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Method for Estimating Surface Transient Storage Parameters for Streams with Concurrent Hyporheic Storage

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A method for estimating surface transient storage parameters for streams with concurrent hyporheic storage

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[1] Application of transient storage models has become popular for characterizing hydrologic and biogeochemical processes in streams. The typical transient storage model represents exchange between the main channel and a single storage zone, essentially lumping together different exchange processes. Here we present a method to inform a transient storage model that accounts for two storage zones (2-SZ) to discriminate between surface transient storage (STS) exchange and exchange with hyporheic transient storage (HTS). This method requires that, in addition to tracer breakthrough curves from the main channel, cross-sectional stream velocity distributions and stream tracer concentration time series data from several main channel locations and adjacent representative STS zones be collected. We apply this method to a constant rate conservative tracer injection in a first-order stream and to an instantaneous slug conservative tracer injection in a fourth-order stream. The 2-SZ model simulations matched observed breakthrough curves of tracer concentration in the main channel and general STS behavior well. Additionally, we compared the optimized parameter sets of the 2-SZ model to one–storage zone model (1-SZ) simulations and found that the lumped storage terms of the 1-SZ model described the time scales of 2-SZ model HTS exchange and attributed the time scales of observed STS exchange to longitudinal dispersion. With additional field data collection efforts and data processing, this method can provide much more useful results than the 1-SZ approach to those interested in discriminating between surface and subsurface transient storage dynamics of streams, which is important for discerning processes important to the cycling and fate of biogeochemicals.

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1. Introduction

[2] Stream water flow paths with significantly reduced downstream velocity in comparison to main channel flow can be defined as transient storage zones [*Bencala and Walters*, 1983; *Harvey et al.*, 1996]. Stream transient storage is driven primarily by fluvial structure [*Harvey and Bencala*, 1993; *Kasahara and Wondzell*, 2003; *Ensign and Doyle*, 2005; *Gooseff et al.*, 2007], vegetation growth and organic debris [*Hart et al.*, 1999; *Chapra and Wilcock*, 2000; *Gooseff et al.*, 2004; *Harvey et al.*, 2003; *Ensign and Doyle*, 2005] and streambed composition [*Harvey et al.*, 1996]. Transient storage can be generally segregated into surface transient storage (STS) and subsurface hyporheic transient storage (HTS). Both storage zone types can be influential to biogeochemical processes by extending residence times and facilitating greater contact with biochemically reactive surfaces compared to water flowing more rapidly down the main channel [*Findlay*, 1995; *Dahm et al.*, 1998; *Baker et al.*, 2000; *Harvey and Wagner*, 2000; *Ensign and Doyle*, 2005]. However, the biogeochemical conditions of each storage zone type are potentially very different [*Runkel et al.*, 2003], for example, HTS water may encounter anoxic conditions and has no exposure to sunlight, whereas STS water is likely to encounter conditions near oxygen saturation and is exposed to sunlight with potential for photochemical reactions.

[3] The p controls on HTS extent and exchange rates are (1) driving forces from hydraulic head and velocity gradients due to bed form and sinuosity [*Harvey and Bencala*, 1993; *Cardenas et al.*, 2004], (2) flow resistance expressed in bed and bank sediment hydraulic conductivities [*Valett et al.*, 1996; *Storey et al.*, 2003], and (3) competing fluxes from groundwater inflow to the channel [*Harvey et al.*, 1996; *Cardenas and Wilson*, 2006]. In contrast, STS depends on (1) discharge, which variously activates side channels, backwaters, and floodplains relative to advective channel flux, and (2) channel morphology, which influences turbulence and detention structures such as pools, wood, vegetation, and large rocks [*Harvey and Wagner*, 2000].

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HTS exchange is generally considered to be Darcian flow through porous media [*Harvey and Bencala*, 1993], while STS exchange is likely via lateral dispersion [*Fischer et al.*, 1979] and turbulent exchange processes [*Ghisalberti and Nepf*, 2002; *Jirka and Uijttewaal*, 2004]. STS exchange mechanisms generally cause more rapid exchange between the main channel (MC) of a stream compared to HTS flow paths [*Hall et al.*, 2002; *Gooseff et al.*, 2004; *Harvey et al.*, 2005].

[4] One major limitation to more accurately understanding how in-stream processes may be affected by transient storage is the aggregation of all STS and HTS exchange into a single storage zone, as represented in many popular transient storage models [*Choi et al.*, 2000; *Hall et al.*, 2002; *Runkel et al.*, 2003; *Ensign and Doyle*, 2005; *Gooseff et al.*, 2004, 2005; *Phanikumar et al.*, 2007]. Reach-scale investigations of transport and storage are often performed using conservative tracers such as salts and dyes to quantify residence time distributions in the form of concentration breakthrough curves (BTCs). These BTCs can then be simulated using a 1-D advection-dispersion solute transport models such as OTIS [*Runkel*, 1998], with one set of parameters characterizing a single storage zone (1-SZ). This method can be very attractive because the experiments are relatively easy to perform, and a limited data set is necessary to inform the model. Additionally, 1-SZ models have been found to accurately characterize the processes of net reach retention [*Choi et al.*, 2000]. Unfortunately the simplicity of this approach can decrease relevance of the results to investigators interested in zone-specific process characterization, particularly biogeochemical reactivity in disparate storage zones (i.e., STS or HTS).

[5] Many tracer studies are based on the assumption that observed transient storage occurs primarily in HTS [e.g., *Valett et al.*, 1996; *Morrice et al.*, 1997; *Haggerty et al.*, 2002; *McKnight et al.*, 2004], and therefore interpret the lumped 1-SZ model parameters as defining HTS exchange. Because of the expected long time scale of hyporheic flow compared to main channel flow, the skewing of tracer BTCs to late times due to hyporheic exchange is a reasonable assumption. Certain biogeochemical processes occur primarily during HTS exchange, as the nature of HTS promotes organic carbon storage and diverse microbial communities [*Findlay*, 1995]. In addition, HTS flow passes through interstitial sediment pores facilitating greater contact between water and biofilms where most biochemical reactions take place [*Valett et al.*, 1996], while STS is mainly dominated by dispersion and recirculation currents in stagnant parts of the water column [*Ensign and Doyle*, 2005]. For these reasons, plus the notion that STS exchange time scales will be rapid compared to HTS exchange, STS exchange has been assumed to be less important to in-stream processes than HTS exchange and has therefore been lumped or neglected in many past stream studies.

[6] The lumped transient storage approach may be appropriate for particular streams or particular study objectives, but even small headwater streams can exhibit STS zones with considerable residence times, as evident from study of a bedrock-lined reach with negligible HTS exchange [*Gooseff et al.*, 2005]. Streams of low gradient (usually higher order) may have weak head and velocity drivers of HTS exchange [*Kasahara and Wondzell*, 2003; *Wollheim et al.*, 2006], suggesting that these systems may accommodate more STS than HTS. STS has been found to be more influential to nutrient uptake than HTS in some systems [*Hill et al.*, 1998; *Gücker and Boëchat*, 2004; *Ensign and Doyle*, 2005], and be the primary storage mechanism in some lowland sand bed streams [*Stofleth et al.*, 2007]. In addition, it is possible that STS can facilitate photochemical reactions not possible during HTS that may be important to biogeochemical cycling [*McKnight et al.*, 2002]. Thus, interstream comparative studies seeking to identify mechanisms of biogeochemical storage and transformation [i.e., *Peterson et al.*, 2001] and model these processes at drainage network scales can benefit greatly by discriminating between HTS and STS.

