



Antecedent flow conditions and nitrate concentrations in the Mississippi River basin

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Abstract. The relationship between antecedent flow conditions and nitrate concentrations was explored at eight sites in the 2.9 million square kilometers (km²) Mississippi River basin, USA. Antecedent flow conditions were quantified as the ratio between the mean daily flow of the previous year and the mean daily flow from the period of record (Q_{ratio}), and the Q_{ratio} was statistically related to nitrate anomalies (the unexplained variability in nitrate concentration after filtering out season, long-term trend, and contemporaneous flow effects) at each site. Nitrate anomaly and Q_{ratio} were negatively related at three of the four major tributary sites and upstream in the Mississippi River, indicating that when mean daily streamflow during the previous year was lower than average, nitrate concentrations were higher than expected. The strength of these relationships increased when data were subdivided by contemporaneous flow conditions. Five of the eight sites had significant negative relationships ($p \leq 0.05$) at high or moderately high contemporaneous flows, suggesting nitrate that accumulates in these basins during a drought is flushed during subsequent high flows. At half of the sites, when mean daily flow during the previous year was 50 percent lower than average, nitrate concentration can be from 9 to 27 percent higher than nitrate concentrations that follow a year with average mean daily flow. Conversely, nitrate concentration can be from 8 to 21 percent lower than expected when flow during the previous year was 50 percent higher than average. Previously documented for small, relatively homogenous basins, our results suggest that relationships between antecedent flows and nitrate concentrations are also observable at a regional scale. Relationships were not observed (using all contemporaneous flow data to-

gether) for basins larger than 1 million km², suggesting that above this limit the overall size and diversity within these basins may necessitate the use of more complicated statistical approaches or that there may be no discernible basin-wide relationship with antecedent flow. The relationships between nitrate concentration and Q_{ratio} identified in this study serve as the basis for future studies that can better define specific hydrologic processes occurring during and after a drought (or high flow period) which influence nitrate concentration, such as the duration or magnitude of low flows, and the timing of low and high flows.

1 Introduction

Many studies show that antecedent moisture conditions influence nutrient export from river basins (Burt and Worrall, 2009; Garrett, 2012; Macrae et al., 2010; Soulsby et al., 2003; Vecchia et al., 2008; Lucey and Goolsby, 1993). Commonly, studies document increased nutrient export following a prolonged dry period (Foster and Walling, 1978; Macrae et al., 2010), though some studies have observed the opposite effect when considering only more recent antecedent conditions (Creed and Band, 1998; Macrae et al., 2010; Welsch et al., 2001). Most observations concerning the influence of antecedent moisture on nutrient export have been made in small basins with generally homogenous land use, land cover, climate, and geology (e.g., Biron et al., 1999; Burt and Worrall, 2009; Cooper et al., 2007; Foster and Walling, 1978; Lange and Haensler, 2012; Macrae et al., 2010; Welsch et al., 2001), and little attention has been given to how this influence plays

out on a large scale. Yet, the degree to which antecedent moisture affects nutrient export from large basins may have profound implications for environmental management and policy, particularly for large basins in agricultural regions that contribute substantial masses of nutrients to coastal waters. Nutrient fluxes from the Mississippi River basin (MRB) are closely related to the spatial extent of the hypoxic zone in the Gulf of Mexico (Donner and Scavia, 2007; Rabalais and Turner, 2001); consequently, the hypoxic zone is often smaller during a drought when low flows from the Mississippi River deliver smaller nutrient loads to the Gulf (Scavia et al., 2003; Turner et al., 2006). However, nitrate and other nutrients may accumulate within the basin during a drought and be subject to flushing by high flows when a drought ends, resulting in higher than normal nitrate concentrations in receiving waters. Conversely, particularly wet antecedent conditions may flush nitrate and other nutrients from the basin with more frequency, depleting the availability of these constituents in the soil and causing lower than anticipated concentrations in streamwater.

Exploring hydrologic processes, such as the influence of antecedent moisture conditions on nitrate export, in large basins (defined in our study as $> 30\,000$ square kilometers (km^2)) is complicated by their diverse mix of land cover, topography, geology and climate, in addition to confounding influences of dams, irrigation, and point and non-point pollution sources. These factors not only hinder the ability to extrapolate results obtained from the investigation of small basins to large basins (Sidle, 2006; Soulsby et al., 2006; Shaman et al., 2004; Sivapalan, 2003) but also make it challenging to use methods typically implemented in small basins, such as the determination of hydrologic storage and flux in soil and groundwater, or direct measurement of flow and concentration from different flow routes (e.g., Rozemeijer et al., 2010). In addition to the diversity of climatic, hydrogeologic, and land use conditions across large basins, there can be substantial spatial variability of precipitation inputs, with some sub-basins experiencing very wet conditions while other sub-basins experience average or even very dry conditions. Since large spatial scales result in highly variable soil water and groundwater storage (spatially and temporally), antecedent moisture conditions in large basins are likely best defined by well-integrated measurement proxies that amalgamate these variable conditions. In this study we use antecedent streamflows at the downstream end of a basin as a proxy for basin-wide antecedent soil moisture.

There are several examples of nutrient studies undertaken in very large basins (e.g., Alexander et al., 2008; Sprague et al., 2011), however, to our knowledge, the relationship between antecedent moisture and nitrate has yet to be explored at a scale as large as the MRB or its major sub-basins. Most hydrologic studies related to antecedent moisture and nitrate have been undertaken at the hillslope scale or in small ($< 100\text{ km}^2$) and meso-scale (100 to 1000 km^2) basins. We identified two studies that cover the largest basin sizes, which

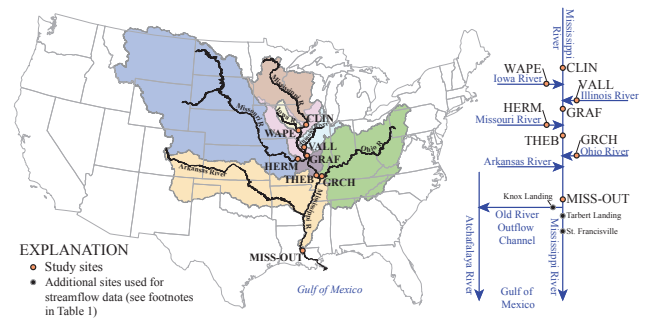


Fig. 1. Map of the continental United States showing Mississippi River basin and study sites, and a schematic line drawing of the relative locations of study sites, major tributaries, and additional sites.

are Vecchia's (2003) study that investigated relationships between other nutrients (ammonia plus organic nitrogen and total phosphorus) and 5-year, 1-year and daily flow anomalies in 30 basins throughout the United States, ranging in size from 114 to $117\,140\text{ km}^2$, and a study by Lucey and Goolsby (1993) that explored the influence of climatic variations on nitrate in an 8900 km^2 basin in Iowa. However, most of the sites in our study are still one or more orders of magnitude larger than even these examples.

