

Nitrogen Mass Balance of a Tile-drained Agricultural Watershed in East-Central Illinois

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Simple nitrogen (N) input/output balance calculations in agricultural systems are used to evaluate performance of nutrient management; however, they generally rely on extensive assumptions that do not consider leaching, denitrification, or annual depletion of soil N. We constructed a relatively complete N mass balance for the Big Ditch watershed, an extensively tile-drained agricultural watershed in east-central Illinois. We conducted direct measurements of a wide range of N pools and fluxes for a 2-yr period, including soil N mineralization, soybean N₂ fixation, tile and river N loads, and ground water and in-stream denitrification. Fertilizer N inputs were from a survey of the watershed and yield data from county estimates that were combined with estimated protein contents to obtain grain N. By using maize fertilizer recovery and soybean N₂ fixation to estimate total grain N derived from soil, we calculated the explicit change in soil N storage each year. Overall, fertilizer N and soybean N₂ fixation dominated inputs, and total grain export dominated outputs. Precipitation during 2001 was below average (78 cm), whereas precipitation in 2002 exceeded the 30-yr average of 97 cm; monthly rainfall was above average in April, May, and June of 2002, which flooded fields and produced large tile and riverine N loads. In 2001, watershed inputs were greater than outputs, suggesting that carryover of N to the subsequent year may occur. In 2002, total inputs were less than outputs due to large leaching losses and likely substantial field denitrification. The explicit change in soil storage (67 kg N ha⁻¹) offsets this balance shortfall. Although 2002 was climatically unusual, with current production trends of greater maize grain yields with less fertilizer N, soil N depletion is likely to occur in maize/soybean rotations, especially in years with above-average precipitation or extremely wet spring periods.

NITROGEN budget calculations in agricultural systems are useful for developing a quantitative understanding of N sources and sinks and assessing overall availability of N to the target crop species as well as efficiency of utilization. These calculations range from simple input/output budgets at the field, watershed, or regional scale to intensive mass balance evaluations at the microplot and small field scale (Watson and Atkinson, 1999). However, accounting for all N fluxes and obtaining a complete N mass balance is extremely challenging due to the inherent complexity of the N cycle and the difficulty in directly measuring various fluxes, particularly denitrification (Davidson and Seitzinger, 2006). Therefore, simple field budgets are more commonly used as performance indicators of nutrient management and as regulatory policy instruments, especially in Europe (Oenema et al., 2003).

In conventional agricultural systems, N budgets generally identify fertilizer N as the major input and N contained in grain as the major output. In the Midwest, where maize (*Zea mays* L.)/soybean (*Glycine max* L.) rotations are the predominant cropping system and tile drainage is extensive, N inputs often include an estimate of soybean N₂ fixation, and N outputs include N leaching from tiles (McIsaac et al., 2002). A mass balance, on the other hand, implies a more rigorous investigation into N pools and fluxes throughout the plant/soil system and often involves applying ¹⁵N to microplots (Stevens et al., 2005). Regardless of the experimental rigor, N accounting and budgeting has been used to evaluate the potential negative impact of agricultural production on water quality and more recently on the soil resource (Jaynes and Karlen, 2008).

Numerous studies in the Midwest have presented field N budgets to evaluate the effects of agricultural practices on N leaching losses (Kladivko et al., 1991; Gentry et al., 1998; Karlen et al., 1998; Andraski et al., 2000; Jaynes et al., 2001; Webb et al., 2004). These studies show that leaching losses can be substantial and are largely dependent on the rate of fertilization, soil type, and precipitation. There are a variety of cultural practices that can improve field N balances and decrease N loss, including timing of N application, variable rate technology, use of nitrification inhibitors and slow release fertilizers,

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Abbreviations: NNI, net nitrogen input.

and cover crops (Randall and Vetsch, 2005; Mamo et al., 2003; Snapp et al., 2005). There have also been N budget calculations on the watershed scale (David et al., 1997; Burkart and James, 1999; McIsaac et al., 2002; Libra et al., 2004). Collectively, these studies have established a clear link between agricultural production and riverine N loads but do not account for all N pools (amount of stored N) and fluxes (movement of N).

Our goal in this study was to directly measure as many of the major N inputs and outputs as possible, supplemented with estimates where needed, to construct a relatively complete N mass balance in an extensively tile-drained agricultural watershed under a maize/soybean production system. We conducted direct measurements of a wide range of N pools and fluxes for a 2-yr period including soil N mineralization, soybean N₂ fixation, tile and river N loads, and ground water and in-stream denitrification. Due to the lack of animal production and municipal wastewater discharge, this agriculturally dominated watershed was well suited to evaluate the linkage between terrestrial N cycling and riverine N load.

Materials and Methods

Site Description

The Big Ditch watershed (101 km²) is a relatively flat and extensively tile-drained area dominated by row crop agriculture (89%) with approximately an equal mixture of maize and soybean planted annually, typical of east-central Illinois watersheds (previously described by Borah et al., 2003; Schaller et al., 2004; Royer et al., 2006; Mehnert et al., 2007). In conjunction with this study, Mehnert et al. (2007) provide a detailed map of the watershed. Our measurements of N pools and fluxes in the Big Ditch watershed were conducted in 2001 and 2002 (riverine and tile N concentrations and loads were calculated on a water-year basis: October 2000 through September 2002). We estimated land area annually planted to maize and soybean throughout the watershed based on the ratio of these two crops in Champaign County, Illinois (Illinois Agricultural Statistics). Local precipitation was estimated by averaging available daily observations from the three closest weather stations (Rantoul, Fisher, and Mahomet), although there were occasional missing values for these stations. Monthly mean precipitation values were also obtained from the eastern Illinois Climate Division operated by the National Oceanic and Atmospheric Administration (National Climate Data Center, 2008). The water-year average precipitation in the climate division during 1971 to 2000 was 97 cm, with a range of 65 cm in 1988 to 141 cm in 1993.

