Relationship between river size and nutrient removal

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[1] We present a conceptual approach for evaluating the biological and hydrological controls of nutrient removal in different sized rivers within an entire river network. We emphasize a per unit area biological parameter, the nutrient uptake velocity (ν_f), which is mathematically independent of river size in benthic dominated systems. Standardization of biological parameters from previous river network models to ν_f reveals the nature of river size dependant biological activity in these models. We explore how geomorphic, hydraulic, and biological factors control the distribution of nutrient removal in an idealized river network, finding that larger rivers within a basin potentially exert considerable influence over nutrient exports. **Citation:** Wollheim, W. M., C. J. Vörösmarty, B. J. Peterson, S. P. Seitzinger, and C. S. Hopkinson (2006), Relationship between river size and nutrient removal, *Geophys. Res. Lett.*, *33*, L06410, doi:10.1029/2006GL025845.

1. Introduction

[2] River networks have the capacity to influence export of terrestrially-derived constituents to coastal systems, making them an important link between land and ocean in the Earth System and a critical component in nutrient pollution control strategies [*Meybeck and Vörösmarty*, 2005]. An unresolved question is how nutrient removal processes scale across the broad range of stream sizes that comprise river networks [*Fisher et al.*, 2004]. Some reports suggest small streams and rivers control nutrient exports from river networks [*Alexander et al.*, 2000; *Peterson et al.*, 2001; *Bernot and Dodds*, 2005], while others emphasize the relative importance of larger rivers [*Seitzinger et al.*, 2002]. Trends in surface water hydraulics with increasing river size determine nutrient removal capacity of constant-length reaches [*Bernot and Dodds*, 2005], but the generalized role of river size requires a basin context. Trends in biological activity with river size have been proposed [*Alexander et al.*, 2000], but the nature of these has been debated [*Lindgren and Destouni*, 2004; *Darracq and Destouni*, 2005]. Here we suggest that differing interpretations of the role of river size can be reconciled if the interactions of biological and hydrological characteristics are clearly identified.

[3] In this letter we explore the factors controlling the strength and distribution of nutrient removal within river networks. We apply an approach, grounded in stream spiraling theory, that identifies the individual and conjunctive roles of biological and hydrological properties controlling nutrient removal in benthic dominated systems [*Donner et al.*, 2004; *Doyle*, 2005]. We first use this approach to evaluate river size dependence of biological activity in several existing river network nitrogen (N) models. We then apply the approach in an idealized river network to explore how biological activity, river network geomorphology, and surface water hydraulics interact to define nutrient removal in full river networks.

2. Methods

[4] Nutrient removal in streams and rivers is determined by the strength of biological processes relative to hydrological conditions. Biological parameters commonly estimated in field studies of stream nutrient spiraling [*Stream Solute Workshop*, 1990] are applied in river network N removal models, including the time specific nutrient uptake rate (k_t [T^{-1}], T = time units) and the apparent nutrient uptake velocity (ν_f [$L\ T^{-1}$], L = length units). As purely biological parameters, k_t is based on per unit volume uptake (volumetric uptake [$M\ L^{-3}\ T^{-1}$]/concentration [$M\ L^{-3}$], M = mass units), and ν_f is based on per unit surface area uptake (areal uptake [$M\ L^{-2}\ T^{-1}$]/concentration [$M\ L^{-3}$]). The parameters can be inter-converted as $\nu_f = hk_t$, where h is water depth [L]. The proportional removal (R [-], unitless) of nutrient inputs to a water body is calculated by relating these parameters to surface water characteristics:

$$R = 1 - \exp\left(\frac{-\upsilon_f}{H_L}\right) \qquad (1)$$

$$R = 1 - \exp(-k_t \tau) \qquad (2)$$

where $\tau = l/v$ and $H_L = h/\tau = Q/(wl)$. τ is residence time [T]; v is average water velocity [$L\ T^{-1}$]; l is reach length [L]; H_L is hydraulic load [$L\ T^{-1}$]; Q is discharge [$L^3\ T^{-1}$]; and w is width [L].

