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Discussions

Antecedent flow conditions and nitrate concentrations in the Mississippi River Basin

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Abstract

The influence of antecedent flow conditions on nitrate concentrations was explored at eight sites in the Mississippi River Basin, USA. Antecedent moisture conditions have been shown to influence nutrient export from small, relatively homogenous basins, but this influence has not been observed at a regional or continental scale. 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 the previous year was drier than average, at these sites, 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 storm events. At half of the sites, when flow during the previous year was 50 % drier than average, nitrate concentration can be from 9 and 27 % higher than nitrate concentrations that follow a year with average daily flow. Conversely, nitrate concentration can be from 8 and 21 % lower than expected when the previous year was 50 % wetter than average. These relationships between nitrate concentration and Q ratio serve as the basis for future studies that can better define specific hydrologic processes occurring during and after a drought, 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; Randall et al., 2003; Soulsby et al., 2003; Vecchia et al., 2008). 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 flows affect 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.

The accumulation of nitrate in farm fields is a function of many influences, including weather conditions, soil characteristics, crop type, crop yield, fertilizer application, and irrigation (Ferguson et al., 2012; Randall et al., 2003). The timing and interaction of these factors during a period of low precipitation leads to a wide range of nitrate storage remaining in the soil after a growing season. In general, farms that had an exceptionally

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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 influence of antecedent flow conditions on nitrate anomalies in the MRB and identify the contemporaneous flow conditions in which antecedent flows are most influential. 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 these relationships for eight sites in the MRB (Fig. 1) using data collected over three decades and across a range of contemporaneous flow conditions.

2 Data compilation

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 (Table 1, Fig. 1). These sites 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 1980 through the fall of 2011 on a

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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.

3 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). The remaining unexplained variability in nitrate concentration may be related in part 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 concentration predicted by a statistical model (based on contemporaneous daily mean flow, season, and trend), herein referred to as nitrate anomalies (Vecchia et al., 2008). If antecedent flows influence nitrate concentration, a statistically significant relationship ($p \leq 0.05$) between antecedent flows, expressed in terms of a hydrologic statistic, and nitrate anomalies should be observed.

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 (Qr_i) for day i is calculated as

$$\mathrm{Qr}_i = \frac{\mathrm{Qyr}_i}{Q_{\mathrm{POR}}} \tag{1}$$

where Qyr_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. The Q ratio serves as a surrogate for overall basin wetness or dryness the previous year, and Q ratios likely relate to other physical, chemical and biological processes in a basin that are affected by preceding moisture conditions. The calculation of Q ratio is straightforward

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and only requires streamflow data. 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. If significant relationships are documented, future studies can help better define the specific hydrologic processes that influence nitrate concentration during and after a drought. 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. A Q ratio value of 1 or near 1 ($\mathrm{Qr}_{\mathrm{avg}} = 1$) indicates the previous year had average mean daily flows. Figure 2 illustrates this concept in the Illinois River (VALL) by showing 3 days that had markedly different antecedent flow conditions. The mean daily flow for the 364 days prior to and including 28 March 2006, was 293 $\mathrm{m^3\,s^{-1}}$ (cubic meters per second), approximately 60 % lower than the mean daily flow for the period of record at this site (approximately 740 $\mathrm{m^3\,s^{-1}}$), resulting in a Q ratio of 0.39 (Fig. 2a). On 16 February 2010, the mean daily flow of the previous year was 1314 $\mathrm{m^3\,s^{-1}}$, approximately 75 % greater than the mean daily flow for the period of record, resulting in a Q ratio of 1.77 (Fig. 2b). Finally, on 5 March 1987, the mean daily flow of the previous year was 709 $\mathrm{m^3\,s^{-1}}$, approximately the same as the mean daily flow for the period of record, resulting in a Q ratio near 1 (0.95) (Fig. 2c). Q ratios 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. 3).

We used the 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 fit separate models for each day, resulting in unbiased estimates of concentration (Hirsch et al., 2010). WRTDS was used to estimate nitrate concentration from 1980 to 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

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$$\mathrm{pc}_i = \beta_0 + \beta_1 t + \beta_2 \ln(Q) + \beta_3 \sin(2\pi t) + \beta_4 \cos(2\pi t) \quad (2)$$

where ln is the natural log, $\beta_0, \beta_1, \ldots, \beta_4$, 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

$$\mathrm{CA}_i = \ln(c_i) - \mathrm{pc}_i \quad (3)$$

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. Thus, a positive nitrate anomaly indicates higher-than-anticipated observed concentration; a negative anomaly indicates a lower-than-anticipated concentration. For details on WRTDS and the modeling of nitrate concentration at these sites, see Hirsch et al. (2010) and Sprague et al. (2011).

Nonparameteric statistical methods were used to explore the influence of antecedent flows on nitrate anomalies because the Q ratio data are positively skewed and contain outliers (Fig. 3). The strength of the correlation between nitrate anomaly and Q ratio 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 Q ratio and is defined as

$$\mathrm{CA}_i = \beta_o + \beta_1 \cdot \mathrm{Qr}_i \quad (4)$$

where $\mathrm{CA}_i$is the nitrate anomaly for day i, Qr_i is the flow ratio on day i, and β_o 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 the median of all Qr_i values (Helsel and Hirsch, 2002). Robust lines were fit for each site using all available data.

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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 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 daily flows (Q ratio = 1) was determined using the following equation,

$$\left(\frac{\exp\left(\beta_1 \cdot \mathrm{Qr}_i\right)}{\exp\left(\beta_1 \cdot \mathrm{Qr}_{\mathrm{avg}}\right)} - 1\right) \cdot 100 = \left(\frac{\exp\left(\beta_1 \cdot \mathrm{Qr}_i\right)}{\exp\left(\beta_1\right)} - 1\right) \cdot 100$$
$$= \text{Percent difference in concentration} \tag{5}$$

where β_1 is the slope coefficient for a given site and flow class (see Tables 2 and 3), $\mathrm{Qr}_{\mathrm{avg}} = 1$ (the Q ratio value for a hypothetical day that had average daily flows the previous year), and Qr_i is the Q ratio for day i. 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). Four hypothetical Q ratio values (0.5, 0.75, 1.25 and 1.5) were applied using Eq. (5). These results are anticipated to parallel those quantified by the robust line relationships (Eq. 4) but apply directly to nitrate concentration instead of nitrate anomaly.

