Substrate size and heterogeneity control anomalous transport in small streams

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1. Key points

Main point 1: Streambed sediment controls anomalous transport.

Main point 2: A truncation of the anomalous behavior is observed.

Main point 3: Our observations provide a strong foundation for building better models.

2. Abstract

In alluvial systems, substrate characteristics play a critical role in slowing downstream transport of both water and solutes. We present results from solute injection experiments testing the influence of sediment size (pea gravel vs. coarse gravel) and heterogeneity (alternating sections vs. well-mixed reaches) on solute transport dynamics in four experimental streams at the Notre Dame Linked Experimental Ecosystem Facility (ND-LEEF). The stream with pea gravel resulted in more long-term retention than the stream with coarse gravel, whereas both streams with heterogeneous substrate (alternated and mixed) fell between with similar late-time scaling. Inverse modeling of solute breakthrough curves suggested that residence times were distributed according to a truncated power-law. While conservative solute transport in all four streams was anomalous, truncation times were influenced by sediment size, with the smaller pea gravel exhibiting a later truncation time than the coarse gravel, and the two streams with heterogeneous substrate having an intermediate cut-off. These results uniquely associate transport scaling with substrate char-

acteristics in fluvial systems, revealing truncation timescales that had been previously predicted, but not observed and quantified in field conditions. Because both benthic (i.e., substrate-water interface) and subsurface hyporheic regions are known biogeochemical hot-spots, relating physical characteristics to the macroscopic transport behavior could be crucial to improve our estimates of solute export from fluvial systems.

3. Index Terms

1830, 1869

4. Introduction

Streams are complex systems, characterized by fast-moving, open channel flows, as well as slow-moving hyporheic flows. As a result, they naturally exhibit broad distributions of velocity (and associated time scales) that influence solute transport, often resulting in *anomalous* transport [*Metzler and Klafter*, 2000; *Bouchaud and Georges*, 1990; *Dentz and Bolster*, 2010]. Using experimental breakthrough curves (BTCs), anomalous transport in streams can be observed as power-law tailing [*Haggerty et al.*, 2002], a feature that cannot be successfully reproduced using classical one dimensional advection/dispersion transport models. This power-law signature is typically attributed to power-law residence times in the slow subsurface.

While conventional models cannot capture these anomalous behaviors, a rich family of emerging models can [e.g., *Haggerty and Gorelick*, 1995; *Berkowitz et al.*, 2006; *Schumer et al.*, 2003]. However, many of these models, in their original formulation, are built on the assumption that the residence time distribution for solute in the slow/immobile regions of the flow is a power-law distribution with infinite variance and even an infinite mean. While mathematically convenient, these assumptions are physically questionable when studying finite systems in the field. As a result, anomalous transport models have been modified to include a cutoff time. At this point, the power-law waiting times are truncated, yielding a finite mean and variance [e.g., *Dentz et al.*, 2004; *Haggerty et al.*, 2002; *Meerschaert et al.*, 2008]. The inclusion of this truncation time yields improved fits to observed data [*Cortis and Berkowitz*, 2004; *McInnis et al.*, 2014]. However, truncation times are typically not observed in field data, and merely inferred by extrapolating fits beyond observational data.

We carefully designed conservative solute additions in experimental streams to determine if we could observe such truncations in controlled field conditions. In particular, we compared BTCs from four streams with contrasting benthic substrates to address the following question: How does the size and heterogeneity of the substrate influence anomalous transport and the occurrence of a truncation time in conservative solute BTCs? We hypothesized that transport in streams with coarser substrate would display shorter truncation times than streams with smaller substrate, while heterogeneous mixtures of coarse and small substrates would fall somewhere in between the two end-member substrates.

