

Natural Organic Matter Transport Modeling with a Continuous Time Random Walk Approach

Daniel P. McInnis, Diogo Bolster, and Patricia A. Maurice*

Department of Civil & Environmental Engineering & Earth Sciences, University of Notre Dame, Notre Dame, Indiana.

Received: September 12, 2013

Accepted in revised form: December 10, 2013

Abstract

In transport experiments through columns packed with naturally Fe/Al oxide-coated quartz sand, breakthrough curves (BTCs) of natural organic matter (NOM) displayed strong and persistent power law tailing that could not be described by the classical advection–dispersion equation. Tailing was not observed in BTCs for a nonre-active tracer (sulforhodamine B); therefore, the anomalous transport is attributed to diverse adsorptive behavior of the polydisperse NOM sample rather than to physical heterogeneity of the porous medium. NOM BTC tailing became more pronounced with decreases in pH and increases in ionic strength, conditions previously shown to be associated with enhanced preferential adsorption of intermediate to high molecular weight NOM components. Drawing from previous work on anomalous solute transport, we develop an approach to model NOM transport within the framework of a continuous time random walk (CTRW) and show that under all conditions examined, the CTRW model is able to capture tailing of NOM BTCs by accounting for differences in transport rates of NOM fractions through a distribution of effective retardation factors. These results demonstrate the importance of considering effects of adsorptive fractionation on NOM mobility, and illustrate the ability of the CTRW model to describe transport of a multicomponent solute.

Key words: adsorptive fractionation; anomalous transport; CTRW; NOM

Introduction

NATURAL ORGANIC MATTER (NOM)—a polydisperse mixture of organic compounds that vary in their physicochemical properties—is ubiquitous in aquatic systems and can have a considerable impact on contaminant and nutrient mobility (Qualls and Haines, 1991; McCarthy, 1998; Chi and Amy, 2004a). Mobility of any material bound to NOM can be retarded by NOM adsorption to porous media or enhanced when NOM itself remains mobile (McCarthy and Zachara, 1989; Maurice, 2009). Adsorption of NOM to minerals is complex and can be controlled by a variety of surface and interfacial forces and mechanisms (Sposito, 1984; Maurice, 2009), depending upon the physicochemical properties of the NOM sample, the properties of the sorbent mineral phases, and solution conditions such as pH and ionic strength (I). The range of adsorption rates and affinities displayed by a given NOM sample is related to its molecular weight (MW) distribution (Cabaniss *et al.*, 2000), although factors such as aromaticity, carboxyl group content, and amino acid residues—which often correlate with MW—can also be impor-

tant (McKnight *et al.*, 1992; Chi and Amy, 2004b). Preferential adsorption to mineral surfaces, most commonly of intermediate to high MW components, may result in adsorptive fractionation, as has been observed in batch experiments (Meier *et al.*, 1999; Namjesnik-Dejanovic *et al.*, 2000; Chorover and Amistadi, 2001; Hur and Schlautman, 2003) and pulsed addition column experiments (Kreller *et al.*, 2013). Such fractionation is enhanced when high NOM surface coverage results in competition between different components for surface sites (Zhou *et al.*, 2001); this tends to occur at low pH and high I (Tipping, 1981; Vermeer *et al.*, 1998; Zhou *et al.*, 2001).

Adsorptive fractionation, most likely combined with adsorption kinetics, leads to complex transport behavior as the various NOM fractions have different mobility. As a result, NOM breakthrough curves (BTCs; see Fig. 2) often contain significant tailing (asymmetry) that cannot be captured by the classical advection–dispersion equation (ADE) for solute transport (Dunnivant *et al.*, 1992; McCarthy *et al.*, 1993; Seders Dietrich *et al.*, 2013). Empirical models have been developed that successfully reproduce observed NOM BTCs under various conditions and identify parameters important in controlling NOM breakthrough (e.g., Zachman *et al.*, 2007). Whereas empirical models are clearly powerful, building them can require large data sets, and extrapolation beyond the specific experimental conditions used to develop

*Corresponding author: Department of Civil & Environmental Engineering & Earth Sciences, University of Notre Dame, 156 Fitzpatrick Hall, Notre Dame, IN 46556. Phone: (574) 631-3469; Fax: (574) 631-9236; E-mail: pmaurice@nd.edu

a model can be risky. Improved understanding and prediction of NOM transport require further development of more mechanistic models that explicitly take into consideration potential sources of NOM BTC tailing.

Transport that does not obey the ADE due to tailing has been described as “nonideal,” “anomalous,” or “non-Fickian” (because the ADE assumes dispersion in accordance with Fick’s law), and is often attributed to sorption isotherm nonlinearity and/or kinetic effects (Bahr and Rubin, 1987). In many cases involving transport of a single solute in a homogeneous porous medium, sorption can be incorporated into the ADE simply by rescaling using a constant effective retardation factor R that accounts for mass transfer between the aqueous and solid phases (Weber *et al.*, 1991). However, in natural systems containing physical and/or chemical heterogeneity, variability in adsorption behavior, hence in R , may be the dominant mechanism leading to tailing (Bellin *et al.*, 1993; Bolster and Dentz, 2012). Although often identified with heterogeneity of the porous medium, anomalous transport and BTC tailing would also be expected in systems where variability in R is associated with a complex solute mixture such as NOM. Such variability has been observed for NOM size fractions, both in laboratory column experiments and field tracer tests. Seders Dietrich *et al.* (2013) analyzed the MW distributions of column influent and effluent using high-pressure size exclusion chromatography (HPSEC) to calculate travel times for individual NOM MW intervals. They observed a broad range of retardation factors ($R = 1.4$ – 7.9) that depended on pH and I and generally increased with MW. McCarthy *et al.* (1996) noted differences in the mobility of NOM size fractions in a shallow, sandy aquifer and argued that predictive modeling of NOM transport requires a multicomponent representation capable of accounting for its physicochemical complexity. Such a representation may be either discrete or continuous (e.g., Annesini *et al.*, 1994).

In the discrete approach, which has been applied to NOM by a number of researchers (Kilduff *et al.*, 1996; Weigand and Totsche, 1998; Schideman *et al.*, 2006), the multicomponent solute mixture is divided into a finite number of pseudocomponents displaying similar adsorption behavior (Ramaswami and Tien, 1986). Adsorption of each pseudocomponent is modeled explicitly. Whereas the wide array of organic compounds within NOM makes it difficult to identify specific pseudocomponents, van de Weerd *et al.* (1999, 2002) reported good agreement between experimental isotherms and a model representing NOM using either 3 or 6 fractions that varied in their local adsorption behavior based on MW and hydrophobicity. Heterogeneity of the porous medium (i.e., physical heterogeneity) was assumed to have a negligible effect on transport of the NOM mixture. This is an important assumption because purely physical heterogeneity can induce tailing in some hydrologic systems (Sugita and Gillham, 1995). Batch adsorption data were used to estimate sorption parameters for each NOM fraction, and the overall BTC was calculated by solving a set of mass balance equations that described sorption of each fraction using a competitive Langmuir isotherm. Multicomponent representation of NOM using this type of approach is typically constrained by computational capabilities; for example, the code used by van de Weerd *et al.* (2002) limited transport simulations to a maximum of three NOM fractions. Additionally, because parameters measured in batch

experiments often fail to accurately predict transport in column experiments (Szecsody *et al.*, 1998), such an approach is not generally applicable.

