Published July 7, 2016

Journal of Environmental Quality

TECHNICAL REPORTS

LANDSCAPE AND WATERSHED PROCESSES

Illinois River Nitrate-Nitrogen Concentrations and Loads: Long-term Variation and Association with Watershed Nitrogen Inputs

Gregory F. McIsaac,* Mark B. David, and George Z. Gertner

Abstract

The Illinois River is a major contributor of nitrate-N to the Mississippi River and the Gulf of Mexico, where nitrate is a leading cause of summertime benthic hypoxia. Corn–soybean production on tile-drained land is a leading source of nitrate-N in this river system, in addition to municipal wastewater discharge. We calculated annual nitrate-N loads in the Illinois River at Valley City from 1976 to 2014 by linear interpolation. Although there was not a significant trend in annual loads during the entire study period, there was a significant downward trend in flow-weighted nitrate-N concentration after 1990 despite high concentrations in 2013 after the 2012 drought. Multivariate regression analysis revealed a statistically significant association between annual flow-weighted nitrate-N concentration and cumulative residual agricultural N inputs to the watershed during a 6-yr window. This suggests that declines in flow-weighted nitrate-N concentration may reflect increasing N use efficiency in agriculture and a depletion of legacy N stored in the watershed. The watershed appears to have transitioned from a state of stationarity in nitrate concentration to nonstationarity. The average annual nitrate-N load at Valley City from 2010 to 2014 was 10% less than the 1980–1996 average load, indicating recent progress toward Illinois' nutrient loss reduction milestone of 15% reduction by 2025 and ultimate target of 45% reduction.

Core Ideas

- Downward trend in annual flow-weighted nitrate-N concentrations since 1990.
- Nitrate-N concentrations correlated with residual agricultural N during the previous 6 yr.
- Nitrate-N concentrations correlated with current year Chicago wastewater discharge.
- Nitrate-N load highly variable due to variation in precipitation and water discharge.
- Average nitrate-N load during 2010–2014 was 10% less than the 1980–1996 baseline period.

To address the problem of summertime benthic hypoxia in the coastal waters in the northern Gulf of Mexico, the USEPA identified a goal of reducing N and P loads in the Mississippi River by 45% (USEPA, 2007). Several states have developed strategies to meet this goal (e.g., IEPA, 2015). Because of the magnitude of the problem and the costs of making large nutrient load reductions, the target date for reducing the hypoxic zone was recently extended from 2015 to 2035, with an intermediate goal of a 20% reduction in nutrient loads by 2025 (USEPA, 2015).

Assessing progress toward these goals will be challenging for several reasons. Annual variation in nutrient loads can be large due to variation in precipitation and stream flow, which can obscure changes due to other factors, such as changes in land use or nutrient management (Hirsch et al., 2010). Groundwater transport of nutrients may result in long lag times between changes in nutrient management and riverine loads (Basu et al., 2010; Tesoriero et al., 2013). Basu et al. (2010) examined the long-term N and P concentrations and loads in 21 catchments in the Mississippi River Basin (MRB) and described the dominant pattern as "stationarity" of annual flow-weighted concentrations, which they attributed to internal storage of nutrients. Using the recently developed method of weighted regression on time, discharge, and season (WRTDS), Sprague et al. (2011) examined nitrate export from the MRB and seven subwatersheds and reported a 10% increase in flow-normalized concentrations and a 9% increase in flow-normalized flux to the Gulf of Mexico from 1980 to 2008. There was little change in five of the subwatersheds, including the Illinois River at Valley City. The two exceptions were the Mississippi River at Clinton and the Missouri River at Herman, where flow-normalized nitrate concentrations and loads had increased more than 55%.

Murphy et al. (2013) examined nitrate concentration and load trends of the same eight locations as Sprague et al. (2011) and reported somewhat larger increases in flow-normalized nitrate concentration (17% increase) and export (14% increase) at the outlet of the MRB from 1980 to 2010 as well as large

J. Environ. Qual. 45:1268–1275 (2016)
doi:10.2134/jeq2015.10.0531

Supplemental material is available online for this article.
Received 21 Oct. 2015.
Accepted 25 Feb. 2016.
*Corresponding author (gmcisaac@illinois.edu).

G.F. McIsaac, M.B. David, and G.Z. Gertner, Dep. of Natural Resources and Environmental Sciences, Univ. of Illinois at Urbana Champaign, 1102 South Goodwin Avenue, Urbana, IL 61801; G. Gertner, current address: 8003 Sand Point Way NE, Unit B26, Seattle, WA 98115. Assigned to Associate Editor Kevin McGuire.

Abbreviations: IEPA, Illinois Environmental Protection Agency; MRB, Mississippi River Basin; MWRDGC, Metropolitan Water Reclamation District of Greater Chicago; RAN, residual agricultural nitrogen; WRTDS, weighted regressions on time, discharge, and season.

increases in the flow-normalized concentrations (≥70%) and loads (≥45%) for the Mississippi at Clinton and the Missouri at Herman. However, they also reported a 14% decline in annual flow-normalized concentration and flux for the Illinois River at Valley City. A slightly smaller decline was also reported for the Iowa River at Wapello, IA, but when spring nitrate flux was examined, only the Illinois River at Valley City registered a decline (15%).

Murphy et al. (2013) also reported a 25% decline in annual flow-normalized nitrate-N flux in the Illinois River at Valley City between 2000 and 2010 and suggested that the decline in nitrate-N may have been related to improved conservation in agricultural N use and/or completion of a system to capture and treat combined sewer overflows in Chicago. Using nitrate-N concentrations measured by the Illinois Environmental Protection Agency (IEPA), Markus et al. (2014) reported similar declines in flow-normalized nitrate-N concentrations and flux but reported no trend in the actual (not flow-normalized) nitrate-N flux. Markus et al. (2014) recommended caution in interpreting WRTDS flow-normalized concentrations and loads because the method is sensitive to a series of years with unusually high flow that occurred toward the end of the record. Markus et al. (2014) compared several methods of estimating loads and flow-weighted concentrations and reported significant downward trends in flow-weighted concentrations from 1975 to 2010, although the statistical significance of the trends depended on the method used to estimate loads. Overall, there appeared to be an increase in concentrations from 1975 to the early 1990s, followed by a decrease to 2010.

