Nitrogen retention in the main channel and two transient storage zones during nutrient addition experiments

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Abstract

The main channel (MC), surface transient storage (STS), and hyporheic transient storage (HTS) zones provide unique habitats in streams. Most nutrient spiraling studies use models that aggregate the influence of the various transient storage zones on uptake and retention. This may explain contradictory results on drivers of nutrient cycling in streams. Here, a new two-storage zone transport model with Michaelis–Menten uptake kinetics was developed to quantify the relative role of the three stream compartments on the physical and biological transport of solutes and compared with a dynamic nutrient spiraling method (tracer additions for spiraling curve characterization). Both approaches are applied to coinjected conservative and reactive tracer tests in a stream with mean annual discharge >1.0 m$^3$ s$^{-1}$. The relative influence of the three stream compartments on in-stream uptake of NO$_3$-N varied between reaches; each stream compartment dominated overall nitrate uptake in at least one subreach. HTS zones generally had greater influence on nitrate concentrations than STS zones because of longer residence times and faster uptake rates. However, a combination of geomorphology, MC-transient storage connectivity, residence time, compartment size, and uptake rate controls overall nutrient uptake capacity of a stream. Overall reach and compartment-specific uptake and uptake efficiency benefit from the upstream action of the transient storage zones during nutrient addition experiments, but STS and HTS contribute in different ways. Physical retention and biological uptake in STS zones contributed equally to overall reach uptake, but biological uptake in HTS zones overshadowed physical retention.

For many fluvial ecosystems, internal nutrient cycling is the dominant source of nutrients for primary producers, especially when lateral inputs are low (Mulholland et al. 1994; Essington and Carpenter 2000). Limiting nutrients, therefore, play a large role in overall stream production and their availability is controlled by the rate of remineralization and subsequent uptake. This is particularly true in large streams, which are less efficient at retaining and recycling nutrients than are smaller fluvial systems (Wetzel 2001). In-stream nutrient cycling also has important implications for ecosystem resistance to and recovery from disturbance (DeAngelis et al. 1990). A common measure of in-stream nutrient cycling is the spiraling length ($S_w$), which quantifies the downstream distance a dissolved nutrient molecule travels before transferring to particulate form and later back to dissolved form (Ensign and Doyle 2006). Focus is generally given to the dissolved component of spiraling length, known as uptake length ($S_u$), because much of the transport occurs in this form (Newbold et al. 1981; Aumen 1990; Ensign and Doyle 2006). Particulate transport primarily occurs during short-lived floods, when large amounts of particulate matter are scoured from the stream bed (Essington and Carpenter 2000). Hyporheic exchange, substrate composition, channel type, light availability, and channel morphology have all been shown to affect the uptake length (Valett et al. 1996; Mulholland et al. 1997; Ensign and Doyle 2006).

Spiraling theory integrates all in-stream processes into a single uptake value, although the advective (main channel [MC]) and nonadvective (transient storage [TS]) stream compartments have unique reaction rates, connectivity, and residence times. The contribution of different stream compartments to nutrient retention depends on the specific combination of physical and biological characteristics between nutrient sources and sinks (Powers et al. 2012). Active TS zones influence solute removal by extending residence times and increasing exposure to biochemically...
Aggregation of TS zone characteristics in analysis of tracer tests may be the origin of various interpretations. Separation of TS zones into surface (surface transient storage [STS]) and hyporheic (hyporheic transient storage [HTS]; Marion et al. 2008; Briggs et al. 2010; Johnson et al. 2014) may clarify the role of TS because these two TS compartments can have significantly different hydraulic and biogeochemical conditions (Thomas et al. 2003). TS zones have faster exchange rates and shorter residence times than HTS, resulting in a greater influence of TS on median transport time (Briggs et al. 2010; Stewart et al. 2011; Johnson et al. 2014). Exchange with STS zones is controlled by lateral dispersion (Fischer et al. 1979) and turbulent processes (Ghisalberti and Nepf 2002) and shows some dependence on discharge and advective velocity (Johnson et al. 2014). Sinuosity is also expected to influence TS zones. HTS exchange is controlled by hydraulic head gradients (Harvey and Bengala 1993) and bed hydraulic conductivity. Therefore, channel properties such as slope, width-to-depth ratio, and channel friction factor that support or inhibit these physical parameters will influence exchange with HTS zones (Johnson et al. 2014). Width-to-depth ratio (W:D), a proxy for the area of contact a stream channel has with its streamed, affects exchange between the MC and subsurface. Channel friction factor, a dimensionless measure of roughness of the channel, is a measure of the energy lost to the substrate surrounding the channel. Water forced into sediments moves more slowly than water in the MC and, therefore, also represents energy lost to the subsurface or substrate of the channel.

Other characteristics that differ between the three stream compartments include temperature, light, and dissolved oxygen (DO) concentration, which greatly influence in-stream productivity and the processing of nutrients (Hauer 2006; Marzadri et al. 2012). If unshaded, STS temperatures are slightly warmer than those in the MC during the summer (Z.C. Johnson, unpubl.) and diel changes in TS temperature slightly lag behind those in the MC (Neilson et al. 2010). HTS temperature reflects the long-term mean of MC temperature and is more modulated, with smaller shifts in temperature over the course of a day (Hannah et al. 2009; Rau et al. 2010; Neilson et al. 2010). HTS temperature can be phase-shifted from the MC signal as a function of flowpath length (Swanson and Cardenas 2010). Light is only available in the MC and STS compartments and decreases with depth. DO concentration is usually greatest in the MC because of its connection with the atmosphere and turbulent mixing. STS DO concentrations are generally smaller (despite the connectivity to the atmosphere) because of slightly higher summer temperatures and lack of turbulent mixing. HTS zones generally have the lowest DO concentrations because respiration in the sediment occurs more quickly than exchange with the MC (Argerich et al. 2011b). As a result, anoxic conditions often exist below a few millimeters (Wetzel 2001; Runkel et al. 2003). Some areas of HTS zones, however, can have high DO concentrations because of strong advective transport carrying oxygen-rich water into the sediments from the MC (Wetzel 2001; Argerich et al. 2011b).

Biogeochemical processes in the STS and HTS compartments are likely to differ and may be important to separate when modeling fluvial nutrient dynamics (Briggs et al. 2009; Stewart et al. 2011; Argerich et al. 2011c). However, the interaction between geomorphology, MC-TS connectivity, residence time, and uptake rate is not well understood. The MC is most often responsible for the majority of observed solute removal (Briggs et al. 2010; Powers et al. 2012) due to a high fraction of median transport time. Exchange between the MC and STS zones is generally much greater than between the MC and HTS zones (Briggs et al. 2010; Stewart et al. 2011) and, on average, water molecules enter STS zones many more times than they enter the HTS zones over a given reach length (Briggs et al. 2009; Briggs et al. 2010). However, the fast exchange rate also means that water molecules spend less time in the STS zones than the HTS zones. High residence times combined with large HTS uptake rates (Stewart et al. 2011) and exposure to sediment biofilms (Gooseff et al. 2003; Gooseff et al. 2006) result in greater solute removal from the STS zones than STS zones. Exchange with HTS zones has also been observed to influence biota in the MC and STS zones by supplying limiting nutrients (Dahm et al. 2006).

In the few studies that differentiate effects of the two types of TS zone, HTS then STS follow the MC in the amount of solute mass retained (Stewart et al. 2011). However, STS has been found to be more influential to nutrient uptake than HTS in some systems (Ensign and Doyle 2005) and be the primary storage mechanism in some small sand bed streams (Stofleth et al. 2008). In addition, STS zones typically accumulate large stocks of organic matter through deposition (Hall et al. 2002) and can accommodate photochemical reactions and N-fixation (Marcarelli et al. 2008) that may be important to biogeochemical cycling (McKnight et al. 2002). High light availability in wide streams with low canopy cover over the channel can promote the growth of aquatic plants and microbes that cycle nutrients (Battin et al. 2008), which may make STS particularly important to biogeochemical processes in larger stream systems. There is, however, a lack of nutrient removal data in large streams (Tank et al. 2008), especially those that differentiate between the MC, HTS, and STS zones.

Because it is difficult to characterize absolute and relative decay rates within and between stream compartments, solute uptake studies typically use many assumptions about
compartment uptake rates (Stewart et al. 2011) and/or lump TS zones into a single compartment (Lautz and Siegel 2007; Runkel et al. 2007; Argerich et al. 2011). Separation of the two TS zones may clarify trends in TS dynamics with increasing stream size and is especially important when the goal is to determine primary drivers of solute retention and calculate the relative influence of the TS zones vs. the MC (Briggs et al. 2010; Johnson et al. 2014). In particular, single storage zone transport models tend to overestimate the fraction of solute uptake occurring in the MC.

