

Modeling denitrification in a tile-drained, corn and soybean agroecosystem of Illinois, USA

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Abstract Denitrification is known as an important pathway for nitrate loss in agroecosystems. It is important to estimate denitrification fluxes to close field and watershed N mass balances, determine greenhouse gas emissions (N₂O), and help constrain estimates of other major N fluxes (e.g., nitrate leaching, mineralization, nitrification). We compared predicted denitrification estimates for a typical corn and soybean agroecosystem on a tile drained Mollisol from five models (DAYCENT, SWAT, EPIC, DRAINMOD-N II and two versions of DNDC, 82a and 82h), after first calibrating each model to crop yields, water flux, and

nitrate leaching. Known annual crop yields and daily flux values (water, nitrate-N) for 1993–2006 were provided, along with daily environmental variables (air temperature, precipitation) and soil characteristics. Measured denitrification fluxes were not available. Model output for 1997–2006 was then compared for a range of annual, monthly and daily fluxes. Each model was able to estimate corn and soybean yields accurately, and most did well in estimating riverine water and nitrate-N fluxes (1997–2006 mean measured nitrate-N loss 28 kg N ha⁻¹ year⁻¹, model range 21–28 kg N ha⁻¹ year⁻¹). Monthly patterns in observed riverine nitrate-N flux were generally reflected in

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model output (r^2 values ranged from 0.51 to 0.76). Nitrogen fluxes that did not have corresponding measurements were quite variable across the models, including 10-year average denitrification estimates, ranging from 3.8 to 21 kg N ha⁻¹ year⁻¹ and substantial variability in simulated soybean N₂ fixation, N harvest, and the change in soil organic N pools. DNDC82a and DAYCENT gave comparatively low estimates of total denitrification flux (3.8 and 5.6 kg N ha⁻¹ year⁻¹, respectively) with similar patterns controlled primarily by moisture. DNDC82h predicted similar fluxes until 2003, when estimates were abruptly much greater. SWAT and DRAINMOD predicted larger denitrification fluxes (about 17–18 kg N ha⁻¹ year⁻¹) with monthly values that were similar. EPIC denitrification was intermediate between all models (11 kg N ha⁻¹ year⁻¹). Predicted daily fluxes during a high precipitation year (2002) varied considerably among models regardless of whether the models had comparable annual fluxes for the years. Some models predicted large denitrification fluxes for a few days, whereas others predicted large fluxes persisting for several weeks to months. Modeled denitrification fluxes were controlled mainly by soil moisture status and nitrate available to be denitrified, and the way denitrification in each model responded to moisture status greatly determined the flux. Because denitrification is dependent on the amount of nitrate available at any given time, modeled differences in other components of the N cycle (e.g., N₂ fixation, N harvest, change in soil N storage) no doubt led to differences in predicted denitrification. Model comparisons suggest our ability to accurately predict denitrification fluxes (without known values) from the dominant agroecosystem in the midwestern Illinois is quite uncertain at this time.

Keywords Crop yields · Mollisol · N₂O · Nitrate · Soil moisture

Introduction

Denitrification is an important component of N biogeochemistry in most ecosystems (Seitzinger et al. 2006), and one of the most difficult to measure

due to great spatial and temporal variability. In addition, measurement techniques often have many limitations in allowing direct quantification of both N₂O and N₂ fluxes (Groffman et al. 2006), due to an atmosphere largely composed of N₂. However, denitrification fluxes are needed to close N mass balances as well as quantify N₂O fluxes to the atmosphere. In agroecosystems, N input and output fluxes are often large, driven primarily by industrially produced fertilizer, biological N₂ fixation and crop harvest of N (David and Gentry 2000; McIsaac et al. 2002). Major fluxes include inputs from fertilizer, fixation, atmospheric deposition and manure, outputs including crop harvest, nitrate leaching, and denitrification, and the internal transformations of N including mineralization, nitrification, immobilization, and crop residue decomposition (McIsaac et al. 2002). Because of high N inputs, agricultural soils are considered critical locations for denitrification as are stream sediments within agricultural watersheds, although the latter are of more limited importance because of limited detention time (Royer et al. 2004; David et al. 2006).

The transfer of gaseous forms of N from agricultural soils to the atmosphere has consequences for agricultural production, water quality, climate change, ozone depletion, and acidic deposition. However, fluxes of N₂ and N₂O have been difficult and costly to measure under agricultural field conditions, and consequently the quantity and location of N losses, and the influence of management practices are poorly understood (Davidson and Seitzinger 2006).

Denitrification measurements indicate that the end products and rates are highly variable in space and time, and are related to soil moisture, nitrate and carbon availability. Although some predictive relationships among these variables have been identified, there is much unexplained variation. Hofstra and Bouwman (2005) conducted a meta-analysis of 336 published measurements of denitrification in agricultural settings throughout the world, and produced estimates of median annual denitrification rates for various conditions and measurement techniques. Denitrification estimated by mass balance tended to be greater than rates based on chamber or core methods. Median annual denitrification for conditions that most closely resemble Midwestern corn production (receiving between 150 and 225 kg N ha⁻¹ fertilizer) ranged from 46 kg N ha⁻¹ year⁻¹ when

estimated by mass balance to $18 \text{ kg N ha}^{-1} \text{ year}^{-1}$ when based on core or chamber techniques. For soils with good drainage, the median values were 29 kg N ha^{-1} when based on mass balance and 11 kg N ha^{-1} when based on core and chamber techniques. For soybean production, which typically receives little or no N fertilizer, median denitrification rates ranged from $24 \text{ kg N ha}^{-1} \text{ year}^{-1}$ for poorly drained soils estimated by mass balance to $6 \text{ kg N ha}^{-1} \text{ year}^{-1}$ for well drained soils estimated by core and chamber methods. There was, however, only one site in the US Corn Belt in this database.

There have been few studies that have made denitrification measurements in North American, tile-drained corn fields. Qian et al. (1997) reported an average of $5.5 \text{ kg N ha}^{-1} \text{ N}_2\text{O} + \text{N}_2$ loss during two growing seasons from corn fields irrigated with high nitrate groundwater in Nebraska. They measured surface gas fluxes using field chambers placed into soils with and without acetylene blockage. When soil moisture exceeded 70% of the pore space, denitrification rates ranged from 0.2 to $1.4 \text{ kg N ha}^{-1} \text{ day}^{-1}$, compared to rates of 0.01 – $0.05 \text{ kg N ha}^{-1} \text{ day}^{-1}$ when soil moisture was less than 60% of pore space. Additionally, when soil moisture was less than 60% pore space, N_2O was the major gas emitted. Denitrification and N_2O flux were highly correlated with water filled pore space at the time of sampling in a dry year, but not in a year of normal precipitation, perhaps because other factors were limiting denitrification.

Measuring denitrification during the growing season in Quebec from a corn field that had been fertilized with 270 kg N ha^{-1} , Kaluli et al. (1999) reported a denitrification rate (using the acetylene block method with intact soil cores) of 19 kg N ha^{-1} from an artificially (tile) drained field, and 60 kg N ha^{-1} when subirrigation was used to maintain the water table within 70 cm of the soil surface. Elmi et al. (2002, 2005a) also reported greater denitrification rates from subirrigated corn compared to corn grown with free drainage in Quebec during five growing seasons (using the acetylene block method with intact soil cores). Cumulative seasonal values of denitrification were not reported, but rates as high as $4.4 \text{ kg N ha}^{-1} \text{ day}^{-1}$ were reported for fields with subirrigation, compared to $2.3 \text{ kg N ha}^{-1} \text{ day}^{-1}$ with free drainage (Elmi et al. 2002). Denitrification rates were usually considerably less than $1 \text{ kg N ha}^{-1} \text{ day}^{-1}$; however, Elmi et al. (2005b) reported an

average of $12.9 \text{ kg N ha}^{-1}$ denitrification during two growing seasons from corn grown with subirrigation and 5.8 kg N ha^{-1} from a sandy loam soil with free drainage in southwestern Quebec (again, using the acetylene block method with intact soil cores). Denitrification measurements were limited to the top 15 cm of the soil, however. Elmi et al. (2005a) also demonstrated significant denitrification occurring in the 15–30 cm depth increment. In both studies (Elmi et al. 2005a, b), N_2O was a smaller fraction of total denitrification under subirrigation, however, the absolute amount of N_2O release from subirrigation was equal to or greater than that from free drainage. While the above studies confirm that soil moisture is an important controlling factor in denitrification, measurements were confined to the growing season. There may also be significant denitrification occurring in the winter and early spring, especially as frozen soils thaw.

It is impossible to measure denitrification in every square meter or every hectare of an agricultural field or a watershed of any size, but modeling can be used to make estimates over large areas based on an understanding of the underlying dynamics. Li et al. (2005b) compared measured values of N_2O flux and denitrification from two wheat fields in China to values simulated by three models (DAYCENT, DNDC, and WNMM). The simple WNMM model estimates were most similar to observed values, but could account for only 45–54% of the daily variation in N_2O flux and 28% of the daily variation in denitrification. In spite of the low correlation between daily observations and simulated values, the cumulative values of observed N gas flux were similar to that predicted by WNMM.

Sogbedji and McIsaac (2006) applied the ADAPT model to the intensively farmed and tile drained Vermilion River watershed in the Illinois River Basin and selected model coefficients to optimize the fit between simulated and observed crop yields and stream nitrate flux. ADAPT is a one dimensional model and simulations were conducted to represent typical conditions in the watershed. The model simulated an average denitrification rate of $5 \text{ kg N ha}^{-1} \text{ year}^{-1}$. In a similar study of the Embarras River watershed, Hu et al. (2007) applied the SWAT model which simulated a denitrification rate of $22 \text{ kg N ha}^{-1} \text{ year}^{-1}$. These SWAT simulations were conducted using a GIS representation of the watershed in

which representative conditions in seven subwatersheds were simulated. In these Illinois applications, both SWAT and ADAPT over estimated soybean N fixation and simulated a significant accumulation of N in the soil over time which has not been observed empirically. It is possible that the denitrification estimates may have also been overestimated due to the excess organic N accumulating from the soybean residue, but there are no denitrification measurements that can be used to verify model simulations.

Boyer et al. (2006) reviewed several modeling approaches and concluded that the models indicate a large role of denitrification in regional and global N budgets, but that model uncertainty is large, and that more extensive and intensive denitrification measurements are needed to better validate and improve existing models. Heinen (2006) presented an overview more than fifty simplified process models for denitrification (excluding microbial growth and soil structural models) that primarily calculated potential denitrification either measured as a soil property or computed from organic C dynamics, or determined it as a first-order decay process. He pointed out how important the soil water content simulation was (because of effects on oxygen), and that the various models prediction of denitrification was most sensitive to parameters affecting this soil function.

