Thinking outside the channel: modeling nitrogen cycling in networked river ecosystems

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Agricultural and urban development alters nitrogen and other biogeochemical cycles in rivers worldwide. Because such biogeochemical processes cannot be measured empirically across whole river networks, simulation models are critical tools for understanding river-network biogeochemistry. However, limitations inherent in current models restrict our ability to simulate biogeochemical dynamics among diverse river networks. We illustrate these limitations using a river-network model to scale up in situ measures of nitrogen cycling in eight catchments spanning various geophysical and land-use conditions. Our model results provide evidence that catchment characteristics typically excluded from models may control river-network biogeochemistry. Based on our findings, we identify important components of a revised strategy for simulating biogeochemical dynamics in river networks, including approaches to modeling terrestrial–aquatic linkages, hydrologic exchanges between the channel, floodplain/riparian complex, and subsurface waters, and interactions between coupled biogeochemical cycles.

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Rivers receive, transport, and process nutrients, contaminants, and other natural and human-derived materials from the landscape and deliver these constituents to downstream waters. Because river networks link terrestrial landscapes to lakes and oceans, perturbations to river ecosystems can influence biogeochemical cycling at local, regional, and global scales. Select human activities, such as fertilizing agricultural lands and burning fossil fuels, have delivered excess nitrogen to rivers, thereby increasing nitrogen export to coastal areas and exacerbating hypoxic zones in nearshore seas worldwide (Diaz and Rosenberg 2008). However, as nitrogen is transported downstream, some may be lost to the atmosphere via denitrification, the microbially mediated reduction of nitrate (NO_3^-) to nitrogen gas. Mass-balance accounting across broad regions suggests that denitrification losses substantially reduce riverine nitrogen loads to the ocean (Seitzinger *et al.* 2006).

In a nutshell:

- Understanding the responses of riverine nitrogen dynamics to anthropogenic perturbations is important for forecasting changes in the global nitrogen cycle
- Key research includes developing more realistic models of river-network hydrogeomorphology and biogeochemistry applicable across different catchments
- Models that can represent a breadth of biogeochemical processes within, and hydrologic connections between, the channel, floodplain/riparian complex, and subsurface waters will advance understanding of river nitrogen cycling

Recent research has focused on modeling nitrogen dynamics in river networks, partly because biogeochemical processes cannot be measured contiguously across river networks. Initial applications of riverine nitrogen models focused on predicting nitrogen export from large watersheds (reviewed by Alexander *et al.* 2002). Additional applications have included efforts to model biogeochemical processes that reduce downstream nitrogen transport, such as denitrification (Alexander *et al.* 2000; Seitzinger *et al.* 2002; Darracq and Destouni 2005; Mulholland *et al.* 2008; Alexander *et al.* 2009). Unfortunately, difficulty in accounting for spatial and temporal variations in the biogeochemical controls of denitrification (Boyer *et al.* 2006) has created major uncertainties in simulation results, which hamper forecasting of river-network biogeochemistry under future scenarios of climate disruptions, urbanization, and human population growth.

Here, we evaluate common modeling approaches and assumptions about river and catchment hydrogeomorphology and biogeochemistry, by scaling in situ denitrifica-

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Table 1. Descriptions of study catchments

Site location	*Biome*	*Basin area (km^2)*	*% agriculture*	*% urban*
Little Tennessee River, North Carolina (NC)	Warm temperate deciduous forest	361	10	7
Mill Creek, Kansas (KS)	Grassland	1008	16	3
Tualatin River, Oregon (OR)	Humid coniferous forest	1828	27	21
Flat Creek, Wyoming (WY)	Semiarid coniferous forest	400	0.4	2
Ipswich River, Massachusetts (MA)	Cool temperate deciduous forest	381	6	31
Little Rabbit River, Michigan (MI)	Cool temperate deciduous forest	126	72	9
Río Piedras, Puerto Rico (PR)	Moist evergreen tropical forest	40	27	42
Rio Grande, New Mexico (NM)	Arid grassland	40 780	0.7	1

Notes: Land-cover data derived from the USGS 2001 National Land Cover Dataset (http://seamless.usgs.gov).

tion measurements from headwater streams (Mulholland *et al.* 2008) to river networks in eight different catchments (Table 1). Using the model results, we identify additional dynamics and catchment characteristics that are important for understanding biogeochemical cycling, illustrate strategies for improving simulation of river biogeochemistry, and prioritize steps for future model development.

A river-network modeling experiment

We conducted simulation experiments using a model of river-network NO_3^- dynamics described by Mulholland *et al.* (2008) to systematically evaluate assumptions about river and catchment hydrogeomorphology and biogeochemistry (WebPanel 1; Figure 1). The model incorporates equations and assumptions commonly used in river-network models to represent downstream changes in channel morphology, hydrology, and biogeochemistry (WebPanel 1), as well as a recently documented reduction in streambed denitrification efficiency with increasing NO_3^- concentration (Mulholland *et al.* 2008).

We treated the model and its assumptions as a hypothesis describing downstream transport and denitrification of NO_3^- in river networks and explicitly tested this hypothesis by evaluating model performance in eight small river networks (Table 1). We conducted sampling of NO_3^- concentrations (the model response variable), channel width, and discharge at locations across each network (Figure 2) during low-flow conditions for 2 years. Observed patterns of downstream changes in width and discharge, combined with network topology from 1:24 000 US Geological Survey (USGS) maps, served to parameterize network morphology and hydrology. We determined model parameters for denitrification from in situ measurements of whole stream-reach denitrification replicated across nine headwater (1st- to 3rd-order) streams in or near each catchment (Mulholland *et al.* 2008; WebTable 1).

We used inverse modeling to estimate the spatial pattern of NO_3^- loading rates to streams by applying a model-independent parameter optimizer (Parameter ESTimation, version 10.1, SS Papadopoulos and Associates Inc). We estimated NO_3^- loading rates necessary for the model to exactly reproduce observed patterns of NO_3^- concentrations across each network. This approach allowed us to calculate spatial variation in NO_3^- loading rates across each catchment (Figure 2), assuming that our hypothesized representation of nitrogen cycling (WebPanel 1) was correct. Thus we were able to falsify our hypothesis (ie reject the model) anywhere that estimated loading patterns were clearly unrealistic. To hedge against rejecting a reasonable representation of river-network biogeochemistry (eg rejecting the model because of the possibility of sampling error or localized dynamics atypical of conditions across the larger catchment), we rejected the model only when >10% of loading estimates for a catchment fell outside of a realistic range (0–6.96 kg km^{-2} d^{-1}, the highest loading estimate from a literature review of 140 catchments; WebTable 2).

