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- Particulate organic carbon transports through deposition and resuspension
- POC transport is accounted for in a multiscale stochastic model framework
- A stochastic model allows upscaling of local observations and prediction

Correspondence to:
J. D. Drummond,
j-drummond@u.northwestern.edu

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Stochastic modeling of fine particulate organic carbon dynamics in rivers

J. D. Drummond[1], A. F. Aubeneau[1], and A. I. Packman[1]

[1]Department of Civil and Environmental Engineering, Northwestern University, Evanston, Illinois, USA

Abstract The majority of particulate organic matter standing stock in streams is <1 mm in diameter, and the mobile phase is primarily very fine particles. Such fine particles transport downstream in a series of deposition and resuspension events mediated by interactions with coarser bed sediment, yielding fine particle retention over a wide range of time scales. This retention controls the opportunity for biogeochemical processing of particulate organic carbon in streams. We present a conceptual model of particulate organic carbon transport in rivers categorized in three cyclic processes: (i) migration of fine particles from the water column to the underlying and surrounding sediments, (ii) fine particle transport and retention within the bed sediments, and (iii) resuspension of fine particles back to the water column. We developed a stochastic model to describe the transport and retention of fine suspended particles in rivers, including advective delivery of particles to the streambed, transport through pore waters, and reversible filtration within the streambed. We then apply this model to observations of fine particle transport in two small streams, and show that the stochastic mobile-immobile model supports improved interpretation of particulate organic carbon dynamics under base flow conditions. Analysis of in-stream solute and particle data shows that particles engage in multiple deposition and resuspension events during downstream transport, and that long-term retention in the streambed produces extended slow releases to the stream even during base flow conditions. We also show how multiscale stochastic modeling can be used to incorporate local observations of particle retention in predictions of whole-stream particle dynamics.

1. Introduction

Streams and rivers of the world transport, transform, or store ~2 Pg of terrestrial carbon per year [*Cole et al.*, 2007]. Although organic carbon can reside in the soil for centuries to millennia without decomposing, up to 70% of this ancient organic carbon is respired within weeks of entering a river network [*Cole and Caraco*, 2001]. This relatively quick in-stream respiration significantly contributes to the high rates of CO_2 emissions from rivers to the atmosphere [*Battin et al.*, 2008]. As a consequence of physical and biological processes, such as gravitational settling and upstream processing of dead leaves and woody debris, the particle size of organic material generally becomes progressively smaller downstream. Thus, fine particulate organic matter (POM) less than 1 mm in diameter accounts for much of the standing stock of organic matter in stream and river ecosystems, and very fine particles less than 52 μm in diameter generally dominates downstream transport [*Cushing et al.*, 1993]. Such very fine POM consists of particulate forms of carbon, nitrogen, and phosphorus and plays a major role in riverine carbon and nutrient dynamics [*Cushing et al.*, 1993; *Hope et al.*, 1994]. Both dissolved organic carbon (DOC) and particulate organic carbon (POC) contribute to the terrestrial flux of organic carbon in river networks. POC represents approximately 40% of the total mass flux, but contributes disproportionately to heterotrophic metabolism by stream microbial communities because POC is generally more labile than DOC [*Stutter et al.*, 2007].

Both conservative solutes and particles are actively exchanged between the water column and the benthic and hyporheic regions in the shallow subsurface surrounding stream channels [*Newbold et al.*, 1981; *Bencala and Walters*, 1983; *Huettel et al.*, 1996; *Packman et al.*, 2000a, 2000b]. As the gravitational settling rate of fine particles is low, POC is mainly removed from the water column by turbulence and advective delivery into the bed due to local pressure variations over streambed topography [*Packman et al.*, 2000a, 2000b; *Ren and Packman*, 2002; *Karwan and Saiers*, 2012; *Fries and Trowbridge*, 2003]. Particles transported into the benthic boundary layer can be trapped in biofilms present at the streambed surface [*Battin et al.*, 2003; *Newbold et al.*, 2005; *Arnon et al.*, 2010], or propagate into the underlying sediments, where they are generally removed by filtration processes [*Packman et al*., 2000a, 2000b; *Arnon et al*., 2010]. Deposited particles have been shown to remobilize during flood events [*Harvey et al*., 2012] and also during base flow conditions [*Cushing et al*., 1993; *Newbold et al*., 2005]. High unsteadiness in particle resuspension generally leads to a wide range of particle residence times in streams. The distribution of particle storage times between deposition and resuspension events controls the opportunity for biogeochemical processing of POC within rivers [*Battin et al*., 2008; *Aufdenkampe et al*., 2011].

Newbold et al. [2005] modeled POM transport in rivers using the advection-dispersion equation for in-stream motion with three distinct storage areas, each characterized by deposition and resuspension rates and an exponential residence time distribution. Model fits to in-stream observations of particle concentrations were not unique and could not be linked to specific controlling processes. Mechanistic models have also been developed for fine particle deposition in sand bed streams with bed forms [*Packman et al*., 2000a; *Karwan and Saiers*, 2012]. Advective hyporheic exchange induced by pressure variations associated with streamflow over stream channel topography, commonly referred to as bed form-induced pumping, delivers particles into the subsurface, contributing to particle deposition by filtration and settling in pore spaces [*Packman et al*., 2000b]. *Karwan and Saiers* [2012] expanded this approach to more realistic flow-boundary interactions using a numerical hydrodynamic model. Enhanced particle deposition has also been observed to occur in the absence of bed forms, indicating that turbulence causes continuous particle deposition and resuspension [*Fries and Trowbridge*, 2003; *McNair*, 2006]. The analysis of *McNair* [2006] further suggested that particles do not usually deposit the first time they hit the bed. Existing models for advective particle removal in streambeds only consider irreversible filtration, whereas organic particles and microbial cells have been shown to slowly release after initial deposition [*Brunke*, 1999; *Cortis et al*., 2006; *Cushing et al*., 1993; *Newbold et al*., 2005]. Particles also attach to streambed biofilms, and subsequently detach because of biofilm erosion or sloughing [*Battin et al*., 2003; *Boulêtreau et al*., 2006].

We present a conceptual model for in-stream fine particle transport in rivers, focused on the dominant processes that mediate the deposition and resuspension dynamics of fine organic particles to the benthic and hyporheic regions. It is difficult to extrapolate deterministic mechanistic models for individual processes to real streams that are highly heterogeneous, and where the transport of fine particles is controlled by the interactions of many different processes occurring over a range of spatial scales and temporal frequencies. Such complex behavior can be described better by stochastic modeling incorporating probability distributions to link the underlying fine particle transport mechanisms to the ensemble large-scale dynamics [*Metzler and Klafter*, 2000]. We present a stochastic modeling framework that can appropriately integrate the multiple deposition and resuspension processes outlined in the conceptual model. Finally we develop a quantitative model for downstream particle transport including the effects of the three processes that we hypothesize to be most important during base flow: advective delivery of fine suspended particles to the streambed, transport through pore waters, and reversible filtration within the streambed. These three mechanisms lead to a wide range of particle residence times within streams, and the associated stochastic model provides a more comprehensive description of observed particle transport than prior deterministic models.

2. Conceptual Model of POC Dynamics in Rivers Transport

The removal of fine particles from streams is driven by deposition in the streambed, settling into slower surface water transport areas, such as pools or dead zones, and retention on floodplains during overbank flow [*Aufdenkampe et al*., 2011; *Blair and Aller*, 2012]. We focus on retention within the stream channel, and consider retention to occur as three cyclic processes: (i) Migration of fine particles from the water column to the underlying and surrounding sediments, (ii) Fine particle transport and retention within the bed sediments, and (iii) Resuspension of fine particles back to the water column (Figure 1).

Particles are delivered to the streambed through a combination of bulk advection, turbulent diffusion, and gravitational settling. Particles are subject to increased turbulence in the near-bed boundary layer, which can either drive the particles into the streambed or remobilize them back into the water column [*McNair*, 2006]. Bottom roughness enhances deposition owing to pressure-driven advective transport across the sediment-water interface [*Fries and Trowbridge*, 2003; *Packman et al*. 2000a, 2000b]. Hyporheic exchange—the two-way flow of water between the water columns and underlying sediments—causes solutes and particles to propagate into the streambed and along pore water flow paths. Pore water flow is induced by

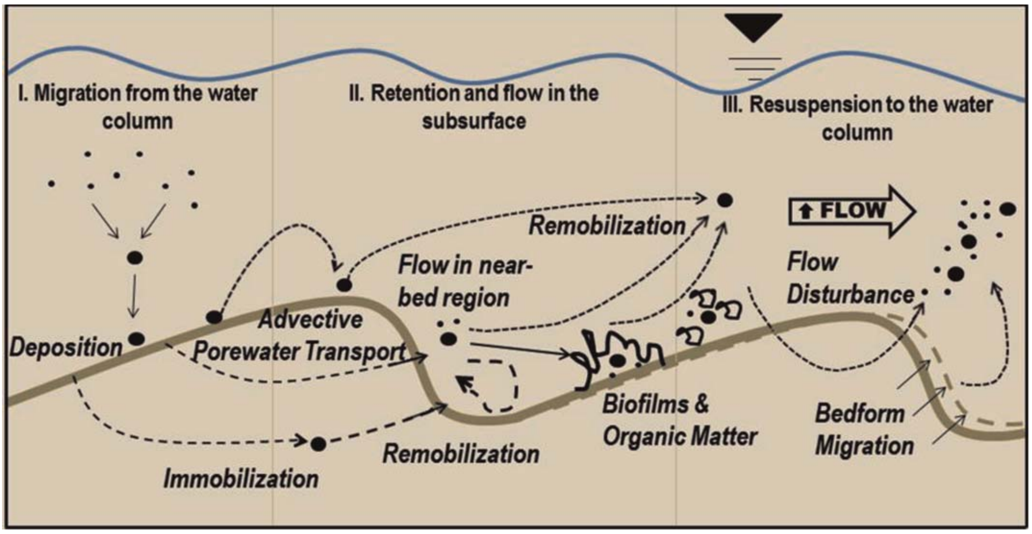

Figure 1. Conceptual model of processes that influence particulate organic carbon retention in streams: (I) migration from the water column, (II) retention and flow in the subsurface, and (III) resuspension to the water column.

pressure variations at the streambed surface, pumping water, solutes and suspended particles from the water column into and through the sediment bed, and eventually back into the water column. Hyporheic exchange of particles differs from solutes because of strong particle deposition during pore water transport. Even though the settling velocities of fine organic matter are low, gravitational settling can be more important within pore waters, where pore water velocities are quite low [*Packman et al*., 2000a, 2000b]. Filtration in the bed leads to particle immobilization [*Packman et al*., 2000a, 2000b; *Karwan and Saiers*, 2012]. However, filtered organic particles are often remobilized, corresponding to reversible filtration [*Cortis et al*., 2006; *Harter et al*., 2000; *Harvey and Garabedian*, 1991]. This slow release of organic particles and microbes after initial deposition has been observed in streams [*Brunke*, 1999; *Cushing et al*., 1993; *Newbold et al*., 2005].

