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Denitrification in the Upper Mississippi River: Potential Limitation by Delivery

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Abstract

Nitrate (NO_3^-) appears to pass conservatively from the Upper Mississippi River to the Gulf of Mexico. Yet, the Upper Mississippi River basin contains large expanses of riparian wetlands and vegetated backwater lakes, hypothetically capable of supporting substantial denitrification. We initiated studies to test this hypothesis in a 27-km reach of the Mississippi River, near La Crosse, Wisconsin. During October 1999, we sampled 60 sites for sediment denitrification, total organic carbon, porewater (interstitial water) total nitrogen (TN), exchangeable ammonium (NH_4^+) and nitrate (NO_3^-); in the overlying water we measured TN, NH_4^+ and NO_3^-. Isolated backwaters tended to have the lowest mean denitrification rates (14.9 mg N/m^2/d ± 4.38 SE), lowest surface water NO_3^- and highest sediment carbon and NH_4^+ concentrations; conversely, sediments near large channels tended to have the highest rates (43.0 mg N/m^2/d ± 9.3 SE) and lower sediment carbon. Monitoring data supports our contention that much of the area with the highest denitrification potential is hydrologically isolated from the NO_3^- source. Denitrification across the entire reach might be enhanced by increased exchange between the main channel and backwaters during summer and fall.

Introduction

- Prior to the 1930's, the natural microbial processes of nitrification and denitrification were at equilibrium in the environment and nitrogen availability for biological use was limited. Since the 1930's, anthropogenic nitrogen fixation has more than doubled the transfer of nitrogen from the atmosphere to biologically available pools. This increase has resulted in marine hypoxia in many near-shore areas worldwide. In the 1990's, the Gulf of Mexico Hypoxic "Dead Zone" developed to cover an area greater than 8,000 square miles.
- Total nitrogen loading to the Upper Mississippi River ranges from 1 to 4 kg/km^2/day. Monitoring data from navigation pool 8 (near La Crosse, Wisconsin; Fig. 4) of the Mississippi River has shown that during high flow, this river reach is a sink for nitrate (Fig. 1). In addition, nitrate concentrations tend to decrease in surface water from high levels in the main channel to low levels in backwaters, especially during periods of low river discharge.

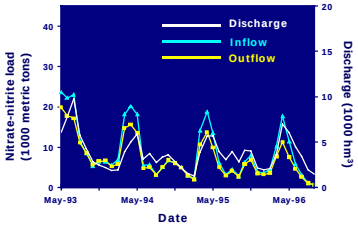


Fig. 1. Seasonal nitrate-nitrite budget and discharge of navigation pool 8, Upper Mississippi River, near La Crosse, Wisconsin.

- Denitrification, an anaerobic microbially mediated process, is a mechanism for nitrogen removal from riverine systems (Fig. 2); it is limited by carbon availability, nitrate delivery rate, the presence of oxygen, and sediment moisture. Organic carbon in sediments has been correlated with sediment moisture and therefore denitrification may follow spatial patterns of sediment moisture and organic content (Fig. 3).

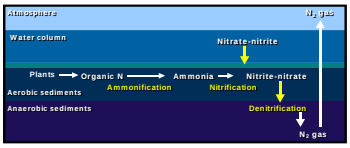
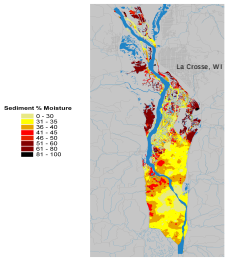


Fig. 2. Nitrogen cycling in riverine sediments.

Fig. 3. Sediment moisture content in navigation pool 8 of the Upper Mississippi River, near La Crosse, Wisconsin. Areas with low moisture content (yellow) have corresponding low sediment carbon content, and high moisture sediments (black areas) have high organic carbon content.



Objectives

- To determine spatial patterns of key components of the nitrogen cycle in the Upper Mississippi River.
- To determine temporal variation in spatial patterns of denitrification and ammonia generation.
- To determine rate limiting steps of these processes in differing habitats under differing hydrologic conditions.
- To develop river management strategies to reduce downstream flux of nitrogen from the Upper Mississippi River basin.

Methods

- Sampling in navigation pool 8 of the Upper Mississippi River, near La Crosse, Wisconsin, USA (Fig. 4), was stratified by into low, medium, and high carbon sediments. In each strata, 20 sampling sites were randomly generated. Global positioning system coordinates were used to locate sites during sample collection over a 3-week period in October 1999.

