River network saturation hypothesis: factors influencing biogeochemical demand of entire river networks relative to supply

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Abstract

River networks are important controllers of material transfer from land to ocean. Understanding the factors regulating this function for different gaseous, dissolved, and particulate constituents is critical as we seek to quantify the local and global effects of climate and land use change. We propose the River Network Saturation (RNS) hypothesis as a generalization of how river network regulation of material fluxes changes with flow conditions due to imbalances between supply and demand at network scales. Demand for a constituent across connected surface waters is broadly defined as any process that removes a constituent from the downstream flux. In contrast to terrestrial ecosystems, saturation of river networks is highly variable in time due to the considerable variation in the supply of constituents associated with changes in flow. All river networks become saturated under very high flow conditions, but the flow thresholds under which saturation occurs depends on the inherent process rates for a given constituent, the presence of saturating kinetics, and the abundance of lentic waters such as lakes, ponds, reservoirs, and fluvial wetlands within the river network. As supply increases, saturation at network scales is initially limited by previously unmet demand in downstream aquatic ecosystems. We explore the RNS hypothesis in the context of different river networks, including, urban, agricultural, lake-abundant, and intermittent. We also explore implications for the gaseous, dissolved, and particulate components of the freshwater carbon cycle at network scales. New approaches using nested *in situ* high-frequency sensors and spatially extensive synoptic techniques offer the potential to test the RNS hypothesis in different river networks. Better understanding of when and where river networks saturate for different constituents will allow for the extrapolation of aquatic function to broader spatial scales, providing information on the influence of river function on continental element cycles, and help identify management priorities.

1. Introduction

Continental freshwater ecosystems are characterized by physical, chemical, and biological processes that influence the flux of materials from land to ocean. Sediment, nitrogen, phosphorus, and carbon can all be retained (temporarily or permanently) or transformed during downstream transport relative to the amount and forms entering from land. This capacity has long been known for some constituents such as sediments and reactive nutrients (e.g. Walling 1983, Alexander et al. 2000, Peterson et al. 2001), but for others such as carbon this phenomenon has become a more recent research focus (Cole et al. 2007). However, the control of constituent fluxes by surface waters is highly variable in time depending on hydrologic conditions (Doyle 2005, Wollheim et al. 2008a, Hall et al. 2009a). The underlying importance of flow has recently been formalized as the Pulse-Shunt concept for carbon (Raymond et al. 2016), but is also generally applicable to all constituents transported by water (e.g. Wollheim et al. 2008a, Alexander et al. 2009). Although flow is a primary control, other factors also determine the influence of the river network on constituent fluxes. A general theory of the capacity of river networks to influence constituent fluxes has not previously been explored. We propose the River Network Saturation (RNS) hypothesis as a conceptual basis for understanding the capacity of entire river networks to remove, retain, and/or transform inputs from land. We demonstrate how the RNS can apply across form - particulate, dissolved, or gaseous - and across constituent - sediment, pathogen, nutrient, organic matter or inorganic carbon. We further suggest that the RNS can be used to elucidate the emergent functional behavior of whole river networks across space and time.

The centrality of hydrology as a control on downstream fluxes is highlighted in the Pulse-Shunt Concept (Raymond et al. 2016). Hydrology controls the amount of material supplied to surface waters, and under elevated flows (the pulse) this material is transported farther downstream (the shunt) because residence times are insufficient to attenuate material inputs. That which is not shunted is retained, removed, or transformed into another form, which may at some later time also be shunted downstream (or retained, removed or further transformed). The underlying physical basis for this dynamic on a stream reach scale has long been understood via the stream spiraling concept (Webster 1979, Newbold et al. 1981). The keys to understanding the capacity of river networks to regulate fluxes are the processes that control removal, retention, or transformation, henceforth referred to as demand.

The balance between the supply of a particular constituent to a river network and the demand for that constituent throughout the river network determines net export to the river mouth. Demand can include biological, chemical, and physical processes. We make the simplifying assumption in this analysis that internal sources are minimal and view demand as a net demand term, as in previous river network studies (Alexander et al. 2001, Helton et al. 2010, Wollheim et al. 2006). All processes can be defined by a net reaction rate, as either a per time constant (time^{-1}), a settling/piston/uptake velocity (length time^{-1}) or areal or volumetric rates (e.g. mass length^{-2} time^{-1}) (Boyer et al. 2006, Ensign and Doyle 2006). Reaction rates of these demand processes vary over orders of magnitude depending on form, from very high (sediments, ammonium, phosphate, simple sugars), to moderate (nitrate, fresh leaf leachate), to low or non-reactive (refractory dissolved organic carbon, chloride) (Table 1). The combination of net reaction rates and hydrologic conditions control the proportion of incoming flux transported further downstream. The RNS considers these interactions in terms of supply and demand of different constituents at the river network scale, which integrate over the many smaller streams that hierarchically combine to form larger streams and rivers within a watershed.

The RNS hypothesis builds on the nitrogen (N) saturation hypothesis from forest watershed systems (Aber et al. 1989) and applies this to river networks. The forest N saturation hypothesis suggested that N limited forests leach little N until deposition increases to sufficient levels and/or demand for N for growth diminishes. Over a long enough period under which inputs exceed net demand, leaching accelerates. Lovett and Goodale (2011) placed the forest N saturation hypothesis in a mass balance context that considers percent of inputs leached as the balance between supply and demand. Forests retain the vast proportion of N entering the system via atmospheric deposition when N deposition is low (supply << demand) or when forests are in early stages of regrowth (demand >> supply). As N deposition increases, or net demand decreases as forests mature, they pass through various stages until supply >> demand. Lovett and Goodale (2011) distinguish kinetic N saturation, in which the rate of N input (supply) exceeds the rate of N sink (demand), from capacity N saturation, in which demand = 0. The RNS hypothesis explores how the saturation concept can be applied to entire river networks.

Future climate in many regions is projected to become more variable, including a greater frequency of extremely high precipitation events and extended dry periods (Melillo et al. 2014). Thus the flow regime of river systems is projected to change in response to meteorological change when floods are no longer considered stationary (Villarini et al. 2009). Because supply and demand of constituents are strongly influenced by flow conditions (Doyle 2005), the ability of river networks to regulate fluxes will likely also change. It is critical to understand this altered function in order to project the changing continental-marine linkages within the Earth system. The RNS attempts to provide a framework to improve understanding of the transport and fate of different constituents by integrating supply and demand across the continuum of flow conditions, including extreme events, and how these processes may differ across watersheds.

A major issue for broad macro-scale questions regarding aquatic function is how to test predictions at the scale of entire river networks. At network scales it is difficult to characterize loading due to the vast number of supply points (e.g. a large number of small streams) that can vary considerably over time. Further, the effects of aquatic processes accumulate along the entire flow path, and their sink strength may fluctuate in space and time, making measurements of network scale removal difficult. Fortunately, a new generation of *in situ*, high-frequency sensors is becoming more affordable and widely deployed, offering the potential for empirical characterization of the variability of both supply and demand within and across watersheds (Rode et al. 2016, Pellerin et al. 2016, Miller et al. 2016). We will demonstrate how such tools can be used to test the RNS.

Here we present the River Network Saturation (RNS) hypothesis, building on previous conceptual work such as the Pulse Shunt Concept, the Stream Spiraling Concept, and the forest N saturation hypothesis. In particular we 1) emphasize the response of demand at network scales (=cumulative processes) relative to terrestrial/landscape supply, which inherently requires a representation of river network topology and geometry, and encapsulates upstream-downstream linkages; 2) use simple models to explore factors that influence river network saturation; 3) provide case studies of how RNS differs in urban, agricultural, lentic, and intermittent river dominated networks, and an example focused on the carbon cycle; and 4) discuss potential approaches for validation of network scale demand for different constituents across flow conditions.

2. River Network Saturation Hypothesis: The Balance between Supply and Demand at Network Scales.

The River Network Saturation (RNS) hypothesis states that the capacity of river network to retain, remove, or transform a constituent entering from land declines with increasing flow due to increasing imbalances between supply and demand for a constituent at network scales (Figure 1a). Further, the flow condition at which saturation occurs is a function of the reactivity of the constituent and characteristics of the river network. To illustrate the RNS hypothesis, we initially assume that reaction rates remain constant throughout the river network, and are not affected by flow conditions. Although a reasonable first approximation (Ensign and Doyle 2006), this simplified condition is not realized in actual river networks. Below, we explore conditions that relax this assumption.

Source/sink behavior of constituents is determined by river network size and structure. River network size fundamentally determines the total surface area and/or volume of lotic and lentic ecosystems where demand processes occur. River network structure determines the delivery of materials to different components of the river network (i.e. initial inputs to headwaters vs. tributaries vs. mainstem; flow path distance through the network; interaction with lake/wetland/riparian systems). Thus, hydrologic connectivity of different river network components, and demand within these components, is also an important factor.

At the network scale, the proportion of a constituent shunted (=exported) across flow conditions is determined by cumulative supply and demand curves for an entire river network (Figure 1a). When demand remains flat with increasing supply, or changes much more slowly than supply, the river system is considered saturated. The RNS hypothesizes that for reactive constituents as flows increase, both supply and demand at network scales also increases, but that demand increases more slowly than supply. The proportion of a constituent that is shunted increases as the river network approaches saturation for the process that retains or transforms the constituent. These dynamics translate to very high percent retention of a constituent at low flows (possibly approaching 100%), and declining retention with increasing flow (Figure 1b). We demonstrate why a logistic curve emerges at network scales below.

Aquatic ecosystems have differing demand (or more generally, processing potential) for various constituents. Examples of major processes include: assimilatory uptake (NH_4, NO_3, orthophosphate), dissimilatory uptake (denitrification of NO_3), microbial oxidation (nitrification of NH_4, DOC), photodegradation (photo reactive DOC), sorption (orthophosphate, organic matter), sedimentation (TSS, particulate organic matter), precipitation (dissolved minerals), and gas exchange (O_2, CO_2, CH_4, N_2O). Some of these processes transform one constituent to another (NH_4 to NO_3, DOC to CO_2), or may be temporary (TSS deposited in rivers that is resuspended under high flows, assimilation of nutrients that are eventually remineralized, dissolution of precipitants). Other processes result in permanent removal, e.g. denitrification, microbial and photochemical oxidation of DOC, gas exchange, or sediment burial in lakes. Here we focus on processes that result in permanent removal (or periods of net uptake). However, we also suggest that the RNS conceptual framework is applicable for temporary storage with remobilization considered as an additional internal supply.