Tile-drained fields of the midwestern cornbelt (including a large part of Illinois) are the major source of N to the Gulf of Mexico, which is the primary nutrient controlling development of hypoxia (USEPA 2007b). However, full N mass balances for this region have been hampered by the difficulty in obtaining direct measurements or making estimates of field denitrification, soybean N₂ fixation, and changes in soil organic N (David and Gentry 2000; McIsaac et al. 2002). Field denitrification estimates from models could be extremely helpful in better documenting N biogeochemistry in these agroecosystems. Our overall objectives were to assess and advance the state of agricultural denitrification modeling by comparing several model simulations of one particular agricultural system and identifying important differences among models that can inform future experimental work. Specific objectives were to: (1) predict denitrification with several models for a typical Illinois, tile-drained, corn and soybean agroecosystem using the same

environmental dataset; (2) compare how the models predict overall denitrification rates, N₂ versus N₂O (where the models provide each) emissions, and the timing of N gas emissions; and (3) discuss these results in the context of what they reveal about the strengths and limitations of current models for similar agroecosystems. This model comparison will help address the following questions: (1) what is the state of modeling important agricultural ecosystems with high N input and output fluxes, (2) what can we learn about how well critical processes are modeled from this comparison, (3) are we confident that some or all of these models can predict denitrification gas losses, and (4) what are the differences between model predictions that can provide hypotheses to guide future experimental work?

Methods

Following the approach used by Tonitto et al. (2007a, b), we used aggregated data from the Embarras River watershed (48,100 ha) in east-central Illinois for data to run our models. These data minimize field-to-field variation, allow for long-term simulations, and integrate both corn and soybean crops each year (Tonitto et al. 2007a). As explained below, however, separate model runs were made, with one set beginning with corn (and then following with soybean in rotation) and the other beginning with soybean (and then following with corn in rotation). To represent outcomes for a landscape equally divided between corn and soybean fields we averaged the results from these simulations; the averaged outcomes were used for comparisons with watershed-scale measured fluxes. Estimates of drainage and nitrate leaching can be difficult to obtain from individual field lysimeter studies, whereas small streams in tile-drained regions are thought to be an accurate integrator of field conditions and nutrient export across the watershed. These agricultural headwater streams have been shown to have little removal of nitrate by denitrification because most export occurs during high flow conditions and retention time is too short for removal processes to be effective (Royer et al. 2004, 2006). We took advantage of a long-term stream dataset for water and nitrate export combined with other knowledge about the average silty-clay

loam Mollisol agroecosystem. Both the watershed and specific field sites have been well studied and described previously (David et al. 1997, 2003; Gentry et al. 1998, 2007; Royer et al. 2004, 2006).

The watershed outlet at Camargo, Illinois (39°47'29"N, 88°11'08"W) is continuously gaged by the United States Geological Survey and these data were used for daily water flux. The Embarras watershed is intensively drained with random tile systems at depths of 1–1.5 m, has flashy hydrographs in response to precipitation events, and is predominately row cropped (>90%) in corn and soybeans. This leads to large exports of nitrate, averaging about 30 kg N ha⁻¹ year⁻¹ (David et al. 1997; Royer et al. 2006). The Mollisols formed in 100–150 cm of loess over medium to fine-textured glacial till, and are mostly silty-clay loams. Flat topography in this area requires artificial drainage to remove subsurface water in early spring and allow timely planting. The dominant soil series is Drummer silty clay loam (fine-silty, mixed, superactive, mesic Typic Endoaquolls), a poorly drained Mollisol that is highly productive with drainage. During the modeling comparison period of 1997 through 2006, annual precipitation was 98 cm (mean of three locations distributed around the watershed), and the annual mean air temperature was 11.5°C (from Urbana, IL data).

Long-term stream chemistry data for this watershed was used to estimate nitrate loss by drainage. Since 1993, water samples were collected weekly from the outlet, and additional samples collected during high-flow periods (as often as daily). Nitrate-N was measured using ion chromatography, and linear interpolation used to estimate concentrations on days samples were not collected (see Royer et al. 2006 for additional details). By combining nitrate concentration data with daily flow, daily riverine export of N as nitrate was estimated. During the modeling period the watershed was planted equally with corn and soybean, with fields rotating crops each year. For corn and soybean yields, we used county level estimates for Champaign County, IL, where the largest part of the watershed is located. Nitrogen fertilizer is typically applied in the fall or spring at rates of 160–200 kg N ha⁻¹ year⁻¹ to corn, and was estimated from surveys to be 190 kg N ha⁻¹ year⁻¹ during the period simulated, with approximately 50% in the fall, and 50% in the spring. Nitrogen fertilizer is not applied to soybean.

As modeled by Tonitto et al. (2007a), each model was parameterized to the system described above, with daily precipitation and temperature files created to allow multi-year runs of each model. A silty clay loam soil was simulated, with a clay fraction of 35%, porosity of 0.477, saturated hydraulic conductivity of 0.025 cm per minute, and field capacity and wilting point of 0.73 and 0.31 (as water-filled porosity or WFPS), respectively. However, adjustments were made to these initial values if needed for calibration of a particular model. The management schedule also followed Tonitto et al. (2007a), with typical corn and soybean production in east-central Illinois. For corn, chisel tillage was on 21 April, with planting and fertilization on 1 May and harvest on 21 October. Fertilization was 95 kg N ha⁻¹ applied as ammonium-nitrate on 1 May, and 95 kg N ha⁻¹ of anhydrous ammonia applied the previous 21 November, following the soybean harvest. Soybean tillage was conducted on 7 May, planting on 21 May, and harvest 5 October, and N fertilizer was not applied. All crop residues were considered to be returned to the field in all models, with only grain exported.

Each modeling team followed the production practices and utilized the soils data described above, and were provided environmental driving variable datasets of daily minimum and maximum air temperature, and daily precipitation for 1993–2006 from three weather stations in or near the watershed. Model parameters were calibrated to fit the observed daily riverine water flux and nitrate-N export, and annual corn and soybean harvest.

Models applied in this comparison included DAYCENT, SWAT, DNDC (two versions), EPIC, and DRAINMOD-N II. Each is described briefly below. The models varied in how they predict denitrification and other N fluxes, as well as simulate soil moisture dynamics, with DNDC being a microbial growth model, and the others simplified process models (as defined by Heinen 2006). Only DRAINMOD-N II was designed to be a tile drainage model, whereas SWAT and EPIC had tile drainage incorporated into later versions. DNDC and DAYCENT have no specific algorithms to simulate tile drainage, and soil parameters are adjusted to simulate water flux below the rooting zone to be similar to the tile drainage water flux. DNDC and DAYCENT were formulated by biogeochemists as tools to better understand C and N dynamics in soils, whereas

DRAINMOD-N II, EPIC, and SWAT were developed by agronomists to assess agricultural production and nutrient, sediment, pesticide losses. Finally, the basis of SWAT was several earlier models, one of which was EPIC, so we might expect some similarities in their predictions of denitrification and other N fluxes.

For all models except SWAT, two sets of simulations were performed to represent cropland in central Illinois, one with corn grown during odd years and soybean during even years and another one with corn grown during even years and soybean grown during odd years. Outputs for grain yields, water leaching, NO_3 leaching, and N gas flux from denitrification were averaged from the two sets of simulations to obtain daily, monthly, and yearly estimates of these variables for the watershed. With SWAT the watershed was divided into seven sub-watersheds and the model was run with approximately half the watershed area in corn and half in soybean for a given year, with rotation of the crops in following years. Therefore, output from each year is similar to the other models in providing an averaged value for corn and soybean.

DAYCENT

DAYCENT (Kelly et al. 2000; Parton et al. 1998; Del Grosso et al. 2001a) is the daily time step version of the CENTURY (Parton et al. 1993) model. DAYCENT simulates exchanges of carbon, nutrients, and trace gases among the atmosphere, soil, and plants as well as events and management practices such as fire, grazing, cultivation, and organic matter or fertilizer additions. Primary model inputs are: soil texture, current and historical land use, and daily maximum/minimum temperature and precipitation. Soil water content, temperature, mineral N concentration, trace gas flux, and SOM decomposition are simulated on a daily time step while plant growth is updated weekly. DAYCENT includes submodels for plant productivity, decomposition of dead plant material and SOM, soil water and temperature dynamics, and N gas fluxes. Flows of C and nutrients are controlled by the amount of C in the various pools, the N concentrations of the pools, abiotic temperature/soil water factors, and soil physical properties related to texture.

The N gas submodel of DAYCENT simulates soil N_2O and NO_x gas emissions from nitrification and

denitrification as well as N_2 emissions from denitrification. N gas flux from nitrification is assumed to be a function of soil NH_4^+ concentration, water content, temperature, and pH (Parton et al. 1996; 2001). Denitrification is a function of soil NO_3^- concentration, labile C availability, WFPS, and soil physical properties related to texture that influence gas diffusivity (Parton et al. 1996; Del Grosso et al. 2000). Denitrification increases exponentially with increasing soil NO_3^- concentration when NO_3^- concentration is low (<50 ppm) and approximately linearly at higher NO_3^- levels. Denitrification increases approximately linearly with soil heterotrophic respiration, a proxy for labile C availability. No denitrification is assumed to occur until WFPS values exceed 50–60%, then denitrification increases exponentially until WFPS reaches 70–80% and it stabilizes as soil water content approaches saturation. The model calculates $\text{N}_2 + \text{N}_2\text{O}$ emissions from denitrification by assuming that the process is controlled by the input (NO_3^- , respiration, WFPS) that is most limiting. N_2O emissions are calculated from $\text{N}_2 + \text{N}_2\text{O}$ gas emissions and an $\text{N}_2:\text{N}_2\text{O}$ ratio function. The ratio of $\text{N}_2:\text{N}_2\text{O}$ gases emitted due to denitrification is assumed to increase as the ratio of e^- acceptor (NO_3^-) to e^- donor (labile C) decreases and as soil gas diffusivity and O_2 availability decrease. N_2O can act as an alternative e^- acceptor and be reduced to N_2 when labile C is in excess compared to NO_3^- . D/D_0 , a relative index of gas diffusivity in soils, is calculated as a function of WFPS and soil physical properties (bulk density and field capacity) that influence gas diffusion rates using equations presented by Potter et al. (1996). As D/D_0 decreases, the residence time of N_2O in soil increases, thus increasing the probability that N_2O will be further reduced to N_2 before diffusing from the soil.