In the work described here, we applied a continuous approach, in which the multicomponent NOM system is represented as a continuum containing an infinite number of individual fractions, and parameters for individual solute particles are sampled from a distribution function. To quantify transport based on this distribution function, we turn to a modeling approach that has enjoyed significant success in capturing anomalous (non-Fickian) transport in the context of heterogeneous porous media: the continuous time random walk (CTRW). This model describes macroscopic transport in terms of a probabilistic distribution for mass transfer at the local scale. In a heterogeneous medium, this distribution may be related to spatial variability in R (Dentz and Castro, 2009). Given that heterogeneous mass transfer may also arise through multicomponent adsorption behavior of a polydisperse solute such as NOM, the CTRW model can be adapted to account for variability in R associated with the solute. Although this work focuses on the CTRW model, other alternative transport models, such as multirate mass transfer or a subordinated ADE model—both of which have been shown mathematically equivalent to a CTRW (Dentz and Berkowitz, 2003; Meerschaert and Scheffler, 2004)—should also be capable of describing NOM transport.

The aim of this research is to explore the following hypotheses: (1) variability in adsorption behavior as a function of MW leads to tailing of NOM BTCs under a broad range of solution conditions, and (2) this tailing can be interpreted through an appropriate mathematical formulation of the CTRW. The modeled data are from a series of column experiments by our group (Seders Dietrich *et al.*, 2013) that used a porous medium consisting of naturally Fe/Al oxide-coated quartz sand and an NOM sample that was previously shown to undergo adsorptive fractionation to the Fe-oxyhydroxide mineral goethite in batch experiments (Pullin *et al.*, 2004). Various conditions of pH (5–8) and background electrolyte concentrations (0.001–0.01 M NaClO₄) were examined. As outlined in Seders Dietrich *et al.* (2013), column effluent MW distributions at four sampling times were determined by HPSEC. After separating the MW distributions into five discrete intervals or bins, observed effective retardation factors (R_o) calculated for each bin generally increased with MW. The research presented here builds upon our prior work by fitting the NOM BTCs using a CTRW model, which we construct assuming a continuous distribution for R . This research represents the first application of the CTRW model to transport a physicochemically diverse, well-characterized solute of widespread environmental importance—NOM.

Theory

Anomalous transport and retardation

One characteristic of solute transport in heterogeneous systems that receives much attention is extended and persistent tailing in BTCs, a feature that simply cannot be modeled using the classical ADE. Tailing—particularly power law tailing—reflects the sensitivity of transport to heterogeneity across multiple scales (Berkowitz *et al.*, 2006). Analytically, it may be shown that non-Fickian transport arising in a heterogeneous porous medium with a random, spatially variable R can be

upscaled (i.e., statistically averaged at an observation scale much larger than the correlation length of the spatial heterogeneity) and described by a CTRW, but not by the ADE with an average (constant) R (Dentz and Castro, 2009; Dentz and Bolster, 2010). Upscaled models typically assume that the underlying random field is stationary and ergodic, such that its properties can be deduced from a single statistical representation of the transport process, or in this case that the full distribution of R is accessible to the solute plume. However, for a given realization of the heterogeneous field, the solute plume may only be sampling the full spatial statistics of the system at late (asymptotic) times, if at all (De Barros and Rubin, 2011). This can mean that for certain applications, an ergodic state is not achieved at timescales of interest; thus, the assumptions of the upscaled model are violated (Fernandez-Garcia and Gomez-Hernandez, 2007). In such cases, CTRW-predicted concentrations are subject to substantial uncertainty (Dentz *et al.*, 2009). On the other hand, in this work, we hypothesize and aim to demonstrate that a description of anomalous transport in a system where variability in R arises from physicochemical diversity of the solute (and not heterogeneity associated with the medium) is not subject to this limitation.

CTRW framework

Earliest applications of the CTRW model focused on electron transport through amorphous semiconductors, in which random potential fluctuations give rise to localized traps (i.e., potential minima) that temporarily delay electron migration (Scher and Lax, 1973). Applications of the CTRW model in hydrology have addressed the trapping of solutes due to various forms of physical and chemical heterogeneity in the porous medium. Conceptually, particles representing a certain mass of solute travel through a medium using a series of random transitions in space and time, which can be described by a joint probability density function (pdf), $\psi(\mathbf{x}, t)$, where \mathbf{x} is the particle displacement and t is time. Macroscopically, solute concentrations can be expressed in terms of this pdf, which should encompass all mechanisms governing transport (i.e., advection, dispersion, and sorption). The concentration distribution $c(\mathbf{x}, t)$ can often be related to $\psi(\mathbf{x}, t)$ through a convolution integral reflecting nonlocality in space and/or time (Berkowitz *et al.*, 2006); we focus here on transport that is nonlocal in time.

Following Berkowitz *et al.* (2006), the continuum form of the one-dimensional solute transport equation is as follows:

$$\frac{\partial c(x, t)}{\partial t} = - \int_0^t M(t-t') \left[\nu_\psi \frac{\partial c(x, t')}{\partial x} - D_\psi \frac{\partial^2 c(x, t')}{\partial x^2} \right] dt' \quad (1a)$$

which may be written in Laplace space as the following equation:

$$u\tilde{c}(x, u) - c_0(x) = -\tilde{M}(u) \left[\nu_\psi \frac{d}{dx} \tilde{c}(x, u) - D_\psi \frac{d^2}{dx^2} \tilde{c}(x, u) \right] \quad (1b)$$

It is convenient to work with Laplace transformed equations to replace the convolution in Equation (1a) with a product. Details on the Laplace transform are provided in the

Supplementary Data (Supplementary Data are available online at www.liebertpub.com/ees). In Equation (1b), u is the Laplace variable, $\tilde{c}(x, u)$ is the Laplace-transformed concentration, $c_0(x)$ is the initial condition for concentration, ν_ψ is the transport velocity (which may be distinct from the fluid velocity), D_ψ is a generalized dispersion coefficient, and

$$\tilde{M}(u) \equiv t_1 u \frac{\tilde{\psi}(u)}{1 - \tilde{\psi}(u)} \quad (2)$$

is what is called the memory function with characteristic time t_1 . The memory function may take on a range of different forms reflecting different types of transport.

The choice of $\tilde{\psi}(u)$, the Laplace-transformed distribution of particle transition times, controls the structure of the memory function and represents the underlying transport mechanism(s). One model that has been applied successfully to a number of test cases is the truncated power law (TPL) (Dentz *et al.*, 2004) as follows:

$$\tilde{\psi}(u) = (1 + t_2 u)^\beta \exp(t_1 u) \Gamma\left(-\beta, \frac{t_2}{t_1} + t_1 u\right) / \Gamma\left(-\beta, \frac{t_2}{t_1}\right) \quad (3)$$

where t_2 is a cutoff time ($> t_1$), β is the power law exponent, and $\Gamma(a, x)$ is the incomplete gamma function. The TPL model is adopted here because it is capable of representing a broad range of tailing behaviors that may arise in natural systems. The exponent β indicates the nature of the dispersion; transport is Fickian for $\beta > 2$ and is increasingly anomalous for decreasing β . The cutoff time allows a transition from anomalous behavior to Fickian behavior at $t \gg t_2$.

