

Variation in Riverine Nitrate Flux and Fall Nitrogen Fertilizer Application in East-Central Illinois

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Abstract

In east-central Illinois, fertilizer sales during the past 20 yr suggest that approximately half of the fertilizer nitrogen (N) applied to corn (*Zea mays* L.) occurs in the fall; however, fall fertilizer N sales were greatly reduced in 2009 as wet soil conditions restricted fall fieldwork, including fertilizer N applications. In 2010, we observed unusually low flow-weighted nitrate concentrations (approximately 40% below the long-term average) in two east-central Illinois rivers (5.7 mg N L⁻¹ in the Embarras River and 5.6 mg N L⁻¹ in the Lake Fork of the Kaskaskia River). Using long-term river nitrate data sets (1993–2012 for the Embarras and 1997–2012 for the Kaskaskia), we examined nitrate concentrations and developed regression models to estimate the association between fall fertilizer N application on riverine nitrate yields in these tile-drained watersheds. During these periods of record, annual riverine nitrate yields ranged from 8 to 57 kg N ha⁻¹ yr⁻¹ (30 kg N ha⁻¹ yr⁻¹ average) for the Embarras River and 2.6 to 59 kg N ha⁻¹ yr⁻¹ (32 kg N ha⁻¹ yr⁻¹ average) for the Kaskaskia. Multivariate linear regression relationships with the current and previous year's annual water yields, previous year's corn yield, and nine-county fall fertilizer sales accounted for 96% of the annual variation in nitrate yield in both watersheds. Running the regression models with fall fertilizer sales set to the 2009 amount suggests that the average reduction in nitrate yield (for the period of record) would be 17 and 20% for the Embarras and Kaskaskia Rivers, respectively. These data suggest that shifting fertilizer N application to the spring can be detected in watersheds as large as 481 km².

ANHYDROUS AMMONIA is a popular source of fertilizer N in corn (*Zea mays* L.) production due, in part, to farmer preference for applying fertilizer in the late fall (USEPA, 2007). Typically, the fall season offers more days suitable for fieldwork with drier soil conditions that decrease the risk of soil compaction (Murrell and Snyder, 2006). Field operations that can be performed in the fall reduce spring workloads, which can lead to earlier corn planting dates and greater yield potential (Murrell and Snyder, 2006). Current Illinois guidelines for fall fertilizer N application suggest using a nitrification inhibitor and waiting until the soil temperature decreases to below 10°C at the 10-cm depth in the late fall (University of Illinois, 2013). In addition, application of fertilizer N in the fall for corn is not recommended for sandy soils or for soils south of Illinois Route 16 (39.3° N lat).

Intensive agriculture in east-central Illinois is predominantly located on poorly drained Mollisols where facilitated drainage such as drainage ditches and tile drainage systems (perforated plastic pipes installed below the soil surface) are common. A recent analysis by David et al. (2010) showed the dominant source of nitrate in surface waters in the Mississippi River Basin was from fertilized cropland containing tile drainage. In addition, studies investigating the timing of fertilizer N applications have shown that fall and winter applications can lead to increased N losses compared with spring applications (Welch et al., 1971; Frye, 1977; Gentry et al., 1998; Randall et al., 2003; Clover, 2005).

An overriding factor that tends to promote fall fertilization is the large size of today's farm operations. The uncertainty of wet spring weather delaying corn planting exerts greater pressure to perform some fieldwork (e.g., N fertilization) in the fall on at least some fields. It is these large-scale management decisions that balance risk and timeliness that compel many producers to employ the practice of fall N application. With the high price ratios of corn grain to fertilizer N, the potential economic cost from N loss associated with fall fertilizer N application is not sufficient to deter many producers from employing this practice.

In east-central Illinois, fertilizer N sales are often greater in the fall than in the spring; however, following the late

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Abbreviations: IEPA, Illinois Environmental Protection Agency; NASS, National Agricultural Statistics Service.

grain harvest of 2009, wet soil conditions restricted the number of days suitable for applying fertilizer N and many fields remained unfertilized until the spring. These unusual circumstances allowed us to investigate the impact of large reductions of fall fertilizer N application on the response of winter and spring riverine N concentrations and yields at a larger spatial scale than previously reported. Therefore, the objective of this study was to examine the response of riverine nitrate concentrations and yields following reduced fall N fertilization for river systems in east-central Illinois in tile-drained agricultural watersheds. In addition, we constructed a multivariate regression model to estimate the impact of N application on annual riverine nitrate loads.

Materials and Methods

East-central Illinois receives on average 100 cm of precipitation annually, of which approximately 10 cm is as snow. The predominant land use in east-central Illinois watersheds consists of row-crop agriculture with nearly all in a corn–soybean [*Glycine max* (L.) Merr.] crop rotation. The area is relatively flat and has been hydrologically modified with numerous drainage ditches and extensive field tile installations (David et al., 1997; Royer et al., 2006; Gentry et al., 2007). Tile systems are generally 1 to 1.5 m below the soil surface and may drain many hectares and cross multiple fields with multiple landowners before outletting into a drainage ditch. Glacial moraines play a large role in defining watershed boundaries and are the source of most headwater streams in this region. In this study, we used river nitrate concentration data from a total of 17 locations in 4 agricultural watersheds in east-central Illinois to investigate the impact of fall fertilizer N application on variations in riverine nitrate flux.

