# Sources of Nitrate Yields in the Mississippi River Basin

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Riverine nitrate N in the Mississippi River leads to hypoxia in the Gulf of Mexico. Several recent modeling studies estimated major N inputs and suggested source areas that could be targeted for conservation programs. We conducted a similar analysis with more recent and extensive data that demonstrates the importance of hydrology in controlling the percentage of net N inputs (NNI) exported by rivers. The average fraction of annual riverine nitrate N export/NNI ranged from 0.05 for the lower Mississippi subbasin to 0.3 for the upper Mississippi River basin and as high as 1.4 (4.2 in a wet year) for the Embarras River watershed, a mostly tile-drained basin. Intensive corn (*Zea mays* L.) and soybean [*Glycine max* (L.) Merr.] watersheds on Mollisols had low NNI values and when combined with riverine N losses suggest a net depletion of soil organic N. We used county-level data to develop a nonlinear model of N inputs and landscape factors that were related to winter–spring riverine nitrate yields for 153 watersheds within the basin. We found that river runoff times fertilizer N input was the major predictive term, explaining 76% of the variation in the model. Fertilizer inputs were highly correlated with fraction of land area in row crops. Tile drainage explained 17% of the spatial variation in winter–spring nitrate yield, whereas human consumption of N (i.e., sewage effluent) accounted for 7%. Net N inputs were not a good predictor of riverine nitrate N yields, nor were other N balances. We used this model to predict the expected nitrate N yield from each county in the Mississippi River basin; the greatest nitrate N yields corresponded to the highly productive, tile-drained cornbelt from southwest Minnesota across Iowa, Illinois, Indiana, and Ohio. This analysis can be used to guide decisions about where efforts to reduce nitrate N losses can be most effectively targeted to improve local water quality and reduce export to the Gulf of Mexico.



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The upper Mississippi River basin (MRB) has been identified as the dominant source of riverine nitrate N flux contributing to the overall load of N to the Gulf of Mexico, where it is a major contributor to the hypoxic zone that forms each summer (USEPA, 2007). Summer 2008 had the second-largest hypoxic zone on record, following high spring rainfall across many areas of the upper basin (USGS, 2008). The upper MRB has the most productive soils in the basin with intensive agricultural production, predominately corn (*Zea mays* L.) and soybean [*Glycine max* (L.) Merr.]. Land use in many subwatersheds is dominated by intensive corn–soybean production, often accounting for 90 to 95% of the landscape. Furthermore, these areas have undergone extensive hydrological modifications including channelization of the headwater streams and intensive tile (subsurface, artificial) drainage in fields to lower water tables and efficiently route water to streams (Baker et al., 2008). However, nitrate N, total and reactive P, and pesticides can readily move to streams during tile flow (e.g., Baker and Johnson, 1981; David et al., 1997, 2003; Gentry et al., 2007), and much of the annual loss can occur during a few days to weeks in the winter and spring (Royer et al., 2006). During these high flow periods there is little opportunity for denitrification to reduce the nitrate N load, so that most of the nitrate N that enters streams during winter and spring reaches the Gulf (Royer et al., 2004; Alexander et al., 2008).

Many modeling methods have been used to better understand the source areas of nitrate in the MRB (e.g., Donner et al., 2004; Booth and Campbell, 2007; Alexander et al., 2008). These methods typically focus on inputs of N (fertilizer, atmospheric deposition, manure, and sewage effluent) and then relate the inputs to riverine loads. One method has used net N inputs (NNI, or sometimes net anthropogenic N inputs [NANI]) to relate inputs and outputs of N at various scales, typically using state (David and Gentry, 2000; McIsaac et al., 2001, 2002) or regional data (Howarth et al., 1996; Boyer et al., 2002; McIsaac and Hu, 2004). Net N input is thought to be the N available for field denitrification losses, additions to the soil N pool, and transport to surface and groundwaters (McIsaac et al., 2002).

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**Abbreviations**: GIS, geographic information system; MRB, Mississippi River basin; NADP, National Atmospheric Deposition Program; NNI, net N inputs; SAB, Science Advisory Board.

McIsaac et al. (2002) were able to predict Mississippi River nitrate N load using NNI and river flow in a nonlinear model and demonstrated that net inputs needed to be lagged up to 9 yr to predict annual loads. Howarth et al. (1996) found that for large regions of the North Atlantic, about 25% of NNI was exported through rivers. David and Gentry (2000) determined that for Illinois, about 50% of NNI was exported through rivers,; they concluded that tile-drained agriculture was the probable cause of this higher loss. McIsaac and Hu (2004) then examined two regions in Illinois using the NNI approach. They observed in the tile-drained region (central Illinois) that NNI was equal to riverine nitrate N export, whereas in the non-tiled region (southern Illinois) riverine export was between 25 and 37% of NNI. Given these patterns, it is not clear if NNI is useful in evaluating the potential for N losses when tile drainage is present.

It is difficult to assess net mineralization of N from the large soil organic N pool present in most agricultural soils, as well as nitrification of the mineralized pool (Dahnke and Johnson, 1990; Griffin, 2008). Each year, a large amount of N is mineralized, with most replaced (on a multiyear basis) through immobilization processes, either by fertilizer or crop residues. In the NNI approach, this pool is assumed to be at a steady state, as there are no consistently reliable annual measurements available. David et al. (2009) evaluated changes in the soil organic N pool from 1957 to 2002 for Mollisols in Illinois and concluded that there were no changes. However, Gentry et al. (2009) in a mass balance of a small watershed in east-central Illinois determined that there may now be a small net depletion of soil organic N occurring most years. In the USEPA Science Advisory Board (SAB) analysis, the possibility of a net depletion was discussed, given that crop harvests have continued to increase while fertilizer additions have been steady, with concomitant high riverine losses of nitrate N (USEPA, 2007). In addition, denitrification losses are difficult to assess and add to the loss of N (David et al., 2009). However, we currently have no systematic collection of field data available to estimate either of these fluxes (i.e., net N mineralization or $N_2O + N_2$) across the MRB.

None of these modeling or NNI approaches have used recent agricultural data at the county scale, combined with perhaps the most critical landscape factor, tile drainage, to examine the source areas of and controls on recent winter and springtime riverine nitrate N flux across the MRB. Therefore, our objectives were (i) to relate agricultural and human inputs and outputs of N across the MRB to annual or winter–spring riverine nitrate export utilizing both state and county scale databases and (ii) to determine the most important drivers and MRB areas leading to riverine nitrate export. We used readily available, multiyear and recent data for the MRB, focusing on the river flow period most associated with Gulf of Mexico hypoxia. This analysis will help to identify where conservation efforts, or changes in agricultural production systems, should be targeted in the MRB if the type of riverine reductions (45% reduction in total N and total P riverine loads compared with 1980 to 1996 average loads) called for in the most recent Gulf Hypoxia Action Plan are to be successful (Mississippi River/Gulf of Mexico Watershed Nutrient Task Force, 2008).