Fine particles are also retained at the streambed surface [*Harvey et al*., 2012; *McNair and Newbold*, 2012]. Interfacial particle deposition is influenced by biofilms—surface-attached microbial communities, which are often encased in a sticky self-produced extracellular polymeric matrix. Benthic biofilms can increase deposition of fine particles from the water column [*Arnon et al*., 2010; *Battin et al*., 2003]; especially in streams with sediments that are less mobile and have high surface area, such as cobbles. By effectively trapping particles at the sediment-water interface, biofilms can reduce deposition within the underlying sediments [*Arnon et al*., 2010]. Once fine particles are trapped within the biofilm matrix, biofilm sloughing can cause remobilization back into the water column [*Boulêtreau et al*., 2006].

With more mobile sediment, such as in sand bed streams, bed sediment transport provides another mechanism of particle capture and release. Moving bed forms capture stream water and can bury POM [*Packman and Brooks*, 2001; *Harvey et al*., 2012]. Deposited fine particles are readily remobilized following scour of the bed sediments, and thus are released during bed form migration [*Packman and Brooks*, 2001]. Particles that deposit deeper in the bed, beneath the active layer of bed sediment transport, will be retained in the bed sediments until they are released by reversible filtration or until the next flood event that scours the bed to that depth [*Rehg et al*., 2005; *Harvey et al*., 2012]. Migration to depths below the region that is commonly scoured leads to long-term retention of particles in the bed [*Rehg et al*., 2005]. Further, remobilized particles can subsequently redeposit, causing cyclic deposition and resuspension that varies over time with the hydrologic and geomorphic characteristics of the stream. Retention of POC by all processes provides increased opportunities for degradation of organic matter by benthic and hyporheic microbial communities, especially near the water-sediment interface [*Stutter et al*., 2007; *Battin et al*., 2008; *Aufdenkampe et al*., 2011].

3. Stochastic Model for POC Dynamics in Rivers

POC dynamics often include both rapid in-stream transport and long-term storage. The relevant range of processes can be described by a mobile-immobile random walk model that provides a probabilistic description of particle motion through distinct series of jumps and waits [*Schumer et al*., 2003; *Benson and Meerschaert*, 2009; *Metzler and Klafter*, 2000]. The sum of the jumps and waiting times determine the overall spatial redistribution and retention time distribution of particles within the stream. Our long-term objective is to develop a model framework for fine particle dynamics in rivers that incorporates all processes outlined in Figure 1. Here the model development is focused on the three processes that we hypothesize to be most important for streams with mobile granular sediment beds (e.g., sand, fine gravel) during base flow: advective delivery of fine suspended particles to the streambed, transport through pore waters, and reversible filtration within the streambed. First, we introduce the stochastic model framework and then demonstrate how it can be used to assess in-stream and subsurface (pore water) particle data through model fitting. We then show how the model can be fully predictive using streambed parameters and a deterministic model within the stochastic model framework. Lastly, we review the processes that controlled fine particle transport in the two streams analyzed here, evaluate the capabilities and limitations of the current model framework relative to prior deterministic model formulations, and discuss the implications for integrated assessments of organic particle transport and biogeochemistry in rivers.

3.1. Stochastic Mobile-Immobile Model Framework

We adopt the decoupled Continuous Time Random Walk (CTRW) framework for the mobile-immobile model, which represents both jump lengths and waiting times as continuous random variables [*Berkowitz et al*., 2006; *Schumer et al*., 2003, 2009; *Meerschaert and Sikorskii*, 2011]. Motion can be represented as a discrete series of jumps and waits, each described by a different distribution. Although this is an idealization, these assumptions have been shown to be valid for cases where material is immobilized for a long time within sediments [*Margolin et al*., 2003; *Schumer et al*., 2003] or where material is delivered into regions where transport is much slower than the main flow [*Boano et al*., 2007; *Schumer et al*., 2009; *Marion et al*., 2008; *Haggerty et al*., 2002]. In rivers, the water column is considered the mobile region, and material retained in benthic or hyporheic zones can often be considered to be effectively immobile [*Schumer et al*., 2003; *Boano et al*., 2007]. This model assumes that pore water transport is much slower than in-stream transport, and hyporheic exchange does not have a significant effect on the overlying velocity field. Further, in-stream motion is assumed to be Brownian, and thus in-stream transport is fully characterized by a mean velocity and dispersion coefficient. In this model formulation, we consider both benthic and hyporheic retention together as an integrated immobile region as it is not possible to distinguish the difference between streambed surface versus subsurface reservoirs without local observations from data or independent models, which are generally not available. With these assumptions, *Boano et al*. [2007] developed a CTRW model for solute transport in rivers:

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

where C is in-stream concentration, x is the longitudinal position, t is the elapsed time, and U and K are the velocity and dispersion coefficients describing Brownian motion in the stream. This formulation is analogous to the advection-dispersion equation (ADE) plus a convolution integral with a memory function, $\mathrm{M}(t)$, representing long-term storage in the system. The memory function represents the mass that is immobilized at time t and is still immobile at a later time ($t+\Delta t$). Such discontinuous motion does not follow the assumptions of Brownian motion, but averages to the ADE at time scales much larger than the longest wait time [*Metzler and Klafter*, 2000; *Zhang et al*., 2012]. For waiting time distributions having infinite variance, termed heavy-tailed distributions, equation (1) never converges to the ADE. Equation (1) can be obtained in other ways. This formulation is equivalent to the multirate mass transfer model (MRMT) and solute transport in rivers model (STIR) [*Haggerty and Gorelick*, 1995; *Marion et al*., 2008] and asymptotically yields the time-fractional advection-dispersion equations (tFADE) [*Schumer et al*., 2003, 2009].

3.2. Memory Function for Particle Immobilization/Remobilization

We use equation (1) to characterize fine particle transport with long waits between motion, as described by the conceptual model depicted in Figure 1. The memory function in equation (1) represents the effects of retention processes such as hyporheic exchange and episodic particle deposition/resuspension dynamics.

This can describe any waiting time distributions, including heavy-tailed power law distributions that do not have a finite mean or variance. In this case, the resulting in-stream breakthrough curves never converge to a Gaussian distribution as predicted by the ADE, but instead have persistent tails that follow a power law distribution [*Metzler and Klafter*, 2000; *Berkowitz et al*., 2006; *Schumer et al*., 2009]. The model can also be generalized for non-Brownian in-stream motion, e.g., Lévy motion incorporating infinite variance jump lengths.

The memory function is dependent on the distribution of waiting times between jumps, $\tilde{\psi}_i(u)$. This is normally written in Laplace space to simplify the expressions. The Laplace transform, L{*f*}(*u*), of a function *f* (*t*) is equal to $\int_0^\infty e^{-ut} f(t)dt$. This yields:

$$\tilde{M}(u) = u\bar{t}\,\frac{\tilde{\psi}_i(u)}{1-\tilde{\psi}_i(u)} \tag{2}$$

where *u* is the Laplace variable and the characteristic time, $\bar{t}$, is the average travel time in the reach, defined as the stream reach length divided by the mean stream velocity. $\tilde{\psi}_i(u)$ changes whether the model represents solute or particle transport, where subscript *i* is then denoted by *S* or *P* respectively. $\tilde{\psi}_i(u)$ depends on the probability of immobilization, $\Lambda_i[\mathrm{T}^{-1}]$, and distribution of residence times in the immobile region, $\tilde{\varphi}_i(\mathrm{u})$:

$$\tilde{\psi}_i(u) = \tilde{\psi}_0[u + \Lambda_i - \Lambda_i * \tilde{\varphi}_i(u)] \tag{3}$$

where $\tilde{\psi}_0$ is the residence time distribution in the mobile region and $\tilde{\varphi}_i(u)$ is the residence time distribution in the immobile region. $\tilde{\psi}_0$ is a much narrower distribution than $\tilde{\varphi}_i(u)$. For the fine organic particles considered here, solute and particle transport are generally identical in the mobile phase, allowing $\tilde{\psi}_0$ to be determined from the fit of equations (1)–(3) to observations of in-stream solute transport. Multiple independent immobilization processes can be convolved together within the memory function by incorporating suitable Λ_i and $\tilde{\varphi}_i(u)$ for each process, as introduced by *Margolin et al*. [2003] and applied to downstream solute transport by *Boano et al*. [2007]. The memory functions are defined for in-stream and subsurface modeling below in sections 3.2.1 and 3.2.2, respectively.

