Sensitivity analysis of conservative and reactive stream transient storage models applied to field data from multiple-reach experiments

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Abstract

The transient storage model (TSM) has been widely used in studies of stream solute transport and fate, with an increasing emphasis on reactive solute transport. In this study we perform sensitivity analyses of a conservative TSM and two different reactive solute transport models (RSTM), one that includes first-order decay in the stream and the storage zone, and a second that considers sorption of a reactive solute on streambed sediments. Two previously analyzed data sets are examined with a focus on the reliability of these RSTMs in characterizing stream and storage zone solute reactions. Sensitivities of simulations to parameters within and among reaches, parameter coefficients of variation, and correlation coefficients are computed and analyzed. Our results indicate that (1) simulated values have the greatest sensitivity to parameters within the same reach, (2) simulated values are also sensitive to parameters in reaches immediately upstream and downstream (inter-reach sensitivity), (3) simulated values have decreasing sensitivity to parameters in reaches farther downstream, and (4) in-stream reactive solute data provide adequate data to resolve effective storage zone reaction parameters, given the model formulations. Simulations of reactive solutes are shown to be equally sensitive to transport parameters and effective reaction parameters of the model, evidence of the control of physical transport on reactive solute dynamics. Similar to conservative transport analysis, reactive solute simulations appear to be most sensitive to data collected during the rising and falling limb of the concentration breakthrough curve.

Keywords: Solute transport; Tracer; Reactive transport; Sensitivity analysis; OTIS; UCODE

1. Introduction

The transient storage model (TSM) simulates stream solute transport and exchange with storage zones (in the form of channel dead zones and hyporheic zones). Since the TSM was introduced by Bencala and Walters [2] to simulate conservative stream Cl transport, the TSM has been widely used in stream solute transport studies to analyze stream solute concentration data collected at one or multiple locations downstream of a single tracer addition point (e.g., [4,7,17,18]). The TSM simulates three conservative stream solute transport processes (advection, dispersion, and transient storage) and lateral inflow [15]:

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\[ \frac{dC}{dt} = -\frac{Q}{A} \frac{\partial C}{\partial x} + \frac{1}{A} \frac{\partial}{\partial x} \left( AD \frac{dC}{dx} \right) + \alpha (C_S - C) \\
+ \frac{q_L}{A} (C_L - C) \\
\frac{dC_S}{dr} = \frac{A}{A_S} (C - C_S) \] (1)

where \( C \) is the solute concentration in the stream (mol L\(^{-1}\)), \( Q \) is the volumetric flow rate (m\(^3\) s\(^{-1}\)), \( A \) is the cross-sectional area of the main channel (m\(^2\)), \( D \) is the dispersion coefficient (m\(^2\) s\(^{-1}\)), \( C_S \) is the solute concentration in the storage zone (mol L\(^{-1}\)), \( A_S \) is the cross-sectional area of the storage zone (m\(^2\)), \( C \) is the stream storage exchange coefficient (s\(^{-1}\)), \( q_L \) is the lateral inflow rate (m\(^3\) s\(^{-1}\) m\(^{-1}\) length of stream, or m\(^2\) s\(^{-1}\)), \( C_t \) is the lateral inflow solute concentration, \( t \) is time (s), and \( x \) is distance downstream (m). Typically, only \( C \) values are measured in the field for comparison to TSM simulations. \( C_S \) values are simulated only, and \( C_t \) values are estimated based on either point measurements or background stream water conditions. Harvey et al. [10] and Wagner and Harvey [23] analyzed the performance of the TSM for conservative solute transport, noting that transport parameters (\( \alpha, A, A_S, D, q_L \)) are sensitive to data at different parts of a stream solute breakthrough curve (BTC). Namely, that the transient storage parameters (\( \alpha \) and \( A_S \)) were most sensitive to the shoulder and tail. Marion et al. [12] compared TSM parameterization with a bed pumping-exchange model and cautioned that TSM simulation with insufficient time/space measurements will result in poorly defined parameter values.

Several recent applications of solute transport TSM simulations have incorporated solute reactions. One approach has been to couple conservative TSM simulations with separate chemical equilibrium models (e.g., MINEQL). Coupled stream solute TSMs and chemical equilibrium models have been used to determine the transport and fate of metal transport in mine drainage streams, based on fundamental understanding of underlying chemical reactions [3,16]. Coupling TSMs to chemical models has the advantage of representing dominant chemical reactions in the context of solute transport and fate involving heterogeneous natural substrates.

