Nitrogen cycling in large temperate floodplain rivers of contrasting nutrient regimes and management

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Abstract
Hydraulic connection between channels and floodplains ("connectivity") is a fundamental determinant of ecosystem function in large floodplain rivers. Factors controlling material processing in these rivers depend not only on the degree of connectivity but also on the sediment conditions, nutrient loads, and source. Nutrient cycling in the nutrient-rich upper Mississippi River (MISS) is relatively well studied, whereas that of less eutrophic tributaries is not (e.g., St Croix River; SACN). We examined components of nitrogen cycling in 2 floodplain rivers of contrasting nutrient enrichment and catchment land use to test the hypothesis that N-cycling rates will be greater in the MISS with elevated nutrient loads and productivity in contrast to the relatively nutrient-poor SACN. Nitrate (NO$_3^-$-N) concentrations were greatest in flowing habitats in the MISS and often undetectable in isolated backwaters except where groundwater inputs occurred. In the SACN, NO$_3^-$-N concentrations were greatest in the flowing backwater where groundwater inputs were high. Ambient nitrification in the MISS was twice that in the SACN and tended to be lowest in the main channel. Denitrification was 3× greater in the MISS than that in the SACN, N-limited in both rivers. Community production/respiration was >1 in the MISS and likely provisioned labile C to fuel microbial metabolism and dissimilatory NO$_3^-$-N reduction, whereas the heterotrophic (production/respiration < 1) nature of the SACN likely limited microbial metabolism and NO$_3^-$-N dissimilation. It appears that N-cycling in the SACN was driven by groundwater, whereas that in the MISS was supported mainly by water column N-sources.

KEYWORDS
connectivity, denitrification, Mississippi River, nitrate, nitrification, productivity, St. Croix River

1 | INTRODUCTION

Channel–floodplain connectivity is a fundamental determinant of ecosystem function in large floodplain rivers (Amoros & Bornette, 2002). The factors controlling material processing in such rivers depend not only on the degree of connectivity and material delivery but also on the resultant sediment carbon and oxygen conditions found on the floodplain. Channels and lateral floodplain habitats of floodplain rivers retain and process nutrients and sediments depending on the degree of hydraulic connection (Noe & Hupp, 2009). Primary determinants of connectivity include river discharge and channel morphology. During floods, hydraulic connection is high, with solutes and particulate matter distributed across the floodplain. As floods subside, hydraulic connection is reduced in isolated habitats, particles settle from the water column, and biological assimilation and biogeochemical processes continue, resulting in declining water column concentrations...
of nitrate and ammonium (Welti, Bondar-Kunze, Singer, et al., 2012; Hein, Baranyi, & Schiemer, 2004).

The geomorphology of large floodplain rivers is similar globally (Lewin, 1978), often consisting of isolated backwaters (IBW), flowing backwater (FBW) channels, and main channels (MC; Lewis Jr., Hamilton, Lasi, Rodriguez, & Saunders III, 2000). In FBW, hydraulic retention time is intermediate between IBW and MC. The rapidly flowing MC typically contains carbon-poor sediments and short hydraulic retention time, limiting certain microbial nitrogen uptake and removal, whereas oxygenated water inhibits denitrification (DEN) and release of sediment-bound phosphorus. In temperate floodplain rivers, IBW tend to exhibit lower water column nitrate and greater phosphorous concentrations during base flow periods than do more connected backwaters (Heiler, Hein, Scheimer, & Bornette, 1995). During extended periods of disconnection, water column nitrate concentrations often decline below detection due to uptake and removal processes and lack of surface water replenishment. Backwaters with groundwater inputs will exhibit less severe nitrate depletion. In contrast, dissolved phosphorus concentrations may increase, as phosphorus-rich sediments become anoxic due to the large microbial oxygen demand and release of sediment-bound phosphorus.