Once $\tilde{\psi}(u)$ is defined, the above equations may be solved for the resident concentration $\tilde{c}(x, u)$ or the mass flux $\tilde{j}(x, u)$, which is related to \tilde{c} as follows:

$$\tilde{j} \equiv \tilde{M} \nu_\psi (\tilde{c} - \alpha_\psi \partial \tilde{c} / \partial x) \quad (4)$$

where $\alpha_\psi = D_\psi / \nu_\psi$ is the dispersivity. The inverse Laplace transform is then applied to convert the Laplace-domain solution to a time-domain solution. The work described here entails the solution of the inverse problem: determination of $\tilde{\psi}(u)$ based on measurement of the solute BTC, which is equivalent to $\tilde{j}(x, u)$ evaluated on the plane $x = L$, where L is the column length.

Many different conceptual models of solute transport may lead to a CTRW. Previous applications of CTRW modeling have successfully captured nonequilibrium and/or nonlinear adsorption (Drazer *et al.*, 2000; Margolin *et al.*, 2003; Deng *et al.*, 2008); however, the CTRW approach has not been applied previously to adsorption from solute mixtures. Detailed derivation of one possible formulation of the CTRW model for a physicochemically diverse solute such as NOM is provided in the Supplementary Data. Briefly, local transport is described in terms of the motion of a finite number of solute particles. Each particle carries an equal fraction of the total solute mass, but represents a unique chemical subset of NOM. Transport of a given particle is governed by a retardation factor R that depends on the particle's chemical characteristics, and is sampled from some probability density

$P(R)$, treating R as an independent, identically distributed random variable. The particle trapping time distribution $\psi(t)$, and hence the memory function $M(t)$, are defined in terms of $P(R)$. In a homogeneous medium, R depends only on the properties of the solute and thus $\psi(t)$ is naturally independent of position. The upscaled concentration, obtained by averaging over the ensemble of solute particles, can be calculated according to Equation (1b) once $M(t)$ is defined.

Materials and Methods

Column experiments

The NOM sample used here was collected by reverse osmosis (RO) processing of surface water at Nelson's Creek (NLC), a first-order stream draining a freshwater wetland in northern Michigan, using a RealSoft PROS/IS RO system. This sample has been well characterized and used in a variety of adsorption and degradation experiments by our group (Pullin *et al.*, 2004; Kreller *et al.*, 2005). The sampling procedure and characteristics of stream water and NOM sample are described by Pullin *et al.* (2004), and details regarding the RO system used to isolate the sample are reported by Serkiz and Perdue (1990). At the time of sampling, NLC had dissolved the organic carbon concentration $[\text{DOC}] = 28.0 \text{ mgC/L}$ and $\text{pH} = 5.52$. The NLC RO concentrate has the following properties (Pullin *et al.*, 2004): molar absorptivity at 280 nm $\epsilon_{280} = 501 \text{ L mol}^{-1} \text{ cm}^{-1}$ and at 350 nm $\epsilon_{350} = 189 \text{ L mol}^{-1} \text{ cm}^{-1}$; weight-average $\text{MW} = 2531 \text{ Da}$ and number-average molecular weight $= 1593 \text{ Da}$ as determined by HPSEC. Fluorescence excitation/emission spectra (Maurice group, unpublished data) contain the two main peaks that are typical for surface waters rich in aquatic humic substances (Goldberg and Weiner, 1989): a very intense A peak at excitation $\lambda = 230 \text{ nm}$ and emission $\lambda = 425 \text{ nm}$ and a less intense H peak at excitation $\lambda = 320 \text{ nm}$ and emission $\lambda = 435 \text{ nm}$. Sample polydispersity $\rho = 1.59$, which is within the range of values ($\rho = 1.52\text{--}2.04$) reported by Cabaniss *et al.* (2000), for 11 NOM samples isolated (by XAD-8 resin) from various locations in the United States. The experimental procedure used in laboratory column studies of the NLC RO concentrate is described here in brief; further details are provided by Seders (2010) and Seders Dietrich *et al.* (2013).

A stock solution of NOM and deionized (MilliQ[®]) water was mixed with the background electrolyte NaClO_4 (0.001–0.01 M) to make sample solutions (5 mgC/L) used in experiments. This influent $[\text{DOC}]$ was chosen based on the adsorption isotherms of the NLC RO concentrate to the Fe oxyhydroxide mineral goethite (Pullin *et al.*, 2004) and adjusting for the surface area of the Fe/Al oxide-coated sand, such that adsorption may be approximated using a linear isotherm—that is, the system is sufficiently dilute (Delle Site, 2001). Solution pH was adjusted to $\sim 5, 6, 7$, or 8 with HCl and/or NaOH. NOM solutions were passed through columns consisting of a borosilicate glass barrel (10 cm long and 1.0 cm inner diameter) packed with naturally Fe/Al oxide-coated quartz sand collected from the U.S. Department of Energy research site in Oyster, VA (Dong *et al.*, 2002), hereafter referred to as the Oyster sand. Characteristics of the Oyster sand (e.g., mineralogy, bulk density, and grain size) are reported by Dong *et al.* (2002), Penn *et al.* (2001), and Seders (2010). The surface chemistry of the sand is altered by the presence of Fe/Al oxides (Penn *et al.*, 2001), which tend

to have relatively high points of zero charge, and hence, higher affinities for NOM than does pure quartz, which tends to have a point of zero charge at $\text{pH} \sim 2$ (Maurice, 2009 and references therein). We model the sand column as an effective homogeneous medium, assuming that nm-scale heterogeneity in the Al, Si, and Fe content of Oyster sand surfaces (as observed by Penn *et al.*, 2001) is likely to average out at the transport scale. Continuous injection of solution through a gravity feed system with continuous flow from the bottom to the top of the column was used in all experiments to pass NOM through the stationary sand grains at a flow rate of $\sim 2 \text{ mL/min}$. A relatively fast flow rate was chosen to minimize the potential for interferences from microbial processes, which could begin to occur after just a few hours, and/or mineral dissolution, which is likely to occur over time when Fe/Al oxide coatings are exposed to NOM. Moreover, this flow rate is likely appropriate for shallow, organic-rich, sandy aquifers especially when pumping is occurring.