The influence of aquatic processes on the amount of constituent transport downstream in a particular water body is defined by the following equation, based on commonly used formulations of aquatic demand in models (Boyer et al. 2006), which clearly identifies the balance between supply and demand (Wollheim 2008a, 2016):

$$R = 1 - \exp\left(-\frac{UWL}{QC}\right) = 1 - \exp\left(-\frac{demand}{supply}\right) \qquad \text{Equation 1}$$

where R is the proportion of a constituent removed by a water body (unitless), U is areal process rate (mass length^{-2} time^{-1}), W is mean channel width (length), L is longitudinal reach length (length), Q is discharge (length^{3} time^{-1}), and C is constituent concentration (mass length^{-3}). In a lake or other lotic water body, WL in Equation 1 can be replaced with surface area. If water column processes dominate, then the numerator in Equation 1 becomes (UDWL) where U is instead a volumetric process rate (mass length^{-3} time^{-1}), and D is depth (length). The numerator represents the demand for the constituent, whereas the denominator represents the supply. The ratio of demand/supply is also equivalent to the Damköhler number (Gu et al. 2007). For modeling purposes, U/C in Equation 1 is often replaced with the uptake velocity, υ_f, because it allows U to vary with C under the assumption that removal rate is a first order reaction (an assumption not always met, which can also be accommodated using this framework, e.g., Wollheim et al. 2008a). Uptake velocity (often applied to dissolved constituents) is equivalent to a settling velocity (applied to particles), or piston velocity (applied to gases), and assumes that processes occur at interfaces, which is the case for many aquatic processes including particle settling, sorption, gas evasion, photo-degradation, and processes that predominantly occur in sediments such as denitrification or microbial respiration. Uptake velocities (υ_f in m yr^{-1}) in water bodies (biotic or abiotic) can range from 0 for conservative solutes like chloride, to extremely high values (> 1000 m yr^{-1}) for reactive nutrients like NH_4 and orthophosphate, simple organic carbon molecules, large particles or evasion of gases in turbulent waters (Table 1).

The RNS applies Equation 1 to individual water bodies (stream and river reaches, lakes, ponds, etc.) throughout the river network, which are linked by flows. Upstream demand alters downstream supply. Individual stream or river reaches are typically dominated by throughputs as opposed to internal cycling or removal especially at moderate to high flows (supply >> demand), whereas many individual lakes and most terrestrial systems are dominated by internal cycling over throughputs (Essington and Carpenter 2001). However, at the scale of river networks, even without ponded waters, supply and demand are closer to balanced because most biogeochemical inputs occur in the headwaters (Alexander et al. 2006), and surface water flow paths interact with considerable surface area where processes occur en route to the basin mouth.

Supply of a given constituent to any given river network generally increases with increasing discharge (Q * C in Equation 1). Some constituent concentrations consistently increase with discharge (e.g. TSS or turbidity, DOC; Raymond and Saiers 2010), so the rate of increase in the constituent load (= supply) will be greater than the increase in discharge. Other constituent concentrations typically exhibit dilution with increases in discharge (e.g. nitrate in urban areas, geogenically derived SRP; Hensley et al. 2017, Koenig et al. In Press), but even under these conditions, supply increases with increases in discharge, because the extent of concentration dilution rarely offsets the discharge increase (i.e. flux is dominated by Q term; Godsey et al. 2009, Basu et al. 2010).

The distribution of constituent supply from the landscape in a river network context is skewed towards smaller streams. The total length of streams in a watershed is always dominated by small streams (Leopold and Maddock 1954, Bishop et al. 2008). Small streams intersect most of the landscape, and therefore intercept a disproportionately large proportion of constituent inputs from land (Alexander et al. 2007). River network geomorphology (fractal) theory describes the distribution and connection of streams and rivers through a network (Rodriguez-Iturbe and Rinaldo 1997). Some small streams bypass intermediate sized rivers and discharge directly into larger rivers. The probabilities are predicted through analytical solutions of river network fractal geometry. The exception to this pattern is point sources due to human activities, which generally enter directly via outfalls to larger rivers (e.g., for N, P, labile organic matter).

The RNS hypothesis considers how demand changes relative to supply. The response in demand to changes in flow is determined by three mechanisms that influence the numerator in Equation 1, manifested as changes in river width, river length, or uptake (here represented as $U/C = \upsilon_f$) as flow increases. River length likely changes minimally (though see discussion of intermittent streams below), while river width increases with hydraulic response to changes in flow depending on channel morphology. Widths tend to increase relatively little with initial increases in storm flow (Leopold and Maddock 1953, Knighton 1998), until bank full thresholds are exceeded and floodplains become connected (which is also explored below). Finally, for now we assume that U relative to C in Equation 1 ($= \upsilon_f$) remains constant with changes in Q to demonstrate the emergent behavior of entire river networks to changes in supply. In reality, reaction rates vary depending on kinetic responses to concentration (zero order, first order, or higher order), light, temperature, or microbial communities, but to demonstrate river network function we initially ignore these.

Three types of network scale saturation can occur: capacity saturation, kinetic saturation (Lovett and Goodale 2011), and spatial saturation. Capacity saturation occurs when there is no net demand, so inputs equal outputs. Kinetic saturation occurs when some net demand (removal) occurs but inputs > outputs. These concepts can be applied to individual water bodies or at river network scales. Spatial saturation is an additional form of saturation we define that emerges at river network scales through connectivity of a series of ecosystems. At some low level of supply, the entire quantity of a constituent may be retained near its point of input to the network. Because loading to river networks is delivered predominantly to small headwater streams, only a small quantity of a constituent is available downstream under low flows. As flow increases, more of the constituent tends to be transported downstream. Essentially there is unrealized demand in downstream reaches under low flows that can be met as excess supply is transported from upstream under higher discharge. We will demonstrate spatial saturation and how it is affected by flow, reaction rates, and other factors.

3. Stages of Network Scale Saturation Response

Four stages of network-scale constituent removal describe the spatial saturation response of entire river networks (Figure 1b). These stages are essentially defined by a logistic response curve. Stage 1 is characterized by complete removal at network scale because demand is so great that constituents are immediately processed as they enter the network. Demand can even exceed external supply if internal sources are available. In this stage, network-scale demand exceeds supply with most removal occurring in headwater streams. Stage 2 continues to show near complete removal at the network scale, but under this condition, demonstrated below, retention by downstream reaches prevents any leakage from the overall network. At the overall network scale, demand continues to keep pace with supply. Stage 3 is characterized by rapid declines in the proportion of constituent removed, resulting in increased breakthrough and export from the river network as loads continue to increase with a slowing increase of the commensurate demand. In Stage 4, the river network essentially has little or no attenuation of input fluxes, because supply overwhelms demand. The rate at which different constituents move through these stages (or remain in a particular stage) depends on hydrological and geomorphological conditions, as well as physical or biological processes that influence the constituent. We demonstrate the mechanisms by which the logistic response curve occurs below.

4. Demonstration of River Network Saturation (RNS) Hypothesis

We use two modeling approaches to demonstrate the RNS hypothesis (Table 2). The first is a statistical model based on river network fractal geometry that accounts for hydraulic characteristics and removal by different river orders, the distribution of direct inputs (i.e., terrestrial sources that first enter the river network) relative to river order, and the flow path water takes from source to basin mouth (Wollheim et al. 2006, Raymond et al. 2016). This model implements Equation 1 and is applied to a hypothetical seventh order river network to explore how flow conditions, reaction rates, and kinetic assumptions affect river network saturation in channel networks (Scenarios 1-3, Table 2). This approach focuses only on the channel network. The second modeling approach uses the Framework for Aquatic Modeling of the Earth System, a spatially distributed routing model previously applied to channel networks (Wollheim et al. 2008a,b, 2015, Stewart et al. 2011, 2013, Samal et al. In Press), modified to account for the role of lakes/reservoirs, beaver ponds, and floodplains to heuristically demonstrate how river network saturation is affected by lentic water bodies (Scenarios 4-8, Table 2). The second model approach is fully spatially explicit, based on the conditions in the Ipswich River network, MA (Wollheim et al. 2008a). We assume chemostatic loading conditions (i.e., loading concentrations remain constant with changing runoff/flow) and that υ_f is not affected by water body type.

For each scenario, we present the response curve of percent of total inputs that are removed by the river network vs. flow (Figure 1b). The scenarios include the effect of increasing flow, increasing uptake velocity, increasing concentrations (with kinetic response of uptake velocity), and increasing aquatic habitat (Table 2). In all scenarios except the kinetic response scenarios, we assume first order kinetics (i.e. U increases linearly with C, so υ_f stays constant). In all scenarios, network scale removal follows a logistic curve with increasing flow. Variation in each term within Equation 1 shifts the logistic curve in Figure 1b to the right or left depending on whether removal proportions are increased or decreased, respectively.

4.A. River Network Saturation Depends on Runoff/Flow (Scenario 1)

As flow increases, supply of a given constituent to the river network increases and demand is eventually overwhelmed so that the percent removal by the river network declines. At network scales, the balance between supply and demand declines non-linearly between low and high flow, resulting in the logistic removal curve. For υ_f typical of denitrification during summer (Scenario 1 in Table 2, υ_f = 35 m yr^{-1} in Figure 2), removal of nonpoint inputs to the river network is near 100% through flows equivalent to about 10% of the mean annual flow. Percent removal decreases rapidly to 34% at mean annual flow, and further declines to < 5% at flows 10-fold higher than the mean annual. The lack of responsiveness below a certain flow threshold (Stage 1 and 2 in Figure 1) indicates excess demand relative to supply at network scales that continues to be met as supply initially increases. The range of flows covered by Stage 1 and 2 is defined in part by the inherent process rates associated with each constituent (section 4.C). The mechanism for this limited response across Stages 1 and 2 is further described in section 4.B.