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4 Results and discussion

4.1 Nitrate anomaly across all contemporaneous flows

When all contemporaneous flows at each site are considered together, the upper Mississippi River (CLIN) and the major tributaries (WAPE, VALL, and GRCH), except the Missouri River (HERM), exhibit statistically significant relationships ($p \leq 0.05$) between Q ratio and nitrate anomaly (Fig. 4), though tau is small, ranging from −0.13 to −0.17 depending on the site (Table 2). 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. 4). In general, the strength of the relationships shown here (Table 2) are weaker than those reported elsewhere for smaller basins (e.g., Biron et al., 1999; Burt et al., 1988; Foster and Walling, 1978; Macrae et al., 2010; Welsch et al., 2001), which is not necessarily surprising given the complexity of solute behavior in large rivers (Webb and Walling, 1984).

In this analysis, the Q ratio 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

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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; Burt and Worall, 2007).

The statistically significant negative relationships ($p \leq 0.05$) between Q ratio and nitrate anomaly (Fig. 4) exhibited in the upper Mississippi River (CLIN), Iowa River (WAPE), Illinois River (ILLI) and Ohio River (GRCH) indicate dry hydrologic conditions the previous year relate to higher nitrate anomalies and wet hydrologic conditions the previous year relate to lower nitrate anomalies. These four sub-basins are likely the most homogenous in the study area. 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 remaning sites further downstream on the Mississippi River (GRAF, THEB and MISS-OUT) and the Missouri River (HERM) do not provide evidence that nitrate anomalies respond to previous antcedent 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 Q ratio and nitrate anomaly when all contemporaneous flows are considered. The lack of an apparent influence of antecedent flow conditions at HERM, THEB or MISS-OUT is necessarily surprising. The Missouri River Basin extends from the Rocky Mountains in the most

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western portion of the basin, through the semi-arid Great Plains and into the humid corn belt in the most eastern portion of the basin (Fig. 1), thus making it the most heterogeneous sub-basin in this study. The wide range of climates and terrains throughout the Missouri River Basin can cause parts of the basin to experience markedly differently hydrologic conditions simultaneously, which may lead to distinct hydrologic processes in this basin compared to others in this study. Further downstream in the Mississippi River, the THEB site (Fig. 1) is primarily a mix of Missouri River water (approximately 39 %) and upstream Mississippi River water (approximately 54 %), neither of which exhibit statistically significant relationships. A significant relationship was not anticipated at the outflow of the Mississippi River (MISS-OUT, Fig. 4) because it is a mix of diverse inputs including Ohio River water (43 %), Missouri River water (14 %), and other water from upper (19 %) and lower (24 %) portions of the basin (Table 1). The travel time of water from different locations in the MRB can take weeks to months to reach MISS-OUT (Nolan et al., 2002), thus the influence of antecedent flows observed at upstream and more homogenous tributaries is likely smeared as water moves downstream and mixes with other water sources.

4.2 Nitrate anomaly by contemporaneous flow class

In most cases, the relationship between Q ratio 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 3) as compared to those derived using all contemporaneous flow data together (Table 2).

4.2.1 Storm response

At the highest contemporaneous flows (> 75th percentile) Q ratio and nitrate anomaly are negatively related ($p \leq 0.05$) at three (CLIN, WAPE and VALL) of the eight sites (Table 3). Contemporaneous flows in this range capture the peak flow and rising and

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falling limbs of major storms within a basin. Also, at mid-high contemporaneous flows (> 50th and < 75th percentile), nitrate anomalies are negatively related to the Q ratio at three of the eight sites (VALL, THEB and GRCH) and positively related at one site (HERM). For these sites, mid-high flows include all or portions of the rising and falling limbs of a hydrograph. During periods with generally elevated flows (during the spring, for example), mid-high flows typically occur near the beginning and end of a storm event. For smaller events or events that occur during a generally lower flow period (during the summer, for example), the mid-high flow range may encompass the entire event, including its peak flow.

In total, six of the eight sites (including GRAF, though the relationship is not statistically significant ($p = 0.06$)) show negative relationships between Q ratio and nitrate anomaly when contemporaneous flows were greater than the 50th percentile of flow (Fig. 5), suggesting a flushing response occurs during storm events that follow extended dry antecedent conditions. This process has been explored extensively in the literature for 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, is also observable at a regional scale. Conversely, wetter antecedent conditions at these sites result in lower nitrate anomalies during storms 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 km^2) and no statistically significant relationships occur at the highest flows for basins larger than 250 000 km^2 (Fig. 5). 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 during high flow events dilution from an expanding variable source area with low nitrate concentrations likely obscures the

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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 Q ratio in the Missouri River (HERM) during mid-high contemporaneous flows (Fig. 5). This observation directly contradicts the flushing response model described for other sites. However, wetter antecedent 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).

A possible conceptualization of this relationship in the Missouri River (HERM) is that the supply of exportable nitrate is reduced by irrigation or other processes during a drought. Approximately 25 % 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 modelling 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 during drier than average climatic conditions. However, the supply-limiting influence of irrigation does not account for the higher nitrate anomalies observed following wetter antecedent conditions.

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Interestingly, the Missouri River Basin also has the greatest number of dams and the largest 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.