An in-line (Hewlett Packard 8453) UV/vis spectrophotometer monitored absorbance of the column effluent at $\lambda = 254 \text{ nm}$ (UV_{254}). Like $[\text{DOC}]$ and other lumped detection parameters, UV_{254} is representative of the total NOM concentration (Dobbs *et al.*, 1972), but does not distinguish among various components of NOM. Therefore, each observed NOM BTC reflects the combined breakthrough of several component fractions. Kreller *et al.* (2005) showed that size exclusion chromatograms for this NOM sample were nearly identical using in-line detection by $[\text{DOC}]$ versus UV_{254} , indicating that absorbance detection is appropriate for this sample. Absorbance detection provides high sensitivity at low sample volumes, which is essential for continuous measurements of column effluent. Effluent absorbance was normalized to the absorbance of the influent solution at 254 nm ($[\text{abs}/\text{abs}_0]_{254\text{nm}}$) and plotted as a function of dimensionless pore volumes to construct NOM BTCs. Transport of the nonadsorbing tracer sulforhodamine B was also studied for each background electrolyte concentration at pH 5 and 8, and tracer concentration detected by UV/vis absorbance at 565 nm. All column experiments were conducted at least in duplicate, but replication was kept to a minimum to conserve the limited supply of NOM samples.

Transport modeling

Equations (1b)–(4) were fit to experimental BTC data using the CTRW toolbox—a collection of MATLAB[®] scripts for fitting CTRW model parameters to experimental data (Cortis and Berkowitz, 2005). The software, user guide, and examples of how to use the toolbox can be downloaded freely at www.weizmann.ac.il/ESER/People/Brian/CTRW/ (accessed Sept 28, 2011). Briefly, the data are input as normalized concentration (measured here as absorbance) versus dimensional time (measured here in minutes); an initial guess for the parameters (v_ψ , D_ψ , β , t_1 , and t_2) is made, and an optimization routine is run to minimize the sum of squared differences between the CTRW model and the experimental data. The boundary conditions corresponding to the experimental setup are a known flux (Robin boundary condition) at the column inlet ($x=0$), and a zero concentration gradient (Neumann boundary condition) at the column outlet ($x=L$). The initial condition ($t=0$) is zero concentration throughout

the column. The one-dimensional solute transport problem [Eq. (1b)] with memory function $\tilde{M}(u)$ defined by the TPL model [Eqs. (2) and (3)] is solved with these conditions imposed, and the flux-averaged concentration in Laplace space ($\tilde{j}/\tilde{M}\nu_\psi$) is numerically inverted to calculate the BTC at the column outlet.

Results and Discussion

Breakthrough of the nonreactive tracer sulforhodamine B, as illustrated in Fig. 1, shows good agreement with the both the ADE and CTRW models. The inflection point of the BTC occurs at ~ 1.6 min, the time needed to exchange one pore volume within the column. Because transport of a conservative (nonadsorbing) tracer is only sensitive to the velocity distribution within a porous medium, and not to the tracer's chemical characteristics, the tracer BTC data serve as an indicator of homogeneous flow within the sand columns. Cortis and Berkowitz (2004) point out that even carefully packed laboratory sand columns are intrinsically heterogeneous and that grain-scale heterogeneity can cause tracer transport to deviate from the ADE, leading to BTC tailing. Our observation of tracer transport in accordance with the ADE suggests that the potential effects of grain-scale heterogeneity in the Oyster sand columns used here are negligible with respect to larger scale transport, and that the columns may be treated as a homogeneous porous medium at the scale of measurement.

In contrast, BTCs for the NOM sample deviate from the ADE model fits, demonstrating the anomalous character of NOM transport due to complex adsorption behavior within the Oyster sand columns (Fig. 2). The CTRW model provides a much closer fit than the ADE to the NOM BTC data, particularly at late times, demonstrating that tailing of NOM BTCs may be described in terms of a broad distribution of trapping times $\psi(t)$ associated with variable effective retardation of different NOM fractions. In general, this distribution depends not only on the physicochemical diversity of the solute, but also on the heterogeneity of the porous medium. However, as described in CTRW Framework section, we

assumed a homogeneous porous medium in deriving $\psi(t)$. Therefore, we attribute adsorptive fractionation of NOM to a diversity of sorption behaviors within the polydisperse NOM mixture, noting that the observed behavior may reflect heterogeneity in adsorption affinity and/or associated kinetic factors. Tailing has also been observed in experiments using NLC NOM and pure mineral sands of hematite or corundum (Seders, 2010; data not shown), lending further support to this assumption.

Examining the BTCs in closer detail, we see how the parameters defining $\psi(t)$ relate to the observed tailing. When plotted as $(1 - [abs/abs_0]_{254nm})$ vs. t on a log-log scale (Fig. 3), the NOM BTCs at late times are observed to follow a straight line defined by $(1 - [abs/abs_0]_{254nm}) = c*t^{-\beta}$, where c is a constant and β is a power law exponent, the same as that defined in the TPL model [Eq. (3)]. The parameters t_1 and t_2 define the time range over which this power-law relationship holds. For $t_1 < t < t_2$, the power-law behavior is observed; for times $t \gg t_2$, transport returns to Fickian (Dentz *et al.*, 2004). Low values of t_1 and extremely large values of t_2 for all the NOM BTCs suggest that power-law behavior is dominant throughout the duration of the experiments. The wide range between t_1 and t_2 can be attributed to the broad distribution of trapping times $\psi(t)$ associated with adsorptive fractionation of the polydisperse NOM sample.

Processes that govern this late time behavior are thought to involve reorganization of NOM molecules on the mineral surface and/or replacement of low MW fractions by those of higher MW (e.g., Zhou *et al.*, 2001). Dunnivant *et al.* (1992) suggested two-stage adsorption through direct association with the solid phase and hydrophobic bonding between adsorbed NOM and NOM in solution. McCarthy *et al.* (1996) argued that BTC tailing could be primarily attributed to competitive adsorption and the multicomponent nature of NOM. Competition among NOM subcomponents was examined by van de Weerd *et al.* (2002), who developed a model to describe redistribution of NOM fractions during transport. Our work extends this idea to a continuous distribution of NOM subcomponents, whose effective transport can be described by $\psi(t)$.

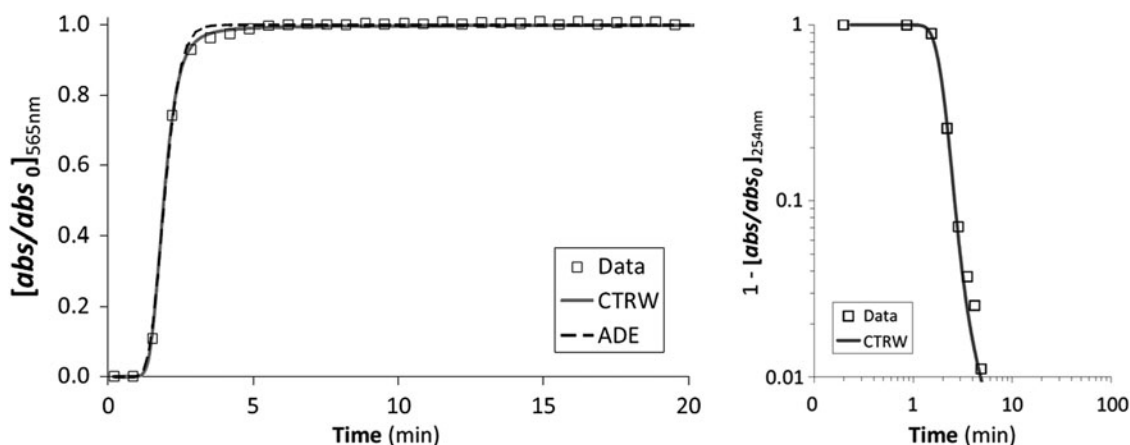


FIG. 1. Breakthrough curves (BTCs) of conservative tracer sulforhodamine B (5 mg/L influent) at pH 5 in 0.001 M NaClO₄ on a linear (left) and log-log (right) scale. Best-fit continuous time random walk (CTRW) (solid line) and advection–dispersion equation (ADE) (dashed line) models are plotted against experimental data (squares). Close agreement between these data and the ADE model suggests homogeneous flow within the column.

