

Separation of river network–scale nitrogen removal among the main channel and two transient storage compartments

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[1] Transient storage (TS) zones are important areas of dissolved inorganic nitrogen (DIN) processing in rivers. We assessed sensitivities regarding the relative impact that the main channel (MC), surface TS (STS), and hyporheic TS (HTS) have on network denitrification using a model applied to the Ipswich River in Massachusetts, United States. STS and HTS connectivity and size were parameterized using the results of in situ solute tracer studies in first- through fifth-order reaches. DIN removal was simulated in all compartments for every river grid cell using reactivity derived from Lotic Intersite Nitrogen Experiment (LINX2) studies, hydraulic characteristics, and simulated discharge. Model results suggest that although MC-to-STs connectivity is greater than MC-to-HTS connectivity at the reach scale, at basin scales, there is a high probability of water entering the HTS at some point along its flow path through the river network. Assuming our best empirical estimates of hydraulic parameters and reactivity, the MC, HTS, and STS removed approximately 38%, 21%, and 14% of total DIN inputs during a typical base flow period, respectively. There is considerable uncertainty in many of the parameters, particularly the estimates of reaction rates in the different compartments. Using sensitivity analyses, we found that the size of TS is more important for DIN removal processes than its connectivity with the MC when reactivity is low to moderate, whereas TS connectivity is more important when reaction rates are rapid. Our work suggests a network perspective is needed to understand how connectivity, residence times, and reactivity interact to influence DIN processing in hierarchical river systems.

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1. Introduction

[2] Identifying the fate of nitrogen (N) in watersheds is important because of increasing anthropogenic N inputs [Galloway *et al.*, 2003]. Human activities such as fertilizer application, N fixation by crops, human and animal waste management, and fossil fuel emissions [Vitousek *et al.*, 1997] have the potential to saturate terrestrial ecosystems with N [Aber *et al.*, 1998] and to overwhelm the removal

capacity of streams [Mulholland *et al.*, 2008] and can ultimately lead to eutrophication of lakes and coastal waters. Nevertheless, the proportion of N retained in many basins is relatively high despite anthropogenic increases in N [Boyer *et al.*, 2002; Howarth *et al.*, 1996]. Terrestrial systems account for much of the N retained in watersheds [Goffman *et al.*, 2004; Wollheim *et al.*, 2005], but aquatic systems also play an important role [Bernhardt *et al.*, 2005], particularly during summer low-flow periods because transport times are longer [Wollheim *et al.*, 2008a]. Here we focus on in-stream denitrification (i.e., N removal), the permanent sink of nitrate, which dominates dissolved inorganic nitrogen (DIN) in many basins. The removal of DIN is important considering organic forms tend to be less than 50% of total dissolved N in northeast rivers [Scott *et al.*, 2007] and inorganic N limits primary productivity in many estuaries [Howarth and Marino, 2006]. A significant challenge is to understand the factors that regulate denitrification at river network scales because of the complex interaction between physical processes and microbial communities.

[3] N removal in aquatic systems is a function of (1) the strength of biological activity [Fellows *et al.*, 2001; Triska *et al.*, 1989], (2) the proportion of solute mass exposed to biologically active surfaces [Harvey *et al.*, 1996], and

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(3) the duration of exposure to these surfaces [Findlay, 1995; Runkel, 1998]. These factors are commonly identified as reaction rates, connectivity, and residence time, respectively. Such factors have been well defined at whole reach scales [Bencala and Duff, 1993; Briggs et al., 2009; Hall et al., 2002; Mulholland and DeAngelis, 2000; Peterson et al., 2001; Thomas et al., 2003] and are controlled by a combination of biologic, hydrologic, and geomorphic components that vary over space and time [Doyle, 2005; Wollheim et al., 2006, 2008a]. Stream channels are composed of different habitats, each potentially with their own reaction rates, connectivity, and residence times. Understanding the relative contribution of these habitats at network scales has not been explored.

[4] Habitats in stream channels can be partitioned into advective and nonadvective zones. The advective zone, or the main channel (MC), comprises the majority of the river cross-sectional area where the highest velocities occur. Nonadvective, or transient storage (TS), zones are flow paths with significantly reduced downstream velocities, e.g., the hyporheic zone or side pools [Choi et al., 2000; Gooseff et al., 2004]. TS zones have been shown to influence DIN fluxes because they extend residence times and increase exposure with biochemically reactive surfaces [Baker and Dahm, 2000; Briggs et al., 2009; Dahm et al., 1998; Ensign and Doyle, 2005; Findlay, 1995; Hancock et al., 2005; Harvey and Wagner, 2000]. TS hydraulic data measured in the field have been paired with nutrient reaction rates to quantify the role of TS in DIN removal at the reach scale. A strong correlation between TS characteristics and DIN removal has been documented in some river segments [Faulkner and Campana, 2007; Hall et al., 2002; Mulholland and DeAngelis, 2000; Thomas et al., 2003], whereas weaker correlations [Hall et al., 2002; Lautz and Siegel, 2007] or no correlation at all [Ensign and Doyle, 2006] have also been reported. The unresolved role of TS in DIN removal has been attributed to heterogeneity of TS hydraulics and biogeochemical processes across systems, within systems, and through time [Thomas et al., 2003].

[5] To further investigate these dynamics, it is necessary to categorize nonadvective zones into surface TS (STS) and hyporheic TS (HTS) [Harvey et al., 2005; Briggs et al., 2009; Marion et al., 2008] because these two compartments can have significantly different hydraulic and biogeochemical conditions [Thomas et al., 2003]. Until recently, traditional field methods have been unable to distinguish the relative control STS and HTS have on water transport [Harvey et al., 2005; Briggs et al., 2009], and this has inhibited more detailed study of DIN removal dynamics in aquatic systems.

[6] STS includes side pools or back eddies along the river channel [Gooseff et al., 2004; Harvey et al., 1996], where water exchange from the channel is controlled by lateral dispersion [Fischer et al., 1979] and turbulent processes [Ghisalberti and Nepf, 2002]. Subsurface HTS is located beneath or adjacent to the water column where water is forced into sediments via Darcian flow through porous media [Harvey and Bencala, 1993], interacts with microbial communities and groundwater, and then resurfaces at some distance downstream. Because of underlying differences in STS and HTS environments, biogeochemical processes in the two compartments are likely to differ.

For instance, STS are depositional zones that typically accumulate large stocks of organic matter [Hall et al., 2002], whereas HTS facilitates considerable water exposure to sediment biofilms and alternating oxic and anoxic environments.

[7] Previous studies have shown that a river network perspective is essential to understand DIN removal processes because of the complex interactions within hierarchical, branching river systems [Benda et al., 2004; Thorp et al., 2006] where downstream river segments buffer upstream inefficiencies associated with increased DIN inputs [Mulholland et al., 2008] and discharge [Wollheim et al., 2008a]. Previous river network models do not incorporate TS processes. Instead, they generally assume that biological rates are independent of river size and changes in N removal are driven by predictable downstream adjustments in river hydraulics [Seitzinger et al., 2002; Wollheim et al., 2006, 2008a]. This is a valid preliminary approach because river size is directly correlated to benthic surface-to-volume ratios. However, this assumption ignores the potentially critical role of water exchange between advective and nonadvective compartments. If TS dynamics are important controls for DIN removal processes, these factors should be incorporated into river network models. Further, separating a lumped TS compartment into STS and HTS is essential so that we can identify where DIN processing is occurring in river cross sections under various reactivity scenarios.

[8] Here we apply a spatially distributed river network model to examine the role of MC, STS, and HTS compartments in Network-Scale DIN removal during a summer base flow period. Our goals with respect to DIN removal by MC, STS, and HTS at network scales are to determine (1) the relative contribution of each compartment, (2) the role of river size, (3) how various combinations of hydraulic and biological parameter values influence removal, and (4) Network-Scale residence times.

2. Methods

2.1. Study Site

[9] The Ipswich River is a Fifth-order coastal watershed located approximately 30 km north of Boston, Massachusetts, and is experiencing rapid suburbanization. The watershed has a shallow average slope (0.06%) [Claessens et al., 2006], drains an area of approximately 400 km², and consists of 36% forest, 30% suburban, 20% wetlands, 7% agriculture, 4% industrial/commercial, and 3% open water [Wollheim et al., 2008a]. Nearly 10% of the basin is impervious. The population density in the basin is 302 people per km², and 60% of the population is served by septic systems. Mean annual precipitation is approximately 1188 mm yr⁻¹, 45% of which is converted to runoff reaching the basin mouth [Claessens et al., 2006]. Mean annual discharge at the basin mouth is 5.4 m³ s⁻¹ and typical summer base flow is approximately 1.0 m³ s⁻¹. The Ipswich River has high nitrate concentrations that are correlated with suburban and agriculture land types [Williams et al., 2004; Wollheim et al., 2005]. Because of an increase in anthropogenic disturbances, there have been significant changes to the system's hydrology [Claessens et al., 2006; Pellerin et al., 2007], DIN inputs [Williams et al., 2004], and DIN retention in headwater catchments [Wollheim et al., 2005].

2.2. River Network Model

[10] The Ipswich River TS DIN removal model was developed to evaluate the role of aquatic TS on DIN removal processes at river network scales. This spatially distributed, gridded river network model simulates DIN fluxes on a daily time step, accounting for serial processing along surface water flow paths. It differs from earlier versions [Wollheim *et al.*, 2008a] by accounting for exchange between the MC and two TS compartments in each pixelated stream reach. Hydraulic and biogeochemical field measurements were used to specify spatially distributed runoff and DIN inputs from land, which are then routed downstream, and to parameterize hydraulic and biological processes that determine aquatic transformations during routing. The Ipswich River network TS DIN removal model is operated within the University of New Hampshire aquatic modeling system, the Framework for Aquatic Modeling in the Earth System (FRAMES) [Wisser *et al.*, 2010; Wollheim *et al.*, 2008a, 2008b].