[7] Recognizing the need to understand where transient storage occurs in streams, researchers have used a variety of methods to better discriminate between STS and HTS exchange. Hydrometric measurements coupled with groundwater flow models can identify HTS extent and exchange coefficients [e.g., *Wroblicky et al.*, 1998; *Kasahara and Wondzell*, 2003; *Cardenas and Wilson*, 2006], but these results are difficult to compare to tracer studies that have a limited "window of detection" of mostly faster exchanging surface and subsurface storage flow paths [*Harvey et al.*, 1996; *Harvey and Wagner*, 2000]. To maintain accuracy in such models, extensive information about the spatial heterogeneity of hydraulic conductivity in the subsurface is required and difficult to acquire [*Harvey et al.*, 1996]. Another approach to identifying where transient storage occurs is by comparing BTCs among stream reaches with varying morphology, such as bed form [*Hall et al.*, 2002; *Gooseff et al.*, 2005] and channel substrate [*Valett et al.*, 1996; *Morrice et al.*, 1997]; and in the same reach with changing conditions, differences such as discharge [*Valett et al.*, 1996; *Hart et al.*, 1999], groundwater flux [*Harvey et al.*, 1996], and manipulations of channel morphology [*Ensign and Doyle*, 2005]. Several of these studies have made simultaneous measurements of solute flux through individual storage zones [*Harvey et al.*, 1996; *Morrice et al.*, 1997; *Fernald et al.*, 2001; *Hall et al.*, 2002; *Harvey et al.*, 2005], which helped confirm that these zones receive tracer and function to temporarily store water. However, making the link to the reach scale from point-scale measurements remains difficult.

[8] A crucial step in proceeding with this kind of storage zone-specific investigation is to incorporate into stream solute transport models terms for both HTS and STS exchange. A two–storage zone solute transport model (2-SZ) with one compartment representing the slower-exchanging HTS, and one compartment representing the faster-exchanging STS allows for the discrimination of storage at the scale of a stream reach. This logical division of surface and subsurface storage may provide valuable insights into the relationships between transient storage exchange and biogeochemical processes. The inclusion of additional storage terms into the 1-SZ model has already been accomplished [*Choi et al.*, 2000], what remains is the development of field techniques that parameterize the 2-SZ model in a realistic way [*Runkel et al.*, 2003].

[9] When additional parameters are added to a model, additional information regarding those parameters may be required to accurately facilitate their estimation. This was demonstrated through Monte Carlo analysis, where *Choi et al.* [2000] showed that unless additional information beyond the MC BTC was incorporated in the 2-SZ modeling process parameter equifinality among different parameter sets could result (i.e., similar simulations for different sets of parameter values). Therefore the challenge in applying the 2-SZ modeling approach is incorporating data with adequate information content pertaining to all model parameters [*Runkel et al.*, 2003].

[10] As STS phenomena are relatively easy to observe and sample, this is a logical place to collect additional data. Previous studies have had some success in estimating STS parameters through physical measurement. For example *Phanikumar et al.* [2007] used wavelet decomposition of acoustic Doppler current profiles to estimate the size of both the flowing MC and STS by delineating the channel into fast and slow moving zones. Similarly some investigations have applied hydrometric measurements of stream velocity to designate average areas for the MC and STS within the stream [*Gücker and Boëchat*, 2004]. When microbial mats were observed to cause much of the STS in Antarctic glacial meltwater streams, *Gooseff et al.* [2004] used data from previous flume studies on microbial mats to constrain STS 2-SZ model parameters. Tracer data has also been collected from stream storage areas during injections to explore how exchange dynamics predicted by the 2-SZ model compare to the natural system [*Harvey et al.*, 2005]. The estimation of STS properties through physical measurement is potentially a promising method to incorporate additional data into the 2-SZ model parameter estimation process, yet few studies have attempted to do so thus far.

[11] Here we propose a method to incorporate data from a combination of hydrometric velocity measurement and STS BTC data, in addition to MC BTC data, to aid in the 2-SZ model parameter estimation process. Our approach is novel, as it includes STS tracer data in the simulation optimization process, while integrating previous work by identifying STS with stream velocity surveys. Using two BTCs in conjunction with an initial constraint on STS size during the optimization process can provide adequate information to support the estimation of additional storage parameters and decrease parameter correlation. We demonstrate the utility of this approach through application to disparate first- and fourth-order streams.

2. Method

2.1. Two–Storage Zone Modeling

[12] The 1-SZ solute transport model, OTIS, incorporates terms into the advection-dispersion equation that account for the processes of transient storage and lateral inflow [*Runkel*, 1998]. Although this 1-SZ model has been shown to characterize the net solute retention in many cases, only inferences can be made as to the individual contribution of exchange with STS or HTS [*Harvey et al.*, 1996; *Choi et al.*, 2000].

[13] The 2-SZ conceptual model (Figure 1) breaks up the lumped storage zone of the 1-SZ model into faster exchanging STS and a slower exchanging HTS by adding additional terms to the original OTIS equations [*Choi et al.*, 2000; *Gooseff et al.*, 2004]:

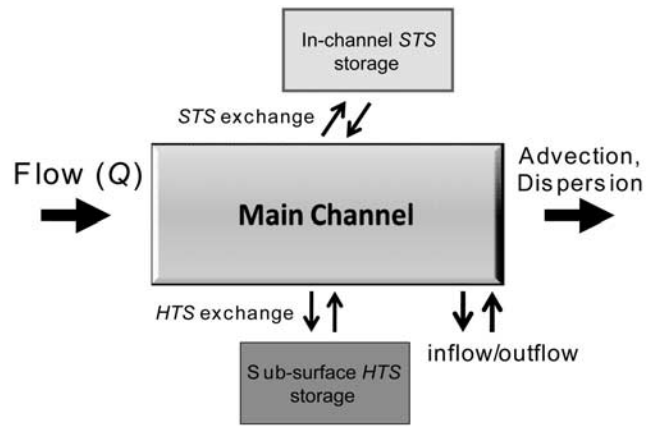

Figure 1. The 2-SZ conceptual model with two compartments of transient storage, each with individual exchange terms.

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial x} + \frac{1}{A}\frac{\partial}{\partial x}\left(AD\frac{\partial C}{\partial x}\right) + \frac{q_L}{A}(C_L - C) + \alpha_{STS}(C_{STS} - C) + \alpha_{HTS}(C_{HTS} - C) \quad (1)$$

$$\frac{\partial C_{HTS}}{\partial t} = \alpha_{HTS}\frac{A}{A_{HTS}}(C - C_{HTS}) \quad (2)$$

$$\frac{\partial C_{STS}}{\partial t} = \alpha_{STS}\frac{A}{A_{STS}}(C - C_{STS}) \quad (3)$$

where t is time and x is distance downstream; C, C_{STS}, C_{HTS} and C_L are solute concentrations in the MC, STS, HTS and groundwater (M/L^3); Q is the in-stream volumetric flow rate (L^3/T); q_L is the groundwater inflow rate (L^3/T/L); D is the MC longitudinal dispersion coefficient (L^2/T); A, A_{STS}, and A_{HTS} are the cross-sectional areas of the MC, STS, and HTS, respectively (L^2); α_{STS} and α_{HTS} are the exchange coefficients for STS and HTS, respectively (1/T).

[14] When additional storage terms are added to the 1-SZ model the MC BTC data alone is not adequate to support unique storage parameter estimates, therefore additional information must be incorporated into this process. The original 1-SZ model requires an estimate of discharge into the study reach, the upstream MC tracer boundary condition, and the reach length [*Runkel*, 1998]. The simulated reach downstream boundary MC BTC is then fit to the observed downstream boundary MC BTC by optimizing A, D, α (general SZ exchange coefficient, 1/T), and A_S (general SZ cross-sectional area, L^2). When applying the 2-SZ model, an initial estimate of A_{STS} is based on hydrometric measurements of stream velocity. In addition, we include information from tracer BTCs collected in representative STS zones into the parameter estimation process.

