative solutes. Instead, a mass loss factor is used

$$m_{rec} = \frac{m_{inj}}{\varphi} \qquad (4)$$

where m_{rec} is the mass recovered, as simulated, at the end of the reach (g), m_{inj} is the mass injected (g), and φ is the mass loss factor (dimensionless) due to irreversible sorption or unsampled tracer in by-passing hyporheic flow. Parameters were estimated within STAMMT-L using a nonlinear least squares algorithm [*Marquardt*, 1963] that minimized the sum of square errors on the logarithms of concentrations. In the bedrock reach simulation (simulation 1), v, D_L, β_{tot}, and α were estimated, and in the combined transient storage alluvial reach simulation (simulation 2), v, D_L, β_{tot}, k, and φ were estimated. The solute BTC observed at the end of the bedrock reach was used as the upstream boundary condition for simulations 2 and 3. In simulation 3, parameter values for D_L, β_{tot}, and α from simulation 1 were used, and v and length of the alluvial reach from simulation 2 was used. For all simulations we report root mean squared error (RMSE) as defined by *Bard* [1974, p. 178] and *Haggerty and Gorelick* [1998]:

$$\mathrm{RMSE} = \left[\frac{\sum_{j=1}^{N_d}\left(\ln\frac{C_{sim,j}}{C_{obs,j}}\right)^2}{N_d - N_p}\right]^{1/2} \qquad (5)$$

where, $C_{sim,j}$ is the jth simulated solute concentration, $C_{obs,j}$ is the jth observed solute concentration, N_d is the number of observed concentration values, and N_p is the number of parameters to be estimated. A RMSE value close to 0 indicates an excellent fit to the observations.

2.3. Rhodamine WT Sorption Isotherm

[12] Bed sediment from the alluvial reach of WS03 was sampled in the spring of 2002. The sample was dried in a drying oven for more than 100 hours. After drying, the sample was sieved and the <2 mm fraction was retained, from which 2.0 g was placed in each of 30 polycentrifuge cuvettes. 30 mL of WS03 stream water was added to each cuvette. After each cuvette was subsequently mechanically shaken for 68 hours and centrifuged for 1 hour, 25 mL of supernatant was decanted and replaced with 25 mL of WS03 stream water. This process was repeated with 12 hours of shaking and the final supernatant was sampled

Table 1. Sizes of Pools in the Upper 304 m Bedrock Reach and Lower 363 m Alluvial Reach, Reported as Means (± Standard Deviation)[a]

	n	Length, m	Width W_P, m	Depth, m	W_E, m
Bedrock	16	1.69 (±0.65)	1.39 (±0.52)	0.32 (±0.17)	0.35 (±0.22)
Alluvial	14	1.85 (±0.93)	1.35 (±0.71)	0.24 (±0.10)	0.46 (±0.35)

[a]Here, n is number, and W_E is eddy width calculated using equation (6).

for RWT fluorescence with the same Turner Designs 10-AU (outfitted with a cuvette holder). None were found to fluoresce. Seven RWT solutions were developed to determine the RWT sorption isotherm, with target concentrations from 0.025 μg L^{-1} to 70 μg L^{-1}. Three replicates of sediment sample and RWT solution (including blanks with WS03 stream water) were shaken for approximately 96 hours. All samples were again centrifuged and supernatant was collected for RWT concentration analysis. Sorbed RWT mass (S) was calculated as the change in concentration during incubation per mass of sediment in the incubation.

2.4. Pool Survey

[13] Pool sizes in both reaches were surveyed 24 June 2004. Pool length, width, maximum depth, average depth, inflow width, and outflow width were measured. Averages and standard deviations of most of these are reported in Table 1. Table 1 also reports an average and standard deviation for the eddy width, computed as

$$W_E = \frac{1}{2}\left(W_P - \frac{W_I + W_O}{2}\right) \tag{6}$$

where W_E is the eddy width (m), W_P is the measured pool width (m), W_I is the measured pool inflow width (m), and W_O is the measured pool outflow width (m). The eddy width for each pool is assumed to be the distance from the centerline running between the edge of the inflow and outflow and the lateral edge of the pool. The fact that the pool sizes were measured after the stream tracer test (under lower discharge conditions) is assumed unimportant because the pool size is controlled primarily by geomorphology and not by discharge.