The other approach to reactive solute transport has been to simulate reactions within the TSM framework (hence forth referred to as Reactive Solute Transport Model, RSTM) by including effective reaction terms. The rates of many chemical and microbial processes, such as microbial nutrient uptake, have been found to have a first order dependence on the concentration of the reactant. McKnight et al. [13], Gooseff et al. [8], and Thomas et al. [22] applied a reactive version of the TSM to stream nutrient transport, and Chapra and Wilcock [5] applied an RSTM to stream dissolved oxygen transport. RSTMs have also been used to simulate first-order decay, reach-scale ion exchange reactions and non-conservative dissolved metal transport [6,9,19,21]. RSTMs simulate an effective reaction solute flux, indicative of comparative reaction rates, but do not fully represent the biogeochemical reactions involved. Wagner and Harvey [24] assessed the performance of an RSTM using hypothetical data sets and Monte Carlo analyses and suggested that an optimized conservative transport parameterization was a prerequisite for improved reactive transport parameter estimation.

In this paper, we simulate data from two field experiments to perform a similar analysis to that of Harvey et al. [10] and Wagner and Harvey [24] for two RSTMs. Parameter-observation sensitivities and correlation coefficients among transport and reaction parameters are investigated to assess the reliability of RSTMs to determine water column and storage zone reactions in and among multiple experimental reaches, utilizing field data. We analyze dependence of reaction parameters upon conservative transport parameters and compare inter-reach parameter sensitivities. Guidance for the design of reactive transport field experiments is advanced through the quantitative analysis of model parameter sensitivities to the temporal and spatial distribution of solute concentration data.

2. Methodology

2.1. Reactive solute transport model (RSTM)

A sensitivity analysis of reaction parameters was conducted for two reactive solute transport studies. In both reactive solute transport studies, Eqs. (1) and (2) were used to determine conservative transport parameters, based on conservative solute transport simulations. The RSTMs evaluated here account for first-order uptake of solute in the stream and storage zone, and sorption to bed sediments:

\[ \frac{dC}{dt} = L(C, C_S) + \rho \lambda_H (C_{SED} - K_d C) - \lambda C \] (3)

\[ \frac{dC_S}{dr} = S(C, C_S) + \lambda_H (\dot{C}_S - C_S) - \lambda_S C_S \] (4)

\[ \frac{dC_{SED}}{dr} = \dot{\lambda}_H (K_d C - C_{SED}) \] (5)

where \( L(C, C_S) \) and \( S(C, C_S) \) represent physical processes in the main water column and the hyporheic zone (right-hand side of Eqs. (1) and (2), respectively), \( \lambda \) is the stream first-order decay coefficient (s\(^{-1}\)), \( \lambda_S \) is the storage zone first-order decay coefficient (s\(^{-1}\)), \( \dot{C}_S \) is the background storage zone solute concentration (mol L\(^{-1}\)), \( C_{SED} \) is the sorbate concentration on the streambed sediment (–), \( K_d \) is the distribution coefficient (m\(^3\) g\(^{-1}\)), and \( \dot{\lambda}_H \) is the first-order rate coefficient for sorption.
onto streambed sediments (s⁻¹), \( \lambda_{\text{HS}} \) is the first-order rate coefficient for sorption onto storage zone sediments (s⁻¹), and \( \rho \) is the mass of accessible sediment per volume of stream water (g L⁻¹). We refer to \( \lambda, \lambda_S, \lambda_{\text{HS}}, \rho \) as effective reaction parameters. These RSTMs are available in the USGS software package OTIS [15]. As with the conservative TSM, simulation of reactive solute transport is based on stream concentrations of solutes at particular stream locations, through time.

2.2. Green Creek NO₃ first-order loss

The first study we analyze is that of McKnight et al. [13], in which the reactive transport of injected NO₃ in Green Creek, Antarctica is simulated using Eqs. (3) and (4) less the sorption terms (i.e., \( \rho = 0, \lambda_{\text{HS}} = 0 \)) as implemented in OTIS [15]. McKnight et al. [13] report that downstream losses of NO₃ were best simulated with uptake in both the stream and the storage zone (\( \lambda > 0, \lambda_S > 0 \)). Optimal RSTM parameter estimates and experimental reach lengths for the Green Creek experiment are reported in Table 1. Note that \( D \) was set to a fixed value of 0.1 m² s⁻¹, and that \( A \), which varied through time with \( Q \), was determined by an independent hydraulic model, and so its values were also set for the TSM or RSTM simulations [13].

2.3. Uvas Creek Sr sorption

The second study we analyze is that of Bencala [1], in which the reactive transport of injected Sr in Uvas Creek, California is simulated using Eqs. (3)–(5), less the first-order loss terms (i.e., \( \lambda = 0, \lambda_S = 0 \)). In this study, we use the optimal parameter estimates reported by Scott et al. [20], who re-evaluated the conservative reactive transport from the Uvas Creek experiment by optimizing the simulations originally presented by Bencala [1] using UCODE, a universal parameter optimization and sensitivity analysis computer code [14]. Optimal parameter estimates are reported in Table 2.

