Environ. Sci. Technol. **2006**, *40,* 2324−2332

Use of Monte Carlo Analysis to Characterize Nitrogen Fluxes in Agroecosystems

SHELIE A. MILLER,*
AMY E. LANDIS, AND THOMAS L. THEIS
Institute for Environmental Science and Policy, University of Illinois at Chicago, 2121 West Taylor Street, Chicago, Illinois 60612

Intensive agricultural systems are largely responsible for the increase in global reactive nitrogen compounds, which are associated with significant environmental impacts. The nitrogen cycle in agricultural systems is complex and highly variable, which complicates characterization in environmental assessments. Appropriately representing nitrogen inputs into an ecosystem is essential to better understand and predict environmental impacts, such as the extent of seasonally occurring hypoxic zones. Many impacts associated with reactive nitrogen are directly related to annual nitrogen loads, and are not adequately represented by average values that de-emphasize extreme years. To capture the inherent variability in agricultural systems, this paper employs Monte Carlo analysis (MCA) to model major nitrogen exports during crop production, focusing on corn-soybean rotations within the U.S. Corn Belt. This approach yields distributions of possible emission values and is the first step in incorporating variable nutrient fluxes into life cycle assessments (LCA) and environmental impact assessments. Monte Carlo simulations generate distributions of nitrate emissions showing that 80% of values range between 15 and 90 kg NO_3^- N/ha (mean 38.5 kg NO_3^- N/ha; median 35.7 kg NO_3^- N/ha) for corn fields and 5−60 kg NO_3^- N/ha (mean 20.8 kg NO_3^- N/ha; median 16.4 kg NO_3^- N/ha) for soybean fields. Data were also generated for grain and residue nitrogen, N_2O, NO_x, and NH_3. Results indicate model distributions are in agreement with available measured emissions.

Introduction

Since the early 19th century, human activities have increased the rate of conversion of nonreactive atmospheric nitrogen to reactive nitrogen eleven-fold (*1*). The substantial increase in the flux of reactive nitrogen contributes to several environmental problems, including global climate change, eutrophication and hypoxia, acid deposition, and production of ground-level ozone (*2*, *3*). The amount of reactive nitrogen is projected to increase with continued population growth. Combustion of fossil fuels contributes only 15% of the anthropogenic reactive nitrogen in the environment, while food production accounts for 75% of anthropogenic nitrogen due to the manufacture of synthetic fertilizer and biological nitrogen fixation from cultivated crops such as legumes and rice (*3*). Significant quantities of nitrogen fertilizer are applied to crops in attempts to increase global and regional food supplies and to enhance nutritional quality of available foods (*4*). In addition to emissions of N_2O and NO_x from the combustion of fossil fuels associated with energy use from fertilizer production and on-farm processes, the agricultural industry is also responsible for NH_3, NO, N_2O emissions evolving from fields, and NO_3^- in surface water runoff. The applied nitrogen is either acquired by crops or released to the environment through a variety of pathways. Figure 1 shows the major fluxes of the agricultural nitrogen cycle relevant to corn and soybean production.

Life Cycle Assessment (LCA) is a tool used to evaluate the environmental impact of a process or product. The analysis examines the entire life cycle of the process or product, from creation to material acquisition through disposal or reuse. LCA documents all relevant mass and energy inputs and emissions through a process called life-cycle inventory (LCI) to determine the intensity of material uses and identify possible areas of improvement. LCA is usually used to compare alternatives and offer policy-makers quantitative information to inform environmentally significant decisions. With the recent rise of bio-based materials offered as alternatives to petroleum products, numerous LCIs have been conducted on agricultural systems (*5*−*9*). While these studies acknowledge that nutrient fluxes are a significant issue, they focus primarily on air emissions, and have not quantified aqueous emissions in a comprehensive manner, due to high variability of nonpoint emissions.