First-order uptake is commonly assumed in TS studies (Baker et al. 2012; Powers et al. 2012; Ye et al. 2012). Michaelis–Menten (M–M) kinetics better represent conditions during a nutrient addition experiment (Ribot et al. 2013) by placing a cap on the uptake rate and controlling the relationship between concentration and uptake. M–M kinetics can also capture multiple-order behavior of biological reactions by allowing for noninstantaneous reactions (Zarnetske et al. 2012). M–M uptake is commonly used to describe total reach uptake (Aumen 1990; Payn et al. 2005; Covino 2010b) but is rarely applied in TS studies (Zarnetske et al. 2012).

Nutrient spiraling breakthrough curve (BTC)-integrated methods are predominantly used in nutrient uptake studies but these only provide one data point for an entire BTC and do not provide concentration-dependent information. However, recently a method was developed to measure spiraling metrics for each concentration measurement (Covino 2010a). This method improves upon BTC-integrated approaches by enhancing confidence in ambient spiraling metrics, characterization of spiraling response curves, and assessment of stream saturation state (Covino 2010a). However, this method also does not differentiate uptake between the three stream compartments. Therefore, a method that combines M–M uptake kinetics and separation between the three stream compartments is needed to clarify how solute uptake is influenced by TS.

In this study of a large N-limited stream, we evaluate (1) the relative biological NO₃-N retention between MC, STS, and HTS compartments, (2) how TS zones affect total reach uptake kinetics, (3) the relative contribution of physical and biological processes to NO₃-N retention, and (4) the total M–M N uptake rates from ambient to saturated conditions. We hypothesize that the biologic TS retention of NO₃-N will reflect some degree of physical TS retention from a previous study (Johnson et al. 2014) but not be controlled by it. We expect lightly shaded STS zones to have a more prominent role in biological N retention than HTS in the lower Truckee River. The two TS zones are not only expected to increase N uptake rates via increased residence times and exposure to metabolically active areas of the stream, but also to increase uptake efficiency via spreading of the N plume (i.e., lower concentrations). The proportion of unrecovered N mass attributed to physical processes is hypothesized to be low because of the relatively low physical exchange of flow with the surroundings in the lower Truckee River. Total NO₃-N uptake rates are expected to be similar but less in the lower Truckee River vs. smaller stream systems. This manuscript extends a previous study of physical solute transport in the lower Truckee River (Johnson et al. 2014) to nutrient spiraling.

**Methods**

**Site description**

We performed conservative (NaCl) and reactive (KNO₃) tracer addition experiments in two reaches of the lower Truckee River, Nevada (Fig. 1). The Truckee River originates from the western shore of Lake Tahoe and flows east over the border between California and Nevada, until the main stem turns north and terminates in Pyramid Lake. From a preliminary transport model experiment and logistical considerations (Johnson et al. 2014), two short reaches between 3.1 km and 3.3 km in length were chosen to represent different physical settings in which to conduct the tracer experiment (Fig. 1). These reaches are separated by the Numana Dam, which for much of the summer diverts some flow from the channel. Site locations were spatially separated from the dam (which also approximately represents the end of the canyon section) to eliminate residual effects. The Upstream reach exists in a steep canyon with relatively low sinuosity (1.02) and slope (1.13 mm m⁻¹). The Downstream reach exists in a more unconstrained section with higher sinuosity (1.10), slope (1.61 mm m⁻¹), and concentration of large channel bars and also encompasses an area of previous hypothetical zone research (Naranjo et al. 2012, 2013). For more details on this section of the Truckee River, see Johnson et al. (2014).

**Velocity transect surveys**

To distinguish between the MC and TS zones, 31 velocity transects were measured along both reaches during the summer of 2012. As previously recommended (Briggs et al. 2009), we measured transects longitudinally every approximately 1–2 bankfull widths to obtain complete coverage which equates to approximately every 80–100 m in the lower Truckee River. A StreamPro (Teledyne RD Instruments) Acoustic Doppler Current Profiler (ADCP) was used to measure the cross-sectional area and velocity profiles. A Marsch-McBirney FloMate (Hach) was also used to more precisely measure the transition between STS (velocities ≤ 0 m s⁻¹) and MC zones. These detailed measurements also enabled the location and magnitude of discharge gained from or lost to the subsurface to be determined. We were not able to measure transects where the depth was less than approximately 0.5 m with the ADCP. In a few cases, the measurement point was moved to deeper water slightly up or downstream. As a result, MC cross-sectional areas may be slightly overestimated. Results from these measurements are summarized in Johnson et al. (2014).
Tracer experiment

In late-summer 2012, a pulse tracer experiment was conducted to estimate the NO$_3$-N retention capacity of two reaches with two TS zones (STS and HTS) of the lower Truckee River (Fig. 1). The two reaches were the same as those described for the “lower” discharge tracer experiment in Johnson et al. (2014). Nitrate (KNO$_3$) served as the reactive tracer and chloride (NaCl) as the conservative tracer. Chloride is a very good conservative tracer for TS experiments because of its lack of sorption, decay, and biological uptake and because its concentration can be easily converted from simple conductivity measurements. However, chloride concentrations via conductivity measurements do not have a particularly low detection limit (>100 $\mu$g L$^{-1}$) and ambient concentrations vary widely. High detection limit can lead to errors at low concentrations, especially in the tail of the BTC. Nitrate is commonly used as a reactive tracer because it does not sorb strongly to sediment and, unlike ammonium, nitrification is not a concern. The only direct loss of nitrate from the system comes from denitrification, in which nitrate is converted to N$_2$ gas. Biological uptake temporarily retains nitrate within organic matter before it is remineralized.

Both tracers were injected sufficiently upstream (>1.6 km) of the first sampling site to allow for complete mixing across the stream. Real-time conductivity values were monitored at the sampling points with temperature-correcting conductivity probes (Yellow Springs Instrument). Conductivity values were converted to Cl$^-$ concentration via calibration curves for each probe ($R^2 > 0.99$). Probes set to one-minute sampling intervals at each site were placed in the MC (thalweg) and adjacent STS zone to parameterize the two-zone storage model. The STS zone at each sampling point was chosen based on accessibility and how representative it was of reach transect measurements conducted earlier in the summer.

Approximately 20 water samples were also taken from the MC and adjacent STS zone. These grab samples were field-filtered with Pall VacuCap 0.45 $\mu$m Filter Units and put on ice to be analyzed for NO$_3$-N within 24 h of collection with an Astoria Pacific Automated Colorimetric Analyzer using Standard Method 4500-NO$_3$ F (Standard Methods 1992). Timing of the passing of the tracer plume was estimated prior to the tracer study from the results of a preliminary numerical experiment and was estimated in real-time based on the passing NaCl plume measured as conductivity.

In the Downstream (3.82 m$^3$ s$^{-1}$) and Upstream (4.11 m$^3$ s$^{-1}$) reaches, 418 kg NaCl and 17 kg KNO$_3$ were injected on distinct occasions separated by 14 days starting at the end of August 2012. On the day of injection, approximately 500 L of river water was pumped into two tanks while NaCl was added. Pumps circulated the solution within the tanks to aid
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in the two-hour dissolution process. When the NaCl was fully dissolved, the solution was pumped back into the river over the course of 20–25 min. KNO3 was dissolved in five gallon buckets and added directly to the river over the course of approximately two minutes when half of the NaCl had been released. Ambient Cl− and NO3-N concentrations in the river were approximately 100 mg L−1 and 4 μg L−1, respectively, for both the injections. The subreach between the injection point and the first sampling point in the Upstream and Downstream reaches will be referred to as UR1 and DR1, respectively. The subreach between the first and second sampling points in the Upstream and Downstream reaches from here will be referred to as UR2 and DR2, respectively.

Total, physical, and biologic NO3-N loss

Discharge within tracer test reaches was measured at the upstream boundary during injection and at our two sampling sites periodically during the experiment using the StreamPro ADCP. Tracer mass recovery (Md) at each sampling point was calculated as

\[ M_d = Q \int_0^t C_T(t) dt \]  

(1)

where \( C_T \) is the time-integrated tracer concentration (measured from conductivity probes and grab samples) and \( Q \) is the local discharge (constant for our experiments). We define total tracer loss (Ltotal) as the difference between tracer mass added (\( M_{add} \)) and mass recovered, \( L_{total} = M_{add} - M_d \). Physical NO3-N loss (NLphys) was estimated from Cl− data using

\[ NL_{phys} = \left( 1 - \frac{C_{M}}{C_{Madd}} \right) N_{Madd} \]  

(2)

where CM is the Cl− mass recovered, CMadd is the Cl− mass added, and Nadd is the NO3-N mass added. Biological NO3-N loss (NLbio) was calculated as the difference between total loss and physical loss, \( NL_{bio} = NL_{total} - NL_{phys} \). Loss in these calculations has units of mass that can easily be converted into percent of injected mass.