The rapid decline in constituent removal as flows continue to increase (Stage 3) occurs because once downstream source limitation is removed (at the end of Stage 2), network-scale demand changes slowly with further increases in flow, while supply increases rapidly. In channel-only river networks (Scenario 1), habitat area increases slowly with increases in discharge (width at-a-site exponent typically ~ 0.1, Table 2), while depth and velocity increase rapidly (Leopold and Maddock 1953, Knighton 1998). As a result, all else being equal, demand increases slowly ($\sim Q^{0.1}$) while supply increases rapidly ($\sim Q^1$). This pattern is equivalent to the effect of declining residence time, but placed in a supply and demand context (note that the terms in Equation 1 are equivalent to $k * \tau$, where τ is residence time; Wollheim 2016). The rate of decline during Stage 3 may differ from that portrayed in this scenario (assuming channel only) because it assumes that new habitat made available with increasing flow ($w \sim Q^{0.1}$) has the same reaction rate as the previously inundated area, but this may not always be the case (e.g. biota may take time to recolonize previously dried habitat). Process rates may decline in channels following storms, e.g. when depth and/or turbidity increases, impeding light or scouring biota on the stream bottom, and reducing demand for nutrients. However, rate of decline in Stage 3 may also slow if connectivity with floodplains or other reactive ecosystems increases (see

4.E). Furthermore, newly inundated habitat area may also serve as a source of some constituents (e.g. SRP, Jones et al. 2015).

4.B. River Network Saturation is Initially Limited by Downstream Systems (Scenario 1)

Network scale saturation does not occur across a range of low flow conditions when non-point sources are relatively low (Scenario 1) because large rivers within the network are initially source-limited and buffer increases in supply. Most runoff and non-point sources enter the network initially in low order streams (dashed line Figure 3, Alexander et al. 2007), so these components of the network are first to process most inputs. In the river network considered in Figures 2 and 3, which is constructed using typical geomorphic ratios (drainage area, number, and length ratios, Wollheim et al. 2006), 60% of inputs occur to first and second order streams. At low flows (< 2% of mean annual), supply to these small streams is similar to demand (even at relatively low reaction rates, υ_f =35 m yr^{-1}), so very little constituent is exported downstream (RO=2% line in Figure 3a). Removal occurs essentially as soon as the constituent enters the network (i.e. removal and direct input curve are similar for Q < 2% of mean annual Q, Stage 1 in Figure 1b).

As constituent supply increases as flows increase, local demand in low order rivers is overwhelmed and a greater proportion is transferred downstream. Because most inputs in river networks occur in smaller streams, large rivers process little of the constituent under lowest flow conditions. Assuming that υ_f is constant throughout the river network, larger rivers have unmet demand at low flow (Koenig et al. 2017). As flow increases, demand in larger rivers can be met, and high network removal proportions maintained. Under these conditions, downstream systems are connected to sufficient supply of the constituent. Integration under the supply curve (dotted line) and under the removal curve in Figure 3 indicates the percent removal of the constituent at the network scale. At 2% mean annual Q, removal by 1st and 2nd order streams is slightly less than their direct inputs, while removal by larger order streams is greater than their direct inputs, because they are also removing excess constituent transported from upstream (Stage 2, Figure 1B).

The contribution of intermediate sized streams to overall network function increases with increasing flows. Over certain flow conditions, the contribution of these intermediate streams actually dominates at network scales (Figure 3a, flows = 10% of mean annual flow). As flows and associated constituent supplies continue to increase, greater breakthrough from intermediate streams occurs, increasing the role of the largest river segments. At higher flows (> 200% of mean annual flow), overall network control of flux declines, but the remaining removal capacity is dominated by the largest rivers. The integration under each curve in Figure 3a corresponds with the total network removal in Figure 2 during the particular flow conditions (with $\upsilon_f = 35$ m yr^{-1}). The specific pattern of response to increasing supply will vary depending on the hydraulic assumptions (downstream width exponent), as well as constituent reaction rates (Wollheim et al. 2006).

4.C. River Network Saturation Depends on Uptake Velocity (Scenario 2)

The previous examples focused on network dynamics at a relatively low reaction rate (Scenario 1, $\upsilon_f = 35$ m yr^{-1}). In Scenario 2, we explored the effect of changes in υ_f on the removal capacity of river networks (Table 2). As υ_f increases across the range of possible values previously observed for different constituents (Table 1), the capacity of the network to remove constituents increases considerably. The higher the υ_f, the broader the range of flows under which network demand is in Stage 1 and 2. At reaction rates typical for ammonium (assimilation plus nitrification, $\upsilon_f = 1000$ m yr^{-1}, Ensign and Doyle 2006), network scale removal remains at essentially 100% through mean annual flow (Koenig et al. 2017). Even at the very highest flow (15-fold higher than the mean annual), removal approaches 60% of inputs. Over most of the flow range, constituent removal is predominately in the low order rivers, but again, at the highest flows large rivers dominate network scale function (Figure 3b). This pattern is consistent with observations that ammonium is rarely observed at concentrations much above the analytical detection limits unless located immediately downstream of a pollution source or in proximity to a reducing environment. Other constituents may have very low reaction rates (e.g. chloride which is conservative). Relatively conservative constituents are therefore always in Stage 4, where removal is minimal and thus hydrological export is equivalent to supply. The constituents summarized in Table 1 have a range of υ_f values and their potential fates under different flow conditions can be quickly assessed using Figure 2.

4.D. River Network Saturation Depends on Uptake Kinetics (Scenario 3)

Under the assumption of first order kinetics, as often invoked in water quality models, the concentration of the constituent itself does not influence removal proportions (the balance between supply and demand) because uptake increases linearly with concentration and reaction rates remain constant. Thus, if supply increases due to increasing concentration (Equation 1; e.g., with land use change), there would be no response to increased loading, and the response curves in Figure 2 would remain unchanged. However, for some constituents such as nutrients (e.g. NH_4, NO_3), reaction rates (as υ_f) can be concentration dependent (Mulholland et al. 2008, Dodds et al. 2002). In this case, uptake (U, demand) will respond non-linearly to concentration (C, supply) depending on the reaction kinetics. This can be described by saturating (Michaelis-Menten) or efficiency loss kinetics (Dodds et al. 2002, O'Brien et al. 2007, Hall et al. 2009b). We can readily model this scenario by considering υ_f as a function of concentration (as in Mulholland et al. 2008, Wollheim et al. 2008a).

Assuming a scenario with efficiency loss of uptake typical of denitrification (leading to permanent removal) applied in the hypothetical 7th order river network (Table 2, Scenario 3), increasing concentrations lead to a shift in the removal curve vs. flow to the left, reducing the capacity of the network to remove nitrate (Figure 4). The range of flows over which the network retains most of the inputs (Stage 1 and 2) declines, and the range over which the network has little or no influence increases (Stage 4). In effect, under the assumption of concentration-dependent υ_f kinetics, increases in supply are exacerbated by a declining capacity of the network to remove the constituent. Further, removal in upstream reaches has the added benefit of enhancing removal efficiency by downstream reaches as constituent concentrations decline with distance downstream (Mulholland et al. 2008). Thus, higher order water bodies become relatively more important at network scales. Concentration dependence of reaction rates will likely not be a factor for constituents like TSS and possibly DOC, but will likely be important for highly reactive constituents (PO_4, NH_4, NO_3).

4.E. River Network Saturation Depends on Abundance of Lakes, Ponds, and Wetlands.

The scenarios so far have only addressed channel networks, and provide a perspective on the underlying role of river network structure and the stream continuum. Actual networks are highly heterogeneous in space and time. In the final set of scenarios, we varied the habitat term in Equation 1, $W \times L$, by incorporating different water bodies. As noted above, Equation 1 can be revised for volumetric processes by replacing U with a volumetric uptake, and habitat = $W \times D \times L$. Although some processes may become more important in the water column of lentic waters, for simplicity we continue to apply the assumption that processes at interfaces dominate (benthic, or air-water). Fluvial wetlands, ponds, lakes, reservoirs and floodplains all introduce additional removal/transformation capacity. Connectivity of fluvial wetlands and floodplains can vary significantly through time depending on Q, as well as due to human activities (e.g. levees). Thus, this final set of scenarios only demonstrates tendencies.

We ran four scenarios for the Ipswich River watershed in Massachusetts (MA), USA, across a range of flow conditions (Scenarios 4-8, Table 2). Scenario 4 assumes only a channel network, as before (cumulative channel surface area = 1.1 km^2 at mean annual flow). Scenario 5 considers lakes/reservoirs as identified by existing GIS layers (surface area = 10.9 km^2). Lakes replace all river channels within their boundaries, and the lake attribute for surface area ($W \times L$ in Equation 1) defines each lakes removal capacity, assuming their area changes little relative to flow. Scenario 6 considers beaver ponds in addition to lakes and channels (surface area = 0.9 km^2). Beaver ponds are assumed to occur randomly throughout the landscape at densities of 0.8 ponds km^{-1} (PIE LTER unpublished data), with individual surface areas to be 10-fold greater than mean annual channel width they replace. Finally, Scenario 7 considers the activation of floodplains at 2-fold the mean annual flow in stream orders 4 and 5, assuming floodplain width is 5-fold the channel width (surface area = 3.9 km^2). In each case, we assume biological activity of the non-channel water body is the same as in river channels (benthic U/C = 35 m yr^{-1}).

A similar logistic curve occurs for each scenario, but constituent removal as a function of flow shifts to the right as additional types of lentic water bodies are considered (Figure 5). The addition of lakes and beaver ponds modestly increases the range of flows in Stage 1 and 2, and reduces the range of flows in Stage 4. At mean annual flows, removal increases from 28% in Scenario 4 to 52% in Scenario 6. Floodplains in 4th and 5th order rivers elevate removal proportions at higher flows, though the difference declines as flow continues to increase. Thus, lentic water bodies add considerable demand, particularly in networks with high loading and reduce the range of flow at which saturation occurs.

5. Case Studies

The following case studies explore the balance between network supply and demand for various constituents and networks with different land use or hydrological regime. We describe how the RNS would apply to help understand four case studies of river network function where the 1) watershed is agriculture-dominated, 2) watershed is urban-dominated, 3) river network is lentic-dominated, and 4) river network dominated by intermittent streams. We also apply the RNS in a fifth case study to understand factors controlling the carbon cycle at river network scales for gaseous, dissolved, and particulate forms.