# Materials and Methods

## Data Sources and Nitrogen Estimates

We constructed a county-level database (1768 counties) for the entire MRB (surface area 3.67 million $km^2$) using several data sources, including annual data from 1997 through 2006. National Agricultural Statistics Service data on crop acres planted and yields were obtained for corn, soybean, wheat (*Triticum aestivum* L.), rice (*Oryza sativa* L.), sorghum [*Sorghum bicolor* (L.) Moench], cotton (*Gossypium hirsutum* L.), alfalfa (*Medicago sativa* L.), and other hay acres for each county and year (USDA, 2008). Animal numbers included head counts of hogs, cattle, broilers, layers, and turkeys utilizing county-level data from the 1997 and 2002 Census of Agriculture, with other years interpolated (USDA, 2008). Fertilizer N sold in each county was estimated by using annual sales at the state level (AAPFCO, 2008), with county usage broken out proportionately from Census of Agriculture fertilizer, lime, and soil conditioner expenditure data from 1997 and 2002 (USDA, 2008), and other years estimated by interpolation. Annual fertilizer sales data are for the period 1 July of the previous year through 30 June of the year indicated, so that they represent the amount applied to the crops for the indicated year. Population data for each county were from the U.S. Census in 2000, when the MRB had a total population of 89.1 million (U.S. Bureau of the Census, 2008). Atmospheric deposition of N (defined as $NO_y$) was from National Atmospheric Deposition Program (NADP) estimates (http://nadp.sws.uiuc.edu) and included wet deposition of nitrate N, with dry deposition estimated as 70% of wet (David and Gentry, 2000; McIsaac et al., 2002; USEPA, 2007). Using ArcGIS v. 9.3 (Environmental Systems Research Institute, 2008), we calculated county-level deposition data from NADP isopleth maps of nitrate deposition for each year from 1997 to 2006, with estimation of dry as described above giving us $NO_y$.

Crop production estimates were used to determine N harvested for each crop and year. For corn, previous work had assumed a protein concentration of 10%, which corresponded to a grain N concentration of 1.6% (David and Gentry, 2000). Data from strip plots in many states now suggest that modern corn hybrids have a much lower protein concentration (e.g., Duvick et al., 2004a,b; University of Illinois, 2009) and that it probably has been decreasing since about 1985 (F.E. Below, personal communication, 2009). We assumed that corn had a 10% protein concentration in 1985 and that it decreased to 8.5% by 2006 (1.36% N). We used linear interpolation between these two values to estimate the corn protein concentration for our data from 1997 to 2006. For soybean, recent strip plot data (University of Illinois, 2009) indicate no change in the 35% protein concentration that we and others have previously used (e.g., David and Gentry, 2000); so we multiplied soybean bushels by 1.52 to obtain N harvested in kg N $bushel^{-1}$. Conversion values for wheat and sorghum bushels were 0.499 and 0.363, respectively (Goolsby et al., 1999). Cotton bales were converted to N harvested by multiplying by 13.6 (Mullins and Burmester, 1990; Brietenbeck and Boquet, 1993; Boquet and Brietenbeck, 2000), and rice hundred weight by 0.58 (Wilson et al., 1998). Alfalfa and hay harvest N conversions were 23.6 and 20 kg N $ton^{-1}$ harvested, respectively (McIsaac et al., 2002).

In previous work, David and Gentry (2000) estimated soybean $N_2$ fixation as 50% of the aboveground N in the plants, assuming an N harvest index of 80%. However, with increasing fertilizer use efficiency in corn and likely less residual nitrate N in soils, we believe $N_2$ fixation by soybean has been increasing. Gentry et al. (2009) measured soybean fixation as 77 and 60% of aboveground biomass N in 2001 and 2002 in a central Illinois watershed using a non-nodulating isoline. For the present study, we assumed soybean $N_2$ fixation was the source of 50% of aboveground N in 1985 and increased linearly to 60% by 2006. Soybean $N_2$ fixation estimated in this way increased on average from 94 to 110 kg N $ha^{-1}$ $yr^{-1}$ from 1997 to 2006 in our dataset. Other representative studies have used either a constant amount of N fixed by soybeans per hectare (Goolsby et al. [1999] used 78 kg N $ha^{-1}$ $yr^{-1}$), assumed a constant amount per bushel (0.91 kg N $bu^{-1}$ by McIsaac et al. [2002], which would give estimates from our data of 81 and 88 kg N $ha^{-1}$ $yr^{-1}$ in 1997 and 2006, respectively), or scaled the estimate as 50% of aboveground N (David and Gentry, 2000, which would give estimates from our data of 84 and 92 kg N $ha^{-1}$ $yr^{-1}$ in 1997 and 2006, respectively). For alfalfa $N_2$ fixation, we used a value of 218 kg N $ha^{-1}$ $yr^{-1}$, and for other hay 116 kg N $ha^{-1}$ $yr^{-1}$ (Goolsby et al., 1999; McIsaac et al., 2002).

To estimate animal manure, we used values derived from Goolsby et al. (1999) for hogs, cattle, broilers, layers, and turkeys of 0.027, 0.16, 0.001, 0.0034, and 0.0044 kg N $d^{-1}$ for each animal, respectively. Per capita values of N consumed by humans was estimated at 4.53 kg N $yr^{-1}$ (David and Gentry, 2000; McIsaac et al., 2002).

We also used a state-level database constructed by McIsaac et al. (2002) that was extended through 2007 using the modified coefficients described above for county-level analysis. For fertilizer N inputs, we used state sales data (AAPFCO, 2008) and did not need to use the Census of Agriculture expenditure data.

## Land Drainage

Tile drainage is a critical aspect of crop production systems in the agricultural Midwest (Baker et al., 2008) and has been in place since the 1860s in many states, with Illinois having most of the original clay tile systems installed between 1880 and 1895 (Baker et al., 2008). Tile systems continue to be replaced and expanded each year, with plastic pipe used since the 1950s. However, there are no public records of these recent installations (landowners have good maps of recent installations), as there were when clay tiles were first installed. The Census of Agriculture conducted every 5 yr by USDA occasionally included questions about drainage, but these questions were imprecise and asked about drainage differently each time; consequently, these data are of limited value. One of the best estimates of tile drainage is thought to be USDA (1987), which used 1978 Census of Drainage data, drainage specialists, and other government data sources, but these data were aggregated at the state level, and there can be large variability in tile drainage intensity across watersheds within a state (McIsaac and Hu, 2004). Because of the importance of tiles in lowering the water table and conveying nitrate N, there has been a great interest in spatially estimating where tiles are located. On small areas (fields to counties), aerial photography has been used to identify tile locations on the basis of differences in soil moisture patterns caused by the tiles (David et al., 2002, 2003). However, this is not feasible on large areas, and therefore soil survey information has been utilized, with drainage class used to estimate tile drained land. In this study, we used the county-level database compiled by Sugg (2007), where areas of row crops and poorly drained soils were calculated and disaggregated to the county level using geographic information system (GIS), allowing an estimate of percentage of the county area in tile drainage to be made. Sugg (2007) provides an excellent summary of what is known about the spatial pattern of tile drainage and gives details of the methods he used. In reviewing these data, we made changes to a few counties in two states, Illinois and Minnesota, where drainage estimates for a few of the counties were quite low for some unknown reason. Adjustments were made to both states on the basis of surrounding county averages, as the counties with low estimates were obvious when plotted because surrounding counties had much higher drainage estimates. For Illinois, a map of tile drainage in 1913 was used (based on cumulative sales of clay tile in each county, reported in Baker et al., 2008) as a basis, and for Minnesota consultation with a state expert (G.W. Randall, personal communication, 2007).