2.4. Sensitivity analyses

Our sensitivity analysis relies on the computation of dimensionless scaled sensitivities (DSS) and composite scaled sensitivities (CSS) of each parameter, evaluated for each observation of stream solute concentration. DSS and CSS measures were developed by Hill [11]. DSS values represent the sensitivity of simulated values (at the times of each observation) to a particular parameter. DSS values were computed using UCODE, as

\[
DSS_i = \left( \frac{\partial y'_i}{\partial b_j} \right) \sigma_i b_i^{-1/2}
\]

where \( i \) denotes the observation index, \( j \) denotes the parameter number index, \( b_j \) is the value of the \( j \)th estimated parameter (in this case, \( b \) is a vector of optimized parameter values, composed of several parameters for each reach), \( y'_i \) is the simulated value associated with observation \( i \), and \( \sigma_i \) is the observation error weight of observation \( i \) (in this case all observation error weights set to 1.0). DSS values are similar to the sensitivity values computed by Harvey et al. [10], indicative of how sensitive the simulation of the \( i \)th observation is to the \( j \)th parameter. Large DSS values suggest increased sensitivity of a simulated value to a parameter. Composite scaled sensitivities, which represent the entire amount of information provided by observation data for optimization of a parameter, are computed as

\[
CSS_j = \left[ \frac{\sum_{i=1}^{ND} (DSS_i)^2 b_j}{ND} \right]^{1/2}
\]

where ND is the total number of observations in all reaches. Whereas a DSS value is calculated for every observation for a given parameter, a single CSS value is computed for every parameter in all of the reaches (e.g., for \( \sigma \) or \( \lambda_S \) in each reach), sensitive to observations in all reaches. Comparatively, large CSS values suggest that there is more information for a particular parameter from the set of observations considered. We present DSS profiles and CSS values to compare conservative and reactive solute transport simulations.

We also assess parameter coefficients of variation (COV), as a measure of parameter optimization confidence. The COV for a parameter is equal to the parameter standard deviation (which is the square root of the parameter variance) divided by the optimized parameter value. UCODE calculates parameter variances as the diagonal of the variance–covariance matrix \( V(b') \),

\[
V(b') = s^2(X^T \Omega X)^{-1}
\]
where \( s^2 \) is the calculated error variance of the optimal fit of the simulation to the observations, \( b' \) is a matrix of the optimally estimated parameter values, \( X \) is a sensitivity matrix (a perturbation of 0.01 or 1% was used to calculate all parameter sensitivities in UCODE), and \( \omega \) is a vector of observation weights (all set to unity in this case) [11]. Larger COV values indicate lower confidence in parameter optimization, because of greater standard deviation of the parameter. It is a dimensionless relative measure of parameter estimate accuracy. Here we present COVs for transport parameters in conservative transport simulations and for effective reaction parameters in reactive transport simulations to compare parameter estimation confidence in both cases.

In order to assess inter-reach parameter dependencies, we also evaluate parameter pair correlation coefficients for reactive solute transport simulations, computed by UCODE as

\[
\text{cor}(y, z) = \frac{\text{COV}(y, z)}{\sqrt{\text{var}(y) \cdot \text{var}(z)}}
\]

where \( \text{COV}(y, z) \) is the covariance of parameters \( y \) and \( z \), and \( \text{var}(y) \) is the variance of parameter \( y \). Magnitudes of ‘cor’ vary from 0 to 1.0, and may be positive or negative. Higher magnitudes ‘cor’ values indicate higher covariance between two parameters, an indication that neither can be independently optimized confidently. In this work, we assume that correlation coefficient magnitudes greater than 0.75 are significant enough to indicate covariance among parameters.

### 3. Results

#### 3.1. Reactive solute transport model 1: first-order decay

The reactive transport of NO\(_3\) in Green Creek was based on conservative transport of Cl, resulting in optimized transport parameters (\( \kappa, A_S \)) (Fig. 1), and found to be simulated accurately by considering first-order decay coefficients in the water column due to algal mat assimilation, and in storage zones due to denitrification in all four reaches (Figs. 2 and 3) [13]. The temporal change in parameter sensitivity to conservative Cl observations shows patterns similar to those shown by Wagner and Harvey [23] where \( \rho \) and \( A_S \) are most sensitive to data in the shoulders and tails of the BTCs. For the case of \( A_S \), the simulations are most sensitive to parameters in the same reach (Fig. 1). In contrast, simulated Cl concentrations in the 3rd and 4th reaches appear to be more sensitive to \( \kappa_2 \) than to \( \kappa_3 \) and \( \kappa_4 \), respectively (where the subscript indicates the reach in which the parameter is assigned). The DSS profiles for conservative Cl transport also indicate that there is appreciable inter-reach sensitivity. Specifically, simulations in one reach were sensitive to parameter values in other reaches (e.g., the Cl simulation in Reach 3 is sensitive to \( \rho \) and \( A_S \) values in all four reaches).