5.A. N_2O Emissions in Agricultural River Networks

In agricultural regions, excess fertilizer or animal waste enter the stream network from non-point runoff with negative consequences such as stream eutrophication and nitrous oxide emissions (N_2O). NH_4 and NO_3 are the two major sources of N_2O through coupled nitrification-denitrification (Mulholland et al. 2004). N_2O is generated mainly via microbial denitrification of NO_3 (Seitzinger 1988; Beaulieu et al. 2010) and is an important greenhouse gas (GHG) (Syakila and Kroeze 2011) that is 289 times more potent that CO_2 (IPCC, 2014) and is responsible for stratospheric ozone destruction (Ravishankara et al. 2009). In this section we explore how agricultural networks respond to alteration of supply of dissolved inorganic nitrogen (DIN= $NH_4 + NO_3$) and how this could impact N_2O emissions during high versus low flow conditions.

Supply of DIN increases considerably in agricultural watersheds due to excess fertilizer applications. Storm flows can quickly transport excess DIN to streams, especially where tile drainage exists, because of lower residence times in soils and bypassing of reactive soils. Thus, both increases in Q and C lead to increasing supply. The fate of NH_4 and NO_3 once in surface waters differs. Uptake velocities, and hence demand, are higher for NH_4 than for NO_3 (Ensign and Doyle 2006, Table 1) due to preferred incorporation of NH_4^+ into biomass and nitrification, with the latter creating in stream sources of NO_3 (Koenig et al. 2017). Further, NO_3 uptake rates follow saturation kinetics such that υ_f declines as NO_3 increases (Mulholland et al. 2008). As a result, at network scales, removal remains in Stage 1 and 2 for a larger range of flows for NH_4 than NO_3 (Figure 2,3). Since N_20 emissions are proportional to NO_3 concentration (Beaulieu et al. 2010), under low flows that characterize Stage 1 N_2O emissions will be source limited in larger rivers and most N_2O emissions will occur in low order streams (Figure 3). As flows increase, DIN supply increases relative to demand (Stage 3 and 4), downstream source limitation will be lessened and N_2O emissions will increase at network scales (spatial saturation).

Field measurements corroborate these dynamics. During low flow conditions (supply < demand) canal ditches and other lower order streams represent the part of the stream network with a major role in N_2O emissions (Garnier et al. 2009, Beaulieu et al. 2011, Marzadri et al. 2017). As flow and associated NO_3 supply increase, intermediate sized and higher order streams begin to contribute higher N_2O emissions (Garnier et al. 2009, Marzadri et al. 2017). However, rates in larger streams under higher flows remain lower than those in small streams at low flows because surface to volume ratio decline with increasing flow, and bottom sediments are where N_2O production occurs (Stewart et al. 2011, Zarnetske et al. 2011, Marzadri et al. 2012). Further, under increasing flow the role of the hyporheic zone in controlling N_2O production declines relative to the water-sediment interface and the water column with an overall reduction in N_2O emissions (Marzadri et al., 2017). As a result, imbalances in supply and demand with increasing flow will lead to greater changes in nitrate export fluxes than in network scale N_2O emissions.

5.B. Urban River Networks

Supply and demand of carbon, nitrogen, and other constituents are greatly altered in urban stream networks compared to networks with less anthropogenic impact (Kaushal et al. 2014, Kaushal et al. 2017), potentially shifting river network saturation curves to the right or the left. Engineered flow paths alter both supply and demand through their impact on flow rates and the efficiency of transport (Elmore and Kaushal 2008). Stream networks may expand into the landscape creating new zero order streams consisting of gutters, storm drains, culverts, pipes etc. (Kaushal and Belt 2012) (increasing L in Equation 1). These new "channels" can behave as a biogeochemical transporter, leading to more supply since terrestrial sites of transformation are bypassed, or a transformer of some processes, depending on flow and seasonality (Kaushal and Belt 2012). In non-engineered stream channels, there is often considerable simplification of channel structure due to wood removal and floodplains are more likely disconnected, reducing biogeochemical demands.

Urban stream networks relative to their natural counterparts may have altered demand because of elevated water temperatures associated with urban heat island effects and lower riparian canopy cover (Kaushal et al. 2010), higher nutrient inputs from chronic groundwater contamination (Kaushal et al. 2011), increased proportions of bioavailable organic matter of microbial origin (Hosen et al. 2014), and increased light availability due to riparian deforestation (Kaushal et al. 2014, Smith and Kaushal 2015). These changes can enhance biological demand (U relative to C) for some constituents (Kaushal et al. 2014, Smith and Kaushal 2015). For example, gross primary production can increase 5-fold and organic carbon lability can increase 4-fold compared to nearby forest reference streams leading to high network retention at baseflows (Kaushal et al. 2014). However, increasing concentrations can also lead to lower removal proportions at network scales due to efficiency loss when U declines relative to C (e.g., NO_3, Mulholland et al. 2008, Figure 4).

During storm flows in urban watersheds, large pulses of constituents may occur (Kaushal et al. 2014, Smith and Kaushal 2015, Pennino et al. 2016) and sources can change, leading to changes in both supply and demand. For example, nitrogen sources can shift from sewage to atmospheric sources (Kaushal et al. 2011, Pennino et al. 2016, Burns et al. 2009), and organic carbon sources can shift from in-stream to terrestrial detrital materials (Smith and Kaushal 2015, Pennino et al. 2016). These may lead to declines in uptake relative to concentration (lower υ_f) compared to lower flows, causing shifts in removal curves to the left (Figure 2). Stream burial can further decrease N uptake and demand along urban stream networks. For example, nitrate is transported approximately 18 times farther downstream in buried than in open streams before being retained, suggesting widespread burial will also shift network scale retention to the left (Beaulieu et al. 2015).

Urban stream hydrology also impacts the microbial community processing of constituents. Urbanized stream microbial communities are subject to higher rates of scouring during storm events than forested systems, leading to decreased uptake (Larsen and Harvey 2017, Reisinger et al. 2017). However, rapid recovery of urban stream biofilms occurs following storms, which enhances nutrient uptake and demand along urban stream networks (Smith and Kaushal 2015, Reisinger et al. 2017). The result is a microbial community that is less resistant to adverse impacts during high flows, but more resilient following such events.

Given the importance of storm contributions to annual N loads, many efforts to retain N along urban stream networks have focused on enhancing N uptake using in-channel stream restoration (Craig et al. 2008, Newcomer Johnson et al. 2016) or floodplain reconnection (Kaushal et al. 2008, Newcomer Johnson et al. 2014, 2016, Scenario 7 in Figure 5). These strategies should be integrated with stormwater management to regulate supply (timing and amount of inputs during storms) relative to demand (benthic surface area) to enhance network removal across flow conditions (Newcomer Johnson et al. 2014; Section 4.E.) for multiple constituents, including particulate carbon and TSS (Filoso et al. 2015, Larsen et al. 2015, Larsen and Harvey 2017). Engineered ponds and wetlands may also increase urban greenhouse gas fluxes, in addition to their service in nutrient retention (Smith et al. 2017). These observations warrant further study. Overall, the size of the restoration effort matters in regulating supply *vs.* demand and these management strategies must consider the balance at network scales.

5.C. Lentic Dominated River Network

Fluvial wetlands can delay river network saturation by increasing demand relative to supply (Fig. 5). This can be especially important in intensively managed agricultural or urban watersheds where supply rates to the network of reactive nitrogen, suspended sediment and phosphorus are often high and difficult to control (Section 5.A and 5.B).

Flow-through wetlands increase total river network demand by increasing surface area, material residence time, demand rate, and total biological demand.

Wetlands and other lentic waters have, by definition, inherently larger water storage volumes than channels of a similar length due to their shape, which increases residence time (W × L × D / Q). Surface areas and residence times in wetlands and other lentic waters are typically orders of magnitude greater than in channels (Roa-Garcia and Weiler 2010, Rueda et al. 2006). For example, using Equation 1 and assuming a constant removal rate of 30 mg N m^{-2} hr^{-1}, nitrate concentration of 20 mg L^{-1} (resulting υ_f = 13.1 m yr^{-1}), Q of 200 L s^{-1}, and a reach length of 300 m, a 300 m wide wetland along this reach would remove 20% of incoming NO_3 compared to 0.2% removed in a 3m wide channel. Residence time is related to both supply and demand (e.g. τ = L/v or W × D × L / Q, where W and L also affect the demand, while Q determines the supply). However, under low flow conditions demand tends to be high in comparison to supply in wetlands potentially leading to source limitation that is maintained over a broader range of flows (Stage 1). As discharge increases, supply increases faster than demand, and material may be transported through lentic waters to downstream reaches (Stage 2). Wetland volume increases during extreme events and reduce the magnitude of peak discharge in downstream portions of the network. This reduction in peak discharge reduces the material supply rate to downstream systems and network demand may keep pace with supply (so flows in Stages 3 and 4 are less frequent).

Total biological demand and areal biological demand rates are high in wetlands and other lentic waters. Due to their width, flow-through wetlands have inherently larger inhabitable benthic surface area than channels (W × L in Equation 1) and thus, potentially higher total biomass and total biological demand. Generally, biological demand in fluvial wetlands (U/C or υ_f) is higher per unit area than in channels (Wollheim et al. 2014), which further enhances nutrient removal in lentic-influenced systems at network scales. Many wetlands are characterized by high vegetative cover, which provides a number of benefits. Vegetation enhances demand rates by direct nutrient assimilation and fuels microbial removal processes through the production of organic carbon (Blodau 2002, Alldred and Baines 2016). Excess organic carbon can enhance nitrate removal via denitrification in downstream channels of the network as well as internal to the wetland (Hansen et al. 2016). Vegetation and its detritus also provide inhabitable surface area, which supports high microbial biomass and thus enhances demand (Power et al. 2009). Lentic waters thus generally delay saturation and move removal curves to the right (Figure 5).

