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How Hydrologic Connectivity Regulates Water Quality in River Corridors

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Research Impact Statement: We quantify river connectivity as the balance between downstream flow and the exchange of water with the bed, banks, and floodplains of rivers, and demonstrate the impact on downstream water quality.

ABSTRACT: Downstream flow in rivers is repeatedly delayed by hydrologic exchange with off-channel storage zones where biogeochemical processing occurs. We present a dimensionless metric that quantifies river connectivity as the balance between downstream flow and the exchange of water with the bed, banks, and floodplains. The degree of connectivity directly influences downstream water quality — too little connectivity limits the amount of river water exchanged and leads to biogeochemically inactive water storage, while too much connectivity limits the contact time with sediments for reactions to proceed. Using a metric of reaction significance based on river connectivity, we provide evidence that intermediate levels of connectivity, rather than the highest or lowest levels, are the most efficient in removing nitrogen from Northeastern United States' rivers. Intermediate connectivity balances the frequency, residence time, and contact volume with reactive sediments, which can maximize the reactive processing of dissolved contaminants and the protection of downstream water quality. Our simulations suggest denitrification dominantly occurs in riverbed hyporheic zones of streams and small rivers, whereas vertical turbulent mixing in contact with sediments dominates in mid-size to large rivers. The metrics of connectivity and reaction significance presented here can facilitate scientifically based prioritizations of river management strategies to protect the values and functions of river corridors.

(KEYWORDS: hydrologic connectivity; river corridor; hyporheic flow; Clean Water Rule.)

INTRODUCTION

Hydrologic connectivity is broadly defined as the magnitude, duration, and timing of water-mediated transfer of materials (Jencso et al. 2009; Larsen et al. 2012). Hydrologic connectivity has been suggested as an integrated measure for understanding how aquatic health is regulated, including carbon and nutrient storage and processing, aquatic metabolism,

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food webs, and biodiversity (Pringle 2003). At present, there are no widely accepted approaches for quantifying connectivity in river networks (Ward et al. 2013; Alexander et al. 2015), limiting the understanding of where and why connectivity matters to the health and functional values of aquatic ecosystems. Quantifying connectivity throughout river corridors is critical to the sustainable management of rivers and their ecosystem services in the face of changing land use, hydrologic alterations, and degrading water quality and ecological health.

Fluvial geomorphic characteristics of river valleys, such as valley slope, sediment type, and runoff characteristics, are all important in determining the extent of a river's hydrologic exchanges with its bed, banks, riparian zones, and floodplains. The resulting river planforms control the timing and partitioning of water conveyance down and across the valley, as well as the partitioning of flows through both surface and subsurface pathways. Biological roughness such as large woody debris adds further complexity, increasing contact between contaminated river water and biogeochemically reactive materials, driving reactions that often result in the transformation or removal of contaminants from flowing waters (Mulholland et al. 2008; Böhlke et al. 2009; Boano et al. 2014). Thus, it is the river corridor, encompassing the main channel and its exchange flows with off-channel areas, rather than the river itself that is the important unit of study (Harvey 2016).

Hynes (1975), Vannote et al. (1980), Ward (1989), and Stanford and Ward (1993) were some of the first to recognize the relationship between river connectivity and aquatic ecosystems. They described important hydrologic linkages in river systems acting in both down-valley and cross-valley directions, with consequent effects on the structure and function of the aquatic ecosystems. Those early ideas about connectivity were updated by Findlay (1995) and Tockner et al. (2000) who respectively described the interplay between main channels and hyporheic zones and floodplains, and by Thorp et al. (2006) and Poole et al. (2006) who advanced concepts of functional process zones and hydrogeomorphic patches. Harvey and Gooseff (2015) argued for defining river connectivity based on direct quantification of the hydrologic exchange flows (HEFs) that connect main channels with their surrounding river corridor.

Although it is understood that longitudinal river flow and lateral HEFs act together to influence water storage and chemical reactivity in river corridors, there still is no widely accepted measure of river connectivity (Alexander et al. 2015; Wohl 2017). Concepts exist for integrating connectivity with biogeochemical processing to understand controls on downstream water quality (Covino 2017), but quantitative approaches are deficient especially at basin to regional scales (however, see Gomez-Velez et al. 2015; Marzadri et al. 2017). The lack of a widely recognized metric of river connectivity, therefore, hinders progress in determining how important river corridor functions such as water purification will evolve with changing land use and climate (Harvey and Gooseff 2015).

In this paper, we quantify river connectivity and demonstrate the effects of common types of river connectivity on denitrification throughout a regional river network (Figure 1). Our goal was to take an important step toward understanding "what type of river connectivity is most important in supporting the denitrification reaction in river corridors of the Northeastern United States (U.S.)," and consequently, "what management strategies will be effective in protecting or enhancing those natural water purification functions?" Our approach builds on the concepts of river turnover length and reaction significance factor (RSF) using metrics that are conceptually simple and broadly applicable across different types of river corridor features. Here we specifically compare the contributions of turbulent vertical mixing to the riverbed with hyporheic flow in the riverbed and riverbank in facilitating denitrification in the Northeastern U.S. We show (1) evidence that reaction zones in the river corridor with an intermediate balance of connectivity with the main channel dominate regional (Northeastern U.S.) denitrification, (2) the primary reaction zones appear to be the riverbed hyporheic zones as opposed to the riverbank hyporheic zones or the streambed's surficial benthic biolayer, and (3) key locations with the highest reaction potential are in small to mid-size rivers of hilly and well-drained areas as opposed to flatter areas or in the largest rivers of the Northeastern U.S. Our proposed metrics are simple and transferable to other areas and contaminants, and when explored further are likely to reveal additional regional patterns of connectivity and reactivity that vary with river size, landscape physiography, flow variability, and related physical, geomorphic, and ecological factors.