The ability of DAYCENT to simulate soil C and N fluxes has been tested with data from various native and managed systems (Del Grosso et al. 2000, 2001b, 2002, 2005). Simulated and observed grain yields for major cropping systems in North America agreed well with data at both the site ($r^2 = 0.90$) and regional ($r^2 = 0.66$) scales (Del Grosso et al. 2005). N_2O emission data from 8 cropped sites and NO_3 leaching data from 3 cropped sites showed reasonable agreement with DAYCENT simulations ($r^2 = 0.74$ and 0.96 for N_2O and NO_3 , respectively) (Del Grosso et al. 2005). The denitrification submodel used in

DAYCENT simulated $\text{N}_2\text{O} + \text{N}_2$ emissions fairly well when compared with incubation data used for model building ($r^2 = 0.74$) and independent field data used for model testing ($r^2 = 0.47$) (Del Grosso et al. 2000). DAYCENT has been used for various applications, most notably to estimate N_2O emissions from agricultural soils for the US Greenhouse Gas Inventory (USEPA 2007a; Del Grosso et al. 2006).

Standard values for all parameters controlling plant growth, leaching, and N gas fluxes were used with the following exceptions. The rooting depth for soybean was increased from 45 to 60 cm and the rooting depth for corn was decreased from 120 to 90 cm. This was done because the standard parameterization for soybeans caused the model to overestimate water and NO_3 leaching in the autumn during some of the years in which soybean was grown. Increasing the rooting depth led to drier soil following harvest so more water could be stored in soil during the autumn, and hence, leaching was decreased during this time period. The rooting depth for corn was decreased because the model tended to underestimate leaching the years corn was grown. The sensitivity of soil water dynamics to rooting depth suggests a potential model improvement. Instead of assuming that rooting depth is constant, DAYCENT could be improved by implementing a dynamic root growth submodel that allowed effective rooting depth to vary throughout the growing season. This would lead to more realistic simulation of water and nutrient uptake by crops, particularly annuals.

SWAT

The Soil and Water Assessment Tool (Arnold et al. 1998; Neitsch et al. 2005) is a physically based, comprehensive simulation model for long-term predictions of hydrological and water quality impacts of alternative land management practices. It can simulate water budgets, sediment yield, and pollution loadings by taking into account a wide range of climatic, soil, topographic, and land use factors. Major simulation components of SWAT include climate, hydrology, plant growth, erosion, and fate of pollutants (including N, P, pesticides, and pathogens). A detailed description of SWAT can be found in Neitsch et al. (2005).

Developed in the early 1990s under the request of USDA Agricultural Research Service, SWAT quickly gained its popularity in the late 1990s, largely due to

its successful integration with GIS, user friendly interface, and ability to simulate a wide variety of environmental processes at large watershed scales. Since its creation, SWAT has been refined and updated. The latest version of the model is SWAT2005, which was released not long ago to replace its popular predecessor SWAT2000. SWAT has been tested and applied under a broad range of geographical settings to solve a wide variety of environmental problems (Gassman et al. 2007).

SWAT can simulate the major nitrogen processes commonly found in agricultural settings. Total denitrification (sum of N_2 and N_2O) is estimated as a function of nitrate, organic carbon, and soil water contents in the soil. The amount of denitrification occurring in a 1 day time step is determined by the following equations:

$$N_{\text{denit,ly}} = \text{NO3}_{\text{ly}} \times [1 - \exp(-\beta_{\text{denit}} \times \gamma_{\text{tmp,ly}} \times \text{orgC}_{\text{ly}} \times t)] \text{ if } \gamma_{\text{sw,ly}} \geq \gamma_{\text{sw,thr}} \quad (1a)$$

$$N_{\text{denit,ly}} = 0 \text{ if } \gamma_{\text{sw,ly}} \leq \gamma_{\text{sw,thr}} \quad (1b)$$

where $N_{\text{denit,ly}}$ is the amount of nitrogen lost to denitrification from soil layer ly, NO3_{ly} is the amount of nitrate in soil layer ly at the beginning of the time step (kg N ha^{-1}), β_{denit} is the denitrification rate coefficient (day^{-1}), $\gamma_{\text{tmp,ly}}$ is the nutrient cycling temperature factor for layer ly, orgC_{ly} is the concentration of organic carbon in layer ly (%), t is the time step (equals 1 day in SWAT), $\gamma_{\text{sw,ly}}$ is the water content factor defined as the ratio of actual soil water content to field capacity of layer ly, and $\gamma_{\text{sw,thr}}$ is the threshold water content factor for denitrification. The values of NO3_{ly} , orgC_{ly} , $\gamma_{\text{tmp,ly}}$, and soil water content are provided by other equations in the model. The soil layer information can be obtained from the State Soil Geographic (STATSGO) database. The values of β_{denit} and $\gamma_{\text{sw,thr}}$ were fixed to 1.4 day^{-1} and 0.95, respectively, in the original version of SWAT2000. However, the version used for this study was slightly modified by its developer to allow users adjustment to β_{denit} (see Louwers 2003 for details) and the value of 0.1 day^{-1} was used. The recently released SWAT2005 has been updated to allow calibrations to both parameters.

A small number of SWAT studies have paid special attention to denitrification from agricultural lands. For a large watershed in Finland (Grizzett et al. 2003), SWAT predicted a denitrification of

1.6 kg N ha⁻¹ year⁻¹ from the agricultural lands with predominantly flat topography and clay soil. Louwers (2003) applied SWAT to the upper Embarras River watershed in Illinois, USA and found the average amount of denitrification during the period of 1978–2002 to be 37 kg N ha⁻¹ year⁻¹. Hu et al. (2007) used SWAT2000 to simulate the same watershed with a more systematic calibration technique and reported watershed average denitrification values of 23 and 20 kg N ha⁻¹ year⁻¹ in the calibration (1994–2002) and validation (1985–2003) periods, respectively. Other reports of direct application of SWAT for denitrification simulation are rare.

The model simulations of Hu et al. (2007) accounted for 74 and 72% of the observed annual and monthly riverine nitrate fluxes, respectively, during the calibration period, but only 36 and 51% during the validation period. The model simulated average annual soybean N fixation of 196 kg N ha⁻¹ year⁻¹, which is considerably greater than the range values (102–124 kg N ha⁻¹ year⁻¹) reported in the literature for the region. This overestimation is likely to have influenced the simulated denitrification.

In this study, the SWAT version 2000 was used to simulate hydrologic and N cycle processes in the upper Embarras River basin. The model was calibrated with observed monthly streamflow and nitrate flux, and annual crop yields from 1994 to 2006. Model configuration and calibration followed the procedures described by Hu et al. (2007), except the farming schedule given by Tonitto et al. (2007a) described above was used, and the harvest index for soybean was adjusted from the default value of 0.31–0.42, the average value suggested by Prince et al. (2001). The latter change reduced the simulated soybean N fixation to 99 kg N ha⁻¹ year⁻¹, which is slightly less than the range reported in the literature for the region. A total of 11 parameters were calibrated, including 6 hydrologic and soil water parameters, 4 nitrogen process parameters, and 2 crop growth parameters. The model simulations started with 1995 weather data to allow a 2-year spin-up period to minimize effects of any erroneous initial conditions.

DNDC

DNDC was developed as a field-scale, process-based, mechanistic model of N and C dynamics in agroecosystems (Li et al. 1992) and has been broadly applied

to assess agricultural management (Li et al. 2004, 2005a, b; Tonitto et al. 2007a, b). DNDC was originally developed to study annual cropping systems, particularly grain systems, but it has also been developed to study forest and grassland ecosystems (Cui et al. 2005a, b; Li et al. 2005b). The primary drivers of DNDC outcomes—climate, soil, vegetation and anthropogenic activity—determine the soil environmental factors: (1) temperature, (2) moisture, (3) pH, (4) Eh, and (5) substrate concentration gradients. Biogeochemical processes of nitrification, denitrification, and fermentation are represented as microbially mediated processes regulated by the soil environmental factors. Model calculations are performed at a daily or hourly time step, though it is generally not possible to validate this level of temporal resolution for application in agricultural management.

DNDC is a process-based model tracking each step of the sequential reactions of denitrification. Trace gas flux in DNDC depends on the interaction between microbial populations and the soil environment. This directly regulates gas flux rates based on biotic controls, rather than relying strictly on N availability and the soil environment. In DNDC, the factors directly controlling denitrification rate are soil Eh, denitrifier activity, and the concentration of substrates (e.g., DOC, NO₃⁻, NO₂⁻, NO, or N₂O). Denitrification rate is driven by two equations: (1) the Nernst equation and (2) the Michaelis–Menten equation. The Nernst equation is a basic thermodynamic formula for determining soil Eh based on soil solution oxidant and reductant concentrations (Stumm and Morgan 1981). The Michaelis–Menten equation is widely applied to describe the kinetics of microbial growth under resource limitation (Paul and Clark 1996); in the denitrification reactions the limiting resources are DOC and electron acceptors (i.e., nitrogen oxidants). The Nernst and the Michaelis–Menten equations can be coupled since they share a common factor, the oxidant concentration. This coupling has been realized in DNDC through a simple kinetic scheme called the “anaerobic balloon.” The anaerobic balloon in DNDC defines the effective anaerobic volumetric fraction of a soil based on the soil bulk Eh. The size of the anaerobic balloon is determined based on the Eh value of a soil layer, and subsequently the soil substrates are allocated inside or outside of the balloon proportional to the anaerobic balloon size.

Only the substrates allocated within the balloon will be involved in the anaerobic reactions (e.g., denitrification etc.), and the substrates allocated outside of the balloon will be involved in the aerobic reactions (e.g., nitrification etc.). When the anaerobic balloon swells, several processes will take place, including (1) more substrate (e.g., DOC, NO_3^- , NO_2^- , NO, or N_2O) will be allocated within the balloon, (2) reduction reaction rates (e.g., sequential denitrification reactions) will increase within the constraints imposed by Michaelis–Menten mediated-microbial growth, and (3) gaseous intermediate products (e.g., N_2O , NO etc.) will take longer to diffuse from the anaerobic to the aerobic fraction, increasing the rate at which N gases are further reduced to N_2 . The coupling of the Nernst and Michaelis–Menten equations enables the simultaneous simulation of nitrification and denitrification in the DNDC model.

The indirect factors controlling denitrification in DNDC include soil temperature, moisture, pH and any C or N-related processes. The production of N_2 and N_2O is regulated by microbial population dynamics. The flux of N gas from the soil to the atmosphere is regulated by soil clay, soil moisture (WFPS), and soil temperature.

DNDC tracks outcomes on a daily time scale. Detailed simulation outcomes are available for soil environmental variables (Eh, moisture and temperature), soil chemistry (inorganic N, organic N, organic C), N and C gas flux, water flux (drainage, runoff, evapotranspiration, ponding, snowpack), crop C and N, and crop yield. In this application, we constrain model outcomes based on field measurements of drainage, nitrate flux, and crop yield.

