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Characterizing multiple timescales of stream and storage zone interaction that affect solute fate and transport in streams

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Abstract. The fate of contaminants in streams and rivers is affected by exchange and biogeochemical transformation in slowly moving or stagnant flow zones that interact with rapid flow in the main channel. In a typical stream, there are multiple types of slowly moving flow zones in which exchange and transformation occur, such as stagnant or recirculating surface water as well as subsurface hyporheic zones. However, most investigators use transport models with just a single storage zone in their modeling studies, which assumes that the effects of multiple storage zones can be lumped together. Our study addressed the following question: Can a single-storage zone model reliably characterize the effects of physical retention and biogeochemical reactions in multiple storage zones? We extended an existing stream transport model with a single storage zone to include a second storage zone. With the extended model we generated 500 data sets representing transport of nonreactive and reactive solutes in stream systems that have two different types of storage zones with variable hydrologic conditions. The one storage zone model was tested by optimizing the lumped storage parameters to achieve a best fit for each of the generated data sets. Multiple storage processes were categorized as possessing I, additive; II, competitive; or III, dominant storage zone characteristics. The classification was based on the goodness of fit of generated data sets, the degree of similarity in mean retention time of the two storage zones, and the relative distributions of exchange flux and storage capacity between the two storage zones. For most cases (>90%) the one storage zone model described either the effect of the sum of multiple storage processes (category I) or the dominant storage process (category III). Failure of the one storage zone model occurred mainly for category II, that is, when one of the storage zones had a much longer mean retention time (t_s ratio > 5.0) and when the dominance of storage capacity and exchange flux occurred in different storage zones. We also used the one storage zone model to estimate a "single" lumped rate constant representing the net removal of a solute by biogeochemical reactions in multiple storage zones. For most cases the lumped rate constant that was optimized by one storage zone modeling estimated the flux-weighted rate constant for multiple storage zones. Our results explain how the relative hydrologic properties of multiple storage zones (retention time, storage capacity, exchange flux, and biogeochemical reaction rate constant) affect the reliability of lumped parameters determined by a one storage zone transport model. We conclude that stream transport models with a single storage compartment will in most cases reliably characterize the dominant physical processes of solute retention and biogeochemical reactions in streams with multiple storage zones.

1. Introduction

Hydraulic exchange between surface water in streams and stagnant or slowly moving water in the surface and subsurface is a key process that affects physical transport times and biogeochemical transformations in stream systems. Table 1 summarizes some of the various types of storage zones that have been observed in natural streams. Many of these storage zones probably coexist within stream systems, for example, streambed materials of different porosity (e.g., coarse gravel deposits versus more poorly sorted alluvial sediments), gravel bars of meandering channels, and slow flowing surface water in areas of thick aquatic vegetation. A stream transport model that considers storage processes usually possess only a single storage compartment (hereinafter the "one storage zone model") [*Bencala and Walters*, 1983; *Newbold et al.*, 1983; *Jackman et al.*, 1984; *Runkel*, 1998; *Wörman*, 1998]. The parameters, including the cross-sectional area of the storage zone (A_s), exchange rate (α), and a rate constant for biogeochemical reactions in a storage zone (λ_s), are therefore usually interpreted as "lumped" parameters that represent a spectrum of storage processes that occur simultaneously in multiple types

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Table 1. Types of Storage Zones

Storage Zone Type	Example	Hydrologic Residence Time	References
Streambed sediments	St. Kevin Gulch, Colo.	6 hours	*Harvey et al.* [1996]
	Pinal Creek, Ariz.	1–25 min	*Harvey and Fuller* [1998]
	Little Lost Man Creek, Calif.	6–25 hours	*Triska et al.* [1993]
Near-stream alluvial sediments (≤5 m from stream)	North Fork Dry Run, Va.	0.3–46 hours	*Castro et al.* [1991]
	St. Kevin Gulch, Colo.	80 hours	*Harvey et al.* [1996]
	Little Lost Man Creek, Calif.	3–130 hours	*Triska et al.* [1993]
Near-stream alluvial sediments (≥5 m from stream)	North Fork Dry Run, Va.	6 days	*Castro et al.* [1991]
	Little Lost Man Creek, Calif.	5–19 days	*Triska et al.* [1993]
	Aspen Creek and Rio Calaveras, N. M.	≤10 days	*Wroblicky et al.* [1998]
Beaver dam subsurface flow paths	Shingobee River, Minn.	Several days	F. J. Triska personal communication, 1998
Aquatic vegetation zone at channel sides	Pinal Creek, Ariz.	4–35 min	*Choi* [1998]
Periphyton-colonized films on streambed	Little Lost Man Creek, Calif.	3 min	*Kim et al.* [1990]

of storage zones. We know, however, that variations in physical and biogeochemical processes in storage zones exert a strong influence over the transport behavior of solutes [*Bourg and Bertin*, 1993; *Triska et al.*, 1993; *Harvey and Fuller*, 1998]. We need a better understanding of how the conventional storage zone model characterizes multiple storage zones. For example, we need to know how the lumped parameters can be interpreted in terms of actual multiple storage processes. In addition, we are interested in knowing under what circumstances a model with only one storage zone fails to characterize storage zones in a meaningful way.