Nitrogen Inputs

Values of atmospheric N deposition in the Big Ditch watershed were from the National Atmospheric Deposition Program/National Trends Network site at Bondville, IL (NADP, 2008), which was located just outside the watershed boundary. Fertilizer N rate for maize was estimated at 184 kg ha⁻¹ based on a farmer survey conducted in the Big Ditch watershed in 2000 (von Holle, 2005). This survey found that about 50% of maize fields received fall application of anhydrous ammonia. Soybean N₂ fixation rates were determined by the difference method, subtracting the amount of above-ground N accumu-

lation of non-nodulated soybean from the N accumulation of nodulated soybean and dividing by the N accumulation of the nodulated soybean (Vasilas and Ham, 1984; Gentry et al., 2001). Values for soybean N fixation in the watershed were determined by multiplying N fixation rate by soybean plant N.

Following the experimental design, plot size, and cultural practices by Gentry et al. (2001) and Bergerou et al. (2004), two adjacent tile-drained fields separated by a small tributary of the Big Ditch that were alternately cropped to maize or soybean in a maize/soybean rotation were selected for microplot study. During the soybean phase of the rotation in these fields, microplots of nodulating and non-nodulating isolines of Williams 82 were established in a randomized block design with four replicates on the predominant silty clay loam soil type (Drummer/Flanagan silty clay loam, fine-silty, mixed, superactive, mesic Typic Endoaquolls) in the watershed. Soybean plants in a 1-m section of row (0.76-m row spacing) were harvested at the late R6 growth stage before leaf drop, divided into two plant fractions (leaves and stalks, and pods and seeds), and dried to a constant weight at 80°C for biomass determination. Dried samples were ground through a 2-mm mesh and analyzed for total N using a combustion technique (Fisons NA 2000 N Analyzer; Fisons Instruments, Strada Rivoltana, Italy).

Nitrogen Outputs

Grain yields of maize and soybean for Champaign County were used for yield values in the Big Ditch watershed (Illinois Agricultural Statistics, 2000–2001). Grain N content was calculated by multiplying grain yield by grain N concentrations of 1.44% for maize and 6.4% for soybean. Grain N concentrations were calculated using an average grain protein concentration of 9% for maize and 40% for soybean (University of Illinois, 2008) and dividing by the average mass ratio of N to grain protein (1:6.25). Total plant N was calculated by dividing grain N by the N harvest index of 0.70 for maize and 0.80 for soybean (David et al., 1997).

Daily river N loads were determined by multiplying daily discharge by inorganic N (including nitrate-N [NO₃-N] and ammonium-N [NH₄-N]) and by total N concentrations. A total of 241 river samples were analyzed during the 2001 and 2002 water years. Linear interpolation was used to estimate N concentrations between sampling dates using SAS 8.2. Water samples were collected on a weekly basis and supplemented with an automated water sampler for periods of rapid change in discharge (ISCO 2900; ISCO, Lincoln, NE). Filtered water samples (0.45 μm) were analyzed for NO₃-N on an ion chromatograph (Dionex, Sunnyvale, CA) and for NH₄-N on a Lachat Quikchem8000 (Lachat, Loveland, CO) flow injection analyzer (American Public Health Association, 1998). For total N, unfiltered aliquots underwent persulfate digestion and were analyzed for NO₃-N by Cd reduction on a Lachat Quikchem8000 (American Public Health Association, 1998).

Shallow ground water and riverine (in-stream) denitrification were determined on the Big Ditch watershed as part of this project and have been previously published (Mehnert et al., 2007; Royer et al., 2004; Schaller et al., 2004). A brief summary is given here; details are available in the publications cited. Mehnert et al. (2007) measured shallow ground water denitrification by monitoring 11

wells installed throughout the watershed. Isotopic ratios of N and O in the nitrate ion were used to suggest the extent of denitrification. Push-pull tests were conducted to determine in situ $\text{NO}_3\text{-N}$ reduction rates. The software GFLOW was used to create a two-dimensional ground water model (Mehnert et al., 2007).

In-stream denitrification was determined on ditch sediments and associated aquatic plants using the chloramphenicol-amended acetylene inhibition procedure (Royer et al., 2004; Schaller et al., 2004). Measurements were made throughout the year within the stream system of the watershed.

A reliable technique for determining field denitrification was not available (Groffman et al., 2006); therefore, we used weather patterns and our knowledge of N budgets to make some general assumptions. Due to dry conditions in 2001, we assumed field denitrification was not an important watershed output. However, with several large precipitation events in April, May, and June of 2002, where rainfall exceeded infiltration rates and soils were saturated for several days, we believe conditions were conducive for field denitrification. We estimated field denitrification in 2002 by difference using the complete watershed N mass balance, assuming total inputs plus grain N derived from soil (explicit change in soil storage) equaled total outputs and solving for missing N.