[11] Nitrogen removal in each grid cell in the river network was simulated on a daily time step using a stream TS model modified from Mulholland and DeAngelis [2000] to incorporate three channel compartments (Figure 1). DIN removal by the channel in each surface water grid cell is partitioned into removal by the MC, STS, and HTS compartments and is calculated as

$$R_i = R_{MC,i} + (TE_{STS,i}R_{STS,i}) + (TE_{HTS,i}R_{HTS,i}), \quad (1)$$

where R_i (dimensionless) is the total proportional removal of DIN within grid cell i , $R_{MC,i}$ (dimensionless),

$R_{STS,i}$ (dimensionless), and $R_{HTS,i}$ (dimensionless) are the proportional removal of DIN that enters into the MC, STS, and HTS compartments within grid cell i , respectively, and $TE_{STS,i}$ (dimensionless) and $TE_{HTS,i}$ (dimensionless) are the fractions of discharge and mass solute entering the STS and HTS compartments within grid cell i , respectively. The transfer (TE), removal (R), and residence time (τ) terms for each compartment in grid cell i are defined as

$$R_{MC,i} = 1.0 - \exp(-v_{f,i}/H_{L,i}), \quad (2)$$

$$TE_{\chi TS,i} = (\alpha_{\chi TS,i} A_{MC,i} L_i) / Q_i, \quad (3)$$

$$R_{\chi TS,i} = 1.0 - \exp(-k_{t,i} \tau_{\chi TS,i}), \quad (4)$$

$$v_{f,i} = k_{t,i} d_{LINUX2}, \quad (5)$$

$$H_{L,i} = Q_i / (w_i L_i), \quad (6)$$

$$\tau_{\chi TS,i} = A_{\chi TS,i} / (\alpha_{\chi TS,i} A_{MC,i}), \quad (7)$$

$$\tau_{MC,i} = L_i / (Q_i / A_{MC,i}), \quad (8)$$

where $v_{f,i}$ is the apparent nutrient uptake velocity ($L T^{-1}$), $k_{t,i}$ is the time-specific DIN uptake rate (T^{-1}), d_{LINUX2} is the average water depth (L) across all Lotic Intersite Nitrogen Experiment (LINUX2) experiments, $H_{L,i}$ is hydraulic load ($L T^{-1}$), w_i is width (L), L_i is reach length (L), $\alpha_{\chi TS,i}$ is the

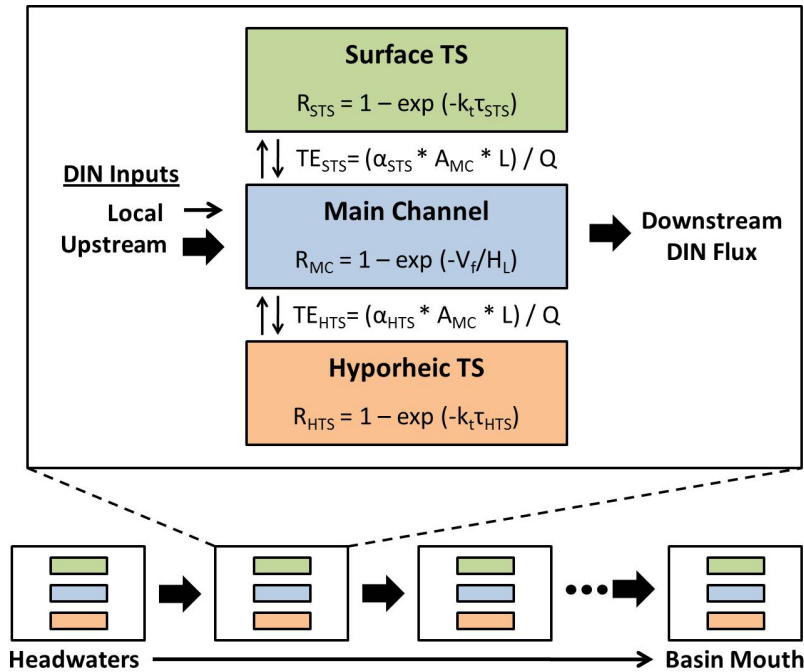


Figure 1. Conceptual model of main channel (MC), surface transient storage (STS), and hyporheic transient storage (HTS) dissolved inorganic nitrogen (DIN) removal for a single river grid cell, derived from Mulholland and DeAngelis [2000] and updated to account for two TS compartments. The resulting DIN flux goes downstream to the next sequential grid cell where the same processes occur and so on to the basin mouth.

exchange coefficient for the STS or HTS compartment (T^{-1}), $A_{MC,i}$ is the cross-sectional area of the MC (L^2), $A_{\chi TS,i}$ is the cross sectional area of the STS or HTS compartment (L^2), Q_i is the average daily discharge ($L^3 T^{-1}$), $\tau_{\chi TS,i}$ is the residence time of water in the STS or HTS compartment (T), and $\tau_{MC,i}$ is the residence time of water in the MC compartment (T).

[12] It is important to note the underlying differences in the two nutrient removal metrics applied in this study. We assume a constant reaction rate on the benthic surfaces in the MC and within the volumetric matrices of STS and HTS. To achieve this, we apply a vertical uptake velocity to the MC (v_f) and time-specific volumetric DIN uptake rates (k_i) to STS and HTS compartments. In practice, this approach keeps the biological reaction rates independent of stream size or TS size (see *Wollheim et al.* [2006] for discussion). While size independence is unlikely in reality, it allows us to explore interactions among MC-TS connectivity and reaction rate intensity at network scales.

[13] The downstream flux of DIN from grid cell i ($FLUX_i$) is calculated as

$$FLUX_i = (UP_i + LC_i)(1.0 - R_i), \quad (9)$$

where UP_i ($M T^{-1}$) is the sum of DIN inputs flowing into grid cell i from immediately upstream grid cells during the time step and LC_i ($M T^{-1}$) is the total DIN input from land generated within grid cell i . The output flux from immediate upstream grid cells become the input flux to the cell immediately downstream and so on downstream for the sequence of cells to the river mouth. Removal is calculated on a daily time step.

2.2.1. Simulated Runoff, River Geomorphology, and DIN Inputs

[14] Spatially distributed daily runoff conditions for the summer base flow period were determined from runoff estimated from U.S. Geological Survey (USGS) gauges and were scaled on the basis of impervious surfaces and contributing area. This procedure to estimate summer flow conditions was applied by *Wollheim et al.* [2008a] and has since been modified to account for the different hydrologic regimes of the densely developed upper drainage basin and the less developed lower basin. Runoff for the upper basin was calculated using discharge measured at USGS gauge station 01101500 at Middleton. Runoff for the lower portion of the watershed was based on the difference in discharge measured at the Middleton gauge and the USGS gauge station 01102000 at Ipswich and then was scaled by the amount of interstation contributing drainage area. A complete water balance was achieved at the basin scale. The month of August 2001 was selected as the primary study period because the range of base flow conditions observed at the river mouth (mean of $1.32 \text{ m}^3 \text{ s}^{-1}$, median of $0.91 \text{ m}^3 \text{ s}^{-1}$, standard deviation of $0.82 \text{ m}^3 \text{ s}^{-1}$, $n = 31$) matched the range in flow conditions at the river mouth during field measurements of hydraulic parameters (mean of $1.30 \text{ m}^3 \text{ s}^{-1}$, median of $1.05 \text{ m}^3 \text{ s}^{-1}$, standard deviation of $0.89 \text{ m}^3 \text{ s}^{-1}$, $n = 6$) [*Briggs et al.*, 2010].

[15] A 120 m grid resolution (STN-120) digital topological river network was used to route water and constituents

downstream. Greater detail on the network is presented by *Wollheim et al.* [2008a]. Discharge is calculated in every grid cell with upstream contributing area greater than 0.5 km^2 . Simulated discharge was then used to calculate river hydraulic geometry with downstream and at-a-site power law relationships [*Leopold and Maddock*, 1953; *Park*, 1977] on the basis of empirical relationships determined in the Ipswich network. Mean annual channel width (W_a , L) and depth (D_a , L) in river grid cell i were calculated from mean annual discharge (Q_a) using power law relationships from 10 USGS streamflow gauges [*Zarriello and Ries*, 2000] and 8 years of field data collected at two headwater stream locations (Plum Island Ecosystem LTER, unpublished data, <http://www.lternet.edu/sites/pie/>):

$$W_a = 9.56 Q_a^{0.65}, \quad (10)$$

$$D_a = 0.45 Q_a^{0.17}. \quad (11)$$

Instantaneous channel width and depth in grid cell i (w_i and d_i , L) at each time step are based on the at-a-site power relationship with instantaneous discharge (q_i , L^3/T):

$$w_i = a_i q_i^y, \quad (12)$$

$$d_i = b_i q_i^z \quad (13)$$

$$A_{MC} = w_i d_i, \quad (14)$$

where $a_i = W_a/Q_a^y$, $b_i = D_a/Q_a^z$, and A_{MC} is the cross-sectional area of the main channel (L^2). The values for y and z are 0.1 and 0.4, respectively, and are based on Ipswich data [*Zarriello and Ries*, 2000] and are typical of rivers worldwide [*Park*, 1977].

[16] Spatially distributed DIN inputs to the river network were derived from empirical relationships between DIN concentration, runoff magnitude, and land use (residential, commercial, and agricultural) [*Wollheim et al.*, 2008a]. DIN input concentrations during low-flow conditions range between 0 and 1.4 mg L^{-1} as determined by a sigmoid function with percent human land use [*Wollheim et al.*, 2008a]. This assumes headwater streams are representative of terrestrial inputs and is consistent with previous findings [*Brookshire et al.*, 2009]. Most DIN enters the Ipswich network in its headwaters as approximately 80% of all watershed area drains directly to first- and second-order river segments. Input concentration estimates match observations best when flow conditions measured at the basin mouth are greater than $1 \text{ m}^3 \text{ s}^{-1}$ [*Wollheim et al.*, 2008a], as was typical of base flow during the model study period.

2.2.2. Network-Scale Hydraulic and Removal Metrics

[17] To understand the function of TS in DIN processing, it is necessary to quantify the hydraulic interactions between advective and nonadvective habitats at reach and network scales. We adjusted several existing metrics to assess the importance of water exchange with two TS compartments and residence times from a network perspective. The fraction of median travel time due to STS or HTS (F_{med}) is a commonly applied metric in evaluating the

relevance of TS control on water transport [Runkel, 2002]. The F_{med} for STS or HTS (χTS) can be calculated as

$$F_{\text{med},\chi\text{TS}} = \left[1 - e^{\left(\frac{-L\alpha\chi\text{TS}}{u}\right)} \right] \frac{A_{\chi\text{TS}}}{(A_{\text{MC}} + A_{\chi\text{TS}})}, \quad (15)$$

where α is the exchange coefficient for the χTS compartment, u is velocity ($L T^{-1}$), and $u = (Q/A_{\text{MC}})$. To compare studies conducted at different scales, a standard distance (L) of 200 m is typically applied (F_{med}^{200}) [Runkel, 2002].

[18] The average flow path distance required for a water molecule to enter HTS or STS once (S_{HTS} or S_{STS}) was derived from the work of Mulholland [1994] and is calculated by dividing the total length of a particular river order by the summation of $\text{TE}_{\chi\text{TS}}$ terms (equation (3)) for the river order:

$$S_{\chi\text{TS},Z} = \frac{\sum_{i=1}^n [L_{Z,i}]}{\sum_{i=1}^n [\text{TE}_{\chi\text{TS},Z,i}]}, \quad (16)$$

where $S_{\chi\text{TS},Z}$ is the flow path distance (L) required to enter the STS or HTS one time for a stream of order Z , n is the total number of grid cells of stream order Z , i is a particular grid cell of stream order Z , and $L_{Z,i}$ is the length of the river in grid cell i (L).