We used long-term river flow and nitrate concentration datasets from two agriculturally dominated watersheds in east-central Illinois (the Upper Embarras River and the Lake Fork of the Kaskaskia River watersheds) to determine annual nitrate yields and flow-weighted mean nitrate concentrations. From June 1993 to September 2012, we collected water samples ($n = 1021$) from the Embarras River at the USGS stream flow gauge #03343400 at Camargo, IL (39°47'30" N, 88°11'09" W), where the watershed area is 48,100 ha. The Illinois Environmental Protection Agency (IEPA) also sampled this location approximately nine times per year. To include the 1993 water-year in our analysis, we used the IEPA reported nitrate concentrations from October 1992 to May 1993. Comparisons between IEPA and our concentration values on nine common sampling dates between 1993 and 1997 indicated no significant difference between the two data sources. From October 1996 through September 2012, we collected water samples ($n = 1124$) at the USGS gauge #05590800 on the Lake Fork of the Kaskaskia River at Atwood, IL (38,600 ha; 39°48'23" N, 88°28'34" W). Maps of these watersheds have been previously published by David et al. (1997) and Gentry et al. (2007). Water samples were collected weekly; however, we also attempted to sample all high flow periods ($>28 \text{ m}^3 \text{ s}^{-1}$) on a daily basis. River samples were filtered (0.45 μm pore size) and analyzed for nitrate by ion chromatography (Dionex). We used linear interpolation to estimate a nitrate N concentration for every daily discharge value to determine daily and annual loads,

and earlier studies have published some of these data (David et al., 1997; Royer et al., 2004, 2006). During extreme flow events, surface runoff typically dilutes river nitrate concentration to about half of the previous day's concentration. Occasionally, when we were unable to sample during high flow, interpolated concentrations were reduced by 50% to avoid overestimation of N loads on days with flow $>50 \text{ m}^3 \text{ s}^{-1}$, as we have done previously (David et al., 1997). Data are expressed on a water-year basis (1 October of the previous year through 30 September of the named year).

Because of low fertilizer N sales in the 2010 water-year, we investigated the pattern of river nitrate concentration during the 2009 through 2011 water-years at our two long-term sampling locations as well as two other watersheds that we were sampling at that time. These other two watersheds include the Upper Salt Fork of the Vermillion River watershed at the USGS gauge #3336900 near St. Joseph, IL (34,720 ha; 40°08'58" N, 88°02'03" W) and a smaller nested watershed within the Embarras, the Black Slough watershed (2500 ha; 39°57'09" N, 88°10'08" W). During this 3-yr investigation, these four sites were sampled approximately 50 times each year. Samples were filtered and analyzed as described above.

To evaluate a larger spatial scale following the low fall N sales of 2010, we performed a synoptic sampling of river nitrate concentrations in early spring and again in late spring of 2010 and 2011. We collected grab samples from 17 river sites in four watersheds in east-central Illinois. The sites included five locations within the Embarras River watershed (Jordan Slough, Long Point Slough, Black Slough, East Branch of the Embarras River, and the USGS gauge near Camargo, IL); three locations in the Kaskaskia River watershed (USGS gauge near Atwood, IL, Lovington East, and Lovington West); six locations in the Sangamon River watershed (Big Ditch, Wildcat Slough, USGS gauge near Fisher, IL, Salt Creek, Salt Creek S. Br., and Salt Creek N. Fork); and three locations in the Upper Salt Fork of the Vermillion River watershed (Salt Fork Ditch, Spoon River, and USGS gauge near St. Joseph, IL).

We graphically plotted cumulative water yield versus cumulative nitrate yield by water-year to examine the response of the watershed during the 1993 through 2012 water-years for the Embarras River and the 1998 through 2012 water-years for the Lake Fork of the Kaskaskia River. Linear regression analysis was also used to examine the relationship between annual river nitrate yield and annual river water yield for both watersheds.

Past research has shown that riverine nitrate concentrations and loads may be correlated with previous year's water yield (McIsaac and Libra, 2003) and corn yield (David et al., 1997; McIsaac et al., 2002). To determine whether these variables may also influence nitrate yields in this setting, multiple linear regression analysis was conducted using an all-subsets approach with annual nitrate yield as the dependent variable and the following variables considered for inclusion: current and previous year's water yields, water-year (a time variable), the previous year's corn yield (indicates an amount of fertilizer remaining postharvest), and annual and fall fertilizer sales.

For each watershed, models with the lowest Mallows' Cp values and those with Cp values approximately equal to one plus the number of variables in the model were subject to further evaluation. The PRESS statistic for each model was calculated

and the model with the lowest PRESS statistic and the least number of variables was selected as the best model (Montgomery et al., 2006). Variance inflation factors were evaluated and model residuals were tested for normality of distribution using the Anderson–Darling A^2 test in SAS version 9.3 (SAS Institute, 2011). Influence of individual water-years on the regression results were evaluated by Cook's D . Paired t -tests were used to evaluate the regional river sampling conducted in 2010 and 2011, with early spring and late spring nitrate concentrations statistically compared between years.

We used Illinois Department of Agriculture monthly tonnage reporting system data for annual (July–June) and fall (July–December) fertilizer N sales from 1992 through 2012 as a proxy for fertilizer N applied in a nine-county area in east-central Illinois (Illinois Department of Agriculture, 2013) having similar cropping systems with tile drainage (David et al., 2010). The annual fertilizer sales values for individual counties are somewhat erratic partly due to changes in dealerships, marketing, and errors in sales reporting. We assumed that combining sales from multiple counties would minimize variation due to these factors. In the multiple regression analysis, we considered as independent variables the sum of the three counties that contain portions of the watershed (Champaign, Piatt, and Douglas Counties) and the sum of a larger nine-county area that included the three core counties and the adjacent counties (De Witt, Ford, Macon, McLean, Moultrie, and Vermillion Counties). We assigned the fall fertilizer sales of the previous year with the named water-year (e.g., fall fertilizer N sales in calendar year 1992 are reflected in the 1993 water-year). In addition, corn acres in these nine counties were summed by year (1993–2012) to determine the change in corn acres through time from USDA National Agricultural Statistics Service (NASS) data using regression analysis.

We used county average corn yields as reported by USDA NASS. For the Embarras watershed, which is almost entirely within Champaign County, we used Champaign County annual average corn yields. The Lake Fork of the Kaskaskia watershed includes approximately equal portions of Champaign and Piatt Counties, so we used the average corn yields from these two counties to represent this watershed.

