



## Compartmental model of nitrate retention in streams

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[1] A compartmental modeling approach is presented to route nitrate retention along a cascade of stream reach sections. A process transfer function is used for transient storage equations with first-order reaction terms to represent nitrate uptake in the free stream and denitrification in the storage regions. In the context of a short-term nitrate injection we define nitrate assimilative capacity as  $1 - \mathcal{A}$ , where the attenuation factor,  $\mathcal{A}$ , is the fraction of injected nitrate mass that is flushed past the outlet of stream. Net exchange with groundwater is modeled by allowing free stream discharge to vary from one reach section to the next. A Monte Carlo simulation was used to compare results of the compartmental model with the OTIS numerical model. Out of 350 Monte Carlo simulations of a stream consisting of five reach sections the highest relative percent difference was 15%, most being well below 10%, as determined using moment analysis on breakthrough curves. Moment analysis on published experimental breakthrough curves showed assimilative capacities did not differ from those determined with the compartmental model by more than about 0.035 and were well within the uncertainty due to possible errors in measured stream metrics and net exchange with groundwater. The results show that the compartmental modeling approach, commonly used in analysis of groundwater data, can also be useful in evaluating nitrate retention in streams.

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### 1. Introduction and Purpose

[2] Many of the most popular ecologically relevant metrics of nitrate processing in streams, measured at the restoration reach scale (hundreds of meters) are based on the assumption of linear underlying kinetics for biogeochemical nutrient uptake and transformation [Newbold *et al.*, 1981; Valett *et al.*, 1996, 1997; Davis and Minshall, 1999; Fellows *et al.*, 2001; Peterson *et al.*, 2001; Thomas *et al.*, 2003; Wilcock *et al.*, 2004; Brookshire *et al.*, 2005]. Jin and Bethke [2002] derived general process-based formulations for electron transfer kinetics in respiration under both aerobic and anaerobic conditions. They have shown that linear kinetics under many conditions fall within the purview of chemiosmotic theory. Other metrics relate to residence time parameters which are based upon the transient storage model of stream solute transport [Thackston and Schnelle, 1970; Nordin and Troutman, 1980; Bencala and Walters, 1983]. These can be determined using short-term nutrient and/or conservative tracer injection experiments. Nonlinear expressions, based on Monod, or Michaelis–Menten kinetics have recently been shown to be tractable in making field measurements [Payn *et al.*, 2005] and in many cases

such nonlinear effects must be considered. Nonlinear kinetics have also been employed in fully numerical methods by Kim *et al.* [1990, 1992] for in-stream processes and by Kinzelbach *et al.* [1991] using multiple Monod kinetics for porous media denitrification processes. Here, the expressions that assume linear dynamics are emphasized because they yield exact analytical results as transfer functions. Furthermore, the metrics most often used by stream ecologists, such as the nutrient uptake length, hydrological retention factor, and fraction of median travel time due to storage [Runkel, 2002], are measured using approaches based on the assumption of underlying linear kinetics. In all cases linearity assumptions reduce the number of parameters that must be determined, and the degree of labor involved in measurement. They result in simple metrics that are likely to have intuitive appeal for decision makers.

[3] From a nutrient management standpoint, the total fraction of the injected mass  $M_0$  that is not attenuated (i.e., the normalized zeroth temporal moment,  $(\int_0^\infty c^*(X, t) dt)/M_0$  where  $c^*$  is the nutrient concentration,  $X$  is the length of the reach of interest, and  $t$  is time) is a direct measure of nutrient assimilative capacity of the stream reach. Here a simple screening level compartmental modeling approach is proposed to relate metrics of nitrate retention and attenuation to stream reach nitrate assimilative capacity. This approach follows along the lines of compartmental models that have been developed for groundwater systems, as described, for example, in Campana *et al.* [2001]. The model is formulated in terms of commonly measured metrics, many of which are already tabulated in growing

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databases [e.g., see *Runkel, 2002; Edwardson et al., 2003; Brookshire et al., 2005*].

## 2. Theoretical Development

### 2.1. Conceptual Model

[4] The conceptual model used here assumes one-dimensional flow and transport with advection, dispersion, transient storage or storage in dead zones, and reaction via nutrient uptake in the mainstream, and denitrification in the storage regions. The stream is represented as divided into segments or cells. The output concentration signal from one cell becomes, via appropriate transformation, the input concentration signal to the cell immediately downstream, and so forth, for the entire cascade of cells in the reach of interest. Within each cell, advection, dispersion, and reaction are quantified as solutions to the governing process equations, and transient storage occurs on a characteristic time distribution. Net gain or loss to groundwater can be represented by allowing discharge to change from one cell to the next.