[19] The number of times a water molecule enters TS along a flow path in the river network could be an important biogeochemical indicator. In a well-mixed water column, the number of TS entries by an average water molecule that begins its flow path at grid cell j to the river mouth is calculated as

$$\text{EN}_{\chi\text{TS},j} = \sum_{i=1}^n [\text{TE}_{\chi\text{TS},i}], \quad (17)$$

where $\text{EN}_{\chi\text{TS},j}$ is the number of entries into STS or HTS for an average water molecule along its flow path from the grid cell of runoff entrance to the network (j) to the basin mouth, i is a particular river grid cell in sequence to the river mouth, n is the total number of river grid cells in sequence to the river mouth and $\text{TE}_{\chi\text{TS}}$ is defined in equation (3). A Basin-scale average ($\text{EN}_{\chi\text{TS},\text{basinavg}}$) is calculated by dividing the total number of entries of runoff to all surface water grid cells (k is the total number of grid cells) by the total volume of runoff generated by all grid cells (RO_j):

$$\text{EN}_{\chi\text{TS},\text{basinavg}} = \frac{\sum_{j=1}^k [\text{EN}_{\chi\text{TS},j}\text{RO}_j]}{\sum_{j=1}^k [\text{RO}_j]}. \quad (18)$$

[20] The total residence time ($\tau_{\text{Flowpath},T}$) that an average water molecule spends in STS, HTS, and MC compartments along its flow path from the grid cell of runoff entrance to the network (j) to the basin mouth is calculated as

$$\tau_{\text{Flowpath},\chi\text{TS},j} = \sum_{i=1}^n [\text{TE}_{\chi\text{TS},i}\tau_{\chi\text{TS},i}] \quad (19)$$

$$\tau_{\text{Flowpath},\text{MC},j} = \sum_{i=1}^n [\tau_{\text{MC},i}], \quad (20)$$

where i is the particular river grid cell, n is the total number of river grid cells in sequence to the river mouth, and $\tau_{\chi\text{TS}}$ and τ_{MC} (T) are defined in equations (7) and (8), respectively.

[21] Basin-scale averages (τ_{basinavg}) for MC, HTS, and STS are calculated by weighting the average residence time in each compartment ($\tau_{\text{Flowpath},\text{MC},j}$, $\tau_{\text{Flowpath},\text{HTS},j}$, and $\tau_{\text{Flowpath},\text{STS},j}$) by the volume of runoff that travels through each flow path (RO_j) for all flow paths in the river network (k):

$$\tau_{\text{basinavg}} = \frac{\sum_{j=1}^k [\tau_{\text{Flowpath},j}\text{RO}_j]}{\sum_{j=1}^k [\text{RO}_j]}. \quad (21)$$

[22] Network-Scale DIN removal in the MC, STS, and HTS of each river order Z as a proportion of total inputs to the entire river network is calculated as

$$\text{RN}_{\text{MC},Z} = \frac{\sum_{i=1}^n [\text{R}_{\text{MC},i}\text{UP}_i + \text{LC}_i]}{\sum_{g=1}^h [\text{LC}_g]}, \quad (22)$$

$$\text{RN}_{\text{STS},Z} = \frac{\sum_{i=1}^n [(\text{R}_{\text{STS},i}\text{TE}_{\text{STS},i})\text{UP}_i + \text{LC}_i]}{\sum_{g=1}^h [\text{LC}_g]}, \quad (23)$$

$$\text{RN}_{\text{HTS},Z} = \frac{\sum_{i=1}^n [(\text{R}_{\text{HTS},i}\text{TE}_{\text{HTS},i})\text{UP}_i + \text{LC}_i]}{\sum_{g=1}^h [\text{LC}_g]}, \quad (24)$$

where Z is a specific river order, i is a river grid cell of river order Z , n is the total number of the Z -order river grid cells, ($\text{UP}_i + \text{LC}_i$) is the total mass entering river grid cell i , g is a particular land grid cell, h is the total number of land grid cells in the model, and LC_g is the local input of DIN from land grid cell g .

2.2.3. Parameterization of Transient Storage Hydraulic Characteristics

[23] Specific TS hydraulic parameters that characterize the connectivity between MC and TS and residence times of TS are required to model DIN removal in nonadvective zones (Figure 2). STS and HTS hydraulic parameters (α_{STS} , α_{HTS} , $A_{\text{STS}}/A_{\text{MC}}$, and $A_{\text{HTS}}/A_{\text{MC}}$) are based on values reported for six tracer experiments conducted during summer low-flow periods in first- through Fifth-order stream segments within the Ipswich and Parker rivers [Briggs *et al.*, 2010]. Because of the lognormal distribution of the data, a log-transformed mean was calculated for each parameter value, retransformed via exponentiation to original units, and applied in the network model [Yevjevich,

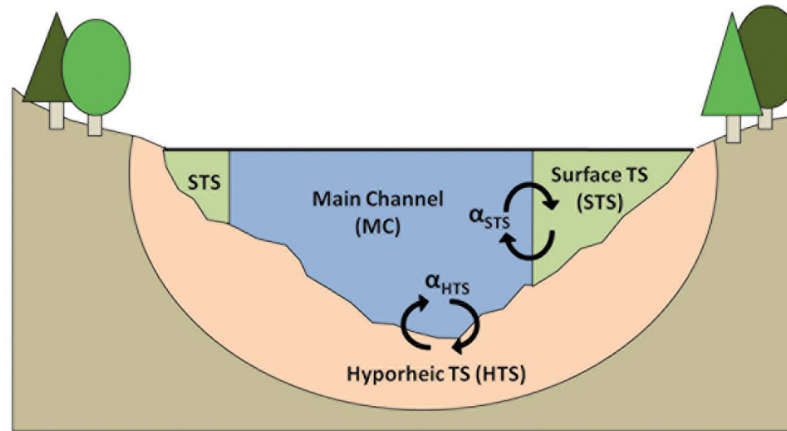


Figure 2. Conceptual diagram of advective (MC) and nonadvective (STS and HTS) compartments in a river cross section. The cross-sectional areas of the blue, green, and orange regions represent A_{MC} , A_{STS} , and A_{HTS} , respectively. Exchange coefficients (α_{STS} , α_{HTS}) characterize the compartment's connectivity with the MC.

1987]. From this point forward, retransformed lognormal mean values are simply referred to as mean values. The mean exchange coefficient for the STS ($1.3 \times 10^{-4} \text{ s}^{-1}$) is about an order of magnitude higher than the mean exchange coefficient for the HTS ($9.5 \times 10^{-6} \text{ s}^{-1}$), while the mean cross-sectional area of the STS relative to the MC ($A_{STS}/A_{MC} = 0.20$) is smaller than the mean value for A_{HTS}/A_{MC} (0.35) (Table 1) [Briggs *et al.*, 2010]. Uncertainty in each parameter mean value was quantified with a 95% confidence interval (Table 1). While these experiments indicate that A_{STS} , A_{HTS} , and A_{MC} increase with contributing drainage area, the relationships provide little evidence that the relative cross-sectional areas (A_{STS}/A_{MC} and A_{HTS}/A_{MC}) change with stream size. However, this could be due to a small sample size, and heterogeneity may overwhelm an underlying gradient.

2.2.4. Biological Activity

[24] Net DIN removal rates were based on denitrification measurements from $^{15}\text{NO}_3$ tracer experiments performed during the summers of 2003, 2004, and 2005 in eight headwater streams in the Ipswich and Parker river watersheds as part of the LINX2 project [Mulholland *et al.*, 2008]. We assume that headwater DIN loss kinetics can be applied throughout the network because previous work has not suggested reactivity rates in large and small rivers differ substantially [Ensign and Doyle, 2006; Pina-Ochoa and Alvarez-Cobelas, 2006; Wollheim *et al.*, 2006]. DIN in the Ipswich River is dominated by NO_3 [Williams *et al.*, 2004; Wollheim *et al.*, 2005]; therefore, we apply NO_3 removal rates directly to DIN. The time-specific biological reactivity rate (k_r) required in TS and the MC to match observed whole-reach denitrification uptake velocities (v_f) was

solved for each of the eight experiments using a single-compartment version of the TS model presented in Figure 1. A lumped compartment model was used here because the LINX2 data were not partitioned between STS and HTS compartments. A denitrification k_r value for each stream was computed using the Solver function in Excel, and a lognormal mean was calculated from all eight streams. The resulting retransformed mean reactivity rate was 0.64 d^{-1} . From this point forward, the retransformed lognormal mean reaction rate is referred to as the mean reactivity rate. This was applied uniformly to STS and HTS throughout the river network. The average depth across all the LINX2 stream experiments was 0.131 m; therefore, applying equation (5) and a k_{MC} value of 0.64 d^{-1} , we calculate a v_f value of 0.084 m d^{-1} . This uptake velocity was applied to MC uniformly throughout the network, under the assumption that MC reactivity occurs at the water-sediment interface and is constant per unit benthic surface area [see Wollheim *et al.*, 2006]. As such, denitrification rates in the STS, HTS, and MC are all calculated from the same reactivity rate ($k_r = 0.64 \text{ d}^{-1}$).

[25] It is highly unlikely that reactivity in the three compartments are identical, but there are very few studies that separate processing rates between advective and nonadvective zones of the stream channel [Thomas *et al.*, 2003]. Generally, HTS is hypothesized to have the highest nitrate removal rates because water would encounter more biofilms and anoxic zones in the subsurface than in surface water [Hall *et al.*, 2002]. STS is a depositional zone for organic matter and could promote favorable conditions for denitrification relative to the MC [Hall *et al.*, 2002]. We applied a k_r directly to the STS instead of the uptake

Table 1. Summary of Transient Storage (TS) Hydraulic and Reactivity Parameters

Statistic	α_{STS}	α_{HTS}	A_{STS}/A_{MC}	A_{HTS}/A_{MC}	k_r
<i>N</i>	6	6	6	6	8
Lognormal mean	-8.95	-11.6	-1.59	-1.06	-0.45
Lognormal standard deviation	0.41	0.76	0.37	1.71	1.1
Retransformed mean (original units)	$1.3 \times 10^{-4} \text{ (s}^{-1}\text{)}$	$9.53 \times 10^{-6} \text{ (s}^{-1}\text{)}$	$0.20 \text{ (m}^2 \text{ m}^{-2}\text{)}$	$0.35 \text{ (m}^2 \text{ m}^{-2}\text{)}$	$0.64 \text{ (d}^{-1}\text{)}$
Retransformed 95% confidence interval (original units)	$0.94 - 1.82 \times 10^{-4} \text{ (s}^{-1}\text{)}$	$0.49 - 18.5 \times 10^{-6} \text{ (s}^{-1}\text{)}$	$0.15 - 0.27 \text{ (m}^2 \text{ m}^{-2}\text{)}$	$0.09 - 1.36 \text{ (m}^2 \text{ m}^{-2}\text{)}$	$0.26 - 1.53 \text{ (d}^{-1}\text{)}$

velocity v_f because denitrification may occur within the volumetric matrices of stagnant, vegetated side pools. We applied uniform reaction rates to all three compartments in order to understand the relative importance of connectivity, residence times, and reaction rates. As such, the findings reported here should be considered as preliminary results, which will be improved as better reaction rate data become available. To test the sensitivity of Network-Scale DIN removal to different processing rates, alternative scenarios were developed that varied (1) the uniform processing rate applied to all three compartments and (2) independent rates in each compartment.