[5] In streams and rivers where generally benthic processes dominate, ν_f is a biological measure that is mathematically independent of surface water hydrological characteristics because it is based on per unit area uptake, and is well suited for comparing biological activity in streams of different sizes [*Wollheim et al.*, 2001]. Thus, our approach uses equation (1), applied in a river network context, to isolate hydrological (defined by H_L) and biological factors (defined by ν_f) controlling removal. We assume first order kinetics are applicable (areal uptake changes linearly with concentration), and do not address more complex kinetics that would alter ν_f with concentration.

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Table 1. Derivation of ν_f From Recently Reported River Network N Removal Models[a]

Model	Equation	Parameter values	Derivation of υ_f
1. SPARROW[b] [*Alexander et al.*, 2000]	$R_1 = 1 - \exp(-k_t\tau)$	k_t = 0.455, 0.118, 0.051, 0.005 d^{-1} for SPQ1-4[b]	$\upsilon_f = k_t h$
2. RivR-N[c] [*Seitzinger et al.*, 2002]	$R_2 = m_1 H_L^{(m_2)}$	m_1 = 0.8845 (-) m_2 = −0.3688l (-)	$\upsilon_f = -H_L \ln[1 - R_2]$
3. POLFLOW[c] [*Darracq and Destouni*, 2005]	$R_3 = \dfrac{1}{(r_{n1}[1000*S + 1]Q^{r_{n2}})}$	r_{n1} = 35 s m^{-3} r_{n2} = 0.4 (-)	$\upsilon_f = -H_L \ln[1 - R_3]$
4. Donner et al. [2004][d]	$R_4 = \upsilon_f/H_L$	υ_{fo} = 28.6 m yr^{-1} (10°C)	$\upsilon_f = \min(\upsilon_{fo}, (\upsilon_{fo}*120/Q))$

[a]R_1−R_4 are the proportional nutrient removal in each model. ν_f in POLFLOW and RivR-N was determined by setting their equations equal to equation (1). For POLFLOW, we derive ν_f using two sets of hydraulic equations to specify H_L with increasing Q, HYD1: w = $8.3Q^{0.52}$, h = $0.29Q^{0.37}$, v = $0.42Q^{0.11}$ (Dave Bjerklie, USGS, personal communication, 2005); HYD2: w = $10.6Q^{0.36}$, h = $0.26Q^{0.40}$, v = $0.36Q^{0.24}$ [*Darracq and Destouni*, 2005] and using 1km reaches as in the POLFLOW calibration. For the RivR-N model we use HYD1 and assume both 10 and 25 km reach lengths.
[b]SPQ1-4 correspond with SPARROW Q class of *Alexander et al.* [2000] defined by 28.3, 283, 850 m^3 s^{-1}.
[c]Variables m1, m2, r$_{n1}$, and r$_{n2}$ are fitted coefficients for the respective models (empirically based for RivR-N and calibrated in POLFLOW) and S is channel slope (-). We assume S = 0.01. Other parameters are defined in the text.
[d]We assume υ_f at 10°C from the full model scaled down linearly at Q > 120 m^3 s^{-1} as by *Donner et al.* [2004].

[6] We use the scale-independent nature of ν_f to standardize and compare biological activity in several previous river network models. The original equations and derivation of ν_f are shown in Table 1. For each model we evaluate how per unit area biological activity varies across stream size, and how hydrological assumptions affect this distribution.

[7] We then apply equation (1) in a model 7th order river network to explore factors controlling the strength and distribution of mean annual nutrient removal. The river network consists of streams in each order class whose number, mean length, and mean drainage area are defined by river network geomorphologic parameters; whose mean depths, widths and velocities are defined by empirical downstream relationships; and whose flow path probabilities are defined using the Geomorphic Unit Hydrograph approach [*Rodriguez-Iturbe and Rinaldo*, 1997] (auxiliary Tables S1 and S2).[1] We apply a base scenario (auxiliary Table S1) to describe the N removal distribution in a river network with typical conditions before exploring the influence of individual factors. The assumption of spatially uniform runoff and N input rates allows isolation of river size related controlling factors.