[5] In a fully dynamic model, the process-dependent solute fluxes at the boundaries between the cells preclude analytic solutions with multiple cells. In a recent article, [*Schmid, 2003*] developed a “moment routing” method, using the transfer function for a one-point initial boundary value problem. In part, it could be considered as a means of overcoming the dynamic conditions at the boundaries, but was primarily presented as a means of parameter estimation, since the introduction of higher-order moment equations can make the number of equations equal to the number of unknowns (parameters).

[6] Here solutions for a semi-infinite domain with nitrate reactions, have been employed. Cell attenuation factors are used to “route” nitrate retention along a cascade of cells. In this approach, solutions are time-integrated to yield total retained mass, providing a measure of total retention or assimilative capacity.

### 2.2. Governing Equations

[7] For a single uniform stream segment (or cell) the transient storage model, with the addition of first-order reactions can be written as

$$\frac{\partial c^*}{\partial t} = K \frac{\partial^2 c^*}{\partial x^{*2}} - u \frac{\partial c^*}{\partial x^*} - \lambda c^* - \epsilon T^{-1} (c^* - c_s^*) \quad (1)$$

with the coupling equation

$$\frac{\partial c_s^*}{\partial t} = T^{-1} (c^* - c_s^*) - \lambda_s c_s^* \quad (2)$$

where  $c^*$  is concentration in the free stream ( $\text{ML}^{-3}$ ),  $c_s^*$  is concentration in the storage region ( $\text{ML}^{-3}$ ),  $K$  is the longitudinal dispersion coefficient ( $\text{L}^2\text{T}^{-1}$ ),  $u = Q/A$  is free stream velocity ( $\text{LT}^{-1}$ ), with  $Q$  representing free stream discharge ( $\text{L}^3\text{T}^{-1}$ ), and  $A$  representing free stream cross-sectional area ( $\text{L}^2$ ),  $\lambda$  is a first-order decay rate associated with biotic nutrient uptake in the free stream ( $\text{T}^{-1}$ ),  $\epsilon$  is the ratio of volume of storage region to volume of free stream,  $T$  is the transient storage residence time ( $\text{T}$ ),  $\lambda_s$  is a first-order decay rate associated with denitrification in the storage region ( $\text{T}^{-1}$ ), and  $x^*$  is

downstream distance ( $\text{L}$ ) below an injection location or measurement location.

[8] We consider an experimental context where the mass of nitrate injected results in concentrations several orders of magnitude greater than ambient, prior to the experiment, so that we can assume the initial condition  $c^*(x^*, 0) = 0$ . Also, likewise for the storage region,  $c_s^*(x^*, 0) = 0$ . We further assume that  $c^*(x^* \rightarrow \infty, t) = 0$  and that the duration of the injection of nitrate is much shorter than the time required for the nitrate pulse to be completely flushed past the downstream measurement location so that it can be approximated by a unit input of mass as follows [*Haggerty et al., 2002*]:

$$c^*(0, t) = \frac{M_0}{Q} \delta(t) \quad (3)$$

where  $M_0$  is the input mass [ $\text{M}$ ] and  $\delta(t)$  is the Dirac- $\delta$  function [ $\text{T}^{-1}$ ].

[9] In order to implement a compartmental modeling approach it will be useful to make equations (1) and (2) dimensionless. Let  $x = x^*/X$ , where  $X$  is the length of the stream reach of interest, and let  $c = c^*(x^*, t)/c^*(0, t)$ ,  $t > 0$ . Furthermore, we are interested in the zeroth moment, and hence the long-term behavior of the system. Therefore the Laplace domain representation of the governing equations will be useful. This follows along the lines of *Nordin and Troutman [1980]*, *Schmid [1995]*, *Czernuszenko and Rowiński [1997]*, *Wörman [2000]*, and *Schmid [2003]*. Following the above substitutions, the Laplace transformation of equations (1) and (2) yields

$$0 = \frac{K}{X^2} \frac{d^2 \bar{c}}{dx^2} - \frac{u}{X} \frac{d\bar{c}}{dx} - \lambda \bar{c} - \epsilon T^{-1} (\bar{c} - \bar{c}_s) \quad (4)$$

and

$$0 = T^{-1} (\bar{c} - \bar{c}_s) - \lambda_s \bar{c}_s \quad (5)$$

where the overbar indicates Laplace transformed quantities. After solving for  $\bar{c}_s$  in terms of  $\bar{c}$ , multiplying through by  $X/u$  leaves

$$0 = \frac{1}{Pe} \frac{d^2 \bar{c}}{dx^2} - \frac{d\bar{c}}{dx} - \overline{Da}(s) \bar{c} \quad (6)$$

where  $s$  is the transform variable,  $Pe = uX/K$  is the Peclet number and  $\overline{Da}$  is a Damkohler number that arises from making equations (1) and (2) dimensionless. After some rearrangement, this is given by

$$\overline{Da}(s) = \frac{X}{u} \left[ \frac{-\epsilon T^{-2}}{s + T^{-1} + \lambda_s} + \epsilon T^{-1} + \lambda + s \right]. \quad (7)$$

[10] Equation (6) is a homogeneous ODE which can be easily solved using the given initial and boundary conditions to give (see Appendix A)

$$\bar{c}(1, s) = \exp \left\{ \frac{Pe \left( 1 - \sqrt{1 + 4\overline{Da}(s)/Pe} \right)}{2} \right\}. \quad (8)$$

This is the process transfer function.