2.3. Observed Data

[26] Observed DIN concentrations at the basin mouth and along longitudinal transects were used to test model results. Observed concentrations at the mouth were based on 2 day composite samples collected by an automated sampler during the months of July, August, and September (2002–2006). The Wilcoxon two-sample test was applied to quantify whether the predicted and observed DIN concentrations at the river mouth have the same median value across various flow conditions. In addition, a synoptic survey of DIN concentrations was conducted on 26 August 2001 at 15 locations along the main stem and tributaries of the Ipswich River. Additional synoptics were collected on other dates and were used to confirm the generality of the results. The Nash-Sutcliffe coefficient was used to compare predicted and observed DIN concentrations along a basin profile of the longest distance from the river mouth to a headwater stream.

2.4. Scenarios

[27] Scenarios were developed to test the sensitivity of river network-scale DIN removal to uncertainties in the magnitudes and spatial distribution of TS hydraulic and biologic parameters (Table 2). In the base scenario (scenario 1), the mean values for each of the five parameters ($A_{HTS}/A_{MC} = 0.35$, $A_{STS}/A_{MC} = 0.20$, $\alpha_{HTS} = 9.5 \times 10^{-6} \text{ s}^{-1}$, $\alpha_{STS} = 1.3 \times 10^{-4} \text{ s}^{-1}$, and MC $v_f = 0.084 \text{ m d}^{-1}$ or $k_f = 0.64 \text{ d}^{-1}$) were applied uniformly to all grid cells, resulting in a continuous gradient in the size of TS throughout the river network. These estimates represent our “best understanding” of parameter values throughout the basin on the basis of empirical findings. To address the uncertainty in network DIN removal associated with these empirical averages, a Monte Carlo analysis was conducted (500 model runs) using randomly selected combinations of the five parameter values (scenario 2, Table 2) from ranges developed from the lognormal mean and standard deviation for each parameter (Table 1). Random values for each

parameter were selected from a lognormal distribution using a rational approximation [Odeh and Evans, 1974; Salas, 1993] and were applied uniformly throughout the river network. Next, sensitivity analyses were conducted to evaluate the response of Network-Scale DIN removal to a hypothetical range in hydraulic (scenario 3) and reactivity parameters (scenario 4) in each compartment. In these scenarios, a single parameter is adjusted while all other parameters are held constant. Finally, the role of spatial heterogeneity was evaluated by testing the sensitivity of network DIN removal to 500 random spatial configurations of hydraulic and biogeochemical parameters (scenario 5). In this scenario, each grid cell was assigned a random parameter value selected from lognormal distributions developed from the lognormal mean and standard deviation for each parameter (Table 1). STS and HTS hydraulic parameters vary independently, while processing rates in the three compartments are identical within a grid cell but vary spatially. This latter scenario simulates how hot spots and cold spots of TS characteristics may influence DIN removal.

3. Results

3.1. MC-STS and MC-HTS Connectivity: Base Scenario

[28] Connectivity between MC and STS was much greater than between MC and HTS. For the base scenario, using the empirical field data exchange coefficients, the longitudinal flow path distance required for an average water molecule to enter the HTS (S_{HTS}) is approximately 10 times the distance of S_{STS} (Table 3). This is expected on the basis of empirical findings [Briggs *et al.*, 2010], which indicate water exchange coefficients (α , T^{-1}) were much greater for the STS than the HTS (Table 1). Model results further quantify this connectivity across stream orders. Per unit length, connectivity is greatest in headwater streams, but per stream order it is greatest in the higher-order reaches because the longer reaches result in more frequent exchange between the channel and TS (Table 3). The average distance required for one entry into HTS is longer than the average reach length for all streams except Fifth-order segments (Table 3).

[29] At the scale of the entire Ipswich network, we find that water molecules enter STS many more times than they enter the HTS. Half of the runoff generated basin wide during base flow periods enters the STS at least 36 times as it travels through the river network (Figure 3). Some water molecules enter the network at the most distant headwater streams and, therefore, are estimated to pass through the STS as much as 75 times during transit to the basin mouth.

Table 2. Summary of Model Scenarios

Scenario	Description	TS Hydraulic Parameters	Reactivity Parameters
1	Base Scenario: uniform parameter values (mean)	Mean network values	Mean network value
2	Uniform parameter values (Monte Carlo analysis)	Uniform network values randomly selected from lognormal distributions	Uniform network values randomly selected from lognormal distributions
3	Sensitivity to TS hydraulic parameters	Hypothetical range	Mean network value
4	Sensitivity to reactivity parameters	Mean network values	Hypothetical range
5	Spatial heterogeneity (Monte Carlo Analysis)	Grid cell values randomly selected from lognormal distributions	Grid cell values randomly selected from lognormal distributions

Table 3. Average Number of Water Molecule Entries Into STS, HTS, and Residence Times for Base Scenario^a

River Order	Mean Reach Length (km)	Average Number of TS Entries per Water Molecule per km		Average Travel Distance Required for One Entry Into TS (km)		Average Number of TS Entries per Water Molecule per Mean Reach Length		Cumulative Residence Time per Water Molecule per Mean Reach Length (days)		
		STS	HTS	STS	HTS	STS	HTS	STS	HTS	MC
1	0.65	3.60	0.26	0.28	3.79	2.34	0.17	0.04	0.07	0.21
2	1.33	2.70	0.20	0.37	5.05	3.60	0.26	0.06	0.11	0.32
3	2.77	2.07	0.15	0.48	6.59	5.74	0.42	0.10	0.18	0.51
4	5.62	1.70	0.12	0.59	8.04	9.54	0.70	0.17	0.30	0.85
5a	13.3	1.26	0.09	0.79	10.8	16.8	1.23	0.30	0.52	1.50
5b	23.5	1.02	0.07	0.99	13.4	23.9	1.75	0.43	0.74	2.12

^aThe average number of surface transient storage (STS) and hyporheic transient storage (HTS) entries per 200 m Ipswich segment are 0.58 and 0.04, respectively.

Predicted connectivity between MC and HTS at network scales is much lower than between MC and STS. On average, 50% of runoff enters the HTS at least 2.6 times during its flow path through the network (Figure 3), and the maximum number of entries for an average water molecule is 5.6. Over 90% of runoff water molecules pass through HTS at least once before exiting the river network.

3.2. MC, STS, and HTS Residence Times: Base Scenario

[30] At the scale of individual TS zones, the model predicts a network-wide average residence time of 0.02 days per entry into the STS and 0.4 days per entry into the HTS before continuing downstream. Predicted residence times match the log-transformed average empirical residence times of 0.02 and 0.4 days for STS and HTS, respectively, measured at the six experiment sites [Briggs *et al.*, 2010].

Residence times per grid cell in the MC compartment (120 m, or 170 m flow length) range from 0.01 to 0.07 day, with shorter durations occurring in downstream river segments. Per mean order length, the cumulative residence time of a water molecule in the MC is almost twice as long as the combined residence time it spends in the STS and HTS (Table 3).

[31] At the network scale, total residence time in TS is determined by the distribution of runoff, geomorphology, the probability of water entering TS in each grid cell, and the residence time of water upon entry into TS. Half the runoff generated at base flows in the Ipswich has a total residence time of at least 3.3 days in the MC, 1.1 days in HTS, and 0.7 day in STS (Figure 4). This suggests that the average runoff molecule will spend a total of nearly 5 days in the river network at low flow, 65% of this time in the MC, 22% in HTS, and 13% in STS.

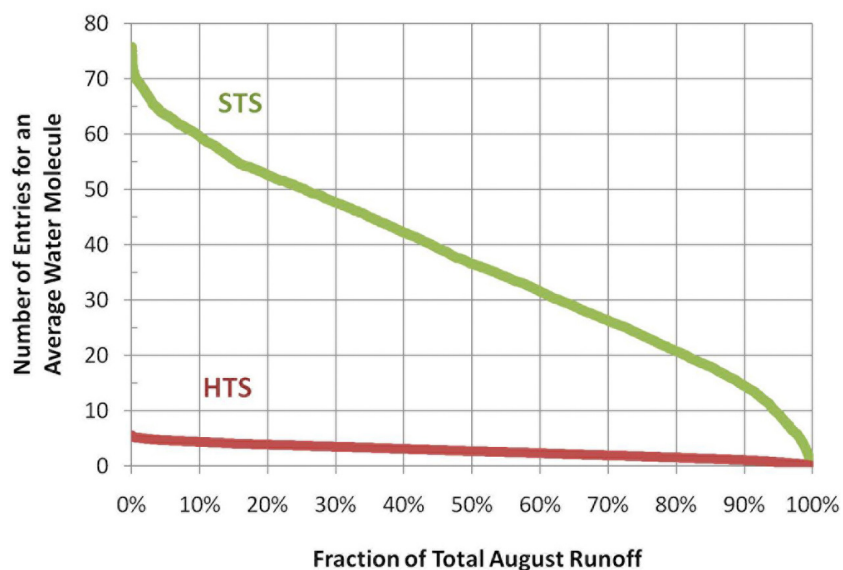


Figure 3. Frequency distribution of basin-wide runoff entering STS and HTS during base flow conditions for scenario 1 (Table 2). Results suggest 50% of runoff enters STS and HTS at least 36 times and 2.6 times, respectively, during its flow path through the channel network. These results are calculated using equation (17) and weighted by the total volume of water that travels along each flow path. Results account for the spatial distribution of runoff inputs to the river network.