QUANTIFYING RIVER CONNECTIVITY AND ITS SIGNIFICANCE TO WATER QUALITY

The spiraling concept recognizes that downstream flow is punctuated by HEFs into and out of storage zones. Although located outside of the main channel, storage zones remain hydrologically connected with the river at time scales ranging from a few minutes to many months. Recirculating water in channel side

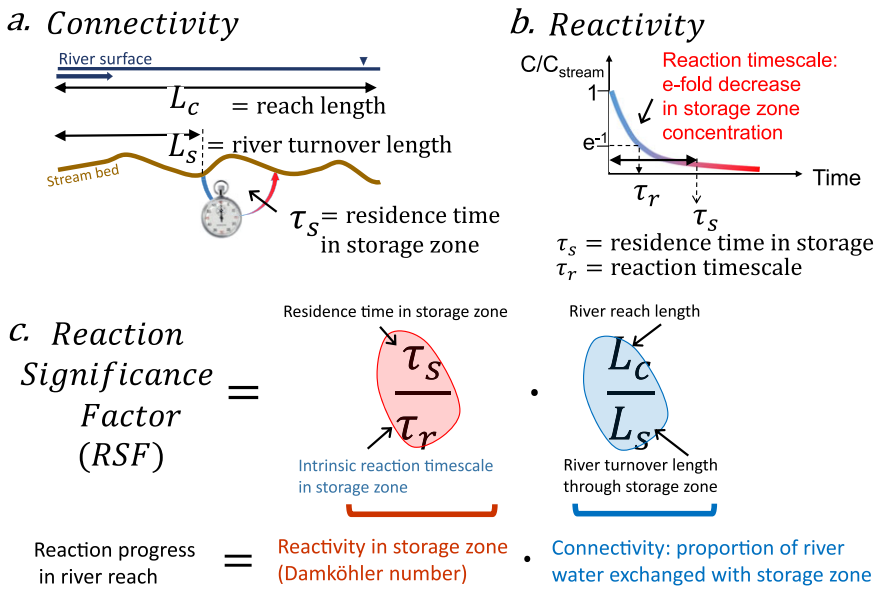

FIGURE 1. River turnover length provides a basis for quantifying river connectivity (a). The ratio of hydrologic residence time and reaction time scale in a storage zone defines the reaction Damköhler number (b). The product of connectivity and reaction Damköhler number quantifies the cumulative reaction progress in a river reach, a dimensionless metric referred to as the reaction significance factor (RSF) (c).

cavities, hyporheic flowpaths through bed and bank, and flows across riparian and floodplain sediments are examples of storage zones that span a continuum from well-connected to much less frequently connected off-channel areas. The extended contact time for river water with the sediments of those storage zones transforms solutes and contaminants in microbially activated and energy-yielding reactions that alter downstream water quality.

ANALYSIS EQUATIONS AND METHODS

Here we describe a generalized approach for quantifying HEFs of several types including (1) hyporheic flow through small bedforms (hyporheic-riverbed HEF), (2) hyporheic flow through river banks, alternating bars, and meanders (hyporheic-riverbank HEF), and (3) turbulent mixing of river water in contact with the riverbed biofilms and shallow sediment HEF.

Quantifying Connectivity

Our metric of river connectivity builds on the concept of river turnover length (Harvey et al. 1996), the average downstream distance that a parcel of water travels in the river before entering a storage zone (i.e., zone with more slowly moving water in close contact with reactive sediments) where most biological processing occurs (Figure 1a). River turnover length is:

$$L_s = \frac{U}{\alpha_s}, \tag{1}$$

where U is the river channel velocity [L/T], and α_s is an exchange rate coefficient [$1/T$] that may be interpreted as a fraction of the river that is exchanged per time with a storage zone (the subscript s is generic for one of many different types of storage zones). As discussed in detail in Appendix, the exchange coefficient in Equation (1) can be expressed in terms of measurable hydrologic quantities:

$$L_s = \frac{U \times d}{q_s} = \frac{Q}{q_s \times w}, \tag{2}$$

where q_s is the hydrologic exchange flux between river and storage zone [L/T], Q is river discharge [L^3/T], d is river depth [L], and w is river width [L]. Equation (2) states that river turnover lengths are negatively associated with connectivity, i.e., turnover lengths are longer in rivers that have lower connectivity with off-channel storage areas.

The inverse of river turnover length, $1/L_s$ [$1/L$], is a measure of the magnitude of river exchange with storage zones *relative* to the magnitude of downstream flow, and therefore is a better metric than river turnover length because it is positively related to connectivity. The inverse of river turnover length

has units of "per river length" and we multiply by a characteristic length for a river reach, L_c [L], to make it dimensionless. The resulting connectivity metric, C, expresses the hydrologic exchange fluxes as a proportion of the river discharge:

$$C = \frac{L_c}{L_s} = \frac{q_s \times w}{Q} L_c, \tag{3}$$

where C is river corridor connectivity, L_c is "characteristic" reach length selected by the investigator, and other variables are previously defined. Another way of thinking of river corridor connectivity, as we define it, is how many times river water is exchanged with storage zones in a river reach of a given length, that is, the number of river water "excursions" through storage zones (Gomez-Velez et al. 2015).

A reach distance, L_c, of 1 km is often selected for use in Equation (3) because it standardizes estimates of connectivity for comparison between different river networks. One kilometer is a convenient standard because it encompasses most of the spatial scales of lateral exchange fluxes, including centimeter-scale flows beneath small bedforms all the way up to flow through river meanders where the wavelength is 20 or more channel widths. Alternatively, the characteristic length for a river reach, L_c, could be selected as a scaling variable, i.e., L_c could vary to reflect the length of National Hydrography Dataset (NHD) reach it represents, in order to facilitate mass balance analysis (e.g., Schmadel et al. 2018), or L_c could vary to match calculations of river water mixing length (e.g., Rutherford 1994; Harvey et al. 2013), which could help isolate variables other than discharge, such as river slope or sediment grain size or other variables, that affect connectivity.