This general pattern of N-cycling is well described for enriched temperate zone floodplain rivers (e.g., Danube: Welti, Bondar-Kunze, Tritthart, Pinay, & Hein, 2011; Seine: Sebilo et al., 2006; and Upper Mississippi River [UMR]: Richardson, Strauss, Monroe, Bartsch, & Soballe, 2004; Strauss, Richardson et al., 2004). Yet the role of ecosystem productivity and process drivers (e.g., nutrient loading), which may have strong influence on N-cycling processes, have not been compared in rivers of contrasting nutrient loading and productivity. The St. Croix National Scenic Riverway (SACN) and the Mississippi National Recreation Area (MISS) are located on temperate floodplain rivers draining catchments of contrasting land use and resultant nutrient and sediment loads and anthropogenic impact (Table 1). Domination of agriculture and greater human population in the MISS catchment results in greater movement of phosphorus and nitrogen from land to river in the MISS, relative to the SACN (Kroening & Andrews, 1997). The St. Croix River is a nationally unique ecosystem with a relatively pristine environment, high biological diversity, exceptional water quality, and progressive management history. More than 30 years since federal designation, the St. Croix River Basin is still predominantly forested (Larson et al., 2002) and the river corridor above St. Croix Falls is representative of pre-European settlement conditions (Minnesota-Wisconsin Boundary Area Commission, 2002). In contrast, the study reach of the MISS corridor begins in rural environments, passes through two large metropolitan cities (Minneapolis and St. Paul), and then returns to a rural setting at its downstream end. Despite substantial water quality degradation, the river valley contains diverse flora and fauna, and much of the river still has some connection to the floodplain, maintaining some historic river ecosystem function (Lafrancois, Magdalene, Johnson, Vandermerlen, & Engstrom, 2013).

Our understanding of habitat-specific N-cycling in less enriched temperate zone floodplain rivers (e.g., SACN) is poorly tested. The striking contrast between the MISS and SACN in nutrient and sediment loading provides an opportunity to evaluate important questions relevant to management regarding the role of natural river ecosystem functioning as a determinant of nutrient retention and cycling (especially nitrogen) by floodplain rivers. In particular, Lake St. Croix, a natural lake within the SACN, is undergoing rapid increases in nitrate concentrations and is categorized as mesotrophic (Vander Meulen & Elias, 2008). The goals of our research were to (a) characterize nutrient conditions in MC, FBW, and IBW of the SACN and MISS over a range of river discharge and (b) investigate biogeochemical processes affecting N-cycling in these habitats.

### 2 | MATERIALS AND METHODS

#### 2.1 | Site description

Our study focused on a set of MC, FBW, and IBW complexes (n = 2 sites per habitat) in each river (Figure 1). Sediment composition was variable but primarily sand in MC sites, a mixture of sand, silt, clay in FBW, and a fine clay and silt in IBW sites. Water depth ranged from 0.5 to 1 m, depending upon discharge (range, SACN: 29.7 to 414.5 m³/s; MISS: 73.6 to 1.359 m³/s).

#### 2.2 | Nitrogen biogeochemistry and sediment nutrient assays

Biogeochemical assays and sediment nutrient measurements were conducted in the SACN and MISS to determine spatial and temporal variation in rates of nitrogen cycling. In May and July 2008 and August 2009, at each site, we collected duplicate sediment cores (7.6-cm diameter, 5-cm depth), which were homogenized, subsampled, and analysed for nitrification, DEN, ammonium (porewater and exchangeable NH₄⁺-N), and porewater nitrate–nitrite (NO₃⁻-N), total carbon (TC), and total nitrogen (TN). Sediment porewater was collected by centrifugation for NH₄⁺-N and NO₃⁻-N and analysed following Richardson et al. (2004). Unionized porewater ammonia concentrations (NH₃-N) were calculated based on in situ pH and temperature measurements, taken during sampling, following Emerson, Russo, Lund, and Thurston (1975). Sediment bulk density, water content (a surrogate of organic matter content), and porosity were determined following Robertson, Coleman, Bledso, and Sollins (1999). Sediment total carbon (C) and nitrogen (N) were analysed on an Elementar™ VarioMax CN analyser (Elementar, Inc., Hanau, Germany). Sediment DEN was measured by the acetylene block technique to determine the ambient