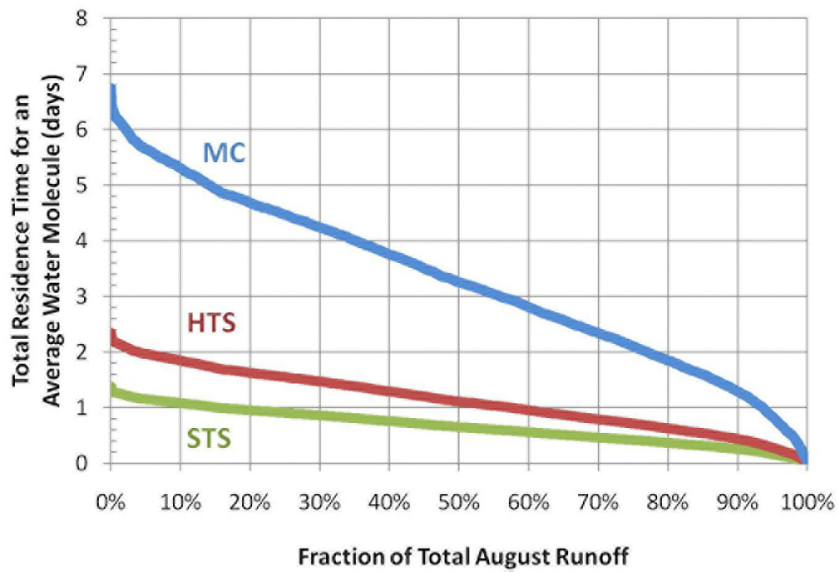


Figure 4. Frequency distribution of the total residence time that water molecules spend in STS, HTS, and MC during base flow conditions for scenario 1 (Table 2). Results suggest 50% of runoff remains in the MC, HTS, and STS for at least 3.3, 1.1, and 0.7 days, respectively, during its flow path through the channel network. These results were calculated using equations (19) and (20) and were weighted by the total volume of water that travels along each flow path. Results account for the spatial distribution of runoff inputs to the river network.

[32] As with connectivity, runoff generated in distant parts of the basin has the longest residence times in STS, HTS, and MC. Only 15% of base flow runoff remains in STS for longer than 1 day during its flow path through the river network (Figure 4). The longest residence time that any grid cell’s average runoff water molecule resides in STS is 1.4 days. Some water molecules can remain in HTS and MC, on average, up to 2.4 and 6.8 days, respectively. Approximately 47% of the watershed surface area generates runoff that remains in HTS for at least 1 day (Figure 5),

whereas only 11% of surface area generates runoff that remains in STS for at least 1 day. Runoff from 92% of the watershed spends at least 1 day of travel time in the MC (not shown).

3.3. Partitioning Network-Scale DIN Removal Among MC, STS, and HTS: Base Scenario

[33] On the basis of our assumptions, the river system was extremely effective at DIN removal under base flow conditions, removing approximately 73% of total DIN

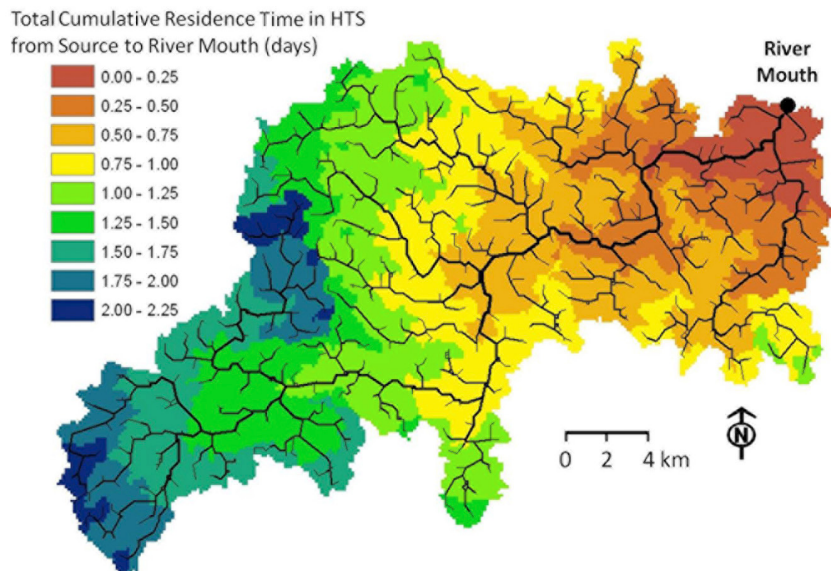


Figure 5. Spatial distribution of the total cumulative residence time of runoff in HTS. Colors represent the total cumulative residence time that runoff will remain in HTS during its flow path from point of generation to the river mouth.

inputs to the network in the base scenario (Figure 6). The MC compartment removed the largest proportion of total DIN inputs (38%), whereas the HTS and STS removed 21% and 14%, respectively (Figure 6). These results reflect the long total residence times in the MC at the network scale compared to total residence times in STS and HTS (Figure 4) and the assumption of similar reactivity in the three zones.

[34] Comparison of reaches of uniform length (200 m) indicates that small streams are the most efficient in removing DIN fluxes (Table 4). The fraction of stream DIN flux removed decreases with increasing stream order. The MC compartment removes the greatest amount of DIN per unit distance, followed by HTS and then STS (Table 4). The effectiveness of MC to remove DIN per uniform length decreases with increasing stream order because depth and velocity increase with river size and a constant uptake velocity (v_f) was applied. The fraction of stream DIN flux removed in the STS and HTS decreases with river size because there is a disproportional increase in discharge relative to A_{MC} in the downstream direction (equation (3)), and this reduces the proportion of water transfer from MC to TS (i.e., there is reduced connectivity). These factors contribute to a greater decline in MC removal than TS removal with increasing river size (Table 4), which results in a change in the relative importance of TS in total removal across river order (Figure 6). The removal percentages in Table 4 are not additive over a string of multiple segments because downstream segments cannot process DIN previously removed by upstream reaches and new DIN inputs are continuously being added along the river continuum.

[35] In terms of total basin DIN inputs from land removed by all river segments, the majority of predicted DIN removal occurred in higher-order river segments (Figure 6). Fifth-order river segments contributed 47% of total predicted network DIN removal while representing only 7.3% of the total river length. This is due to the downstream

Table 4. Average Percent DIN Flux Removed per 200 m Stream Segment^a

Stream Order	MC	STS	HTS	Total
1	7.3%	0.8%	1.3%	9.4%
2	4.3%	0.6%	0.9%	5.9%
3	2.6%	0.5%	0.7%	3.8%
4	1.8%	0.4%	0.6%	2.8%
5a	0.9%	0.3%	0.4%	1.7%
5b	0.6%	0.2%	0.4%	1.2%

^aThese values represent the average percent removal of dissolved inorganic nitrogen (DIN) flux that enters a 200 m segment and do not reflect the proportion of total basin inputs removed by the entire network.

location of Fifth-order reaches where a large proportion of total network inputs enter the upstream ends of these segments. Although the Fifth-order reach represents only 7.3% of total river length, it is all in one continuous segment, and therefore, it is the longest part of the total flow path traveled by an average water molecule.

[36] Generally, the proportion of total DIN inputs removed by stream order increases from first- to Fifth-order streams (Figure 6). The exception is third-order streams, which contribute greater DIN removal than fourth-order streams because of the relatively short total lengths of fourth-order streams in the Ipswich river network (5.9% of total river length) [Wollheim *et al.*, 2008a]. Headwater streams (orders 1 and 2) contribute a relatively small amount to total network removal, even under these base flow conditions. On the basis of the values applied in this study, the MC compartment dominates removal across river order because of the substantial total residence time it provides as water flows downstream and because identical reaction rates were assigned to all three compartments. The HTS contributes more removal than the STS compartment for all river orders. TS plays a more important role in downstream reaches because there is a greater decline in MC removal than TS removal with increasing river size

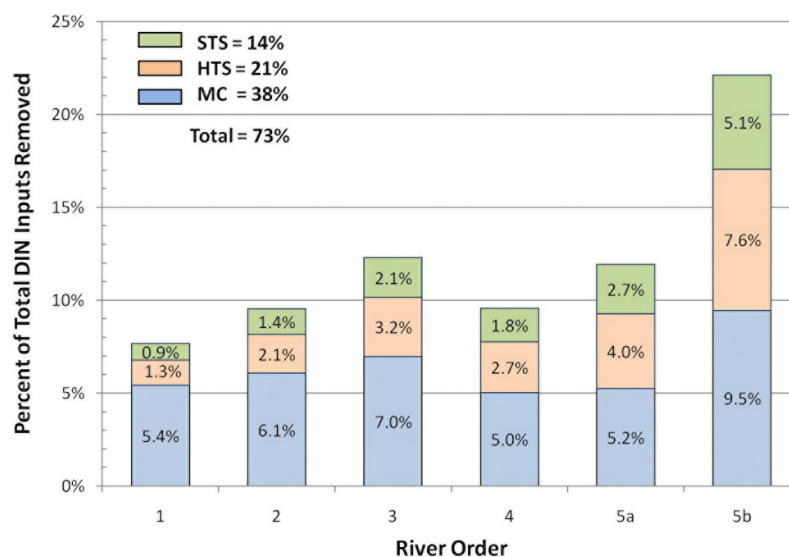


Figure 6. Proportion of total network inputs removed by MC, STS, and HTS throughout the river network during the month of August 2001. Fifth-order river segments with contributing drainage areas greater than 140 km² were classified as 5b.

(Table 4). The sensitivity of network DIN removal to various combinations of parameter values is explored in sections 3.5, 3.6, and 3.7.

3.4. Comparison With Observations

[37] Predicted and observed NO_3 concentrations are similar at the river mouth during base flow conditions (Figure 7). A Wilcoxon two-sample test indicates there is no significant difference between median values among observed and predicted concentrations for flows under $3 \text{ m}^3 \text{ s}^{-1}$ ($p > 0.05$). Although model results fall within the noise of observed data, predicted variability in DIN concentrations is much less than that observed across all flows (Figure 7). Moreover, the model generally underpredicts NO_3 concentrations during flows at the basin mouth between 1.0 and $2.0 \text{ m}^3 \text{ s}^{-1}$ (this equates to a runoff depth of between 0.27 and 0.53 mm d^{-1}) and overpredicts NO_3 concentrations during higher discharges. Assuming DIN inputs in the model are correct, these results suggest predicted network removal is too high for flows between 1.0 and $2.0 \text{ m}^3 \text{ s}^{-1}$ and too low for flow above $2.0 \text{ m}^3 \text{ s}^{-1}$. Predicted removal is too low during high discharges because TS hydraulics may adjust with discharge and the model does not account for these changes. TS hydraulics in the model are based on those identified in the field during low-flow conditions in the six tracer experiments ($1.4 \text{ m}^3 \text{ s}^{-1}$) conducted by Briggs *et al.* [2010].