Throughout the MRB and other basins in agricultural regions, nitrate accumulates in farm fields due to a variety of influences, including weather conditions, soil characteristics, crop type and yield, fertilizer application, and irrigation (Ferguson et al., 2013; Randall et al., 2003). The timing and interaction of these factors during a period of low precipitation leads to a wide range of nitrogen storage remaining in the soil after a growing season. In general, farms that had an exceptionally low crop yield the previous growing season have elevated soil nitrate concentrations, whereas farms that had average or above-average yields have low soil nitrate concentrations (Sawyer, 2013). During a drought, irrigation is often a determining influence for crop yield and thus the amount of nitrate likely to accumulate in the soil (Sawyer, 2013). Most farmland in the MRB is not irrigated (Table 1) and elevated soil nitrate concentrations are typically anticipated across much of the basin following a drought (Dinnes et al., 2002; Ferguson, et al., 2013; Randall et al., 2003; Rehm et al., 2009; Sawyer, 2013).

In this paper, we explore the relationship between antecedent flows and nitrate anomalies in the MRB and identify which contemporaneous flow conditions exhibit the strongest relationships. Nitrate anomalies are the unexplained variability in nitrate concentration after filtering out season, long-term trend, and contemporaneous flow effects. Our objective is to quantify relationships between antecedent flows and nitrate anomalies for eight sites in the MRB (Fig. 1) using data collected over three decades and across a range of contemporaneous flow conditions.

2 Study area description

Eight sites in the MRB are used in this study, four Mississippi River main-channel sites and four sites in major tributary basins: the Iowa River, Illinois River, Missouri River and Ohio River (Fig. 1). These basins are regional to continental in scale with drainage areas ranging from approximately 32 thousand km² to over 2.9 million km² (Table 1). In total, the MRB drains approximately 41 % of the continental United States and is the largest river basin in North America (National Stream Quality Accounting Network; <http://water.usgs.gov/nasqan/docs/missfact/missfactsheet.html>).

Basin and climate characteristics vary greatly between the eight sites in this study (Table 1). Generally, the Ohio River basin receives the most precipitation, leading to high streamflows and runoff, whereas the Missouri River basin is the driest. The Missouri River basin is also the most hydrologically altered in terms of number of dams and relative storage (Table 1). The smallest basins have the highest percentage of farmland. Basin and climate characteristics also vary widely within each basin. For example, average annual precipitation (1961–1990, The National Atlas; <http://www.nationalatlas.gov/>) in the northwest portion of the Missouri River basin is approximately 250 millimeters per year (mm yr⁻¹) as compared to 950 mm yr⁻¹ near the downstream end of the basin, in the vicinity of the Missouri River at Hermann (HERM, Fig. 1). Similarly, in the Ohio River basin, annual precipitation ranges from about 1900 mm yr⁻¹ in the southeastern portion of the basin to about 950 mm yr⁻¹ in northern portions of the basin. For the sites in this study, there appears to be a great deal of within-basin variability as well as between-basin variability (described in Table 1) and these variations in basin and climate characteristics add considerable complexity to the identification and interpretation of relationships between antecedent flow and nitrate.

Throughout the MRB, nitrate and other forms of nitrogen in streamwater come from multiple sources including urban runoff, wastewater discharges, atmospheric deposition, and runoff and subsurface flow from agricultural (crop and animal) lands. According to the US Geological Survey’s SPARROW (SPATIally Referenced Regression On Watershed attributes) decision support system (Mississippi/Atchafalaya Basin Total Nitrogen Model – 2002; <http://cida.usgs.gov/sparrow/>), which models in-stream water quality in relation to upstream sources and basin and climate characteristics, agricultural sources such as fertilizer, waste from confined animals, or legume crops dominate the total nitrogen load to the Gulf of Mexico (MISS-OUT) as compared to atmospheric deposition or population-related sources (Table 2). Furthermore, across all sites the relative proportion of total nitrogen from agriculture is at least 3 times greater than total nitrogen from population-related sources. Contributions of total nitrogen from population-related sources (6 to 22 %, depending on the basin) and atmospheric deposition (15 to 32 %) can be substantial but agriculture (51 to 79 %) is the

Table 1. Site information and basin characteristics for eight sites in the Mississippi River basin. [USGS, US Geological Survey: sq km, square kilometers; cms, cubic meters per second; mm yr⁻¹, millimeters per year].

Site	USGS site number	Site name	Basin area (sq km)	Mean daily streamflow (cms)	Mean annual runoff (mm yr ⁻¹)	Mean annual precipitation ⁴ (mm yr ⁻¹)	Farmland in basin ⁵ (percent)	Irrigated land in basin ⁶ (percent)	Cropland that is irrigated ⁵ (percent)	Number of dams in basin ⁷	Relative storage ^{7a} (years)
CLIN	05420500	Mississippi River at Clinton, Iowa	221 703	1605	228	787	43	1.3	4.0	1531	0.59
WAPE	05465500	Iowa River at Wapello, Iowa	32 375	304	297	887	79	0.2	0.2	223	0.08
VALL	05586100	Illinois River at Valley City, Illinois	69 264	743	339	955	67	1.9	2.3	653	0.10
GRAF	05587455	Mississippi River below Grafton, Illinois ¹	443 665	3722	265	855	56	1.2	2.6	4824	0.34
HERM	06934500	Missouri River at Hermann, Missouri	1 353 269	2694	63	539	36	4.1	25.6	19 233	1.89
THEB	07022000	Mississippi River at Thebes, Illinois	1 847 180	6912	118	631	41	3.3	19.2	25 540	0.95
GRCH	03612500	Ohio River at Dam 53 near Grand Chain, Illinois ²	526 027	8460	508	1187	31	0.2	15.4	5827	0.31
MISS-OUT	—	Mississippi River above Old River Outflow Channel, Louisiana ³	2 914 514	19 700	213	783	38	3.4	0.7	39 678	0.58

¹ Streamflow measured at Mississippi River at Grafton, Illinois (USGS site number 05587450). ² Streamflow measured at Ohio River at Metropolis, Illinois (USGS site number 03611500). ³ MISS-OUT is meant to provide an approximation of streamflow and concentration just upstream of the Old River Outflow Channel. Streamflow is the sum of Mississippi River at Harbert Landing, Mississippi (US Army Corps of Engineers site 01100) and Old River Outflow Channel near Knox Landing, Louisiana (US Army Corps of Engineers site 02600) and nitrate data were sampled at Mississippi River near St. Francisville, Louisiana (USGS site number 07373420). ⁴ Prism data produced by Oregon State, (4 km) 1970–2011. <http://www.prism.oregonstate.edu/>. ⁵ US National Atlas, 2002. <http://www.nationalatlas.gov/datasfp.html> and <http://www.usgs.gov/>. ⁶ USGS MODIS-derived data, 2002. <http://earthworming.usgs.gov/USirrigation/> and Perez and Brown, 2010. ⁷ National Inventory of Dams: data set produced by the Army Core of Engineers, 2009; <http://crunch.ucr.edu/nid/>. ^{7a} data set updated (duplicates removed and approximately 70 percent verified). ^{7a} Relative storage = total storage in basin (from National Inventory of Dams)/total annual streamflow.