5.D. Intermittent River Networks

Intermittent river networks are commonly found in regions where infrequent monsoonal systems result in extreme events. Intermittent river networks exhibit a highly dynamic hydrological regime that includes periods with no running water and the alternation of wet and dry phases. Wet and dry cycles affect network-scale supply and demand through impacts on terrestrial inputs, hydrologic transport, and stream processes (e.g., Acuña et al. 2004, Datry et al. 2014). We hypothesize that the shape of the network scale removal vs. flow relationship (Figure 1b) in intermittent river networks will exhibit a hysteresis response depending on whether the network is wetting (flow increasing) or drying (flow decreasing). We expect lower demand at a given flow or supply level during the wetting phase than during the drying phase because biotic function has to recover from declines following the dry period.

During the transition from wet to dry conditions (contraction phase), the shape of the retention curve (Figure 1B) will likely be similar to those in other river networks because biotic function has been established. As dry conditions become extreme, aquatic microbial communities become detrimentally impacted. Gross primary production is disproportionately suppressed compared to heterotrophic respiration (Timoner et a. 2014, Acuña et al. 2015), meaning that net removal of organic matter can increase during network contraction even if overall microbial metabolic activity is decreasing. Intermittent river networks enter into Stage 1 as flow declines, but then gradually disconnect from terrestrial ecosystems and some proportion of the network evolves towards dessication (Bernal and Sabater 2012). Stream segments that retain water are disconnected from each other such that hydrological connectivity across longitudinal, lateral, and horizontal axes becomes extremely low and spatially variable (Bernal et al. 2013). Segments with surface water continue to require constituents, so demand in these patches remains high relative to supply (Martí et al. 1997, Valett et al. 1996) resulting in high network scale removal

(Stage 1, Figure 1). These studies suggest that U x W x L decrease at a slower rate than Q x C (Equation 1) during the contraction phase, although there can be spatial heterogeneity in this balance (Acuña et al. 2007; von Schiller et al. 2011, Datry et al. 2014).

After a dry summer period, heavy rainfalls in autumn lead to a resumption of surface flow, and increasing supply of nutrients and organic matter from land and internal stream bed sources from material that has accumulated during dry conditions (Butturini et al. 2003, Vázquez et al. 2007, Loecke et al. 2017). During the initial transition from dry to wet conditions, flow is relatively low compared to mean annual flows, while the concentration of nutrients and dissolved organic matter in stream water can increase several-fold (Bernal et al. 2005, von Schiller et al. 2015). So both Q and C in equation 1 increase during the wetting phase. At the same time microbial activity is initially delayed during rewetting but recovers relatively quickly as microbes are stimulated by an influx of new resources (Romani and Sabater 1997, Sabater et al. 2016). Nutrient supply initially overwhelms nutrient demand after rewetting, especially in low order streams. As a result, demand relative to supply is initially low, causing lower removal efficiencies and a removal vs. flow curve shifted to the left compared to the drying phase (Figure 1b).

5.E. Carbon Cycle and Network Saturation

The carbon cycle in inland waters provides an excellent opportunity to demonstrate the generality of the RNS hypothesis. Like other elements, carbon occurs in different forms in surface water, including dissolved gases (carbon dioxide, methane), dissolved inorganic and organic carbon (DOC, DIC), and particulate inorganic and organic carbon (POC, PIC). All are subject to supply, transport, and uptake processes, but the rates of uptake or transformation, as well as the ability of river networks to transport and mobilize each of these carbon forms varies tremendously (Table 1). Thus, the balance between supply and demand and the resulting stage of network saturation (Figure 1) likely also differ considerably among carbon forms. Supply can also include sources that are produced *in situ*, e.g. DOC leached from aquatic vegetation, CO_2 produced in sediments (Hotchkiss et al. 2015, Vidon and Serchan 2016, Werner et al. 2012), or resuspension of previously deposited POC during high flows.

Dissolved gases in excess of saturation can enter river systems from terrestrial ecosystems via runoff or from production within aquatic systems. At network scales, "demand" (in this case, exchange across the water-air interface) is high relative to supply, because gas exchange rates are relatively high (Table 1), particularly in steeper sloped headwater streams. For gas inputs from terrestrial ecosystems, the network remains in Stage 1 or 2 for a wide range of flows (Figure 1). Abril et al. (2014) explored how far downstream CO_2 from a source location is advected before it is lost to the atmosphere via gas exchange. Their approach can be reformulated in terms of supply and demand using Equation 1 by considering R as the proportion of excess pCO_2 that is degassed across the air-water interface in a water body (R_{pCO2_excess}), which is a function of the piston velocity (υ_f), W, L, and Q. Here "demand" in terms of areal flux of CO_2 emitted from a water body is in part a function of concentration (excess above saturation), so concentration influences both the demand and the supply, and as supply increases, so generally does the demand. While Abril et al. (2014) consider the effect of depth and velocity, in the RNS conceptual model and Equation 1 these are represented by the equivalent Q/W.

Gas loss accumulates along the surface water flow path as determined by how each factor in Equation 1 changes (C in terms of excess CO_2, υ_f, W/Q, and L). In their exercise, Abril et al. (2014) estimated that CO_2 could be transported 10-100 km downstream depending on the gas transfer velocity similar to effects shown in Figure 2. Interestingly for gases, as Q increases during storms both velocity times depth (= Q/W) and υ_f increase, which leads to simultaneous and offsetting increases in both supply and demand (Raymond et al. 2012), resulting in increased terrestrial CO_2 emissions from surface waters of a network (Beaulieu et al. 2008; Butman and Raymond 2011). Most streams remain oversaturated for GHG despite high loss rates, suggesting that in-stream production offsets gas evasion with distance downstream (Werner et al. 2012, Vidon and Serchan 2016).

The process is more complex for DOC. Demand for DOC is driven by biological activity (microbial mineralization), physical processes (flocculation, adsorption), as well as photochemical oxidation (Lu et al. 2013, Cory et al. 2014). DOC occurs in a variety of forms, each with their own reactivity, which again can be represented by υ_f (Mineau et al. 2016, Table 1). The predominant forms of DOC, and hence reactivity, vary over space and time.

Generally DOC concentrations increase with runoff, so supply increases nonlinearly with flow (Wilson et al. 2013, Raymond et al. 2010, Hu et al. 2016). If υ_f remains constant, then the pattern in Figure 1 will be followed (Jin et al. 2015), and level of υ_f determines the flow at which networks become saturated (Figure 2). However the predominant form of terrestrial DOC can change during storms as different soil pools are connected to stream flow (Creed et al. 2015), which because υ_f varies with form, can result in altered demand for DOC during storms. Previous studies have reported both increases and decreases in DOC bioavailability in streams as flow (and supply) increases (Holmes et al. 2008; Fellman et al. 2009; McLaughlin and Kaplan, 2013; Wiegner et al, 2009). Thus during storms, removal may transition from one removal curve (in Figure 2) to another depending on how predominant composition and υ_f change.

However, because sediments likely contribute substantially to DOC reactivity at whole reach scales (Sobczak et al. 2003), and the proportional exchange between water column and sediments declines with increasing flow (Battin et al. 2008), reach-scale υ_f should also tend to decline with increasing flows (the role hyporheic zones is implicit in reach-scale υ_f, Mulholland and Deangelis 2000). Since DOC uptake is modulated by biology, υ_f will also be dependent on temperature, with generally lower υ_f in cold months compared to warm months. Thus DOC exported during a snow melt event would be expected to have lower demand relative to supply than DOC exported during a summer rainstorm. However, if the biological lability of DOC is higher during these months (e.g. because of lower reactivity in soils) (Holmes et al. 2008), then aquatic reactivity could increase, offsetting to some degree colder temperatures.

Thus, a complex set of factors interacts to determine what proportion of DOC entering river networks is removed (oxidized) or exported, likely affecting the shape of the removal curve. Relatively little reach-scale research has explored the variability of DOC υ_f throughout river networks. Although the effects of water temperature, light, microbial communities, flow regime, nutrient regime, and local DOC form have all been documented (Hall et al. 2016, Thomas et al. 2005, Griffiths et al. 2012, Mineau et al. 2016), understanding the controls on DOC υ_f will require additional research.

The dynamics of POC highlight another degree of complexity. Unlike DOC, POC can be stored in depositional features such as pools, meander bars, lentic waters and floodplains. In-stream storage sites can become important sources during storms (Dhillon and Inamdar 2014). Similar to CO_2, the distance that POC will be transported from a discrete source will depend on water turbulence but also the physical characteristics of the particle (together affecting net sedimentation rate, υ_f). Once deposited, the fate of POC will be determined by its reactivity (per time biological decay), conditions of the depositional zone and the potential for re-entry into the water column due to future turbulent events (mobilization of internal sources).

To integrate these three major forms of carbon (POC, DOC, CO_2), we expect the following: 1) the majority of terrestrial inputs of CO_2 and CH_4 will evade in most river networks of larger watersheds across flow conditions because "demand" increases with supply (Stage 1 or 2); 2) terrestrial inputs of most POC will be deposited somewhere within the river network due to high settling velocities, particularly in networks with abundant lentic water bodies and connected floodplains (Stage 1 and 2); 3) POC deposited within the stream network will contribute to net heterotrophy, and is therefore a source of CO_2 that is also rapidly evaded, and/or DOC leachate that is transported downstream; and 4) terrestrial DOC is shunted through the network across flow conditions when lability (demand) is low (Stage 3 and4) but is removed when lability is high (Stages 1 and 2).

6. Validation Approaches

The RNS hypothesis describes network scale function. While river network models are helpful for understanding these potential dynamics, observations of function at the network scale would facilitate testing of models and allow empirical comparison of function of different river networks and how they respond over time and space. Typically, observations of flow and concentrations are collected at basin mouths to test the predictions of river network models (Wollheim et al. 2008a, Alexander et al. 2009). However, such measurements do not isolate the effects of loading and river network transformation. As a result models can simulate the right answer for the wrong reason. As high frequency, *in situ* nutrient sensors become more affordable the potential arises to deploy them in ways that address network scale function. Researchers are beginning to use *in situ* sensors for these purposes. For example, Miller et al. (2016) used a single station approach to estimate network scale retention of NO_3 over the course of a year in the Potomac R. watershed. The sensor was deployed at the watershed outlet, and winter concentrations were assumed to reflect loading from land, on the assumption that biotic processes are low during winter. This approach also assumed that inputs from land are derived from two sources, groundwater and soil runoff, which varied as determined through a hydrograph separation approach. Each of these sources was held constant over the year, an assumption not likely to hold in many cases. Such an approach could be improved through more detailed characterization to temporal and spatial variation of the NO_3 sources, which would require a network of sensors

An alternative approach is to deploy a network of sensors in both headwaters and at the basin mouth and estimate network removal using an end member mixing analysis involving both reactive and conservative solutes (Wollheim et al. In Press). With this approach, storm event scale flux of both reactive nitrate and conservative chloride vs. total storm runoff in multiple headwaters are used to derive the anthropogenic end member. The end members for anthropogenic and non-anthropogenic land uses can then be used to predict the nitrate:chloride flux ratio at the basin mouth based on land use fractions assuming conservative mixing , and then compared to observed nitrate:chloride flux ratio at the basin mouth. Derivation of an anthropogenic end member from multiple headwaters also allows for estimation of uncertainty. This approach therefore isolates both the loading and network transformation signal at storm event or under stable base flow scales. This technique could also be applied at different times of year and over time, avoiding some of the assumptions of Miller et al. (2016). Further, these results would be an independent test of river network model predictions.