While anomalous transport has been observed in many fluvial systems, the importance of tailing in BTCs remains uncertain because tails represent a small fraction of the total mass of conservative solute injected into a stream. Given that different hydraulic processes control the various features of tracer BTCs, whether or not tailing behavior is significant will depend on context. Transport in the open channel fast flow (i.e., advection and dispersion) will control the leading edge and peak of the BTC, while the tail represents the fraction of the tracer mass that has traveled through slower regions of flow. Short-term retention, represented by a BTC tail that is exponentially-distributed, is related to surface retention in pools and other slow regions of the open channel, while power-law tails generally correspond to subsurface flow paths [*Gooseff et al.*, 2005; *Ensign and Doyle*, 2005; *Cardenas*, 2008]. It is well known that the surface and subsurface environments play contrasting roles with regard to biogeochemical processing and transformation, and the subsurface hyporheic zone has been characterized as a bioreactive hot spot [*Fischer et al.*, 2005]. Thus, discerning how long solutes spend in different regions of the flow is critical to improved understanding and prediction of reactive transport in fluvial systems. Here, we interpret our experimental BTCs for conservative transport using a continuous time random walk (CTRW) model that clearly distinguishes residence times in diverse regions of the flow. This approach can readily be modified to include chemical reactions that can vary in different regions of the flow, ultimately allowing us to probe their relative influence on reactive transport and biological transformations [*Aubeneau et al.*].

5. Methods:

Site description: We conducted a series of conservative tracer additions in four replicate streams located at the Notre Dame Linked Experimental Ecosystem Facility (ND-LEEF). This facility was ideal to test our hypotheses because it contains four constructed stream channels that are shallow with regulated flow provided from a groundwater-fed reservoir. The groundwater had very low background fluorescence, meaning it would not influence RWT measurements [Drummond et al., 2012]. Each stream is 60m long and 0.35m wide and the bottom of each channel is lined to prevent any flow loss as water moves through the channel; discharge was held at 1.5 $L.s^{-1}$ in all four streams. To test the influence of benthic substrate on transport, we lined one stream with pea gravel ($D_{50} = 0.5cm$), one with coarse gravel ($D_{50} = 5cm$), another with alternating 2m sections of pea gravel and coarse gravel, and the final stream with a uniform 50:50 mixture of pea gravel and coarse gravel (Figure 1). We define "substrate size" to mean coarse gravel, fine gravel, or a mixture of the two, while "sediment heterogenity" or "sediment structure" refers to the distribution of different gravels (e.g., homogeneous, mixed, alternating).

Conservative tracer additions: Rhodamine (RWT) pulses were introduced in the surface water at the top of each stream and BTCs were recorded at a downstream station 48m from the injection point. Using the work of *Wang et al.* [2012] suggests that the streams will be well mixed at a length of around 45m. This is a conservative estimate considering that our streams meander and are quite rough. Additionally, all concentration measurements were taken with two Hydrolab MS5 Minisondes (Hach, Loveland, CO), separated by a finite distance at a given breakthrough location. The resulting measurements were virtually identical (available for download *Aubeneau* [2014b]), suggesting that the solutes were indeed well mixed by this point. Finally, because the same setup was used for all treatments, if pre-asymptotic dispersion were a contributing factor it would have a similar impact on each experiment and thus could not explain the differences we observed between treatments. We also repeated the experiments over time, and in early experiments, the features decribed in this paper appeared consistently. We introduced 10mg of RWT in 1L of injectate solution, with a goal to achieve peak RWT concentrations of 100 $\mu g L^{-1}$ at the bottom of each reach. Each sonde was equipped with a Turner Designs fluorometer with a RWT detection limit of 0.01 $\mu g L^{-1}$. We calibrated each sonde individually over its entire dynamic range. The RWT additions yielded concentration data ranging over 4 orders of magnitude.

Model Description: We used a Continuous Time Random Walk (CTRW) transport model [*Berkowitz et al.*, 2006]:

$$\frac{\partial C(x,t)}{\partial t} = \int_0^t M(t-t')[-U\frac{\partial C(x,t')}{\partial x}dt' + K\frac{\partial^2 C(x,t')}{\partial x^2}]dt', \quad (1)$$

where, in Laplace space, M is:

$$\tilde{M}(u) = u\bar{t}\frac{\tilde{\psi}(u)}{1-\tilde{\psi}(u)}. \quad (2)$$

C represents the modeled tracer concentration, U and K are the velocity and dispersion in the water column, x is the distance downstream and t is time. t' is a dummy time variable, $\bar{t}$ is the advective time in the water column and u is the Laplace variable. M is a memory function where $\tilde{\psi}(u)$ represents the waiting time distribution in the system, expressed as:

$$\tilde{\psi}(u) = \frac{1}{1+u+\Lambda-\Lambda\tilde{\varphi}(u)}. \quad (3)$$

This formulation represents a one storage zone model, whose global structure is controlled by the residence time distribution in that storage zone. In this study we propose a truncated power-law residence time distribution for $\tilde{\varphi}(u)$ [*Aban et al.*, 2006]. Λ is the exchange rate between the water column and the storage zone. In the time domain, it reads