Table 2. Relative contributions of total nitrogen load by source estimated using the SPARROW model (SPATIally Referenced Regression On Watershed attributes) decision support system (Mississippi/Atchafalaya Basin Total Nitrogen Model – 2002; <http://cida.usgs.gov/sparrow/>).

Site	River	Relative contributions of total nitrogen load by source (percent) ¹		
		Atmospheric deposition	Agri-culture ²	Population-related ³
CLIN	Mississippi	22	68	10
WAPE	Iowa	15	79	6
VALL	Illinois	15	64	22
GRAF	Mississippi	18	71	11
HERM	Missouri	21	69	10
THEB	Mississippi	19	69	12
GRCH	Ohio	32	51	18
MISS-OUT	Mississippi	25	61	14

¹ May not sum to 100 due to independent rounding. ² Includes fertilizer, waste from confined animals and legume crops. ³ Includes wastewater treatment plants and urban sources.

dominant source of total nitrogen for the eight basins in this study (Table 2).

3 Data compilation

The eight sites used in this study (Table 1) are a part of a network of long-term data-collection sites throughout the United States that are maintained by the US Geological Survey (USGS) through the National Water-Quality Assessment (NAWQA) and National Stream-Quality Accounting Network (NASQAN) Programs. Streamflow and dissolved nitrate plus nitrite concentrations (referred to as nitrate hereafter) were compiled and prepared for each site according to the techniques outlined in Aulenbach et al. (2007). Daily mean streamflow data used in this study are from 1979 through the fall of 2011. Nitrate data were compiled from samples collected between 1980 and the fall of 2011 on a semi-monthly to monthly frequency (e.g., 9–18 samples per year). Nitrate data were collected across a range of streamflow conditions, including base and peak flows.

4 Methods

In the main channel of the Mississippi River and in several of its major tributaries, nitrate concentrations have been related to season, long-term trend over time, and contemporaneous daily mean flow (Sprague et al., 2011). A portion of the remaining unexplained variability in nitrate concentration may be related to antecedent flow conditions. In this study, a statistical model is used to quantify the unexplained variability in nitrate concentration after filtering out these effects. This unexplained variability is the deviation of the observed log nitrate concentration from the log nitrate concen-

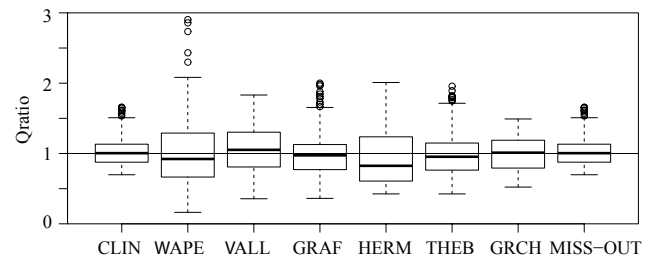


Fig. 2. Box plot of Q_{ratio} values by site.

tration predicted by a statistical model (based on contemporaneous daily mean flow, season, and trend), herein referred to as nitrate anomalies (Vecchia et al., 2008). To evaluate if antecedent flow conditions can help to explain variations in nitrate concentrations, we tested whether nitrate anomalies were significantly ($\alpha = 0.05$) related to a measure of antecedent flow conditions.

In this study, we define antecedent flow as a ratio between mean daily flow of the previous year and mean daily flow of the period of record, for a given site (Q_{ratio}). The Q_{ratio} (Q_{r_i}) for day i is calculated as

$$Q_{r_i} = \frac{Q_{yr_i}}{Q_{POR}}, \quad (1)$$

where Q_{yr_i} is the mean daily flow for the previous year (day i through the previous 364 days), and Q_{POR} is the mean daily flow for the period of record. Q_{ratio} values greater than 1 indicate higher than average mean daily flows for the previous year; values less than 1 indicate lower than average flows. Q_{ratio} s for the eight sites used in our study range from 0.16 to 2.90 and the majority are within ± 0.25 of 1 (Fig. 2).

By using streamflow integrated over the year as a large-basin surrogate for the kinds of hydrologic storage and flux measures that might be used in small-basin-process models, we are able to acquire a general measure of basin moisture that is likely related to other physical, chemical and biological processes in a basin that are affected by preceding moisture conditions. The choice of a one-year averaging period used to compute the Q_{ratio} makes this antecedent flow measure independent of the time of year and season. It is possible that more complex statistical formulations with seasonal terms or an averaging period other than one year would have a stronger statistical association with nitrate anomalies, but model parsimony led us to commit to this simpler formulation. Using Q_{ratio} to describe antecedent flows characterizes hydrologic conditions broadly and allows for an initial examination of how nitrate concentration responds following a drought or high flow period. If significant relationships are documented, future studies can help better define the specific hydrologic processes that influence nitrate concentration during and after a drought or high flow period.

We used the published Weighted Regressions on Time, Discharge, and Season model (WRTDS; Hirsch et al., 2010)

to determine nitrate anomalies. WRTDS uses time, contemporaneous flow, and seasonal variables to estimate solute concentrations for large river basins that have several decades of flow and concentration data. Locally weighted regression is used to make unbiased estimates of the log of nitrate concentration for each day (Hirsch et al., 2010). WRTDS was used to estimate nitrate concentration from 1980 through the fall of 2011 for the eight sites in this study. The residuals from this modeling effort are the nitrate anomalies analyzed in this study. Predicted log nitrate concentration (pc_i) for day i is modeled in WRTDS as

$$pc_i = \beta_0 + \beta_1 t + \beta_2 \ln(Q) + \beta_3 \sin(2\pi t) + \beta_4 \cos(2\pi t), \quad (2)$$

where \ln is the natural log, $\beta_0, \beta_1, \dots, \beta_4$ are fitted coefficients, t is time, and Q is daily mean streamflow (Hirsch et al., 2010). Nitrate anomaly (CA_i) for day i is defined as

$$CA_i = \ln(c_i) - pc_i \quad (3)$$

where c_i is the observed nitrate concentration on day i , and pc_i is the predicted log nitrate concentration on day i . By using WRTDS, nitrate anomalies can be conceptualized as the portion of the concentration signal that is not accounted for by contemporaneous discharge, season or long-term trend. Since nitrate anomalies are simply the residuals from the model these values represent a combination of measurement error, inadequacies of the model's functional form, estimation error of the coefficients, and the influence of other variables that are not considered by the model. In this case, we explicitly consider the role that antecedent streamflow, a variable not included in the model, might play. Thus, a positive nitrate anomaly indicates higher-than-anticipated observed concentration; a negative anomaly indicates a lower-than-anticipated observed concentration. For details on WRTDS and the modeling of nitrate concentration at these sites, see Hirsch et al. (2010) and Sprague et al. (2011).