4.2.2 Baseflow response

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. 5, Table 3). These flow ranges generally occur between storm events and represent baseflow conditions. For other sites, the lack of significant relationships during baseflow suggests the groundwater system is not closely influenced by surface conditions, at least over a time span of one year. Among all tributaries to the Mississippi River, the Ohio River contributes about 43 % of flow to the Mississippi River (Table 1); therefore if flow at GRCH is low, flow at MISS-OUT is likely to also be low. Since low flow conditions at GRCH and MISS-OUT are closely related, it is likely any interpretation about the influence of antecedent flows on nitrate anomalies for GRCH also applies to the low flow response observed at MISS-OUT. However, insight into the influence of previous drought on baseflow conditions and nitrate concentration at very large scales is limited and the relationships documented at GRCH and MISS-OUT are not readily interpretable.

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4.3 Potential effect on nitrate concentration

For each statistically significant relationship ($p \leq 0.05$, Tables 2 and 3), Eq. (5) and the appropriate slope coefficient were used to translate nitrate anomalies to the percent change in nitrate concentration that would occur following a wet or dry year ($Qr_i > 1$ or $Qr_i < 1$, respectively) relative to the nitrate concentration expected following a year with average flows ($Qr_{avg} = 1$). For example, the three different Q ratio values for the Illinois River (VALL) in Fig. 2 represent dry antecedent flow conditions (Fig. 2a, $Qr_i = 0.39$), wet antecedent flow conditions (Fig. 2b, $Qr_i = 1.77$), and near-average antecedent flow conditions (Fig. 2c, $Qr_i = 0.95$). All three dates in Fig. 2 (28 March 2006; 16 February 2010; and 5 March 1987) had mid-high contemporaneous flows. Thus, the concentration anomaly on each of the three dates can be calculated using Eq. (4) and the intercept (0.42) and slope (−0.34) values from Table 3 for VALL at mid-high flow conditions. The resulting calculations indicate concentration anomalies are expected to be positive (0.29), negative (−0.18) and near zero (0.10), respectively, for these three dates. To put the results into terms of percent change in concentration, Eq. (5) was used to estimate that nitrate concentrations on these three dates will be +23 % different, −23 % different, or indistinguishable (+2 %), respectively, from nitrate concentrations expected following an average flow year.

4.3.1 All contemporaneous flows

Rather than apply Eq. (5) to each day in the period of record at each site, four hypothetical Q ratio scenarios were used to describe the potential response of nitrate concentration to different antecedent flow conditions. Hypothetical Q ratios and Eq. (5) were applied by site and only for the flow conditions that had significant robust line relationships ($p \leq 0.05$, Table 4). The results from this analysis are consistent with those presented for nitrate anomalies. Considering all contemporaneous flow conditions together, when the previous year's flow is 50 % wetter or drier than average, nitrate concentration is about ±10 % different from expected nitrate concentration at the two smallest tributary

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sites (WAPE, and VALL). In the upper Mississippi River (CLIN) and Ohio River (GRCH), the difference in nitrate concentration could be expected to be as much as 27 % higher or 21 % lower than expected (Table 4).

4.3.2 Storm response

Analogous to the nitrate anomaly results, nitrate concentration responds more strongly to antecedent flow conditions when contemporaneous flow data are subdivided into flow classes. For contemporaneous flow classes that capture all or part of a storm event (contemporaneous flows > 50th percentile), when the previous year's flow is 25 % drier than average, nitrate concentration may be about 6 to 10 % higher than expected, for most sites where nitrate anomaly is negatively related to the Q ratio (Table 4). Nitrate concentration increases to about 11 to 19 % different from expected when the previous year's flow is 50 % drier than average. Nitrate concentration is more sensitive to antecedent flow conditions in the upper Mississippi River (CLIN) and when the previous year was 25 to 50 % drier than average, nitrate concentration can be 16 to 34 % higher than expected at high flows (Table 4). At these sites, differences in nitrate concentration are slightly smaller in magnitude and negative when the previous year is wetter than average (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 the previous year was 25 or 50 % drier than average, nitrate concentration is 8 or 16 % lower than expected, respectively. With the exception of HERM, these patterns at mid-high and high contemporaneous flow conditions are consistent with the conceptual model of soil nitrate flushing during storm events following a drought.

4.3.3 Baseflow response

Nitrate concentration appears to be 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).

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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. 5). For mid-low and low flow classes, when the previous year's flow is 25 % drier than average, nitrate concentration may be about 9 to 20 % greater than expected. As antecedent flow conditions become increasingly dry (50 % of average flow) nitrate concentration can be 19 to 44 % higher than expected (Table 4). Similarly, during baseflow conditions when the previous year's flow is 25 and 50 % wetter than average, nitrate concentration can be between 8 and 30 % lower than expected.

4.3.4 Recent observations in Iowa (2012–2013)

Nitrate sensors deployed in several Iowa rivers during the spring of 2013 provide some empirical support for the results presented in this study. From May 2012, through February 2013, much of the central United States experienced moderate to extreme hydrologic drought. By the following spring (2013), much of the State of Iowa (Fig. 1) had recovered and was moderately to very wet (National Oceanic and Atmospheric Administration, 2013). For example, peak discharge between early-October and mid-June of 2013 would rank as the 5th highest annual peak discharge in the 111-yr flood record at the WAPE site on the Iowa River. At this site, daily mean flow from March through May was predominately mid-high (50th to 75th percentile) to high (greater than 75th percentile) and the mean of the daily Q ratios over this period was 0.49, indicating that flow during the previous year was approximately 50 % lower than average. Considering the contemporaneous flow conditions, we used Eq. (5) and observed (though provisional) daily streamflow data to predict the concentration differences for each day during this 3-month period. These predictions indicate nitrate concentration at WAPE was likely between 7 to 19 % higher (13 % higher on average) during these months than would have been expected if the previous year had had average daily flows. Provisional nitrate sensor data from Iowa indicate extremely high nitrate concentrations in many rivers during the spring and summer of 2013. Around mid-May, nitrate concentration

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peaked at about 40 mg L^{-1} in a small stream in north-central Iowa and elevated nitrate concentrations (some approximately 20–30 mg L^{-1}) were also observed in larger rivers throughout the state. In many instances, nitrate concentrations recorded by the sensors were some of the highest concentrations recorded since the start of continuous nitrate monitoring in 2008 (written communication on 15 May, and 26 June 2013, Jessica Garrett, USGS; Beeman, 2013). These recent observations in Iowa are consistent with the conceptual model of a flushing response following prolonged dry conditions described in this study.