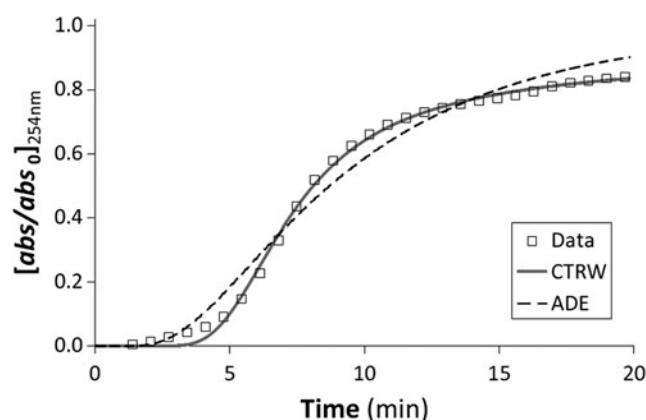


FIG. 2. Comparison of best-fit CTRW (solid line) and ADE (dashed line) models to data for natural organic matter (NOM) (5 mgC/L influent) in 0.001 M NaClO₄ at pH 5 (squares). Strong tailing of the experimental BTC that cannot be fit using the ADE is captured by the CTRW model.

Our results reveal that the extent of BTC tailing is sensitive to solution conditions. Greater tailing and decreased overall mobility of NOM are observed at lower pH and higher I (Fig. 4), conditions that should both act to increase NOM sorption (Tipping, 1981; Vermeer *et al.*, 1998; Zhou *et al.*, 2001). These results are consistent with previously observed

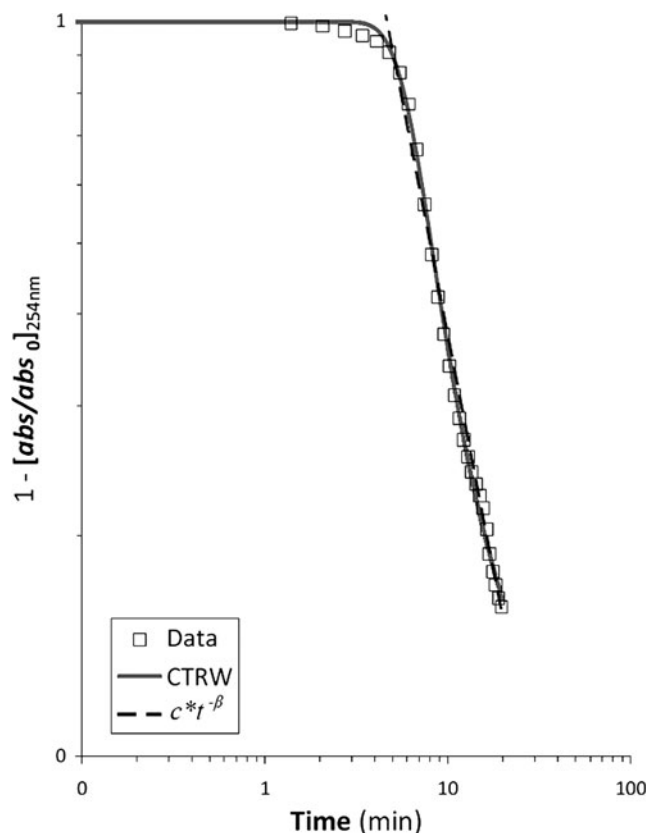


FIG. 3. Log-log plot of NOM breakthrough (5.0 mgC/L influent) in 0.001 M NaClO₄ at pH 5 (squares) highlighting power-law tailing $\propto t^{-\beta}$ ($\beta = 1.28$, dashed line) at late times. The CTRW model (solid line) is able to capture this late time behavior.

trends in NOM transport with pH and I (Sojitra *et al.*, 1996; Chang *et al.*, 1997). BTCs for the full range of solution conditions examined are included in the Supplementary Data. Breakthrough of NOM under different conditions varies substantially: a rapid rise in the concentration at early time is observed at pH 8 in 0.001 M NaClO₄, whereas at pH 5 and 0.01 M, the BTC is much more dispersed and shifted toward later time. Nevertheless, in all cases examined, the late time behavior is characterized by extended tailing as the NOM concentration gradually approaches its maximum value. The CTRW model is consistently able to capture tailing of NOM BTCs in the experiments examined here. Changes in the degree of adsorptive fractionation are reflected by changes in the CTRW model parameters.

Best-fit parameters of the CTRW model to data under various experimental conditions are listed in Table 1. Of particular interest is the value of β , which is determined by the nature of the dispersion. It can be shown that the TPL model with $\beta > 2$ yields Fickian transport behavior at times $t > t_1$ (a central limit process), whereas $\beta < 2$ is characteristic of anomalous/non-Fickian transport (Dentz and Berkowitz, 2003). Thus, the ADE can be considered as a limiting case of the CTRW formulation. Values of $\beta > 2$ for transport of the conservative tracer (Table 1) are consistent with observations that the ADE fits these data well. In this case, the parameters v_ψ and D_ψ correspond to the average pore velocity v and dispersion coefficient D used in the ADE, although in general, these two sets of parameters are not equivalent. In experiments with NOM, the transport velocity v_ψ tends to increase as pH increases and ionic strength decreases, but no clear trends are observed in D_ψ . Values of β for NOM transport range from 1.28 to 1.45, with larger values (i.e., less tailing) at higher pH and lower background electrolyte concentrations (hence lower I).

Modeling transport of a sorbing solute is inherently challenging. The conventional approach is to use tracer tests and batch experiments to isolate and identify parameters for advection, dispersion, and sorption; however, this approach has recently been called into question. A study by Rubin *et al.* (2012) suggests that coupling between the processes limits applicability of parameters determined from tracer tests and batch experiments. These authors examined sorption of a single component in a heterogeneous medium, finding that sorption led to enhancement of BTC tailing relative to that of a conservative tracer. However, working within the CTRW framework, they were unable to relate transport parameters for the sorbing solute to those of the nonsorbing tracer, nor could they establish a relationship between CTRW model parameters and sorption isotherm parameters determined from batch experiments. They therefore attributed the enhanced BTC tailing to unresolved chemical heterogeneity. In contrast, we have applied CTRW to resolve the effects of variable sorption behavior among a distribution of NOM components in a physically homogeneous porous medium, assuming an effective retardation of each component, which is consistent with the observations made by Seders Dietrich *et al.* (2013). Our CTRW modeling approach incorporates a continuous distribution of solute travel times, which can be understood in terms of a distribution function for R . Enhanced tailing of NOM BTCs thus may be interpreted in terms of different adsorptive properties of various components in a polydisperse solute mixture under a broad range of solution conditions.

