Effect of habitat type on in-stream nitrogen loss in the Mississippi River

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with 4 figures and 1 table

Abstract: Eutrophic and hypoxic coastal waters are often associated with high nutrient inputs from riverine systems. For example, nitrogen (N) export from the Mississippi River into the Gulf of Mexico has been identified as an important factor causing eutrophication and seasonal hypoxia. Modelling studies of N flux in large rivers, including the Mississippi River, suggest that much of the N that enters rivers remains in solution and is exported downstream. However, patterns of N cycling in the Mississippi River are complex and vary according to habitat type and season. Here we use spatial habitat data and empirically derived denitrification rates to extrapolate N loss to various reaches in 2,400 km of the Mississippi River from Minneapolis, Minnesota to the Atchafalaya diversion. Our results indicate that 9.5% of the total N load is lost through denitrification in the river and that reaches containing large areas of impoundments and backwater lakes exhibit elevated rates of N loss. The northern 1,041 km reach of the river contains significant areas of impoundments and backwater lakes and yielded a total N loss from denitrification of 89,172 t N y⁻¹. In comparison, total N loss from the southern 1,352 km open river was 69,872 t N y⁻¹. Our results are consistent with high throughput of N in large rivers, but specify that habitat diversity, channel complexity, and retention time are important factors affecting nitrogen loss in rivers.

Keywords: Mississippi River, nitrogen, denitrification, habitat type, habitat diversity, modeling

Introduction

Large rivers are the primary conduits that transport nitrogen (N) leached from the landscape to coastal systems. Increasing interest has been directed toward understanding and managing N flux in rivers because of the often adverse effects of additional N on coastal systems (Howarth et al. 1996, Alexander et al. 2000). Delivery of reactive nutrients, especially N, from large rivers into coastal systems has been cited as a primary cause of coastal eutrophication resulting in conditions such as decreased biodiversity, losses of submerged aquatic vegetation, oxygen depletion, and blooms of harmful algae (Nixon 1995, Carpenter et al. 1998). Nitrogen flux, regardless of channel size, is the net result of reach-scale N loadings and exports. The difference between loadings and exports is accountable through in-stream N losses and retention. A primary mechanism of in-stream N loss is denitrification, the anaerobic respiration of organic carbon using oxidized N ions (e.g., NO₃⁻ and NO₂⁻) as microbial electron acceptors. Denitrification is considered a permanent loss from systems because its final product, N₂, can freely diffuse out of the aquatic environment and into the atmosphere. In contrast, N retention is not a loss of N from a system but rather a temporary storage. Nitrogen retention in riverine systems is primarily a combi-
tion of abiotic and microbial sequestration in benthic materials and biotic uptake in the channel.

Much has been learned about N flux in streams and small rivers through a variety of empirical techniques including the use of stable isotope tracers and process level studies. In general, these studies have determined that in-stream N loss and retention in small streams are directly linked to N concentrations, biological activity, channel morphology, and hydrology (Duff & Triska 2000, Peterson et al. 2001). Low-N headwater streams generally have high in-stream N loss and retention because of their high surface-to-volume ratio with the biologically active benthos (Peterson et al. 2001). These relatively high processing rates can result in retention or loss of all N inputs within a few kilometers (< 1 day). Larger streams generally exhibit lower uptake rates primarily because of increases in discharge, depth, and water velocity (Wollheim et al. 2001). Streams with higher N concentrations such as those associated with agricultural runoff generally have higher loss rates, however lower residence time and high inputs often overwhelm the losses (Kemp & Dodds 2002, Bohlke et al. 2004, Mulholland et al. 2008).