[8] To determine the strength of N removal across river size, we calculate the proportional nutrient removal in streams of increasing order (i) per km of river length, (ii) per individual river reach whose length is defined by order, assuming inputs enter the upstream end, and (iii) integrated over all streams and rivers for each order in the 7th order basin, accounting for the distribution of initial inputs and flow path probabilities. Removal by each stream order for (i) and (ii) is straightforward (equation (1)). For (iii), we apply the following model to calculate the difference between export from all order ω streams (F_ω) and inputs to them:

$$F_\omega = P(0, 1_{up}) * I_\omega * \exp(-\upsilon_f/H_{Lup(\omega)})$$
$$+ [1 - P(0, 1_{up})] * I_\omega * \exp(-\upsilon_f/H_{Lmid(\omega)}) \qquad \omega = 1$$
$$F_\omega = F_{\omega-1} * P(\omega - 1, \omega_{up}) * \exp(-\upsilon_f/H_{Lup(\omega)}) \qquad (3)$$
$$+ \left[\sum_{k=1}^{\omega-1} F_k * P(k, \omega_{mid}) + I_\omega\right] * \exp(-\upsilon_f/H_{Lmid(\omega)}) \quad \omega > 1,$$

where I_ω is nutrient input to all streams of order ω via direct drainage from land (auxiliary Table S1); $H_{Lup(\omega)}$ and

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[1]Auxiliary material is available at ftp://ftp.agu.org/apend/gl/2006gl025845.

$H_{Lmid(\omega)}$ are hydraulic loads for stream order ω for inputs to the upstream end and on average to the midpoint of the reach, respectively; and $P(i, j_{up})$ and $P(i, j_{mid})$ are the probabilities of order i draining to order j at the upstream end and on average at the mid point, respectively (auxiliary Table S2). In first order streams, $P(0, 1)$ is the proportion of I_1 entering the upstream end via two 0 order groundwater flow paths. $H_{Lup(\omega)}$ is based on the entire mean length of order ω, and mean Q and w at the midpoint, whereas $H_{Lmid(\omega)}$ assumes half the length and Q and w at the downstream end (auxiliary Table S1). Adequately distributing N inputs along stream reaches is necessary to avoid biases in nutrient removal [*Lindgren and Destouni*, 2004]. The approximation that local and non-upstream tributary inputs occur at the mid point of each stream order results in acceptably small biases (<10%) that are effectively constant across order compared to an explicit representation of linearly distributed inputs.

3. Results and Discussion
3.1. Biological Activity and River Size in Existing Models

[9] Biological activity in each model, when normalized on a per unit surface area basis (ν_f) (Table 1), is river size dependant, either increasing or decreasing with depth (Figure 1). With the exception of the *Donner et al.* [2004] model where a decline in ν_f at high Q is explicitly assumed, the patterns in ν_f are unacknowledged in the original
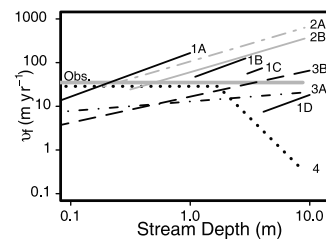

Figure 1. Relationship between ν_f and depth in various models (Table 1). 1A−1D correspond with Sparrow SPQ1-4 in Table 1; 2A = RivR-N with 10 km reaches; 2B = RivR-N with 25 km reaches; 3A = POLFLOW using HYD1, 3B = POLFLOW using HYD2; 4 = Donner. Observed is based on mean for denitrification in rivers [*Howarth et al.*, 1996].
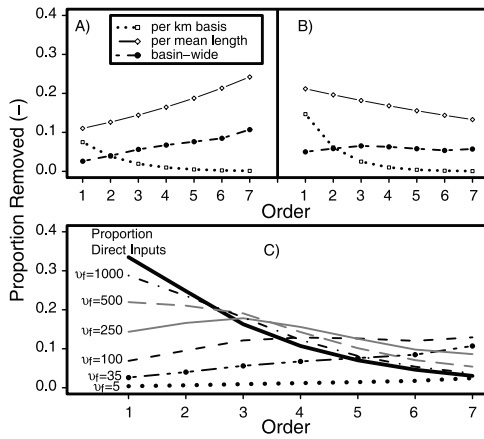
Figure 2. Nutrient removal within river networks. (a) Nutrient removal as a proportion of upstream inputs per km and per mean length of order, and as a proportion of basin wide inputs to the network, using the base scenario. (b) Same as A except the hydraulic width exponent is reduced from 0.52 to 0.36. (c) Proportion of basin wide inputs to the network removed by each stream order for various levels of uniform ν_f (m yr^{-1}) using the base scenario. The proportion of direct drainage inputs to each order also shown.

studies. These scale dependencies affect interpretation of the role of stream size in relation to nutrient removal.

