Limited nitrate retention capacity in the Upper Mississippi River

Luke C Loken1,2,7, John T Crawford3, Mark M Dornblaser3, Robert G Striegl3, Jeffrey N Houser4, Peter A Turner5,6 and Emily H Stanley2

1 U.S. Geological Survey, Wisconsin Water Science Center, Middleton, WI 53562, United States of America
2 Center for Limnology, University of Wisconsin-Madison, Madison, WI 53706, United States of America
3 U.S. Geological Survey, Water Mission Area, Boulder, CO 80303, United States of America
4 U.S. Geological Survey, Upper Midwest Environmental Science Center, La Crosse, WI 54603, United States of America
5 Department of Soil, Water, and Climate, University of Minnesota-Twin Cities, St. Paul, MN 55108, United States of America
6 Department of Global Ecology, Carnegie Institution for Science, Stanford, CA 94305, United States of America
7 Author to whom any correspondence should be addressed.

Abstract

The Mississippi River and other large rivers have the potential to regulate nitrogen export from terrestrial landscapes, and thus mitigate eutrophication in downstream aquatic ecosystems. In large rivers, human-constructed impoundments and connected backwaters may facilitate nitrogen removal; however, the capacity of these features is poorly quantified and incompletely incorporated into model frameworks. Using a high-resolution and spatially intensive sampling technique, we assessed the contribution of individual navigation pools, as well as impounded open waters and backwater wetlands within them, to overall nitrate retention by mapping the entire length (1370 km) of the Upper Mississippi River (UMR) main channel. Based on this single spatial survey of water chemistry, the river appeared to act primarily as a passive nitrate transporter, retaining only 12.5% of the incoming load, most of which occurred in the upper 150 km of the river, which includes the largest and only naturally impounded reach of the river. Although reservoirs typically are nitrogen sinks, our data indicate that UMR dams do not impede river flows to the extent necessary to promote substantial changes in water residence times and subsequent nitrogen removal. Backwaters routinely had lower nitrate concentrations than the main channel, but their limited hydrologic connectivity to the through-flowing river channel constrained their influence on downstream export. As a whole, the UMR did not remove a substantial proportion of its nitrate load despite optimal N removal conditions, numerous impoundments, and the presence of extensive backwater habitats. These results suggest that efforts to reduce delivery of nitrogen to the Gulf of Mexico should emphasize mitigation strategies that target upland nutrient sources rather than relying on removal within the Mississippi River.

1. Introduction

Human activities have increased nitrogen (N) loading to world rivers in recent centuries [1, 2], leading to a prevalence of eutrophication and degraded water quality of rivers and downstream waterbodies [3, 4]. The Mississippi River exemplifies this global crisis, as agricultural runoff to the river has elevated river N concentrations [5, 6] and been implicated as a key driver of the expansion of the Gulf of Mexico’s oxygen-depleted ‘dead zone’ [7–9]. In the United States alone, anthropogenic N inputs to freshwater ecosystems cause an estimated $70 billion in potential damage costs annually [10]. In an effort to improve water quality, the United States has set a goal of reducing N loading to the Gulf of Mexico by 45% by 2035 [9]. However, tackling a problem of this magnitude is challenging [11] as there are trade-offs among environmental, societal, and political goals [12, 13] and it requires coordination across half of the contiguous United States.
Many effective mitigation strategies target nutrients near their sources [11]. While these restoration efforts may improve conditions locally, changes are undetectable at the broader basin scale due to the distributed nature of non-point and legacy N sources [14–16]. Alternatively, promoting N removal in larger rivers is attractive as they receive water and material from distant upland sources and thus have the potential to regulate N export from their entire watersheds.

N processing in headwater streams can significantly buffer the effects of N enrichment [17, 18], but quantifying removal in larger rivers is more challenging due to data limitations [19, 20] associated with their large size and substantial spatial and temporal complexity. The few process-based studies and several modelling approaches offer conflicting conclusions that N retention in larger rivers is alternatively trivial [21, 22] or significant [19, 23–26] and increases in importance as N loading intensifies [27]. Medium and large channels compose a majority of the global river area [28] and if removal rates scale with benthic surface area, these systems could retain significant amounts of the N they receive from their upstream networks. While these model-based evaluations provide valuable guidance, often they are based on spatially limited datasets extrapolated from small streams, and fail to identify variability in N processing potential among distinct river segments and habitats. Thus, high-resolution, spatially extensive data are needed to evaluate N processing at finer spatial scales in these large and heterogeneous systems.