On the basis of these criteria, we accepted the model in only two of the eight catchments: the Little Tennessee River, North Carolina, and Mill Creek, Kansas (Figure 2). Thus, we con-

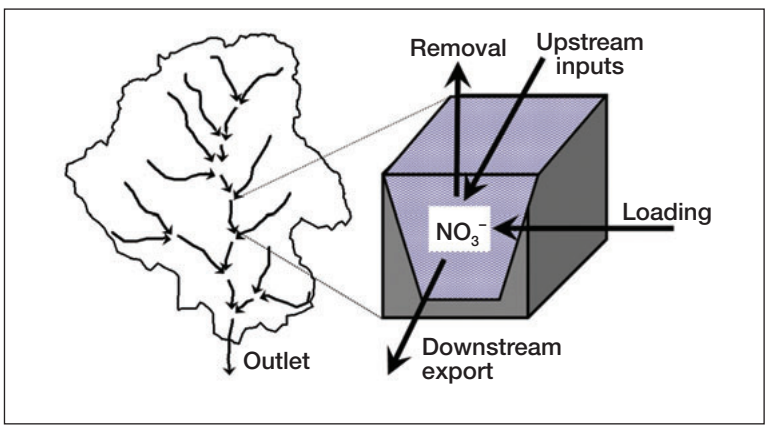

Figure 1. *River-network model structure. Following the methods presented by Mulholland* et al. *(2008), river networks were divided into segments, defined as the length of stream between tributary junctions. Water and NO_3^- flux into (upstream inputs and loading from the terrestrial landscape) and out of (downstream export and removal via denitrification) each segment were modeled. Fluxes are described in WebPanel 1.*

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clude that aspects of these two river networks are largely consistent with model assumptions, including: (1) catchment topography drives water and NO_3^- accumulation; (2) channel width increases in proportion to discharge; (3) streambed denitrification is the primary mechanism of nitrogen removal; and (4) NO_3^- concentration is the primary determinant of streambed denitrification rate.

In the remaining six catchments, we used model results, catchment characteristics, and findings from published research to identify deviations between model assumptions and catchment dynamics as potential sources of model failure. This information highlights important shortcomings in existing approaches to simulating river-network biogeochemistry and provides a basis for prioritizing needs for future model improvements.

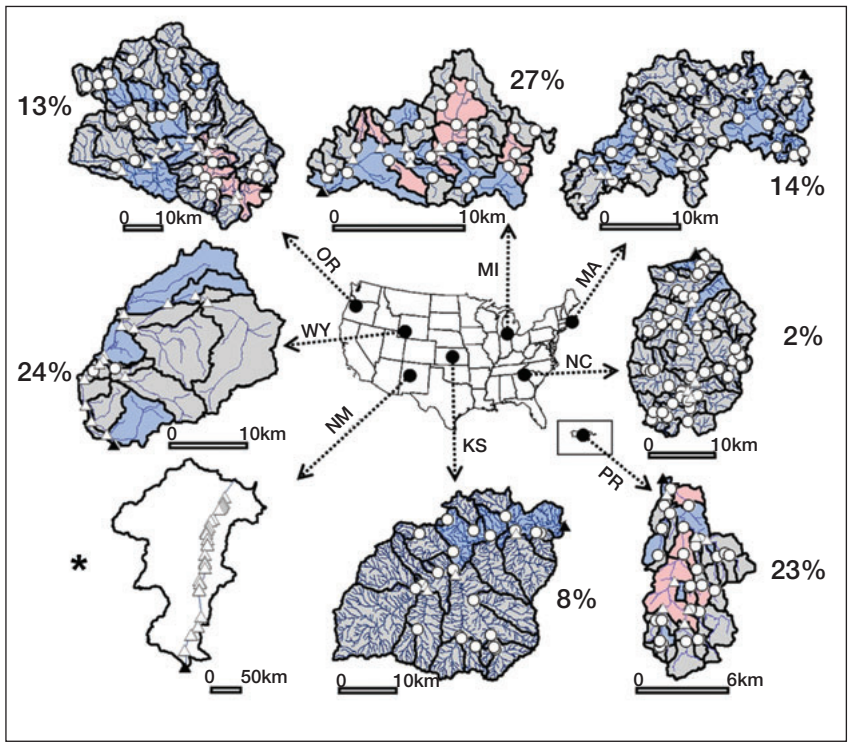

*Figure 2. Maps of the eight modeled catchments, which include stream hydrography (blue lines), discharge sampling points (triangles; solid triangles indicate catchment outlet), NO_3^- sampling points (circles), and catchment contributing area (CCA) for each NO_3^- sampling point (black lines). Color of CCA represents average simulated loading estimates that are realistic (gray; between 0 and 6.96 kg km^{-2} d^{-1}), unrealistic (high = red; > 6.96 kg km^{-2} d^{-1} and low = blue; < 0 kg km^{-2} d^{-1}), or indeterminable given model assumptions (white; see text). The percent of CCAs with unrealistic modeled NO_3^- loading estimates is indicated for each catchment. *See text for discussion of NM river-flow issues.*

Model assumptions versus catchment conditions

Our assessment suggests that model errors likely result from important deviations between catchment conditions and commonly applied model assumptions, including assumptions that: (1) oversimplify catchment hydrology; (2) oversimplify river-network hydrogeomorphology; (3) incorporate unidirectional uptake of nitrogen rather than cycling in the context of other elements (ie stoichiometric constraints); and (4) focus on base-flow or annual mean conditions, ignoring the ecological relevance of seasonal cycles and temporal dynamics.

Catchment hydrology and nitrogen delivery to streams

Five of the modeled catchments provide examples of the influence of catchment hydrology on river-network biogeochemistry. In the Tualatin River, Oregon (13% unrealistic loading rates; Figure 2), two wastewater treatment facilities discharge 60 million gallons (over 227 million L) per day of treated wastewater into the river (Clean Water Services unpublished data), and agricultural water withdrawals occur throughout the network (Oregon Water Resources Department, www.wrd.state.or.us). When we reparameterized our model to incorporate the spatial arrangement of nitrogen and water delivery from these point-source inputs, unrealistic loading estimates were nearly eliminated from the model results (reduced from 13% to 3%).

The Río Piedras, Puerto Rico; Little Rabbit River, Michigan; and Flat Creek, Wyoming catchments had high percentages of unrealistic loading rates (23%, 27%, and 24%, respectively; Figure 2). Most land in the Little Rabbit River catchment is agricultural (72% of catchment area; Table 1), with numerous high-density animal operations (USDA 2002) and extensive tile drainage systems (eg Figure 3a). The Río Piedras catchment has 42% urban land cover (Table 1) and contains many straight-pipe sewage lines from residential buildings to streams (eg Figure 3b). Water withdrawals from Flat Creek reduce flow substantially (eg to dryness; Figure 3c) in its headwaters, before water is added downstream by both a diversion from Gros Ventre River and spring flows. In these three catchments, anthropogenic delivery systems (eg tile drains, sewers, irrigation systems), rather than catchment topography, dominate patterns of water and nitrogen delivery to streams, thus violating important model assumptions (WebPanel 1).