## Nitrogen Balances

We calculated several N balances using our database, all on a county-level basis. Components included all manure, which was calculated as the sum of cattle, hog, broiler, layer, and turkey manures. Crop N was the sum of corn, soybean, wheat, rice, cotton, and sorghum N harvested. All hay was the sum of alfalfa and other hay N harvested. Crop fixation was the sum of soybean, alfalfa hay, and other hay fixation. Net N inputs were calculated as (fertilizer N + $NO_y$ deposition + all manure + crop fixation + people N) – (crop N + all hay N). Nitrogen balance was (fertilizer N + $NO_y$ + all manure + people N) – (corn N + wheat N + rice N + cotton N + sorghum N).

## Riverine Nitrogen Concentrations, Loads, and Modeling

For the analysis of the large subbasins of the MRB, we used the state-level nutrient mass balances and USGS annual nitrate N concentrations and river flow measurements to construct yields (mass loss per unit area, kg N $ha^{-1}$) as reported in the SAB hypoxia report (USEPA, 2007) for the 1979 through 2007 water years. Water years are defined as runoff from 1 October of the previous year through 30 September of the indicated year. To investigate the relative roles of hydrology and tile drainage, we compared the large subbasins to two smaller watersheds that are intensively tile drained: the Des Moines River in Iowa and the Embarras River in Illinois. We obtained nitrate N concentrations (~22 values $yr^{-1}$) and daily flow data for the Des Moines River for the 2001 through 2006 water years from the Des Moines River Water Quality Network (Iowa State University, 2010). We also had nitrate N yields for the Embarras River at Camargo in east-central Illinois for the 1991 through 2008 water years, most previously reported in David et al. (1997) and Royer et al. (2006). Annual nitrate N loads for both the Des Moines and Embarras rivers were calculated using interpolation to expand the nitrate concentrations following Royer et al. (2006).

We used 153 unique watersheds with available nitrate N concentration and river flow data in the MRB where we could calculate January to June nitrate yield estimates. Data were obtained from USGS, USEPA, and state agency Web sites for 1997 through 2006. Sites were only included that met the following criteria: continuous flow monitoring by the USGS and at least three nitrate N concentration measurements each year (January–June) during this time period. Typically, there were about 40 winter–spring nitrate N concentrations for a given location. The nitrate N concentrations were averaged for the six-month period, multiplied by average river flow during this period, and then divided by the watershed area for a yield estimate. Watershed level estimates of all independent variables were made by aggregating all county data (averaged for 1997 to 2006) in the watershed using ArcGIS. The median watershed area in this analysis was 1982 km$^2$, with a range from 79 to 50,360 km$^2$ (Table 1). We used a correlation analysis to identify variables that were related to the January-to-June nitrate N yield for each watershed. A nonlinear model was then developed using the SAS NLIN procedure, with estimates of the variation explained in the final model by the individual terms using GLM (SAS Institute, 2003). We compared the distribution of important watershed characteristics for all counties in the basin with the 153 watersheds to be confident our model calibration watersheds reflected the entire basin (Table 1). To expand the final model to all counties in the MRB, we obtained January-to-June runoff data at the HUC8 level from the USGS for January to June each year from 1997 to 2006 (USGS, 2010a) and then used GIS to obtain runoff for each county, taking an overall 10-yr average. See USGS (2010b) for an explanation of hydrologic unit cords (HUCs).

# Results

## Large Subbasin Analysis

For the entire MRB, fertilizer N inputs have increased at 0.13 kg N ha$^{-1}$ yr$^{-1}$ since 1980 (linear regression equation, $n$ = 26, $r^2$ = 0.46, $p$ < 0.0001) to about 20 kg N ha$^{-1}$ yr$^{-1}$ for the MRB (Fig. 1). Nitrogen fixation has also steadily increased as soybean productivity has increased. Atmospheric deposition ($NO_y$) is a small component (8%) of the recent inputs (1997–2006), as inputs are dominated by fertilizer (52%) and $N_2$ fixation (40%). Crop harvest removal dominates outputs (~25 to 30 kg N ha$^{-1}$ yr$^{-1}$) during the past 30 yr, although the recent estimates have decreased by about 2 kg N ha$^{-1}$ yr$^{-1}$ compared with other recent work (e.g., USEPA, 2007) due to our adjustment in corn protein concentrations. Manure has shown a steady decline due to decreasing animal numbers across the basin and is now about 8 kg N ha$^{-1}$ yr$^{-1}$, with human consumption only 1 kg N ha$^{-1}$ yr$^{-1}$. Net N inputs during the 1997 to 2006 period have averaged 18.3 kg N ha$^{-1}$ yr$^{-1}$, with no trend. When looking at the same fluxes for the upper Mississippi River basin (Fig. 2), all N fluxes are much greater due to a greater dominance of agriculture across the landscape. Fertilizer inputs have been steady in this subbasin,

**Table 1. Distribution of watershed (model, *n* = 153), Mississippi River basin county (MRB, *n* = 1768), and counties with nitrate N yields >7.5 kg N ha$^{-1}$ (>7.5, *n* = 259) characteristics and January to June nitrate N yields averaged for 1997 to 2006.**