Nutrient spiraling

Three common nutrient spiraling parameters reported are uptake length (\( S_u \)), uptake velocity (\( V_u \)), and stream-bed areal uptake rate (\( U \)). Uptake length is the average distance a solute molecule travels downstream before being removed from the water column, \( S_u = \frac{1}{k_u} \), where \( k_u \) is the longitudinal uptake rate (m−1). \( k_u \) is calculated by plotting the natural log of the ratio of reactive to conservative tracer concentration for injectate and background corrected BTC sample vs. stream distance. \( k_u \) is the slope of this line. Uptake velocity is a measure of the biotic demand relative to concentration, \( V_u = \frac{Q}{S_u} \), where \( Q \) is discharge and \( S_u \) is the average wetted stream width. It normalizes \( S_u \) for the effects of depth and velocity, so streams of different sizes can be directly compared (Tank et al. 2008). Stream-bed areal uptake rate quantifies the nutrient mass taken up per area of streambed per unit time (Aumen 1990; Earl et al. 2006), \( U = V_u \frac{[NO3-N]}{C} \), where the term in brackets is the geometric mean of NO3-N concentrations. These spiraling equations can be applied in a BTC-integrated or dynamic fashion (Covino 2010a). The BTC-integrated method, used in many previous studies (Ensign and Doyle 2006; Lautz and Siegel 2007; Tank et al. 2008), combines all grab sample data into a single value that cannot capture changes in spiraling as concentration increases. Instead, each BTC datum can be used to evaluate how biologic uptake responds in a dynamic way to variable NO3-N concentration (Covino 2010a). In this approach, known as Tracer Additions for Spiraling Curve Characterization (TASCC), spiraling values are obtained for each grab sample and spiraling metrics vs. concentration curves can be developed. Because spiraling metrics estimated from nutrient addition experiments reflect the spiraling of added nutrient and not total nutrient spiraling, ambient spiraling metrics need to be estimated to calculate total nutrient spiraling. Variations of the three spiraling parameter equations are used to calculate ambient, BTC-integrated, dynamic, and total uptake kinetics (Covino 2010a).

These uptake curves are useful for assigning appropriate kinetic models and kinetic model parameterization (Covino 2010b). We used a M–M model

\[ U = \frac{U_{max} C_g}{K_m + C_g} \]  

(3)

to fit dynamic total areal uptake rate (\( U \)) data to estimate maximum uptake rate (\( U_{max} \)) and the half-saturation concentration (\( K_m \)). \( C_g \) is the geometric mean of conservative (i.e., estimated conservative transport of reactive tracer) and total (i.e., not background-corrected) observed nutrient concentration. These methods closely followed those of Covino et al. (2010b). One exception was estimation of NO3-N concentrations expected if it were to travel conservatively. We calculated this using previously estimated model parameters from Cl− tracer data (Johnson et al. 2014) and set decay to zero. This was necessary because input signals for Cl− and NO3-N had different time-lengths of injection. To calculate \( U_{max} \) and \( K_m \), we minimized the squared residuals between modeled and observed \( V_u \) and \( U \) values while adjusting \( U_{max} \) and \( K_m \) values. This method has less error associated with it than transforming the data and fitting linear regressions (Chapra 1997).

Two-zone storage modeling

A modified one-dimensional transport with inflow and storage (OTIS) model (Runkel 1998) was used prior to collecting field data to direct logistics for the tracer study described above. The original code is publicly available (http://pubs.er.usgs.gov/usgspubs/wri/wri984018) and has been widely used in a variety of applications. This model uses the
Crank–Nicolson finite difference method to solve the advection–dispersion–TS equations derived by Bencala and Walters (1983). In this study with conservative and reactive tracers, the traditional OTIS code was modified to allow for multiple storage zones

\[ \frac{\partial C}{\partial t} = -\frac{Q}{A} \frac{\partial C}{\partial x} + \frac{1}{A} \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) + \frac{q_{\text{LIN}}}{A} (C_{\text{LIN}} - C) + x_{\text{HTS}}(C_{\text{HTS}} - C) + x_{\text{STS}}(C_{\text{STS}} - C) - \lambda C \]  

(4)

\[ \frac{\partial C_{\text{HTS}}}{\partial t} = -x_{\text{HTS}} \frac{A}{A_{\text{HTS}}} (C_{\text{HTS}} - C) - \lambda_{\text{HTS}} C_{\text{HTS}} \]  

(5)

\[ \frac{\partial C_{\text{STS}}}{\partial t} = -x_{\text{STS}} \frac{A}{A_{\text{STS}}} (C_{\text{STS}} - C) - \lambda_{\text{STS}} C_{\text{STS}} \]  

(6)

where \( C \) is the MC solute concentration (mg L\(^{-1}\)), \( Q \) is the volumetric flow rate (m\(^3\) s\(^{-1}\)), \( A \) is the MC cross-sectional area (m\(^2\)), \( D \) is the dispersion coefficient (m\(^2\) s\(^{-1}\)), \( x \) is the distance downstream (m), \( t \) is time (s), \( q_{\text{LIN}} \) is the lateral inflow rate per unit length (m\(^3\) s\(^{-1}\) m\(^{-1}\)), \( C_{\text{LIN}} \) is the solute concentration in the lateral inflow (mg L\(^{-1}\)), \( C_{\text{HTS}} \) is the solute concentration in the HTS zone (mg L\(^{-1}\)), \( C_{\text{STS}} \) is the solute concentration in the STS zone (mg L\(^{-1}\)), \( C_{\text{HTS}} \) is the cross-sectional area of the HTS zone (m\(^2\)), \( C_{\text{STS}} \) is the cross-sectional area of the STS zone (m\(^2\)), \( x_{\text{HTS}} \) is the MC-HTS exchange coefficient (s\(^{-1}\)), \( x_{\text{STS}} \) is the MC-STS exchange coefficient (s\(^{-1}\)), \( \lambda_{\text{HTS}} \) is the MC first-order decay coefficient (s\(^{-1}\)), \( \lambda_{\text{STS}} \) is the STS decay coefficient (s\(^{-1}\)), and \( \lambda_{\text{STS}} \) is the STS decay coefficient (s\(^{-1}\)). The stream, in this model, is represented by a series of completely mixed cells, each having adjacent cells for TS (STS and HTS are arranged in parallel). The amount of solute retained in storage is proportional to the difference in concentrations between the MC and TS zone (i.e., there is no advective transport into or out of the TS zone). Solute exchange with TS zones, therefore, is controlled by the ratio of MC cross-sectional area to TS zone area (\( A:A_{\text{TS}} \)) and the MC-TS first-order exchange coefficient (\( \alpha \)). Lateral inflow and outflow were kept equal because there was no indication of a net change in discharge during our experiments. From here, we will refer to the lateral inflow or outflow as \( q_{\text{LAT}} \).

Physical transport, estimated with the conservative tracer (NaCl), describes how water molecules and solutes are physically moved through the system and storage zones. Critical modeling parameters include \( D, A, A_{\text{HTS}}, A_{\text{STS}}, x_{\text{HTS}}, x_{\text{STS}}, \lambda_{\text{HTS}}, \lambda_{\text{STS}}, \) and \( q_{\text{LAT}} \) for physical transport. The nonconservative tracer (KNO\(_3\)) is also controlled by these physical factors as well as biological uptake which takes the form of a first-order decay coefficient (\( \lambda_{\text{HTS}}, \lambda_{\text{STS}} \)) in the modified-OTIS model. Therefore, the difference between the conservative tracer and nonconservative tracer represented in a BTC is the result of biological uptake of NO\(_3\)-N.

Model optimization

All Cl\(^-\) and NO\(_3\)-N concentration values used in the model were background-corrected by subtracting measured ambient concentrations. Optimization and calculation of 95% confidence intervals (CIs) of the two-storage zone model parameters were performed using the inverse modeling software UCODE_2005 (Poeter 2005). Optimization of the model parameters via nonlinear regression was completed by iteratively adjusting the parameter values until a global minimum in residuals between observed and simulated concentration values was achieved (Poeter and Hill 1997). More weight was applied to the MC BTC than the STS BTC to reflect the error between the reach average STS zone and the one we collected samples from. Notwithstanding, the STS BTC still provides an additional guide for the optimization process. Simultaneous 95% CI analysis was performed for all parameters using the UCODE_2005 sensitivity analysis mode when the weighted least squares objective function displayed little change. For more details on UCODE, the reader is directed to Poeter (2005). Conservative model parameters (i.e., \( D, A, A_{\text{STS}}, A_{\text{HTS}}, x_{\text{HTS}}, x_{\text{STS}}, \) and \( q_{\text{LAT}} \)) were estimated in a previous study (Johnson et al. 2014) and used here. In this study, to allow for the calculation of concentration-dependent uptake coefficients for the three stream compartments, we converted the first-order decay coefficients (Eqs. 4–6) following (Aumen 1990)

\[ \dot{\lambda} = \frac{V_{\text{f}}}{h} = \frac{U_{\text{max}}}{(K_m + c)} \]  

(7)

where \( U_{\text{max}} \) is \( U_{\text{max}}/h \) and \( h \) is the mean compartment depth (m). This way, M–M uptake kinetics can be separated between the three stream compartments.