3.2.1. In-Stream Modeling

We apply equation (1)–(3) here for both solute and particle transport in rivers. For solutes, the memory function represents hyporheic exchange. We assume an exponential distribution of residence times in the mobile region, $\psi_0\ (t) = e^{-t}$, or in Laplace space, $\tilde{\psi}_0(\mathrm{u}) = 1/(1\ +\ \mathrm{u}\ )$. In this case, the probability of immobilization of solutes, Λ_S, is the probability of hyporheic exchange per unit time. Similarly, the residence time distribution for solutes, $\tilde{\varphi}_S(u)$, is based on the time solutes are retained within the streambed by hyporheic exchange. Solute residence time distributions have often been found to be heavy-tailed power laws, where $\varphi_S\ (t) = t^{\beta_S}$, or in Laplace space $\tilde{\varphi}_S\ (u)\ =\ 1/(1\ + u^{-(1+\beta_S)})$, for $-2 < \beta_S < -1$ [*Haggerty et al*., 2002; *Cardenas*, 2008; *Wörman and Wachniew*, 2007; *Stonedahl et al*., 2012].

Equation (1) then reflects convolution of solute advection and dispersion within the main channel and the memory function describing hyporheic exchange.

For fine particles, the memory function is modified to incorporate the additional particle deposition and resuspension processes shown in Figure 1. We first describe the procedure for fitting observed in-stream particle breakthrough curves without specific, local observations in the streambed, benthic, or hyporheic regions. We assume advective delivery of suspended particles is controlled by hyporheic exchange and gravitational settling is minimal due to the low settling velocity of such fine particles. In this case, hyporheic exchange of solute and particles is similar, and $\Lambda_P \approx \Lambda_{S.}$ Deposition and resuspension of particles within the hyporheic zone is then described by the particle residence time distribution in the immobile region, $\tilde{\varphi}_P(u)$.

$$\tilde{\varphi}_P(u) = \tilde{\varphi}_S[u + \Lambda_{HP} - \Lambda_{HP} * \tilde{\varphi}_{HP}(u)] \tag{4}$$

where $\tilde{\varphi}_S$ is the residence time distribution for transport in the immobile region determined by fitting solute data using equations (1)–(3), Λ_{HP} is the probability of immobilization of particles within the immobile

Table 1. Overview of Model Parameters Within the Mobile-Immobile Framework[a]

	In-Stream Data		Subsurface Data	
Residence Time Distribution for:	Solute $\left(\tilde{\psi}_S\right)$	Particles $\left(\tilde{\psi}_P\right)$	Solute $\left(\tilde{\psi}_{CS}\right)$	Particles $(\tilde{\psi}_{CP})$
Mobile	$\tilde{\psi}_0$	$\underbrace{\tilde{\psi}_0}_{\text{Solute data}}$	$\tilde{\psi}_{C0}$	$\underbrace{\tilde{\psi}_{C0}}_{\text{Solute data}}$
Immobile	$\Lambda_S, \tilde{\varphi}_S$	$\tilde{\varphi}_P = f\left(\underbrace{\Lambda_S, \tilde{\varphi}_S}_{\text{Solute data}}, \Lambda_{HP}, \tilde{\varphi}_{HP}\right)$, where $\Lambda_{HP} \approx \Lambda_{CP}$and $\tilde{\varphi}_{HP} \approx \tilde{\varphi}_{CP}$	N/A	$\Lambda_{CP}, \tilde{\varphi}_{CP}$

[a]Whole-stream analysis of in-stream breakthrough curves uses the in-stream data parameters. Subsurface data parameters are used when analyzing data within an immobilization area, such as for the column experiment demonstrated herein.

region, and $\tilde{\varphi}_{HP}(u)$ is the residence time distribution of particles in the hyporheic region. Fine particles are immobilized within the immobile regions due to settling, filtration, or attachment to organic matter or biofilms present at the subsurface-surface interface, which is controlled by Λ_{HP}. Fine particles are also resuspended due to turbulence, reversible filtration or sloughing of biofilms, yielding a residence time distribution for particle resuspension represented by $\tilde{\varphi}_{HP}(u)$. We represent the particle-specific residence time distribution in the hyporheic region as a power law distribution, $\varphi_{HP}(t) = t^{\beta_P}$ or in Laplace space $\tilde{\varphi}_{HP}(u) = 1/(1 + u^{-(1+\beta_P)})$, for $-2 < \beta_\mathrm{P} < -1$. The parameters describing solute and particle transport and immobilization are summarized in Table 1.

3.2.2. Subsurface Modeling

Additional, local observations of solute and particle transport within the benthic and hyporheic regions can be included in a multiscale mobile-immobile model. We consider the case where supplemental information is obtained from direct observations of solute and particle transport in streambed sediment. The distribution of waiting times between jumps specific to 1-D transport along a pore water flow path is $\tilde{\psi}_{Ci}(u)$:

$$\tilde{\psi}_{Ci}(u) = \tilde{\psi}_{C0}[u + \Lambda_{Ci} - \Lambda_{Ci} * \tilde{\varphi}_{Ci}(u)] \tag{5}$$

where $\tilde{\psi}_{C0}$ is the residence time distribution associated with pore fluid flow, Λ_{Ci} is the probability of immobilization in the sediments, and $\tilde{\varphi}_{Ci}(u)$ is the distribution of residence times in the immobile region of the sediments. Since conservative solutes are not immobilized, $\Lambda_{CS} = 0$ and $\tilde{\psi}_{CS}(u) = \tilde{\psi}_{C0}(u)$. Immobilization of fine particles due to gravitational settling and reversible filtration within the sediments are represented by Λ_{CP} and $\tilde{\varphi}_{CP}(u)$ in equation (5). Local parameters Λ_{CP} and $\tilde{\varphi}_{CP}(u)$ obtained by fitting observations or derived from a local-scale theoretical model can then be used within equation (4) by setting $\Lambda_{HP} \approx \Lambda_{CP}$ and $\tilde{\varphi}_{HP}(u) \approx \tilde{\varphi}_{CP}(u)$, linking the hyporheic exchange terms in the in-stream model to measured or predicted local particle retention and release processes.

Alternatively, the memory function for fine particles, $\tilde{M}(u)$, can be defined in terms of a first-order filtration coefficient for particle deposition, λ_f, and the residence time distribution for resuspension of filtered particles, $\tilde{\varphi}_{Cf}(u)$:

$$\tilde{M}(u) = \lambda_f - \lambda_f * \tilde{\varphi}_{Cf}(u) \tag{6}$$

Here λ_f is equivalent to the irreversible filtration coefficient in classic colloid filtration theory, while $\tilde{\varphi}_{Cf}$ incorporates reversible filtration by allowing for ongoing resuspension of filtered particles. This relates the mobile-immobile equations to classic colloid filtration theory that has been previously used as the basis for deterministic models of particle capture in streambeds [e.g., *Packman et al.*, 2000a]. The parameters used in the multiscale model are summarized in Table 1.

3.3. Predictive Modeling With Hyporheic Parameters

This multiscale model framework for particles can be extended to be fully predictive by using a theoretically derived model for hyporheic exchange [e.g., *Packman et al.*, 2000; *Karwan and Saiers*, 2012]. In some instances, it is possible to predict filtration parameters based on knowledge of the particle properties, bed sediment properties, and pore water flow [*Tufenkji and Elimelech*, 2004]. Hyporheic exchange can be predicted using the bed form-induced pumping model [*Elliot and Brooks*, 1997], or other process-based or semianalytical exchange models. Here we consider hyporheic exchange resulting from pumping into and out of streambed sediments, calculated from the advective flow pattern induced by the dynamic pressure variations over a dune. The input parameters include hydraulic conductivity, bed form height and wavelength, stream depth, streambed depth, and in-stream velocity. The pumping model output includes both the flux of solute into immobilization and residence time distribution of solute in immobilization, Λ_S and $\tilde{\varphi}_S(u)$ in equation (3). For fine particles, the pumping model can use the fitted column parameters from equation (6) to incorporate reversible filtration within each time step of the model. The pumping model output is $\tilde{\varphi}_P(u)$, the residence time distribution of particles in immobilization and can be used within equations (1)–(3).

3.4. Numerical Solution Method

We solved these equations with a modified version of the CTRW toolbox [*Cortis and Berkowitz*, 2005; A. F. Aubeneau et al., A stochastic model for reactive transport in rivers, submitted to *Freshwater Science*, 2014]. We expanded the types of waiting time distributions that can be simulated. Specifically, we added the option to use either a power law distribution or numerically generated residence time distribution, e.g., obtained from particle tracking simulations of the pumping process. We also included the multiscale model for fine particle immobilization in the memory function, as described by equations (3) and (4). Finally we updated the procedure used to fit in-stream data by implementing an unconstrained nonlinear search coupled with a least squares criteria.

3.5. Summary of Model Capabilities and Limitations

The stochastic mobile-immobile model is able to represent a wide range of spatial and temporal time scales, including many of the individual processes shown in Figure 1. While deterministic models are available for some of the component processes, it is difficult to integrate these over the wide range of spatial and temporal scales relevant in highly variable river systems. Additional processes illustrated in Figure 1 can be included within the memory function by means of the appropriate immobilization probabilities and residence time distributions, provided that they can be characterized independently with data or independent models. For example, retention and resuspension due to interaction with benthic biofilms can be represented with an independent immobilization probability and residence time distribution. However, the current model framework is limited to classic IID assumptions (independent and identically distributed variables), and thus cannot describe cases where multiple processes covary or where there is an underlying nonstationary (spatial or temporal variability) in the governing probability distributions [*Metzler and Klafter*, 2000]. Notable cases beyond the scope of the current modeling framework are long-term feedbacks between hyporheic exchange, fine particle deposition, streambed structure, and biofilm growth; and flood disturbances that simultaneously change hyporheic flow, bed morphology, and particle dynamics.