Nonparametric statistical methods were used to explore relationships between antecedent flows and nitrate anomalies because the Qratio data are positively skewed and contain outliers (Fig. 2). The strength of the correlation between nitrate anomaly and Qratio was determined using Kendall's tau, and the relationship was quantified using the Kendall–Theil robust line (Helsel and Hirsch, 2002). The robust line describes the response of nitrate anomaly to Qratio and is defined as

$$CA_i = \beta_0 + \beta_1 \cdot Qr_i, \quad (4)$$

where CA_i is the nitrate anomaly for day i , Qr_i is the Qratio on day i , and β_0 and β_1 are the fitted coefficients for the intercept and slope, respectively. Rather than using ordinary least squares to estimate the coefficients, the slope is based on the median slope of all pairwise slopes between CA_i and Qr_i values, and the intercept is back-calculated using this median slope and a point defined by the median of all CA_i values and

Table 3. Kendall's tau and robust line results of nitrate anomaly and Qratio relationships, using all contemporaneous flow data. Statistically significant relationships ($p \leq 0.05$) are italicized [n , number of observations].

Site	River	Tau	<i>p</i> value	Intercept	Slope	<i>n</i>
<i>CLIN</i>	<i>Mississippi</i>	<i>-0.13</i>	<i>< 0.01</i>	0.60	-0.48	315
<i>WAPE</i>	<i>Iowa</i>	<i>-0.15</i>	<i>< 0.01</i>	0.29	-0.20	312
<i>VALL</i>	<i>Illinois</i>	<i>-0.17</i>	<i>< 0.01</i>	0.22	-0.18	370
GRAF	Mississippi	-0.03	0.50	0.10	-0.05	308
HERM	Missouri	0.06	0.06	-0.03	0.12	429
THEB	Mississippi	-0.05	0.09	0.12	-0.09	431
<i>GRCH</i>	<i>Ohio</i>	<i>-0.16</i>	<i>< 0.01</i>	0.37	-0.34	378
MISS-OUT	Mississippi	-0.05	0.15	0.16	-0.12	401

the median of all Qr_i (Helsel and Hirsch, 2002). Robust lines were fit for each site using all available data.

Additionally, to identify the contemporaneous flow conditions in which concentrations are most sensitive to antecedent flows, data at each site were divided into flow classes according to the daily mean flow on the day of sample collection, and robust lines were fit to each site and flow class. Contemporaneous flow classes consist of four percentile ranges based on the observed streamflow across the period of record: low (< 25th percentile), mid-low (> 25th and < 50th percentile), mid-high (> 50th and < 75th percentile), and high (> 75th percentile) contemporaneous flows.

Finally, to quantify the effect of antecedent flow on nitrate concentration, as opposed to nitrate anomaly, the percent difference in nitrate concentration relative to a previous year that had average mean daily flow (Qratio = 1) was determined using the following equation:

$$\text{Percent difference in concentration} = \left(\frac{\exp(\beta_1 \cdot Qr_i)}{\exp(\beta_1)} - 1 \right) \cdot 100 \quad (5)$$

where β_1 is the slope coefficient for a given site and flow class. Because the denominator in Eq. (5) gives the expected nitrate concentration following a year with average flow conditions, the resulting percent difference from this equation gives the anticipated increase or decrease in nitrate concentration for a given antecedent flow condition (Qr_i) relative to nitrate concentration following a year with average antecedent flow conditions. Four hypothetical Qratio values ($Qr_i = 0.5, 0.75, 1.25$ and 1.5) were applied using Eq. (5) at each site and flow class. These results will parallel those quantified by the robust line relationships (Eq. 4), but apply directly to nitrate concentration instead of nitrate anomaly.

5 Results and discussion

5.1 Nitrate anomaly and antecedent flow across all contemporaneous flows

When all contemporaneous flows at each site are considered together, the upper Mississippi River (CLIN) and the

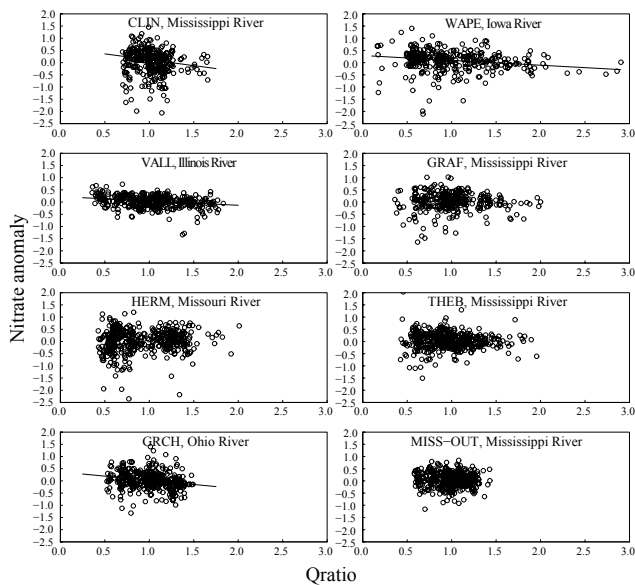


Fig. 3. Plots of nitrate anomaly versus Qratio by site, using all contemporaneous flow data. Statistically significant relationships ($p \leq 0.05$) are denoted with a solid black line.

major tributaries (WAPE, VALL, and GRCH), except the Missouri River (HERM), exhibit statistically significant relationships ($p \leq 0.05$) between Qratio and nitrate anomaly (Fig. 3), though tau is small, ranging from -0.13 to -0.17 depending on the site (Table 3). All sites have negative slopes and the steepest slope occurred in the upper Mississippi River (CLIN). Downstream Mississippi River sites (GRAF, THEB, and MISS-OUT) and the Missouri River (HERM) do not demonstrate significant relationships across the observed range of flows (Fig. 3). Note that all three basins larger than 1 million km² had non-significant correlations but four out of the five basins smaller than 1 million km² had significant correlations. In general, the relationships between antecedent flow and nitrate shown here are weak to moderately strong with low to moderate correlation (Table 3), which is not necessarily surprising given the complexity of solute behavior in large basins (Webb and Walling, 1984).