[10] The ν_f patterns arise because biological and hydrological characteristics are not independently represented in the model equations. For example, the calibrated parameters in the POLFLOW equation (Table 1) incorporate both trends in biological process rates and the downstream hydraulic relationships. Thus, ν_f derived from these parameters is dependant on the underlying hydraulic assumptions, increasing at a greater rate under the HYD2 than HYD1 hydraulic scenarios (Table 1 and Figure 1). The greater ν_f increase derived using HYD2 occurs because w changes slowly with Q (w $\sim$ Q$^{0.36}$), requiring a rapid increase in areal uptake to achieve the predicted rate of removal as Q increases. It is therefore difficult to interpret whether trends in removal with river size arise from hydrological or biological factors.

[11] The ν_f trend with increasing depth in the RivR-N model is similarly influenced by downstream hydraulics, but is also a function of how the river network is partitioned (Figure 1). In the RivR-N equation (Table 1), removal declines relatively slowly with H$_L$, requiring increased areal biological activity at higher H$_L$'s (ν_f increases from 2–300 m yr^{-1} over H$_L$ of 1–10000 m yr^{-1}). Because H$_L$ depends on both the hydraulic assumptions and the specified length of reaches (H$_L$ = Q/wl), ν_f will also depend on these factors. Thus, a network partitioned into many shorter segments will have higher removal than the same network partitioned into fewer longer segments (Figure 1). In the original application [*Seitzinger et al.*, 2002], the network consisted of vector river reaches that increased in length with order, so a relatively constant ν_f was maintained. Nevertheless, this equation also blends biological and hydrological characteristics, making it difficult to evaluate the factors controlling nutrient removal with river size.

[12] River size dependence of areal biological activity (ν_f) is inherent when applying a constant k$_t$ across river size

as in SPARROW. The per unit area biological activity required to meet a given k$_t$ is less in shallower systems (e.g., 1A in Figure 1) as originally acknowledged [*Alexander et al.*, 2000]. The k$_t$'s calibrated for different Q classes in the Mississippi correspond with roughly constant ν_f in all but the highest class (ranges overlap for 1A−1C in Figure 1), suggesting size independent areal process rates through much of the basin.

[13] Recent studies addressing gradients in biological activity with river size have used k$_t$ as the basis for comparison. However, as described above, k$_t$ does not define the purely biological component in benthic-dominated systems because it is in part a function of h. Declining k$_t$ with stream size is not necessarily an artifact as recently argued [*Lindgren and Destouni*, 2004], but is expected if per unit area biological activity is constant. When scaling biological activity within basins, the underlying nature of ν_f and k$_t$ (areal vs. volumetric uptake) should be considered.

[14] The class of river network models compared here uses a single equation to simplify representation of biological removal processes. A per-area biological parameter (ν_f) in such models [*Donner et al.*, 2004] is ideal because, unlike other parameters, it removes confounding hydrological characteristics, allowing a clearer understanding of biological and hydrological controls across scale. Numerous factors could ultimately define trends in ν_f across river size, including the changing role of hyporheic zones [*Mulholland and DeAngelis*, 2000], or factors controlling the river continuum [*Vannote et al.*, 1980], but there is little empirical evidence of such trends and model results are inconsistent (Figure 1). Moreover, the assumption of uniform ν_f is useful for exploring the role of river size within river networks, as we demonstrate next.

3.2. Controls of Nutrient Removal Distribution in River Networks

[15] The relative importance of nutrient removal by different sized rivers depends on whether comparisons are based on segments of uniform length, reaches defined by order length, or the total length of all streams of given order within basins. Using the base scenario with constant ν_f, low order streams remove a greater proportion of upstream inputs on a per km basis than high order streams (Figure 2a) [*Bernot and Dodds*, 2005]. In terms of H$_L$, the decline in τ (due to increased velocity) and increase in h (decreased surface to volume ratio) with stream order result in reduced capacity to retain nutrients per unit length.

