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Network Controls on Mean and Variance of Nitrate Loads from the Mississippi River to the Gulf of Mexico

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Abstract

Excessive nitrate loading to the Gulf of Mexico (GoM) has caused widespread hypoxia over many decades. Despite recent reductions in nitrate loads observed at local scales, decreases in nitrate loading from the Mississippi River basin (MRB) to the GoM have been small (1.58% during 2002–2012) with a low level of analytical confidence in this trend. This work seeks to determine the reasons why local-scale improvements have not translated into reductions at the outlet of the Mississippi River. We estimated annual nitrate loads from 166 sites in the MRB over the 2002 to 2012 period to examine trends and variability. The Upper Mississippi and Ohio Rivers together dominate the average nitrate load to the GoM, but very large interannual variability is driven primarily by the Upper Mississippi River. Within the Upper Mississippi River basin, decreasing trends in nitrate loading were common and the greatest improvements occurred at sites with the highest initial nitrate loads (the worst water quality). However, these improvements were balanced with increasing nitrate loads in other parts of the basin, such that the mean trend in load was near zero. Although load reductions in either the Ohio or Upper Mississippi basins have the potential to reduce the loads to the GoM, the improvements have not yet been large enough or widespread enough to lead to a change at the outlet. This analysis provides a basin-wide perspective on recent nitrate trends and the contribution of tributary basins to the mean and variability of nitrate loading to the GoM.

Core Ideas

- High nitrate loads to the Gulf of Mexico remained stable in the 2002 to 2012 period.
- Nitrate load trends in the Mississippi River Basin were mostly small and offsetting.
- Larger, more widespread decreases are needed to achieve larger reductions at the outlet.
- Variation in nitrate load is driven mostly by the Upper Mississippi River subbasin.
- Mean reductions in gulf hypoxic zone size could be disrupted by large interannual variation.

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Nutrient loading to the Gulf of Mexico (GoM), which has myriad ecological and economic consequences (CENR, 2000; NRC, 2000; Craig et al., 2005; Smith et al., 2017), has remained relatively constant over recent decades (Sprague et al., 2011), despite focused efforts at reduction (USDA, 2012). The GoM is representative of a worldwide phenomenon of nutrient-driven hypoxia in coastal ecosystems (Diaz and Rosenberg, 2008). Enhanced nutrient inputs to agricultural land support high crop yields and food production, but delivery of excess nutrients to marine ecosystems such as the GoM disrupts fisheries and ecosystem structure through eutrophication (Diaz and Rosenberg, 2008). In addition to the distal impacts to the GoM via nutrient loading from the Mississippi River basin (MRB), there is also the potential for more localized impacts from elevated nutrient concentrations in surface waters, including increased costs for drinking water treatment (USEPA, 2015), increased risk of bladder cancer in some populations (Jones et al., 2016), negative effects on the health of small children (Ward et al., 2005), and increased risk of biodiversity loss (Mozumder and Berrens, 2007).

A group of federal and state agencies and tribes, known as the Hypoxia Task Force, has established goals of reducing nutrient loading to the GoM from the MRB. Their stated goal is to reduce total nitrogen (N) and total phosphorus loading to the GoM by 45% from a 1980 to 1996 baseline period by the year 2035, a level that is predicted to limit the GoM hypoxic zone to <5000 km^2. An interim reduction goal of 20% by 2025 has been established (Hypoxia Task Force, 2017). In this work, we focus on N, specifically in the form of nitrate, which is the dominant form of N loading to the GoM (Goolsby et al., 2000). In addition to the stated goals of reducing average nutrient loads, it is also recognized that loads during high runoff years will need to be addressed to consistently achieve these targets with respect to the size of the hypoxic zone (Donner and Scavia, 2007). Therefore, the sources of interannual variations need to be considered in reduction strategies.

The Hypoxia Task Force and others have recognized nutrient load improvements in a number of small watersheds within the MRB (USDA, 2012). Ultimately, however, these improvements have not translated to corresponding reductions in nitrate

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Abbreviations: FN, flow-normalized; GoM, Gulf of Mexico; MRB, Mississippi River basin; NWIS, National Water Information System; UMR, Upper Mississippi River; WRTDS, weighted regressions on time, discharge, and seasons.

loading to the GoM (Sprague et al., 2011), as will also be shown here. The lack of progress has been linked to legacy N sources in the basin (Van Meter et al., 2018) and localized differences in N storage capacity in groundwater systems (Green et al., 2014). However, it is also becoming increasingly recognized that the variability and expression of temporal trends are dependent on basin-wide organization of subwatersheds due to lag effects, macroscale differences in subbasin characteristics, and differential travel times in the basin (Zeiger and Hubbart, 2016; Zhang et al., 2016; Abbott et al., 2018)

The primary goal of this work is to identify reasons why local improvements have not resulted in reduced loads at the outlet of the Mississippi River. We focused specifically on the objectives of reducing the long-term mean nutrient load, and interannual variability, which can lead to an extremely large hypoxic area in high runoff years. Our approach was to examine estimated nitrate loading from a large monitoring dataset and ask (i) how have changes in mean conditions upstream contributed to changes in conditions at the outlet, and (ii) where has interannual variability upstream contributed to interannual variability at the outlet.

Materials and Methods

Data Sources and Processing

Water quality data used in this analysis originated from a broad range of federal, state, local, and tribal sources. Because the data originated from a variety of sources, it was necessary to harmonize information to standard reporting units, sample handling, remark codes, and parameter names. In cases where metadata were not sufficient for adequate interpretation, the observations were excluded from the analysis (Oelsner et al., 2017; Sprague et al., 2017). Nevertheless, the resulting data aggregation was unprecendented in scope and provided a large number of sites with nitrate trends in the MRB. The parameters nitrate and nitrate plus nitrite were found to be equivalent for the purposes of this analysis, so water quality data used for nitrate trends include both parameters (Oelsner et al., 2017). All observations were expressed as milligrams of N per liter.

Daily stream discharge data were required for the trend and load estimation model, weighted regressions on time, discharge, and seasons (WRTDS; Hirsch et al., 2010; Hirsch and DeCicco, 2015). In most cases, discharge data originated from the USGS National Water Information System (NWIS; USGS, 2016). Water quality and stream discharge data typically originated from the same monitoring location. In cases where the originating locations differed, water quality and stream discharge were merged using an indexing algorithm. Monitoring locations were matched to stream flow lines in the National Hydrography Dataset (NHDPlus) V2 Medium Resolution (McKay et al., 2012) and snapped to the closest gauge on the same named river. Matches were checked manually and removed in cases where discontinuities existed between the water quality and stream gaging locations (i.e., hydrologic modifications, large point inputs, major tributaries, etc.) or if the calculated upstream watershed area differed by >10% between the monitoring stations. Stations with matched water quality and streamgage data were further checked for data coverage. For load and trend analysis, stations were required to have at least four samples per year in 70% of the years in the trend period. Additionally, at least four samples per year were required in the first 2 yr and last 2 yr in the trend period. Sites were also checked for adequate coverage of samples during high flow. More detailed descriptions of the gage matching routines are given in Oelsner et al. (2017).