5 Conclusions

Except for the Missouri River (HERM), our results show a negative relationship between antecedent flow conditions and nitrate anomaly during mid-high and high contemporaneous flows for the major tributaries and two of the four Mississippi River main-channel sites (Fig. 5). In general, when the previous year was drier than average, nitrate concentration is higher than expected relative to nitrate concentrations following a year with average flow conditions. This response is likely due to the accumulation of soil nitrate during a drought and subsequent flushing with moderately high to high flow events when the drought ends. When the previous year was wetter than average nitrate concentrations are lower than expected 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 (Fig. 5), indicates the influence of antecedent flow on nitrate anomaly not only varies by contemporaneous flow class but also regionally. The heterogeneity of the Missouri River Basin coupled with high levels of irrigation and dam storage (Table 1) make interpretation difficult but may indicate lower nitrate supply in this basin following a drought, compared to other study basins.

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Due to the large scale of these basins and their inherent complexity, the flushing response observed at these sites is dampened (Tables 2 and 3) compared to observations from smaller basins (e.g., Biron et al., 1999; Burt et al., 1988; Foster and Walling, 1978; Macrae et al., 2010; Welsch et al., 2001). Yet, nitrate concentrations following a drier or wetter than average year appear to be up to 27 or −21 % different from nitrate concentrations expected following a year with average flow (Table 4). These percent differences in nitrate concentrations typically increase in magnitude when contemporaneous flows are considered (Table 4) and can be as much as 34 % different from expected during storm events and high flows (CLIN) or up to 44 % different from expected during baseflows (GRCH). 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.

While this study identifies significant relationships between antecedent flow conditions and nitrate concentration, it does little to explain the cause of these relationships, thus we 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 Worall, 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?

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– 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 classes. 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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References

Ashby, J. A., Bowden, W. B., and Murdoch, P. S.: Controls on denitrification in riparian soils in headwater catchments of a hardwood forest in the Catskill Mountains, U.S.A., Soil Biol. Biochem., 30, 853–864, 1998.

Aulakh, M. S. and Bijay-Singh: Nitrogen losses and fertilizer N use efficiency in irrigated porous soils, Nutr. Cycl. Agroecosyst., 27, 197–212, 1997.

Aulenbach, B. T., Buxton, H. T., Battaglin, W. A., and Coupe, R. H.: Flow and nutrient fluxes of the Mississippi-Atchafalaya River Basin and subbasins for the period of record through 2005, US Geological Survey Open-File Report 2007-1080, http://toxics.usgs.gov/pubs/of-2007-1080/, last access: September 2013, US Geological Survey, 2007.

Beeman, P.: Nitrate spike tests Des Moines water supplies, Des Moines Register, available online at: http://www.desmoinesregister.com/article/20130701/NEWS/307010028/Nitrate-spike-tests-Des-Moines-water-supplies?odyssey=tab%7Ctopnews%7Ctext%7CFrontpage, last access: 30 June 2013.

Bernal, S. and Sabater, F.: Changes in discharge and solute dynamics between hillslope and valley-bottom intermittent streams, Hydrol. Earth Syst. Sci., 16, 1595–1605, doi:10.5194/hess-16-1595-2012, 2012.

Biron, P. M., Roy, A. G., Courschesne, F., Hendershot, W. H., Cote, B., and Fyles, J.: The effect of antecedent moisture conditions on the relationship of hydrology to hydrochemistry in a small forested watershed, Hydrol. Process., 13, 1541–1555, 1999.

Bowman, J. A. and Collins, M. A.: Impacts of irrigation and drought on Illinois ground-water resources, ISWS/RI-109/87, State of Illinois, Department of Energy and Natural Resources, Illinois state water survey, Illinois, 31 pp., 1987.

Brown, J. B., Sprague, L. A., and Dupree, J. A.: Nutrient sources and transport in the Missouri River basin, with emphasis on the effects of irrigation and reservoirs, J. Am. Water Resour. Assoc., 47, 1034–1060, 2011.

Burkart, M. R. and Stoner, J. D.: Chapter 7, Nitrogen in groundwater associated with agricultural systems, in: Nitrogen in the Environment: Sources, Problems, and Management, Academic Press/Elsevier, Amsterdam, Boston, 177–202, 2008.

Burt, T. and Worrall, F.: Non-stationarity in long time series: some curious reversals in the ‘memory’ effect, Hydrol. Process., 21, 3529–3531, 2007.

Burt, T. P. and Worrall, F.: Stream nitrate levels in a small catchment in south west England over a period of 35 years (1970–2005), Hydrol. Process., 23, 2056–2068, 2009.

Burt, T. P., Arkell, B. P., Trudgill, S. T., and Walling, D. E.: Stream nitrate levels in a small catchment in south west England over a period f 15 years, Hydrol. Process., 2, 267–284, 1988.

Cooper, R., Thoss, V., and Watson, H.: Factors influencing the release of dissolved organic carbon and dissolved forms of nitrogen from a small upland headwater during autumn runoff events, Hydrol. Process., 21, 622–633, 2007.

Creed, I. F. and Band, L. E.: Export of nitrogen from catchments within a temperate forest: Evidence for a unifying mechanism regulated by variable source area dynamics, Water Resour. Res., 34, 3105–3120, 1998.

de Klein, C. A. M. and van Logtestijn, R. S. P.: Denitification in grassland soils in the Netherlands in relation to irrigation, N-application rate, soil water content and soil temperature, Soil Biol. Biochem., 28, 231–237, 1996.