### TABLE 1 | Catchment population and land use characteristics for the Upper Mississippi River (MISS, above the Minnesota River) and St. Croix River (SACN, above the confluence with the MISS)

| Variable                        | Basin          | MISS | SACN |
|---------------------------------|----------------|------|------|
| Basin size (km²)                | 51,840         | 20,040 |
| Basin population (no. ind.)     | 2,358,393      | 313,501 |
| Population density (ind/km²)    | 45.6           | 15.6  |
| Forested area (km²)             | 20,910         | 11,651 |
| Percent basin forested          | 40.7           | 58.4  |
| Agricultural area (km²)         | 17,574         | 4,843  |
| Percent basin agriculture       | 34.2           | 24.3  |
| Urban area (km²)                | 1,515          | 275.2  |
| Percent basin urbanized         | 3.0            | 1.4   |
DEN rate (no amendment), or C amended or N amended (C or N limitation), and the combined C and N to determine potential rates (DEN enzyme assay; denitrification assay [DEA]; see Richardson et al., 2004, for method details). Potential nitrification was determined by a modification to the ISO method 15685 (ISO, 2012) where assay buffers and ammonium were omitted from the amendments.

2.3 | Water quality and nutrient concentrations

Water column samples were collected mid-depth at each site concurrent with sediment sampling (in 2008 and 2009) and measured for TN, NO$_3^-$-N, NH$_4^+$-N, total phosphorus (TP), and soluble reactive phosphorus (SRP). Water was immediately filtered (Whatman® model GD/X 0.45 μm nominal pore size) prior to analysis of NO$_3^-$-N, NH$_4^+$-N, and SRP. Samples for NH$_4^+$-N and NO$_3^-$-N were analysed following Richardson et al. (2004). SRP samples were frozen (~20 °C) until analysis using the ascorbic acid method (American Public Health Association, 1998). TN and TP samples were unfiltered, acidified to pH ~2, and refrigerated (~4 °C). TN was determined using persulfate digestion, followed by the automated cadmium reduction method, and TP was determined using persulfate digestion, followed by the ascorbic acid method (American Public Health Association, 1998). Dissolved oxygen (DO, mg/L), pH, temperature (°C), and conductivity (μS/cm) were measured at mid-depth, at all sites, with a 600XL sonde (Yellow Springs Instrument Company, Inc., Ohio, USA; Table S1). Quality assurance procedures followed Soballe and Fischer (2004). Instantaneous nutrient loads in the MC for each river over a range of discharge were determined following standard U.S. Geological Survey procedures (Conn et al., 2015; Table S2).

2.4 | Productivity and metabolism

Water quality sondes were deployed in each river at MC, FBW, and IBW sites for continuous measurements of DO and temperature for 1 week prior to water sampling (during July–August 2007 and May–June 2009). Open-channel, single-point ecosystem metabolism was estimated using diurnal changes in DO (Owens & Crumpton, 1995). Photosynthetically active radiation was measured at the same locations with an LI-COR model LI-250 metre (Lincoln, Nebraska, USA) and underwater quantum sensor to estimate euphotic zone depth in accordance with Wetzel (2001). Gross and net production and respiration were modelled using the single-station method (Bales & Nardi, 2007).