Integrating Connectivity with Biogeochemical Processing

Biological processing is often more efficient in HEFs of the river corridor because many important reactions, for example, denitrification, precipitation or sorption of trace metals, mercury methylation, toluene degradation, etc., take place in close contact with microbially and geochemically active sediments. Therefore, hydrologic exchange with storage zones may dominate net river corridor reactivity and nutrient retention and strongly influence downstream water quality.

To integrate river connectivity and sediment reactivity, we used RSF (Harvey and Fuller 1998; Harvey et al. 2013). RSF is a dimensionless metric that quantifies the cumulative fraction of removal of a reactive constituent from a river reach as the product of river connectivity with storage zones and reactivity in storage zones (Figure 1):

$$\mathrm{RSF} = \mathrm{Da} \times C, \tag{4}$$

where the components of C, the river connectivity with storage zones [dimensionless] were previously defined and Da is the reaction Damköhler number [dimensionless], which characterizes reaction progress during a single excursion through a storage zone as a ratio of time scales $\frac{\tau_s}{\tau_r}$, where τ_s is the average residence time of river water in storage [T] and τ_r is the intrinsic reaction time scale rate in storage [T] (Figure 1).

The reaction Damköhler number, Da, is a commonly used measure of reactivity (Bahr and Rubin 1987) that expresses the balance between the time available for reactions to proceed in the storage zone and the intrinsic time scale of the reaction (Figure 1b). HEF paths with too little time in storage ($\mathrm{Da} \ll 1$) process only small amounts of the reactant, referred to as "reaction limited." On the other hand, HEF paths with too much time in storage are "transport limited," with water stored for longer residence times becoming biogeochemically inactive after the reactant has been used up. Following first-order reaction dynamics, less than one percent of the reactant remains when $\mathrm{Da} \geq 4.7$ (Figure 1b; Gomez-Velez et al. 2015) and therefore Da values between 0.1 and 1 are expected to be more efficient processors of the reactant because (1) reactant concentrations (and thus reaction rates) remain high in storage zones because of continual replenishment from the river through relatively fast exchanging flowpaths, and (2) biogeochemically inactive storage is avoided.

Research Methods

To illustrate the use of the connectivity and reaction significance metrics, we compared the contributions from hyporheic zones and river turbulent mixing across the 184,289 river reaches of the Northeastern U.S. catalogued by the NHDPlus (Version 2.1, https://www.epa.gov/waterdata/nhdplus-national-hydrography-dataset-plus accessed on May 6, 2017). Calculations were made for each NHD reach to determine the average characteristics of "riverbed hyporheic flow" that results from hydrodynamic forcing mainly in the vertical direction through ripples and dunes on the riverbed, and characteristics of "riverbank hyporheic flow" that results from hydrostatic forcing mainly in the horizontal direction through alternating bars, banks, and meander bends. Hyporheic flow calculations follow the modeling approach developed by Gomez-Velez and Harvey (2014) and

refined for application in NHD river reaches by Gomez-Velez et al. (2015). Calculations of turbulent mixing to the riverbed were made using a turbulent vertical eddy diffusivity coefficient based on theory and data from Rutherford (1994). Using this diffusivity coefficient, an exchange rate coefficient for river water exchanged with a thin layer of riverbed was approximated for each NHD reach based on reach attributes and mass transfer theory (Larsen et al. 2014). Both hyporheic and turbulent river mixing calculations used mean annual river discharge and channel slope estimates from NHD, and channel geometry and related features from publicly available sources (see Appendix).

RESULTS AND DISCUSSION

Highest Reaction Significance Associated with Intermediate Connectivity

Turbulent vertical mixing of river water to the riverbed dominates overall river connectivity (Figure 2a). In contrast, hyporheic connectivity with the riverbed is intermediate in magnitude and hyporheic connectivity with riverbanks is lowest. Both riverbed and riverbank hyporheic connectivity decline substantially in the transition from mid-size to large rivers (stream order 4–5). The abrupt decrease in hyporheic connectivity appears to be caused by a decline in riverbed and bank grain size in larger rivers and the associated lower hydraulic conductivity of that sediment. The transition to less substantial hyporheic flow coincides with broad fluvial geomorphic changes in channels from a "sediment translation" regime to a "sediment deposition" regime where channels have smaller grain size (Wohl et al. 2015).

The reaction Damköhler number is highest in the riverbank hyporheic exchange flows that tend to have greater residence times through relatively long flowpaths through alternating bars and riverbanks (Figure 3b). In contrast, the Damköhler numbers for riverbed hyporheic flow are intermediate through the relatively short flowpaths beneath river bedforms. Damköhler numbers are much smaller for turbulent vertical river mixing because of very short residence times of turbulent mixing with the biolayer on the riverbed surface.