$$\varphi(t) = \frac{\alpha t_a^{\alpha} t^{-\alpha-1}}{1-(t_a/T)^{\alpha}} \qquad t_a \le t \le T \quad (4)$$

where t is time, α is the power law exponent, t_a is the lower limit, taken as the advective time in the breakthrough curve, and T is the truncation time. Λ is the exchange rate between the water column and the storage zone. In order to fit observed data with this model we minimized a weighted objective function where the weights are assigned as inversely proportional to the observed values, thus appropriately weighting tails, following the methods outlined in *Chakraborty et al.* [2009]. To ensure that we converge on global minima during the optimization scheme we used a multistart approach [*Chakraborty et al.*, 2009]. Model parameter estimates were then obtained using the inner product of the Jacobian to approximate the asymptotic covariance matrix of the parameters [*Seber and Wild*, 2003].

6. RESULTS:

The RWT BTCs measured in all four experimental streams (Figure 2) demonstrate that, as hypothesized, substrate size and heterogeneity played an important role in the emergent transport behavior of the conservative solute. The BTCs from all four streams, with contrasting benthic substrate composition, show similar qualitative behavior with a power-law tail following the peak concentration and a subsequent truncation of this power-law distribution. The tracer was retained longer in the stream with pea gravel (2500s) than in the stream lined with coarse gravel (600s), while both channels with heterogeneous substrate (i.e., alternating and mixed) had similar tailing behavior that resembled the coarse gravel behavior early on, but persisted longer over time (1100 to 1400s). The truncation of the anomalous tailing, one of the dominant features we had predicted would occur, stands out strongly in the BTCs from all four streams, and includes a rapid reduction (i.e., truncation) in concentration at these cutoff times.

The CTRW model fits for the four contrasting streams are shown in Figure 3, with the corresponding model parameters summarized in Table 1. In all cases, we found excellent agreement between model and observed data (RMSE <1%) with all features, including peak, tail and truncation time being faithfully captured by the CTRW model. We also found that uncertainty estimates on the model parameters were very small, typically several orders of magnitude smaller than the obtained parameter values, which gives us high confidence in these optimized parameter values for all BTCs.

The CTRW model parameters reflect differences in BTCs across streams, presumably driven by substrate differences. For example, residence time in the storage zone had a similar power-law slope in the coarse gravel, the well-mixed gravel and the alternating treatment (-1.9), but was shallower in the stream with pea gravel (-1.76), confirming our prediction that substrate size influences the tailing behavior. Interestingly, at least for these controlled systems, these data suggest that it is not the slowest time scale, associated with the pea gravel, but rather the faster scale, associated with the coarse gravel that dictates the structure of the power-law tail. Benthic substrate size and distribution (i.e., heterogeneous or homogeneous) also controlled the hyporheic exchange rate (Λ), where the stream with pea gravel had the lowest exchange rate (0.07 s^{-1}), and the coarse gravel had a 25% higher exchange rate (0.10 s^{-1}). Again, both the heterogeneous streams, with well-mixed and alternating substrate, showed intermediate behavior, with an exchange rate of $0.08s^{-1}$ for the mixed substrate and $0.09s^{-1}$ for the stream with alternating substrate.

Finally, as we predicted, the observed truncation time of anomalous tailing in the stream with pea gravel tapered off 2444 s after the peak, which corresponds to ∼10 advective travel times, while anomalous tailing in the stream with coarse gravel tapered off after only 600 s, which was ∼2 travel times. Streams with heterogeneous substrate once again had intermediate behaviors, although the anomalous behavior was sustained slightly longer in the alternating configuration (1406 s) than in the stream with well-mixed substrate (1141 s). These observed truncations were not related to type C errors described in Drummond et al. [2012], as they happened at concentrations one order of magnitude higher than the instrument detection limit and also during injections with even higher concentrations (data not shown).

7. DISCUSSION:

While previous research has shown that the presence of benthic substrate induces anomalous transport in streams [*Gooseff et al.*, 2005], here we present strong empirical evidence that substrate size and structural composition controls the characteristics of anomalous transport and how long they will persist. Consistent with our predictions, we observed that transport in streams with smaller substrate (i.e. pea gravel) displayed both heavier tails and longer truncation times than streams with coarser sediment, with heterogeneous mixtures of coarse and small substrate falling in between these two end-members. These empirical data, using experimentally manipulated streams in the field, are important to understanding transport in stream systems and, more fundamentally, to understanding controls on anomalous transport.