Nitrogen losses in most large rivers are probably small relative to N load, but rates of N-cycle processes are seldom directly measured in these systems because the analytical techniques commonly employed to study N flux in smaller systems are usually financially or practically prohibitive in large rivers (Fennel et al. 2009). As a result, studies of larger rivers have often used analyses of N budgets or statistical and computer models to elucidate patterns of N concentrations or to determine the effects of N-cycle processes (Howarth et al. 1996, Caraco & Cole 1999, Alexander et al. 2000, McIsaac et al. 2001, Seitzinger et al. 2002, Donner et al. 2004, Wollheim et al. 2006, Alexander et al. 2009). While these types of studies can be quite powerful and informative, they are often far removed from the fine spatial and temporal scales at which the processes are actually occurring. In all lotic systems, various geomorphic and human influences influence the hydrology and physical structure of the system and can be important determinants of N flux. On one extreme, large floodplain rivers can be very wide and contain a complex network of large and small channels, backwater lakes, and wetlands (e.g., Amazon River, Upper Mississippi River, and portions of the Danube River). Many of these habitats characteristically have increased water retention time and organic rich sediments which could be capable of high N processing (Mitsch et al. 2001, Richardson et al. 2004, Strauss et al. 2004). However, connectivity of flow among these areas is critical to realizing the high potential (Hein et al. 2004). On the other extreme, decreased N processing likely occurs in homogeneous confined channels where water transport is relatively unimpeded resulting in short residence times (e.g., Ohio River, Lower Mississippi River, and Rhine River).

Only a few studies have directly measured denitrification in large rivers and have found absolute rates to be variable and related to habitat types, nitrate concentration, sediment carbon, and temperature or season (Garcia-Ruiz et al. 1998, Richardson et al. 2004, Yan et al. 2004). One of these studies was our recent investigation on a 27-km reach of the Upper Mississippi River where we reported that denitrification exhibited distinct spatial and temporal patterns (Richardson et al. 2004). Nitrogen loss from denitrification was greatest during the spring and summer seasons and disproportionately more N was lost in the backwater lakes and in the impounded area created by the lock and dam system used to facilitate navigation. Nitrogen loss was low in the flowing channels at all times of the year. These spatial and temporal rates were then used to estimate that 7% of the NO$_3^-$ entering the system is lost through denitrification and another 13% is retained in the reach. In this study, we extrapolate our earlier results to estimate N loss through denitrification for nearly 2,400 km of the Mississippi River, from Minneapolis, Minnesota to the Atchafalaya diversion (ca. 500 km upstream of the confluence with the Gulf of Mexico). This analysis provides reach-scale and total river N loss as well as provides information on importance of certain channel features to overall N loss. A better understanding of these channel features in the Mississippi River can be useful if promoting N loss in the river is a desirable management goal.

**Methods**

The 3,700 km Mississippi River drains about 41% of the land area in the conterminous United States (Fig. 1A) and supplies an annual N flux of nearly 1.56 x 10$^8$ t N to the northern region of the Gulf of Mexico (Goolsby & Battaglin 2001). Of the total amount of N that is transported in the Mississippi River much is in the inorganic form of NO$_3^-$ and can be accounted for by anthropogenic N inputs, primarily inorganic N fertilizers, within the drainage basin (McIsaac et al. 2001, Booth & Campbell 2007). For this study, the Mississippi River was divided into two main reaches based on geography and river features: the northern segment containing the navigation pools and the southern open river. The northern stretch of the river (north of Cairo, Illinois) is termed the Upper Mississippi River, but only part of that reach (north of St. Louis, Missouri) is segmented into a series of navigation pools delineated by locks and dams (Fig. 1B). The navigation pools, numbered sequentially 1 through 26 from the north, main-
tain distinct aquatic habitats including the main channel, side channels, impoundments, and backwaters. The open river (south of St. Louis) lacks the diversity of habitats and consists of a main channel and occasional side channels.

More detailed descriptions of the main channel, side channel, impounded, and backwater habitats can be found elsewhere (Wilcox 1993, Strauss et al. 2004, Houser & Richardson 2010) and will only be summarized here. In the Mississippi River, flow is concentrated in the main channel resulting in a high kinetic energy habitat that is deep (> 3 m), usually devoid of aquatic vegetation, and predominately sandy sediment with low carbon (C) and N availability. However, N concentrations in the water column are dominated by NO$_3^-$ and are generally higher than those in the other habitats. Side channels are shallower than the main channel, often contain macrophytes along the channel margins, and the sediments are a mixture of sand and silt with a low C and N content. Impounded areas are effectively depositional areas with sediments primarily composed of silt and clay. These sediments have a higher C and N content than those of the main and side channels and sometimes contain macrophytes in shallow areas. The backwater habitats are often described as lentic or wetland-like environments (except during high flow conditions) and characteristically con-