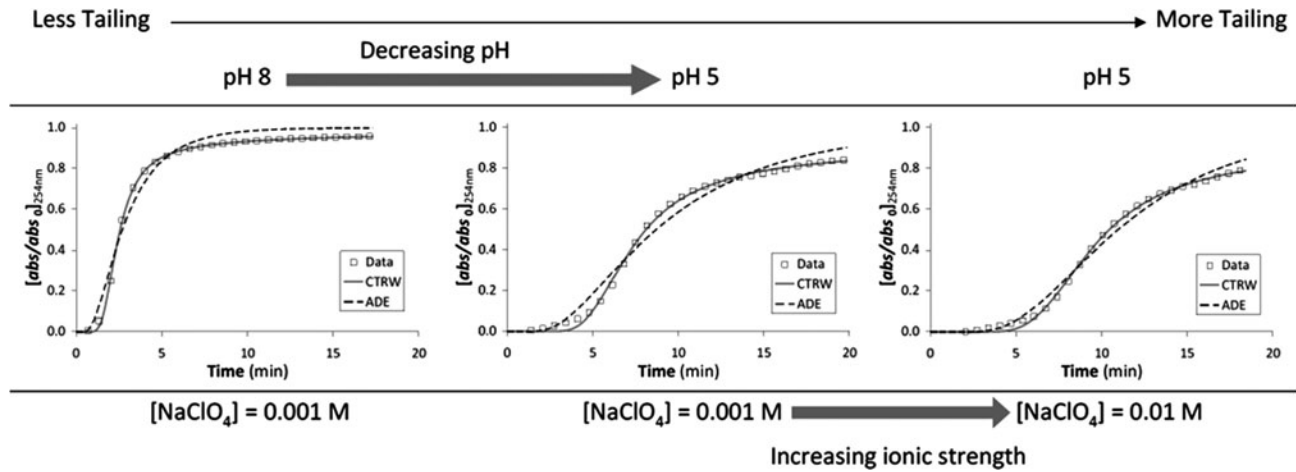


FIG. 4. Best-fit CTRW (solid line) and ADE (dashed line) models to experimental data (squares) at various conditions of pH and background electrolyte (NaClO_4) concentration. In all cases examined, the CTRW model provides a closer fit to the experimental data than does the ADE. Departures from the ADE are attributed to the physicochemical diversity of NOM, which leads to heterogeneous interactions with the sorbent. Greater tailing is observed at lower pH and higher ionic strength.

Conclusions

Seders Dietrich *et al.* (2013) showed that different NOM fractions (defined by MW) in the sample used here have different mobilities as quantified by observed retardation factors, most likely due to different adsorption affinities, but perhaps also due, at least in part, to adsorption kinetics. This variability in R leads to BTC tailing that cannot be captured by the classical ADE model, but as shown here, the tailing can be captured using the CTRW approach. To the best of our knowledge, this is the first application of the CTRW approach to a highly heterogeneous solute (NOM), expanding beyond its original applications to a heterogeneous porous medium. Whereas variability in the adsorption behavior of the NOM components provides a plausible explanation for the observed BTC tailing, potential use of the model in a predictive sense will require further exploration of the relationship between the parameters of the CTRW model and specific experimental conditions, such as pH, I and background electrolyte identity; physicochemical properties of the chosen adsorbent and NOM sample; and hydrologic parameters such as flow rate. A more detailed characterization of how R varies with different NOM

components by MW is also needed—additional experiments using polymer standards of known MW (currently underway) may provide insight into the relative importance of molecular size and chemical composition. Additional column experiments with NOM, combining analysis of column influent and effluent MW distributions as described by Seders Dietrich *et al.* (2013) with additional modeling should further enhance our quantitative understanding. It is also important to note that the use of the CTRW does not formally require the assumption of constant effective retardation for individual components; indeed, its earliest applications make no such assumptions (Scher and Lax, 1973). This is merely one manner in which to rigorously derive a CTRW as shown in the Supplementary Data. The assumption is consistent with the initial observations of Seders Dietrich *et al.* (2013), but further research is needed to explore this assumption in greater detail. As more data emerge, the mechanistic understanding of the CTRW and its parameters will certainly evolve. These are topics of our ongoing research.

Tailing of NOM BTCs may have important implications for contaminant transport and groundwater remediation. NOM impacts subsurface transport of a wide variety of

TABLE 1. BEST-FIT CTRW MODEL PARAMETERS FOR NOM (5 MG/L INFLUENT) AND TRACER (SULFORHODAMINE B, 5 MG/L INFLUENT) BREAKTHROUGH CURVES UNDER VARIOUS EXPERIMENTAL CONDITIONS

Solute	I (M)	pH	v_ψ (cm/min)	D_ψ (cm ² /min)	β	t_1 (min)	t_2 (min)
NOM	0.001	5	3.76	0.39	1.28	1.78×10^{-2}	2.36×10^4
		6	6.19	0.51	1.33	8.28×10^{-3}	4.88×10^4
		7	6.18	0.48	1.44	1.60×10^{-2}	1.61×10^6
		8	7.87	0.99	1.45	1.65×10^{-2}	5.60×10^3
	0.01	5	2.99	0.51	1.28	1.29×10^{-2}	1.02×10^6
		6	2.83	0.80	1.35	1.76×10^{-2}	8.53×10^5
		7	3.54	0.25	1.35	1.19×10^{-2}	1.18×10^4
		8	3.61	0.46	1.37	1.57×10^{-2}	4.31×10^3
Tracer	0.001	5	5.03	0.91	2.01	6.14×10^{-3}	1.45×10^5
	0.001	8	5.21	0.22	2.02	1.21×10^{-2}	6.85×10^5

I , ionic strength [M NaClO_4]; v_ψ , transport velocity; D_ψ , generalized dispersion coefficient; β , power-law exponent; t_1 , characteristic time marking the onset of power-law behavior; t_2 , cutoff time marking the transition from power-law behavior to (Fickian) exponential decay; CTRW, continuous time random walk; NOM, natural organic matter.

contaminants, including heavy metals, radionuclides, and aromatic hydrocarbons (Johnson and Amy, 1995; Jordan *et al.*, 1997; McCarthy, 1998; Wernert *et al.*, 2003), and different components of NOM have different affinities not only for mineral surfaces but also for various contaminants (Cabaniss *et al.*, 2000). The CTRW model should ultimately provide a more reliable framework than the traditional ADE model for predicting transport of NOM-bound contaminants in the laboratory and in the field.

Acknowledgments

We thank the National Science Foundation (NSF) for funding this research through a graduate fellowship (to D. McInnis, DGE-0822217) and grants EAR02-21966 and EAR-1113704. Experimental data were supplied by Dr. Lindsay A. Seders Dietrich; UV/Vis spectrophotometry measurements were conducted in the Center for Environmental Science & Technology (CEST) at the University of Notre Dame. Finally, we thank Mr. Matthew Staffelbach for his assistance in the preparation of this article.