In addition to detecting whether trends in riverine nutrient loads have occurred, the agencies responsible for water quality policy, management, and regulation need to identify the causes for the trends or lack of trends to develop appropriate responses. Identifying the causes can be difficult in watersheds with multiple nutrient sources, such as the Illinois River, which receives large quantities of both point and nonpoint source inputs. None of the studies analyzing water quality trends mentioned in the preceding paragraphs attempted to quantify changes in nutrient use and cycling in the watersheds. Such studies are needed to understand the legacy stores and lag times between changes in nutrient management on the land and changes in riverine export (Basu et al., 2010). Here, we present such a study focused on N and the Illinois River Basin.

The Illinois River is a disproportionate contributor of nitrate-N to the Mississippi River and the Gulf of Mexico (David and Gentry, 2000). From 1980 to 2014, the Illinois River provided 3.5% of the water delivered to the Gulf and about 11% of the nitrate load. The primary source of Illinois River nitrate is tile-drained cropland, but municipal wastewater from the Chicago metropolitan area also contributes about 12.5% (David et al., 2015).

Previous research in tile-drained watersheds has demonstrated that the quantity of nitrate-N carried by streams and rivers is correlated with stream flow, fertilizer application amount and timing, and crop yields (Gentry et al., 2014; Jones et al., 2016). Droughts that reduce corn yields can leave considerable N fertilizer in the soil that is susceptible to loss through drain tiles in the subsequent wet season (Lucey and Goolsby, 1993). After the 2012 drought, unusually high nitrate-N concentrations were observed in Illinois and Iowa (Gentry et al., 2014; Jones et al., 2016). Murphy et al. (2013) and Markus et al. (2014) did not include these years in their trend analyses, and doing so in this study may lead to different conclusions about long-term trends. Understanding the relationships among riverine nitrate flux, weather, and crop production variables can aid interpretation of trends or lack of trends and can suggest reasons for progress, or lack of progress, toward meeting nutrient loss reduction goals.

The objectives of this study were (i) to examine annual variation and trends in nitrate-N flow-weighted concentrations and loads the Illinois River at Valley City during 1976–2014 and (ii) to investigate statistical associations between nitrate-N concentrations and loads and the major point and nonpoint sources of N to the watershed.

Materials and Methods

Watershed Description

The Illinois River above Valley City drains 69,264 km^2 covering central Illinois, northwestern Indiana, and southeastern Wisconsin. Approximately 61% of the land area was classified as cropland in the late 1990s (Goolsby et al., 1999). Much of this land has artificial subsurface "tile" drainage and is planted to a corn–soybean rotation (David et al., 2010). The upper portion of the Illinois River watershed is heavily urbanized, and the river receives wastewater discharge from the Chicago metropolitan area as well as fresh water diverted from Lake Michigan through the Chicago Sanitary and Ship Canal.

Data

Daily water discharge and 517 discrete nitrate-N concentration observations (parameter codes 00630 and 00631) for the Illinois River at Valley City were obtained from the US Geological Survey National Water Information System (station 05586100). Additionally, 339 nitrate-N concentration observations were obtained from the IEPA through the EPA STORET system and through personal communication with IEPA staff. There was considerable duplication in the sampling dates and reported concentrations in the two data sources. Concentrations reported on the same date by the different agencies were averaged. A total of 631 sampling dates were used in the analysis starting in December 1974 and ending in November 2014. Samples were collected an average of 16 d per water year, ranging from 7 in 1985 to 39 in 1991. Before 1991, samples were generally collected every 4 to 6 wk. From 1991 through 2014, samples were generally collected every 4 wk, although there were occasionally months without sampling, as well as weekly sampling during the summers of 1991 and 1993. Sampling dates and river discharge are illustrated in Supplemental Fig. S1.

Annual nitrate-N loads were calculated by linear interpolation: concentrations between sampling dates were assumed to vary linearly with time. We considered using weighted regressions on time, discharge, and season (WRTDS) but determined that it was inappropriate. Hirsch and De Cicco (2015) state that flow normalization in the WRTDS method should not be used if river flows are not "substantially stationary" over the study period. The 5-yr average discharge for the Illinois River at Valley City during 2007 to 2011 was the greatest on record since 1939. Furthermore, in developing the WRTDS method, Hirsch et al. (2010) assumed that changes in concentrations with time and discharge would be smooth and gradual. However, sudden changes in nitrate-N concentration can occur in agricultural watersheds after droughts (Lucey and Goolsby, 1993). Pellerin et al. (2014) recently demonstrated that Mississippi River monthly nitrate-N loads calculated from linear interpolation of concentrations between sampling times could be more accurate than loads estimated with WRTDS. Finally, WRTDS-estimated concentrations and loads for a given year are based on a multiple year window, both forward and backward in time. This would confound attempts to establish causal linkages between changes in the watershed and subsequent changes in nitrate-N loads.

Stenback et al. (2011) demonstrated that the LOADEST method for estimating river loads, with the adjusted maximum likelihood estimator procedure, had a tendency to produce estimates of nitrate load that were at least 25% greater than the observed nitrate load for 33% of the rivers examined in Iowa. More recently, Williams et al. (2015) examined six different methods of estimating nitrate loads for small (>4 km^2) tile-drained watersheds in Ohio and in Ontario, Canada, and concluded that linear interpolation provided the best balance between accuracy and precision for estimating annual nutrient loads.

Daily nitrate-N discharges from the Metropolitan Water Reclamation District of Greater Chicago (MWRDGC) were available from 1983 to 2014 (MWRDGC, 2015), and we aggregated these to annual values. Although this is not the only wastewater discharge in the basin, it is the largest single source of urban wastewater and the only source with available discharge records dating back to 1983. Our analysis assumes that nitrate-N discharged from other urban areas was highly correlated with the discharge from the MWRDGC.