The case of the Rio Grande, New Mexico, is even more extreme. Patterns of base flow in the system are so completely dominated by dams, headgates (eg Figure 3d), and other flow regulation structures that no semblance of a convergent flow network remains along the river corridor. The hydrology of the river deviates so far from the underlying hydrologic basis of our model (ie topographi-

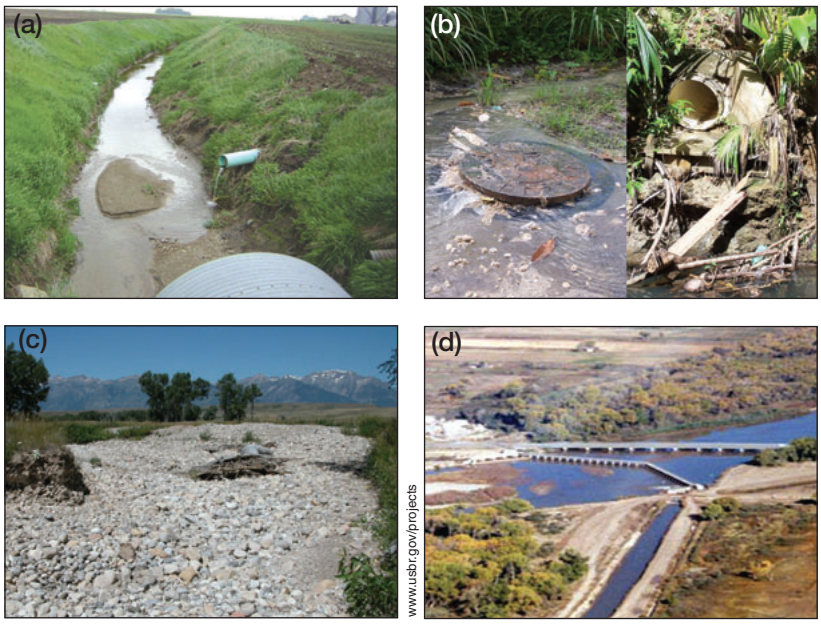

Figure 3. *Examples of anthropogenic alterations to hydrology and nitrogen delivery that deviate from assumptions within modeled catchments. (a) Agricultural tile drains, Rabbit River, MI, catchment. (b) Sanitary sewer overflow (left) and straight-pipe sewer discharge (right), Río Piedras, PR, catchment. (c) Alluvial stream reach irrigated to dryness, Flat Creek, WY, catchment; (d) Water abstraction, Isleta diversion, Rio Grande, NM.*

cally driven flow accumulation) that we were unable to apply our model to the system (Figure 2).

These five catchments illustrate the importance of incorporating the spatial patterns of water and nitrogen delivery to river networks into models. Indeed, previous modeling work has shown that accounting for the spatial arrangement of nitrogen inputs to rivers can improve model estimates of nitrogen export (Alexander *et al.* 2002), and spatial and temporal heterogeneity in water and nitrogen delivery increases uncertainty in modeled nitrogen export (Lindgren and Destouni 2004). Despite the need to incorporate spatiotemporal patterns of nitrogen delivery, many river-network models rely on a mass-balance or a statistical approach to estimate nitrogen sources, resulting in steady-state mean annual estimates of nitrogen delivery to rivers. Such model applications are useful and appropriate for scaling up annual catchment nitrogen exports, based on data from distributed monitoring stations. However, more realistic representations of spatiotemporal variation in water and nitrogen delivery will be necessary for imperatives such as forecasting river biogeochemical responses to continued human population growth coupled with climate change.

River hydrogeomorphology

Both the Ipswich River, Massachusetts, and Flat Creek, Wyoming, catchments provide intriguing examples of hydrogeomorphic controls on river-network biogeochemistry. The Ipswich River has extensive water withdrawals for urban use in its headwaters (Zarriello and Ries 2000) and it flows through numerous wetland complexes, which comprise 20% of catchment land cover (eg Figure 4a). The Flat Creek network, in addition to hydrologic alteration (described above), has a large wetland (~2.3 km^2) along the main stem of Flat Creek, and high rates of exchange between the channel and an extensive hyporheic zone (the area directly beneath the channel and floodplain where surface and subsurface waters are freely exchanged) typical of western US alluvial streams (eg Figure 4b). In both catchments, our analysis yielded large percentages of negative loading estimates (Figure 2), indicating that our model underpredicts nitrogen removal in many reaches of each network.

Incorporating headwater withdrawals from the Ipswich River into the model did not reduce the percentage of unrealistic loading estimates. However, loading estimates were negatively correlated with the fraction of stream length intersecting wetlands (WebFigure 1), suggesting that wetlands are an important nitrogen sink not represented by the model. In Flat Creek, biotic removal of NO_3^- in the hyporheic zone (sensu Triska *et al.* 1989; Dahm *et al.* 1998; Hill *et al.* 1998; Dent *et al.* 2001) probably creates an NO_3^- sink that is not addressed by the model and therefore is a potential cause of the estimated negative loading rates.

The Ipswich River and Flat Creek networks illustrate the importance of considering patterns of hydrologic connections among river channels and adjacent wetlands, riparian corridors, floodplains, and hyporheic zones (Figure 5). As flow paths from different river ecosystem components converge throughout a river network, they create important spatial areas and times of biogeochemical reactions (eg McClain *et al.* 2003; Hall *et al.* 2009) that vary in magnitude and frequency along stream courses. The potential importance of small lakes (Harrison *et al.* 2009), floodplains (within the Ipswich River catchment; Wollheim *et al.* 2008), and hyporheic zones (Thouvenot *et al.* 2007) on river-network nitrogen cycling has been acknowledged in some modeling studies. However, apart from reservoirs (eg Seitzinger *et al.* 2002; Bosch 2008), the influence of non-channel hydrogeomorphology has not been incorporated into river-network biogeochemical models, including our own (WebPanel 1). Associated simplifying assumptions mean that such models do not represent natural mechanisms of nitrogen retention or the effects of common perturbations that disrupt them. For instance, streams with well-connected, intact riparian zones/floodplains may both denitrify and store nitrogen in vegetation and sediments for long periods, reducing and delaying downstream transport. Yet agricultural and urban development in stream corridors, stream chan-

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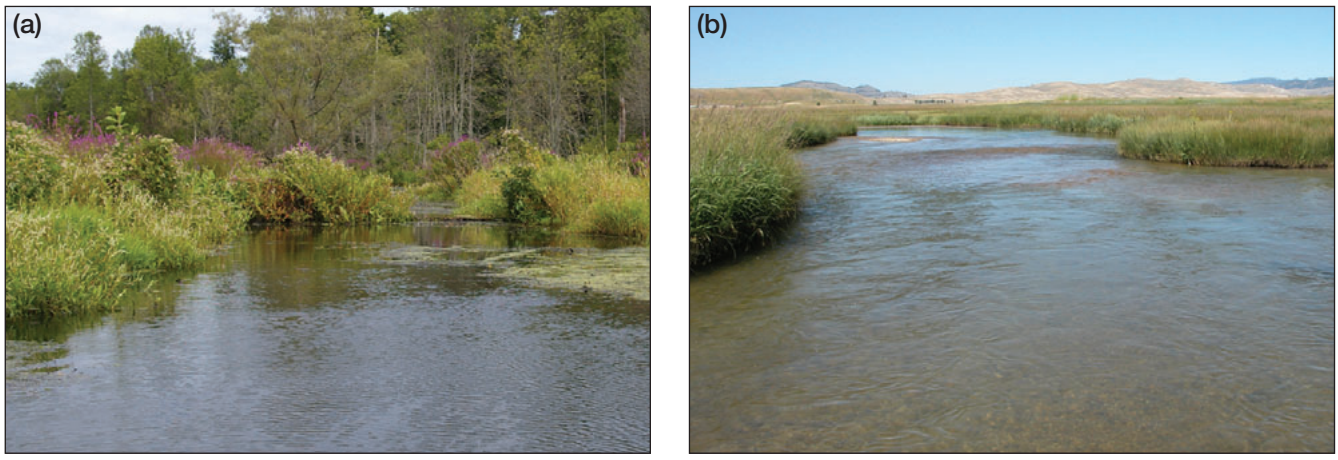

