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Dynamics of N removal over annual time periods in a suburban river network

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[1] River systems are dynamic, highly connected water transfer networks that integrate a wide range of physical and biological processes. We used a river network nitrogen (N) removal model with daily temporal resolution to evaluate how elevated N inputs, saturation of the denitrification and total nitrate removal processes, and hydrologic conditions interact to determine the amount, timing and distribution of N removal in the fifth-order river network of a suburban 400 km^2 basin. Denitrification parameters were based on results from whole reach $^{15}NO_3$ tracer additions. The model predicted that between 15 and 33% of dissolved inorganic nitrogen (DIN) inputs were denitrified annually by the river system. Removal approached 100% during low flow periods, even with the relatively low and saturating uptake velocities typical of surface water denitrification. Annual removal percentages were moderate because most N inputs occurred during high flow periods when hydraulic conditions and temperatures are less favorable for removal by channel processes. Nevertheless, the percentage of annual removal occurring during above average flow periods was similar to that during low flow periods. Predicted river network removal proportions are most sensitive to loading rates, spatial heterogeneity of inputs, and the form of the removal process equation during typical base flow conditions. However, comparison with observations indicates that removal by the river network is higher than predicted by the model at moderately high flows, suggesting additional removal processes are important at these times. Further increases in N input to the network will lead to disproportionate increases in N exports due to the limits imposed by process saturation.

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1. Introduction

[2] Anthropogenic nitrogen (N) inputs to watersheds can negatively impact freshwater and coastal ecosystems by altering primary productivity, oxygen status, and community composition [*Anderson et al.*, 2002; *Bricker et al.*, 1999]. Despite such impacts, most watershed N inputs are stored or denitrified (henceforth referred to as removal) somewhere along the sequence of ecosystems that link N source areas and receiving waters [*Boyer et al.*, 2002]. Most watershed N removal occurs in terrestrial or riparian systems prior to entering surface waters, but removal by aquatic systems is also an important sink [*Bernhardt et al.*, 2005] and can account for a significant proportion of total inputs to aquatic systems [*Alexander et al.*, 2000]. Because aquatic systems are the final filter prior to material export from watersheds [*Meybeck and Vörösmarty*, 2005], understanding their capacity to respond to increased N inputs is of considerable interest.

[3] Nutrient removal by river systems is determined by a combination of geomorphic, hydrologic, and biological factors that vary over space and time [*Doyle*, 2005; *Wollheim et al.*, 2006]. Because river systems are highly connected networks, the consequences of local land use, nutrient loading rates, hydrologic conditions and geomorphic setting can be felt far downstream [*Alexander et al.*, 2000; *Mulholland et al.*, 2008]. River systems are also extremely dynamic as hydrologic conditions vary in response to storms or seasonal changes in climate. Temporal variation in biological activity and loading adds to this dynamic quality. Spatial and temporal heterogeneity interact with inherent gradients in stream size to determine nutrient removal by entire networks.

[4] To play a significant role in annual N removal, river systems must have the capacity to remove nutrients during periods of high flow when most solute and particulate transport occurs. Empirical observations have suggested that small streams draining agricultural catchments have

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limited N removal capacity over annual timescales [*Royer et al.*, 2006]. *Doyle* [2005] used a reach model to demonstrate that removal drops rapidly with increasing discharge in individual stream reaches. However, downstream systems, including larger rivers, lakes, and reservoirs can potentially buffer increased flux from upstream systems [*David et al.*, 2006; *Royer et al.*, 2006]. Thus, a full understanding of N removal by river systems over highly variable annual flow conditions requires a whole river network perspective.

[5] Aquatic denitrification and other removal processes can respond nonlinearly or saturate with increasing nitrogen concentrations [*Earl et al.*, 2006; *Garcia-Ruiz et al.*, 1998b; *Mulholland et al.*, 2008]. Most river network N models have assumed that N removal is a first-order process, i.e., as N concentrations increase, process rates increase proportionally, implying that removal efficiency remains constant with increased loading [*Alexander et al.*, 2000; *Donner et al.*, 2002; *Seitzinger et al.*, 2002]. Recent network models that have incorporated nonlinear kinetics have shown that overall N removal efficiency by river systems declines as inputs increase, and that larger, higher order rivers increase in relative importance compared to smaller, low order streams [*Mulholland et al.*, 2008]. The latter response was unexpected, further demonstrating that a network perspective is needed to fully understand the implications of nonlinear kinetics. Interactions of ecosystem saturation, hydrologic variability and spatial heterogeneity of inputs have not previously been addressed in a river network context.

[6] Here, we explore how denitrification influences the N removal capacity of an entire fifth-order river network throughout the annual hydrograph. Our focus is on N removal occurring within channels (i.e., associated with the streambed between the banks, including hyporheic zones) expressed in a river network context. Denitrification parameters are based on measurements made by the LINX2 study [*Mulholland et al.*, 2008] in headwater streams of the Plum Island watersheds during summers, and extended to the rest of the year assuming temperature is the primary rate control. Our goals are to (1) evaluate the degree to which denitrification in river systems can control nutrient export from watersheds when accounting for hydrologic variability over annual time periods, (2) identify the size class of stream (i.e., Strahler order) that contributes most to N removal at the basin scale, (3) understand the influence of nonlinear kinetics on river network N removal capacity in a watershed with spatially varying N inputs, and (4) determine discrepancies with observations to identify additional research needs. Our application of rates measured in summers to other time periods should be viewed with caution, since many seasonal phenomena are not considered. However, this analysis begins to address the importance of N removal processes within entire river networks beyond mean annual or summer low flow periods. We use a variety of scenarios of biological activity and loading to aquatic systems to both understand how these factors control river network N removal and to address uncertainties in scaling biological activity in space and time.

2. Study Area

[7] The Ipswich R. network drains a 400 km^2 watershed located approximately 30 km from Boston in northeastern Massachusetts. Land cover in the basin includes residential suburban (30%), upland forest (36%), agriculture (7%), industrial/commercial (4%), open water (3%), and wetlands (20%). Forest vegetation is primarily mixed hardwood. Almost 10% of the watershed is impervious. Population density for the basin as a whole is 302 km^{-2}, with roughly 60% on septic systems. Urbanization has led to numerous impacts including changes in the hydrologic cycle [*Claessens et al.*, 2006; *Pellerin et al.*, 2007; *Zarriello and Ries*, 2000], increased N inputs and fluxes [*Williams et al.*, 2004], and reduced N retention in headwater catchments [*Wollheim et al.*, 2005]. Mean annual precipitation is 1188 mm a^{-1}, of which 45% is converted to runoff reaching the basin mouth [*Claessens et al.*, 2006]. Mean annual discharge at the basin mouth is $\sim$5.4 m^3 s^{-1}. Peak flows can approach 100 m^3 s^{-1}. Typical summer base flow is about 1 m^3 s^{-1}, although during droughts, flows can drop to <0.1 m^3 s^{-1}, in part due to groundwater withdrawals [*Zarriello and Ries*, 2000]. The basin is a shallow gradient coastal plain watershed with approximately 0.06% average slope along the main stem [*Claessens et al.*, 2006] and grading into somewhat steeper slopes in the headwaters (mean = 0.6% in first-order streams). Because of the flat topography, there are abundant wetland areas, including extensive floodplain areas adjacent to river channels. The Ipswich R. watershed drains to Plum Island Sound, one of the largest salt marshes in the northeast. The watershed and Sound are part of the Plum Island Long-term Ecological Research site.

3. Methods

[8] We apply a river network N removal model that integrates key geomorphic, hydrological, biological, and dissolved inorganic nitrogen (DIN) loading characteristics of the suburban Ipswich R. watershed. These characteristics are specified a priori using available empirical information and assumptions, detailed below. The analysis focuses on denitrification in stream channels and its ability to attenuate the flux of DIN within an entire river network over annual time periods. In the Ipswich, DIN is dominated by NO_3 [*Williams et al.*, 2004; *Wollheim et al.*, 2005], so we apply the denitrification rate models (section 3.4) directly to DIN. Note that we do not model in-stream NH_4 dynamics in this paper. The model uses a daily time step, and is applied to the 2000–2003 time frame, encompassing wet and dry years.

3.1. River Network Model

[9] The Ipswich river network N removal model is implemented within the UNH aquatic modeling system, the Framework for Aquatic Modeling in the Earth System (FrAMES). FrAMES is a grid-based modeling approach that allows incorporation of different biological process algorithms at various spatial scales [*Wollheim et al.*, 2008].

[10] For each time step, N flux leaving each grid cell *i* via a river channel is calculated as:

$$Flux_i = (Upstream_i + Local_i) * (1 - R_i) \qquad (1)$$

where $Upstream_i$ is the sum of inputs flowing into grid cell *i* from upstream grid cells during the time step, and $Local_i$ is input from land to stream within the local grid cell *i*. R_i is

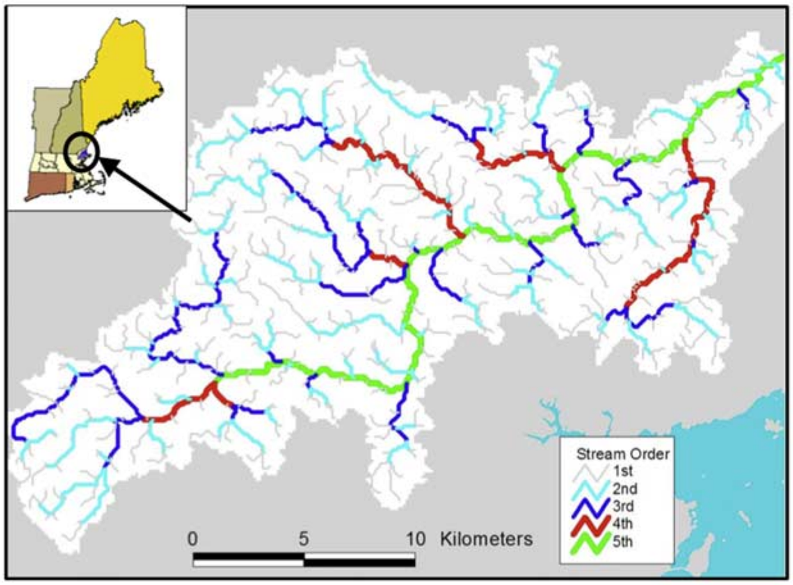

Figure 1. Ipswich R. network, showing different stream orders.