The DNDC model has previously been applied to study the Embarras watershed in Illinois for the period 1992–2002 (Tonitto et al. 2007a, b). In that work, DNDC was modified to approximate dynamics of tile-drainage, which is currently not explicitly modeled in DNDC; the DNDC model was calibrated using data from 1993 to 1997 and validated using data from 1998 to 2002. For the current model comparison, we simulated the period 1996–2006, with 1996 being removed from the summary of model outcomes. In the current work, we simulate the Embarras watershed using two versions of DNDC, DNDC82h used previously to simulate the Embarras watershed and a slightly earlier version of the model, DNDC82a. In the current application DNDC82h is

simulated using what was considered a ‘best case’ parameter set (Tonitto et al. 2007a), with parameters DID = 0.2 (proportion of water lost from freely available water pool), DVD = 0.05 (power function coefficient describing the amount of water that is lost from the soil pore space), day_leach_water = 700 (power function coefficient, which determines the fraction of nitrate that is leached from a given soil layer and ultimately leached from the system), pool_leach_nitrate = 10 (initial value of nitrate pool available for leaching), and PLN = 0.01 (describes the fraction of the leached nitrate pool that is available for plant uptake). DNDC82a was applied with similar parameter modifications, but with some different final coefficients (DID and DVD = 0.05, day_leach_water = 250, pool_leach_nitrate = 30, and PLN = 0.01). Because results were quite different between the two versions, both sets of results are presented.

DRAINMOD-N II

DRAINMOD-N II (Youssef 2003; Youssef et al. 2005) is a field-scale, process-based model that simulates C and N dynamics in drained cropland for a wide range of soil types, climatic conditions and farming practices. As the name implies, DRAINMOD-N II is a companion model to DRAINMOD (Skaggs 1978), a widely used hydrologic model for artificially drained soils.

DRAINMOD is a one dimensional model that simulates water and heat flow for high water table soils with artificial drainage systems. It uses the water balance approach with functional relationships to describe the main hydrologic processes and predict subsurface drainage, surface runoff, infiltration, water table depth, soil water content and evapotranspiration in response to given climatological conditions, soil and crop properties, and drainage and irrigation management. DRAINMOD simulates heat flow using finite difference solution to the heat equation and predicts the temperature distribution throughout the soil profile. The model uses an empirical approach to predict the relative grain yield as affected by planting date delays, soil water related stresses, and soil salinity on crop yield. The model is well documented (e.g. Skaggs 1978, 1999) and several reports of model validation and application (e.g. Skaggs et al. 1981;

Skaggs 1982; Fouss et al. 1987) have shown that DRAINMOD can reliably predict water table fluctuations and drainage volumes.

DRAINMOD-N II simulates organic carbon (OC) dynamics using a C-cycle similar to that of the CENTURY model (Parton et al. 1993). It considers three below-ground soil organic matter fractions (active, slow, and passive), a surface microbial pool, two above-ground and two below-ground litter pools (metabolic and structural). Each pool is characterised by the C to N ratio (C:N), and the potential rate of decomposition. Nitrogen mineralization and immobilization processes are simulated as consequences of C cycling in the system during SOM decomposition (Youssef et al. 2005).

DRAINMOD-N II simulates a detailed N cycle that considers both mineral N and organic N (ON) and their interaction as affected by C cycling. The ON compartment is divided into pools that correspond to the OC pools. The model operates in three modes. The simplest is based on the original version of Brevé et al. (1997) and ignores ammoniacal-N ($\text{NH}_x\text{-N}$); all mineral N is considered to be in the $\text{NO}_3\text{-N}$ form. In the second mode, referred to as the 'normal' mode, $\text{NH}_x\text{-N}$ is considered to be in the $\text{NH}_4\text{-N}$ form. In the last mode, referred to as the 'volatilization' mode, the $\text{NH}_x\text{-N}$ is considered to be in the $\text{NH}_4\text{-N}$ and ammonia-N ($\text{NH}_3\text{-N}$) forms, which are in a pH-dependent equilibrium. The model automatically switches between the normal and the volatilization modes according to simulated soil pH. The model simulates atmospheric deposition, application of mineral N fertilizers, application of organic N sources, plant uptake, mineralization, immobilization, nitrification, denitrification, NH_3 volatilization, and N losses via subsurface drainage and surface runoff.

Nitrogen transport is simulated using a multiphase form of the one dimensional advection-dispersion-reaction (ADR) equation. For a reactive species, a linear adsorption isotherm is used to relate its concentration in the soil solution to the solid phase. Henry's law is used to relate a solute's concentration to the gaseous phase. DRAINMOD-N II solves the ADR equation using a first-order, explicit finite difference scheme (Youssef et al. 2005). The hydrological parameters driving reactive N transport in DRAINMOD-N II are based on DRAINMOD's output.

The model simulates farming practices such as tillage and plant residue management and the application of mineral N fertilizers and animal manure. It simulates a tillage event by identifying a plough depth within which the soil and any plant residues laying on the soil surface are mixed according to a tillage intensity factor. With the exception of anhydrous NH_3 , the model applies all fertilizer N in solid form, which dissolves according to a zero-order rate whenever soil water exceeds a threshold value. Anhydrous NH_3 is injected into the soil profile in the gaseous phase. The model simulates the application of animal waste which may contain both mineral and organic N.

Nitrification, denitrification, and urea hydrolysis are modelled in DRAINMOD-N II using Michaelis-Menten kinetics. The model simulates the influence of organic carbon on denitrification rate using an exponential depth function. It uses an empirical response function to simulate nitrification inhibition caused by inhibitors that might be applied with N fertilizers. DRAINMOD-N II uses environmental response functions to simulate the effect of environmental factors including soil temperature, soil moisture and soil pH on C and N transformation (Youssef et al. 2005).

Model predictions include daily concentrations of mineral N (i.e. NO_3^- and NH_4^+) in soil solution and drainage outflow, organic C content of the top 20 cm soil layer, and cumulative rates of simulated N processes on daily, monthly, and annual basis. DRAINMOD N II has been successfully tested using field data from artificially drained soils with contrasting soil types, climatic conditions, and farming practices (e.g. Youssef et al. 2006; Bechtold et al. 2007). For this Illinois corn/soybean comparison the Nash-Sutcliffe modeling efficiency was used as a statistical measure of agreement between model predictions and observations.

The potential evapotranspiration (PET), estimated by DRAINMOD using the Thornthwaite method, is corrected using monthly correction factors that are derived for Illinois conditions (R. Cooke, personal communication) and fine tuned during model calibration. Hydraulic soil properties, including the lateral saturated hydraulic conductivity and the soil water characteristic data, were based on field measurements (D. Pitts, unpublished data). Other chemical and physical soil properties were obtained

from published soil survey data for the Drummer soil in Vermilion County, IL (NRCS 1996). Tile drainage was simulated using a drain depth of 1.2 m (Tonitto et al. 2007a) and a calibrated drain spacing of 30.0 m. Soil organic matter inputs were based on default inputs for the Century model (Parton et al. 1993). Nitrogen transport and transformation parameters were based on default values for the DRAINMOD-N II model (Youssef et al. 2005, 2006). Input parameters for nitrification and denitrification processes were adjusted during model calibration.

EPIC

The EPIC model is a field-scale agroecosystem model that simulates crop production as a function of weather, soil conditions, and production practices employed (e.g., tillage types, tillage frequency, crop rotations). EPIC was developed and is maintained by researchers at Texas A&M University, and was designed originally to explore the impacts of soil erosion on crop productivity (Williams et al. 1983). The model has evolved continuously since 1985, with continued refinements to the carbon and nutrient cycling sub-models, and additional capacity introduced related to water quality and the response of crops to atmospheric CO₂ (Gassman et al. 2005). EPIC, and the models that have evolved from it such as APEX, have been applied extensively to cropping systems worldwide on a variety of soils and cropping systems (see He et al. 2006 for a review), and a number of validation studies have been performed to explore its handling of nutrient cycling and nutrient loss (Gassman et al. 2005), including tile drainage (e.g., Chung et al. 2001).

EPIC's nutrient cycling sub-routine tracks soil N movement through five organic C/N pools and two inorganic pools. The five organic C/N pools consist of two surface litter pools—metabolic and structural litter—and three subsurface pools—microbial biomass, an active soil humus pool (called “slow” humus) and a stable (or “passive”) soil humus pool. The user can specify the fraction of humus assigned to the stable pool, or EPIC will estimate it based on the years in which the plot has been in cultivation, with longer cultivation times leading to a larger stable humus pool and lower aggregate mineralization rates. Nitrogen moves into the organic pools through plant residues, roots, green manures, or fertilizers, and out of the organic pools through sediment losses or

through mineralization to the inorganic ammonium pool, which also receives inputs from ammonium fertilizers. The ammonium pool increases based on mineralization and fertilizer inputs, and decreases via nitrification losses to the nitrate pool, or volatilization into the atmosphere as NH₃.

The nitrate pool in EPIC represents the pool of N that is available for plant uptake. Nitrogen enters this pool through precipitation deposition, fertilization, and nitrification, and exits through runoff, subsurface flow, leaching, denitrification and plant uptake. There are multiple opportunities for user calibration of these processes. Denitrification, for instance, is modeled as a first-order transformation that is triggered when soil saturation exceeds a user-specified level. The Denitrification Soil–water threshold variable in EPIC is the fraction of field capacity soil water storage that triggers denitrification. In the model runs performed in this study, this value was set a 1.0. The denitrification rate constant is also user specified, as is the minimum soil nitrate concentration, which constrains the amount of N available for denitrification. Plant demand for N is determined by the crop's N use efficiency parameters; once N is taken up by the plant, it is either removed from the field with yield or returned to the organic N pools as residue or root weight. The amount of N removed is a function of total biomass, harvest index, and fraction of N in yield. Nitrogen fixation allows crops to augment the amount of N returned to the organic pools.

EPIC governs movement of N along these paths by calculating for each N pool the potential input and output transformations, aggregated into potential total demand and supply for each pool, and then actual transformations based on adjusted potential transformations (in cases where demand is estimated to exceed supply). The rate functions describing input and output transformations incorporate information about soil temperature, soil water, soil texture, and limitations on maximum conversions or minimum concentrations, together with information on erosion, leaching, and crop production processes, and contain multiple user-input parameters that can be used to adjust or calibrate those relationships. A thorough description of the functions underlying the various transformation processes in the organic C/N cycle appears in Izaurre et al. (2006).

It has been argued that EPIC is well-suited for modification to simulate trace gas fluxes in the soil

(Izaurre et al. 2006), but the model currently does not explicitly model the trace gas outputs from soil processes such as nitrification and denitrification. EPIC calculates N loss to denitrification, for instance, but does not distinguish whether that N is lost as N₂ or N₂O.