2.5 | Statistical analyses

Our goal was to identify large differences in patterns of N-cycling rates between rivers and among habitats of the two rivers and to identify drivers of these rates and patterns. Analysis of variance (JMP®, 2016; Table S3) was used to test for differences in magnitude of response variables among rivers, habitats, interaction of habitats × rivers, and sample periods (dates). An information-theoretic approach was used to identify the best models that predicted DEA rates based on a suite of predictor variables. Separate analyses were conducted for each river that resulted in a set of predictor variables that had the minimum Akaike Information Criteria (AIC) for observed DEA rates. We present the best models based on Burnham and Anderson (2002) where competing models with Δi values <2 are the best Kullback–Liebler model.

\[ \Delta_i = AIC_i - AIC_{\text{min}} \]
where $AIC_{min}$ is the minimum AIC value for all models and $AIC_i$ is the ith competing model. Similarities in the suite of predictors were compared to conceptual models in an attempt to describe processes occurring under the different nutrient regimes in each river. We used model averaging, which tends to shrink estimates of weaker terms, yielding better predictions. Models were averaged with respect to $AIC_i$ weight following:

\[
AIC_i \text{ weight} = \exp[-0.5 \times (AIC_i - AIC_{min})]
\]

We averaged models with 1 to 8 terms using a cut-off $AIC_i$ weight quantile of 0.95 and present predictor coefficients with confidence intervals that do not include zero (JMP®, 2016).

3 | RESULTS

3.1 | Water column nutrients

Water column NO$_3$-N concentrations (Figure 2a,b) were, on the average, ~10× greater in the MIS than those in the SACN. Average NO$_3$-N concentrations were highest in the FBW in MISS and lowest in IBW. In the SACN, the FBW had the highest average NO$_3$-N concentrations, whereas the MC had the lowest.

Water column NH$_4$+N concentrations (Figure 2c,d) were, on average, greater in the SACN than those in the MISS. In the MISS, NH$_4$+N concentrations in the FBW and MC were similar, whereas those in the IBW were lower. This pattern contrasts that seen in the SACN, where the FBW contained NH$_4$+N concentrations 4× those of the MC and the IBW. Particularly striking was the large increase in NH$_4$+N in the FBW of SACN in July 2008.

TN concentrations (Figure 2e,f) were, on average, >3× greater in the MISS than those in the SACN. TN concentrations in the MC and FBW of the MISS were identical, and IBW was 1 mg/L lower. In contrast, TN concentrations in the FBW of the SACN were greater than in the MC and the IBW. TN concentrations increased in all habitats as flooding occurred. This was particularly pronounced in the MISS during the flood of 2008 when TN concentrations dropped over 1 mg/L in all habitats after flooding subsided in July. In the SACN, the pattern was confounded by TN concentrations that were elevated in the FBW after floods subsided. Local inputs of groundwater and a nitrogen-rich tributary likely caused this pattern (Kroening & Andrews, 1997).

SRP concentrations (Figure 2g,h) were >3× greater in the MISS than those in the SACN. Average SRP concentrations in the MISS were greatest in the FBW and lowest in the IBW. SRP showed strong habitat-specific and year differences. In 2007, SRP in the IBW in the MISS was half that in the MC or FBW during both July and August, whereas in 2008, flooding appeared to homogenize concentrations across all habitats in May, with divergence and increased concentrations occurring in July under lower river discharge. SRP concentrations in the MISS showed similar patterns in 2009 but with lower river discharge. In the SACN, average SRP concentrations were similar across all habitats on the aggregate, but with IBW showing lower concentrations in 2007 and 2008. Floods in 2008 also caused a greater homogenization than in 2007 and 2009, followed by divergence across habitats.

TP concentrations (Figure 2i,j) in the MISS were 3× greater than those in the SACN. In the MISS, TP concentrations were slightly lower in the FBW and the MC than the IBW. In the SACN, MC concentrations were lower than the IBW or FBW. In contrast, TP concentrations in the SACN in May ranged from 0.05 mg/L in the FBW to 0.09 mg/L in the IBW. In late July 2008, TP concentrations in the MC and IBW declined slightly from those in May, whereas those in the FBW nearly doubled (0.09 mg/L).