the daily unitless removal proportion in the grid cell defined as:

$$R_i = 1 - \exp\left(-\frac{U_i}{C_i * H_L}\right) \quad (2)$$

where U_i is the areal process rate in the river channel within grid cell i (mg m^{-2} d^{-1}), C_i is nutrient concentration in the surface water (mg m^{-3}) and H_L is the hydraulic load in the grid cell (m d^{-1}). U/C is equivalent to υ_f, the vertical or uptake velocity (m d^{-1}) of the nutrient molecule [*Stream Solute Workshop*, 1990]. Equation (2) is based on equations previously used in river network models to govern the transfer of materials (e.g., $R = 1 - \exp(-k\tau)$ or $R = 1 - \exp(-\upsilon_f/H_L)$, where k is the time specific uptake rate (d^{-1}), and τ is residence time (d) [*Alexander et al.*, 2000; *Kelly et al.*, 1987; *Wollheim et al.*, 2006] but is modified to allow incorporation of nonlinear process rates. H_L is equivalent to h/τ, or Q/A, where h is water depth (m), Q is discharge (m^3 d^{-1}), and A is benthic surface area (m^2). H_L represents the average depth of water through which a nutrient molecule must travel to reach the stream bottom in the period of time water resides in the water body (here, a stream reach). When scaling removal processes that occur mainly on the stream bottom (e.g., denitrification) throughout river systems, the form υ_f/H_L or U/C * H_L allows application of a single biological rate (υ_f) or set of nonlinear rate parameters without having to adjust for changes in water depth (see *Wollheim et al.* [2006] for more discussion). Equation (2) incorporates the strength of biological activity relative to the hydrological throughput, thus describing the capacity of a specified water body to remove nutrients. Note that equation (2) can be rearranged as $R = 1 - \exp(-F_b/F_i)$ where F_b is the total benthic flux within the reach (U * A; mg d^{-1}) and F_i is the total flux into the reach (Q * C; mg d^{-1}).

3.2. River Network Geomorphology

[11] We use a digital topological river network at 120 m grid cell resolution (STN-120m) developed for the watersheds draining to the Plum Island Sound estuary (the Ipswich and the Parker watershed). STN-120m was developed from a 30m digital elevation model with USGS hydrography (MASSGIS, http://www.state.ma.us/mgis/massgis.htm) burned in using the AGREE program [*Hellweger and Maidment*, 1997]. The resulting river network is fifth order (Figure 1), with attributes described in Table 1. The drainage density of the network is 1.4 km^{-1}. The area, number, and length ratio are 4.5, 4.9, and 2.7, respectively, but are somewhat skewed by the unusually long fifth-order main stem, without which the values are 4.1, 4.0, and 2.1, respectively. The entire watershed was partitioned into roughly 2 km^2 subbasin areas (~139 grid cells/subbasin) for which runoff and nutrient loads into the river network were determined based on subbasin land use characteristics (see below).

3.3. Hydrologic Conditions

[12] Daily runoff within each subbasin area (RO_{sub}, mm d^{-1}) was based on daily runoff from the entire basin (RO_{ips}, mm d^{-1}) measured at the USGS gage at Ipswich (Station 01102000). RO_{ips} was scaled to each subbasin according to a scaling factor that is a function of imperviousness in each subbasin:

$$RO_{sub} = RO_{ips} * F\_IMP_{sub} \quad (3)$$

where $F\_IMP_{sub} = (22.4 + 0.27 * IMP_{sub})/25$ derived from *Wollheim et al.* [2005], where IMP_{sub} is the % of impervious land in the subbasin. F_IMP_{sub} is an empirical scaling factor derived from measured runoff in urban and forested catchments in the basin and accounts for the greater runoff observed in suburban catchments due to imperviousness [*Pellerin et al.*, 2007; *Wollheim et al.*, 2005]. Daily discharge throughout the river network was calculated based on flow accumulation of runoff from upstream grid cells.

[13] Mean annual channel width within each grid cell was determined from mean annual discharge (Q) as W_{mean} =

Table 1. Geomorphic Characteristics of the Ipswich River Network Derived From the 120 m Resolution Gridded River Network

Stream Order	Mean Direct Drainage[a] (km^2)	Mean Area (km^2)	Mean Length (km)	Numbers (-)	Direct Drain to Order[b] (Proportion)
1	0.52	0.52	0.65	432	0.57
2	0.81	2.35	1.33	103	0.21
3	1.77	9.60	2.77	28	0.11
4	3.39	34.5	5.62	6	0.05
5	25.3	404	41.9	1	0.07

[a]Mean direct drainage is the average area of watershed surface draining directly to each stream of a given order class.
[b]Direct drain to order is the proportion of the entire Ipswich basin draining initially into each stream order.

$8.3Q_{mean}^{0.5}$ based on a wide range of streams [*Leopold and Maddock*, 1953; *Park*, 1977]. Channel width in grid cell i (W_i) at each time step is based on the at-a-site power relationship: $W_i = a_i Q_i^c$, where a_i is derived for each grid cell from W_{mean}, Q_{mean}, and c = 0.11. The value for c is based on hydraulic information available for the Ipswich [*Zarriello and Ries*, 2000] and is typical of many rivers worldwide [*Park*, 1977].

3.4. Biological Activity

[14] Two measures of biological activity are implemented in separate model runs: (1) denitrification of surface water nitrate only (henceforth referred to as DENIT), and (2) denitrification plus DIN assimilation (referred to as DENIT+ASSIM). Actual permanent DIN removal by channels would likely be intermediate between these two measures, as some assimilated N is ultimately denitrified via coupled mineralization-nitrification-denitrification [*Seitzinger et al.*, 2006] or transported as particulates during high flow events. Both measures are based on the results of $^{15}NO_3$ tracer additions conducted in nine headwater streams (first and second order) in the Ipswich basin as part of the LINX2 experiment [*Mulholland et al.*, 2008]. These experiments indicate that nitrate concentrations are the major control of both denitrification and total nitrate uptake rates across streams. Thus, we applied relationships driven by concentration only, using a Michaelis-Menton type relationship that well describes the results from the Ipswich streams (S. M. Thomas and B. J. Peterson, manuscript in preparation, 2008):

$$U_i = \frac{U_{\max} C_i}{K_s + C_i} \tag{4}$$

where U_{max} is the maximum areal uptake rate (mg m^{-2} d^{-1}), K_s is the concentration at which half the maximum uptake is achieved (mg m^{-3}), C_i is concentration in cell i (mg m^{-3}). Uptake velocity, υ_f, is U/C and the maximum uptake velocity, υ_{f-max}, is U_{max}/K_s [*Newbold et al.*, 2006]. The parameters for each measure (DENIT, DENIT+ASSIM) were determined using a least squares procedure in Excel using the Solver function to fit the relationship between υ_f and C across the PIE LINX streams (n = 8 for DENIT, n = 7 for DENIT+ASSIM) (Table 2). Model predicted versus observed rates have r^2 of 0.69 and 0.67 for DENIT and DENIT+ASSIM, respectively. The resulting parameter values for denitrification (Table 2) are similar to previous reports [*Garcia-Ruiz et al.*, 1998b]. An alternative to the Michaelis-Menten model, the Efficiency Loss model [*Mulholland et al.*, 2008; *O'Brien et al.*, 2007], can also be used to describe the PIE results and was applied as an alternative scenario (see section 3.8).

[15] The parameters controlling the denitrification process rates are based on measurements taken in headwater streams during summers. Given the lack of measurements in higher order streams and the finding that concentration is the

Table 2. Model Parameters for the DENIT and DENIT+ASSIM Base Scenario

Parameter	Definition	Value
Hydraulic		
a	Downstream direction width constant (m)	8.2
b	Downstream direction width exponent (-)	0.52
d	At-a-site width exponent (-)	0.11
Biological (Michaelis-Menten)		
DENIT		
υ_{f-max}	Maximum uptake velocity (m a^{-1})	83.7
U_{max}	Maximum uptake rate (mg m^{-2} h^{-1})	3.4
K_s	Half saturation constant (mg L^{-1})	0.359
DENIT+ASSIM		
υ_{f-max}	Maximum uptake velocity (m a^{-1})	278
U_{max}	Maximum uptake rate (mg m^{-2} h^{-1})	7.7
K_s	Half saturation constant (mg L^{-1})	0.243
Q10	Factor change in U_{max} for every 10°C temp. change (-)	2
T_{ref}	Reference temperature to which Umax refers (°C)	20
N inputs		
Asym	Asymptote of loading concentration (mg L^{-1})	1.4
Scale	Scale factor on the land use axis	12.2
X_{mid}	Land use (%) at inflection point of the curve	40.3 + 19.5 * log10(Q)

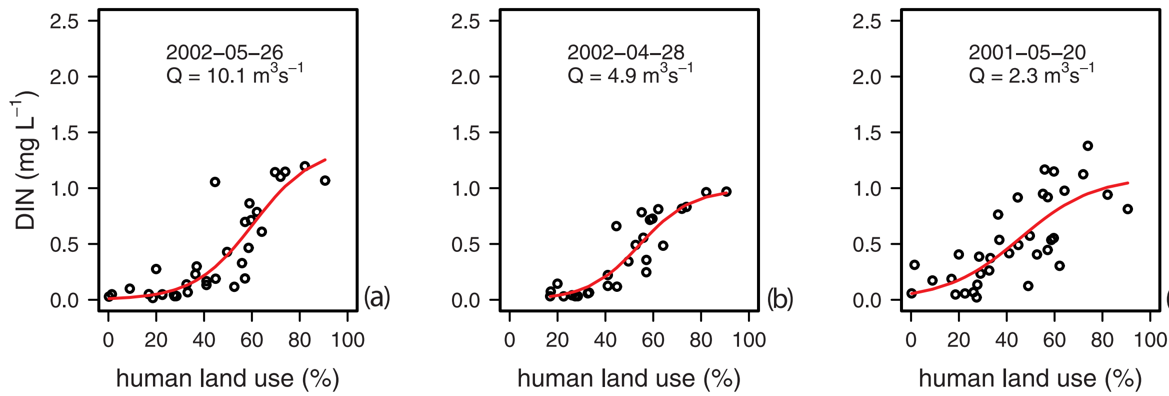

Figure 2. Examples of empirical DIN concentrations versus percent human land use (residential + agriculture + industrial) in the Ipswich basin for 3 sample days with different flow conditions (as indicated by discharge (Q) at the basin mouth). Line represents the logistic model fitted for the sample day.