Figure 4. *Examples of river hydrogeomorphology that deviate from assumptions within modeled catchments. (a) Riverine wetlands, Ipswich River, MA, catchment. (b) Spring-fed alluvial stream reach with high hyporheic exchange, Flat Creek, WY, catchment.*

nel engineering, and water abstraction tend to sever hydrologic connections between channel and non-channel components of streams (Cardenas and Wilson 2004; Kondolf *et al.* 2006), leaving the primary location of nitrogen uptake and storage as the channelized streambed, from which carbon and nutrients are easily remobilized and transported downstream (eg Noe and Hupp 2005). These critical changes in riverine biogeochemical processing cannot be adequately investigated by models that consider only channel water and the streambed as the hydrogeomorphic basis of stream ecosystems.

Nitrogen cycling and stoichiometry

Consistent with other models of river-network nitrogen dynamics (Boyer *et al.* 2006; Wollheim *et al.* 2006), our model (WebPanel 1) assumes that denitrification is the primary nitrogen removal pathway and views the nitrogen cycle as a one-way flux of nitrogen from channel water (Figure 5). In our parameterization dataset (Mulholland *et al.* 2008), "direct" denitrification accounted for a wide percent of total NO_3^- taken up by biota (0.05–100%; median 16%). However, in most streams, NO_3^- assimilation into biomass was the largest removal flux, and assimilated nitrogen may either be stored temporarily and re-released to the water column as inorganic or organic nitrogen, or removed permanently via coupled nitrification–denitrification (eg Whalen *et al.* 2008) or other microbial pathways (eg reviewed by Burgin and Hamilton 2007; Figure 5). Unfortunately, the field methods (Mulholland *et al.* 2008) used to parameterize our model (WebPanel 1) quantify neither the subsequent cycling nor the ultimate fate of the nitrogen removed from the water column by assimilation. Furthermore, our parameterization dataset is based on denitrification measurements from headwater (1st- to 3rd-order) streams. Measuring the role of large rivers in biogeochemical cycling (eg Tank *et al.* 2008) will provide improved empirical estimates of denitrification throughout river networks, allowing us to parameterize and verify models. Coupled field and modeling efforts that attempt to iteratively investigate and simulate nitrogen storage, cycling, and mass balance in streams and rivers would further accelerate understanding of spatiotemporal patterns of nitrogen cycling within, and export from, river networks.

Our model also incorporates a decline in denitrification efficiency (υ_{fden}) with increasing NO_3^- concentration (Mulholland *et al.* 2008; Böhlke *et al.* 2009; WebPanel 1). The relationship is especially apparent when data from the eight catchments are combined (Mulholland *et al.* 2008). Yet the strength of the relationship varies markedly when considered for each of the eight catchments individually (WebTable 1), suggesting that NO_3^- concentration was a primary driver of υ_{fden} in some study catchments (eg Little Tennessee River, North Carolina; $r^2 = 0.72$), but not in others (eg Río Piedras, Puerto Rico; $r^2 = 0.01$). Stoichiometric relationships between nitrogen and other elements (eg carbon, Bernhardt and Likens 2002; phosphorus, Cross *et al.* 2005; sulfur, Burgin and Hamilton 2008) or whole-stream respiration rates (Mulholland *et al.* 2008) may also drive nitrogen cycling rates. However, such dynamics cannot be addressed by river-network models that track nitrogen dynamics in isolation and use statistical representations of nitrogen uptake. More mechanistic models that consider microbial biomass and respiration, along with coupling of the nitrogen cycle to other elemental cycles (ie an ecological stoichiometry approach), would improve the heuristic value and predictive power of simulations (see also Boyer *et al.* 2006), yielding more robust approaches for scaling biogeochemical cycles in river networks.

Temporal dynamics

Most river-network models, including our own (WebPanel 1), simulate steady-state (eg base-flow or mean annual) hydrologic conditions (but see Wollheim *et al.* 2008; Böhlke *et al.* 2009). Steady-state hydrologic assumptions prevent simulation of dynamics that may

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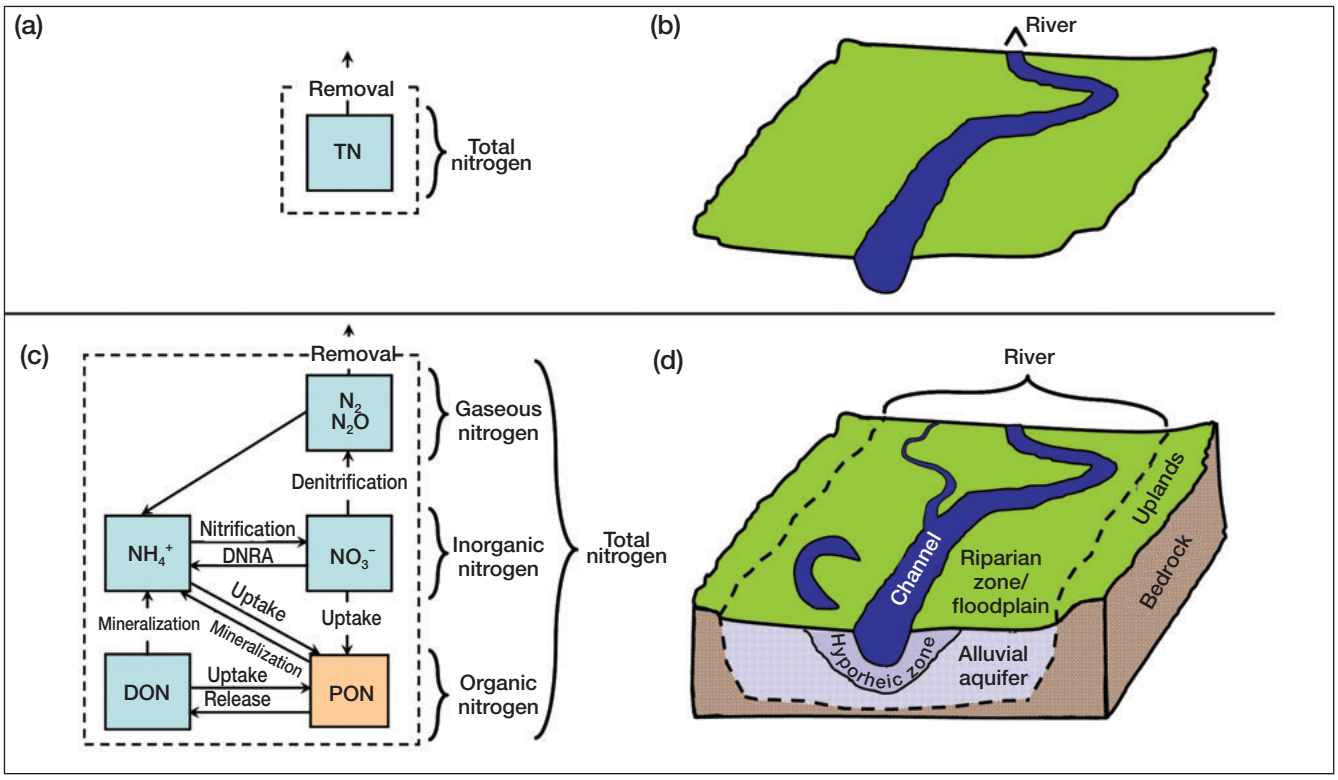

