Relating Net Nitrogen Input in the Mississippi River Basin to Nitrate Flux in the Lower Mississippi River: A Comparison of Approaches

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ABSTRACT

A quantitative understanding of the relationship between terrestrial N inputs and riverine N flux can help guide conservation, policy, and adaptive management efforts aimed at preserving or restoring water quality. The objective of this study was to compare recently published approaches for relating terrestrial N inputs to the Mississippi River basin (MRB) with measured nitrate flux in the lower Mississippi River. Nitrogen inputs to and outputs from the MRB (1951 to 1996) were estimated from state-level annual agricultural production statistics and NO_y (inorganic oxides of N) deposition estimates for 20 states that comprise 90% of the MRB. A model with water yield and gross N inputs accounted for 85% of the variation in observed annual nitrate flux in the lower Mississippi River, from 1960 to 1998, but tended to underestimate high nitrate flux and overestimate low nitrate flux. A model that used water yield and net anthropogenic nitrogen inputs (NANI) accounted for 95% of the variation in riverine N flux. The NANI approach accounted for N harvested in crops and assumed that crop harvest in excess of the nutritional needs of the humans and livestock in the basin would be exported from the basin. The U.S. White House Committee on Natural Resources and Environment (CENR) developed a more comprehensive N budget that included estimates of ammonia volatilization, denitrification, and exchanges with soil organic matter. The residual N in the CENR budget was weakly and negatively correlated with observed riverine nitrate flux. The CENR estimates of soil N mineralization and immobilization suggested that there were large (2000 kg N ha^{-1}) net losses of soil organic N between 1951 and 1996. When the CENR N budget was modified by assuming that soil organic N levels have been relatively constant after 1950, and ammonia volatilization losses are redeposited within the basin, the trend of residual N closely matched temporal variation in NANI and was positively correlated with riverine nitrate flux in the lower Mississippi River. Based on results from applying these three modeling approaches, we conclude that although the NANI approach does not address several processes that influence the N cycle, it appears to focus on the terms that can be estimated with reasonable certainty and that are correlated with riverine N flux.

Nitrogen enrichment of the biosphere is an issue of global concern (Vitousek et al., 1997). In many estuaries and coastal marine environments, biologically available N limits primary production. Consequently, anthropogenic additions of N to these systems contribute to a process of cultural eutrophication and periodic hypoxia and anoxia in lower portions of the water column (Rabalais et al., 1999; National Research Council, 2000; Diaz, 2001; Goolsby et al., 2001). Enrichment of freshwaters with nitrate may also pose human health risks and increase treatment costs for drinking water supplies.

Nitrate N flux from the Mississippi River basin (MRB) to the Gulf of Mexico has increased approximately threefold from 1955 to 1998 (Goolsby et al., 1999; Goolsby and Battaglin, 2001), and is considered to be a primary cause of hypoxia in the Gulf (Rabalais et al., 1999, 2001; National Research Council, 2000). Efforts to reduce N delivery to coastal waters can be guided by models that quantify the relationship between N inputs to drainage basins and the subsequent riverine N flux to the coasts.

As part of the U.S. White House Committee on Environment and Natural Resources (CENR) effort to assess factors influencing the extent of hypoxic waters in the northern Gulf of Mexico, Goolsby et al. (1999) developed a nearly comprehensive accounting of N inputs and outputs for the MRB (Table 1). This CENR N assessment included estimates for N mineralization, immobilization, and denitrification in the soil, and N volatilization from crop canopies, although considerable uncertainty in these estimates was recognized. Estimated total N input to the MRB from 1980–1996 was approximately equal to estimated total N outputs (including riverine N export), which suggested that all N inputs and outputs were accounted for. In-stream denitrification was not included in the assessment, however, and this flux may be substantial (Alexander et al., 2000). To include in-stream denitrification and maintain a balanced N budget, estimates of other terms would have to be modified. Additionally, the difference between terrestrial N inputs and outputs (not including riverine N flux, that is, the residual that would be available for transport to surface waters) was weakly and negatively correlated with observed nitrate flux from the MRB to the Gulf of Mexico (Fig. 1). In contrast, McIsaac et al. (2001) estimated that net anthropogenic input (NANI) to the basin increased during this time and was highly correlated with riverine N flux. Nitrate is only one form of riverine N, but the analysis of Goolsby and Battaglin (2001) indicates that increases in nitrate account for essentially all of the increase in total N concentration in the lower Mississippi River during the 20th century. Thus, nitrate flux is highly correlated with total N flux in the Mississippi River, and consequently total N flux was also negatively correlated with the CENR N budget residual, and positively correlated with NANI.

Goolsby and Battaglin (2001) presented a three-term regression model that accounted for 89% of the variation in annual nitrate flux from the MRB during 1955–1999. The three terms were annual water yield, CENR

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Abbreviations: CENR, Committee on Natural Resources and Environment; MRB, Mississippi River basin; NANI, net anthropogenic nitrogen input; NNI, net nitrogen input.

Table 1. Components of the Committee on Natural Resources and Environment (CENR) N budget (Goolsby et al., 1999). Terms in italic type were also included in the calculation of net anthropogenic nitrogen input (NANI).

N inputs	N outputs
Soil N mineralization	*N in crop and pasture harvest*
N fertilizer	Crop senescence losses
N fixation	Immobilization
Atmospheric NH_3 deposition (wet only)	Manure N volatilization
Atmospheric NO_y deposition (wet and dry)	Soil denitrification
Animal manure N less volatile losses	Fertilizer volatilization
Municipal sewage	
Industrial point source inputs	

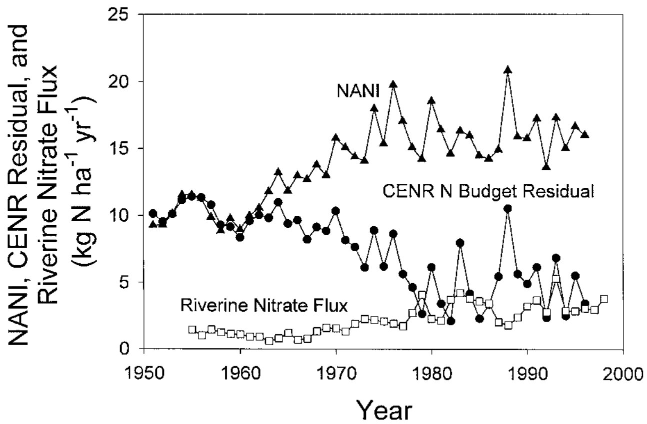

Fig. 1. Time series of Committee on Natural Resources and Environment (CENR) N budget residual (input − output), net anthropogenic N inputs (NANI), and estimated riverine nitrate flux in the lower Mississippi River based on nitrate concentration measurements at St. Francisville, LA and discharge measurements at Tarbert's Landing and the Old River outflow to the Atchafalaya River.

N budget residual from the previous year, and fertilizer N input from two years previous to the current year. The combination of fertilizer use and average annual stream flow accounted for 86% percent of the variation in nitrate flux. The N budget residual term accounted for an additional 3% of the variation in nitrate flux, but the sign of the coefficient was negative. Thus, even when the influences of hydrologic processes were considered, the CENR N budget residual for the MRB was weakly and negatively correlated with the observed riverine nitrate flux in the Mississippi River.

It is possible that the weak negative correlation between riverine N flux and the CENR N budget residual was due to differences in the mobility of different forms of N input (e.g., manure vs. fertilizer) and differences in N transport efficiencies of different soil types, landscapes, and watersheds. The lack of a positive correlation may also be due to inaccuracies in the CENR estimates of N inputs and outputs to the basin, especially in estimating N exchanges with soil organic matter, denitrification in the soil, and N volatilization from crop canopies. There is considerable uncertainty associated with estimates of these terms. Using data from the 1992 Census of Agriculture, Burkart and James (1999) presented an agricultural N budget for the Mississippi River that was in many ways similar to the CENR approach. Unlike the CENR budget, however, Burkart and James (1999) included no estimate of immobilization of N in soil organic matter and 73% of the volatilized ammonia was estimated to be redeposited within the MRB. Burkart and James (2001a) later modified their budget to include an estimate of immobilization that was similar to the CENR estimate of immobilization. In spite of this, both the CENR and Burkart and James (1999, 2001a) budgets estimated net soil organic N losses (the difference between mineralization and immobilization) of approximately 60 to 40 kg N ha^{-1} yr^{-1}, which is not consistent with observations that indicate soil organic N has been relatively constant on soils that have been under continuous cultivation for 60 yr or more (Jenny 1941; Buyanovsky et al., 1997; Aref and Wander, 1998).