dominant control in a wide variety of streams [*Mulholland et al.*, 2008], we assumed that the same parameters could be applied throughout the river network. There is also a similar lack of measurement outside the warm season. To scale throughout the year, we assumed temperature was the main determinant of denitrification seasonality [*Garcia-Ruiz et al.*, 1998a], such that lower activity occurs during colder temperatures. We used a Q_{10} approach to adjust $U_{\max}$ over the course of the year based on water temperature:

$$U_{\max\_t} = U_{\max} * Q_{10}^{\frac{T-Tref}{10}} \quad (5)$$

where $U_{\max\_t}$ is the adjusted $U_{\max}$ for time t, T is the water temperature at time t, $U_{\max}$ is calculated from the LINX additions (Table 2), T_{ref} is the mean water temperature during the LINX additions (= 20°C), and Q_{10} is the factor change in $U_{\max}$ for every ten degree change in water temperature. We assumed Q_{10} = 2 [*Seitzinger*, 1988]. Water temperature was approximated from air temperature [*Donner et al.*, 2002; *Mosheni et al.*, 1998]. Gridded air temperature was based on interpolated weather station data for MA and NH from National Climate Data Center climate stations. Based on variations in NO3 and temperature, the resulting υ_f's range between 5 – 100 m a^{-1} using DENIT and 10 – 280 m a^{-1} using DENIT+ASSIM up to 5 mg N L^{-1}. Uptake velocities can be slightly higher than $\upsilon_{f\max}$ because of the temperature function. This approach for scaling rates throughout the year ignores the role of seasonally important phenomena such as litter fall, high light inputs in spring prior to leaf out, and submerged aquatic vegetation phenology.

3.5. N Inputs

[16] The spatial and temporal distribution of DIN inputs to the river network were approximated from empirical relationships between DIN concentration and land use developed from headwater surveys in the Ipswich (Figure 2) and runoff conditions (section 3.3). Limitations of this approach are discussed below. DIN loading concentrations in the Ipswich are well described by a logistic (sigmoid) function of land cover:

$$[DIN] = \frac{Asym}{1 + \exp\left(\frac{X_{mid} - LU_{sub}}{Scale}\right)} \quad (6)$$

where LU_{sub} is the % residential + commercial + agricultural land in the subbasin, *Asym* is the asymptote of the relationship (i.e., maximum concentration), *Scale* describes the *LU* range over which concentrations rise, and X_{mid} is LU_{sub} at which the inflection point occurs. Parameters were estimated from 21 headwater surveys conducted over a range of flow conditions (Figure 2). *Asym* varied primarily between 1 and 1.4 mg N L^{-1} and *Scale* averaged 12.2. Neither was related to flow conditions or time of year. In contrast, X_{mid} increased with runoff (X_{mid} = 40.3 + 19.5 * $\log_{10}$(Q), r^2 = 0.51, $p < 0.001$), suggesting a dilution effect as runoff increased. Model fits were better when flow conditions as measured at the basin mouth were greater than 1 m^3 s^{-1} (r^2 between 0.35 and 0.6) indicating greater uncertainty in our modeled inputs at low flow ($r^2 <$ 0.3). For the base scenarios we assumed *Asym* = 1.4 mg N L^{-1}. The sensitivity analysis explored how different *Asym* values impact the results. The resulting DIN input concentration model is shown in Figure 3. DIN input flux was determined from DIN concentration and runoff for each 2 km^2 subbasin (section 3.2). The sigmoid function is empirically based, but is consistent with increased N inputs due to human activities in suburban catchments, and suggests that thresholds of suburbanization exist below which DIN concentrations change little and above which DIN begins to increase.

[17] This regression-based approach gives a reasonable estimate of the magnitude of input concentrations and their distribution within the basin. Two key assumptions are (1) the concentrations measured in headwater streams are indicative of terrestrial loading concentrations and are not impacted by aquatic processing upstream of the sampling point, and (2) the regression can be applied throughout the basin, including direct inputs to higher order streams and rivers. We attempted to minimize the violation of assump-

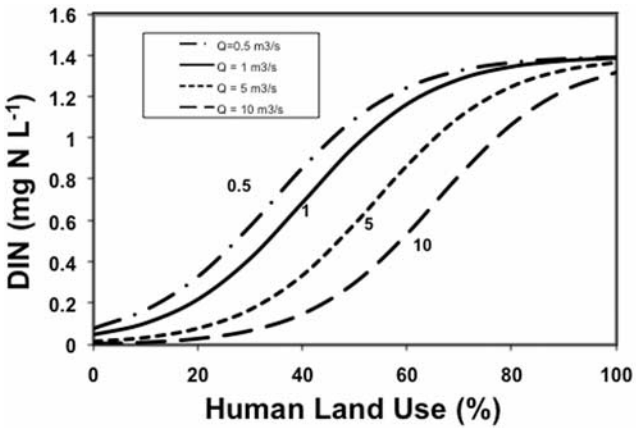

Figure 3. Modeled relationship between DIN input concentrations and percent human land use (residential + agriculture + industrial) for several flow conditions represented by discharge at the basin mouth. The downward shift demonstrates a dilution effect with increasing flow levels.

tion 1 by sampling headwater sites with relatively short upstream lengths (<1 km) that should reflect terrestrial inputs. This assumption is reasonable under higher flow conditions when residence times are short, and likely helps explain the greater predictability of the empirical loading relationships (equation (6)) at higher flows. Violation of the second assumption will likely have minimal effect because a relatively small proportion of land drains directly to higher order streams (Table 1), and because near-stream land use along higher-order streams remains primarily natural forest or wetland with low DIN loading rates. There are no known point sources within the basin [*Williams et al.*, 2004].

3.6. Frequency Analysis

[18] The distribution of N removal throughout the year was assessed by extending the flow frequency analysis of nutrient removal in individual channels described by *Doyle* [2005] to entire river networks. Daily watershed flow conditions (based on discharge at the downstream USGS gauging station) were binned into 19 logarithmically distributed classes. For each flow class, we calculated (1) the average whole river network removal proportion within the flow class (R), (2) the proportion of annual DIN inputs calculated to enter the river network (I), and (3) the input weighted removal proportions, RI (= R × I). The integral of RI corresponds with the total proportion of inputs removed by the river network over the entire model period. The approach is modified slightly from that described by *Doyle* [2005] in that we focus on the frequency distribution of inputs to the river network (I), rather than Q, to assess the effectiveness of river network removal in relation to timing of N inputs. We also determined the effective discharge (Q_{eff} = the flow category with the highest RI), and the functionally equivalent discharge (Q_{fed} = the flow level for which R is equivalent to the annual removal proportion) [*Doyle*, 2005].

3.7. Observed Data

[19] Observed DIN export concentrations are based on grab samples collected at least monthly at the mouth of the Ipswich R. by the Plum Island LTER. More frequent samples were collected between April 2000 and May 2001 [*Williams et al.*, 2004]. Annual observed export fluxes from the basin mouth are based on interpolated concentrations and observed Q. We did not distinguish storm events in this analysis. In addition, headwater and main stem samples were collected synoptically over a range of flow conditions (n = 21 surveys). Headwater samples were used to develop the DIN input model described in 3.5.

[20] We compared model predicted and observed areal fluxes (kg km^{-2} d^{-1}) from the headwaters and from the basin mouth for each synoptic survey. Headwater areal flux for each survey was calculated by summing the product of the observed DIN concentration and modeled discharge and then dividing by the sum of headwater catchment area. The cumulative headwater catchment area that was sampled represented ∼14% of the basin area, and was 44% urban (compared with 40% urban for the basin as a whole). We also compared the relative prediction error (PE) at the basin mouth with the median, 25th and 75th percentile PE from the headwater sites. PE is defined as (P − O)/O * 100, where P and O are predicted and observed values, respectively [*Alexander et al.*, 2002]. PE < 0 indicates the model prediction is too low, while PE > 0 indicates it is too high.

3.8. Scenarios

[21] The true magnitude and distribution of N inputs to the aquatic system over time, as well as the assumptions regarding the scaling of biotic N removal over space and time, are highly uncertain. In order to constrain the role of river network N removal, we applied several different scenarios of loading to and processing by the aquatic system. These scenarios also serve to better understand how the river system responds to different conditions. Single factor changes were made to each of the base scenarios (DENIT and DENIT+ASSIM, Table 2). Responses of both integrated river network removal and the role of different sized streams over annual timescales were quantified.

[22] To evaluate uncertainty in the DIN inputs to the river system, we applied scenarios with (1) no dilution effect (i.e., X_{mid} is the average (52.4%) of all 21 logistic relationships, so that input concentrations are uniform over time); (2) differing degrees of anthropogenic loading associated with human land use change (four scenarios where Asym was set to 0.5, 1.0, 2.0, and 2.8 mg N L^{-1}); and (3) spatially uniform inputs to better understand how the distribution of N inputs affects river network function (by applying each days mean flow-weighted input concentration to the entire basin).

[23] To evaluate our assumptions about process rates and kinetics, we modified the Michaelis-Menten (MM) base scenarios to (1) keep process rates independent of time (i.e., no temperature effect, Q10 = 1), (2) apply first-order kinetics, as in most previous river network models, and (3) to apply the Efficiency Loss (EL) model of rate changes with increasing concentration [*Mulholland et al.*, 2008; *O'Brien et al.*, 2007]. The first-order kinetic scenarios apply an average uptake velocity calculated from the same streams used to develop the kinetic relationship (υ_f = 40 m a^{-1} for DENIT; υ_f = 116 m a^{-1} for DENIT+ASSIM (S. M. Thomas and B. J. Peterson, manuscript in preparation, 2008)). The

Table 3. Observed and Predicted Conditions in Each Year for the DENIT and DENIT+ASSIM Scenarios

Parameter	2000	2001	2002	2003
Mean Annual Q (m^3 s^{-1})	6.1	5.2	3.0	6.2
Predicted Inputs (t a^{-1})	93.1	67.6	54.9	93.8
Predicted Exports (t a^{-1})				
DENIT	79.7	55.4	44.6	80.7
DENIT+ASSIM	63.2	44.0	33.6	65.6
Predicted Removal (%)				
DENIT	14.4	18.1	18.8	14.0
DENIT+ASSIM	32.1	34.9	38.8	30.1
Observed Exports (t a^{-1})	37.2	55.4	21.4	56.8
Observed Removal (%)	60.0	18.0	61.0	39.4
Export Prediction Error (%)				
DENIT	114	0	108	42
DENIT+ASSIM	70	−21	57	15

EL model has the form of $\log(\upsilon_f) = -f \log(C) + e$, where e and f are fitted parameters. The EL model suggests that process rates decline with increasing concentration but do not saturate as in the MM model. For denitrification in PIE streams, $\log(\upsilon_f) = -0.479(\log(NO_3)) + 2.709$ ($r^2 = 0.63$) and for total nitrate removal $\log(\upsilon_f) = -0.552(\log(NO_3)) + 3.17$ ($r^2 = 0.78$). Model fits are comparable to those for the MM model, but the shape of the curve with concentration differs somewhat (S. M. Thomas and B. J. Peterson, manuscript in preparation, 2008).