Figure 5. *River-network models typically describe (a) one-way total nitrogen flux from (b) river channels. A more holistic conceptual model of nitrogen cycling in river ecosystems recognizes (c) multiple forms of nitrogen that undergo numerous transformations and (d) the role of non-channel river ecosystem components in nitrogen dynamics, including the hyporheic zone, alluvial aquifer, and floodplain/riparian complex. DON = dissolved organic nitrogen; PON = particulate organic nitrogen;* NH_4^+ *= ammonium;* NO_3^- *= nitrate;* N_2 *= dinitrogen gas;* N_2O *= nitrous oxide; DNRA = dissimilatory nitrate reduction to ammonium.*

drive most biogeochemical processing or transport. For instance, in river channels, the fraction of catchment nitrogen exported downstream is highest during peak flows, when streambed biotic nitrogen removal efficiency is lowest (Royer *et al.* 2004; Alexander *et al.* 2009). In contrast, transient hydrologic connections with non-channel ecosystem components may buffer excess nitrogen export during high flows (Richardson *et al.* 2004; Hall *et al.* 2009). For example, transient hydrologic simulation of the Ipswich River network explored how variations in daily runoff influenced predicted denitrification patterns (Wollheim *et al.* 2008). The model appeared to underpredict nitrogen removal during periods of peak flow in the river network, suggesting that nitrogen may be removed by off-channel components of the stream ecosystem (eg when floodwaters spill onto floodplains or into adjacent wetlands). Indeed, storm pulses expand hydrologic connections among river ecosystem components (Stanley *et al.* 1997), wetting ephemeral channels and floodplains, and thereby initiating contact between different suites of solutes and activating biogeochemical processes in areas adjacent to river channels (Valett *et al.* 2005). Developing models that can both incorporate and scale dynamic hydrology across river networks presents a formidable challenge, yet is a critical necessity for improving models of river-network biogeochemistry.

■ The way forward

Four fundamental and widely applied assumptions caused our model to fail in six out of eight catchments. Our model: (1) assumes that catchment topography drives water and nitrogen accumulation in river networks; (2) represents streams as channels, ignoring the floodplain, wetland, riparian, and hyporheic components of streams; (3) simulates nitrogen uptake in isolation rather than nitrogen cycling in the context of ecological stoichiometry; and (4) assumes a steady-state discharge regime. We believe, therefore, that overcoming these assumptions will extend the applicability and predictive accuracy of river-network biogeochemical models across a range of catchments. On the basis of these findings, we recommend several specific strategies to help extend and improve current modeling approaches.

Integration of river-network and catchment ecohydrologic models

Hydrologic and physical properties of catchments strongly control nitrogen delivery to rivers, but river-network models do not normally simulate hydrologic nitrogen delivery to rivers. Ecohydrologic models (reviewed by Boyer *et al.* 2006; Kulkarni *et al.* 2008) simulate hydrologically explicit hillslope nitrogen dynamics across catchments, even predicting

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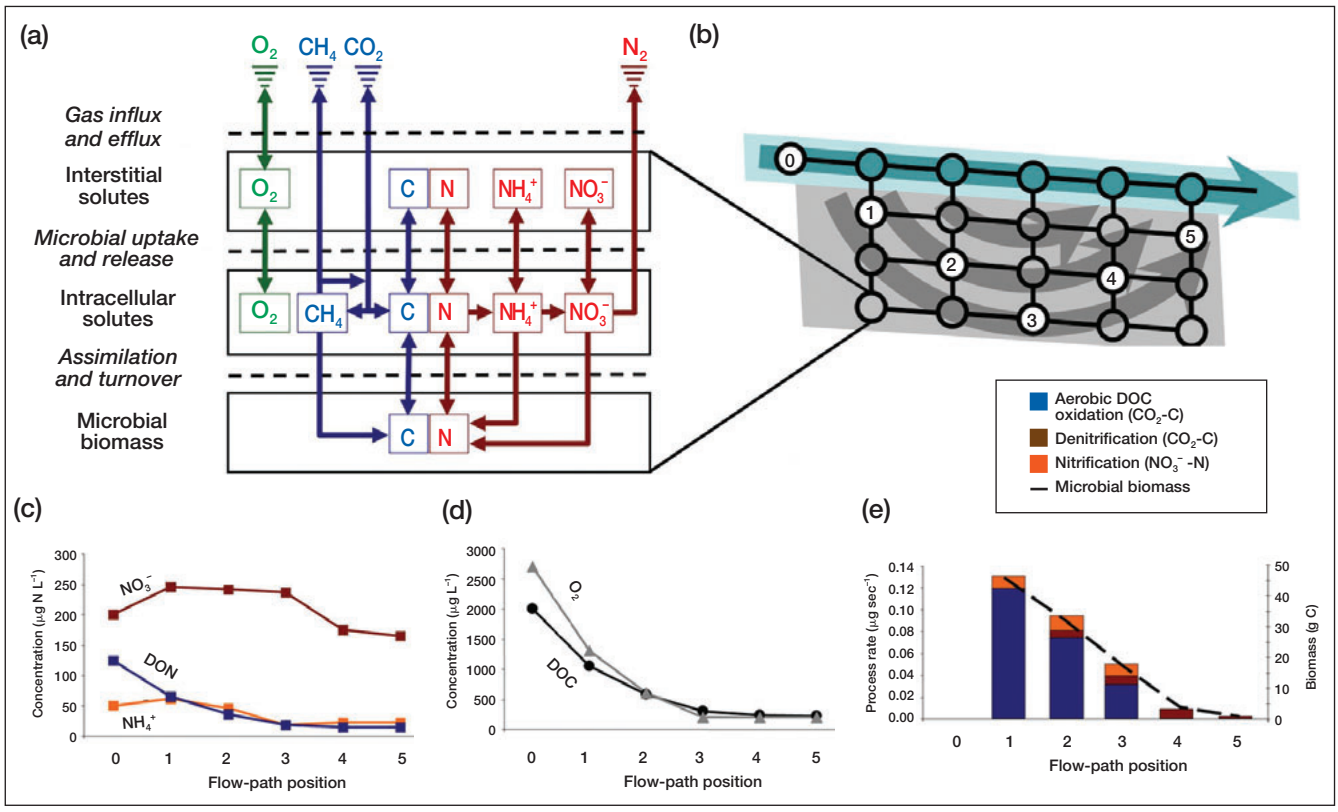