| Characteristic | Basin | Min. | 25th percentile | Median | 75th percentile | Max. |
|---|---|---|---|---|---|---|
| Crop fraction (%) | Model | 0 | 0.6 | 7.7 | 45.4 | 86.1 |
| | MRB | 0 | 1.1 | 14.3 | 45.9 | 100 |
| | >7.5 | 0 | 52.2 | 67.1 | 77.4 | 100 |
| Tile drainage (% of area) | Model | 0 | 0 | 0 | 0.8 | 53.5 |
| | MRB | 0 | 0 | 0 | 0.8 | 81.7 |
| | >7.5 | 0 | 8.9 | 25.2 | 48.4 | 81.7 |
| NOy (kg N ha$^{-1}$) | Model | 0.7 | 3.1 | 3.8 | 4.5 | 6.4 |
| | MRB | 0.8 | 3.3 | 4.1 | 4.8 | 7.5 |
| | >7.5 | 2.0 | 4.2 | 4.9 | 5.4 | 6.1 |
| Fertilizer N (kg N ha$^{-1}$) | Model | 0 | 3.9 | 12.6 | 41.9 | 84.6 |
| | MRB | 0 | 5.5 | 16.6 | 41.1 | 107 |
| | >7.5 | 0 | 49.1 | 62.4 | 72.9 | 97.9 |
| Manure N (kg N ha$^{-1}$) | Model | 0 | 4.6 | 11.2 | 20.3 | 75.3 |
| | MRB | 0 | 5.1 | 10.5 | 18.1 | 132 |
| | >7.5 | 0 | 5.1 | 9.5 | 17.2 | 132 |
| Human N (kg N ha$^{-1}$) | Model | 0 | 0.4 | 0.7 | 1.5 | 66.6 |
| | MRB | 0 | 0.3 | 0.6 | 1.3 | 98.4 |
| | >7.5 | 0.2 | 0.6 | 1.1 | 1.9 | 98.4 |
| N Balance (kg N ha$^{-1}$) | Model | 0.6 | 10.2 | 27.6 | 40.4 | 89.8 |
| | MRB | −2.1 | 13.9 | 26.1 | 38.8 | 184 |
| | >7.5 | 13.8 | 32.9 | 39.4 | 47.9 | 184 |
| Net N Inputs (kg N ha$^{-1}$) | Model | 2.2 | 15.5 | 27.7 | 38.3 | 92.4 |
| | MRB | −5.2 | 17.6 | 27.1 | 37.5 | 177 |
| | >7.5 | 1.6 | 24.0 | 30.9 | 39.4 | 177 |
| Area (km$^2$) | Model | 79 | 953 | 1982 | 4623 | 50,360 |
| Flow Jan. to June (cm) | Model | 0 | 6.3 | 16.7 | 28.4 | 58.8 |
| Yield Jan. to June (kg N ha$^{-1}$) | Model | 0 | 0.2 | 1.3 | 5.2 | 24.3 |

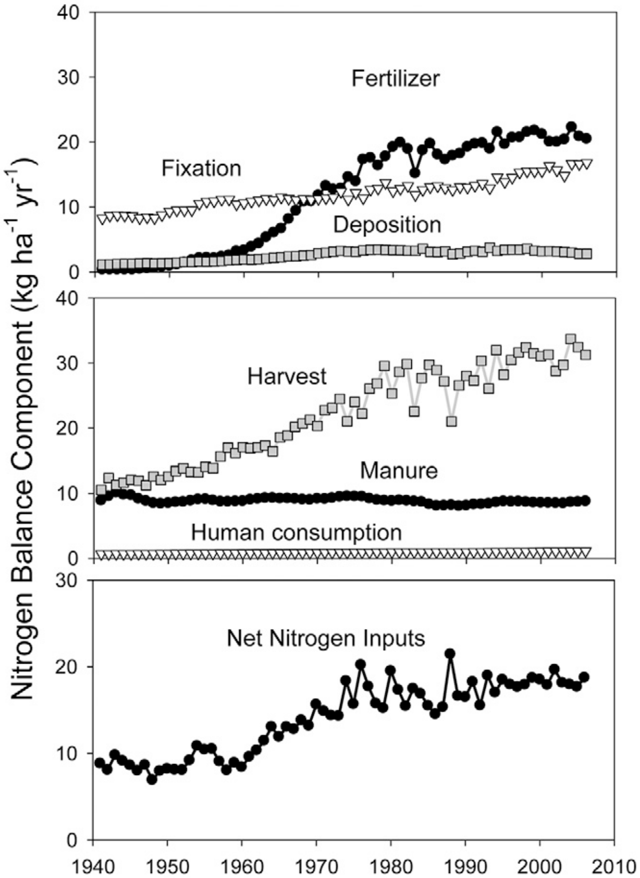


**Fig. 1. Annual inputs and outputs of N along with net N inputs for the entire Mississippi River basin for 1940 through 2006.**

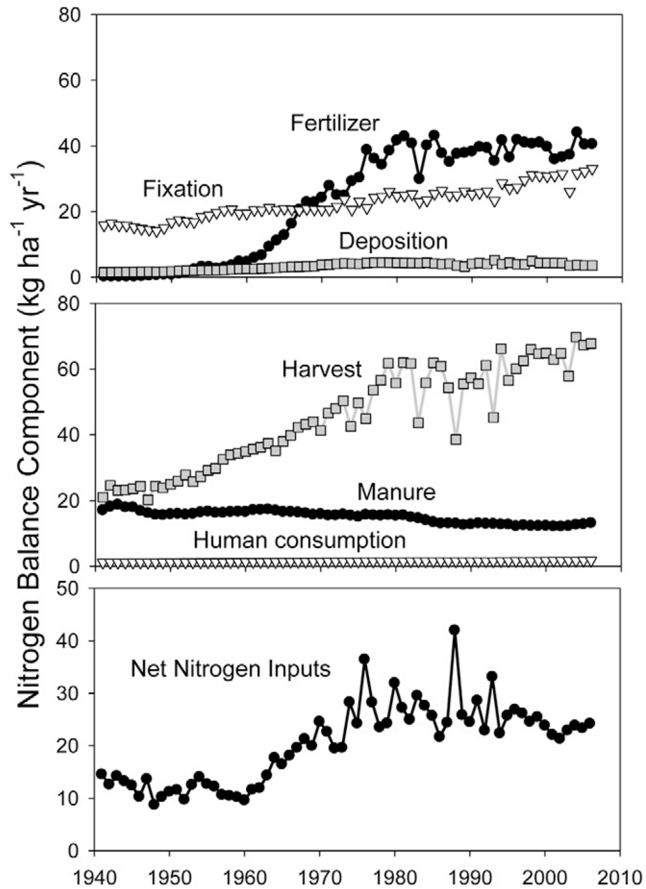


**Fig. 2. Annual inputs and outputs of N along with net N inputs for the upper Mississippi River subbasin for 1940 through 2006.**

at about 40 kg N ha$^{-1}$ yr$^{-1}$, and NNI has decreased at a low rate since the late 1970s (from 1975 through 2006 linear regression slope = –0.17 kg N ha$^{-1}$ yr$^{-1}$, $r^2$ = 0.14, $p$ = 0.037) and averaged 24 kg N ha$^{-1}$ yr$^{-1}$ during 1997 to 2006, about 6 kg N ha$^{-1}$ yr$^{-1}$ more than for the overall basin.

For the period 1997 to 2006, riverine nitrate yield for the Ohio, upper Mississippi, lower Mississippi, and Missouri subbasins averaged 5.9, 7.2, 1.1, and 0.8 kg N ha$^{-1}$ yr$^{-1}$, respectively. We plotted annual riverine nitrate N yield as a fraction of NNI (averaged for the previous 4 yr) for each of the subbasins versus annual water yield to illustrate the variability among the subbasins (Fig. 3). For the overall MRB nitrate N as a fraction of NNI is about 0.25, with the range among subbasins from 0.05 for the lower Mississippi to 0.30 for the upper Mississippi. There also was a great range within a subbasin depending on river flow. For example, for the upper Mississippi subbasin, riverine nitrate/NNI ranged from 0.11 in the dry year of 1989 (12.5-cm flow) to 0.60 in 1993 (47.7-cm flow). The Des Moines River had an average riverine nitrate/NNI of 0.53, whereas the Embarras River was 1.4 for 1991 through 2005. Three recent points on the Embarras (2006–2008) had riverine nitrate/NNI values much higher for a given flow than the previous period, reaching 4.2 in the wet year of 2008.