Load Estimation

For stations that matched data criteria, WRTDS was run for the length of the water quality record using the EGRETci package in R (Hirsch et al., 2010; Hirsch and DeCicco, 2015). Benefits of WRTDS include a strong ability to detect changes; flexible relationships between concentration, discharge, and season that are allowed to change over time; and that the time series of estimates do not follow a fixed or predetermined "shape" so can be either monotonic or non-monotonic (Hirsch et al., 2010). The WRTDS is a weighted regression approach that places weight calibration points based on their proximity to estimated values in the model domain. The weighting scheme is a tricube function with adjustable parameters. For our analysis, the half-window width was set to 10 yr, one or two natural log units (for sites with drainage areas greater or less than 250,000 km^2, respectively), and 0.5 yr in the time, streamflow, and seasonal dimensions, respectively. The WRTDS provides daily estimates of load, concentration, and flow-normalized (FN) versions of these outputs. The daily estimates are also aggregated to monthly, seasonal, and annual values. The FN concentrations and loads are meant to remove the random hydrologic variation, which is known to affect concentration, load, and trend estimation and allow greater focus on changes in water quality that occur as a result of management actions or other long-term changes in the watershed.

The flow normalization algorithm works by producing estimates of load and concentration that occur at mean flow conditions for each day of the year. A primary assumption is flow stationarity, the absence of long-term directional trends, over the period of record. We used FN trends and loads primarily to describe behavior of sites during the period 2002 to 2012. The short duration of the trend period makes it unlikely that streamflow trends affected our interpretation, but it should be noted that when the assumption of flow stationarity is violated, water quality trends can be masked or trends in flow can be mistakenly attributed to changes in water quality (Choquette et al., 2019; Murphy and Sprague, 2019).

Trend analysis focused on the time period of 2002 to 2012 because it offered the greatest number of sites having appropriate data for modeling, which offered an expanded view of nutrient loading patterns and trends relative to previous reports on the MRB (Sprague et al., 2011). However, analyses of watershed load contributions and variability in subwatershed load time series used all available model output and therefore included data prior to 2002. The FN load estimates were aggregated at the annual level for each monitoring site, and loads were reported in units of 10^6 kg N yr^{-1}. Trends in FN annual load were calculated as net change

$$\text{Net change} = L_{t2} - L_{t1} \quad [1]$$

where is L_{t2} the annual FN load in the year at the end of the trend period and L_{t1} is the annual FN load at the beginning of the trend period. Trend likelihood was determined using a bootstrapping approach, in which the water quality record for a site

was subsampled and the WRTDS model rerun up to 100 iterations (Hirsch and DeCicco, 2015). Each iteration produced different estimates for L_{t1} and L_{t2} and likelihood was determined by the proportion of iterated model runs showing $L_{t2} > L_{t1}$ or vice versa. Sites with >70% coherence among bootstrapped results were considered to be showing a likelihood of that trend result.

Load Summation and Network Analysis

We assessed how much the major tributary monitoring sites within the MRB accounted for the total load at the outlet to the GoM. This analysis was performed to determine the influence of unmeasured inputs (i.e., from point sources, smaller tributaries in the lower basin, or diffuse groundwater inputs downstream of the tributary watersheds) on nitrate loading from the Mississippi River to the GoM. If the contribution of unmeasured sources was large, then our ability to interpret trends using existing monitoring locations would be limited. In this study, the outlet site was defined as the Mississippi River near St. Francisville (NWIS Station ID 07373420). Nitrate concentration data for this site were used in conjunction with streamflow data from the Mississippi River at Tarbert Landing (NWIS Station ID 07295100) and Old River Outflow Channel (NWIS Station ID 07381482) to estimate loads. We defined the "major tributaries" to the Mississippi River as the Ohio River (Ohio River at Dam 53 near Grand Chain, IL, Station ID 03612500), Upper Mississippi River (UMR; Mississippi River below Grafton, IL, Station ID 05587455), Missouri River (Missouri River at Hermann, MO, Station ID 06934500), and Arkansas River (Arkansas River at David D. Terry Lock & Dam below Little Rock, AR, Station ID 07263620). Each has distinct differences in population, climate, hydrology, and land use patterns, with the UMR having the highest densities of crops, fertilizer, and manure applications (Table 1).

We summed the load from the tributaries and then compared that with the estimated load at the outlet to determine whether the combined loads from major tributaries were good approximations of the actual estimated load at the outlet. The fraction each tributary contributed to total nitrate loading at the outlet of the basin (F_t) was calculated by dividing the load at each tributary (L_t) by the load at the outlet (L_o) as $F_t = L_t/L_o$. An analogous calculation was performed within the UMR. This load fraction calculation allowed us to determine the relative contribution of individual basins to the annual nitrate load, and whether there was switching of dominance among tributaries and subtributaries. For the UMR analysis, we combined the Iowa River (Iowa River at Wapello, IA, Station ID 05465500), Des Moines River (Des Moines River downstream of Ottumwa, IA, Station ID 05489500), and Skunk River (Skunk River at Augusta, IA, Station ID 0474000) into one larger subtributary group that we call the eastern Iowa tributaries. These basins all had similar concentration–discharge (C–Q) relationships, similar land use, and, when combined, were comparable in discharge and load to the Illinois River (Illinois River at Hardin, IL, Station ID 05586100). The other subtributaries to the UMR that we included in this analysis were the UMR at Clinton, IA (Station ID 05420500), and the Minnesota River at Fort Snelling State Park, MN (Station ID 05330920).

Changes in the Concentration–Discharge Relationships

The C–Q relationship for nitrate and its evolution over time was assessed for the UMR, Ohio, and select subtributaries in the MRB to determine if there were any patterns with respect to the mean and variance of nitrate loads. The C–Q relationship is typically expressed as being negative, positive, or flat (also known as homeostatic; Godsey et al., 2009; Moatar et al., 2017). Negative slopes are usually interpreted as showing dilution of point sources and/or that base-flow inputs are dominant, and positive slopes are interpreted as showing situations where surface runoff processes and nonpoint sources dominate (Moatar et al., 2017). These two situations can also be referred to as supply limited (negative slope) or transport limited (positive slope), each having implications for the interaction between precipitation within a basin and the total load of nitrate. In the case of supply limitation, greater discharge will lead to comparatively small increases in load, whereas under transport limitation, greater discharge will lead to large increases in load. As already mentioned, WRTDS allows for flexible C–Q relationships that can change over years and seasons. Changes to the C–Q relationship can occur due to management practices, changes in storage of the constituents of interest, and changes in the transport function in watersheds. Therefore, having a flexible C–Q relationship over time, such as the WRTDS model used in this study, provides a more realistic modeling framework for water quality constituents over extended time periods. We extracted information regarding the C–Q relationships from annual mean flows and concentrations.

Statistical Tests

All analyses were completed using the R Statistical Programming Language (R Core Team, 2017). To test whether trends in nitrate

Table 1. Characteristics of each of the four major tributaries to the outlet of the Mississippi River.