Detty, J. M. and McGuire, K. J.: Topographic controls on shallow groundwater dynamics: implications of hydrologic connectivity between hillslopes and riparian zones in a till mantled catchment, Hydrol. Process., 24, 2222–2236, 2010.

Dinnes, D. L., Karlen, D. L., Jaynes, D. B., Kaspar, T. C., Hatfield, J. L., Colvin, T. S., and Cambardella, C. A.: Nitrogen management strategies to reduce nitrate leaching in tile-drained Midwestern soils, Agron. J., 94, 153–171, 2002.

Donner, S. D. and Scavia, D.: How climate controls the flux of nitrogen by the Mississippi River and the development of hypoxia in the Gulf of Mexico, Limnol. Oceanogr., 52, 856–861, 2007.

Emmerich, W. E. and Heitschmidt, R. K.: Drought and Grazing: II. Effects on runoff and water quality, J. Range Manage., 55, 229–234, 2002.

Ferguson, R., Shapiro, C., Wortmann, C., Shaver, T., and Hergert, G., University of Nebraska-Lincoln Extension, CropWatch, Nebraska crop production & pest management information, Checking for Residual nitrate this spring: http://cropwatch.unl.edu/web/cropwatch/archive?articleID=5121463, last access: 21 June 2013, posted: 6 March 2013.

Foster, I. D. L. and Walling, D. E.: The effects of the 1976 drought and autumn rainfall on stream solute levels, Earth Surf. Proc., 3, 393–406, 1978.

Garrett, J.: Concentrations, loads and yields of select constituents from major tributaries of the Mississippi and Missouri Rivers in Iowa, Water Years 2004–2008, US Geological Survey Scientific Investigations Report 2012-5240, http://pubs.usgs.gov/sir/2012/5240/sir2012-5240.pdf, last access: September 2013, US Geological Survey, 72 pp., 2012.

Groves, S. J. and Bailey, R. J.: The influence of sub-optimal irrigation and drought on crop yield, N uptake and risk of N leaching from sugarbeet, Soil Use Manage., 13, 190–195, 1997.

Helsel, D. R. and Hirsch, R. M.: Statistical methods in water resources, Techniques of water-resources investigations, Book 4, chapter A3, http://pubs.usgs.gov/twri/twri4a3/html/pdf_new.html, last access: September 2013, US Geological Survey, 522 pp., 2002.

Hirsch, R. M., Moyer, D. L., and Archfield, S. A.: Weighted regressions on time, discharge, and season (WRTDS), with an application to Chesapeake Bay river inputs, J. Am. Water Resour. Assoc., 46, 857–880, 2010.
Hornberger, G. M., Bencala, K. E., and McKnight, D. M.: Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado, Biogeochemistry, 25, 147–165, 1994.
Lange, J. and Haensler, A.: Runoff generation following a prolonged dry period, J. Hydrol., 464–465, 157–164, 2012.
Macrae, M. L., English, M. C., Schiff, S. L., and Stone, M.: Influence of antecedent hydrologic conditions on patterns of hydrochemical export from a first-order agricultural watershed in Southern Ontario, Canada, J. Hydrol., 389, 101–110, 2010.
National Oceanic and Atmospheric Administration: National Climatic Data Center, Climate Monitoring Group Palmer Hydrological Drought Index – May 2012 to April 2013: http://www.ncdc.noaa.gov/oa/climate/research/prelim/drought/palmer.html, last access: 21 June 2013.
Nolan, J. V., Brakebill, J. W., Alexander, R. B., and Schwarz, G. E.: ERF1_2 – Enhanced River Reach File 2.0: http://water.usgs.gov/GIS/metadata/usgswrd/XML/erf12.xml, last access: 2 June 2013.
Pervez, M. S. and Brown, J. F.: Mapping irrigated lands at 250-m scale by merging MODIS data and national agricultural statistic, Remote Sensing, 2, 2388–2414, 2010.
Rabalais, N. N. and Turner, R. E.: Hypoxia in the northern Gulf of Mexico: description, causes and change, in: Coastal Hypoxia: Consequences for living resources and ecosystems, Coastal and Estuarine Studies, American Geophysical Union, Washington, D.C., 1–36, 2001.
Randall, G. W., Vetsch, J. A., and Huffman, J. R.: Nitrate losses in subsurface drainage from a corn-soybean rotation as affected by time of nitrogen application and use of Nitrapyrin, J. Environ. Qual., 32, 1764–1772, 2003.
Rehm, G., Schmitt, M., and Eliason, R.: University of Minnesota-Extension, Using soil nitrate test in Minnesota, WW-07310: http://www.extension.umn.edu/distribution/cropsystems/DC7310.html, last access: 21 June 2013, posted: 2009.
Sawyer, J.: Iowa State University-Extension, Soil profile nitrate in corn fields following the 2012 drought: http://www.extension.iastate.edu/CropNews/2013/0221sawyer.htm, last access: 21 June 2013, posted: 21 February 2013.

Scavia, D., Rabalais, N. N., Turner, R. E., Justic, D., and Wiseman, W. J.: Predicting the response of Gulf of Mexico hypoxia to variation in Mississippi River nitrogen load, Limnol. Oceanogr., 48, 951–956, 2003.

Soulsby, C., Petry, J., Brewer, M. J., Dunn, S. M., Ott, B., and Malcolm, I. A.: Identifying and assessing uncertainty in hydrological pathways: a novel approach to end member mixing in a Scottish agricultural catchment, J. Hydrol., 274, 109–128, 2003.

Sprague, L. A., Hirsch, R. M., and Aulenbach, B. T.: Nitrate in the Mississippi River and its tributaries, 1980 to 2008: Are we making progress?, Environ. Sci. Technol., 45, 7209–7216, 2011.