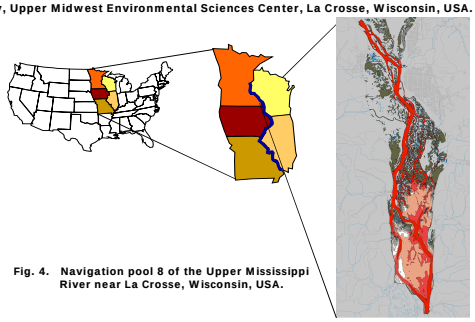


Fig. 4. Navigation pool 8 of the Upper Mississippi River near La Crosse, Wisconsin, USA.

- At each sampling site, sediment cores were collected and analyzed for potential denitrification rate (acetylene block), total carbon (loss-on-ignition), interstitial ammonium (total, unionized, and KCl-exchangeable), and sediment particle size (hydrometer), bulk density, and percent moisture (gravimetric). Sediment pH and temperature were measured in the field.
- At each site, surface water and porewater samples were collected, field-filtered and acid preserved for analysis of total nitrogen, nitrate-nitrite, and ammonium following standard methods. Surface water pH, dissolved oxygen, conductivity, and temperature were measured on site.

Results

- Surface water nitrate-nitrogen concentrations ranged from 0 to 1.44 mg N/L and total nitrogen concentrations ranged from 0.3 to 2.4 mg N/L at the 60 sites. Except for one site, surface water ammonium-nitrogen concentrations were low, ranging from 0.002 to 0.164 mg N/L (Fig. 5).
- Sites in areas of high flow, main and side channels (yellow arrows), had higher concentrations of both nitrate-nitrogen and total nitrogen compared to low flow, isolated backwaters (white arrows; Fig. 5).

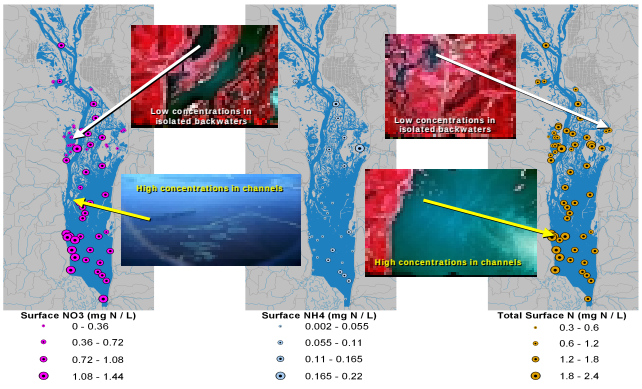


Fig. 5. Surface water concentrations (mg N/L) of nitrate-nitrogen, ammonium-nitrogen, and total nitrogen at 60 sites in navigation pool 8 of the Upper Mississippi River, near La Crosse, Wisconsin.

- Potential denitrification rates were variable among the 60 sites and ranged from 0 to over 100 mg N/m^2/day (Fig. 6).
- Higher denitrification rates were observed near high flow water in main and side channels with high nitrate concentrations (yellow arrows; Fig. 6).
- Isolated backwater areas with little or no flow had low rates of denitrification (white arrows; Fig. 6).
- Patterns in sediment carbon did not predict patterns of denitrification rate (DR) except within high sediment carbon strata. In the top 50% of sediment carbon, we observed the following relationship:

$$DR = 4.8([NO_x]) + 0.11([\text{sediment carbon}]) - 0.37$$

$$R^2 = 0.73,\ p = 0.0001$$

- Other sites with increased denitrification were in macrophyte beds near the main or side channels or near zebra mussel beds (Fig 6).

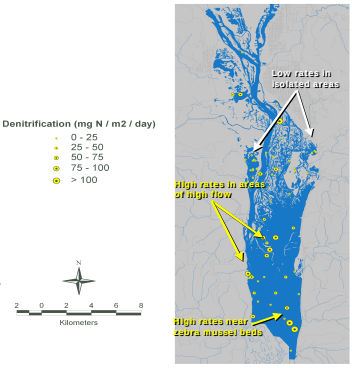


Fig. 6. Potential denitrification rates (mg N/m^2/day) at 60 sites in navigation pool 8 of the Upper Mississippi River, near La Crosse, Wisconsin. Arrows indicate areas with high (yellow) or low (white) denitrification rates.

Conclusions

- Navigation pool 8 of the Upper Mississippi River is likely denitrifying below the potential maximum due to nitrate limitation in areas of the pool with the highest denitrifying potential. The hydraulic isolation of the backwater areas from the nitrate-laden water of the main channel limits the supply of nitrate to sediments with the highest denitrification potentials.
- Sediment carbon appears to play a secondary role as a determinant of nitrate removal in navigation pool 8 of the Upper Mississippi River.
- In the Upper Mississippi River system, isolated, backwater areas may be potential active sites of denitrification and ultimate removal of nitrogen from the system. Floods that reconnect backwater areas with the nitrate-laden water of the main channel likely play a critical role in reduction of nitrate to nitrogen gas (denitrification).