Groundwater investigations are informative about approaches that might be used to characterize multiple storage processes in stream systems. Aspects of the problems, such as physical retention in dead-end pores [*Selim et al.*, 1976; *Cameron and Klute*, 1977], size, geometry and porosity of grains [*Wood et al.*, 1990; *Harmon and Roberts*, 1994], and chemistry and mineralogy of coatings on sediment surfaces [*Weber et al.*, 1991; *Barber et al.*, 1992], are now routinely considered. Recently, *Haggerty and Gorelick* [1995] showed that transport of reactive solutes within heterogeneous aquifer materials could most accurately be characterized by models with distributions of multiple mass transfer processes.

The one storage zone models that have been used almost exclusively in stream systems are clearly not sufficient for all purposes. For example, *Harvey et al.* [1996] showed how a one storage zone model could detect rapid exchange with subsurface water in gravel bars but was insensitive to slower exchange that was occurring with the subsurface water in finer-grained alluvium that surrounds the channel. Some investigators have used the aggregated dead zone (ADZ) stream transport model [*Beer and Young*, 1983], which is flexible because it allows more than one storage zone to be considered. For example, *Castro and Hornberger* [1991] found that solute retention times in hyporheic zones are sometimes better described by two different storage zones rather than by just a single storage zone. Beyond two storage zones, they found that the improvement in model fit was not justified by the additional parameters. In general, the task of describing multiple storage zones by optimizing a large number of parameters will be difficult.

Because of wide usage of the one storage zone model in the past, our study is needed to provide guidelines to evaluate the reliability of previous modeling results and to develop practical guidelines for designing future studies. There are some inherent limitations of transport models with a single storage zone. For example, *Harvey and Wagner* [2000] showed that parameters determined from one experiment cannot be extrapolated for other flow conditions or reach lengths. These strict limitations on the transferability of one storage zone modeling have also been observed in groundwater investigations [*Young and Ball*, 1995; *Haggerty and Harvey*, 1997]. The results from the present study are therefore only applicable to model behavior when applied for a specific set of experimental conditions, i.e., stream velocity and reach length. Despite that limitation, we believe that stream-tracer experiments and one storage zone modeling will be used even more widely in the future because of the simplicity of the technique and the efficiency of the analysis.

The goal of the present study was to interpret and understand exactly how the one storage zone model characterizes storage processes in stream systems with multiple storage zones. To achieve our goal, we used a Monte Carlo modeling approach to represent a broad range of possible conditions that could be encountered in different geographic settings. We extended an existing solute transport model (OTIS) [*Runkel*, 1998] to describe transport processes in a two-storage stream system that represents the simplest case of multiple-storage stream systems. We believe our results from simple numerical experiments using a model of a two-storage stream system can be generalized because we feel that most natural stream systems are probably characterized by only one or two dominant storage zones. *Castro and Hornberger*'s [1991] finding that two storage zones were always sufficient to model multiple storage processes at their field site supports our contention. Our approach was to use numerical techniques to evaluate a wider range of conditions than could be sampled in the field. Our results therefore provide the guidelines necessary to interpret and understand one storage zone modeling results in terms of the characteristic and dominant storage processes in stream systems.

2. Extension of Stream Transport Model

One-dimensional transport models that consider advection and dispersion in natural channels [*Fischer et al.*, 1979] were extended in the 1970s to consider both groundwater inflow and interaction between an active channel and stagnant or slowly moving zones of flow [*Thackston and Schnelle*, 1970; *Valentine and Wood*, 1977; *Bencala and Walters*, 1983]. The storage zone model (sometimes referred to as the transient storage model) divided the hydrologic system into two interacting compartments: the actively flowing main channel and the storage zone capable of exchanging stream water with the main channel. The conventional storage zone model assumes that a single model compartment can adequately describe the multiple storage processes resulting from the many different timescales of storage interactions in a stream system (Figure 1).