4. Simulation of Particle Transport in Streams

We demonstrate how the stochastic modeling framework can represent fine particle dynamics observed in the field. We use two data sets for this comparison, one from a field injection of ^{14}C-labeled natural fine POM (FPOM) in a small gravel-and-cobble-bed mountain stream [*Minshall et al*., 2000; *Newbold et al*., 2005], and the second from a field injection of fluorescent microspheres in a small sand bed coastal stream [*Harvey et al*., 2012]. Both particle injections were paired with conservative solute injections, providing the ability to discriminate particle deposition and resuspension from in-stream mixing and hyporheic exchange. The first data set contains only in-stream measurements of FPOM and a conservative solute. Based on the combination of FPOM and solute tracer measurements, the model can differentiate the processes that control fine particle deposition and resuspension from hydrodynamic in-stream transport and hyporheic exchange. The second data set includes both in-stream data and local measurements of solute and fine particle transport and retention within the streambed sediment. This provides the ability to separately assess in-stream and subsurface processes, and supports predictive models for upscaling from the local scale to the reach scale.

4.1. Natural Organic Particle Transport in a Gravel Bed Stream

Newbold et al. [2005] performed solute and particle injections in Middle Bloomington Creek, Idaho. The study reach was comprised of mainly cobble, gravel, and some sand with average slope = 0.018, discharge = 225 L s^{-1}, depth = 0.31 m, and velocity = 0.29 m s^{-1} at time of the injection [*Minshall et al*., 2000; *Newbold et al*., 2005].

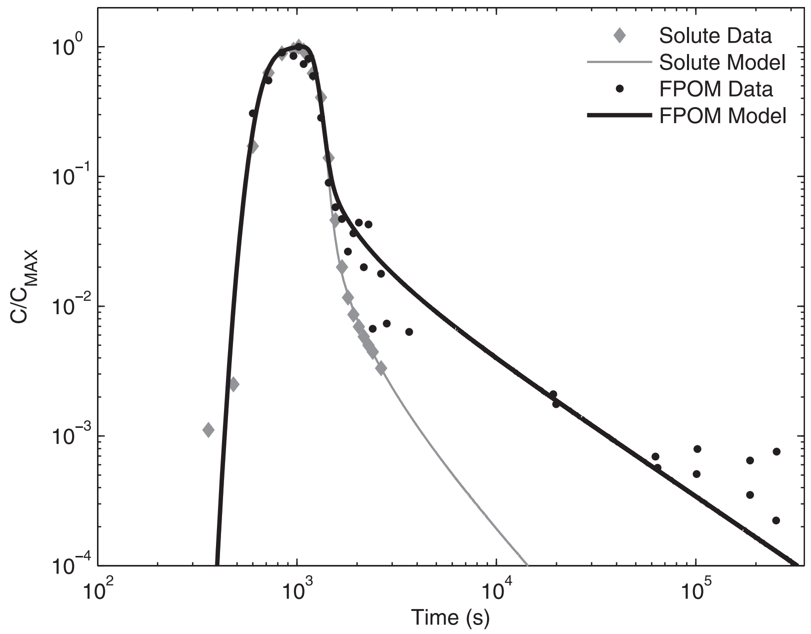

Figure 2. Observations and model fits of in-stream breakthrough curves for a conservative solute (Rhodamine) and FPOM. In-stream transport and hyporheic exchange of solute resulted in a wide range of retention times, shown with power law tailing (slope = −1.65). FPOM showed increased retention compared to solute with a heavier power law tail (slope = −1.05), with quick deposition and slow FPOM release.

Both a conservative solute tracer (Rhodamine) and ^{14}C-labeled FPOM were injected over 8 min, and breakthrough curves were measured at multiple distances downstream from the injection point for up to 5 days. We apply the model to data collected 250 m downstream of the injection site.

We first fit the stochastic model to solute data to characterize in-stream transport and hyporheic exchange, then used these fitted parameters to model fine particle transport. The best fit values of in-stream velocity and dispersion were 0.37 and 0.9 m^2 s^{-1}, respectively. These values are similar to those previously reported by *Newbold et al*. [2005]. Hyporheic exchange was best described by a power law residence time distribution, $\tilde{\varphi}_S(u)=\frac{1}{1+u^{-(\beta_S+1)}}$, where the power law slope β_S is -1.65 and a probability of immobilization $\Lambda_S = 6.0\times10^{-3}\text{s}^{-1}$. We assumed an exponential travel time distribution in the mobile region $\tilde{\psi}_0(u)=1/(1+u)$. The resulting fit of the observed solute BTC is shown in Figure 2. The wide range in solute retention times produces a breakthrough curve with power law tailing.

We simulated FPOM transport using the in-stream (*U, K*), and hyporheic exchange $(\Lambda_S, \ \tilde{\varphi}_S)$ parameters obtained from the solute fit, with an additional probability of immobilization of fine particles, Λ_{HP}, and residence time distribution of resuspension, $\tilde{\varphi}_{HP}$, within the hyporheic region, as given in equation (4). Particle deposition and resuspension within the hyporheic region were best fit with a probability of immobilization $\Lambda_{HP}= 4.0\times10^{-1}\text{s}^{-1}$ and a power law resuspension time distribution, $\tilde{\varphi}_{HP}=\frac{1}{1+u^{-(\beta_P+1)}}$, where the power law slope β_P is -1.2.

Both solute and particle breakthrough curves show power law tails, but the FPOM breakthrough curve has a heavier power law tail, with a slope of -1.05 compared to the solute breakthrough curve slope of -1.65, demonstrating there is increased retention of fine particles in this stream (Figure 2). The increased retention is due to the continuous deposition and resuspension of particles within the streambed, which is captured by the immobilization probability and resuspension time distribution in the model $(\Lambda_{HP}, \tilde{\varphi}_{HP})$. Previous models were not able to capture both the quick processes of advection-dispersion that control the breakthrough curve peak behavior and the slower FPOM resuspension that controls the long-term tail dynamics. The stochastic modeling framework improves the description and interpretation of particle transport by distinguishing hyporheic exchange that influences both solute and particle transport from specific particle deposition/resuspension processes.

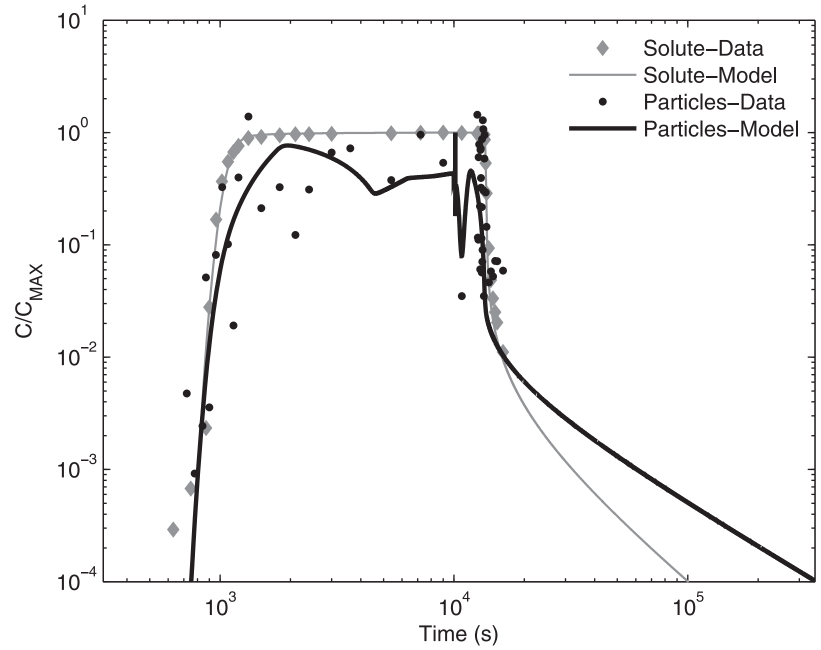

Figure 3. Observations and model fits of in-stream breakthrough curves for a conservative solute (Bromide) and fine fluorescent particles. In-stream transport and hyporheic exchange parameters were determined from solute data fit, while fine particle hyporheic removal and resuspension parameters were based on best fit parameters of a column experiment. Fine particles showed increased retention and a heavier power law tail (slope = −1.26) compared to solute (slope = −1.70).

4.2. Tracer Particle Transport in a Sand Bed Stream

Harvey et al. [2012] coinjected bromide as a conservative tracer and fluorescent microspheres (Day Glo AX Pigment-Aurora Pink) for 3.5 h in Clear Run, a second-order stream located in Wilmington North Carolina. The stream channel is regularly meandering with a bed comprised of well-sorted medium sand covered by dune-shaped bed forms [*Harvey et al*., 2012]. At the time of the injection, approximate mean hydrologic, geomorphic, and hydrogeologic conditions were: discharge = 60 L s^{-1}, velocity = 0.19 m s^{-1}, porosity = 0.4, bed form wavelength = 0.12 m, bed form height = 0.01 m, depth = 0.06 m, and streambed hydraulic conductivity = 4.8×10^{-4} m s^{-1}. The tracer particles were synthetic fluorescent organic microspheres, 1–10 μm in diameter, consisting of amorphous melamine formaldehyde polymers and acrylic resins, that have similar density (1.36 g cm^{-3}) as natural organic seston [*Cushing et al*.,1993], and similar negative surface charge (zeta potential = −29 mV) as riverine fine particulate organic matter. *Harvey et al*. [2012] measured in-stream solute and particle breakthrough curves at sites 47 and 221 m downstream of the injection location for 1 h past the injection cut off time, and also measured mobile particle concentrations in pore water at various depths within the sediment bed at 187 m downstream of the injection location. *Harvey et al*. [2012] also observed particle resuspension resulting from an experimental flood event, but that resuspension event will not be considered here as the model framework presented in section 3 is restricted to base flow processes. We apply the model to data collected at 221 m downstream of the injection.