Traditionally, N retention has been thought to decline with river size because of increasing water velocities and decreasing surface-to-volume ratios [17, 21]. While this convention may apply to idealized river channels, many large channels can be structurally complex and include floodplains, backwaters, and low-velocity reaches. These habitats are widely associated with amplified N retention [26–29], thus their frequent exclusion from models (but see [27]) may lead to underestimations of actual N retention rates in larger channels. Human modifications to river corridors add another layer of complexity by reducing connectivity to lateral habitats and increasing the abundance of lentic features via damming. While reservoirs often act as N sinks [30, 31], disconnecting rivers from floodplains and backwaters is expected to diminish N removal capacity [32, 33]. In large river channels, we expect that some structural attributes (e.g. backwaters, impoundments) to be associated with N retention, while others with N transport (e.g. levees, channels), and given that these features and associated habitats are not well incorporated into a single framework, it is unclear the net effect of this habitat heterogeneity on whole-river N processing.

We focused our investigation on the Upper Mississippi River (UMR), which like many of the world’s rivers, has been impacted by a range of human activities. Cultivated cropland comprises 49% of the UMR watershed [34] and contributes to chronic N loading to the river [5, 6, 15]. Typical of many rivers draining agricultural landscapes, nitrate (NO$_3^-$) constitutes the majority of the total-N pool [34–37] and concentrations frequently exceed human toxicity thresholds in ground and surface waters [38–40]. Humans have also extensively changed the hydrology and geomorphology of the UMR [41]. Along the UMR mainstem, dams impede river flows, countless channel-training structures focus flow into the main navigation channel and reduce lateral water exchange [22], and in some sections of the river constructed levees drastically disconnect the historic floodplain [42]. These physical alterations have changed the configuration of riverine habitats and their connectivity to the main channel, potentially altering the UMR’s N processing capacity and its ability to regulate export to the Gulf of Mexico.

Here, we ask what is the spatial pattern of NO$_3^-$ in the UMR, what proportion of the incoming NO$_3^-$ load does the UMR remove, and how do distinct riverine habitats influence NO$_3^-$ dynamics and export? Our strategy was to generate and analyze datasets of NO$_3^-$ in the UMR that are both spatially intensive and extensive, allowing us to identify locations of NO$_3^-$ depletion and calculate NO$_3^-$ removal at multiple spatial scales. This involved measuring NO$_3^-$ concentrations along the entire length (1370 km) of the UMR during warm baseflow conditions that are typically associated with elevated N retention capacity [43, 44], and repeatedly assessing NO$_3^-$ patterns and retention in a single 38 km river segment composed of a high proportion of backwaters and impounded area compared to channel habitat [22]. Backwaters and impounded areas may promote NO$_3^-$ removal in the UMR; however, their reactivity and hydrologic connectivity vary through time and across space, controlling their influence on main channel chemistry and whole-river N retention.

2. Methods

2.1. Site description

We define the UMR as the 7th to 10th order river [45] located between Minneapolis, MN (44.98° N, 93.25° W) and the confluence with the Ohio River near Cairo, IL (36.98° N, 89.13° W; figure 1). Along this 1370 km river segment, 29 low-head dams exist today that were originally constructed to facilitate navigation. The dams are managed to maintain a 2.74 m depth in the river’s navigation channel [42] during low-flow periods but allow the river to flow relatively unrestricted during high discharge [41]. The UMR is unusual among impounded rivers in that its dams do not prevent floods nor have large storage capacity. While nearly half of the original floodplain (mostly in the upper UMR) remains unlevied and hydrologically connected to the river [41, 42], a myriad of channel training structures and wing dams focus flows into the river’s navigation channel and thus limit lateral water exchange.
Spatial heterogeneity within the UMR is driven by the presence of dams and variation in hydrologic connectivity to the river thalweg. Dams of the UMR divide the river into ‘navigation pools’ defined as the river section between two successive dams. Within each navigation pool, the river can be classified into four distinct aquatic areas (main channel, side channel, backwater, and impoundment; see figure 5), reflecting river morphology [46] and hydrologic connections with the main channel. Impoundments are immediately upstream of dams and include the aquatic area flooded by the dam. Backwaters are present throughout the river corridor and are distinguished by limited hydrologic connectivity to the through-flowing river [47]. The UMR main channel and side channels are characterized by relatively high water velocity and kinetic energy, which prevent accumulation of fine sediments and organic matter [47]. In contrast, backwaters and other lentic areas accrue fine, carbon-rich sediments [48]. The proportion of each aquatic area varies among pools. Below dam 13 (near Clinton, IA; 41.90° N 90.16° W), the river has fewer connections with backwaters and channel areas dominate [22] due to distinct geomorphology and an extensive levee system built to mitigate flooding and facilitate floodplain agriculture [41, 49]. In contrast, pools in the upper river (i.e. Pools 1–13) support a more diverse assemblage of aquatic areas [50] because the river is allowed to flow laterally into backwater habitats. In addition to impounded areas created by dams, one natural lake (Lake Pepin) exists within the UMR main channel and shares many features with traditional reservoirs. Lake Pepin is the widest naturally occurring part of the Mississippi River and was formed above the Chippewa River delta in Pool 4 (44.42° N, 92.10° W).
2.2. Sampling design