Stites, W. and Kraft, G. J.: Nitrate and chloride loading to groundwater from an irrigated north-central U.S. sand-plain vegetable field, J. Environ. Qual., 30, 1176–1184, 2001.

Turner, R. E., Rabalais, N. N., and Justic, D.: Predicting summer hypoxia in the northern Gulf of Mexico: Riverine N, P, and Si loading, Mar. Pollut. Bull., 52, 139–148, 2006.

Vecchia, A. V., Martin, J. D., and Gilliom, R. J.: Modeling variability and trends in pesticide concentrations in streams, J. Am. Water Resour. Assoc., 44, 1308–1324, 2008.

Walling, D. E. and Foster, I. D. L.: Variations in the natural chemical concentration of river water during flood flows, and the lag effect: some further comments, J. Hydrol., 26, 237–244, 1975.

Webb, B. W. and Walling, D. E.: Stream solute behavior in the River Exe basin, Devon, UK, Dissolved loads of rivers and surface water quantity/quality relationships, Proceedings of the Hamburg Symposium, August 1983, IAHS Publ, 141, 153–169, 1984.

Welsch, D. L., Kroll, C. N., McDonnell, J. J., and Burns, D. A.: Topographic controls on the chemistry of subsurface stormflow, Hydrol. Process., 15, 1925–1938, 2001.

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Table 1. Site information and basin characteristics for eight sites in the Mississippi River Basin. (USGS, US Geological Survey; km^2, square kilometres; $m^3 s^{-1}$, cubic meters per second; $mm\,yr^{-1}$, millimetres per year; cm, centimetres.)

Site	USGS site number	Site name	Basin area (km^2)	Mean daily streamflow ($m^3 s^{-1}$)	Mean annual runoff ($mm\,yr^{-1}$)	Mean annual precipitation[4] (cm)	Farmland in basin[5] (%)	Irrigated land in basin[6] (%)	Cropland that is irrigated[5] (%)	Number of dams in basin[7]	Relative storage[7a] (yr)
CLIN	05420500	Mississippi River at Clinton, Iowa	221 703	1605	228	79	43	1.3	4.0	1531	0.59
WAPE	05465500	Iowa River at Wapello, Iowa	32 375	304	297	89	79	0.2	0.2	223	0.08
VALL	05586100	Illinois River at Valley City, Illinois	69 264	743	339	96	67	1.9	2.3	653	0.10
GRAF	05587455	Mississippi River below Grafton, Illinois[1]	443 665	3722	265	85	56	1.2	2.6	4824	0.34
HERM	06934500	Missouri River at Hermann, Missouri	1 353 269	2694	63	54	36	4.1	25.6	19 233	1.89
THEB	07022000	Mississippi River at Thebes, Illinois	1 847 180	6912	118	63	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	119	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	78	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 Tarbert 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 was 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, county-level, http://nationalatlas.gov/atlasftp.html and http://www.agcensus.usda.gov/. [6] USGS MODIS-derived data, 2002, http://earlywarning.usgs.gov/USirrigation/ and Pervez and Brown, 2010. [7] National Inventory of Dams dataset produced by the Army Core of Engineers, 2009, http://crunch.tec.army.mil/, dataset updated (duplicates removed and approximately 70 % verified). [7a] Relative storage = total storage in basin (from National Inventory of Dams)/total annual streamflow

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Table 2. Kendall's tau and robust line results of nitrate anomaly and Q ratio relationships, using all contemporaneous flow data. Statistically significant relationships ($p <= 0.05$) are bolded.

Site	River	Tau	p value	Intercept	Slope	n^{*}
CLIN	**Mississippi**	**−0.13**	**0.00**	**0.60**	**−0.48**	**315**
WAPE	**Iowa**	**−0.15**	**0.00**	**0.29**	**−0.20**	**312**
VALL	**Illinois**	**−0.17**	**0.00**	**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
GRCH	**Ohio**	**−0.16**	**0.00**	**0.37**	**−0.34**	**378**
MISS-OUT	Mississippi	−0.05	0.15	0.16	−0.12	401

* n is the number of observations.

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Table 3. Kendall's tau and robust line results of nitrate anomaly and Q ratio relationships, by contemporaneous flow class. Statistically significant ($p < = 0.05$) are bolded.

		Low flow conditions (daily $Q^1 < 25$th)					Mid-low flow conditions (25th $<$ daily $Q^1 < 50$th)					Mid-high flow conditions (50th $<$ daily $Q^1 < 75$th)					High flow conditions (daily $Q^1 > 75$th)				
Site	River	Tau	p value	Interc[2]	Slope	n[3]	Tau	p value	Interc[2]	Slope	n[3]	Tau	p value	Interc[2]	Slope	n[3]	Tau	p value	Interc[2]	Slope	n[3]
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**	**0.00**	**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**	**0.00**	**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**	**0.00**	**0.42**	**−0.34**	**94**	**−0.25**	**0.00**	**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

[1] daily Q = daily streamflow; [2] Interc = intercept; [3] n = number of observations.

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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. Q ratio scenarios describe when the previous year was 50 and 25 % drier than average (Q ratios 0.5 and 0.75, respectively) and 25 and 50 % wetter than average (Q ratios 1.25 and 1.5, respectively). These scenarios are only applied to relationships that were statistically significant ($p <= 0.05$, see Tables 2 and 3).