Results and discussion

Modeling results

Each of the models was able to simulate corn and soybean yields within 12% of the observed average, with most differences <5% (Table 1). However, most of the models over predicted soybean average yield, although the overall range was from -0.7 to 7.3% of the yearly mean value. Both versions of DNDC under predicted corn yields, but were within 2.5% of soybean yields.

Water is a primary flux controlling many biogeochemical processes, and in this tile drained region about 30% of precipitation ends up as streamflow, most routed through tiles, then lateral seepage, and a small amount as surface runoff. The tile flow carries the large nitrate loads found throughout the cornbelt (David et al. 1997; Mitchell et al. 2000; Royer et al. 2006), and it is important to model tile water flux accurately to obtain good estimates of nitrate flux (Hu et al. 2007). Each of the models except DNDC82h

accurately estimated average annualized drainage water flux during the 10 year period, with a range of 28.2–31.2 cm compared to the observed value of 30.2 cm; DNDC82h simulated 20.3 cm. On a monthly basis (Fig. 1), there was considerable variation in water flux, with *r*² values ranging from 0.44 for DNDC82h to 0.85 for SWAT. DRAINMOD-N II, EPIC, DAYCENT, and DNDC82a had monthly water flux *r*² values of 0.81, 0.73, 0.66, and 0.57, respectively. Modeling efficiency (EF) can also be used to compare predicted and observed values (Tonitto et al. 2007a, b), and is defined as

$$EF = \frac{\sum_{t=1}^N (O(t) - \bar{O})^2 - \sum_{t=1}^N (S(t) - O(t))^2}{\sum_{t=1}^N (O(t) - \bar{O})^2},$$

where (S) is model simulations, and (O) is field observations during the course of the simulation (*t* = time). Values between 0 and 1 indicating the model results are better than using the mean value of the observations, and values < 0 worse. The best performing models are those with EF close to 1. Modeling efficiency for water flux varied from 0.38 to 0.85, with the three agronomic models performing the best (Table 2). The underprediction of average annualized drainage in the DNDC82h simulations results from two model trends. DNDC82h underpredicted stream flow in 9 of the 10 years the one exception being the drought year of 2000. Additionally, DNDC82h is completely unable to capture dynamics in 2003. In 2003, DNDC82h predicts

Table 1 Mean annual crop yields, drainage water flux, and N fluxes for 1997 through 2006 for a central-Illinois corn and soybean agroecosystem

Flux	Observed	SWAT	DAYCENT	DRAINMOD-N II	EPIC	DNDC82a	DNDC82h
Corn yield (kg C ha ⁻¹)	4,230	4,250	4,370	4,510	4,150	3,910	3,710
Soybean yield (kg C ha ⁻¹)	1,400	1,440	1,500	1,460	1,420	1,400	1,390
Stream flow (cm)	30.2	30.1	30.7	28.2	31.2	30.2	20.3
Nitrate-N (kg N ha ⁻¹)	28	21	26	22	26	28	26
Fertilization (kg N ha ⁻¹)	95	95	95	95	95	95	95
N ₂ Fixation (kg N ha ⁻¹)		49	79	96	74	72	78
Grain N harvest (kg N ha ⁻¹)		138	129	152	134	115	111
Denitrification (kg N ha ⁻¹)		17	5.6	18	11	3.8	21
N ₂ O (kg N ha ⁻¹)			3.0			2.4	8.6
N ₂ (kg N ha ⁻¹)			2.6			1.4	13
Δ soil N storage (kg N ha ⁻¹)		-22	5.5	-7	-2	19	15
N balance (kg N ha ⁻¹) ^a		-32	13	-1	-2	20	15

^a Nitrogen balance = fertilization + N₂ fixation - (grain N harvest + denitrification + nitrate-N)

Fig. 1 Observed and modeled water flux for a central-Illinois corn and soybean agroecosystem

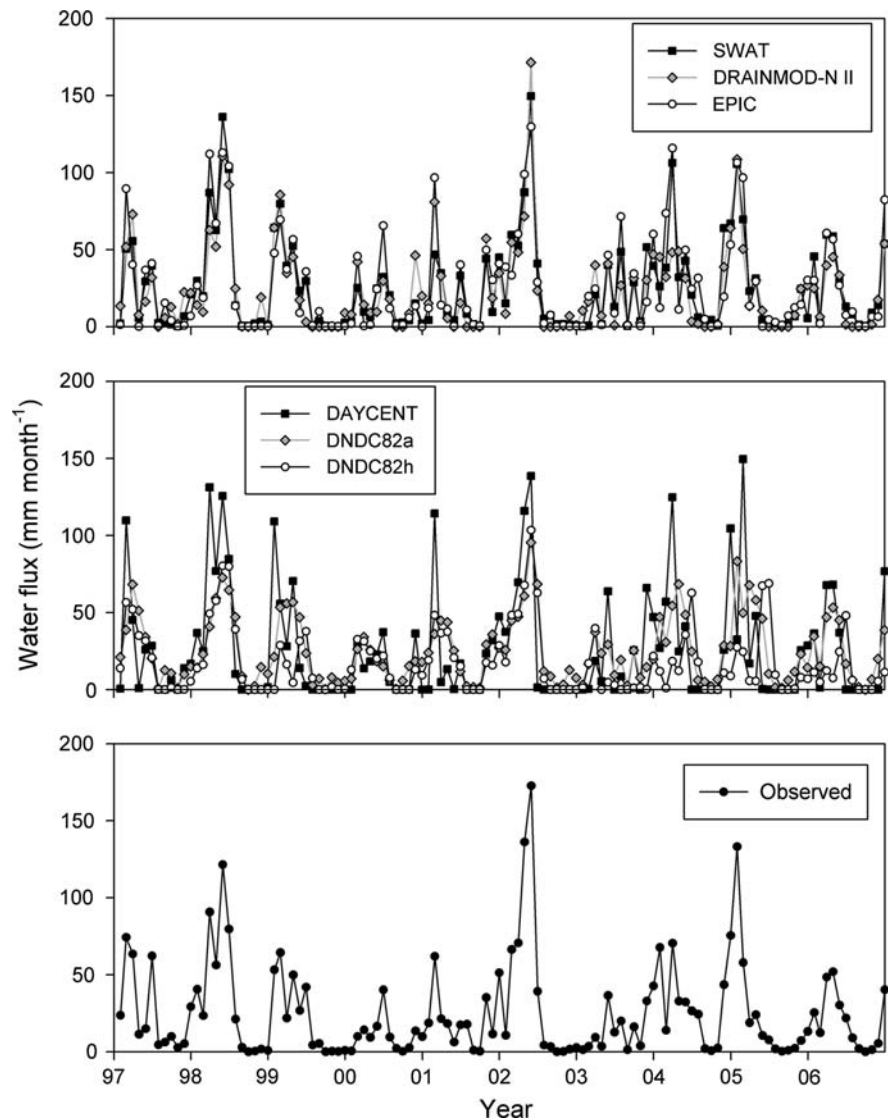


Table 2 Modeling efficiency (EF) comparing measured monthly water and nitrate flux data for 1997 through 2006 for a central-Illinois corn and soybean agroecosystem

Model	Modeling efficiency (EF)	
	Water flux	Nitrate-N leaching
SWAT	0.85	0.68
DAYCENT	0.53	0.49
DRAINMOD-N II	0.80	0.53
DNDC82a	0.56	0.23
DNDC82h	0.38	0.38
EPIC	0.69	-0.46

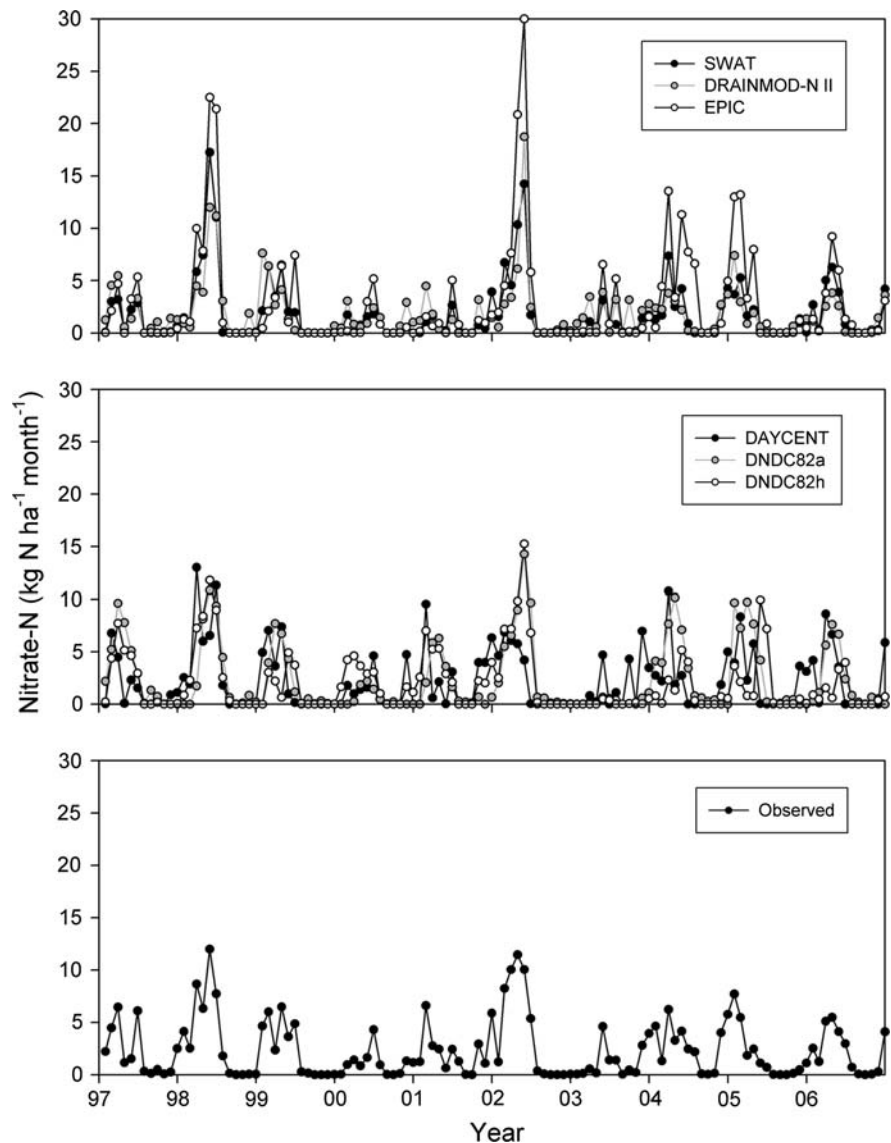
essentially no tile drainage (2.4 cm) and above average runoff (7 cm). The other simulated years result in annual tile drainage ranging from 12 to 36 cm and runoff ranging from 0 to 4.4 cm (with most years below 1 cm). This shift in 2003 from water loss as leaching to water loss via runoff has significant implications for nitrate availability in the soil profile.