Power-law RTDs have been observed in many natural systems [*Schumer et al.*, 2009]. Streamflow exhibits fractal scaling on the daily to monthly timescales, allowing inferences about catchment residence times [*Harman et al*, 2009]. Different mechanisms have been shown to produce power-law hydrograph recessions [*Thompson and Katul*, 2011]. At shorter timescales, the presence of alluvium in the stream is known to induce power-laws [*Gooseff et al.*, 2005]. Even though power-law RTDs are common, observed power-law exponents are rarely related to specific system characteristics, even though bed topography [*Stonedahl et al.*, 2012] and discharge [*Zarnetske et al*, 2007] have been shown to exert some control. In this study, we demonstrate how the benthic substrate itself, in the absence of bed topography or discharge variability, can influence changes in observed power law slopes, with the smaller sediments inducing heavier tails. Because in the smaller sediment, there is a higher ratio of solid surfaces to water volume, the amount of drag on the flow is also higher and therefore the conductivity smaller. This leads to slower hyporheic velocities, or equivalently to longer retention times, translated in the smaller power-law exponents. However, we also observed that the BTC tails in mixed sediments were closer to the coarser end-member. Coarse substrate may dominate the BTC signature because the pore flow in coarse gravels is faster than in fine substrate, suggesting fine gravel contributions may be functionally too small in magnitude to dominate when a mixed substrate is present. This could be linked to the fast exchange caused by the high roughness from coarse gravel or the preferential flow-paths established through the coarse pore-network. Our experiments did not provide adequate data to test these hypotheses, but offer them as an avenue for future exploration. Our observations provide a strong foundation for building physically-based models that link substrate characteristics to emergent anomalous transport behavior.

Truncated power-law RTDs in the storage zone provided an excellent description of the observed transport behavior. Even though truncated power-law distributions have been observed in other systems (i.e., economics, seismology, power outages [e.g. *Clauset et al.*, 2009]) and have been proposed in studies of environmental transport [*Zhang and*

Meerschaert, 2011], they have proved elusive to observe in practice, and as a result, few environmental datasets using field data have conclusively demonstrated their existence. Not only did we observe well-defined truncation times in these experiments, but our results also confirmed that the longest transport timescale was directly influenced by the substrate. Currently, it remains unclear whether hydraulic conductivity (i.e. advective process) or dispersivity (i.e. diffusive process) drove this. Nevertheless, these field results provide solid empirical evidence of a truncation time in the elution of a conservative solute from stream sediments. In real streams, benthic substrates would typically be much more heterogeneous than in these experimental streams, and the addition of fine sediments and biofilms will contribute heterogeneous microhabitats that could take much time to resolve. However, we reemphasize that this dataset provides a solid foundation on which to start building models for storage zone RTDs based on physical characteristics of the substrate.

While data from this study explore the role of substrate on conservative transport, we highlight the value of these results to improve our understanding of reactive transport in streams, as streambeds are biogechemical hotspots [*Fischer et al.*, 2005]. The interplay between the amount of hyporheic exchange and the actual hyporheic residence time should be important for biologically catalyzed reactions. Our results indicate that smaller sediments induced less total exchange between the surface and subsurface, but that the mass of conservative tracer that did enter the hyporheic zone remained trapped for much longer. The proposed CTRW model distinguishes clearly between surface, interfacial and hyporheic processes, providing an easy method to investigate their effect on both conservative and reactive transport.