Major tributary basin and monitoring location	Basin area	Population	Avg. air temperature	Annual precipitation	Agriculture	Manure from farms	Farm N fertilizer	Area soy	Area corn	Avg. discharge
	× 1000 km^2	persons km^{-2}	°C	cm	%	kg km^{-2}		%		m^3 s^{-1}
Missouri (Missouri River at Hermann, MO; 06934500)	1345.3	9.2	7.46	54.1	32.42	888.5	2387.4	5.64	8.36	2726
Ohio (Ohio River at Dam 53 near Grand Chain, IL; 03612500)	527.4	55.7	11.63	118.52	35.33	914.5	2219.7	7.27	8.78	8677
Upper Mississippi (Mississippi River below Grafton, IL; 05587455)	446.9	48.5	7.64	85.92	62.38	1461.1	5649.3	16.25	27.29	3636
Arkansas (Arkansas River at David D Terry Lock & Dam below Little Rock, AR; 07263620)	408.7	16.9	12.62	71.97	30.78	1199.4	1586.3	1.41	2.78	1420

loading were associated with water quality patterns among basins, a linear regression was used to assess the relationship between trends in FN nitrate loads and the initial FN nitrate load at the beginning of the trend period. This initial load can be considered the nitrate load that would have occurred in that year under average hydrologic conditions. In both of these analyses, trends in FN load were expressed in units of 10^6 kg N yr^{-1}.

We were also interested in the patterns of variability, and in determining which parts of the basin contributed most strongly to the overall variability in nitrate loads at the outlet of the Mississippi River. We focused on the Ohio River and the UMR because of their primacy in overall nitrate loads in the MRB (Sprague et al., 2011). We tested how each tributary contributed to variability in nitrate loading using the equality of variance (F test, also known as the variance ratio test; Helsel and Hirsch, 1992) of the annual loads (not FN) between the major tributaries and the outlet using the function *var.test* in R. Type I error was guarded against by adjusting p values for multiple comparisons according to the Benjamini and Hochberg (1995) procedure. The source of variation was also evaluated analytically by sequentially holding each individual major tributary load constant and comparing the resulting simulated outlet load variance to the actual outlet load variance. Prior to using the test for equality of variance, we verified that the data followed a normal distribution using the Shapiro–Wilk test. We also performed the variance ratio test within the UMR to test for sources of variability among the subwatersheds. We were unable to break down sources of variation within the Ohio River basin or other major tributaries because of the scarcity of sites that passed data screening for inclusion in the load and trend analysis using WRTDS.

Results

Flow-normalized nitrate loading to the GoM from the MRB decreased by 1.58% during the period of 2002 to 2012, although the likelihood of the downward trend was very low (i.e., not coherent among bootstrapped WRTDS model runs), meaning that a downward trend was about as likely as not (Supplemental Fig. S1). This recent small decrease was preceded by a period of increasing FN nitrate loads in the 1970s and early 1980s. For example, the FN nitrate load increased from 554×10^6 to 833×10^6 kg N yr^{-1} between 1972 and 2012, an increase of 50%. The record of annual loads (i.e., not FN), including the focal trend period (2002–2012), was marked by wide interannual variability with a range of export between 390×10^6 and 1261×10^6 kg N yr^{-1}.

Throughout the MRB, trends in FN nitrate load were mostly modest, slightly increasing or decreasing, between 2002 and 2012 (Fig. 1), with most sites falling within a narrow range of the central tendency (Fig. 2; median change = -0.036×10^6 kg N yr^{-1}; mean change = -2.69×10^6 kg N yr^{-1}). In general, sites with the highest initial FN loads experienced the greatest decreases over the 10-yr period (Fig. 2, Kendall correlation, $\rho = -0.41$, $p < 0.0001$). Mean and median nitrate yield were 1.00 and 0.65 g N m^{-2} yr^{-1}, respectively, whereas the change in yield over the period of 2002 to 2012 had a mean and median of −0.15 and −0.01 g N m^{-2} yr^{-1}. Likewise, the largest decreases in yield occurred in the basins with the highest initial yields (Fig. 2; Kendall correlation, $\rho = -0.38$, $p < 0.0001$), so although improvements occurred in the basins with the worst initial water quality in terms of nitrate fluxes, these improvements were not widespread enough to result in improvements at the outlet of the basin and offset by increases elsewhere.

Decreasing nitrate trends were primarily found in the UMR. The largest improvements were typically found at sites monitored in the central and eastern region of Iowa (Fig. 1). Outside of the UMR, no sites in the Arkansas basin improved, one site within the Missouri basin improved, and four sites within the Ohio basin improved (not including the outlet of the Ohio River).

Over the period of 1992 to 2012, the sum of nitrate loads from the major tributaries was 78 to 110% (mean and SD: 95 ± 8%) of the load at St. Francisville (Supplemental Fig. S2). This result indicates that the influence of unmeasured nitrate inputs (i.e., from point sources, smaller tributaries in the lower basin, or diffuse groundwater inputs downstream of the tributary watersheds) was minimal. Therefore, insight about the basin-scale controls on nitrate load can be gained by analyzing patterns in nitrate load from the tributaries. Tributary contributions to overall nitrate loading followed an expected pattern, with the Arkansas River having the lowest average contribution (2.3%), the Missouri River contributing 13.5% on average. Over the period of 1992 to 2012, the Ohio River averaged 34.8% of the total nitrate load, ranging from 22.6 to 45.2% of the total nitrate load. However, contributions from the Ohio River were greater earlier in the record, reaching as high as 64.4% in 1973. Contributions from the UMR ranged between 26.1 and 63.4%, averaging 44.1% (Fig. 3). Although the Ohio River had greater average discharge, the similarity in nitrate load between the Ohio River and the UMR occurred because nitrate concentrations were higher overall in the UMR (Table 1). Despite the overlapping range of nitrate contribution between the Ohio and the UMR (means = 35 and 44%, respectively), their behavior over time has been very different. There was a decrease in the proportional contribution of the Ohio River in the 1970s and early 1980s, leading to generally similar load contributions as compared with the UMR in the most recent period (2002–2012), although the UMR accounted for more of the total load to the GoM in most years (Fig. 3). We suggest that if the load from the MRB increased until the 1980s, the proportional load from the Ohio River decreased, and there was little to no change in the absolute Ohio River load, then the UMR load must have increased. Other studies have noted increases in nitrate loads from the UMR over similar time periods, although the approaches and tests of significance differed (Sprague et al., 2011; Stets et al., 2015).

