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Nitrate in the Mississippi River and Its Tributaries, 1980 to 2008: Are We Making Progress?

Lori A. Sprague,[*,†] Robert M. Hirsch,[‡] and Brent T. Aulenbach[§]

[†]U.S. Geological Survey, Denver Federal Center, Box 25046 MS 415, Denver, Colorado 80225, United States

[‡]U.S. Geological Survey, 432 National Center, Reston, Virginia 20192, United States

[§]U.S. Geological Survey, 3039 Amwiler Road, Suite 130, Atlanta, Georgia 30360, United States

S Supporting Information

ABSTRACT: Changes in nitrate concentration and flux between 1980 and 2008 at eight sites in the Mississippi River basin were determined using a new statistical method that accommodates evolving nitrate behavior over time and produces flow-normalized estimates of nitrate concentration and flux that are independent of random variations in streamflow. The results show that little consistent progress has been made in reducing riverine nitrate since 1980, and that flow-normalized concentration and flux are increasing in some areas. Flow-normalized nitrate concentration and flux increased between 9 and 76% at four sites on the Mississippi River and a tributary site on the Missouri River, but changed very little at tributary sites on the Ohio, Iowa, and Illinois Rivers. Increases in flow-normalized concentration and flux at the Mississippi River at Clinton and Missouri River at Hermann were more than three times larger than at any other site. The increases at these two sites contributed much of the 9% increase in flow-normalized nitrate flux leaving the Mississippi River basin. At most sites, concentrations increased more at low and moderate streamflows than at high streamflows, suggesting that increasing groundwater concentrations are having an effect on river concentrations.

INTRODUCTION

The hypoxic zone in the northern Gulf of Mexico is one of the largest in the world[1] and its size is related to the flux of nitrate from the Mississippi River basin.[2] Nitrate flux from the Mississippi River basin is strongly influenced by changes in streamflow, which in turn is influenced by changes in precipitation and runoff.[3−5] This climate-driven variability in nitrate flux has been shown to be one of the primary factors influencing interannual variability in the size of the hypoxic zone.[3,6] The random nature of climate-driven variability makes it a confounding factor in the assessment of planned progress toward nutrient reduction goals—for example, low fluxes during a series of dry years may be the result of random variations in streamflow rather than reductions realized through specific conservation practices. Estimates of nitrate flux that are independent of random variations in streamflow can provide greater insight into the effects of conservation practices implemented in the basin.

We use a new approach—designed for large, long-term data sets—to overcome such challenges by estimating nitrate concentration and flux with and without the influence of streamflow variability.[7] These estimates were made for eight sites in the Mississippi River basin, including main-stem and major tributary sites. Changes in nitrate concentration and flux between 1980 and 2008 were examined, with a particular focus on the non-streamflow related changes that occurred during this period. Large increases in nitrate concentration and flux since the 1950s have previously been documented in the Mississippi River basin.[4,5,8−11] Our analysis builds on previous studies by integrating more recent data, including data collected during the recent period of rapidly increasing corn prices.[12] In addition to the estimation of a time series of concentration and flux with and without the influence of streamflow variability, the new approach departs from methods used in previous studies by allowing a flexible decomposition of nitrate behavior into time trend, seasonal components, and streamflow-related components. Rather than focusing on hypothesis testing, this method describes the evolving system and helps elucidate changes in particular seasons and streamflow conditions.

METHODS

Analysis of Change in Concentration and Flux. The Weighted Regressions on Time, Discharge, and Season (WRTDS) method[7] was used to make estimates of nitrate concentration for every day of the period of record at each site. Concentration is modeled in

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WRTDS as

$$\ln(c) = \beta_0 + \beta_1 t + \beta_2 \ln(Q) + \beta_3 \sin(2\pi t) + \beta_4 \cos(2\pi t) + \varepsilon \quad (1)$$

where ln is natural log, c is concentration, β_i are fitted coefficients, Q is daily mean streamflow, t is decimal time, and ε is the unexplained variation. Estimates of daily concentration are multiplied by the respective daily mean streamflow to estimate daily flux. WRTDS differs from similar models used in previous studies in that the fitted coefficients do not apply throughout the entire domain of the data. Instead, a unique set of coefficients is estimated for every combination of Q and t in the period of record. For every combination of Q and t, the coefficients in eq 1 are estimated using weighted regression. The weights on each observation in the calibration data set are based on the distance in time, streamflow, and season between the observation and (Q,t). This process results in unbiased estimates of daily concentration and flux.