LCA was initially developed for industrial systems, where processes are usually carefully structured and controlled, with known or measurable material and energy fluxes. Traditional LCAs often use average data to generate generic depictions of material and energy fluxes to simplify an analysis and generate a representative inventory; however, large deviations should be documented to provide a complete system description. While average data may be acceptable for industrial systems with low operational variability, such values seldom represent the inherent fluctuations of natural and agricultural systems. Concentrating solely on extreme values is equally problematic, as it can bias the results of the analysis, and not adequately depict the impacts for the majority of years.

Agricultural processes differ from many industrialized processes because of inconsistent material fluxes due to nonpoint emissions, uncertain input variables (e.g., nitrogen fixation and soil mineralization), the temporal scale needed to produce a product, the interdependence of crops in rotation, and the high degree of system variability which depends on geography, weather patterns, soil type, and agricultural practices. If average data are used to characterize agricultural systems, "extreme" data, such as wet or drought years, may not be captured. Average data may be appropriate for use in situations where aggregate emissions cause long-term environmental impacts (e.g., carbon dioxide emissions leading to global climate change); however, impacts associated with nitrogen emissions are temporally relevant. For example, the size of a hypoxic zone for a given year will vary proportionately with nitrate emissions into the watershed that year (*10*, *11*). These complexities underscore the importance of conducting a comprehensive and reproducible LCI for agricultural systems.

To reduce variability among parameters when examining agricultural systems, researchers often prefer to limit the analysis to a relatively small geographic region, assuming that the relative uniformity of system variables, such as climate and soil type, will allow greater precision in inventory

* Corresponding author phone: 312-996-1081; fax: 312-355-0760; e-mail: smille24@uic.edu.

10.1021/es0518878 CCC: $33.50
© 2006 American Chemical Society
Published on Web 02/23/2006

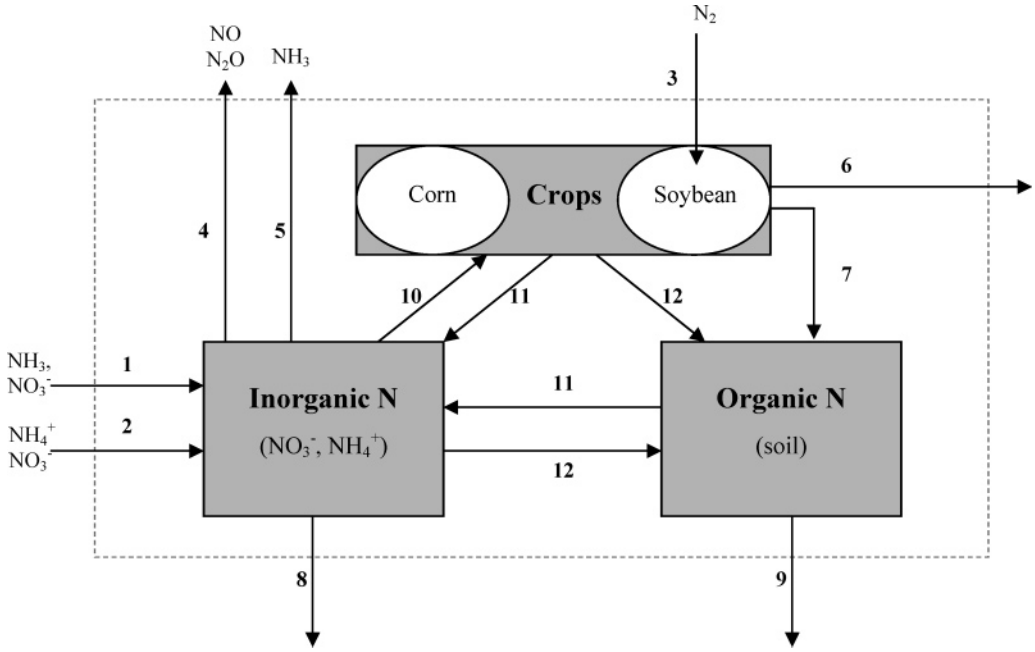


FIGURE 1. Diagram of the nitrogen cycle in agricultural soils. (1) fertilizer application; (2) atmospheric deposition; (3) N_2 fixation; (4) nitrification/denitrification; (5) volatilization; (6) crop grain; (7) crop residue; (8) runoff; (9) erosion; (10) uptake; (11) mineralization; (12) denitrification/immobilization