[15] Exchange between the MC and STS is controlled by a complicated turbulence field at the interface of the two STS [*Weitbrecht et al.*, 2008], yet the general behavior of this exchange can be characterized by analyzing the BTC

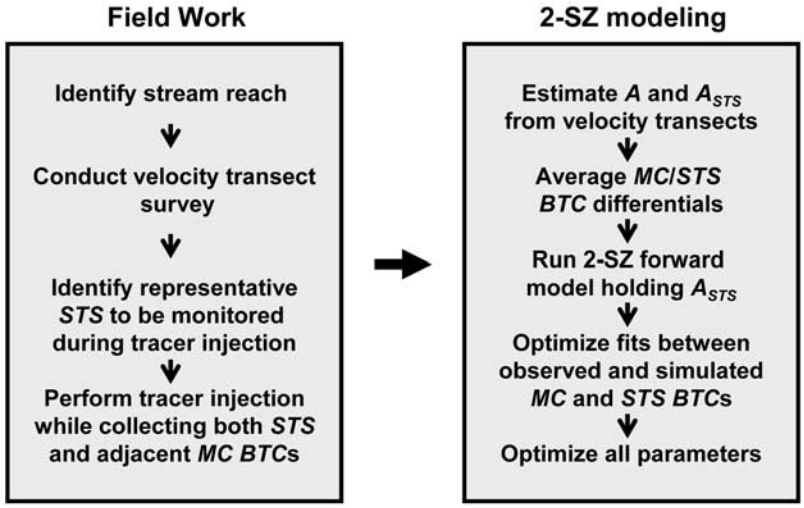

Figure 2. Flowchart for informing the 2-SZ model and achieving parameter optimization.

differentials observed between adjacent MC/STS locations. The MC BTC at a point adjacent to the STS zone serves as the input to the zone, the offset and modification of the STS BTC relative to this input characterizes how each STS zone exchanges stream water. Thus, we calculate the difference between STS BTCs and adjacent MC BTCs at each time step. This approach yields a general storage signature for each STS zone which can easily be aggregated, and used as additional information in the model optimization process. By using the adjacent MC BTC as the input signal for each observed STS zone the cumulative effects of stream transport up to that point are removed, rendering the MC/STS differential pattern from various reach locations directly comparable. This approach assumes that exchange characteristics are not affected by STS loading with a progressively more dilute tracer concentration with reach length during slug injections.

[16] Collecting data to estimate STS parameters is superior to doing so for HTS parameters as STS zones are easier to identify in the field, sample from, and typically contain internal velocity patterns that promote some mixing. A result of this mixing is that a solute BTC collected from a single point within a STS zone can reasonably represent the hydrologic functioning of that entire STS zone. Conversely HTS exchange can be difficult to locate without repeated tracer injection, and any single HTS sampling location may only capture the dynamic of a specific flow path, therefore characterizing less of the system heterogeneity. As discussed in detail by *Harvey et al.* [1996], individual HTS sampling locations are not likely to represent the exchange dynamics simulated by the transient storage solute transport model.

2.2. Field Data Collection

[17] To implement the proposed 2-SZ model we need estimates for both A_{STS} and BTC data from some representative group of STS zones (Figure 2). There are various techniques that can be applied to this data collection, depending on the physical characteristics of the system and what tracer is being used. Although the measurements of stream velocity used to estimate A_{STS} are usually not practical to perform during tracer injection, they should be made under similar hydrologic conditions as discharge can greatly affect the magnitude and distribution of STS storage.

[18] A_{STS} is estimated using a survey of velocity distributions across transects normal to flow direction. The number of transects necessary to adequately characterize the reach varies on the basis of the degree of heterogeneity present, but spacing of $\sim$1–2 bankfull widths provides good coverage, assuming that reach length is on the order of 20 bankfull widths or more. A reach length of at least 20 bank full widths should be sufficient to sample stream morphology, while transect spacing of 2 bankfull widths or less should capture the interfeature variability dynamics of the stream. Regular intervals between these transects reduces potential sampling bias along the reach. Once the velocity distributions have been recorded, delineation between areas contributing to MC flow from those of STS can be made. This process serves to provide preliminary model parameter estimates of the cross-sectional areas of storage (A_{STS}) and MC flow (A) for each cross section. The threshold between STS and MC flow will vary among STS zones, and possibly between reach-specific cross sections depending on the observed velocities and magnitude of heterogeneity (Figure 3). Once an estimate for A_{STS} has been established for every cross section the fraction of the total channel cross section this represents is determined, and these fractions are averaged over all transects and applied to the mean channel cross-sectional area to estimate reach-representative A_{STS}. Averaging the fraction of A_{STS} is superior to using the actual areas because equal weight is given to each cross section. Using an initial constraint on A_{STS} functions to decrease possible correlation between the various storage parameters and guide the modeling process toward the observed magnitude of A_{STS}. Although an initial estimate is also generated for A, this is used as a starting point, not a model constraint. Parameter sensitivity, or the amount of information contained in the data regarding a parameter [*Hill and Tiedeman*, 2007], is usually high for A while information for other parameters is generally lower; so constraining this parameter would only hinder the optimization process.

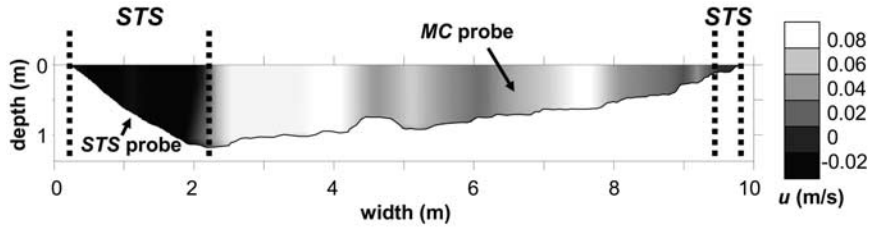

Figure 3. Example velocity survey from a transect located 463 m downstream of the Ipswich River reach input (shown at 3X vertical exaggeration). STS (here $u \leq 0$) was calculated to make up 21% of the total channel area for this cross section. Probe locations for an MC/STS pair are shown, and the delineation between MC and STS velocities is noted with the dashed lines.

[19] Once a variety of STS zones are identified through the velocity surveys, a subset of these locations are chosen for sampling. STS locations should be chosen to best represent the dominant type(s) of STS observed during the velocity survey. Adequate coverage will vary on the basis of the degree of heterogeneity expressed by STS over the given reach. Tracer BTCs in both the STS zone and adjacent MC are collected during the injection. This data augments the incoming boundary MC tracer BTC and the lower-boundary MC BTC information. Finally, discharge is measured at the top and bottom of the reach. This serves to provide an estimate of net streamflow change, which can be translated to lateral inflow or outflow along the reach.

2.3. Two–Storage Zone Model Parameter Estimation

[20] Collected data must be processed to facilitate the parameter optimization procedure (Figure 2). The raw MC/STS BTC differentials are on different time and concentration scales on the basis of their relative location along the reach. Generally the farther the STS zone is from the reach head, the lower the concentration and longer the duration of the input signal (adjacent MC BTC) because of dispersion, lateral inflow, and transient storage exchange along the reach.

[21] To render the various STS zone differentials directly comparable to one another and to the downstream boundary MC BTC, the STS zone BTCs must all be normalized to similar time and concentration scales. Therefore the differentials of tracer concentration per time step between each MC/STS pair are normalized to both the time and concentration scale of the downstream boundary MC BTC. First the time of center mass for each MC BTC is normalized to the time of center mass of the lower-boundary MC BTC. Time of center mass is referred to as the median travel time when dealing with an instantaneous slug injection [*Runkel*, 2002], and can be calculated through the relationship:

$$\frac{\int_0^t QC(x=L,t)dt}{\int_0^\infty QC(x=L,t)dt} = 0.5 \tag{4}$$

To avoid normalization bias by reach location, $t = 0$ is taken as the time of initial tracer arrival at each MC location. This approach accounts for the changing input BTC characteristics downstream on the basis of the time of center mass. Time of center of mass is not affected by the extreme values occurring in the BTC tails, which often get progressively more pronounced as the tracer travels downstream. The normalization of time since MC tracer arrival for each MC/STS pair is performed by applying the following calculation:

$$\text{normalized}(t) = \frac{t_{CM}^{LB}}{t_{CM}^{STS}}(t) \tag{5}$$

where t is time since MC arrival, t_{CM}^{LB} is the time of center mass calculated from the lower-boundary MC BTC, and t_{CM}^{STS} is the time of center mass calculated for the MC BTC adjacent to each STS zone. Next the peak concentration of each MC BTC is normalized to the lower-boundary MC BTC peak in a similar manner to account for the dilution of the input signal to each STS zone over the reach.