Grain Nitrogen Derived from Soil

Estimates of maize fertilizer N recovery and soybean N_2 fixation were used to calculate a value for grain N derived from soil. Fertilizer N recovery in maize was determined by measuring the difference between fertilized and unfertilized above-ground plant N accumulation and dividing by the fertilizer N rate. Unfertilized maize N accumulation can also be used as a proxy for net soil N mineralization during the growing season (Gentry et al., 2001). Four plots of unfertilized maize were established in the alternate field adjacent to the soybean microplots during the maize phase of the rotation. Four plant samples from a 6.1-m row length (0.76-m row spacing) of unfertilized maize were harvested at physiological maturity, divided into three plant fractions (leaves and stalks; tassel, husk, and cob; and grain), and dried to a constant weight at 80°C for biomass determination (Gentry et al., 1998). Dried samples were ground through a 2-mm mesh and analyzed for total N using a combustion technique (Fisons NA 2000 N Analyzer). Above-ground plant N accumulation of fertilized maize was based on county estimates of grain N divided by N harvest index. Using the percent fertilizer recovery, we calculated maize grain N derived from fertilizer and assumed the remainder was from soil. For soybean, we calculated grain N derived from fixation and assumed the remainder was from soil.

Tile Drainage

Three agricultural drainage tiles along the Big Ditch were monitored during 2001–2002. These tiles cumulatively drained 25.5 ha, with the majority of the effective drainage area planted to soybean in 2001 and maize in 2002. The effective drainage area of each tile was determined by assuming the ratio of river discharge to precipitation for the watershed is the same for tiles, dividing annual tile volume by annual precipitation, solving for area, and averaging effective tile drainage area over the

2 yr. Tile discharge was gauged using a Sigma 900 MAX (Hach Co., Loveland, CO) area velocity sampler, and water samples were collected on a flow proportional basis using an automated water sampler (ISCO 2900). Water samples were analyzed for $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, and total N as described previously. Tile water flow-weighted mean N concentrations and loads were determined to compare and contrast to riverine N.

Nitrogen Balance Calculations

We calculated simple field N balances for maize (fertilizer N minus grain N) and for soybean (N_2 fixation minus grain N). We calculated simple watershed N balances as inputs (deposition, fertilizer N, soybean N_2 fixation) minus outputs (maize and soybean grain N), comparing riverine N loads with these watershed balances. Finally, we calculated the overall watershed N mass balances as the inputs (deposition, fertilizer N, soybean N_2 fixation) minus the outputs (maize and soybean grain N, stream N load, in-stream and ground water denitrification, field denitrification).

Results and Discussion

Precipitation and Crop Yield

Weather patterns and annual precipitation in Champaign County varied greatly during 2001 and 2002; however, crop yields were similar in both years. The 2001 water year was particularly dry (78 cm measured in local rain gages and an average of 91 cm measured in the climate division), and crop yields (0% moisture) were 8.27 and 2.68 Mg ha⁻¹ for maize and soybean, respectively. Although annual precipitation was low in 2001, rainfall occurred at timely intervals during the growing season that resulted in crop yields that were within 5% of the 1997–2000 averages. The 2002 water-year precipitation was 110 cm in local rain gages and 112 cm for the climate division, which was the third wettest water year since 1971. The county average maize yield declined by 7% to 7.7 Mg ha⁻¹, whereas soybean yield increased by 17% to 3.2 Mg ha⁻¹. The 2002 growing season began with a wet, cool April and May but became hot and dry during late June and early July, which negatively affected maize production; however, the soybean crop benefited from rainfall in mid-August. Overall, crop yields in Champaign County in 2001 and 2002 were similar to adjacent counties and were above the state average.

Maize Fertilizer Nitrogen Recovery and Soybean N_2 Fixation

Fertilizer N recovery values were 51 and 38% in 2001 and 2002, respectively (Table 1). Net soil N mineralization as indicated by unfertilized maize N accumulation was 77 and 90 kg ha⁻¹ in 2001 and 2002, respectively. These estimates suggest that the drier conditions of 2001 limited soil N mineralization. Based on the difference in N accumulation of nodulated and non-nodulated soybean isolines, we determined N_2 fixation rates to be 77 and 60% of the total N accumulation in the above-ground biomass in 2001 and 2002, respectively (Table 1). By multiplying fixation rate and total above-ground N accumulation (grain N divided by N harvest index), we estimated soybean N_2 fixation in the watershed to be 163 and 150 kg N ha⁻¹

in 2001 and 2002, respectively. Nitrogen accumulation of the non-nodulating soybean isolate can also be used as an indication of net soil N mineralization and was less for 2001 than 2002 (32 and 63 kg ha⁻¹, respectively). Compared with unfertilized maize, N accumulation by the non-nodulating soybean was less in both years (Table 1). This may in part be due to differences in growing period, root architecture, and N absorption patterns of maize and soybean; however, maize has been shown to stimulate soil N mineralization by as much as 50% (Sanchez et al., 2002). Overall, the drier growing season of 2001 created conditions that increased maize N fertilizer recovery and soybean N₂ fixation.

Field Nitrogen Balance

For simple field N balances, we used only fertilizer N or N₂ fixation for inputs and grain N for output; we did not consider atmospheric N deposition here. Subtracting maize grain N from the fertilizer N rate of 184 kg N ha⁻¹, we found field N balances to be positive, indicating a net gain of 65 and 73 kg N ha⁻¹ for maize fields in 2001 and 2002, respectively. Maize yields would need to be >13 Mg ha⁻¹ (assuming 1.44% grain N) to remove more N than was supplied at this fertilization rate. For soybean, field N balances were negative for both years because N from fixation was less than grain N output. Subtracting soybean grain N from plant N₂ fixation (grain N divided by N harvest index multiplied by N₂ fixation rate), we found net removal of N in soybean fields to be 7 and 51 kg ha⁻¹ in 2001 and 2002, respectively. Although a soybean crop is often given a N credit when preceding maize (Gentry et al., 2001), studies report a negative balance in soybean fields (Heichel and Barnes, 1984; Zapata et al., 1987).