The temporal change in NO\(_3\) simulation sensitivity in each reach to a parameter generally shows that the greatest overall magnitude (discounting the outlier values) of sensitivity is found in the same reach in which the parameter is assigned (i.e., the simulations in reach one have, on average, the greatest sensitivity to \( \lambda_1 \)). Further, DSS profiles of a given \( \lambda \) or \( \lambda_S \) for observations within a particular reach respond greatly to the time of peak concentrations for that reach (Figs. 2 and 3). For example, the temporal DSS profile for the observations in Reach 2 show peak sensitivity to \( \lambda_{S1} \) at the peak storage zone concentration of NO\(_3\) in Reach 2 (Fig. 3). In the storage zone, simulated NO\(_3\) concentrations were much lower than those in the stream (Figs. 3 and 2, respectively).

There are single anomalous sensitivities of large magnitude for all reaches from effective reaction parameters in any reach. For example, for a single observation in Reach 1, a high sensitivity to \( \lambda_2 \) was calculated (Fig. 2). It is informative to note that these spikes in the DSS profiles occur at the time of the rise (shoulder) and drop (tail) of the BTC for the reach in which a parameter is effective. For example, the DSS profiles for the observations in Reach 2 show spikes in DSS profiles for \( \lambda_1 \) at the time of the NO\(_3\) tail in Reach 1, at approximately 4.2 h (Reach 2). These spikes may also

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reach number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length (m)</td>
<td>38</td>
</tr>
<tr>
<td>( D ) (m(^2) s(^{-1}))</td>
<td>0.01</td>
</tr>
<tr>
<td>( A ) (m(^3))</td>
<td>0.31</td>
</tr>
<tr>
<td>( A_S ) (m(^2))</td>
<td>0</td>
</tr>
<tr>
<td>( \kappa ) (s(^{-1}))</td>
<td>0</td>
</tr>
<tr>
<td>( q_L ) (m(^2) s(^{-1}))</td>
<td>0</td>
</tr>
<tr>
<td>( \lambda_S ) (s(^{-1}))</td>
<td>4.4 \times 10^{-5}</td>
</tr>
<tr>
<td>( \rho ) (g L(^{-1}))</td>
<td>5.4 \times 10^4</td>
</tr>
</tbody>
</table>

Note. \( K_a \) was set to 70 \times 10^{-6} m\(^3\) g\(^{-1}\) for all reaches (as per Bencala [1]), \( \lambda_{HS} \) was set to 1.0 for all reaches, and \( C_i \) was set to 11.39 mM.
be a consequence of the sensitivity estimation by UCODE, which is not exact.

CSS values show that, with respect to $a$, Green Creek Cl simulations are most sensitive to $a_2$ (CSS = 38.5) and least sensitive to $a_4$ (CSS = 1.15) and with respect to $A_S$, most sensitive to $A_{S,1}$ (CSS = 4.04) and least sensitive to $A_{S,4}$ (CSS = 1.00) (Fig. 4A). There is an apparent spatial pattern in the CSS values of $A_S$, decreasing downstream, and in $a$, decreasing below Reach 2 (Fig. 4A). CSS values also show that reactive NO$_3$ transport simulations are most sensitive to $A_{S,1}$ (CSS = 16.4), and least sensitive to $A_{S,3}$ (CSS = 0.3), and transient storage exchange rate coefficients ($a$) in all four reaches had consistently moderate CSS values, ranging from 9.3 to 11.0 (Fig. 4B). Alternatively, CSS values for in-stream NO$_3$ reaction rate coefficients ($\lambda$) varied from 6.0 in Reach 1, to 12.6, the greatest $\lambda$ CSS value, in Reach 2, to 1.0 in Reach 3, to 1.9 in Reach 4. Storage zone reaction rate coefficient CSS values ranged from 0.57 in Reach 4 to 6.14 in Reach 1. There are no apparent, consistent spatial patterns of reactive simulation CSS values.

Parameter COV values for conservative transport simulation of Cl in Green Creek are variable for $D$ in all four experimental reaches. Although $D$ was fixed in all 4 reaches in these simulations, UCODE allows for a sensitivity analysis of even fixed variables. Parameter COV values were variable for $A_S$ and $a$ which were optimized from the Cl data (Table 3). Given that $D$ was fixed, it is interesting to note that the range of COVs for $D$ is fairly small, and generally acceptable, all <0.1. These results indicate that $A_S$ is most accurately estimated in Reach 1 and least accurately estimated in Reach 4, and that $a$ is most accurately estimated in Reach 2 and least accurately estimated in Reach 4. For the RSTM simulations in Green Creek, reaction parameter COVs in the stream vary from $9.18 \times 10^{-3}$ to 0.646, with $\lambda$ being most accurate in Reach 2, least accurate in Reach 4 (Table 4). The storage zone effective reaction parameter COVs range from 0.159 in Reach 4 to 123 in Reach 3 (Table 4). In all cases, COV values for $\lambda$ are smaller than those for $\lambda_S$, indicating that effective stream reaction processes are better supported by the data than storage zone reaction processes. However, COVs for $\lambda_S$ are all less than 1, with the exception of Reach 3, indicating that storage zone effective reaction parameters can be confidently characterized by simulating in-stream concentration data.
The ‘cor’ values for all 20 transport and reaction parameters ($D, \sigma, A_S, \lambda$, and $\lambda_S$ in four reaches) for reactive NO$_3$ simulations reveal three highly correlated pairs of parameters, one reaction–transport pair and two transport parameter pairs, one of which reveals inter-reach correlation (Table 5). The occurrence of $D$ values in these ‘cor’ pairs is most likely a result of setting $D$ to a fixed value in the original conservative TSM.