Using a spatially explicit sampling platform (see below), we investigated NO₃ dynamics in the UMR using two approaches. First, to compare NO₃ retention among navigation pools with varying proportions of backwater, channel, and impounded areas, we mapped the entire length (1350 km) of the UMR navigation channel from August 1–13, 2015. We chose this time period to coincide with warm baseflow conditions, which were expected to promote higher NO₃ retention compared to other times of the year [43, 44]. We collected most of our measurements in the river’s navigation channel, but also sampled major tributaries (supplementary table 1 available at stacks.iop.org/ERL/13/074030/mmedia) and non-channel aquatic areas. To analyze the longitudinal pattern in river chemistry, measurements from the main channel were snapped to a line running through the center of the navigation channel.

Second, we investigated temporal within-pool patterns of NO₃ by characterizing Pool 8 (43.77° N, 91.24° W) on 8 dates between July 2014 and August 2016. We chose Pool 8 because it has relatively low tributary inputs and a large proportion of area designated as backwaters and impoundment (supplementary table 2). We expected these aquatic areas to be important for NO₃ processing [22]. During each survey, we attempted to sample the same locations, including the entire length of main channel, selected backwaters, and major tributaries. However, due to weather, navigability, and equipment malfunction, Pool 8 maps vary slightly among sample dates. To assess the within-pool patterns at a finer temporal resolution, we combined our Pool 8 maps with water chemistry data from the Long Term Resource Monitoring element (LTRM) of the US Army Corps of Engineers’ (USACE) Upper Mississippi River Restoration (UMRR) program (www.umesc.usgs.gov/ltrmp.html). We selected five sites representing a gradient in connectedness to the main channel. Three of the sites (Target Lake, Lawrence Lake, Main Channel) were sampled by both the LTRM program and our repeat surveys. The fourth LTRM site (Stoddard Island) is located within a semi-connected backwater flow path. The last site is a FLAME-only (Fast Limnology Automated Measurement platform; see below) site located in a side channel (Turtle Slough).

2.3. Sensor platform

We characterized the spatial pattern of surface water conditions using the FLAMEs-only (Fast Limnology Automated Measurement platform) [51]. Briefly, river water (≈0.2 m depth) was continuously pumped at a rate of 2.84 L min⁻¹ to a series of onboard sensors including a Satlantic SUNA V2 optical nitrate analyzer (10 mm path length) and a YSI EXO2 (outfitted with specific conductivity (SPC) and turbidity sensors for this study) equipped with manufacturer-supplied flow-cells. Water was then delivered to a sprayer-type equilibrator [51], stripping the water of dissolved gases. Methane was analyzed using a Los Gatos Research ultraportable greenhouse gas analyzer (UGGA) and nitrous oxide by a Teledyne analyzer. More information regarding the spatial pattern of these gases can be found in Crawford et al [52] and Turner et al [53]. Sensor outputs were georeferenced using an onboard GPS and corrected for hydrologic lags and sensor response rates using methods outlined in Crawford et al [51]. The GPS, YSI, and UGGA recorded data at 1 Hz. Nitrous oxide measurements were denoised using a wavelet technique and subjected to 30 s block averaging [53]. Because the SUNA overheats when operated continuously unsubmerged, we configured it to capture data at ~0.1 Hz and cooled it with ice water using an aquarium circulation pump and homemade water jacket.