4.2.1. In-Stream Solute Simulation

Following the same procedure used for Bloomington Creek, we first fit the stochastic model to solute data to characterize in-stream transport and hyporheic exchange and then used these fitted parameters to model fine particle transport in the stream. The best fit results for in-stream velocity and dispersion were 0.21 m s^{-1} and 0.19 m^2 s^{-1}, respectively. Hyporheic exchange was best described by a power law residence time distribution, $\tilde{\varphi}_S(u)=\frac{1}{1+u^{-(\beta_S+1)}}$, with a power law slope $\beta_S = -1.70$, and a probability of immobilization $\Lambda_S=9.0\times10^{-3}s^{-1}$. We assumed an exponential residence time distribution in the mobile region $\tilde{\psi}_0(u)=1/(1+\gamma)$. We used a square-wave input for the conservative solute as the upstream boundary condition to match the 3.5 h injection. The resulting fit of the observed solute breakthrough curve is shown in Figure 3.

4.2.2. Subsurface Solute and Fine Particle Simulation

We performed a supplemental column experiment to obtain well-constrained information on particle filtration and resuspension within the streambed. We coinjected a conservative tracer and the same fluorescent microspheres used in the field into a 6 cm long by 2.5 cm diameter glass column wet packed with Clear Run streambed sediment, and observed the resulting breakthrough curves at the column outlet. The flow rate through the column was kept constant at 14.5 L s^{-1}. Lithium chloride (LiCl) was used for the conservative tracer at a concentration of 400 ppm in a background solution of deionized water. The fine particles injected into the column were DayGlo Fluorescent AX Pigments (Aurora Pink) identical to those used in Clear Run. The average injection concentration was 1.2×10^5 particles mL^{-1}, slightly greater than the plateau concentration of fine particles at the sediment-water interface at Clear Run, 1.1×10^4 particles mL^{-1}, in a background of deionized water with added 5 g L^{-1} of sodium hexametaphosphate surfactant (Alfa Aesar) in order to disperse and wet the fluorescent particles, which are slightly hydrophobic. The same procedure was used in the field injection experiment. The tracer solution and particle suspension were injected from separate beakers into the column for 1 h. At the end of the injection, the influent was switched to DI water for an additional 10 h. The solute and particle concentrations were measured in the column effluent at least every 3 min throughout and immediately following the 1 h injection, and then at least every 30 min for the remainder of the experiment.

Following procedures employed by *Harvey et al.* [2012], particle concentrations were analyzed by flow cytometry on a Becton Dickinson LSR II (San Jose, CA) equipped with FACSDiva 6.0 software and 488, 635, and 405 nm lasers. The emission filters used for the particles were 525/50 (Alexa Fluor 430) and 582/15 (PE) and results were analyzed using FlowJo version 8.8.6 (Tree Star, Inc.). Forward scatter, side scatter, and fluorescent parameters were displayed in a log scale to include the range of size and fluorescence of the fluorescent pigment particles. Accucount 5 μm Microspheres (Spherotech) were added to each sample and used as a reference population for the direct determination of the sample volume analyzed by the flow cytometer. Lithium was analyzed by inductively coupled plasma/atomic emission spectroscopy (Varian® VISTA).

The solute transported conservatively through the column, as indicated by the mobile-immobile model best fit using a power law residence time distribution in the mobile region $\tilde{\psi}_0(u) = \frac{1}{1+u^{-(\beta_0+1)}}$, with a power law slope $\beta_0 = -1.995$, and dispersion coefficient $= 1 \times 10^{-6}$ m^2 s^{-1}. The best-fit probability of immobilization due to reversible filtration was $\Lambda_{CP} = 3.5 \times 10^{-2}$ s^{-1}. The residence time distribution of particles immobilized due to reversible filtration was best represented by a power law with $\beta_{CP} = -1.35$ $\left(\tilde{\varphi}_{CP} = \frac{1}{1+u^{-(\beta_{CP}+1)}}\right)$. The model fits of the observed solute and particle column breakthrough curves are shown in Figure 4. We also fit the column data with the reversible filtration model, yielding a best fit filtration coefficient, $\lambda_f = 5$ m^{-1}. The residence time distribution of particles resuspended within the column was best represented by a power law with $\beta_{CP} = -1.35$ $\left(\tilde{\varphi}_{CP} = \frac{1}{1+u^{-(\beta_{CP}+1)}}\right)$. The reversible filtration model fit is included in Figure 4.

4.2.3. In-Stream Fine Particle Simulation

Fine particle transport in Clear Run was simulated using the hyporheic exchange terms (Λ_S and $\tilde{\varphi}_S$) obtained from fitting the in-stream solute tracer breakthrough curve, and particle deposition and resuspension terms obtained from the column experiment, $\Lambda_{HP} = 3.5\times10^{-2}s^{-1}$ and $\tilde{\varphi}_{HP} = \frac{1}{1+u^{-(\beta_P+1)}}$, where the power law slope $\beta_P = -1.35$. Since the fine particle injectate concentration during the 3.5 h injection was not uniform, we used the actual measured concentrations of the injectate as the upstream boundary condition. The explicit multiscale particle transport model (equations (1)–(5)) allows in-stream particle transport to be predicted from the combination of observations of in-stream conservative solute transport and *ex situ* observations of pore water transport and reversible filtration in streambed sediments. The resulting simulated particle breakthrough curve is shown in Figure 3.

4.2.4. Prediction of Fine Particle Transport

The stochastic mobile-immobile model is predictive in cases where the memory function can be defined by either independent observations or a process-based model. We predict in-stream fine particle transport using the combination of (1) pumping model simulations of hyporheic exchange, (2) in-stream transport properties inferred from the solute tracer injection, (3) parameters to characterize pore water transport and reversible particle filtration inferred from the column filtration experiment, and (4) colloid filtration theory applied to upscale the column results to pore water transport in the streambed. We use a modified version of the pumping model described by *Packman et al.* [2000] to represent particle transport and filtration in

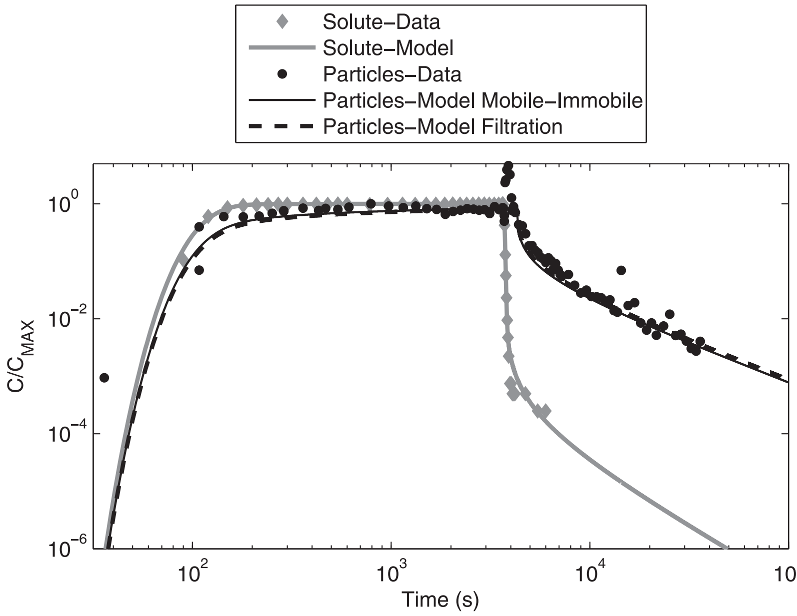

Figure 4. Conservative solute and fine particle model fits within a column experiment using sand bed stream sediment. The particle data were fit to both the mobile-immobile model and colloid filtration model with resuspension.

the streambed. The mean pore water velocity in the field was calculated using the pumping model to be 1.34×10^{-5} m s^{-1}. The hyporheic residence time distribution of solute flow along streamlines predicted by the pumping model is shown in Figure 5. This distribution was used in the stream-scale CTRW model to predict overall downstream, with the in-stream velocity and dispersion coefficient for Clear Run reported by *Harvey et al.* [2012]: $U = 0.21$ m s^{-1} and $K = 0.19$ m^2 s^{-1}. The resulting solute breakthrough curve is compared with the observed in-stream transport in Figure 6. In order to apply the column experiment particle

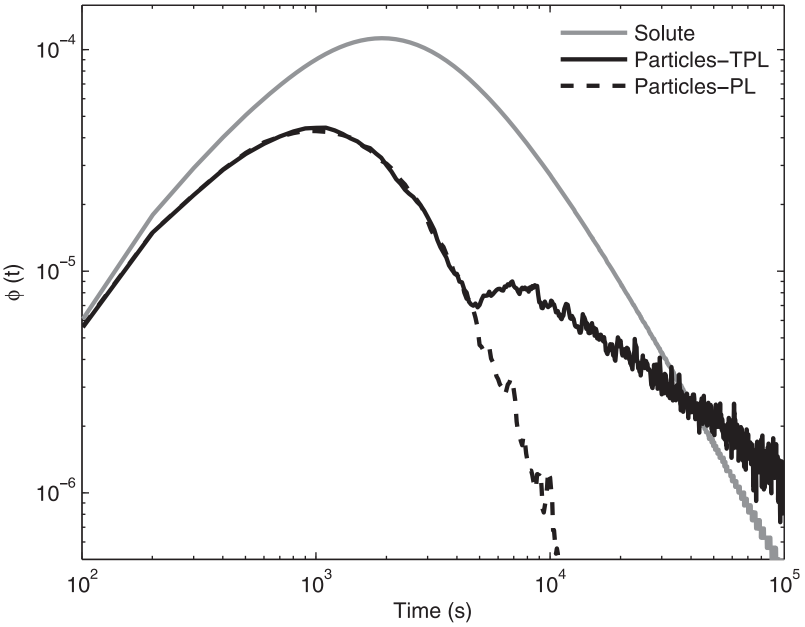

Figure 5. Hyporheic residence time distribution of solute and particles predicted from pumping model. Advective transport induced by bed forms results in a wide range of hyporheic residence times, shown by a power law tailing behavior. Particles with an infinite power law distribution of resuspension times showed irreversible filtration, while a truncated power law distribution showed slow release of particles from the streambed.