Net Nitrogen Input

Simple watershed N balances have been used to compare riverine N loads with net nitrogen input (NNI); however, basin size, intensity of agricultural production, and extent of artificial drainage influence the relationship. For example, Howarth et al. (1996) found riverine N load to be about 22% of NNI for the entire Mississippi River basin. David and Gentry (2000) estimated the combined riverine N load for the major rivers of Illinois to be 51% of the NNI. In watersheds within Illinois, McIsaac and Hu (2004) found large differences in riverine N load to NNI, based on the presence or absence of tile drainage. Riverine N load represented 25 to 37% of NNI in non-tile drained watersheds, whereas riverine N load was 100% of NNI for watersheds containing extensive tile drainage. These results suggest that the value for NNI cannot account for both N leaching and denitrification in tile-drained regions.

For the Big Ditch watershed, N fertilizer provided 83 and 85 kg N ha⁻¹ in 2001 and 2002, respectively (Table 2). Although we used the same fertilizer N rate for both years of the study, there was a slight increase in maize acres in the watershed in 2002. Soybean N₂ fixation contributed 71 and 64 kg N ha⁻¹ to the entire watershed in 2001 and 2002, respectively (Table 2). By summing atmospheric N deposition, fertilizer N, and N₂ fixation and subtracting total grain N, we calculated NNI for the Big Ditch watershed to be 30 and 17 kg N ha⁻¹ in 2001 and 2002. For this relatively small and extensively drained agricultural watershed, riverine N loads represent 70 and

294% of NNI for the 2 yr. In accordance with McIsaac and Hu (2004), our calculation of NNI could not account for both riverine N flux and denitrification during the wet year of 2002.

Riverine and Tile Nitrogen Load

Discharge and N loads exiting the Big Ditch watershed varied greatly between the two water years. Total discharge was 19 and 34 million m³ (19 and 34 cm) for the 2001 and 2002 water years, respectively, which represented 24 and 31% of the annual precipitation. During the 1994–2003 water years, annual discharge for this stream ranged from 8 to 38 cm, with an average value of 26.5 cm (Royer et al., 2006).

Based on the entire watershed area, riverine total N loads were 21 and 50 kg N ha⁻¹ for the 2001 and 2002 water years, respectively (>90% of the total N was NO₃-N). Flow-weighted mean NO₃-N concentrations for the Big Ditch were 10.2 and 14.8 mg N L⁻¹ for the 2001 and 2002 water years, respectively. Although precipitation was low in 2001, there were two large discharge events in February (Fig. 1). These precipitation events generated overland runoff as indicated by the dilution of riverine NO₃-N concentrations during peak discharge, producing relatively small total N loads. During 2002, numerous flow events occurred, and riverine NO₃-N concentrations tended to increase through May (Fig. 1). With 50% of the fertilizer N applied in the fall in this watershed, we speculate that this was an important source of river and tile NO₃-N during the wet spring.

In 2002, N load and annual flow-weighted mean NO₃-N concentrations in the Big Ditch were the highest recorded during the 10 yr from 1994 to 2003 (Royer et al., 2006). During this period, NO₃-N flux was highly correlated with water yield ($r^2 = 0.72$), but two years were outliers: in 1994 the observed NO₃-N flux was 12 kg N ha⁻¹ less than the trend line, and in 2002 the observed NO₃-N flux was 13 kg N ha⁻¹ greater. Precipitation throughout the region in 1993 was the greatest on record, as were river flows, and this appeared to flush NO₃-N out of the soil and ground water so that NO₃-N concentrations tended to be lower in 1994. Precipitation and flows during 1999–2001 were below average, allowing accumulation of NO₃-N in soil and shallow ground water, which appeared to have been mobilized during the high flows of 2002.

Total N load per unit area for three tiles located in the Big Ditch watershed were similar to river loads for both years. Based on the total effective drainage area for all three tiles, cumulative N loads were 22.7 and 59.9 kg ha⁻¹, and flow-weighted mean NO₃-N concentrations were 11.7 and 19.2 mg L⁻¹ for the 2001 and 2002 water years, respectively. Similar to the Big Ditch, tile NO₃-N concentration decreased during the large discharge events in February of 2001 and tended to increase with discharge for each successive flow event in 2002. After tile flow cessation, river NO₃-N concentration quickly decreased below detection limits for both years. This similar pattern of river and tile NO₃-N suggests that tiles were the major source of riverine N.

Denitrification (In-Stream and Shallow Ground Water)

In-stream denitrification was estimated to be no more than 1 kg N ha⁻¹ yr⁻¹ (Table 2). Although in-stream denitrification

Table 1. Maize and soybean crop parameters used to calculate nitrogen balances in the Big Ditch watershed during 2001 and 2002.