Despite the general accuracy of the average annual water flux predictions, there was much greater variation in predicted annual nitrate fluxes, demonstrating the difficulty in simulating the N cycle in this agroecosystem. This was primarily due to the

considerable variation in monthly water flux predictions discussed above. Accurate winter and spring water flux predictions are critical to accurate predictions of nitrate flux. The observed nitrate flux was $28 \text{ kg N ha}^{-1} \text{ year}^{-1}$, and model predictions ranged from 21 to $28 \text{ kg N ha}^{-1} \text{ year}^{-1}$. Nitrate flux is greatest during late winter to spring, and the models all simulated this temporal pattern well on a monthly basis, with r^2 values ranging from 0.51 to 0.76 (Fig. 2). Although the temporal variation predicted by the models (driven primarily by water flux) matched the observations, the models varied in how much nitrate was in the water, leading to the large

range in average predictions and a wide range in EF values (Table 2). EPIC, DAYCENT, DNDC82a, and DNDC82h predicted nitrate fluxes $26\text{--}28 \text{ kg N ha}^{-1} \text{ year}^{-1}$ (within 10% of the observed value), whereas SWAT and DRAINMOD-N II were 25 and 21% lower, respectively than observed. SWAT had the best EF value (0.68), with EPIC having a negative value (-0.46) due to two periods where modeled nitrate flux was quite different than observed. Modeling efficiency for the other models varied from 0.23 to 0.53. Again, the two best models in predicting monthly nitrate flux, based on EF, were agronomic based and included tile drainage.

Fig. 2 Observed and modeled monthly nitrate-N leaching fluxes for a central-Illinois corn and soybean agroecosystem



Modeled average annual denitrification fluxes for 1997–2006 were highly variable, and ranged from 3.8 to 21 kg N ha⁻¹ year⁻¹, with a median value of 17 kg N ha⁻¹ year⁻¹ (Table 1). DNDC82a and DAYCENT had relatively low annual fluxes of 3.0–6.7 kg N ha⁻¹ year⁻¹ (Table 3), whereas SWAT and DRAINMOD-N were substantially higher ranging from 11 to 29 kg N ha⁻¹ year⁻¹. EPIC was intermediate to these two sets of models, ranging from 5.4 to 16 kg N ha⁻¹ year⁻¹. Finally, DNDC82h had the largest range of all, from 3.1 to 88 kg N ha⁻¹ year⁻¹. It is perhaps significant that the models that underestimated riverine nitrate flux also predicted high denitrification values. The most extreme annual denitrification value of 88 kg N ha⁻¹ year⁻¹ derives from poor simulation of drainage and nitrate flux in 2003 by DNDC82h (simulated drainage was 9.4 cm compared to 18.5 cm observed, and simulated nitrate flux was 1.6 kg N ha⁻¹ compared to 15.7 observed). Additionally, 2003 resulted in exceptionally low simulated corn yield, resulting in more soil N available for denitrification. DNDC82h had been previously calibrated and validated against data through 2002 (Tonitto et al. 2007a, b), and the run was extended for this work through 2006. The model estimated much larger denitrification fluxes beginning in 2003, and behaved very differently for these four additional years than it had previously. The increase in denitrification after 2003 in DNDC82h occurs mostly as higher N₂ loss, with only moderate increase in N₂O flux predicted. During this time period, soybean fields exhibited their highest range of N-fixation (164–177 kg N ha⁻¹), simultaneously

accompanied by low nitrate leaching. The moderately high denitrification predicted from 2004 to 2006 is mostly explained by this altered N balance in the simulation of soybean dynamics.

The models typically predicted greatest denitrification fluxes in late spring, and most had the largest fluxes during the same months (Fig. 3), but there were exceptions from this pattern. Modeled denitrification fluxes are highly variable (Table 4). Correlation coefficients ranged from 0.04 to 0.75, with most about 0.5. These correlation coefficients indicate that one model's monthly denitrification flux explains only about 25% of another models. The two models that were most related for monthly flux predictions were SWAT and EPIC, with an $r = 0.75$, which reflects how they calculate denitrification similarly and that EPIC was one of the models that formed the basis for the SWAT model (Neitsch et al. 2005). DRAINMOD-N II predictions of denitrification in 2002 had the least correlation with the other models, primarily due to predictions of denitrification during the summer and fall. DRAINMOD-N II is different from all other models in that it explicitly simulates water table fluctuation in response to other hydrologic processes that enables the model to simulate denitrification in the entire soil profile, not just the surface soils as in the other models. Therefore, the predicted daily denitrification is the integration of denitrification that is simulated in the whole profile during the day. We do not have field data to compare to these predictions, but the DRAINMOD-N II results suggest a prolonged period of denitrification that the other models do not.

Table 3 Annual denitrification fluxes for 1997 through 2006 for a central-Illinois corn and soybean agroecosystem

Year	SWAT (kg N ha ⁻¹ year ⁻¹)	DAYCENT (kg N ha ⁻¹ year ⁻¹)	DRAINMOD-N II (kg N ha ⁻¹ year ⁻¹)	EPIC (kg N ha ⁻¹ year ⁻¹)	DNDC82a (kg N ha ⁻¹ year ⁻¹)	DNDC82h (kg N ha ⁻¹ year ⁻¹)
1997	12	5.7	16	7.5	3.0	3.1
1998	26	5.6	29	11	4.2	3.9
1999	11	5.1	15	8.6	3.2	23
2000	22	6.6	17	5.4	3.7	4.5
2001	9.9	5.8	14	11	3.7	3.2
2002	22	4.2	24	14	4.4	3.5
2003	13	6.7	18	8.2	4.8	88
2004	23	5.5	18	16	3.6	32
2005	11	4.4	12	16	3.8	28
2006	18	6.7	17	15	4.1	38

Fig. 3 Modeled monthly denitrification fluxes for a central-Illinois corn and soybean agroecosystem. Note y-axis scale differences

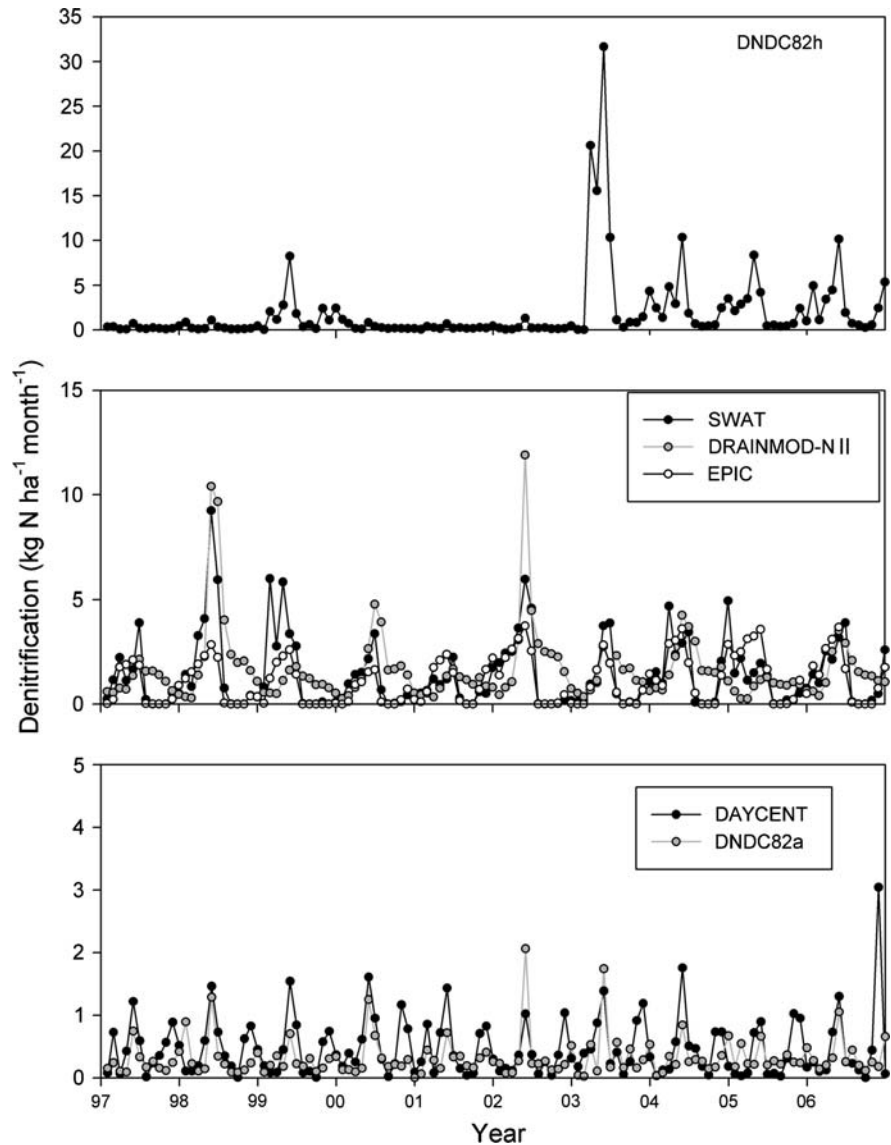


Table 4 Correlation coefficients (r) among the various models for monthly denitrification fluxes for 1997–2006 ($n = 120$)