[22] At this point the MC/STS concentration differentials are directly aggregated through a simple arithmetic average. The resultant average MC/STS differential pattern can then be fit during the optimization process providing important information concerning how the STS zones respond to the tracer injection, which is ultimately a function of α_{STS} and A_{STS}. The use of an arithmetic average implies that reach location has little bearing on the MC/STS differential pattern after normalization. Test applications of this approach support this assumption by showing no clear trends in the MC/STS differential patterns with location along the study reach.

[23] Once the model is initially parameterized with an estimate of A_{STS} on the basis of the stream velocity survey, the remaining parameter values can be optimized. Optimization is achieved by iteratively adjusting parameter values until a global minimum [*Poeter and Hill*, 1997] in residuals of the difference of simulated and observed concentration values is achieved. The observed values in this case are the lower-boundary MC BTC and the average MC/STS differential pattern. The observed lower-boundary MC BTC is compared directly with the simulated lower-boundary MC BTC produced by the 2-SZ model. The average MC/STS differential pattern is fit by applying these differentials to the observed lower-boundary MC BTC and minimizing the residuals between the resultant BTC and the 2-SZ model simulated STS BTC. We apply more weight to the observed lower-boundary MC BTC than the average MC/STS differential pattern to reflect the cumulative errors present in the MC/STS differential aggregation process. Despite this lower weight, the MC/STS differential pattern provides an additional guide for the modeling process. Finally when a minimum residual is achieved, the A_{STS} parameter is also opened to estimation to achieve the true global minimum in residuals which reflects the best fit to the observed data.

2.4. Two–Storage Zone Model Parameter Evaluation

[24] Experimental reach length can be evaluated with the Damköhler number (*DaI*) [*Wagner and Harvey*, 1997]. The *DaI* is calculated as

$$DaI = \alpha \frac{(1 + A/A_S)L}{u} \tag{6}$$

where L is the reach length (m) and u is average stream velocity (m/s). The optimal *DaI* range is within 2 orders of magnitude of 1 (0.1–10), i.e., peak storage zone sensitivity. A *DaI* within this range indicates that there has been adequate tracer exchange over the reach length between the MC and storage to support the estimation of model storage parameters. Optimal parameter values for the 2-SZ model can be used to evaluate the relevance of each storage process to overall transport. One metric that can be useful for this evaluation is the fraction of median transport time due to storage, or F_{MED} [*Runkel*, 2002]:

$$F_{MED} = \frac{t_{MED} - t^m_{MED}}{t_{MED}} \tag{7}$$

where t_{MED} is the median travel time calculated from the lower-boundary MC BTC simulation with transient storage, and t^m_{MED} is the median travel time calculated from the lower-boundary MC BTC simulation without transient storage (i.e., α = 0). The median travel time of an instantaneous slug is determined using equation (4). For a constant rate addition, it is determined as the time to reach half of the plateau concentration. To facilitate comparison among reaches of differing length, simulations using the optimal parameters can be run over a common length. Here, we have chosen a reach length of 200 m (i.e., F^{200}_{MED}), consistent with the synthesis of *Runkel* [2002]. When applying the 2-SZ model, each storage zone type can be removed, to estimate F^{200}_{MED} for the alternate storage zone.

[25] We also compute the mean storage zone residence times, T_{STO} for both storage zones individually as [*Thackston and Schnelle*, 1970]

$$T_{STO} = \frac{A_S}{\alpha A} \tag{8}$$

where A_S and α can refer to either STS or HTS. A comparison of T_{STO} values between STS and HTS may indicate important differences in potential biogeochemical processing between the storage zones. This complements the F^{200}_{MED} analysis, providing additional information about the possible relevance of storage to in-stream processes. For example, a storage zone with a fast α may have a strong effect on the median transport time and therefore a high F^{200}_{MED}, but do little to promote biogeochemical processes as the actual residence time within that storage zone may be low.

3. Application

3.1. Site Description

[26] The Ipswich River watershed is located on the north shore of Massachusetts and drains 404 km^2 of rapidly urbanizing area into the Plum Island Sound. The surficial geology is dominated by shallow soils and glacial deposits, and the basin structure is predominantly igneous and metasedimentary Paleozoic and Precambrian bedrock [*Carlozzi et al.*, 1975]. Stream size within the basin ranges from first-order tributaries to the fifth-order lower Ipswich River main stem. The low-order streams drain a combination of wetland, agricultural land, woodland and urban areas; and are primarily medium to low gradient. The Ipswich River main stem is a meandering river of low gradient whose highest elevation is 24 m above sea level [*Williams et al.*, 2004]. In addition to abundant beaver activity, the Ipswich River is impeded by three main stem anthropogenic dams and discharge is monitored in both the towns of Middleton and Ipswich by USGS gauging stations. In an effort to illustrate the broad range of application of the 2-SZ method, examples from the first-order Lockwood Brook in Boxford and a section of the fourth-order upper Ipswich River main stem in North Reading are presented.

Table 1. Physical Characteristics of the Two Experimental Reaches

Reach	Length (m)	Order	Contributing Area (km^2)	Slope	Average Width (m)	Average Depth (m)
Lockwood Brook	219	1	1.1	0.022	1.52	0.05
Ipswich River	547	4	93.6	0.0005	7.3	0.44

3.2. Ipswich Basin Experimental Approach

[27] Dissolved NaCl was used as a conservative tracer (Cl^-) and applied through a constant rate injection in the first-order stream and as an instantaneous slug injection in the fourth-order stream (Table 1). The instantaneous slug injection was used instead of a constant rate injection for the fourth-order stream experiment because it was deemed more practical in the context of a large system. The results of these two methods are directly comparable because they yield the same information regarding reach-scale residence time distributions [*Payn et al.*, 2008]. Both tracer experiments were monitored by temperature correcting YSI EC 300 and Campbell Scientific 547A conductivity probes (connected to Campbell Scientific data loggers). Conductivity was later converted to concentration through a measured relationship between standards of known concentration ranging from 0 to 500 mg NaCl/L and resultant conductivity calculated for each probe using reach-specific water [*Gooseff and McGlynn*, 2005]. The two boundary condition BTCs were recorded using loggers attached to a single probe, while loggers with two probes were used to monitor three adjacent MC/STS locations during each injection. Data was normally recorded at 1 min intervals during the tracer injections and 2 s intervals during dilution gauging discharge measurements.