Annual residual agricultural N was estimated from crop and livestock production statistics from USDA and fertilizer sales information. We followed the methods described in David et al. (2010) using the same assumptions and crop coefficients, which are briefly summarized here. For each county in the Illinois River Basin, we obtained annual corn, soybean, and wheat acreage and yields from the USDA National Agriculture Statistics Service (USDA–NASS, 2015) and converted crop yields to harvested N (David et al., 2010). For corn, we used a variable grain N concentration based on an estimated protein concentration of 10% (1.6% N) before 1985, which we estimated then linearly declined to 8.5% by 2006 (1.36% N) and finished at 8.0% in 2014 (1.3% N). Annual cattle and hog inventories for each year and country were also obtained and converted to manure estimates using 0.16 and 0.027 kg N d^{-1}, respectively (David et al., 2010). Biological N_2 fixation by hay, alfalfa, and soybean was estimated using annual county-level harvest data, again using coefficients and equations reported in David et al. (2010). The value for alfalfa fixation was 218 kg N ha^{-1} yr^{-1}, and the value for other hay fixation was 116 kg N ha^{-1} yr^{-1}. For soybean fixation, we followed David et al. (2010) and assumed fixation increased from 50% of aboveground N in 1985 to 60% by 2006 and to 63% in 2014. For fertilizer inputs, we used statewide N sales per hectare of land rather than county-level data from Illinois Commercial Fertilizer Sales reports (Illinois Department of Agriculture, 2015) and assumed that the Illinois River Basin had the same level of fertilizer application as the rest of the state. This is because more recent county-level sales were not available and because county-level sales are not as robust as state-level values. An annual residual agricultural N (RAN) was calculated as fertilizer N + legume N fixation − N harvested adjusted for manure N applied. To estimate the accumulation and depletion of residual N over multiple years, we also calculated multiple-year cumulative RAN ($CRAN_X$), which included prior year riverine nitrate-N losses as follows:

$$\mathrm{CRAN}_X(t) = \sum_{i=1}^{X} \mathrm{RAN}(t-i) - \sum_{i=1}^{X-1} \text{river nitrate-N flux}(t-i) \qquad [1]$$

where X is the number of years included in the calculation, and t is the current year.

Previous research has demonstrated that fertilizer application timing influences nitrate-N losses to tile drains (Randall and Mulla, 2001). However, we did not have data on timing of N fertilizer application. Gentry et al. (2014) noted that fall N fertilizer applications in east-central Illinois were likely to have been reduced when harvest and post-harvest field operations (e.g., N fertilizer application) were delayed by heavy rainfall in October and November in 2009. These conditions produced unusually high river discharge in November. High rainfall in October typically recharges soil moisture without producing much increase in stream discharge. Thus, we used November river discharge as a proxy measure for reduced fall fertilizer application.

Statistical Analysis

To identify factors that might explain annual variations in annual nitrate-N loads and flow-weighted concentrations, we used an all-subsets approach to multiple linear regression with annual nitrate-N concentrations and load as dependent variables and the following candidate independent variables: annual river discharge; the previous year's annual discharge; November discharge; RAN lagged 1 yr; $CRAN_2$, $CRAN_3$, $CRAN_4$, $CRAN_5$, $CRAN_6$, and $CRAN_7$ (as defined in Eq. [1]); and the annual nitrate-N discharge reported by the MWRDGC. Because the MWRDGC discharge data were only available from 1983 to 2014, the regression analysis was limited to that time period.

Mallow's Cp and the PRESS Statistic were used to identify the "best" models (Montgomery et al., 2006). SAS Proc Reg was used to calculate Cp values for each combination of dependent variables. The regression equations with Cp values within about 0.25 units of the number of estimated parameters in the model (including the intercept) were considered for additional analysis. The PRESS statistic was calculated for these models, and the equations with the lowest PRESS statistic were subject to further diagnostic testing for normal distribution of residuals, variance inflation factors less than 5, and autocorrelation of the residuals. The Durbin–Watson approach was used to test for autocorrelation of residuals.

The significance of linear trends with time was tested with linear regression and with the Kendall–Tau procedure (Kendall and Gibbons, 1990).

Results

There was considerable variation and no significant linear trend in the annual nitrate-N flux over the entire 1976–2014 period (Fig. 1). The greatest nitrate-N flux occurred in 1993, which was the highest annual discharge recorded at Valley City since the start of recording in 1939. The lowest nitrate-N fluxes were calculated for drought years 2003 and 2012. There were, however, two periods of statistically significant decline in annual fluxes from 1982 to 1989 ($p < 0.01$ by both linear regression and Kendall–Tau) and from 1993 to 2006 ($p = 0.052$ by linear regression; $p = 0.10$ by Kendall–Tau). There was also an increase in nitrate-N flux from 2006 to 2010, significant at $p = 0.08$ by linear regression and $p = 0.09$ by Kendall–Tau.

These trends in nitrate-N flux coincide with similar trends in river discharge (Fig. 2). River discharge declined significantly from 1983 to 1989 ($p < 0.01$) and from 1993 to 2006 ($p < 0.02$) as determined by linear regression and Kendall–Tau. River discharge increased significantly from 2006 to 2010 ($p = 0.02$ by linear regression; $p = 0.086$ by Kendall–Tau). The 5-yr average discharge from 2007 to 2011 was the greatest since 1939. For 1976 to 2014, the R^2 value for the linear relationship between nitrate load and water discharge was 0.80, which is the lower limit for indicating stationarity (Basu et al., 2010). For 1976 to 1995, the R^2 was 0.88, and it declined to 0.73 from 1996 to 2014, indicating the river system has transitioned from stationarity to nonstationarity.

Annual flow-weighted nitrate-N concentrations (annual load divided by annual discharge) varied between 2.86 and 6 mg N L^{-1} (Fig. 3). There was a significant downward trend ($p < 0.01$ by both linear regression and Kendall–Tau) in flow-weighted nitrate-N concentrations from 1990 to 2014, with the 2014 concentration being the lowest on record and 2013 being the fifth highest on record. Concentrations were not correlated with annual discharge.