If first-order decay was used, three parameters would have been fit ( \( \dot{\lambda}, \lambda_{\text{HTS}}, \) and \( \lambda_{\text{STS}} \)). To keep the number of adjustable variables to three, we assumed \( K_m \) values for the different stream compartments based on the reported half-saturation concentrations for the dominant processes for each compartment. The compartment-specific \( K_m \) values were the same for each subreach. Periphyton has been shown to be the dominant factor controlling DO concentrations and water quality in the lower Truckee River (Warwick et al. 1999; Kish et al. 2006; Bartlett and Warwick 2009) and substantial stocks were observed in the channel during the experiments, especially in the Downstream reach. Therefore, we used a periphyton half-saturation concentration of 25 mg L\(^{-1}\) which was applied in a previous Truckee River study (Caupp et al. 1997) for the MC. We used the ratio between \( K_m \) and ambient nitrate concentration ( \( C_{\text{amb}} \)) from the literature to determine the appropriate \( K_m \) value for the compartments rather than use the absolute \( K_m \) values reported because \( C_{\text{amb}} \) affects uptake kinetics (Reuter and Axler 1992; Ribot et al. 2013) and most nitrate uptake studies were conducted in streams with higher \( C_{\text{amb}} \) than the lower Truckee River. Our MC \( K_m \) value resulted in a \( K_m:C_{\text{amb}} \) ratio of 5.21–13.2 which is similar to the range in ratio values for epilithic periphyton communities of 7.13–12.6 (Reuter and
Axler 1992). For the STS zones, we assumed that the dominant process occurring was algal uptake similar to that in the MC. However, because these are depositional zones they can also have significant epipelic algal communities. Epipelic communities have been shown to have higher $K_m$ values than epilithic communities due to higher ambient nitrogen availability from interstitial nitrogen which results in lower nitrogen limitation (Reuter and Axler 1992). For the HTS zones, we assumed the dominant process was denitrification and used a $K_m$ value of 15 $\mu$g L$^{-1}$. This resulted in a $K_m$ : $C_{amb}$ ratio of 3.13–7.89 for our subreaches, which is similar to other reported $K_m$ : $C_{amb}$ ratios for denitrification of 0.72–7.30 (Evrard et al. 2013) and 5.16–17.39 (Herrman et al. 2008).

Therefore, $U_{max,MC}$, $U_{max,STS}$, and $U_{max,HTS}$ represent the maximum volumetric uptake rate within each of the three compartments and are adjusted to the NO$_3$-N data in place of $\lambda$, $\lambda_{STS}$, and $\lambda_{HTS}$. To minimize issues of equifinality of model parameter sets (Gooseff et al. 2013), a combination of numerical optimization and visual checks was used. All three uptake rates were initially opened to optimization before $U_{max,HTS}$ alone was optimized to the tail data and $U_{max,MC}$ and $U_{max,STS}$ were held constant. Lastly, $U_{max,MC}$ and $U_{max,STS}$ were reopened to optimization while $U_{max,HTS}$ was held constant. In this way, the HTS uptake was optimized to the late-time tail data where it primarily affects the BTC and the MC and STS uptake were optimized to the rest of the BTC. STS primarily affects the early- to mid-time tail of the BTC and affects the timing of the peak more than HTS. Further improvement of this method could include individual stream-specific characterizations of $K_m$ in the three compartments.

The cumulative uptake of NO$_3$-N ($N_{cum}$) for each of the three stream compartments within a subreach was determined within the model by calculating the mass taken up in a compartment for a specific time-step and location and summing for all time-steps and locations in a subreach

$$N_{cum} = \sum_{i=1}^{n} \sum_{j=1}^{m} \lambda_{ij}C_{ij}A_{ij}L_{C}\Delta t$$  \hspace{1cm} (8)

where $i$ and $j$ represent the spatial and temporal dimensions, respectively, $L_{C}$ is the cell length (10 m for this study), and $\Delta t$ is the time-step (10 s for this study). With this equation, differences in relative NO$_3$-N uptake can be compared between using first-order decay and M–M uptake rates and between compartments. This information is important for comparing and contrasting the roles of the three storage zones in nutrient retention and transport. To investigate the influence, the two TS zones have on total uptake kinetics the numerical model is rerun as each TS zone is turned off in two steps; only the decay capabilities of one of the TS zones is turned off (i.e., set $U_{max}$ to zero) and a second set of

### Table 1. General Truckee River subreach and reach characteristics.*†‡

| Subreach or reach | $Q$ (m$^3$ s$^{-1}$) | Solute $u$ (m s$^{-1}$) | $L$ (m) | Slope (mm m$^{-1}$) | Sinuosity‡ | $h_{MC}$ (m) | $h_{STS}$ (m) |
|------------------|---------------------|------------------------|--------|-------------------|-----------|-------------|-------------|
| DR1              | 3.822               | 0.196                  | 1859   | 1.522             | 1.048     | 0.697       | 0.611       |
| DR2              | 3.822               | 0.243                  | 1475   | 1.726             | 1.163     | 0.601       | 0.606       |
| Downstream Reach | 3.822               | 0.211                  | 3344   | 1.612             | 1.096     | 0.661       | 0.608       |
| UR1              | 4.105               | 0.240                  | 1660   | 1.404             | 1.016     | 0.668       | 0.538       |
| UR2              | 4.105               | 0.204                  | 1504   | 0.822             | 1.023     | 0.805       | 0.676       |
| Upstream Reach   | 4.105               | 0.225                  | 3164   | 1.128             | 1.019     | 0.723       | 0.605       |

*Values in bold represent overall reach (injection to second sampling point) averages.
†$h_{STS}$ values represent mean STS depth.
‡Dimensionless.

### Table 2. BTC results for the Truckee River tracer tests in the Downstream (DR) and Upstream (UR) reaches.*†

| Tracer | Subreach | Mass recovered (%) | Detection length (h) | Peak concentration ($\mu$g L$^{-1}$) |
|--------|----------|--------------------|----------------------|--------------------------------------|
| KNO$_3$ | DR1      | 71.2               | 3.97                 | 113                                  |
|        | DR2      | 38.7               | 4.57                 | 54.5                                 |
|        | UR1      | 84.9               | 3.35                 | 166                                  |
|        | UR2      | 68.0               | 3.90                 | 73.0                                 |

*The BTC of the subreach in bold is shown in Figure 2.
†Mass recovered values are relative to total mass injected.
cumulative uptake is calculated, then the exchange with the TS zone is turned off (i.e., set $z$ to zero) and a third set of cumulative uptake is calculated. The two-step process is then repeated for the other TS zone and the decrease in NO$_3$-N mass taken up is compared between the two steps for each TS zone. This way, the overall influence of the STS and HTS zones is separated by both biologic ($U_{\text{max}}$) and physical ($z$) factors.

**Results**

**Total, physical, and biological NO$_3$-N loss**

General Truckee River reach characteristics are summarized in Table 1, which is a modified version of the table from Johnson et al. (2014). The reader is also referred to that manuscript for Cl$^-$ data. The NO$_3$-N BTC characteristics of the MC are summarized in Table 2 and an example BTC is shown in Figure 2. We refer to NO$_3$-N mass “loss” as the mass of solute not recovered at a downstream sampling site. The physical fraction of this loss (NL$_{\text{phys}}$) is assumed to be primarily lost to groundwater. Hydrologic turnover is the gross input and output of lateral discharge ($q_{\text{LAT}}$) where, as a percentage of the channel discharge, DR1 (4.2%) was greatest followed by UR1 (4.0%), DR2 (3.1%), and UR2 (3.0%). A portion of NL$_{\text{phys}}$ may also be caused by extended residence times in HTS zones or subsurface flow paths circumventing our sampling points; however, the latter is expected to be small. Differences in HTS exchange rates may partially explain differences in physical mass lost in the Truckee subreaches. DR2 showed some evidence of fast exchanging HTS zones (Johnson et al. 2014) and had relatively low physical loss of solute mass compared with the other subreaches. Biological loss (NL$_{\text{bio}}$) refers to the portion of mass lost due to biologic processes and is only a loss in the timeframe of our experiment. The only true direct loss of nitrate in streams occurs via denitrification while all other nitrate uptake represents temporary storage in organic matter because it will eventually be remineralized (Ensign and Doyle 2006). Nitrite can be used to oxidize ammonium into N$_2$ gas in a process known as anammox (Zhu et al. 2013), but nitrite concentration is negligible in the lower Truckee River. However, nitrate can be reduced to ammonia (Samuelsson 1985) and continue along any of the pathways for ammonia including anammox. In the lower Truckee River reaches, riparian uptake is expected to be a minor contributor to biological NO$_3$-N uptake because of limited riparian vegetation.