3. Results

[14] Discharge at the WS03 stream gauge was nearly constant during the tracer drip and during the data collection period at the end of the bedrock reach, but increased significantly a few days later, while measurable tracer concentrations were still being collected at the end of the alluvial reach (Figure 2). Because of the high discharges, the autosampler water intake was displaced from the stream prior to complete recovery of the injected tracer. Solute transport was simulated as flux (Q^*C), rather than concentrations, similar to the approach of *Haggerty et al.* [2002]. This approach assumes that hyporheic RTD and β_{tot} are constant with discharge, which is reasonable for the small changes in discharge through the time of most of our data collection. For reporting purposes, we give concentrations.

[15] The continuous stream tracer experiment resulted in a steady state concentrat the bedrock reach, and complete flushing of the tracer within 12 hours of end the drip (Figure 3a). The tracer BTC was best simulated (RMSE = 0.19) as an exponential exchange process, with β_{tot} = 0.14, v = 0.30 m s^{-1}, D_L = 0.89 m^2 s^{-1}, φ = 1.00, and α = 9.17 $\times$ 10^{-5} s^{-1}, which corresponds to a mean storage residence time (α^{-1}) of 3.03 hours. The alluvial reach BTC is simulated appropriately with a power law RTD, RMSE = 0.08 (Figure 3b). Simulation 2 best fit the stream observations with β_{tot} = 105.2, v = 0.12 m s^{-1}, D_L = 0.10 m^2 s^{-1}, k = 1.28, and φ = 1.03, which corresponds to a mean transient storage residence time (harmonic mean of integration limits in equation (3) $\alpha_{\min}$ = 10^{-7} s^{-1}, $\alpha_{\max}$ = 10^{-1} s^{-1}, an estimate of a mean transient storage residence time for a power law RTD) of 1166 hours. This mean cannot be estimated with confidence because it is far beyond the limits of our data, a result typical of power law BTCs and RTDs. The parameter values are very similar to those found by *Haggerty et al.* [2002] for the same alluvial reach. Approximately 31.5 g of RWT (active ingredient) was injected over the 4 hour drip, 26.4 g (84% of injected mass) recovered at the end of the bedrock reach, and 23.2 g (74% of injected mass) recovered at the end of the alluvial reach. The lower recovery at the end of the alluvial reach is expected as the very end of the solute BTC tail was not sampled due to the high discharges (Figure 3). While these recovery rates are not ideal, there is significant potential for our mass balances to be in error because measured discharge at the end of the bedrock reach may not be accurate.

[16] Simulation 3, of solute transport in the alluvial reach using the bedrock transport parameters (β_{tot}, D_L, and α), and a v of 0.12 m s^{-1}, does not fit the solute data observed at the end of the alluvial reach well, RMSE = 1.87. Early time simulated concentrations arrive prior to the observations and simulated plateau concentrations are higher than observed concentrations (Figure 3b), indicating that the alluvial reach has a more extensive storage zone, and likely a different longitudinal dispersion than the bedrock reach. Late time

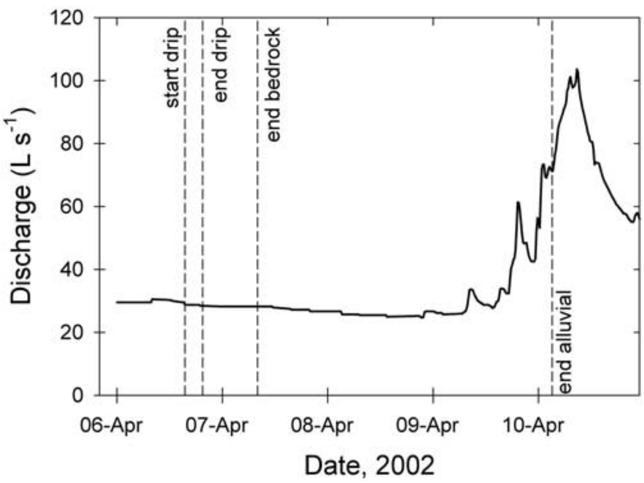

Figure 2. Watershed 3 hydrograph for 6–10 April 2002, recorded at the WS03 gauge house, 667 m downstream of the RWT drip location. The bedrock reach ends 304 m downstream from the drip location. Start and end of continuous drip of tracer is noted, as well as the end times of sampling at the end of the bedrock reach and end of the alluvial reach.