Multivariate Regression Results with Flow-Weighted Nitrate-N Concentration

The best model for annual flow-weighted concentration included the variables $CRAN_6$ and MWRDGC nitrate-N discharge (Table 1) and accounted for about 34% of the variation, with each variable providing similar explanatory power. Variance inflation factors were 1.6 or less, and there was no significant autocorrelation of residuals ($p < 0.01$) or temporal trend in the residuals. Observed flow-weighted nitrate-N concentrations, model estimates, and the model residuals are presented graphically in Supplemental Fig. S2. The hypothesis that the residuals fit a normal distribution could not be rejected at $p > 0.15$. When the model-estimated concentrations were used to estimate annual loads, the result accounted for 85% of the variation in the loads calculated from measured concentrations.

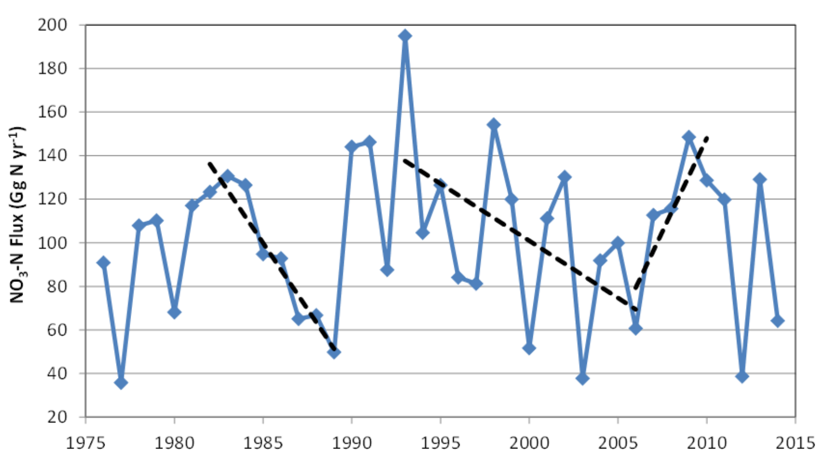

Fig. 1. Annual nitrate-N loads in the Illinois River at Valley City calculated by interpolation. The dashed lines illustrate the statistically significant trends from 1982 to 1989 ($p = 0.0002$), from 1993 to 2006 ($p = 0.052$), and from 2006 to 2010 ($p = 0.08$) as determined by linear regression.

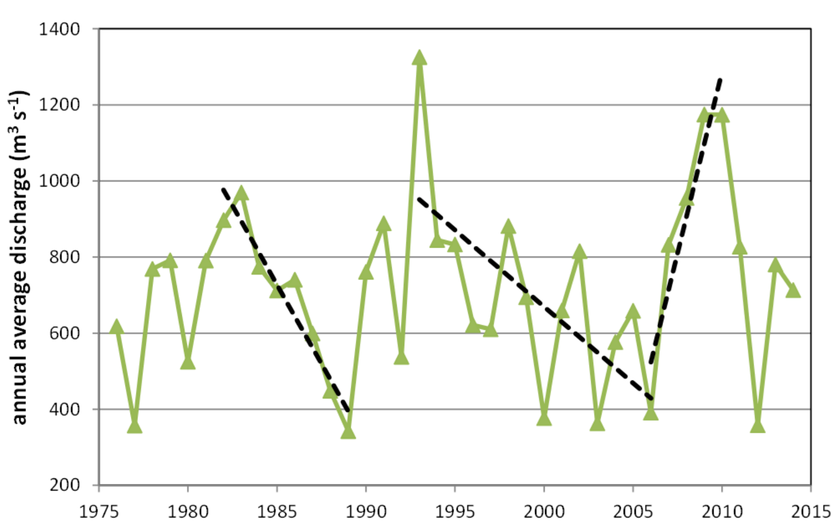

Fig. 2. Average annual river discharge for the Illinois River at Valley City. The dashed black lines illustrate the statistically significant trends from 1982 to 1989 ($p = 0.0002$), from 1993 to 2006 ($p = 0.009$), and from 2006 to 2010 ($p = 0.02$), as determined by linear regression.

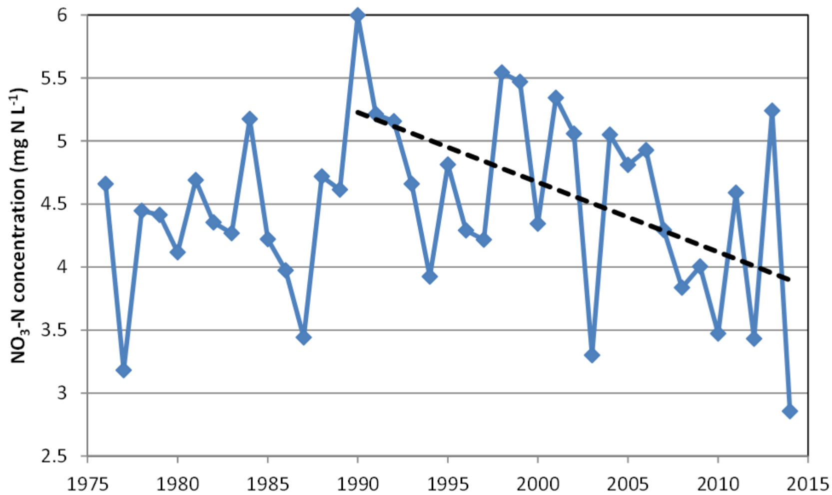

Fig. 3. Annual flow-weighted nitrate-N concentrations for the Illinois River at Valley City. The dashed black line illustrates the statistically significant (p = 0.008) trend from 1990 to 2014, as determined by linear regression.