The potential reaction significance for downstream water quality is greatest for riverbed hyporheic zones in fourth-order streams and smaller, consistent with having intermediate values of reaction Damköhler number and intermediate values of connectivity (Figure 2). Too little connectivity with riverbank hyporheic flowpaths leads to transport limitation in storage zones that become biogeochemically inactive (i.e., after reactants have been used up). Conversely, too much turbulent connectivity with the riverbed biolayer (e.g., biofilms) likely creates reaction-limited

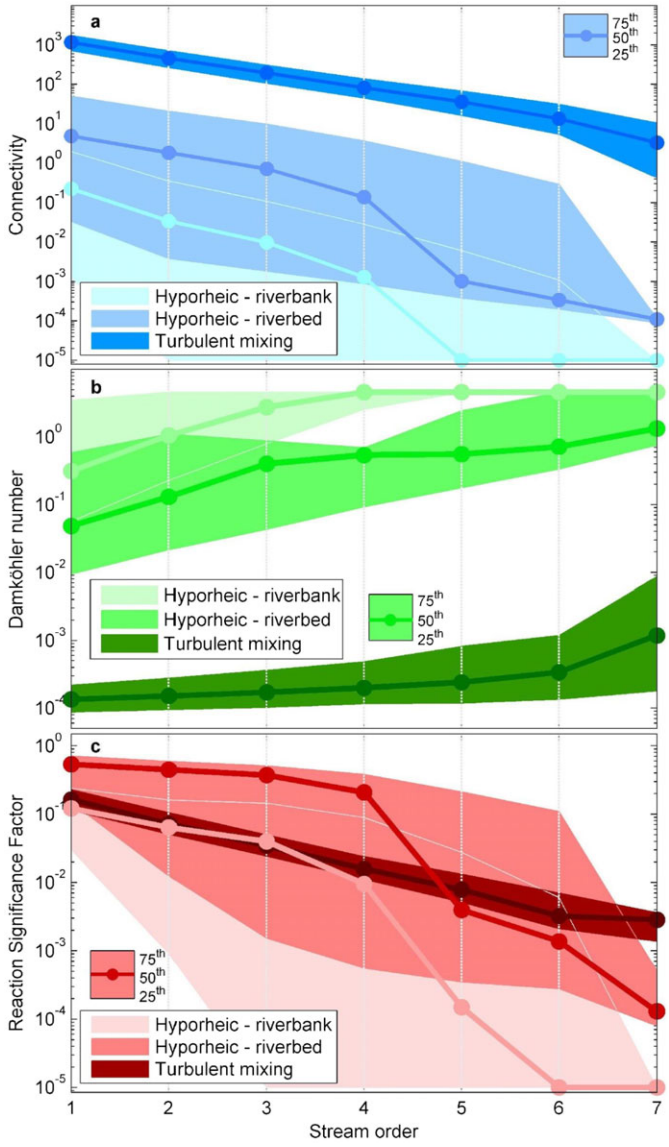

FIGURE 2. River connectivity, reaction Damköhler number, and potential reaction significance as a function of Strahler stream order for the approximately 184,000 river reaches of the Northeastern United States. Riverbed hyporheic flow had intermediate levels of connectivity compared to turbulent mixing to the riverbed which had the highest levels and riverbank hyporheic flow which had the lowest levels of connectivity (a). For the reaction Damköhler number, riverbed hyporheic flow was intermediate between high values for riverbank hyporheic flow and low values for turbulent mixing (b). The highest contributor to potential reaction significance was riverbed hyporheic flow in streams of order 1–4 (c). In larger rivers, turbulent mixing to the riverbed is a greater contributor to reaction significance. Circles indicate mean values and shaded areas encompass 25th–75th percentile values for each stream order.