The UMR and the Ohio River differed greatly in the variances of annual nitrate load (not FN). When compared with the outlet of the MRB, the variance of the Ohio River was significantly lower, but the UMR was not statistically different, having a variance ratio of 0.87 (Table 2). This statistic indicates that ~87% of the variance at the outlet of the MRB can be attributed to the UMR, whereas only ~10% of the variance could be attributed to the Ohio River. We tested the contribution of the UMR and the Ohio River to the observed variance at the outlet using a second method. By holding each tributary load at its long-term average individually and then comparing the resulting change in the variance at the outlet, we found that only holding the UMR constant would reduce the variance at the outlet significantly ($p = 0.036$, $F = 4.58$; Table 2), whereas holding the Ohio River constant did not significantly alter the variance ($p = 0.34$, $F = 1.30$;

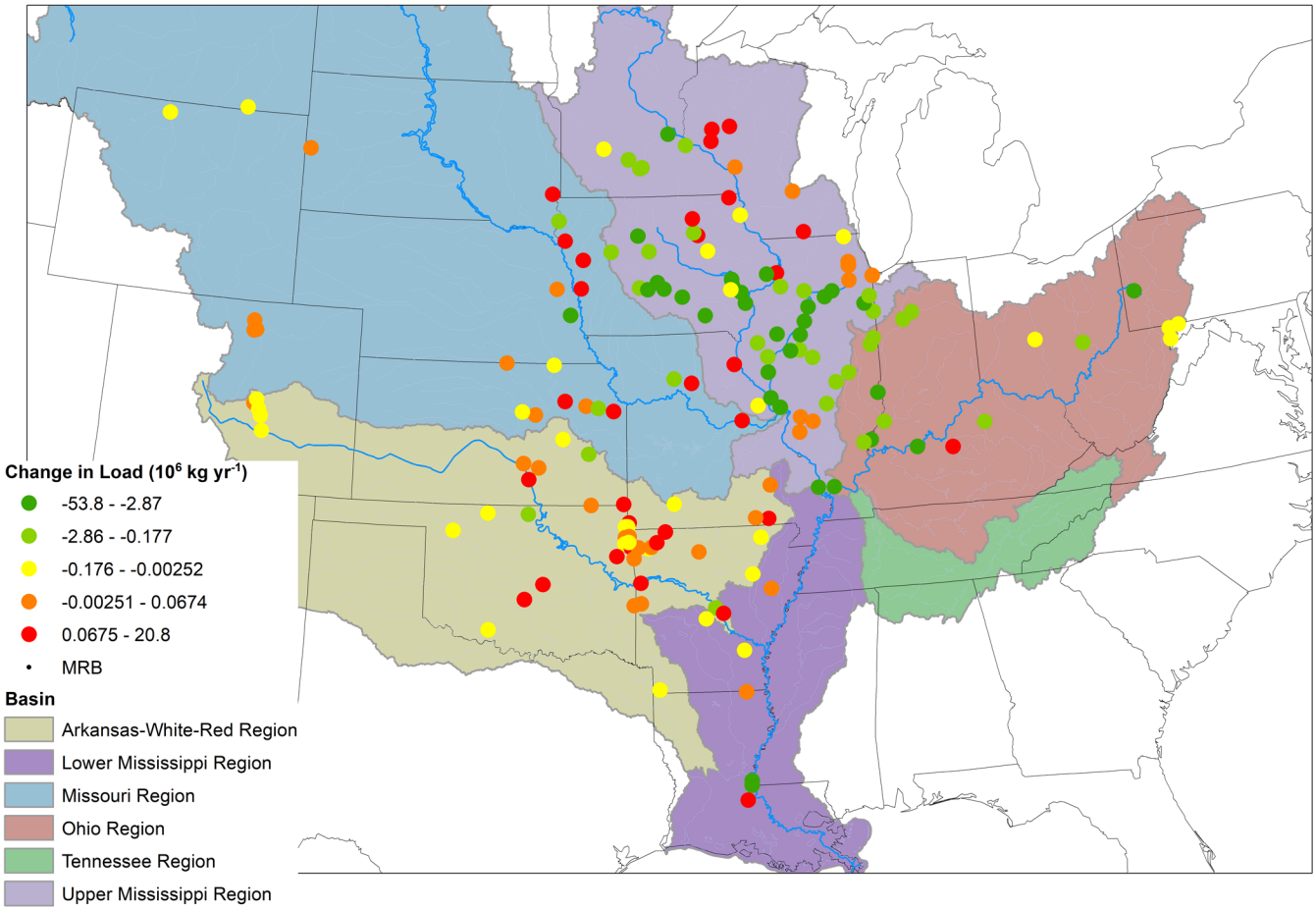

Fig. 1. Map of changes in flow-normalized nitrate load in the 2002 to 2012 modeling period. Green (negative) values indicate improving water quality, whereas red values indicate increasing nitrate load from watersheds. Outlines indicate major tributary watershed boundaries.

Table 2). Therefore, although the UMR and Ohio River basins are similar in their contribution of nitrate to the MRB, they behave differently in that there is unequal contribution to variability in nitrate loads to the GoM among subbasins of the MRB, with the UMR causing most of the interannual variability.

Water quality conditions in the UMR, as evidenced by the *C*–*Q* relationship, have changed over time and among seasons (Supplemental Fig. S3; also see Turner et al., 2006), but a notable feature of the *C*–*Q* relationship for all months and years in the UMR is the persistent positive slope, as is shown by *C*–*Q* plots generated from annual flow and concentration data (Fig. 4). Unlike the UMR, the Ohio River (near Grand Chain, IL) showed a mixture of both positive and negative *C*–*Q* relationships for nitrate (Supplemental Fig. S4), resulting in a slightly positive or flat *C*–*Q* relationship overall (Fig. 4). The difference in *C*–*Q* relationships suggests that a similar amount of flow variability results in a greater range of nitrate loads from the UMR than the Ohio River.

Because of the unique role of the UMR in controlling the variability in nitrate loads in the MRB, we examined the structure of subtributaries in the UMR in greater detail. A similar analysis in the Ohio River basin was prevented due to a lack of data on subtributaries. Our analysis revealed that the network structure in the UMR contrasts with that of the larger MRB. Subtributary loadings in the UMR showed substantial overlap among many more basins (Fig. 5). Any one of the subtributaries of the UMR (eastern Iowa, Illinois River, Minnesota River, or UMR above Clinton, IA) had the potential to dominate the total nitrate load leaving the UMR in a given year. The eastern Iowa tributaries had an especially large range in contribution to the nitrate load leaving the UMR (10.2–3.9%). The large contribution, and large range among years, has also been documented for the state of Iowa as a whole (Jones et al., 2018). The eastern Iowa tributaries and the Illinois River were responsible for the largest proportions of the load, whereas the Minnesota River was generally responsible for the smallest proportion, with its contribution generally at 12.7%, although it contributed up to 30% in some years due to high flows (Fig. 5).

The variances in annual loads from the subtributaries, however, were very different (Table 2). The variance of the eastern Iowa tributaries was greater than that of the Illinois River and the UMR station at Clinton, IA. It is acknowledged that the UMR is the main driver of variability at the outlet of the MRB and that variability arises from specific subtributaries of the UMR, so how do they compare? Compared with the outlet of the UMR (at Grafton, IL), eastern Iowa had the highest relative variance (26%), whereas the Illinois and UMR at Clinton, IA, only showed ~7% of the variance. We also simulated the effect of removing the variation induced by eastern Iowa and the Illinois Rivers and compared the resulting variance at the outlet using the variance ratio test. This simple model showed that by holding the load from these tributaries constant, the variance in nitrate load to the GoM would be reduced by half, although the results were only marginally significant ($p = 0.12$, $F = 2.504$; Table 2).