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Table 1. *Best fit parameters (±standard errors) from the CTRW model.*

Stream	**Velocity** ($m.s^{-1}$)	**Dispersion** ($m^2.s^{-1}$)	**Exchange rate** (s^{-1})	**Truncation time** (s)	**Slope**
Small Gravel	0.22 ± 1.10^{-10}	0.018 ± 5.10^{-3}	0.072 ± 3.10^{-10}	2444 ± 1.5	$-1.76 \pm 1.5.10^{-3}$
Coarse Gravel	$0.2 \pm 4.5.10^{-10}$	0.02 ± 3.10^{-4}	0.097 ± 3.10^{-9}	600 ± 2	$-1.89 \pm 4.8.10^{-11}$
Alternating	0.13 ± 7.10^{-3}	0.02 ± 3.10^{-3}	0.088 ± 8.10^{-3}	1406 ± 9	-1.89 ± 4.10^{-3}
Mixed	0.14 ± 1.10^{-9}	0.016 ± 3.10^{-4}	0.08 ± 2.10^{-9}	1141 ± 2	-1.9 ± 1.10^{-10}

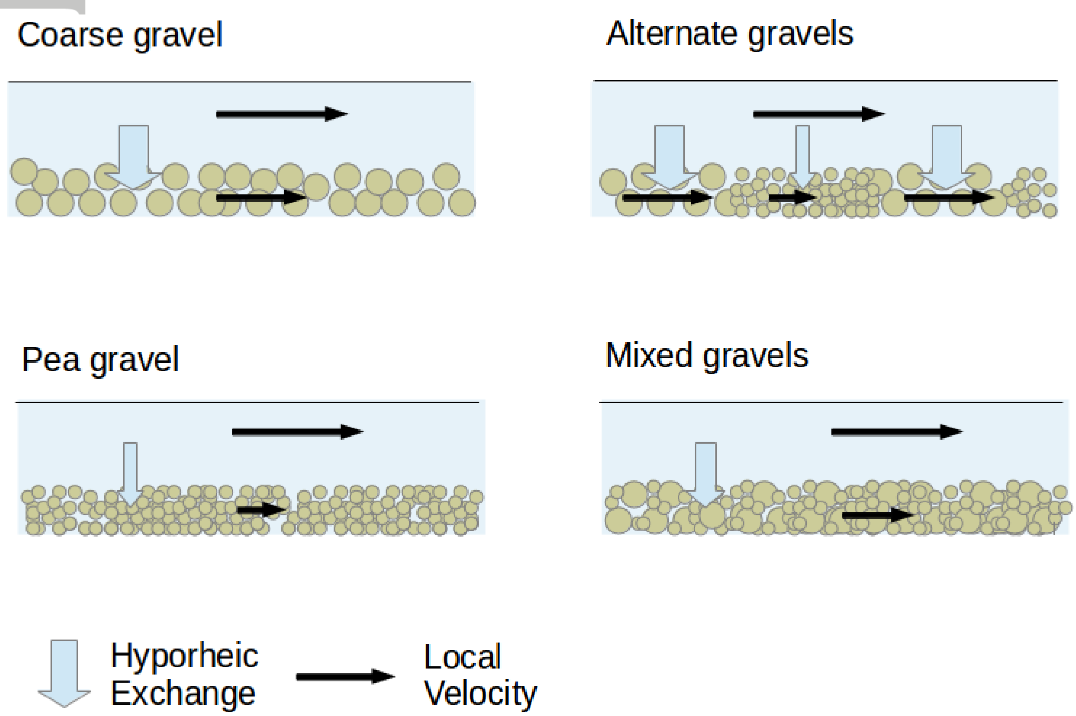

Figure 1. *Schematic experimental setup.* We expected higher hyporheic exchange (blue arrows) and hyporheic velocity (black arrows) in the coarse gravel than in the pea gravel treatment, and intermediate behavior in the heterogeneous treatments.