[38] Modeled NO_3 concentrations on 26 August 2001 match observations quite closely along the basin profile (Nash-Sutcliffe coefficient of 0.60) (Figure 8). Modeled results are representative of typical summer concentrations based on measurements from eight synoptic surveys conducted during summers between 2001 and 2003 (Figure 8). More recent samples also indicate that DIN is high for the first several upstream kilometers before dropping off. A model run that mixed terrestrial DIN loads without any In-stream biological activity (i.e., $v_f = 0 \text{ m d}^{-1}$ in MC and $k_r = 0 \text{ d}^{-1}$ in STS and HTS compartments) suggests removal processes in river networks are extremely important in regulating DIN concentrations along the basin profile, and the simple dilution of DIN inputs alone cannot explain DIN concentrations throughout the river system (Figure 8).

3.5. Uncertainty in Mean Network Parameters

[39] A Monte Carlo analysis was conducted to evaluate the range in estimates of DIN removal by the different channel compartments due to uncertainty in the hydraulic and reactivity parameter values. The range in TS hydraulic parameters we applied captures the spectrum of parameter values identified across 246 published tracer experiments [Battin *et al.*, 2008]. The model predicts network DIN removal to range from 11% to 100% (Figure 9a) with first, second (median), and third quartiles of 54%, 74%, and 90%, respectively. In 500 model runs, the median removal value for the MC was 35% (first and third quartiles were 22% and 49%, respectively), 15% for the HTS (first and third quartiles were 6% and 31%, respectively), and 13% for the STS (first and third quartiles were 7% and 18%, respectively). A Wilcoxon two-sample test suggests there is a statistically significant difference among the removal proportions provided by each compartment ($p < 0.05$). Therefore, the Monte Carlo analysis provides further indication that the MC removes the greatest proportion of total basin DIN inputs, followed by the HTS, and then the STS. However, this evaluation pertains only to uncertainties due to the uniform hydraulic parameters of a channelized system with identical and uniform reaction rates in the three compartments.

3.6. Spatial Heterogeneity

[40] Simulation of 500 combinations of spatially heterogeneous TS and reactivity parameter values results in a small range of total Network-Scale DIN removal from 83% to 88% (Figure 9b). The median network removal for all model runs is 85%, which is a relatively small, but statistically significant, increase from a homogenous network (74% of total basin inputs). Spatial heterogeneity increased the median network DIN removal from scenario 2 in the MC (from 35% to 43%), the STS (from 13% to 18%), and the HTS (from 15% to 24%) (Figure 9b). All increases are statistically significant ($p < 0.05$). Network removal is consistently higher across the 500 model runs compared to scenario 2 because a spatially heterogeneous distribution of random parameters ensures the existence of a number of “hot spots” (locations of high DIN removal) scattered

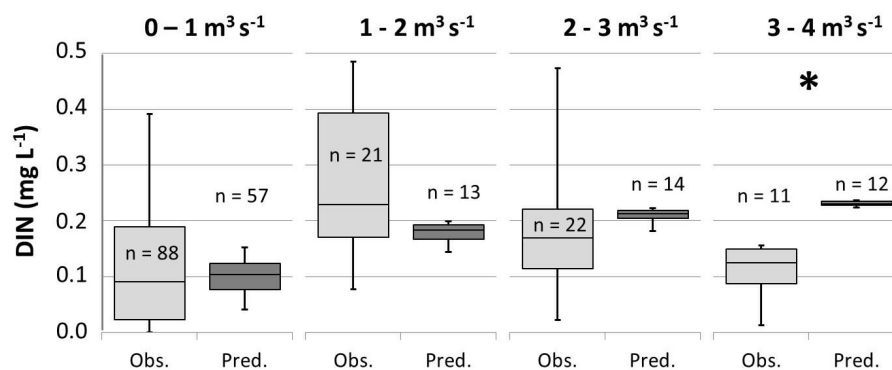


Figure 7. Observed and predicted DIN concentrations for various summer flow conditions (binned on the basis of discharge at the river mouth). The asterisk indicates statistically significant difference between observed and predicted median values. Observed concentrations are based on 2 day composite samples taken during the months of July, August, and September from 2002 to 2006. Predicted concentrations are average daily DIN concentrations for the months of July, August, and September 2001.

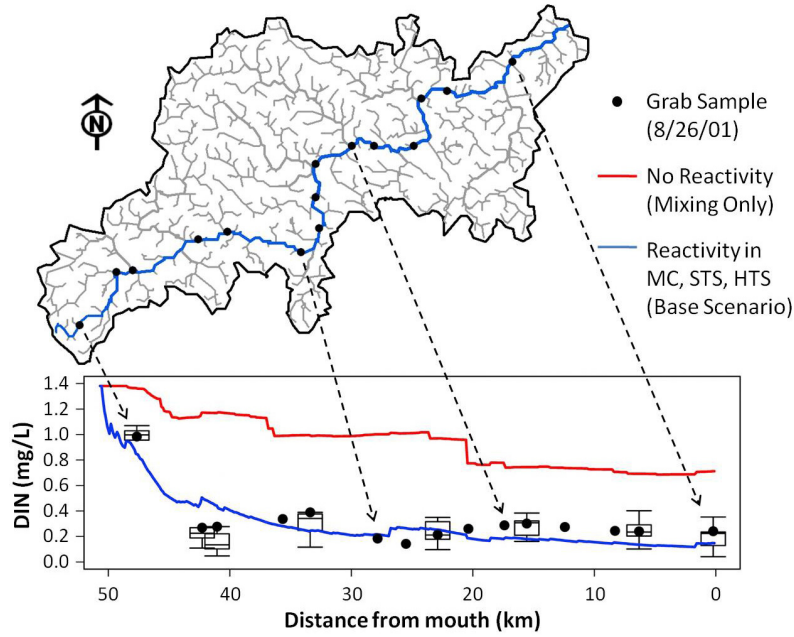


Figure 8. Comparison of observed and predicted DIN concentrations along the basin profile for 26 August 2001 (Nash-Sutcliffe coefficient of 0.60). Box plots indicate quantiles for eight synoptic surveys taken during the summers of 2001–2003. The mixing scenario (red line) describes predicted DIN concentrations as a function of downstream mixing and no reactivity. The reactivity scenario (blue line) shows DIN concentrations as predicted by the base scenario (scenario 1, Table 2).

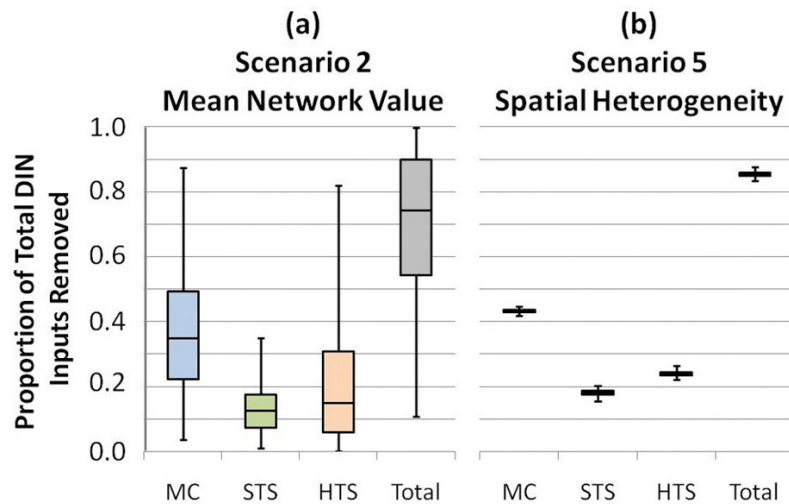


Figure 9. Monte Carlo results for (a) scenario 2 and (b) scenario 5. Box plots indicate the sample minimum, lower quartile, median, upper quartile, and maximum for 500 model runs. In scenario 2, parameter values were selected and applied uniformly throughout the network. In scenario 5, all parameter values vary spatially. A Wilcoxon two-sample test indicates there is a statistically significant difference among median removals for each compartment between scenarios 2 and 5.

throughout the river network. These hot spots are able to buffer upstream inefficiencies in DIN processing in “cold spots” that were assigned low parameter values. Hot spots are created via a combination of one or more of the TS hydraulic parameters or biologic reactivity parameters.

3.7. Sensitivity Analysis

[41] Sensitivity analyses were performed to evaluate how network DIN removal adjusts with changes in hydraulic characteristics and reaction rates in each compartment and to understand the interactions of different parameter values at network scales. Given the hypothetical ranges in Ipswich TS hydraulic parameters, DIN removal is more sensitive to the size of TS (A_{HTS} , A_{STS}) than to TS exchange coefficients (α_{STS} , α_{HTS}) (Figures 10 and 11). Assuming typical reaction rates, removal is not highly sensitive to exchange coefficients because α has a dual effect. Exchange coefficients control the fraction of discharge that enters TS (connectivity) and also control the residence time of water in storage, and these have offsetting effects (Figure 11).

[42] In terms of reaction rates, network DIN removal is the most sensitive to the magnitude of reactivity in MC (data not shown) because cumulative network residence times of runoff in that compartment are significantly greater than in STS and HTS (Figure 4). To evaluate the importance of the individual reaction rates in STS and HTS with regard to network DIN removal, a sensitivity analysis was conducted under the hypothesis that MC reactivity is negligible [Hall et al., 2002] (Figure 12). Results indicate that specific patterns emerge when various reaction rates are applied to each compartment because of the hydraulic characteristics of the STS (high connectivity and short unit residence times) and HTS (low connectivity and long unit residence times). When reaction rates in STS and HTS are identical, STS dominates removal when reactivity is high ($k_t > 2.85 \text{ d}^{-1}$), whereas HTS dominates under lower reactivity (Figure 12). High reaction rates result in instant DIN removal upon entrance to the compartment, and therefore,

total network removal becomes more a function of how much water passes through each compartment (connectivity) rather than how long water remains in storage (residence time). Even when reaction rates in the HTS are 10 times higher than in the STS, the STS can exert greater control on DIN fluxes when its reaction rates are elevated ($k_t > 4.2 \text{ d}^{-1}$) because it is highly connected to the MC (Figure 12).