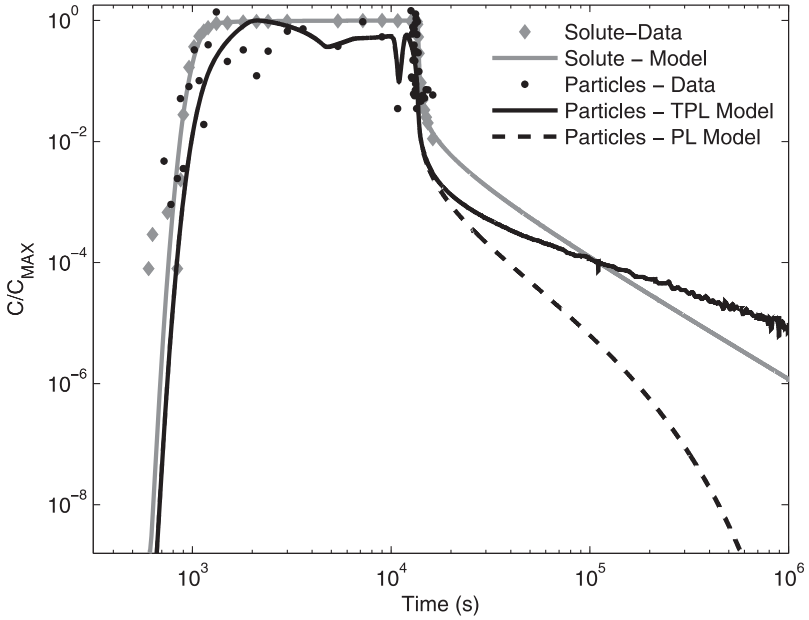

Figure 6. Observed and predicted conservative solute and fine particle in-stream breakthrough curves. The model output is a prediction based on bed form and stream parameters and not a fit. Both solute and particle with truncated power law (TPL) resuspension predictions exhibit power law tailing at longer time scales, with the particle power law tail heavier than the solute. The particle prediction for an infinite power law (PL) distribution of resuspension times shows only immobilization without noticeable resuspension, which resulted in an exponential removal.

parameters to field conditions, we modify the filtration coefficient using colloid filtration theory. For physicochemical filtration in saturated porous media:

$$\lambda_f = \frac{3}{2}\frac{1-\theta}{d_c}\alpha\eta_0 \tag{7}$$

where θ is the porosity, d_c is the sediment diameter, α is the attachment efficiency, and η_0 is the contact efficiency. Because we performed laboratory filtration experiments with the same tracer particles and sediments from the stream, only the pore water velocity (and thus η_0) varied between the lab and field. We corrected the filtration coefficient using the relationships developed by *Tufenkji and Elimelech* [2004] based on the mean pore water velocity predicted by the pumping model, yielding an estimate of $\lambda_f = 55$ m^{-1} for field conditions. The residence time distributions for solute and particles, $\varphi_S(t)$ and $\varphi_P(t)$, predicted from the pumping model are shown in Figure 5. We simulated reversible filtration in the streambed using both infinite and truncated power law residence time distributions for reversible filtration following the power law distribution observed in the column experiment ($t^{-1.35}$, truncation time = 1 h). This resuspension time distribution was included in the local-scale CTRW model for reversible filtration along pumping streamlines to predict the overall residence time distribution of particles in the hyporheic zone. The hyporheic residence time distributions are shown in Figure 5. An infinite power law local resuspension time distribution with slope -1.35 causes the bed to be essentially a sink for particles. However, the truncated power law distribution causes filtered particles to be slowly resuspended from the streambed back into the water column. The hyporheic residence time distributions shown in Figure 5 were then used in the stream-scale CTRW to predict overall downstream particle transport. The resulting breakthrough curves are compared with the observed in-stream transport in Figure 6. The limited tail of the breakthrough curve, resulting from the artificial flood imposed in the field experiment, does not allow the long-term particle resuspension behavior to be differentiated based on in-stream observations.

5. Discussion

Fine particles, including particulate organic carbon, can be retained in streams long-term and remobilized in events that significantly disturb streambed sediments and biofilms. The results presented here demonstrate that fine particles also cycle continuously between the stream and subsurface under base flow conditions. Although the cyclic process of exchange between the water column and streambed has been described previously by the nutrient spiraling concept [*Newbold et al*., 1981], here we showed that the time scales of storage implied by conventional spiraling and transient storage metrics are much too short. We now understand that there is stronger river-hyporheic interaction that delivers fine particles into the benthic and hyporheic regions, and provides long-term biophysical opportunity for biogeochemical processing [*Battin et al*., 2008]. The availability of substrates and nutrients (C, N and P) associated with fine particles in streams provides a key link between catchment processes and aquatic ecological cycles [*Battin et al*., 2008; *Aufdenkampe et al*., 2011; *Dawson et al*., 2012]. Recent estimates of CO_2 outgassing from streams and rivers suggest that land-derived organic carbon plays an important role in the net heterotrophy of fluvial ecosystems [*Battin et al*., 2008; *Butman and Raymond*, 2011; *Mayorga et al*., 2005]. Fresh and labile POC is expected to be consumed quickly and locally without significant transport downstream, but this process is regulated by the delivery and retention of associated particles in benthic and hyporheic microbial communities. The timing and magnitude of ecological connectivity from up- to down-stream is therefore strongly controlled by fine particle deposition and resuspension events.

The significant longitudinal connectivity of POC has been previously described by the river continuum concept [*Vannote et al*., 1980], but here we developed a conceptual model for fine particle transport in rivers that details the individual processes that control downstream transport and storage within stream channels. This includes advective delivery of fine suspended particles to the streambed, transport through pore waters, and reversible filtration within the streambed. Our conceptual model, described in terms of basic deposition, retention, and resuspension processes, provides the basis for improved interpretation of the effects of stream, sediment, and periphyton characteristics on POC dynamics. It is quite similar to the overall nutrient spiraling view [*Webster and Patten*, 1979; *Newbold et al*., 1981], but updated to incorporate recent advances in understanding of the physics of hyporheic exchange and fine particle deposition/resuspension processes. While the conceptual model provides an updated framework for the understanding of particle propagation through rivers, the stochastic mobile-immobile model provides a way to quantify propagation of fine particles through the river continuum. We showed that the stochastic mobile-immobile model framework provides an appropriate description of the continuum of rates that control solute and particle storage in rivers. Retention is defined by a memory function that can account for any distribution of storage time scales. Explicit separation of hyporheic exchange processes, relevant to all dissolved and suspended materials, from particle-specific deposition and resuspension clarifies the distinct roles of hydrodynamic transport and particle immobilization in net downstream particle transport. By evaluating solute and particle transport observed in two streams having very different hydrological and morphological characteristics (one gravel/cobble bed mountain stream and one sand bed coastal plain stream), we showed that this stochastic modeling framework is generally needed to represent the combination of quick deposition and slow resuspension of particles in rivers.

Previous models underestimated the interaction of both solutes and particles with the streambed for the streams considered here. First-order particle removal models often assume that deposition is irreversible. This leads to an underestimation of deposition rates because some particles observed in-stream have previously deposited and returned from the streambed. Even when resuspension has been incorporated, such as in the model described in *Newbold et al*. [2005], particle residence time distributions were assumed to be exponential. However, we found that hyporheic retention generally follows power law residence time distributions that occur over much longer time scales. In fact, the best fit residence time distributions were heavy tailed, meaning that they have infinite mean values. The stochastic mobile-immobile model distinguishes the deposition process, described by a probability of immobilization, from resuspension, characterized by the hyporheic residence time distribution and particle resuspension time distribution. This clarifies that observed in-stream particle breakthrough curve data exhibit multiple deposition/resuspension events with long-term (heavy-tailed) storage. Power law tailing has persistently been found for both solutes and fine particles [*Haggerty et al*., 2002; *Schumer et al*., 2003; *Cortis et al*., 2006], indicating that storage time scales are very long and that particles interact with the bed multiple times during downstream transport. Recent experiments and models show that surface-subsurface fluxes and hyporheic exchange induced by geomorphological features exhibits fractal behavior, leading to a power law residence time distribution of solutes in storage that cannot be represented well by first-order models [*Haggerty et al*., 2000; *Cardenas*, 2008; *Drummond et al*., 2012].

The stochastic model framework for fine particle transport in streams is flexible in its ability to synthesize diverse in-stream and subsurface processes based on a combination of local observations and application of predictive models for specific processes. In both the sand bed and gravel bed streams considered here, information on in-stream transport and hyporheic exchange was obtained from conservative solute data. Differing degrees of information on particle immobilization and remobilization were used to parameterize the particle transport models for each stream. In Bloomington Creek (the gravel bed stream) fine particle transport is expected to be dependent on hyporheic exchange, subsurface filtration, and trapping in benthic biofilms. However, only in-stream observations were available. For this case, sequential fitting of the in-stream solute and particle breakthrough curves revealed the distinct time scales of hyporheic exchange relative to particle retention at the whole-stream scale. Additional independent observations or estimates of subsurface filtration and biofilm trapping in this type of stream could be independently parameterized in the stochastic model to distinguish the specific contribution of each process to downstream transport. In Clear Run (the sand bed stream) we supplemented in-stream observations with an *ex situ* experiment to characterize pore water transport and reversible particle filtration in the streambed sediments. By incorporating this information into a multiscale stochastic model, we were able to show that reversible filtration within the streambed produces long-term retention of particles at the whole-stream scale. This model was made predictive by incorporating discrete process models for hyporheic pumping exchange and reversible particle filtration into the mobile-immobile stochastic model for the whole stream. Similar approaches can be used to characterize the effects of interaction between other stream-borne constituents, such as contaminants and nutrients, with streambed sediments.