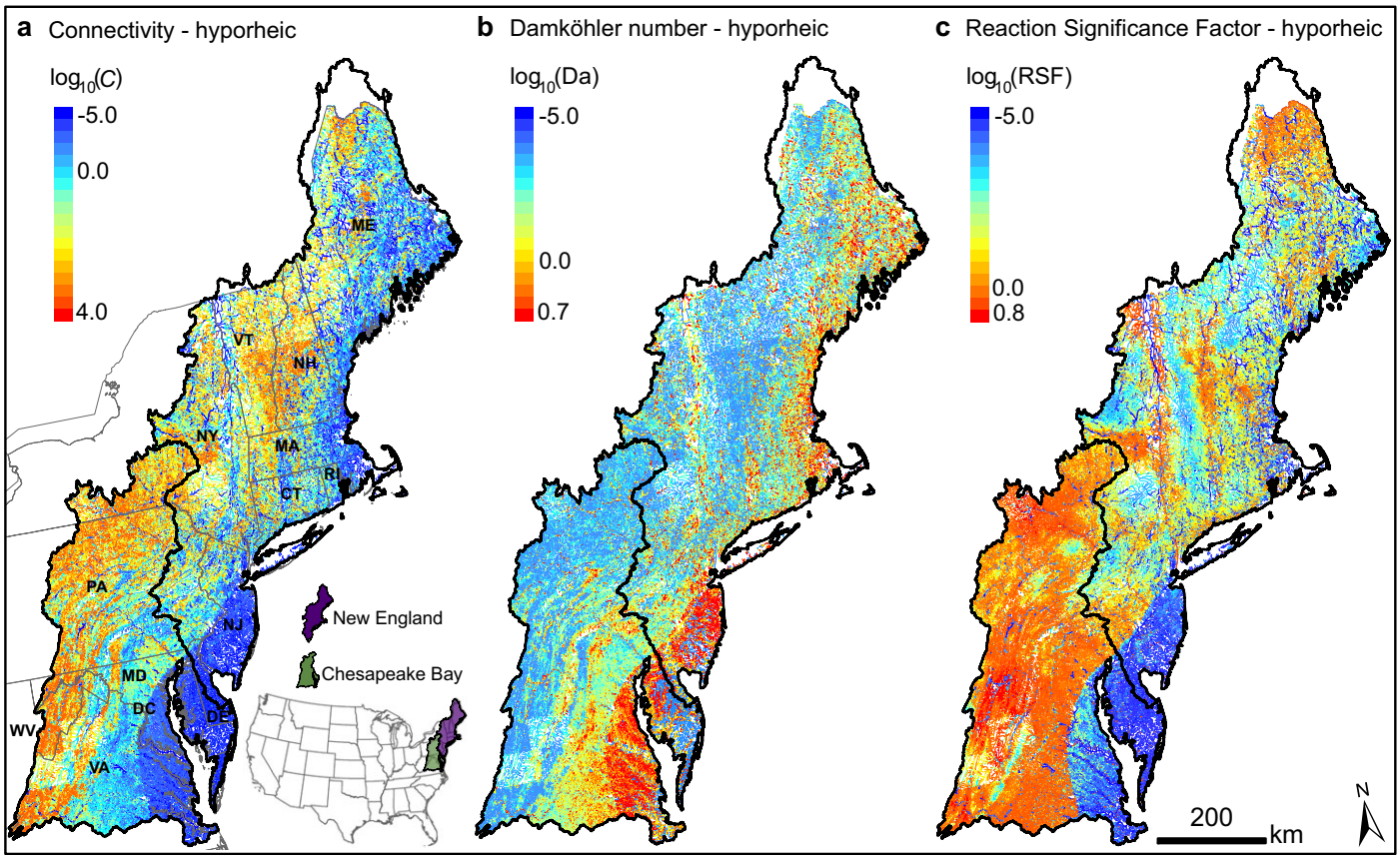

FIGURE 3. Map of dimensionless metrics of riverbed hyporheic flow connectivity (a), reaction Damköhler number (b), and potential RSF (c) with warm colors representing high values and cool colors representing low values on logarithmic scales. For the riverbed hyporheic zone, the potential RSF is highest in headwaters of mountainous or hilly areas, followed by mid-size channels, and lowest in major valleys and much of the Atlantic Coastal Plain.

conditions, without enough time or without the right chemical conditions for a reaction such as denitrification to progress before water is returned to the river channel.

The potential dominance of riverbed hyporheic zones is therefore achieved by an intermediate level of connectivity through small bedforms that tend to have reaction time scales and transport time scales that are closer to being in balance (or slightly reaction limited), with Da values ranging between 0.08 and 1. Therefore, an intermediate amount of river connectivity with a hydrologic exchange zone, where the residence time in storage and the reaction times are relatively well balanced, is best poised to optimize reaction progression and achieve favorable cumulative downstream effects.

A transition occurs in fifth-order rivers from potential dominance of reactions by riverbed hyporheic processing to dominance by turbulent mixing with the riverbed biolayer. Although preliminary, this finding suggests there may be a river-size threshold where a transition in hydrogeomorphology strongly influences the solute processing regime of river corridors.

Where and Why Is Potential Reaction Significance Highest in the Northeastern U.S.

The interaction of connectivity with the intrinsic reactivity of sediments in river corridor storage zones determines how reaction significance varies spatially on the landscape. For example, the highest values of the potential reaction significance metric, RSF, occur in headwaters of the Piedmont, Valley and Ridge, and Appalachian Plateau provinces of Virginia, Maryland, Pennsylvania, and southern New York. In those areas, there are moderate to steep slopes and coarse-grained streambeds that have relatively high hydraulic conductivity with appropriate time for interaction with sediments that match the time scale of biogeochemical reactions such as denitrification. In contrast, the lowest potential reaction significance for riverbed hyporheic flow occurs in the Atlantic Coastal Plain with low slopes and finer grained streambeds where hyporheic flow is considerably less. Intermediate values of connectivity and potential reaction significance occur in major river valleys (e.g., Connecticut, Hudson, and Susquehanna River Valleys)

and lowest values occur in the very low slope regimes of the Atlantic Coastal Plain in the eastern portions of New Jersey, Delaware, Maryland, and Virginia (Figure 3).

The RSF metric quantifies the potential for the dentrification reaction to progress in riverbed hyporheic zones. The actual amount of denitrification depends on sources of nitrogen to the aquatic system. Information about nitrogen sources in the Northeastern U.S. (e.g., Ator et al. 2011; Moore et al. 2011; Schmadel et al. 2018) indicates that riverbed hyporheic denitrification is most likely to be important where relatively high values of RSF overlap with high nitrogen sources, i.e., in the hilly farmland areas of the Appalachian Plateau, Ridge and Valley, and Piedmont provinces of north-central Pennsylvania and south-central New York, all within the Susquehanna River basin (Figure 3c). There are a few additional areas, such as the Mohawk River Valley in east-central New York and the Great Valley in west-central Virginia where moderate to high RSF values occur in nitrogen-rich areas. The hilly farmlands with abundant nitrogen sources also tend to have streams of moderate slope that provide energy to drive hyporheic flow and coarse-grained streambeds with relatively high hydraulic conductivity that conducts substantial hyporheic flow. Atlantic Coastal Plain streams and rivers in Delaware, Maryland, and Virginia possess lower slope and finer channel grain size, characteristics which are typically associated with lower river connectivity with hyporheic zones. As a result, we found very low values of potential reaction significance in hyporheic zones for Coastal Plain streams (Figure 3b).

Other modeling studies indicate substantial evidence for removal of nitrogen in coastal plain streams (e.g., Ator et al. 2011); however, typical studies at regional scales cannot identify the specific subenvironments where the reaction occurs. Our findings indicate that denitrification is more likely to be associated with turbulent vertical mixing of river water with the riverbed's surface biolayer on the sediment, compared with denitrification in hyporheic zones (Figure 3c). This finding should be interpreted cautiously, because our calculations only account for reaction in hyporheic zones and turbulent mixing to riverbeds. The denitrification reaction, however, can occur in other sub-environments such as on epiphyton of submerged vegetation in streams and rivers (Smith et al. 2006), in submerged leaf packs in rivers (Groffman et al. 2006), and on fine suspended material in rivers (Zhu et al. 2018), as well as in ponded waters and wetlands, indicating the importance of identifying the specific processes involved.