Maize crop	2001	2002
	—kg N ha ⁻¹ —	
Fertilizer N rate	184	184
Grain yield, kg ha ⁻¹	8270	7730
Grain N	119	111
Grain N derived from soil	59	69
Fertilized plant N	170	159
Unfertilized plant N	77	90
Fertilizer N recovery	51	38
Soybean crop		
Fertilizer N rate	0	0
Grain yield, kg ha ⁻¹	2680	3160
Grain N	172	202
Grain N derived from soil	36	74
Nodulated plant N	136	156
Non-nodulated plant N	32	63
N ₂ fixation rate	77	60

rates have been shown to be substantial during the summer months in east-central Illinois (Royer et al., 2004; Opdyke et al., 2006), tile drainage has generally ceased at this time (David et al., 1997). In contrast, the majority of river NO₃-N was exported when tile drainage was occurring, stream water residence time was short, and temperatures were cool (Royer et al., 2004). These factors combined to make in-stream denitrification a negligible N output from the Big Ditch watershed.

Denitrification in shallow ground water was greater than in-stream denitrification; however, it was a minor output from the watershed. Mehnert et al. (2007) found that 1.8 and 5.7 kg ha⁻¹ of N were denitrified from ground water in this watershed during the 2001 and 2002 water years, respectively, representing 6 and 34% of NNI. These estimates were considered minimum values because the hydrologic model only accounted for steady state ground water flow and ignored transient flow events, such as flow from precipitation events. It is likely that the existence of extensive tile drainage decreases the potential for shallow ground water denitrification in this watershed.

Nitrogen Mass Balance

The overall annual mass balances of the Big Ditch watershed are shown in Fig. 2 and 3. Assuming field denitrification was <1 kg ha⁻¹ in 2001, N inputs (158 kg N ha⁻¹) were greater than outputs (152 kg N ha⁻¹), indicating a positive N mass balance of 6 kg N ha⁻¹. Although we calculated a value of -44 kg N ha⁻¹ for grain N derived from soil, the positive N balance indicates that net soil N depletion did not occur in 2001. It is likely that dry years with moderate grain yields and small leaching and denitrification losses create surplus N, allowing carryover of N to the subsequent year (David et al., 1997).

Gaseous N losses from soils are considered the most difficult measurements to conduct on a large spatial scale and were not directly measured in this study. Although the 2001 watershed N mass balance suggests that as much as 6 kg N ha⁻¹ could be lost from soils via processes such as denitrification and nitrification, soils were not inundated when temperatures were favorable for denitrification. Nitrification of ammoniacal fertilizers (especially at fertilization rates greater than sufficient) has been shown to pro-

Table 2. Cropland area, inputs, outputs, and explicit change in soil storage for the Big Ditch watershed in 2001 and 2002.

	2001	2002
Cropland area		
Maize, ha	4547	4658
Soybean, ha	4381	4269
Inputs	—kg N ha ⁻¹ —	
Deposition	4	5
N fertilizer	83	85
Soybean N fixation	71	64
Total	158	154
Outputs		
Maize grain N	54	51
Soybean grain N	75	86
Big Ditch total N load	21	50
In-stream denitrification	<1	1
Ground water denitrification	2	6
Field denitrification	<1	27
Total	152	221
Explicit change in soil storage		
Maize grain N derived from soil	-26	-32
Soybean grain N derived from soil	-18	-35
Total	-44	-67

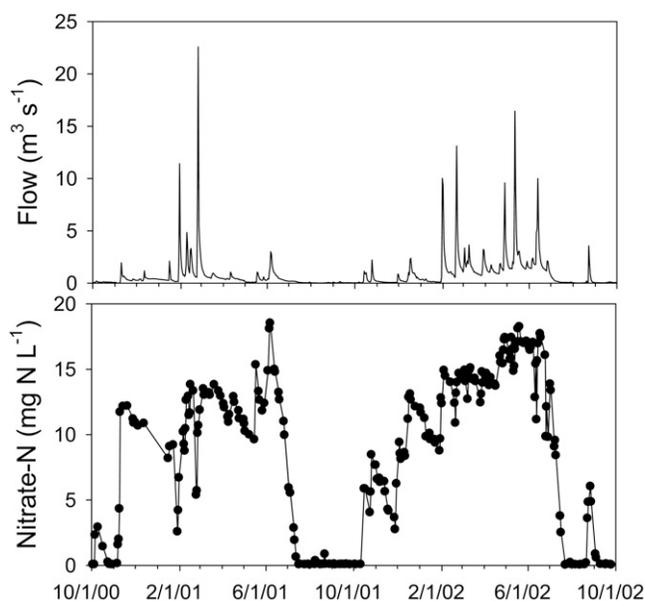


Fig. 1. Big Ditch discharge and NO₃-N concentrations.

duce gaseous N loss; however, fertilizer N rates in the Big Ditch watershed were not considered excessive, which would minimize the importance of this N output in our mass balance calculations (McSwiney and Robertson, 2005). In general, the extensive tile drainage that exists throughout east-central Illinois is thought to decrease the occurrence of field denitrification (McIsaac and Hu, 2004). Therefore, in the drier year of 2001, we believe field denitrification was not likely an important watershed output.