4. Discussion

4.1. Dynamics Among TS Hydraulics, Reaction Rates, and DIN Removal

[43] The implications of Reach-scale hydraulic characteristics for the MC (advective and short unit residence times), STS (high connectivity and short unit residence times), and HTS (low connectivity and long unit residence times) are difficult to interpret unless evaluated in the context of a dynamic, holistic river system. Assuming constant reaction rates across the three zones, the MC provided the largest contribution of DIN removal, followed by HTS and then STS (Figure 6). High connectivity (Figure 3) by itself does not necessarily imply high DIN processing contributions at large scales, as has been previously suggested [Valett et al., 1996]. Instead, the cumulative network residence time that water remains in each compartment is more important (Figure 4). The large contribution of the MC in defining network residence time has also been demonstrated in other systems [Darracq et al., 2010; Dunn et al., 2007]. However, its importance in Network-Scale DIN removal in this study (Figure 6) is based on the assumption that reactivity is similar there as in STS and HTS. While reactivity in the MC may be high for certain processes, this assumption may not apply for others, such as denitrification [Thomas et al., 2003].

[44] Sensitivity analyses indicate all three compartments have the potential to be the dominant control on Network-Scale DIN removal depending on the combination of hydraulic and reactivity parameters in each compartment

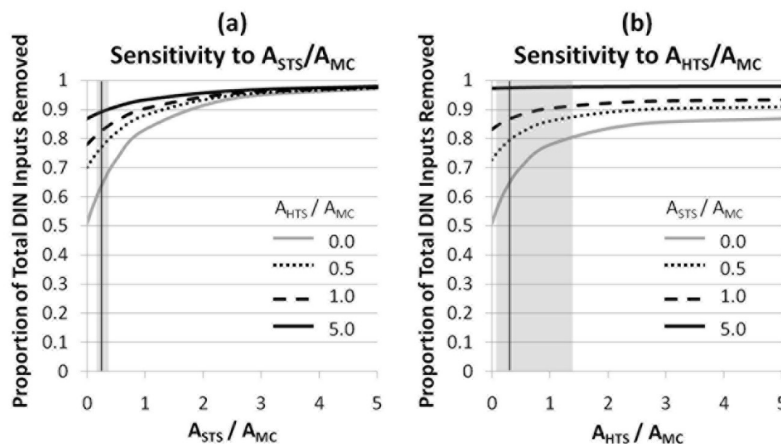


Figure 10. Response of Network-Scale DIN removal to (a) A_{STS}/A_{MC} and (b) A_{HTS}/A_{MC} . All other parameters are constant, with values set as the mean values provided in Table 1 (reaction rates are considered low to moderate). Figures 10a and 10b present the same data but with different x axes. The mean values for A_{STS}/A_{MC} and A_{HTS}/A_{MC} are marked with vertical lines, and the 95% confidence intervals are indicated with gray shading.

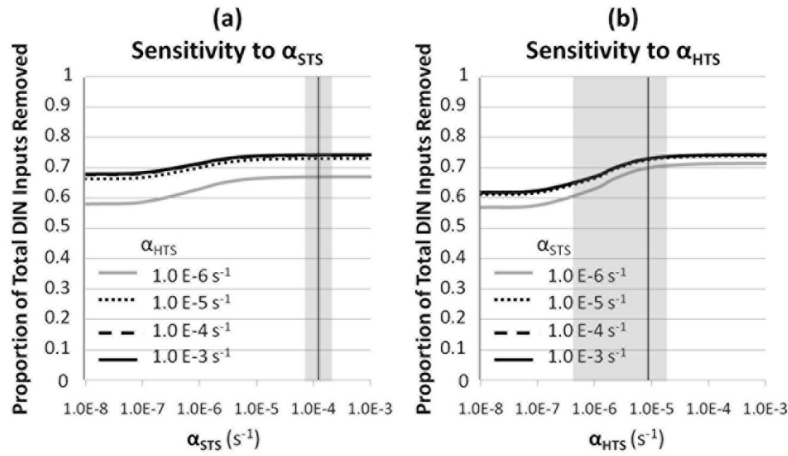


Figure 11. Response of Network-Scale DIN removal to (a) α_{STS} and (b) α_{HTS} . All other parameters are constant, with values set as the mean values provided in Table 1 (reaction rates are considered low to moderate). Figures 11a and 11b present the same data but with different x axes. The mean values for α_{STS} and α_{HTS} are marked with vertical lines, and the 95% confidence intervals are indicated with gray shading.

(Figure 9a). Previous studies have shown complex dynamics among TS hydraulics, reaction rates, and DIN removal at the reach scale. For example, an increase in the size of TS and/or its connectivity with the MC results in increased DIN removal [Gooseff *et al.*, 2004; Mulholland and DeAngelis, 2000; Triska *et al.*, 1989; Valett *et al.*, 1996]. A single compartment TS model indicated that nutrient uptake length (the average distance a nutrient molecule travels downstream before being removed from the system) decreases with greater relative size of TS (A_{TS}/A_{MC}) for a given water exchange rate (α_{TS}) [Mulholland and DeAngelis, 2000]. Nutrient uptake length also declines as α_{TS} increases at a given A_{TS}/A_{MC} [Mulholland and DeAngelis, 2000]. Further implications arise at network scales. Our

model suggests biologic reactivity in TS compartments affects the sensitivity of Network-Scale DIN removal to TS size (A_{TS}/A_{MC}) and connectivity (α_{TS}). We found the size of TS (A_{TS}/A_{MC}) is more important than its connectivity (α_{TS}) with the MC when reactivity rates are low to moderate ($k_r < 2.85 \text{ d}^{-1}$), whereas TS connectivity is more important when reaction rates are elevated ($k_r > 2.85 \text{ d}^{-1}$) (Figure 12). These dynamics explain the relatively greater importance of the HTS compared to STS when a relatively low reaction rate ($k_r = 0.64 \text{ d}^{-1}$) is applied (Figure 6) and the dominance of STS on network removal when reactivity is elevated (Figure 12).

[45] The HTS is likely to dominate TS DIN removal in river networks even if reaction rates are identical in both

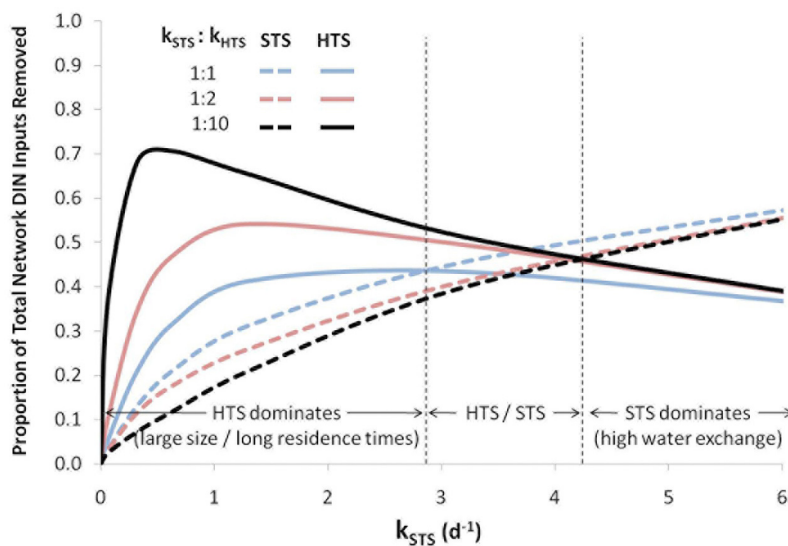


Figure 12. Proportion of total DIN inputs removed by an individual TS compartment under various reactivity levels in each zone. The MC is assumed to be inactive in this summary ($v_f[\text{MC}] = 0.0 \text{ m d}^{-1}$); however, the patterns shown here hold for evaluations with $v_f[\text{MC}] > 0 \text{ m d}^{-1}$ (data not shown).

TS compartments. Denitrification rates are relatively low in streams [(M. B. Green et al., Effective denitrification scales predictably with water residence time across diverse systems, submitted to Plos ONE, 2011) *Hall et al.*, 2009], and because average network residence times are greater in HTS than STS (Figure 4), network scale removal by HTS is relatively more important. It should be noted that these earlier studies identified whole-reach-scale reaction rates and do not account for reactivity in specific habitats within the reach. We underestimate the contribution of the HTS relative to STS in network DIN removal for a couple reasons. First, our estimates of MC-HTS connectivity disregard the faster-moving hyporheic exchange that is known to be an important facilitator of denitrification in streams [*Gooseff et al.*, 2004; *Bohlke et al.*, 2009]. Some of this faster-moving HTS exchange could be lumped into our estimation of α_{STS} . Second, theoretical considerations [*Hall et al.*, 2002; *Runkel et al.*, 2003] suggest denitrification rates are likely to be elevated in the HTS compared to MC and STS. This would suggest HTS is very important in regulating DIN fluxes in river systems because we applied a conservative estimate of HTS reactivity (i.e., we used similar reaction rates in all three compartments in each model run) (Figure 9a). Still, our results highlight the need for more field investigations into the individual reaction rates in the MC, STS, and HTS.

4.2. Quantifying Network-Scale Residence Times

[46] The average residence time of a water molecule in a river network controls its potential for biogeochemical transformation. In our analysis, residence time is defined as the time of transport in the surface channel network (i.e., MC, STS, and HTS compartments) based on recovered tracer only and does not include flow paths prior to entrance into the river (i.e., subsurface flow) or the potential for long-term losses of stream water from the network (i.e., groundwater recharge and possible later return) that are incorporated in other studies [*Covino and McGlynn*, 2007; *McDonnell et al.*, 2010; *McGuire et al.*, 2002; *Payn et al.*, 2009]. The roles of wetlands, ponds, and lakes were not included but could substantially increase network residence times. Because of the complex nature of dendritic and cascading river systems, there are no existing metrics that can be used to characterize the average residence time of runoff in a river network. The most commonly used metric for characterizing Reach-scale water transport times due to TS is F_{med}^{200} [*Runkel*, 2002]. F_{med}^{200} accounts for the interaction between advective and nonadvective controls on reach travel time and mass transport [*Runkel*, 2002]. However, F_{med}^{200} is not suitable for identifying the average residence time of water molecules in storage and is inadequate for characterizing the role of TS on transport times at large scales [*Runkel*, 2002].

[47] Application of F_{med}^{200} is appropriate for characterizing median transport times at reach scales but not at the scale of an entire river network. Reach-scale experiments in Ipswich River segments indicate that STS (average F_{med}^{200} STS = 10.6%) exerts greater control on median transport times than HTS (average F_{med}^{200} HTS = 0.92%) [*Briggs et al.*, 2010]. The reason F_{med}^{200} is greater for STS than for HTS is because STS-MC connectivity (α_{STS}) is high enough over short segment distances for median travel

times to be affected by the temporary retention of water in STS. HTS is relatively unimportant for median transport times in 200 m segments because HTS-MC connectivity (α_{HTS}) is too low for a significant number of water molecules to enter the compartment. This is supported by our model, which indicates average water molecules enter the STS 0.58 times per 200 m reach but enter the HTS only 0.04 times over the same distance (Table 3). Because 200 m is not long enough to capture the effect that typical α_{HTS} have on water transport, we suggest F_{med}^{200} is predominantly a measure of highly connected TS zone control on median transport times at the reach scale alone.