Fig. 1. The Mississippi River watershed (A) covers 41% of the conterminous United States (shaded area on map). The two main reaches analyzed in this study (B) were the reach containing the navigation pools (Minneapolis, Minnesota to St. Louis, Missouri) and the open river reach (St. Louis, Missouri to the Atchafalaya River diversion in Louisiana). The circles located on the river are the nodes of the 30 sub-reaches used. Select sub-reaches of the northern reach and all the open river (OR) reaches are labelled. Navigation pool 7 (C) is a representative example of the aquatic habitat spatial data used to extrapolate N loss in the river.
Table 1. Habitat-specific seasonal rates of denitrification (standard error) used to extrapolate N-loss in the Mississippi River. Rates were measured in Navigation Pool 8 of the Upper Mississippi River and described previously by Richardson et al. (2004). See text for additional details.

<table>
<thead>
<tr>
<th>Season</th>
<th>Backwater</th>
<th>Impounded</th>
<th>Main channel</th>
<th>Side channel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winter</td>
<td>0.143 (0.055)</td>
<td>0.251 (0.063)</td>
<td>0.109 (0.043)</td>
<td>0.085 (0.019)</td>
</tr>
<tr>
<td>Spring</td>
<td>0.325 (0.032)</td>
<td>0.366 (0.048)</td>
<td>0.074 (0.018)</td>
<td>0.142 (0.051)</td>
</tr>
<tr>
<td>Summer</td>
<td>0.398 (0.042)</td>
<td>0.457 (0.038)</td>
<td>0.133 (0.035)</td>
<td>0.189 (0.059)</td>
</tr>
<tr>
<td>Autumn</td>
<td>0.224 (0.023)</td>
<td>0.215 (0.022)</td>
<td>0.094 (0.027)</td>
<td>0.101 (0.018)</td>
</tr>
</tbody>
</table>

The seasonal rates of denitrification used for this analysis (Table 1) were measured from 469 samples collected from Pool 8. These denitrification rates and a detailed description of methods of measurement and extrapolation have been described previously (Richardson et al. 2004). These rates are the basis of those used here except to improve winter estimates we measured an additional 20 sites (5 sites from each habitat) during winter 2004 using the same methods. Denitrification estimates were determined using a modification of the acetylene block technique that incorporates NO3− production via nitrification. To calculate denitrification, we used three different metrics: i) unamended nitrification measured using the nitrapyrin technique (Strauss et al. 2004); ii) unamended denitrification with 100 mg L−1 chloramphenicol to inhibit new enzyme synthesis (Richardson et al. 2004); and iii) denitrification enzyme activity (DEA), i.e., denitrification after adding NO3− (14 mg N L−1), glucose (12 mg C L−1), and chloramphenicol (Richardson et al. 2004).

In this system, unamended denitrification rates must be considered an underestimate of actual in situ denitrification because of the low (often absent) NO3− concentrations in the sediment. The acetylene added to the sediment to measure denitrification also inhibits nitrification (NO3− production) on which denitrification is dependent. Conversely, DEA must be considered an overestimate of actual in situ denitrification because of the added NO3− and glucose. However, in some samples this may be a value close to the actual denitrification rate, but it would be very inappropriate to consider this as an actual denitrification rate in all sediment samples. We consider DEA as an upper limit. Our estimate of in situ denitrification is neither an extrapolation of DEA nor an extrapolation of unamended denitrification, but rather a metric that lies between the two and has been termed estimated denitrification rate (EDR) (Richardson et al. 2004). To calculate EDR we examine two different values. The first value is (A) the sum of unamended denitrification rate and unamended nitrification rate. This value represents the total amount of NO3− that could be denitrified in a sediment sample. It is assumed that the measured nitrification rate represents the actual in situ NO3− contribution and that all of the NO3− produced via nitrification is denitrified. The nitrification rates used here were measured without an NH4+ amendment, but might have been somewhat elevated because they were measured in aerobic slurries. However, an aerobic surficial layer has been present in all of the sediment samples we have assessed (Strauss et al. 2004). It is also important to keep in mind that sediment samples very rarely have detectable levels of NO3−. Thus, our assumption does appear to be valid. The second value used to calculate EDR is (B) the DEA rate. EDR is the smaller of the two values (A or B). We use DEA in the calculation because we consider the value to be an upper limit and under no circumstances should a denitrification
rate be greater than the DEA rate. In the event that the sum of unamended denitrification and unamended nitrification is high, EDR is bounded by the rate of DEA.

