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

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SEPARATION OF RIVER NETWORK SCALE NITROGEN REMOVAL AMONG MAIN

CHANNEL AND TWO TRANSIENT STORAGE COMPARTMENTS

BY

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Bachelor of Science, Hobart and William Smith Colleges, 2003

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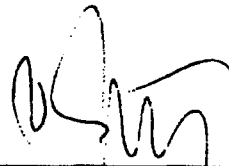
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ABSTRACT

SEPARATION OF RIVER NETWORK SCALE NITROGEN REMOVAL AMONG MAIN

CHANNEL AND TWO TRANSIENT STORAGE COMPARTMENTS

by

Robert J. Stewart

University of New Hampshire, December 2009

Reach scale experiments have shown that transient storage (TS) could be an important control on dissolved inorganic nitrogen (DIN) export to coastal waters. Here, the relative roles the main channel (MC), surface TS (STS) and hyporheic TS (HTS) have in DIN removal at the network scale are investigated using a model applied to the Ipswich River in Massachusetts. Collaborative field investigations in 1st through 5th order reaches of the Ipswich River provided the mean and range for the hydraulic parameters controlling TS connectivity and residence time. DIN removal was simulated in the MC, STS and HTS compartments for every river grid cell using hydraulic characteristics, simulated discharge, and a constant reaction rate. Application of mean network parameters resulted in removal of 73.1% of total DIN inputs with the MC, HTS, and STS contributing 38.2%, 20.9%, and 14.0% respectively. Sensitivity analyses suggest large rivers and hotspots greatly impact DIN fluxes.

CHAPTER I

INTRODUCTION

Understanding processes controlling nitrogen removal (e.g. denitrification) in ecosystems has become important due to the increase in anthropogenic nitrogen (N) inputs to our environment. Human activities such as fertilizer application, N fixation by crops, human and animal waste management, and fossil fuel emissions (Vitousek 1997) saturate terrestrial ecosystems with N (Aber et al. 1998), degrade the quality of streams that drain them (Peterson et al. 2001) and can ultimately lead to eutrophication of lakes and coastal waters. However, evidence suggests that the proportion of N retained in basins can be relatively high despite anthropogenic increases in N (Howarth et al. 1996; Boyer et al. 2002). Terrestrial systems account for most of the N removed in watersheds, but aquatic systems also play an important role (Bernhardt et al. 2005), particularly during summer low flow periods (Wollheim et al. 2008). A significant challenge in aquatic ecology is to identify the specific locations responsible for denitrification in streams (Thomas et al. 2003) and to quantify these processes at large scales.

N removal in aquatic systems is a function of 1) the strength of biological activity (Triska et al. 1989; Fellows et al. 2001), 2) the proportion of mass solute exposed to biologically active surfaces (Harvey et al. 1996), and 3) the duration of exposure to these surfaces (Findlay 1995; Runkel 2000). These factors are determined by a combination of biologic, hydrologic, and geomorphic components and subsequently vary over space and time (Doyle 2005; Wollheim et al. 2006; Wollheim et al. 2008). There have been a number of investigations looking into these factors at fine scales (Bencala et al. 1993; Mulholland and DeAngelis 2000; Peterson et al. 2001; Hall et al. 2002; Thomas et al. 2003; Briggs et al. 2009). One factor that could be important is the degree of water exchange between advective and non-advective habitats (Triska et al. 1989; Valett et al. 1996; Thomas et al. 2003; Gooseff et al. 2004).

The advective zone, or the main channel (MC), consists of the majority of the river cross-sectional area where the highest velocities occur. Non-advective, or transient storage (TS), zones are flow paths with significantly reduced downstream velocities (Bencala and Walters 1983; Harvey et al. 1996). Transient storage zones are hypothesized to influence dissolved inorganic N (DIN) fluxes because they extend residence times and facilitate water exposure with biochemically reactive surfaces (Findlay 1995; Dahm et al. 1998; Baker et al. 2000; Harvey and Wagner 2000; Ensign and Doyle 2005; Hancock et al. 2005; Briggs et al. 2009). 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 (Mulholland and DeAngelis 2000; Hall et al. 2002; Thomas et al. 2003; Faulkner and Campana 2007). Some studies found a strong correlation

between transient storage characteristics and DIN removal in river segments (Triska et al. 1989; Valett et al. 1996; Thomas et al. 2003; Gooseff et al. 2004) while others found a weaker correlation (Hall et al. 2002; Lautz and Siegel 2007) or no correlation at all (Ensign and Doyle 2006). The role of TS in DIN removal varies because TS hydraulics and biogeochemical processes are heterogeneous across systems, within systems, and through time (Thomas et al. 2003). Further, non-advective zones can be categorized into surface transient storage (STS) and hyporheic transient storage (HTS) (Briggs et al. 2009) and these two compartments can have significantly different hydraulic and biogeochemical processes (Thomas et al. 2003). Because traditional field methods cannot distinguish the relative control that the STS and HTS have on water transport (Briggs et al. 2009), it is understandable that there is not a general consensus on the role of TS on DIN removal.

STS includes side pools or back eddies along the river channel (Harvey and Wagner 2000) where water exchange from the channel is controlled by lateral dispersion (Fischer et al. 1979) and turbulent processes (Ghisalberti and Nepf 2002). Sub-surface 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, then resurfaces at some distance downstream. STS and HTS characteristics are expected to adjust along a river network in response to gradients in channel morphology (Gooseff et al. 2007; Battin et al. 2008) but may do so at separate rates because of underlying differences in hydraulic dynamics (Briggs et al. 2009, in revision). Due to differences in STS and HTS

characteristics, biogeochemical processes in the two compartments are likely to also differ. For instance, STS are depositional zones that typically accumulate large stocks of organic matter (Hall et al. 2002) whereas HTS facilitates water exposure to sediment biofilms and alternating oxic and anoxic environments.

To better understand DIN removal in aquatic systems, the STS and HTS must be considered separately. As part of this collaborative study, a new method was developed to partition between the hydraulics of these non-advective compartments (Briggs et al. 2009). This work refined traditional lumped hydraulic parameters such as the TS exchange coefficient (α_{TS}), TS zone size (A_{TS}), and the fraction of median travel time through a stream reach that is due to temporary retention in transient storage (F_{med}^{200}) (Runkel 2002) into α_{STS}, α_{HTS}, A_{STS}, A_{HTS}, $F_{med}^{200}STS$ and $F_{med}^{200}HTS$ (Briggs et al. 2009). A subsequent field study was conducted to inform a river network DIN removal model with a range in STS and HTS hydraulic parameters found in channelized sections throughout a 5th order river network (Briggs et al. 2009, in revision). Here, I use this model to quantify how much DIN removal occurs in the MC, STS and HTS at the river network scale during a summer baseflow period.

It is important to take reach scale observations of TS and place them in a broader context. Previous studies have shown that a river network perspective is essential to understand DIN removal processes because downstream river segments buffer upstream inefficiencies associated with increased DIN inputs (Mulholland and al. 2008) and discharge (Wollheim et al. 2008). However, there have been few studies that

have taken a river network approach to quantifying DIN removal in stream ecosystems. Generally, these studies have assumed that biological rates are independent of river size and changes are driven by predictable downstream adjustments in river hydraulics (Seitzinger et al. 2002; Wollheim et al. 2006; Wollheim et al. 2008). This is a valid approach because river size is directly correlated to benthic surface-to-volume ratios but this assumption ignores the potentially critical role of water exchange between advective and non-advective compartments. However, to the best of my knowledge, there are no river network models that incorporate TS processes.

Here, I develop a river network model and parameterize the model with empirical TS measurements to quantify basin scale DIN removal in MC, STS and HTS compartments during a summer baseflow period. The model basin is the Ipswich River located in northeastern Massachusetts. The goals of this study with respect to DIN removal by MC, STS, and HTS compartments at network scales are to determine 1) the relative importance of each compartment, 2) the role of stream size, 3) the importance of spatial heterogeneity or gradients (e.g. hotpsots), and 4) the sensitivity to hydraulic and biologic parameters in each zone.

CHAPTER II

METHODS

Study Site

The Ipswich River is a coastal 5th order watershed located approximately 30 km north of Boston, Massachusetts, and is experiencing rapid suburbanization (Figure 1). The watershed is shallowly sloped (0.06%) (Claessens et al. 2006), drains an area of approximately 400 km^2 and consists of 36% forest, 30% suburban, 20% wetlands, 7% agriculture, 4% industrial/commercial, and 3% open water (Wollheim et al. 2008). Nearly 10% of the basin is impervious. The population density in the basin is 302 people per km^2, and 60% of the population is served by septic systems. Mean annual precipitation is approximately 1188 mm per year, 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 m^3 s^{-1} and typical summer baseflow is about 1 m^3 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). Due to 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).

Ipswich River Network
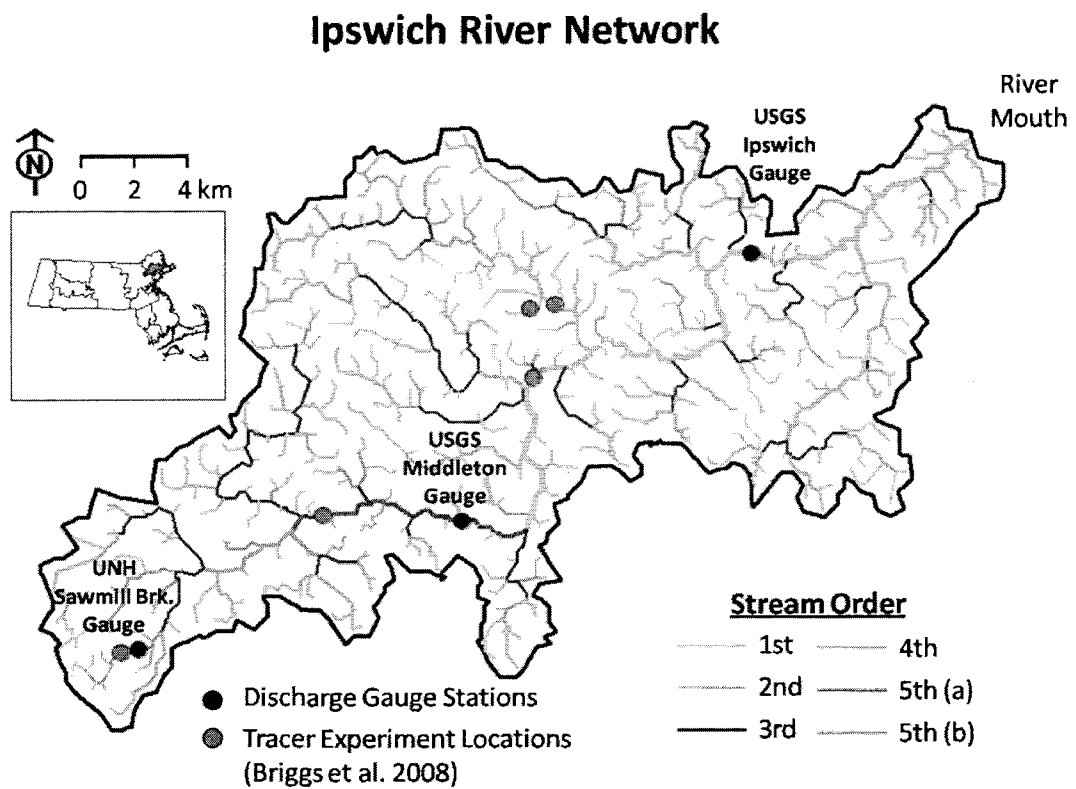
Figure 1 The Ipswich River is a 5th order river network and has two USGS gauge stations on its mainstem (USGS Ipswich Gauge No. 0110200 and USGS Middleton Gauge No. 01101500). Five tracer experiments were conducted in Ipswich River segments and a sixth was completed in the neighboring Parker River (Briggs et al. 2009, in review).

River Network Model

The Ipswich River DIN removal model was developed to evaluate the role of TS on DIN removal processes at basin scales. Hydraulic and biogeochemical parameters quantified in the field were used in this spatially-distributed, gridded river network model to simulate DIN inputs, hydrology, hydraulic processes, and denitrification during a summer baseflow period. The Ipswich river network DIN removal model is operated within the UNH aquatic modeling system, the Framework for Aquatic Modeling in the Earth System (FrAMES) which has been employed in a number of previous hydrological studies (Wollheim et al. 2008; Wollheim et al. 2008; Wisser et al. 2009). The model has been populated with Ipswich-specific empirical data collected through various field investigations and data sets downloaded from national inventories. The month of August, 2001 was selected as the primary study period because the range of flow conditions observed at the river mouth (mean = 1.32 m^3 s^{-1}, median = 0.91 m^3 s^{-1}, standard deviation = 0.82 m^3 s^{-1}, n = 31) matched the range in flow conditions observed at the river mouth during field evaluations of hydraulic parameters (mean = 1.30 m^3 s^{-1}, median = 1.05 m^3 s^{-1}, standard deviation = 0.89 m^3 s^{-1}, n = 6) (Briggs et al. 2009, in revision). Field evaluations of hydraulic parameters occurred during the summers of 2007 and 2008 but simulations were not conducted during this time period because there was not sufficient DIN monitoring data to compare model results with.

DIN Removal Approach

Nitrogen removal in each river grid cell was simulated using a stream TS model derived from Mulholland and DeAngelis (2000) (Figure 2). Since DIN in the Ipswich River is dominated by NO_3, removal is applied specifically to NO_3. Total DIN removal for each grid cell is the combination of removal in the MC, STS, and HTS compartments and is calculated as:

$$Removal_i = Removal_{MC} + (Transfer_{STS} * Removal_{STS}) + (Transfer_{HTS} * Removal_{HTS}) \quad (1)$$

Where $Removal_i$ is the total proportional removal of DIN within grid cell i (unitless), $Removal_{MC}$ (unitless) is the proportional removal of DIN in the MC compartment within grid cell i, $Transfer_{STS}$ (unitless) is the fraction of discharge and mass solute entering the STS compartment from the MC within grid cell i, $Removal_{STS}$ (unitless) is the proportional removal of DIN from the STS compartment within grid cell i, $Transfer_{HTS}$ (unitless) is the fraction of discharge and mass solute entering the HTS compartment from the MC within grid cell i, and $Removal_{HTS}$ (unitless) is the proportional removal of DIN from the HTS compartment within grid cell i. The transfer and removal terms for each compartment are defined as:

$$Removal_{MC} = 1.0 - exp\,(-\upsilon_f\,/\,H_L) \quad (2)$$

$$Transfer_{xTS} = (\alpha_{xTS} * A_{MC} * L)\,/\,Q \quad (3)$$

$$Removal_{xTS} = 1.0 - exp\,(-k_t * \tau_{xTS}) \quad (4)$$

$$\upsilon_f = k_t * d \quad (5)$$

$$H_L = Q / (w * L) \tag{6}$$

$$\tau_{xTS} = A_{xTS} / (\alpha_{xTS} * A_{MC}) \tag{7}$$

$$\tau_{MC} = L / (Q / A_{MC}) \tag{8}$$

where υ_f is the apparent nutrient uptake velocity (m d^{-1}), k_t is the time-specific DIN uptake rate (d^{-1}), d is water depth (m), H_L is hydraulic load (m d^{-1}), w is width (m), L is reach length (m), α_{xTS} is the exchange coefficient for the STS or HTS compartment (d^{-1}), A_{MC} is the simulated cross-sectional area of the MC (m^2), A_{xTS} is the cross sectional area of the STS or HTS compartment (m^2), Q is the simulated average daily discharge in the grid cell i (m^3 d^{-1}), τ_{xTS} is the residence time of water in the STS or HTS compartment (d), and τ_{MC} is the residence time of water in the MC compartment (d). It is important to note the underlying differences in the two nutrient removal metrics applied in this study. A vertical uptake velocity is applied to the MC (υ_f) whereas time-specific volumetric DIN uptake rates (k_t) are applied to STS and HTS compartments. Therefore, when applying spatially uniform reaction rates to all three compartments, the υ_f value for the MC will remain constant throughout the network, but the k_t value for the MC will vary because it is a function of river depth (Alexander et al. 2000).