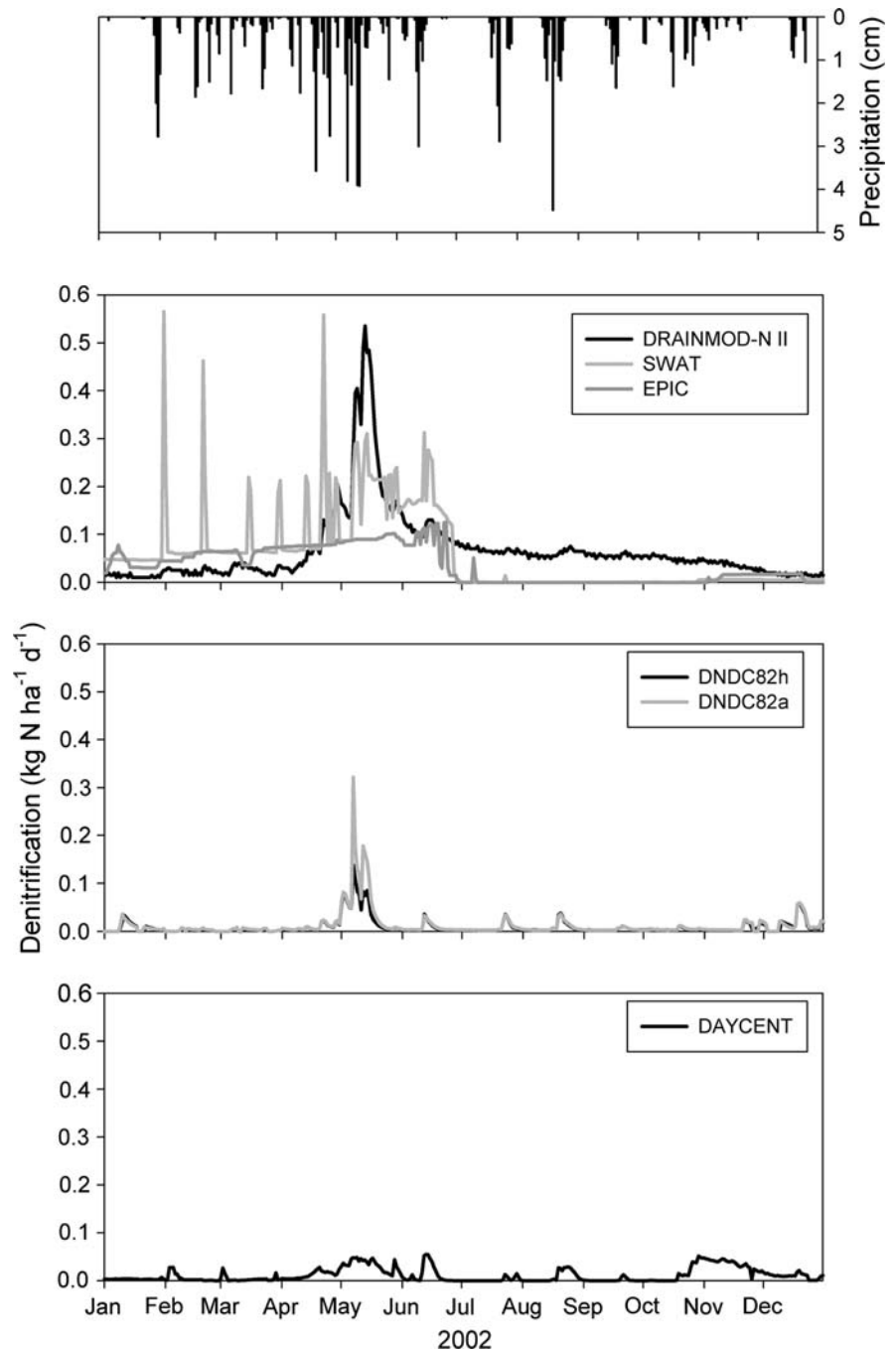
All are significant ($p < 0.0001$) with the exception of DND82h and DRAINMOD-N II ($p > 0.1$)

	DAYCENT	DRAINMOD-N II	EPIC	DNDC82a	DNDC82h
SWAT	0.22	0.56	0.75	0.46	0.25
DAYCENT		0.31	0.28	0.46	0.29
DRAINMOD-N II			0.31	0.55	0.04
EPIC				0.45	0.38
DNDC82a					0.43
DNDC82h					

To further illustrate these differences in denitrification predictions among the models, we examined denitrification in 2002 on a daily basis (Fig. 4). This

was a wet year, with numerous precipitation events greater than 2 cm throughout the year, although most were in the spring. Modeled denitrification fluxes for

Fig. 4 Modeled daily denitrification fluxes for a central-Illinois corn and soybean agroecosystem for 2002, along with daily precipitation



the year ranged from 3.5 to 24 kg N ha⁻¹ year⁻¹, illustrating that the various models were translating the driving variable of precipitation to corresponding denitrification rates very differently. SWAT predicted short, intense denitrification fluxes throughout the winter and spring months (daily flux rates of >0.2 kg N ha⁻¹ day⁻¹), with little denitrification

after June. The SWAT total denitrification flux for the year was 22 kg N ha⁻¹ year⁻¹, similar to the DRAINMOD-N estimate of 24 kg N ha⁻¹ year⁻¹. DRAINMOD-N had low denitrification fluxes until the wet period in May and June, when high rates were predicted. This increase in denitrification remained at about 0.1 kg N ha⁻¹ day⁻¹ from June through the

rest of the year, declining to zero only in December. For these two models, annual rates were similar, but the predicted daily denitrification values were very different.

All models predicted high denitrification rates for many days in May and June 2002 ($>0.1 \text{ kg N ha}^{-1} \text{ day}^{-1}$), although the DAYCENT maximum flux for the year was only $0.06 \text{ kg N ha}^{-1} \text{ day}^{-1}$ (Fig. 4). Denitrification values in fertilized corn fields greater than $1 \text{ kg N ha}^{-1} \text{ day}^{-1}$ have been reported (Qian et al. 1997; Elmi et al. 2002), but this modeling exercise attempted to simulate average conditions over a large watershed, which included unfertilized soybeans, from which lower denitrification rates are expected.

Our denitrification results for 2002 (Fig. 4) were the average of separate corn and soybean runs for a given year. We also examined these fluxes in the individual simulations for corn or soybean in 2002 (Table 5). The overall mean values for denitrification were 14.5 and $9.4 \text{ kg N ha}^{-1} \text{ year}^{-1}$ for corn and soybean simulations for 2002, respectively. All models had greater denitrification under corn compared to soybean, although the relative difference was quite variable (from 8 to 58% greater denitrification under corn compared to soybean). We would expect greater denitrification under corn because of the large nitrate pool that would be present during spring following fertilization. This is shown to occur for DRAINMOD-N II, where a clear response to fertilizer inputs occurs in May and June (Fig. 5). EPIC had a similar pattern of denitrification during 2002 in both corn and soybean, although the corn flux was always much greater (Fig. 5), and similar patterns were found for DNDC82a and h, as well as DAYCENT

Table 5 Modeled annual denitrification fluxes for a central-Illinois corn and soybean agroecosystem for 2002, with separate corn and soybean predictions

	Corn ($\text{kg N ha}^{-1} \text{ year}^{-1}$)	Soybean ($\text{kg N ha}^{-1} \text{ year}^{-1}$)
SWAT	23.6	21.7
DAYCENT	4.8	3.6
DRAINMOD-N II	34.1	14.3
EPIC	16.1	9.7
DNDC82a	4.8	3.6
DNDC82h	3.8	3.2

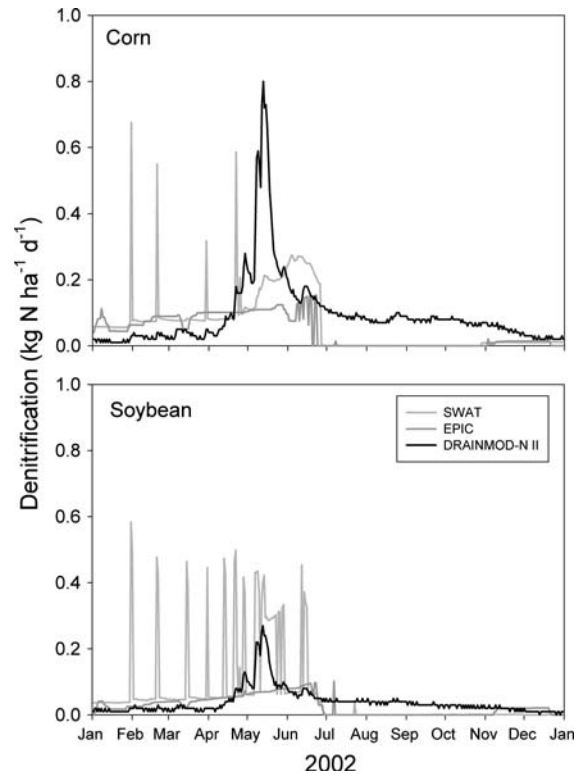


Fig. 5 Modeled daily denitrification fluxes for a central-Illinois corn and soybean agroecosystem, showing separate corn and soybean predictions

(daily fluxes not shown). SWAT was the one model that had a different response (Fig. 5). Denitrification occurred at rates $>0.2 \text{ kg N ha}^{-1} \text{ day}^{-1}$ on 7 different days prior to the multi-day denitrification period in May under soybean, but on only 4 days under corn. The simulated denitrification in May and June, which would reflect the period following fertilization, was also not that different from SWAT predictions (11.9 and $10.4 \text{ kg N ha}^{-1}$ for the 2 month period for corn and soybean, respectively). As previously discussed, it is interesting that SWAT responded little to the corn fertilization, but that EPIC (which was one of the models that was the basis for SWAT) had a much larger increase in simulated denitrification. SWAT has a relatively high soil moisture threshold for denitrification to occur (95% of field capacity) and no denitrification is simulated below this threshold. Thus, in order to simulate sufficient denitrification in the short periods when the threshold is exceeded, the rate of denitrification must be set to a high level in calibration.

Only two of the models predicted N_2O and N_2 components of total denitrification (DAYCENT and DNDC). DAYCENT predicted an even split of 50% of denitrification in each gas, whereas DNDC82a simulated N_2O as 63% of total denitrification. DNDC82h simulated N_2O ranging from 40 to 75% of annual flux in low denitrification years, and ranging from 22 to 54% of annual denitrification in high flux years.

Because simulated denitrification in each model depends on a soil nitrate pool that can be reduced if soil moisture status conforms to model-specific conditions, overall N biogeochemistry directly controls denitrification trends. Nitrogen additions by soybean fixation and internal cycling by mineralization combined with grain harvest of N all affect the nitrate pool and overall status of the soil. Similarly, the models track a large soil organic N storage pool that can be added to or mineralized and depleted. Ammonia volatilization is not presented because it was roughly balanced by the input of ammonium in atmospheric deposition and it represents a small portion of total N flux for this system. The individual components of the N cycle (except ammonia volatilization) were highly variable among the models (Table 1). Soybean N_2 fixation (on a landscape basis) varied from 49 to 96 kg N ha⁻¹ year⁻¹, whereas grain N harvest varied from 111 to 152 kg N ha⁻¹ year⁻¹. Finally, the average change in soil storage each year ranged from -22 to 19 kg N ha⁻¹ year⁻¹. We also compared a calculated N balance to the change in soil N storage, and found that for some models these values were nearly equal, whereas for others the difference ranged from 6 to 10 kg N ha⁻¹ year⁻¹. This great variation in N fluxes directly affects modeled soil nitrate that is available for plant uptake, leaching, or denitrification. As an example, DNDC82a had a change in soil N storage of 19 kg N ha⁻¹ year⁻¹, the largest of any of the models. We attempted to reduce this increase to zero by adjusting model coefficients, but were not able to without greatly affecting other N fluxes. Because nitrate leaching was known and calibrated to, there was little nitrate available for denitrification. If the soil storage had been zero, then an additional 19 kg N ha⁻¹ year⁻¹ would have been available for crop uptake and denitrification, perhaps greatly increasing the denitrification flux.