[28] The same method of MC/STS concentration differential aggregation discussed above was applied to both the constant rate and slug experimental data (Figure 4). Velocity transect measurements (made at 60% depth of the water column) in each reach were performed normal to flow with a top-setting wading rod equipped with an electromagnetic velocity meter (Marsh-McBirney model Flomate 2000). The meter had a resolution of 0.01 m/s, and velocity values of ≤ 0 were interpreted as STS storage for all velocity transects. A

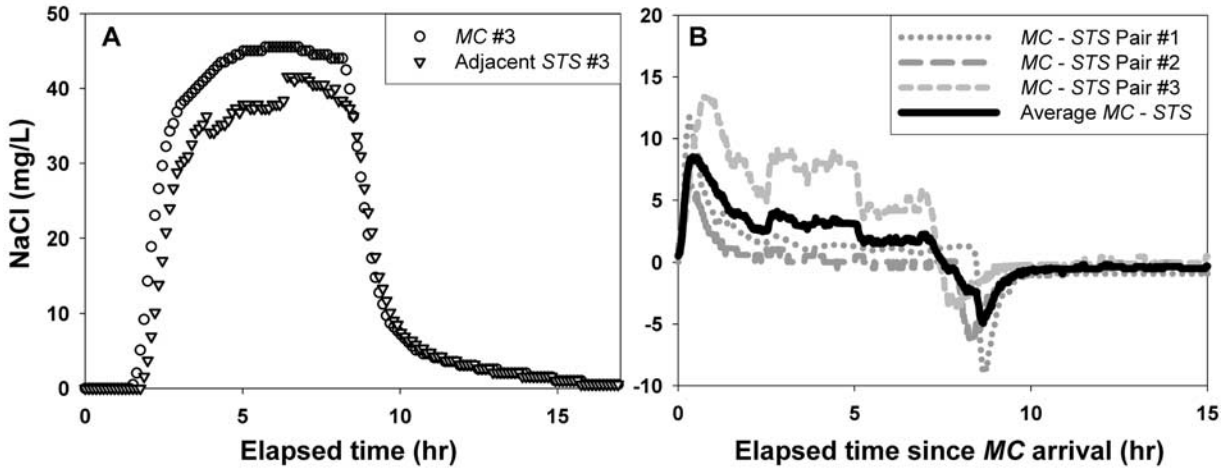

Figure 4. (a) Lockwood Brook constant rate injection BTC data from the adjacent pair of MC/STS probe locations at 180 m (pair 3). (b) The normalized concentration differentials per normalized time step for this pair and two others; these differentials are averaged to determine the general MC/STS differential pattern which is used to inform the 2-SZ model.

Trutrack WT-HR water level rod was installed within a pool near the head of each reach to monitor stage changes over the course of the experiments.

[29] The fit between observed and simulated concentration data was optimized using nonlinear regression by means of UCODE_2005 [*Poeter et al.*, 2005]. This was done for both the 1-SZ and 2-SZ versions of the 1-D transport model OTIS for the purposes of comparison. With UCODE_2005 a weighted least squares objective function is minimized through the perturbation of parameter values providing the "best fit" between weighted observations and their simulated equivalents [*Poeter et al.*, 2005]. The observations being fit to in this case were the lower-boundary MC BTC and the aggregate MC/STS differential pattern (2-SZ model only). The weighting of observations should reflect the perceived error in those measurements; therefore the MC/STS differential pattern was weighted less than the lower-boundary MC BTC because it was an average of measured values, not the measured values themselves. Final observation weights were adjusted to bring the calculated error variance close to 1.0 as calculated by UCODE_2005, which indicates that the model fit is consistent with the observation weighting scheme [*Hill and Tiedeman*, 2007].

[30] UCODE_2005 provides several metrics with which to evaluate the performance of the model. Perhaps the most important of these is a sensitivity analysis for each parameter based on a forward or central perturbation technique. Parameter sensitivity reflects the abundance of information contained within the observation data pertaining to that specific parameter. All parameters should display composite scaled sensitivities above 1.0 and within 2 orders of magnitude of the most sensitive parameter in order to have a reasonable chance of being estimated; parameters that fall outside of this interval likely cannot be estimated accurately. In addition to sensitivities UCODE_2005 reports 95% confidence intervals and correlations for each parameter in the set. Both a sensitivity and confidence interval analysis is presented for all estimated parameters.

3.3. First-Order Lockwood Brook Experiment

[31] Lockwood Brook is a first-order tributary that was also studied during the LINX II (Lotic Intersite Nitrogen Experiment) investigation. Lockwood Brook ranges from medium to low gradient, and the upper 219 m 0.022 gradient section was used for this experiment (Figure 5). A solution of 100 g/L NaCl and stream water was injected at 63 mL/min for 6.68 h on 13 July 2007 at low-flow conditions. This reach had an average width of 1.52 m and depth of 0.05 m at the time of the injection. It was bound by unconsolidated sediments consisting predominantly of sands and cobbles. The morphology of the channel was dominated by extended riffle and run sequences, with limited step/pool structures formed around channel obstructions. There was no substantial macrophyte growth within the stream, resulting in morphology-driven STS transient storage. Changes in water level within a pool located 15 m upstream of the reach were negligible during the course of the experiment.

[32] Velocity transect measurements were performed normal to flow approximately every 10 m, yielding 21 total transects. The data from these transects were used to provide initial parameter estimates for both A and A_{STS}. Solute BTC data was recorded at the 0m and 219m MC locations, while MC/STS pairs were monitored at 50 m, 111 m and 180 m from the head of the reach. This reach was found to display predominantly side channel margin type STS structures, so these areas were preferentially monitored along with one larger pool. Discharge at the reach head was calculated to be 1.9 L/s during the time of the experiment, and the stream was found to be net gaining using dilution gauging measurements.

3.4. Fourth-Order Ipswich River Main Stem Experiment

[33] A slug input of 22.6 kg NaCl dissolved into stream water at ~200 g/L in a large trash can was injected into a fourth-order section of the Ipswich River on 26 July 2007 during low-flow conditions (Figure 5). The gradient for this 547 m reach was only 0.0005, and half of this elevation

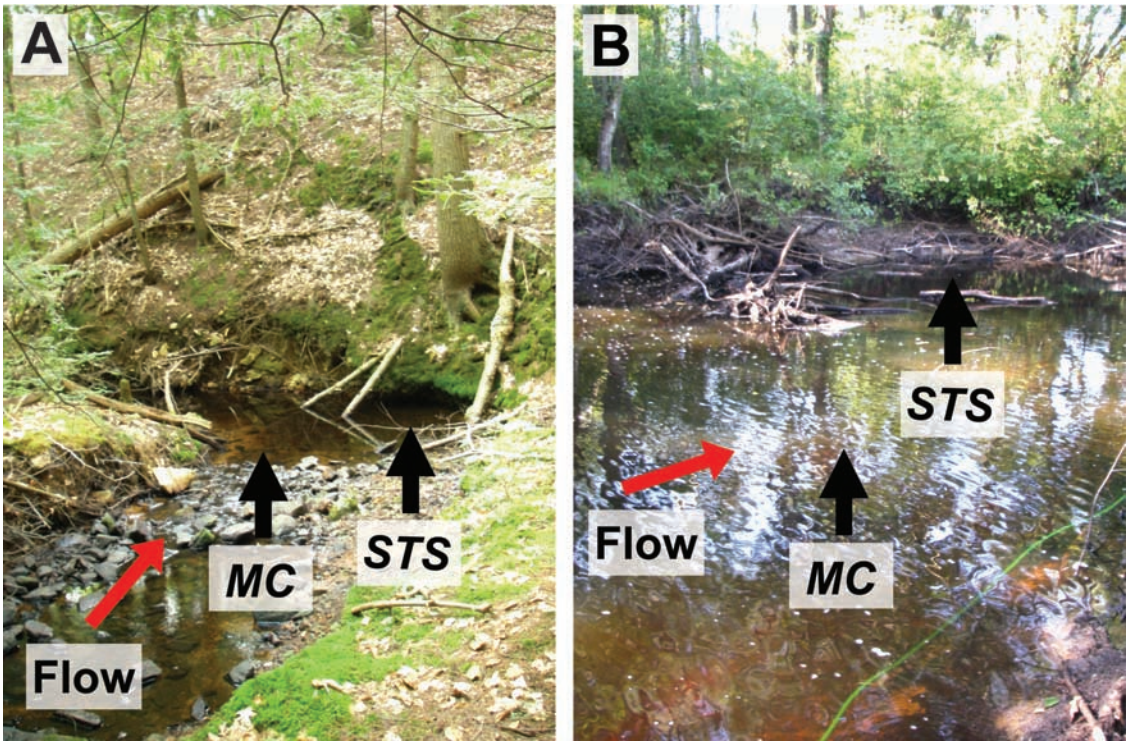

Figure 5. Typical stretches of (a) the first-order Lockwood Brook and (B) the fourth-order Ipswich River. MC/STS pair probe locations are shown at 111 m (Figure 5a) and 463 m (Figure 5b) from their respective reach heads.

change was controlled by a short riffle over submerged remnant bridge materials. Consequently this reach was slow flowing, with a median travel time of 8.35 h. The channel was bound mainly by gravel, sand and mud with the exception of the occasional boulder, and macrophytes were present but not abundant. This reach drained an area 85 times larger than that of Lockwood Brook, resulting in a much greater average channel width (7.3 m) and depth (0.44 m). Water level recorded in a backwater area indicated that discharge was steady during the experiment.