One advantage of this process is that it can estimate a wider class of regression surfaces than parametric functions.[13] Because WRTDS estimates a unique set of coefficients for every combination of Q and t in the period of record, the relations among concentration, streamflow, and time are not fixed. It is possible for both the magnitude and the sign of the coefficients to change, which allows for inflection points in the pattern of concentration changes with streamflow and (or) time.

Because the estimates of daily concentration and flux are strongly influenced by random variations in streamflow, flow-normalized (FN) estimates of daily concentration and flux also are computed in WRTDS. The FN estimates are designed to remove the variation in nitrate concentration or flux due to random streamflow variations (but not the variation due to nonrandom seasonal streamflow variations); the effects of antecedent streamflow conditions are not removed. The temporal variation in streamflow is removed in WRTDS by assuming that the streamflow that occurred on any given day of the record is one sample from the probability distribution of streamflows for that particular day of the year. To compute the FN estimate of concentration for a given date (for example, assume we have n years of record and we are estimating the FN concentration for August 10, 1999), WRTDS uses n weighted regressions to estimate concentration on that date with the streamflow value set to each one of the n historical streamflow values for that day of the year (here, every August 10 in the period of record). The FN concentration on that date is then calculated as the mean of the estimated concentration values from each of those n weighted regressions. Similarly, the FN flux is the mean of the estimated flux values from each of those n weighted regressions. In this report, FN estimates are referred to as FN concentration or FN flux; non-FN estimates are referred to as estimated concentration or estimated flux. All estimated and FN concentrations and fluxes are reported as nitrate as nitrogen. For more detail on the model, see the Supporting Information.

For many of the analyses herein, the daily estimates were summarized into calendar-year annual means (for concentration) and calendar-year annual totals (for flux). Changes in annual mean concentration were examined in three ways:

$$\text{Net change} = c_{t_2} - c_{t_1} \quad (2)$$

where c_{t_1} is the annual mean concentration in year t_1 and c_{t_2} is the annual mean concentration in year t_2,

$$\text{Net change in percent} = \left(\left(c_{t_2} - c_{t_1}\right)/c_{t_1}\right)*100 \quad (3)$$

and

$$\text{Rate of change in percent per year} = \left(\left(\left(c_{t_2} - c_{t_1}\right)/c_{t_1}\right)*100\right)/n \quad (4)$$

where n is $t_2 - t_1$. Changes in total annual flux were examined in a similar manner. These descriptions of change are only shown for the FN values because they are much more stable than the estimated values, which display a great deal of year-to-year streamflow-driven variation. This makes FN concentration and flux ideal for evaluating progress toward nutrient reduction goals. However, for studies of ecological processes in the watershed or in the Gulf of Mexico, estimated concentration and flux would be ideal. Tables of estimated and FN annual mean concentration and total annual flux for each study site are provided in the Supporting Information.

WRTDS can be used to estimate the expected value of c for any given combination of Q and t. In our final application of WRTDS, we generated color contour plots that show expected concentrations over a range of streamflow conditions on each date. The estimated concentration for any given date (used in the computation of estimated annual mean concentration and total annual flux) is the value on the contoured concentration surface for the actual Q on that day. The FN concentration for any given date (used in the computation of FN annual mean concentration and total annual flux) is the mean of the values from the vertical slice on the contour surface for that day, weighted by the observed probability distribution of streamflows on that day of the year. These contour plots are a useful way of visualizing the evolving characteristics of water quality at a site, showing changes in concentration over time as a function of both season and streamflow. We generated contour plots for two 5-year snapshots in time—an early period from 1980 to 1984 and a recent period from 2004 to 2008.

Data Compilation. The U.S. Geological Survey maintains a network of long-term data collection sites in the Mississippi River basin through its National Stream-Quality Accounting Network (NASQAN) and National Water-Quality Assessment (NAWQA) programs. Data from NASQAN and NAWQA sites were screened for characteristics appropriate for WRTDS:[7] sample size greater than 200, period of record longer than 20 years, a complete record of streamflow at the site or at a nearby location, data censoring in no more than 1% of the data set, and data gaps no longer than 4 years. The final sites included four on the main-stem Mississippi River and four in major tributary basins: the Ohio, Iowa, Illinois, and Missouri River basins (Tables 1 and SI-S1; Figure SI-S1). The sources and preparation of the dissolved nitrate plus nitrite (hereinafter nitrate) concentration and streamflow data used in this study are detailed in Aulenbach et al.[14] Aulenbach et al.[14] cover data collected through 2005; similar approaches were used with data collected after 2005. The analysis presented here is based on 3368 individual water-quality samples and 110 732 individual daily streamflow values.