The downstream flux of DIN from grid cell i (Flux$_i$) is calculated as:

$$\text{Flux}_i = (\text{Upstream}_i + \text{Local}_i) * (1.0 - \text{Removal}_i) \tag{9}$$

where Upstream$_i$ (kg d^{-1}) is the sum of DIN inputs flowing into grid cell i from immediately upstream grid cells during the time step, and Local$_i$ (kg d^{-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 and results are processed using monthly averages.

Surface TS

$\text{Removal}_{STS} = 1 - \exp(-k_r \tau_{STS})$

$\uparrow\downarrow$ STS Transfer = $(\alpha_{STS} * A_{MC} * L) / Q$

DIN Inputs

Local $\rightarrow$

Upstream $\blacksquare\!\!\rightarrow$

Main Channel

$\text{Removal}_{MC} = 1 - \exp(-V_f/H_L)$

$\blacksquare\!\!\rightarrow$ **Downstream DIN Flux**

$\uparrow\downarrow$ HTS Transfer = $(\alpha_{HTS} * A_{MC} * L) / Q$

Hyporheic TS

$\text{Removal}_{HTS} = 1 - \exp(-k_r \tau_{HTS})$

Headwaters $\longrightarrow$ **Basin Mouth**
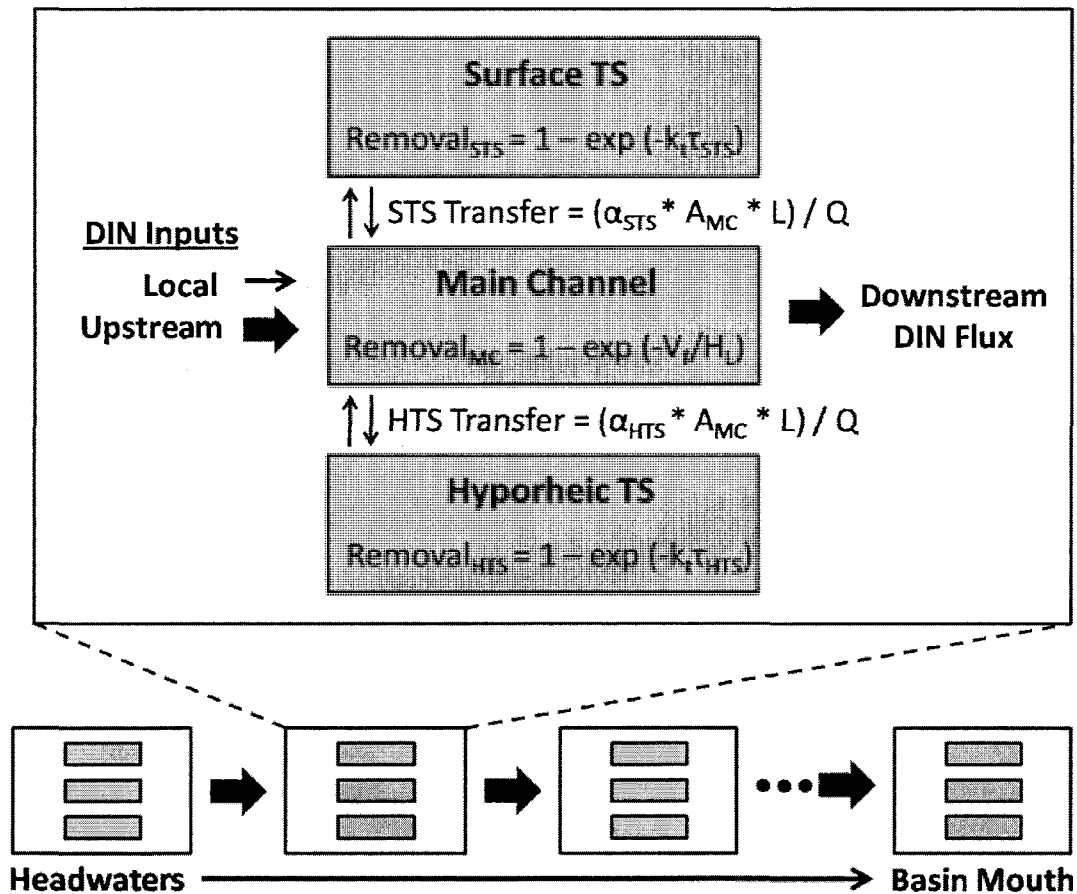
Figure 2 Conceptual model of MC, STS, and HTS DIN removal for a single river grid cell, derived from Mulholland and DeAngelis (2000) and updated to account for two TS compartments instead of one lumped zone. The resulting DIN flux from a river grid cell goes downstream to the next sequential grid cell and so on to the basin mouth for every flow path in the river network.

The fraction of median travel time due to STS or HTS (F_{med}) is a useful and commonly applied metric in evaluating the relevance of TS on water transport (Runkel 2002). The fraction of median travel time due to STS or HTS (xTS) is calculated as:

$$F_{med} xTS = (1 - e^{-L(\alpha/u)}) * A_{xTS} / (A_{MC} + A_{STS} + A_{HTS}) \qquad (10)$$

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

To assess the importance of exchange with TS at network scales, I have adjusted several existing metrics and created a few new ones. First, the average flow path distance required for an average water molecule to enter HTS or STS once (S_{HTS} or S_{STS}) was derived from Mulholland (1994) and is calculated by dividing the total length of a particular river order by the summation of Transfer$_{xTS}$ terms (equation 3) for the river order:

$$S_{xTS, z} = \frac{\sum_{i=1}^{n} [L_{z, i}]}{\sum_{i=1}^{n} [Transfer_{xTS, z, i}]} \qquad (11)$$

Where $S_{xTS, z}$ is the flow path distance (m) 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, and L_z is the length of each grid cell of stream order Z (m).

The number of times an average water molecule enters TS along a flow path from the grid cell of runoff generation, j, to the river mouth is calculated as:

$$\text{Entries}_{xTS, j} = \sum_{i=1}^{n} [\text{Transfer}_{xTS, i}] \tag{12}$$

where $\text{Entries}_{xTS, j}$ is the number of entries into STS or HTS for an average water molecule along its flow path from the grid cell of runoff generation, j, to the basin mouth, i is the local river grid cell, and n is the total number of river grid cells in sequence to the river mouth. A basin-scale average ($\text{Entries}_{xTS, basin\ avg}$) is calculated by dividing the total number of entries of runoff from all grid cells (k is the total number of grid cells) by the total volume of runoff generated by all grid cells (Runoff_j):

$$\text{Entries}_{xTS,\ basin\ avg} = \frac{\displaystyle\sum_{j=1}^{k} [\text{Entries}_{xTS, j} * \text{Runoff}_j]}{\displaystyle\sum_{j=1}^{k} [\text{Runoff}_j]} \tag{13}$$

The total residence time (d) that an average water molecule spends in STS, HTS, and MC compartments along its flow path from the grid cell of runoff generation, j, to the basin mouth is calculated as:

$$\text{Tstor}_{Flowpath, xTS, j} = \sum_{i=1}^{n} [\text{Transfer}_{xTS, i} * \tau_{xTS, i}] \tag{14}$$

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$$\text{Tstor}_{\text{Flowpath, MC, j}} = \sum_{i=1}^{n} [\tau_{\text{MC, i}}]$$

(15)

Where i is the local river grid cell, n is the total number of river grid cells in sequence to the river mouth, and τ_{xTS} and τ_{MC} (d) are defined in equations 7 and 8, respectively. A basin-scale average ($\text{Tstor}_{\text{basin avg}}$), is calculated by weighting the average residence time in each compartment ($\text{Tstor}_{\text{Flowpath, MC, j}}$, $\text{Tstor}_{\text{Flowpath, HTS, j}}$, $\text{Tstor}_{\text{Flowpath, STS, j}}$) by the volume of runoff that travels through each flow path (Runoff_j):

$$\text{Tstor}_{\text{basin avg}} = \frac{\sum_{j=1}^{k} [\text{Tstor}_{\text{Flowpath, j}} * \text{Runoff}_j]}{\sum_{j=1}^{k} [\text{Runoff}_j]}$$

(16)

Hydrologic Conditions

A hydrologic approach was applied that provided an accurate portrayal of baseflow conditions throughout the river network, while also giving slightly greater weight to urban portions of the basin which tend to have somewhat higher flows. USGS gage data were used to calculate mean basin runoff for the upper and lower portions of the Ipswich basin. Daily runoff for the upper basin (RO_{mid}, mm d^{-1}) was

based on discharge measured at the USGS gage station 01101500 at Middleton and then scaled using the contributing drainage area to the gage. Runoff for the lower portion of the watershed was calculated based on the difference in discharge measured at the Middleton gage and the USGS gage station 01102000 at Ipswich and then scaled by the amount of inter-station contributing drainage area (RO_{ips}, mm d^{-1}) (Figure 1). To account for an increase in runoff due to imperviousness, the Ipswich River basin was partitioned into approximately 2 km^2 subbasin areas and percent impervious surfaces were calculated for each (Wollheim et al. 2008). Runoff from each subbasin was derived from RO_{mid} and RO_{ips}, depending on whether the subbasin is in the upper or lower portion of the watershed, and was scaled based on a factor that is a function of subbasin imperviousness:

$$RO_{sub} = RO_x * F\_IMP_{sub} \qquad (17)$$

$$F\_IMP_{sub} = (22.4 + 0.27 * IMP_{sub})/25 \qquad (18)$$

where RO_x is RO_{mid} or RO_{ips} (mm d^{-1}), IMP_{sub} is the percent of impervious area in the subbasin, and F_IMP_{sub} is an empirical scaling factor that accounts for a greater proportion of runoff generated in urban catchments than in forested catchments (Wollheim et al. 2005; Pellerin et al. 2007). Daily discharge in each river grid cell was calculated by flow accumulation of runoff from upstream grid cells. The approach used here follows that used in a study by Wollheim et al. (2008).

Comparisons of predicted and observed daily discharges for the month of August, 2001, were made at the USGS Ipswich gauge (324 km^2 drainage area, 11.7%

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impervious), USGS Middleton gauge (115 km^2 drainage area, 16.4% impervious), and the UNH Sawmill Brook gauge (4.1 km^2 drainage area, 24.6% impervious). Measures of correlation and difference between predicted and observed discharge were quantified using the observed mean ($\bar{O}$), predicted mean (P), the standard deviation of the predicted discharge (S_p), the standard deviation of the observed discharge (S_o), the intercept of the regression line (a), the slope of the regression line (b), the mean absolute error (MAE), the root mean square error (RMSE), and the Nash-Sutcliffe coefficient (NS). The MAE, RMSE, and NS measures are calculated as follows (Willmott 1982):

$$MAE = \frac{\sum_{i=1}^{n} [P_i - O_i]}{n} \tag{19}$$

$$RMSE = \left[\frac{\sum_{i=1}^{n} [P_i - O_i]^2}{n} \right]^{0.5} \tag{20}$$

$$NS = 1 - \left[\frac{\sum_{i=1}^{n} [O_i - P_i]^2}{\sum_{i=1}^{n} [O_i - \bar{O}]^2} \right] \tag{21}$$

River Network Geomorphology

A digital topological river network with 120 m grid cell resolution (STN-120m) was used that was previously applied by Wollheim et al. (2008). The network was originally developed using 30-meter resolution digital elevation model (DEM) with USGS hydrography (1:25,000) burned in using the AGREE program (Hellweger and Maidment 1997). Grid cells that are not intersected by hydrography are strictly land cells and do not have a river component. The resulting drainage network is a 5th order river system (Table 1, Figure 1). Due to a long 5th order river segment that is not typical of observed scaling relationships (Horton 1945), I partitioned the 5th order reach into 5a and 5b segments to avoid skewing results based on river size. The 5a segment was identified as having a contributing area of 140 km^2, as would be expected in the Strahler stream order system (Horton 1945) based on the configuration of the Ipswich River and its network drainage area ratio of 4. The 5b segment is downstream of the 5a section and constitutes the remaining length of the mainstem.

Table 1 Geomorphic characteristics of the Ipswich River network.

Stream Order	Mean Direct Drainage Area[a] (km^2)	Mean Stream Length (km)	Stream Count	Direct Drainage Area[b] (fraction)
1	0.52	0.65	432	0.57
2	2.35	1.33	103	0.21
3	9.60	2.77	28	0.11
4	34.5	5.62	6	0.05
5a	148	13.3	1	0.03
5b	404	23.5	1	0.04

[a]Average watershed area draining directly to each stream order
[b]Proportion of total watershed area draining directly to each stream order

River hydraulic geometry was simulated using downstream power law relationships specific to the Ipswich network that adjust cross-sectional form to accommodate the mean annual discharge. Mean annual channel width (W_i) and depth (D_i) in river grid cell i were calculated using mean annual discharge (Q_i) with the following set of equations:

$$W_i = 9.56 * Q_i^{0.65} \tag{22}$$

$$D_i = 0.45 * Q_i^{0.17}. \tag{23}$$

These power law relationships were derived from Ipswich River hydraulic data at 10 USGS streamflow gauges (Zarriello 2000), and 8 years of field data collected at two headwater stream locations. Instantaneous channel width and depth in grid cell i (w_i and d_i) at each time step is based on the at-a-site power relationship with instantaneous discharge (q_i):

$$w_i = a_i * q_i^y \tag{24}$$

$$d_i = b_i * q_i^z, \tag{25}$$

$$A_{MC} = w_i * d_i \tag{26}$$

where $a_i = W_i / Q_i^y$, $b_i = D_i / Q_i^z$, and A_{MC} is the cross sectional area of the main channel (m^2). The values for y and z are 0.1 and 0.4, respectively and are based on Ipswich data (Zarriello 2000) and are typical of rivers worldwide (Park 1977).

Transient Storage Hydraulic Characteristics

To model DIN removal in non-advective zones, specific TS hydraulic parameters are needed to characterize the TS compartment's connectivity with the MC and residence times (Figure 3). River network STS and HTS hydraulic parameters are based on values reported for 6 tracer experiments conducted as part of this collaborative study during summer low flow periods in 1st through 5th order stream segments within the Ipswich and Parker Rivers (Briggs et al. 2009, in revision) (Figure 1). Assuming that the four transient storage parameters (α_{STS}, α_{HTS}, A_{STS}/A_{MC}, and A_{HTS}/A_{MC}) are typical of most hydrology data and are log-normally distributed (Yevjevich 1972), a log-transformed mean was calculated for each parameter value. The mean values were then re-transformed via exponentiation to original units and applied throughout the river network. From this point forward, re-transformed lognormal mean values are simply referred to as mean values. The mean exchange coefficient for the STS (1.3×10^{-4} s^{-1}) is about an order of magnitude higher than the mean exchange coefficient for the HTS (9.5×10^{-6} 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 2). Uncertainty in each parameter mean value was quantified with a 95% confidence interval (CI) (Table 2). While these experiments indicate that A_{STS}, A_{HTS}, and A_{MC} increase with contributing drainage area, it remains uncertain whether the relative cross-sectional areas (A_{STS}/A_{MC} and A_{HTS}/A_{MC}) change with stream size because of a limited sample size. Various spatial distributions of STS and HTS parameter values were evaluated with the model as alternative scenarios (see below).

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Table 2 Summary of TS hydraulic and reactivity parameters.