3.2 | Porewater dissolved inorganic nitrogen

Average concentrations of sediment porewater NH$_3$-N (Figure 3a,b) in the MISS were ~2× those in the SACN. Among habitats in the MISS, NH$_4$+N concentrations were highest in the FBW and lowest in the IBW. Sediment NH$_3$-N concentrations in the SACN were highest in the MC and lowest in the FBW. Sediment NH$_3$-N concentrations were highly variable over time (Figure 3a,b). During July 2008, no NH$_3$-N porewater samples were analysed from the SACN.

Exchangeable NH$_4$+N in sediment porewater of the MISS was ~7× greater than that in the SACN (Figure 3c,d). In the MISS, concentrations of NH$_3$-N were highest in the FBW and lowest in the IBW. In contrast, in the SACN, concentrations of exchangeable NH$_4$+N were highest in the FBW and lowest in the IBW. Generally, there were no differences by date within rivers, but MISS sediments generally contained substantially greater concentrations of exchangeable NH$_3$-N than SACN. Porewater NO$_3$-N concentrations were ~7× greater in sediments of the SACN than that of the MISS (Figure 3e,f). Concentrations of porewater NO$_3$-N, in the SACN, were highest in the sediments of the FBW and lowest in the IBW. In the MISS, the highest NO$_3$-N concentrations were found in MC sediments and lowest in the IBW.

3.3 | Sediment C and N

The total C (% of total mass) in the top 5 cm of sediments was ~5× greater in the MISS than that in the SACN (Figure 4). Average % C in the MISS was greatest in FBW, whereas in the SACN, the IBW sediments had the greatest % total C. Sediment total % N in the SACN IBW was 3× greater than in other SACN habitats. Sediment % total N in MISS were similar across all habitats. The great disparity in sediment total C between the two rivers resulted in a 2× greater C:N (atoms) in the MISS relative to the SACN.

3.4 | Potential nitrification

Average rates of potential nitrification were 6× greater in the MISS than those in the SACN (0.49 ± 0.13 μg-N/cm²/h), ranging from 1.9 to 5.6 μg-N/cm²/h in MISS and 0.005 to 1.3 μg-N/cm²/h in SACN (Figure 5). Rates were also greater in July (MISS: 3.8 ± 0.7 μg-N/cm²/h; SACN: 0.7 ± 0.2 μg-N/cm²/h) than in May (MISS: 2.3 ± 0.5 μg-N/cm²/h; SACN: 0.3 ± 0.1 μg-N/cm²/h). Nitrification was greater in IBW in both rivers during July (2008 and 2009), with differences most pronounced in July 2009 (MISS: 5.6 ± 0.08 μg-N/cm²/h; SACN: 1.3 ± 0.2 μg-N/cm²/h).

3.5 | Denitrification

Ambient DEN rates in the MISS averaged ~3× greater than those in the SACN (MISS: 0.44 ± 0.3 μg-N/cm²/h; SACN 0.15 ± 0.1 μg-N/cm²/h; Figure 6). In the MISS, the greatest rates of ambient DEN were found in the MC (0.72 ± 0.5 μg-N/cm²/h) and lowest in the IBW.
In the SACN, greatest rates of DEN occurred in the FBW (0.45 ± 0.17 μg-N/cm²/h) and lowest in the IBW (undetectable). DEN rates in both rivers were strongly N-limited (only slightly C-limited) as indicated by the large increase of DEN with the addition of NO₃⁻-N and NO₃⁻-N + C (=DEA). Sediments from the MISS, with
added NO₃, exhibited average DEN rates of 10.0 ± 1.1 μg-N/cm²/h, whereas those in the SACN averaged 2.4 ± 0.5 μg-N/cm²/h. Rates were further elevated with the addition of NO₃⁻⁻N+C.

In the MISS, the IBW was most strongly N- and C-limited, whereas the MC was the least. Addition of C-alone had little effect on DEN in any habitat. The IBW generally exhibited the strongest N limitation on all dates (Figure 6a,b,c), whereas FBW and MC showed less distinct limitation. In the SACN, the IBW also exhibited the strongest N limitation, particularly in summer when water temperatures were highest and river discharge was lowest.