[16] However, when considering the entire length of a stream of given order, the proportional removal of upstream inputs by larger streams is several-fold greater than for smaller streams (Figure 2a). In terms of H$_L$, greater residence time (τ) in higher order rivers due to longer reaches outweighs the effect of increasing h, so that H$_L$ declines with stream order. The opposite trend occurs under certain hydraulic scenarios as when w increases slowly in the downstream direction (Figure 2b) [*Seitzinger et al.*, 2002]. Whether H$_L$ increases or decreases with order can be determined from the simultaneous factor changes in Q, l, and w from one order to the next as defined by the geomorphic and hydraulic parameters.

[17] When considered in terms of nutrients loaded to the entire river network (equation (3)) the role of large rivers in

the base scenario remains elevated relative to small rivers (Figure 2a) because (i) on a per length of order basis, large rivers are effective at removing nutrients, and a large proportion of inputs enter the upstream end (auxiliary Table S2), (ii) some proportion of land surface bypasses small rivers and drains directly to larger rivers (auxiliary Table S1), and, (iii) all nutrient inputs not removed by smaller rivers eventually pass through large rivers. Similar basin-scale results were obtained by *Seitzinger et al.* [2002], but are here grounded in the use of ν_f.

[18] The basin wide distribution of nutrient removal is sensitive to the strength of biological activity. The base scenario assumes $\nu_f = 35$ m yr^{-1}, a reasonable value for denitrification or for TN removal over annual time scales (Figure 1). With increasing basin wide ν_f, as might occur seasonally or for certain processes [*Peterson et al.*, 2001], the basin wide distribution of removal moves progressively upstream, eventually reflecting the distribution of direct inputs to the network (Figure 2c). The role of larger rivers declines because few nutrients are transferred from upstream. Nutrient removal by the entire 7th order network increases sigmoidally with log(ν_f) as the role of smaller streams increases (auxiliary Figure S1).

[19] Hydrologic and geomorphic river network characteristics also influence nutrient removal via the distribution of benthic surface area [*Donner et al.*, 2004]. We varied within observed ranges key factors that control the H_L distribution (runoff, hydraulic width parameters, length ratio) to test sensitivity of removal relative to the base scenario ($\nu_f = 35$ m yr^{-1} in each). Estimates of whole network removal ranged between 27 and 72% of aquatic N inputs (46% in the base scenario), with 1st–4th orders accounting for 32–58% of removal (41% in the base scenario) (auxiliary Figure S2). The hydraulic/geomorphic scenarios we explored affect the magnitude of the difference between small and large rivers. Large rivers can remain important at the basin scale even when the removal capacity of individual reaches defined by order declines (Figure 2b), resulting from the relatively high transfer of nutrients from upstream when $\nu_f = 35$ plus local direct inputs, consistent with *Seitzinger et al.* [2002].

[20] This theoretical analysis demonstrates how biological and hydrological characteristics interact to determine the magnitude and distribution of nutrient removal under a variety of conditions. Many factors will complicate these patterns in real networks, including trends in ν_f, local variability in ν_f or hydraulic/geomorphic conditions, non-uniform distribution of nutrient loads (e.g., point or concentrated non point inputs), and higher order kinetics. The impact of these deviations can be better evaluated if the underlying controls and their interactions are understood.

4. Conclusion

[21] We applied an approach for scaling biological activity throughout river networks that allows clear identification of the hydrologic, geomorphic, and biological controls of nutrient removal in benthic dominated systems. Other modeling approaches, while valid, use biological parameters that intermingle biological and hydrological characteristics, making it difficult to independently understand these controls. We tried to reconcile differing perspectives on the role of river size with respect to nutrient removal, finding

that the importance of small and large rivers depends on the level of aggregation for which removal is reported, the underlying hydraulic and geomorphic factors, and the magnitude of biological activity. At ν_f corresponding with measured denitrification or calibrated TN removal, larger rivers can exert considerable influence on nutrient exports. Anthropogenic alterations of large rivers could have a disproportionate impact on basin exports. Additional empirical studies of nutrient dynamics in larger rivers, which are relatively underrepresented, are needed. Quantifying the factors contributing to the nutrient removal capacity of river networks will improve our ability to model and manage nutrient exports to coastal zones as human modifications of the earth system increase.

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