In 2002, with large N leaching losses and likely substantial field denitrification, total inputs (154 kg N ha⁻¹) were less than all measured outputs (194 kg N ha⁻¹) (Table 2). This negative balance suggests a reduction in stored soil N in 2002. Here we treat explicit change in soil storage (-67 kg N ha⁻¹) as an input, offsetting the balance shortfall and solving for field denitrification. By assuming that N input plus the absolute value for explicit change in soil storage is

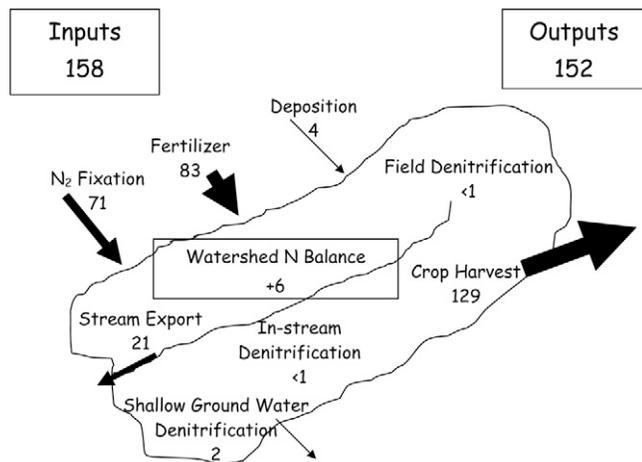


Fig. 2. Nitrogen mass balance for the Big Ditch watershed in 2001, showing summed inputs and outputs as well all major measured and estimated fluxes. All units are kg N ha⁻¹ yr⁻¹, and arrows are proportional to fluxes.

equal to total N outputs (due to the extensive flushing of N from soil and shallow ground water), we estimated that 27 kg N ha⁻¹ was lost from the watershed via field denitrification in 2002 (Table 2). Although few studies have quantified field denitrification, a study in east-central Illinois (Torbert et al., 1992, 1993) found that when Drummer soil was artificially flooded for more than five consecutive days, nearly 50% of the fertilizer N applied was lost via denitrification. As indicated by the numerous river and tile discharge events during May and June of 2002, frequent precipitation at that time created saturated soil conditions in the Big Ditch watershed for extended periods at temperatures favorable for denitrification. In extensively tile-drained regions, only small amounts of N enter shallow ground water because tile and stream networks quickly transport N downstream and out of the watershed (Mehner et al., 2007; Royer et al., 2006). Therefore, we believe that denitrification in the upper soils was likely the most important source of gaseous N loss during the wet year of 2002.

David et al. (2009) compared five models that simulate the N cycle in agricultural systems and predicted denitrification (SWAT, DAYCENT, DRAINMOD-N II, EPIC, and DNDC) for the Embarras River watershed in Champaign County, directly south of the Big Ditch watershed. The Embarras River watershed has similar soils, cropping patterns, fertilizer N use, and riverine N exports as in the Big Ditch watershed (Royer et al., 2006). The models predicted an average denitrification flux for 2002 of 13.5 kg N ha⁻¹. For the agronomic-based models SWAT, DRAINMOD-N II, and EPIC, field denitrification rates were estimated to be 22, 24, and 14 kg N ha⁻¹ yr⁻¹, respectively, which is similar to our estimate of 27 kg N ha⁻¹ yr⁻¹; the two biogeochemistry models DAYCENT and DNDC had estimates of 3.5 to 4.2 kg N ha⁻¹ yr⁻¹, respectively. Using our estimate for field denitrification, we find a gross loss of N via leaching and denitrification (field, shallow ground water, and in-stream) of 84 kg N ha⁻¹ for the Big Ditch watershed in 2002.

Overall, our watershed mass balance analysis indicates that N fertilizer is the largest input, that grain N is the largest output, and that total outputs are greater than total inputs. During

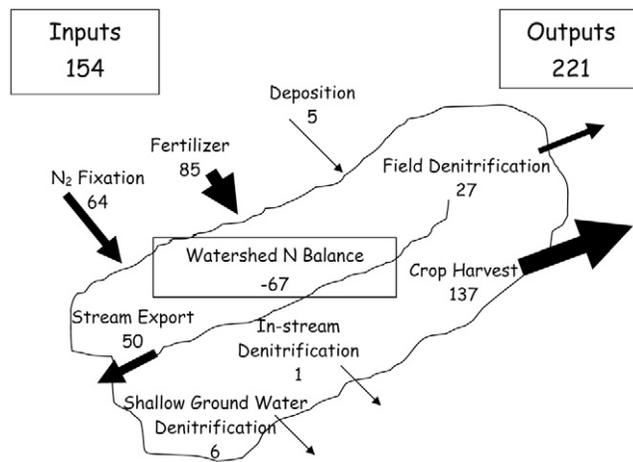


Fig. 3. Nitrogen mass balance for the Big Ditch watershed in 2002, showing summed inputs and outputs as well all major measured and estimated fluxes. All units are kg N ha⁻¹ yr⁻¹, and arrows are proportional to fluxes.

the past 20 yr, US fertilizer N sales have remained relatively constant, whereas crop yields and N harvested (especially maize since the introduction of GMO traits) have increased (USEPA, 2007). Given this perceived increase in maize N utilization efficiency, it would be expected that riverine N loads in the Mississippi River watershed would be declining. Surprisingly, riverine loads in tile-drained regions have not declined much, if at all, during this period (USEPA, 2007). In our analysis of the Big Ditch watershed, the N mass balance could not be closed without considering the explicit change in soil storage. Therefore, our results suggest that a maize/soybean rotation depletes soil N in this extensively tile-drained watershed, especially during an extremely wet year. In addition, tile drainage losses can be substantial (>50 kg N ha⁻¹ yr⁻¹), even with a favorable crop N balance, as indicated by a NNI of 17 kg ha⁻¹ in 2002. Finally, there is little doubt that NO₃-N leaching, largely mediated through tile drainage networks, is the major source of N in surface waters in east-central Illinois, contributing to local water quality problems and nutrient loading in the Gulf of Mexico.