estimates (*12*). Complex models, such as CENTURY and EPIC (*13*, *14*), are often used to model nitrogen fluxes in agricultural systems. While these models can be effective, the output data are only applicable to the selected region, and cannot be readily projected to other regions. The promotion of biocommodities, such as ethanol or bio-diesel, impacts a large geographic area. Corresponding impact assessments require information pertinent to the entire region. Ideally, comprehensive inventories of many small regions can be compiled into larger regional assessments. However, this is a lengthy and data-intensive process, and there is a need to address nutrient-related impacts in the near term. This paper describes the use of a probabilistic approach addressing a large geographic area to complement site-specific modeling techniques. The goal of this study is to determine the extent of nitrogen emission variability in agricultural systems, and to provide a framework for integrating these data into biocommodity LCAs. In addition, decision-makers may wish to use probability distributions to determine appropriate nitrogen control measures.

Increased nitrogen loading into watersheds is one of the most serious problems facing coastal areas in the United States, with the Gulf of Mexico and the Chesapeake Bay facing the most severe damage (*3*). Increased nitrate concentrations allow unchecked algal growth, which depletes water of dissolved oxygen and light, leading to large regions of hypoxia. These hypoxic zones are not only detrimental to aquatic life, but to local economies dependent upon fisheries. Since 1993, the hypoxic zone in the Gulf of Mexico has averaged 16 000 km^2 during the summer, with a maximum area of 22 000 km^2 in 2002 (*11*).

Management of the hypoxic zone in the Gulf depends on a reduction in the total nitrogen load to the Mississippi River Basin (MRB), for which agriculture is mostly responsible. The National Oceanic and Atmospheric Administration (NOAA) has estimated that a 40% reduction in total nitrogen flux from 1996 levels would reduce the size of the hypoxic zone in the Gulf of Mexico to acceptable levels (*15*). The cause−effect phenomenon of the hypoxic zone is not well understood, and greater understanding of nitrate inputs and their transport to the Gulf of Mexico is needed. The results presented in this paper depict ranges of nitrogen exports from the agricultural sector to the MRB, and can be coupled with models such as SPARROW (SPAtially-Referenced Regression On Watershed attributes), which estimates the fraction of MRB nitrogen that is delivered to the Gulf of Mexico (*16*). This will inform overall system characterization, and lead to better and more effective management practices (*17*).

Experimental Section

Study Area. This analysis forecasts probable distributions for nitrogen fluxes in corn−soybean rotations for the U.S. Corn Belt, defined as the collection of states producing 80% or more of the national corn and soybean production (*18*, *19*). These include Iowa, Illinois, Nebraska, Minnesota, Indiana, Ohio, South Dakota, Wisconsin, and Missouri. Data collected from 1990 to the present are used in the analysis to ensure that the analysis reflects current agricultural practices.

Statistical Methods. Monte Carlo analysis (MCA) is a tool that simulates a probable range of outcomes given a set of variable conditions and can be applied within a risk assessment or LCI framework to capture parameter variability. MCA is a technique used to quantify variability and uncertainty by using probability distributions (*20*, *21*). Any independent variable with a range of estimates or possible values can be assigned a probability distribution. Output distributions are generated by repeatedly and randomly sampling values from the probability distributions. A simulated outcome distribution can show the most likely scenario, as well as extreme cases which occur infrequently. Using ranges of data that incorporate the system variability in terms of geography, annual variation, and agricultural practices will allow decision-makers to see a range of possible outcomes in addition to the average values for the entire system.