4. Results

4.1. Whole River Network N Removal

[24] DIN removal by the entire river network predicted by the model accounted for a relatively small proportion of total DIN inputs to the river network over annual timescales. Modeled annual DIN inputs ranged from 55 to 94 t a^{-1} (t = 1 t = 1000 kg) whereas predicted DIN exports at the basin mouth ranged from 45 to 81 t a^{-1} assuming surface water denitrification (DENIT), and 34 to 66 t a^{-1} assuming additional losses of assimilated DIN (DENIT+ASSIM) (Table 3). Over the entire 4-year period, the river network removed 15.8% of inputs using DENIT (inter-annual range, 14–19%) and 33% using DENIT+ASSIM (range 30–39%) (Table 3). Higher percent removal occurred in the 2 drier years.

[25] Most DIN entered the river network during higher flow conditions when removal efficiency is reduced, even with the dilution effect incorporated in the loading model (Figure 4). Using DENIT, river network removal approached 100% of inputs during extremely dry conditions (Q at the basin mouth < 0.2 m^3 s^{-1}), declined rapidly to about 40% of inputs when flows are 1 m^3 s^{-1} (typical summer flow conditions), and fell to <15% when flows were >5 m^3 s^{-1} (long-term mean annual discharge = 5.3 m^3 s^{-1}) (R in Figure 4). Using DENIT+ASSIM, the removal curve shifts to the right. Most annual inputs occurred when flow was >5 m^3 s^{-1} (I in Figure 4).

[26] Multiplication of the removal (R) and input (I) curves provides the input flux weighted removal curve, or the distribution of annual removal across flow categories (RI, Figure 4). Flow conditions between 2 and 8 m^3 s^{-1} dominated annual removal for both DENIT and DENIT+ASSIM. Q_{eff}, which is the flow level during which the greatest annual N removal occurs, is 3.2 and 5.0 m^3 s^{-1} for DENIT and DENIT+ASSIM, respectively. Integration under the flux-weighted removal curve (Figure 4) gives the annual removal for DENIT (15.3%) and DENIT+ASSIM (32.2%). Slight discrepancies compared to Table 3 occur because of the binning procedure used in the frequency analysis. Q_{fed}, which is the flow level during which removal proportions are equivalent to the integrated mean annual removal, was 3.5 and 5.1 m^3 s^{-1} for DENIT and DENIT+ASSIM, respectively.

[27] Despite reduced removal efficiency during above average flow conditions (>5 m^3 s^{-1}), the proportion of annual aquatic removal occurring during these flows is similar to removal near base flow (<2 m^3 s^{-1}) and intermediate flows (2–5 m^3 s^{-1}) for both DENIT and DENI-

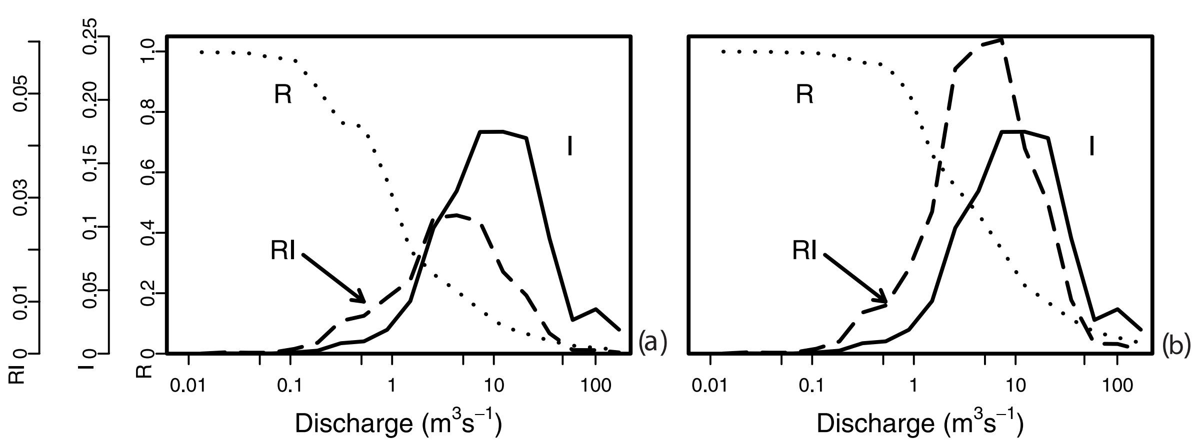

Figure 4. Distribution of annual inputs to the river network occurring during various flow categories (I, unitless) and mean network removal proportion during each flow category (R; unitless) for (a) DENIT and (b) DENIT+ASSIM over the 4-year study period. RI is the product of R and I and is the distribution of annual removal by the river network as a function of flow level. Flow levels are based on discharge measured at the USGS gauging station extrapolated to the basin mouth. Integration under RI gives the total proportion of annual inputs removed by the aquatic network.

Table 4. Percentage of Annual Runoff, DIN Inputs, DIN Export, and Aquatic Removal Occurring in Each Discharge Category

Discharge Category[a] (m^3 s^{-1})	Annual Runoff (%)	Annual DIN Inputs (%)	Annual DIN Exports (%)	Annual DIN Removal (%)	DIN Inputs in Flow Category Removed[b] (%)
DENIT					
<2	6.9	12.6	8.5	35.3	42.5
2–5	19.7	27.2	25.6	35.7	20.0
>5	73.5	60.3	65.9	28.9	7.3
DENIT+ASSIM					
<2	6.9	12.6	5.4	27.8	70.6
2–5	19.7	27.2	22.2	37.8	44.4
>5	73.5	60.3	72.4	34.4	18.3

[a]Based on flows at the basin mouth.
[b]Last column shows the percentage of inputs during the flow category that are removed within the flow category.

T+ASSIM (Table 4). During the 4-year period, 29–34% of all aquatic removal was predicted to occur during above average flow periods even though a much smaller proportion of inputs during high flow periods are removed (7.3–18.3%). Removal during low flow periods is significant with respect to annual removal budgets (representing 28–35% of annual removal), despite these periods representing a small proportion of annual inputs (12.6%) (Table 4).

4.2. Distribution of Removal by Stream Order

[28] Most of the predicted annual DIN removal occurred in higher order river channels, including the fourth-order tributaries and the fifth-order main stem (Table 5). Although fourth- and fifth-order channels represent 13% of total river length in the Ipswich (Table 1), application of DENIT resulted in 60% of the predicted river network removal over the 4-year period occurring in these reaches (Table 5). Application of DENIT+ASSIM resulted in a slightly reduced role of larger rivers (57% of total removal) compared to DENIT, but the change is small compared to the much greater total network removal than in DENIT (Table 3). Small rivers are slightly more important in the DENIT+ASSIM scenario because biological process rates are higher, resulting in more removal in low order streams nearer to where material first enters the network [e.g., *Wollheim et al.*, 2006]. Low-order rivers (orders 1–3) also contribute significantly to whole network N removal over annual timescales (~40% of total removal). Removal by lower order streams is greater in drier years, but the small interannual differences suggest that the removal distribution is relatively insensitive to typical interannual hydrologic variability (Table 5).

[29] N removal was dominated by lower order streams during low flows (Figure 5). Assuming similar temperatures (i.e., biological activity) across the flow range, removal by first through third order streams approaches the distribution of inputs to the network (~90%, Table 1) at extremely low flows (Figure 5). As flows increase, the proportion of network removal occurring in smaller rivers declines rapidly and stabilizes at ~40%. The higher rates of biological activity using DENIT+ASSIM increases the flow range over which low order rivers account for most removal, but the asymptotes are similar to DENIT.

Table 5. Percent of Total Aquatic DIN Removal Accounted for by Different Stream Orders Over the 4-Year Period for the DENIT and DENIT+ASSIM Scenarios[a]

Stream Order	DENIT Scenario	DENIT+ASSIM Scenario
First	9.6 (8.9–10.6)	10.9 (9.9–12.2)
Second	13.6 (12.8–14.3)	14.8 (13.9–16.0)
Third	16.7 (16.3–17.2)	17.3 (17.0–17.8)
Fourth	13.0 (12.9–13.1)	12.9 (12.7–13.1)
Fifth	47.2 (45.3–49.0)	44.2 (41.2–46.2)

[a]Range in annual values shown in parentheses.

4.3. Comparison With Observations

[30] Predicted and observed areal fluxes in the headwater streams, aggregated over all headwaters in each synoptic survey, are similar across the range of flow conditions, suggesting that the loading model (Figure 3) represents inputs to the river system reasonably well (Figure 6a). At the basin mouth, predicted and observed areal fluxes during the synoptic surveys are also similar up to flows of ~3 m^3 s^{-1} (Figure 6b). Above this flow level, with one exception, observations at the basin mouth are 2–5 fold lower than predicted. DIN concentration prediction errors (PE) at the basin mouth also demonstrate this pattern (Figure 7a).

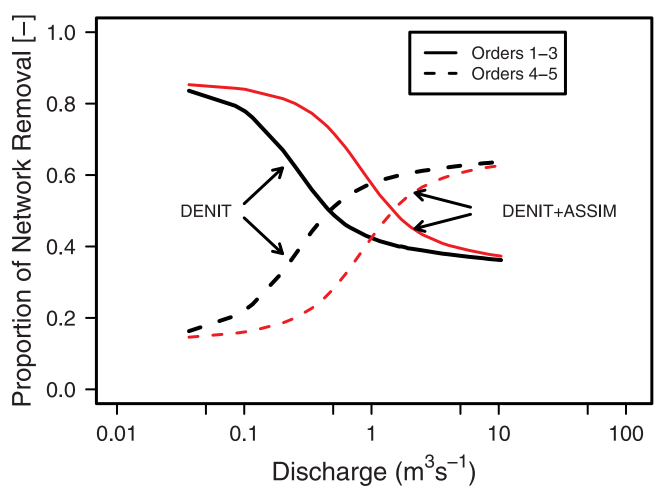

Figure 5. Proportion of whole river network DIN removal occurring in small (orders 1–3) and large (orders 4–5) streams as a function of flow condition as indicated by discharge at the basin mouth for DENIT and DENIT+ASSIM.