2.4. Retention metrics

To assess the ability of the river to modulate NO₃ export, we calculated instantaneous uptake rates and the percentage of NO₃ retained in each UMR pool. Retention was assessed at the pool scale because typically all water exiting a pool is funneled through a narrow channel section at the dam. Thus, the NO₃ signal at the pool outlet incorporates inputs and processing for that pool. Calculating retention at finer spatial scales for the entire UMR was not feasible due to variable and unknown lateral water exchange and dissimilar water velocity and boat speeds [54]. We calculated NO₃ retention (R₉O₃) and uptake (U₉O₃) for each pool by solving each pool’s instantaneous NO₃ mass balance using input (NO₃-in) and export (NO₃-out) concentrations.

\[
\text{NO}_3^{\text{in}} = \frac{\sum Q \times \text{[NO}_3]}{\sum Q} \quad (1)
\]

\[
R_{\text{NO}_3} = \frac{\text{NO}_3^{\text{in}} - \text{NO}_3^{\text{out}}}{\text{NO}_3^{\text{in}}} \quad (2)
\]

\[
U_{\text{NO}_3} = (\text{NO}_3^{\text{in}} - \text{NO}_3^{\text{out}}) \times \frac{\sum Q}{\text{SA}} \quad (3)
\]

For NO₃-in, we computed the discharge-weighted input concentration using conditions at the upstream dam and 13 major tributaries (supplementary table 1). NO₃-out is the concentration at the downstream dam, and SA is the pool surface area. For Mississippi River discharge (Q), where available, we used daily ratings from US Geological Survey (USGS) gauging stations (n = 7, supplementary table 3) [55]. For pools without a USGS gauging station (n = 19), we obtained discharge at the dams provided by USACE (www.mvd.usace.army.mil). Tributary discharge was obtained for the most downstream USGS gauge [55]. Lake Pepin—located in Pool 4—a 3,000 km long impoundment, so we split Pool 4 at the outlet of Lake Pepin and analyzed each as separate pools. We calculated NO₃ retention for 27 pools using data from the August longitudinal transect. Pool 8 retention was...
computed from the eight repeated surveys and from two winter sampling events. Winter retention was calculated using NO$_3^-$ determined from discrete water samples collected in January of 2015 and 2016 (see supplementary material for laboratory methods).

We also calculated the percent change in turbidity and SPC. Concentrations of NO$_3^-$ in equations (1) and (2) were replaced with measurements of turbidity and SPC. Positive retention of turbidity indicated net removal of suspended material. Retention or production of SPC was used to identify measurable inputs that were not accounted for in the water mass balance. Lastly, longitudinal profiles of NO$_3^-$, turbidity, and SPC were compared to expectations based on conservative mixing using discharge-weighted tributary loading.

Underlying our retention model are the assumptions of steady-state conditions and closed water budgets. We acknowledge that neither are entirely true, and these deviations add uncertainty to our retention estimates. For example, small tributaries, waste water treatment plants (WWTPs), and groundwater all contribute flow to the river and change the NO$_3^-$ load. While these water fluxes were small compared to the Mississippi River discharge (supplementary material), we expanded our NO$_3^-$ retention model to include uncertainty associated with additional water sources. Rather than modelling each water source individually, we modified equations (1)–(3) by adding a single water source term ($Q_x$) that represents the summation of additional water sources.

$$\text{NO}_3^{-\text{in-x}} = \frac{\sum_{in} Q \times [\text{NO}_3^-] + (Q_x \times [\text{NO}_3^-_{-x}])}{\sum_{in} Q + Q_x}$$

$$R_{\text{NO}_3^{-x}} = \frac{\text{NO}_3^{-\text{in-x}} - \text{NO}_3^{-\text{out}}}{\text{NO}_3^{-\text{in-x}}}$$

$$U_{\text{NO}_3^{-x}} = \frac{(\text{NO}_3^{-\text{in-x}} - \text{NO}_3^{-\text{out}}) \times \sum_{in} Q + Q_x}{SA}$$

Because additional water sources could concentrate or dilute river NO$_3^-$, we calculated $R_{\text{NO}_3^{-x}}$, using the minimum and maximum concentrations (0 and 6.37 mg N L$^{-1}$) observed in this study (supplementary figure 1) for NO$_3^{-x}$. For each pool, $Q_x$ was assigned to be either the difference between outgoing and incoming discharge ($-\Delta S$ see supplementary material) or the average $-\Delta S$ among all pools, whichever was larger. The average $-\Delta S$ among pools was 35.5 m$^3$ s$^{-1}$, which was comparable to discharge records for the larger unsampled tributaries in this study and much greater than estimated contributions from groundwater and WWTPs (supplementary table 3). By multiplying $Q_x$ by a high and low NO$_3^-$ concentration equation (4), we incorporated uncertainty from missing water sources into our pool-scale retention models.