Our overall findings suggest that the greatest potential or biogeochemical processing in hyporheic zones occurs in streams smaller than fifth order where streams have intermediate connectivity with hyporheic zones. Reactions such as organic matter respiration and denitrification are performed with high efficiency in such hyporheic zones because the reaction time scale in streambed hyporheic zones is intermediate and well matched with the residence time of streambed hyporheic flow, resulting in highest overall potential reaction significance and greatest potential effects on downstream water quality (Figures 2 and 3). In contrast, the connectivity provided by turbulent river mixing is several orders of magnitude greater than hyporheic connectivity. However, turbulent river mixing generally cannot perform reactions as efficiently compared to streambed hyporheic zones because of the very short residence time in contact with the benthic biolayer. On the other hand, riverbank hyporheic flowpaths are poorly connected with long residence times in storage that become transport limited after nitrate is completely used up. Other processes such as turbulent exchange with the benthic biolayer have different optima. For example, in moderate to larger rivers (fifth order and above), turbulent exchange with the benthic biolayer can potentially dominate reactions because of lowered connectivity with hyporheic zones (Figure 2).

Controls on River Connectivity

Riverbed hyporheic-zone connectivity is intermediate between turbulent river mixing with the benthic biolayer, which has the highest connectivity, and riverbank hyporheic-zone connectivity, which is lower (Figure 4). Diffusion of river solutes across the sediment interface is the lowest contributor to connectivity, although depending on river characteristics, Figure 4 shows that diffusion may in some circumstances be as important as hyporheic flow. The relative rankings are apparent on a bivariate (log–log) plot showing the extent of different types of hydrologic exchange fluxes versus river discharge (Figure 4). The higher values of connectivity plot toward the upper left of Figure 4 because connectivity is defined as hydrologic exchange flux (y-axis) as a proportion of river discharge (x-axis) (Equation 2).

Consistent with theory, Figure 4 shows that hydrologic exchange fluxes of each type tend to be positively related with river discharge. Greater hydrologic exchange in higher discharge rivers may occur if channel width:depth ratios are greater, because of the greater contact area with the bed and banks. Higher discharge rivers also may have greater connectivity because higher discharge rivers tend to flow faster with greater hydraulic energy to drive hydrologic exchange (Boano et al. 2014). However,

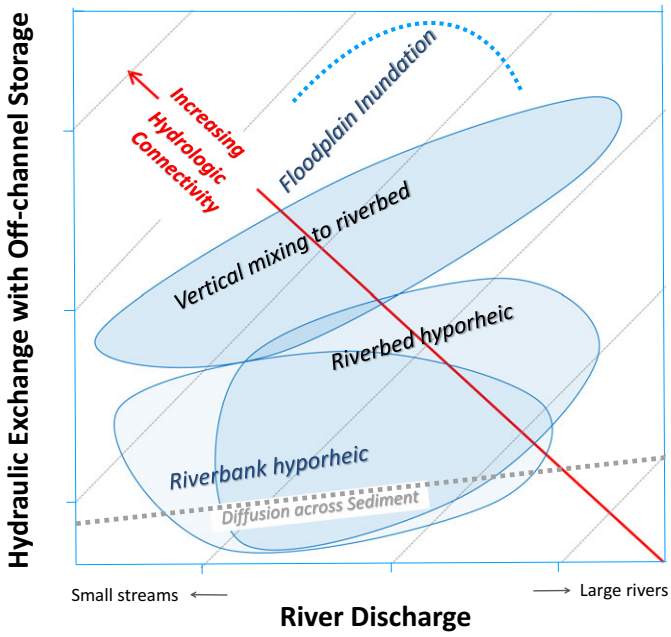

FIGURE 4. River connectivity contributions in Northeastern U.S. from turbulent vertical river mixing to the riverbed, riverbed hyporheic exchange flow, riverbank hyporheic exchange flow, and diffusion across sediment, plotted on log-transformed axes. Light gray isolines are contours of equal connectivity with connectivity increasing toward upper left quadrant. Several trends are apparent including (1) turbulent vertical mixing exceeds hyporheic exchange as a mechanism of connectivity and (2) connectivity is highest in small streams compared to large rivers, even though hydrologic exchange fluxes are generally greater at higher discharge.

the trend of increasing hydrologic exchange fluxes with greater river discharge does not mean that large rivers have the greatest connectivity. In fact the opposite is generally true with small streams generally having the highest connectivity because of coarser sediment that contributes to greater channel roughness and higher hydraulic conductivities that permit more hyporheic flow (Boano et al. 2014). Also, as expressed by the definition of connectivity as "the extent of hydrologic exchange as a proportion of river flow," larger rivers require much more hydraulic exchange with storage areas to achieve a given level of connectivity. A much smaller hydrologic flux can be effective in exchanging small streams, which indicates the strong scaling of river connectivity with the *inverse* of river discharge, and explains the strong trend of greater river connectivity in smaller streams (Figure 4; also see Equation 2).

River widening onto riparian areas and floodplains during high flow events is an important contributor to river connectivity and reactivity, increasing denitrification (Ensign et al. 2008). Because floodplain effects have not been systematically measured over large areas, we can only speculate about its importance on a regional basis. Floodplain inundation contributions to connectivity are probably generally small in headwater streams because of the steep landscapes; however, floodplain inundation is more often likely to be an important contributor in mid-size or larger rivers. Unlike the other contributors, the magnitude of floodplain connectivity probably is not dampened by the effect of greater discharge, and floodplain inundation could conceivably dominate over all other types of connectivity in mid-size to large rivers (Figure 4).