Results and Discussion

River Water and Nitrate Yields

During the 20 water-years from 1993 through 2012, the annual water yield of the Embarras River at Camargo, IL, averaged 35 cm, which represented approximately 36% of the annual precipitation (Fig. 1). The largest annual water yield during the past 40 yr (data not shown) at Camargo, IL, occurred in 1993 (66 cm), which was the wettest year on record. However, the largest riverine nitrate yield occurred in 2002 (57 kg N ha⁻¹ yr⁻¹), which was a wet year that followed 2 yr with below-average precipitation (Fig. 1). The three driest years (2000, 2003, and 2012) produced the smallest water and nitrate yields. The average annual nitrate yield exiting the Embarras River watershed during this time period was 30 kg N ha⁻¹ yr⁻¹. During the period of record for the Kaskaskia River (1998–2012), annual water yields and riverine nitrate yields were similar to those of the Embarras River, ranging from 2.6 to 59 kg N ha⁻¹ yr⁻¹ with an average of 32 kg N ha⁻¹ yr⁻¹ (Fig. 1).

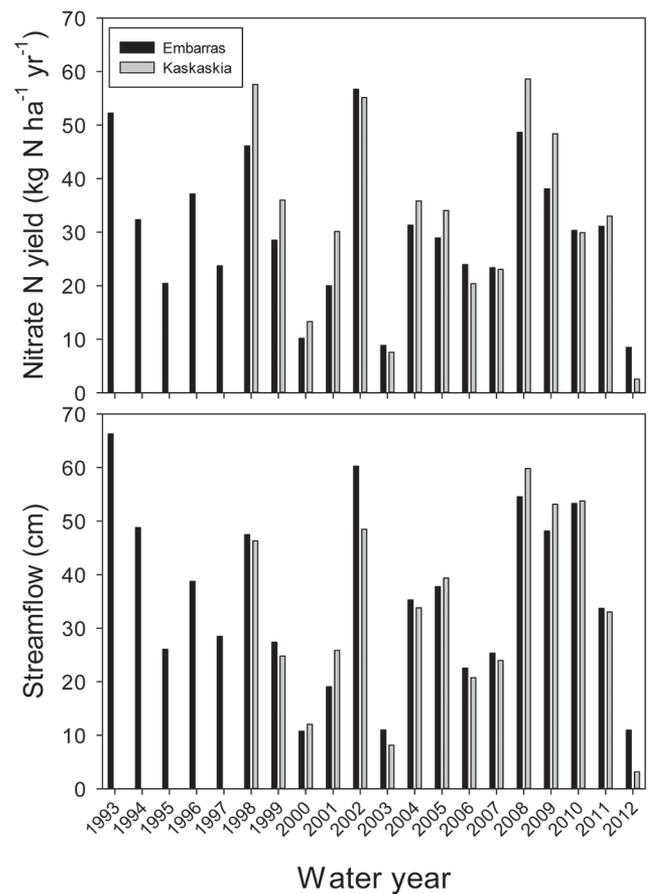


Fig. 1. Annual nitrate yield and stream flow for the Embarras River watershed at Camargo, IL, and Lake Fork of the Kaskaskia River watershed at Atwood, IL.

Nitrate in both river systems exhibited a seasonal pattern such that concentrations were usually <1 mg N L⁻¹, or below our detection limit of 0.1 mg N L⁻¹, at the beginning of most water-years. Concentrations increased through the winter months, peaked in late spring, and quickly decreased through the summer months (Fig. 2). During 1993, however, nitrate concentrations in the Embarras River generally remained above 5 mg N L⁻¹ during the summer except for four high-flow events that diluted nitrate concentrations. This was exceptional since every subsequent year nitrate concentrations decreased below 1 mg N L⁻¹ during the late summer and fall (Fig. 2). Researchers working in the Embarras River watershed in 1993 documented that tile drainage occurred through the summer of 1993 and into the fall (David et al., 1997). These researchers demonstrated that the period of elevated riverine nitrate coincided with the period of tile flow and that riverine nitrate quickly declined below 1 mg N L⁻¹ following cessation of tile drainage. Additionally, David et al. (1997) demonstrated that the pattern of nitrate concentration in one tile in the Embarras River watershed could explain 70% of the variation in riverine nitrate concentration and concluded that tiles are a major source of nitrate to surface waters.

The greatest annual flow-weighted mean nitrate concentration during the period of record was 10.6 mg N L⁻¹ in 2006 for the Embarras River and 14.7 mg N L⁻¹ in 1999 for the Kaskaskia River (Fig. 2). The least annual flow-weighted mean nitrate concentrations for both watersheds (5.6 mg N L⁻¹ for the Embarras River and 5.7 mg N L⁻¹ for the Kaskaskia

River) occurred in the 2010 water-year. In addition, the seasonal pattern of nitrate concentrations was notably different in 2010 compared to all other years, described in more detail below.

Fertilizer N Sales and River Nitrate Concentrations

Annual fertilizer sales in the nine counties of east-central Illinois ranged from 102,000 to 150,000 Mg N yr⁻¹ with an average value of 124,000 Mg N yr⁻¹ (Fig. 3). There was more variation in fall fertilizer N sales, which ranged from 26,000

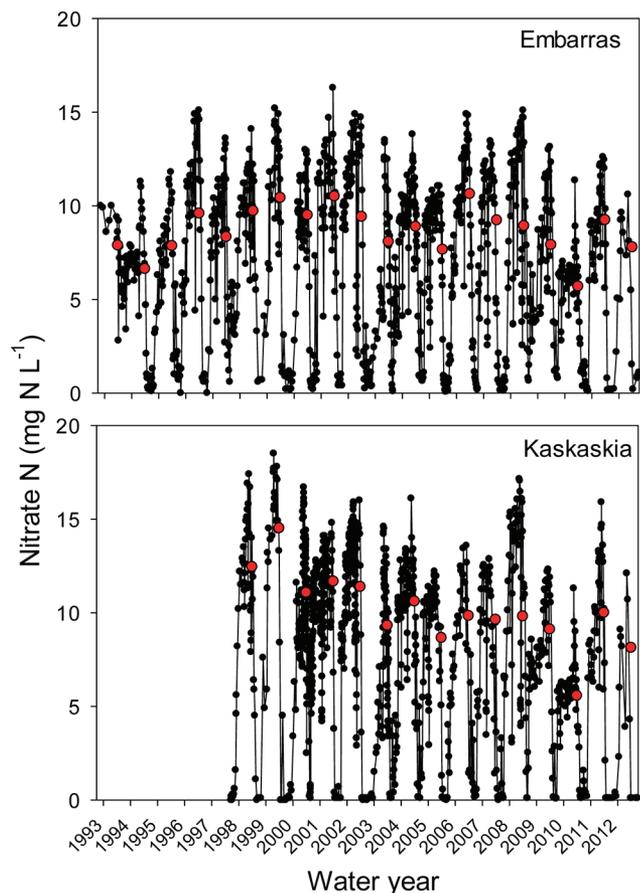


Fig. 2. Nitrate concentrations in grab samples (black dots) and flow-weighted annual nitrate concentrations (red dots) in the Embarras River at Camargo, IL, and Kaskaskia River at Atwood, IL.