		All contemporaneous flow conditions Drier (Q ratio) Wetter				Low flow conditions Drier (Q ratio) Wetter				Mid-low flow conditions Drier (Q ratio) Wetter				Mid-high flow conditions Drier (Q ratio) Wetter				High flow conditions Drier (Q ratio) Wetter			
Site	River	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												

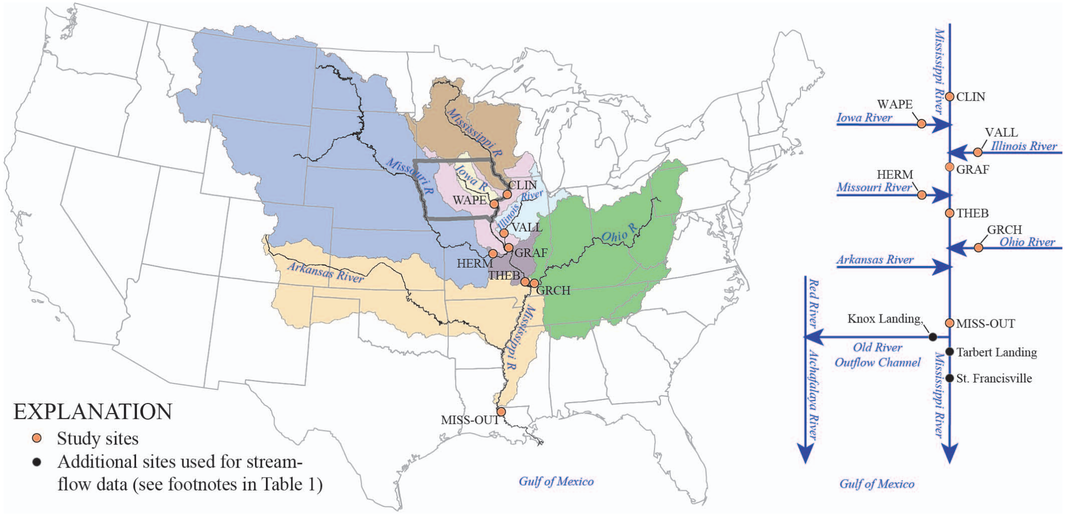

Fig. 1. Map of the continental United States showing Mississippi River basin and study sites, and a schematic line drawing of the relative locations of study sites, major tributaries, and additional sites. Bolded area is the state of Iowa.

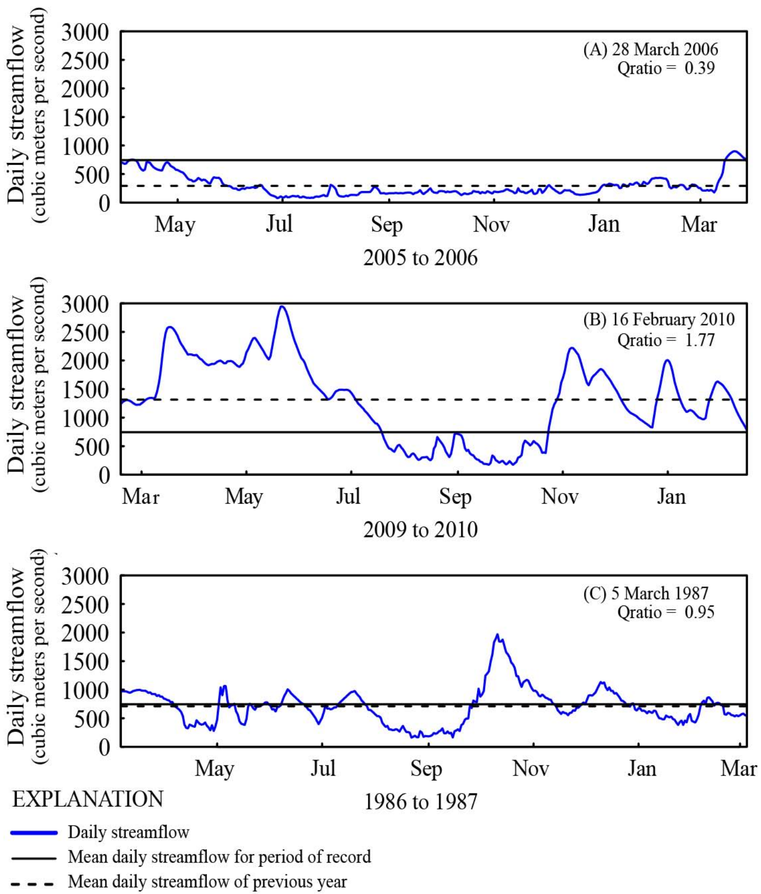

Fig. 2. Example of dry **(A)**, wet **(B)**, and near average **(C)** antecedent flow conditions at VALL (Illinois River) for three specific dates. Plot depicts daily streamflow for the 364 days prior to and including the date indicated on each plot.

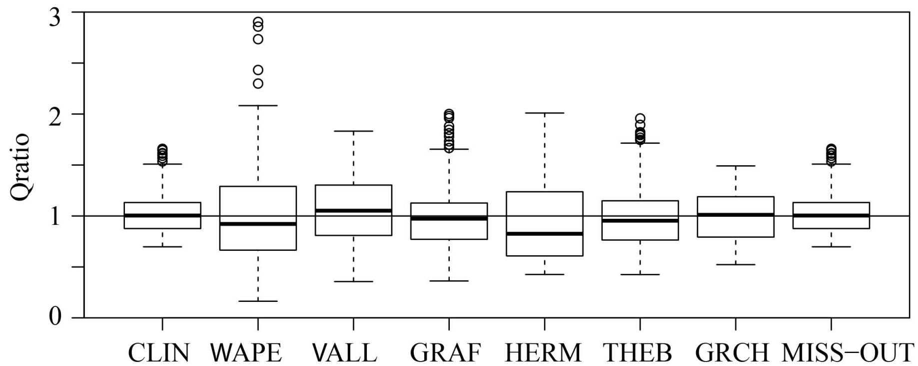

Fig. 3. Boxplot of Q ratio values by site.