The storage process in streams is usually formulated mathematically as a first-order mass transfer process that couples the stream and the storage zone. That formulation implies that the storage zones are perfectly mixed and that the hydrologic retention times in storage zones are exponentially distributed [*Levenspiel*, 1972]. A transport model that includes two storage zones or a distribution of storage zones might have greater flexibility to simulate two different distributions of retention times. The result could be very different from a one storage zone model depending on the physical dimensions (A_s) and exchange timescale (α) of each storage zone. The concept for extending the model from the one storage zone model to the two storage zone model is shown in Figure 1. The governing equations of the extended two storage zone model are

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial x} + \frac{1}{A}\frac{\partial}{\partial x}\left(AD\frac{\partial C}{\partial x}\right) + \frac{q_L}{A}(C_L - C) + \alpha_1(C_{s1} - C) + \alpha_2(C_{s2} - C) - \lambda C, \quad (1)$$

$$\frac{\partial C_{s1}}{\partial t} = \alpha_1\frac{A}{A_{s1}}(C - C_{s1}) - \lambda_{s1}C_{s1}, \quad (2)$$

$$\frac{\partial C_{s2}}{\partial t} = \alpha_2\frac{A}{A_{s2}}(C - C_{s2}) - \lambda_{s2}C_{s2}, \quad (3)$$

where t and x are the time and direction along the stream; C, C_{s1}, C_{s2}, and C_L are solute concentrations in the main channel, the storage zones 1 and 2, and the groundwater inflow, respectively (M/L^3); Q is the instream volumetric flow rate (L^3/T); q_L is the groundwater inflow rate ($L^3/T/L$); D is the longitudinal dispersion coefficient in the main channel (L^2/T); A, A_{s1}, and A_{s2} are the cross-sectional areas of the main channel and the two storage zones, respectively (L^2); α_1 and α_2 are the exchange rates of storage zones 1 and 2, respectively ($1/T$). The two storage zones included in the extended model operate independently, according to their own storage capacity, exchange, and biogeochemical reaction parameters $(A_{si}, \alpha_i, \text{and } \lambda_{si})_{i=1,2}$. We modified the U.S. Geological Survey (USGS) code OTIS [*Runkel*, 1998] to include a second storage zone (equations (1)–(3)) and solved these equations numerically.

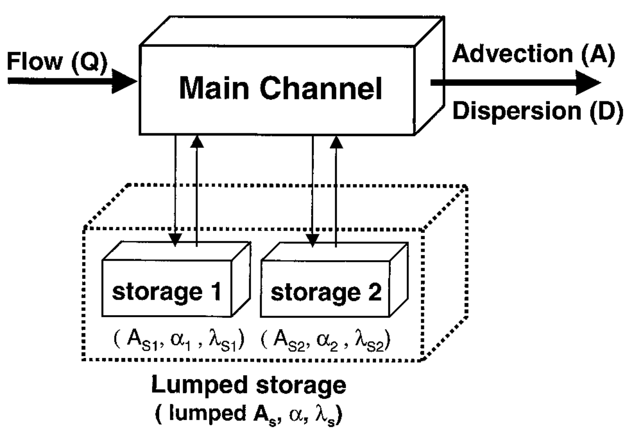


Figure 1. Conceptual framework of the one and the two storage zone transport model.

Table 2. Parameter Ranges of Two-Storage Transport Model Used in the Evaluation of One-Storage Transport Model

	Dynamic Transport, Nonreactive Solute	Steady State Transport, Reactive Solute
A_{s1}, m^2	0.1–2.0	0.1–2.0
A_{s2}, m^2	0.1–2.0	0.1–2.0
α_1, s^{-1}	1.0E-05 to 1.0E-03	1.0E-05 to 1.0E-03
α_2, s^{-1}	1.0E-05 to 1.0E-03	1.0E-05 to 1.0E-03
Q, m^3 s^{-1}	0.08	0.08
A, m^2	1.0	1.0
D, m^2 s^{-1}	0.4	0.4
L, m	150.0	150.0
λ_{s1}, s^{-1}	0.0	1.0E-03
λ_{s2}, s^{-1}	0.0	1.0E-05

Read 1.0E-05 as 1.0×10^{-5}.

3. Evaluation of the One Storage Zone Transport Model

For the numerical experiments we used the two storage transport model (Equations (1)–(3)) to generate theoretical data sets representing a broad range of transport processes in two storage stream systems. Two related transport scenarios were investigated: dynamic transport of a nonreactive solute and steady state transport of a reactive solute. The one storage transport model was evaluated on the basis of the accuracy with which instream solute concentrations generated by models with two storage zones were reproduced by single sets of lumped storage parameters (A_s and α) and lumped biogeochemical rate constants (λ_s). Figure 2 is a flowchart describing the evaluation approach in this study.