Regression Results with Annual Nitrate-N Load

When annual nitrate-N load was the dependent variable, the best model selected accounted for 86% of the variation in annual loads and included the following dependent variables: annual average discharge, November average discharge, $CRAN_6$, and MWRDGC nitrate-N discharge (Table 2). Variance inflation factors were 2.0 or less, and there was no significant autocorrelation of residuals (p < 0.01) or temporal trend in the residuals. The hypothesis that the residuals fit a normal distribution could not be rejected at $p > 0.15$. Annual discharge accounted for 78% of the variation in load, $CRAN_6$ and November discharge each accounted for 3.6%, and MWRDGC nitrate-N discharge accounted for about 1%. Observed nitrate-N loads versus model estimates and the model residuals are presented graphically in Supplemental Fig. S3.

Residual Agricultural N and Metropolitan Water Reclamation District of Greater Chicago Nitrate-N Discharges

During the 1980s and early 1990s, the annual RAN averaged about 22 kg N ha^{-1}, with a peak of 43 kg N ha^{-1} for the drought year of 1988 (Fig. 4). From 1998 through 2010, the RAN was consistently less than 20 kg N ha^{-1} and declined to 7.7 kg N ha^{-1} in 2008. During this period, corn yields and N harvested in the corn increased more than fertilizer plus manure N had been applied to corn, which resulted in more efficient utilization of agricultural N, even after accounting for a decline in the N concentration in harvested corn. After 2008, RAN increased to 21.5 kg N ha^{-1} in 2011 and to 37.4 in the drought year of 2012. However, a series of years of high precipitation and high river discharge (2007–2011) led to riverine nitrate-N loads that were larger than the RAN, thus leading to negative values of $CRAN_6$ from 2010 to 2012. This may reflect a small depletion of soil organic N, which becomes vulnerable to leaching after mineralization and nitrification during the growing season. Gentry et al. (2009) demonstrated this effect at a smaller scale on a small watershed in east-central Illinois. The drought of 2012 caused large increases in the $CRAN_6$, but the 2013 and 2014 values were considerably less than the values calculated for the 1980s due to the recent legacy of lower RAN and high riverine N losses. The stationarity of flow-weighted nitrate concentrations observed in the late 1970s and 1980s may have been due to relatively constant net N inputs as well as N storage in the basin.

Basu et al. (2010) did not include the Illinois River in their analysis; nor did they examine changes in net N inputs over time. The USEPA Science Advisory Board (USEPA, 2007) reported

Table 1. The results of ordinary least squares regression with the annual flow-weighted nitrate-N concentration as the dependent variable.†

Variable‡	Parameter estimate	SE	t value	Approximate $P > \|t\|$
Intercept	1.49	0.70	2.12	0.043
$CRAN_6$, kg N ha^{-1} yr^{-1}	0.0224	0.0042	5.29	<0.0001
MWRDGC NO_3–N discharge, Gg N yr^{-1}	0.170	0.045	3.79	0.0008

† Durbin Watson = 2.35; critical range at 1% significance, 1.351–1.1.

‡ CRAN6, cumulative residual agricultural N over the previous 6 yr; MWRDGC, Metropolitan Water Reclamation District of Greater Chicago.

Table 2. Results of multiple regression with annual nitrate-N load as the dependent variable.†

Variable‡	Parameter estimate	SE	t value	Approximate $P > \|t\|$
Intercept	−43.5	24.3	1.79	0.00
Annual avg. discharge, m^3 s^{-1}	0.15	0.013	11.11	<0.0001
November avg. discharge, m^3 s^{-1}	−0.016	0.009	1.77	0.09
$CRAN_6$, Gg N yr^{-1}	0.43	0.14	3.17	0.004
MWRDGC NO_3–N discharge, Gg N yr^{-1}	2.40	1.60	1.51	0.14

† Durbin Watson = 1.90; critical range at 1% significance, 1.509–0.897.

‡ CRAN6, cumulative residual agricultural N over the previous 6 yr; MWRDGC, Metropolitan Water Reclamation District of Greater Chicago.

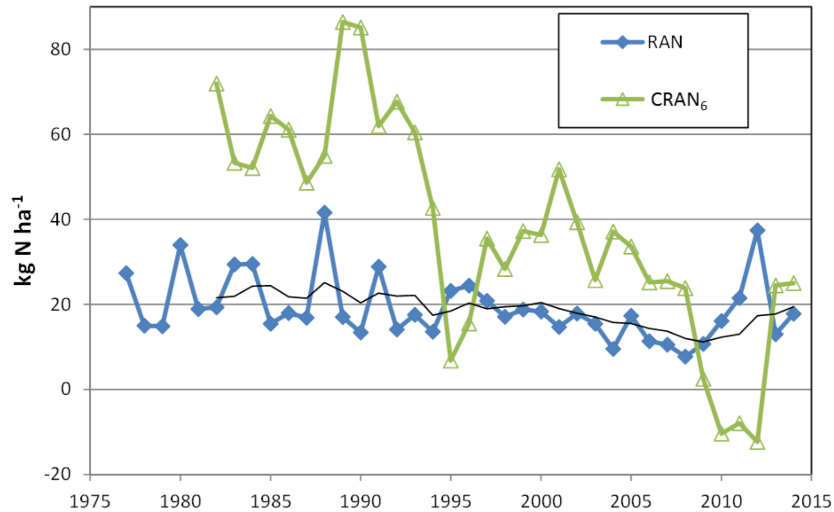

Fig. 4. Variation in residual agricultural N (RAN) and cumulative residual agricultural N over the previous 6 yr ($CRAN_6$) over time. The thin black line is a 6-yr moving average value for RAN.

that net N inputs to the MRB as a whole have been relatively constant since about the mid-1970s, although there has been variation in trends among the sub-basins. Evaluation of the factors affecting stationarity should consider variations in nutrient sources and sinks.

Wastewater nitrate-N discharged from the MWRDGC increased after 1987, peaked in 2009 at 16.6 Gg N yr^{-1}, and declined by about 2.0 Gg N yr^{-1} from 2010 to 2012 (Fig. 5). On average, the MWRDGC nitrate-N discharge represented about 12.5% of the nitrate-N carried in the river but was as high as 36% during low flow years and as low as 6.5% during years with high flow and high nitrate-N flux.