Figure 6. *Simulation of multi-element biogeochemical cycles along a hyporheic flow path. (a) Schematic of a prototype biogeochemical model (AM Helton* et al. *unpublished) that simulates microbial uptake and utilization and/or production of dissolved organic matter, oxygen, nitrate, ammonium, and methane. The model operates by assuming that microbial assemblages will use the suite of metabolic pathways that will maximize microbial growth, as co-limited by the availability of carbon, nitrogen, and oxygen as electron donors/acceptors and the stoichiometric ratio of carbon and nitrogen required for building biomass. (b) Simulated hydrologic flow paths in a simple two-dimensional implementation of a mechanistic model of surface water flow and hyporheic exchange (hydrology model described by Poole* et al. *2006). We combined the two models to simulate hydrologic solute flux and (c) concentrations of different nitrogen forms (DON = dissolved organic nitrogen), (d) dissolved oxygen and dissolved organic carbon (DOC), and (e) microbial activity and biomass along an idealized hyporheic flow path (numbered circles in [b]).*

observed patterns and timing of water and nutrient delivery to streams (Band *et al.* 2001). Such catchment ecohydrologic models could be linked to river-network models, to provide spatially explicit and temporally dynamic estimates of water and nutrient delivery to streams – an important first step for understanding biogeochemical dynamics at the terrestrial–aquatic interface.

Catchment ecohydrologic models, however, still typically rely on topography as the primary determinant of catchment water and solute routing. Yet existing modeling techniques that accurately represent the hydrologic dynamics of human-dominated catchments generally require detailed and difficult-to-obtain information, such as patterns of tile drainage in agricultural lands or sewer system maps in urbanized settings (eg Hsu *et al.* 2000; Northcott *et al.* 2002). Thus, improved simulation of river-network biogeochemistry may also arise from the development of new, less data-intensive techniques that could quantify water and nutrient routing dynamics in urban and agricultural catchments without requiring detailed maps and descriptions of sewer or drain systems.

Modeling stoichiometric controls on biogeochemical cycles

River-network nitrogen models tend to simulate one-way removal of nitrogen. Such an approach has been quite successful when used to quantify annual nitrogen budgets of large catchments (Alexander *et al.* 2002). However, the nitrogen cycle is driven by multiple nitrogen pools and fluxes (Figure 5) and its relationships with other elemental cycles (eg carbon and oxygen). A more mechanistic representation of nitrogen dynamics might therefore help to explain complex patterns of biogeochemical dynamics within river networks, and improve forecasts of biogeochemical responses to land-use or climate-change perturbations.

Biogeochemical cycling depends on the changing availability of various electron donors and acceptors, given the thermodynamically constrained metabolism of microorganisms (Hedin *et al.* 1998; Fisher *et al.* 2004). Thus, stoichiometric constraints on microbial metabolism link multiple elemental cycles in complex yet predictable ways. Indeed, microbial ecology models can predict carbon and nitrogen

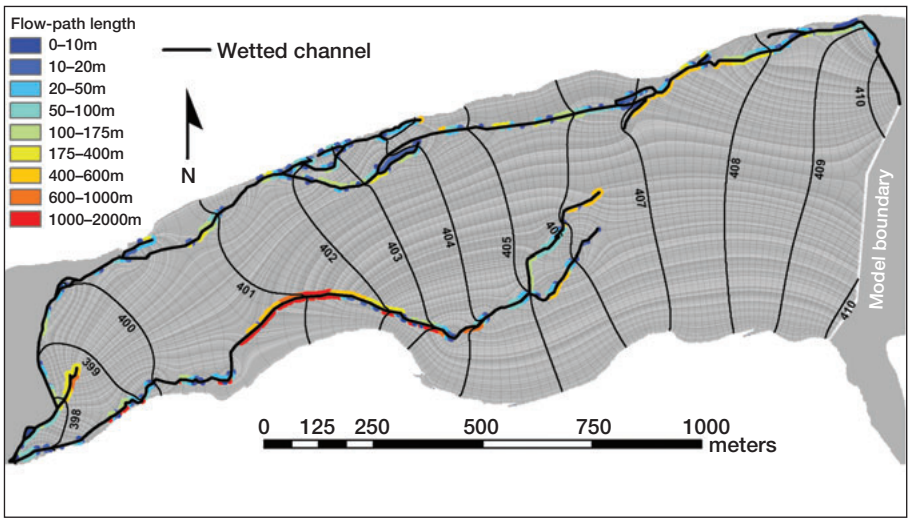

Figure 7. *Simulated spatial juxtaposition of individual flow paths within a floodplain aquifer (modified from Poole* et al. *2008; ©2008 John Wiley and Sons Ltd. Reproduced by permission). Heavy black lines show the center of active channels. Colors along the channels denote subsurface (hyporheic) flow-path length at each point of flow-path discharge back to the channel. Absence of color along the channel denotes points of hyporheic recharge from the channel. Black contours represent simulated water table elevations (m). Simulated aquifer flow paths are indicated by gray background striations.*

uptake, assimilation, and loss, based on the assumption that the aggregate metabolic activity of the microbial assemblage present will respond to oxygen, carbon, and nitrogen availability in such a way as to maximize overall growth (eg Vallino *et al.* 1996; Figure 6a). Such an approach, based on the first principles of thermodynamics (ie free energy yield from metabolic pathways), provides an avenue for addressing shifting drivers of the nitrogen cycle across systems. This comprehensive biogeochemical approach also highlights important contemporary research challenges, including: quantifying the fraction of nitrogen forms that make up the total nitrogen pool, understanding the interaction of nitrogen with other elements, and understanding the role and shifting frequency of alternate nitrogen removal pathways (eg coupled nitrification–denitrification).

Using river hydrogeomorphology to scale biogeochemistry

Although river-network models typically incorporate general trends of channel geometry and in-channel hydrology (eg WebPanel 1), they often disregard geomorphic variation in, and hydrologic connections between, the channel, riparian zone/floodplain, and hyporheic zone (Figure 5), even though such connections are key to understanding river biogeochemical dynamics (McClain *et al.* 2003; Groffman *et al.* 2009). Thus, to simulate river-network biogeochemistry, a reliable approach for scaling biogeochemistry to flow paths is needed. For example, we have begun to integrate the aforementioned stoichiometric biogeochemical model (Figure 6a) into a spatially explicit and temporally dynamic model of hydrologic flow paths (Poole *et al.* 2006; Figure 6b). Initial results suggest the combined models yield realistic patterns of nitrogen (Figure 6c), oxygen, and organic carbon (Figure 6d), as well as microbial biomass and respiration (Figure 6e), along hyporheic flow paths. By using the hydrologic model to simulate floodplain surface and subsurface flow paths (Figure 7), we will be able to develop realistic, multi-element models of whole floodplain biogeochemistry.