The period of record differed among the eight sites. The longest record, at MSSP-OUT, ran from 1967 to 2010; the shortest record, at IOWA-WAP, ran from 1977 to 2009. All available data were used for calibration in WRTDS (version 3_b) (Table SI-S1). With smoothing approaches such as WRTDS, estimates will

Table 1. Study Sites[a]

site abbreviation	site name
MSSP-CL	Mississippi River at Clinton, IA
IOWA-WAP	Iowa River at Wapello, IA
ILLI-VC	Illinois River at Valley City, IL
MSSP-GR	Mississippi River below Grafton, IL
MIZZ-HE	Missouri River at Hermann, MO
MSSP-TH	Mississippi River at Thebes, IL
OHIO-GRCH	Ohio River at Dam 53 near Grand Chain, IL
MSSP-OUT	Mississippi River above Old River Outflow Channel, LA

[a] More detail on site locations and characteristics is available in Figure SI-S1 and Table SI-S1.

generally be less reliable at the beginning and end of the records. For this reason, even though data from years prior to 1980 were used in calibrating the model, estimates for the earliest years of each record were excluded, and a common starting year of 1980 was used. The importance of understanding recent conditions drove our decision to report results through 2008, even though estimates for the last several years likely will change when re-estimated in the future with the addition of new data. This is not unlike the development of economic statistics, which are commonly subject to revision as newer data become available. Estimates for years in which no samples were collected (1988−1990 and 1994 at MSSP-CL and 1995 at MSSP-GR) were not reported.

RESULTS AND DISCUSSION

Changes in Concentration and Flux. Estimated annual mean concentration and total annual flux were affected by random variations in climate and streamflow and thus were more variable from year to year than their flow-normalized counterparts at all sites (Figure 1). The large fluxes during high-streamflow years are an indication that larger decreases in flux may be required to meet nutrient reduction goals in wetter years,[3] which presents a policy challenge. For example, a recent report by the U.S. Environmental Protection Agency Science Advisory Board acknowledged that flux varies considerably from year to year in response to changes in precipitation and streamflow; to address this issue, they recommended nitrogen reduction targets based on 5-year running averages of estimated flux.[15] FN concentration and flux are independent of random variations in streamflow and thus can provide a more reliable means of tracking progress toward nutrient reduction goals and greater insight into the effects of watershed activities such as land-use change, implementation of conservation practices, or changes in fertilizer use. As such, the FN values will be our focus from this point forward.

In general, percentage changes in FN concentration and flux between 1980 and 2008 were relatively large at MIZZ-HE and the four sites on the main-stem Mississippi River but were small at the three tributary sites in the Upper Mississippi and Ohio River basins (Table 2). FN concentration and flux increased between 9 and 76% at MSSP-CL, MSSP-GR, MIZZ-HE, MSSP-TH, and MSSP-OUT. Changes were smaller and ranged from −3 to 3% at IOWA-WAP, ILLI-VC, and OHIO-GRCH. The largest percentage increases in FN concentration and flux occurred at MSSP-CL (76 and 67%, respectively) and MIZZ-HE (75 and 57%, respectively); these increases were over three times larger than at any other site. Notably, MSSP-CL and MIZZ-HE were among the four sites with the lowest FN concentration and yield (flux per unit area) at the start of the study period (Table 2). Changes were much smaller at the sites with the highest FN concentrations and yields in 1980: IOWA-WAP and ILLI-VC.

Because it does not assume linearity of changes over the entire record, WRTDS allows for a comparison of rates of change between different parts of the record. At most sites, the rate of change was greater between 2000 and 2008 than between 1980 and 2000 (Table 3). FN concentration and flux increased during both periods at MIZZ-HE and the four sites on the main-stem Mississippi River. The difference between the two periods was greatest at MSSP-CL and MIZZ-HE, where the rate of increase was about 2−3% higher between 2000 and 2008 than between 1980 and 2000. This was due in part to the pattern of change in FN concentration and flux between 1980 and 2008—at MSSP-CL and MIZZ-HE, as well as at MSSP-TH and MSSP-OUT, FN concentration and flux increased during the 1980s, were relatively stable or decreased in the 1990s, and then increased consistently after 2000 (Figure 1). In contrast, FN concentration and flux decreased between 2000 and 2008 after remaining stable or increasing between 1980 and 2000 at the tributary sites OHIO-GRCH, IOWA-WAP, and ILLI-VC.