Discussion

The trends in concentration and load we examined are similar to those in Markus et al. (2014), who reported no significant trend in nitrate-N loads in the Illinois River at Valley from 1976 to 2010 but noted a downward trend in flow-weighted nitrate-N concentration from the early 1990s to 2010. The effects of the 2012 drought on nitrate-N concentration appear to have been limited to 2013 because the 2014 concentration was the lowest since 1976.

Jones et al. (2016) also reported a significant decline in April–July nitrate-N concentrations from 1999 to 2014 in 9 of 41 stream locations in Iowa and no significant trend in loads. This occurred despite an increase in N fertilizer application, increased area planted to corn, and a decline in fertilizer use efficiency. Nitrate-N loads were correlated with precipitation, which was highly variable (Jones et al., 2016).

Although correlations do not prove causation, our results suggest that annual nitrate-N loads in the Illinois River are sensitive to hydrology, multiyear RAN, and nitrate-N discharges from the MWRDGC. The decline in flow-weighted nitrate-N concentrations after 1990 occurred at the same time that N fertilizer and manure use in corn production was becoming more efficient as reflected in the reduction of RAN and $CRAN_6$. Murphy et al. (2013) suggested that improved conservation may have led to the declining nitrate-N concentrations they documented in the Illinois River. Other than better alignment of N fertilizer application rates with corn N needs, it is difficult to document specific conservation practices. To our knowledge, there is no evidence of widespread adoption of other conservation practices that target and reduce nitrate loss in this basin, such as the use of winter cover crops, treatment wetlands, or drainage water management. We believe that relatively constant N fertilization rates combined with steadily increasing corn yields have improved N use efficiency and likely contributed to the nitrate-N concentration declining in the Illinois River.

The significance of the 6-yr cumulative agricultural N budget may reflect a combination of fast and slow hydraulic pathways

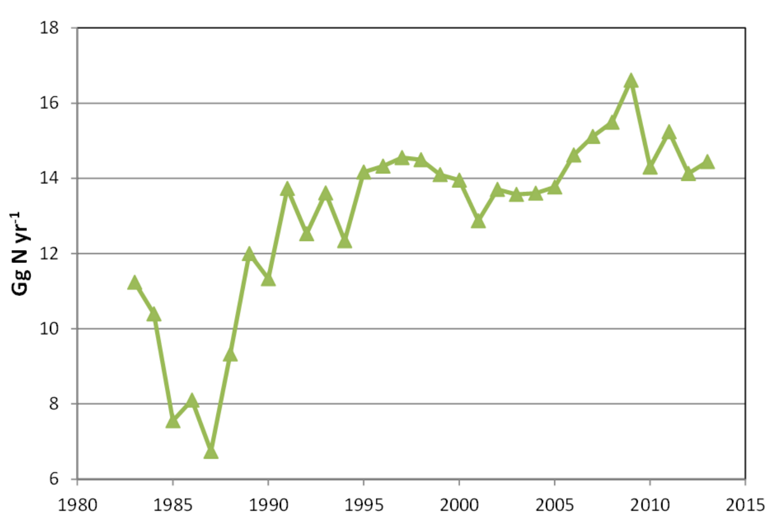

Fig. 5. Annual nitrate-N discharges from the Metropolitan Water Reclamation District of Greater Chicago.

(tile flow and shallow groundwater flow, respectively). Jaynes (2015) reported excess N fertilizer to a tile-drained field in Iowa increased nitrate-N in tile drainage water for at least 4 yr after application (monitoring was concluded after 4 yr), although the greatest increase occurred 6 mo to 2 yr after application. Transport characteristics of nitrate-N are similar to chloride. David et al. (2016) reported that annual chloride concentrations in two small tile-drained watersheds in central Illinois were significantly correlated with chloride inputs during the previous 2 to 6 yr. The Illinois River Basin includes areas without tile drainage, primarily in the western side of the basin, and these areas are expected to deliver nitrate-N through groundwater discharge, which is a slower pathway than tile flow. Nitrate yields from these areas are generally much lower than from tile-drained watersheds (McIsaac and Hu, 2004; Hong et al., 2013) and therefore would have less impact on the magnitude of nitrate loads in the Illinois River.

The residence and transport times for nitrate-N in the watershed reaching the watershed outlet at Valley City are likely to be influenced by rates of precipitation and drainage. Residence times are likely to be longer during dry periods and shorter during wet periods (David et al., 1997). This may be illustrated by the differences between the watershed response to the 1988 drought and the 2012 droughts. The 1988 drought reduced crop yields, which led to the highest RAN of the study period (41.8 kg N ha^{-1}). In 1989, the flow-weighted nitrate-N concentration was only slightly above average, but riverine nitrate-N loads were the fourth lowest of the study period because the water discharge was the lowest of the study period. The timing of rainfall in 1989 was favorable for crop production, which led to a low RAN, but there was little drainage water to transport the RAN to the river. Much of the 1988 and 1989 RAN remained stored in the watershed. In 1990, water discharge was near the 1976–2014 average and had the highest flow-weighted nitrate-N concentration of the 1976–2014 study period.

The 2012 drought led to a RAN of 37.4 kg N ha^{-1} and was followed in 2013 by watershed drainage that was slightly above the 1976–2014 average, with moderately high nitrate-N concentrations and loads that were only slightly above average. Thus, the timing of the nitrate-N appearance at Valley City can vary depending on the quantity of drainage water transporting the nitrate. Van der Velde et al. (2010) demonstrated this for a small tile-drained catchment in The Netherlands.