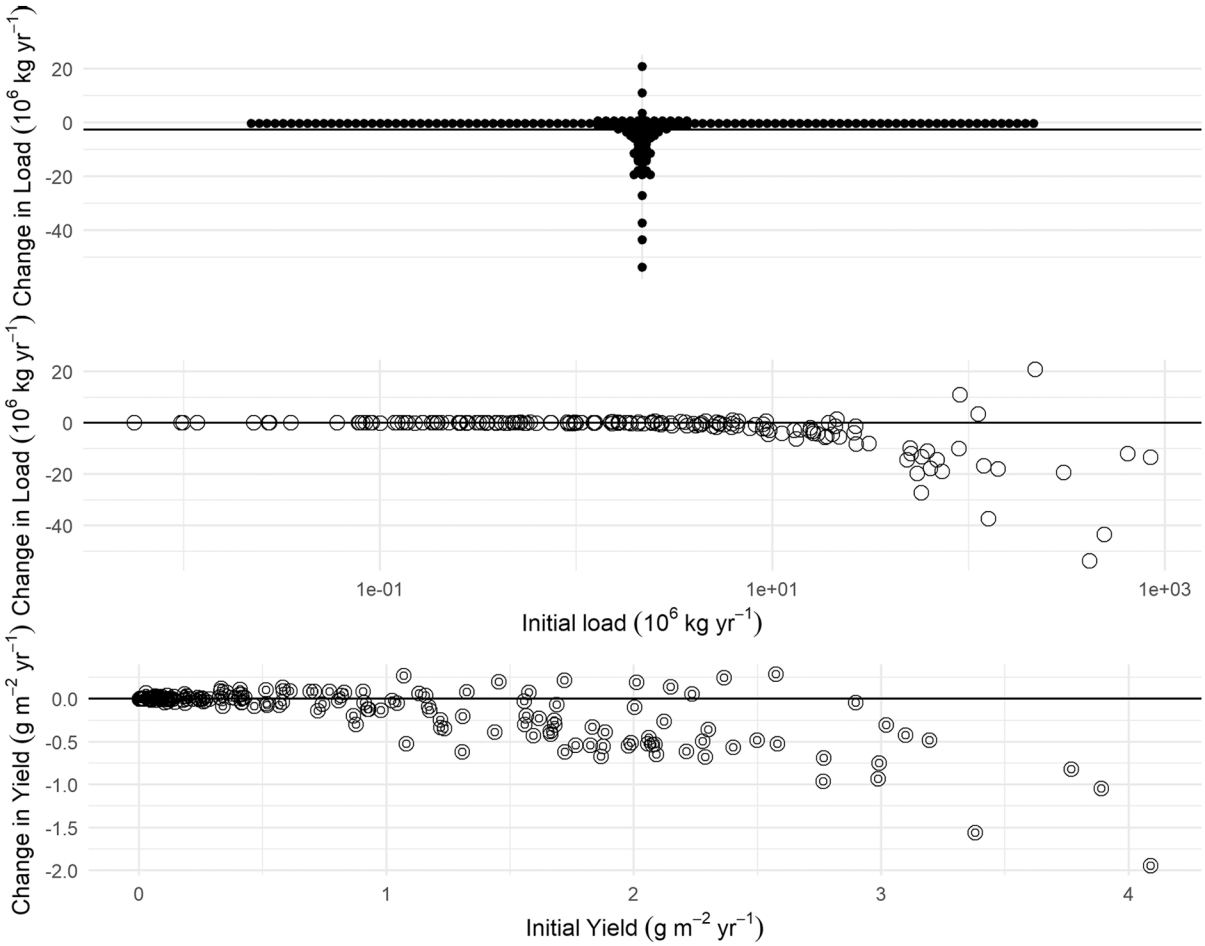

Fig. 2. Dot-plot showing changes in flow-normalized nitrate load in the Mississippi River basin during the 2002 to 2012 trend period (top panel). Scatterplot of initial (2002) nitrate load vs. the change in flow-normalized nitrate load from 2002–2012 (middle panel). Initial nitrate yield vs. change in nitrate yield (bottom panel).

Similar to the UMR as a whole, the prominent subtributaries with respect to total nitrate load showed mostly positive *C*–*Q* relationships (Fig. 6). Three subtributaries (East Iowa, Minnesota, and Illinois) overlapped in *C*–*Q* space, with the Minnesota River having the steepest slope. However, the Minnesota River had a much narrower range in discharge relative to the other two. The steep slope and high intercept relationship was much less pronounced downstream at the UMR monitoring site at Clinton, IA (Fig. 6). In contrast, two selected sites draining large portions of the state of Wisconsin (the Wisconsin River and Chippewa River) had mostly flat *C*–*Q* relationships and did not exhibit wide ranges in either discharge or concentration as compared with the Minnesota, eastern Iowa, or Illinois Rivers.

Discussion

The nitrate load to the GoM changed relatively little, if at all, in the 2002 to 2012 period when accounting for interannual variations in water discharge (Supplemental Fig. S1) and is still far from reaching the reductions established by the Hypoxia Task Force (Sprague et al., 2011; Van Meter et al., 2018). We found that most of the trends in nitrate loading within the MRB were close to zero and that increasing and decreasing loads and yields were balanced such that mean and median changes in the MRB were near zero (Fig. 2).

The sites that experienced the greatest decreases in loading had the highest nitrate concentrations initially (Fig. 2). Put another way, the worst sites have improved, but the improvement has not been large enough nor widespread enough to affect nitrate loading to the MRB. It is unclear at this point whether management actions specifically targeted to the sites with the highest initial concentrations drove the patterns of nitrate trends in this study. Legacy N has dampened temporal trends in the MRB, meaning that the response of water quality to management actions is typically muted or delayed (Van Meter et al., 2018). Along the same line of inquiry, an analysis of N trends in Iowa rivers found the strongest decreases in basins with the smallest groundwater N storage capacity (Green et al., 2014), suggesting that the basins most likely to show changes were those with limited capacity for legacy N storage. Our finding of strong decreases in N loading at monitoring locations in central and eastern Iowa was also described by Green et al. (2014) and supports this idea. Nevertheless, these changes were small compared with the load at the outlet of the Mississippi River and largely offset by increases in other parts of the basin including the Arkansas River, Missouri River, and other parts of the UMR watersheds (Fig. 1). Although a reduction in nitrate loading from any basin ultimately reduces nitrate loading at the outlet, at present, we cannot detect the impact of these improvements at the outlet because their contribution is small relative to the total load and they are potentially being offset by increases elsewhere.