Another perspective on the results is to consider the relative contribution of each subwatershed to the 0.69×10^8 kg change in FN flux observed between 1980 and 2008 at MSSP-OUT (Table 2). In addition to the change in FN flux estimated for the MSSP-CL, IOWA-WAP, ILLI-VC, MIZZ-HE, and OHIO-GRCH subwatersheds in Table 2, the change in FN flux from the nested subwatersheds (Figure SI-S1) can be estimated: the change from the nested area above MSSP-GR (MSSP-GR minus MSSP-CL, IOWA-WAP, and ILLI-VC) was 0.06×10^8 kg; the change from the nested area above MSSP-TH (MSSP-TH minus MIZZ-HE and MSSP-GR) was -0.54×10^8 kg; and the change from the nested area above MSSP-OUT (MSSP-OUT minus MSSP-TH and OHIO-GRCH) was 0.29×10^8 kg. Taken together, the changes in FN flux from each of the subwatersheds indicate that the increase in FN flux at MSSP-OUT between 1980 and 2008 was driven primarily by the increases at MSSP-CL and MIZZ-HE, and to a lesser extent, the nested area above MSSP-OUT. This holds true despite the large decrease in FN flux in the nested area above MSSP-TH. The decrease in this nested subwatershed, which is about 3% of the total area above MSSP-TH, may have been due to decreased nonpoint source inputs, decreased point source inputs, increased in-channel losses (denitrification), or decreased in-channel gains (nitrification). It is unlikely that nonpoint source inputs from this relatively small area were large enough to contribute to such a large change on their own, and large decreases in nonpoint source inputs were not evident in nearby subwatersheds. It is also unlikely that in-channel losses changed substantially over time; generally in-channel losses of nitrate in large rivers are small[16] and the supply of nitrate likely was not limiting at any point during this period. It is possible that changes in point source inputs from the St. Louis metropolitan area were a contributing factor—for example, in 1992 and 1993, two-stage secondary treatment was added at the Bissell Point Treatment Plant, the largest wastewater-treatment facility in Missouri that discharges to the Mississippi River between Grafton and Thebes.[17] Upgrades at this and other point sources during the period may have resulted in substantial changes to inputs of both nitrate and ammonia to the Mississippi River, with a combined effect of substantially decreasing the net flux of nitrate (although no facility-specific histories of fluxes of nitrate and ammonia could be obtained).