Large differences in total and biological NO$_3$-N mass loss were observed between the two reaches. Overall mass loss of injected NO$_3$-N was almost two times greater in the Downstream reach (61.3%) than Upstream reach (32.0%). Relative reach length, the Downstream (18.4% km$^{-1}$) and Upstream (10.1% km$^{-1}$) NO$_3$-N removal values are much lower than the approximately 64% over a 1-km reach reported from other studies (Peterson et al. 2001; Mulholland et al. 2009). In the Downstream reach, biological (47.2%) processes were consistently responsible for a greater proportion of total NO$_3$-N mass loss than physical (14.1%) processes (Fig. 3A). In the Upstream reach (Fig. 3B), the proportions were much closer with physical (16.4%) loss exceeding biological uptake (15.6%). The second sampling site (DR2 and UR2) retention values in Figure 3 are shown relative to the mass recovered from the first sampling site (DR1 and UR1), rather than total mass injected. The Upstream reach had a faster mean solute velocity (22.5 cm s$^{-1}$) and lower mean temperature (19.5°C) than the Downstream reach (21.1 cm s$^{-1}$ and 22.4°C, respectively) which could explain some of the difference in NO$_3$-N uptake between reaches.

**Total uptake kinetics using the TASCC method**

As recommended by Covino et al. (2010a), we simultaneously calculated areal uptake rates using both dynamic and mass balance approaches which produced similar results (slope = 1.04, $R^2 = 0.997$). Henceforth, we will refer to the dynamic values calculated (Table 3). Consistent with M-M kinetics, uptake length ($S_w$) increased (Fig. 4), uptake velocity ($V_I$) decreased (Fig. 5), and areal uptake rate ($U$) increased (Fig. 6) with increased NO$_3$-N concentration. There was no significant difference in ambient uptake length ($S_{w-amb}$) between the Downstream (668–1790 m) and Upstream reaches (1510–2110 m; Table 3). There was also no significant difference in $V_{I-amb}$ between the Downstream (4.58 mm min$^{-1}$ to 13.0 mm min$^{-1}$) and Upstream (4.66 mm min$^{-1}$ to 3.39 mm min$^{-1}$) reaches. The ambient areal uptake rate ($U_{amb}$), however, was significantly larger in the Downstream reach (22.9 $\mu$g m$^{-2}$ min$^{-1}$ to 52.2 $\mu$g m$^{-2}$ min$^{-1}$) than the Upstream reach (10.8 $\mu$g m$^{-2}$ min$^{-1}$ to 14.0 $\mu$g m$^{-2}$ min$^{-1}$). Maximum areal uptake rate ($U_{\text{max}}$) values were between 1.5 and 3.1 times greater in the Downstream reach (122–230 $\mu$g m$^{-2}$ min$^{-1}$) than Upstream reach (73.6–82.9 $\mu$g m$^{-2}$ min$^{-1}$). Maximum volumetric uptake rate ($U_{\text{max}}$) values (Table 3) were calculated by dividing $U_{\text{max}}$ by the subreach mean MC.
depth (Table 1) and were between 1.4 and 4.2 times greater in the Downstream reach (175–383 \( \mu g \) m\(^{-3} \) min\(^{-1} \)) than Upstream reach (91.4–124 \( \mu g \) m\(^{-3} \) min\(^{-1} \)). The ambient and maximum uptake rates indicate that the Downstream reach had a greater capacity to retain NO\(_3\)-N than the Upstream reach. \( K_m \) values were not statistically different between the Downstream (11.2–15.4 \( \mu g \) L\(^{-1} \)) and Upstream (8.86–11.2 \( \mu g \) L\(^{-1} \)) reaches, although the Downstream reach values were generally larger. Combined with previous nutrient data from grab samples, this suggests that the Upstream reach is slightly more N-limited than the Downstream reach which may affect the density of aquatic biota.

A total N (TN) to total P (TP) ratio below 22 is often indicative of N-limitation while values above 44 are often indicative of P-limitation (Green and Fritsen 2006). Water quality samples collected from these reaches in August, 2011 showed greater TN:TP molar ratios in the Downstream reach (9.2–9.7) over the Upstream reach (8.4–8.7). Background NO\(_3\)-N concentrations in the August 2011 samples (4.8 ± 0.3 \( \mu g \) L\(^{-1} \)) were slightly greater than in 2012 (3.5 ± 0.4 \( \mu g \) L\(^{-1} \)).

**Fig. 3.** Relative influence of physical and biological processes on NO\(_3\)-N mass loss in the (A,C,E) Downstream and (B,D,F) Upstream reaches calculated with our transport model. Physical and biological losses (A,B) relative to total NO\(_3\)-N added, (C,D) relative biologic losses in the MC, STS, and HTS compartments, and (E,F) relative physical NO\(_3\)-N retention (as measured by \( k_{MED} \)) in the three stream compartments.
Water quality samples obtained on 20 September 2012 from downstream of our study reaches in Nixon, NV, showed slightly greater NO3-N concentration (6.0 μg L⁻¹) and also indicated N-limitation (TN : TP = 13.9). Comparison between in-stream ambient concentration (Camb) and Km has also been used to determine degree of nutrient limitation (Muhlholland et al. 2002), where Km : Camb > 1 indicates limitation. In the lower Truckee River, the Upstream reach showed greater Km : Camb values (2.9–5.9) than the Downstream reach (2.6–3.2; Table 3). Therefore, biotic growth in both of the reaches is strongly N-limited.

Model-based separation of physical retention and biological loss in MC, STS, and HTS compartments

The fraction of median transport time due to a specific storage zone measured over a standard 200 m reach length (F MED) is the most useful metric to assess the relevance of each storage process to overall physical transport (Runkel 2002) but does not inform biological uptake. The relative physical retention, described by F MED, in the Truckee MC, STS, and HTS compartments was previously described (Johnson et al. 2014). To summarize, the MC was consistently responsible for the majority of the median transport time in both reaches (Fig. 3E,F). TS (STS + HTS) had a larger effect on the median transport time in the Downstream reach than the Upstream reach. STS was consistently responsible for a

Table 3. M–M NO3-N spiraling parameters in the Truckee River Downstream (DR) and Upstream (UR) subreaches estimated from the Tracer Additions for Spiraling Curve Characterization (TASCC) method.* †

| Parameter | DR1 | DR2 | UR1 | UR2 |
|-----------|-----|-----|-----|-----|
| Camb (μg L⁻¹) | 4.80 | 4.30 | 3.10 | 1.90 |
| Sw-amb (m) | 1790 | 668 | 2110 | 1510 |
| Vf-amb (mm min⁻¹) | 4.58 | 13.0 | 4.66 | 5.39 |
| Uamb (μg m⁻² min⁻¹) | 22.9 | 52.2 | 14.0 | 10.8 |
| Umax (μg m⁻³ min⁻¹) | 122 | 230 | 82.9 | 73.6 |
| Km (μg L⁻¹) | 15.4 | 11.2 | 8.86 | 11.2 |

*Ambient nitrate concentrations (Camb) were measured with grab samples.
†Umax values were calculated using mean MC depth (hMC) values from Table 1.

Fig. 4. Dynamic and BTC-integrated uptake lengths (Sw) with linear regression in the (A) Downstream and (B) Upstream subreaches calculated using the TASCC method.

Fig. 5. Dynamic and BTC-integrated uptake velocities (Vf) with M–M fit in the (A) Downstream and (B) Upstream subreaches calculated using the TASCC method.
greater percentage of median transport time than HTS in both reaches.

With M–M decay (Table 4), the fits to the observed MC (mean $R^2 = 0.967 \pm 0.009$) and STS (mean $R^2 = 0.938 \pm 0.023$) BTCs were good and the M–M uptake coefficients for the three stream compartments varied between subreaches. The MC M–M maximum uptake rate ($U_{\text{max,MC}}$) varied between 29.8–428 $\mu$g m$^{-3}$ min$^{-1}$, the STS uptake rate ($U_{\text{max,STS}}$) from 13.8–507 $\mu$g m$^{-3}$ min$^{-1}$, and the HTS uptake rate ($U_{\text{max,HTS}}$) from 294 $\mu$g m$^{-3}$ min$^{-1}$ to 610 $\mu$g m$^{-3}$ min$^{-1}$. The range in $U_{\text{max,HTS}}$ is at the lower end of the range reported for denitrification (Evrard et al. 2013) of 210–1750 $\mu$g m$^{-3}$ min$^{-1}$. $U_{\text{max,MC}}$ was significantly greater in the Downstream reach than the Upstream reach. Uptake rates in the HTS zones were higher than the MC and STS zones in every Truckee River subreach, in agreement with some previous findings (Stewart et al. 2011; Argerich et al. 2011c). STS uptake rates alternated between being larger and smaller than that of the MC in these subreaches, which is also similar to a previous study (Powers et al. 2012). Confidence in the MC uptake rates was greater than confidence in the STS and HTS uptake rates (Table 4) showing that overall nitrate uptake was most sensitive to the MC uptake rate. However, sensitivity to STS or HTS uptake rate increased where these zones were responsible for a higher fraction of the total nitrate uptake. For example, in UR1 the relative confidence (i.e., maximum confidence value divided by optimized value) in the HTS uptake rate was slightly better than that of the MC and in UR2 the relative confidence in the STS uptake rate was similar to that of the MC.