To describe the potential response of nitrate concentration to different antecedent flow conditions, four Qratio values ($Qr_i = 0.50, 0.75, 1.25$ and 1.50) were applied using Eq. (5) at the sites with significant robust line relationships ($p \leq 0.05$, Table 3). At the two smallest tributary sites (WAPE and VALL) when the previous year's flow is 50 percent higher or lower than average ($Qr_i = 1.5$ or 0.5 , respectively) nitrate concentration is about 10 percent lower or higher than expected, respectively (Table 4). These positive or negative differences in nitrate concentration are relative to the nitrate concentration that follows a (hypothetical) year that had average mean daily flow ($Qr_i = 1.0$). In the upper Mississippi River (CLIN) and Ohio River (GRCH), the difference in nitrate concentration could be as much as 27 percent higher

or 21 percent lower than expected when the previous year's flow is 50 percent lower or higher than average, respectively. At these same sites, nitrate concentration could be only about ± 10 percent different than expected when the previous year's flow deviates about 25 percent from average flow conditions (Table 4). Therefore, the influence of antecedent flow conditions on nitrate concentration may be twice as strong at the sites with slightly larger basin areas (CLIN and GRCH), as compared to the sites with the smallest basin areas in our study (WAPE and VALL).

In this analysis, the Qratio describes previous flow conditions in a basin and also serves as a proxy for changes to other physical, chemical and biological processes that are affected by inter-annual variation in the overall moisture of a basin. Grouped into two broad categories, variations in antecedent flow conditions often coincide with changes to (1) the mass and availability of nitrate in soil (supply), and (2) hydrologic processes that move nitrate through the basin to the stream (transport). Many processes control the accumulation of available nitrate in the soil during a drought, and most are closely related to soil moisture conditions. These may include increased plant stress resulting in low nitrate uptake and low crop yields (Groves and Bailey, 1997), decreased microbial processes resulting in more limited denitrification (Ashby et al., 1998; de Klein and van Logtestijn, 1996) and decreased runoff and leaching (Emmerich and Heitschmidt, 2002; Stites and Kraft, 2001). The timing of fertilizer application before or after a rainfall or irrigation event also influences the amount of available nitrate in the soil (Aulakh and Bijay-Singh, 1997). Additionally, droughts and periods of low flow typically coincide with lowered water tables, decreased hydrologic storage, and decreased hydrologic connectivity, all of which inhibit nitrate transport to streams (Bernal and Sabater, 2012; Detty and McGuire, 2010; Macrae et al., 2010). Wetter antecedent conditions can cause these supply- and transport-limiting processes to have the opposite effect of minimizing the accumulation of nitrate in the soil through denitrification, crop uptake and other processes, while also increasing hydrologic connectivity and the frequency with which nitrate is transported to groundwater or a stream. Although supply- and transport-limiting processes interact to encourage or inhibit nitrate export, the varying influence of these processes can result in inconsistent relationships between antecedent flow conditions and nitrate concentration among different basins (Macrae et al., 2010) and even over time within a single basin (Burt and Worrall, 2009, 2007).

The statistically significant negative relationships ($p \leq 0.05$) between Qratio and nitrate anomaly (Fig. 3) exhibited in the upper Mississippi River (CLIN), Iowa River (WAPE), Illinois River (VALL) and Ohio River (GRCH) indicate that below-average mean daily streamflow the previous year relates to higher nitrate anomalies (and concentrations), and above-average mean daily flow the previous year relates to lower nitrate anomalies (and concentrations).

Table 4. Percent difference in nitrate concentration relative to nitrate concentration expected following a year with average flow conditions (see Eq. 5). Positive and negative percent differences describe the increase or decrease of nitrate concentration, respectively, in response to four hypothetical antecedent flow conditions. Qratio scenarios describe when mean daily streamflow the previous year was 50 and 25 percent lower than average (Qratios 0.50 and 0.75, respectively) and 25 and 50 percent higher than average (Qratios 1.25 and 1.50, respectively). These scenarios are only applied to relationships that were statistically significant ($p \leq 0.05$).

Site	River	All contemporaneous flow conditions				Low flow conditions				Mid-low flow conditions				Mid-high flow conditions				High flow conditions			
		Drier (Qratio)		Wetter		Drier (Qratio)		Wetter		Drier (Qratio)		Wetter		Drier (Qratio)		Wetter		Drier (Qratio)		Wetter	
		0.5	0.75	1.25	1.5	0.5	0.75	1.25	1.5	0.5	0.75	1.25	1.5	0.5	0.75	1.25	1.5	0.5	0.75	1.25	1.5
		(percent change)				(percent change)				(percent change)				(percent change)				(percent change)			
CLIN	Mississippi	27	13	-11	-21													34	16	-14	-26
WAPE	Iowa	10	5	-5	-9													13	6	-6	-12
VALL	Illinois	9	5	-4	-8								19	9	-8	-16		13	6	-6	-11
GRAF	Mississippi																				
HERM	Missouri													-16	-8	9	19				
THEB	Mississippi													11	6	-5	-10				
GRCH	Ohio	19	9	-8	-16	44	20	-17	-30	19	9	-8	-16	15	7	-7	-13				
MISS-OUT	Mississippi					20	9	-9	-17												

At these sites, it appears soil nitrate that accumulates during dry periods increases the supply of nitrate, which may influence nitrate export later in the year. The remaining sites further downstream on the Mississippi River (GRAF, THEB and MISS-OUT) and the Missouri River (HERM) do not provide evidence that nitrate anomalies are related to antecedent flow conditions, at least when considering all contemporaneous flows together. Interestingly, the GRAF site, located on the Mississippi River below the confluence with the Illinois River (Fig. 1), has relatively similar climate and basin characteristics as CLIN, WAPE and VALL (Table 1), yet does not show a statistically significant relationship between Qratio and nitrate anomaly when all contemporaneous flows are considered.