3.2. Reactive solute transport model 2: streambed sorption

The results of the optimized Cl and Sr dynamics in the Uvas Creek experiment using the conservative TSM and the sorption RSTM, respectively, match the stream observations very well (Figs. 5–8). Similar to the figures reported by Wagner and Harvey [23], conservative Cl transport simulation is primarily sensitive to the rising and descending limbs of the BTCs (Figs. 5 and 6), though magnitudes of sensitivity vary. Uvas Creek Cl transport simulations also indicate considerable inter-reach sensitivities. For example, simulated BTCs in Reaches 3, 4, and 5 are more sensitive to $A_3$ and $q_{L,3}$ than $A_4$ or $A_5$ and $q_{L,4}$ or $q_{L,5}$, respectively (Fig. 5).

Temporal DSS profiles were computed for the flow-related transport parameters $A$ and $q_L$ (Fig. 7), the transient storage parameters $\sigma$ and $A_S$ (Fig. 8), and for the effective reaction parameters $\lambda$ and $\lambda_H$ (Fig. 9) with
respect to reactive Sr transport. DSS profiles for A show that the greatest sensitivity to a particular parameter is to the observations within the same reach, and that the magnitude of DSS profiles decreases consistently downstream (Fig. 7). DSS profiles of qL show that qL,3 has the greatest magnitudes, and simulated Sr concentrations in Reaches 3, 4, and 5 are also highly sensitive to qL,3 (Fig. 7). DSS profiles of Sr transport to the transient storage exchange coefficient (a) show a strong downstream influence, with simulated values in Reaches 3 and 4 being sensitive to a3 and less sensitive to Sr simulations in Reach 5 (Fig. 8). Alternatively, simulated Sr values are not very sensitive to AS, with only a single substantial DSS profile in Reach 4 to AS in Reach 5 (Fig. 8).

Temporal DSS trends for λH of each reach show repeated, but diminishing patterns from the reach in which the parameter is effective, in response to the BTC of the reach of interest (Fig. 9). For example, the simulation sensitivity to λH,1 shows the strongest response in Reach 1, with a decrease during near-plateau concentrations, and then a strong decrease during the tail with a slow exponential increase through the rest of the BTC. This pattern of sensitivity to λH,1 is repeated, but diminished, in Reaches 2–5. Alternatively, ρ DSS profiles show the inverse patterns, mirroring those of λH, also decreasing in magnitude downstream from the reaches in which they are effective (Fig. 9).

Uvas Creek conservative Cl transport CSS values indicate that simulation data in all reaches is most sensitive to qL,3 (CSS = 4.55), and least sensitive to AS,5 (CSS = 0.21) (Fig. 10A). No consistent downstream trends of CSS values for conservative Cl transport in Uvas Creek are apparent. Uvas Creek reactive Sr transport CSS values indicate that simulation data is most sensitive to ρ1 (CSS = 1.03), and least sensitive to AS,3 (CSS = 1.11 × 10^-6) (Fig. 10B). Reactive Sr CSS patterns also indicate a decreasing sensitivity to A downstream (Fig. 10B). Effective reaction parameter CSS values are the largest of all parameters in each reach, with CSSs of ρ consistently being slightly larger than those of λH (Fig. 10).

Optimized simulations of conservative transport of Cl in Uvas Creek yielded COVs ranging within the same order of magnitude for A and z (all <0.1) but several orders of magnitude for D, AS, and qL (all <0.5, Table 6). According to these results, D is most accurately optimized in Reach 5, least accurately optimized in Reach 3; A is most accurately optimized in Reach 1 and least accurately optimized in Reach 5; AS is most accurately optimized in Reach 5, least accurately optimized in Reach 4; z is most accurately optimized in Reach 4, least accurately optimized in Reach 5; qL is most accurately optimized in Reach 5, least accurately optimized in Reach 3, least accurately optimized in Reach 2 (Table 6). Similar to the Green Creek RSTM simulations, the reaction parameter COV values are similar in magnitude. Both λH and ρ are most accurately optimized in Reach 1, least accurately optimized in Reach 4 (Table 7).