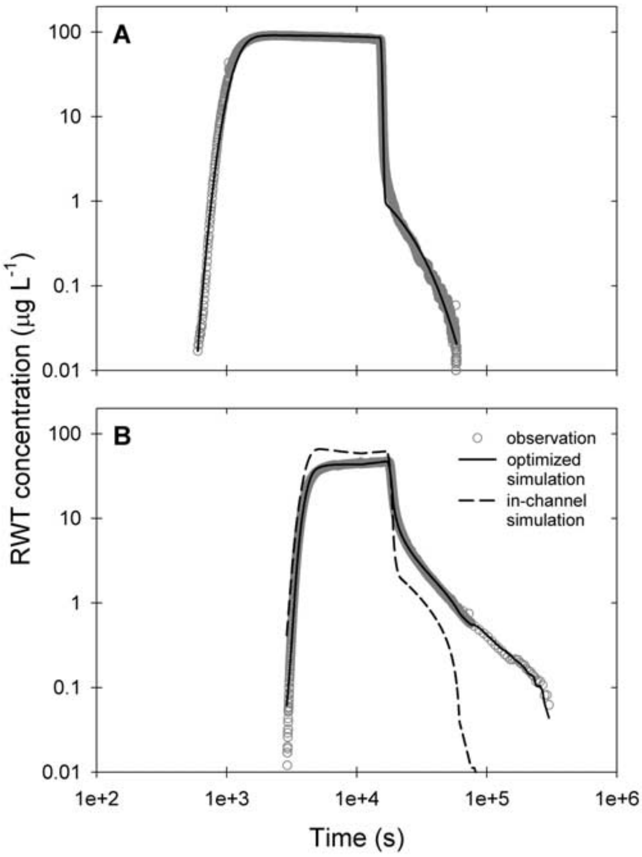

Figure 3. Observations and simulations of WS03 RWT tracer experiment, 6 April 2002 in (a) the 304 m bedrock reach (simulation 1) and (b) the downstream 367 m alluvial reach (simulations 2 and 3). All times are relative to the start of the drip (time 0 s).

simulated concentrations are underestimated by the exponential simulation (Figure 3b), indicative of the slower hyporheic exchange in the alluvial reach, compared to the in-channel storage exchange, as simulated.

[17] Pool and eddy sizes and the number of pools are similar in both reaches (Table 1). Velocity as estimated from tracer test data is smaller in the alluvial reach (0.12 m s^{-1}) than in the bedrock reach (0.30 m s^{-1}). *Valentine and Wood* [1977], *Uijttewaal et al.* [2001], and *Weitbrecht* [2004] report in-channel (dead zone) transient storage residence time distributions that are exponential, with a mean residence time t_α of the form

$$t_\alpha = \frac{a_m W_E}{\kappa a_i v} \quad (7)$$

where κ is an empirical constant; a_m (m) and a_i (m) are the respective dead zone and channel depths. Given that similar dynamics are operating in both alluvial and bedrock reaches, we assume that κ and the ratio a_m/a_i are similar in both. In-channel mean transient storage residence time is proportional to the ratio of eddy widths to channel velocity. Therefore, if transient storage is controlled by in-channel processes, we would expect both the bedrock and alluvial reaches to have transient storage zones with exponential RTDs, and a mean t nt storage residence time approximately 3.3 times greater in the alluvial reach than in the bedrock reach (W_E/v is 3.3 times larger in the alluvial reach than the bedrock reach). However, the alluvial reach has a power law RTD, and has a mean transient storage residence time estimated to be 385 times greater than the bedrock reach, suggesting that hyporheic exchange dictates the late time breakthrough curve behavior.