Still, direct application of a spatially explicit, flow-path-centric approach (Figure 6) to an entire river network is not feasible because of the intensive data needs for parameterization and verification, along with the computational requirements needed to execute such a model. We believe, however, that river-network models incorporating both hydrogeomorphic and stoichiometric controls on biogeochemistry could be developed within the next decade. One promising approach would pair stream biogeochemical models with contemporary efforts by hydrologists to use theoretical approaches (Cardenas 2008) and simulation modeling (Deng and Jung 2009) as a means of scaling up the net effect of localized, off-channel hydrologic processes, such as hyporheic water exchange. Thus, the next generation of models might emerge from coupling network-scale hydrologic residence-time distributions with a robust understanding of flow-path biogeochemistry. Maturation of emerging geospatial technologies, such as LIDAR (Light Detection and Ranging; Jones *et al.* 2007, 2008) and SRTM (Shuttle Radar Topography Mission; Farr *et al.* 2007), will ultimately improve the practicality of quantifying hydrogeomorphic variation (sensu Wörman *et al.* 2006) across river networks to parameterize associated models of river-network hydrologic residence time distributions.

■ Conclusions

We recommend an admittedly ambitious roadmap for developing the next generation of river-network models. Rather than attempting to implement all of our recommendations simultaneously, which may lead to overly cumbersome models that are difficult to parameterize and run, incremental improvements coupled with experimentation is more likely to succeed. We have outlined three specific paths to improve river-network biogeochemistry models, which can be accomplished incrementally and independently of one another. First, we propose using ecohydrologic models to improve estimated spatiotemporal patterns of water and nutrient delivery to river networks. Human alterations will complicate these patterns, and

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methods to scale their effects – for example, effects of storm-sewer and tile drainage systems on nutrient and water routing to whole river networks – will be essential, particularly as human impacts become increasingly prevalent. Second, we propose incorporating multiple elemental cycles and ecological stoichiometry into river-network models. Our initial approach (Figure 6) integrates first principles of thermodynamics (ie free energy yield from metabolic pathways) with governing equations for surface and groundwater fluxes, and should therefore be widely applicable. Maturation of such an approach, however, will require increased collaboration between empirical, simulation, remote sensing, geographical, and computer sciences to create, model, and understand datasets describing biogeochemical fluxes across an array of environmental conditions and scales. Finally, we propose integrating biogeochemical models and floodplain-scale hydrology models (eg Figure 7), which will provide important insights into the biogeochemical dynamics of multiple interacting flow paths within fluvial landscapes. The challenge will be to develop methods to scale these integrated biogeochemistry–hydrology models to whole river networks.

Developing models that can accurately represent hydrogeomorphic and biogeochemical dynamics across river networks will require the melding of concepts and approaches from both terrestrial and aquatic biogeochemical modeling, as well as hydrologic modeling and remote-sensing sciences. Application of these models will yield insights into the river-network biogeochemistry necessary for understanding carbon and nutrient cycling across a variety of fluvial landscapes and among diverse biomes. As anthropogenic activities, such as land-use conversion and fossil-fuel production, push ecosystems toward unprecedented states, a holistic and mechanistic approach to biogeochemical modeling of rivers will provide a valuable tool for forecasting the responses of biogeochemical cycles across river networks worldwide.

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WebPanel 1. A model for scaling denitrification to river networks

We developed a model of NO_3^- loading, transport, and denitrification in stream and river networks (described in detail by Mulholland *et al.* 2008) to scale up empirical measures of stream-reach denitrification. The model is based on a steady-state, mass-balance approach and hydrogeomorphic scaling principles commonly used to represent river geomorphology and hydrology, including: (1) steady-state hydrologic flux; (2) accumulation of water in streams and rivers from their drainage areas as they flow downstream; (3) uniform water yield for each sampled subcatchment (see Figure 2); and (4) channel width increasing downstream in proportion to discharge. In accordance with typical river-network model assumptions, denitrification is the primary nitrogen removal pathway (Wollheim *et al.* 2006).

The model calculates denitrification within stream segments and routes water (Q; $m^3\ d^{-1}$) and NO_3^- ($NO3$; $g\ d^{-1}$) between segments linked together into networks (see Figure 1). Upstream inputs to a stream segment (i) of water (Q_{ui}) and NO_3^- ($NO3_{ui}$) are equal to the sum of exports from upstream segments.

$$Q_{ui} = \Sigma(Q_{i-1}) \quad \text{(Eq 1)} \qquad NO3_{ui} = \Sigma(NO3_{i-1}) \quad \text{(Eq 2)}$$

Lateral water (Q_{Li}) and NO_3^- ($NO3_{Li}$) inputs from the terrestrial landscape are equal to the product of the area draining directly to stream segment i (A, m^2) and the area specific loading rate (Y) of water ($m^3\ m^{-2}\ d^{-1}$) and NO_3^- ($kg\ m^{-2}\ d^{-1}$).

$$Q_{Li} = A_i Y_{Qi} \quad \text{(Eq 3)} \qquad NO3_{Li} = A_i Y_{NO3i} \quad \text{(Eq 4)}$$

We calculated downstream exports using a steady-state mass-balance approach where downstream fluxes of water (Q_{ei}) and NO_3^- ($NO3_{ei}$) equal the sum of inputs minus outputs.

$$Q_{ei} = Q_{ui} + Q_{Li} \quad \text{(Eq 5)} \qquad NO3_{ei} = NO3_{ui} + NO3_{Li} - NO3_{Ri} \quad \text{(Eq 6)}$$

$NO3_{Ri}$ is the NO_3^- removed from stream segment i via denitrification, and is the product of the fraction of NO_3^- denitrified (R) and the sum of NO_3^- inputs to the segment.

$$NO3_{Ri} = R_i(NO3_{ui} + NO3_{Li}) \quad \text{(Eq 7)}$$

The fraction of NO_3^- denitrified from each stream segment is determined by:

$$R = 1 - e^{-\upsilon_{fden}/H_L} \quad \text{(Eq 8)}$$

where hydraulic load (H_L, $m\ s^{-1}$) is the ratio of discharge to streambed surface area (length times width of each stream segment; Wollheim *et al.* 2006). Stream length was determined from USGS stream hydrography data (1:24 000). Stream width (w) was calculated using modeled discharge (Q) for each stream segment (Leopold and Maddock 1953):

$$w = aQ^b \quad \text{(Eq 9)}$$

Parameters a and b were estimated empirically for low-flow conditions within each catchment (WebTable 1). Because water yields and width parameters were derived from low-flow measurements, the model scenarios apply to low-flow conditions within each catchment.