[34] Velocity transects normal to flow were recorded approximately every 25 m for a total of 21 transects over the reach. Data from the velocity transects indicated that the distribution of STS was governed by channel morphology and the presence of woody debris. An example of the complicated transect velocity distributions from this reach is depicted in Figure 3, located 463 m downstream of the reach input. Solute BTC data was recorded at adjacent MC/STS locations 51 m, 346 m and 463 m from the slug injection, along with the lower-boundary MC BTC at 547 m. Unfortunately the slug was found to be poorly mixed at the 51 m location, and consequently only the data from the remaining two MC/STS pairs were used during the modeling exercise. The STS zone located at 346 m was formed behind a longitudinal deposit of coarse sand deposited perpendicular to MC flow, while the STS zone at 463 m was a side pool created by a snag of woody debris (Figure 3). Discharge was calculated to be 46 L/s during the time of the experiment using the wading method and there was no empirical evidence from the salt slug to indicate lateral inflow along this reach.

3.5. Lockwood Brook Results

[35] The fits of the simulated lower-boundary MC BTC to observed lower-boundary MC BTC data by both the 1-SZ model and 2-SZ models (Figure 6) were both very good, and had a nearly identical squared sum of unweighted residuals between the lower-boundary MC BTCs (29.1 and 24.3, respectively). In addition, the simulated STS BTC fit some aspects of the average MC/STS differential pattern well (Figure 6), demonstrating a similar magnitude of lag from the MC BTC. Composite scaled sensitivities were within the optimal range (2 orders of magnitude from the highest sensitivity) for all estimated parameters of both the 1-SZ and 2-SZ models (Figure 7), with A having the highest sensitivity in both cases.

[36] The optimized parameters for both the 1-SZ model and 2-SZ model (Table 2) exhibit both expected similarities and some important differences. The estimate of A generated from the velocity survey (0.08 m^2) was a good proxy for both the 1-SZ and 2-SZ model fits, although both optimized values were reduced from this original estimate by 12.5% and 25%, respectively. The original constraint used for A_{STS} (0.03m^2) was decreased during final model runs when all parameters were left open to optimization. Both models agreed well with field observations including a positive hydrologic gain over the stream reach, generating nearly identical estimates of lateral inflow. The "lumped" transient storage parameters of the 1-SZ model were similar to the HTS parameters of the 2-SZ model, yet the 2-SZ model also incorporated a much faster exchanging smaller STS zone. The optimal D estimate was much higher (~2.5X) for the 1-SZ model compared to the 2-SZ model.

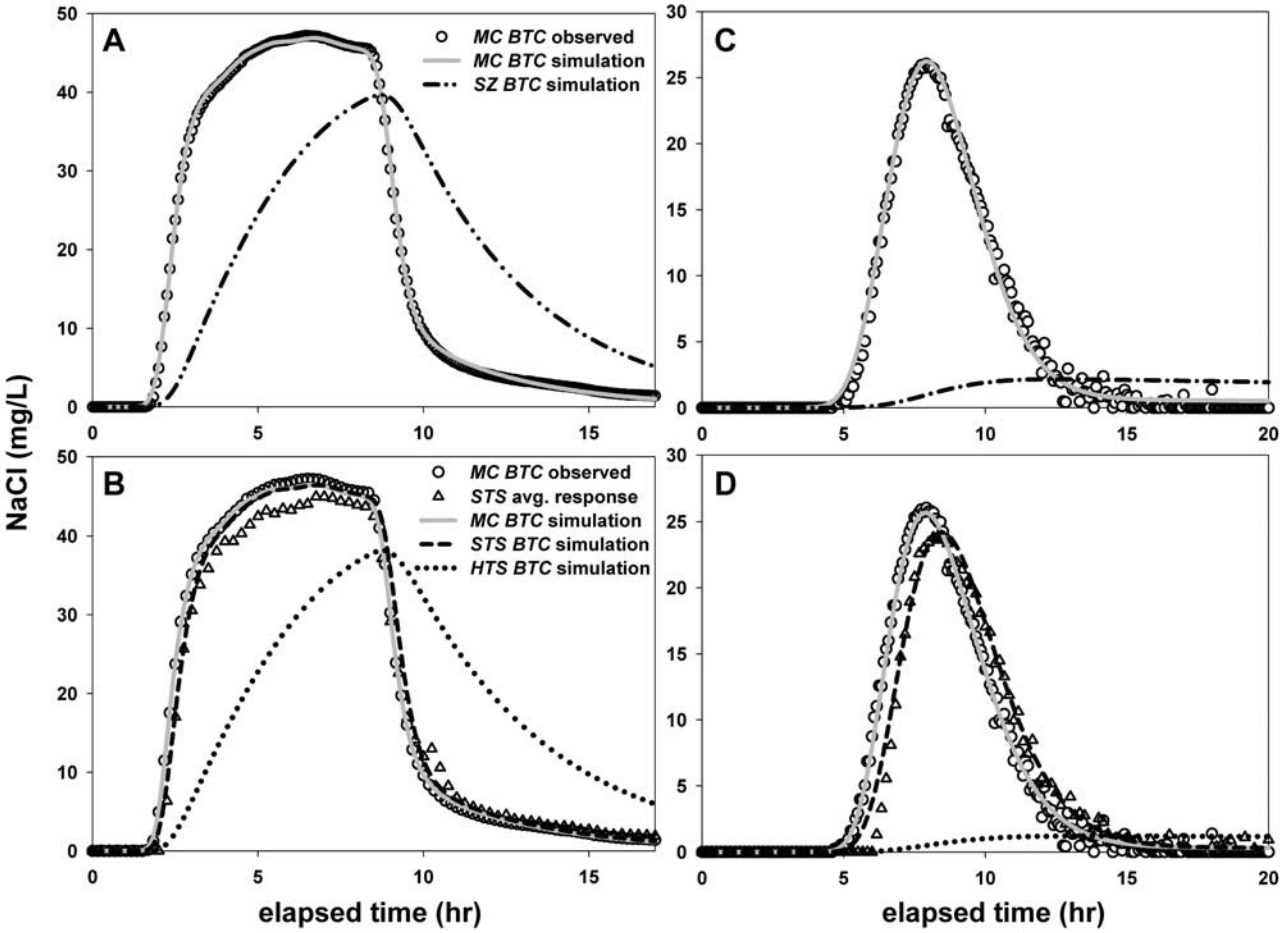

Figure 6. Tracer breakthrough curve observations and simulations of the first-order Lockwood Brook stream tracer experiment from the (a) 1-SZ model and (b) 2-SZ model and of the fourth-order Ipswich River tracer experiment from the (c) 1-SZ model and (d) 2-SZ model.

[37] An analysis of the appropriate reach length based on the 1-SZ model results yielded a *DaI* of 1.0 (the optimal value). When the F^{200}_{MED} analysis was applied to both the 1-SZ and 2-SZ HTS results, they were again quite similar, indicating that only ~3% of median transport time was due to exchange with transient storage (Table 2). Conversely, interaction with the fast exchanging STS affected median transport time by 13% in the 2-SZ model. The average storage zone residence time (T_{STO}) was considerable for the 1-SZ model (2.93 h) and the 2-SZ HTS (3.24 h). The 2-SZ STS average residence time was much lower, averaging only 0.18 h.