The lack of an apparent relationship at HERM, THEB or MISS-OUT is not necessarily surprising given that these sites have drainage areas in excess of 1 million km² whereas other sites have drainage areas less than 600 000 km². The diversity of basin characteristics in the drainage area above HERM, THEB and MISS-OUT is very substantial and the Qratio is likely a poor indicator of the moisture status of the particular areas in these basins that are major contributors of nitrate to streamwater. For example, during the 2011 Missouri River flood the upper reaches of the basin provided most of the flood water and this area has very limited row crop agriculture, thus the water delivered to streams in this region had relatively low concentrations of nitrate; however, most high flow events in the Missouri River basin tend to originate in lower portions of the basin that are highly agricultural and deliver relatively high concentrations of nitrate to streams (Kalkhoff, 2013). Further complicating factors include lag times associated with groundwater discharges (Sanford and Pope, 2013) and the travel time of water through basins (Krichner et al., 2001) and large river networks. For example, at the outflow of the Mississippi River (MISS-OUT), streamwater from different locations in the MRB can take weeks to months to reach MISS-OUT (Nolan et al., 2002),

thus the relationships between antecedent flows and nitrate anomalies observed upstream in more homogenous tributaries are likely smeared as water moves downstream and mixes with water from other sources. Also, transport processes in some basins have been found to be more dependent on the permeability and storage capacity of the soil and bedrock as compared to other basins where flow-path lengths and the density of drainage networks are important influences (Hrachowitz et al., 2013).

5.2 Nitrate anomaly and antecedent flow by contemporaneous flow class

In most cases, the relationship between Qratio and nitrate anomaly is stronger when the flow condition on the day of sample collection (contemporaneous flow) is considered. Robust line coefficients and tau are typically greater in magnitude for specific contemporaneous flow classes (Table 5) as compared to those derived using all contemporaneous flow data together (Table 3).

5.2.1 Relationships at mid-high and high contemporaneous flows

At the highest contemporaneous flows (> 75th percentile) Qratio and nitrate anomaly are negatively related ($p \leq 0.05$) at three (CLIN, WAPE and VALL) of the eight sites (Table 5). Also, at mid-high contemporaneous flows (> 50th and < 75th percentile), nitrate anomalies are negatively related to the Qratio at three of the eight sites (VALL, THEB and GRCH) and positively related at one site (HERM). In total, six of the eight sites (including GRAF, though the relationship is not statistically significant ($p = 0.06$)) show negative relationships between Qratio and nitrate anomaly when contemporaneous flows were greater than the 50th percentile of flow (Fig. 4), suggesting a flushing response occurs during elevated flows that follow extended dry antecedent conditions. Flushing responses during storm events have been explored

Table 5. Kendall's tau and robust line results of nitrate anomaly and Qratio relationships, by contemporaneous flow class. Statistically significant values ($p \leq 0.05$) are italicized [daily Q, daily streamflow; Interc, intercept; n , number of observations].

Site	River	Low flow conditions (daily Q < 25th)					Mid-low flow conditions (25th < daily Q < 50th)					Mid-high flow conditions (50th < daily Q < 75th)					High flow conditions (daily Q > 75th)				
		Tau	<i>p</i> value	Interc	Slope	<i>n</i>	Tau	<i>p</i> value	Interc	Slope	<i>n</i>	Tau	<i>p</i> value	Interc	Slope	<i>n</i>	Tau	<i>p</i> value	Interc	Slope	<i>n</i>
CLIN	Mississippi	-0.09	0.46	0.57	-0.51	39	-0.06	0.49	0.40	-0.26	60	-0.11	0.12	0.57	-0.45	93	-0.18	< 0.01	0.71	-0.59	122
WAPE	Iowa	-0.09	0.29	0.22	-0.32	58	-0.14	0.09	0.30	-0.20	65	-0.12	0.08	0.29	-0.15	91	-0.20	< 0.01	0.36	-0.25	96
VALL	Illinois	-0.07	0.34	0.13	-0.10	79	-0.05	0.58	0.08	-0.05	70	-0.34	< 0.01	0.42	-0.34	94	-0.25	< 0.01	0.31	-0.24	125
GRAF	Mississippi	0.09	0.31	-0.10	0.23	63	0.12	0.12	-0.12	0.23	78	-0.14	0.06	0.26	-0.21	81	-0.11	0.13	0.15	-0.16	85
HERM	Missouri	0.10	0.14	-0.29	0.53	98	0.04	0.54	0.09	0.10	105	0.19	< 0.01	-0.35	0.35	103	-0.02	0.71	0.08	-0.05	123
THEB	Mississippi	0.01	0.86	0.01	0.03	85	-0.08	0.23	0.17	-0.16	93	-0.12	0.05	0.26	-0.21	115	-0.08	0.18	0.18	-0.11	130
GRCH	Ohio	-0.20	< 0.01	0.70	-0.73	87	-0.16	0.04	0.41	-0.35	79	-0.17	< 0.01	0.28	-0.29	111	-0.11	0.12	0.20	-0.16	101
MISS-OUT	Mississippi	-0.14	0.05	0.38	-0.36	91	-0.02	0.77	0.12	-0.06	84	-0.06	0.34	0.20	-0.14	109	0.02	0.69	-0.06	0.06	115

extensively in the literature for small forested and agricultural basins (Biron et al., 1999; Burt et al., 1988; Foster and Walling, 1978; Hornberger et al., 1994; Macrae et al., 2010; Walling and Foster, 1975), and is primarily attributed to the rapid movement of nitrate during a storm when the water table intersects soil horizons that have accumulated elevated stocks of nitrate during periods of low moisture. Our results suggest that a flushing response, previously documented for small, relatively homogenous basins during storms, is also observable at a regional scale during elevated streamflows. Conversely, at these sites above-average mean daily flow the previous year relates to lower nitrate anomalies during mid-high and high flows, possibly because the mass of stored nitrate has been depleted by increased export from the basin and uptake by plants earlier in the year. Noticeably, the flushing response at the highest flows (> 75th percentile) is evident only for the smallest basins (< 250 000 km²) and no statistically significant relationships occur at the highest flows for basins larger than 250 000 km² (Fig. 4). With the exception of GRAF (Fig. 1), these smaller basins (CLIN, WAPE and VALL) have the highest percentage of farmed land (Table 1), which suggests that during high flows, dilution from an expanding variable source area with low nitrate concentrations likely obscures the influence of antecedent flow conditions (Creed and Band, 1998) in larger study basins, whereas dilution in smaller, more intensely farmed basins appears less common.

Contrary to other sites in the MRB, nitrate anomaly is positively related to the Qratio in the Missouri River (HERM) during mid-high contemporaneous flows (Fig. 4). This observation directly contradicts the flushing response model described for other sites. However, higher antecedent flow conditions have been related to increased nitrate export in other studies, though in these studies antecedent conditions were typically considered over time periods shorter than a year and in basins smaller than those considered in this study (e.g., Welsch et al., 2001; Macrae et al., 2010). Additionally, of all the basins in this study, the Missouri River is considered the most heterogeneous; the variation in weather and terrain throughout this basin can cause parts of the Missouri River to experience markedly different hydrologic conditions simultaneously.