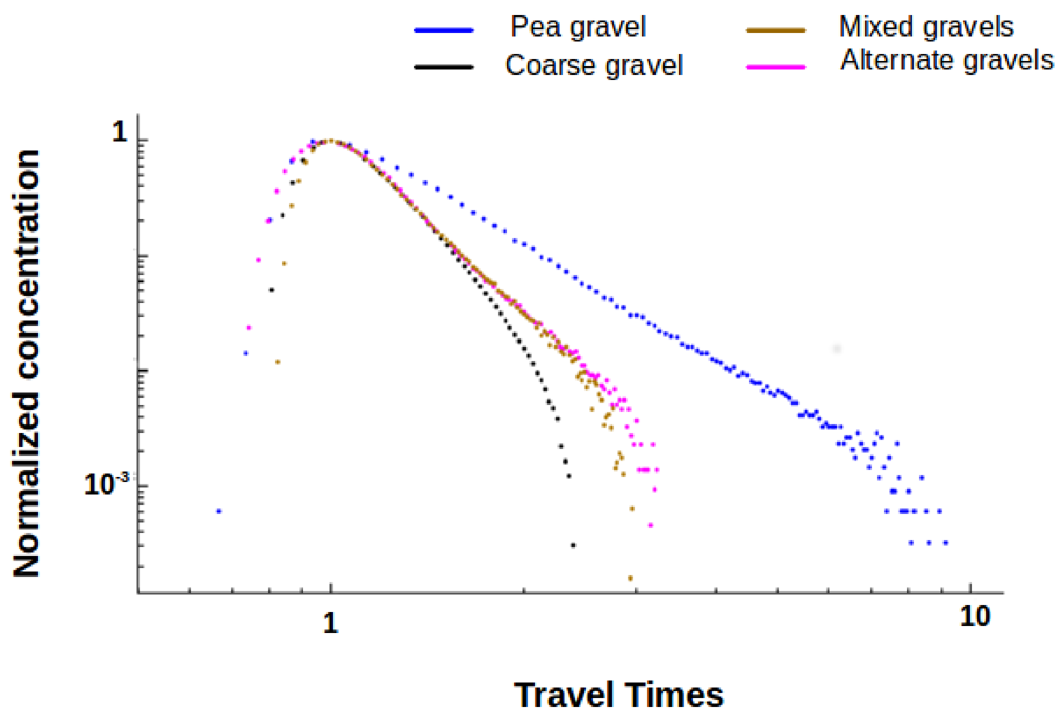

Figure 2. *Observed breakthrough curves.* The pea gravel induces a heavier tail than the coarse gravel, while the heterogeneous treatments produce similar tails that resemble the coarse gravel early on but extend longer.

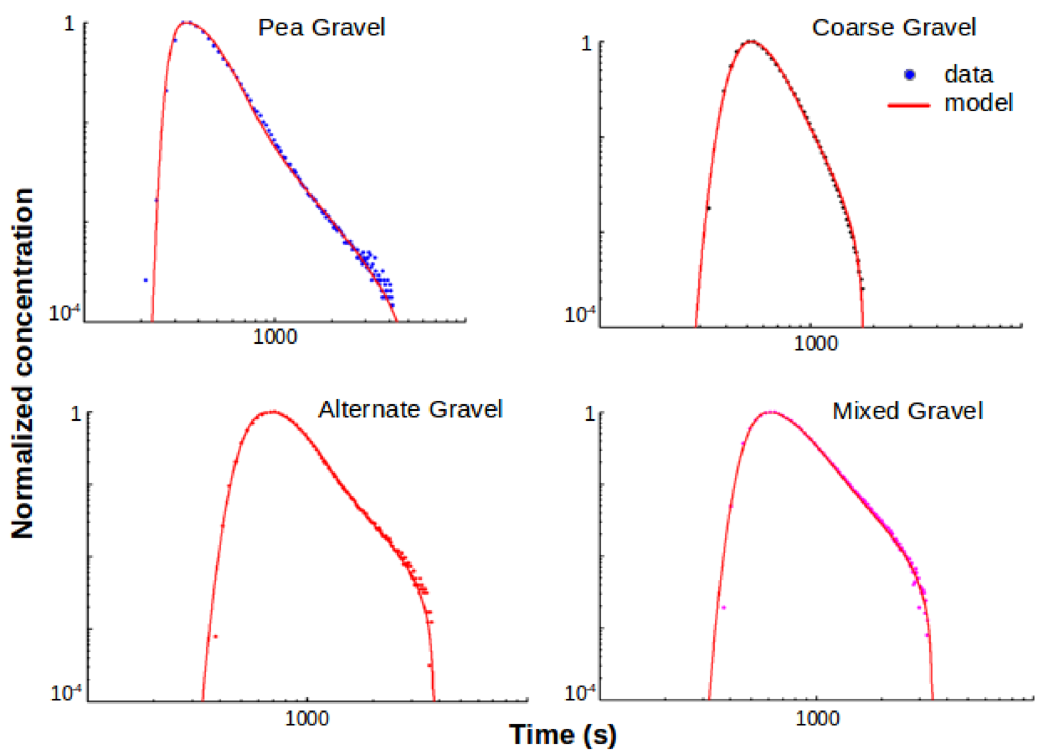

Figure 3. *Model fits.* The CTRW model with a truncated power-law RTD captures the solute behavior at all recorded timescales, including observed truncation times.