In the sorption RSTM, three general types of parameter correlations were found with ‘cor’ magnitudes >0.75, transport parameter pairs (among parameters A, ρ, AS, qL), transport–reaction, and between reaction parameters (Table 8). We interpret correlations between parameters in different reaches (i.e., ρ2 and A1) to be an indication of dependencies between parameters and
observations across reaches. This is an independent potential line of evidence that can be corroborated with parameter DSS and CSS data to assess inter-reach dependencies. Because the conservative solute transport data was used to determine optimal parameter estimates of transport parameters, it is likely that the transport parameter correlation pairs reported in Table 8 are an artifact of the use of reactive solute data in the correlation coefficient analysis. Scott et al. [20] have shown that the conservative transport model for Uvas Creek did not result in any highly correlated parameter pairs. Our focus in this paper is on the estimation of effective reaction parameters, thus we are not exploring possible relationships among the parameters of physical transport estimated from observations of conservative tracers. Only two parameter pairs were identified as mixed transport \((A, \alpha, A_S, q_L)\) and effective reaction \((k_H, q)\), neither of which were inter-reach pairs (Table 8). Two reaction parameter pairs with \(|c_{212}/c_{213}| > 0.75\) were also found, neither of which were inter-reach pairs (Table 8). These high correlations for \(k_H\) and \(q\) in Reaches 1 and 4 suggest that the parameters cannot be independently estimated with confidence.

### 4. Discussion

#### 4.1. Modeling approach

The goal of nonlinear parameter estimation based on an inverse approach is to improve the accuracy of the model used in simulating system responses with a minimum amount of predictive uncertainty. In this case, we seek to estimate RSTM parameters with minimal uncertainty. The uncertainty in numerical model simulations is a function of three interrelated inverse modeling components: model conceptualization, model parameterization, and quality (space/time) of measurement information. We have focused on model parameterization for two sets of stream tracer measurements. TSM model conceptualization has been analyzed by Harvey et al. [10] and Wagner and Harvey [23], and RSTM model conceptualization has been analyzed by Wagner and Harvey [24]. Stream tracer data quality (in time and space) was analyzed in all three of these studies.
Fig. 5. Observed and simulated stream solute breakthrough curves and dimensionless scaled sensitivity (DSS) values for channel transport parameters \((A, q_L)\) from an optimized simulation of conservative Cl transport in Uvas Creek, California. DSS plots represent the sensitivity of stream concentrations to each parameter value in each reach. Parameter subscripts denote the parameter for each reach.

Fig. 6. Observed and simulated stream solute breakthrough curves and dimensionless scaled sensitivity (DSS) values for transient storage parameters \((\alpha, A_S)\) from an optimized simulation of conservative Cl transport in Uvas Creek, California. DSS plots represent the sensitivity of stream concentrations to each parameter value in each reach. Parameter subscripts denote the parameter for each reach.
Fig. 7. Observed and simulated stream solute breakthrough curves and dimensionless scaled sensitivity (DSS) values for channel transport parameters ($A$, $q_L$) from an optimized simulation of reactive Sr transport in Uvas Creek, California. DSS plots represent the sensitivity of stream Sr concentrations to each $A$ and $q_L$ value in each reach. Parameter subscripts denote the parameter for each reach.

Fig. 8. Observed and simulated stream solute breakthrough curves and dimensionless scaled sensitivity (DSS) values for transient storage parameters ($\alpha$, $A_S$) from an optimized simulation of reactive Sr transport in Uvas Creek, California. DSS plots represent the sensitivity of stream Sr concentrations to each $\alpha$ and $A_S$ value in each reach. Parameter subscripts denote the parameter for each reach.
We have taken the approach of estimating physical transport parameters from observations of a conservative tracer. An alternative approach, not explored in this work, is to simultaneously attempt to optimize all parameters (physical transport and effective reaction parameters) for the simulation of reactive solute data. We argue that such an approach would only confuse our understanding of solute transport within a stream-storage zone system. For example, if one were to determine an optimized value of $\alpha$ from the reactive solute transport analysis for a particular reach that is different than a value that was found for the conservative transport simulation, what would that mean? How could one resolve which value was more appropriate? Optimized conservative transport parameter values can be evaluated by simulating the observations for another conservative solute. One could certainly use parameter fit statistics to argue for one approach or the other, but without corroboration of the conservative transport data, a different value for a transport parameter would likely better match the model for perhaps the wrong reason (with a likely simultaneous change to one of the reaction parameters). However, we would also submit that if conservative and reactive solute data were collected at different times or different locations, then one might only optimize conservative transport as a first step toward reactive transport optimization, which might include simultaneous regression of all parameters.

### 4.2. Effective reaction parameter sensitivities

The effective reaction parameters that control reactive solute transport in these RSTMs are reach-integrated values that are indicative of the time scale of reaction processes, as determined at the reach scale, in the field. These values may not reflect the rate coefficients of specific chemical or microbial reactions, especially in such heterogeneous physical and biogeochemical systems as streams. Rather, they should be interpreted as an indication of the potential for effective mass loss to occur within a particular reach and of dominant reactions that control solute concentrations at the time scale of transport processes.