A possible explanation for this relationship in the Missouri River (HERM) is that the supply of exportable nitrate during a drought is reduced by irrigation. Approximately 25 percent of cropland in the Missouri River basin is irrigated, making it the most irrigated basin in this study (Table 1). During droughts, irrigation may remove nitrate from the soil horizon by leaching, denitrification, or uptake by crops (Aulakh and Bijay-Singh, 1997; Dinnes et al., 2002). Leached nitrate typically moves downward below the active root zone, leading to elevated nitrate concentrations in groundwater (Burkart and Stoner, 2008; Stites and Kraft, 2001). Increased denitrification occurs with irrigation because elevated soil moisture conditions increase microbial activity (de Klein and van Logtestijn, 1996; Groves and Bailey, 1997). Which process dominates during a drought is debatable and may depend on soil properties, fertilizer application rates, and climate (Aulakh and Bijay-Singh, 1997; Brown et al., 2011). In the Missouri River basin, a recent modeling effort found that increases in irrigation relate to decreases in total nitrogen export on a regional scale (Brown et al., 2011). Irrigation likely occurs at a higher rate when the weather is drier than average, according to a study in Illinois (Bowman and Collins, 1987), therefore, lower nitrate anomalies in the Missouri River (HERM) following a drought may occur because processes associated with irrigation do not allow for the accumulation of nitrate in soil during drier-than-average climatic conditions. However, the supply-limiting influence of irrigation does not account for the higher nitrate anomalies observed following a year with higher antecedent flows.

Interestingly, the Missouri River basin also has the greatest number of dams and the highest relative storage of any basin (Table 1). The reservoirs in this basin hold approximately 1.89 times the annual flow of the Missouri River at HERM, which is more than twice the relative storage of any other site in this study (Table 1). Therefore, flow conditions at HERM, and low flows in particular, are not just the result of natural hydrologic conditions but are also influenced by release decisions made by dam operators. The confounding processes of irrigation and dam storage in addition to the geophysical and climatological heterogeneity of the Missouri River basin make even rudimentary interpretation problematic.

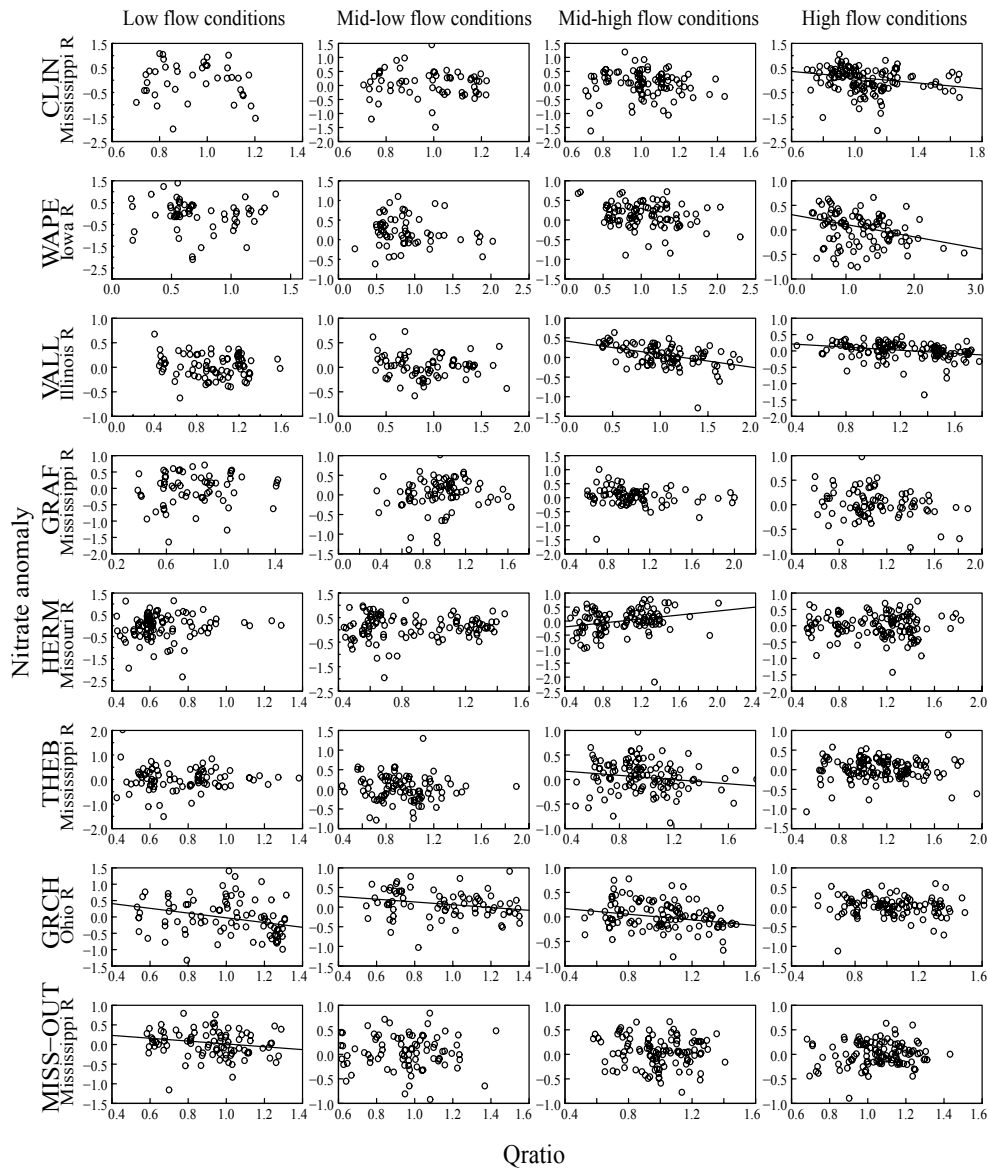


Fig. 4. Plots of nitrate anomaly versus Qratio, by site and contemporaneous flow class. Statistically significant relationships ($p \leq 0.05$) are denoted with a solid black line. Low flow conditions: < 25th percentile, mid-low flow conditions: > 25th and < 50th percentile, mid-high flow conditions: > 50th and < 75th percentile, and high flow conditions: > 75th percentile. Note horizontal and vertical axes are specific to each plot.