As an example, we applied the statistical model used in Scenario 1 (Table 1; Wollheim et al. 2006) to the fourth order river network in which Wollheim et al. (In Press) deployed the end member sensor approach (the Oyster River watershed, with drainage area = 50 km^2). Model predictions of retention across flow conditions indicate that both the model and the observations exhibit a decline in network scale nitrate retention with increasing storm size, and predictions were within the uncertainty of the observations

(Figure 6a). However, the observations suggest the model contains incomplete dynamics (e.g. negative retention or mobilization of nitrate during the largest storm events, which is not considered in the statistical model). Deployment of nested sensor networks in a variety of river networks, for a variety of constituents, could be used to test aspects of the RNS hypothesis.

Other approaches have relied on synoptic sampling throughout river networks at various snapshots in time using similar principles. For example, Wollheim et al. (2008a) used twenty different synoptic surveys over a two-year period to estimate network retention across different flow conditions. The synoptic survey approach relies on regressions of nitrate concentration vs. land use in headwaters, which are then compared to concentrations at the network outlet. Results suggested that retention in the Ipswich River network was high at low flow, declined with increasing flow, but then increased again at higher flow conditions when abundant fluvial wetlands were connected (as demonstrated by the floodplain scenario in Figure 5). Figure 6b shows nitrate concentrations, measured during three separate synoptic sampling events in a single watershed within the Upper Mississippi River basin, decreasing as modeled nitrate mass travel time increased. In this study most sites with the cumulative travel times greater than ~ 10 hours (Figure 6b black markers, a metric of time spent in a surface water flow path) had > 8% lentic waters (Czuba et al. in review). This demonstrates the potential management strategy of increasing network demand to counteract high supply rates in intensively managed landscapes (Hansen et al. accepted). In a nested watershed study in the Adirondack Mountains, NY, Vidon et al. (2014) showed that stream network features (e.g. presence of lakes and wetlands, headwater vs. lowland) had a dominant role on the bioavailability of DOC across flow conditions. These different approaches could be used to test model predictions, and to compare the function of different river networks with respect to the RNS and the balance of supply and demand.

7. Limitations

The models presented here are simple and do not consider many factors that likely also affect network scale function. For example, the models did not represent in-stream sources, which are likely important for sediment and particulate organic matter that settles in streams, or DOC mobilization and nutrient mineralization from stream organic matter or biota. The observations of whole network retention vs. storm size (Figure 6) suggest that mobilization of nutrients from internal stream sources may become important. We also did not consider the spatial and temporal heterogeneity of reaction rates. For example, storm events can cause aquatic process rates to decline with recovery times that vary among different river networks (Reisinger et al. 2017). The impact of short and long-term disturbances on network function can be explored with approach we have outlined here.

8. Conclusions

The RNS is a general hypothesis that can serve as a framework for understanding aquatic function at network scales and can be used to generate more detailed hypotheses on riverine retention and transport processes (Table 3). It can be applied generally to multiple constituents, including gaseous, dissolved and particulate species. It suggests how and why network scale removal follows a non-linear pattern with increasing flow as a function of constituent reaction rates and kinetics and the availability of reactivity surface area. It also demonstrates the importance of larger streams and rivers in buffering network scale saturation with increasing flows.

The RNS hypothesis looks at network scale function across a range of flow conditions. Understanding the resulting response curves is critical as climate variability and the number of extreme events changes. Extreme events can include catastrophic floods, or a greater frequency of drought and intermittent river networks. To evaluate how systems respond to extreme events, we must place river networks in the context of more common conditions. For example, we can hypothesize that under typical flow conditions, there is a certain response curve (Figure 1b), but that following disturbances caused by extremely high flows (where biota is scoured) or extremely low flows (where biota is dessicated), there will be a shift in the response curve to the left (reduced network scale function). Alternatively, we could also hypothesize that fresh organic matter introduced during extreme high flows enhances some functions or that source limited areas following dry periods result in rapid uptake, causing shifts to the right (enhanced network scale function). The RNS complements the idea that aquatic systems do geomorphic work and have an effective discharge of removal (Doyle 2005) as was applied to understand network scale N removal (Wollheim et al. 2008a). The effective discharge approach integrates over some time period to determine the flow conditions under which river networks receive the most material and when they remove the most inputs, to determine when they transport the most material (geomorphic work). As flow frequencies shift, the work that can be done by river networks will also shift. The RNS can be used to understand these responses.

There are a number of research priorities that would help enhance understanding of network scale function and better test the RNS. First, nested *in situ* sensors for more constituents should be deployed in a greater variety of watersheds. Affordable, *in situ* sensors are becoming more available for a variety of reactive nutrients (e.g. EPA Nutrient Sensor Action Challenge), and should be deployed in headwaters of representative land uses and at their basin mouths. Conductivity sensors should always be co-deployed to allow correction for conservative solute transport and dilution, as is typically done in reach-scale studies (Stream Solute Workshop 1990). Aggregation to storm event scales is likely needed to allow comparison across spatial scales, as storm events have different time scales in smaller headwaters compared to larger rivers. These approaches are likely most appropriate for intermediate sized rivers (Wollheim et al. In Press). In larger watersheds, nested networks at multiple hierarchical levels may be needed to account for spatial variability in loading dynamics. As sensors become more affordable, such approaches may become feasible.

Second is the need to better understand and quantify spatial heterogeneity of function among water bodies embedded within river networks. Obviously, increased residence times of large lakes, reservoirs, and connected floodplains needs to be integrated, as well as their reaction rates for different constituents. But also important is the role of more advection dominated lentic waters, including beaver ponds, fluvial wetlands, and small reservoirs. We hypothesize that the range of conditions existing in heterogeneous river networks enhances overall network function by allowing different processes to dominate in different parts of the flow path that could alleviate source limitation (e.g., conditions that alternately favor nitrification and denitrification). This phenomenon will require incorporation of linkages among multiple biogeochemical cycles (e.g., carbon, oxygen, nutrient interactions, Schlesinger et al. 2011, Helton et al. 2017) that also account for the links between microbial communities and functions. Finally, a greater understanding of process rates across the range of flow conditions and response to disturbances are needed. Many tools developed to study streams and rivers require low flow conditions and are not easily applied at high flows (Ensign and Doyle 2006, Tank et al. 2008). More effort is needed to estimate reaction rates at higher flows, in higher order reaches, and repeatedly so as to better understand the range of variability and the role of ancillary drivers such as concentration, light, and temperature.

The RNS hypothesis helps to understand the complex interplay between demand and supply associated with flow and loading concentrations that can lead to a changing role played by smaller vs. larger streams, and the role of aquatic systems in regulating fluxes to downstream systems. For some constituents, the concern is what proportion of inputs reach downstream systems. For others, the concern is how much of a constituent is actually evading from the network. And for others, the concern is how much of a constituent is accumulating within the network. Anthropogenic changes lead to changes in supply, as well as to both direct and indirect changes in demand. To better understand the role of aquatic systems in continental constituent cycles, and better manage aquatic ecosystem function, including receiving waters, understanding the interplay of supply and demand and how these lead to network scale function will be critical.

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Tables

Table 1. Median reaction rates for different constituents in surface waters. All uptake velocities are standardized to units of meters per year to facilitate comparison among different constituents. * = quiescent water.

Constituent	υ_f (m yr^{-1})	Source
Chloride	0	Assumption
Ammonium	2680	Ensign and Doyle (2006)
Phosphate	1150	Ensign and Doyle (2006)
Nitrate-Total (using solutes)	740	Ensign and Doyle (2006)
Nitrate-Total (using ^{15}N)	220	Mulholland et al. (2008)
Nitrate-Denitrification (using ^{15}N)	25	Mulholland et al. (2008)
Dissolved Organic Carbon		
- Simple Compounds	1500	Mineau et al. (2016)
- Leaf Leachates	580	Mineau et al. (2016)
- Bulk (summer low flow)	4-37	Wollheim et al. (2015)
Particles	18-93,000*	Cheng (1997)
Sands	>150,000*	Ferguson and Church (2004)
Bacteria (*E. coli*)	40-300	Drummond et al. (2015)
Gases	37-37,000	Raymond et al. (2012)

Table 2. Scenarios used to demonstrate different aspects of the river network saturation hypothesis.