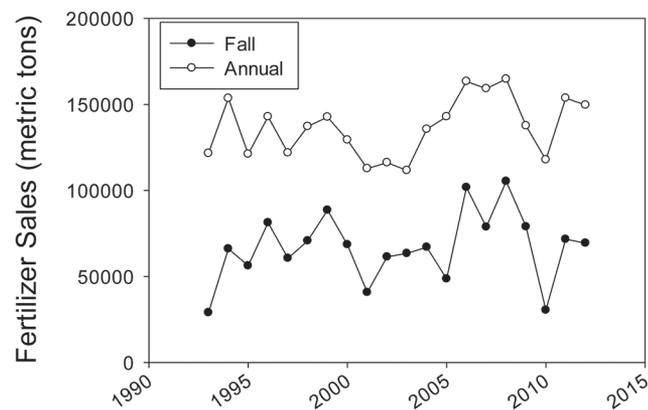


Fig. 3. Annual and fall N fertilizer sales as reported to the Illinois Department of Agriculture for the nine-county, tile-drained region of east-central Illinois.

to 96,000 Mg yr⁻¹ with an average of 61,000 Mg yr⁻¹. The percentage of annual fertilizer sold in the fall ranged from 24 to 64%, with an average of 48%. Corn acreage for the nine counties increased significantly at a rate of 5400 ha yr⁻¹ for the period of 1993 through 2012 (regression of year vs. nine-county planted corn ha had $R^2 = 0.57$ and $p < 0.0001$). Acreage planted to corn during this 20-yr period increased about 13%, with most of the increase after 2004.

The 2009 growing season in east-central Illinois was cooler and wetter than average, delaying crop harvest. For example, corn harvest in the east-central region of Illinois was only 61% completed by 22 November 2009, compared to the 5-yr average of 98% (USDA, 2009). Precipitation in October (19.8 cm) and November (17.5 cm) limited the number of days suitable for fieldwork. As a result, the application of fertilizer N in the fall was also restricted. Based on the nine counties, fertilizer N sales in east-central Illinois in the fall of 2009 (2010 water-year) were less than half of the 20-yr average fall sales.

We present (Fig. 4) a more detailed view of the seasonal pattern of riverine nitrate concentration during the 2010 water-year for the two long-term datasets as well as two other nearby watersheds (the Upper Salt Fork is adjacent to the Embarras watershed, and the Black Slough watershed is nested within the Embarras watershed). Figure 4 includes the previous and

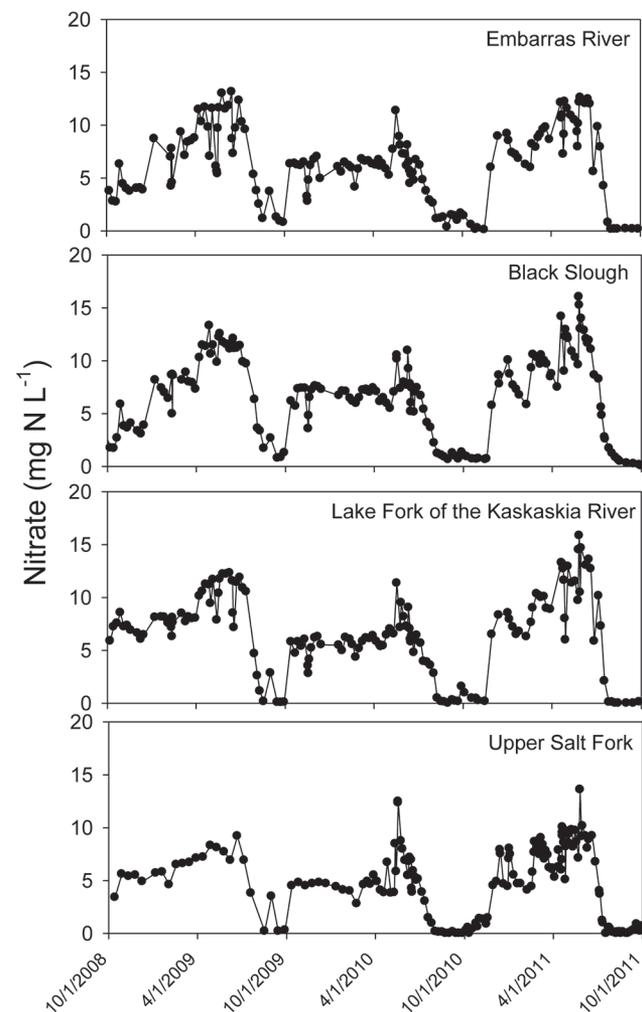


Fig. 4. Nitrate concentrations in four east-central Illinois rivers during the 2009 through 2011 water-years.

subsequent water-years to compare and contrast the unusual pattern of riverine nitrate concentration in 2010. In the 2009 and 2011 water-years, nitrate concentration generally increased throughout the tile drainage season; however, in 2010 the concentrations held steady through early May at approximately 5 or 6 mg N L⁻¹, depending on the watershed. There was a spike in riverine nitrate concentration in all four watersheds following a rain event in May 2010. Due to the warm and dry weather in the months of March and April, farmers had been able to apply fertilizer N by this time.