The first step was to select 500 sets of storage parameters for the two storage stream system (A_{s1}, A_{s2}, α_1, and α_2). These sets of storage zone parameters have uniform distributions with ranges (Table 2) that encompass typical variation occurring in natural systems [*Wagner and Harvey*, 1997]. The q_L and C_L were set to zero for all simulations, because these two parameters do not affect the storage processes. After running the two storage zone model with 500 different sets of storage parameters (A_{s1}, A_{s2}, α_1, and α_2), the one storage zone model was then optimized to estimate the lumped storage parameters (A_s and α), via inverse modeling (OTIS-P; *Runkel* [1998]). The sets of lumped storage parameters were evaluated with respect to their accuracy with which theoretical in-stream solute concentrations of the two storage stream system were reproduced. The accuracy was represented by calculating the root-mean-square-error (RMSE), defined as

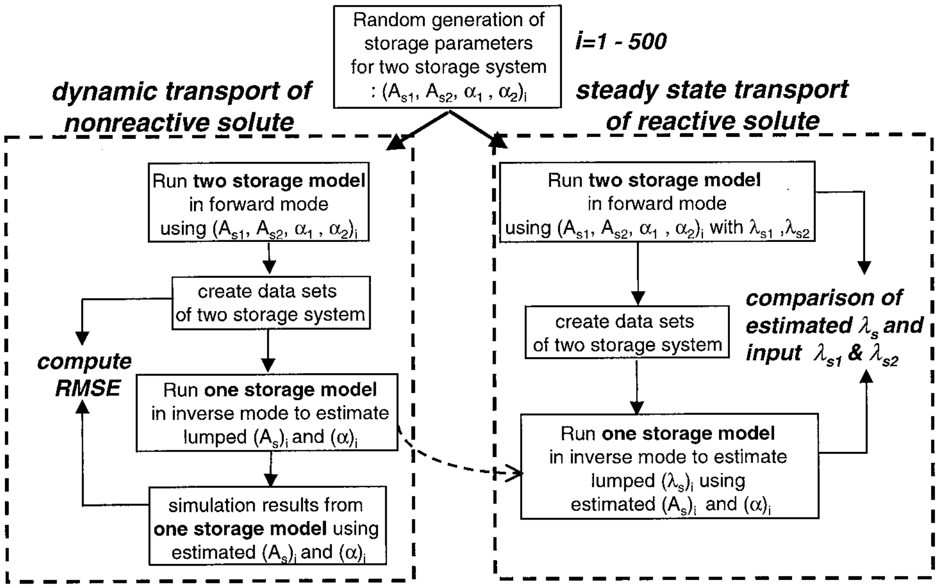


Figure 2. Flowchart describing the evaluation of the one storage zone transport model.

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{i=1}^{N} (C_2^i - C_1^i)^2}{N}}, \tag{4}$$

where C_2^i is the concentration of solute produced by the two storage zone model with A_{s1}, A_{s2}, α_1, and α_2; C_1^i is the concentration of solute simulated from the one storage zone model with lumped parameters, A_s and α; and N is the number of time-concentration data points for each simulation. A high RMSE implies that the lumped storage parameters A_s and α failed to accurately describe the physical storage processes occurring in the two-storage stream system. Typical modeling outcomes with high and low RMSE are shown in Figure 3. We found that the error that was introduced by modeling a two-storage system with lumped storage parameters (A_s and α) was usually obvious when the RMSE exceeded 0.035. For our purpose, we defined outcomes with a RMSE >0.035 as situations where the one storage zone transport model failed to describe the physical transport processes occurring in a multiple-(two)-storage stream system.

3.1. Dynamic Transport of Nonreactive Solutes

The RMSE varied widely for the 500 simulations, ranging from approximately 10^{-6} to 0.07 with an average RMSE of 0.013. The question that arises from the variations of RMSE is, Under which conditions is the one storage zone model able to reliably describe the dominant storage processes associated with a two-storage stream system? To answer this, we focused our investigation on identifying the key variable that explains variation in RMSE. One variable that could possibly explain much of the variation in RMSE is the ratio of the retention times t_{s1} and t_{s2} (R_{t_s}) for the two storage zones, where