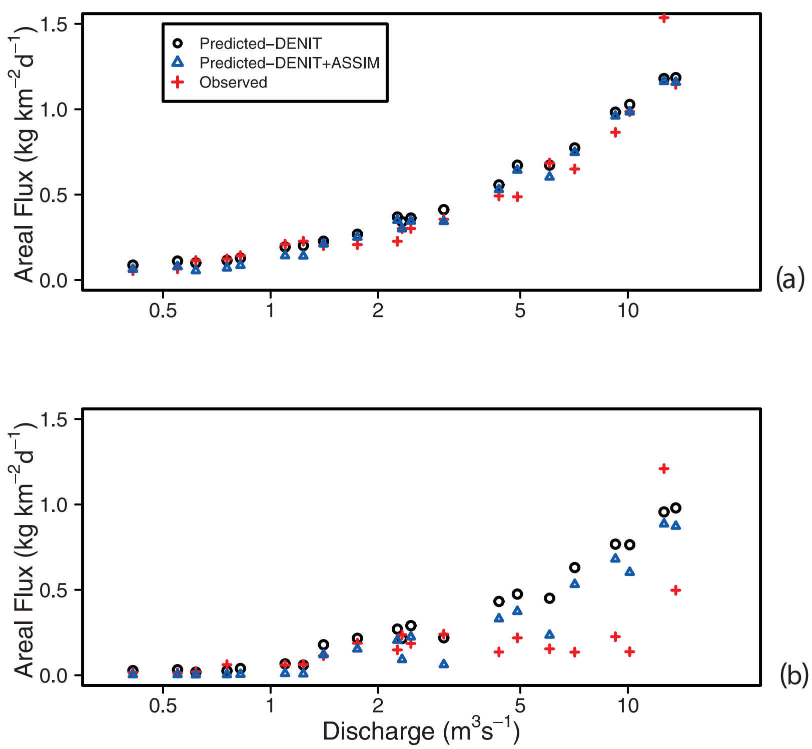

Figure 6. Observed and predicted areal fluxes versus flow condition as indicated by discharge at the basin mouth for (a) for the headwaters and (b) at the basin mouth. Areal flux in the headwaters is based on the sum of total flux across all headwater sample sites, divided by the sum of catchment area.

Errors at the basin mouth track errors in the inputs up to ~3 $m^3\ s^{-1}$, but diverge from the input errors (headwater PE) above this flow level. The pattern of error at the basin mouth using DENIT+ASSIM is similar, but errors are negative at low flows (Figures 6b and 7a). The large basin mouth PE's at higher flows, while errors in the inputs are similar across flow conditions (Figure 7a), suggests that for these sample days, predicted network removal is too low, rather than predicted inputs too high. Observed removal (1 − observed export fluxes/predicted inputs) corresponds reasonably well with the model at lower flows, but diverges considerably at higher flows (Figure 7b, compare with R in Figure 4).

[31] The magnitude and seasonality of model predicted DIN concentrations correspond reasonably well with observations across the 4-year period (Figure 8). Both observed and predicted values reach maxima during winter periods, and low levels during summer low flow periods. Summer low flows were progressively lower from 2000 to 2002, and both predicted and observed summer DIN concentrations were also progressively lower across these years. Concentrations predicted using the two measures of biological activity (DENIT, DENIT+ASSIM) more or less bracket observations during mid-summers and mid-winters. However, periods of significant discrepancies occurred, especially during high flow spring periods (right edges of gray shading in Figure 8), when the lowest observed DIN concentrations for the year generally occur, and during rare flushing events associated with some winter storm events (in 2001, 2003; Figure 8).

[32] Annually, DIN flux PE's at the basin mouth are 0 to 114% (annual predictions are up to twofold higher than observed) using DENIT and −21 to 70% using DENIT+ASSIM (Table 3). The overestimate is the result of high predicted fluxes during intermediate flows (Figure 6b), when significant inputs to the network occur (Figure 4). Model predicted fluxes at the basin mouth can be overestimated in both dry (e.g., 2002) and wet years (e.g., 2000).

4.4. Sensitivity Analysis

[33] A variety of scenarios were used to explore the sensitivity of N removal to different loading and biological processing assumptions. All the scenarios consider processes within channels only. Based on the set of single factor change scenarios (section 3.8), removal over the 4-year period by the entire Ipswich River network ranged between 11 and 25% of inputs using the denitrification parameters (DENIT), and between 21 and 52% using the total nitrate uptake parameters (DENIT+ASSIM) (Table 6). The relative importance of small (first through third order) and large (fourth through fifth order) rivers was little affected across the various scenarios. None of the scenarios could explain the high observed removal at flows >5 $m^3\ s^{-1}$. Results from specific scenarios provide additional insight into river network behavior.

4.4.1. Increasing DIN Inputs

[34] The four scenarios where DIN input rates increased from 71 to 400 kg $km^{-2}\ a^{-1}$ (a 5.6 fold increase) resulted in a 6.4 fold increase in DIN export using DENIT and a 7.6 fold increase using DENIT+ASSIM (ASYM scenarios, Table 6). Annual basin-wide removal efficiencies dropped from 22.3 to 10.8% of inputs for DENIT and from 44.1 to 23.7% using DENIT+ASSIM, indicating the expression of a

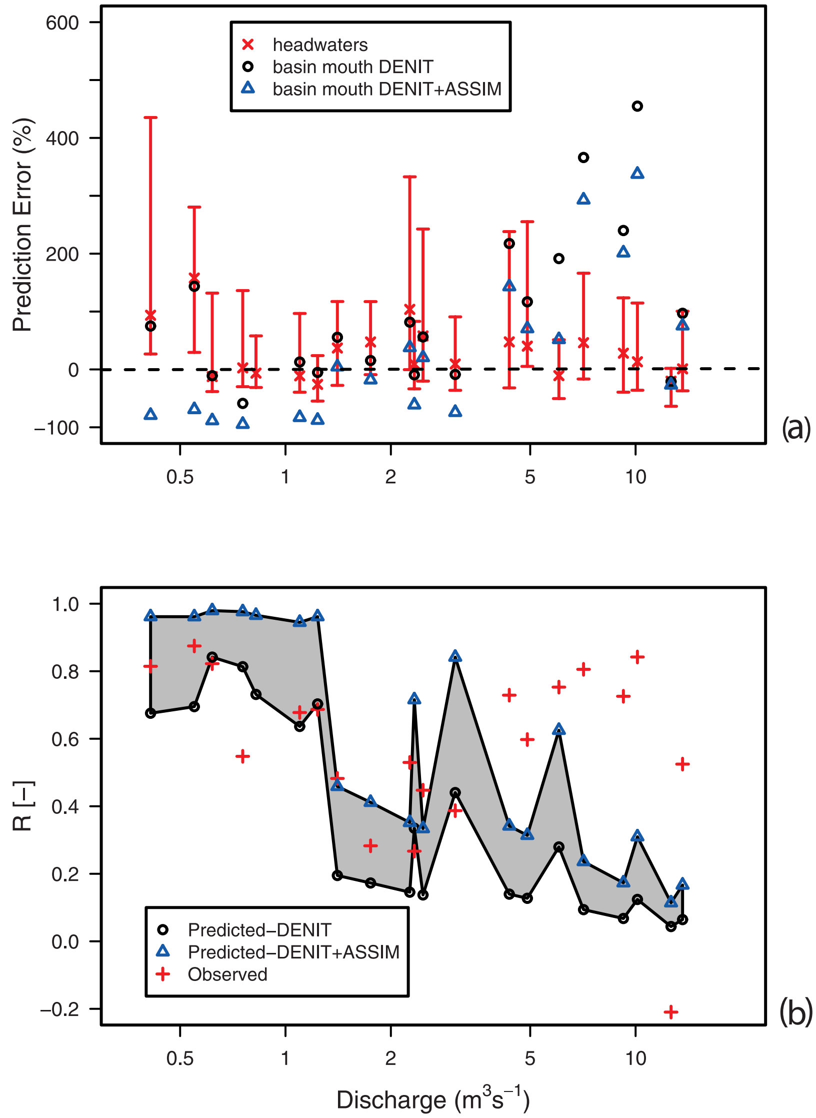

Figure 7. (a) Relationship between DIN concentration prediction errors and flow condition (as indicated by discharge at the basin mouth) at the headwater sampling sites (median, with error bars defined by the 25th and 75th percentiles), and at the basin mouth using the DENIT and DENIT+ASSIM scenarios. (b) Observed and predicted (for DENIT and DENIT+ASSIM) river network removal versus flow condition for each synoptic survey.

saturation effect. The role of large rivers (fourth and fifth order) increased modestly with increased inputs (57 to 61% and 52 to 59% of total network removal for DENIT and DENIT+ASSIM, respectively).

4.4.2. Temporal Variability of DIN Inputs

[35] The dilution effect (Figure 3) leads to disproportionately low inputs to the aquatic system during high flow periods (e.g., 74% of annual runoff, but only 60% of annual DIN inputs occur at flows >5 $m^3\ s^{-1}$; Table 4). If the dilution effect is removed (Temporally Uniform scenario, Table 6), annual inputs to the river system are 29% greater due to greater inputs during high flow periods. As a result, annual removal by the network declines from 15.9% to 11.6% (DENIT) or from 33.3 to 24.8% (DENIT+ASSIM). The relative importance of small versus large streams changes little (Table 6).

4.4.3. Spatial Variability in Loading

[36] Heterogeneity of land use in the Ipswich leads to disproportionate DIN inputs in the most distant headwaters of the basin (lower left corner of Figure 1). If inputs to the river system are uniformly distributed spatially (but with identical total inputs), annual river network removal increases slightly, from 15.9% to 16.4% of inputs (DENIT) and from 33.3 to 34.4% (DENIT+ASSIM). At the same time, the contribution of smaller streams to network removal increases 5–6% (Table 6), likely because uniform loading allows more small streams to increase their removal efficiency because concentrations are not as elevated.