Seasons were characterized as 3-month time periods: winter (December – February), spring (March – May), summer (June – August), and autumn (September – November). The sediment and water samples used for determining the denitrification rates used in this study were collected during a variety of high, intermediate, and low flow conditions that correspond, respectively, to high, intermediate, and low water column NO$_3^-$ concentrations. Therefore, it is assumed that the seasonal rates of N loss calculated here are averages of the variable rates expected under different hydrological regimes.

We also assumed that habitat-specific denitrification rates were similar in all reaches of the river. To examine this assumption we measured denitrification in Pools 4, 8, and 25 during summer 2002. Denitrification rates were measured using the same methods described previously at 20 sites (5 sites in each habitat: main channel, side channel, backwater, and impounded) in each pool. Rate differences among pools for each habitat were not significant (p > 0.10, 1-way ANOVA), suggesting our assumption may be valid. However, if the rates we used did exhibit longitudinal variability, one might expect the rates to increase downstream because of the warmer water temperatures. In this case our rates would underestimate N loss and make the results of our calculations more conservative.

Seasonal N loss was calculated for each sub reach of the river by multiplying the habitat-specific denitrification rates by the respective wetted surface areas of each habitat and the duration of each season. Spatial habitat data for the Upper Mississippi River was extracted from USGS GIS data files available online (USGS 2005). An example of the USGS spatial data is shown in Figure 1C. Spatial data for the open river was collected from a GIS data file supplied by the U.S. Army Corps of Engineers. Annual reach-level N loss was then calculated by summing the seasonal N loss values. Measurement error was extrapolated from initial estimates to reach-level and river-level estimates using standard error propagation formulas (Pitman 1993).

Our cumulative N loss estimates were then added to published Mississippi River annual total N flux estimates (Goolsby et al. 1999, Wasley 2000) for each reach to estimate cumulative N fluxes in the absence of denitrification. The proportion of total N loss from denitrification was then calculated by dividing the cumulative annual N loss by the N flux in the absence of denitrification. Data and calculated values were then compared between the 1,041 km stretch of the river containing navigation pools and the 1,352 km open river to elucidate the effects of the habitat type on N loss differences between the two reaches.

**Results**

Extraction and summation of spatial data revealed that the total aquatic surface area was smaller in navigation pool reach (1,236 km$^2$) compared to the open river (1,719 km$^2$). Mean longitudinal aquatic surface areas (surface area normalized by reach length) were more similar but still somewhat smaller in the navigation pool reach: 1.2 km$^2$ km$^{-1}$ compared to 1.3 km$^2$ km$^{-1}$ (Fig. 2A). Among the four aquatic habitats, the main channel occupies the greatest relative area in both the navigation pool reach and the open river, 43% and 70%, respectively. The remaining three habitats have similar areal coverage in the navigation pools; whereas in the open river, only side channels have appreciable surface coverage. The overall large
mean longitudinal surface area of the main channel habitat in the navigation pool reach is a result of the large area occupied by this habitat in the southern half of the reach (Pools 14–26); the main channel habitat is less extensive in the northern pools (Fig. 2B). In the northern pools, backwaters and impoundments typically cover the largest amount of surface area of the four habitat types.

Despite the lower longitudinal aquatic surface areas in the navigation pool reach, N loss was 85.7 t y⁻¹ km⁻¹ in the navigation pools, 66% greater than that in the open river (Fig. 3A). In the navigation pools the largest percentage of N loss was from impoundments and backwaters, 34 and 32%, respectively, even though the main channel occupied the greatest surface area. In the open river, the majority of N loss (65%) occurred in the main channel. The pattern of total N loss in each of the sub-reaches was similar to the pattern of total surface area (Fig. 2B and 3B), however in the navigation pools the proportion of N loss was greatest from impoundments and backwaters.