The estimated N immobilization in the CENR and Burkart and James (2001a) N budgets is partly based on ^{15}N studies that recover 40% of applied inorganic ^{15}N in soil organic matter at the end of the growing season. This is partly due to crop uptake of ^{15}N and return of crop residues to the soil. This method, however, does not include immobilization of other sources of N, such as biologically fixed N, or N mineralized from the soil that is taken up by the crop and subsequently returned to the soil in crop residues. Thus, CENR and Burkart and James (2001a, 2001b; unpublished data, 2002) appear to have underestimated the return of N to the soil organic N pool.

Most recently, Burkart and James (2001b; unpublished data, 2002) calculated agricultural N budgets for the MRB using Census of Agriculture data between 1949 and 1997 in which they revised their earlier approach (Burkart and James, 1999, 2001a) to estimating mineralization of soil organic matter and did not estimate atmospheric N deposition. Recognizing the relative steadiness of organic N in soils that have been under cultivation for several decades, they estimated mineralization based on the estimated N content in the previous year crop residue. The value of this estimate was similar to the estimated mineralization based on soil organic matter content. The estimate of immobilization by Burkart and James (2001b; unpublished data, 2002), however, does not include all of the N in crop residues returned to the soil and, therefore, it continues to be considerably less than mineralization, which is not consistent with steady soil organic N. Furthermore, the Census of Agriculture was conducted only once every five years and did not occur during several significant drought years in the 1980s. These droughts are important features of the N budget as they led to reduced crop N harvest and probably increased N transport to rivers in subsequent wet years. Unlike the CENR N budget, there has been no quantitative assessment of whether the Burkart and James (1999, 2001a,b; unpublished data, 2002) N budget residual is correlated with riverine N flux.

In contrast to the nearly comprehensive N accounting approaches of CENR and Burkart and James (1999), the approaches of Howarth et al. (1996) and Caraco and Cole (1999) do not include denitrification, volatilization, or exchanges with soil organic matter. Yet, these approaches correlate well with measurements of riverine N flux across a wide range of settings, and may therefore provide insight into the variables that are most relevant to N transport in rivers.

Howarth et al. (1996) found that a linear relationship with regional net anthropogenic N input (NANI) accounted for 73% of the between-river variation in long-term (10–20 yr) average riverine N flux from 12 major river basins in the temperate region draining to the northern Atlantic Ocean. Net anthropogenic nitrogen input was calculated as the difference between anthropogenic N inputs (NO_y deposition, fixation associated with crop production, and food, feed and fertilizer imports) and outputs (food and feed exports) (Table 1). Using the same approach, Jordan and Weller (1996) accounted for 73% of the variation in the riverine nitrate flux among U.S. rivers in the 1980s, although nonlinearity was observed. Riverine nitrate flux was low when NANI was less than 20 kg N ha^{-1} yr^{-1}, but increased dramatically as NANI exceeded this value. In both studies (Howarth et al., 1996; Jordan and Weller, 1996), riverine N fluxes were approximately 20% of NANI, and consequently the fate of the remaining 80% of the NANI was unquantified. This N could have been denitrified, or stored in soils or ground water. The consistency of the percentage of NANI that becomes riverine N flux may be due to the relatively high mobility of the nitrate ion, which tends to be the dominant form of riverine N in systems with large NANI. Additions of N to the landscape tend to increase nitrate in the soil, which is then subject to leaching and transport to surface water.

Caraco and Cole (1999) developed the following model that used gross anthropogenic N inputs and hydrologic transport efficiency to account for 80 to 90% of the between-river variation in average annual riverine nitrate flux in 35 major rivers throughout the world:

$$NF = 0.7(PSIN + 0.4 \times WY^{0.8} \times WSIN) \quad [1]$$

where NF is the average annual nitrate N flux (kg N ha^{-1} yr^{-1}), PSIN is the point source input of sewage (kg N ha^{-1} yr^{-1}), WY is the annual water yield (m yr^{-1}), and WSIN is the watershed inputs of N fertilizer and NO_y deposition (kg N ha^{-1} yr^{-1}). This equation and the NANI approach had been primarily used to examine between-basin variation in long-term average annual N flux.

Recently, McIsaac et al. (2001) developed a model that used the NANI approach in combination with water yield that accounted for 95% of the variation in annual nitrate flux in the lower Mississippi River for the 1960–1998 period:

$$NF_m = 0.66 \times WY^{0.93} \times \exp(0.13 \times NANI_{2\text{–}5} + 0.06 \times NANI_{6\text{–}9}) \quad [2]$$

where NF_m is the annual nitrate N flux in lower Mississippi River (kg N ha^{-1} yr^{-1}), $NANI_{2\text{–}5}$ is the average annual net anthropogenic N input during the previous 2 to 5 yr (kg N ha^{-1} yr^{-1}), $NANI_{6\text{–}9}$ is the average annual net anthropogenic N input during the previous 6 to 9 yr (kg N ha^{-1} yr^{-1}), and WY is the annual water yield (m yr^{-1}).

It is not known how well Eq. [1] estimates temporal variation in riverine nitrate flux in the lower Mississippi River, and whether it would represent an improvement over Eq. [2]. It is also not known how using a more complete N budget residual in place of NANI in Eq. [2] would influence the performance of the model. Ultimately, a comprehensive model that simulates N inputs, transformations, and transport is needed to estimate changes in riverine N fluxes that will result from changes in terrestrial N inputs and outputs. Currently, correlation with partial N budget residuals appears to account for much of the variation in riverine N flux from temperate regions (Howarth et al., 1996; McIsaac et al., 2001). Systematically adding N flux terms to partial N budgets or subtracting terms from comprehensive N budgets, and evaluating the subsequent correlation with observed riverine nitrate flux, will identify combinations of N input and output estimates that are correlated with riverine N flux and those that are not. This may help identify N budget terms that have significantly different transport properties, or that have been inaccurately estimated in previous N budgets.

The objective of our study was to examine the relationships between temporal variation in riverine nitrate N flux in the lower Mississippi River during 1960 to 1998 and alternative combinations of terrestrial N inputs and outputs to the MRB. The relationships considered include the Caraco and Cole (1999) model (Eq. [1]) and the equation of McIsaac et al. (2001) (Eq. [2]) with several alternative net N input terms. The alternative net N input terms considered include NANI, the CENR N budget residual, modifications of NANI to include components of the CENR N budget (Goolsby et al., 1999), and modifications of the CENR N budget residual including an approximation of the approach of Burkart and James (2001a). This analysis will provide a basis for understanding differences in predictions and inferences drawn from these alternative N budget approaches. Additionally, this analysis will help identify research that will improve our understanding of the relationship between terrestrial N cycles and riverine nitrate flux in the MRB.