Statistic	α_{STS}	α_{HTS}	A_{STS}/A_{MC}	A_{HTS}/A_{MC}	k_t
N	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
Re-transformed Mean (original units)	1.3×10^{-4} (s^{-1})	9.53×10^{-6} (s^{-1})	0.20 (m^2/m^2)	0.35 (m^2/m^2)	0.64 (d^{-1})
Re-transformed 95% Confidence Interval (original units)	0.94×10^{-4} - 1.82×10^{-4} (s^{-1})	0.49×10^{-6} - 18.5×10^{-6} (s^{-1})	0.15 - 0.27 (m^2/m^2)	0.09 - 1.36 (m^2/m^2)	0.26 - 1.53 (d^{-1})
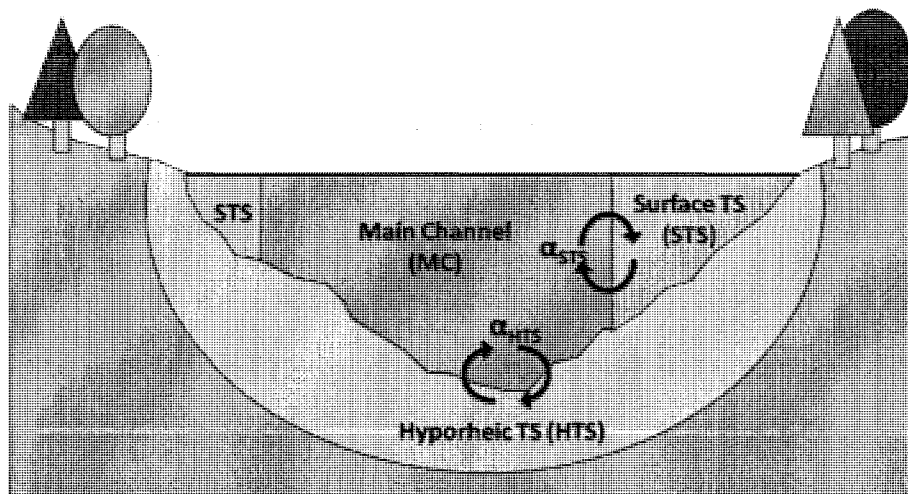
Figure 3 Conceptual diagram of advective (MC) and non-advective (STS and HTS) compartments in a river cross-section. The blue, green, and orange areas represent A_{MC}, A_{STS}, and A_{HTS}, respectively. Exchange coefficients (α_{STS}, α_{HTS}) characterize the compartments connectivity with the MC.

DIN Inputs

Spatially distributed DIN inputs to the river network were derived from empirical relationships between DIN concentration and land use and are described in full by Wollheim et al. (2008). Using this relationship, the model simulates runoff DIN concentrations as a function of percent human land cover (residential + commercial + agricultural land) and runoff conditions (Wollheim et al. 2008). Percent human land cover for the Ipswich basin is provided in Figure 4. Load concentration estimates match observations best when flow conditions measured at the basin mouth are greater than 1 $m^3 s^{-1}$ (Wollheim et al. 2008) and, therefore, are suitable for this study.
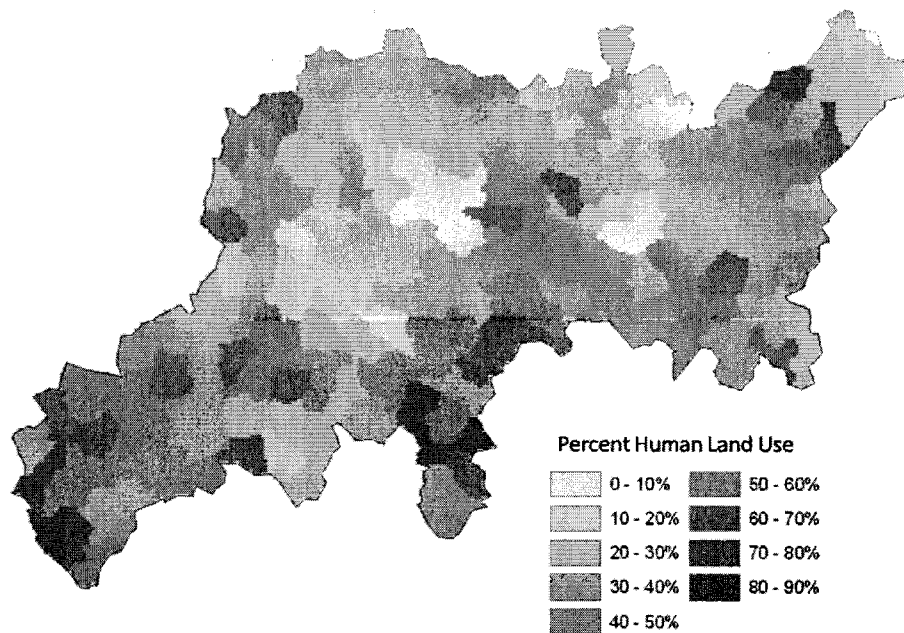
Figure 4 Percent human land use in the Ipswich basin (residential, commercial and agricultural land types). Data is source is MassGIS land use layer (2005) based on 0.5 m resolution ortho photographic imagery captured in April 2005.

Biological Activity

DIN uptake values were based on results from $^{15}NO_3$ tracer experiments performed during the summers of 2003, 2004 and 2005 in eight headwater streams in the Ipswich River as part of the LINX2 project (Mulholland and al. 2008). The time-specific biological reactivity rate (k_t) required in TS and the MC to match observed reach DIN uptake velocities (υ_f) was solved for each of the eight experiments using a single-compartment version of the TS model presented in Figure 2. A lumped compartment model was used here because the LINX2 data were not partitioned between STS and HTS compartments. A k_t value for each experiment was computed using the Solver function in Excel and a lognormal mean was calculated from all 8 experiments. The resulting re-transformed mean reactivity rate was 0.64 d^{-1} and was applied uniformly throughout the river network in the MC, STS and HTS. The average depth across all the LINX2 stream experiments was 0.131 m, therefore a k_{MC} value of 0.64 d^{-1} in these headwater streams equates to a υ_f value of 0.084 m d^{-1}. From this point forward, the re-transformed lognormal mean reaction rate is referred to as the mean reactivity rate.

It should be noted that 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 non-advective zones of the stream channel (Thomas et al. 2003). Generally, HTS is considered to have the highest processing rate for nitrate removal because water would encounter a greater degree of biofilms and anoxic zones there than it would in surface water (Hall et al. 2002). STS is a depositional zone for organic matter and could promote these conditions along the water-sediment interface

and therefore, it is likely that STS has a greater processing rate than the MC (Hall et al. 2002). 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.

Observed Concentration Data

Observed DIN concentrations at the basin mouth are based on two-day composite samples taken from an automated sampler by the Plum Island LTER during the months of July, August and September (2002 – 2006). Comparisons are made between predicted and observed DIN concentrations at the river mouth. In addition, a synoptic survey of DIN concentrations was conducted on August 26, 2001 at 15 locations along the mainstem and tributaries of the Ipswich River. A comparison was made between predicted and observed DIN concentrations along a basin profile of the longest distance from the river mouth to a headwater stream and the prediction error (PE) was calculated at the river mouth. PE is calculated as $(P - O) / O * 100$, where P and O are predicted and observed values, respectively (Alexander et al. 2002). Negative PE values indicate the model prediction is too low while positive PE values indicate it is too high.

Scenarios

A number of scenarios were developed to test the sensitivity of river network scale DIN removal to uncertainties in the magnitudes and spatial distributions of TS zone

hydraulic parameters (Table 2). In the base scenario (Scenario 1a), the mean value for each of the five parameters ($A_{HTS}/A = 0.35$, $A_{STS}/A = 0.20$, $\alpha_{HTS} = 9.5E6\ s^{-1}$, $\alpha_{STS} = 1.3E4\ s^{-1}$, and $k_t = 0.64\ d^{-1}$) was applied uniformly throughout the river network. These estimates represent our "best understanding" of parameter values throughout the basin, based on 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 5 parameter values (Scenario 1b, Figure 5b, Table 3) from ranges developed from the lognormal mean and standard deviation for each parameter (Table 2). Random values for each parameter were selected from a lognormal distribution using a rational approximation (Odeh and Evans 1974; Salas 1993) and applied uniformly throughout the river network.

Next, a sensitivity analysis was conducted to evaluate how network scale DIN removal would respond to a heterogeneous spatial distribution of parameter values. The magnitude and spatial distribution of runoff and DIN inputs to the river network remain the same for all scenarios. The cross-sectional area of the MC (A_{MC}) varies identically with discharge in all scenarios (equation 26). These scenarios are discussed in greater detail, below.

Spatial Heterogeneity (Scenario 2). It is unreasonable to expect that TS hydraulic characteristics and processing rates will be spatially uniform throughout the river network. I explored the sensitivity of network DIN removal to 500 random configurations of spatial heterogeneity in TS hydraulic and biogeochemical parameters.

Each grid cell in the river network was assigned random parameter values (Figure 5c) selected from lognormal distributions developed from the lognormal mean and standard deviation for each parameter (Table 2). Random values were selected from the lognormal distribution using a rational approximation (Odeh and Evans 1974; Salas 1993). Processing rates in the MC, STS, and HTS are identical within a grid cell, but vary spatially. In contrast, STS and HTS hydraulic parameters vary independently.

Spatial Heterogeneity and Increase in A_{TS}/A_{MC} with River Size (Scenario 3).
Results from Briggs et al. (2009) suggest that A_{HTS}/A_{MC} and A_{STS}/A_{MC} may increase with river size for contributing drainage areas up to 200 km^2. This relationship was not significant because of limited data points. A scenario was developed to evaluate the impact of this potential scaling relationship on network scale DIN removal with an embedded degree of spatial heterogeneity (Figure 5d). It was assumed the lognormal means for A_{STS}/A_{MC} and A_{HTS}/A_{MC} generally increase with basin size, based on fits to the empirical data (Briggs et al. 2009, in revision). Heterogeneity was introduced by selecting random parameter values from a lognormal distribution around the empirical means and standard deviations (Table 2). No empirical data were available for river segments with drainage areas greater than 200 km^2, so parameter values in these segments were selected from the full distribution range. Reactivity rates (k_t) and connectivity parameters (α_{STS}, α_{HTS}) were distributed heterogeneously throughout the river network as they were in Scenario 2, with no constriction based on contributing drainage area.

Sensitivity to TS Hydraulic Parameters (Scenario 4). The sensitivity of total network DIN removal to various combinations of exchange coefficients (α_{STS}, α_{HTS}) and TS zone sizes (A_{STS}/A_{MC}, A_{HTS}/A_{MC}) was investigated in Scenario 4. A hypothetical range in TS hydraulic parameters was established from 0 to 10 times the mean network values provided in Table 2. DIN processing rates are kept constant throughout the river network ($k_t = 0.64$ d^{-1})

Sensitivity to Reactivity Parameters (Scenario 5). It is highly unlikely that processing rates in the three compartments are identical. The sensitivity of total network DIN removal to various combinations of individual processing rates in the three compartments was evaluated in Scenario 5. A hypothetical range in k_t values from 0.0 to 10 times the mean empirical value of 0.64 d^{-1} was used. In this scenario, all TS hydraulic parameters (α_{STS}, α_{HTS}, A_{STS}/A_{MC}, and A_{HTS}/A_{MC}) were kept constant throughout the river network as the mean values provided in Table 2.

Table 3 Summary of model scenarios.

No.	Description	TS Hydraulic Parameters	Reactivity Parameters
1a.	Base Scenario: uniform parameter values (mean)	Mean network values	Mean network value
1b.	Uniform parameter values (Monte Carlo Analysis)	Uniform network values randomly selected from log-normal distributions	Uniform network values randomly selected from log-normal distributions
2.	Spatial heterogeneity (Monte Carlo Analysis)	Grid cell values randomly selected from log-normal distributions	Grid cell values randomly selected from log-normal distributions
3.	Spatial heterogeneity with increase in A_{TS}/A_{WC} with river size (Monte Carlo Analysis)	Grid cell values randomly selected from log-normal distribution and adjusted based on contributing drainage area	Grid cell values randomly selected from log-normal distributions
4.	Sensitivity to TS hydraulic Parameters	Hypothetical range	Mean network value
5.	Sensitivity to reactivity parameters	Mean network values	Hypothetical range
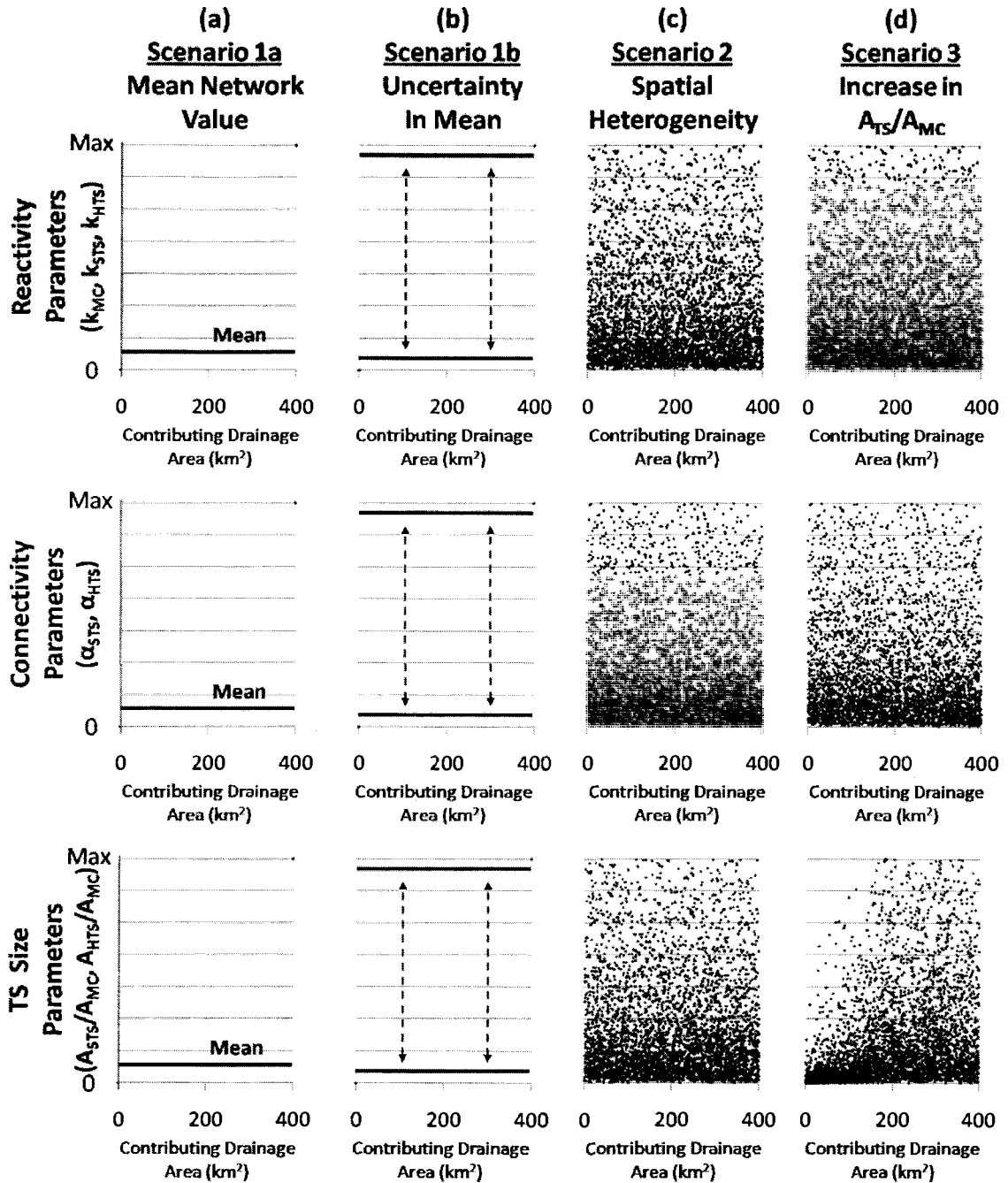
Figure 5 Conceptual diagram of spatially varying grid cell parameter values for a single model run for a.) Scenario 1a, b.) Scenario 1b, c.) Scenario 2 and d.) Scenario 3. Each point represents an individual grid cell with a specified contributing drainage area. Scenario 1a applies a mean network parameter uniformly throughout the river network. Scenario 1b randomly selects parameter values and applies them uniformly throughout the network. Scenario 2 applies a random distribution of parameter values throughout the river network. Scenario 3 applies a trend of increasing TS size with drainage area (up to 200 km^2), with all other parameters distributed heterogeneously.