The variable $CRAN_6$ estimates the residual agricultural N that may remain in the soils and groundwater of the basin from the previous six growing seasons after taking into account the nitrate-N exported in river discharge in the previous 5 yr. It does not account for denitrification losses, which are impossible to estimate at a large scale. This approach may not be successful in other basins where denitrification has a greater influence on nitrate-N export. Furthermore, calculating CRAN over a different number of years may be more appropriate in basins with different hydrologic throughput and pathways. Nonetheless, this and similar studies using relatively simple N budgets can provide plausible explanations for the causes of variations in nitrate-N concentrations and loads. These budgets and more mechanistic models could likely be improved by more accurate data on the quantities and timing of N fertilizer applications.

Nitrate-N discharged from MWRDGC (and possibly other urban point sources) was relatively steady from 1991 to about 2005. An increase from 2005 to 2009 may have contributed to increased flux at Valley City. Since 2009, nitrate-N discharges from MWRDGC decreased, whereas $CRAN_6$ has remained relatively low. Thus, a combination of reduced inputs from point sources and nonpoint sources appears to have contributed to the decline in concentrations after 2009.

The negative correlation between November river discharge and annual nitrate-N loads may be due to greater rainfall during the fall causing delays in harvesting and fall N fertilizer application. This would result in less N fertilizer application during the fall and lower riverine nitrate-N concentrations in the spring, as discussed in Gentry et al. (2014), who examined nitrate loads from two smaller tile-drained, corn–soybean watersheds in east central Illinois that do not drain to the Illinois River. Jaynes (2015) also demonstrated that shifting fertilizer application timing from the fall to the spring reduces nitrate-N concentration in tile drainage and increases nitrate-N uptake by corn.

The ultimate goal of the Illinois Nutrient Loss Reduction Strategy is to reduce nitrate-N loads in all rivers by 45% from the 1980–1996 baseline loads, with an intermediate milestone of reducing loads 15% by 2025 (IEPA, 2015). Despite the lack of a recent downward trend in nitrate-N load in the Illinois River at Valley City, the 2010–2014 average load was 96,700 Mg N yr^{-1}, which is a 10% reduction from the 1980–1996 average load of 107,300 Mg N yr^{-1}. It is encouraging that this reduction occurred despite adverse hydrologic conditions (water discharge 4% above the 1980–1996 average and 10% above the 1975–2005 average in addition to extreme drought in 2012). Without the unusually high flows from 2007 to 2011, there may have been a downward trend in loads similar to the downward trend in flow-weighted concentration. On the other hand, the high flows from 2007 to 2011 may have moved stored nitrate-N out of groundwater and soils, reducing $CRAN_6$ and thereby contributing to reduced nitrate-N loads in subsequent years.

Our results suggest there will be a further decline in the average annual nitrate-N loads in the Illinois River at Valley City if (i) future river flows return to the 1975–2005 average, (ii) urban discharge rates remain steady or decline, and (iii) residual agricultural N values are maintained below about 20 kg N ha^{-1}. However, if future river discharges continue to be greater than the long-term average, this will likely lead to shorter residence times of nitrate-N in the watershed and possibly greater loads of riverine nitrate-N from fertilizer and mineralized from soil organic N. Meeting nutrient loss reduction goals with higher average precipitation and river discharge may require greater conservation efforts than estimated in the Illinois Nutrient Loss Reduction Strategy (IEPA, 2015).

Acknowledgments

This article is based on research partially supported by the National Institute of Food and Agriculture, USEPA, under Agreement No. 2011-039568-31127. The authors thank the Illinois Environmental Protection Agency for providing financial resources and data and facilitating this research, Corey Mitchell for assisting with MWRDGC data, and an anonymous reviewer and Dr. Kevin McGuire for making constructive suggestions.

References

Basu, N.B., G. Destouni, J.W. Jawitz, S.E. Thompson, N.V. Loukinova, A. Darracq, S. Zanardo, M. Yaeger, M. Sivapalan, A. Rinaldo, and P.S.C. Rao. 2010. Nutrient loads exported from managed catchments reveal emergent biogeochemical stationarity. Geophys. Res. Lett. 37:L23404. doi:10.1029/2010GL045168

David, M.B., L.E. Drinkwater, and G.F. McIsaac. 2010. Sources of nitrate yields in the Mississippi River basin. J. Environ. Qual. 39:1657–1667. doi:10.2134/jeq2010.0115

David, M.B., C.A. Mitchell, L.E. Gentry, and R.K. Salemme. 2016. Chloride sources and losses in two tile-drained agricultural watersheds. J. Environ. Qual. 45:341–348. doi:10.2134/jeq2015.06.0302

David, M.B., and L.E. Gentry. 2000. Anthropogenic inputs of nitrogen and phosphorus and riverine export for Illinois, USA. J. Environ. Qual. 29:494–508. doi:10.2134/jeq2000.00472425002900020018x

David, M.B., L.E. Gentry, D.A. Kovacic, and K.M. Smith. 1997. Nitrogen balance in and export from an agricultural watershed. J. Environ. Qual. 26:1038–1048. doi:10.2134/jeq1997.00472425002600040015x

David, M.B., G.F. McIsaac, G.D. Schnitkey, G.F. Czapar, and C.A. Mitchell. 2015. Science assessment. IEPA 2015 Illinois nutrient loss reduction strategy. www.epa.illinois.gov/Assets/iepa/water-quality/watershed-management/nlrs/nlrs-final-revised-083115.pdf (accessed 21 Mar. 2016).

Gentry, L.E., M.B. David, and G.F. McIsaac. 2014. Variation in riverine nitrate flux and fall nitrogen fertilizer application in east-central Illinois. J. Environ. Qual. 43:1467–1474. doi:10.2134/jeq2013.12.0499

Gentry, L.E., M.B. David, F.E. Below, T.V. Royer, and G.F. McIsaac. 2009. Nitrogen mass balance of a tile-drained agricultural watershed in east-central Illinois. J. Environ. Qual. 38:1841–1847. doi:10.2134/jeq2008.0406

Goolsby, D.A., W.A. Battaglin, G.B. Lawrence, R.S. Artz, B.T. Aulenbach, R.P. Hooper, D.R. Keeney, and G.J. Stensland. 1999. Flux and sources of nutrients in the Mississippi-Atchafalaya River Basin: Topic 3. Report of the integrated assessment on hypoxia in the Gulf of Mexico. NOAA Coastal Ocean Program Decision Analysis Series No. 17. NOAA Coastal Ocean Program, Silver Spring, MD.