METHODS

Riverine Nitrate Concentrations and Flux

Riverine nitrate concentration was measured at St. Francisville, Louisiana, between 1955 and 1999 as described by Goolsby et al. (1999). Annual water yield was based on discharge measured at Tarbert's Landing, Mississippi, and the flow diverted to the Atchafalaya River via the Old River outflow. Ninety-eight percent of the entire MRB lies upstream of these measurement locations. Between 1955 and 1967, water samples were collected daily and combined for periods of 10 to 30 d to form a composite sample that was analyzed for nitrate with the phenoldisulfonic acid method. Nitrate flux during this period was estimated by multiplying the composite concentration by the discharge measured during the period that samples were collected. After 1967, water samples were taken approximately once per month and were not composited. Nitrate flux for this period was calculated using the rating curve approach as described by Cohn et al. (1992) and Goolsby et al. (1999). In employing the rating curve method, it was observed that the concentration at St. Francisville depended on discharge at Tarbert's Landing and the proportion of discharge coming from the Mississippi River above the Missouri River, which has considerably greater nitrate concentration than the Missouri or the Ohio Rivers. The rating curve that accounted for the greatest portion of variation in nitrate concentration at St. Francisville was based on discharges from the Mississippi River at Alton, Illinois, and discharge at the mouths of the Missouri and Ohio Rivers.

In the early 1970s, the method of determining nitrate concentrations was changed to automated cadmium reduction. There does not appear to be any change in concentrations or flux estimates associated with the changes in methodologies employed during different periods (Goolsby et al., 1999; Goolsby and Battaglin, 2001). Annual flow-weighted nitrate concentrations were calculated by dividing the estimated annual flux by the annual discharge.

Estimating Nitrogen Inputs

With minor exceptions, we used methods described by Goolsby et al. (1999) to estimate annual N inputs and outputs for the 20 states that cover 89% of the MRB (Table 2). Specific N inputs and outputs of these states were summed and expressed per unit area (3.39 million km^2) of the 20 states. This N use intensity was assumed to represent the entire drainage basin including the 11% of the drainage basin that lies outside of these states. Approximately 8% of the 20-state region lies outside of the MRB, and approximately half of this area (4% of the 20 state region) is in the western portions of Montana, Colorado, and Wyoming, where N use intensity is low due to low precipitation and limited irrigation development. Inclusion of this area in the estimation of N use intensity in the MRB will cause a systematic underestimation of the actual N use intensity in the basin by approximately 4%. Because the N use intensity in this region has changed little between 1950 and 1996, this relatively constant error will have little influence in our analysis of the relationship between temporal variation in N use intensity in the basin and temporal variation in riverine nitrate flux.

Table 2. States used to estimate N inputs and outputs for the Mississippi River basin (MRB), area of each state in the basin, and total state area.

State	Area of state in MRB	Total state area
	1000 km^2	
Arkansas	137	137
Colorado	150	270
Iowa	146	146
Illinois	146	146
Indiana	85	94
Kansas	213	213
Kentucky	104	104
Louisiana	92	121
Minnesota	128	219
Missouri	181	181
Mississippi	61	123
Montana	314	381
Nebraska	201	201
Ohio	77	107
Oklahoma	181	181
South Dakota	198	200
Tennessee	109	109
Wisconsin	101	146
West Virginia	53	63
Wyoming	182	253
Total	2857	3394

Major N inputs and outputs compiled for this analysis are presented in Fig. 2. Nitrogen fertilizer input was taken from state-level fertilizer sales statistics compiled by Alexander and Smith (1990), Battaglin and Goolsby (1995), and USDA (1998). The NO_y deposition from 1984 to 1996 was estimated based on the National Atmospheric Deposition Program measurement of wet NO_3^- deposition and assuming dry NO_3^- deposition to be 0.7 times the wet (Goolsby et al., 1999). In contrast to the CENR analysis, which assumed constant NO_3^- deposition prior to 1984, we used the approach of David and Gentry (2000) and assumed that NO_y deposition from 1951 to 1984 was proportional to national estimated NO_x emissions (USEPA, 2000). For each year prior to 1984, the 1984 to 1996 average NO_y deposition was multiplied by the ratio of annual estimated NO_x emissions to the estimated 1984 to 1996 NO_x emissions. For instance, estimated national NO_x emissions in 1951 were 43% of 1984 to 1996 average emissions; therefore, the estimated NO_y deposition for 1951 was 43% of the 1984 to 1996 estimated deposition. Howarth et al. (1996) estimated that, on average, 94% of NO_y deposition was anthropogenic in origin. In our calculation of NANI, we did not distinguish between anthropogenic and non-anthropogenic portions of NO_y and included all of the estimated NO_y deposition as an input.

The NANI approach assumes that deposition of atmospheric ammonia and organic N is largely derived from local

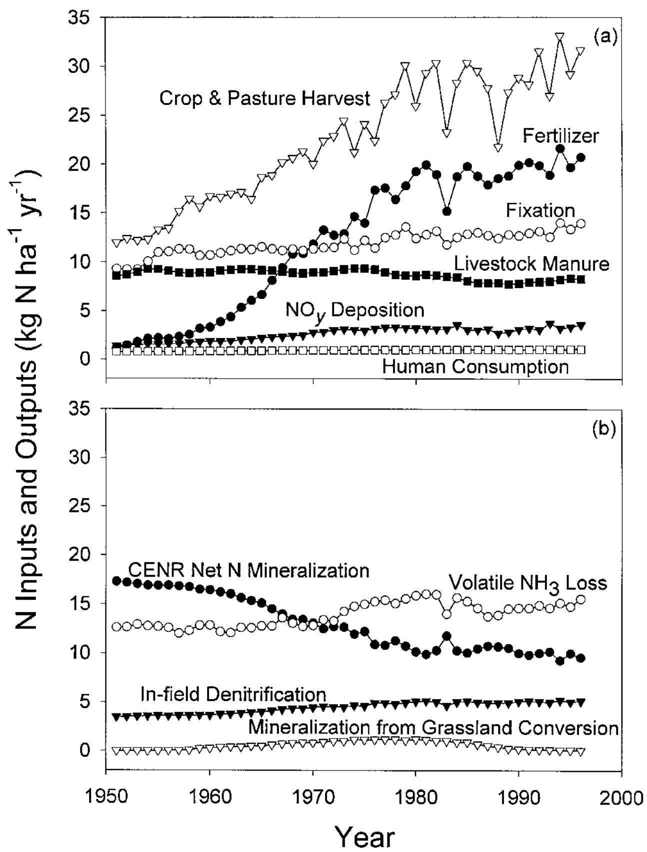

Fig. 2. Estimated N inputs to and outputs from the 20-state region covering the Mississippi River basin used to (*a*) calculate net anthropogenic nitrogen input (NANI) and (*b*) estimate soil N mineralization resulting from conversion of hay and pasture to cropland, in addition to Committee on Natural Resources and Environment (CENR) estimates of net mineralization of soil organic N (mineralization − immobilization), crop senescence losses, and in-field denitrification.

volatilization of fertilizer and manure, and thus constitutes an internal cycle rather than a new input (Howarth et al., 1996; Ferm, 1998; Fahey et al., 1999). Ferm (1998) reviewed literature on NH_x deposition in Europe and noted considerable uncertainty in measurements of short-range deposition from particular sources. Transport length is influenced by wind velocity, precipitation, and NO_x and SO_x concentrations. In spite of this variability, several studies concluded that approximately 50% of the volatilized ammonia was redeposited within 50 km of the source. This was consistent with calculations using a simple model that suggested half of the volatilized ammonia would be deposited every 65 to 130 km from the source. Analysis of deposition outside of the Netherlands (a major source area in Europe) indicated that deposition beyond 300 km appeared to be halved every 400 km. Burkart and James (1999, 2001a) applied a modification of the Ferm (1998) results to the MRB and estimated that 73% (4 of 5.5 Tg N yr^{-1}) of the ammonia volatilized in the MRB was redeposited within the basin. Burkart and James (1999, 2001a) assumed 75% redeposition of NH_x within 400 km of the source, which is a lower redeposition rate than suggested by the analysis of Ferm (1998). At a minimum, Ferm's analysis suggests 75% of volatilized ammonia would be redeposited within 300 km of its source. If we take the mid-range of Ferm's short distance transport calculations, which indicate that NH_x deposition is halved every 100 km up to 300 km, this suggests that 87.5% of volatilized NH_x would be redeposited within 300 km of the source. If Ferm's results are applicable to the MRB, then Burkart and James' (1999, 2001a) modification of Ferm's results underestimates redeposition of ammonia volatilized within the basin. Additionally, Burkart and James (1999, 2001a) did not consider deposition of NH_x in the basin that originated from ammonia volatilized outside the western (upwind) boundary of the basin. Such an influx of N would probably be small, but it would replace some of the volatilized NH_x that was estimated to drift out of the eastern (downwind) boundary of the basin. This omission by Burkart and James (1999, 2001a) further contributes to an overestimation of net loss of volatile NH_x from the MRB.