Conclusions

Our comparison of N cycling in the Big Ditch watershed was conducted during 2 yr of differing N leaching patterns driven by precipitation. The watershed N balance calculations indicate that N inputs were greater than outputs (+6 kg ha⁻¹) in the drier year (2001) but were much less than outputs (-67 kg ha⁻¹) in the wetter year (2002), indicating soil N depletion. In years with modest leaching losses and minimal denitrification, N may accumulate and carry over to the next year, thus partly offsetting net depletion of soil N. Our analysis suggests that soil N depletion can occur in maize/soybean rotations in years with above-average precipitation or extremely wet spring periods. With current production trends of higher grain yields with flat or even declining fertilizer N rates, these data suggest the likelihood that soil N depletion may be exacerbated.

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References

- American Public Health Association. 1998. Standard methods for the examination of water and wastewater. 20th ed. APHA, Washington, DC.
- Andraski, T.W., L.G. Bundy, and K.R. Brye. 2000. Crop management and corn nitrogen rate effects on nitrate leaching. *J. Environ. Qual.* 29:1095–1103.
- Bergerou, J.A., L.E. Gentry, M.B. David, and F.E. Below. 2004. Role of N₂ fixation in the soybean N credit in maize production. *Plant Soil* 262:383–394.
- Borah, D.K., M. Bera, and S. Shaw. 2003. Water sediment, nutrient, and pesticide measurements in an agricultural watershed in Illinois during storm events. *Trans. ASAE* 46:657–674.
- Burkart, M.R., and D.E. James. 1999. Agricultural-nitrogen contributions to hypoxia in the Gulf of Mexico. *J. Environ. Qual.* 28:850–859.
- David, M.B., and L.E. Gentry. 2000. Anthropogenic inputs of nitrogen and phosphorus and riverine export for Illinois, USA. *J. Environ. Qual.* 29:494–508.
- David, M.B., L.E. Gentry, D.A. Kovacic, and K.M. Smith. 1997. Nitrogen balance in and export from an agricultural watershed. *J. Environ. Qual.* 26:1038–1048.
- David, M.B., S.J. Del Grosso, X. Hu, E.P. Marshall, G.F. McIsaac, W.J. Parton, C. Tonitto, and M.A. Youssef. 2009. Modeling denitrification in a tile-drained, corn and soybean agroecosystem of Illinois, USA. *Biogeochemistry* 93:7–30.
- Davidson, E.A., and S. Seitzinger. 2006. The enigma of progress in denitrification research. *Ecol. Appl.* 16:2057–2063.
- Gentry, L.E., F.E. Below, M.B. David, and J.A. Bergerou. 2001. Source of the soybean N credit in maize production. *Plant Soil* 236:175–184.
- Gentry, L.E., M.B. David, K.M. Smith, and D.A. Kovacic. 1998. Nitrogen cycling and tile drainage nitrate loss in a corn/soybean watershed. *Agric. Ecosyst. Environ.* 68:85–97.
- Groffman, P.M., M.A. Altabet, J.K. Böhlke, K. Butterbach-Bahl, M.B. David, M.K. Firestone, A.E. Giblin, T.M. Kana, L.P. Nielsen, and M.A. Voytek. 2006. Methods for measuring denitrification: Diverse approaches to a difficult problem. *Ecol. Appl.* 16:2091–2122.
- Heichel, G.H., and D.K. Barnes. 1984. Opportunities for meeting crop nitrogen needs from symbiotic fixation. p. 49–59. *In* Organic farming: Current technology and its role in sustainable agriculture. Spec. Publ. No. 46, ASA, CSSA, SSSA, Madison, WI.
- Howarth, R.W., G. Billen, D. Swaney, A. Townsend, N. Jaworski, K. Lajtha, J.A. Downing, R. Elmgren, N. Caraco, T. Jordan, F. Berendse, J. Freney, V. Kudryarov, P. Murdoch, and Z. Zhao-Liang. 1996. Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: Natural and human influences. *Biogeochemistry* 35:75–139.
- Illinois Department of Agriculture. 2000–2001. Illinois Agricultural Statistics. Illinois Agricultural Statistics Service, Springfield, IL.
- Jaynes, D.B., T.S. Colvin, D.L. Karlen, C.A. Cambardella, and D.W. Meek. 2001. Nitrate loss in subsurface drainage as affected by nitrogen fertilizer rate. *J. Environ. Qual.* 30:1305–1314.
- Jaynes, D.B., and D.L. Karlen. 2008. Sustaining soil resources while managing nutrients. p. 149–158. *In* Upper Mississippi River Sub-basin Hypoxia Nutrient Committee. Final report: Gulf Hypoxia and Local Water Quality Concerns Workshop. Am. Soc. Agric. Biol. Eng., St. Joseph, MI.
- Karlen, D.L., L.A. Kramer, and S.D. Logsdon. 1998. Field-scale nitrogen balances associated with long-term continuous corn production. *Agron. J.* 90:644–650.
- Kladivko, E.J., G.E. VanScoyoc, E.J. Monke, K.M. Oates, and W. Pask. 1991. Pesticide and nutrient movement into subsurface tile drains on a silt loam soil in Indiana. *J. Environ. Qual.* 20:264–270.
- Libra, R.D., C.F. Wolter, and R.J. Langel. 2004. Nitrogen and phosphorus budgets for Iowa and Iowa watersheds. Iowa Geological Sur. Tech. Info. Ser. No. 47. Iowa Dep. Natural Resources, Des Moines, IA.