This paper describes a stochastic approach to generate emissions data for nitrogen species in generic watersheds, using linear fractionation of input variables. Nitrogen inputs are allocated to export categories by appropriate fractionation parameters, which assign a portion of the input nitrogen to each export category. A probability distribution is assigned to each input variable and fractionation parameter, from

TABLE 1. Model Equations and Input Parameters[a]

description	equation	corresponding flux(es) in Figure 1
(1) mass N in	$N_{in} = N_f + N_{atm,w} + N_{atm,d} + N_{fix} + N_{res}$	1 + 2 + 3 + 7
(2) mass N out	$N_{out} = N_{grain} + N_{N_2O} + N_{NO_3} + N_{NH_3}N_{NO}$	4 + 5 + 6 + 8
(3) mass N in grain	$N_{grain} = H \times f_{grain}$	6
(4) mass N in residue	$N_{res} = H \times HI \times f_{res}$	7
(5) mass direct emissions of N2O from fertilizer and mineralized N	$N_{N_2O} = (f_{N_2O,ni} \times N_f) + (f_{N_2O,de} \times N_{min})$	4
(6) NO produced from nitrification/denitrification reactions	$N_{NO} = (f_{NO,ni} \times N_f) + (f_{NO,de} \times N_{min})$	4
(7) mass N volatilized as NH3	$N_{NH_3} = f_{NH_3} \times N_f$	5
(8) mass N fixed (soy only)	$N_{fix} = f_{fix}(N_{grain} + N_{res})$	3
(9) mass NO_3^- from fertilizer (corn only)	$N_{NO_3,c} = N_f \times f_{NO_3}$	8
(10) mass NO_3^- from mineralization (soy only)	$N_{NO_3,s} = N_{min} \times f_{NO_3}$	8

[a] Equations 1−7 apply to both corn and soybeans, which are denoted by *c* or *s* in the subscript. Corresponding flux(es) indicates the numbered flux(es) diagrammed in Figure 1. (N_{in} = total nitrogen inputs to system; N_f = rate of fertilizer application; $N_{atm,w}$ = wet atmospheric deposition as either ammonium or nitrate; $N_{atm,d}$ = dry atmospheric deposition; N_{fix} = nitrogen fixed via biological nitrogen fixation; N_{out} = total nitrogen exports; N_{grain} = nitrogen exported to grain; N_{res} = nitrogen exported through residue; N_{N_2O} = direct N_2O emissions via nitrification and denitrification reactions; N_{NO} = NO emissions via nitrification and denitrification reactions; N_{NO_3} = nitrogen runoff as NO_3^-; N_{min} = mineralized nitrogen from soil and crop residue; N_{NH_3} = nitrogen volatilized as NH_3; H = grain harvested; f_{grain} = nitrogen fraction of harvested grain; HI = harvest index (mass residue/mass grain); f_{res} = nitrogen fraction of residue; f_{fix} = fraction of total plant nitrogen obtained through biological nitrogen fixation; $f_{N_2O,ni}$ = fraction of applied fertilizer nitrified to N_2O; $f_{N_2O,de}$ = fraction of mineralized nitrogen denitrified to N_2O; $f_{NO,ni}$ = fraction of applied fertilizer nitrified to NO; $f_{NO,de}$ = fraction of mineralized nitrogen denitrified to NO; f_{NH_3} = fraction of applied fertilizer volatilized to NH_3; f_{NO_3} = fraction of fertilizer to NO_3^- runoff).

which values are selected to generate export distributions. Similar approaches have been used to predict nitrogen fluxes in The Netherlands (*22*) and the variability of soil mineralization (*23*). Because MCA generates distributions based on stochastic inputs, it does not generate distinct point values typical of deterministic models. Instead, it generates a range of values based on the probability of occurrence, thus it is not a predictive model.