Biological N_2 fixation in association with legume crops, hay, and pastures was estimated based on values reported in the literature for soybean [*Glycine max* (L.) Merr.] (0.91 kg N bu^{-1}), alfalfa (*Medicago sativa* L.) (218 kg N ha^{-1} yr^{-1}), non-alfalfa hay (116 kg N ha^{-1} yr^{-1}), eastern grassland pasture (15 kg N ha^{-1} yr^{-1}), and western grassland pastures (1 kg N ha^{-1} yr^{-1}) (Goolsby et al., 1999; David and Gentry, 2000). Western pastures were those in the states west of Minnesota, Iowa, Missouri, Arkansas, and Louisiana. Soybean production and area devoted to hay and pasture were taken from state-level historical statistics compiled by USDA (1998).

Nitrogen harvested in corn (*Zea mays* L.), soybean, wheat (*Triticum aestivum* L.), sorghum [*Sorghum bicolor* (L.) Moench], and hay was estimated from state-level crop production statistics multiplied by the average N content of each product (Table 3). Except for soybean, these values were identical to those used by Goolsby et al. (1999). For soybean, Goolsby et al. (1999) used a value of 1.78 kg N bu^{-1}, which is considerably greater than 1.5 kg N bu^{-1} used by Burkart and James (1999, 2001a) or 1.61 kg N bu^{-1} used by Kellogg et al. (2000). We used the value of Kellogg et al. (2000).

Harvested material from pastures was estimated to be a fraction of the yield reported for non-alfalfa hay (classified as "all other hay" in USDA statistics) depending on the type of pasture. Cropland used as pasture was assumed to produce half the yield of non-alfalfa hay in that state, eastern pastures were assumed to produce one-fourth the yield of non-alfalfa hay, and western pastures were assumed to produce one-tenth the yield of non-alfalfa hay (Goolsby et al., 1999).

The NANI approach consists of the sum of N inputs in fertilizer, biological fixation, and atmospheric NO_y deposition, minus the net N exported from the basin in food and feed products (Howarth et al., 1996). The net N export from the basin in food and feed products was calculated as the sum of N in harvested crops, hay, and pasture, minus the N retained in animal wastes and retained for human consumption. The N excreted in livestock waste was estimated based on population sizes and estimates of excreted N per capita for different species and age classes (Table 4). Actual N consumption by domestic animals in the basin will be greater than the excreted N by the amount that is assimilated into animal tissues and animal products (e.g., milk and eggs). The N in meat, milk, and eggs will be available for human consumption or export from the basin, and in our approach it implicitly remains with the harvested crops that is available for export or human consumption in the MRB. The N consumed by humans in the MRB was estimated to be 4.53 kg N $person^{-1}$ yr^{-1} based on analysis of protein consumption and age structure of the Illinois population (David and Gentry, 2000).

Human population was estimated from state-level U.S. Census data and interpolation between census years. Livestock population sizes were taken from year-end inventories of populations in state-level production statistics compiled by USDA (1998). The year-end inventories were assumed to be representative of average populations during the entire year for all species except for steers, turkeys, and two thirds of heifers, which were assumed to produce manure N for an average of 170, 122, and 170 d, respectively (Goolsby et al., 1999).

Net anthropogenic nitrogen input does not address exchanges with soil organic N and implicitly assumes that organic N mineralization and immobilization are approximately equal. This latter assumption is reasonable if soil organic N content is relatively steady over time. Jenny (1941) concluded that soil organic N declines rapidly after initial cultivation and achieves

Table 3. Nitrogen content in crop and pasture products used to estimate annual N harvested in the Mississippi River basin.

Crop	Harvest unit	N
		kg
Alfalfa	ton	23.6
Corn for grain	bu	0.331
Corn for silage	ton	3.27
Sorghum for grain	bu	0.363
Sorghum for silage	ton	6.70
Soybean	bu	1.61
Wheat	bu	0.499
Other hay	ton	20.0
Pasture	ton	20.0

Table 4. Estimates of N excreted in animal manure.

Animal	N excreted
	kg d^{-1}
Hogs and Pigs	0.027
<60 lb	0.009
60–119 lb	0.027
120–179 lb	0.031
>180 lb	0.041
Milk cows	0.204
Beef cows	0.150
Dairy heifers	0.141
Steers and bulls	0.150
Slaughter cattle	0.104
Chickens and hens	0.0015
Pullets and broilers	0.0010
Tom turkeys	0.0054
Hen turkeys	0.0034
Sheep and lambs	0.023
Horses and ponies	0.127

a new steady state value after about 60 yr. The new steady state level will depend on the crop management system and crop yields. The limited number of measurements and simulation studies that are available to assess changes in soil organic matter in the MRB suggest that soil organic N levels in cultivated soils have been, on average, approximately constant from 1950 to 1999 (Paul et al., 1997; Buyanovsky et al., 1997; Donigian et al., 1997; Patwardhan et al., 1997; Aref and Wander, 1998). Some studies have simulated or measured increases in organic carbon in the top 20 cm of the soil profile after 1970, which appears to be due to increases in crop yields and changes in tillage practices (Donigian et al., 1997; Patwardhan et al., 1997). In some locations, it has been demonstrated that the soil organic C increase in the top 20 cm from reduced tillage is roughly equal to a decrease lower in the soil profile such that no net change has occurred in the soil profile (Needleman et al., 1999; Wander et al., 1998; Yang and Wander, 1999). Additionally, Buyanovsky et al. (1997) reported that there was no change in soil N in long-term research plots in Missouri where an increase in soil organic carbon was measured. Aref and Wander (1998) reported that soil organic N content in long-term plots in Illinois has been steady since about 1955 where continuous corn and corn–soybean were grown. A slight increase in soil organic N was detected in Illinois plots in a corn–oat (*Avena sativa* L.)–hay rotation (Aref and Wander, 1998), but this rotation became relatively uncommon in the basin after 1960.

The CENR N budget estimated the average soil N mineralization from cropland in the MRB to be 2% of the average soil organic matter content as reported in the STATSGO database (Goolsby et al., 1999). The CENR N budget estimated immobilization of N in cropland soils to be 40% of N applied as fertilizer and 40% of the nitrate from atmospheric deposition. This was based on a limited number of studies that used ^{15}N to track the fate of fertilizer N applied to the soil. This approach does not consider all forms of N that can be returned to the soil organic matter. Nitrogen in crop residues that contribute to soil organic N can come from fixation, or early season mineralization of organic matter. Manure N also contributes to the soil organic N pool.

The cumulative difference between estimated mineralization and immobilization in the CENR budget produced an estimated net depletion of 2000 kg N ha^{-1} in soil organic N from cropland in MRB between 1950 and 1996. This would represent 25 to 50% of the organic N in the top 30 cm of many cropland soils. A loss of this magnitude is not consistent with observations or simulation modeling results that suggest steady or increasing soil organic matter in soils that have been in row crop production for 60 yr or more (Jenny, 1941; Paul et al., 1997; Aref and Wander, 1998). Little is known about long-term changes in soil N below 30 cm. Because soil organic matter declines with depth, a loss of 2000 kg N ha^{-1} from below 30 cm would represent an even greater percentage of the soil organic N deeper in the profile.