Conceptually, uptake velocity for denitrification (υ_{fden}) is the downward velocity of NO_3^- molecules through the water column necessary to meet observed streambed denitrification demand for NO_3^-. Mulholland *et al.* (2008) demonstrated that υ_{fden} decreases with increasing in-stream NO_3^- concentration ($[NO3]$), following a power function. Thus, the model determines υ_{fden} for each stream segment according to:

$$\upsilon_{fden} = c\,[NO3]^d \quad \text{(Eq 10)}$$

We derived parameters c and d empirically for each catchment using observed values of υ_{fden} and $[NO3]$ from 5–9 experimental stream reaches located within or adjacent to each modeled network (WebTable 1).

WebTable 1. Site-specific parameter values for river-network modeling

Site abbreviation	*Channel width* *a, b* (r^2)	*Uptake velocity* (υ_{fden}) *c, d* (r^2)
NC	7.3, 0.45 (0.90)	8.2E-1, –1.2 (0.72)
KS	7.2, 0.35 (0.74)	2.3E-4, –0.48 (0.61)
OR	7.2, 0.35 (0.74)	7.6E-1, –1.2 (0.18)
WY	7.0, 0.33 (0.50)	8.5E-1, –0.10 (0.88)
MA	7.4, 0.27 (0.37)	4.0E-4, –0.47 (0.60)
MI	10.4, 0.45 (0.93)	1.1E-1, –0.93 (0.53)
PR	6.6, 0.35 (0.27)	3.4E-6, –0.063 (0.01)
NM	nd	4.2E-5, –0.36 (0.23)

Notes: The width coefficient (a) and exponent (b) were used to determine channel width for each stream segment (using Eq 9 in WebPanel 1). The denitrification coefficient (c) and exponent (d) were used to determine denitrification uptake velocity (υ_{fden}) for each stream segment (using Eq 10 in WebPanel 1). nd = no data.

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WebTable 2. Literature review used to determine the realistic range of modeled NO_3^- loading estimates

Location	*Number of catchments*	*Catchment area (km^2)*	*% agriculture*	*% urban*	*Loading estimate (kg N km^{-2} d^{-1})*	*Method used to estimate loading*	*Reference*
Loch Vale Watershed, Colorado Front Range	1	6.6	0	0	0.69	Modeled direct total N loading to aquatic ecosystems	Baron and Campbell (1997)
Upper Mississippi	3	492 000 (422 000–1 320 000)	nd	nd	1.93 (0.28–2.52)	Measured NO_3^- river export	Carey *et al.* (2001)
Embarrass River, Illinois	1	482	91	4.5	6.54	Measured NO_3^- river export	David *et al.* (1997)
Gwynns Falls, Maryland	3	0.32 (0.08–0.81)	0 (0–100)	0 (0–47)	1.78 (0.14–4.49)	Measured total N river export	Groffman *et al.* (2004)
Lake Michigan basin	18	2398 (153–15 825)	42 (5–82)	2 (0.2–20)	0.86 (0.47–3.63)	Measured total N river export	Han *et al.* (2009)
Southeast US	14	2125 (63–56 894)	16 (2–42)	0.5 (0.05–5)	1.30 (0.71–2.50)	Measured total N river export	Harned *et al.* (2004)
LTER sites across North America	13	0.38 (0.06–10)	nd	nd	0.19 (0.03–1.18)	Measured dissolved inorganic N river export	Kane *et al.* (2008)
Oldman River, Alberta, Canada	1	28 200	nd	nd	0.76	Measured total N river export	Rock and Mayer (2006)
US West Coast	18	8995 (1531–279 438)	6 (0.4–24)	1 (0–20)	0.32 (0.19–4.57)	Measured total N river export	Schaefer *et al.* (2009)
Sierra Nevada and Rocky Mountains	28	1.6 (0.2–19.1)	nd	nd	0.20 (0.008–0.85)	Measured dissolved inorganic N river export	Sickman *et al.* (2002)
Central Valley, California	23	2736 (461–61 721)	6 (0–74)	2 (0–6)	0.31 (0.06–2.59)	Measured total N river export	Sobota *et al.* (2009)
Northeast US	16	11 945 (475–70 189)	10 (1–61)	3 (0– 22)	5.51 (2.74–6.96)	Modeled estimates of NO_3^- leaching to ground and surface waters	Van Breeman *et al.* (2002)
Ipswich River basin, Massachusetts	1	404	7	35	1.85	Estimated direct total N loading to river network by 1st-order streams	Williams *et al.* (2004)
Summary	140	1791 (0.06–1 320 000)	10 (0–100)	1.2 (0–47)	0.49 (0.008–6.96)		

Notes: Catchments in the literature review span a wide range of geographic regions, catchment areas, and land-use conditions. When references included more than 1 year of loading data for a particular catchment, the average value was used. Data are reported as median (range). The highest reported nitrogen loading rate was 6.96 kg N km^{-2} d^{-1}. nd = no data.

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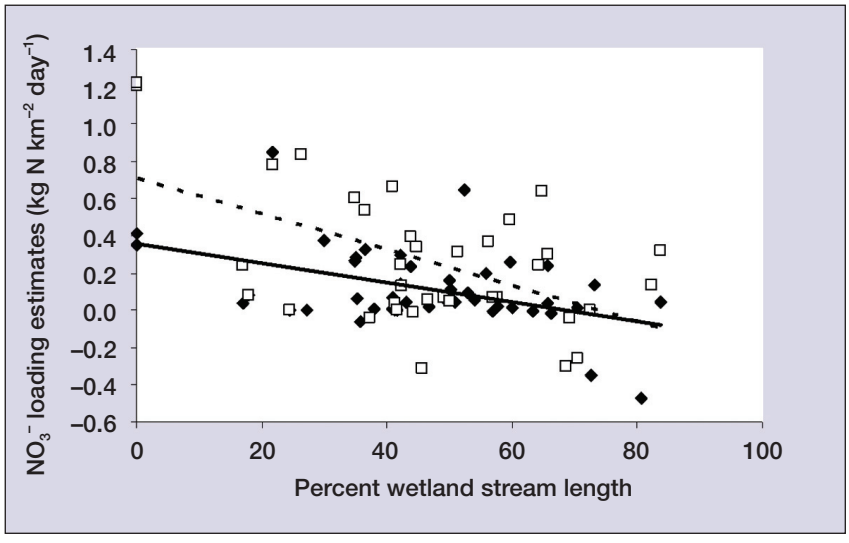

WebFigure 1. *Modeled NO_3^- loading estimates from the Ipswich River, MA, versus upstream percent wetland stream length (ie ratio of stream length passing through wetlands to total stream length). Wetland extent determined from 2001 National Land Cover Dataset (http://seamless.usgs.gov). Loading estimates derived from network modeling were negatively correlated with percent wetland stream length for both years of estimated loading rates (2003 $r^2 = 0.21$, $P < 0.002$, solid line and diamonds and 2004 $r^2 = 0.31$, $P < 0.002$, dashed line and open squares), suggesting that the model underpredicts denitrification in channels flowing through wetlands.*