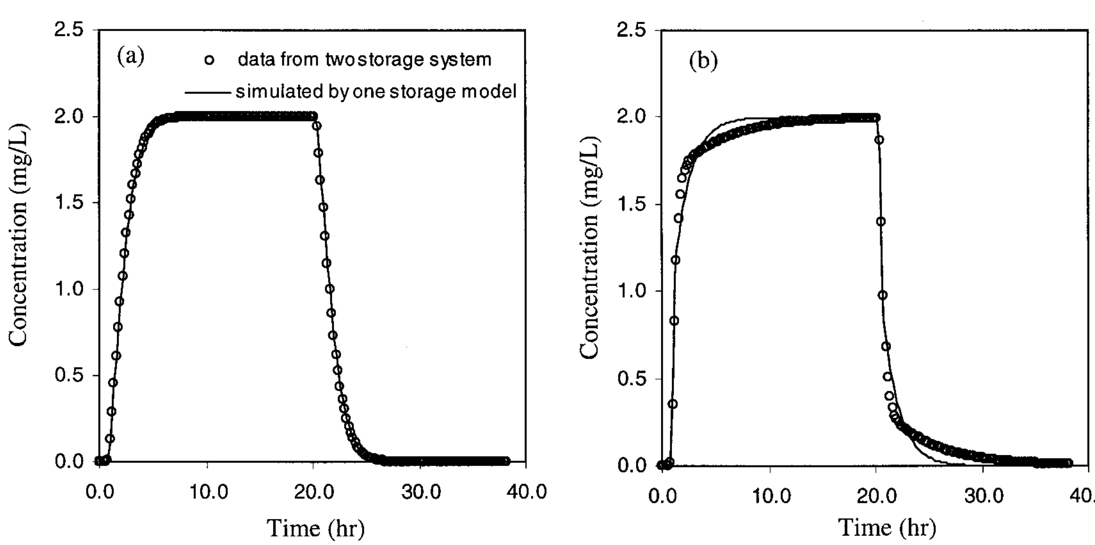


Figure 3. Simulation results from the one storage zone model based on the numerical data generated by a two storage zone model. (a) Good fit (RMSE = 0.002). (b) Poor fit (RMSE = 0.038).

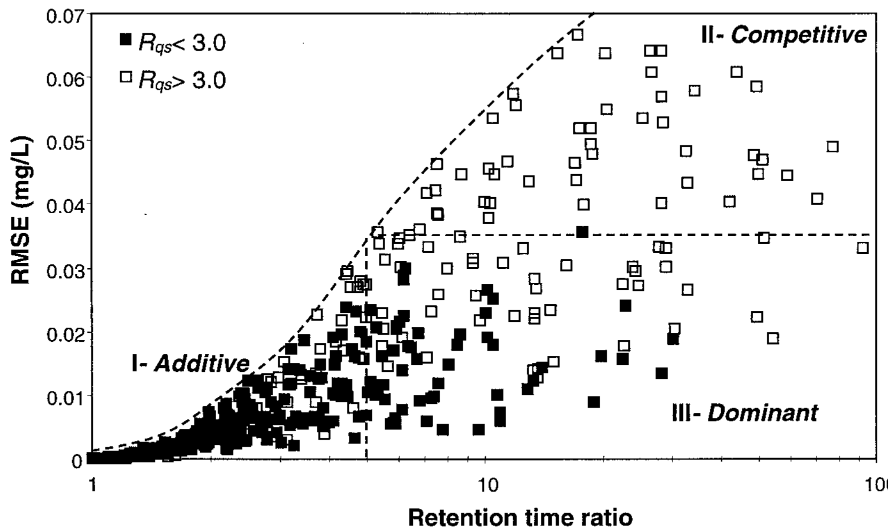


Figure 4. Evaluation results of the one storage zone model for nonreactive transport in the two-storage stream system. The 500 cases are classified into similar exchange flux ($R_{q_s} < 3.0$; solid squares) and contrasting exchange flux ($R_{q_s} > 3.0$; open squares). Also, the 500 cases are classified into three categories (additive, competitive, and dominant) by similarity in timescale (R_{t_s}) and distribution of storage capacity (A_s) and exchange flux (R_{q_s}).

$$t_s = \frac{A_s}{\alpha A}. \tag{5}$$

It is important to note that R_{t_s} is defined as the ratio of the longer retention time over the shorter retention time, so that R_{t_s} is always ≥ 1.