The CENR analysis of soil organic N did not explicitly consider the N that is incorporated into nonharvested crop residues that are normally returned to the soil. More recent analyses indicated that estimates of N remaining in the nonharvested portion of grain crops (leaves, stems, roots) are similar to the CENR estimate of soil N mineralization based on soil organic matter content (Burkart and James, 2001b; unpublished data, 2002). If the annual quantity of N mineralized from soil organic matter calculated by Burkart and James (1999) is roughly equal to the N that is returned to the soil in crop residues (Burkart and James 2001b; unpublished data, 2002), then it would appear that soil organic N is roughly in steady state, which is the assumption of the NANI approach.

Neither the CENR nor the NANI approach estimates the changes in soil organic N content that can result from conversion of grasslands and wetlands to annual crop production, or the reverse. Mineralization of soil organic N associated with conversion of hay and pasture to annual crop production may have rendered significant quantities of N available for transport to the Mississippi River at certain times. Between 1950 and 1980, there was a 12 million ha decline in area in hay and pasture in the MRB. During the same time, the area devoted to soybean production increased dramatically as the corn–soybean rotation replaced the older corn–oat–meadow rotation. After 1982, there was an expansion of land in perennial vegetation, initially due to a reduction in grain prices, and then due to the implementation of the Conservation Reserve Program after 1985.

We estimated the net nitrogen mineralized from these land use changes as follows. We assumed that the 12 million ha reduction in hay and pasture area was entirely due to conversion to row crop production, and assumed a net mineralization of 40 kg N ha^{-1} yr^{-1} from the soil for the first 10 yr and 20 kg N ha^{-1} yr^{-1} for the second 10 yr (Meisinger and Randall, 1991). We further assumed that 12 million of the 16 million ha increase in hay and pasture after 1982 was largely the same area that was converted from hay and pasture to cropland in the 1960s and 1970s. We therefore reduced the mineralization coming from prior conversions in proportion to the cumulative percentage of the 16 million ha that was converted to hay or pasture after 1982.

With Eq. [1], nitrate flux estimates were calculated using estimates of point source N input from municipal sewage based on sewage production of 4.53 kg N person^{-1} yr^{-1} (David and Gentry, 2000). This is greater than the global average value of 1.8 kg N person^{-1} yr^{-1} suggested by Caraco and Cole (1999), who assumed that half of the global population was sewered. We assumed 100% of the population of the MRB was sewered and ignored gaseous N losses in the sewage treatment process. Industrial point source N inputs were estimated to be 0.08 Tg N yr^{-1} (0.24 kg N ha^{-1} yr^{-1}) for the MRB by (Goolsby et al., 1999) based on discharges permitted by USEPA for 1996. Previous estimates of industrial point source N inputs suggest about 30% greater inputs during the 1970s, but this may have been due to differences in estimation methods used (Goolsby et al., 1999). Estimates of industrial point source N inputs were small in relation to other inputs and, following Goolsby et al. (1999), were assumed to be constant over time at the 1996 value.

Model Testing

The Caraco and Cole (1999) model (Eq. [1]) was used to estimate annual nitrate N flux for the MRB, and these estimates were compared with riverine nitrate flux estimates based on measurements of stream flow and nitrate concentration in the lower Mississippi River described above. Nitrate flux estimates were calculated with Eq. [1] using inputs from the 20 states. In an attempt to identify the lag time between N inputs and riverine export, we performed several regression analyses using N inputs averaged over a range of years (1 to 12 yr) and lagged over a different range (0 to 6 yr) prior to each year of observed nitrate flux. The lag and the range of years that provided the model to best fit the observed data were reported. The fit between model estimates and observed data was evaluated by the slope of the line between observed and simulated nitrate flux, coefficient of determination, root mean square error, and the residual autocorrelation function.

Net anthropogenic nitrogen input was calculated as the difference between anthropogenic N inputs (fertilizer, fixation, and NO_y deposition) and net food and feed export (N harvested in crops, hay, and pasture minus N retained in animal manure and N consumed by human residents) from the 20 states. Additional N input terms were added to NANI and output terms subtracted from NANI to evaluate the effect of including these terms on the relationship between resulting net nitrogen inputs (NNI) and riverine nitrate N flux. The relationship with riverine nitrate N flux was evaluated using nonlinear regression analysis to estimate coefficients for the following function:

$$\mathrm{NF} = a \times (\mathrm{WY}^b) \exp(c \times \mathrm{NNI}_{2\text{–}5} + d \times \mathrm{NNI}_{6\text{–}9}) \quad [3]$$

where a, b, c, and d are parameters estimated by regression; $\mathrm{NNI}_{2\text{–}5}$ is the average annual net N input during the previous 2 to 5 yr (kg N ha^{-1} yr^{-1}); $\mathrm{NNI}_{6\text{–}9}$ is the average annual net N input during the previous 6 to 9 yr (kg N ha^{-1} yr^{-1}), and other terms are the same as previously defined.

The N input terms that were added to NANI were CENR N net mineralization (mineralization − immobilization), and our estimate of N mineralization resulting from land-use conversions. The N output terms that were subtracted from NANI were the CENR estimate of in-field denitrification, the CENR estimate of crop volatilization losses, and 27% of the CENR estimate of crop volatilization losses (assuming 73% is redeposited within the drainage basin as was estimated by Burkart and James [1999, 2001a]). The values of these terms appear in Fig. 2b.

We also conducted several nonlinear regression analyses using as the NNI the CENR N budget residual in its original form and various modifications of the CENR N budget residual in which specific input and output fluxes were removed (by subtracting and adding, respectively). The CENR N budget residual was originally calculated using only the nonvolatile fraction of animal manure N as an input, even though volatilization from manure was subtracted as an output. In several of our analyses, we added the volatile component of manure to the CENR N budget residual. We also discovered and corrected a few minor errors in the data that had been used to calculate N fixation and harvest in pastures and non-alfalfa hay. The Burkart and James (2001a) N budget approach was approximated by adding to the CENR N budget residual the volatile component of manure N, and 73% of all N volatilization losses (manure, plant senescence, and fertilizer) to account for redeposition in the basin, subtracting municipal and industrial N sources, N fixation in pastures and non-alfalfa hay, and adding N harvested in pastures (which were not considered by Burkart and James). When this procedure was used, the N budget residual for 1992 was 5.57 Tg (16.4 kg ha^{-1}), which is similar to the value of 6 Tg (17.7 kg ha^{-1}) reported by Burkart and James (2001a) for that year. The values are not identical because Burkart and James (2001a) used county-level census data and used somewhat different values for N content of harvested crops and N fixation rates.

The correspondence between observed riverine nitrate flux and that estimated by the regression model was evaluated by root mean square error and coefficient of determination. The significance of the residual autocorrelation function was evaluated using the Ljung–Box Q statistic.

RESULTS

Temporal Variation in Riverine Nitrate Flux, Water Yield, and Net Anthropogenic Nitrogen Input

Estimated riverine nitrate flux based on measurements at St. Francisville declined from 1.4 to 0.7 kg N ha^{-1} yr^{-1} between 1955 and 1966, then increased from 0.8 to 4.1 kg N ha^{-1} yr^{-1} between 1967 and 1979, and subsequently fluctuated around 3.3 kg N ha^{-1} yr^{-1} (Fig. 1). During the same time period, NANI increased from an average of 10.4 kg N ha^{-1} yr^{-1} in the 1950s to 17.3 kg N ha^{-1} yr^{-1} in the 1990s. Much of this increase occurred in the 1960s, after N fertilizer use had increased without an equal increase in crop N harvest. Annual water yield was highly variable, and tended to increase from an average of 0.16 m yr^{-1} prior to 1972 to 0.21 m yr^{-1} after 1972 (Fig. 3).