3.6. Ipswich River Main Stem Results

[38] Here the 2-SZ model simulated the observed downstream boundary MC BTC more accurately than the 1-SZ model (Figure 6), with an unweighted residual sum of squares of 258.0 and 499.0, respectively. The simulated STS BTC was a good fit to that generated from the average MC/STS differential pattern (Figure 6), capturing the general timing and magnitude of the observations. The composite scaled sensitivities were all within 2 orders of magnitude from the highest sensitivity and above 1.0 (the optimal range), except for 1-SZ A_S and 2-SZ A_{HTS} which displayed sensitivities that were 3 orders of magnitude lower than the most sensitive parameter (A) (Figure 7). This indicated there

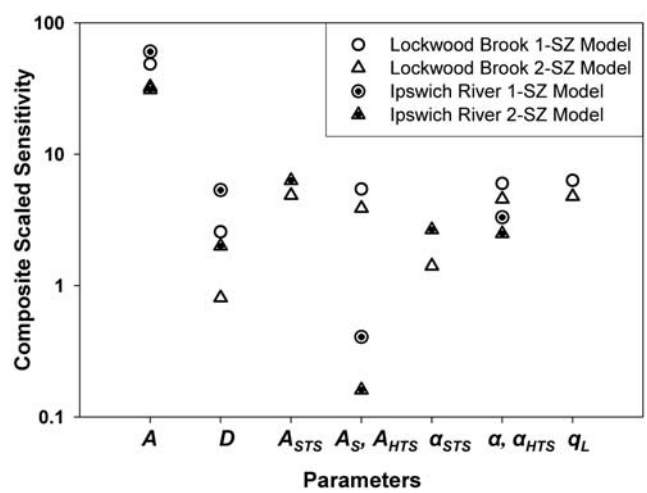

Figure 7. The composite scaled parameter sensitivities for both the Lockwood Brook and the Ipswich River models. All parameter sensitivities were within the optimal range, 2 orders of magnitude of the highest sensitivity in the set, except for the Ipswich River 1-SZ model A_S and Ipswich River 2-SZ model A_{SHZ} terms.

Table 2. Optimized Parameter Values and Storage Metrics From Both the 1-SZ and 2-SZ Models of the First-Order Lockwood Brook Reach and Fourth-Order Ipswich River Reach[a]

Parameter	Simulations			
	1-SZ Lockwood Brook	2-SZ Lockwood Brook	1-SZ Ipswich River	2-SZ Ipswich River
D (m^2 s^{-1})	0.103 (0.098–0.109)	0.046 (0.030–0.070)	0.193 (0.191–0.195)	0.096 (0.089–0.103)
A (m^2)	0.070 [*0.08*] (0.070–0.070)	0.060 [*0.08*] (0.057–0.064)	2.59 [*2.48*] (2.58–2.59)	2.08 [*2.48*] (2.04–2.12)
A_S, A_{HTS} (m^2)	0.027 (0.026–0.028)	0.028 (0.027–0.030)	3.73 (3.19–4.27)	6.72 (5.36–8.42)
A_{STS} (m^2)	NA	0.010 [*0.03*] (0.007–0.014)	NA	0.53 [*0.75*] (0.49–0.58)
α, α_{HTS} ($\times 10^{-5}$ s^{-1})	3.65 (3.53–3.77)	4.04 (3.81–4.28)	0.930 (0.910–0.950)	1.12 (1.09–1.15)
α_{STS} ($\times 10^{-5}$ s^{-1})	NA	26.3 (16.3–42.5)	NA	12.8 (11.2–14.7)
q_L ($\times 10^{-5}$ m^2 s^{-1})	0.108 (0.105–0.111)	0.110 (0.106–0.114)	0.0	0.0
F^{200}_{MED}, $F^{200}_{MED}HTS$ (%)	3.1	2.5	0.6	0.7
$F^{200}_{MED}STS$ (%)	NA	12.7	NA	18.7
T_{STO}, $T_{STO}HTS$ (h)	2.93	3.24	43.02	80.13
$T_{STO}STS$ (h)	NA	0.18	NA	0.55
DaI	1.0	*N/A*	0.5	NA

[a]The 95% confidence intervals are given in parentheses. Note the similarities between the 1-SZ model storage terms and the corresponding 2-SZ model HTS terms. A comparison between the 2-SZ optimized A and A_{STS} values and the original velocity transect estimates (italicized values in brackets) shows good agreement in all cases except Lockwood Brook A_{STS}. NA means not applicable.

was much less information present within the observations with which to estimate these parameters compared to the rest of the set; though the 95% confidence intervals on these estimates were reasonably small (Table 2).

[39] Both values of A of the 1-SZ and 2-SZ models agree well with the estimate generated by the velocity survey (2.48 m^2), being 4% larger and 16% smaller than the original estimate, respectively (Table 2). The initial constraint for A_{STS} (0.75 m^2) was decreased during final optimization by 29%, which was a much smaller reduction than that which occurred with the first-order stream model. The storage parameters of the 1-SZ model were similar to the 2-SZ HTS parameters; both displayed a large, slow-exchanging zone of transient storage. The exchange coefficient was 1 order of magnitude larger for STS than for the corresponding HTS. Again as with the first-order reach, the D estimate of the 1-SZ model was considerably greater (~2X) than that of the 2-SZ model.

[40] The DaI calculated from the 1-SZ parameters (0.5) was within the optimal range, suggesting this reach length was reasonable, although some storage parameter sensitivities remained low. The F^{200}_{MED} determined for both the 1-SZ model and the 2-SZ model HTS was very low, suggesting these estimated storage zones were so slow in exchange that they had little effect on median transport time (Table 2). The F^{200}_{MED} determined for the 2-SZ model STS was 18.7%, indicating a very different story was being told by the 2-SZ model. The small exchange coefficients and large sizes of the single storage zone of the 1-SZ model and the HTS of the 2-SZ model yielded very long T_{STO} values of 43.0 and 80.1 h, respectively; while the 2-SZ model STS T_{STO} was a much more rapid 0.6 h.

4. Discussion

4.1. Application to Study Reaches

[41] The primary objectives of applying the 2-SZ transient storage model to these contrasting first- and fourth-order reaches was to illustrate both the utility of this approach in better representing the natural system, and effectiveness of adding additional STS information to the 2-SZ model parameter optimization process. The underlying assumption that many streams exhibit both a slow exchanging HTS and faster exchanging STS observed in previous studies [*Hall et al.*, 2002; *Gooseff et al.*, 2004; *Harvey et al.*, 2005] also seems to be supported here. The velocity transect surveys yielded good proxies for A as determined by optimization of the Lockwood Brook and Ipswich River models. This result can be viewed to indicate that either transect resolution was adequate to accurately describe this most sensitive parameter, or assuming this to already be the case, that the model represents both systems well. The initial velocity transect estimate of A_{STS} in the fourth-order 2-SZ model was close to the optimized value, while the value of A_{STS} decreased threefold from initial estimate to optimized parameter estimate in the first-order 2-SZ model. This large reduction may be explained by inaccuracies incurred using the Marsh-McBirney electromagnetic velocity meter along the edges of the very shallow first-order stream. The bulk of the STS along the transects was recorded at stream edges in less than 6 cm of water with a cobbled bottom. Unfortunately, options for determining velocity distribution in very shallow flow are limited at this time, although more information may be gained from instruments which report flow in multiple planes. Overall the initial estimates were judged to be good starting points for the optimization process, providing solid basic information about the systems. Additionally, the survey fulfilled the crucial role of identifying the existence of STS in both streams, and representative areas to be monitored during the injections.