Summation of N loss from the navigation pools reaches yielded a total N loss from denitrification of 89,172 t N y⁻¹. Total N loss from the open river was 69,872 t N y⁻¹ and the entire Mississippi River included in our analysis had a total in-stream N loss of 159,044 t N y⁻¹. Moving downstream, we calculated that denitrification cumulatively removes as much as 32.5% of the total N load through Pool 13, 15.2% of the load through the navigation pool reach, and 9.5% up to the Atchafalaya Diversion (Fig. 4). The overall effect of denitrification on N flux in the Mississippi River is shown in Fig. 4. In total, we calculate that denitrification reduces the total N load in the Mississippi River by 9.5%.

**Discussion**

In this study, our goal was to examine spatial patterns of N loss in the Mississippi River based on spatial extrapolations of rates of denitrification to cover 2,393 km of the river from Minneapolis, Minnesota to the Atchafalaya River diversion in Louisiana. The areal denitrification rates were measured from samples collected seasonally from a variety of habitats in the Mississippi River (Richardson et al. 2004) and were extrapolated using data collected from publically available GIS coverages. Our analysis predicted a total annual loss of 159,044 t N or 9.5% of the N load in the Mississippi River. Other modelling studies of N flux in large rivers consistently suggest that once N enters large riverine systems, the majority is transported to the river’s terminal. Howarth et al. (1996) pre-
dict 5–20 % of N is retained or lost in moderately loaded rivers. Caraco and Cole (1999) estimated that > 80 % of variability in NO₃⁻ export among major world rivers can be explained by point and nonpoint N loadings. This result implies that the effects of N cycling on N budgets are likely small in large rivers. In a modelling study of 16 drainage networks in the eastern United States, Seitzinger et al. (2002) found that larger lotic systems (5th–9th order) remove about 40 % of N entering the channel. However, they also report that the largest rivers (8th order) removed less than 15 % of the N. In the Mississippi River, a 10th order system, Donner et al. (2004) calculated that 18–28 % of the total N is lost through denitrification and Alexander et al. (2000) estimated that > 90 % of the N that enters the Mississippi River is transported to the Gulf of Mexico. Another model of particular note is the recent conceptual model by Wollheim et al. (2006) which suggests that large rivers “potentially exert considerable influence over nutrient export.” Their model estimates nutrient loss in river networks by examining system hydrology and applying a general nutrient loss model estimate, nutrient uptake velocity (vₓ), which varies linearly with nutrient concentration. This approach simplifies the system by assuming all areas within a particular river reach exhibit a uniform nutrient loss. In comparison, our approach is also an areal application of nutrient loss rates, but we use the spatial heterogeneity within a river reach by extrapolating empirically derived loss rates based on habitat type and season. Our assumption is that the significant effects of hydrology and nutrient concentrations are accounted for in the seasonally acquired rates. As a result, one limitation of our approach is that we are unable to account for transitory or localized effects of varying nutrient concentrations. Nevertheless, the total in-stream N loss we calculated for the Mississippi River (9.5 %) is consistent with these other studies.

This agreement implies that researchers can still gain insights at large spatial scales by measuring process rates using traditional biogeochemical and ecosystem ecology methods and scaling rates up to whole systems. For example, in addition to the total N loss within the Mississippi River, our study further describes reach level N loss. Our analysis found that N loss was higher in reaches that contained a more diverse assemblage of habitats. Reaches of the river that contained a higher proportion of backwater lakes and impoundments, especially upstream of Navigation Pool 13, exhibited higher N loss compared to more simple reaches containing only the main channel and side channels. This result was not necessarily surprising because the sediments in these habitats are rich in C and N and the denitrification rates used in the extrapolation were 1.31–4.95 times greater for backwaters and impounded areas compared to main and side channels.