[11] An important shortcoming of the formulation given by equation (1) of the transient storage model is the assumption that nutrient uptake in the main channel, expressed through the product  $\lambda c$ , is independent of stream velocity. Nutrient uptake is typically measured using nutrient injection experiments in the stream, rather than by batch experiments that would yield direct estimates of  $\lambda$ . Therefore it is important to employ a formulation of the governing equations in terms of the measured nutrient uptake. *Newbold et al.* [1981] defined nutrient uptake length  $S_w$  as the average distance a nutrient molecule travels downstream before it is taken up by biotic assimilation. In nutrient spiraling theory there is a return flux following algal senescence, mineralization, and nitrification. Here the decay is interpreted as the amount of uptake in excess of temporary biotic assimilation as suggested by *Stream Solute Workshop* [1990]. Although it remains an open research question how nutrient uptake length should be incorporated in the governing equations of the transient storage model [e.g., see *Runkel, 2003*], it is commonly expressed as a simple linear function of free stream velocity [*Newbold et al.*, 1981; *Stream Solute Workshop, 1990*; *Packman et al.*, 2006]:

$$\lambda \approx \frac{u}{S_w}. \quad (9)$$

[12] An additional metric often determined is the average distance a solute travels downstream before entering the storage zone. This can be expressed in terms of the parameters given in equations (1) and (2) as

$$L_s = Tu\epsilon^{-1}. \quad (10)$$

[13] In terms of these metrics, (7) can be rewritten

$$\overline{Da}(s) = \frac{X}{L_s} \left[ 1 - \frac{1}{1 + T(s + \lambda_s)} \right] + \frac{X}{S_w} + s \frac{AX}{Q}. \quad (11)$$

[14] The transfer function is useful in several different contexts as long as the properties in the cell ( $0 < x^* \leq X$ ) can be assumed to be reasonably uniform (i.e.,  $Pe$  and  $\overline{Da}$  are assumed not to vary with  $x$ ). As pointed out by *Hart* [1995] and by *Schmid* [1997], this assumption is completely valid, since short-term injection experiments which are used to determine nutrient uptake parameters are conducted over the entire reach section, and hence they serve as effective parameters. This assumption will be relaxed to incorporate a cascade of reach sections in the compartmental modeling context below. Solutions to equation (6) have screening level applications. For example, the final value theorem of Laplace transformation states [e.g., see *LePage, 1961*, p. 315].

$$\lim_{s \rightarrow 0} s \overline{c}(1, s) = \lim_{t \rightarrow \infty} c(1, t). \quad (12)$$

This identity is useful for recovering time-averaged solutions from Laplace domain solutions without Laplace inversion, as long as the initial conditions yield expressions for  $s \overline{c}(1, s)$  where  $\lim_{s \rightarrow 0}$  is defined. For example, the final value theorem can be used to derive the following well-

known identity for the  $k$ th temporal moments of the response of the system

$$\int_0^\infty t^k c(1, t) dt = (-1)^k \frac{d^k [\overline{c}(1, s)]}{ds^k} \Big|_{s=0} \quad (13)$$

which arises easily using equation (12) and the definition of the Laplace transform and its derivative. In this paper, we will consider only the case where  $k = 0$ , corresponding to the zeroth moment. The zeroth moment for nitrate passing through a cell is a measure of the total mass not retained in the stream cell, hence the transfer function for the case  $c(0, t)\delta(t)$  can be used directly to define an attenuation factor for nitrate within a single cell as follows:

$$AF \equiv \lim_{s \rightarrow 0} \overline{c}(1, s). \quad (14)$$

It is natural to define assimilative capacity as  $1 - AF$ , with zero representing no assimilative capacity, and one representing complete assimilation. The Laplace transform variable appears in the Damkohler number of equation (8), which becomes

$$\overline{Da}(s = 0) = \frac{X}{L_s} \left[ 1 - \frac{1}{1 + T\lambda_s} \right] + \frac{X}{S_w} \quad (15)$$

with  $s \rightarrow 0$ .