Scenario	Model	Network	Width-Down stream vs. Q	Width-At-a-site vs. Q	Uptake Velocity (m yr^{-1})	Mean Annual Runoff (mm yr^{-1})	Daily Runoff (mm yr^{-1})	Loading Conc.	Types of Water Bodies
1. Role of Flow	Statistical Network	7th order	$w=8.3Q^{0.52}$	$w=aQ^{0.1}$	35	500	1-10000	Constant, first order	Channels only
2. Role of Uptake Velocity	Statistical Network	7th order	$w=8.3Q^{0.52}$	$w=aQ^{0.1}$	10-1000	500	1-10000	Constant, first order	Channels only
3. Role of saturating kinetics	Statistical Network	7th order	$w=8.3Q^{0.52}$	$w=aQ^{0.1}$	vf = 10^-0.79 * log C + 2.709 * 365	500	1-10000	0.2 - 10 mg L^{-1}	Channels only
4. Role of Channels Only	Spatially explicit Network	5th Order	$w=8.0Q^{0.58}$	$w=aQ^{0.1}$	35	352	3.65-3650	Spatially varying, based on land use	Channels only for Ipswich River network
5. Role of Lakes	Spatially explicit Network	5th Order	$w=8.0Q^{0.58}$	$w=aQ^{0.1}$	35	352	3.65-3650	Spatially varying, based on land use	Scenario 4 + GIS Lakes
6. Role of Beaver ponds	Spatially explicit Network	5th Order	$w=8.0Q^{0.58}$	$w=aQ^{0.1}$	35	352	3.65-3650	Spatially varying, based on land use	Scenario 5 + 0.8 ponds km^{-1}, BP W = 10x mean channel W
7. Role of Floodplains	Spatially explicit Network	5th Order	$w=8.0Q^{0.58}$	$w=aQ^{0.1}$	35	352	3.65-3650	Spatially varying, based on land use	Scenario 5 + floodplains on Order 4 and 5 streams, w/ activation @ 2x mean annual Q, w/ FP W 5x channel W

Table 3. Examples of specific hypotheses generated by the RNS.

Specific Hypotheses
1. Urban and agriculture dominated networks are closer to saturation (Stage 4) for nitrogen than other networks because of increased loading, efficiency loss, and anthropogenic disturbance of the channel networks.
2. Urban and agricultural networks will see greater shift in the removal response curve following extreme events than other river networks due to greater disturbance caused by flow variability.
3. Intermittent river networks will experience less hysteresis in the removal curve following drying than river networks where drying occurs only rarely because the former are adapted to periodic drying.
4. River networks with abundant lakes and fluvial wetlands are less likely to reach saturation (Stage 4) than other river networks because of greater overall constituent demand.
5. River networks with abundant lakes and fluvial wetlands will show smaller changes in network scale removal during and following extreme events than river networks with fewer lakes and fluvial wetlands because they buffer changing conditions that influence both rates of supply and demand.
6. Urban and agriculture dominated networks are further from saturation (Stage 4) for organic carbon than other networks due to an increased demand that results from overall higher lability of organic carbon accompanied by conditions facilitating organic carbon removal such as more abundant nutrients and deforestation of riparian zones
8. Extreme climatic events (i.e., more frequent, large-size storms) will lead to increased loads of more labile organic compounds exported to coastal oceans and stimulate microbial food webs therein, because of greater supply vs. demand imbalances.

Figure 1. The river network saturation hypothesis, showing a) the change in supply and demand across a range of flow conditions, and b) the resulting shape of network scale removal proportions as function of flow conditions. Four stages are identified, including Stage 1: when removal by network occurs immediately at point of entry and there is little export; Stage 2: when constituents begin to be transported further downstream but are removed by previously source limited ecosystems downstream; Stage 3: when removal increases at a much slower rate than supply; Stage 4: when removal by the network is small relative to supply.

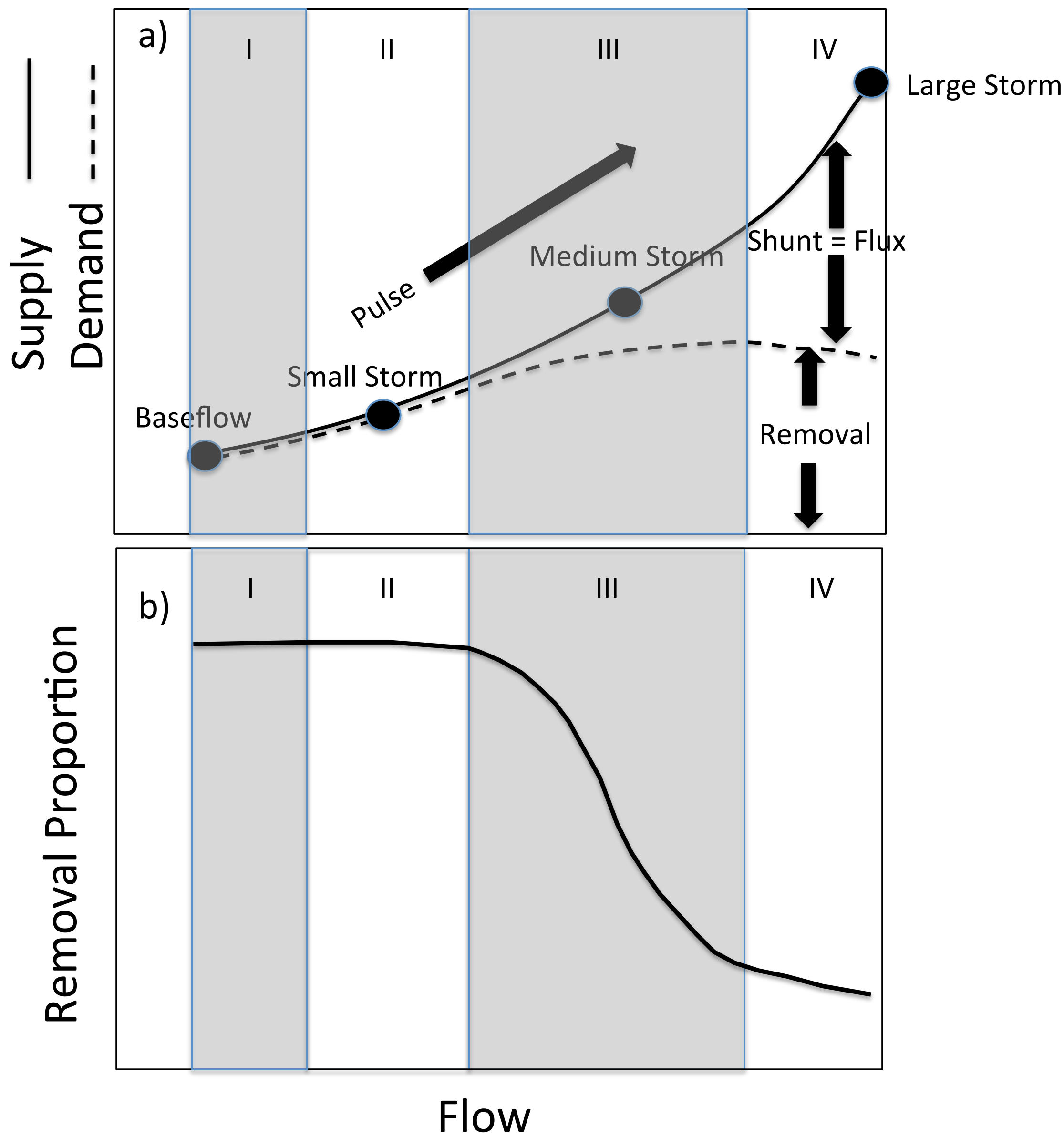


Figure 2. Network scale removal proportions as a function of flow as a proportion of mean annual flow conditions assuming different constituent reaction rates (Scenarios 1 and 2). υ_f in units of m yr^{-1}.

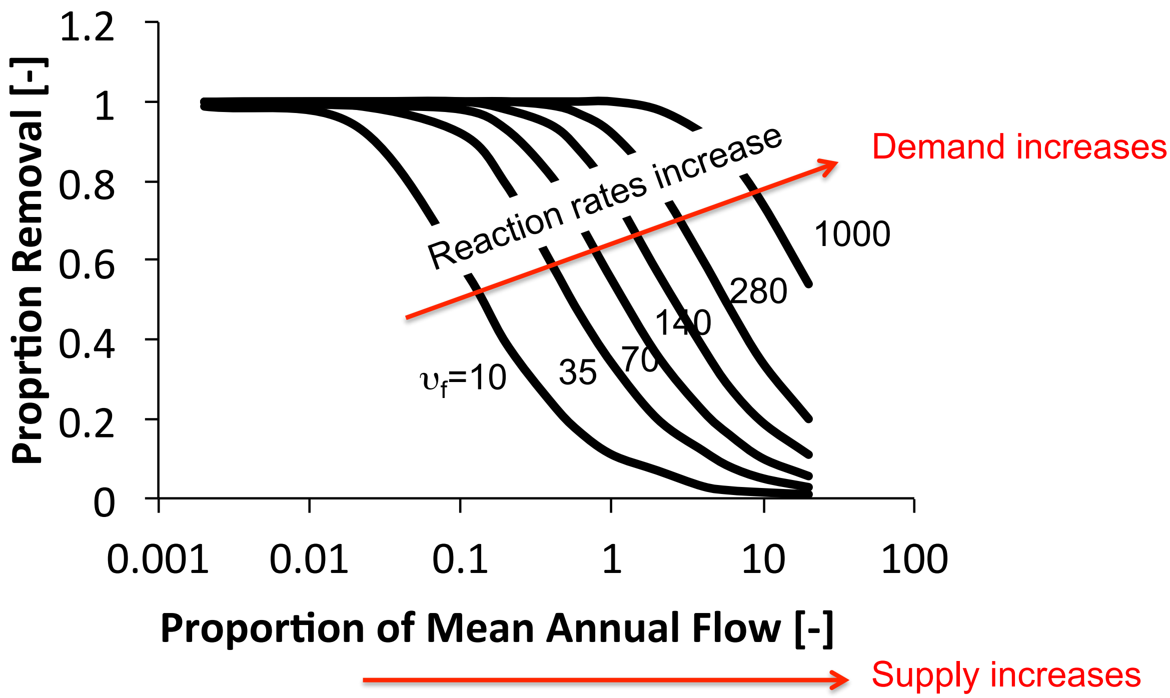
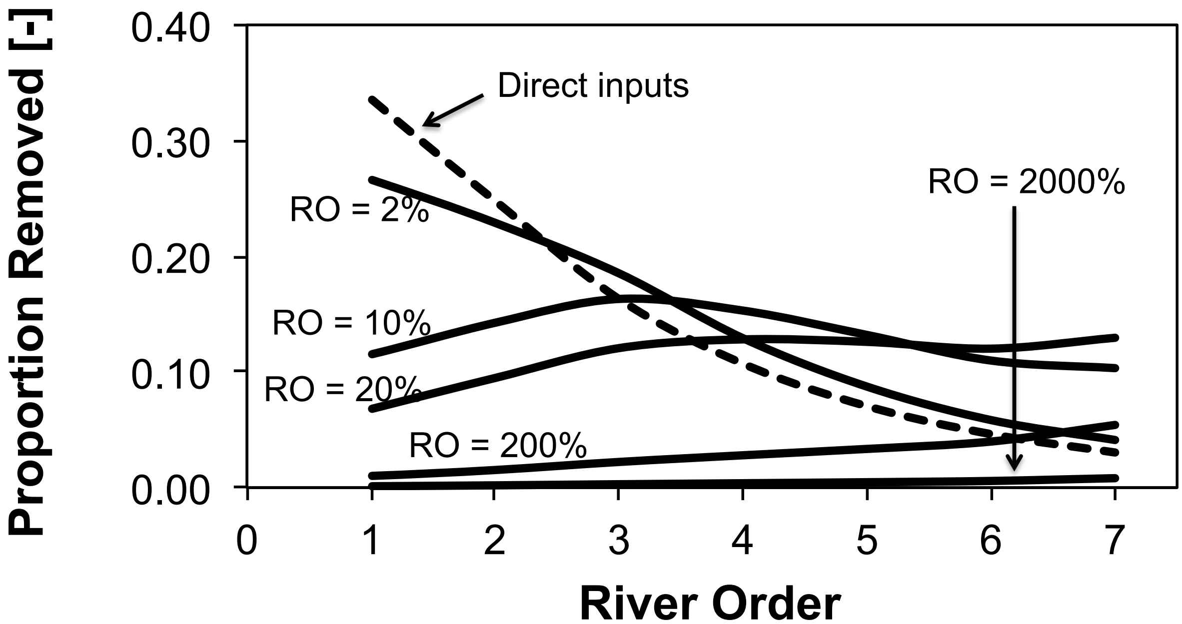