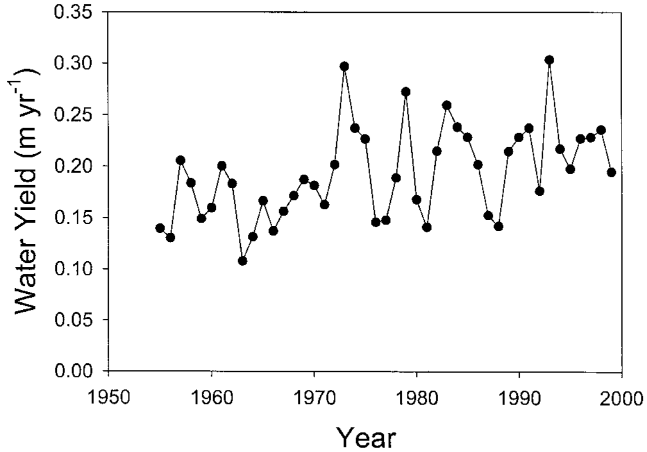

Fig. 3. Time series of annual water yield measured at Tarbert's Landing, and the Old River outflow.

Caraco and Cole Model

The nitrate flux estimates of the Caraco and Cole (1999) model (Eq. [1]) were highly correlated with observed values ($r^2 = 0.88$), but the slope and intercept of the regression of observed vs. simulated riverine nitrate flux values were significantly ($P < 0.001$) greater than 1 and less than zero, respectively (Fig. 4). This indicates that the model tended to overestimate low nitrate flux

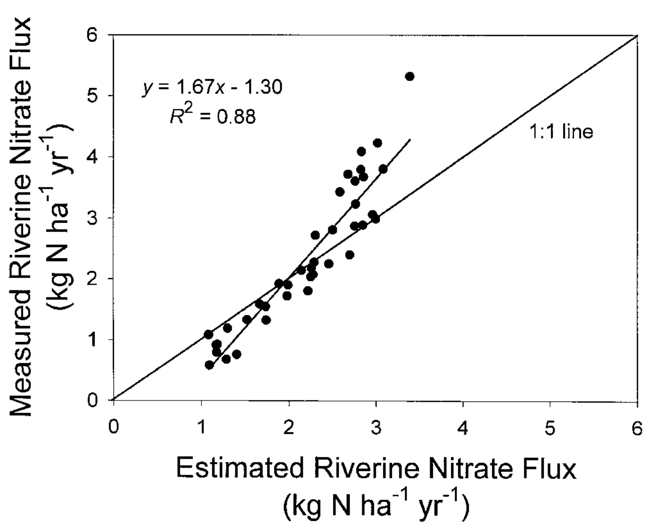

Fig. 4. Comparison of observed nitrate N flux in the Mississippi River at St. Francisville (1960–1998) to that predicted by the Caraco and Cole (1999) model (Eq. [1]) using watershed N inputs averaged over four years prior to the prediction year and lagged one year.

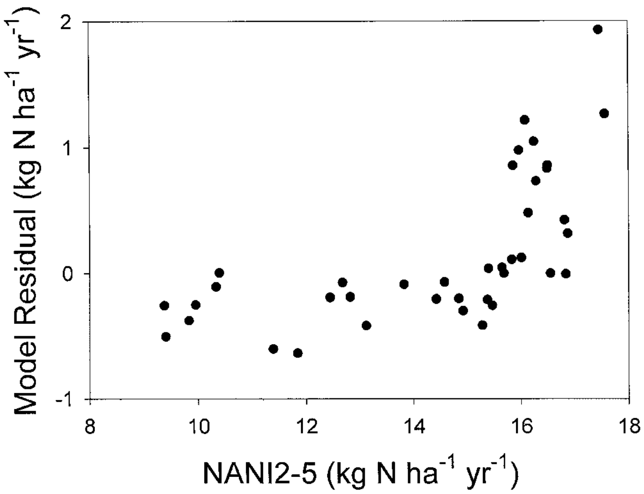

Fig. 5. Difference between observed nitrate flux and that predicted by Eq. [1] (residuals) plotted as a function of net anthropogenic nitrogen input averaged for the previous two to five years (NANI2–5).

values and underestimate large values. This result was not significantly influenced by lagging or averaging N inputs over different time periods because the largest deviations between prediction and observation occurred after 1978, when N fertilizer input and atmospheric deposition were relatively constant. Underestimation of nitrate flux by the Caraco and Cole model may be a consequence of inaccurate estimates of point source inputs. Our estimate of municipal sewage input (4.53 kg N person^{-1} yr^{-1}) is unlikely to be an underestimate as it considers all residents in the basin to contribute to sewage and does not account for gaseous N losses in sewage treatment. Additionally, the largest model residuals (observed − predicted nitrate N flux) tended to occur following periods of low N harvest in crops relative to N inputs, which is reflected in large values of NANI averaged over four years and lagged two years (NANI2–5) (Fig. 5). Thus, N_2 fixation and N harvest terms in the NANI approach, which are not included in the Caraco and Cole (1999) model, appear to provide information that is correlated to subsequent changes in nitrate flux from the MRB.

Relation between Net Nitrogen Input Terms and Riverine Nitrate Flux

Water yield alone without any N input terms in Eq. [3] accounted for 59% of the variation in water riverine nitrate flux (Table 5, Model 1). When NANI was used as NNI (Model 2), the equation accounted for 95% of the variation in riverine nitrate flux. Adjusting NANI to include our estimate of soil N mineralization resulting from conversion of hay and pasture to cropland had relatively little influence on the estimated equation parameters (Model 3). The coefficients of net NNI (*c* and *d*) were reduced slightly, mean square error was increased, and R^2 was reduced. Autocorrelation of residuals was not significant. Subtracting the CENR estimate of in-field denitrification from NANI (Model 4) also had a minor influence on the equation parameters and diagnostic statistics.

Table 5. Nonlinear regression results with Eq. [3] using alternative net nitrogen inputs (NNI) to account for annual riverine nitrate flux in the lower Mississippi River from 1960 to 1998.

Model	NNI	Model parameter estimates				RMSE†	R^2	Ljung–Box *Q*
		a	*b*	*c*	*d*			
1	no N input (water yield only)	29.0*	1.55*	–	–	0.577	0.588	75.2*
2	NANI‡	0.66*	0.93*	0.131*	0.055*	0.073	0.950	7.21
3	NANI + soil N mineralization from hay and pasture conversion	1.06*	1.02*	0.099*	0.059*	0.099	0.932	8.69
4	NANI − CENR§ in-field denitrification	1.09*	0.95*	0.144*	0.081*	0.087	0.940	7.37
5	NANI − CENR in-field denitrification − NH_x volatilization losses	34.9*	1.11*	0.103*	0.136*	0.378	0.742	47.76*
6	NANI − CENR in-field denitrification − 27% NH_x volatilization loss	2.07*	0.94*	0.151*	0.105*	0.116	0.921	9.74
7	NANI − CENR in-field denitrification − NH_x volatilization + mineralization − immobilization	69.2*	1.39*	−0.071*	−0.062*	0.257	0.824	24.84*
8	NANI − CENR in-field denitrification − 27% NH_x volatilization losses + mineralization − immobilization	531	1.45*	−0.082*	−0.082*	0.378	0.741	43.43*
9	CENR N budget residual	40.0*	1.32*	−0.061*	−0.056*	0.196	0.866	18.60*
10	CENR N budget residual + volatile manure N	60.5*	1.31*	−0.058*	−0.045*	0.214	0.854	20.60*
11	CENR N budget residual + volatile manure N + 0.73 × volatile N losses	280	1.31*	−0.062*	−0.064*	0.277	0.810	36.44*
12	CENR N budget residual + volatile manure N + 0.73 × ammonia volatilization − pasture fixation + pasture harvest − other hay fixation − municipal and industrial point sources	498	1.47*	−0.098*	−0.043	0.352	0.759	35.61*
13	CENR N budget residual + volatile manure N − mineralization + immobilization	34.5	1.81*	−0.103	−0.059	0.537	0.633	41.76*
14	CENR N budget residual + volatile manure N + 0.73 × ammonia volatilization − industrial sources − mineralization + immobilization	0.948	1.06*	0.160*	0.143*	0.324	0.779	56.87*
15	CENR N budget residual + volatile manure N + ammonia volatilization − NH_x deposition − industrial sources − mineralization + immobilization	0.446	0.982*	0.173*	0.132*	0.186	0.873	28.96*

* Significant at the 0.05 probability level.
† Root mean square error.
‡ Net anthropogenic nitrogen input.
§ Committee on Natural Resources and Environment.