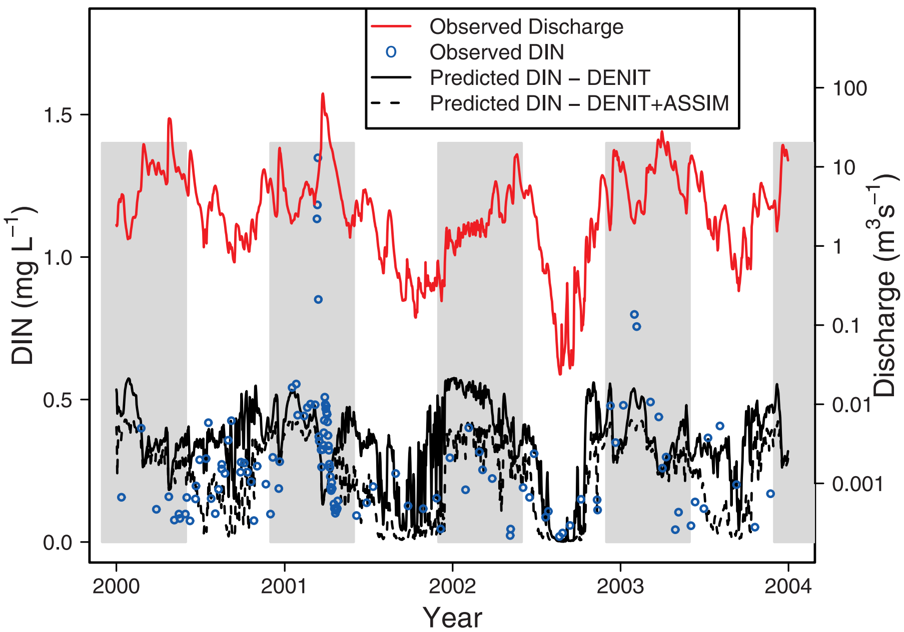

Figure 8. Time series of observed discharge, observed DIN, and model predicted DIN (both DENIT and DENIT+ASSIM scenarios) at the basin mouth. Gray shaded regions represent the winter and spring high flow periods (December–May) for each year.

4.4.4. Biological Assumptions

[37] The temperature control had a large impact on network removal, but did not influence the relative role of different stream sizes (Table 6). When the biological rates are unmodified by the Q10 factor ("No Q10"), so that high summer rates are applied all year, annual removal increases from 16 to 25% using DENIT, and from 33 to 52% using DENIT+ASSIM. In contrast, annual network removal using the first-order kinetics model changed little from the base scenario (~1% change), but shifted to low order streams. Application of the Efficiency Loss (EL) model resulted in modest declines in network removal for DENIT (from 15.9% using MM to 12.6% using EL), and larger declines for DENIT+ASSIM (from 33.3% using MM to 21.0% using EL). The declines occur because uptake velocities using EL (section 3.8) are lower than those using MM (Table 2) over the range of concentrations typical in the Ipswich (0.1 – 1 mg N L^{-1}), with a greater difference between the two models for total nitrate removal (S. M. Thomas and B. J. Peterson, manuscript in preparation, 2008).

5. Discussion

5.1. Flow Control of River Network N Removal

[38] The capacity of a river network to remove N inputs is highly dependent on flow conditions. Denitrification and total nitrate removal within river networks are clearly strong controls of nutrient exports during low flows, even with the relatively low and saturating process rates typical of surface water denitrification (υ_f = 10 to 100 m a^{-1}). Because many estuaries are strongly influenced by nutrient inputs during summer low flow periods when biological activity is high and residence times are long [*Hopkinson and Vallino*, 1995], the flow range corresponding with significant river network removal is an important consideration. Under current loading rates in the Ipswich, more than 40% of inputs to the network can be removed from flows up to 1 m^3

Table 6. Results of Sensitivity Analysis[a]

	Base	No Q10	First-Order Kinetics	Efficiency Loss	Temporally Uniform Loading	Spatially Uniform Loading	Asym = 0.5	Asym = 1.0	Asym = 2.0	Asym = 2.8
Predicted Inputs (t/4 years) (kg km^2 a^{-1})	309 (200)	309 (200)	309 (200)	309 (200)	398 (257)	309 (200)	110 (71)	221 (143)	442 (286)	619 (400)
DENIT										
Predicted Exports (t/4 years)	260	232	257	270	352	258	86	181	383	552
Predicted Removal (% of inputs)	15.9	25.0	17.1	12.6	11.6	16.4	22.3	18.2	13.2	10.8
% Aquatic Removal by first through third	39.7	39.6	44.0	40.6	39.3	44.5	42.7	40.6	38.9	38.8
% Aquatic Removal by fourth through fifth	60.3	60.4	56.0	59.3	60.8	55.3	57.2	59.3	60.8	61.4
DENIT+ASSIM										
Predicted Exports (t/4 years)	206	149	203	244	299	203	62	138	316	472
Predicted Removal (% of inputs)	33.3	52.0	34.3	21.0	24.8	34.4	44.1	37.4	28.4	23.7
% Aquatic Removal by first through third	42.9	43.3	48.8	41.9	42.2	48.5	47.6	44.4	41.5	40.5
% Aquatic Removal by fourth through fifth	57.2	56.7	51.2	58.2	57.9	51.5	52.4	55.6	58.5	59.4

[a]Model scenarios are single factor changes relative to the base scenario and are defined in section 3.8. Observed export over the 4 years is 170 t.

s^{-1} (DENIT) which corresponded with 22% of the time over the 4-year period. This represents an important linkage between river network and estuarine processes.

[39] Over annual timescales, our model suggests that the ability of networks of river channels to control DIN exports is relatively low because most inputs occur during high flow periods when the capacity for removal is reduced. This result for an entire river network is consistent with expectations based on field and modeling studies conducted at reach scales [*Doyle*, 2005; *Royer et al.*, 2006]. However, observed N concentrations indicate that the Ipswich river network possibly sustains high removal rates during higher flow conditions as well (Figure 7b), especially in late spring (e.g., points at right side of gray shaded areas in Figure 8). One possible reason is that the temperature control we used to scale denitrification rates throughout the year (equation (5)) is inadequate. However, even application of summer rates throughout the year ("No Q10" scenario; Table 6) did not result in high enough removal rates to match those observed at higher flows (>5 m^3 s^{-1}). Another possible reason for the discrepancy is that the modeled inputs to the river network were too high during high flow periods. *Williams et al.* [2004] suggest that extremely low concentrations in spring are a result of source limitation (i.e., by the end of May, N sources have been flushed by previous high flows). However, none of the headwater synoptic surveys used to develop the loading relationships provided evidence of large declines in inputs with increasing flow to explain the extremely low export concentrations (Figure 7a), nor do temporally frequent DIN time series obtained from high N urban headwater streams in the basin [*Wollheim et al.*, 2005]. Therefore, it seems that additional removal mechanisms than those measured in channels during summer low flows are active at other times of year.

[40] Biological activity potentially intensifies during spring at certain flow levels because light levels are high with minimal shading prior to full leaf out, leading to high N assimilation by primary producers [*Mulholland and Hill*, 1997]. High order streams in the Ipswich develop fairly extensive submerged vegetation, suggesting at least temporary N storage that may ultimately be denitrified following senescence later in the year. Alternatively, floodplains are connected during high spring flows when temperatures are also relatively warm, possibly stimulating removal [e.g., *Baker and Vervier*, 2004]. None of these mechanisms are accounted for in our current model.

[41] High flow periods can account for a significant proportion of annual aquatic N removal in our model scenarios, even with our under estimate of removal proportions during high flows. Removal at reach scales may be small and undetectable at high discharge using field methods, but at the network scale small amounts of removal accumulate along flow paths potentially leading to consequential removal, accounting for between 7 and 18% of inputs during higher flows (>5 m^3/s).

[42] Our model results are consistent with other estimates of river network removal for the Ipswich and other river networks. *Williams et al.* [2004], using a mass balance approach, estimated that 15% of DIN inputs were removed by the river system between May 2000 and April 2001. For the same period, our model predicts 12.7–28.3% removal using DENIT and DENIT+ASSIM. However, this period had lower observed removal than other years (Table 3), and may not be indicative of typical annual removal, in part because flows remained high throughout the summer and because extremely high flows occurred at the start and end of this period (Figure 8). *Donner et al.* [2004] using a daily time step model, predicted 24% annual removal in the Mississippi, and slightly less in the smaller, higher runoff Allegheny. The Allegheny also showed relatively little inter-annual variability in network removal despite considerable inter-annual variability in precipitation [*Donner et al.*, 2004], similar to what we found in the Ipswich (Table 3). Comparisons across models are difficult, however, because loading rates, uptake kinetics, river hydraulics, and network resolutions simultaneously differ.

5.2. Impact of Modeling Mean Annual Versus Time Varying N Removal

[43] Many river network models have been applied at mean annual time steps [*Alexander et al.*, 2000; *Seitzinger et al.*, 2002; *Wollheim et al.*, 2008] and therefore do not consider the role of hydrologic variability in network N removal (except see *Donner et al.* [2002]). *Doyle* [2005] proposed the concept of functionally equivalent discharge (Q_{fed}) to identify the specific flow level at which reach-scale removal is equivalent to the total removal proportion over the annual hydrograph. Q_{fed} is potentially useful at the whole river network scale to assess errors that arise when modeling river network removal using mean annual conditions. In the Ipswich Base scenarios, Q_{fed} was surprisingly similar to the mean annual discharge (Q_{mean}) of 5.1 m^3 s^{-1} (Q_{fed} = 4.8 m^3 s^{-1} for DENIT and 5.6 m^3 s^{-1} for DENIT+ASSIM), suggesting that, given the model assumptions, mean annual conditions provide a reasonable approximation of the annual capacity for river network channel processes to remove N inputs.

[44] The correspondence between Q_{fed} and Q_{mean} arises because the distribution of N input peaks during flow conditions higher than Q_{mean}, while removal is skewed toward N inputs occurring during flows less than Q_{mean}. There is therefore a tendency for Q_{fed} to approach the mean annual flow condition (Figure 4). If the relative skewness of N inputs and removal changes, a greater difference between Q_{fed} and Q_{mean} can result. For example, Q_{fed} increased to 6.4 m^3 s^{-1} under the scenario of temporally uniform N loading concentrations (which shifts I in Figure 4 to the right), indicating that a mean annual model will overestimate N removal in this case. Thus, the degree of error in modeling N exports using mean annual conditions will depend on the timing of N inputs relative to the distribution of N removal capacity across flow in the targeted basin. The high observed removal at higher flows (Figure 7b) suggests that actual Q_{fed} in the Ipswich will be higher than Q_{mean}, and suggests a better understanding of processes during high flow is needed.