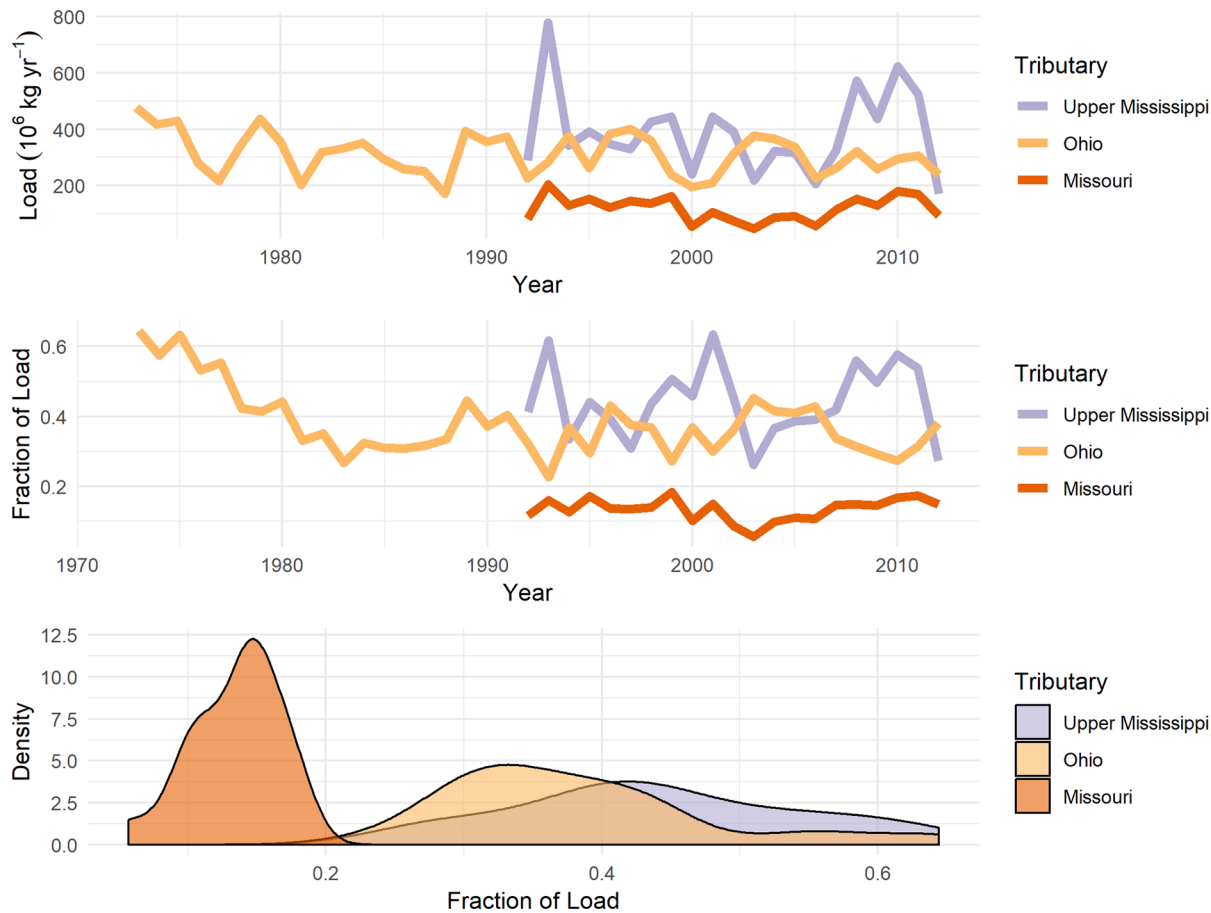

Fig. 3. Time series of major tributary nitrate load (top panel), time series nitrate load fraction to the outlet of the Mississippi River (middle panel), and histogram of nitrate load fraction by major tributary (bottom panel). The Upper Mississippi station is at Grafton, IL. Histograms were based on the entire nitrate load record available for each site in our dataset.

The UMR and Ohio River contributed similar amounts of nitrate to the GoM on average over this recent time period, 44 and 35%, respectively. Meanwhile, the other major tributaries to the Lower Mississippi, the Missouri, and the Arkansas Rivers contributed relatively little to the total nitrate load. These stark differences in nitrate loading among the major tributaries can be attributed to, among other drivers, the large differences in climate, hydrology, agricultural practices, and watershed size (see Table 1). The UMR and Ohio River have exhibited contrasting load histories (Fig. 3), and *C*–*Q* relationships (Fig. 4), and thus have had different impacts on the total nitrate load entering the GoM.

Table 2. Results of the variance ratio test (*F* test) comparing the variance in nitrate loads between monitoring stations within the Mississippi River Basin during the 2002 to 2012 time period.

Comparison	*P* value (Benjamini and Hochberg corrected)	Variance ratio
Basins		
Ohio vs. Outlet	0.002	0.1
UMR† vs. Outlet	0.84	0.9
UMR vs. Ohio	0.003	9.2
Iowa vs. Illinois	0.01	3.9
Iowa vs. Clinton	0.01	3.9
Iowa vs. Grafton	<0.0001	0.3
Illinois vs. Grafton	<0.0001	0.07
Clinton vs. Grafton	<0.0001	0.07
Simulations		
Outlet vs. Illinois and eastern Iowa variance removed	0.12	2.5
Outlet vs. UMR variance removed	0.036	4.6
Outlet vs. Ohio variance removed	0.34	1.3

† UMR, Upper Mississippi River.

Site-based load and trend models, such as WRTDS, reconstruct load histories at single stations but do not incorporate information from upstream locations and thus give little insight into the ways in which patterns occurring at tributary and subtributary scales affect water quality at the station of interest. For example, when patterns emerge due to the behavior of spatially distinct source areas, further insight is gained from analysis of nested monitoring locations. Our results from the UMR tributaries indicated frequent switching of dominance among basins. That is, each major subtributary had the capacity to drive the yearly load from the UMR as a whole. On average, the Illinois River, the group of tributaries emerging from eastern Iowa, and the UMR at Clinton, IA, were nearly equally responsible for the nitrate load from the UMR, comprising an average of 31, 26, and 26% respectively (Fig. 5). The impact of the state of Iowa is even more evident when its load contribution via the Missouri River is taken into account (see Jones et al., 2018). The geographical patterns with respect to nitrate loads were similar to those documented in nationwide regression models such as SPAtially Referenced Regression On Watershed attributes (SPARROW),