[18] Our experiment suggests mean transient storage residence times of approximately 9500 times the ratio of the eddy width to the stream velocity (i.e., κ = 1/9500), compared to 35–100 times this ratio recommended by *Valentine and Wood* [1977] and *Uijttewaal et al.* [2001] for groynes (wing dams designed to control sediment transport in large rivers). Part of the difference may be that RWT sorbs to bed material. However, it is also possible that natural pools have larger residence times than groynes, based on their hydraulic geometry. Additional research on dead zone hydraulic geometry and retention is warranted.

[19] The results of the RWT sorption experiments suggest that the sorption isotherm is linear for RWT and WS03 streambed sediments (Figure 4), as noted by the very high correlation coefficient for a linear model fit. The resulting K_d value is 0.0332 L g^{-1} of sediment.

4. Discussion

[20] Stream tracer results are typically confounded by in-channel storage processes that may contribute to transient storage. Our approach was to conduct a stream tracer experiment in adjacent bedrock and alluvial stream reaches. The stream tracer tailing from transient storage in the bedrock reach is due to in-channel dead zone storage processes because there is no hyporheic zone. As expected, the stream tracer pulse was flushed from the bedrock reach much faster (within 11.84 hours of the end of the injection) than in the immediate downstream alluvial reach, in which tracer was measured flushing out for at least 4 days after the end of the injection.

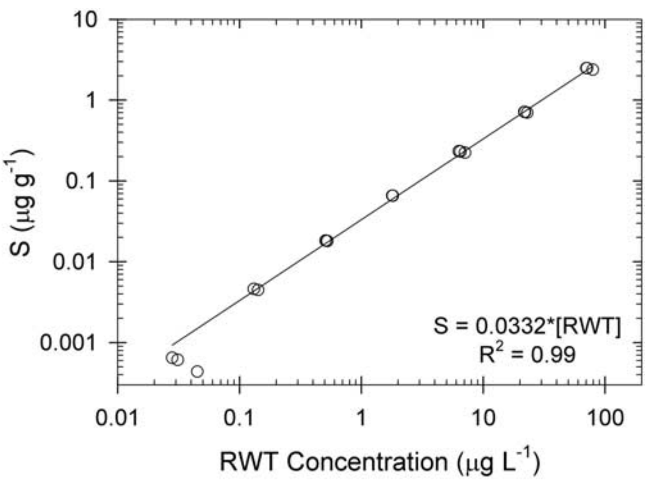

Figure 4. Rhodamine WT (RWT) sorption isotherm for WS03 streambed sediments (<2 mm size fraction), where S is the sorbed mass of RWT per mass of sediment. Three replicates were run for each RWT concentration value. Resulting K_d value is 0.0332 L g^{-1}.

[21] Our study design used RWT in a continuous injection so that we could take advantage of the greater tracer concentration precision (4 orders of magnitude from 0.01 ppb to 100 ppb), than more commonly used ionic tracers. The advantage of using RWT is that we can more precisely quantify transient storage dynamics because of the greater measurable concentration range of RWT compared to ionic tracers. *Wondzell* [2005] conducted NaCl stream tracer experiments in the same reaches of WS03 to determine the role of morphology and discharge on reach-scale transient storage behavior. Wondzell's solute transport simulations using OTIS-P (exponential RTD model [*Runkel*, 1998]) yielded qualitatively similar results – a smaller storage zone in the bedrock reach than in the alluvial reach, and a shorter mean transient storage residence time in the bedrock reach (<1 hour) than in the alluvial reach (as much as 25 hours). Wondzell's results show lower transient storage residence times than ours. The difference is likely due to the combination of two effects: (1) the exponential residence time model in combination with NaCl data is much less sensitive to long residence times and (2) RWT sorbs.