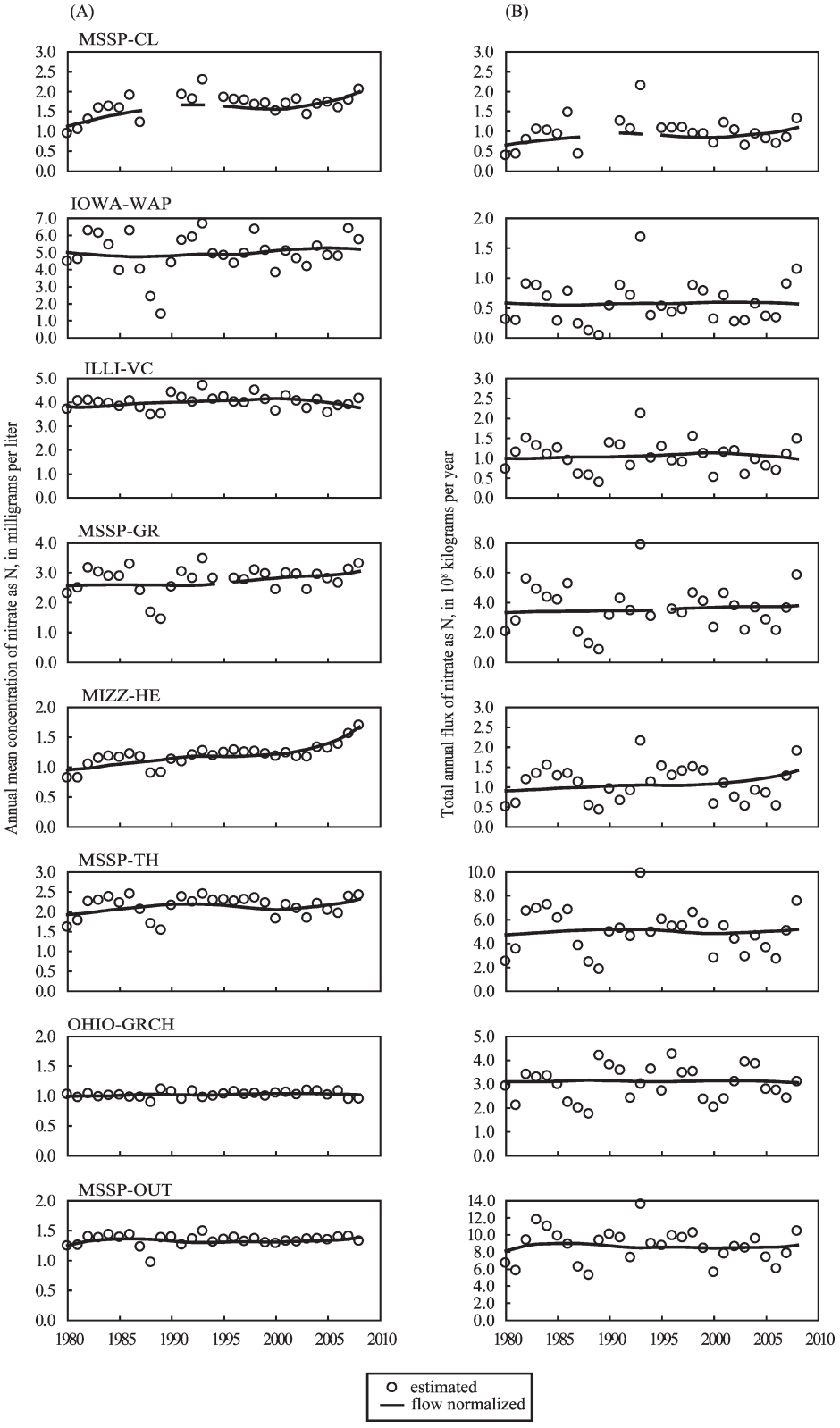

Figure 1. (A) Annual mean estimated and flow-normalized nitrate concentration and (B) total annual estimated and flow-normalized nitrate flux from 1980 to 2008.

As with any change evaluation, these estimates of change are dependent on the choice of starting and ending points. Using a much earlier starting point, 2-fold increases in nitrate concentration and flux in the Mississippi River basin since the 1950s have been documented.[4,5,8,10,11] A previous study of changes at OHIO-GRCH, MSSP-TH, and MSSP-OUT during a more

Table 2. Net Change in Flow-Normalized Nitrate Concentration and Flux between 1980 and 2008

	flow-normalized concentration of nitrate as N			flow-normalized flux of nitrate as N			
		change, 1980−2008				change, 1980−2008	
site	annual mean flow-normalized concentration in 1980, mg/L	mg/L	%	total annual flow-normalized flux in 1980, 10^8 kg/yr	total annual flow-normalized yield (flux per unit area) in 1980, kg/km^2/yr	10^8 kg/yr	%
MSSP-CL	1.13	0.86	76	0.66	297	0.44	67
IOWA-WAP	5.02	0.17	3	0.59	1,813	−0.02	−3
ILLI-VC	3.81	−0.04	−1	0.99	1,433	−0.01	−1
MSSP-GR	2.56	0.49	19	3.33	751	0.47	14
MIZZ-HE	0.96	0.72	75	0.90	67	0.51	57
MSSP-TH	1.93	0.38	20	4.74	257	0.44	9
OHIO-GRCH	0.99	0.03	3	3.10	590	−0.04	−1
MSSP-OUT	1.25	0.13	10	8.11	278	0.69	9