In addition to uncertainty from missing water sources, retention calculations should be interpreted cautiously due to model assumptions. Our assessment of N retention by the UMR was based on the spatial pattern of NO$_3^-$ at a single point in time. We lack information on fine-scale temporal variability of tributary inputs and within-river processing, which is needed to fully evaluate river N dynamics. This mass balance approach may also be prone to error due to spatial lags and changing pool volumes, but it provides a relative comparison among pools that vary drastically in their geomorphology, hydrology, and input chemistry [22, 42, 50, 56]. Our approach is more appropriate for larger fluvial systems, such as the Mississippi River, where groundwater contributes minimally to reach-scale water budgets [57, 58] and the quantity of hyporheic exchange tends to be small [59]. Additionally, we sampled the entire length of the UMR in August when flows [49] and NO$_3^-$ concentrations [60, 61] are generally more stable. UMR discharge during August 2015 between Pools 1 and 19 was comparable to monthly averages since 1970 (supplementary figure 4). However, a rain event occurred on August 8th that affected some of our main channel measurements in the lower UMR. Prior to this date, we sampled Pools 1 to 17 and tributary discharge was ~60% of mean annual discharge (supplementary table 1). After the rain event, flows increased in the Iowa, Des Moines, and Illinois Rivers (and many smaller tributaries) near or above their annual means, which we sampled from August 8–10. During this time, we witnessed horizontal stratification at tributary confluences, as inputs from each river were visually distinct from water in the mainstem and tended to hug their respective banks. Complete mixing ensued after flowing through the next dam. Our sampling path followed the navigation channel (e.g. figure 5) that meanders between banks. Thus, measurements alternated between the UMR mainstem and multiple tributary plumes, contributing to erratic measurements (figure 2) and unreliable retention estimates for pools 18–24.

3. Results and discussion

3.1. Longitudinal NO$_3^-$ patterns

The basin-wide pattern in NO$_3^-$ was largely driven by tributary inputs as concentrations increased notably downstream of the Minnesota, Iowa, and Des Moines Rivers (figures 1 and 2). These rivers drain predominantly agricultural watersheds and make substantial contributions to total riverine N loads [6, 62]. Turbidity also increased downstream of the Minnesota and Des Moines Rivers (figure 2), signaling that these rivers also delivered high sediment loads to the UMR. Our observed NO$_3^-$ longitudinal pattern (figure 2) matched results from a similar spatial survey conducted in the summer of 1991, where concentrations were lowest in the middle section of the UMR and elevated downstream of the same N-rich tributaries [56]. After accounting for tributary inputs,
the main channel maintained fairly constant NO$_3$ concentrations over long distances, and—aside from Pools 2 through 4 (see below)—concentrations did not diverge substantially from expectations based on conservative mixing (figure 2).

The UMR did not retain (i.e. reduce) a substantial proportion of its NO$_3$ load (figure 3), despite the presence of numerous impoundments and extensive backwater habitats, validating the impression that smaller streams are more important than larger rivers for NO$_3$ removal at the watershed scale [21]. Based on our single snapshot survey, the entire UMR retained 12.5% of the incoming NO$_3$ load (supplementary table 2). Although there are large uncertainties in each pool’s NO$_3$ retention estimate (figure 3), our evaluation for the entire UMR is in the range calculated by upscaling [22] and modelling [21] approaches for the entire Mississippi River and similar to the percent retained via denitrification in the River Elbe based on a Lagrangian approach [26]. Because our survey occurred during optimal N removal conditions [43, 44], we predict that this summer baseflow retention estimate is larger than the annual average. Seasonal Pool 8 retention estimates are consistent with this prediction as they hint at greater NO$_3$ retention during warm low-flow conditions (supplementary figure 6). Although the UMR retention estimate was only 12.5%, this translates to a mass of 138 metric tons of N that is not exported down river each day. The NO$_3$ load reduced by the UMR is ~3% of the total

Figure 2. Longitudinal profile of nitrate (NO$_3$; upper panel), turbidity (middle), and specific conductivity (lower) in the navigation channel of the Upper Mississippi River. River km 0 is the most upstream sampling site in Minneapolis, MN. Measurements occurring in backwaters, side channels, and tributaries were excluded. Gray line indicates the expected concentration assuming instantaneous mixing of major tributaries and conservative transport. Red dotted lines indicate dam locations (1, 2, etc.). Blue dashed lines indicate locations of major tributary confluences (MN—Minnesota; SC—St. Croix; Ch—Chippewa; Ri—Root; WI—Wisconsin; Rk—Rock; IA—Iowa; DM—Des Moines; IL—Illinois; MO—Missouri). Lake Pepin (blue polygon) is in Pool 4 above the confluence with the Chippewa River.
amount of NO\textsubscript{3} discharged to the Gulf of Mexico \cite{63} and \(\sim 5\%\) of the load reduction goal set by US Environmental Protection Agency \cite{9}. Thus, the percent of NO\textsubscript{3} removed by the UMR may have been small, but the total mass of NO\textsubscript{3} retained was meaningful.