[22] RWT sorbs to streambed sediments. However, we have found this sorption to be characterized by a linear isotherm for WS03 sediments (Figure 4), indicating that RWT BTCs are indicative of transport dynamics and not simply a result of sorption-desorption processes. Sorption is likely to be stronger in the alluvial reach (greater surface area and more organic material) than in the bedrock reach, and because it is linear, sorption does not change the shape of the power law RTD observed in the alluvial reach. It should also be noted that the sorption isotherm reported here for RWT is likely an overestimate of the true in situ isotherm for hyporheic sediments in the streambed, because we focused on the fine fraction of the hyporheic sediment sample acquired, and because field sediment conditions (sediment surface contact with hyporheic waters, temperatures, etc.) are different than those we established in the laboratory. Sorption may, however, increase the estimated mean transient storage residence time in the alluvial reach. Thus our estimate of mean transient storage residence time based on the stream RWT recovery may be larger than for water. This may explain some of the differences between our results and Wondzell's, where our estimated mean transient storage residence time in the alluvial reach (>1000 hours) are significantly greater than Wondzell's (up to 25 hours). Our mean transient storage residence time for the bedrock reach (3.03 hours) is of the same order as Wondzell's (0.71 hours). This comparison suggests that additional research on discrimination of in situ hyporheic RWT sorption processes is warranted.

[23] Although our results are based on a single experiment during particular discharge conditions, it appears appropriate to model in-channel storage with an exponential RTD. This is consistent with the concept of in-stream eddy diffusion, whereby mass is transferred from the thalweg to eddies and back again, as proposed in early stream solute transport studies that included "dead zones" [e.g., *Valentine and Wood*, 1977]. Eddy residence time in streams, while not well studied theoretically, should have a mean residence time that scales with eddy size and inversely with stream velocity. However, it is also important to note that streamflow in the bedrock reach was moderate during this experiment, which will have an impact on the residence time of bedrock pools, and the ratio of active pool volume to dead zone volume. At very low flows, one may find a very different RTD as turnover times in the pools increase.

[24] As found previously by *Haggerty et al.* [2002], the alluvial reach requires a power law RTD for the transient storage zone. This transient storage is dominated by hyporheic exchange, though the early time portions of the RTD are undoubtedly affected by in-channel storage. However, given the large differences in both the volumes and mean transient storage residence times between the bedrock reach and alluvial reach (β_{tot} = 0.14 and 105, and mean transient storage residence time = 3.03 and 1166 hours, respectively), it is likely not a great exaggeration to attribute most of the transient storage in the alluvial reach to hyporheic exchange. Though, had a photoreactive biogeochemical process also been considered, the reach-scale reaction processes may have been very sensitive to this balance between in-channel and subsurface storage.

[25] These results suggest that perhaps a two storage zone model, similar to those of *Castro and Hornberger* [1991], *Choi et al.* [2000], and *Gooseff et al.* [2004] is an appropriate first step toward modeling in-channel storage and hyporheic transient storage with a conventional model. Previous efforts by *Choi et al.* [2000] and *Gooseff et al.* [2004] have assessed multiple storage exponential storage zone dynamics. However, hyporheic exchange should be represented by power law [e.g., *Haggerty et al.*, 2002; *Gooseff et al.*, 2003] or, as other studies have suggested, a lognormal [*Wörman et al.*, 2002] RTD. Under some conditions it may be appropriate to simplify the hyporheic exchange representation to an exponential RTD. Appropriate circumstances for simplification would be (1) an RTD with small variance, (2) a lack of need for late time or small-concentration accuracy (as is common with salt tracers), or (3) a lack of need for changing space or timescales in the model.

[26] Appropriate characterization of in-channel RTDs is important for discriminating possible photochemical versus subsurface biogeochemical transformations [*Gooseff et al.*, 2003, Figure 7]. On the basis of these findings, future research into in-channel storage zones is certainly warranted, perhaps in other bedrock reaches at varying discharge rates, or in stream reaches underlain by permafrost, because simultaneous discrimination between in-channel and hyporheic storage in typical stream channels is difficult.