CHAPTER III

RESULTS

Discharge

The hydrological model adequately predicts discharge throughout the river network during baseflow conditions (Figure 6a, 6b, and 6c). Predicted flows at the Ipswich (gauge number 00102000) and Middleton (gauge number 00101500) USGS gauge locations closely match observed discharges as indicated by Nash-Sutcliffe values of 1.00 at each site (Table 4). The variability in predicted discharge is similar to the variability in observed discharge at these two gauge locations (Table 4). The RMSE and MAE are among the best metrics of model performance (Willmott 1982) and indicate there is very little difference between observed and predicted flows at these two locations on the main stem. Predicted discharge at the Sawmill Brook station was significantly lower than observed discharge during four days that had relatively high flow levels (8/3, 8/4, 8/10, and 8/12/2001). Therefore, the model may overestimate DIN removal in small urban catchments during precipitation events because discharge is inversely proportional to removal efficiency (Wollheim et al. 2008). Omitting these four days from the data set indicates the model slightly overestimates baseflow levels (Figure

6c). Therefore, the model provides a conservative estimate of DIN removal in urban

headwater catchments during normal baseflow conditions.
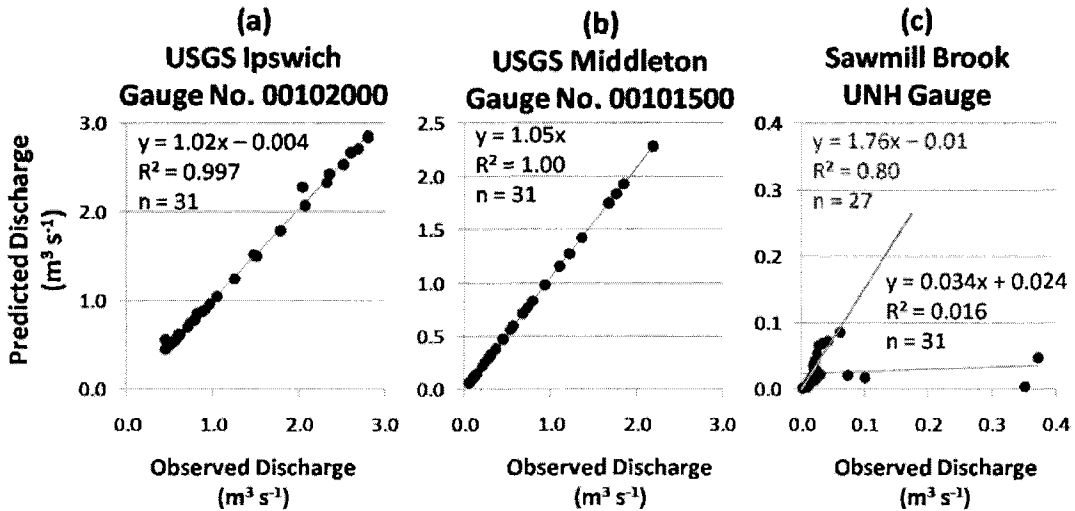
Figure 6 Scatter plots of observed versus predicted daily average discharge for the month of August, 2001, at a.) USGS Ipswich gauge number 00102000, b.) USGS Middleton gauge number 00101500, and c.) Sawmill Brook gauge maintained by the Water Systems Analysis Group at the University of New Hampshire. Observed and predicted flows at the Sawmill Brook gauge are highly correlated for flows less than 0.07 $m^3 s^{-1}$ (n = 27).

Table 4 Quantitative measures of runoff model performance at three gauge locations for the month of August, 2001. The Nash-Sutcliffe (NS) value for Sawmill Brook is negative which indicates the observed mean is a better predictor than the model.

Gauge	$\bar{O}$ $m^3 s^{-1}$	P $m^3 s^{-1}$	S_o $m^3 s^{-1}$	S_p $m^3 s^{-1}$	n	a	B	R^2	MAE	RMSE	NS
USGS Ipswich	1.32	1.35	0.82	0.84	31	0.00	1.02	1.00	0.03	0.05	1.00
USGS Middleton	0.63	0.67	0.59	0.62	31	0.00	1.05	1.00	0.03	0.04	1.00
UNH Sawmill[1]	0.02	0.03	0.01	0.02	27	-0.01	1.76	0.8	0.01	0.02	-0.57

[1]Four days (8/3, 8/4, 8/10, and 8/12/2001) were removed from the data set because of high flows associated with precipitation events.

MC-STS and MC-HTS Exchange: Base Scenario

Empirical results (Briggs et al. 2009, in revision) indicate that hydrological conductivity, determined as the per time water exchange coefficient (α, s^{-1}), is greater between the MC and STS than between the MC and HTS (Table 2). Model results further quantify this connectivity at the reach and network scales. For the base scenario, in which the mean TS hydraulic characteristics are applied throughout the river network and A_{MC} increases with discharge, model results suggest the 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 5). Per unit length, water has the greatest opportunity to enter TS in headwater streams, and connectivity decreases as river size increase (Table 5). However, water is more likely to enter TS in a higher order reach because these reaches are longer (Table 5).

Table 5 Average number of water molecule entries into STS, HTS for base scenario.

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	
		STS	HTS	STS	HTS	STS	HTS
1	0.65	3.60	0.26	0.28	3.79	2.34	0.17
2	1.33	2.70	0.20	0.37	5.05	3.60	0.26
3	2.77	2.07	0.15	0.48	6.59	5.74	0.42
4	5.62	1.70	0.12	0.59	8.04	9.54	0.70
5a	13.3	1.26	0.09	0.79	10.8	16.8	1.23
5b	23.5	1.02	0.07	0.99	13.4	23.9	1.75

Average number of STS entries per 200 m Ipswich segment = 0.58
Average number of HTS entries per 200 m Ipswich segment = 0.04

At basin scales, and given the geomorphology of the Ipswich, half of the runoff generated basin-wide during baseflow periods enters the STS at least 36.6 times as it

travels through the river network (Figure 7). Some water molecules enter the network at the most distant headwater streams and, therefore, can pass through the STS approximately 75.8 times. 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 2.68 times during its flow path through the network (Figure 7) 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.
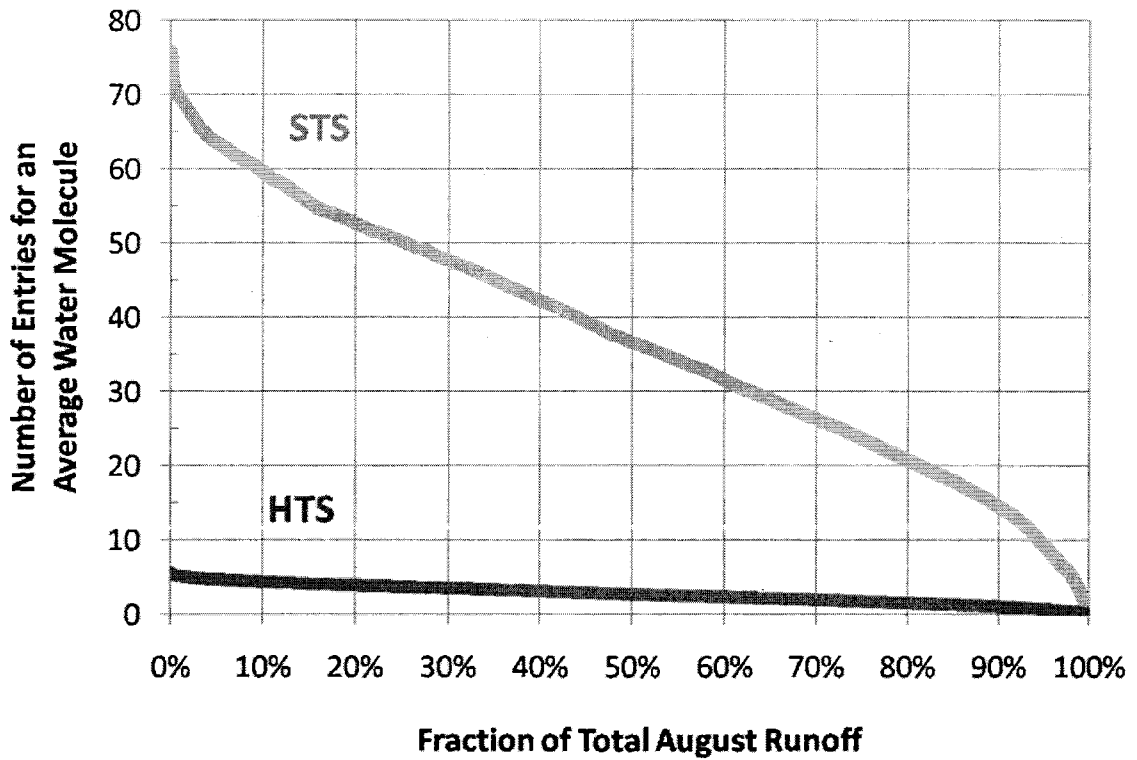
Figure 7 Cumulative frequency distribution of basin wide runoff entering STS and HTS during baseflow conditions for Scenario 1a. These results are calculated using equation 12 and weighted by the total volume of water that travels along each flow path. Results account for the spatial distribution of runoff inputs to the river network.

MC, STS, and HTS Residence Times: Base Scenario

The model predicts a network-wide average STS residence time of 0.018 days per entry to this zone before continuing downstream (Table 6). This is similar to the average empirical residence time of 0.019 days per entry measured at the 6 experiment sites (Briggs et al. 2009, in revision) (Table 6). The average modeled residence time in the HTS compartment, 0.42 days, is much lower than the empirical average of 1.03 days (Briggs et al. 2009, in revision). Residence times in the MC compartment per grid cell (120 m, or 170 m flow length) range from 0.01 day to 0.07 day with shorter durations occurring in downstream river segments. The fraction of median travel time due to temporary retention in TS compartments over a 200 m segment (F_{med}^{200}) is a function of both connectivity and residence time. Model results were similar to observations in that F_{med}^{200}STS was significantly higher than F_{med}^{200}HTS (Table 6).

Table 6 Comparison of observed and modeled TS residence times.

	Average Residence Time per Entry (d)		F_{med}^{200}	
	STS	HTS	STS	HTS
Observed[a] (Briggs et al., 2009)	0.019	1.03	10.6%	0.92%
Predicted[b] (Model Results)	0.018	0.42	5.23%	0.92%

[a] Average results for 6 experiment locations conducted during baseflows (Briggs et al., 2009b)
[b] Average network results during baseflow conditions (this study)

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 baseflows in the Ipswich has a total residence time of at least 3.26 days in the MC, 1.11 days in HTS,

and 0.65 days in STS (Figure 8). 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, 22.1% in HTS, and 12.9% in STS. These results assume the river network consists of channelized reaches only, and do not reflect the role of wetlands and lakes. Only 15.3% of baseflow runoff remains in STS for longer than one day during its flow path through the river network (Figure 8). The longest residence time that any grid cell's average runoff water molecule resides in STS as it moves through the network is 1.38 days. Some water molecules can remain in HTS and MC on average up to 2.35 days and 6.75 days, respectively. Approximately 47.4% of the watershed surface area generates runoff that remains in HTS for at least one day (Figure 9), whereas only 10.8% of surface area generates runoff that remains in STS for at least one day (Figure 10). Runoff from 92.0% of the watershed area remains in the MC for at least one day.

The fraction of median transport time (F_{med}) due to MC, STS, and HTS is different depending on whether evaluated at reach or network scales. Based on reach scale F_{med}^{200} results (Briggs et al. 2009, in revision), the MC contributes the most to median travel times (88.5%), followed by STS (10.6%) and HTS (0.92%) (Table 6). However, at the network scale, a greater proportion of median transport time is due to TS and HTS becomes more important than the STS (Figure 8). Model results indicate the fraction of total basin residence time due to MC, STS and HTS are 65%, 12.9% and 22.1%, respectively. This discrepancy indicates that F_{med}^{200} is not a scale independent measure of transport times. The importance of HTS retention on median travel times emerges only at large scales because although MC-HTS exchange is relatively small for any given

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reach, at the scale of the entire flow path, there is a high probability of water entering

HTS at some point. The limitation in the F_{med}^{200} metric is visited further in the discussion

section.
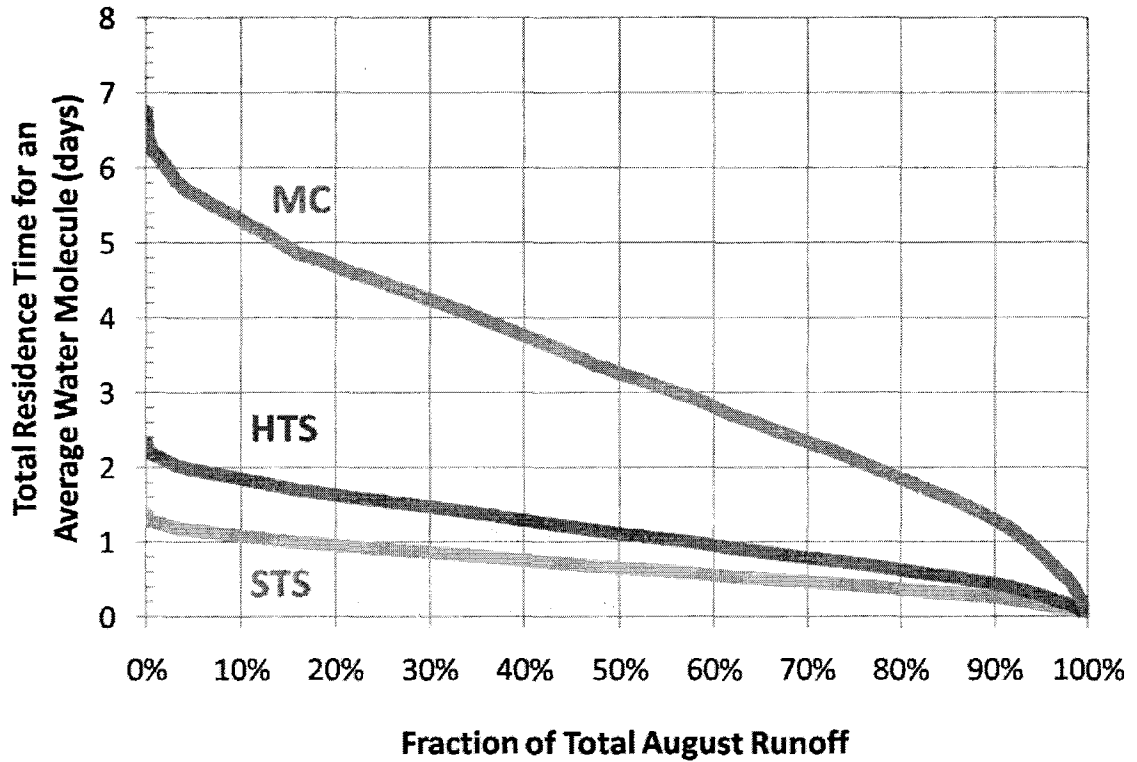
Figure 8 Cumulative frequency distribution of the total residence times that water molecules spend in surface transient storage (STS), hyporheic transient storage (HTS) and main channel (MC) during baseflow conditions in Scenario 1a. These results were calculated using equations 14 and 15 and were weighted 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.
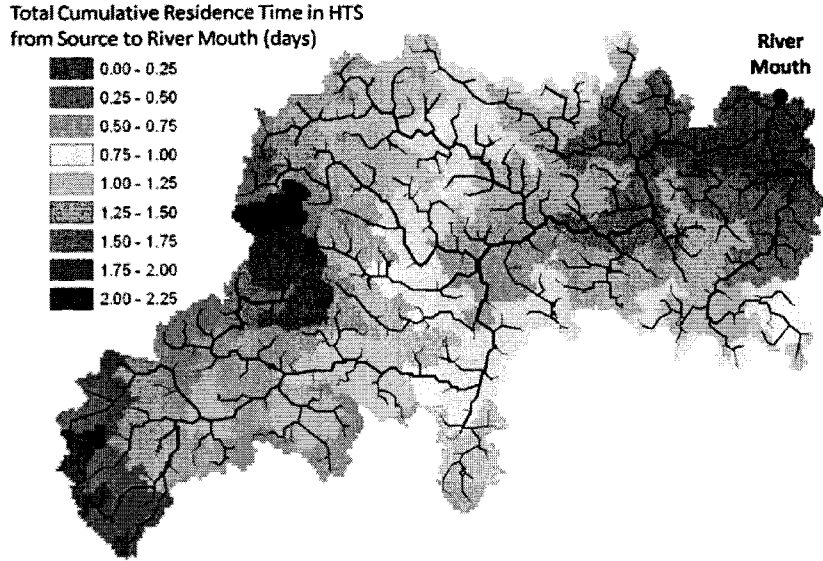
Figure 9 Spatial distribution of the total cumulative residence time of runoff in HTS. Colors represent the total cumulative residence time that runoff will remain in HTS during its flow path from point of generation to the river mouth.
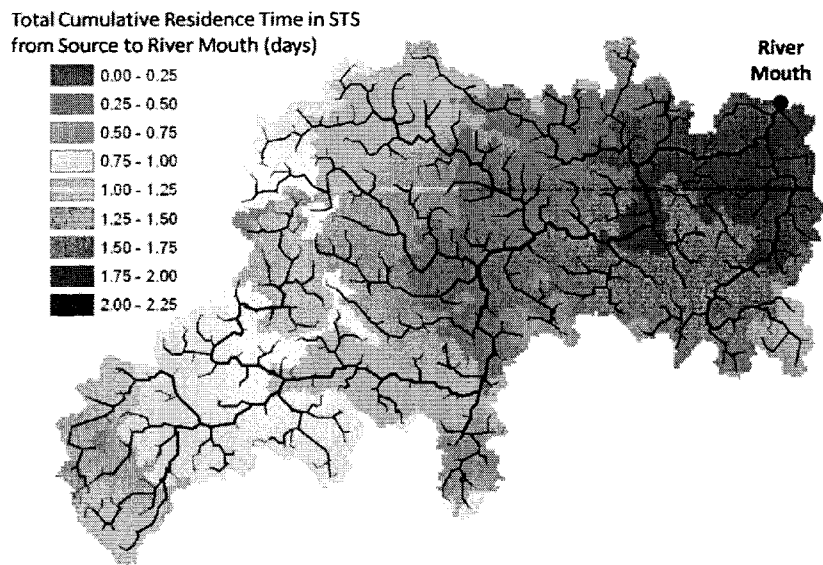
Figure 10 Spatial distribution of the total cumulative residence time of runoff in STS. Colors represent the total cumulative residence time that runoff will remain in STS during its flow path from point of generation to the river mouth.