Synoptic sampling of 17 river and ditch locations in early and late spring indicated that nitrate concentrations were lower in the 2010 water-year, compared with 2011, across this region of the state (Fig. 5). When averaged across all sites in 2010, nitrate concentrations were 26% lower in early spring and 29% lower in late spring compared with 2011 nitrate concentrations at similar dates. The flow-weighted mean nitrate concentrations in 2011 were nearly equal to the long-term average at the gaged outlets of the Embarras and Kaskaskia watersheds. These data corroborate our findings that nitrate concentrations in surface waters throughout east-central Illinois were unusually low during the spring of the 2010 water-year.

Bivariate Linear Regression

When cumulative riverine nitrate yield was plotted against cumulative water yield for each water-year for the Embarras and Kaskaskia Rivers (Fig. 6), it was clear that for each additional cm of water yield, there was a smaller incremental yield of nitrate during 2010 than for any of the 35 water-years of our study. The next closest year was 1994 for the Embarras River, which followed the wettest year on record, producing year-round tile flow in this part of the state. Although fertilizer sales were low in the fall of 1992 (1993 water-year), the unusual circumstance of continuous tile flow throughout the summer added greatly to the riverine load, increasing nitrate yield and flow-weighted mean nitrate concentration that year, which likely reduced the amount of nitrate available for leaching during the subsequent water-year (1994).

Annual riverine nitrate yield was highly correlated with annual water yield (Table 1), but 2010 deviated from the bivariate regression line more than any other year for both rivers (Fig. 7). For the Embarras River, linear regression with water yield accounted for 87% of the variation in nitrate yield, but the regression equation overestimated nitrate yields for 1994 and 2010 by 25 and 44% (8.0 and 13.4 kg N ha⁻¹, respectively). When these 2 yr were removed from the analysis, the regression equation with the remaining water yields accounted for 95% of the variation in nitrate yield. Similarly, for the Kaskaskia River, regression with water yield alone accounted for 79% of the variation in annual nitrate yield, but the regression equation substantially overestimated nitrate yield for 2010 by 71% (21.3 kg N ha⁻¹). When 2010 was removed from the analysis, annual water yield accounted for 92% of the variation in nitrate yield.

Multivariate Linear Regression

For the Embarras River, the multivariate model with the lowest values of Mallows' Cp and PRESS statistics and the least number of variables contained four terms: current year water

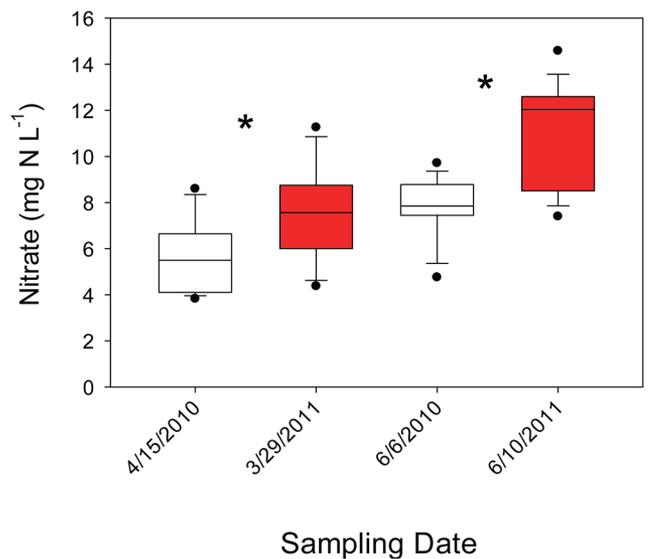


Fig. 5. Box plots of nitrate N concentrations from regional sampling of east-central streams during spring of 2010 and 2011 ($n = 17$). Asterisks indicate a significant difference between early spring 2010 and 2011 samples and late spring 2010 and 2011 samples using paired t -tests ($p < 0.0001$).

yield, previous year's water yield, previous year's corn yield, and the nine-county fall fertilizer sales (Table 1). Variance inflation factors were all less than 1.1, and the hypothesis that the residuals were normally distributed could not be rejected at the $p > 0.25$ level according to the Anderson–Darling A^2 test. Annual fertilizer

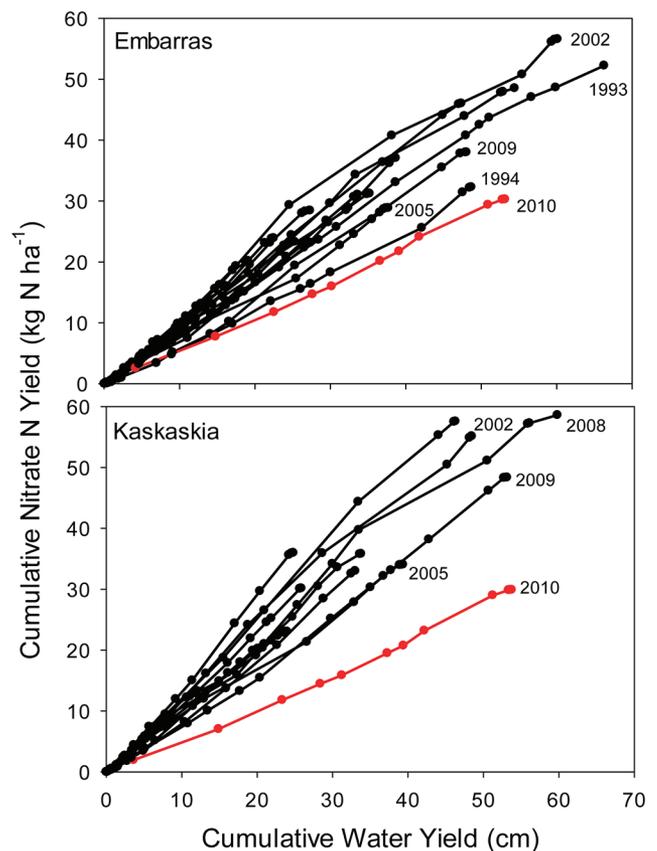


Fig. 6. Cumulative water yield vs. cumulative nitrate N yield by water-year for the Embarras River at Camargo, IL, and the Lake Fork of the Kaskaskia River at Atwood, IL. Selected years identified.