## County-Level Analysis

As expected, fertilizer N inputs by county (Fig. 4) and fraction of the county in crops (crop fraction) were highly correlated ($r$ = 0.94, $n$ = 1768, $p$ < 0.0001). The fraction of the county that

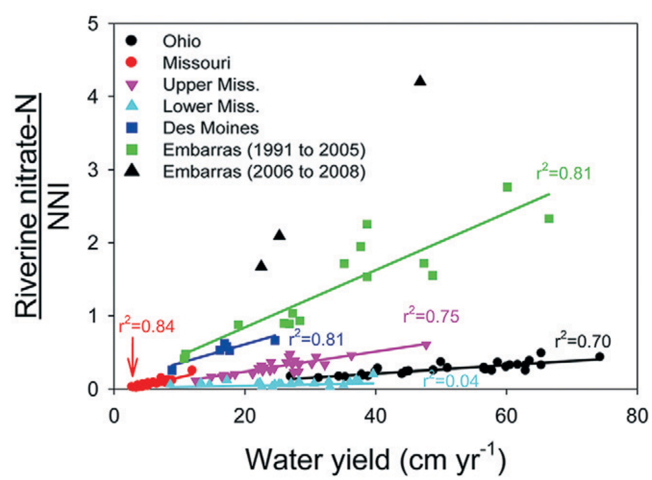


**Fig. 3. Annual riverine nitrate N loads divided by net N inputs (NNI; average of previous 4 yr) plotted against annual water yield of the river for the major Mississippi River subbasins (1979–2007), as well as the Des Moines River in central Iowa (2001–2006) and Embarras River in east-central Illinois (1991–2008).**

was tile drained was also strongly correlated with fertilizer N ($r$ = 0.61, $p$ < 0.0001) as well as crop fraction ($r$ = 0.60, $p$ < 0.0001). The tile drainage pattern on the MRB landscape clearly shows the U.S. Cornbelt, where artificially drained Mollisols have the highest productivity and are therefore primarily in corn and soybean rotations (Fig. 5). Net N inputs were weakly correlated with fertilizer N inputs ($r$ = 0.41, $p$ < 0.0001) and crop