Application of the first-order decay model (Eqs. (3) and (4)) resulted in CSS values (Fig. 4) for $\lambda$ and $\Lambda$ that appear to be largely driven by a few large magnitude DSS values (Figs. 2 and 3). These increased DSSs tend to coincide with the times on the solute BTCs of high sensitivity for $\alpha$ and $\Lambda$, the shoulder and tail (Figs. 1–3), as demonstrated by Wagner and Harvey [23]. There are two potential reasons for this temporal pattern. Firstly, for the stream solute concentrations, the processes of transient storage and reactions both act as a loss of reactive solute mass to the stream (even if only temporarily in the case of transient storage) and the RSTM is more sensitive to solute loss at the shoulder and tail of the BTC than elsewhere in the BTC.
Secondly, for storage zone reaction parameters, storage zone reactions are ultimately dependent upon the mass transfer of solute to the storage zone, and therefore transient storage parameters \(x\) and \(A_S\). Thus simulated values are likely to be sensitive to \(\lambda_S\) values at the same times of the BTC when the simulated values are highly sensitive to \(x\) and \(A_S\). This result suggests that the sampling of the shoulder and tail of the reactive BTC is important when designing field sampling protocol. Wagner and Harvey [23] and Gooseff and McGlynn [7] demonstrate that high frequency sampling during the BTC shoulder and tail improve conservative solute transport simulation fit by decreasing the coefficient of variation and 95% confidence intervals for \(x\) and \(A_S\).

Substantial inter-reach parameter sensitivity was evident. That is, simulated values in particular reaches were shown to be sensitive to parameters in other reaches. This was true of both transport \((A, x, A_S, q_L, \lambda)\) and effective reaction \((\lambda, \lambda_S, \rho, \lambda_H)\) parameters. Parameters assigned to any one reach influence simulated values in other reaches. In some cases, first-order decay terms in both the stream (Fig. 2) and the storage zone (Fig. 3) are most influential to observations in reaches other than the ones to which they are assigned. A downstream sensitivity, in which downstream observations are sensitive to parameters assigned to any one reach influence simulated values in other reaches.

### Table 6

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Uvas Creek reach number</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D (m^2 s^{-1}))</td>
<td>(1)</td>
</tr>
<tr>
<td>(A (m^2))</td>
<td>(5.00 \times 10^{-3})</td>
</tr>
<tr>
<td>(A_S (m^2))</td>
<td>–</td>
</tr>
<tr>
<td>(x (s^{-1}))</td>
<td>–</td>
</tr>
<tr>
<td>(q_L (m^2 s^{-1}))</td>
<td>–</td>
</tr>
</tbody>
</table>

Note. \(K_0\) was set to \(70 \times 10^{-6}\ m^3 \ g^{-1}\) for all reaches (as per Bencala [1]), \(\lambda_{HS}\) was set to \(1.0\) for all reaches, and \(C_L\) was set to \(11.39 \ mM\). “–” denotes no COV value because that parameter was fixed or not used in that particular reach (see Table 2 for details).

### Table 7

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Uvas Creek reach number</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\lambda_H (s^{-1}))</td>
<td>(1)</td>
</tr>
<tr>
<td>(\rho (g L^{-1}))</td>
<td>(0.109)</td>
</tr>
</tbody>
</table>

Note. \(K_0\) was set to \(70 \times 10^{-6}\ m^3 \ g^{-1}\) for all reaches (as per Bencala [1]), \(\lambda_{HS}\) was set to \(1.0\) for all reaches, and \(C_L\) was set to \(11.39 \ mM\). “–” denotes no COV value because that parameter was fixed or not used in that particular reach (see Table 2 for details).

### Table 8

<table>
<thead>
<tr>
<th>Parameter pair correlations (cor &gt; 0.75)</th>
<th>Transport–reaction pairs</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\lambda_H, x)</td>
<td>(\lambda_H, q_L)</td>
</tr>
<tr>
<td>(\lambda_H, A)</td>
<td>(\lambda_H, A_S)</td>
</tr>
<tr>
<td>(\lambda_H, \rho)</td>
<td>(\lambda_H, \lambda_S)</td>
</tr>
</tbody>
</table>

There are a total of 30 parameters in the model of the five experimental reaches, though 6 are set to 0 and therefore have no sensitivity. Subscripts denote reach number.
tive to an upstream parameter, is not surprising, as our physical and simulated reaches are sequential, and upstream processes and reactions obviously influence downstream transport of solute. There were some cases of upstream sensitivity—that, for example, simulations of NO$_3$ in Reach 3 were sensitive to $\lambda_S$ indicative of the fact that solute concentrations upstream of a given location are influenced by downstream solute flux, to the extent that the flux is influenced by the concentration gradient in the stream. This finding does not have a clear physical explanation, however it may be a consequence of the spatial concentration gradients that are required within the solute transport model. These inter-reach sensitivities are evidence of the overall sensitivity to a system-wide downstream mass flux, which is temporally varying throughout the transport simulations, and evidence that the inclusion of downstream observations can have an influence on estimating parameters of solute transport upstream of the observation location.