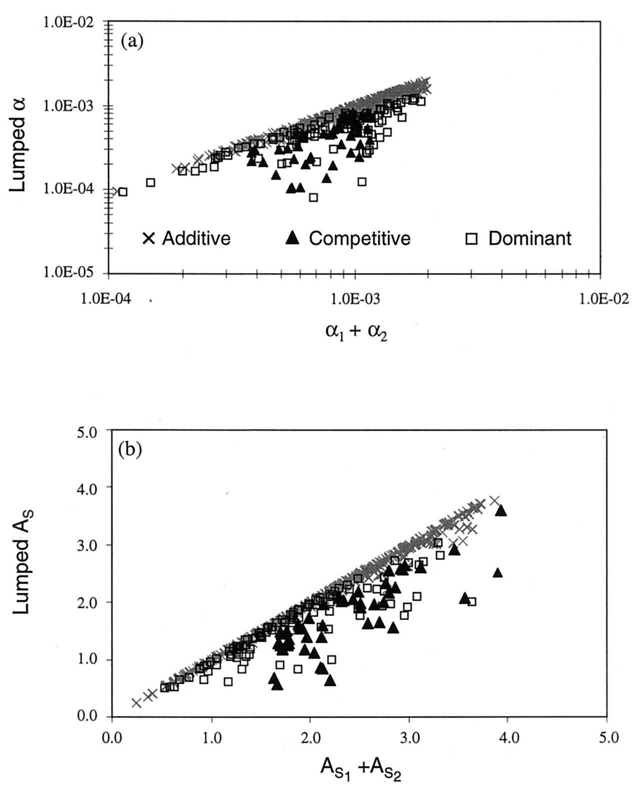


Figure 5. Comparison between lumped storage parameters (A_s and α) and the sum of two different storage parameters assigned to two storage zones ($A_{s1} + A_{s2}$ and $\alpha_1 + \alpha_2$). (a) Results for exchange coefficient (α). (b) Results for cross-sectional area of storage zone (A_s).

The RMSE increased as the retention time ratio R_{t_s} increased (Figure 4). Simulation results with high RMSE (>0.035) covered just 9.0% of the 500 total cases and can be observed only in the range of higher retention time ratio ($R_{t_s} > 5.0$). However, the RMSE showed wide variation between different simulation cases, even though they have the same retention time ratio, especially in the range of higher retention time ratio ($R_{t_s} > 5.0$) (Figure 4). In order to explain this variation the RMSE of 500 cases were classified into two groups according to the ratio of exchange fluxes at two storage zones, q_{s1} and q_{s2} (R_{q_s}), where

$$q_s = A\alpha. \tag{6}$$

Following the definition of R_{t_s}, R_{q_s} is the ratio of the larger exchange flux over the smaller exchange flux, so that R_{q_s} is always ≥ 1. As shown in Figure 4, one group (solid squares) had a similar ratio ($R_{q_s} < 3.0$), and the other group (open squares) had a contrasting ratio ($R_{q_s} > 3.0$). The simulation results with RMSE >0.035 were observed only when two different storage zones had contrasting exchange fluxes ($R_{q_s} > 3.0$).

The two storage zone stream system was characterized by one storage zone modeling in the following ways (Figure 4): I, "Additive" characteristics, similar retention time in storage zones ($R_{t_s} < 5.0$); II, "Competitive" characteristics, contrasting retention time in storage zones ($R_{t_s} > 5.0$) with dominance of storage capacity and exchange flux in different storage zones; and III, "Dominant" characteristics, contrasting retention time in storage zones ($R_{t_s} > 5.0$) with dominance of both storage capacity and exchange flux in a single storage zone.

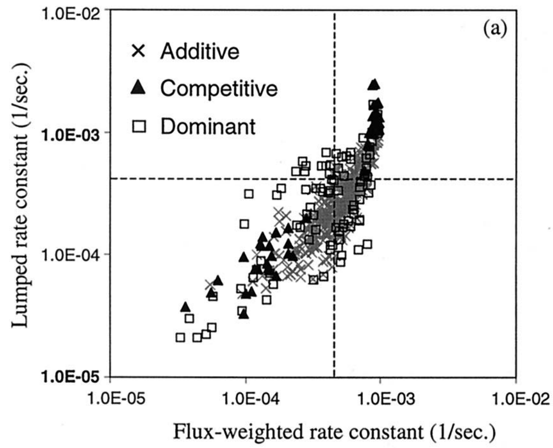
Figure 5 shows relationships between lumped storage parameters (A_s and α) and actual storage parameters (A_{s1}, A_{s2}, α_1, and α_2) of two storage zones. For the additive category, the lumped storage parameters A_s and α are approximately equal to the sum of parameter values of two storage zones (Figure 5). For the competitive and dominant categories the lumped storage parameters are always less than the sum of parameter values of two storage zones. For the dominant category the lumped parameters characterize the storage zone with larger size and faster exchange. The competitive category is distinguished by the more unpredictable nature of lumped parameters in comparison with the sum of parameter values of two storage zones (Figure 5).