Hirsch, R.M., D.L. Moyer, and S.A. Archfield. 2010. Weighted regressions on time, discharge, and season (WRTDS), with an application to Chesapeake Bay River inputs. J. Am. Water Resour. Assoc. 46:857–880. doi:10.1111/j.1752-1688.2010.00482.x

Hirsch, R.M., and L.A. De Cicco. 2015. User guide to Exploration and Graphic for River Trends (EGRET) and data retrieval: R packages for hydrologic data (Version 2.0), USGS Techniques and Methods 4-A10. http://pubs.usgs.gov/tm/04/a10/ (accessed 10 Oct. 2015).

Hong, B., D.P. Swaney, and R.W. Howarth. 2013. Estimating net anthropogenic nitrogen inputs to U.S. watersheds: Comparison of methodologies. Environ. Sci. Technol. 47:5199–5207. doi:10.1021/es303437c

Illinois Department of Agriculture. 2015. Tonnage report summaries. Monthly tonnage reporting system. https://www.agr.state.il.us/fertilizer-reports (accessed 21 Mar. 2016).

Illinois Environmental Protection Agency (IEPA). 2015. Illinois nutrient loss reduction strategy. www.epa.illinois.gov/topics/water-quality/watershed-management/excess-nutrients/nutrient-loss-reduction-strategy/index (accessed 10 Oct. 2015).

Jaynes, D.B. 2015. Corn yield and nitrate loss in subsurface drainage affected by timing of anhydrous ammonia application. Soil Sci. Soc. Am. J. 79:1131–1141. doi:10.2136/sssaj2015.01.0033

Jones, C.S., A. Seeman, P.M. Kyveryga, K.E. Schilling, A. Kiel, K.S. Chan, and C.F. Wolter. 2016. Crop rotation and Raccoon River nitrate. J. Soil Water Conserv. (in press).

Kendall, M., and J.D. Gibbons. 1990. Rank correlation methods. 5th ed. Edward Arnold, London.

Lucey, K.J., and D.A. Goolsby. 1993. Effects of short-term climatic variations on nitrate concentrations in the Raccoon River, Iowa. J. Environ. Qual. 22:38–46. doi:10.2134/jeq1993.00472425002200010005x

Markus, M., M. Demissie, M. Short, S. Verma, and R. Cooke. 2014. Sensitivity analysis of annual nitrate loads and the corresponding trends in the lower Illinois River. J. Hydrol. Eng. 19:533–543. doi:10.1061/(ASCE)HE.1943-5584.0000831

McIsaac, G.F., and X. Hu. 2004. Net N input and riverine N export from Illinois agricultural watersheds with and without extensive tile drainage. Biogeochemistry 70:253–273. doi:10.1023/B:BIOG.0000049342.08183.90

Metropolitan Water Reclamation District of Greater Chicago. 2015. Water reclamation plant data. https://www.mwrd.org/irj/portal/anonymous?NavigationTarget=navurl://14d6b38927bee2ff03c32994983903f0 (accessed 10 Sept. 2015).

Montgomery, D.C., E.A. Peck, and G.G. Vining. 2006. Introduction to linear regression analysis. 4th ed. John Wiley & Sons, Hoboken, NJ.

Murphy, J.C., R.M. Hirsch, and L.A. Sprague. 2013. Nitrate in the Mississippi River and its tributaries, 1980– 2010: An update. USGS Scientific Investigations Report 2013–5169. http://pubs.usgs.gov/sir/2013/5169/ (accessed 10 Sept. 2015).

Pellerin, B.A., B.A. Bergamaschi, R.J. Gilliom, C.G. Crawford, J. Saraceno, C.P. Frederick, B.D. Downing, and J.C. Murphy. 2014. Mississippi River nitrate loads from high frequency sensor measurements and regression-based load estimation. Environ. Sci. Technol. 48:12612–12619. doi:10.1021/es504029c

Randall, G.W., and D.J. Mulla. 2001. Nitrate nitrogen in surface waters as influenced by climatic conditions and agricultural practices. J. Environ. Qual. 30:337–344. doi:10.2134/jeq2001.302337x

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

Stenback, G.A., W.G. Crumpton, K. Schilling, and M. Helmers. 2011. Rating curve estimation of nutrient loads in Iowa rivers. J. Hydrol. 396:158–169.

Tesoriero, A.J., J.H. Duff, D.A. Sadd, N.E. Spahr, and D.M. Wolock. 2013. Vulnerability of streams to legacy nitrate sources. Environ. Sci. Technol. 47:3623–3629. doi:10.1021/es305026x

USDA–NASS. 2015. Statistics by state. http://www.nass.usda.gov/ (accessed 10 Sept. 2015).

USEPA. 2007. Hypoxia in the northern Gulf of Mexico: An update by the EPA Science Advisory Board. EPA-SAB-08-004. USEPA, Washington, DC.

USEPA. 2015. States develop new strategies to reduce nutrient levels in Mississippi River, Gulf of Mexico. http://yosemite.epa.gov/opa/admpress.nsf/0/C1FEEC0BA93871DB85257DEA005F017F (accessed 10 Oct. 2015).

Van der Velde, Y., G.H. de Rooij, F.C. van Geer, and H.P. Broers. 2010. Nitrate response of a lowland catchment: On the relation between stream concentration and travel time distribution dynamics. Water Resour. Res. 46:W11534. doi:10.1029/2010WR009105

Williams, M.R., K.W. King, M.L. Macrae, W. Ford, C. Van Esbroeck, R.I. Brunke, M.C. English, and S.L. Schiff. 2015. Uncertainty in nutrient loads from tile-drained landscapes: Effect of sampling frequency, calculation algorithm, and compositing strategy. J. Hydrol. 530:306–316. doi:10.1016/j.jhydrol.2015.09.060