Modeled denitrification in response to environmental variables

We compared each of the models' daily denitrification flux for 2002 to further explore predicted dynamics. DNDC82a and DNDC82h demonstrated a similar temporal trend in denitrification, with most N gas loss occurring during peak flux between May and June (Fig. 4). In terms of the magnitude of N gas flux, 2002 is a relatively low denitrification year for DNDC82h, but an average to high flux year for DNDC82a. Peaks in N_2O production always correlate with high soil NO_3^- status, in part because DNDC models N_2O production as a result of both the denitrification pathway as well as a constant fraction of nitrification. The highest N_2 flux events likewise correlate to soil NO_3^- status, however, smaller N_2 flux events show N_2 flux dependence on soil moisture status. The correlation of N_2 production to soil moisture status derives from the expansion of the anaerobic balloon, with increased soil moisture increasing the size of the anaerobic balloon, therefore allowing a higher proportion of N_2O to reduce completely to N_2 . Although precipitation events clearly regulate soil moisture, a direct correlation between denitrification and precipitation is difficult to discern during the growing season due to the effect of evapotranspiration on soil moisture. In contrast to years with high simulated denitrification, 2002 had low daily N_2 and N_2O fluxes. In terms of temporal dynamics, 2002 simulations showed insignificant N_2 and N_2O flux prior to planting and following harvest, relative to years with high simulated denitrification. Compared to the suite of models tested in this research, DNDC behaves most similarly to DRAINMOD-N II in terms of timing of peak dynamics, though DRAINMOD-N II has higher N gas flux throughout 2002 and particularly during the growing season.

In SWAT, the denitrification process is primarily controlled by soil NO_3^- content and moisture level in a discontinuous fashion (see Eq. 1aa, b). The denitrification spikes in the SWAT daily output (Fig. 4) tend to follow major precipitation events in the late winter and spring. During this period, the large soil NO_3^- pool developed from fertilization makes high denitrification possible. When moisture in the nitrate-rich soil layers exceeds the threshold level in Eq. 1aa, b denitrification process is triggered, which causes

abrupt denitrification fluxes. The relatively flat pattern of denitrification flux between the spikes reflects the denitrification occurring in (presumably deeper) nitrate-poor soil layers, where soil moisture maintains steadily above the threshold level during late winter and spring months. We also found that the simulated annual denitrification flux by SWAT is significantly correlated with the total precipitation from January to July ($R^2 = 0.5$). The sharp decline in denitrification at late June to early July reflects the rapid depletion of soil NO_3^- pool and soil moisture at this period. The depletion of soil NO_3^- may be a collective effect of immobilization, increasing crop uptake, and earlier denitrification loss. Loss of soil moisture is likely due to low rainfall and intensified evapotranspiration driven by high temperature and rapid plant development at this period. For the rest of the year, simulated denitrification remained extremely low even when large rainfall events occur, suggesting that SWAT simulated a persistently low soil NO_3^- pool after early July.

Among the 11 calibrated SWAT parameters, denitrification was most sensitive to soil available water capacity (defined as field capacity minus wilting point), saturated hydraulic conductivity, and denitrification rate. Saturated hydraulic conductivities were increased by 10% from default values, which reduced the duration of soil saturation and reduced the simulated denitrification. The denitrification rate coefficient was largely reduced from its default value of $1.4\text{--}0.1 \text{ day}^{-1}$, suggesting that the default value in SWAT may cause substantial over-prediction in denitrification flux under the studied conditions. Available water capacity values were not changed by calibration. In general, SWAT simulated some denitrification patterns that were notably different from the other models. Future field observations are needed to verify which patterns are realistic.

The primary controls on denitrification rates in DAYCENT are soil NO_3 concentration, soil water content, and heterotrophic CO_2 respiration. Of these, CO_2 respiration (a proxy for labile C availability) had the highest correlation ($r^2 = 0.12$) with daily denitrification rates. It is not surprising that none of the driving variables are highly correlated as single factors with denitrification at a daily scale because the model assumes that the law of the minimum applies; i.e. denitrification is controlled by the substrate (NO_3 or labile C availability) or

environmental condition (water content) that is most limiting. At the annual scale, DAYCENT simulated denitrification rates were highly correlated ($r^2 = 0.57$) with available soil water (the difference between precipitation and water drained). This makes sense because the more water that is stored in the soil the more opportunities are available for denitrification to occur.

Denitrification in EPIC does not begin until soil saturation exceeds a user-specified threshold level. At that point, denitrification is calculated in a soil layer using a simple first-order equation that calculates the amount denitrified as a conversion factor multiplied by the soil layer nitrate concentration. The conversion factor is user-specified, but the value provided is actually a maximum level that is driven to zero as soil temperature and/or organic carbon levels in that layer go to zero. The daily denitrification results provided by EPIC reflect these dynamics; denitrification rates are low in the winter when soils are cool and dry, then increase in the spring when temperatures, moisture, and, nitrate concentrations (as a result of fertilization) increase. These concentrations quickly decrease, however, during the growing season as available nitrate and soil moisture levels decline. Because EPIC's results are calculated layer-by-layer, they appear less sensitive to discrete fertilization and precipitation events than other model results; fertilization affects the upmost soil layer, which tends to be the driest, so unless it is accompanied by precipitation, denitrification may be inhibited despite the large increase in soil nitrate concentration. Similarly, high spring precipitation events rapidly increase the soil moisture in upper soil layers that may already be nitrate depleted, so they do not necessarily trigger denitrification events. EPIC's denitrification profile can be easily altered by the user by changing either the soil moisture threshold or the maximum denitrification conversion factor; the general dynamics described above continue to hold, but aggregate denitrification levels vary significantly with these variables.

DRAINMOD-N II predicts denitrification within the soil profile as a function of the $\text{NO}_3\text{-N}$ and organic C availability, soil water, soil temperature and soil pH. It uses Michaelis–Menten kinetics to model process rate dependency on $\text{NO}_3\text{-N}$. Denitrification rates estimated with the Michaelis–Menten equation are then reduced using an exponential depth

function to implicitly simulate the effect of organic C decline with depth on the process rate. Once the water-filled pore space reaches a user-defined threshold value, denitrification proceeds at an increasing rate until it reaches a maximum at complete saturation. The effect of soil temperature on the process rate is simulated using a form of the Van't Hoff function with variable Q_{10} . As temperature increases, the process rate increases exponentially and then levels off until reaching its optimum rate and then declines with further increases in temperature. The user can set the model to either ignore or simulate the effect of soil pH on the process rate using a pH-response function (Youssef et al. 2005).

For 2002, DRAINMOD-N II predicted relatively low denitrification rates during the winter months because of low temperatures. In the spring and early summer, denitrification increased until it peaked at 4.0–5.5 kg N ha⁻¹ day⁻¹ during April and May. The combination of warm weather, wet conditions, and high NO₃-N concentrations in the soil profile led to high predicted denitrification rates in both April and May. Precipitation was 15.5 cm in April and 20.7 cm in May 2002. Fertilizer applied to corn fields in November 2001 and May 2002 led to high NO₃-N concentrations in the top 25–50 cm soil layer. The intermittent anaerobic conditions for this N-rich soil layer following major rainfall events was predicted to lead to major denitrification losses. Following the April and May peaks, predicted denitrification continued to decline to less than 0.1 kg N ha⁻¹ day⁻¹. Compared to the other models, however, DRAINMOD-N II predicted significantly higher denitrification rates during late summer and fall. DRAINMOD-N II predictions of persistent denitrification during summer and fall can be attributed to the denitrification that occurs below the water table where NO₃-N concentration may reach 10 mg L⁻¹ below corn fields.

Each of the models evaluated in this study uses the same environmental drivers of denitrification, but varied in how they are used to predict denitrification. This leads to considerable variation in denitrification predictions at all time scales. Because direct measurements of denitrification flux for our modeled agroecosystem were not available, we were not able to calibrate models for this flux. The biogeochemist constructed models (DNDC and DAYCENT) had more similar results to each other (and overall lower

simulated denitrification fluxes) compared to the agronomist and crop oriented models (DRAINMOD-N II, EPIC, and SWAT). These latter models predicted much greater denitrification fluxes than DNDC and DAYCENT, but generally did better at predicting drainage water and nitrate, which may be a result of their greater sophistication in modeling crop evapotranspiration and/or explicit incorporation of tile drainage into each model.

Conclusions

We modeled denitrification in a tile-drained Mollisol with corn and soybean in rotation using five well described and widely utilized models. Following calibration, generally all models were able to make reasonable predictions of crop yields, water flux, and nitrate flux, with the latter flux having more model to model variability than the others. Models that explicitly included tile drainage and were crop based (SWAT, DRAINMOD-N II, and EPIC) generally had results that grouped together and were different than the biogeochemistry focused models (DNDC and DAYCENT). For denitrification, for which a measured value was not available, models predicted 10 year average fluxes ranging from 3.8 to 21 kg N ha⁻¹ year⁻¹, a factor of 5.5. Within year variation was much larger, and some of the models predicted daily denitrification in response to driving variables quite differently. Other components of the N cycle included in each model that determine the nitrate pool available for leaching and denitrification also showed considerable variability. Because the many aspects of the N cycle are interconnected and affect soil nitrate concentrations, differences in the prediction of a component such as crop N harvest can lead to differences in denitrification. The divergence among the models compared suggest our ability to accurately predict denitrification fluxes (without known values) from the dominant agroecosystem in the midwestern Illinois is quite uncertain at this time.

Systematic measurements of denitrification are needed to further test and refine the existing models, as well as provide data for all important N fluxes that are simulated in each model. An idealized example would be a multi-year detailed N biogeochemical study on a tile-drained corn and soybean field, with measurements of all major N fluxes, including:

deposition, fertilizer, fixation, harvest, stover return of N, N mineralization, seasonal soil nitrate pools, tile drainage losses, changes in soil N pools, and denitrification losses, supported by a full range of physical measurements (e.g., precipitation, soil temperature, soil moisture, leaching fluxes). This would allow the most complete assessment of our ability to model denitrification. A simpler approach would be to measure just a few of the major N fluxes (i.e., fertilizer, harvest N) combined with physical measurements and measured denitrification. This would give a measured value for modeled denitrification to be compared to, but would not constrain the models with many of the other N fluxes that are known to affect denitrification. Therefore, modeled denitrification could compare well to measured, but accuracy of many other N fluxes would be unknown.

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