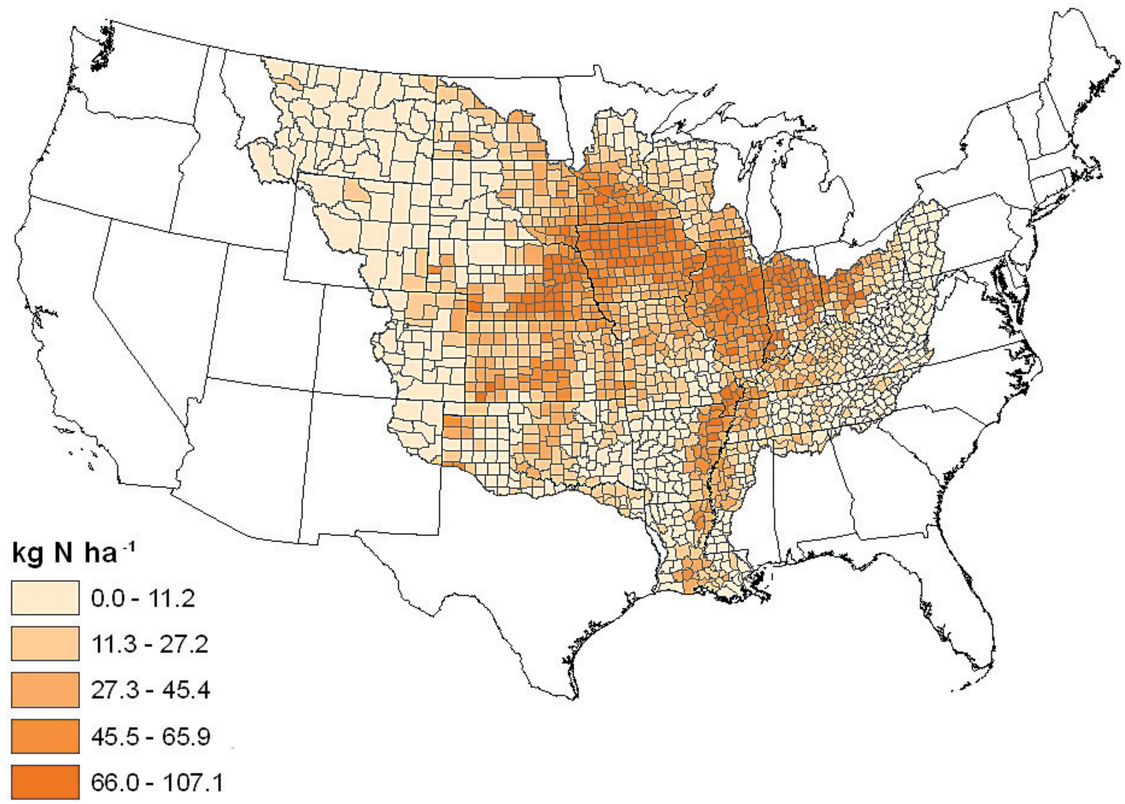


**Fig. 4. Average annual fertilizer N inputs by county for the Mississippi River basin for 1997 to 2006.**

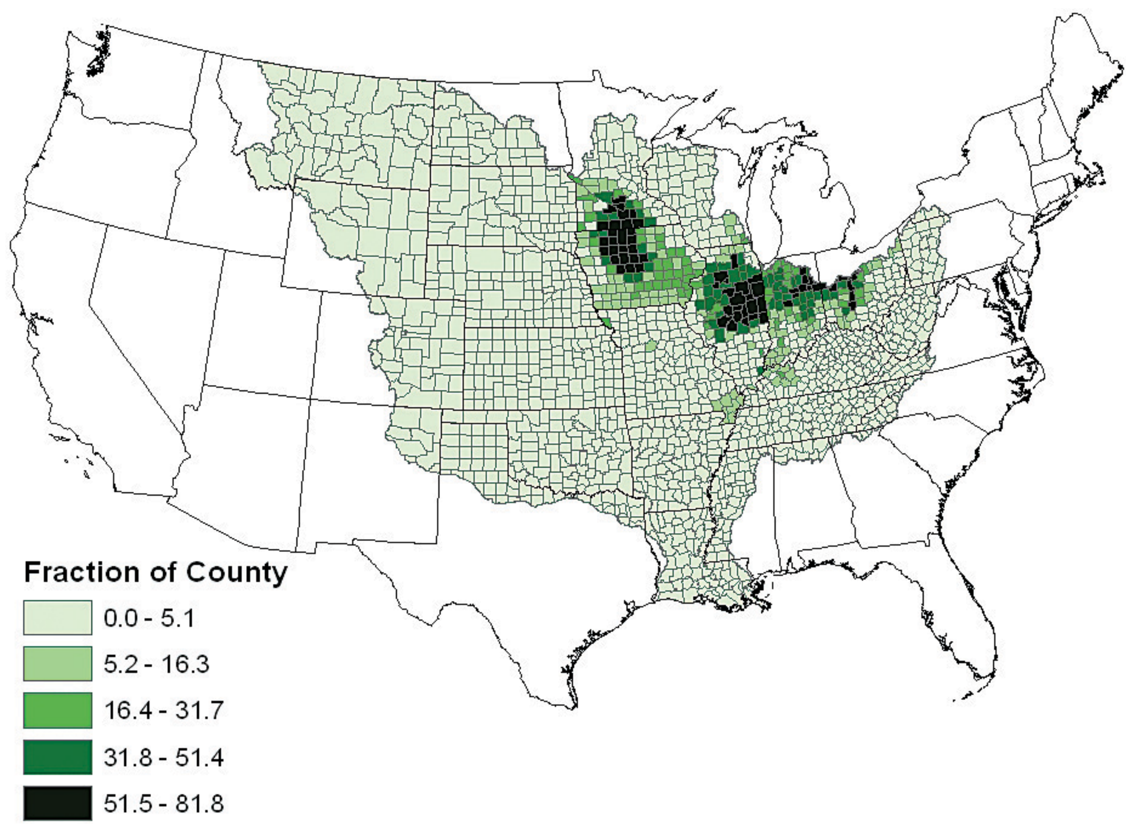


**Fig. 5. Fraction of county area that is tile drained in the Mississippi River basin.**

fraction ($r$ = 0.23, $p$ < 0.0001) and showed no clear spatial pattern across the MRB (Fig. 6). In forested or grassland areas, NNI values were generally <10 kg N ha$^{-1}$ and were greatest in areas with high animal numbers that generated manure. These areas were typically outside of the Cornbelt, so that NNI was only weakly correlated with drainage ($r$ = 0.07, $p$ < 0.03).

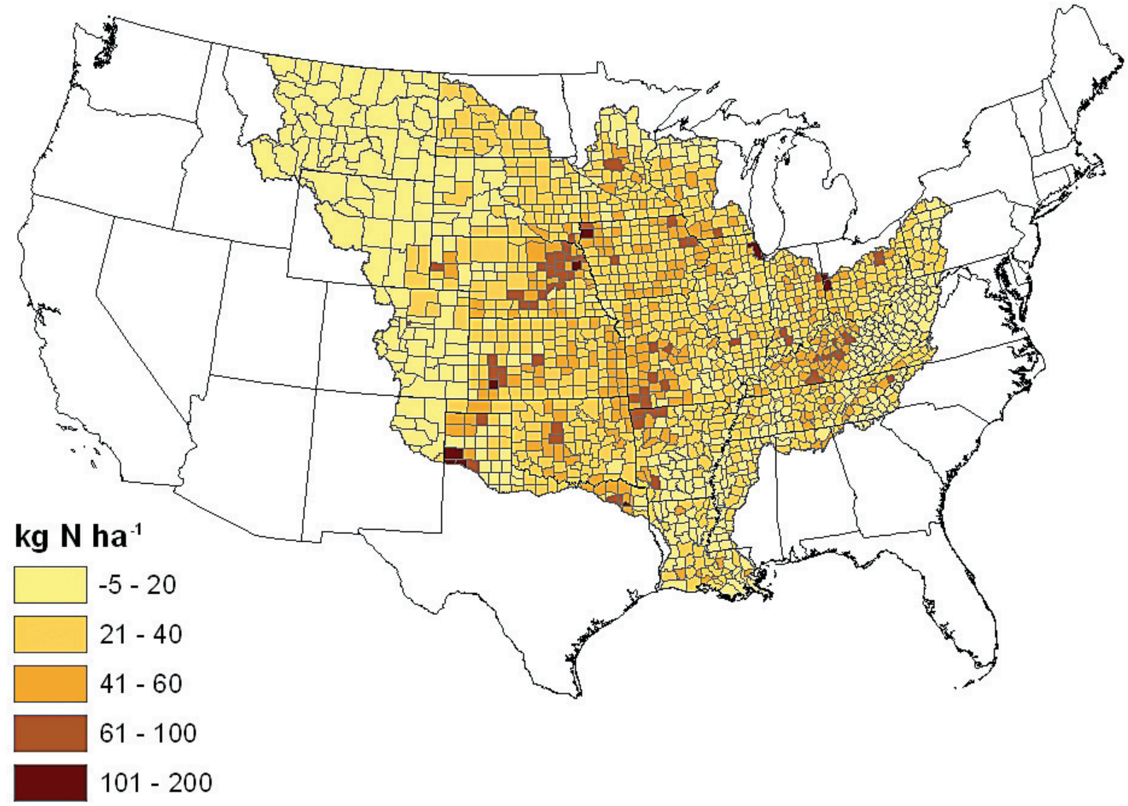


**Fig. 6. Average annual net N inputs by county for the Mississippi River basin for 1997 to 2006.**

We evaluated a wide range of models to predict watershed riverine nitrate N yield from our various N inputs, balances, and landscape factors for the 153 watersheds in the MRB for which we had riverine flux data available. Both linear and nonlinear models were evaluated using characteristics in Table 1 as well as others we thought might explain nitrate N yields. The model with the best fit that was developed used average county values aggregated to a watershed scale for 1997 to 2006 with a nonlinear regression analysis to estimate coefficients with the following form:

Modeled nitrate N yield (January to June kg N ha$^{-1}$)
= cm of river flow $x$ (0.0112 × kg fertilizer N ha$^{-1}$)$^{0.7783}$
+ 0.1988 × kg N consumed by humans ha$^{-1}$ + 0.21750
× fraction of the county tile drained

The overall $R^2$ for this model was 0.82, and all model parameters had 95% confidence limits that did not overlap with zero. As determined by GLM, all terms were significant ($p < 0.0001$), with river flow × fertilizer N accounting for 76% of the model explained variation, drainage 17%, and human consumption 7%. The distribution of important characteristics for our model compared with all counties in the MRB indicates that our model watersheds were generally representative of the overall MRB (Table 1). The county-based MRB had a greater median crop fraction than did our 153 watersheds, but the distribution was similar. Most other characteristics had similar medians and distribution, although the county maximums were always greater than those for the modeled watersheds. The predicted versus estimated January-to-June nitrate N yields show the range in values and fit of the final model (Fig. 7). The residuals had no trend with nitrate N yield. The second-best model had the same form and terms, with the exception of crop fraction in place of fertilizer ($R^2$ = 0.80), suggesting it is not fertilizer alone leading to nitrate N losses but the combination of the most productive soils (high in organic matter) that are tile drained and heavily cropped leading to nitrate N export.