The relative contribution to the biological and total NO$_3$-N retention described by M–M uptake kinetics in the three stream compartments varied between subreaches (Fig. 3A–D). The general trend (injection to second sampling site) in the Downstream reach (MC > HTS > STS) was different than that in the Upstream reach (HTS > STS > MC) and neither showed consistent dependence on $F_{\text{200 MED}}$. These differences in biologic processing of NO$_3$-N between the reaches may be due to a combination of differences in aquatic biota type and density in the three stream compartments and physical exchange characteristics with the TS zones.

**STS and HTS influence on total reach uptake**

Model-simulated uptake decreased when decay within the STS or HTS zones was turned off (i.e., $U_{\text{max}} = 0$; Fig. 7) or exchange with either of those zones was turned off (i.e., $x = 0$).

**Table 4.** Optimized M–M NO$_3$-N spiraling parameters to main channel (MC) and surface transient storage (STS) BTCs in the Truckee River Downstream (DR) and Upstream (UR) subreaches using our multistorage transport model.*

| Parameter                  | DR1          | DR2          | UR1          | UR2          |
|----------------------------|--------------|--------------|--------------|--------------|
| $U_{\text{max,MC}}$ (µg m$^{-3}$ min$^{-1}$) | 137 (92.2–203) | 428 (310–591) | 29.8 (11.3–78.8) | 36.0 (16.0–81.2) |
| $K_{\text{M,MC}}$ (µg L$^{-1}$)   | 25.0         | 25.0         | 25.0         | 25.0         |
| $U_{\text{max,STS}}$ (µg m$^{-3}$ min$^{-1}$) | 50.9 (4.63–560) | 507 (196–1310) | 13.8 (0.72–266) | 338 (138–827) |
| $K_{\text{M,STS}}$ (µg L$^{-1}$) | 27.5         | 27.5         | 27.5         | 27.5         |
| $U_{\text{max,HTS}}$ (µg m$^{-3}$ min$^{-1}$) | 294 (128–677) | 610 (169–2200) | 482 (190–1220) | 401 (138–1160) |
| $K_{\text{M,HTS}}$ (µg L$^{-1}$) | 15.0         | 15.0         | 15.0         | 15.0         |
| MC $R^2$                  | 0.968        | 0.957        | 0.991        | 0.954        |
| STS $R^2$                 | 0.976        | 0.871        | 0.952        | 0.952        |

*Values in parentheses represent 95% confidence intervals for the maximum volumetric uptake rates ($U_{\text{max}}$).

HTS stands for “hyporheic transient storage.”
The contribution of physical (exchange) and biological uptake (decay) varied for the two TS zones. Physical exchange with the STS zones was responsible for 6.3–84.4% of the loss in total nitrate uptake when STS zones were removed from the model \((z = 0)\) and biological uptake in the STS zones was responsible for 15.6–93.7%. Overall, the influence on total nitrate uptake was nearly evenly split between physical and biological processes for STS zones. The influence of physical and biological processes varied less for the HTS zones. Physical exchange with the HTS zones was responsible for 6.5–38.2% of the loss in total nitrate uptake when HTS zones were removed from the model \((z = 0)\) and biological uptake in the HTS zones was responsible for 61.8–93.5%. Overall, the influence on total nitrate uptake was dominated by biological uptake for HTS zones.

When STS exchange was turned off, mean decreases in total nitrate uptake varied greatly between subreaches in the Upstream reach (8.0%–49.3%) but were more consistent in the Downstream reach (12.5%–16.1%). Decay was responsible for 18.6%–73.7% of the decrease in total uptake in the Downstream reach and 15.6%–93.7% in the Upstream reach for STS zones. The absence of the STS zones not only resulted in the loss of NO\(_3\)-N uptake attributed to those zones but also a decrease in NO\(_3\)-N loss attributed to the MC and HTS compartments (Fig. 8). This is most likely due to a loss in uptake efficiency resulting from higher NO\(_3\)-N concentrations and a less dispersed NO\(_3\)-N plume. The absence of STS reduced NO\(_3\)-N mass loss attributed to the MC by 5.6% and the HTS zones by 2.1% overall in the Downstream reach and the MC by 10.4% and the HTS zones by 2.4% overall in the Upstream reach. Loss of NO\(_3\)-N uptake totaled 14.8% in the Downstream reach and 33.6% in the Upstream reach.

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**Fig. 7.** Effect of transient storage uptake on the simulated percent cumulative NO\(_3\)-N mass loss (%\(N_{\text{cum}}\)) in the MC, STS, and HTS compartments and on the compartment sum (total) from (A) DR1 (100% = 407 g NO\(_3\)-N), (B) DR2 (100% = 704 g NO\(_3\)-N), (C) UR1 (100% = 145 g NO\(_3\)-N), and (D) UR2 (100% = 222 g NO\(_3\)-N) during three modeling scenarios: (1) Both transient storage zones fully active, (2) HTS uptake turned off \((U_{\text{max,HTS}} = 0)\), and (3) STS uptake turned off \((U_{\text{max,STS}} = 0)\).

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reach when STS was turned off, which is greater than the relative NO$_3$-N mass loss attributed to STS alone in both reaches (10.8% and 29.7%, respectively) when both TS zones are active (Fig. 3C,D). This indicates a degree of dependence between the three compartments for nutrient uptake during an addition experiment.

When HTS was turned off, the relative decreases in total nitrate uptake also varied between subreaches in the Upstream reach (17.7%–82.9%) and the Downstream reach (17.2%–54.6%). The influence of physical vs. biological processes was more consistent between the subreaches. Decay was responsible for 61.8%–82.3% of the decrease in total nitrate uptake in the Downstream reach and 92.1%–93.5% in the Upstream Reach for HTS zones. The absence of the HTS zones also resulted in the loss of NO$_3$-N uptake attributed to the MC overall in the Downstream reach (6.8%) and Upstream reach (4.0%) but no significant change (<1%) in the mass loss attributed to STS overall in either reach (Fig. 8). Loss of NO$_3$-N uptake totaled 31.0% in the Downstream reach and 43.8% in the Upstream reach when HTS was turned off, which is also greater than the relative NO$_3$-N mass loss attributed to HTS alone in both reaches (26.8% and 42.8%, respectively) when both TS zones are active (Fig. 3C,D).

The loss of one TS zone generally affected the MC more than the other TS zone (Fig. 8). However, removal of a TS zone did not always result in a significant loss of NO$_3$-N uptake attributed to the MC or the other TS zone in a sub-reach. It appears that the dependence between the three stream compartments is the strongest when high concentration plumes pass by (i.e., closer to the injection point) and is weaker at lower concentrations. At high concentration and fast time of passage, the TS zones retain solute and spread the plume which enables more efficient uptake in all three compartments further downstream. Near our second sampling sites the plume is already spread enough to allow for more efficient uptake in the three compartments over longer periods of time regardless if the other TS zones are present upstream. Additionally, the geomorphology, TS size, MC-TS connectivity, and degree of nutrient limitation will affect the point downstream at which the loss of one TS zone will no longer affect the retention taking place in the MC and other TS zone.

To confirm this explanation, we ran the transport model several times for each subreach to calculate the point at which (longitudinal threshold) the loss of STS or HTS no longer significantly affected the NO$_3$-N mass taken up in the MC or other TS zone. We found that the threshold when
removing STS is longer than when removing HTS and both are longer closer to the injection (i.e., DR1 and UR1) than further from the injection point (i.e., DR2 and UR2). The longer threshold for STS is likely a result of its greater effect on the median transport time. Confirming that reach characteristics were a factor in determining specific subreach responses to the loss of a TS zone, we observed differing responses between the subreaches to the loss of STS or HTS. The loss of STS resulted in a greater decrease (10.4%) in NO3-N mass retained by the MC than did the loss of HTS (4.0%) in the Upstream reach. In the Downstream reach, the opposite was true but the effect on the mass retained by the MC was closer between the loss of the HTS (6.8%) or STS (5.6%) zones. This result complements the relative biological NO3-N loss results (see above) showing that the contribution of STS relative to HTS was greater in the Upstream Reach.

Discussion

Physical and biological processes

In-stream cycling of nitrogen is strongly controlled by biota (Horne and Goldman 1994; Duff and Triska 2000; Wetzel 2001). Success of in-stream biota depends on a limited range of temperature, substrate, water velocity, oxygen content, and light availability (Wetzel 2001), which leads biota to seek out habitats within the stream that meet these criteria. The physical processes regulating exchange with TS zones control the biologic processing capabilities by driving the types and density of biota that can exist there. Thus, TS zones should affect uptake kinetics (i.e., maximum uptake rate and half-saturation concentration). However, biota can affect some of these physical parameters for their benefit. For example, macrophyte beds can dramatically decrease velocity, increase organic matter content, and modify nutrient cycling (Clarke 2002). The physical processes controlling biological distribution and processing are not currently understood well enough to use only physical characteristics of a stream to predict biological processes.