Author Disclosure Statement

No competing financial interests exist.

References

- Annesini, M.C., Giona, M., and Gironi, F. (1994). Continuous model for complex mixture adsorption. *Ind. Eng. Chem. Res.* 33, 2764.
- Bahr, J.M., and Rubin, J. (1987). Direct comparison of kinetic and local equilibrium formulations for solute transport affected by surface reactions. *Water Resour. Res.* 23, 438.
- Bellin, A., Rinaldo, A., Bosma, W.J.P., van der Zee, S.E.A.T.M., and Rubin, Y. (1993). Linear equilibrium adsorbing solute transport in physically and chemically heterogeneous porous formations: 1. Analytical solutions. *Water Resour. Res.* 29, 4019.
- Berkowitz, B., Cortis, A., Dentz, M., and Scher, H. (2006). Modeling non-Fickian transport in geological formations as a continuous time random walk. *Rev. Geophys.* 44, RG2003.
- Bolster, D., and Dentz, M. (2012). Anomalous dispersion in chemically heterogeneous media induced by long range correlations. *J. Fluid Mech.* 695, 366.
- Cabaniss, S.E., Zhou, Q., Maurice, P.A., Chin, Y., and Aiken, G.R. (2000). A log-normal distribution model for the molecular weight of aquatic fulvic acids. *Environ. Sci. Technol.* 34, 1103.
- Chang, Y., Li, C., and Benjamin, M.M. (1997). Iron oxide-coated media for NOM sorption and particulate filtration. *J. Am. Water Work Assoc.* 89, 100.
- Chi, F.-H., and Amy, G.L. (2004a). Transport of anthracene and benz(a)anthracene through iron-quartz and three aquifer materials in laboratory columns. *Chemosphere* 55, 515.
- Chi, F.-H., and Amy, G.L. (2004b). Kinetic study on the sorption of dissolved natural organic matter onto different aquifer materials: the effects of hydrophobicity and functional groups. *J. Colloid Interface Sci.* 274, 380.
- Chorover, J., and Amistadi, M.K. (2001). Reaction of forest floor organic matter at goethite, birnessite and smectite surfaces. *Geochim. Cosmochim. Acta* 65, 95.
- Cortis, A., and Berkowitz, B. (2004). Anomalous transport in "classical" soil and sand columns. *Soil Sci. Soc. Am. J.* 68, 1539.
- Cortis, A., and Berkowitz, B. (2005). Computing "anomalous" contaminant transport in porous media: The CTRW MATLAB toolbox. *Ground Water* 43, 947.
- De Barros, F.P.J., and Rubin, Y. (2011). Modelling of block-scale macrodispersion as a random function. *J. Fluid Mech.* 676, 514.
- Delle Site, A. (2001). Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. A review. *J. Phys. Chem. Ref. Data* 30, 187.
- Deng, J., Jiang, X., Zhang, X., Hu, W., and Crawford, J.W. (2008). Continuous time random walk model better describes the tailing of atrazine transport in soil. *Chemosphere* 71, 2150.
- Dentz, M., and Berkowitz, B. (2003). Transport behavior of a passive solute in continuous time random walks and multirate mass transfer. *Water Resour. Res.* 39, 1111.
- Dentz, M., and Bolster, D. (2010). Distribution- versus correlation-induced anomalous transport in quenched random velocity fields. *Phys. Rev. Lett.* 105, 244301.
- Dentz, M., Bolster, D., and Le Borgne, T. (2009). Concentration statistics for transport in random media. *Phys. Rev. E* 80, 010101.
- Dentz, M., and Castro, A. (2009). Effective transport dynamics in porous media with heterogeneous retardation properties. *Geophys. Res. Lett.* 36, L03403.
- Dentz, M., Cortis, A., Scher, H., and Berkowitz, B. (2004). Time behavior of solute transport in heterogeneous media: transition from anomalous to normal transport. *Adv. Water Resour.* 27, 155.
- Dobbs, R.A., Wise, R.H., and Dean, R.B. (1972). Use of ultraviolet absorbance for monitoring total organic carbon content of water and wastewater. *Water Res.* 6, 1173.
- Dong, H., Onstott, T.C., Deflaun, M.F., Fuller, M.E., Scheibe, T.D., Streger, S.H., Rothmel, R.K., and Mailloux, B.J. (2002). Relative dominance of physical versus chemical effects on the transport of adhesion-deficient bacteria in intact cores from South Oyster, Virginia. *Environ. Sci. Technol.* 36, 891.
- Drazer, G., Rosen, M., and Zanette, D.H. (2000). Anomalous transport in activated carbon porous samples: power-law trapping time distributions. *Physica A* 283, 181.
- Dunnivant, F.M., Jardine, P.M., Taylor, D.L., and McCarthy, J.F. (1992). Transport of naturally occurring dissolved organic carbon in laboratory columns containing aquifer material. *Soil Sci. Soc. Am. J.* 56, 437.
- Fernandez-Garcia, D., and Gomez-Hernandez, J.J. (2007). Impact of upscaling on solute transport: travel times, scale dependence of dispersivity, and propagation of uncertainty. *Water Resour. Res.* 43, W02423.
- Goldberg, M. C., and Weiner, E. R. (1989). Fluorescence measurements of the volume, shape, and fluorophore composition of fulvic acid from the Suwannee River. In: *Humic Substances in the Suwannee River, Georgia: Interactions, Properties, and Proposed Structures*. US Geological Survey Open-File Report 87-557, pp. 179–204.
- Hur, J., and Schlautman, M.A. (2003). Molecular weight fractionation of humic substances by adsorption onto minerals. *J. Colloid Interface Sci.* 264, 313.
- Johnson, W.P., and Amy, G.L. (1995). Facilitated transport and enhanced desorption of polycyclic aromatic-hydrocarbons by natural organic matter in aquifer sediments. *Environ. Sci. Technol.* 29, 807.
- Jordan, R.N., Yonge, D.R., and Hathhorn, W.E. (1997). Enhanced mobility of Pb in the presence of dissolved natural organic matter. *J. Contam. Hydrol.* 29, 59.