We then applied the model to each county in the MRB to predict an average January-to-June riverine nitrate N yield for 1997 to 2006 (Fig. 8). The results indicated there were 259 counties with predicted nitrate N yields >7.5 kg N ha$^{-1}$, 375 counties in the 3 to 7.5 kg N ha$^{-1}$ class, and 1135 counties in the <3 kg N ha$^{-1}$ class. As we would expect from the final variables in the model, highest loads were found across

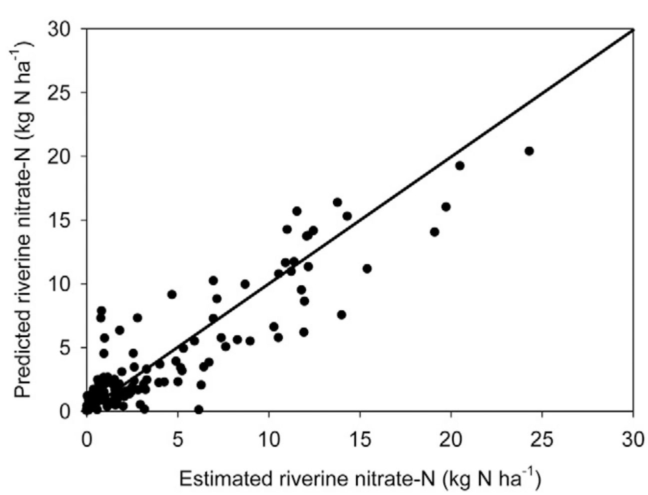


**Fig. 7. Predicted riverine nitrate N yields, January to June, for 153 unique subwatersheds in the Mississippi River basin for 1997 to 2006 compared with estimated yields from measurement data.**

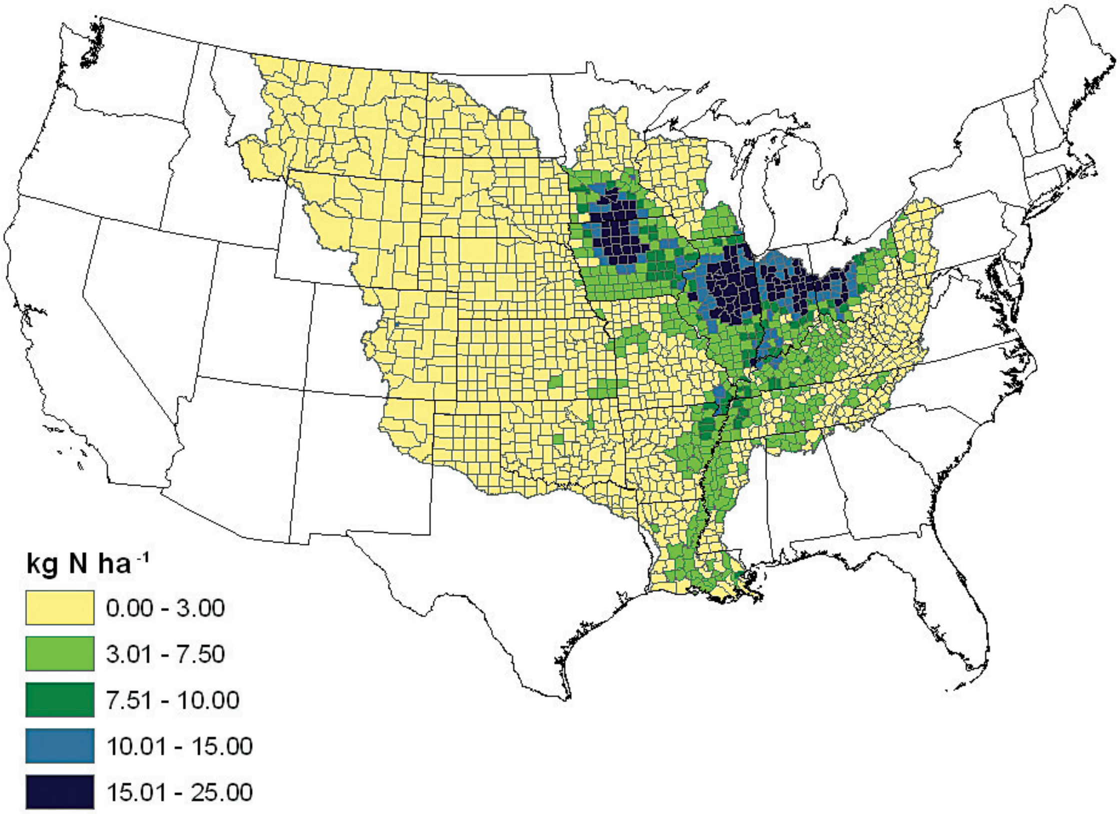


**Fig. 8. Predicted average riverine nitrate N yield, January to June, for all counties in the Mississippi River basin for the period 1997 to 2006.**

the Cornbelt from southern Minnesota into the Des Moines lobe of Iowa, across northern central Illinois, Indiana, and into Ohio. This map is consistent with the large measured loads from the upper Mississippi and Ohio basins and shows which counties in these subbasins would have the largest nitrate N yields. Watershed characteristics for the counties with nitrate N yields >7.5 kg N $ha^{-1}$ are given for reference in Table 1.

## Discussion

Our analysis at the large subbasin and county scales shows the overwhelming importance of fertilized crops on a tile-drained landscape leading to the greatest riverine nitrate N yields, with localized effects of sewage effluent. As Baker et al. (2008) pointed out, the most productive soils that are high in organic matter (with high soil N mineralization rates) have modified drainage, are intensively cropped, and therefore have the greatest fertilizer inputs, creating an agricultural system that is leaky with respect to nitrate N. Despite increasing crop harvests, NNI has only remained steady within the MRB due to slightly increasing fertilizer N inputs, decreasing corn protein concentrations, and increased $N_2$ fixation by soybean. The importance of hydrology on nitrate N yields was also observed, leading to a greater fraction of NNI exported by rivers in watersheds with higher water yields, more intense cropping, and increased tile drainage. For small watersheds such as the Embarras River, riverine nitrate N export was several times NNI, suggesting a carryover of N from one year to the next, or an additional source of nitrate N. The additional source is probably a net mineralization of soil organic N, as modern transgenic corn hybrids are perhaps accessing available soil N more efficiently than older hybrids. Other recent studies also noted that N balances, when including riverine export, may now be negative in tile-drained Mollisols with corn and soybean rotations in the upper Mississippi Basin (Jaynes et al., 2001; Jaynes and Karlen, 2008; Gentry et al., 2009).

Because another source of N is probably important to overall N balances and riverine losses combined with the role of tile drainage in increasing losses, we found that NNI was not a good predictor of riverine nitrate N loss across the MRB. In watersheds such as the Embarras, the difference between N inputs and outputs is now close to zero, without including riverine export or denitrification. However, riverine nitrate N losses are still quite large. McIsaac and Hu (2004) first documented this pattern when they assessed NNI in tile-drained versus non-tile-drained regions of Illinois. Vitousek et al. (2009) also noted that although N balances in Illinois were now smaller than they were previously, environmental impacts of intensive agricultural production on tile-drained fields were not declining.