5.3. Role of River Size

[45] Larger rivers potentially play an important role within entire river networks when integrated over annual timescales. Previous work has emphasized smaller rivers [*Alexander et al.*, 2000; *Peterson et al.*, 2001], which, in the Ipswich model, also account for a significant proportion of annual DIN removal (~40%) and are dominant at low flows (Figure 5). Smaller rivers dominate when substrates are highly reactive, as for ammonium [*Peterson et al.*, 2001;

Wollheim et al., 2006] and at lower flows because removal occurs near the point of original loading. However, as has been suggested on the basis of some river network models applied at mean annual time steps [*Ensign and Doyle*, 2006; *Seitzinger et al.*, 2002; *Wollheim et al.*, 2006], larger rivers are potentially considerable sinks as well when reactivity is less intense or flows are higher. Large rivers are significant under the assumption that uptake velocity is independent of river size because the rate at which rivers widen and lengthen with increasing discharge results in disproportionate increases in benthic habitat in the downstream direction [*Ensign and Doyle*, 2006; *Wollheim et al.*, 2006].

[46] The role of large rivers is highly dependent on the assumption that biological process rates are independent of stream size. Calibrations involving the SPARROW model suggest that uptake velocities decline with increasing stream size [*Alexander et al.*, 2000; *Moore et al.*, 2004], whereas synthesis of empirical observations of total nitrate assimilation and denitrification uptake velocities [*Ensign and Doyle*, 2006; *Garcia-Ruiz et al.*, 1998b; *Pina-Ochoa and Alvarez-Cobelas*, 2006] show little evidence for such declines. Consistent rate measurements along stream continua are needed to better address this assumption.

[47] Larger rivers are able to act as buffers that slow but do not prevent the increase in river network N exports with increasing non-point N loads, or with increasing flow conditions. Our results are consistent with recent modeling that suggests nonlinear process rates lead to an increasing role of large rivers as non-point N loads increase [*Mulholland et al.*, 2008]. This occurs because downstream systems are source limited under low N load conditions when most removal occurs near the point of entry to the network. As N loads increase, uptake velocities decline, and more N is transferred to larger rivers where it can then be removed. In networks with heterogeneous nonpoint inputs such as the Ipswich, both dilution and upstream removal combine to reduce N concentrations along riverine flowpaths, leading to greater uptake velocities in downstream systems. Several model scenarios support this interpretation. For example, an assumption of first-order kinetics (no process saturation) led to a relatively greater role of smaller streams, whereas elevated loads (increasing saturation) led to a lesser role for smaller streams (Table 6). Spatially uniform loading also increased the role of lower order rivers.

[48] We find a similar increase in the role of large rivers with increasing flow (Figure 5). Under low flow conditions, all removal occurs upstream so little material reaches large rivers. As flows begin to increase, smaller rivers become leakier, but downstream rivers can remove this excess material with the result that there is little response in whole network removal over a range of low flows (the flat portions of R in Figure 4). However, this compensation disappears relatively quickly as flows increase. The increasing role of larger rivers is in agreement with suggestions that excess material exported from smaller streams can be processed in downstream rivers, lakes, and reservoirs [*David et al.*, 2006; *Royer et al.*, 2006], and indicates the need for a river network perspective. River networks with significant reservoir or lake abundance will likely show an even greater buffering capacity as flows increase [*David et al.*, 2006]. The tendency for downstream systems to increase in importance will be greatly affected by factors such as point source inputs and hydraulic modifications (e.g., channelization, levees, dredging).

5.4. Michaelis-Menten Versus Efficiency Loss Models of N Removal

[49] Two nonlinear models of N process rates, Michaelis-Menten (MM) and Efficiency Loss (EL), were applied to the denitrification rates measured in the Plum Island LINX streams, and both fit the observations equally well. The MM model is more appropriate at the cellular level, and does not account for microbial communities adapting to chronically higher nutrient levels [*O'Brien et al.*, 2007]. This adaptation is suggested for why process rates in the EL model show declining efficiency with increased nutrients but do not saturate. In the Ipswich, it is difficult to distinguish the two models because of the small set of observations in the PIE denitrification rate data set (n = 8), the relatively small range of concentrations (0.05 to 1.4 mg L^{-1}), and few measurements at intermediate concentrations within this range. The MM model results in higher uptake velocities than the EL model at intermediate concentrations [*O'Brien et al.*, 2007] that are typical in Ipswich streams. As a result, application of the EL model resulted in lower network removal percentages than did the MM model (Table 6 and Figure 9a).

5.5. N Saturation at River Network Scale

[50] The concept of N saturation has long been a topic of interest in terrestrial systems [*Aber et al.*, 1989] and is being increasingly applied to rivers as it becomes clear that nitrate removal processes are less efficient at high concentrations [*Earl et al.*, 2006; *O'Brien et al.*, 2007]. In our application of this concept to an entire river network, we found that removal efficiencies decline with increased anthropogenic N inputs. Over the range of loading scenarios explored (from 0.35 to 2x contemporary loads), removal proportions declined roughly by half (Table 6). Similar results occur using both the MM and EL models over the range of inputs considered. Thus, increasing inputs combined with nonlinear removal processes will lead to disproportionate increases in export from the river network and increased potential impacts on downstream ecosystems.

[51] The effects of saturation are most evident over a certain range of flow where biological processes have the greatest influence on network removal. Using the DENIT MM model, at very low and very high flow, network removal is not sensitive to changes in N loading (Figure 9b), indicating hydrology is the dominant control. However, at typical summer low flow (1 $m^3 s^{-1}$) removal declined from 0.61 in the low N load scenario (60 kg km^{-2} a^{-1}) to 0.47 at contemporary loadings (200 kg km^{-2} a^{-1}). A further doubling of inputs from 200 to 400 kg km^{-2} a^{-1} (increasing maximum headwater stream DIN concentrations to $\sim$3 mg N L^{-1}) would further reduce removal at 1 $m^3 s^{-1}$ to 0.3. Thus, N saturation magnifies changes in N inputs related to human activities: the percentage change in exports will be greater than the percentage change in inputs from land, with the greatest effect occurring during typical low flow periods that influence processes in some estuaries. Similar results were found applying the Efficiency Loss model to the different N loading scenarios. N removal in our system is responsive to load variations because our DIN

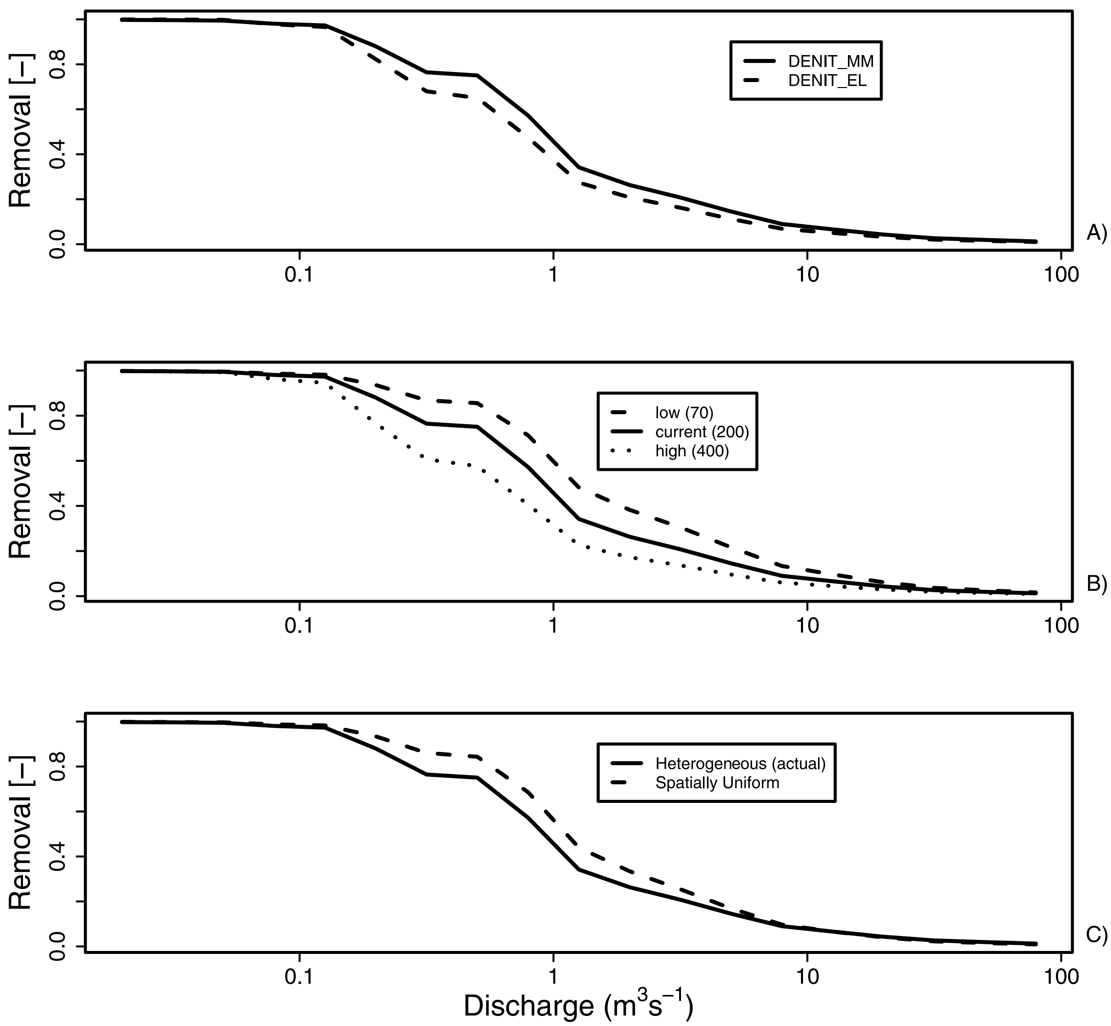

Figure 9. Comparison of river network DIN removal as a function of flow condition as indicated by discharge at the basin mouth for different scenarios: (a) Michaelis-Menten (MM) versus Efficiency Loss denitrification process specification, (b) a series of increasing N inputs to the river system (basin wide average of 70, 200, and 400 kg km^2 a^{-1}), and (c) with heterogeneous (spatially distributed) N inputs versus homogenous (spatially uniform) inputs. The solid line is identical in each figure, and is the predicted network removal from the base DENIT scenario.

levels fall within the dynamic portion of the MM and EL relationships. If DIN were already higher, changes in removal with similar increases in DIN would be smaller.