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Network Scale DIN Removal Among MC, STS, and HTS Compartments: Base Scenario

The river system was extremely effective at removing DIN under baseflow conditions. DIN removal predicted by the model base scenario for August 2001 accounted for 73.1% of total DIN inputs to the river network (Figure 11). The MC compartment removed the largest proportion of total DIN inputs (38.2%), whereas the HTS and STS removed 20.9% and 14.0%, respectively (Figure 11). These results are supported by the long total residence times in the MC at the network scale compared to total residence times in STS and HTS (Figure 8).

A comparison based on uniform segment lengths (200 m) indicates that small streams were the most efficient in removing DIN fluxes (Table 7). The fraction of stream DIN flux removed decreased with increasing stream order. The MC compartment is the most efficient at removing DIN flux per unit distance, and HTS is more efficient than STS (Table 7). 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 decreased with river size because there is a disproportional increase in A_{MC} in the downstream direction and this reduces the proportion of water transfer from MC to TS (equation 3). The removal percentages in Table 7 are not additive over a string of multiple 200 m segments because downstream segments cannot processes any DIN removed by upstream reaches and new DIN inputs are continuously being added along the river continuum.

Table 7 Average percent DIN flux removed per 200 meter stream segment. These values represent the average percent removal of DIN flux that enters a 200 m segment and do not reflect the proportion of total basin inputs removed by the entire network.

Stream Order	MC	STS	HTS	Total
1	7.27%	0.83%	1.25%	9.35%
2	4.31%	0.62%	0.94%	5.88%
3	2.63%	0.48%	0.72%	3.83%
4	1.82%	0.39%	0.59%	2.80%
5a	0.93%	0.29%	0.44%	1.67%
5b	0.56%	0.23%	0.35%	1.15%

In terms of total basin DIN inputs removed by all river segments, the majority of predicted DIN removal occurred in higher order river segments (Figure 11). 5th order river segments contributed 46.5% of total predicted network DIN removal while representing only 7.3% of the total river length. This is largely due to the downstream location of 5th order reaches where a large proportion of total basin inputs enter the upstream ends of these segments. Although the 5th order reach represents only 7.3% of total river length, it is all in one continuous segment, and therefore is the longest part of the total flow path traveled by an average water molecule.

Generally, the proportion of total DIN inputs removed by stream order increases from 1st to 5th order streams (Figure 11). The exception is 3rd order streams which contribute greater DIN removal than 4th order streams due to the relatively short total lengths of 4th order streams in the Ipswich river network (5.9% of total river length). Headwater streams (orders 1 – 2) contribute a relatively small amount to total network removal. The MC compartment dominates removal across river order, because of the

substantial total residence time of water there and because identical reactivity rates were assigned to all three compartments. The HTS contributes more removal than the STS compartment for all river orders, but the effectiveness of STS relative to HTS increases with river size.
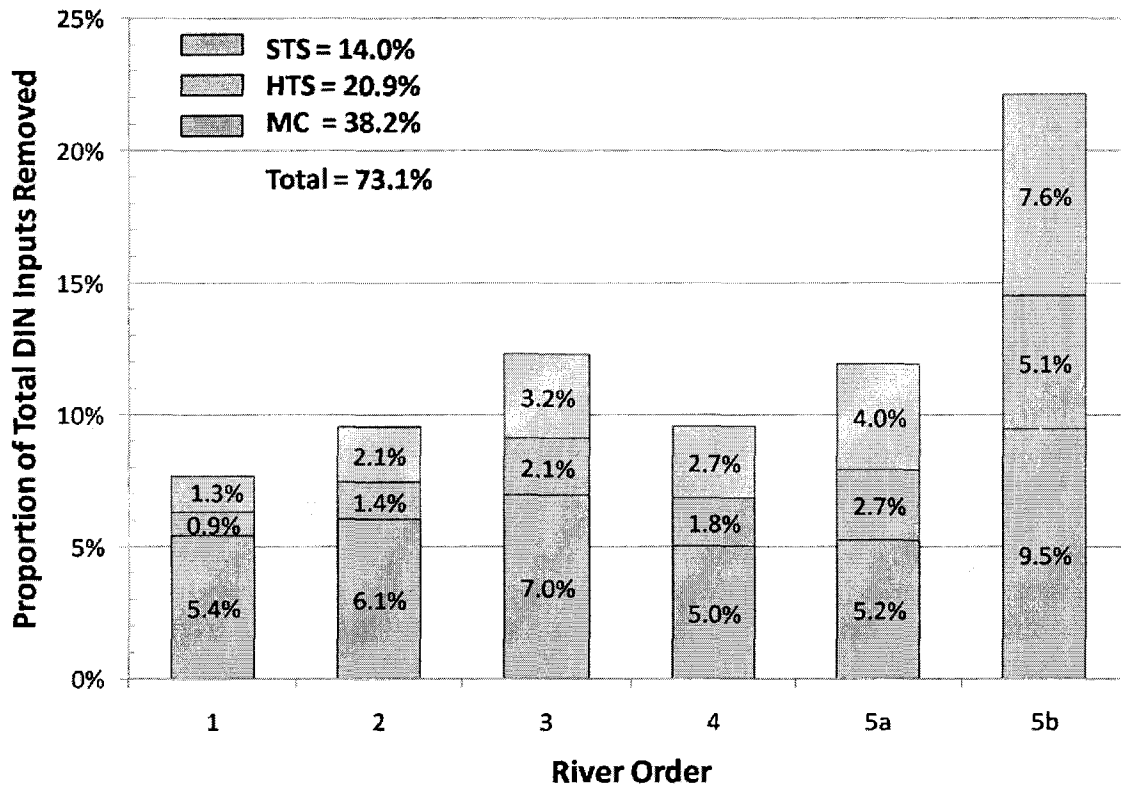
Figure 11 Proportion of total network inputs removed during August 2001 by main channel (MC), surface transient storage (STS), and hyporheic transient storage (HTS) throughout the river network for August 2001 flow conditions. 5th order river segments with contributing drainage areas greater than 140 km^2 were classified as '5b'.

Comparison with Observations

Predicted and observed NO_3 concentrations are similar at the river mouth during summer flow levels (Figure 12). Predictions fall short of capturing the observed variability in DIN concentrations at all flow levels (Figure 12). The model generally

under-predicts NO_3 concentrations during flows between 1.0 and 2.0 m^3 s^{-1}, whereas

the model over-predicts NO_3 concentrations during higher discharges. These results

suggest that predicted network removal is too high for flows between 1.0 and 2.0 m^3 s^{-1}

and too low for flow above 2.0 m^3 s^{-1} measured at the basin mouth. Predicted removal

is too low during high discharges because TS hydraulics may adjust with discharge and

the model does not account for these changes. The TS hydraulics in the model are

optimized for the flow conditions observed during the 6 tracer experiments (1.4 m^3 s^{-1})

conducted by Briggs et al. 2009.

Modeled NO_3 concentrations match observations quite closely along the basin

profile, tending to straddle the observed values (Figure 13). The prediction error (PE) at

the basin mouth is -30% for typical baseflow conditions. A model run that mixes

terrestrial DIN loads without any in-stream biological activity (i.e. k_t = 0 d^{-1} in MC, STS,

and HTS compartments) suggest 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 at the basin mouth

(Figure 13, red line).
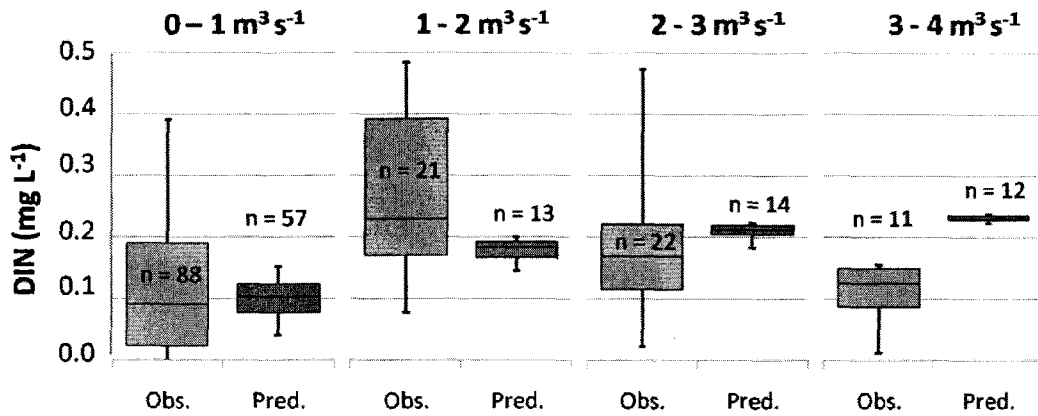
Figure 12 Observed and predicted DIN concentrations for various summer flow conditions (binned based on discharge at the river mouth). Observed concentrations are two-day composite samples taken during the months of July, August and September from 2002 – 2006. Predicted concentrations are average daily DIN concentrations for the months of July, August and September, 2001
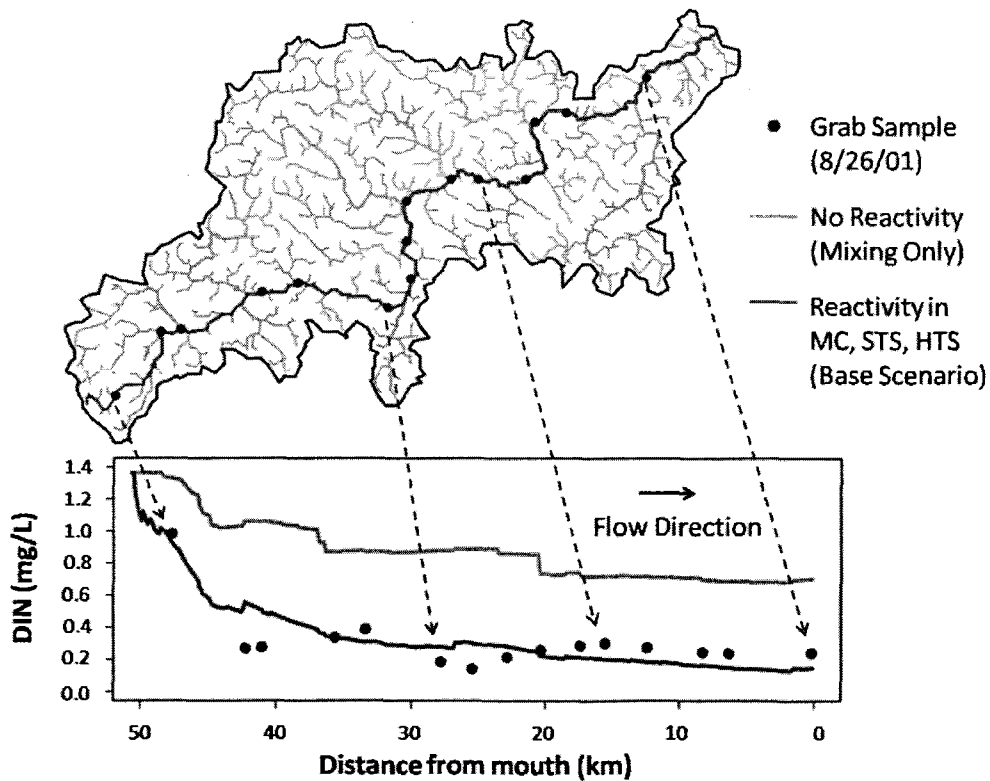
Figure 13 Comparison of observed and predicted DIN concentrations along the basin profile for August 26, 2001. The mixing scenario (red line) describes predicted DIN concentrations as a function of downstream mixing and no reactivity, the reactivity scenario (blue line) shows DIN concentrations as predicted by the base scenario (reactivity in MC, STS, HTS).

Sensitivity Analysis

A number of scenarios were evaluated to test the sensitivity of river network scale DIN removal to varying magnitudes and spatial distributions of TS hydraulic parameters and biogeochemical characteristics (Table 3). Results for each scenario are discussed in detail, below.

Uncertainty in Mean Network Parameters (Scenario 1b)

In this scenario, the model randomly selected a value from a lognormal distribution for each parameter and applied these values uniformly throughout the entire river network. Based on the uncertainty in the empirical mean network parameters, the model predicts a range in total network DIN removal from 10.8% to 99.6% (Figure 14a) with first, second, and third quartiles of 54.2%, 74.3% and 90.0%, respectively (Table 9). The median removal value for the MC was 34.8% (first and third quartiles were 22.2% and 49.3%, respectively), 14.8% for the HTS (first and third quartiles were 5.8% and 30.7%, respectively), and 12.5% for the STS (first and third quartiles were 7.3% and 17.5%, respectively). It should be noted the median removal values for each compartment are mutually exclusive and do not correspond to the same model run.

The Wilcoxon Two-Sample test is a nonparameteric statistical method used to determine if two groups of observations were drawn from the same distribution. This test was used to determine whether there is a statistical difference between the predicted removal by the MC, STS, and HTS in the 500 model runs. In this instance, the

null hypothesis (H_o) was that the contribution of DIN removal in two compartments X (STS) and Y (HTS) have a common cumulative distribution function over the model runs. The alternative hypothesis (H_a) was that a randomly selected value from population X is smaller than a randomly selected value from population Y. This test was used to evaluate comparisons for STS-HTS, STS-MC, and HTS-MC.

The Wilcoxon two-sample tests indicate that H_o is rejected in all cases (Table 8) and suggests there is a statistical difference in the removal proportions provided by each compartment in the 500 model runs. Therefore, the Monte Carlo analysis supports the finding that the MC removes the greatest proportion of total basin DIN inputs, followed by the HTS, and then the STS. However, this evaluation assumes reaction rates in the three compartments are identical. Further, it is acknowledge the importance of each compartment is based on empirical findings measured in channelized segments only. Wetlands, lakes, and beaver dams may have a significant role in network scale removal, but are not reflected in these calculations.

Table 8 Wilcoxon two-sample test.