The mobile-immobile stochastic model allows for specific POC transport processes to be parameterized individually and then convolved together to determine the overall residence time distribution of POC in stream. The model can account for both fast transport processes and long-term retention of particles in-stream. A particular advantage of the mobile-immobile model framework we present here is that it distinguishes the effects of hydrodynamic transport processes that affect all stream-borne constituents (e.g., hyporheic exchange) from specific mechanisms of particle deposition and retention. Processes that produce fractal behavior, such as the slow resuspension of fine particles within the streambed sediments, are represented in the model through the use of heavy-tailed power law distributions that incorporate a wide range of time scales. This analysis is particularly useful for problems where residence time is critical to overall system dynamics, as well as for constituents that remain important at low concentrations. The whole-ecosystem transformation of many reactive and biologically important constituents depends on delivery and retention in regions of high microbial activity, notably the benthic and hyporheic regions. In this context, the stochastic model presented here provides an improved description of the biophysical opportunity for microbial metabolism of carbon, nutrients, and biodegradable contaminants in rivers. Similarly, the model describes the retention of hazardous substances within the river corridor and thus both the rate of long-term accumulation of these materials at the whole-system scale and the ongoing slow rate of release. While we applied the model here to short-term tracer injection data, it can also be used to simulate long-term dynamics based on distributed inputs. This is useful, for example, for describing the retention of pathogens in streambeds, which provides the opportunity for colonization of streambed sediments followed by slow release of infectious organisms during base flow, and extremely large export at high flows [*Benjamin et al*., 2013; *Kistemann et al*., 2002; *Muirhead et al*., 2004; *Yakirevich et al*., 2013].

Floodplains are often well connected to streams via flood pulses, contributing to in-stream POC inputs [*Junk et al*., 1989; *Aufdenkampe et al*., 2011]. The long-term storage associated with floodplains represents much larger spatial and temporal scales than captured in the data sets analyzed here, but can be considered within the same conceptual framework. It is very difficult to characterize the full range of particle storage time scales in the field, so current studies either address in-stream transport or floodplain storage, but not normally both together. The stochastic mobile-immobile approach can be extended to include interactions with floodplains at base flow, but cannot currently incorporate large fluctuations in flow, such as flood events. This is due to the classic IID assumptions (independent and identically distributed variables) within the stochastic approached presented here, requiring that all governing distributions are stationary over space and time, and remain uncoupled over all scales. Important cases that cannot be represented using these assumptions include strong variations in streamflow (i.e., floods) that cause substantial changes in the behavior of many constituents, long-term feedbacks in streambed properties associated with fine particle accumulation or biofilm growth, and threshold processes associated with onset of bed sediment transport.

These processes can potentially be considered within the same stochastic modeling framework presenting by employing new advancements in mathematics such as correlated CTRW models for nonstationary processes [*Le Borgne et al*., 2011], or by explicitly analyzing the coupled dynamics of solutes, suspended particles, and bed sediments with multicomponent, multiscale stochastic models. Here we demonstrated how stochastic models can be used to improve interpretation of organic particle dynamics in rivers. Upscaled, long-term simulations will require advancements in both stochastic transport theory and observation of spatially-distributed particle transport and transformation processes.

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References

Arnon, S., L. P. Marx, K. E. Searcy, and A. I. Packman (2010), Effects of overlying velocity, particle size, and biofilm growth on stream-subsurface exchange of particles, *Hydrol. Processes*, *24*, 108–114, doi:10.1002/hyp.7490.

Atkinson, C. L., S. W. Golladay, S. P. Opsahl, and A. P. Covich (2009), Stream discharge and floodplain connections affect seston quality and stable isotopic signatures in a coastal plain stream, *J. N. Am. Benthol. Soc.*, *28*(2), 360–370, doi:10.1899/08-102.1.

Aufdenkampe, A. K., E. Mayorga, P. A. Raymond, J. M. Melack, S. C. Doney, S. R. Alin, R. E. Aalto, and K. Yoo (2011), Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere, *Front Ecol. Environ.*, *9*(1), 53–60, doi:10.1890/100014.

Battin, T. J., L. A. Kaplan, J. D. Newbold, and C. M. E. Hansen (2003), Contributions of microbial biofilms to ecosystem processes in stream mesocosms, *Nature*, *426*, 439–442, doi:10.1038/nature02152.

Battin, T. J., L. A. Kaplan, S. Findlay, C. S. Hopkinson, E. Marti, A. I. Packman, J. D. Newbold, and F. Sabater (2008), Biophysical controls on organic carbon fluxes in fluvial networks, *Nat. Geosci.*, *1*, 95–100, doi:10.1038/ngeo101.

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*(3), 718–724, doi:10.1029/WR019i003p00718.

Benjamin, L., E. R. Atwill, M. Jay-Russell, M. Cooley, D. Carychao, L. Gorski, and R. E. Mandrell (2013), Occurrence of generic *Escherichia coli*, *E. Coli* O157 and *Salmonella* spp. in water and sediment from leafy green produce farms and streams on the Central California coast, *Int. J. Food Microbiol.*, *165*, 65–76, doi:10.10.1016/j.ijfoodmicro.2013.04.003.

Benson, D. A., and M. M. Meerschaert (2009), A simple and efficient random walk solution of multi-rate mobile/immobile mass transport equations, *Adv. Water Resour.*, *32*, 532–539, doi:10.1016/j.advwatres.2009.01.002.

Berkowitz, B., A. Cortis, M. Dentz, and H. Scher (2006), Modeling non-fickian transport in geological formations as a continuous time random walk, *Rev. Geophys.*, *44*, RG2003, doi:10.1029/2005RG00178.

Blair, N. E., and R. C. Aller (2012), The fate of terrestrial organic carbon in the marine environment, *Annu. Rev. Mar. Sci.*, *4*, 401–23, doi: 10.1146/annurev-marine-120709-142717.

Boano, F., A. I. Packman, A. Cortis, R. Revelli, and L. Ridolfi (2007), A continuous time random walk approach to the stream transport of solutes, *Water Resour. Res.*, *43*, W10425, doi:10.1029/2007WR006062.

Boulêtreau, S., F. Garabétian, S. Sauvage, and J.-M. Sánchez-Pérez (2006), Assessing the importance of a self-generated detachment process in river biofilm models, *Freshwater Biol.*, *51*, 901–912, doi:10.1111/j.1365-2427.2006.01541.x.

Brunke, M. (1999), Colmation and depth filtration within streambeds: Retention of particles in hyporheic interstices, *Int. Rev. Hydrobiol.*, *84*(2), 99–117.

Butman, D., and P. A. Raymond (2011), Significant efflux of carbon dioxide from streams and rivers in the United States, *Nat. Geosci.*, *4*, 839–842, doi:10.1038/NGEO1294.

Cardenas, M. B. (2008), Surface water-groundwater interface geomorphology leads to scaling of residence times, *Geophys. Res. Lett.*, *35*, L08402, doi:10.1029/2008GL033753.

Chapin, F. S., III, et al. (2006), Reconciling carbon-cycle concepts, terminology, and methods, *Ecosystems*, *9*, 1041–1050, doi:10.1007/s10021-005-0105-7.

Cole, J. J., and N. F. Caraco (2001), Carbon in catchments: Connecting terrestrial carbon losses with aquatic metabolism, *Mar. Freshwater Res.*, *52*, 101–110, doi:10.1071/MF00084.

Cole, J. J., et al. (2007), Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget, *Ecosystems*, *10*, 171–184, doi:10.1007/s10021-006-9013-8.

Cortis, A., and B. Berkowitz (2005), Computing 'anomolous' contaminant transport in porous media: The CTRW MATLAB tool-box, *Ground Water*, *43*(6), 947–950, doi:10.1111/j.1745-6584.2005.00045.x.

Cortis, A., T. Harter, L. Hou, E. R. Atwill, A. I. Packman, and P. G. Green (2006), Transport of *Cryptosporidum parvum* in porous media: Long-term elution experiments and continuous time random walk filtration modeling, *Water Resour. Res.*, *42*, W12S13, doi:10.1029/2006WR004897.

Cushing, C. E., G. W. Minshall, and J. D. Newbold (1993), Transport dynamics of fine particulate organic matter in two Idaho streams, *Limnol. Oceanogr.*, *38*(6), 1101–1115, doi:10.4319/lo.1993.38.6.1101.

Dawson, J. J. C., Y. R. Adhikari, C. Soulsby, and M. I. Stutter (2012), The biogeochemical reactivity of suspended particulate matter at nested sites in the Dee basin, NE Scotland, *Sci. Total Environ.*, *434*, 159–170, doi:10.1016/j.scitotenv.2011.08.048.

Drummond, J. D., T. P. Covino, A. F. Aubeneau, D. Leong, S. Patil, R. Schumer, and A. I. Packman (2012), Effects of solute breakthrough curve tail truncation on residence time estimates: A synthesis of solute tracer injection studies, *J. Geophys. Res.*, *117*, G00N08, doi:10.1029/2012JG002019.

Elliot, A. H., and N. H. Brooks (1997), Transfer of nonsorbing solutes to a streambed with bed forms: Theory, *Water Resour. Res.*, *33*(1), 123–136, doi:10.1029/96WR02784.