Interactions between River Connectivity and Reactivity

Our results suggest that river connectivity plays an important role in processing of biogeochemically active solutes, with especially pronounced effects in streams smaller than fifth order (Figure 2). Those small- to medium-sized streams and rivers have intermediate levels of connectivity with hyporheic zones in the streambed that happen to be appropriately scaled in terms of their residence times for efficient processing of organic matter and nitrogen through reactions such as organic matter respiration and denitrification.

The riverbed hyporheic zone has an intermediate reaction time scale of approximately 10 h, whereas the benthic biolayer has higher reactivity, with a faster time scale of processing (approximately one hour). The riverbed hyporheic zone also has an intermediate rate of connectivity with residence time scales of approximately 10 h, compared to turbulent river mixing which has a residence time scale of minutes. Consequently, the overall reaction significance is highest in riverbed hyporheic zones, where time scales of connectivity and reactivity are well matched (Figures 2 and 3). In contrast, turbulent river mixing generally cannot perform as efficiently compared to the riverbed hyporheic zone because of the mismatch between the very short residence time and comparatively longer reaction time scale in the benthic biolayer. That does not mean turbulent mixing is not a contributor to reactions. In moderate to larger rivers (fifth order and above), it appears that turbulent exchange with the benthic biolayer can dominate reactions (Figure 2).

The finding that storage zones with an intermediate amount of connectivity have the highest reaction significance generally agrees with Covino (2017), who hypothesized that there is an intermediate connectivity peak where the most efficient biological processing occurs. Our integrated metrics of connectivity and reaction significance provide a quantitative basis for assessing effects of river connectivity. We demonstrated their use in the Northeastern U.S., but the approaches are entirely compatible with all river reach

and basin scale modeling of water quality that considers reactions in "storage areas" (e.g., Wollheim et al. 2014; Helton et al. 2011; Stewart et al. 2011; Marzadri et al. 2017). While some of these previous approaches have also modeled unequal reactions across rivers and their storage zones, our RSF is an approach that can be consistently applied across all regions of the continental U.S. to evaluate what are the most important contributions to river corridor connectivity and reactivity that influence downstream water quality. At present, only hyporheic zones and turbulent mixing have been modeled, and there is need to consider more types of reaction zones such as floodplains. Also, the river network that we considered does not include the smallest streams, which are difficult to map comprehensively (Allen et al. 2018). Eventually there will be improvements in regional mapping that will allow their inclusion. Currently, the approach also ignores temporal variability in favor of keying in on well-established temporal averaging as expressed by mean annual flow conditions. Our approach therefore represents only a starting point for comprehensive regional analyses that will in the future be extended to examine effects of more detailed landscape features and temporal influences.

SUMMARY AND CONCLUSION

The importance of connectivity to downstream water quality is through its control over interactions between river water and off-channel water in closer contact with sediments of the riverbed, banks, and floodplain. Prior advancements have been through field tracer studies and modeling that incorporates HEFs into river water quality models (see Newbold et al. 1981; Bencala et al. 1984; Harvey and Fuller 1998; Runkel 1998; Alexander et al. 2007; Runkel 2007; Stewart et al. 2011). However, there are very few regional studies that identify the dominant areas of processing of riverborne contaminants. Without specific attribution of processes, it will be difficult to predict future changes responding to specific stressors, or to evaluate the relative effectiveness of management strategies intended to lessen downstream impacts.

Hydrologic connectivity has been suggested as an integrated measure for understanding the regulation of biogeochemical reactions affecting carbon and nutrient storage and processing, aquatic metabolism, food webs and energetics, as well as affecting biological habitats and biodiversity. The longitudinal and lateral fluxes in rivers, i.e., downstream flow and hydrologic exchange with bed and banks, are related components of connectivity. The balance between longitudinal and lateral fluxes determines the extent of downstream hydrologic transport relative to the extent of hydrologic storage and biological processing in off-channel compartments of the river corridor.

In this paper, we presented a dimensionless metric of connectivity, C, that integrates longitudinal and off-channel connections to quantify the balance between downstream flow and HEFs with the riverbed and riverbank. We combined our integrated metric of connectivity with a biological reactivity metric in riverbed and riverbank storage zones to quantify the reaction significance of the river corridor to downstream water quality. Our results suggested that intermediate levels of connectivity, where downstream flow and hydrologic exchanges with reactive storage zones are in balance, protect downstream water quality the most by promoting efficiency in contaminant processing. The importance of intermediate levels of connectivity is explained by the potential RSF, a dimensionless metric that considers both hydrologic and biogeochemical factors involved in water-quality functions. RSF demonstrates that reaction progress is substantial where *both* the *intrinsic reactivity* of the sediment zone and *connectivity* of the river with the sediment zone are both at least intermediate and if the time scale of storage and reaction in hydrologic exchange zones is well matched. Our connectivity and reaction significance metrics explain the relative importance and combined influence of hydrologic connectivity and sediment reactivity as it varies according to river size and flow, as well as across river corridors. The metrics of connectivity and reaction significance are easily applied over large river networks, including across the conterminous U.S. Next steps include applications that account for flood inundation, seasonal trends, and addressing scientifically based prioritization of river management strategies to protect the values and functions of river corridors.

APPENDIX

Here we explain how our metrics of connectivity and potential reaction significance were expanded in terms of measurable parameters to permit quantification. For simplicity, it was assumed that hydrologic exchange fluxes into riverbed and riverbank hyporheic storage zones, and turbulent mixing to the riverbed benthic surface storage zone, all occur independently of one another. Stonedahl et al. (2013) tested that assumption and found that the amount of exchange with riverbed hyporheic zones had no easily

discernible effect on the amount of exchange with riverbank hyporheic zones.