A comprehensive review of the patterns of N dynamics in the Mississippi River has not been published nor is one appropriate here, but the patterns of denitrification can be summarized as being spatially complex and influenced by season, discharge, and site specific phenomena. In general, backwater and impounded habitats exhibit a higher water retention time and provide a nearly ideal low redox environment for denitrification because of the mostly anaerobic and organic-rich sediments. Water column NO₃⁻ concentration are typically lower than those in the main channel but can be elevated in flow-through areas or for short periods during high discharge events when channel waters flow at a higher rate through these habitats (Houser & Richardson 2010). Immediately following NO₃⁻ pulses, denitrification and macrophyte uptake cause water column concentrations to decline rapidly (Houser & Richardson 2010, James 2010, Kreiling et al. 2010). High discharge will also often inundate the floodplain and result in N loss through soil denitrification (Schramm et al. 2009). Interstitial NO₃⁻ concentrations are also low and often below detection in backwater and impounded habitats, however a surficial aerobic layer supports an active community of nitrifying bacteria producing NO₃⁻ (Strauss et al. 2004). Presumably nitrification and denitrification are coupled in these areas resulting in high rates of N loss via denitrification (Richardson et al. 2004, Strauss et al. 2006). Main and side channel habitats typically have lower rates of denitrification despite the higher water column NO₃⁻ concentrations due to the paucity of electron donors in the inorganic sediments (i.e., sand). However, appreciable denitrification can occur in certain areas where organic materials accumulate such as beds of the invasive zebra mussel (Dreissena polymorpha) or macrophyte beds along the channel edges (Richardson et al. 2004, Bruesewitz et al. 2006).

The Mississippi River ecosystem has been constantly evolving since the Wisconsin glaciation retreated north out of the region 10,000 years ago, however human modifications to the system in the last 150 years have expedited and directed the dramatic physical, chemical, and biological changes. Beginning in the 1800s, frequent flooding of the floodplain and an increasing desire to use the river for navigation initiated large-scale engineering efforts to modify the river. In the Lower Mississippi River, meander cutoffs, levees, and revetments have shortened the river by over 240 km, disconnected the river from 90 % of its historical floodplain, decreased the water residence time, and increased the gradient of this segment of the river (Shields 1995, Kesel 2003, Knox 2008, Schramm et al. 2009). In the Upper Mississippi River, major river modifications began in the late 1800s with sediment dredging (which continues to this day) and the installation of wing and closing dams to focus water within a specific
Navigable channel (Fremling 2005). To further facilitate navigation, the lock and dam system was constructed in the 1930s. Major effects of the lock and dams have been the creation of the open water impoundments (see Fig. 1C) and the raising of the water level thereby increasing the overall water surface area and flooding portions of the floodplain. All of these river modifications have altered the river’s capacity to retain or remove N. In the Lower Mississippi River, decreasing the water residence time and the total surface area of the contact between sediment and water have undoubtedly greatly diminished the N removal capacity. Moreover, much of the floodplain that was disconnected from the river included wetlands which are hotspots for N removal. Conversely, in the Upper Mississippi River, the river modifications may have increased N removal because of the increase in sediment/water surface area and the creation of impoundments and connected backwater lakes.

During the same time as the river’s ability to retain or remove N was altered, N loading into the system and N flux through the system was increasing. Data indicate that in the latter half of the 20th century N inputs into the Mississippi River Basin and N flux in the river have increased dramatically (Goolsby & Battaglin 2001, Goolsby et al. 2001, McIsaac et al. 2001). This increased N flux has been likely to be at least partly responsible for the increasing size of the Gulf of Mexico zone of hypoxia. It is unknown if the pre-1800s Mississippi River system could have processed this increased N load, but it is clear that the historic river state could have processed higher N loads than it does today. Mechanisms for reducing and mitigating this high N load must occur on a variety of different levels and have been reviewed in detail by Mitsch et al. (2001). Many of these mechanisms include river management and restorations that would increase habitat diversity in the Mississippi River and reconnect the river to portions of its historic floodplain. Our results support these recommendations because habitat diversity and river channel complexity are driving factors that influence retention time, depth, and other physical/chemical variables that lead to increased riverine N loss.

Acknowledgements

The authors recognize the contributions of J. Rogala who conducted an earlier analysis on a partial data set. C. Lowenberg, D. Olsen, and J.C. Nelson assisted with the GIS processing. We also thank B. Johnson, B. Knights, J. Houser and two anonymous reviewers for comments on an earlier draft of this manuscript.

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Received 21 September 2010
Modified version received 3 January 2011
Accepted 4 January 2011