Table 1. Results of linear regression analysis with annual nitrate N yield as the dependent variable for the Embarras and Kaskaskia Rivers.

River system	Independent variable	Regression coefficient	t	p > [t]	R ²
Embarras	Water yield (cm)	0.76	9.63	<0.0001	0.87
Kaskaskia	Water yield (cm)	0.88	7.02	<0.0001	0.79
Embarras	Water yield (cm)	0.80	18.6	<0.0001	
	Lag† (water yield) (cm)	-0.18	-4.03	0.0011	
	Lag (corn yield) (Mg ha ⁻¹)	-1.28	-2.45	0.0268	
	Fall fertilizer (Mg)	0.00014	3.83	0.0017	0.96
Kaskaskia	Water yield (cm)	1.07	15.0	<0.0001	
	Lag (water yield) (cm)	-0.28	-4.02	0.0024	
	Lag (corn yield) (Mg ha ⁻¹)	-5.53	-4.80	0.0007	
	Fall fertilizer (Mg)	0.00017	3.14	0.01	0.96

† The lag of water yield and corn yield refers to the previous year's value for these variables (e.g., for the 2010 water-year, lag (water yield) refers to the 2009 water yield).

sales were not selected for the model. Three years were identified as having high influence (Cook's *D* > *n*/4): 1994, 1996, and 2010. When these 3 yr were removed and the model selection process repeated, the same four-variable model was selected based on the lowest Cp. Although there were some differences in model coefficients (described in Supplemental Material), the influence of these 3 yr on the regression results appeared to be relatively minor and likely due to the combination of conditions that occurred during those years rather than data errors.

For the Kaskaskia River, the multivariate model with the lowest values of Cp and PRESS statistics and the least number of variables included the same four terms as the model for the Embarras River described above. Variance inflation factors were less than 1.33 and the hypothesis that the residuals were

normally distributed could not be rejected at *p* > 0.25 according to the Anderson–Darling *A*² test. Two years were identified with high influence (Cook's *D* > *n*/4): 2003 and 2010. When these 2 yr were removed from the analysis and the selection process repeated, the same four-variable model was selected. Differences in coefficients are presented in the Supplemental Material. The high influence of these years appeared to be due to conditions occurring during those years rather than data errors.

For the Embarras River, the four-term model accounted for 96% of the variation in annual nitrate yield. Nitrate yields in 1994 and 2010 were still overestimated by this equation but to a lesser degree (2.1 and 4.6 kg N ha⁻¹), and these are the largest residuals in absolute value (Fig. 7). For the Kaskaskia River, the equation also accounted for 96% of the variation in nitrate yield. Nitrate yield for 2010 was overestimated by 6.3 kg N ha⁻¹, which is the greatest deviation between model estimated and observed nitrate yield but is similar in magnitude to other residuals and less than one-third the magnitude of the 2010 residual for the model based on water yield alone.

For both watersheds, the current year water yield accounts for most of the annual variation in nitrate yield. The negative coefficient on previous year's water yield indicates a low water yield in a previous year contributes to a higher nitrate yield in the current year. Nitrate is likely to remain stored in the soil profile when drainage and water yield are low, but this stored nitrate is available for leaching in the subsequent water-year. Conversely, nitrate is likely to have been flushed out of the soil profile or denitrified during a wet year with high water yield, leaving less to contribute to nitrate yield in the subsequent year. A previous year's corn yield would also influence soil N available for leaching in the subsequent water-year. Low corn yields leave more N and high yields leave less N, which is consistent with the negative sign of the coefficients for this variable in both watersheds.

The improved fit of the multivariate models suggests different factors may account for the lower-than-expected nitrate yields (as predicted by the bivariate model) in the Embarras River in 1994 and 2010. Fall sales of fertilizer N in the 1994 water-year were nearly equal to the 20-yr average value, and the 1993 corn yields were 12% less than average. These two factors would contribute to average or above-average nitrate yield in 1994. Water yield in 1993 (66 cm) was nearly twice the average annual water yield, and thus, this is likely the dominant factor associated with the lower-than-expected riverine nitrate yield in 1994, presumably due to increased denitrification or flushing of nitrate out of the

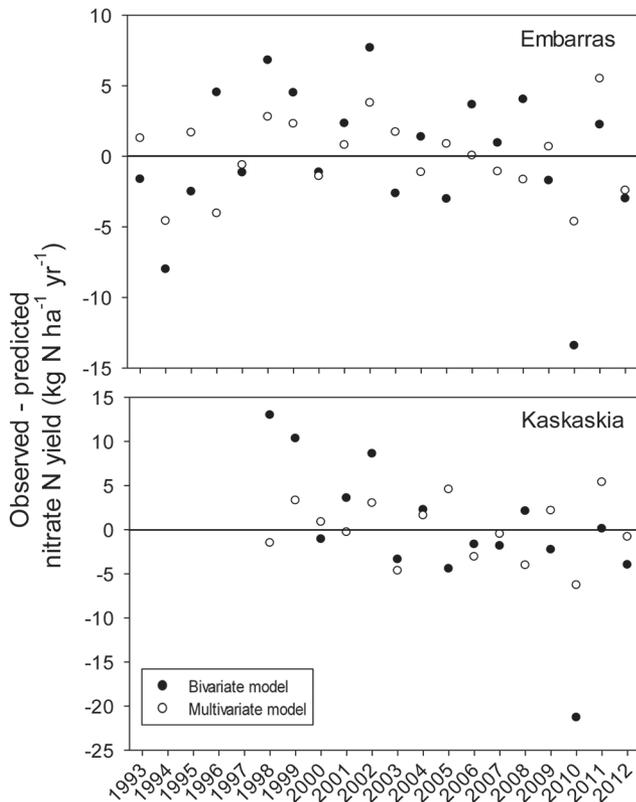


Fig. 7. Bivariate and multivariate model residuals for annual nitrate N yield for the Embarras River at Camargo, IL, and Kaskaskia River at Atwood, IL.

soil profile. In 2010, all three factors potentially contributed to lower-than-expected river nitrate yield; fall fertilizer sales were only 50% of the long-term average, while 2009 water yield and corn yield were 134 and 119%, respectively, of their long-term averages. Based on the deviations from the long-term averages, reduction in fall fertilizer appears to have been the dominant factor in the 2010 water-year.