Table 3. Rate of Change in Flow-Normalized Nitrate Concentration and Flux between 1980 and 2000 and between 2000 and 2008, in Percent Per Year

site	flow-normalized concentration		flow-normalized flux	
	1980−2000	2000−2008	1980−2000	2000−2008
MSSP-CL	1.9	3.5	1.4	3.7
IOWA-WAP	0.1	0.2	0.1	−0.6
ILLI-VC	0.5	−1.2	0.7	−1.7
MSSP-GR	0.5	1.0	0.5	0.4
MIZZ-HE	1.4	4.7	1.0	3.9
MSSP-TH	0.3	1.6	0.1	0.9
OHIO-GRCH	0.2	−0.2	0.1	−0.3
MSSP-OUT	0.2	0.7	0.2	0.5

contemporaneous period (1980−2006) compared the mean of annual flow-adjusted nitrate fluxes during a baseline period of 1980 to 1996 to the mean from 2000 to 2006 and found no significant change.[9] Our change estimates were based on a starting year of 1980 rather than the mean of an extended 1980−1996 period in which MSSP-TH and MSSP-OUT experienced a substantial rise in nitrate flux and then a fall. In addition, our analysis included two additional years of data collected during a period of increasing biofuel crop production, which may be contributing to increased nitrogen flux to the Gulf of Mexico.[18] These examples illustrate how study objectives and the choice of starting and ending points can influence study conclusions.

As part of its Conservation Effects Assessment Project, the U.S. Department of Agriculture (USDA) recently compared two model scenarios for the Upper Mississippi River basin—a baseline scenario that modeled the watershed with the conservation practices in place between 2003 and 2006 and a no-practice scenario that modeled the watershed as if no conservation practices were in place. Based on this comparison, the USDA reported[19] that conservation practices have resulted in improvements in river quality in the Upper Mississippi River basin, represented by MSSP-GR. While our results show that FN nitrate concentration and flux at MSSP-GR were relatively stable between 1980 and 1995, they increased between 1995 and 2008 (Figure 1), ultimately resulting in a net increase of 19 and 14%, respectively, between 1980 and 2008 (Table 2). The apparent disparity in results may be related to temporal changes in other watershed conditions that were held constant in the USDA model comparison (conditions such as land use and point and nonpoint source nutrient inputs). These changes may have counteracted improvements realized through the implementation of conservation practices. Conservation practices may still have had a positive effect—increases in nitrate concentration and flux might have been larger without these practices in place.

Spring nitrate flux has been found to be a strong predictor of the size of the summer hypoxic zone in the Gulf of Mexico.[2,20] Spring (April, May, and June) FN nitrate flux typically contributed about 40−50% of the annual FN nitrate flux at the study sites (Figure SI-S2). Although a disproportionately high percentage of the annual FN flux occurred in the spring, this percentage remained fairly constant between 1980 and 2008 at all sites (Figure SI-S2). Aulenbach et al.[14] found that when flux estimates were not flow normalized, spring nitrate flux contributed a wider range of the annual nitrate flux (30−50%) from the Mississippi and Atchafalaya Rivers between 1979 and 2005 and that the relative contributions were more variable from year to year in response to climatic variations. Our findings show that when flux estimates were flow normalized, year-to-year variations in spring nitrate flux were similar to those in annual nitrate flux. The temporal correspondence suggests that the effects of watershed activities on nitrate flux were not limited to the spring period of high streamflows, high nutrient inputs, and high productivity, but rather were sustained throughout the year. This may be due in part to groundwater inputs of nitrate to these rivers, which occur throughout the year.

Changes in Concentration at Different Streamflows. Up to this point, the results have primarily focused on annual values. Annual concentration is weighted more toward conditions over the many days of low to moderate streamflow throughout the year, whereas annual flux is weighted more toward conditions on the relatively fewer days of the year with higher streamflow, when much of the flux occurs. This is true for both estimated values, because streamflow changes from day to day, and for FN values, because the probability distribution of streamflow changes from day to day (for instance, streamflow is often high on days in the spring, when snowmelt and storm events increase flow in