DEA was significantly greater in the MISS (p < .0001) and across habitats (p < .0001) in both rivers (Table S3). Sampling period was not significantly different among habitats in either river. Multiple regression models (Table 2) developed for the MISS and SACN indicate differences in drivers of DEA between the two rivers. In MISS, river discharge was important in all models, as was nitrification, sediment porosity, and surface water (NO₃⁻⁻N or NH₄⁺⁻N). Sediment C:N ratio was also identified in one model as a significant driver of DEA. In the SACN, the best models predicting DEA included ambient nitrification, porewater NO₃⁻⁻N, and sediment water content.

3.6 | Metabolism

Ecosystem metabolism in 2007 and 2009 showed differences between the two rivers. Across all habitats, average gross primary production was greater in the MISS (9.5 mg O₂/L/d ± 2.1) than that in the SACN (3.0 mg O₂/L/d ± 0.89; Table 3). Average respiration (R) was slightly greater in the MISS (7.3 mg O₂/L/d ± 0.9) than that in the SACN (5.6 mg O₂/L/d ± 1.0). Average net primary production (NPP) was greater in the MISS (2.2 mg O₂/L/d ± 1.2) than that in the SACN (−2.6 mg O₂/L/d ± 0.86). The ratio of gross primary production/R, an index of ecosystem metabolic status, indicates that the MISS is
predominantly autotrophic during the growing season (P/R = 1.3) and was substantially greater than the SACN (P/R = 0.5), which appears to be predominantly a heterotrophic system (with respiration the dominant ecosystem metabolic process). In the MISS, NPP was positive in channels and backwaters (MC: 3.2 mg O₂/L/d ± 2.7; IBW: 1.2 mg O₂/L/d ± 0.39) and the P/R ratio was always >1. In contrast, habitats of the SACN generally exhibited negative NPP (MC: −1.9 mg O₂/L/d ± 1.1; IBW: −4.73 mg O₂/L/d; FBW: −3.48 mg O₂/L/d), and the P/R ratio was usually <1.

**DISCUSSION**

The SACN and MISS rivers exhibit spatial patterns in nitrogen biogeochemistry similar to other floodplain systems. The two rivers, however, display substantial differences in habitat-specific nitrogen cycling rates, sources of nitrate driving N-cycling, and rate of primary...
production, a source of labile carbon needed to fuel the nitrogen biogeochemical reactions (Fischer, Kloep, Wilzcek, & Pusch, 2005; Wetti et al., 2012). Both rivers contain intact floodplains and connection between channels and floodplains. Further, in both rivers, channels and backwaters function as in other large floodplain rivers: main and secondary channels typically contain most of the nitrate; backwater lakes are typically devoid of NO$_3^−$ (Heiler et al., 1995).

Yet the SACN and MISS are strikingly different rivers with contrasting nutrient loads, nitrogen cycling rates, and productivity. Average nitrogen and phosphorus concentrations in the MISS are at $\sim 2\times$ those in the SACN; average rates of DEN in the MISS are $\sim 3\times$ greater than those in the SACN; average rates of potential nitrogen nitrification in the MISS are $\sim 6\times$ those in the SACN. Rates of potential DEN in the MISS were $4\times$ greater than those in the SACN. Rates of ambient DEN in the MISS were similar to those reported by Richardson et al. (2004) in the UMR Pool 8 in the MC (during summer), IBW, and FBW (during spring floods). Ambient DEN rates of the SACN were similar to those reported for flooded riparian soils of the Rhine River (Olde Venterink, Hummelink, & Van Den Hoorn, 2003), which also varied depending on NO$_3^−$ delivery and carbon availability. Nitrification rates in the MISS in this study were consistent with those in Strauss et al. (2004) measured in the UMR Pool 8. Nitrification likely supported the high rates of DEN found in the MISS relative to that in the SACN.