It is important to note that reactive solute transport experiments and subsequent simulations are likely to be case-specific, with respect to reaction rates and reactive solute dynamics. Our first-order uptake simulation resulted in almost the entire injected mass of NO$_3$ disappearing within the set of experimental reaches. Yet, in the sorption RSTM example Sr was obviously more persistent and significant concentrations passed the lowest stream sampling point. Complete loss of a reactive solute at a particular sampling point increases uncertainty in parameter estimates for that reach because one cannot confidently identify the location at which complete uptake occurred. In the case of the Green Creek experiment, because at least one sample had measurable NO$_3$ concentration in Reach 4, it is likely that most of the reach was responsible for uptake of NO$_3$. Thus, practitioners must also consider the relative effect of a reaction within a reach (e.g., Reaction Loss Factor, as defined by Wagner and Harvey [24]) when planning reactive solute transport experiments.

4.3. Implications for reactive solute transport experiment design

In the reactive NO$_3$ transport model, storage zone and streambed effective reaction parameters are determined from stream NO$_3$ concentration data. We expected that NO$_3$ simulations would be more sensitive to $\lambda$ than $\lambda_S$ (characterized by DSS and CSS), because the storage zone reaction location is disconnected from the stream and its effect is dampened by the time scale of exchange. But, $\lambda_S$ CSS values are, in general, on par with CSS values for $\lambda$ (Fig. 4B), suggesting that there are comparatively just as many conditioning measurements to support $\lambda_S$ parameterization as there are for $\lambda$. The interpretation that stream solute data provide an adequate basis for optimizing storage zone parameters (e.g., $\lambda_S$) is also supported by the COV results, which indicated comparable estimation confidence for both $\lambda$ and $\lambda_S$ (Table 4).

For the reactive Sr sorption model, we expected that sensitivities of $\rho$ and $\lambda_H$ would be lower than for the physical transport parameters ($A$, $A_S$, $q_L$, $x$), but CSS values for $\rho$ and $\lambda_H$ in each reach are higher than for every other parameter in the respective reach (Fig. 8). Similarly, $\rho$ and $\lambda_H$ DSS values tend to be larger in magnitude than DSS values for $A$, $A_S$, $q_L$, and $x$ at the same time (Figs. 7–9). This suggests that, with respect to reactive Sr transport, the reaction parameters ($\rho$ and $\lambda_H$) are the most influential on Sr simulations. Similar to the case for Green Creek, both reaction parameters are comparably optimized in all reaches, according to the COV analysis (Table 7).

The numerous correlated transport–reaction parameter pairs in both reactive transport models and the high CSS values of transport parameters with respect to reactive solute observations and simulations, both support the conclusion that the estimation of the transport parameter values ($A$, $A_S$, $q_L$, $x$) is the foundation for subsequent optimization of reaction parameters. Thus, we propose that the advice of Wagner and Harvey [23] and Gooseff and McGlynn [7], with respect to high temporal frequency sampling of conservative solute BTCs for robust TSM parameter optimization holds true for reactive solute transport simulation and analysis, particularly because reactive transport should be parameterized after conservative transport is optimized. This is an expected result, in agreement with Wagner and Harvey [24].

The greatest DSS values were found during the rise and fall of the BTCs. These times were found to be the most sensitive to transient storage parameters in conservative solute transport [10,20]. Thus, these times of the BTCs are very important to both conservative and reactive solute transport parameter identification. Likely, it is the relationship between transient storage parameters and reaction rate parameters that emphasizes these portions of the BTCs.

5. Conclusions

The increasing interest in simulation of reactive stream solutes has lead to increased use of RSTMs. Our sensitivity analyses of two RSTMs applied to two particular reactive transport data sets shows that effective reaction parameters have the greatest sensitivity to observations within their own reach, but are also sensitive to observations in reaches immediately upstream and downstream. Our findings also suggest that stream reactive solute data are adequate to confidently estimate storage zone reaction parameters in the examples presented, given the formulation of the net solute
losses in these RSTMs. Simulations of reactive solutes are also shown to be just as sensitive to model transport parameters as they are to effective reaction parameters, evidence of the dependence of reactive solute dynamics on physical transport. Effective reaction parameters appear to be most sensitive to BTC rise (shoulder) and fall (tail). These issues should be kept in mind when designing reactive stream tracer experiments so that appropriate sampling of reactive BTC concentrations can be achieved, and subsequent characterization of the effective reaction processes can be realized.

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This work was supported by the Utah Agricultural Experiment Station, a National Research Council Postdoctoral Fellowship to DTS, the US Geological Survey Toxic Substances Hydrology Program, and NSF OPP 92-11773. We would like to acknowledge A. Packman, S. Mehl, M. Friedel and an anonymous reviewer whose comments greatly improved this paper.

References