[15] By approaching equations (1) and (2) as an initial boundary value problem, and with  $\lambda$  as an independent parameter, equations (6) and (7) of *Schmid* [1995] constitute, likewise, a closed form expression of the attenuation factor for a cell. When normalized by the injection mass  $M_0$ , these can be used in place of our equations (8) with (15). The results will differ slightly however, due to different initial and boundary conditions assumed in the derivation.

### 2.3. Compartmental Modeling Approach

[16] For a cascade of  $n$  cells in series representing the stream reach of interest, each cell with a different set of parameter values representing the heterogeneity of the stream, the attenuation factor for a single cell is  $AF_i = \lim_{s \rightarrow 0} \overline{c}_i(1, s)$ . It follows that the total nitrate attenuation factor for the reach is

$$\mathcal{A} = \prod_{i=0}^n AF_i \quad (16)$$

where  $AF_0$  is the attenuation factor for the first cell in the cascade, which has  $c(0, t) \equiv \delta(t)$ . Therefore, as long as the stream can be represented as a series of discrete cells, each with uniform properties, longitudinal heterogeneity can be effectively accounted for in the total attenuation for the reach of interest by  $\mathcal{A}$ . Likewise, the effect of net flux of nitrate to or from groundwater can be modeled by using the differing values of  $Q$ , with  $u_i = Q_i/A_i$ , from one cell to the next. This is valid because in the limit as  $t \rightarrow \infty$  the effect of the boundaries between cells is averaged.

## 3. Results and Discussion

[17] In order to test the validity of equation (16), two approaches were used. In the first, comparisons were made

**Table 1.** Domains of Uniformly Distributed Values Used in Monte Carlo Simulations

Metric	Minimum	Maximum	Units
$Pe$	$1.0 \times 10^{-2}$	$1.2 \times 10^6$	-
$\overline{Da}(s=0)$	$0.0 \times 10^0$	$1.5 \times 10^2$	
$S_w$	$1.0 \times 10^0$	$1.5 \times 10^8$	m
$\epsilon$	$1.0 \times 10^{-4}$	$7.1 \times 10^3$	
$T = \frac{\epsilon}{\alpha}$	$2.0 \times 10^{-1}$	$2.75 \times 10^8$	s
$L_s$	$1.4 \times 10^0$	$3.0 \times 10^8$	m
$Q$	$2.5 \times 10^{-3}$	$4.0 \times 10^0$	$m^3 s^{-1}$
$A$	$0.0 \times 10^0$	$4.0 \times 10^0$	$m^2$
$A_s$	$0.0 \times 10^0$	$4.0 \times 10^0$	$m^2$
$K$	$1.0 \times 10^{-2}$	$2.0 \times 10^1$	$m^2 s^{-1}$
$\alpha$	$0.0 \times 10^0$	$1.0 \times 10^{-3}$	$s^{-1}$
$\lambda$	$0.0 \times 10^0$	$1.0 \times 10^{-3}$	$s^{-1}$
$\lambda_s$	$0.0 \times 10^0$	$1.0 \times 10^{-2}$	$s^{-1}$

with numerical simulation results using the numerical model OTIS [Runkel, 1998] which can be used to solve equations (1) and (2) in a longitudinally heterogeneous stream. In the second, estimates of attenuation were obtained using published results of a field tracer test. The basis for the former is that, in general, exact time-domain solutions to equations (1) and (2) can only be obtained using numerical methods. A time-domain solution has been developed that requires only numerical integration [Schmid, 1997]. We have chosen to use OTIS as a means of verification because it can directly incorporate heterogeneity in the form of a series of reach sections with differing parameters. Comparison with actual data in section 3.2 will show the applicability of the compartmental approach with data that are well-suited for validation.

### 3.1. Model Verification Using Numerical Simulation

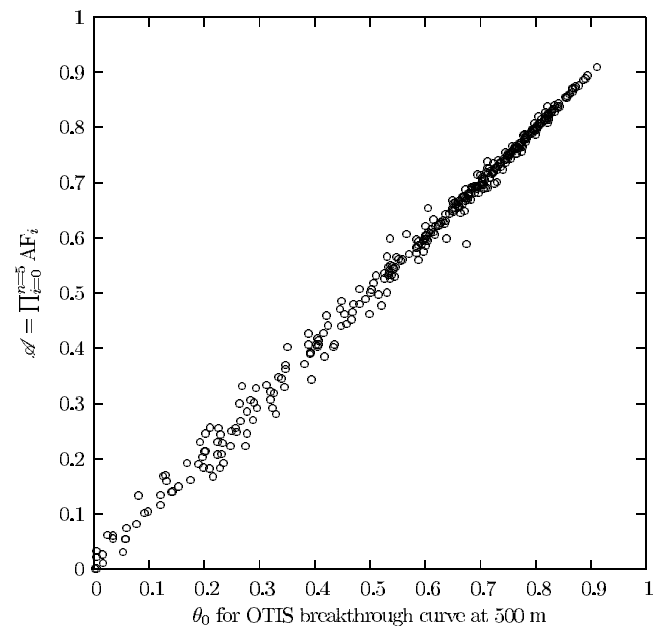
[18] It should be emphasized that the modeling approach presented here is based on the zeroth moment, which is the total mass load of nitrate not retained by the stream system. For a single cell, this is defined by equation (13) as  $\int_0^\infty c(1, t) dt$ . Therefore field sampling data consisting of concentrations or output from a numerical model must be integrated numerically. Alternatively, it could be determined by analytically integrating a parametric model of the concentration signal at the downstream distance of interest. OTIS has been validated with several data sets with nonzero values for terms in equations (1) and (2). These are reported in the main documentation for the OTIS model [Runkel, 1998]. For reactive transport of nitrate with storage and uptake, where all terms were nonzero, OTIS has been used with data obtained by McKnight *et al.* [2004] and in direct support of that study.