The hydrologic exchange fluxes were computed by replacing the empirical exchange rate coefficient in Equation (1) with measurable values of the hydrologic flux moving out and then back into a river channel of well-defined geometry:

$$\alpha_s = \frac{q_s}{d}, \tag{A1}$$

where q_s is the hydrologic exchange flux per unit area [$L^3/L^2/T$] of riverbed, d is the river depth [L], and α_s is an exchange rate coefficient representing fraction of the river exchanged per time [1/T] (Harvey et al. 1996). Note that for simplicity this formulation normalizes any hydrologic exchange flux to streambed area even if the flux occurs horizontally across the channel banks or across the top of the floodplain. Below we discuss more about the estimation of the component fluxes, specifically riverbed and riverbank hyporheic fluxes and turbulent mixing to the riverbed. The hydrologic residence time in storage zones, τ_s, is quantified as:

$$\tau_s = \frac{d_s}{q_s}, \tag{A2}$$

where d_s is the equivalent water depth or thickness of the storage zone, not accounting for the depth occupied by sediment in subsurface storage zones, and normalized to the streambed area.

Substituting the measurable parameters of Equation (A1) in Equation (1) of the main text, river turnover length is:

$$L_s = \frac{U \times d}{q_s} = \frac{Q}{q_s \times w}, \tag{A3}$$

where Q is the river discharge [L^3/T], w is the river width [L], and U is the river velocity [L/T]. Furthermore, using the identity in Equation (A1) and substituting into Equation (2) of the main text defines river connectivity as the "proportion of river flow exchanged with lateral storage areas in a river reach", which permits RSF (Equation 4 main text) to be expanded:

$$\mathrm{RSF} = \frac{\tau_s}{\tau_r} \times \frac{q_s w}{Q} L_c, \tag{A4}$$

where τ_s is the average residence time in a particular type of storage zone as measured or calculated by hydrologic models (see Equation (A2) and hyporheic and turbulent mixing sections below) [T]. Variables not defined in the Appendix are defined in the main text.

RSF computations were made using approximations of a one-hour time scale for reactivity for the turbulent river mixing to the riverbed's biolayer (1 cm) and a 10-h time scale for reactivity for hyporheic exchange flows, which may vary in depth beneath the riverbed from 1 cm (beneath bedform ripples) to 4 m and up to 100 m horizontally away from the river. A reaction time scale of one hour is appropriate for relatively fast decomposition of labile organic matter and for removal of dissolved nitrate by denitrification in a 1-cm "biolayer" comprised of a mixed layer of algal biofilms and sediment grains on the riverbed surface (Smith et al. 2006; Alexander et al. 2009; Böhlke et al. 2009; Harvey et al. 2013). The assignment of a slower reaction time scale (10 h) is appropriate for deeper sediment in hyporheic exchange flow according to the data compiled from hyporheic studies by Gomez-Velez et al. (2015).

Hyporheic Flow

Measurements and modeling of hydrologic exchange fluxes, q_s, and subsurface residence times, τ_s, have been undertaken in many rivers for both hydrodynamically driven and hydrostatically driven flows associated with various bedform morphologies (Boano et al. 2014; Cardenas 2015; Harvey 2016). Gomez-Velez and Harvey (2014) built upon the well-established modeling of Wörman et al. (2007), Marzadri et al. (2010), Boano et al. (2009), Cardenas (2009), and Gomez et al. (2012) to develop a multi-scale model of hyporheic exchange flow for large river networks called NEXSS (Networks with Exchange and Subsurface Storage). NEXSS is a multi-scale model based on fluvial geomorphic and hydraulic theory that estimates the distribution of hyporheic flow associated with ripples, dunes, alternating bars, and meanders. NEXSS is based on relatively simple analytical flow models that are solved numerically with particle tracking to compute q_s and τ_s. In NEXSS, separate calculations are made for "riverbed hyporheic exchange flow," resulting from hydrodynamic forcing of vertical hyporheic fluxes through ripples and dunes, and "riverbank hyporheic exchange flow" resulting from hydrostatic forcing of lateral hyporheic fluxes through alternating bars, banks, and meander bends. Gomez-Velez et al. (2015) used publicly available measurements of river width, depth, river discharge, groundwater discharge, stream slope, and grain size information throughout the upper Mississippi River basin as inputs to a NEXSS model. Here we used the identical code and publicly available data sources to perform riverbed hyporheic flux and

riverbank hyporheic flux calculations for mean annual flow conditions for the approximately 184,289 river reaches catalogued by NHDPlus Version 2.1 for the Northeastern U.S.

Turbulent Vertical Mixing of River Water in Contact with the Riverbed

We assume that vertical mixing of the water column is a key hydrologic flux bringing river water in contact with the biofilm and sediment surface layer (biolayer) of the riverbed. Turbulent vertical river mixing with the riverbed's biolayer was parameterized based on an estimate of the turbulent eddy diffusivity for vertical mixing in rivers, D_v $[L^2/T]$ (Rutherford 1994):

$$D_v = 0.067u^*d, \tag{A5}$$

where u^* is the river shear velocity $[L/T]$ and d is the river depth $[L]$. Shear velocity was approximated from river measurements as:

$$u^* = \sqrt{gdS}, \tag{A6}$$

and where S is the river slope $[L/L]$ and g is the gravitational constant $[L/T^2]$ (Rutherford 1994). Based on an approximate series solution (Haggerty and Gorelick 1995; Larsen et al. 2014), the exchange rate coefficient for vertical turbulent mixing to the riverbed is:

$$\alpha_v = 3\frac{D_v}{d_v^2}, \tag{A7}$$

where α_v is the exchange rate coefficient for vertical turbulent mixing to a riverbed biolayer of thickness d_s $[L]$, for which a value of 1 cm for d_v was chosen. Substituting α_v from (Equation A7) into Equation (A1) and following Equations (A2–A4) permits estimation of connectivity and reaction significance for turbulent river mixing to benthic surfaces.

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