3.2. Steady State Transport of Reactive Solutes

A first-order reaction rate constant in a single storage zone is the approach often used to characterize reactive transport in streams. In a stream system with multiple storage zones, this approach assumes that a single lumped rate constant represents the sum of biogeochemical reactions occurring in many different storage zones, no matter how different are their physical dimensions and biogeochemical conditions. Using the previous 500 sets of the storage parameters (A_{s1}, A_{s2}, α_1, and α_2) and two fixed rate constants ($\lambda_{s1} = 1.0 \times 10^{-3}$ and $\lambda_{s2} = 1.0 \times 10^{-5}$) assigned for the storage zones (Table 2), the two storage zone model was executed to produce 500 sets of distance-concentration data for steady state transport cases with biogeochemical reactions. The one storage zone model with lumped parameters A_s and α was applied to each of the 500 data sets to estimate lumped rate constants (λ_s). The lumped rate constants were compared with the flux-weighted rate constants ($\hat{\lambda}$), defined as

$$\hat{\lambda}_s = \frac{q_{s1}}{(q_{s1} + q_{s2})}\lambda_{s1} + \frac{q_{s2}}{(q_{s1} + q_{s2})}\lambda_{s2}. \tag{7}$$

The flux-weighted rate constant is a weighted arithmetic mean that averages rate constants for two different storage zones. It represents the combined effect of biogeochemical reactions in two storage zones. Many of the lumped rate constants show a positive correspondence with the flux-weighted rate constants (Figure 6). This result implies that the net effect of biogeochemical reactions in two different storage zones can reasonably be characterized by the single lumped rate constant.



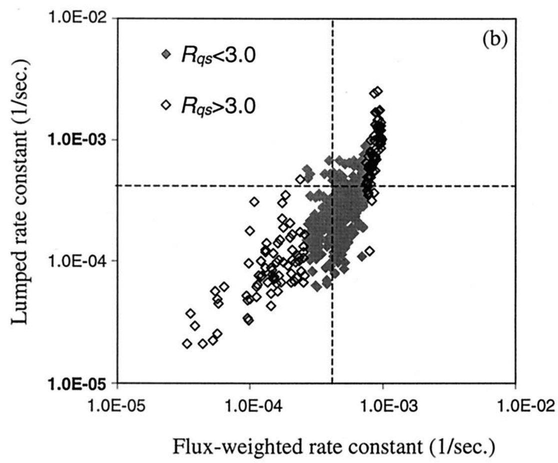


Figure 6. Comparison between lumped and flux-weighted rate constants. For the numerical experiment, two rate constants (1.0×10^{-3} and 1.0×10^{-5}) were assigned to two storage zones. The 500 lumped rate constants are classified as (a) additive, competitive, or dominant categories and (b) similar and contrasting exchange flux. The arithmetic average of the two rate constants is represented by dashed lines in both Figures 6a and 6b.

4. Discussion

In the past, most transport modeling in streams with the transient storage model has assumed a lumped single storage compartment with one characteristic dimension and timescale. Multiple exchange timescales are increasingly being observed in field studies, such as exchange with a streambed gravel bar and deeper alluvium sediments [*Castro and Hornberger*, 1991; *Harvey et al.*, 1996]. Our numerical evaluation of multiple storage zones indicated that a characteristic dimension and timescale of storage could be meaningfully described by a one storage zone model in over 90% of 500 simulation cases (Figure 4). Our results therefore suggest that only rarely will we be able to recognize the effects of multiple storage zones in streams when a one storage zone model is used. This result explains why inverse modeling of field tracer experiments to determine lumped storage zone parameters has typically been judged to be successful, even in stream systems where multiple storage zones are known to exist. However, since the goal of the modeling is to quantify processes and not just to fit data precisely, it is necessary to know how the actual storage processes are characterized by the lumped storage parameters.

On the basis of the key hydrologic conditions of each storage zone, similarity in timescale (R_{t_s}), and distribution of dominance in storage capacity and exchange flux, the multiple-storage stream systems can be classified into three categories: I, additive; II, competitive; and III, dominant storage zone systems (Figure 4). Figure 5 shows that if the solute retention times of two storage zones are very similar, the actual storage parameters are essentially added (I, additive) to identify the lumped storage parameter. If a specific storage zone has contrasting retention time and is dominant in both storage capacity and exchange flux, that storage zone will dominate the storage effect (III, dominant). The characteristic storage processes of both additive and dominant categories are quantified with good precision by the one storage zone model with the lumped storage parameter set A_s and α. However, if a specific storage zone has contrasting retention time but is only dominant in either storage capacity or exchange flux (II, competitive), the characteristic transport processes of a two-storage stream system cannot be reliably quantified by any possible combination of lumped A_s and α parameters.