[19] In OTIS, the Dirac- $\delta(t)$  pulse was simulated as the boundary condition for the upper boundary cell by using a narrow normal distribution frequency function (mean, 54 s; standard deviation 7.2 s). It was scaled so that its zeroth moment was unity. A simple trapezoidal rule quadrature routine (see equation (17)) was then applied on the output to estimate zeroth moments,  $\theta_0$ , at locations corresponding to compartmental cell boundaries. The discrete solution print times were every 3.6 s (corresponding to 0.001 hours, the basic unit of print time in OTIS). We modified OTIS so that the simulations were

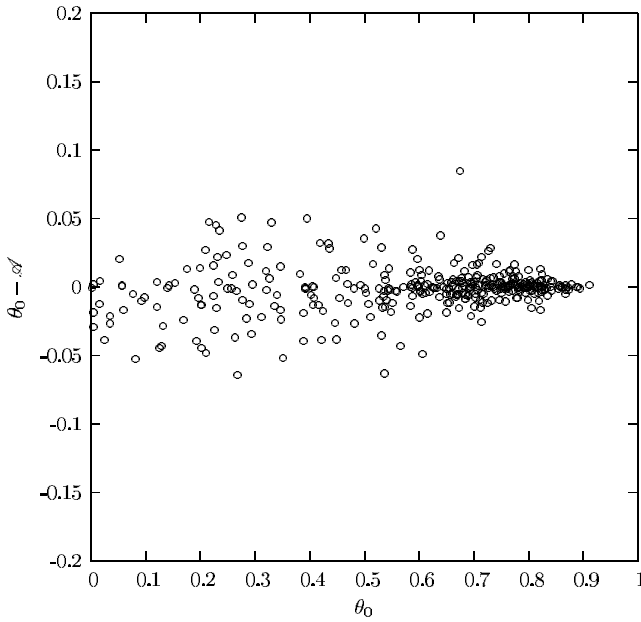
each run until all concentrations were approximately zero, corresponding to flushing of nitrate from the system. The stream system was treated as consisting of five segments or cells, each 100 m in length, with a unique realization of parameters randomly sampled from a uniform distribution within the plausible domains shown in Table 1. The plausible domains were taken from values that represent, in our best judgment, the full ranges encountered in field measurements.

[20] OTIS was used in the trial runs as follows. For the numerical computation a time step of 0.0001 hours was used (print for quadrature increment was 0.001 hours), and the total stream system distance was 700 m. This was done in order to place the downstream boundary sufficiently far away from the last location of interest (500 m) so that any effects of the zero-concentration gradient boundary would be negligible [Runkel, 1998]. The number of computation node points was 8400 and the spatial nodal increment was 8.3 cm. For each simulated stream system,  $Q$  was constant within that system, so that heterogeneity in groundwater exchange was handled by random (independent) deviates of  $A$  and  $A_s$ .

[21] The results are shown in Figure 1, which shows the values of  $\theta_0$  computed using equation (17) on the breakthrough curve at the 500 m location, versus the results of using the attenuation factor given by equation (16). The Monte Carlo simulation used 350 trials corresponding to 350 stream systems. Agreement appeared to be very good, with slightly more deviation in the systems which had very high total nitrate retention under the model. In one trial the relative percent difference was 15%. In all other trials it was less than 10%. Figure 2 shows the residuals about zero as



**Figure 1.** Scatterplot of  $\mathcal{A} = \prod_{i=0}^{n-1} AF_i$  versus  $\theta_0$  for OTIS output breakthrough curve at the end of a five-segment simulated stream. Parameters were randomly selected from a uniform random distribution and allowed to vary within the domains reported in Table 1.