Our results show that the MISS is “supercharged” with fuel needed to drive nitrogen biogeochemistry at high rates, compared to the SACN system, which has a leaner supply of nitrogen and carbon to drive the biogeochemical engine. In the MISS, DEA was generally much greater than reported in the UMR Pool 8 (Richardson et al., 2004). DEA from the SACN were much lower than those in the MISS and similar to those of the UMR Pool 8 reported during spring floods when floodwaters were cool and nitrate laden. Rates of DEA in the Danube River are highly variable but are intermediate to those of the SACN and MISS (e.g., 0.02 to 19.8 μg/N/cm$^2$/h; Wetti et al., 2011).

Both the MISS and SACN exhibited N-limited DEN. In IBW, DEN was nearly undetectable except when nitrate was delivered via flooding. Carbon limitation was not observed in either river. Other
studies have shown that nitrogen limitation is a general phenomenon related to delivery of nitrate (e.g., Richardson et al., 2004; Welti et al., 2012). Additionally, the consortia of denitrifying bacteria vary in their response to fluctuating porewater oxygen concentrations, exhibiting reduced DEA in habitats with variable oxygen concentration (Tatariw, Chapman, Sponseller, Mortazavi, & Edmonds, 2013), as likely found in the MC of both the MISS and SACN. Further, regression models suggest that nitrate is being supplied differently to denitrifiers in the two rivers. In the MISS, water column sources of both nitrate and ammonia likely control DEN (Figure 7). Sediment porosity is an important factor, especially in the MISS, allowing sediments to be provisioned with water column nitrogen. Further, sediment porewater in the MISS is depleted of nitrate suggesting that sediment nitrate consumed by DEN is not replenished by groundwater. Sediment total carbon and nitrification rates are also substantially greater in the MISS than those in the SACN, likely supporting the high rates of DEN. However, the role of surface water in the MISS is complicated (Figure 7). Negative relationships among surface water dissolved inorganic nitrogen (DIN: NO$_3^-$-N + NH$_4^+$-N) and DEA are likely linked to habitat patterns of nitrate availability—in that highest DEAs occurred in IBW—areas typically depleted of surface water DIN, and lowest DEAs in MC, where DIN and discharge is relatively high but DEA is lower. Typically, porewater nitrate is also low in the MISS, but porosity is quite high allowing surface water nitrate to penetrate into sediments to support DEA. Nitrification is relatively high in the MISS, further provisioning sediment nitrate in support of elevated DEA rates.

In contrast, DEA in the SACN is relatively low and likely dependent on groundwater sources of DIN. Surface waters are low in DIN, and river discharge likely supplies little DIN to denitrifiers. In the SACN, greater concentrations of porewater nitrate and greater sediment water content suggest that groundwater, supplemented with nitrification, provides nitrate in excess of metabolic demands of the sediment microbial community (Welti et al., 2012). The relatively low sediment carbon content and low rates of primary production in the SACN likely further limit microbial metabolism and N-cycling (Stelzer, Scott, & Bartsch, 2014). In these two rivers of contrasting productivity, it is highly likely that N-cycling rates in the MISS are being supported by carbon produced in the water column and captured in sediments (Tatariw et al., 2013).