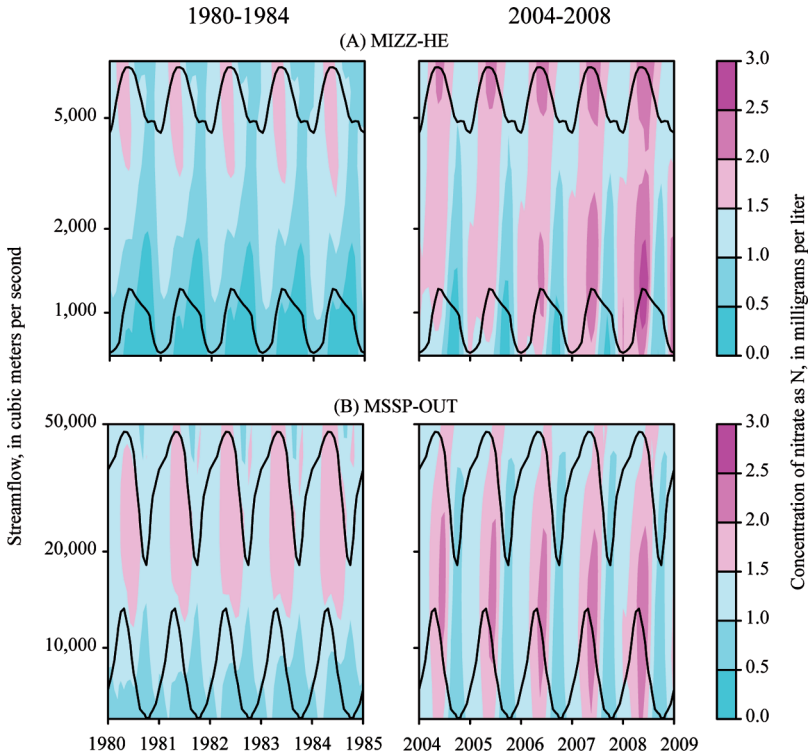

Figure 2. Contour plots of expected nitrate concentration (mg/L). Upper black line represents the 95th percentile of streamflows; lower black line represents the 5th percentile of streamflows.

these rivers). During the study period, percentage changes in annual FN concentrations were greater than percentage changes in annual FN flux at all sites (Table 2), indicating that concentration changes at low and moderate streamflows were greater than concentration changes at higher streamflows. A comparison of contour plots of expected concentrations in the early period (1980−1984) and the recent period (2004−2008) shows that this was true at most sites (Figures 2 and SI-S3). These contour plots show WRTDS estimates of concentration as a function of time and streamflow. Any vertical line shows how concentration would have varied with streamflow on a particular day of a particular year; any horizontal line shows how concentration would have varied over time (seasonally and annually) at a particular streamflow. Because the probability distribution of streamflow changes from day to day, the 5th and 95th smoothed estimates of the percentiles of streamflow on each day are plotted as black lines. In the subsequent discussion of contour-plot results, two sites are highlighted as case studies to illustrate the changes between the early and recent periods and are shown in Figure 2; the other sites are described more generally and are shown in Figure SI-S3.

At MIZZ-HE (the first case study, shown in Figure 2A) and MSSP-CL (Figure SI-S3A), concentrations increased between the early and recent period at all streamflows. Increases at MIZZ-HE were largest at low streamflows, whereas increases at MSSP-CL were largest at high and moderate streamflows. Using MIZZ-HE as an example, concentrations at low streamflows increased by a factor of 2 or more between the early and recent period. For example, around May 1 and at a streamflow of 2000 $m^3\ s^{-1}$ (approximately the 25th percentile streamflow for this time of year), concentrations increased from about 1.0 to more than 2.5 mg/L. In contrast, concentrations around May 1 increased very little at higher streamflows—at a streamflow of 5000 $m^3\ s^{-1}$ (approximately the 75th percentile for this time of year), concentrations only increased 5%, from about 1.8 to 1.9 mg/L.

At MSSP-OUT (the second case study, shown in Figure 2B), MSSP-GR, IOWA-WAP, MSSP-TH, and OHIO-GRCH (Figure SI-S3B−E), concentrations increased at low and moderate streamflows but decreased at high streamflows in some or all seasons. At MSSP-GR and MSSP-TH, increases at low and moderate streamflows were greater than decreases at high streamflows, whereas decreases at IOWA-WAP, OHIO-GRCH, and MSSP-OUT at high streamflows were more comparable to increases at low and moderate streamflows, particularly in the spring and summer. Notably, concentrations at high streamflows in the spring, when nitrate fluxes were highest, decreased at MSSP-TH, OHIO-GRCH, and MSSP-OUT.