While the majority of the river appeared to have acted mostly as a passive NO\textsubscript{3} transporter, the upper four pools were particularly important for shaping UMR-wide N removal during our longitudinal survey. Lake Pepin, which represents 2\% of the UMR length, received only 8\% of the total NO\textsubscript{3} load (above the Missouri River) yet was responsible for 29\% of the UMR’s total NO\textsubscript{3} load reduction. Pools 2 and 3 also contributed a notable proportion of the total NO\textsubscript{3} removed by the river (\(\sim 13\%\) each). Similar to Lake Pepin, these pools are located in the upper UMR and received only a small fraction of the total NO\textsubscript{3} load (<10\%). Thus, over half of the NO\textsubscript{3} retained in the UMR occurred in the uppermost 150 km. While our data imply that some pools below Lake Pepin produced or consumed NO\textsubscript{3} (figure 3), these sources or sinks were typically balanced in subsequent pools, making the majority of the river close to net-neutral in terms of its NO\textsubscript{3} mass balance.

We were not surprised to find minimal NO\textsubscript{3} retention in the lower UMR (Pools 14–26; figure 3). The lower UMR is dominated by channel habitat due to its extensive levee system \cite{42}. These pools have short water residence times and large hydraulic loads (supplementary table 2), thus limiting the opportunity for substantive N processing. In addition to high flushing rates through channels, NO\textsubscript{3} uptake efficiencies and denitrification rates are likely low due to the predominance of mineral-rich sediments \cite{48} and limited hyporheic exchange \cite{59}. Notably, several major NO\textsubscript{3} sources flow into river in parallel.

Figure 3. Nitrate (NO\textsubscript{3}) retention (upper panel) and uptake (lower panel) in Upper Mississippi River navigation pools. Pool 1 is the most upstream pool located in Minneapolis, MN. Retention calculated as percent difference between discharge weighted input and output NO\textsubscript{3} concentration during August 1–13, 2015 survey. Error bars represent retention and uptake estimates after including an uncertainty term in each pool’s water budget. Pools 18 to 24 had unreliable estimates due to high tributary flows and erratic main channel chemistry. Retention and uptake in Lake Pepin plotted as light blue. The y-axis on the lower panel is truncated to improve visualization.
with this diminution of a capacity for N retention, which means that these loads have little chance of being retained in river and are likely to be discharged into the Gulf of Mexico.

In contrast to the lower UMR, Pools 1–13 are composed of a large proportion of backwaters and impounded areas [22], which would be expected to promote NO₃ removal. We observed modest retention (10%–18%) in five upper UMR pools (figure 3). Pools identified as NO₃ sinks tended to be large, composed of more than 50% non-channel habitat, and had low hydraulic loads (supplementary table 2). However, not all pools of this type were NO₃ sinks (e.g. Pool 9), and Pools 2 and 3 retained moderate amounts of NO₃ yet have relatively small surface areas. Higher NO₃ uptake rates in Pools 2 and 3 (figure 3) may have been facilitated by high concentrations of NO₃, which has been linked to N removal and denitrification in lentic and lotic systems [27, 30, 63].

Among pools, we did not find a clear driver of NO₃ retention (supplementary figure 2) as most pools had low NO₃ uptake rates and did not remove a large fraction of incoming NO₃ (figure 3). Further, uncertainty in our retention estimates may have precluded the detection of potential drivers. In some sections of the UMR, NO₃ removal via denitrification may have been balanced (or exceeded) by nitrification. Nitrification may be important in the UMR [46] because water residence times through hyporheic zones tend be shorter than the timescales necessary to favor denitrification over nitrification [59, 65]. Additionally, mean water residence times through pools are short (<3 days; supplementary table 2), which limits the mitigating effect of backwaters on downstream N export. Further, most flow bypasses backwaters as it is directed through the main navigation channel by channel-training structures. Thus, most of the UMR flow—and its N load—is shunted downriver through the river’s main channel, resulting in minimal overall N processing.

3.2. Lake Pepin
Lake Pepin is a natural lake that behaves much like a reservoir in terms of its capacity to sequester NO₃. Lake Pepin retained 47% of incoming NO₃ (figure 3), making it the major NO₃ sink in the UMR. It has nearly ten times the water residence time of other UMR pools and one of the highest NO₃ removal efficiencies (supplementary table 2). As NO₃ declined in Lake Pepin, we observed sequential spikes in nitrous oxide and methane (figure 4). This sequence strongly suggests removal of at least some fraction of the NO₃ via denitrification and the associated production and downstream displacement of nitrous oxide, followed by methanogenesis after the dissipation of much of the NO₃ and nitrous oxide. While this longitudinal change is consistent with thermodynamic constraints on microbial metabolism [66], to our knowledge, such a pattern has not been observed in surface waters of fluvial systems. Its detection was facilitated by the high spatial density of measurement, and points to substantial anaerobic metabolism within Lake Pepin that is associated with the likely permanent removal of a portion of the incoming N load to the benefit of downstream waterbodies.