[42] We recorded the difference between several MC and adjacent STS solute BTCs, and averaged these MC/STS differential patterns to be fit during the optimization process. The average patterns seemed to represent the general nature of STS activity recorded during both the first-order constant rate and fifth-order instantaneous slug injection. Although the fits of simulated STS BTCs based on the average MC/STS differential patterns were not as close as the simulated/observed lower-boundary MC BTC fits, the general magnitude and timing was represented well. The first-order reach STS zones were likely to be concentrated areas of groundwater infiltration and had consistently lower background specific conductivity compared to the adjacent MC. This concentrated lateral inflow is not represented by the model, and probably accounts for the "diluted"

observed STS BTC plateau which is not well simulated (Figure 6).

[43] A sensitivity analysis of both 2-SZ parameter sets suggested that we were successful in providing adequate information with which to estimate additional storage parameters, avoiding model equifinality. Sensitivity to the A_{HTS} parameter was low in the Ipswich River 2-SZ model, but this effect was mirrored in the 1-SZ model as well. This was probably due to the extremely small HTS exchange coefficient retaining much of the HTS signal beyond our tracer "window of detection."

[44] A comparison between the 1-SZ and 2-SZ model parameter sets for both experiments yielded some interesting similarities. First, the lumped 1-SZ parameters were comparable to their corresponding HTS parameters in the 2-SZ model, especially for the first-order reach. This semblance was naturally mirrored in their transient storage metrics as well, although $T_{STO}HTS$ was considerably longer than its 1-SZ counterpart for the fourth-order reach. Second, D dropped significantly between the 1-SZ and 2-SZ models in both cases. This indicates that the effect of STS exchange on transport is on a similar time scale as the dispersion process, in the 1-SZ model. We know that STS exists in both cases because it was observed through field measurement. Thus, we conclude that the 2-SZ model is a better representation of the natural system.

[45] This is especially evident in the fourth-order models where the 1-SZ model lumped storage terms produced an F^{200}_{MED} estimate of 0.6%; yet the 2-SZ model yielded an F^{200}_{MED} STS of 18.7%. This implies that within the 1-SZ model the processes of advection and dispersion were almost completely responsible for the main "spread" of tracer mass, while the incorporation of observed STS exchange with the 2-SZ model strongly effected median transport time. This is evident in the poorer simulation timing of tracer arrival and tailing by the 1-SZ model; fits which are improved when the second storage zone is included. Finally, these results support the notion that the 1-SZ model parameters are sensitive to HTS exchange, as indicated in past work [e.g., *Bencala and Walters*, 1983; *Morrice et al.*, 1997; *Haggerty et al.*, 2002], even in systems such as this fourth-order river where STS exchange may be expected to dominate the BTC signal.

[46] Although the 1-SZ model may be effective in separating in-channel hydrologic processes from hyporheic exchange, this approach remains problematic to those interested in discriminating STS dynamics from longitudinal D. A separation of these two processes using the 2-SZ model is extremely important to many interested in a variety of in-stream processes, especially in systems such as the Ipswich River where transport seems to be most influenced by STS exchange. Ipswich River STS zones have been observed to contain abundant woody debris and macrophyte growth, both of which can host reactive biofilms. Combined with the potential for photochemical reactions, STS may be more influential to stream chemistry than the corresponding very slow exchanging HTS.

4.2. General Application of the 2-SZ Model

[47] Application of a 2-SZ model to stream solute transport, as described above, is an important step toward discriminating the general location of transient storage. *Choi et al.* [2000] performed a Monte Carlo sensitivity analysis of the 2-SZ model and concluded that the information contained in the lower-boundary MC BTC was not adequate to uniquely parameterize the model. The approach here overcomes this equifinality issue by providing additional data to incorporate into the optimization process: initial estimates of STS size, and STS BTC dynamics. This follows the preceding applications of 2-SZ models by *Gooseff et al.* [2004] and *Harvey et al.* [2005], who both used data beyond the observed lower-boundary MC BTC to inform the modeling process. As noted by *Harvey et al.* [1996], it is not feasible to gather "reach representative" information about *HTS* transient storage because point measurements in the subsurface often capture information about a single flow path. HTS flow paths are heterogeneous, and it is therefore difficult to characterize them as a single transient storage zone. *Stofleth et al.* [2007] were able to make estimates of reach-averaged specific discharge between the stream and groundwater, assumed to be strongly related to hyporheic flux on the basis of piezometric vertical head gradient measurements. Though they note a shortcoming of the research was that the piezometers were all installed at a common depth within the streambed, and did therefore could not capture the vertical heterogeneity of the subsurface. Conversely, in addition to being more easily sampled, STS can be more readily identified empirically and evaluated through hydrometric velocity measurements. Furthermore, many STS zones function as a mixed unit, so tracer data collected within them can be more informative on general STS exchange processes. The choice of which STS zones to monitor during the tracer experiment is subjective, but if these areas are chosen to best represent the distribution of STS observed during the velocity transect survey they provide valuable information about "average" reach STS exchange.

[48] In comparison with the prevalently used 1-D transport model with lumped storage terms, the 2-SZ model is both a more accurate and informative representation of the stream and its exchange processes, in a way that is meaningful to stream biogeochemistry. However, the underlying limitations of the stream tracer approach remain. The sensitivity of tracer modeling can be biased toward faster exchanging storage processes (for both STS and HTS), especially during times of high base flow [*Harvey et al.*, 1996]. The resulting "window of detection" for storage exchange may not capture large-scale interactions [*Battin et al.*, 2008]. Additionally, the fast exchange bias renders a reliable comparison of storage exchange parameters at varying hydrologic conditions difficult. However, despite the limitations of tracer experiments, they remain an important tool to understanding how storage exchange functions on the reach scale. As with any mathematical representation of a natural system much complexity is lost, but the potential of the 2-SZ model to well describe the dominant storage zone exchange dynamics remains.

[49] Understanding the impact of transient storage on water quality is the premise for the majority of stream transient storage research. Parsing stream transient storage for the sake of better understanding biogeochemical processes is a great advancement that this method can facilitate. It is recognized that the biogeochemical conditions of STS and HTS can differ strongly. The ability to estimate prop-

erties such as zone specific exchange coefficients and residence times allows an evaluation of where certain biogeochemical reactions may be taking place within the stream system. Much attention has been paid to the remediation potential of small HTS dominated headwater streams [*Peterson et al.*, 2001], but the impact of STS dominated transport remains unclear. When used in conjunction with reactive nutrient additions [e.g., *Runkel*, 2007], the 2-SZ model results can be critical to accessing whether STS dominated systems may have appreciable impact on water quality.

5. Conclusions

[50] Using a 2-SZ model that assumes fast STS exchange/slow HTS exchange to simulate stream transport is reasonable and provides a more realistic representation of storage processes than simulation results of the 1-SZ model. We propose a method to incorporate STS BTC data and hydrometric stream velocity data into the 2-SZ 1-D transport model parameter estimation process to avoid model equifinality. This method was applied to a first-order stream tracer experiment (constant rate injection) and a fourth-order stream tracer experiment (instantaneous injection) to illustrate its potential. A sensitivity analysis of both parameter sets indicated that this method was successful in providing sufficient information to warrant the incorporation of additional storage parameters.

[51] For the purposes of comparison, the original 1-SZ model was also applied to the same data sets. These results indicated that although both models generated similar fits to MC BTC data, the 1-SZ model failed to interpret the effects of observed STS exchange, and compensated for this by increasing longitudinal D. Conversely the 2-SZ model adequately simulated observed STS characteristics, yielding a more informative description of the natural system. Using 2-SZ model results, metrics such as F_{MED}^{200} and T_{STO} can be applied to the storage zones independently, revealing comparative relevance to hydrologic retention and potentially to biogeochemical processing. Our findings support the application of the 1-SZ model when investigating hyporheic exchange alone, as these "lumped" storage parameters seem to be most sensitive to HTS exchange.

[52] The evolution of 1-D transport modeling to include independent terms for both surficial and subsurface storage is logical and effective when additional information beyond the MC BTC is incorporated into the optimization process. We advocate that these storage zones need to be considered as distinct in studies of transient storage because they likely function very differently in biogeochemical processing and ultimately in how streams maintain water quality.

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