The overall net effect of biogeochemical reactions in multiple storage zones is estimated by a flux-weighted rate constant which considers the reaction rate of each storage zone and the relative exchange flux of each storage zone within the stream. When flux-weighted and lumped rate constants were compared, we found a positive linear relationship with the uncertainty less than 1 order of magnitude (Figure 6). The lumped rate constants of the additive category underestimate slightly the flux-weighted rate constants, while those of the dominant and competitive categories are unbiased but more variable (Figure 6a). In order to interpret the lumped rate constant in terms of two actual rate constants the lumped rate constants were also classified into two groups by the ratio of exchange fluxes q_s ($R_{qs} < 3.0$ and $R_{qs} > 3.0$) (Figure 6b). The lumped rate constants for the cases of $R_{qs} < 3.0$ represent approximately the arithmetic average value of rate constants in both storage zones. However, the lumped rate constants for the cases of $R_{qs} > 3.0$ tend to better represent one or the other storage zone. Consequently, the lumped rate constant represents approximately the average rate constant in all storage zones when the exchange fluxes of two storage zones are very similar. Otherwise, the lumped rate constant represents the storage zone with the dominant exchange flux with the stream. Therefore the distribution of exchange fluxes among storage zones is a key variable controlling the lumped rate constant.

Even though the one storage transport model can almost always provide a reasonable characterization of multiple storage processes, there are some uncertainties in transferring those results to different hydrologic conditions. *Harvey and Wagner* [2000] showed that the storage parameters determined by the one storage zone model for one flow condition were not transferable to longer reaches or other flow conditions because of the shifting sensitivity to other storage timescales. There are two ways we can envision overcoming these significant drawbacks of one storage zone modeling. First, it might be possible to determine parameters for multiple storage zones by inverse modeling. A powerful method of optimization would be needed to estimate multiple sets of storage parameters or their distribution. For example, the time series modeling approach used with the ADZ model appears to provide a robust method to identify individual characteristics of multiple storage zones [*Castro and Hornberger*, 1991]. Alternatively, parameters for multiple storage zone models could possibly be estimated by independent field measurements to estimate storage parameters of multiple storage zones. For example, *Harvey and Fuller* [1998] used a minidrivepoint sampler [*Duff et al.*, 1998] to estimate storage parameters for the hyporheic zones on the basis of measurements of the penetration depth and retention time of stream tracer in streambed sediments. For example, A_s was estimated as

$$A_s = d_s w n, \tag{8}$$

where d_s is the penetration depth of tracer in streambed measured by the minidrivepoint sampler, w is the averaged stream width, and n is the average porosity of the streambed sediments. Both of the alternatives discussed above have advantages and drawbacks, and neither can be expected to work in all instances.

5. Conclusion

In this paper, we presented results of numerical experiments justifying the use of the one storage zone model in stream systems with multiple storage zones. Our justification is in the form of guidelines for interpreting the modeling results from the one storage zone model. In general, the one storage zone model identifies either the additive effect of several storage zones with similar timescales of retention or the effect of one dominant storage zone. The one storage zone model fails to characterize multiple storage zones for a very limited set of hydrologic conditions, i.e., the competitive category (where one storage zone dominates storage capacity but not exchange flux). Our results suggested that the competitive category represents a rare set of hydrologic conditions in which a two-storage stream system can be easily distinguished from a one-storage stream system. The rarity of the competitive situation probably explains why previous investigators almost always achieved good modeling fits to their stream tracer data.

In the case of reactive transport the lumped rate constant that was determined by fitting experimental data is a good estimate of the flux-weighted rate constant. In general, it will be difficult to determine relative contributions of several storage zones to overall biogeochemical reactions from stream tracer experiments. Alternatively, biogeochemical reactions might be estimated independently for each storage zone. For example, *Harvey and Fuller* [1998] used subsurface measurements of tracer transport and solute reaction to quantify reactive uptake of a solute contaminant in hyporheic flow paths beneath the stream.

In most stream systems the physical and biogeochemical storage processes associated with multiple types of storage zones can be characterized by a one storage zone model with lumped storage parameters. In some cases, model accuracy can possibly be improved by an extension of the model to include two storage zones [*Castro and Hornberger*, 1991], but the improvements in fit are usually minor. The biggest drawback of the transport model with only one storage zone is that lumped parameters (A_s, α, and λ_s) cannot be extrapolated to longer reaches or different flow regimes [*Harvey and Wagner*, 2000]. On the other hand, transport modeling that explicitly defines multiple storage zones will require that the hydrologic conditions for each of the multiple storage zones be fully characterized by independent methods [e.g., *Haggerty and Gorelick*, 1995]. This independent characterization is an expensive and time-consuming task. We believe that the one storage zone model will continue to be used in future studies because of its efficiency and simplicity, despite limitations to specific conditions and reach length. The results of numerical evaluations in this paper provide the guidelines from which we can correctly understand the modeling results from the one storage zone transport model when it has been applied to stream systems with multiple storage zones.

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