When the CENR-estimated ammonia volatilization losses from fertilizer, manure, and crop canopy were subtracted from NANI minus CENR denitrification (Model 5), the mean square error increased by a factor of four, R^2 was reduced to 0.74, and the autocorrelation of the residuals was significant. If we assume that 73% of the ammonia volatilization losses were redeposited within the MRB, and subtract only 27% of these losses from NANI minus the CENR denitrification (Model 6), the resulting parameter values and diagnostic statistics were similar to those for NANI alone. If the CENR estimate of net soil mineralization (mineralization − immobilization) was added to NANI minus CENR denitrification and minus ammonia volatilization losses (Model 7), the coefficients of the resulting NNI terms were negative, the mean square error increased, the R^2 declined, and autocorrelation of the residuals was significant. If we modify Model 7 with the assumption that 73% of the volatilized ammonia is redeposited within the MRB (Model 8), the coefficients of NNI remain negative, the MSE increases and the R^2 decreases to 0.74.

When we used the CENR N budget residual as the NNI term in Eq. [3] (Model 9), the equation accounted for 87% of the variation in observed riverine flux, but coefficients of the NNI terms were significantly less than zero and the residual autocorrelation function was significant. These results did not change significantly when the volatile N component of manure was added to the CENR N budget (Model 10) and when 73% of the volatile ammonia losses were assumed to be redeposited in the MRB (Model 11). When estimated N fixation in pastures and non-alfalfa hay were subtracted and N harvest in pasture was added (Model 12) to approximate the approach of Burkart and James (2001a), only the coefficient of NNI2–5 was significantly less than zero. Removing soil N mineralization and immobilization from the CENR N budget (Model 13) caused neither of the coefficients of NNI to be statistically different than zero. When 73% of the volatilized ammonia was assumed to be redeposited within the basin and soil was assumed to be at steady state (Model 14), both coefficients of NNI were statistically greater than 0, although this model accounted for only 78% of the variation in riverine nitrate flux and the residual autocorrelation function was significant. Assuming that 100% of the volatilized ammonia was redeposited within the MRB and removing ammonia deposition as an input (Model 15), the model accounted for 87% of the variation in riverine nitrate flux, but the residual autocorrelation coefficient was significant. The major difference between the NNI for Model 15 and for Model 4 was that atmospheric NO_y deposition was assumed to be proportional to NO_x emissions prior to 1984 in NANI, as opposed to the constant 1984–1996 average used in the CENR N budget and Model 15.

Improved fit between estimated observed riverine nitrate flux for Models 3 through 15 might be obtained if NNI values were averaged and lagged over different numbers of years. The results with Models 3, 4, and 6, however, were similar to the results using NANI alone, and taking averages and lags over alternative years is unlikely to have a large effect. Because Model 5 did not include redeposition of volatile NH_x, it was not considered a realistic model. For Models 7 through 12, taking averages and lagging over different periods of years would not change the negative coefficients of NNI because these values of NNI declined over the study period while riverine nitrate flux increased. For Model 13, there was essentially no trend in NNI during the study period. Additional linear and nonlinear regression analysis using different averaging and lag times with NNI for Models 14 and 15 did not produce significantly different results.

DISCUSSION

Our results with Models 9 and 10 are in some ways similar to results of Goolsby and Battaglin (2001), who reported a negative coefficient for the CENR N budget residual in a regression model to account for annual variation in riverine nitrate flux in the lower Mississippi River. The components of the N cycle that seemed to have the greatest effect on the relationship between NNI and riverine nitrate flux were the CENR estimate of soil N mineralization and immobilization. Because estimated immobilization (considered an N output) increased over time, this led to a significant decline in annual net mineralization (Fig. 2) and contributed to a negative correlation between NNI and riverine nitrate flux. When mineralization (a constant) and immobilization were removed from the CENR N budget, the resulting NNI had essentially no correlation with riverine nitrate flux, rather than a negative correlation when mineralization and immobilization were included. As discussed in the Methods section, the CENR estimate of mineralization was much greater than immobilization. This suggests that large losses have occurred in cropland soil organic matter since 1950, which is not consistent with measurements of organic N changes in plots under long-term cultivation (Aref and Wander, 1998; Paul et al., 1997). It appears that the CENR estimate of immobilization does not account for all forms of N that contribute to the soil organic N pool.

Our estimate of N mineralization from changes in land use and the CENR estimate of denitrification from NANI had relatively little influence on the relationship between the resulting NNI and riverine nitrate flux. Adding our estimate of soil mineralization as an input reduced coefficients of NNI2–5 by about 30%. This would produce a slightly different simulated effect of reducing N fertilizer use than reported previously by McIsaac et al. (2001). Rather than a 12% fertilizer use reduction needed to achieve a 33% reduction in riverine nitrate flux, including this estimate of soil N mineralization in NNI suggests a 14% reduction in fertilizer use would be needed to achieve a 33% reduction in nitrate N flux. This is still substantially less than the 24% reduction in fertilizer use suggested by Doering et al. (1999). Additionally, it is unlikely that a 14% reduction in fertilizer use would have reduced crop yields much, if at all. Crop yields tend to asymptotically approach an economic optimum as fertilizer application rates increase (Cerrato and Blackmer, 1990; Bullock and Bullock, 1994). If producers had been applying optimal rates of N fertilizer, then a 14% reduction in fertilizer input would have caused a small reduction in crop yields that would have reduced growers' profits. There is evidence that farmers had been applying fertilizer and manure N in excess of crop requirements (Legg et al., 1989). Fertilizer applied per bushel of corn harvested has decreased by about 30% since the mid 1980s, in part because application of fertilizer and manure N had exceeded crop requirements. Based on regional simulation studies, Doering et al. (1999) described the economic effect of a 20% reduction in fertilizer application as "modest."

Like immobilization, estimated ammonia volatilization losses were an output that increased over time (Fig. 2) and thus contributed to a negative correlation between NNI and nitrate flux. If 73% of the volatilized ammonia were redeposited within the basin, as estimated by Burkart and James (1999, 2001a), the effect on the relationship between NNI and riverine flux is considerably reduced. The assumption of whether 73 or 100% of the volatilized ammonia is deposited in the basin appears to have a considerable effect on how well the modified CENR Models 14 and 15 fit the observed data. The assumption in the CENR analysis that NO_y deposition was constant prior to 1984 contributed to a relatively small rate of change in the residual N from 1951 to 1996, and consequently the assumption of how much ammonia is redeposited has a considerable effect on that slower rate of change in NNI. In contrast, the assumption in our calculation of NANI that NO_y is proportional to NO_x emissions produces a greater rate of increase in NANI and consequently whether we assume 100 or 73% redeposition of volatilized ammonia has relatively little effect on the rate of change of NANI or the relationship with riverine nitrate flux.

As discussed in the Methods section, there is evidence that indicates that Burkart and James (1999, 2001a) underestimated the percentage of ammonia that is redeposited in the basin. Additionally, there is evidence that indicates that the estimates of crop senescence losses used by CENR and Burkart and James (1999, 2001a) are too large. Based on an extensive literature review, Holtan-Hartwik and Bockman (1994) estimated that net ammonia volatilization from crops is on the order of 1.5 kg N ha^{-1} yr^{-1}, but may be as large as 6 kg N ha^{-1} yr^{-1} under higher temperatures and growing conditions that lead to poor grain fill. These values are roughly an order of magnitude less than the CENR estimates. Holtan-Hartwik and Bockman (1994) favored results based on direct measurement of ammonia flux from fields using micrometeorological methods, which would partially account for redeposition within the field of origin. Larger values of crop senescence losses are frequently based on field ^{15}N studies and field N balances in which missing N is assigned to crop senescence losses. Using labeled isotope methods, Francis et al. (1993) estimated that N volatile losses from a maize canopy may be as large as 81 kg N ha^{-1} yr^{-1}, but they also indicated that this N was not necessarily lost from the crop–soil system, since an unknown portion may be redeposited in the field of origin. In a more recent study, Francis et al. (1997) further concluded that N volatilization losses from crop canopies estimated from the disappearance of N isotopes in microplots overestimate the net N loss from the canopy at the field scale because an unknown portion of the isotope N is lost from the microplots via gaseous exchange with neighboring plants outside the plots. Additionally, Francis et al. (1993) also indicated that canopy volatilization was not a new net loss from the soil crop system, but a more precise accounting of N that had previously been thought to volatilize or denitrify from the soil. If crop volatilization losses are to be included in N budgets, then estimates of denitrification and volatilization from the soil should be based on studies that used measurement techniques capable of isolating these losses from canopy volatilization losses.