NO₃ retention in Lake Pepin observed in this study was high relative to modelled estimates for large rivers [27] as well as prior estimates for Lake Pepin [34]. Pronounced retention was probably due to river conditions during our study. We sampled during relatively low discharge (~70% of median annual discharge), resulting in a slower flushing rate and allowing more time for biogeochemical processing. Additionally, removal efficiencies may have been elevated due to warm temperatures and high light availability, which control denitrification [44] and primary production [67, 68], respectively. The combined high demand and prolonged time available for processing in August likely drove maximum retention in comparison to the summer average [34] that incorporates a broader range of environmental conditions. Yet our results are consistent with long-term data [34] that hint at notable retention in Lake Pepin, and at the same time, limited retention in other sections of the river.

3.3. Impoundments
While human-constructed impoundments retain substantial amounts of N in other river systems [30, 31], UMR impoundments did not alter NO₃ transport during our single survey. NO₃ concentrations did not decline longitudinally in the navigation channels above dams. Additionally, when we sampled laterally across impounded areas, NO₃ concentrations...
remained similar to the bordering navigation channel (e.g. figure 5). Both impounded areas and channels are locations of locally high N concentrations [69], suggesting minimal N processing in impoundments. UMR impounded areas differ dramatically from the larger storage reservoirs such as are present on other large rivers (e.g. the Missouri and Columbia Rivers). UMR impoundments are shallow and flush quickly due to relatively low dam height (3.9 m mean vertical lift; www.mvp.usace.army.mil) to facilitate navigation rather than water storage [42]. This, combined with sizeable discharge, produces large hydraulic loads and short water residence times (supplementary table 2) compared to reservoirs across the Mississippi River basin [31]. Consequently, dams on the UMR do not increase water residence times to the extent necessary to significantly reduce NO_3 loads in the river.

3.4. Backwaters
Backwaters of Pool 8 (and other pools) consistently had lower NO_3 than the main channel (figure 5), and these sites are known to remove N [43, 48]. Across the UMR, limited hydrologic connectivity to the main channel allows differences in N concentrations to develop during baseflow, but spatial differences diminish during high flow periods [48] as hydrologic connectivity increases between the river channel and backwaters. A clear example of the development of nutrient heterogeneity in response to loss of connectivity is provided by Lawrence Lake (a backwater lake located in Pool 8; see figure 5). In June 2004, flooding of the Root River delivered NO_3-rich water to this backwater habitat [48]. As flow receded and connectivity between the lake and the UMR main channel was diminished NO_3 declined rapidly from 6 to 1 mg N L\(^{-1}\) over a 2 week period [48], indicating high N removal capacity. Thus, variability in biogeochemical processing can drive lateral differences in NO_3 when hydrologic connectivity diminishes and these backwater habitats become functionally isolated from the through flowing river.

Although we observed stark lateral differences in NO_3 within pools (figure 5), the influence of backwaters on downstream export appeared limited. We found no relationship between backwater area and NO_3 retention across UMR pools (supplementary figure 5). Additionally, average NO_3 retention in Pool 8 was low (0.6%; supplementary figure 6) despite it being backwater-rich [22]. Comparatively, our removal estimate for Pool 8 is lower than another mass balance study [46] that estimated the pool retained 14% of its annual NO_3 load. However, another study [70] indicated overall NO_3 production in Pool 8 as annual exports were greater than inputs, suggesting that Pool 8 backwaters may not have a modulating effect on NO_3 export. By definition, backwaters have reduced connectivity to the river channels, which hinders their ability to continually intercept NO_3 loads. Similar hydrologic ‘short-circuiting’ occurs in stream transient storage zones [71] and flow through wetlands [72], where N loads bypass locations of elevated N processing potential. While backwaters have elevated NO_3 removal capacity, their limited connectivity to the main channel minimizes their net effect on downstream NO_3 export.