Fries, J. S., and J. H. Trowbridge (2003), Flume observations of enhanced fine-particle deposition to permeable sediment beds, *Limnol. Oceanogr. Methods*, *48*(2), 802–812, doi:10.4319/lo.2003.48.2.0802.

Fries, J. S., and G. L. Taghon (2010), Particle fluxes into permeable sediments: Comparison of Mechanisms mediating deposition, *J. Hydraul. Eng.*, *136*(4), 214–221, doi:10.1061/(ASCE)HY.1943-7900.0000169.

Haggerty, R., and S. M. Gorelick (1995), Multiple-rate mass transfer for modeling diffusion and surface reactions in media with pore-scale heterogeneity, *Water Resour. Res.*, *31*(10), 2383–2400, doi:10.1029/95WR10583.

Haggerty, R., S. A. McKenna, and L. C. Meigs (2000), On the late-time behavior of tracer test breakthrough curves, *Water Resour. Res.*, *36*(12), 3467–3479, doi:10.1029/2000WR900214.

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.

Harter, T., S. Wagner, and E. R. Atwill (2000), Colloid transport and filtration of *Cryptosporidium parvum* in sandy soils and aquifer sediments, *Environ. Sci. Technol.*, *34*, 62–70, doi:10.1021/es990132w.

Harvey, R. W., and S. P. Garabedian (1991), Use of colloid filtration theory in modeling movement of bacteria through a contaminated sandy aquifer, *Environ. Sci. Technol.*, *25*, 178–185, doi:10.1021/es00013a021.

Harvey, J. W., et al. (2012), Hydrogeomorphology of the hyporheic zone: Stream solute and fine particle itneractions with a dynamic streambed, *J. Geophys. Res.*, *117*, G00N11, doi:10.1029/2012JG002043.

Hope, D., M. F., Billett, and M. S. Cresser (1994), A review of the export of carbon in river water: Fluxes and processes, *Environ. Pollut.*, *84*, 301–324, doi:10.1016/0269-7491(94)90142-2.

Huettel, M., W. Ziebis, and S. Forster (1996), Flow-induced uptake of particulate matter in permeable sediments, *Limnol. Oceanogr.*, *41*(2), 309–322, doi:10.4319/lo.1996.41.2.0309.

Junk, W. J., P. B. Bayley, and R. E. Sparks (1989), The flood pulse concept in river-floodplain systems, *Can. Spec. Publ. Fish. Aquat. Sci.*, *106*, 110–127.

Karwan, D. L., and J. E. Saiers (2012), Hyporheic exchange and streambed filtration of suspended particles, *Water Resour. Res.*, *48*, W01519, doi:10.1029/2011WR011173.

Kistemann, T., T. Claßen, C. Koch, F. Dangendorf, R. Fischeder, J. Gebel, V. Vacata, and M. Exner (2002), Microbial load of drinking water reservoir tributaries during extreme rainfall and runoff, *Appl. Environ. Microbiol.*, *68*(5), 2188–2197, doi:10.1128/AEM.68.5.2188-2197.2002.

Le Borgne, T., D. Bolster, M. Dentz, P. de Anna, and A. Tartakovsky (2011), Effective pore-scale dispersion upscaling with a correlated continuous time random walk approach, *Water Resour. Res.*, *47*, W12538, doi:10.1029/2011WR010457.

Margolin, G., M. Dentz, and B. Berkowitz (2003), Continuous time random walk and multirate mass transfer modeling of sorption, *Chem. Phys.*, *295*, 71–80, doi:10.1016/j.chemphys.2003.08.007.

Marion, A., M. Zaramella, and A. Bottacin-Busolin (2008), Solute transport in rivers with multiple storage zones: The STIR model, *Water Resour. Res.*, *44*, W10406, doi:10.1029/2008WR007037.

Mayorga, E., A. K. Aufdenkampe, C. A. Masiello, A. V. Krusche, J. I. Hedges, P. D. Quay, J. E. Richey, and T. A. Brown (2005), Young Organic matter as a source of carbon dioxide outgassing from Amazonian rivers, *Nature*, *436*, 538–541, doi:10.1038/nature03880.

McNair, J. N. (2006), Probabilistic settling in the Local Exchange Model of turbulent particle transport, *J. Theor. Biol.*, *241*, 420–437, doi:10.1016/j.jtbi.2005.12.006.

McNair, J. N., and J. D. Newbold (2012), Turbulent particle transport in streams: Can exponential settling be reconciled with fluid mechanics?, *J. Theor. Biol.*, *300*, 62–80, doi:10.1016/j.jtbi.2012.01.016.

Meerschaert, M. M., and A. Sikorskii (2011), *Stochastic Models for Fractional Calculus*, De Gruyter, Studies in Mathematics 43, De Gruyter, Berlin.

Metzler, R., and J. Klafter (2000), The random walk's guide to anomalous diffusion: A fractional dynamics approach, *Phys. Rep.*, *339*, 1–77, doi:10.1016/S0370-1573(00)00070-3.

Minshall, G. W., S. A. Thomas, J. D. Newbold, M. T. Monaghan, C. E. Cushing (2000), Physical factors influencing fine organic particle transport and deposition in streams, *J. N. Am. Benthol. Soc.*, *19*, 1–16, doi:10.2307/1468278.

Muirhead, R. W., R. J. Davies-Colley, A. M. Donnison, and J. W. Nagels (2004), Faecal bacteria yields in artificial flood events: Quantifying instream stores, *Water Res.*, *38*, 1215–1224, doi:10.1015/j.watres.2003.12.010.

Newbold, J. D., J. W. Elwood, R. V. O'Neill, and W. Van Winkle (1981), Measuring nutrient spiralling in streams, *Can. J. Fish. Aquat. Sci.*, *38*, 860–863, doi:10.1139/f81-114.

Newbold, J. D., S. A. Thomas, G. W. Minshall, C. E. Cushing, and T. Georgian (2005), Deposition, benthic residence, and resuspension of fine organic particles in a mountain stream, *Limnol. Oceanogr. Methods*, *50*(5), 1571–1580, doi:10.4319/lo.2005.50.5.1571.

Packman, A. I., and N. H. Brooks (2001), Hyporheic exchange of solutes and colloids with moving bed forms, *Water Resour. Res.*, *37*(10), 2591–2605, doi:10.1029/2001WR000477.

Packman, A. I., N. H. Brooks, and J. J. Morgan (2000a), A physicochemical model for colloid exchange between a stream and a sand streambed with bed forms, *Water Resour. Res.*, *36*(8), 2351–2361, doi:10.1029/2000WR900059.

Packman, A. I., N. H. Brooks, and J. J. Morgan (2000b), Kaolinite exchange between a stream and streambed—Laboratory experiments and evaluation of a colloid transport model, *Water Resour. Res.*, *36*(8), 2363–2372, doi:10.1029/2000WR900058.

Rehg, K. J., A. I. Packman, and J. Ren (2005), Effects of suspended sediment characteristics and bed sediment transport on streambed clogging, *Hydrol. Processes*, *19*, 413–427, doi:10.1002/hyp.5540.

Ren, J., and A. I. Packman (2002), Effects of background water composition on stream-subsurface exchange of submicron colloids, *J. Environ. Eng.*, *128*(7), 624–634, doi:10.1061/(ASCE)0733-9372(2002)128:7(624).

Schumer, R., D. A. Benson, M. M. Meerschaert, and B. Baeumer (2003), Fractal mobile/immobile solute transport, *Water Resour. Res.*, *39*(10), 1296, doi:10.1029/2003WR002141.

Schumer, R., M. M. Meerschaert, and B. Baeumer (2009), Fractional advection-dispersion equations for modeling transport at the Earth surface, *J. Geophys. Res.*, *114*, F00A07, doi:10.1029/2008JF001246.

Stonedahl, S. H., J. W. Harvey, J. Detty, A. Aubeneau, and A. I. Packman (2012), Physical controls and predictability of stream hyporheic flow evaluated with a multiscale model, *Water Resour. Res.*, *48*, W10513, doi:10.1029/2011WR011582.

Stutter, M. I., S. J. Langan, and B. O. L. Demars (2007), River sediments provide a link between catchment pressures and ecological status in a mixed land use Scottish River system, *Water Res.*, *41*, 2803–2815, doi:10.1016/j.watres.2007.03.006.

Tufenkji, N., and M. Elimelech (2004), Correlation Equation for Predicting Single-Collector Efficiency in Physicochemical filtration in Saturated Porous Media, *Environ. Sci. Technol.*, *38*, 529–536, doi:10.1021/es034049r.

Vannote, R. L., G. W. Minshall, K. W. Cummins, J. R. Sedell, and C. E. Cushing (1980), The river continuum concept, *Can. J. Fish. Aquat. Sci.*, *37*, 130–137, doi:10.1139/f80-017.

Webster, J. R., and B. C. Patten (1979), Effects of watershed perturbation on stream potassium and calcium dynamics, *Ecol. Monogr.*, *49*, 51–72, doi:10.2307/1942572.

Wörman, A., and P. Wachniew (2007), Reach scale and evaluation methods as limitations for transient storage properties in streams and rivers, *Water Resour. Res.*, *43*, W10405, doi:10.1029/2006WR005808.

Yakirevich, A., Y. A. Pachepsky, A. K. Guber, T. J. Gish, D. R. Shelton, and K. H. Cho (2013), Modeling transport of *Escherichia coli* in a creek during and after artificial high-flow events: Three-year study and analysis, *Water Res.*, *47*(8), 2676–2688, doi:10.1016/j.watres.2013.02.011.

Zhang, Y., M. M. Meerschaert, and A. I. Packman (2012), Linking fluvial bed sediment transport across scales, *Geophys. Res. Lett.*, *39*, L20404, doi:10.1029/2012GL053476.