**Figure 2.** Scatterplot of the residuals about zero as differences  $\theta_0 - \mathcal{A}$  versus  $\theta_0$  for the Monte Carlo simulation.

the differences  $\theta_0 - \mathcal{A}$  versus  $\theta_0$  for the values in Figure 1. It shows no apparent trend in the residuals.

### 3.2. Validation With Field Data

[22] In order to validate the field application of equation (16) the results of a nutrient injection experiment conducted by *McKnight et al.* [2004] were used. In that study a short-term release of  $\text{NaNO}_3$  solution was conducted on a reach of Green Creek in the McMurdo Dry Valleys of Antarctica. The resulting time series of nitrate concentrations were measured at three downstream locations until all of the measurable injected nitrate was effectively flushed from the stream system [*McKnight et al.*, 2004]. The study reported OTIS parameters that were obtained by inverse numerical modeling. The resulting parameter ranges are shown in Table 2. Zeroth temporal moments at each location were determined using trapezoidal rule quadrature. This is computed from time and concentration measurements by *Haas* [1996]

$$\theta_0 = \sum_{j=2}^n \left( \frac{c^*[j] + c^*[j-1]}{2} \right) (t[j] - t[j-1]) \quad (17)$$

where now  $c^*[j]$  represents a measured concentration [ $\text{ML}^{-3}$ ]. The quantity  $\theta_0$  will be hereafter referred to as the experimental zeroth moment ( $\text{TML}^{-3}$ ). Since the breakthrough concentration profiles exhibited considerable noise, it was desirable to estimate the uncertainty. To do this, the method developed by *Brooks and Wise* [2005] was used. Specifically, the uncertainty in terms of variance in the experimental zeroth moment is given by their equation (B1):

$$\text{var}(\theta_0) = \frac{1}{4} \Delta t_1^2 \text{var}(c^*[1]) + \sum_{j=1}^{n-2} \left[ \frac{1}{4} (\Delta t_j^2 + \Delta t_{j+1}^2) \cdot \text{var}(c^*[j+1]) \right] + \frac{1}{4} \Delta t_n^2 \text{var}(c^*[n]) \quad (18)$$

where  $j$  is the index of the measurement,  $\Delta t_j \equiv t[i+1] - t[i]$ ,  $c^*[j]$  is the  $j$ th measured concentration in time,  $n$  is the total number of observations for the measurement location, and  $\text{var}(c^*[\cdot])$  is the estimated variance associated with the measurement of the particular value of  $c^*$ . This variance is interpreted as measurement uncertainty due to several possible factors including random variation in transverse and depthwise nitrate concentration in the stream cross section, random analytical error, and, in the case of the *McKnight et al.* data, effects of nonsteady discharge,  $Q$ . In their paper, the effect of nonsteady  $Q$  was accounted for by a flow routing adjustment. Here, we necessarily assume that for each application of the transfer function,  $u = Q/A$ , was constant. In terms of the experimental zeroth moment, unsteady discharge is assumed to be a component of random error. In order to estimate the total error associated with each  $c^*[j]$ , a generalized autoregressive conditional heteroscedasticity (GARCH) model was used with the time series for each measurement location. This approach corrects for autocorrelation in  $c^*[\cdot]$  and allows computation of  $\text{var}(c^*[j])$  by assuming constant variance (homoscedasticity) occurs only in the error residual. This was implemented using SAS/ETS software, version 9, via its AUTOREG procedure [*SAS Institute Inc.*, 2002]. The error was estimated by assuming normally distributed errors for all times, thus

$$\text{var}(c^*[j]) = \left( \text{UCL}(\hat{c}^*[j]) - c^*[j] \right)^2 \quad (19)$$

where  $\text{UCL}(\hat{c}^*[j])$  is the upper confidence limit in the GARCH predicted concentration ( $\hat{c}^*[j]$ ) for  $t[j]$ , as computed from the GARCH time series model. The results are presented in Table 3. Table 3 shows the results of the trapezoidal rule integration using the nitrate time series for each reach section, along with the uncertainty expressed as lower and upper confidence limits. For the confidence limits presented in Table 3, we used the uncertainty estimate given by equation (18), which accounts for covariance in the time series of concentration measurements. It is derived by assuming that  $\Delta t_j$  and  $c^*[j]$  are bivariate normally distributed [*Brooks and Wise*, 2005]. It was also assumed that the resulting variance estimate from the experimental zeroth moment given by equation (18) represents the square of the standard error. Then we assumed the one-sided confidence limits could be approximated by using the zeroth moment estimate from equation (17), i.e.,  $\theta_0 \pm 2\sqrt{\text{var}(\theta_0)}$ . This approach provides an indication of the degree of uncertainty associated with the experimental zeroth moments given in Table 3.