[48] When evaluating transport times at the scale of entire river networks, HTS can substantially affect travel times because nearly all water molecules enter HTS at least once before exiting the river system (Figure 3). A single entrance into HTS has a greater effect on median network transport time than many entrances into STS because of the orders of magnitude greater residence time in HTS. As such, although HTS-MC connectivity is much lower than STS-MC connectivity, HTS exerts greater control on transport times over long flow path distances (Figure 4). As discussed in section 4.1, a longer network residence time of water in the HTS than in STS results in greater potential for denitrification in the subsurface zone (Figure 6), particularly when considering that reaction rates in the HTS are expected to be higher than in the other compartments [*Hall et al.*, 2002; *Runkel*, 2002].

[49] A number of studies have failed to find a significant relationship between DIN uptake and F_{med}^{200} in small river segments [*Ensign and Doyle*, 2006; *Lautz and Siegel*, 2007; *Mulholland et al.*, 2009]. This is not surprising considering (1) F_{med}^{200} at reach scales is primarily a metric of STS processes and (2) HTS removes more DIN than STS at reach scales assuming low to moderate reaction rates (Table 4). Therefore, assuming STS processes also dominate F_{med}^{200} in other empirical studies, we would expect little correlation between F_{med}^{200} and DIN removal. We propose application of equations (19) and (20) as a proxy for comparing the potential for biogeochemical processing among various compartments within flow paths or between flow paths. Further, we suggest equation (21) should be used for quantifying average residence times in entire river networks. These findings are based on an empirical model in the Ipswich basin where residence times in STS relative to HTS are minimal. More two-compartment TS studies are needed elsewhere to confirm the generality of these findings.

4.3. Large Rivers As Important Regulators of DIN Flux

[50] Larger streams in a river network have been shown to remove a greater proportion of total basin DIN inputs than smaller streams [*Ensign and Doyle*, 2006; *Wollheim et al.*, 2006], though small streams increase in importance at lower flows [*Wollheim et al.*, 2008a]. These earlier studies did not explicitly account for the role of TS. Incorporation of two TS zones yielded similar results. However, our study suggests that the relative role of TS during low flow increases in larger rivers (Table 4). This is because removal processes in the MC and TS become less efficient per unit distance downstream but efficiency reduces more quickly in the MC than in TS. Reduced efficiency in downstream

reaches occurs because of scaling relationships between channel depth and width and increasing discharge [Wollheim *et al.*, 2006]. The downstream scaling relationships used in this analysis for channel width and depth (and thus MC residence time) are similar to those applied in previous network studies [Wollheim *et al.*, 2008a; Alexander *et al.*, 2009]. Removal processes in the MC are less efficient in large rivers because of a decreased benthic surface width to discharge ratio. Removal per unit length due to TS also declines in larger reaches because water transfer to TS is a function of A_{MC} and discharge (equation (3)), and discharge increases at a greater rate than A_{MC} in the downstream direction [Leopold and Maddock, 1953]. As discussed in sections 2.2 and 2.4, a vertical uptake velocity is applied to the MC (v_j), whereas time-specific volumetric DIN uptake rates (k_r) are applied to STS and HTS compartments. Therefore, given our empirical TS hydraulic implementation [Briggs *et al.*, 2010], STS and HTS become more effective downstream relative to the MC because the ratio of width to discharge declines faster than the ratio of A_{MC} to discharge. These findings support earlier studies that stress the importance of evaluating river processes with a network perspective [David *et al.*, 2006; Royer *et al.*, 2006; Wollheim *et al.*, 2006, 2008a; Alexander *et al.*, 2009] and corroborate expectations for a realistic cascading river system [Bernot and Dodd, 2005]. More research in larger rivers is needed to further verify these findings [e.g., Briggs *et al.*, 2009; Tank *et al.*, 2008].

4.4. Hot Spots Versus Continuous Gradients in River Networks

[51] A consensus on the general distribution of physical and biological characteristics in river networks has yet to be agreed upon [Thorp *et al.*, 2006]. The concept of a “continuous gradient” of physical conditions from headwaters to a river’s mouth [Vannote *et al.*, 1980] is still largely accepted, particularly in small- to medium-sized rivers [Thorp *et al.*, 2006]. However, a significant amount of evidence has been growing that suggests river networks consist of discontinuous patches of various physical and biological complexities [Benda *et al.*, 2004; Perry and Schaeffer, 1987; Pina-Ochoa and Alvarez-Cobelas, 2006; Poole, 2002; Statzner and Higlner, 1985; Thorp *et al.*, 2006]. As such, TS characteristics and biogeochemical processing are likely to be heterogeneous in space and time, potentially leading to hot spots [McClain *et al.*, 2003] of removal at river network scales.

[52] We investigated the potential role of spatial heterogeneity during base flow conditions in river networks by randomly selecting parameter values for each river grid cell from lognormal distributions that were fit by each parameter’s empirical mean and standard deviation (Table 2). In this way, hot spots were created stochastically throughout the river network because of combinations of increased TS connectivity, residence time, or reactivity and resulted in localized areas of high removal. The presence of hot spots modestly enhances overall network removal over a network characterized by a gradient of hydraulics and uniform biological activity (Figures 9a and 9b). This suggests that although we match observed DIN concentrations in our base scenario (Figures 7 and 8), we may do so for the wrong reason. That is, at low flows, uniform parameters

applied to the network may match observed removal even though most might be occurring in hot spots. In terms of Network-Scale DIN removal processes, it may not matter whether river networks consist of both hot and cold segments (patchy removal strength) or have generally uniform characteristics throughout because of the buffering capacity of cascading systems. Cascading systems enable unsaturated downstream segments to capture leakage from upstream inefficiencies. More work should be focused on quantifying the role that heterogeneity plays in Network-Scale biogeochemical processes [Pina-Ochoa and Alvarez-Cobelas, 2006], particularly with increasing flow conditions [Botter *et al.*, 2010] when a gradient representation of river networks becomes considerably less efficient than observations suggest is the case [Wollheim *et al.*, 2008a].

4.5. Key Uncertainties

[53] The model presented in this study is a valuable tool for integrating geomorphic, hydrological, and biological characteristics at basin scales but is limited by a number of uncertainties. Although we address the uncertainty associated with mean network parameters, we do not expect the few measurements taken to represent the entire range of characteristics that exist in the Ipswich basin. TS hydraulic measurements ($n = 6$) were taken in channelized stream segments during low flows over a 2 year period and do not account for the presence of wetland-dominated reaches, beaver ponds, and lakes. Further, our model uses water exchange coefficients from tracer experiments that have a limited “window of detection” of transfer with surface and subsurface flow paths [Harvey and Wagner, 2000; Harvey *et al.*, 1996]. Also, no measurements were taken in reaches with drainage areas greater than 200 km², which represents more than half of the total length of the Fifth-order river segment and nearly 20% of total DIN removal. The contribution of HTS and STS DIN removal in larger rivers reported here could be an overestimate considering A_{TS}/A_{MC} has been found to decrease with increasing river order [Harvey and Wagner, 2000], while we applied a constant ratio throughout the network. As a result, the importance of TS in large rivers comes with a large degree of uncertainty. To reduce uncertainty in the model, more field studies are needed to partition between STS and HTS hydraulics, particularly in large river segments. Furthermore, future network models should integrate the role of gaining and losing reaches and longer-term residence times.

[54] There are a number of limitations associated with our biological assumptions. First, biological reactivity parameters were based on measurements taken within the Ipswich basin ($n = 8$), but only in small headwater streams, integrated over entire reaches, and at a different time (2003–2005) [Mulholland *et al.*, 2008]. Further, we derived the denitrification rate assuming hydraulic exchange parameters between MC and a single TS compartment. Earlier studies have suggested that reactivity in the HTS is greater than in the MC and STS [Hall *et al.*, 2002], but more studies are needed to quantify the specific reaction rates in the three compartments [Thomas *et al.*, 2003]. Isolation of reaction rates in these different compartments is extremely difficult, and our own attempts at quantifying reaction rates in each zone are ongoing. In addition, studies have shown that DIN removal processes are less efficient at

high concentrations [Earl et al., 2006; O'Brien et al., 2007]. Efficiency loss was not incorporated into this model because the rate at which processing decreases in TS with increasing concentration is unknown. Including efficiency loss would only add additional parameters to the model and increase complexity. As a result, the findings presented here could be an overestimation of DIN removal under high DIN concentrations [O'Brien et al., 2007], as demonstrated by Wollheim et al. [2008a] at network scales without explicit consideration of TS. Future Network-Scale TS models should incorporate the concept of N saturation when more TS data become available. Finally, the interaction of DIN processing with other element cycles, such as carbon and oxygen, was not included in this study but could play a significant role.

[55] Some hydrologic factors in the model also need further consideration. Groundwater withdrawals are quantitatively significant in summer relative to base flows in certain portions of the watershed [Zarriello and Ries, 2000] and could be a source of error in this study. Because withdrawals are concentrated in high-DIN portions of the basin, their omission leads to model predictions that could be higher than would be expected.

5. Conclusions

[56] DIN removal processes in advective and nonadvective compartments in river systems are the result of interactions among connectivity, residence time, and the strength of biological reactivity. We applied a spatially distributed river network model to identify the important dynamics of TS at large scales. We found that although HTS does not appear to be highly connected to the MC, most runoff enters the HTS at least once at the scale of the entire network and residence times in the subsurface are long. As a result, HTS exerts greater control over water transport and DIN removal at network scales than STS. Assuming reaction rates are similar in all three compartments, the MC exerts the greatest control on DIN removal, followed by the HTS and then STS. These predictions will improve following more field investigations of specific reaction rates in each compartment. Despite uncertainties in TS hydraulic and biological parameters, large rivers were found to have a considerable role in regulating DIN fluxes, supporting the need for a network perspective to fully understand biogeochemical processes in river systems [Battin et al., 2008; Seitzinger et al., 2002; Wollheim et al., 2006, 2008a]. Further, although hot spots tend to elevate DIN removal, the interactions of TS hydraulics and reactivity at network scales can provide similar total network processing capacity at low flows when assuming a uniform distribution of those factors. Because of current limitations in field methods, this model accounts only for hydraulic processes within channelized sections of the Ipswich and does not account for wetlands and lakes. These omitted features, as well as changing hydraulics of TS, have the potential to play significant roles in DIN processing over the entire range of flow conditions and could be incorporated in future studies. Moving forward, more emphasis should be put on quantifying the average residence time a water molecule remains in specific habitats along its entire flow path through a river network over a range of flow conditions to better understand large-scale biogeochemical processes.

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