5. Conclusions

[27] To the best of our knowledge, this is the first attempt to discriminate in-channel transient storage from hyporheic exchange in a field study. Our findings suggest that in-channel storage processes may be appreciable, particularly with respect to biogeochemical transformation timescales. The qualitative difference in RWT BTCs at the end of the bedrock reach and the end of the alluvial reach suggest that there is significantly greater and longer timescale transient storage in the alluvial reach. Further, the transient storage behavior in the reaches is quantitatively different: the bedrock reach demonstrates exponential-type transient storage behavior, whereas the alluvial reach demonstrates

power law residence time behavior. We conclude that these differences in transient storage behavior are directly related to the different transient storage processes: in-channel eddy exchange versus hyporheic exchange, in-channel features, and channel composition.

[28] Additional stream tracer experiments in bedrock reaches, utilizing sensitive tracers (such as RWT), are warranted to further investigate the potential for in-channel storage dynamics in a range of channel complexities. We expect that a database of these storage zone sizes will be one approach toward discriminating in-channel transient storage from hyporheic transient storage. In addition, experiments in modified bedrock reaches, with added alluvium may also sufficiently increase our understanding of in-channel transient storage dynamics.

[29] **Acknowledgments.** We are grateful to Kevin McGuire, Gregory Stewart, Nick Scheidt, and Jeff Ninnemann for assistance with field work, and to Jeff McDonnell for loan of equipment. We would also like to thank Kevin McGuire for a helpful review of this manuscript. This work was supported by NSF grant EAR 99-09564.

References

Bard, Y. (1974), *Nonlinear Parameter Estimation*, Elsevier, New York.
Bencala, K. E., and R. A. Walters (1983), Simulation of solute transport in a mountain pool-and-riffle stream: A transient storage model, *Water Resour. Res.*, *19*, 718–724.
Castro, N. M., and G. M. Hornberger (1991), Surface-subsurface water interactions in an alluviated mountain stream channel, *Water Resour. Res.*, *27*, 1613–1621.
Choi, J., J. W. Harvey, and M. H. Conklin (2000), Use of multi-parameter sensitivity analysis to determine relative importance of factors influencing natural attenuation of mining contaminants, *Water Resour. Res.*, *36*, 1511–1518.
Gooseff, M. N., S. M. Wondzell, R. Haggerty, and J. K. Anderson (2003), Comparing transient storage modeling and residence time distribution (RTD) analysis in geomorphically varied reaches in the Lookout Creek basin, Oregon, USA, *Adv. Water Resour.*, *26*, 925–937.
Gooseff, M. N., D. M. McKnight, R. L. Runkel, and J. H. Duff (2004), Denitrification and hydrologic transient storage in a glacial meltwater stream, McMurdo Dry Valleys, Antarctica, *Limnol. Oceanogr.*, *49*, 1884–1895, doi:10.1002/hyp.5790.
Graf, J. B. (1995), Measured and predicted velocity and longitudinal dispersion at steady and unsteady flow, Colorado River, Glen Canyon Dam to Lake Mead, *Water Resour. Bull.*, *31*, 265–281.
Haggerty, R., and S. M. Gorelick (1998), Modeling mass transfer processes in soil columns with pore-scale heterogeneity, *Soil Sci. Soc. Am. J.*, *62*(1), 62–74.
Haggerty, R., and P. C. Reeves (2002), STAMMT-L version 1.0 user's manual, *ERMS 520308*, 76 pp., Sandia Natl. Lab., Albuquerque, N. M.
Haggerty, R., S. A. McKenna, and L. C. Meigs (2000), On the late-time behavior of tracer test breakthrough curves, *Water Resour. Res.*, *36*, 3467–3479.
Haggerty, R., S. M. Wondzell, and M. A. Johnson (2002), Power-law residence time distribution in the hyporheic zone of a 2nd-order mountain stream, *Geophys. Res. Lett.*, *29*(13), 1640, doi:10.1029/2002GL014743.
Hall, R. O., E. S. Bernhardt, and G. E. Likens (2002), Relating nutrient uptake with transient storage in forested mountain streams, *Limnol. Oceanogr.*, *47*, 255–265.
Harvey, J. W., and K. E. Bencala (1993), The effect of streambed topography on surface-subsurface water exchange in mountain catchments, *Water Resour. Res.*, *29*, 89–98.
Marquardt, D. W. (1963), An algorithm for least-squares estimation of nonlinear parameters, *J. Soc. Ind. Appl. Math.*, *11*, 431–441.
McKnight, D. M., G. M. Hornberger, K. E. Bencala, and E. W. Boyer (2002), In-stream sorption of fulvic acid in an acidic stream: A stream-scale transport experiment, *Water Resour. Res.*, *38*(1), 1005, doi:10.1029/2001WR000269.
Mulholland, P. J., E. R. Marzolf, J. R. Webster, D. R. Hart, and S. P. Hendricks (1997), Evidence that hyporheic zones increase heterotrophic metabolism and phosphorous uptake in forest streams, *Limnol. Oceanogr.*, *42*, 443–451.
Runkel, R. L. (1998), One-dimensional transport with inflow and storage (OTIS): A solute transport model for streams and rivers, *U.S. Geol. Surv. Water Resour. Invest. Rep., 98-4018*.
Savant, S. A., D. D. Reible, and L. J. Thibodeaux (1987), Convective transport within stable river sediments, *Water Resour. Res.*, *23*, 1763–1768.
Thackston, E. L., and K. B. Schnelle Jr. (1970), Predicting effects of dead zones on stream mixing, *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.*, *96*(SA2), 319–331.
Thomas, S. A., H. M. Valett, J. R. Webster, and P. J. Mulholland (2003), A regression approach to estimating reactive solute uptake in advective and transient storage zones of stream ecosystems, *Adv. Water Resour.*, *22*, 965–976.
Uijttewaal, W. S. J., D. Lehmann, and A. van Mazijk (2001), Exchange processes between a river and its groyne fields: Model experiments, *J. Hydraul. Eng.*, *127*(11), 928–936.
Valentine, E. M., and I. R. Wood (1977), Longitudinal dispersion within dead zones, *J. Hydraul. Div. Am. Soc. Civ. Eng.*, *103*, 975–1006.
Weitbrecht, V. (2004), Influence of dead-water zones on the dispersive mass transport in rivers, Ph.D. dissertation, Univ. of Karlsruhe, Karlsruhe, Germany.
Wondzell, S. M. (2005), Effect of morphology and discharge on hyporheic exchange flows in two small streams in the Cascade Mountains of Oregon, USA, *Hydrol. Processes*, in press.
Wörman, A., A. I. Packman, H. Johansson, and K. Jonsson (2002), Effect of flow induced exchange in hyporheic zones on longitudinal transport of solutes in streams and rivers, *Water Resour. Res.*, *38*(1), 1001, doi:10.1029/2001WR000769.