	HTS – STS Comparison		HTS – MC Comparison		MC – STS Comparison	
	STS (X)	HTS (Y)	HTS (X)	MC (Y)	STS (X)	MC (Y)
Sum of Ranks (W)	231736	268764	184956	315544	151540	348960
n	500	500	500	500	500	500
|Z|	4.054		14.298		21.615	
Prob. > |Z|	<0.0001		<0.0001		<0.0001	
Result	Reject H_o, accept H_a		Reject H_o, accept H_a		Reject H_o, accept H_a	

Spatial Heterogeneity (Scenario 2)

Model runs of 500 combinations of spatially heterogeneous parameter values result in a small range of total network scale DIN removal from 83.4 to 87.7% (Figure 14b). The median network removal for all model runs is 85.4%, which was a considerable increase from Scenario 1b (74.3% of total basin inputs). Spatial heterogeneity increased the median network DIN removal from Scenario 1b in the MC (from 34.8 to from 43.3%), the STS (from 12.5 to 18.0%) and the HTS (from 14.8 to 24.0%) (Figure 14b, Table 9). Network removal is consistently higher across the 500 model runs compared to Scenario 1b because a spatially heterogeneous distribution of random parameters ensures the existence of a number of "hotspots" scattered throughout the river network. These hotspots are able to buffer upstream inefficiencies in DIN processing in river grid cells 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.

Spatial Heterogeneity and Increase in A_{TS}/A_{MC} with River Size (Scenario 3)

An increase in A_{STS}/A_{MC} and A_{HTS}/A_{MC} with contributing drainage area results in an increase in median network removal from Scenario 1b from 74.3 to 89.3% (Table 9, Figure 14c). Network removal remains consistently high (from 87.7 to 92.3%) in the 500 model runs evaluated (Figure 14c). Increasing TS size with contributing area (with heterogeneity) results in an insignificant increase (3.9%) in median network DIN removal compared to the scenario using mean TS size with heterogeneity (Scenario 2). 5th order rivers remove considerably more inputs in Scenario 3 (42.2% of total DIN inputs) than

they do in Scenario 2 (34.1% of total DIN inputs) (Table 9). The increase in 5th order removal occurs exclusively in the TS compartments, and most of this increase can be attributed to HTS. Conversely, removal by the MC in this scenario shifts upstream because inefficiencies in STS and HTS in small streams increases the exposure of the MC to a greater proportion of total basin DIN inputs in the headwaters. Therefore, the difference between Scenario 2 and Scenario 3 with regards to network DIN removal is not the total proportion of inputs removed, but the general location where this removal occurs in the network.
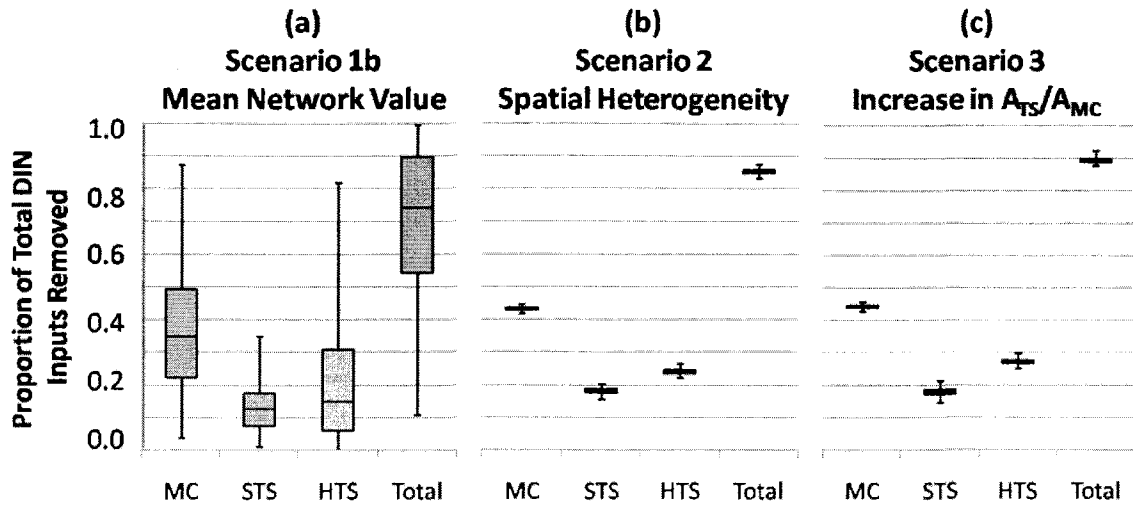
Figure 14 Monte Carlo model results for a) Scenario 1b, b) Scenario 2 and c) Scenario 3. Box plots indicate the sample minimum, lower quartile, median, upper quartile, and sample maximum for 500 model runs.

Table 9 Monte Carlo results for each scenario. Data shown are medians (and first and third quartiles) for 500 model runs. Results for 5th order river segments are in italics. Note that median values for each compartment are mutually exclusive, and do not correspond to the same model run.

Scenario	Proportion of Total Basin DIN Removed			
	MC	STS	HTS	Total
Mean Network Value (1b)	34.8 (22 - 49) *11.6 (8 - 16)*	12.5 (7 - 18) *6.0 (4 - 9)*	14.8 (6 - 31) *7.4 (3 - 15)*	74.3 (54 - 90) *30.5 (23 - 33)*
Spatial Heterogeneity (2)	43.3 (43 - 44) *13.6 (13 - 14)*	18.0 (18 - 19) *8.7 (8 - 9)*	24.0 (24 - 25) *11.7 (11 - 12)*	85.4 (85 - 86) *34.1 (34 - 35)*
Spatial Heterogeneity and increase in A$_{TS}$/A$_{MC}$ (3)	44.3 (44 - 45) *12.4 (12 - 13)*	17.8 (17 - 19) *11.4 (11 - 12)*	27.2 (27 - 28) *18.3 (18 - 19)*	89.3 (89 - 90) *42.2 (42 - 43)*

Sensitivity to TS Hydraulic Parameters (Scenario 4)

Network scale DIN removal is sensitive to STS and HTS hydraulic parameters. Model results suggest that without TS (A$_{STS}$ = A$_{HTS}$ = 0.0) and a constant υ_f (based on k_t = 0.64 d^{-1} in the headwaters) the MC is able to remove approximately 50% of total inputs

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during baseflow conditions (Figure 15a, 15b). Network scale removal increases from 50% with increases in the A_{HTS}/A_{MC} and A_{STS}/A_{MC} parameters (Figure 15a, 15b). Removal is particularly sensitive to high A_{STS}/A_{MC} values because the STS compartment is highly connected to the MC. This is consistent with the notion that large STS features, such as wetlands, beaver ponds, and floodplains are important controls of DIN retention.

Network scale DIN removal is not particularly sensitive to TS exchange coefficients, α_{STS} and α_{HTS} (Figure 16b). Given the mean values for A_{STS}/A_{MC}, A_{HTS}/A_{MC}, and identical reactivity rates in all three compartments, the critical range in α_{HTS} values is between 1×10^{-7} s^{-1} to 1×10^{-5} s^{-1}, where removal slightly increases with increasing HTS exchange coefficient values. Network scale DIN removal does not respond to changes in α above or below this range. The critical range in α_{HTS} values overlaps the uncertainty in the mean value for this parameter (Figure 16b). The critical range in α values is relatively smaller in the STS than in the HTS and is between 1×10^{-7} s^{-1} to 5×10^{-6} s^{-1}. Variation in network mean α_{STS} value does not have an impact on the predicted total network scale DIN removal because it does not overlap the critical range in α_{STS} values (Figure 16a). Network scale DIN removal is not highly sensitive to exchange coefficients because α has a dual effect. Exchange coefficients control the fraction of discharge that enters TS, but also control the residence time of water in storage and these have offsetting effects.

Figure 15 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 2. Figure 15a and 15b present the same data but with different x-axes. The mean values for A_{STS}/A_{MC} and A_{HTS}/A_{MC} are indicated with vertical lines, and the 95% confidence intervals are marked with grey shading.

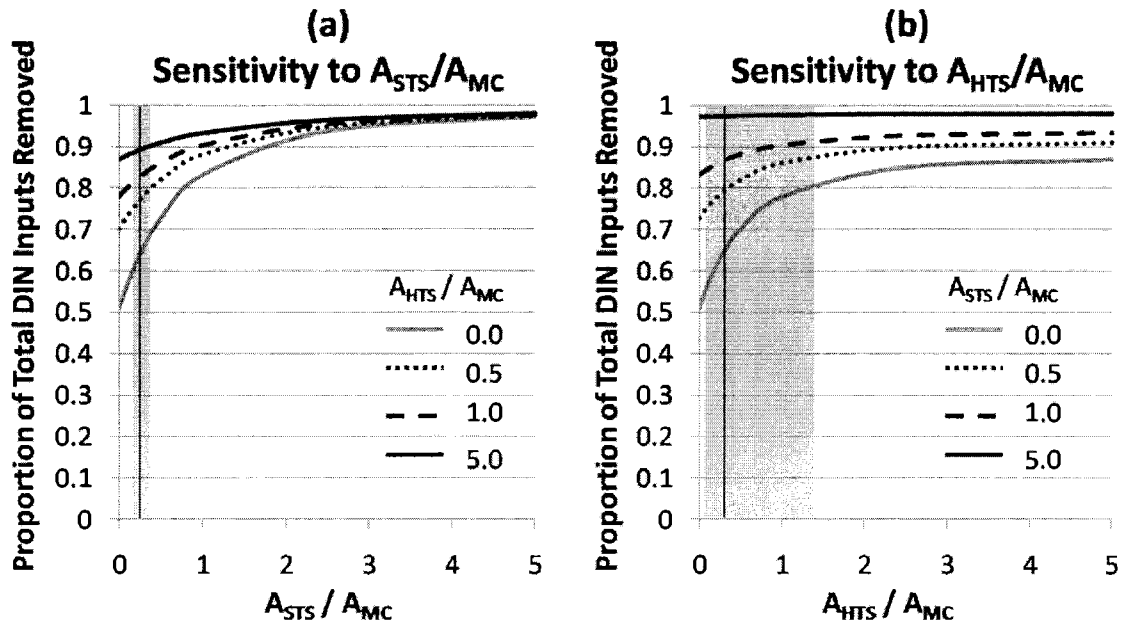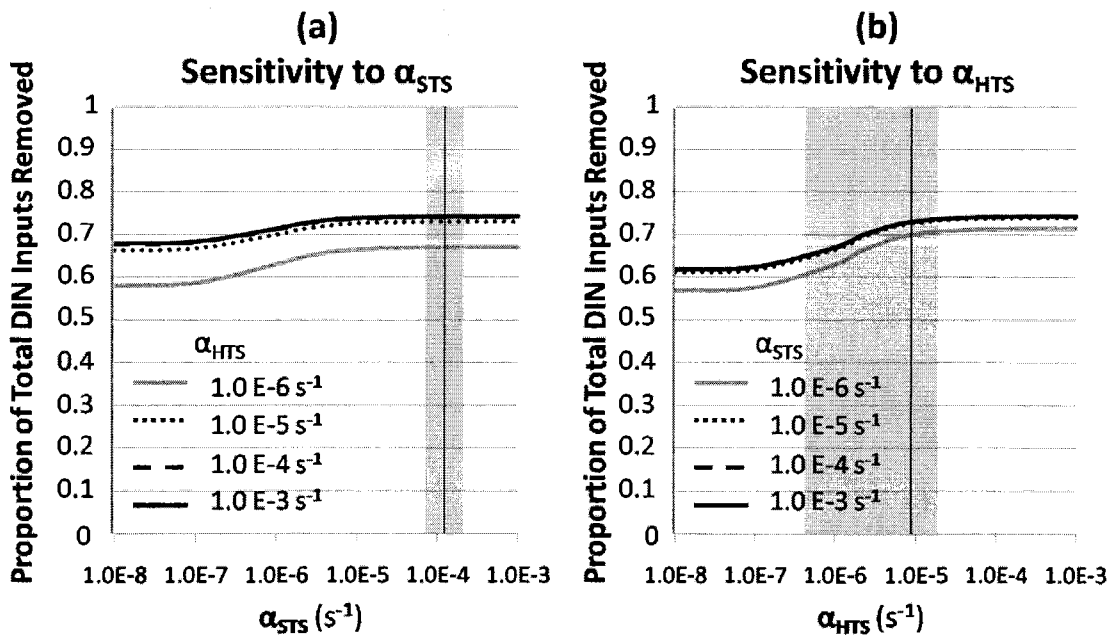**Figure 16** Response of network scale DIN removal to a) α_{STS}, and b) α_{HTS}. All other parameters are constant with values set as the mean values provided in Table 2. Figure 16a and 16b present the same data, but with different x-axes. The mean values for α_{STS} and α_{HTS} are indicated with vertical lines, and the 95% confidence intervals are marked with grey shading.

<u>Varying Processing Rates in MC, STS, and HTS (Scenario 5)</u>

Total network DIN removal is sensitive to processing rates in the STS, HTS, and MC. When the MC is biologically inactive (υ_f = 0 m d^{-1}, k_{MC} [headwaters] = 0 d^{-1}), basin scale DIN removal responds to changes in k_{STS} and k_{HTS} (Figure 17a). This sensitivity diminishes with higher reactivity rates in the STS and HTS as network DIN removal approaches 1 (Figure 17a). However, as MC reactivity increases, total network removal becomes less responsive to k_{STS} and k_{HTS} to the point where removal is entirely dominated by MC processes (Figure 17d). The high sensitivity of network DIN removal to MC reactivity (υ_f) is supported by the hydraulic model results, which indicate runoff spends the majority of its residence time in the MC (Figure 8). Therefore, network scale DIN removal is more responsive to MC reactivity than it is to reaction rates in STS and HTS.

It is important to evaluate the system under the assumption that MC reactivity is low because theoretical implications suggest reaction rates in STS and HTS are elevated relative to MC (Hall et al. 2002). Due to the hydraulic characteristics of the STS (high connectivity, low residence time) and HTS (low connectivity, high residence time), the STS has a greater opportunity to dominate network scale DIN removal if processing rates are high, whereas the HTS has a greater opportunity to do so under lower rates (Figure 18). Assuming MC is biologically inactive (υ_f = 0.0 m d^{-1}) model results indicate that if k_{STS} > k_{HTS}, the STS compartment would contribute a greater proportion of total DIN removal than HTS despite providing shorter total residence times (Figure 18, green lines). If reaction rates in the STS and HTS are identical, the HTS will contribute more

removal than the STS when reaction rates are low whereas the STS will contribute more removal than the HTS when reactivity is high (Figure 18, blue lines). However, it is hypothesized that reaction rates are higher in HTS than in STS (Hall et al. 2002; Runkel et al. 2003). Assuming reaction rates in HTS are double those in STS, the STS can still contribute a greater proportion of total network removal than HTS if reactivity in the STS is greater than 4.0 d^{-1} (Figure 18, red lines). This is because when reactivity is high, DIN is instantly removed upon entrance to TS and removal becomes more a function of how much water passes through TS then how long water remains in storage. When reaction rates in HTS are ten times those in STS, the STS can still remove more DIN at the network scale than the HTS if k_{STS} is greater than 4.25 d^{-1} (Figure 18, black lines).