In the MISS, elevated sediment ammonium and nitrification, but low concentrations of sediment nitrate, suggests that DEN was rapid enough to remove nitrate at rates greater than nitrification. Further, in the MISS, a positive relationship between nitrification and DEA suggests a tight coupling between these processes and potential nitrate limitation. Sediment ammonium concentrations in the MISS are likely linked to high sediment carbon and nitrogen concentrations via mineralization and oxygen limitation of nitrifiers to process this ammonium. In the MISS, percent sediment total C and N and C:N ratios were generally two to five times greater than those measured in the SACN sediments, particularly in the flowing channels. These elevated C and N concentrations in the sediments suggest that high rates of organic matter accumulation occur in the MISS. Dodds et al. (2013) found the lower Mississippi River (nr. Baton Rouge, Louisiana, USA) to be almost completely heterotrophic except for short periods in winter. Although Houser, Bartsch, Richardson, Rogala, and Sullivan (2015) found the MISS (nr. La Crosse, Wisconsin, USA) MC to be autotrophic during the growing season, associated with elevated chlorophyll a concentrations and a drawdown of soluble phosphorus. The elevated rates of primary production (e.g., P/R ratio 1.1 to 1.6) in the MISS channels suggest that the source of this sediment organic matter is likely autochthonously produced phytoplankton. Entrainment of phytoplankton into river sediments can provide a high-quality source (Canuel, 2001) of both carbon and nitrogen to drive N-cycling processes (Fischer et al., 2005). Movement of particulate C into benthic sediments is common in sandy sediments of large rivers and likely supports heterotrophic biogeochemical processes (Fischer, Sukhodolov, Wilczek, & Engelhardt, 2003). The high concentrations of C and N may also be derived from bacterial secondary productivity in sediments. Fischer et al. (2005) measured bacterial carbon production in channel sediments of the Elbe River in Germany (0.95 g C m$^{-2}$ h$^{-1}$), which was three to five times greater than that in nearshore areas and N-cycling was a significant portion of the carbon budget.

In contrast to the MISS, origins of C and N in the SACN are likely to be substantially different and derived less from autochthonous but more from allochthonous sources. Reduced nutrient concentrations of the SACN limit water column productivity. Further, channels of the SACN course through wooded riparian zones where the forest canopy and shading often reach mid-channel. Water column metabolism in the SACN was typically more heterotrophic (P/R ranging 0.1 to 0.9) than that in the MISS. Sediment C and N in the SACN reflect the reduced

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**FIGURE 7** Graphical representation of the best predictors of denitrification assay (DEA) rates for the Upper Mississippi (MISS) and St. Croix (SACN) rivers based on regression model averaging with an Akaike Information Criteria (AIC), weight quantile of $\geq 0.95$. Black arrows represent positive effects of the model coefficient for each independent variable, and negative effects are dashed arrows. Water content is a surrogate for sediment total carbon. Grey arrows indicate variable relationship with DEA rates.
water column productivity, such that C (%) and N (%) were at least half that of the sediments in the MISS. The implications are that labile C available to fuel microbial activity in the SACN is much reduced relative to those of the MISS; further, sediment ammonium concentration are less than half than those in the MISS, whereas sediment nitrate is 30 times that in the MISS sediments. We suspect that local groundwater inputs were the source of nitrate because nitrification rates were relatively low and likely not capable of producing such large concentrations of nitrate, particularly in the presence of relatively high DEA.

Differences between these two rivers in nutrient loading and productivity are likely related to differences in catchment land use and sewage outfall volume (Kloiber, 2004). In particular, greater human population densities, greater agricultural land use, and less forest result in greater nutrient loading in the MISS than in the SACN. These patterns have existed for at least a century (Lafrancois, Magdalene, & Johnson, 2009) but with indications of declining phosphorus and increasing nitrogen load in the SACN and MISS rivers. Management of agriculturally derived sediments may be contributing to declining P loads, whereas increasing nitrate loads likely originate from a number of sources including atmospheric, agricultural, and urban (Kloiber, 2004; Kroening & Andrews, 1997).

5 CONCLUSIONS

Two large floodplain rivers in the UMR catchment of differing nutrient load and productivity showed similar spatial patterns of nitrogen biogeochemical functioning. DEN rate tended to be highest in backwater lakes and side channels where sediment C and N accumulate. However, rates of nitrogen cycling and carbon and nitrogen accumulation in sediments were much greater in the MISS where loads of N and P and productivity are much greater than in the SACN. We suggest that the fuel needed to support high rates of N-cycling is paradoxically provided by these elevated nutrient inputs from surrounding agricultural and urban landscapes. Current anthropogenic nutrient inputs likely far overwhelm the capacity of these rivers to naturally remove the inputs before being transported downstream.

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SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

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