Using MSSP-OUT as an example of the second case study, around May 1 and a streamflow of 20 000 $m^3\ s^{-1}$ (approximately the 25th percentile for this time of year), concentrations increased 12%, from about 1.7 to 1.9 mg/L. In contrast, around May 1 and a streamflow of 35 000 $m^3\ s^{-1}$ (approximately the 75th percentile for this time of year), concentrations decreased about 17%, from about 1.8 to 1.5 mg/L. In the early period, the highest springtime concentrations occurred at higher streamflows (around 30 000 $m^3\ s^{-1}$, approximately the 70th percentile for spring); by 2008, the highest concentrations were occurring at lower streamflows (around 20 000 $m^3\ s^{-1}$). This means that during high streamflow periods in the spring, the flux can be expected to be lower than it would have been for the same high streamflows in the earlier years of the record. Conversely, during low streamflow periods in the spring, the flux can be expected to be higher than it would have been in the earlier years of the record. Integrating the changes in the relation between streamflow and concentration

over the full flow-duration curve, these changes have not resulted in a decrease in the annual or spring mean flux of nitrate to the Gulf of Mexico. They could, however, have the effect of moderating the influence of high streamflow, leading to a reduction in the size and intensity of the hypoxic zone in critical high-streamflow years. This tendency is worthy of further investigation in terms of its cause and its effect. The high-streamflow conditions that occurred in 2011 will provide valuable new information about these changes.

Finally, changes in concentration were small at all streamflows at ILLI-VC (Figure SI-S3F), and the direction of change was mixed among seasons.

An interesting feature in many of the contour plots was the dual peak in concentration around January and again around June (see, for example, IOWA-WAP in Figure SI-S3C). These peaks may reflect the effects of fall and spring fertilizer applications—USDA data from Minnesota, Iowa, and Illinois indicate that up to 50% of the fertilizer applied to corn acreage each year is applied in the fall.[15] Nitrification of fall-applied anhydrous ammonia can be inhibited by low temperatures during the winter,[21] but in areas or years with warmer winter temperatures, nitrification can contribute to substantial leaching of nitrate through tile drains.[22] Dual peaks in nitrate concentration have been observed in the spring and late fall/early winter in Raccoon River, Iowa,[23] the Upper Four Mile Creek watershed in Ohio and Indiana,[24] and the Upper Illinois River basin in Illinois, Indiana, and Wisconsin.[25] Changes in the timing and magnitude of the fall and spring peaks in nitrate concentration between the early and recent periods suggest that fertilizer application practices and(or) nitrate transport pathways in these watersheds may be changing. Additional evaluation was beyond the scope of this study, but further investigation may prove helpful in shaping future nutrient management strategies.

The contour plots show that concentrations increased at low and moderate streamflows at most of the study sites and the magnitude of changes in concentration at low and moderate streamflows was greater than or comparable to that at higher streamflows. Concentration changes were not confined to high streamflows in the growing season, which are a focus of many conservation practices. These results are a strong indication that nitrate concentrations in groundwater also increased in many parts of the basin, a finding that is consistent with previous studies of groundwater trends in the region. Nitrate concentrations in aerobic groundwater underlying agriculture in the South Platte alluvial aquifer in Colorado increased about 5.0 mg/L between 1994 and 2002, and nitrogen isotope ratios indicated that fertilizer was the predominant source.[26] Nitrate concentrations in groundwater also increased about 4.5 mg/L in the glacial deposits of Wisconsin between 1994 and 2002, and these changes were associated with changes in fertilizer inputs in the region.[27]

The results from this study show that little consistent progress has been made in controlling nitrate concentration and flux in the Mississippi River basin since 1980, and that concentration and flux are increasing in some parts of the basin. No substantial net decreases in FN nitrate concentration or flux occurred at the study sites between 1980 and 2008. Rather, FN concentration and flux increased between 9 and 76% at the four main-stem sites and MIZZ-HE and changed very little at the three other tributary sites. The largest increases occurred at MSSP-CL and MIZZ-HE, which were among the sites with the lowest nitrate values at the start of the study period. The increases at these two sites contributed much of the 9% increase in FN nitrate flux leaving the Mississippi River basin at MSSP-OUT. Nitrate concentrations decreased in the spring at high streamflows at MSSP-TH, OHIO-GRCH, and MSSP-OUT, suggesting that some progress has been made in reducing nitrate transport in spring runoff in these watersheds. At these and most other sites, however, increases in nitrate concentration at low to moderate streamflows were greater than or comparable to changes at high streamflows. The increase in concentrations at low streamflows during all seasons is a strong indication that increasing nitrate concentrations in groundwater are having a substantial effect on river concentrations in the basin. As a result, conservation practices designed to reduce infiltration to groundwater may help with managing nitrate in these rivers.

■ ASSOCIATED CONTENT

Supporting Information. Additional details on the study sites and the WRTDS model, as well as model estimates of nitrate concentration and flux (annual and spring). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 303-236-6921; fax: 303-236-4912; e-mail: lsprague@usgs.gov.

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