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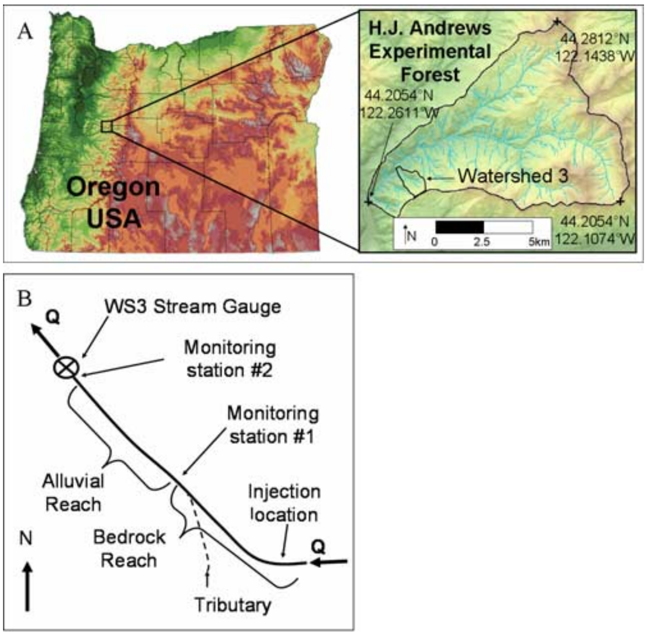

Figure 1. (a) Location map of watershed 3 (WS03) in the H.J. Andrews Experimental Forest and (b) schematic of experimental reaches.