Figure 3. Distribution of total inputs removed by each river order within a 7th order river network as a function of runoff (RO) conditions represented as % of mean annual flow a) assuming uptake velocity = 35 m yr^{-1} and b) assuming uptake velocity = 1000 m yr^{-1}. Dotted line shows direct inputs where terrestrial sources first enter the river network, and are assumed to be constant across flow conditions. Scenarios 1 and 2.



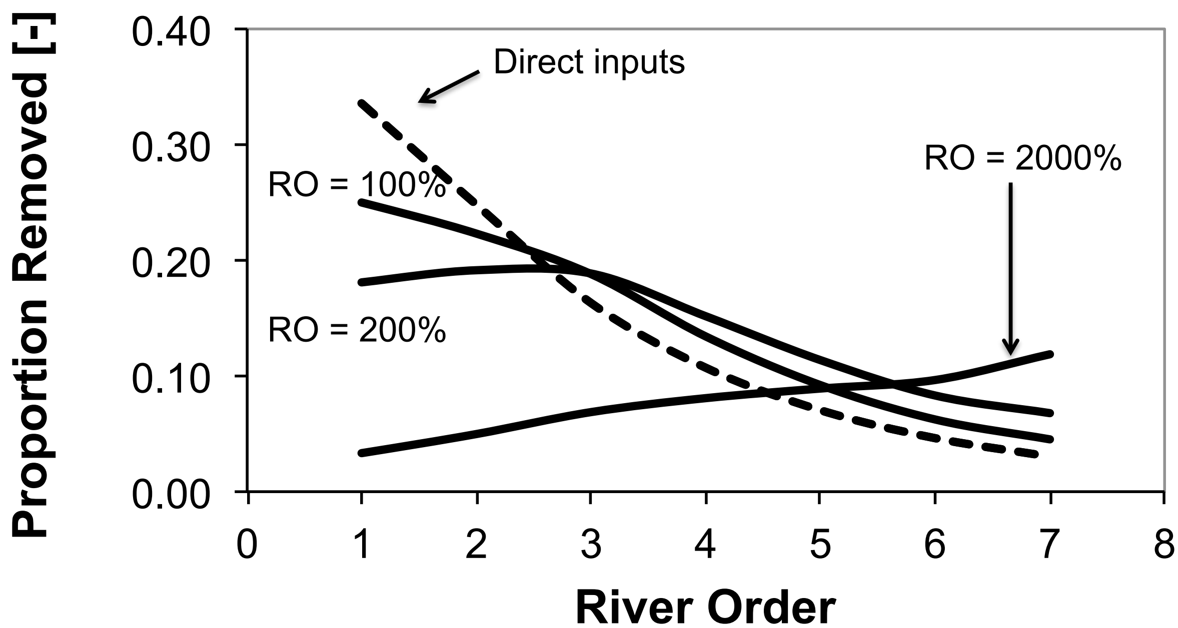


Figure 4. Network scale removal proportions as a function of flow as a proportion of mean annual flow conditions for different loading concentration (0.2, 1, and 10 mg N L^{-1}, Scenario 3), assuming the uptake velocity vs. concentration relationship reported in Mulholland et al. 2008 and Wollheim et al. 2008a, appropriate for denitrification of nitrate.

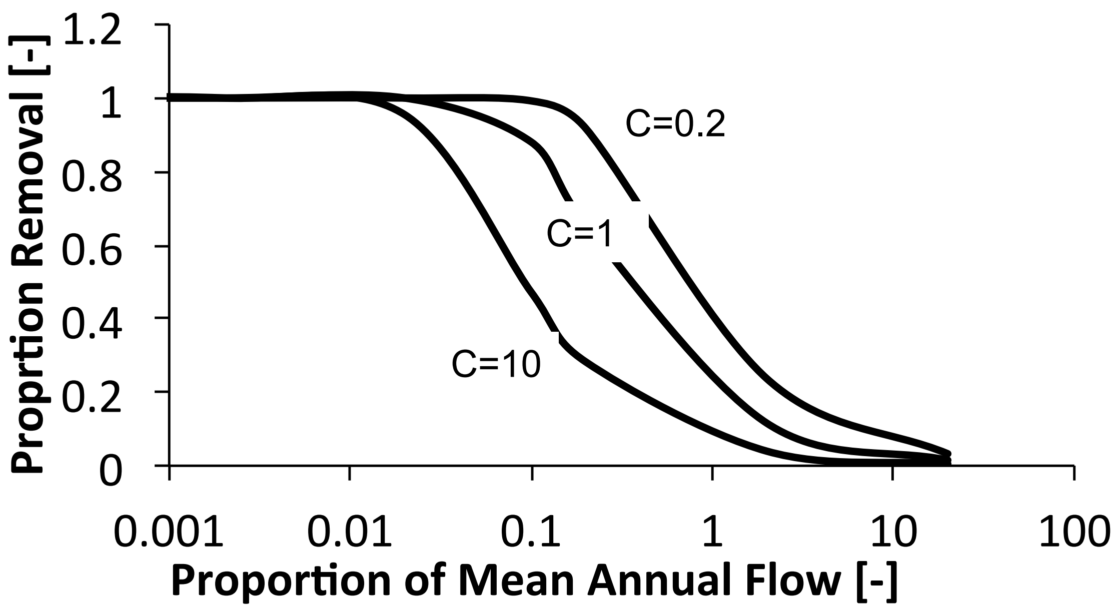


Figure 5. Network scale removal proportions as a function of flow conditions accounting for different types of aquatic systems in the Ipswich River watershed (Drainage Area = 400 km^2), containing a 5th order river network. S4 = channel network only; S5 = S4 + GIS lakes; S6 = S5 + beaver ponds at density 0.8 km^{-1}, W = 10x mean annual channel width; S7 = S5 + flood plain activation at 2x mean annual runoff in order 4 and 5 streams where floodplain width is 5x the mean annual channel width.

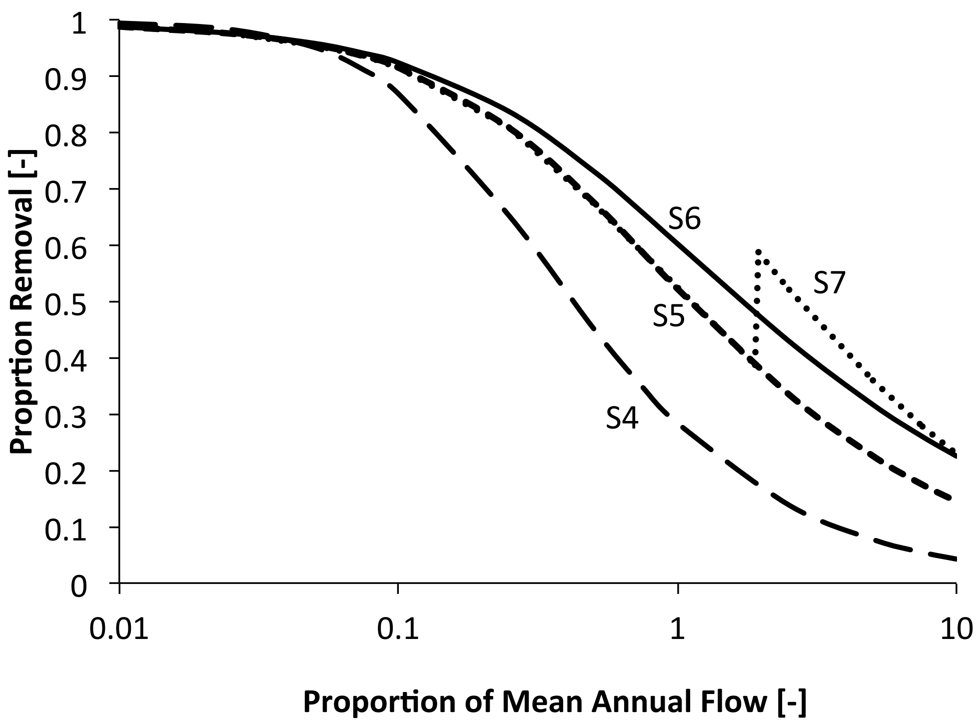


Figure 6. Empirical estimates of river network scale function as a) proportion of nitrate removed by river networks for different storm sizes estimated from nested *in situ* sensors and an end member mixing analysis applied in the Oyster R. Watershed, NH (Wollheim et al. In Press) compared to model predictions for this watershed assuming $\upsilon_f = 35$ m yr^{-1}, and b) change in nitrate concentration with increasing cumulative residence time in the Upper Mississippi during synoptic surveys conducted during three different years. Closed points are sites where upstream watershed area contain > 8% lentic waters.