The CENR estimate of canopy volatilization from soybean is particularly important because that is the only crop that substantially increased in planted area over the study period, and thereby contributes to a positive trend in the overall ammonia losses. The estimate of canopy volatilization from soybean was, however, based on a technique that very likely overestimated the quantity of N volatilized from the crop–soil system. Stutte et al. (1979) estimated that 45 kg N ha^{-1} volatilized from a soybean canopy based on a measurement technique that involved removing water vapor and soluble N compounds from the gaseous stream that was being recirculated over a soybean leaf. Other studies have shown that plants absorb or release ammonia N depending on the difference in ammonia concentrations inside and outside the leaves (Farquhar et al., 1980). By continuously removing ammonia from the air supplied to the leaves they were monitoring, Stutte et al. (1979) had created conditions that enhanced volatile N loss from the plant and, therefore, estimated a greater volatile N flux than would occur under ambient atmospheric ammonia concentrations (Stutte and Weiland, 1978; Wetselaar and Farquhar, 1980). Using micrometeorological techniques, Harper et al. (1989) observed that two soybean canopies in Georgia emitted and adsorbed ammonia from the atmosphere during different portions of the growing season, and on balance absorbed 5 to 10 kg N ha^{-1} during the growing season. If the estimate of volatilization from soybean canopy were substantially reduced, it would have a considerable effect on impact on the trend in ammonia volatilization losses.

The exponential relationship between NNI and riverine nitrate flux of Eq. [3] may be a consequence of N inputs exceeding the N assimilation capacities of the terrestrial and/or riverine systems. In-stream denitrification appears to be limited by contact between water and sediment (Alexander et al., 2000), and biological uptake is limited by phosphorus concentrations based on the N to P ratios of rivers in the basin (Howarth et al., 1996; David and Gentry, 2000). Nitrate additions to the riverine system beyond the assimilation capacity would lead to fluxes being an increasing fraction of the

N inputs. Measurements and modeling of edge-of-field N losses indicate that in-field denitrification can consume significant quantities of excess fertilizer N, resulting in a linear relationship between N inputs and edge-of-field losses (Mitsch et al., 1999; Doering et al., 1999), although exponential relationships are sometimes observed at the field scale (Zucker and Brown, 1998). Thus, the observed exponential relationship between N inputs and nitrate flux could be a consequence of N saturation of the terrestrial and/or riverine systems.

The exponential relationship between N inputs and nitrate flux may also be a consequence of changes in factors influencing nitrate transformation and transport that are not included in Eq. [3]. Drainage of wetlands in the basin could have contributed to increased nitrate delivery, although construction of reservoirs would have had the opposite effect. Reductions in organic waste discharges into streams may have also had an influence on nitrate loads in the lower Mississippi River. In-stream denitrification is inversely related to streamflow and dissolved oxygen concentration, and it may have also declined slightly as a consequence of reduced point-source discharges of organic wastes to the river system (Smith et al., 1987, 1993). The effect of point-source reductions is likely to have been greatest in the mid- to late 1970s, when the greatest reductions in industrial biological oxygen demand (BOD) discharges occurred (USEPA, 1990). Because denitrification requires near-anoxic conditions, these wastes (and their subsequent removal) probably would have had an effect only where and when waste loads produced nearly anoxic conditions in the water column. This tended to occur during low stream flow, which would also correspond to periods of low nitrate flux, with or without the wastes. For this reason, the effect of the BOD inputs and their removal on nitrate flux was probably small.

The exponential relationship might also be due to changes in characteristics of NANI. Inorganic N fertilizers may be more readily transported to surface waters than the organic forms of N that were used for crop fertility prior to 1960. Additionally, changes in the spatial distribution of N use in the basin may have also influenced N transport to surface waters.

Finally, the exponential relationship between N inputs and nitrate flux may be a consequence of a trend in the inaccuracies in estimating N inputs or NANI. The estimate of biological N fixation probably introduces the greatest uncertainty into NANI. We assumed that N fixation has been constant with respect to soybean yields and the area planted to other legumes. If, however, N fixation rates have increased over time, perhaps due to genetics and/or production practices, the actual NANI in recent years would be greater than our estimate, and the true relationship between NANI and riverine nitrate flux would have less curvature and would be more nearly linear.

In-field and in-stream denitrification are not included in NANI, but the high correspondence with observed riverine nitrate flux in spite of these omissions may be a consequence of the general mobility of the nitrate ion. Additionally, the combination of in-field and in-stream denitrification may be relatively constant for a given level of N input to the basin because of the contrasting conditions that promote denitrification in-field vs. in-stream. In-field denitrification tends to be greater during years with high precipitation that cause soils to be saturated with water for greater lengths of time. These conditions also increase stream flow, which reduces in-stream residence time and thus reduces in-stream denitrification. Conversely, during relatively dry years, soils will be saturated less frequently, leading to less in-field denitrification, but low stream flow and longer in-stream residence time that promote in-stream denitrification. The NANI approach does not address several processes that are involved in the N cycle, but it appears to focus on the terms that can be estimated with reasonable certainty and that are correlated with riverine N flux in temperate river basins where soil organic N is relatively constant. It is not clear whether the correlation with riverine N is due to greater certainty of the estimates or greater mobility of the N fractions estimated in NANI.

CONCLUSIONS

The Caraco and Cole (1999) model, using N inputs in fertilizer, sewage, and atmospheric NO_y deposition, produced annual riverine nitrate flux estimates that were highly correlated with observed annual nitrate flux in the lower Mississippi River from 1960 to 1996, but it tended to overestimate low annual nitrate fluxes and underestimate large nitrate fluxes. The approach using an exponential function of NANI, which included a wider range of N inputs and outputs (biological N fixation and crop N harvest), accounted for more of the observed variation in annual nitrate flux the lower Mississippi River during this time period.

Comparison of alternative combinations of N inputs and outputs indicated that the key assumptions that lead to high correlation between net N inputs and riverine nitrate flux for the lower Mississippi from 1960 to 1998 are: (i) soil organic N was at a long-term steady state, (ii) volatilized ammonia was largely ($\geq$73%) redeposited within the basin, and (iii) NO_y deposition prior to 1984 was proportional to estimated NO_x emissions.

Nitrogen input and output combinations that violated the first two assumptions by including mineralization estimates that were considerably greater than immobilization, and/or assuming NH_3 volatilization was not redeposited in the basin, produced N budget residuals that were weakly and negatively correlated with observed values of riverine nitrate flux. The third assumption increased the correlation of models that did not violate the first two assumptions.

Nitrogen budgets include errors due to the difficulty in accurately estimating large fluxes of N, and the resulting residual N may be uncorrelated or negatively correlated with relevant measures of riverine N. Inferences about water quality drawn from such budgets may be misleading. On the other hand, positive correlations do not prove cause and effect. To better understand the factors influencing N transport to the Gulf of Mexico, we suggest continued monitoring and more intensive research on the dynamics of soil organic N, in-field and in-stream denitrification, and biological N fixation, as well as the effects of spatial distribution of N use on delivery to the Gulf of Mexico.

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