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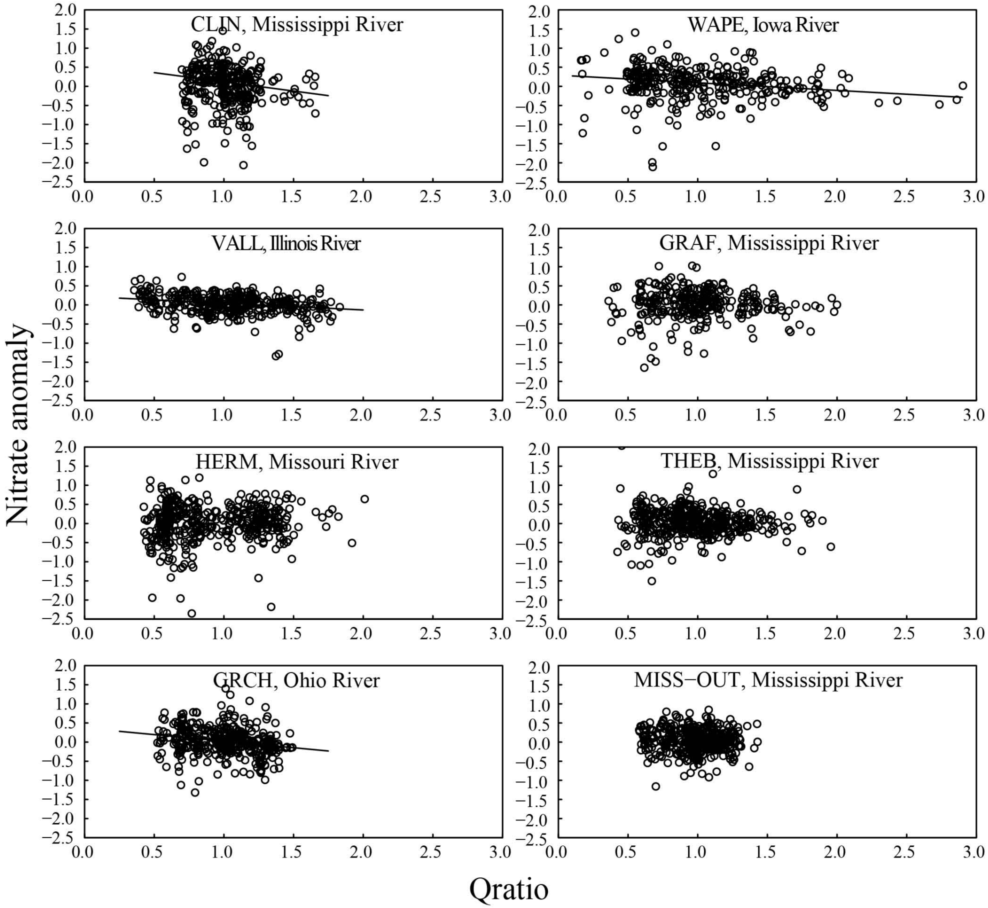

Fig. 4. Plots of nitrate anomaly versus Q ratio by site, using all contemporaneous flow data. Statistically significant relationships ($p \leq 0.05$) are denoted with solid black line.

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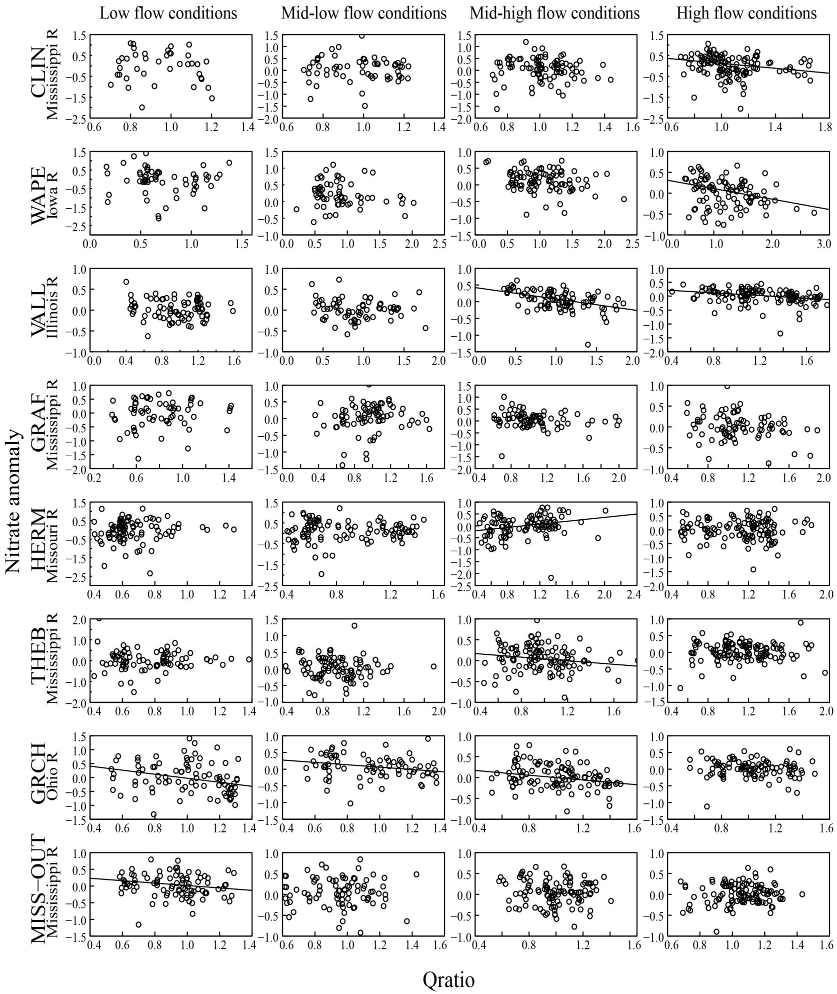

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Fig. 5. Plots of nitrate anomaly versus Q ratio, by site and contemporaneous flow class. Statistically significant relationships ($p \leq 0.05$) are denoted with solid black line. Low flow conditions: < 25th percentile, mid-low flow conditions: > 25th and < 50th percentile, mid-high flow conditions: > 50th and < 75th percentile, and high flow conditions: > 75th percentile. Note scale on axis is specific to each plot.

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