[23] In the third column of Table 3, these values were normalized by dividing each zeroth moment by the zeroth

**Table 2.** Ranges of Metrics Based on Parameter Estimates Obtained Using Inverse Modeling With Unsteady Flow With OTIS and  $A \in [0.02, 0.07] \text{ m}^2$  and  $Q \in [0.3, 3.0] \text{ L s}^{-1}$ , as Reported by *McKnight et al.* [2004].

Reach, m	$L_s$ , m	$T$ , s	$\overline{Da}(s=0)$	$Pe$
0–50	126–3,723	19,592–67,459	0.10–2.47	2.2–65.2
50–226	24–695	30,079–104,070	0.27–6.41	8.2–232.4
226–327	17–459	20,638–71,542	0.32–7.69	4.7–125.2

**Table 3.** Comparison of Experimental Zeroth Moments for Nitrate From the Study of *McKnight et al.* [2004] Versus Monte Carlo Simulation ( $N = 30000$ ) Results Using the Transfer Function With Uniform Distributions of  $Q \in [0.3, 3.0] \text{ L s}^{-1}$ ,  $A \in [0.02, 0.07] \text{ m}^2$ , as Reported in That Study<sup>a</sup>

Reach, m	Experiment, $\mu\text{M h}$			Normalized			$\mathcal{A}$		
	LCL	$\theta_0$	UCL	LCL	$\theta_0$	UCL	Q1	Median	Q3
0	165 <sup>b</sup>	165 <sup>b</sup>	165 <sup>b</sup>	1.000	1.000	1.000	1.000	1.000	1.000
0–50	97	115	133	0.585	0.696	0.806	0.552	0.693	0.780
50–226	37	43	50	0.223	0.262	0.301	0.112	0.261	0.384
226–327	7	8	9	0.040	0.047	0.054	0.018	0.082	0.168

<sup>a</sup>LCL, lower confidence limit approximated by  $(\theta_0 - 2\sqrt{\text{var}(\theta_0)})$ , as described in the text. UCL, upper confidence limit approximated by  $(\theta_0 + 2\sqrt{\text{var}(\theta_0)})$ , as described in the text.

<sup>b</sup>Extrapolated to match normalized results from  $\mathcal{A}$ .

moment for the injection point. The actual mass used for the injection was not explicitly reported by *McKnight et al.* [2004], so this was estimated by extrapolation. It was adjusted until it yielded normalized zeroth moments for each of the four reaches that were as closely equivalent to those computed using equation (16) as possible. This moment occurred with a value of 165 ( $\mu\text{M h}$ ). The injection zeroth moment was assumed not to have uncertainty. The values given by equation (16) are reported in Table 3. The distributions of  $\mathcal{A}$  were distinctly nonnormal. Therefore the first quartile (Q1), median, and third quartile (Q3) were reported rather than parametric statistics. The transfer function model showed good agreement with the experimental results.

#### 4. Conclusions

[24] A compartmental modeling approach was developed for relating nitrate retention and attenuation metrics to quantifying actual nitrate assimilative capacity. Using a short-term nutrient injection, total assimilative capacity can be defined as  $1 - \mathcal{A}$ , where  $\mathcal{A}$  is the attenuation factor, which is the normalized zeroth moment, for the stream reach.  $\mathcal{A}$  is the total mass of nitrate injected that is flushed through the stream reach. For a heterogeneous reach this can be interpreted in the compartmental approach as  $\mathcal{A} = \prod_{i=0}^n \text{AF}_i$  where  $\text{AF}_i$  is the attenuation factor for an individual cell or compartment and the initial compartment has as input a Dirac- $\delta$  pulse. The values of  $\text{AF}_i$  are determined using the normalized process transfer function for the transient storage model with first-order reactions representing nutrient uptake in the free stream, and denitrification in the storage regions. The compartmental model therefore is a representation of the stream as a cascade of uniform reach sections with differing parameters. This approach also allows net flux to or from groundwater to be represented by allowing differing values of free stream discharge from one cell to the next.

[25] Comparison of this approach with results of Monte Carlo simulations, using the OTIS numerical model, showed that the highest relative percent difference was 15% lumping all cell exit concentrations in a 100 meter cell length, 5 cell cascade. For the Monte Carlo simulations, parameter values were allowed to vary uniformly within

parameter domains that have been measured and published in field studies.

[26] Using the compartmental approach with parameters and breakthrough curves from a published field experiment was also evaluated. By using an experimental moment analysis on a three cell cascade the differences between the observed assimilative capacity and that predicted using the compartmental approach were all less than about 0.035. These were well within the propagated uncertainties from imprecise concentration and parameter measurement.

[27] The compartmental modeling approach has commonly been used to evaluate tracer data in regional groundwater studies. The results presented here show that this approach can also be applied in the determination of nitrate retention and total assimilative capacity.