When any two compartments are biologically inactive (k_t = 0.0 d^{-1}), the effectiveness of the single active compartment can be considerable due to a buffering effect. For instance, assuming that denitrification occurs only in the HTS, and a mean reactivity rate is applied (k_{HTS} = 0.64 d^{-1}), 37.6% of total basin DIN inputs are removed (Figure 17a). When STS is the only active compartment, 25.8% of total basin DIN inputs are removed assuming the same processing rate (Figure 17a). The MC removes 50.8% of inputs when it is the only active compartment (k_{MC} = 0.64 d^{-1} [headwaters]) (Figure 17b). The removal contribution for each of the compartments when they are the single active zone exceeds the contribution of the compartment in the base scenario when other zones are active (Figure 11).
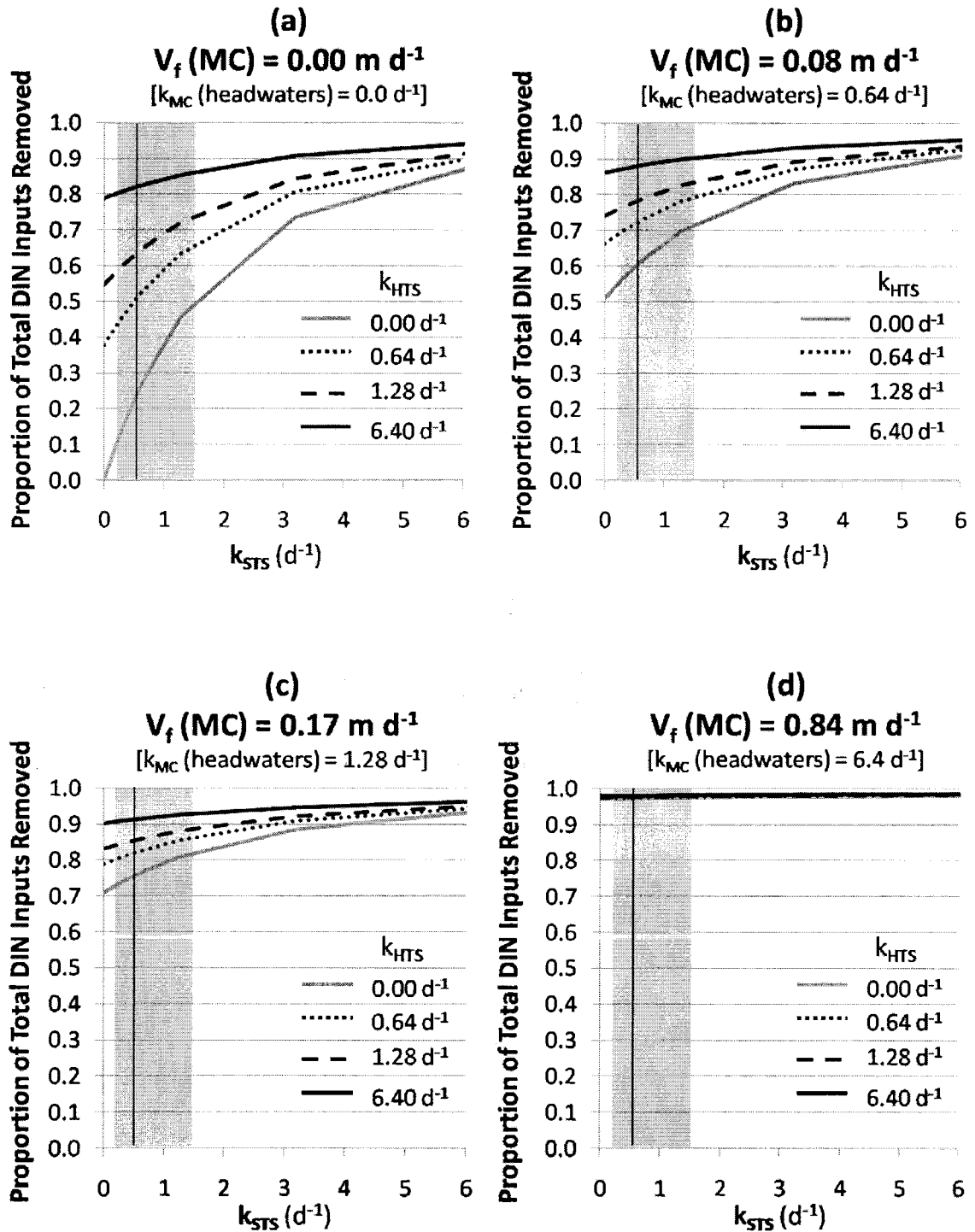
Figure 17 Response of total river network DIN removal to varying reaction rates in the MC, STS, and HTS. All TS hydraulic parameters are constant with values set as the mean values provided in Table 2.
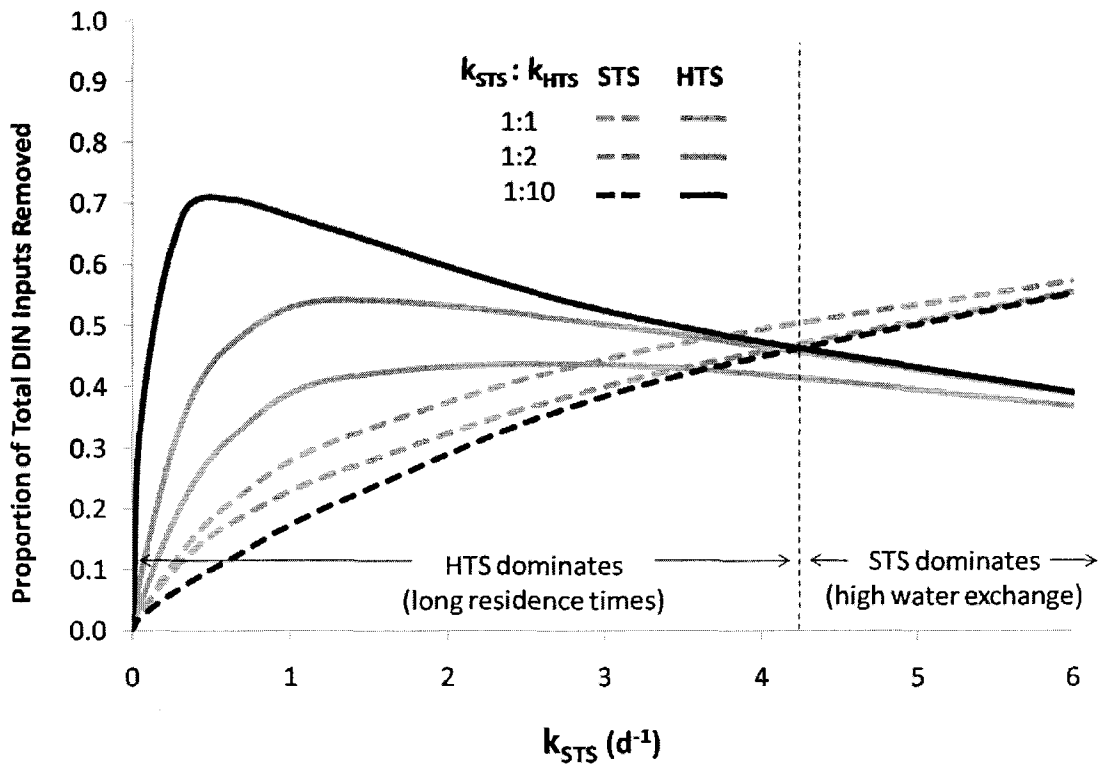
Figure 18 Proportion of total DIN Inputs removed by an individual TS compartment under various reactivity levels in each zone. The MC is assumed to be inactive in this summary (υ_f [MC] = 0.0 m d^{-1}), however the patterns shown here hold for evaluations with υ_f [MC] > 0 m d^{-1} (data not shown).

CHAPTER IV

DISCUSSION

Influence of TS on Network Scale DIN Removal

Transient storage zones in streams can exert considerable control over N removal dynamics (Triska et al. 1989; Valett et al. 1996; Thomas et al. 2003; Gooseff et al. 2004). Most studies of TS in streams have focused at reach scales and considered TS as a single compartment (Choi et al. 2000; Hall et al. 2002; Runkel et al. 2003; Gooseff et al. 2004; Ensign and Doyle 2005; Gooseff et al. 2005). Recent advances in field methodology allow separate estimation of hydraulic parameters for both surface and hyporheic zones (Briggs et al. 2009). In an evaluation of the role of TS on DIN removal, I partitioned between the MC, STS, and HTS compartments using empirically derived TS parameters and found that assuming identical reaction rates in all three zones the MC exerts the most control on DIN removal both at reach and network scales followed by HTS, and then STS (Figure 14a). The large role of the MC is due to the fact that all water passes through the MC in a particular river segment, whereas only a fraction passes through a segment's HTS and STS compartments. Although STS is relatively more connected to channel flow than the HTS, residence times in the HTS are significantly

longer (Table 6) which results in a greater proportion of stream DIN flux removed in HTS than in STS at the reach scale (Table 7). At network scales, HTS removes a greater proportion of total DIN inputs than STS because nearly all runoff will enter the HTS at least once and water must enter the STS many times to compete with the total residence time provided by a single entrance into HTS. However, these results assume a constant reaction rate in all three compartments which is unlikely according to empirical studies (Thomas et al. 2003) and theoretical considerations (Hall et al. 2002; Runkel et al. 2003). Uncertainty in the mean network values indicates that we have an unclear picture of the roles the three compartments play at network scales because DIN removal in the STS and HTS compartments are sensitive to hydraulic and biologic parameters. Sensitivity analyses indicate all three compartments have the potential to be the dominant control on network scale DIN removal depending on reaction rates in the compartments (Figures 17 and 18).

Model results suggest a uniform increase in the size of TS and/or its connectivity with the MC increases network DIN removal (Figures 15 and 16). These relationships are supported by earlier modeling studies. 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 an increase in the relative size of TS (A_{TS}/A_{MC}) for a given water exchange rate (α_{TS}) (Mulholland and DeAngelis 2000). This earlier model also suggests nutrient uptake length declines as α_{TS} increases at a given A_{TS}/A_{MC} (Mulholland and DeAngelis 2000). A number of empirical studies that quantified TS hydraulics and nutrient uptake rates in streams have generally

found similar results (Triska et al. 1989; Valett et al. 1996; Gooseff et al. 2004). However, these previous studies do not address the potential impact that reaction rates have on the importance of A_{TS}/A_{MC} and α_{TS}.

The model results presented here suggest that biologic reactivity in TS compartments can affect the sensitivity to TS size (A_{TS}/A_{MC}) and connectivity (α_{TS}). Network scale DIN removal is not highly sensitive to exchange coefficients when reaction rates are low to moderate (Figure 16a, 16b) because α affects both connectivity and residence times in TS pools, and these effects are offsetting. However, when TS reactivity is high, DIN is removed rapidly upon entrance into TS and therefore network scale removal becomes more a function of how much water is exposed to each compartment than the duration of storage. Therefore, 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 ($k_t < 2.85$ d^{-1}) whereas TS connectivity is more important when reaction rates are elevated ($k_t > 2.85$ d^{-1}) (Figure 18). This explains the relatively greater importance of the HTS compared to STS when a mean reaction rate ($k_t = 0.64$ d^{-1}) is applied (Figure 11, 14a) and the dominance of the STS on network removal when reactivity is elevated (Figure 18).

The Effect of TS on Transport Times at the Network Scale

A commonly used metric to characterize water transport times in rivers due to TS is F_{med}^{200} (Runkel 2002). F_{med}^{200} is a unique metric because it accounts for the

interaction between advective and non-advective controls on reach travel time and mass transport (Runkel 2002). However, as noted by Runkel (2002) and discussed here, F_{med}^{200} is inadequate in characterizing the role of TS on transport times at large scales.

Field 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. 2009, in revision). The reason for this is because STS-MC connectivity 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 is too low for a significant number of water molecules to enter the compartment. This is supported by model results which indicate average water molecules enter the STS 0.58 times per 200 m reach, but enter the HTS only 0.04 times (Table 5). Because 200 m is not long enough to capture the effect that HTS has on water transport, I suggest F_{med}^{200} is predominantly a measure of STS control on median transport times.

When evaluating transport times at the scale of entire river networks, HTS can substantially affect median travel times because nearly all water molecules enter HTS at least once before exiting the river system (Figure 7). A single entrance into HTS has a greater effect on median network transport time than many entrances into STS due to the orders of magnitude greater residence time in HTS (Table 6). As such, although HTS-MC connectivity is much lower than STS-MC connectivity, HTS exerts greater control on median transport times over long flow path distances (Figure 8).

Consider, for example, two cars on a cross-country trip from New York, NY to Los Angeles, CA (3,000 miles). When in motion, the two cars travel at an identical speed of 50 miles per hour. However, Car A makes a half hour stop every 50 miles, whereas car B makes a 6 hour stop every 500 miles. For the first 200 miles, the percent of total transport time due to stoppage for car A and car B, respectively, are 33.3% (4 hours of travel, 2 hours of stoppage) and 0.0% (4 hours of travel, 0 hours of stoppage). However, we cannot use the first 200 miles to characterize how stoppage time has affected each cars total trip from NY to CA. The percent of total transport time for the entire NY-CA trip due to stoppage is 33.3% for car A, and 37.7% for car B. This stresses the importance of considering entire flow paths when evaluating basin scale processes.

The effects that STS and HTS have on median water transport times ($F_{med}STS$, $F_{med}HTS$) are a function of the reach length evaluated (Figure 19). Assuming the mean network TS parameters used in the base scenario of this study, median transport times due to TS switch from being STS dominated to being HTS dominated at a segment length (L) of about 20 km (Figure 19). F_{med} values for STS and HTS asymptote at high L values (Figure 19) due to the size of the TS compartment (A_{HTS} or A_{STS}) relative to the total size of the MC and all TS compartments ($A_{MC} + A_{HTS} + A_{STS}$). These calculations indicate that the fraction of median transport times due to STS and HTS cannot exceed 17% and 26%, respectively given the mean hydraulic parameters applied in this study (Figure 19). The calculations of F_{med} using equation 10 are similar to the network model predictions for the average fraction of total residence time in STS and HTS of 11.7% and 22.3%, respectively (Figure 8). This suggests that the average flow path length in the Ipswich

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River is close to the length required for the F_{med} relationship to asymptote, but discrepancies occur because advective velocities (u) in the model increase in the downstream direction which reduces the effect of TS retention. Since the fraction of transport time due to TS is a function of stream length evaluated, F_{med}^{200} cannot be used to characterize the role of TS on mass transport at large scales.

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). This is not surprising considering 1) I have shown F_{med}^{200} is primarily a metric of STS processes (Figure 19), and 2) HTS removes more DIN than STS at reach scales assuming low to moderate reaction rates (Table 7). Therefore, assuming STS processes also dominate F_{med}^{200} in other empirical studies, I would expect little correlation between F_{med}^{200} and DIN removal. However, I have based this finding on an empirical model in the Ipswich basin where channelized river segments are shallowly sloped and STS processes could be much more important than what has been modeled here. More two-compartment TS studies are needed in steeper watersheds to verify these findings.

$$F_{med} = (1-e^{-L(\alpha/u)}) A_{XTS}/(A_{MC}+A_{STS}+A_{HTS})$$
(Runkel, 2002)

HTS
STS
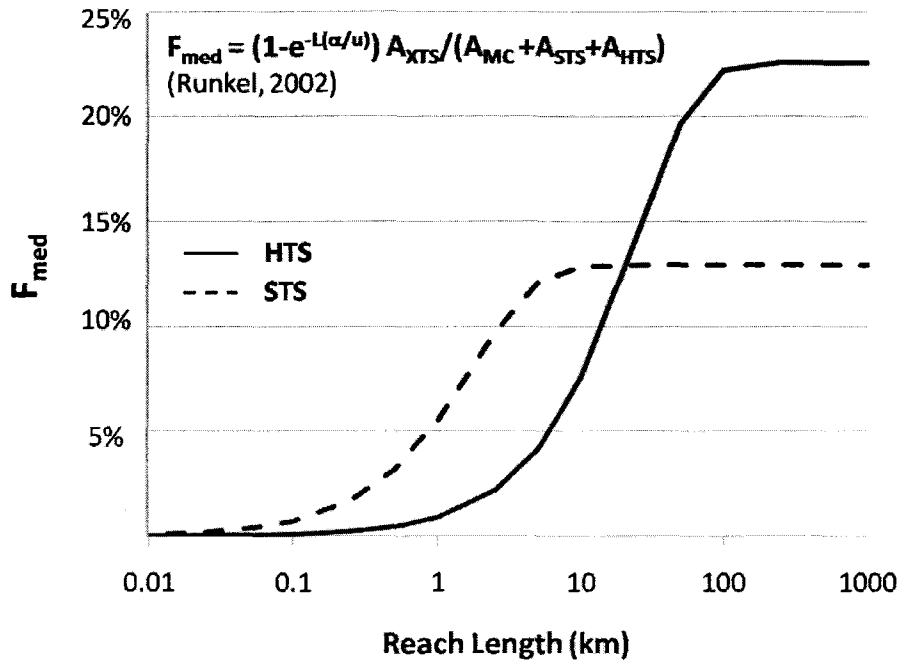
Figure 19 F_{med} (Runkel, 2002) calculations using mean parameter values and a discharge of 1.0 m^3 s^{-1}. MC cross sectional area (A) and velocity were calculated from Q using power law relationships for the Ipswich River provided in equations 22 and 23.