TS zones should affect rates of nutrient uptake because they provide sites for microbial (especially HTS) and plant (STS only) communities to flourish (Thomas et al. 2003; Lautz and Siegel 2007; Argerich et al. 2011c). However, their physical traits should also aid in overall nutrient uptake and uptake efficiency during nutrient addition experiments by spreading the plume via the physical retention of solute molecules within their boundaries. While biological uptake is expected to dominate, physical retention dependent on residence times should also significantly influence overall nutrient uptake. Because STS zones generally affect the median transport time of solutes more than HTS, their physical influence is expected to be greater than that of HTS zones.

Here, we expand upon recently developed methods that allowed for the physical separation and reliable characterization of the three stream compartments and the dynamic calculation of in-stream solute uptake to explore the relative contribution of the three compartments to solute retention and transport. Adequate characterization of a stream is the first step. Sufficient description of the MC (including slope and sinuosity) and STS areas is required for selection of appropriate sampling points and reliable model parameter estimations and interpretation of data. Velocity transect surveys every 1–2 bankfull widths fill this need over a greater reach length (>20 bankfull widths; Briggs et al. 2009) and allow the measurement of gross gains and losses of discharge along the reach of interest. The gross gains and losses of discharge represent the turnover of water in a downstream direction (Covino and McGlynn 2007; Covino 2009) when gains not labeled with the tracers replace and offset losses labeled with tracers. Therefore, hydrologic turnover is an important factor and together with long-term storage and in-stream nutrient uptake regulate overall nutrient spiraling dynamics (Covino 2010b).

The second step involves conducting a simultaneous conservative and nonconservative tracer experiments and sampling in the MC and adjacent representative STS zone at multiple points along a stream. Concomitantly injecting conservative and reactive tracers allows for the separation of physical and biological parameters. For nitrate, the biological loss could result from in-stream uptake by algae or microbes, denitrification by microbes, or dissimilatory nitrate reduction to ammonium by microbes (Powers et al. 2012). Physical loss of reactive tracer mass, calculated using conservative tracer data, is a combination of gross losses of discharge to the surrounding subsurface, long-term retention in hyporheic zones, and hyporheic flow paths circumventing sampling points. Solute mass can be diluted by gross discharge gains, but not lost. Lost solute mass may be stored in groundwater, return to the channel at some point, or be taken up biologically by riparian vegetation outside of the stream channel but each of these still serve to delay downstream transport and contribute to overall solute retention (Covino 2010b).

Repeating the second step at multiple discharge levels would improve the method. Mixing and injecting the conservative and reactive tracers together is best, but only if this does not dilute the reactive tracer past the point where saturated conditions will be met at the downstream sampling sites. If coinjecting the conservative and reactive tracers is not possible, then the use of a model is necessary to describe the conservative transport of the reactive tracer for use in calculating total uptake kinetics with the TASCC method. Coinjection of conservative and reactive tracers has been used in many previous studies, but these studies only estimated uptake within the MC (Mulholland et al. 2002; Tank et al. 2008; Covino 2010b) or as first-order uptake occurring in aggregated TS zones and MC (Thomas et al. 2003; Argerich et al. 2011a; Lin and Webster 2012). Following the
separation of physical processes from biological is the separation of the influence of the three stream compartments on physical and biological solute retention.

To separate the physical and biological contributions to solute retention between the three stream compartments, a two TS zones transport model with M–M decay capabilities is required along with model parameter optimization. Calculating dynamic total uptake with first-order decay in the model will not work for a nutrient addition experiment because solute concentrations vary greatly leading to M–M uptake behavior (Covino 2010a, b; Zarnetske et al. 2012) unless concentrations remain below $K_m$. First-order decay underestimates solute uptake at low concentrations and overestimates uptake at high concentrations in all three compartments compared to M–M uptake (Z.C. Johnson unpubl.), which leads to errors in the interpretation of compartment-specific uptake. Optimization of the conservative parameters occurs first and these are used in the optimization of the biologic uptake parameters (decay) for the reactive tracer. The real-time measurement of the conservative tracer usually enables a more confident estimation of its model parameters over the less-intensively sampled reactive tracer. Newly developed in situ measurement of nitrate (Pellerin et al. 2009, 2012) may make optimization of the decay parameters more reliable in future studies. With the separation of physical from biological tracer mass loss and physical and biological retention between the three compartments, the influence of the two TS zones on total solute uptake within a stream and how those contributions change longitudinally can be addressed.

Application to a large stream

Different physical and biological stream characteristics were found in adjacent reaches of the lower Truckee River. Separation of overall physical and biological NO$_3$–N mass loss revealed markedly different ratios of physical to biological loss in these reaches. Inclusion of gross gains and losses throughout our study reaches increased model performance but were balanced and did not result in significant net gains or losses in any reach. Physical loss was always greater than hydrologic turnover in the lower Truckee River, likely indicating some loss of solute via long-term storage in the hyporheic zone.

In the lower Truckee River, ambient uptake length ($S_{w_{\text{amb}}}$) was generally shorter and ambient uptake velocity ($V_{w_{\text{amb}}}$) and areal uptake rate ($U_{w_{\text{amb}}}$) were generally greater in the Downstream reach than the Upstream reach. This indicates a greater background nutrient uptake capacity in the Downstream reach which may derive from differences in temperature, velocity, biological communities, and TS characteristics. Significantly larger $U_{\text{max}}$ values and generally larger $K_m$ values in the Downstream reach also appear to support a difference in biological communities. $U_{\text{max}}$ has been shown to be an exclusively biological parameter while $K_m$ reflects a complex combination of biological and physical mechanisms (Aksnes and Egge 1991). $U_{\text{max}}$ or $U_{w_{\text{max}}} (U_{\text{max}}/h)$ controls the maximum amount of solute taken up and reflects the biomass and biota type present in the system. $K_m$ is often considered to reflect the relative ability of an organism to use a nutrient when present in low concentrations (Reuter and Axler 1992) and the $K_m$ values were similarly low in the N-limited Truckee River reaches. Therefore, N-limitation alone cannot explain the potential differences in biological communities between the reaches. The ratio of $U_{\text{max}}$ and $K_m$, also known as specific affinity, has been suggested as a better measure of substrate affinity than either of the two parameters alone (Aksnes and Egge 1991; Reay et al. 1999). Specific affinity is the initial slope of the M–M function and is independent of uptake mechanism. With larger maximum uptake rates, similar half-saturation concentrations, and shallower mean depth, the Downstream reach also shows greater specific affinity than the Upstream reach.

The lower Truckee River had overlapping ambient and M–M total uptake parameter ranges with the only comparable study (Covino 2010b), which took place in a headwater stream system. However, relative physical losses (% 100 m$^{-1}$) were significantly smaller in both Truckee reaches and relative biological losses were significantly greater in the Truckee Downstream reach than this headwater stream system. The lower fraction of physical loss of NO$_3$–N in the Truckee River is most likely due to significantly lower gross losses of discharge, as larger stream systems tend to lose a lower fraction of water to their surroundings (Covino 2010b). Less long-term storage in the hyporheic zones of the Truckee River could also account for some of this difference. The larger biological loss of NO$_3$–N in the Downstream reach of the Truckee River may be due to differences in biological communities, $W:D$ ratios (3.9–16.8 in the small streams), and size. Similar areal uptake rates ($U$) will result in a greater mass of solute taken up in a stream with greater streambed area, which is true for the lower Truckee River. Ambient NO$_3$–N concentrations were also slightly lower in the Truckee River and may reflect greater N-limitation. However, because TN and TP data are not available from Covino et al. (2010b) we cannot be sure about differences in nutrient limitation.

We had more difficulty in fitting nutrient spiraling regression lines to the first sampling site data (DR1 and UR1) than the second sampling site data (DR2 and UR2) in our study (Figs. 4–6) using the TASCC method. This may in part be due to corrections applied to compare nonconcurrent reactive and conservative tracer injections. Differences in the calculated reactive-to-conservative ratios could have affected the calculations of uptake length, uptake velocity, and areal uptake rate. Size differences between the streams may have also influenced the reactive-to-conservative ratios.