3.5. Study limitations
While our study was spatially extensive, we recognize its limitations and the assumptions in our methods. The broad-scale pattern in NO_3 and the pool-specific retention estimates were based on a single snapshot in time. Thus, these results miss temporal heterogeneity in water chemistry and in N transformation rates [44, 63]. Additionally, our evaluation ignored lateral and vertical variation within the main channel, which we expected to be small compared to longitudinal and temporal variation due to fast flow velocities. Although disregarding this variation is frequent [e.g. 20, 21, 63], at times there were clear lateral differences in UMR water chemistry associated with horizontal stratification. Additionally, our retention estimates include uncertainty associated with missing water sources and non-steady state conditions. In five pools, our water budgets had percent errors greater than 10% (supplementary table 3) and in four pools SPC did not behave conservatively (>5% percent error; supplementary table 2), indicating there may be missing or temporally dynamic water sources. Even with these limitations and model uncertainties, this data-dense survey coupled with repeat mapping of Pool 8 align with modelling [21] and upscaling [22] approaches that collectively point to limited retention in the Mississippi River even at times of year when conditions are most amendable to N losses.

3.6. Strategies for increasing Mississippi River N removal
The data and analysis presented in this paper do not support the notion that nutrient management strategies targeting the Mississippi River mainstem will be effective in substantially reducing N export to the Gulf of Mexico. In its current state, human channel modifications have pushed the UMR toward a regime of N transport rather than N removal. While enlarging or creating impounded areas and increasing flooding to backwaters may enhance N retention, such an increase would likely be small. To be effective, any nutrient management strategy based solely on enhancing these habitats would need to consider the spatial arrangement of sources and be scaled to the size of the river. For example, impoundments on the Mississippi River would need to be positioned downstream of major sources and be massive in size to effectively intercept and retain N loads. In addition to construction costs, expanding impounded areas would require coordinating and purchasing huge swaths of privately owned land, making it nearly impossible. Additionally, the long term N dynamics in impounded waters are not well understood [31], and potential environmental gains may be offset
Figure 5. Temporal and spatial pattern of nitrate (\(\text{NO}_3\)) in Mississippi River Pool 8. (a) \(\text{NO}_3\) across Pool 8 on four dates (maps; upper right) where yellow and red colors indicate higher concentrations. (b) Seasonal pattern of \(\text{NO}_3\) for select Pool 8 stations (time-series; middle right) US Army Corps of Engineers Upper Mississippi River Restoration Long Term Resource Monitoring element (LTRM) fixed sampling sites (lines and circles) and FLAME samples (∗). Symbol color reflects relative connectivity to main channel where dark blue indicates least connected and brown—most connected (i.e. Lawrence Lake is the least connected). Consistent stations between FLAME and LTRM share color. (c) Mississippi River and Root River discharge (time-series, lower right). (d) USGS defined aquatic areas (basemap; lower left) largely driven by hydrologic connectivity to the main channel and water velocities. The river flows from north to south.

by harmful societal and ecological consequences [73]. Alternatively, reconnecting backwaters may promote \(\text{NO}_3\) retention, but hydraulic through-flow would need to be optimized for maximal water residence times and scaled to be commensurate with riverine hydraulic loads [73]. It has been suggested that reconnecting \(~10,000\) ha of backwaters to the UMR would be necessary to remove \(~40\)% of the UMR \(\text{NO}_3\) load at the confluence with the Chippewa River [73]. However, more than \(~80\)% of the load enters farther downstream, indicating fundamental shortcomings of this strategy at the whole river scale. Routing Mississippi River flows through large corridor wetlands—namely the Atchafalaya River Wetland—was also ineffective in retaining N as hydraulic loads outweighed N processing potential [75]. Large-scale water diversions also pose potential detrimental environmental consequences, such as cyanobacteria blooms and fish kills, related to increased sediment and nutrient delivery to backwaters [42]. Although the Mississippi River is an attractive site for watershed N remediation, the results presented here indicate that management strategies targeting the river do not offer a rapid nor easily implemented solution to the eutrophication of the Mississippi River and the hypoxia in the Gulf of Mexico. Emphasis should remain on the reduction of N inputs [42] and management strategies targeted closer to upland sources [11], rather than relying on removal in the Mississippi River.
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ORCID iDs

Luke C Loken @ https://orcid.org/0000-0003-3194-1498  
John T Crawford @ https://orcid.org/0000-0003-4440-6945  
Mark M Dornblaser @ https://orcid.org/0000-0002-6298-3757  
Robert G Striegl @ https://orcid.org/0000-0002-8251-4659  
Jeffrey N Houser @ https://orcid.org/0000-0003-3295-3132  
Peter A Turner @ https://orcid.org/0000-0003-0839-1408  
Emily H Stanley @ https://orcid.org/0000-0003-4922-8121

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