#### Appendix A

[28] Equation (6) has the characteristic equation  $0 = (1/Pe)\Gamma^2 - \Gamma - \overline{Da}(s)$ , where  $\Gamma^2 \equiv d^2/dx^2$  and  $\Gamma \equiv d/dx$ . The general solution is  $\bar{c} = \varphi_1 \exp(\Gamma_1 x) + \varphi_2 \exp(\Gamma_2 x)$ , where  $\varphi_1$  and  $\varphi_2$  are constants of integration, and, by the quadratic formula the roots are  $\Gamma_1 = (1 + \sqrt{1 + 4\overline{Da}(s)/Pe})Pe/2$  and  $\Gamma_2 = (1 - \sqrt{1 + 4\overline{Da}(s)/Pe})Pe/2$ . The far-field boundary condition, in which we assumed that

$$x^* \rightarrow \infty, c^* \rightarrow 0 \quad (\text{A1})$$

can be expressed in terms of the dimensionless variables in the Laplace domain as

$$\bar{c}(Pe \rightarrow \infty, s) = 0. \quad (\text{A2})$$

This leads to  $\Gamma_1 = 0$ , so that

$$\bar{c} = \varphi_2 e^{\Gamma_2 x}. \quad (\text{A3})$$

We have assumed the boundary condition at the injection site to be given by equation (3). Therefore, at location  $x = 0$  immediately below the injection point the following holds [*Fischer et al.*, 1979, p. 50], and noting that the Laplace transform of  $\delta(t)$  is equal to 1:

$$1 = \bar{c}(0, s) - \frac{1}{Pe} \frac{\partial \bar{c}}{\partial x} \Big|_{x=0} \quad (\text{A4})$$

[29] Substituting equation (A3) and its derivative into this gives

$$1 = \varphi_2 e^{\Gamma_2 x} \Big|_{x=0} - \frac{\varphi_2 \Gamma_2}{Pe} e^{\Gamma_2 x} \Big|_{x=0} \quad (\text{A5})$$

which leads to

$$\varphi_2 = \frac{1}{1 - \Gamma_2/Pe}. \quad (\text{A6})$$

Now substituting this result into equation (A3) yields

$$\bar{c} = \frac{1}{1 - \Gamma_2/Pe} e^{\Gamma_2 x}. \quad (\text{A7})$$

[30] At the exit point of the stream reach mass balance requires that

$$\bar{c}_{\text{exit}} = \bar{c}(1, s) - \frac{1}{Pe} \left. \frac{\partial \bar{c}}{\partial x} \right|_{x=1} \quad (\text{A8})$$

Now substituting equation (A7) into (A8) yields after simplification

$$\bar{c}_{\text{exit}} = \exp \left\{ \frac{Pe \left( 1 - \sqrt{1 + 4Da(s)/Pe} \right)}{2} \right\}. \quad (\text{A9})$$

## Notation

$AF_i$	attenuation factor for cell $i$ .
$A$	free stream cross-sectional area $L^2$ .
$\mathcal{A}$	cumulative total nitrate attenuation factor.
$c$	dimensionless nitrate concentration.
$c^*$	nitrate concentration, $ML^{-3}$ .
$c_s^*$	nitrate concentration in storage region, $ML^{-3}$ .
$c_{\text{exit}}$	dimensionless cell exit nitrate concentration.
$\frac{K}{Da}$	longitudinal dispersion coefficient, $L^2T^{-1}$ .
$\frac{Da}{Da}$	Damkohler number.
$j$	time series index of measurement.
$k$	order of temporal moment.
$L_s$	average distance prior to entering storage ( $Q/(A\alpha)$ ), $L$ .
$n$	number of observations of nitrate time series at a given location.
$N$	total number of Monte Carlo trials.
$Pe$	Peclet number, equivalent to $uX/K$ .
$u$	average free stream velocity, $LT^{-1}$ .
$Q$	volumetric flow rate, $L^3T^{-1}$ .
Q1	first quartile of Monte Carlo outputs for $\mathcal{A}$ .
Q3	third quartile of Monte Carlo outputs for $\mathcal{A}$ .
$s$	Laplace transform variable.
$S_w$	nutrient uptake length, $L$ .
$t$	time, $T$ .
$T$	storage zone residence time, $T$ .
$x$	dimensionless downstream distance.
$x^*$	downstream distance, $L$ .
$X$	length of reach section (cell), $L$ .
$\alpha$	mass transfer coefficient, $T^{-1}$ .
$\delta(t)$	Dirac delta function, $T^{-1}$ .
$\theta_0$	experimental zeroth moment for heterogeneous stream system.
$\lambda$	first-order decay rate associated with nutrient uptake, $T^{-1}$ .
$\lambda_s$	storage zone loss rate for nitrate, $T^{-1}$ .
$\mu_k$	$k$ th temporal moment, $T^k$ .

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