We used the multivariate regression models to estimate the impact on annual riverine nitrate N yield if fall fertilizer sales had been the 2010 water-year value in all years during the period of record for a given watershed. For the Embarras River, the model estimated an average of 17% reduction of nitrate yield during the 1993 through 2012 water-years. For the Kaskaskia River, the estimated reduction was 20% of the annual nitrate yield when fall fertilizer was set to the 2010 sales. These results are similar to a controlled and replicated plot-scale study conducted in east-central Illinois that reported a 25% reduction in nitrate N loss through tiles by shifting all N fertilization from fall to spring (Clover, 2005).

Although the nine-county fall fertilizer sales for the 2010 water-year were 50% of the long-term average, the relationship between these sales and actual N application is uncertain. For example, N fertilizer may be purchased and not applied due to weather constraints. University of Illinois Extension specialists estimated that not more than 15% of the annual amount of anhydrous ammonia was applied in the fall of 2009 (University of Illinois Extension, 2010). Sales of anhydrous ammonia in the fall are typically greater than 60% of the total annual sales of anhydrous ammonia. Thus, the actual fall N application in the study watersheds in 2009 may have been considerably less than 50% of the long-term average. The similarity between our estimate of the long-term average reduction in nitrate yield by using fall fertilizer sales from the 2010 water-year, along with the reduction reported by Clover (2005), also suggests that there was little fall N applied that year.

Gowda et al. (2008) used a spatial process model combining geographical information system (GIS) and Agricultural Drainage And Pesticide Transport (ADAPT) modeling to examine nitrate losses for a small (365 ha) watershed in central Iowa (Walnut Creek). Their simulation indicated a 13% reduction in annual nitrate loss by changing the timing of N fertilization from fall to spring. Although annual precipitation is less in Iowa than Illinois, their results may also suggest that nitrate loss associated with fall N fertilization on tile-drained fields decreases with increasing latitude as soils remain continuously frozen throughout much of the winter season.

Management Implications

The *Illinois Agronomy Handbook* (University of Illinois, 2013) states that fall N applications should not be performed on soils that are sandy or organic, that are very poorly drained or have excessive drainage, or that rarely freeze or experience temperatures that decline very slowly from 10°C to freezing. The installation of tile drainage in poorly drained Mollisols increases the risk of nitrate leaching losses, especially in systems using fall fertilizer N application. Tile systems are now often installed in a grid pattern where an entire field is drained (not just low lying subbasins). We speculate that increased tile drainage densities (pattern tile systems on top of older random tile systems) across

the landscape will increase nitrate leaching from fields to ditches, making fall fertilizer N more susceptible to leaching. In addition, the USDA revised the plant hardiness zone map in 2012 (USDA, 2012), citing greater detail and accuracy due to the inclusion of more years of data. The new map generally moves the zones north by approximately 150 km in Illinois. The previous hardiness zone boundary was positioned near the southern boundary, where fall fertilizer N application is considered feasible (University of Illinois, 2013). Research has shown that nitrification inhibitors such as nitrapyrin degrade faster with increasing temperature (Hendrickson and Keeney, 1979; Keeney, 1980; Wolt, 2004). The appropriateness of fall N fertilizer application on tile-drained land in east-central Illinois may need to be revisited in light of warmer winters and the research results presented here.

The fertilizer industry is currently encouraging corn producers to limit their fall fertilizer N application rate to 50% of planned overall applications, whereas they currently apply 100%. This would be part of an N management system that considers applying fertilizer N in split applications (fall, spring, and sidedress). From an agronomic standpoint, research studies have shown that spring and sidedress (after crop emergence) applications of fertilizer N can lead to better fertilizer recovery (e.g., Randall and Vetsch, 2005) with reduced optimum fertilizer rates (Bundy 1986; Randall and Goss, 2001). These studies suggest that N applications closer to the period when corn requires the greatest amount of available soil N will likely decrease nitrate leaching losses and possibly increase crop yields with an overall lower fertilization rate. However, fertilizer timing changes, as well as other in-field and edge-of-field approaches in the tile-drained regions of the Corn Belt, would be required to reduce nitrate losses from current amounts (Robertson and Vitousek, 2009).

Summary and Conclusions

Unusually wet fall weather in east-central Illinois during the 2010 water-year reduced the number of days suitable for fieldwork, which restricted the amount of fertilizer N applied that fall. Riverine nitrate concentrations and nitrate yields were unusually low during the winter and early spring of 2010 in two east-central Illinois watersheds. Although fall fertilizer sales are an imperfect measure of fall fertilizer application, it was a significant term in regression models that accounted for 96% of the variation in annual nitrate yield in these watersheds. When the regression models were used to estimate riverine nitrate yields for all years using the value of fertilizer sales in the fall of the 2010 water-year, the average reduction in nitrate yield was 17 and 20% for the Embarras and Kaskaskia Rivers, respectively. This result is similar to a plot scale study that compared tile nitrate losses from fall-applied N to spring-applied N (Clover 2005). The similarity suggests that little fall N was applied in the study watersheds during the 2010 water-year and that shifting N fertilizer application to the spring can be detected in watersheds as large as 481 km². More accurate quantification of fertilizer N application rates and timing would allow for more precise estimates of the influence of fertilizer management on nitrate transport to surface waters; however, our results suggest that water quality can respond to N management more quickly and at a larger scale than previously reported.