- Kilduff, J.E., Karanfil, T., Chin, Y.-P., and Weber, W.J., Jr. (1996). Adsorption of natural organic polyelectrolytes by activated carbon: a size-exclusion chromatography study. *Environ. Sci. Technol.* 30, 1336.
- Kreller, D.I., Turner, B.F., Namjesnik-Dejanovic, K., and Maurice, P.A. (2005). Comparison of the effects of sonolysis and γ -radiolysis on dissolved organic matter. *Environ. Sci. Technol.* 39, 9732.
- Kreller, D.I., Schlautman, M.A., and McGunigale, S.L. (2013). Combined HPLC/HPSEC study of Suwannee river fulvic acid adsorptive fractionation on α -aluminum oxide. *J. Colloid Interface Sci.* 390, 242.
- Margolin, G., Dentz, M., and Berkowitz, B. (2003). Continuous time random walk and multirate mass transfer modeling of sorption. *Chem. Phys.* 295, 71.
- Maurice, P.A. (2009). *Environmental Surfaces and Interfaces from the Nanoscale to the Global Scale*. Hoboken, NJ: John Wiley & Sons, Inc., pp. 210–213.
- McCarthy, J.F. (1998). Colloid-facilitated transport of contaminants in groundwater: mobilization of transuranic radionuclides from disposal trenches by natural organic matter. *Phys. Chem. Earth* 23, 171.
- McCarthy, J.F., Williams, T.M., Liang, L., Jardine, P.M., Jolley, L.W., Taylor, D.L., Palumbo, A.V., and Cooper, L.W. (1993). Mobility of natural organic-matter in a sandy aquifer. *Environ. Sci. Technol.* 27, 667.
- McCarthy, J.F., Gu, B., Liang, L., Mas-Pla, J., Williams, T.M., and Yeh, T.-C.J. (1996). Field tracer tests on the mobility of natural organic matter in a sandy aquifer. *Water Resour. Res.* 32, 1223.
- McCarthy, J.F., and Zachara, J.M. (1989). Subsurface transport of contaminants. *Environ. Sci. Technol.* 23, 496.
- McKnight, D.M., Bencala, K.E., Zellweger, G.W., Aiken, G.R., Feder, G.L., and Thorn, K.A. (1992). Sorption of dissolved organic-carbon by hydrous aluminum and iron-oxides occurring at the confluence of Deer Creek with the Snake River, Summit County, Colorado. *Environ. Sci. Technol.* 26, 1388.
- Meerschaert, M.M., and Scheffler, H.-P. (2004). Limit theorems for continuous-time random walks with infinite mean waiting times. *J. Appl. Prob.* 41, 623.
- Meier, M., Namjesnik-Dejanovic, K., Maurice, P.A., Chin, Y.-P., and Aiken, G.R. (1999). Fractionation of aquatic natural organic matter upon sorption to goethite and kaolinite. *Chem. Geol.* 157, 275.
- Namjesnik-Dejanovic, K., Maurice, P.A., Aiken, G.R., Cabaniss, S., Chin, Y.-P., and Pullin, M.J. (2000). Adsorption and fractionation of a muck fulvic acid on kaolinite and goethite at pH 3.7, 6, and 8. *Soil Sci.* 165, 545.
- Penn, R.L., Zhu, C., Xu, H., and Veblen, D.R. (2001). Iron oxide coatings on sand grains from the Atlantic coastal plain: high-resolution transmission electron microscopy characterization. *Geology* 29, 843.
- Pullin, M.J., Proggess, C.A., and Maurice, P.A. (2004). Effects of photoirradiation on the adsorption of dissolved organic matter to goethite. *Geochim. Cosmochim. Acta* 68, 3643.
- Qualls, R.G., and Haines, B.L. (1991). Geochemistry of dissolved organic nutrients in water percolating through a forest ecosystem. *Soil Sci. Soc. Am. J.* 55, 1112.
- Ramaswami, S., and Tien, C. (1986). Simplification of multi-component fixed-bed adsorption calculations by species grouping. *Ind. Eng. Chem. Process Des. Dev.* 25, 133.
- Rubin, S., Dror, I., and Berkowitz, B. (2012). Experimental and modeling analysis of coupled non-Fickian transport and sorption in natural soils. *J. Contam. Hydrol.* 132, 28.
- Scher, H., and Lax, M. (1973). Stochastic transport in a disordered solid .1. Theory. *Phys. Rev. B* 7, 4491.
- Schideman, L.C., Marinas, B.J., and Snoeyink, V.L. (2006). Three-component competitive adsorption model for fixed-bed and moving-bed granular activated carbon adsorbers. Part II. Model parameterization and verification. *Environ. Sci. Technol.* 40, 6812.
- Seders, L.A. (2010). *Experimental Studies of Geochemical Reactions That Affect the Mobility of Metals and Nanoparticles of Environmental Interest*. Ph.D. Dissertation, University of Notre Dame, Notre Dame, IN. Available at www.nd.edu/~fein/Publications/SedersLA_dissertation.pdf (accessed April 20, 2012).
- Seders Dietrich, L.A., McInnis, D.P., Bolster, D., and Maurice, P.A. (2013). Effect of polydispersity on natural organic matter transport. *Water Res.* 47, 2231.
- Serkiz, S.M., and Perdue, E.M. (1990). Isolation of dissolved organic matter from the Suwannee River using reverse osmosis. *Water Res.* 24, 911.
- Sojitra, I., Valsaraj, K.T., Reible, D.D., and Thibodeaux, L.J. (1996). Transport of hydrophobic organics by colloids through porous media. 2. Commercial humic acid macromolecules and polyaromatic hydrocarbons. *J. Colloid Surf. A Physicochem. Eng. Asp.* 110, 141.
- Sposito, G. (1984). *The Surface Chemistry of Soils*. New York: Oxford University Press.
- Sugita, F., and Gillham, R.W. (1995). Pore scale variation in retardation factor as a cause of nonideal reactive breakthrough curves: 1. Conceptual model and its evaluation. *Water Resour. Res.* 31, 103.
- Szecsody, J.E., Zachara, J.M., Chilakapati, A., Jardine, P.M., and Ferency, A.S. (1998). Importance of flow and particle-scale heterogeneity on $\text{Co}^{\text{IV/III}}$ EDTA reactive transport. *J. Hydrol.* 209, 112.
- Tipping, E. (1981). The adsorption of aquatic humic substances by iron oxides. *Geochim. Cosmochim. Acta* 45, 191.
- van de Weerd, H., van Riemsdijk, W.H., and Leijnse, A. (1999). Modeling the dynamic adsorption/desorption of a NOM mixture: Effects of physical and chemical heterogeneity. *Environ. Sci. Technol.* 33, 1675.
- van de Weerd, H., van Riemsdijk, W.H., and Leijnse, A. (2002). Modeling transport of a mixture of natural organic molecules: Effects of dynamic competitive sorption from particle to aquifer scale. *Water Resour. Res.* 38, 1158.
- Vermeer, A.W.P., van Riemsdijk, W.H., and Koopal, L.K. (1998). Adsorption of humic acid to mineral particles. 1. Specific and electrostatic interactions. *Langmuir* 14, 2810.
- Weber, W.J., Jr., McGinley, P.M., and Katz, L.E. (1991). Sorption phenomena in subsurface systems: concepts, models, and effects on contaminant fate and transport. *Water Res.* 5, 499.
- Weigand, H., and Totsche, K.U. (1998). Flow and reactivity effects on dissolved organic matter transport in soil columns. *Soil Sci. Soc. Am. J.* 62, 1268.
- Wernert, V., Frimmel, F.H., and Behra, P. (2003). Mercury transport through a porous medium in presence of natural organic matter. *J. Phys. IV* 107, 1361.
- Zachman, B.A., Rajagopalan, B., and Summers, R.S. (2007). Modeling NOM breakthrough in GAC adsorbers using non-parametric regression techniques. *Environ. Eng. Sci.* 24, 1280.
- Zhou, Q., Maurice, P.A., and Cabaniss, S.E. (2001). Size fractionation upon adsorption of fulvic acid on goethite: equilibrium and kinetic studies. *Geochim. Cosmochim. Acta* 65, 803.