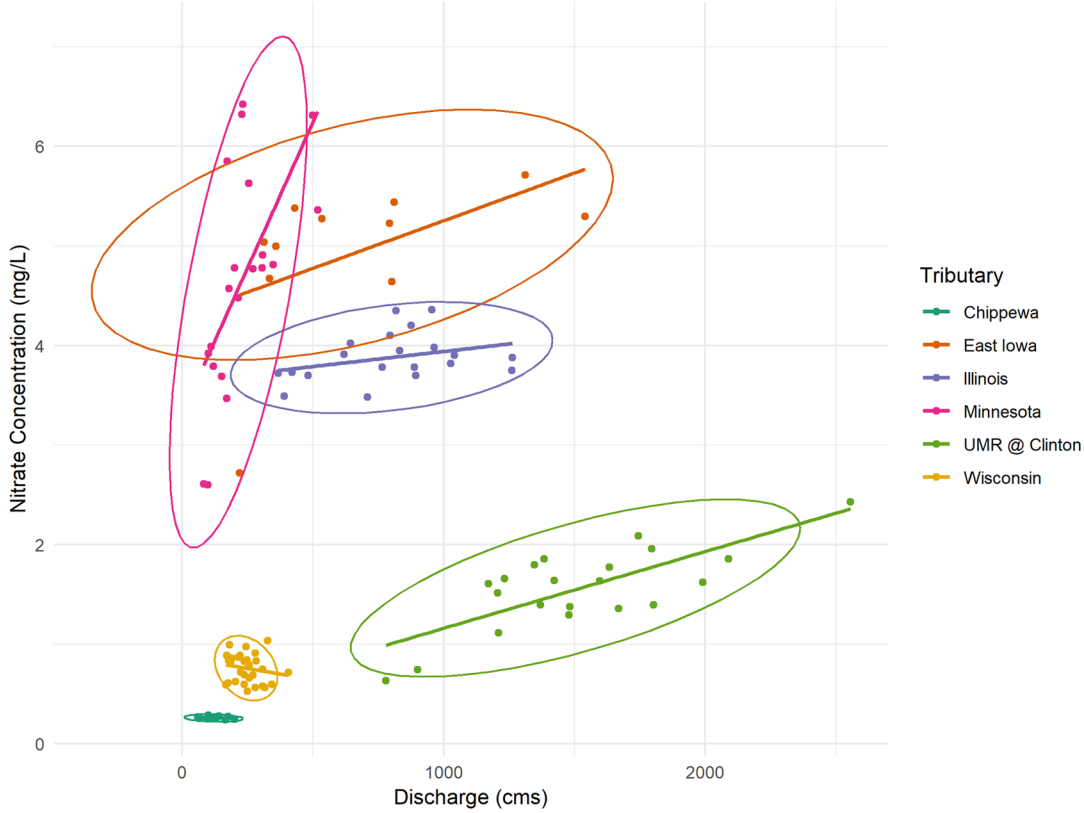

Fig. 4. Concentration vs. discharge relationships for the three major tributaries to the outlet of the Mississippi River. The Upper Mississippi station is at Grafton, IL. Discharge is given in units of cubic meters per second (cms).

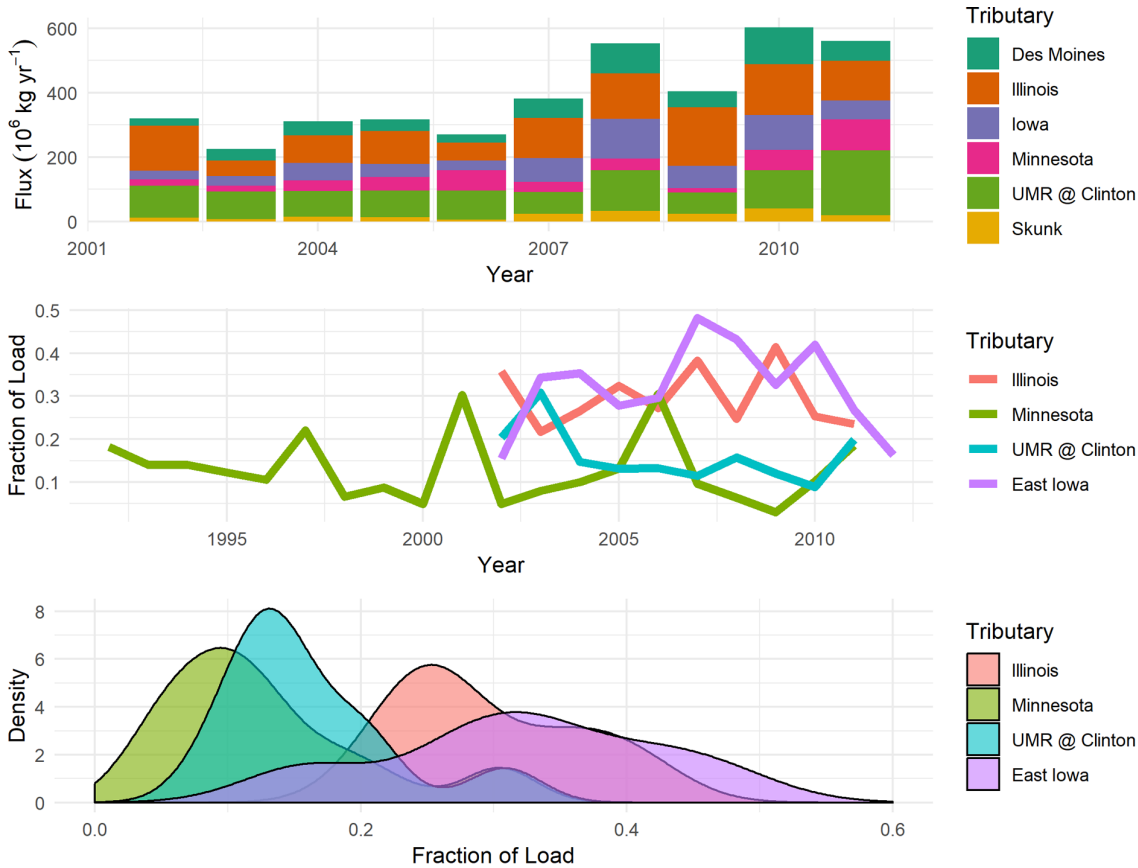

Fig. 5. Time series of the nitrate load from selected subtributaries of the Upper Mississippi River (UMR, top), time series of the fraction of nitrate load at the outlet of the UMR (middle) by major tributary, and histogram of the fractions of nitrate load at the outlet of the UMR by major tributary (bottom). The UMR station is at Clinton, IA. Histograms were based on the entire nitrate load record available for each site in our dataset.