- Mamo, M., G.L. Malzer, D.J. Mulla, D.R. Huggins, and J. Strock. 2003. Spatial and temporal variation in economically optimum nitrogen rate for corn. *Agron. J.* 95:958–964.
- McIsaac, G.F., and X. Hu. 2004. Net N input and riverine N export from Illinois agricultural watersheds with and without extensive tile drainage. *Biogeochemistry* 70:251–271.
- McIsaac, G.F., M.B. David, G.Z. Gertner, and D.A. Goolsby. 2002. Relating net nitrogen input in the Mississippi River basin to nitrate flux in the lower Mississippi River: A comparison of approaches. *J. Environ. Qual.* 31:1610–1622.
- McSwiney, C.P., and G.P. Robertson. 2005. Nonlinear response of N₂O flux to incremental fertilizer addition in a continuous maize (*Zea mays* L.) cropping system. *Glob. Change Biol.* 11:1712–1719.
- Mehner, E., H.H. Hwang, T.M. Johnson, R.A. Sanford, W.C. Beaumont, and T.R. Holm. 2007. Denitrification in the shallow groundwater of a tile-drained agricultural watershed. *J. Environ. Qual.* 36:80–90.
- NADP. 2008. National Atmospheric Deposition Program. Available at <http://nadp.sws.uiuc.edu> (verified 7 May 2009).
- National Climate Data Center. 2008. Daily precipitation and temperature for Illinois sites. Available at <http://www.ncdc.noaa.gov/oa/climate/stationlocator.html> (verified 26 April 2009).
- Oenema, O., H. Kros, and W. de Vries. 2003. Approaches and uncertainties in nutrient budgets: Implications for nutrient management and environmental policies. *Eur. J. Agron.* 20:3–16.
- Opdyke, M.R., M.B. David, and B.L. Rhoads. 2006. The influence of geomorphological variability in channel characteristics on sediment denitrification in agricultural streams. *J. Environ. Qual.* 35:2103–2112.
- Randall, G.W., and J.A. Vetsch. 2005. Nitrate losses in subsurface drainage from a corn-soybean rotation as affected by fall and spring application of nitrogen and nitrapyrin. *J. Environ. Qual.* 34:590–597.
- Royer, T.V., J.L. Tank, and M.B. David. 2004. The transport and fate of nitrate in headwater, agricultural streams in Illinois. *J. Environ. Qual.* 33:1296–1304.
- Royer, T.V., M.B. David, and L.E. Gentry. 2006. Timing of riverine export of nitrate and phosphorus from agricultural watersheds in Illinois: Implications for reducing nutrient loading to the Mississippi River. *Environ. Sci. Technol.* 40:4126–4131.
- Sanchez, J.E., E.A. Paul, T.C. Willson, J. Smeenk, and R.R. Harwood. 2002. Corn roots effects on the nitrogen-supplying capacity of a conditioned soil. *Agron. J.* 94:391–396.
- Schaller, J.L., T.V. Royer, M.B. David, and J.L. Tank. 2004. Denitrification associated with plants and sediments in an agricultural stream. *J. N. Am. Benthol. Soc.* 23:667–676.
- Snapp, S.S., S.M. Swinton, R. Labarta, D.R. Mutch, J.R. Leep, J. Nyiraneza, and K. O'Neil. 2005. Evaluating benefits and costs of cover crops for cropping systems niches. *Agron. J.* 97:322–332.
- Stevens, W.B., R.G. Hoefl, and R.L. Mulvaney. 2005. Fate of nitrogen-15 in a long-term nitrogen rate study: II. Nitrogen uptake efficiency. *Agron. J.* 97:1046–1053.
- Torbert, H.A., R.G. Hoefl, R.M. Vandenheuvel, and R.L. Mulvaney. 1992. Effect of moisture regime on recovery and utilization of fertilizer N applied to corn. *Commun. Soil Sci. Plant Anal.* 13:1409–1426.
- Torbert, H.A., R.G. Hoefl, R.M. Vandenheuvel, R.L. Mulvaney, and S.E. Hollinger. 1993. Short-term excess water impact on corn yield and nitrogen recovery. *J. Prod. Agric.* 3:337–344.
- University of Illinois. 2008. Department of Crop Science Variety Testing. Available at <http://vt.cropsi.illinois.edu> (verified 7 May 2009).
- USEPA. 2007. Hypoxia in the Northern Gulf of Mexico, an update by the EPA Science Advisory Board. EPA-SAB-08-004. USEPA, Washington, DC.
- Vasilas, B.L., and G.E. Ham. 1984. Nitrogen fixation in soybeans: An evaluation of measurement techniques. *Agron. J.* 76:759–764.
- von Holle, C.K. 2005. Agricultural nitrogen use and producer attitudes in tile-drained watersheds of east-central Illinois. M.S. Thesis, University of Illinois at Urbana-Champaign.
- Watson, C.A., and D. Atkinson. 1999. Using nitrogen budgets to indicate nitrogen use efficiency and losses from whole farm systems: A comparison of three methodological approaches. *Nutr. Cycl. Agroecosyst.* 53:259–267.
- Webb, J., S. Ellis, R. Harrison, and R. Thorman. 2004. Measurement of N fluxes and soil N in two arable soils in the UK. *Plant Soil* 260:253–270.
- Zapata, F., K.A. Danso, G. Hardason, and M. Fried. 1987. Time course of nitrogen fixation in field-grown soybean using nitrogen-15 methodology. *Agron. J.* 79:172–176.