[52] Emergent properties arise when finer scale processes result in new patterns at coarser scales [*Cadenasso et al.*, 2006]. Relatively simple rules governing subsets of system behavior, when integrated, result in behavior at the whole system level that would be difficult to determine a priori without integration through models. Nutrient removal by entire river networks is an example of such an emergent property. For example, in our model the specified hydrologic, hydraulic, geomorphic, biological, and N loading characteristics result in a certain level of mass removal by the entire river network. As N inputs increase, a relationship between inputs and whole network removal emerges. Using the MM process model, the overall basin response follows a saturating curve which can be used to estimate the limits of river network removal with increasing N inputs, given the hydrological conditions and model assumptions (Figure 10a). For DENIT, the maximum removal rate is 27 t a^{-1}, with a half saturation DIN input level of 93 t a^{-1}. For DENIT+ASSIM, the maximum removal rate is 65 t a^{-1}, with a half saturation input of 119 t a^{-1}. The current DIN input rate is about 80 t a^{-1}, which is approaching the half saturation level, suggesting that further increases in inputs will result in disproportionate increases in exports. Application of the Efficiency Loss process model shows a similar magnitude of response, but with a different shape (Figure 10b). Application of the first-order process model (using the low N load scenario as the starting point) results in constant removal proportions with increased loading. Such curves could potentially be a useful way to evaluate how river systems with different characteristics (river network morphology, hydrology) are expected to respond to increased loading given different process assumptions

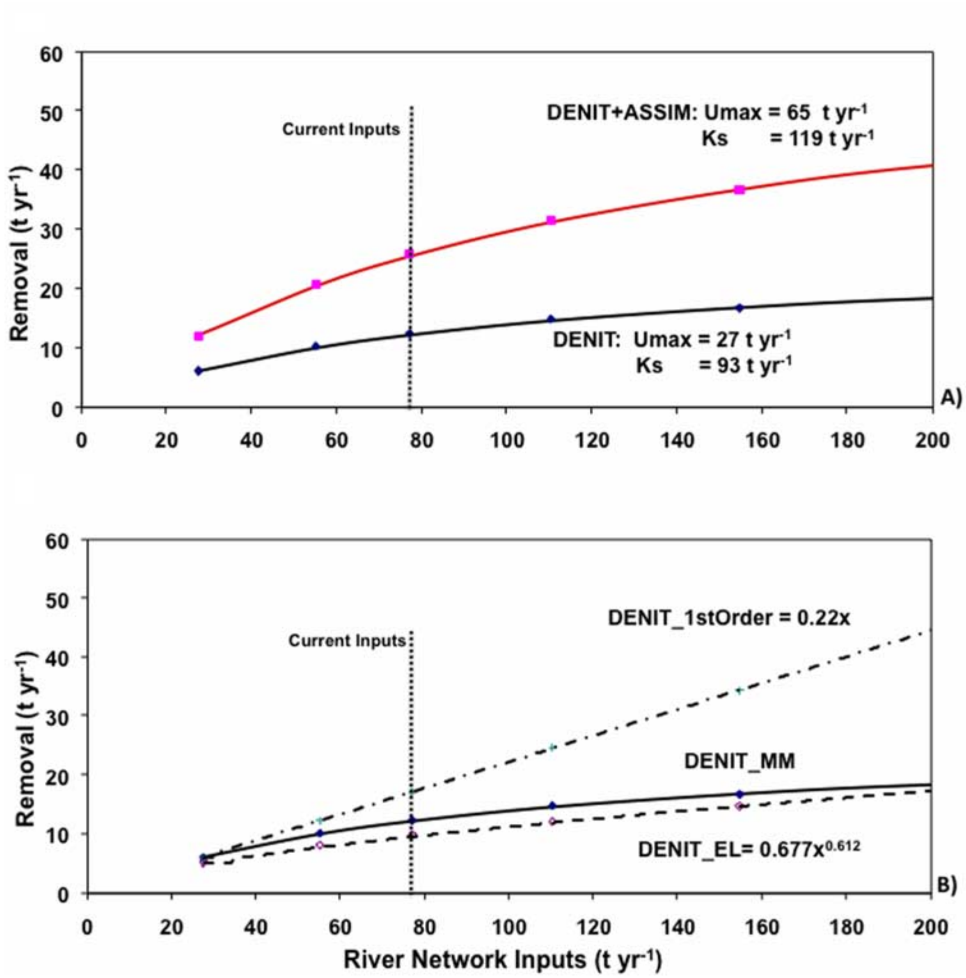

Figure 10. Relationship between river network removal and river network inputs based on different scenarios of loading to the river network (equivalent to 70, 140, 200, 286, and 400 kg km^2 a^{-1}) (a) using the DENIT and DENIT+ASSIM base scenarios that apply the saturating Michaelis-Menten (MM) process model and (b) comparing the first-order, efficiency loss (EL) and MM process models for DENIT. Current estimated inputs to the Ipswich R. network is 70 t a^{-1} (200 kg km^2 a^{-1}).

and could inform management of nutrient inputs within watershed.

5.6. Role of Spatial Variability of N Inputs

[53] Spatial heterogeneity is potentially an important influence on ecosystem processes [*Turner*, 1989]. For river network N removal in the Ipswich over annual timescales, it appears that land use heterogeneity is secondary to hydrological control. Land use heterogeneity in the Ipswich results in disproportionate DIN input to headwaters most distant from the basin mouth [*Williams et al.*, 2004; *Wollheim et al.*, 2005], potentially leading to elevated removal because a disproportionate amount of DIN must travel the entire Ipswich R. main stem and would be subject to removal processes en route. However, we found that spatially uniform inputs led to slightly greater removal and that this occurred in smaller first through third order streams (Table 6). Apparently, the uniform distribution of inputs results in lower concentrations and higher uptake velocities in smaller streams that compensate for the additional length of stream that some N experiences under the heterogeneous conditions. The difference is small over annual timescales, because hydrological factors dominate annual removal efficiency. But the effect is more noticeable under base flow conditions (Figure 9c), suggesting that the importance of land use heterogeneity is a dynamic function of flow condition.

5.7. River Network Model: Key Uncertainties

[54] The N processing rates we incorporated into the model reflect relatively few measurements (n = 8) in small stream channels taken over a limited time period (summer low flow). Although we scaled these over space and time using reasonable a priori assumptions, there are many phenomena not considered in the model. As a result, model predictions only roughly correspond with observations, underestimate removal, and overestimate mean annual exports from the basin. Nevertheless, the model is useful as a preliminary step for understanding how river networks behave given a particular process specification, in this case nonlinear removal processes over a range of hydrologic conditions.

[55] Biological factors that require further attention include seasonal controls of process rates, changes in biological activity with stream size, and interactions with other element cycles (especially carbon and oxygen). Model predicted removal is highly sensitive to the seasonality assumption. Scenarios with no seasonality (No Q10 in Table 6) resulted in the greatest change in annual removal relative to other scenarios. Many factors are involved in explaining seasonality, requiring a coupled C, N, P, O biogeochemical model [e.g., *Billen and Garnier*, 2000]. Factors to consider include the timing of leaf fall, leaf out, floodplain inundation, periods of aquatic vegetation biomass accumulation, DOC in streams across the landscape (e.g., wetland dominated areas) and so forth. Moreover, explicit representation of individual N cycle processes (nitrification, assimilation, mineralization, denitrification, PON suspension, DON production) will likely further lead to interesting river network dynamics, as each of these vary over different temporal and spatial resolutions. The assumption of similar kinetics across stream size (on a per area basis) is reasonable a priori [*Ensign and Doyle*, 2006], but requires further testing. Hot spots and hotmoments of biogeochemical activity are evident in the Ipswich River network [*Williams et al.*, 2004], and certain sections of the river system with low dissolved oxygen have much lower DIN than expected (unpublished data). In addition, transient storage zone characteristics should also influence uptake velocities [*Mulholland and DeAngelis*, 2000; *Runkel*, 2007], and it is not known how they scale with increasing stream size.

[56] Hydrologic dynamics not currently considered that may be important include spatially variable precipitation and runoff conditions (runoff heterogeneity is currently influenced only by impervious surfaces), differential flow variability in different stream sizes [*Doyle*, 2005], channel/floodplain routing (as opposed to simple flow accumulation), water withdrawals [*Claessens et al.*, 2006], and heterogeneity/discontinuities in channel morphology (e.g., wider wetland dominated reaches, beaver ponds), which likely also affect biological rates. Finally, better constraints on the N inputs to the river system are needed. Our loading specification only roughly represents the timing and distribution of DIN inputs. For example, the input relationships can't represent the rare but extremely elevated export concentrations that sometimes occur during intermediate flows, or considerable unexplained variability (e.g., Figure 2). However, given that the inputs reasonably reflect loading rates and patterns (Figure 6a), we believe that the results provide a reasonable indication of river network behavior with respect to N removal for different process specifications.

6. Conclusion

[57] N removal dynamics of entire river networks are the result of the temporal and spatial variation of hydrological, biological, and geomorphic characteristics, interacting with the amount, distribution, and timing of N inputs. Many of these characteristics are being altered by human activities, and should be considered simultaneously to understand changes in the ability of aquatic systems to attenuate N fluxes. The net effect of these anthropogenic impacts is currently unknown but has important management implications. Based on our model, river systems can be significant sinks during lower flows, but are only a moderate sink during higher flows. Our model however accounts only for channel processes. Observations suggest that the network as a whole, including floodplains, is able to remove a much greater proportion of inputs during higher flow periods. Increases in N inputs are likely to lead to disproportionate increases in N exports due to saturation of removal processes, and the effect will be most noticeable under flow conditions that can influence estuarine processes. Other river networks with alternative network geomorphology (including lakes), biological activity, hydraulic characteristics or N input patterns will show different responses to increasing N inputs. The analysis presented here provides a potentially useful way of comparing the expected responses to anthropogenic change in different watersheds and evaluating ecosystem services provided by river systems.

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