Spatial Distribution of TS and the Impact of Hotspots

TS characteristics and biogeochemical processing are likely to be heterogeneous in space and time (Jones and Mulholland 2000), potentially leading to hotspots (McClain et al. 2003) of removal at river network scales. Here, spatial heterogeneity was simulated by randomly selecting parameter values (kt, α_{STS}, α_{HTS}, A_{STS}/A_{MC}, and A_{HTS}/A_{MC}) 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, hotspots were created stochastically throughout the river network due to a combination of increased TS connectivity, residence time, or reactivity and resulted in localized areas of high removal. Spatial heterogeneity in the Ipswich River network results in removal

increases in the MC, STS and HTS compartments compared to the base scenario. These results indicate that hotspots buffer the inefficiencies of upstream "cold spots", leading to greater removal compared to application of uniform parameters (Scenario 1) (Figure 14a, 14b). Overall, these results suggest that hotspots in river networks potentially enhance removal at basin scales.

Areas of high removal could come in the form of lakes (David et al. 2006), beaver ponds (Correll et al. 2000), wetlands (Johnston et al. 1990; Johnston 1991; Johnston et al. 2001) and floodplains (Pinay et al. 2000). These features are generally well connected to the MC, provide substantial cross-sectional areas and may have high reactivity rates because they expose water to large stocks of organic material. Future work should be conducted to quantify the number and magnitude of hotspots required to maintain high removal despite upstream processing deficiencies.

Previous research has investigated how TS characteristics scale throughout river networks (Harvey and Wagner 2000; Battin et al. 2008; Briggs et al. 2009, in revision). A study in the Ipswich River suggests that A_{STS}/A_{MC} and A_{HTS}/A_{MC} may increase with river size (Briggs et al. 2009, in revision) and this relationship was embedded in Scenario 3 with a degree of spatial heterogeneity (Figure 5d). Results for Scenario 3 (Figure 14c, Table 9) indicate only a small increase in network scale removal compared to a simple spatial heterogeneous scenario (Scenario 2) (Figure 14b). Although the increase in TS size in downstream segments does not significantly increase total network DIN removal, it does shift the locations where removal occurs (Table 10). Spatial heterogeneity

(Scenario 2) increases the role of 1st through 4th order rivers relatively more than it does 5th order rivers (Table 10). In contrast, increasing A_{TS}/A_{MC} downstream (Scenario 3) substantially increases the importance of 5th order river segments (Table 10). This reflects the nature of river networks in which reductions in upstream efficiency are compensated by increases in downstream processing and vice versa. As such, overall removal changes little between the spatial configurations of Scenario 2 and Scenario 3, while location of removal changes more (Table 10).

Table 10 Percent change in median removal compared to Scenario 1b. Percent changes in 5th order reaches compared to base scenario are provided in parentheses.

Scenario	MC	STS	HTS	Total
Spatial Heterogeneity (2)	+24.4% (+17.2%)	+44.0% (+45.0%)	+62.2% (+58.1%)	+14.9% (+11.8%)
Spatial Heterogeneity w/ increasing TS/MC size (3)	+27.3% (+6.9%)	+42.4% (+90.0%)	+83.8% (+147%)	+20.2% (+38.4%)

Role of River Size

Model results indicate large streams remove a greater proportion of total basin DIN inputs than smaller streams. This contradicts some earlier studies that suggest headwater streams are a fundamental control on N retention (Alexander et al. 2000; Peterson et al. 2001). However, our results indicate that small streams (orders 1-3) still contribute a reasonable proportion (39.8%) of total basin DIN removal (Figure 11). This finding is supported by an earlier study of network scale DIN removal that reported small streams provide approximately 40% of network scale denitrification during similar

baseflow conditions (Wollheim et al. 2008). Similar to the study presented here, Wollheim et al. (2008) derived reaction rates (k_t) from the LINX2 project (Mulholland and al. 2008) however they assumed no transfer between advective and non-advective compartments. Despite this, the findings of Wollheim et al. (2008) provided supporting evidence of the buffering capacity of river networks.

Large rivers play a fundamental role in regulating DIN exports from river systems in the model because 1) on a per mean reach length basis, water molecules enter TS compartments more times in larger rivers, 2) all DIN input not removed by smaller rivers eventually pass through large river segments, and 3) some DIN inputs to the river network bypass smaller streams and drain directly to large rivers (Ensign and Doyle 2006; Wollheim et al. 2008). The significant role of large rivers in our model is also in part due to the assumption that uptake velocity in the MC is independent of river size (Wollheim et al. 2008). The rate at which rivers widen and lengthen with increasing discharge creates a disproportional increase in benthic habitat in larger downstream reaches (Ensign and Doyle 2006; Wollheim et al. 2006; Wollheim et al. 2008). 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; Wollheim et al. 2008).

Removal processes in TS and MC become less efficient per unit distance in downstream reaches (Table 7). However, the removal contribution of TS relative to the MC increases in the downstream direction in the base scenario (Table 7). TS provides

approximately 29% of total DIN removal in 1st order streams and 57% of the total

removal in 5th order streams (Figure 11). Removal processes in TS and MC become less

efficient in downstream reaches because of scaling relationships between channel

depth, channel width and increasing discharge. Removal in the MC becomes less

efficient in large reaches because of decreasing benthic surface area to volume ratios in

the downstream direction (Wollheim et al. 2006). Removal in TS becomes less efficient

in larger reaches because water transfer to TS is a function of A_{MC} and discharge, and

discharge increases disproportionally with A_{MC} in the downstream direction. STS and

HTS become more effective downstream relative to the MC because the ratio of depth

to discharge decreases faster than the ratio of A_{MC} to discharge.

The spatial distribution in TS characteristics throughout the river network can

affect the role of larger rivers (Table 10). Spatial heterogeneity of TS connectivity, size

and/or reactivity (Scenario 2) tends to reduce the leakiness of upstream systems by

creating hotspots in smaller river segments, thereby reducing the relative role of 5th

order river segments in network scale removal. However, downstream systems still

have the potential to buffer upstream processing inefficiencies. When the cross-

sectional area of TS relative to MC increases with river size (Scenario 3), so does the

importance of STS and HTS DIN processing in 5th order river segments (Table 10).

Because Scenario 3 limits the size of TS relative to the MC area in smaller streams, the

MC compartment becomes more important in upstream segments, but most of the

buffering occurs downstream.

Implications for Land Use Management

Anthropogenic disturbances have altered the N cycle by substantially increasing N inputs (Howarth et al. 1996; Vitousek 1997). Increased DIN loading to rivers is a result of a growth in non-point sources (Howarth et al. 1996), NO_x emissions (Vitousek 1997), septic and point source waste (Williams et al. 2004), and fertilizer additions to lawns (Valiela and Bowen 2002). Patterns of land use greatly influence the distribution of these inputs to river systems. Knowing the distribution of inputs relative to removal (especially hotspots) in a river network, would be helpful for watershed management. The configuration of land use in the Ipswich basin results in a disproportional amount of DIN inputs to headwater streams (Williams et al. 2004; Wollheim et al. 2005). This may lead to high network removal because DIN must travel through long distances before reaching the river mouth. However, watersheds with a more uniform distribution of land use and DIN inputs may not result in an increase in DIN export because streams may be able to uptake more nutrients when concentrations are low (Wollheim et al. 2008). Recent studies have shown that processing rates decline in efficiency with increased nutrients but do not saturate (O'Brien et al. 2007, Mulholland et al. 2008). The model used here assumes DIN processing increases linearly with concentration because there is no data available for efficiency loss in TS compartments. The concept of efficiency loss and the impact it may have on this study is discussed in the following section.

The model outlined in this study can be applied to identify zones of influence for water quality at key locations in the river network. The zone of influence for a particular

location on a river is the drainage area that contributes to the DIN observed at that point. The zone of influence for estuarine health is only 11.5% of the total watershed area for the base scenario (Figure 20), indicating that the river network removes DIN inputs from 88.5% of the watershed by the time runoff exits the basin. This stresses the importance of having higher standards in land use management practices in areas that have short flow path distances to the basin mouth if one is interested in managing for estuarine health during summer periods. Future work should focus on how this zone of influence varies with changing flow conditions, not just for nutrients, but for other related pollutants such as fecal coliform which can significantly impact the health of shell fish in the estuarine Ipswich. Zones of influence for town water supply intakes are also important (Figure 21). The zones identified for the Salem/Beverly and Lynn town water supply intakes (Figure 21) are likely to be underestimated in size because water withdrawals occur only during winter periods at high flows when streams are less efficient in removal (Claessens et al. 2006).
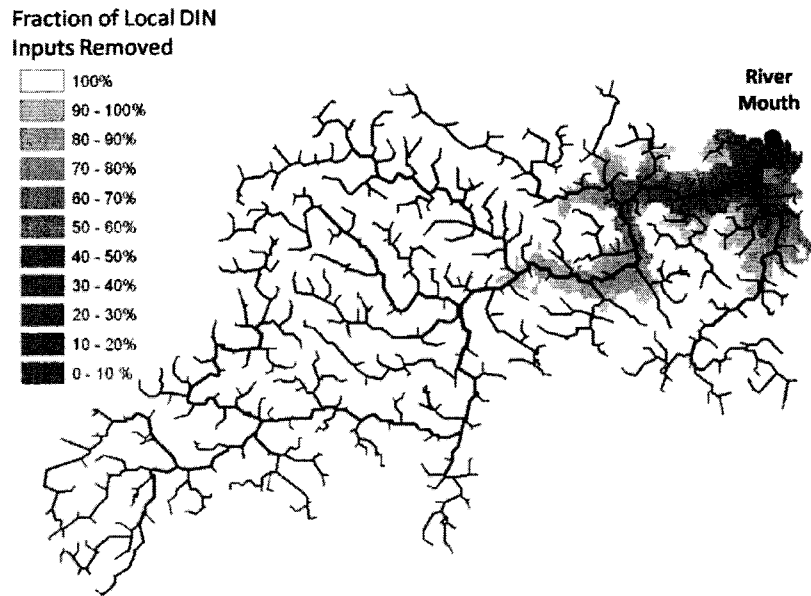
Figure 20 Zone of influence for estuarine health. Shaded areas represent the fraction of local DIN inputs removed before reaching river mouth for base scenario (Scenario 1a). White regions of the basin have local DIN inputs removed entirely before runoff reaches the river mouth.
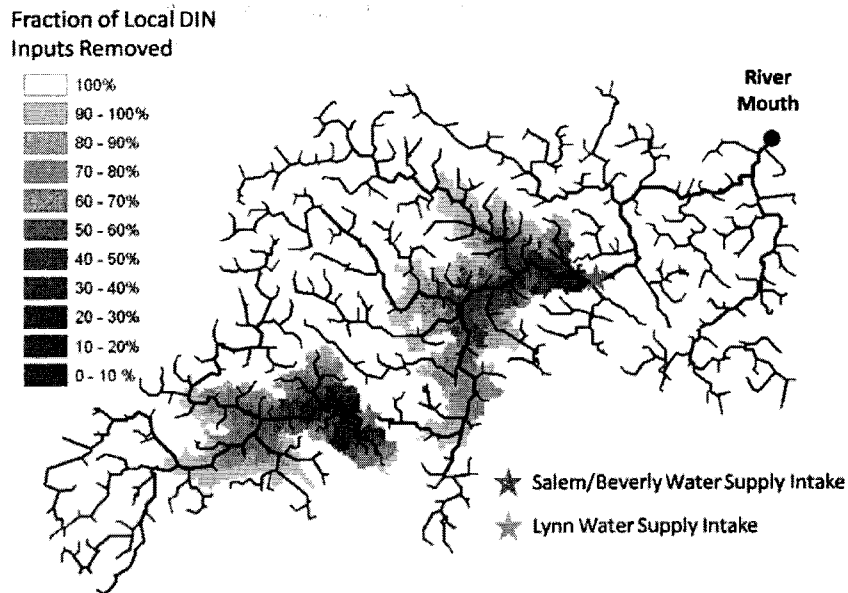
Figure 21 Zones of influence for town water supply intakes. Shaded areas represent the fraction of local DIN inputs removed before reaching each intake under base scenario conditions (Scenario 1a). White regions of the basin have local DIN inputs removed entirely before runoff reaches the river mouth.

Key Model Uncertainties

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. The model was applied only at summer baseflow because this is when hydraulic and reactivity parameter measurements were conducted. In order to model these processes over annual time scales, we first need a better understanding of how hydraulic parameters scale with increasing flow (at-a-site). Furthermore, to model removal across the annual hydrograph, the model would need to incorporate additional systems (i.e. floodplains) that are not currently represented.

Although I address the uncertainty associated with mean network parameters, I 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 two year period and do not account for the presence of large wetlands and lakes. Furthermore, no measurements were taken in reaches with drainage areas greater than 200 km^2 which represents more than half of the total length of the 5th order river segment. 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.

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 at a different time (2003-2005) and assuming a single TS compartment (Mulholland and al. 2008). Furthermore, a simplified approach was used to partition reaction rates between the MC and TS compartments. 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). As part of this collaborative study there is an ongoing field effort looking into the specific reaction rates in the MC, STS, and HTS compartments but these results are not yet available. Further, studies have shown that DIN removal processes are less efficient at high concentrations (Earl et al. 2006; O'Brien et al. 2007; Mulholland et al. 2008). Efficiency loss was not incorporated into this model because the rate at which processing decreases in TS with increasing concentration is unknown. 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 in Wollheim et al. (2008) at network scales without explicit consideration of TS. Future network scale TS models should incorporate the concept of N saturation when more TS data becomes 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.

There are a number of hydrologic factors that also need further consideration. Although observed and predicted flows fit well at the USGS gauge stations at Ipswich and Middleton on the main stem, the model significantly underestimates flows in flashy urban headwater streams during precipitation events (Figure 6). Spatially variable

precipitation and runoff conditions would significantly improve flow estimates in headwater catchments. Furthermore, channel routing would substantially increase our understanding of the timing of water transport and DIN fluxes through the river network but simple flow accumulation is acceptable for this study since the focus was on average summer baseflow conditions.. Surface and groundwater withdrawals from the Ipswich River should be incorporated into the model when evaluating DIN removal at annual timescales. The omission of surface withdrawals should not impact these results because these occur predominantly during winter periods (Claessens et al. 2006), but groundwater withdrawals could have an effect. Processes associated with wetlands, lakes and beaver ponds are also important and should be incorporated into future models. The removal reported here is underestimated based on hydraulic considerations alone, but full accounting for wetlands, lakes and beaver dams requires characterization of reactivity which might also vary over time.

CHAPTER V

CONCLUSION

DIN removal processes in advective and non-advective compartments in river systems are the result of reach scale interactions among connectivity, residence time, and the strength of biological reactivity. Although HTS does not appear to be highly connected to the MC at small scales, most runoff enters the HTS at least once at the scale of the entire network. As a result, HTS is more important in controlling water transport at network scales than STS. Recent advancements in field techniques have built upon our knowledge of hydraulics in non-advective zones, but there remain key questions regarding the specific biological processing rates in each compartment. Although evidence points to reactivity rates being the greatest in HTS (Hall et al. 2002), this study indicates that without more information on how these rates vary between compartments we cannot fully understand DIN removal processes among the three compartments at network scales. Assuming reaction rates are identical in all three compartments, the MC exerts the greatest control on DIN removal, followed by the HTS, and then STS. The relative importance of STS and HTS in network scale DIN removal depends on the reaction rate applied to both compartments. The HTS removes more

DIN than STS when a low reactivity is applied because HTS provides longer residence times, whereas STS removes more DIN than HTS when a high reaction rate is applied because STS is more connected with the MC.

Despite uncertainties in TS hydraulic and biological parameters, large rivers were found to have a considerable role in regulating DIN fluxes. However, the importance of river size on DIN removal can be offset by the spatial distribution of TS characteristics throughout the river network. Hotspots potentially have a critical role in maintaining high levels of DIN removal in river networks and this work supports earlier studies that suggest a network perspective is needed to fully understand processes in river systems (Seitzinger et al. 2002; Wollheim et al. 2006; Battin et al. 2008; Wollheim et al. 2008). Due to 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 have the potential to play significant roles in DIN processing during baseflow periods and should be incorporated in future studies. The work presented here helps understand the fate of DIN in aquatic systems and the relationships among connectivity, TS size and reactivity.

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