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References

- Bundy, L.G. 1986. Review: Timing nitrogen applications to maximize fertilizer efficiency and crop response in conventional corn production. *J. Fert. Issues* 3:99–106.
- Clover, M.W. 2005. Impact of nitrogen management on corn grain yield and nitrogen loss on a tile drained field. M.S. thesis, University of Illinois at Urbana-Champaign.
- 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., 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
- Frye, W.W. 1977. Fall- vs spring-applied sulfur coated urea, uncoated urea, and sodium nitrate for corn. *Agron. J.* 69:278–282. doi:10.2134/agronj1977.00021962006900020019x
- Gentry, L.E., M.B. David, T.V. Royer, C.A. Mitchell, and K.M. Starks. 2007. Phosphorus transport pathways to streams in tile-drained agricultural watersheds. *J. Environ. Qual.* 36:408–415. doi:10.2134/jeq2006.0098
- Gentry, L.E., M.B. David, K.M. Smith, and D.A. Kovacic. 1998. Nitrogen cycling and tile drainage nitrate loss in a corn/soybean watershed. *Agric. Ecosyst. Environ.* 68:85–97. doi:10.1016/S0167-8809(97)00139-4
- Gowda, P.H., D.J. Mulla, and D.B. Jaynes. 2008. Simulated long-term nitrogen losses for a midwestern agricultural watershed in the United States. *Agric. Water Manage.* 95:616–624. doi:10.1016/j.agwat.2008.01.004
- Hendrickson, L.L., and D.R. Keeney. 1979. Effect of some physical and chemical factors on the rate of hydrolysis of nitrapyrin (N-Serve). *Soil Biol. Biochem.* 11:47–50. doi:10.1016/0038-0717(79)90117-2
- Illinois Department of Agriculture. 2013. Tonnage report summaries. Monthly tonnage reporting system, Illinois Dep. of Agric. <http://www.agr.state.il.us/programs/fert2/> (accessed 12 Dec. 2013).
- Keeney, D.R. 1980. Factors affecting the persistence and bioactivity of nitrification inhibitors. In: J.J., Meisinger, G.W. Randall, and M.I. Vitosh, editors, *Nitrification inhibitors: Potentials and limitations*. ASA Spec. Publ. 38. ASA, Madison, WI. p. 33–46.
- McIsaac, G.F., M.B. David, G.Z. Gertner, and D.A. Goolsby. 2002. Relating N inputs to the Mississippi River Basin and nitrate flux in the Lower Mississippi River: A comparison of approaches. *J. Environ. Qual.* 31:1610–1622. doi:10.2134/jeq2002.1610
- McIsaac, G.F., and R.D. Libra. 2003. Revisiting nitrate concentrations in the Des Moines River. *J. Environ. Qual.* 32:2280–2289. doi:10.2134/jeq2003.2280
- Montgomery, D.C., E.A. Peck, and G.G. Vining. 2006. *Introduction to linear regression analysis*. 4th ed. John Wiley & Sons, Hoboken, NJ. p. 141–142.
- Murrell, T.S. and C.S. Snyder. 2006. Fall-applied nitrogen in the corn belt: Questions and answers for corn. International Plant Nutrition Institute. <http://www.ipni.net/article/IPNI-3027> (accessed 12 Dec. 2013).
- Randall, G.W., and M.J. Goss. 2001. Nitrate loss to surface water through subsurface tile drainage. In: R.F., Follett, and J.L. Hatfield, editors, *Nitrogen in the environment: Sources, problems, and management*. Elsevier Science B.V., Amsterdam. p. 95–122.
- Randall, G.W., and J.A. Vetsch. 2005. Nitrate losses in subsurface drainage from a corn-soybean rotation as affected by fall and spring application of nitrogen and nitrapyrin. *J. Environ. Qual.* 34:590–597. doi:10.2134/jeq2005.0590
- Randall, G.W., J.A. Vetsch, and J.R. Huffman. 2003. 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. doi:10.2134/jeq2003.1764
- Robertson, G.P., and P.M. Vitousek. 2009. Nitrogen in agriculture: Balancing the cost of an essential resource. *Annu. Rev. Environ. Resour.* 34:97–125. doi:10.1146/annurev.environ.032108.105046
- Royer, T.V., M.B. David, and L.E. Gentry. 2006. Timing of riverine export of nitrate and phosphorus from agricultural watersheds in Illinois: Implications for reducing nutrient loading to the Mississippi River. *Environ. Sci. Technol.* 40:4126–4131. doi:10.1021/es052573n
- Royer, T.V., J.L. Tank, and M.B. David. 2004. The transport and fate of nitrate in headwater agricultural streams in Illinois. *J. Environ. Qual.* 33:1296–1304. doi:10.2134/jeq2004.1296
- SAS Institute. 2011. SAS/STAT software. Version 9.3. SAS Inst., Cary, NC.
- University of Illinois. 2013. Illinois Agronomy Handbook. Dep. of Crop Sciences, Univ. of Illinois at Urbana-Champaign. <http://extension.cropsci.illinois.edu/handbook/> (accessed 12 Dec. 2013).
- University of Illinois Extension. 2010. Applying nitrogen after planting. The Bulletin: Pest management and crop development information for Illinois. Issue No. 6, Article 5, May 14, 2010. University of Illinois Extension, Urbana, IL. <http://bulletin.ipm.illinois.edu/article.php?id=1311> (accessed 12 Dec. 2013).
- USDA. 2009. Illinois weather and crops. National Agricultural Statistics Service, Illinois Field Office. http://www.nass.usda.gov/Statistics_by_State/Illinois/Publications/Crop_Progress_&_Condition/Historical_Reports/2009/wc-vol30-no39.pdf (accessed 12 Dec. 2013).
- USDA. 2012. USDA plant hardiness zone map. Agricultural Research Service. <http://planthardiness.ars.usda.gov/PHZMWeb/> (accessed 12 Dec. 2013).
- USEPA. 2007. Hypoxia in the northern Gulf of Mexico: An update by the EPA Science Advisory Board. EPA-SAB-08-003. USEPA, Washington, DC.
- Welch, L.F., D.L. Mulvaney, M.G. Oldham, L.V. Boone, and J.W. Pendleton. 1971. Corn yields with fall, spring, and sidedress nitrogen. *Agron. J.* 63:119–123. doi:10.2134/agronj1971.00021962006300010037x
- Wolt, J.M. 2004. A meta-evaluation of nitrapyrin agronomic and environmental effectiveness with emphasis on corn production in the Midwestern USA. *Nutr. Cycling Agroecosyst.* 69:23–41. doi:10.1023/B:FRES.0000025287.52565.99