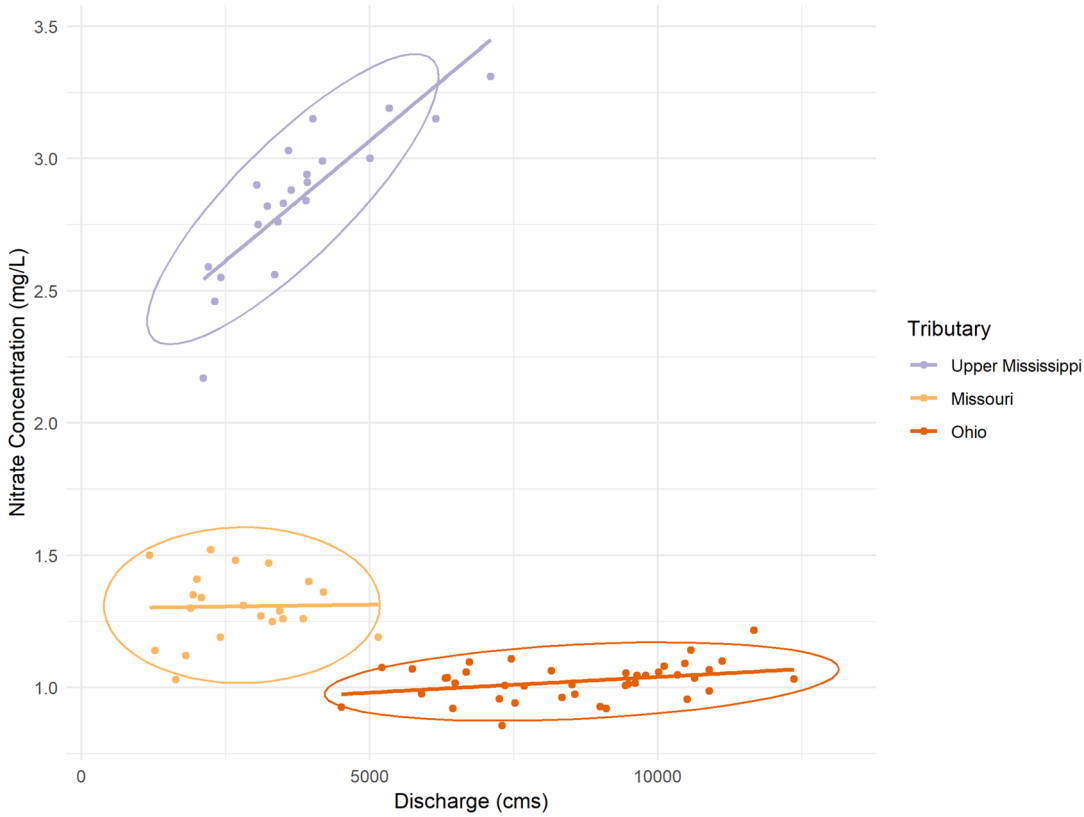

Fig. 6. Concentration vs. discharge relationship for selected subtributaries of the Upper Mississippi River. The Upper Mississippi River station is at Clinton, IA. Discharge is given in units of cubic meters per second (cms).

with agricultural areas in Minnesota, Iowa, and Illinois having the greatest nutrient loading (Preston et al., 2011). However, this study enhances the loading estimates beyond the single time-point average conditions previously documented and provides information on patterns and sources of variation.

Despite the relatively similar contributions from the UMR and the Ohio River to the average nitrate load to the GoM, we found that the UMR is likely responsible for most of the interannual variability in nitrate loads to the GoM (∼90%, see Table 2). The dominance of the UMR in controlling interannual variability in MRB nitrate loads can be attributed to the magnitude of nitrate loads, variability in Q, and the dynamic nature of the C–Q relationship in that basin (Supplemental Fig. S3). First, nitrate loads from the UMR were ∼25% larger than those from the Ohio River during 2002 to 2012, and the UMR variance was more than nine times larger than the Ohio River variance (Fig. 1, Table 2). The greater average loads in the UMR mean that it would have a greater variance even if the CVs were the same between the basins. Second, the variation in Q is larger in the UMR than in the Ohio River (37 vs. 15%, respectively; 2002–2012). Finally, the Ohio River is weakly transport limited or possibly homeostatic as evidenced by the mostly flat C–Q relationships (Fig. 4; Moatar et al., 2017), and it has seen rather large decreases in nitrate load contributions in the 1970s and 1980s (Fig. 3). Weak transport limitation or homeostasis of the Ohio River implies that loads are unlikely to increase dramatically, even in the event of substantially higher precipitation in that basin. On the other hand, the highly agricultural UMR (Table 1) is strongly transport limited as demonstrated by the positive C–Q relationships (Supplemental Fig. S3). Transport limitation, possibly due to legacy nutrient accumulation (Van Meter et al., 2017), has also been suggested by others (Basu et al., 2010). Transport limitation implies that concentration and discharge increase in tandem such that loading accelerates under greater precipitation and runoff in the UMR basin, which may be exacerbated by trends in climate within the basin (Donner et al., 2002). Therefore, in high runoff years, which do not occur completely at random through time (Maurer and Lettenmaier, 2003; Twine et al., 2005), the UMR will yield an even larger load of nitrate to the GoM than average resulting in a large interannual variability in loads. Given the importance of springtime nutrient loading to the GoM (Booth and Campbell, 2007), seasonality of loads is also of interest. Although a thorough analysis is beyond the scope of this manuscript, data in Sprague et al. (2011) shows that spring nitrate loading from the UMR has a CV twice as large as that of the Ohio River (42 vs. 23%, respectively, not shown). This suggests that the variability in the UMR occurs at the annual scale, as well as during the spring.

We found that the eastern Iowa tributaries and the Illinois River were responsible for most of the interannual variation in nitrate loads at the scale of the UMR, as reflected by the variance ratio tests. The other large subtributaries within the UMR had less impact on variability. A similar test of the influence of the Illinois and eastern Iowa tributaries on the outlet of the MRB suggested that they contributed substantially to the overall variance (50%), but we cannot say with certainty due to the short period of record (Table 2). The high variability in these subtributaries is likely the result of their C–Q relationships, which have high intercepts and steep slopes (Fig. 6), which lead to especially large loads during wet years. We suggest that similarities in C–Q

(transport vs. supply limitation regimes) may reflect similar underlying hydrologic and biogeochemical drivers within these basins, similar to what has been shown for other nutrients and sediments (Underwood et al., 2017). The Minnesota River also overlaps the Iowa tributaries and the Illinois River with respect to the C–Q space, but even the greatest load from the Minnesota never matched the Illinois or Iowa tributaries, partly because the total water discharge from the Minnesota was smaller, even in high runoff years.

Conclusion

To achieve progress toward mean N reduction goals in the MRB and maintain the target size of the hypoxic zone over multiple years, both the mean load and interannual variability in loads must be addressed. Large reductions throughout the MRB will reduce the mean nitrate load transported to the GoM, but additional targeted reductions within basins exhibiting the greatest variability will also be needed to reduce the interannual variability in loads. Our work suggests that without actions to reduce the nitrate inputs within targeted tributaries that have high-intercept and steeply-sloped C–Q relations, high precipitation years will still result in large hypoxic areas, as was the case very recently (Van Meter et al., 2018), even if the multiyear average load goals were met (Donner and Scavia, 2007). The evidence of progress in eastern Iowa and elsewhere within the UMR (Fig. 1) offers insights and approaches to tackling the nitrate load reductions in other basins, especially those that share similar characteristics such as high-intercept and steeply sloped C–Q relationships or land use patterns or have similar drivers of nutrient loading (Underwood et al., 2017).

Supplemental Material

Four additional figures can be found in the supplemental material. They include a graph of nitrate loads from the Mississippi River during the period of 1972 to 2012; a comparison of the nitrate load at the outlet of the Mississippi River basin and the hypothetical load obtained by summing the loads at the major tributaries; a graph of the monthly concentration–discharge relationship at the Upper Mississippi River; and a graph of the monthly concentration–discharge relationship at the Ohio River.

Conflict of Interest

The authors declare no conflict of interest.

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