The Truckee River results represent sorely needed data from stream systems with discharge greater than 1 m$^3$ s$^{-1}$ (Tank et al. 2008). However, only a limited comparison was
possible between this and other studies which did not produce new insight into why some streams have similar or dissimilar nutrient uptake kinetics. Discharge did not appear to be a significant factor separating nutrient spiraling patterns between stream systems. Separation of uptake between the three stream compartments may clarify the reasons for the similarities and differences between stream systems. In a BTC-integrated \( S_w \) and \( V_t \) data comparison between the lower Truckee River, the Snake River (Tank et al. 2008), and 10 small stream systems (Tank et al. 2008; Covino 2010a,b), the Snake River was the largest discharge system (12.0 m\(^3\) s\(^{-1}\)) and had one of the longest uptake lengths (2500 m), but also had the second greatest uptake velocity (7.4 mm min\(^{-1}\)). The Truckee River was the second largest discharge system in this comparison and its uptake lengths were longer and uptake velocities smaller than the larger Snake River. The other 10 stream systems (12 total data points) had much lower discharge (mean = 0.172 ± 0.029 m\(^3\) s\(^{-1}\)), generally shorter uptake lengths (mean = 2316 ± 599 m), and generally lower uptake velocities (mean = 2.38 ± 0.67 mm min\(^{-1}\)) than the large Snake River. The Truckee’s uptake lengths were generally longer than those in the 10 small stream systems but the uptake velocities overlapped.

Our modeling approach was compared to TASC’CC by setting all maximum areal uptake rate, half saturation, and mean depth values equal for the three compartments in the model. Maximum uptake rate and half-saturation concentration were then optimized. We used mean MC depths (\( h_{MC} \)) measured from the subreach for the mean compartment depth values, which was necessary to compare maximum areal uptake rates. From this comparison, we found no significant differences between the two methods for calculating total reach uptake kinetics when the individual characteristics of the stream compartments are not separated. Our model’s \( U_{\text{max}} \) (173 μg m\(^{-2}\) min\(^{-1}\)) and \( K_m \) (20.7 μg L\(^{-1}\)) values were slightly larger than TASC’CC’s (142 μg m\(^{-2}\) min\(^{-1}\) and 12.6 μg L\(^{-1}\), respectively) in the Downstream reach and slightly smaller (54.3 μg m\(^{-2}\) min\(^{-1}\) and 3.37 μg L\(^{-1}\), respectively) than TASC’CC’s (69.0 μg m\(^{-2}\) min\(^{-1}\) and 10.9 μg L\(^{-1}\), respectively) in the Upstream reach. While TASC’CC will give you information about overall reach nutrient removal, it says nothing of the complex combination of physical and biological processes occurring in the different stream compartments that lead to the overall behavior.

The relative contribution of the three stream compartments to biological NO\(_3\)-N mass loss was determined by optimizing the modified-OTIS model with NO\(_3\)-N BTC data sampled from the MC and an adjacent STS zone. Separation of the two TS zones is important for the lower Truckee River because the STS zones are significantly influenced by discharge (Q) and advective velocity (Q:A) while HTS zones are influenced by width-to-depth ratio and channel friction factor (Johnson et al. 2014). In the lower Truckee River, we observed varied influence of the three compartments on biological loss of NO\(_3\)-N when using M–M uptake in the model. The MC was consistently responsible for the greatest fraction of biological loss in the Downstream reach while TS contributions to biological loss were greater overall than the MC’s in the Upstream reach. The latter could simply be a result of low MC uptake in the Upstream reach and was different than the physical influence of the TS zones (\( F_\text{TOT}^{\text{NS}} \)) relative to the MC. The dominant nitrate uptake or loss processes occurring in the different stream compartments likely includes benthic uptake from periphyton in the MC (Warwick et al. 1999; Kish et al. 2006; Bartlett and Warwick 2009), algal (epipelvic and epilthic) uptake in the STS zones, and denitrification in the HTS zones, although these were not explicitly determined in this study. Maximum uptake rates were greatest in the HTS zones followed by the MC and STS zones. These results agree with other studies that have shown that the HTS zone is a “hot spot” for biogeochemical turnover (Argerich et al. 2011c) but the MC tends to dominate overall nutrient uptake (Stewart et al. 2011). Generally, each of the three compartments in the Downstream reach were responsible for more NO\(_3\)-N mass loss than their counterparts in the Upstream reach, which could suggest that the biologic communities in the MC and TS zones were different between the reaches. Average water temperature during these experiments was slightly higher and average solute velocities lower in the Downstream reach and could also contribute to the difference in uptake. Despite longer average HTS residence times in the Upstream reach, biological loss of NO\(_3\)-N attributed to HTS was greater in the Downstream reach. This indicates that the limited connectivity with the HTS zones, which led to longer residence times, may have inhibited solute uptake (Argerich et al. 2011c). Size of the HTS zones was not a significant factor because there was no significant difference between reaches (Johnson et al. 2014). Solute uptake in the Truckee, therefore, is likely dependent on a combination of many factors including uptake rate, connectivity to TS zones, residence time, and compartment size.

Both TS zones showed some influence on the uptake kinetics of our study reaches, where overall nitrate uptake values decreased without one of the TS zones. These decreases in uptake are a combination of the loss of uptake in the inactive TS zone and the loss of uptake in the MC and other active TS zone resulting from the loss of the inactive TS zone. This interdependence between the stream compartments was confirmed when we observed decreased uptake occurring in the MC and active TS zone when one of the TS zones was turned off (Fig. 8). However, this dependence was more pronounced closer to the injection point.

Differences were observed in biological and physical influences between STS and HTS zones which indicates dependence of solute uptake on residence time, connectivity, and between the compartments. While HTS areas were generally larger than STS areas, the differences were not large (Johnson et al. 2014). Without the separation of STS and HTS biological uptake properties in addition to physical characteristics,
we would not have predicted the varying influences of the TS zones between the two reaches. Despite reduced shading conditions in the lower Truckee River, HTS generally had more influence in nutrient uptake kinetics than STS where the loss of HTS resulted in a greater decrease in uptake values in three out of the four subreaches. This is primarily a result of the greater uptake rate in the HTS zones and, in the case of physical retention, average residence time. However, increased residence time does not necessarily result in higher uptake totals when connectivity limits the amount of solute entering the TS zone and size limits how many can enter and stay within the TS zone.

The physical vs. biological influence on nitrate uptake in the TS zones varied for zone type and subreach. Overall reach nitrate uptake was nearly equally influenced by STS physical and biological processes but these relative influences varied between subreaches. HTS biological processes were consistently more important to overall reach nitrate uptake than HTS physical processes. Despite greater influence on median transport time, STS physical retention had a similar influence on overall reach nitrate uptake as HTS physical retention. In general, the HTS zones were slightly larger than the STS zones which means that differences in residence times between the TS zones is primarily controlled by differences in exchange rate (connectivity). Differences in connectivity, residence time, and processing capabilities between the two TS zones led to the large differences in the overall nutrient uptake in the two TS zones. Similar to our results, a previous study observed higher uptake rates in TS zones with higher residence times and less connectivity (Powers et al. 2012). For STS zones, biological uptake is controlled by how many solute molecules are exposed to the biologic communities within the storage zone because they are in most cases very well mixed and connected to the MC, have uptake rates similar to or less than the MC, and have small residence times. In contrast, HTS zones are limited by the supply of solutes and oxygen because they are not as well connected to the MC and can serve as a source (nitrification) or sink (denitrification) of nitrate (Triska et al. 1989; Argerich et al. 2011b; Zarnetske et al. 2012). Therefore, HTS zones are more dependent on residence times and with higher reaction rates more thoroughly process the solute molecules that the biologic communities are able to come in contact with.

It has been observed that HTS dominate physical TS processes in small streams while STS dominate in large streams (Johnson et al. 2014). As discharge or advective velocity changes within a stream system, STS zones are predictably affected but HTS zones are not (Ward et al. 2012; Johnson et al. 2014). As width-to-depth ratios and channel friction factor change within a stream system, HTS zones are predictably affected but STS zones are not. STS has been hypothesized to dominate in-stream metabolism where a large quantity of shallow STS zones and rapid exchange exists, whereas HTS would dominate in streams with large quantity of rapid HTS exchange and deep, very slow STS exchange or a lack of STS (Argerich et al., 2011c). This may be true for physical retention (i.e., $F^{200}_{MED}$), but $F^{200}_{MED}$ does not give any information about biological processes. The Truckee River possesses many relatively shallow, fast-exchanging STS zones but we showed in this study that HTS zones dominated in-stream metabolism nonetheless. Because these two TS zones are fundamentally different biologically as well, the processing and transport of solutes in a stream system will depend on the background physical properties of the stream, connectivity between the MC and TS zones (which is also related to residence time), biological uptake rates, compartment sizes, and how these two TS zones interact with each other and the MC.

Without model separation of physical and biological uptake in the STS and HTS zones, contradictory results concerning the TS role in solute retention and transport easily occur. The methods used in this study can easily be applied to stream systems of various sizes, repeated over ranges of discharge, and can help clarify the role TS zones have on solute retention and transport within and between stream systems. Repeating these methods over a range of discharge levels and stream types will further clarify primary drivers of solute retention and transport in fluvial systems. Independently defining the dominant biological process(es) and half-saturation concentrations for each compartment will likely result in more reliable estimations of uptake rates and each compartment’s role in overall solute transport.

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