Our modeled nitrate N yield for each county in the MRB illustrates clearly that the combination of fertilized corn on tile-drained watersheds is the dominate source of riverine nitrate N yields in the upper MRB, with another source area in southeastern Missouri and northeastern Arkansas. This result is consistent with the recent findings of Broussard and Turner (2009), who found that corn production contributes to riverine nitrate export across the United States. Atmospheric deposition of N and animal manure were not found to be significant explanatory variables in our model. Only human consumption, which is an indicator of sewage effluent inputs, was an additional important term in our model.

The model we developed was quite similar to that recently published by Booth and Campbell (2007), using data from 1990 to 2002, where they predicted spring nitrate N flux for the MRB. Their model was similar in form, with runoff × fertilizer accounting for 59% of the modeled load and human consumption 11%, which is similar to our corresponding values of 76 and 7%, respectively. However, they also reported animal manure (13% of modeled load) and atmospheric nitrate deposition (17%) as significant sources of nitrate N yields. Booth and Campbell (2007) did not include a term for tile-drainage, however, which we found explained 17% of our model variation and also affected the exponent on runoff × N fertilizer term. Booth and Campbell (2007) had an exponent of 3.083 on fertilizer N, whereas our final model had an exponent of 0.7783, and they stressed the nonlinear response of the river flow × fertilizer N term. However, when we used a nonlinear model without the tile drainage term (and including manure, similar to the Booth and Campbell (2007) model), the river flow × fertilizer term had an exponent of 2.682, similar to theirs. This suggests that the nonlinear nature of the fertilizer term found by Booth and Campbell (2007) may be a result of tile drainage increasing as fertilizer N increases across the MRB, with the increased tile drainage leading to a greater fraction of N loss as we observed in the large subbasin analysis. Our model explicitly shows this effect, whereas the larger fertilizer N exponent (>1) by Booth and Campbell (2007) indirectly reflects the interaction of tile drainage and fertilizer N inputs. The model of Booth and Campbell (2007) could lead to the conclusion that high fertilizer inputs alone could lead to large riverine fluxes, although with little tile drainage this is unlikely as McIsaac and Hu (2004) observed. When the tile drainage term was excluded in our analysis, there was a greater error sums of squares and several of the coefficients had 95% confidence limits that overlapped with zero. Overall, given the similarity of the major terms in both models that explained nitrate N yield, our map (Fig. 8) of nitrate N yield is quite similar to the Booth and Campbell (2007) Fig. 5, which showed the modeled nitrate N flux from agricultural sources.

We determined that human consumption of N, which is an indirect measure of sewage effluent N inputs to rivers, was statistically significant, but a relatively unimportant term in our model, explaining only 7% of the variation in nitrate N yield. This is similar to Booth and Campbell (2007), who found that it explained 11% in their model, and to the load data analyzed by the USEPA SAB (USEPA, 2007), where it was estimated that 14% of spring riverine nitrate N load to the Gulf of Mexico was from point sources, which were dominated by sewage effluent. Although reductions in point-source N would help reduce nitrate N yields in some streams of the MRB, in the overall scale of nitrate N losses, these reductions would probably have small impacts on winter–spring nitrate N loads delivered to the Gulf of Mexico.

The SPARROW model was been developed to identify sources and transport processes of both total N and P delivery to the Gulf of Mexico from the MRB (Alexander et al., 2008; Robertson et al., 2009). SPARROW incorporates in-stream removal processes for N and P, includes a tile-drainage factor, and estimates a long-term annual nutrient load using nutrient concentrations and daily flow measurements from 1975 to 1995, standardized to the 1992 base year, which was also the only year used for nutrient-source data. Our analysis does not attempt to predict nitrate N delivery to the Gulf of Mexico, but we would suggest that during the higher flow periods of winter and spring there is limited in-stream removal of nitrate N, as discussed by Royer et al. (2004, 2006). SPARROW indicated that 52% of the N delivered to the Gulf was from corn and soybean production, whereas 16% was from atmospheric deposition, 5% from manure on pasture and rangelands, and 9% from urban–human sources (Alexander et al., 2008). Again, this result is consistent with our model in that land supporting corn and soybean production (and the associated fertilizer N) is the primary driver, with human sources a small but important N input. A major difference from our results is the importance of atmospheric deposition, as well as other sources such as forests (5%). Robertson et al. (2009) present maps of all HUC8 watersheds within the MRB for both total N yields and total N delivered to the Gulf of Mexico using SPARROW. Their map of total N yields (their Fig. 3A) includes our high nitrate N yielding counties but incorporates a broader area of watersheds with high total N yields. These differences in estimated N sources and watershed yields of total N may be due to several factors: SPARROW includes just 1 yr of nutrient input data (1992), predicts annual N fluxes, predicts total N rather than nitrate N, and uses N data from 1975 through 1995.

We suggest that improved practices are needed to reduce nitrate N losses in the top 259 counties (where the modeled January–June nitrate N yields were >7.5 kg N $ha^{-1}$). Our analysis shows that these counties have high crop and drainage fractions, high fertilizer N inputs, and greater N balances compared with the overall MRB (Table 1). Reducing nitrate N loss from tile-drained fields will be difficult if they remain in corn and soybeans, given that for the best-yielding (i.e., highest crop production) fields the N balance may be negative. Our results and many other recent studies demonstrate that corn and soybean fields with tile drainage are quite leaky with respect to nitrate N, even when current best management practices are followed (Baker et al., 2008; Hatfield et al., 2009). As pointed out by the USEPA SAB (USEPA, 2007) and Hatfield et al. (2009), shifting to more complex crop rotations is needed to have a major effect on N losses. These rotations could include winter cover crops to capture nitrate N and legumes to fix N, which would better couple carbon and N cycles and reduce nitrate N losses (Tonitto et al., 2006; Drinkwater and Snapp, 2007). Other practices such as shifting from fall to spring N fertilization, side-dressing N, and changes in the type of N fertilizer all may help reduce nitrate losses. However, without increasing cropping system diversity, these changes are not likely to greatly reduce losses (USEPA, 2007; Broussard and Turner, 2009; Gardner and Drinkwater, 2009). Water table management has great promise for reducing losses (Skaggs and Youssef, 2008; Cooke et al., 2008), although there are still many questions about the fate of the retained water and nitrate N. Off-field practices that increase denitrification such as tile bioreactors (Blowes et al., 1994; Greenan et al., 2009; Chun et al., 2009, 2010), denitrification wall or trenches (Schipper and Vojvodic-Vukovic, 2001; Jaynes et al., 2008), wetlands at tile outlets (Kovacic et al., 2000; USEPA, 2007), or modification of drainage ditches (Powell et al., 2007ab) also could be adopted. These off-field methods allow current production systems to be used, while removing nitrate N at the edge of fields, but may exacerbate nitrous oxide emissions. Given the current agricultural policies in place, however, where commodity payments are dominant, producers have little incentive to install these off-field systems or make other changes to current crop production systems (Booth and Campbell, 2007).

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