For the six sites with significant robust line relationships at mid-high or high (> 50th percentile) contemporaneous flow classes ($p \leq 0.05$, Table 5) four Qratio values ($Qr_i = 0.5, 0.75, 1.25$ and 1.5) were applied using Eq. (5) to describe the potential response of nitrate concentration to different antecedent flow conditions. When the previous year’s flow is 25 percent lower than average ($Qr_i = 0.75$), nitrate concentration may be about 6 to 9 percent higher than expected, for most sites where nitrate anomaly is negatively related to the Qratio (Table 4). Nitrate concentration increases to about 11 to 19 percent, different from expected when the previous year’s

flow is 50 percent lower than average ($Qr_i = 0.50$). Nitrate concentration appears to be more sensitive to antecedent flow conditions during high contemporaneous flows in the upper Mississippi River (CLIN); when flows the previous year were 25 to 50 percent lower than average, nitrate concentration can be 16 to 34 percent higher than expected (Table 4). At these sites, differences in nitrate concentration are slightly smaller in magnitude and lower than expected when the previous year had higher-than-average flows (Table 4). In the Missouri River, percent differences in nitrate concentration are similar in magnitude to those at other sites but opposite

in direction; when flows the previous year were 25 to 50 percent lower than average, nitrate concentration is 8 to 16 percent lower than expected, respectively. With the exception of HERM, these patterns are consistent with the conceptual model of soil nitrate flushing during high and mid-high flows following a drought.

5.2.2 Relationships at mid-low and low contemporaneous flows

Only the Ohio River (GRCH) and Mississippi outflow (MISS-OUT) demonstrate a significant negative response ($p \leq 0.05$) to the previous year's flow at mid-low (> 25th and < 50th percentile) or low (< 25th percentile) contemporaneous flows (Fig. 4, Table 5). Other studies of meso-scale basins (< 1000 km²) have found that, when not considering storm flows, inter-annual variations in climate act as a hydrologic driver that influences the mixing of groundwater with different residence times (but rather stable nitrate concentration) resulting in variations of nitrate concentration and flux in streamwater (Gascuel-Oudoux et al., 2010). In this context, the significant relationships during mid-low and low contemporaneous flows suggest the groundwater systems for GRCH and MISS-OUT may be influenced by annual variations in surface conditions or climate. However, the age of groundwater discharge to large rivers can be highly variable depending on geology, terrain and soil characteristics (Sanford and Pope, 2013). Throughout the MRB, the lack of statistically significant (Table 5) or visually strong (Fig. 4) relationships between antecedent flow and nitrate anomaly at mid-low and low contemporaneous flows may simply indicate that there is no overland flow flushing the stored nitrate to the river during these flow conditions. However, it may also imply that surface runoff (overland flow) and shallow groundwater with residence times less than one year are likely the main pathways influenced by antecedent flow conditions. To better capture the influence of preceding moisture conditions on nitrate export during low and mid-low flows, multi-year metrics of antecedent flows (or moisture conditions) may be needed.

Using Eq. (5) and four Q_{r_i} values ($Q_{r_i} = 0.5, 0.75, 1.25$ and 1.5) to translate nitrate anomalies to nitrate concentration, it appears that nitrate concentration is more sensitive to changes in antecedent flow during low and mid-low contemporaneous flows in the Ohio River (GRCH) and Mississippi outflow (MISS-OUT) than during high and mid-high flows at most other sites (Table 4). However, while the relationships between Q_{ratio} and nitrate anomaly at mid-low and low flows at GRCH and MISS-OUT are statistically significant ($p \leq 0.05$), they do not appear as visually strong as those at other sites or higher contemporaneous flow conditions (Fig. 4). For mid-low and low flow classes, when the previous year's flow is 25 percent lower than average ($Q_{r_i} = 0.75$), nitrate concentration may be about 9 to 20 percent greater than expected. As antecedent flow conditions become in-

creasingly low (50 percent of average flow, $Q_{r_i} = 0.50$) nitrate concentration can be 19 to 44 percent higher than expected (Table 4). Similarly, during mid-low or low contemporaneous flow conditions when the previous year's flow is 25 percent and 50 percent higher than average ($Q_{r_i} = 1.25$ and 1.50 , respectively), nitrate concentration can be between 8 and 30 percent lower than expected at GRCH and MISS-OUT (Table 4).

6 Conclusions

Many of the sites in our study, except the Missouri River (HERM), show a negative relationship between antecedent flow conditions and nitrate anomaly when specific contemporaneous flow classes are considered, or when all contemporaneous flows are considered together, suggesting that the influence of antecedent moisture conditions on nitrate export is observable at a large scale. The higher-than-expected nitrate concentrations that occur if streamflow during the previous year was lower than average likely are due to the accumulation of soil nitrate during a drought, and subsequent flushing with moderately high to high flows when the drought ends. Conversely, when the previous year's flow was higher than average, lower nitrate concentrations possibly occur because more nitrate is likely taken up by crops, removed from the system through denitrification, or transported with greater frequency (at lower concentrations) to the stream and groundwater earlier in the year. The positive relationship observed in the Missouri River (HERM) during mid-high contemporaneous flow conditions indicates relationships between antecedent flow and nitrate anomaly not only vary by contemporaneous flow class and basin size, but also regionally. How higher-than-expected nitrate concentrations following a drought will affect the hypoxic zone in the Gulf of Mexico is debatable, and is likely influenced by factors such as the timing of delivery to the Gulf (during the spring versus the fall, for example), the magnitude of flows transporting nitrate through the basin, the spatial and temporal variability of sub-basins experiencing drought and flushing, and changes to nutrient management practices throughout the basin.

In this study we identified significant relationships between antecedent flow conditions and nitrate concentration for regional-scale basins and propose several questions to encourage future studies on this topic at similar scales.

- What are the controlling influences for relationships between antecedent flow conditions and nutrient export, and how do these relationships change based on climate, basin characteristics, and management practices?

- Do relationships between antecedent flows and nitrate export change over time, as documented in other basins with long temporal records (Burt and Worrall, 2009; Burt and Worrall, 2007)?
- Which specific aspects of drought conditions (such as the magnitude and duration of low flows, and the timing of low and high flows) most influence nitrate accumulation in an agricultural basin and its subsequent flushing to a stream?
- Based on these results, might it be possible to develop a better statistical model of nitrate export that simultaneously uses both current and antecedent flow conditions to estimate concentration?
- How would one go about using new, high-frequency nitrate sensor data to improve understanding on how antecedent flows influence solute concentration? Will these new, richer data sets facilitate understanding of storage, transport, and processing of nitrogen within watersheds at this scale?

The results of our analysis suggest that nitrate transport in the Mississippi River basin is not a simple product of current hydrologic conditions and nitrate concentrations, but rather an integration of current conditions with past inputs of water and changes in nitrate supply that vary regionally and with contemporaneous flow class. Therefore, an improved understanding of the evolving pattern of nitrate fluxes from the entire Mississippi River basin will require detailed analysis of the diverse patterns of nitrate export from the various sub-basins and their interaction with similarly variable spatial and temporal patterns of climate and management practices. As a result, the evaluation of progress in nutrient management will benefit from consideration of antecedent influences.

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