All reported MCA simulations in this analysis were generated using 50 000 trials, which ensured the reproducibility of the forecasts. The simulations were generated using Crystal Ball 5.5, a statistical software program (*24*).

Model Equations and Distributions. The model for this system consists of 17 equations and 29 input parameters to determine exports from an agricultural system, using basic units of kg N/ha per year. The model equations can be found in Table 1. These simulation equations calculate the range of nitrogen species in terms of total system inputs and exports for corn and soybean growing seasons. Each parameter is assigned a distribution based on a variety of literature sources. The sources and the rationale used to create the parameter distributions used in the MCA can be found in the Supporting Information. Annual mass closure was not enforced in the model, because nitrogen inputs and exports do not necessarily reconcile in a given year.

For this analysis, the primary inputs of nitrogen into the system are defined as synthetic nitrogen fertilizer, biological nitrogen fixation, crop residues from previous years, and atmospheric nitrogen deposition, as depicted in Figure 1. Some nitrogen budgets include mineralized nitrogen as an input. Existing soil mineralization estimates take into account mineralization of crop residues, and are not considered part of the nitrogen budget (*25*−*28*). Fertilizers in the form of anhydrous ammonia and ammonium nitrate are commonly used throughout the study region. For the purposes of the model, their partitioning behaviors are treated equally, since the range associated with NO_3^- fractionation takes into account runoff and uptake rates of both types of fertilizer. Nitrogen from manure application is not included in this analysis; manure is applied to only 18% of corn crops and 6% of soybean crops in the study area (*19*, *29*, *30*). It is important to note that manure fertilizers have higher volatilization rates during application and incorporation. Application of manure may significantly change the outcome of the model and should be treated separately, therefore only studies using synthetic fertilizer were used for comparison purposes.

The exports included in the analysis are nitrogen in harvested grain, N_2O, NO_x (primarily as NO), NH_3, and NO_3^-. Nitrogen contained in crop residues is assumed to stay within the system and is considered an input instead of an export. Additional exports not described by distributions due to lack of data include nitrogen compounds bound within transported sediment and the release, or senescence, of NH_3 during the decomposition of plant matter.

Many of the model parameters fall within a narrow range, except for the nitrogen fractionation parameter (f_{NO_3}), which studies have shown to vary from 3 to 80% of applied fertilizer (*27*). The assigned distribution reflects this degree of variability. Nitrate emissions from fields are highly variable, depending largely on weather patterns, agricultural practices, and soil properties. Drought years yield extremely low nitrate emissions from fields, unlike the high nitrate emissions during wet years. As discussed later, reported values for nitrate fluxes from agricultural fields demonstrate large variabilities that this model is able to capture. An empirically derived fraction of applied fertilizer is often used as a surrogate variable to estimate nitrate runoff, due to system complexities and uncertainties associated with mechanistic modeling (*31*).

It is common practice to estimate nitrate runoff as a fraction of applied fertilizer; however, it is important to note that only 25% of soybeans receive fertilizer, yet agricultural fields discharge appreciable nitrate runoff during soybean growing seasons. Field study data by Klocke et al. (*33*) report nitrate emissions of up to 105% of nitrogen fertilizer applications over the course of a six-year corn−soybean rotation. Because a significant amount of applied fertilizer is taken up by crops, this demonstrates that a portion of the system's nitrate runoff is independent of fertilizer application. One of the novel elements of the model used in this analysis is the estimation of nitrate emissions from soybean fields. Nitrate emissions from corn fields are calculated using the standard method of using a fraction of applied fertilizer. To determine the nitrate load during soybean growing seasons, this model uses mineralized nitrogen multiplied by the nitrate conversion rate for fertilizer, as shown by eq 10 (Table 1). This method was chosen based upon the assumption that mineralized nitrogen behaves similarly to applied nitrogen fertilizer in the soil matrix, so the same fractionation parameter is used.

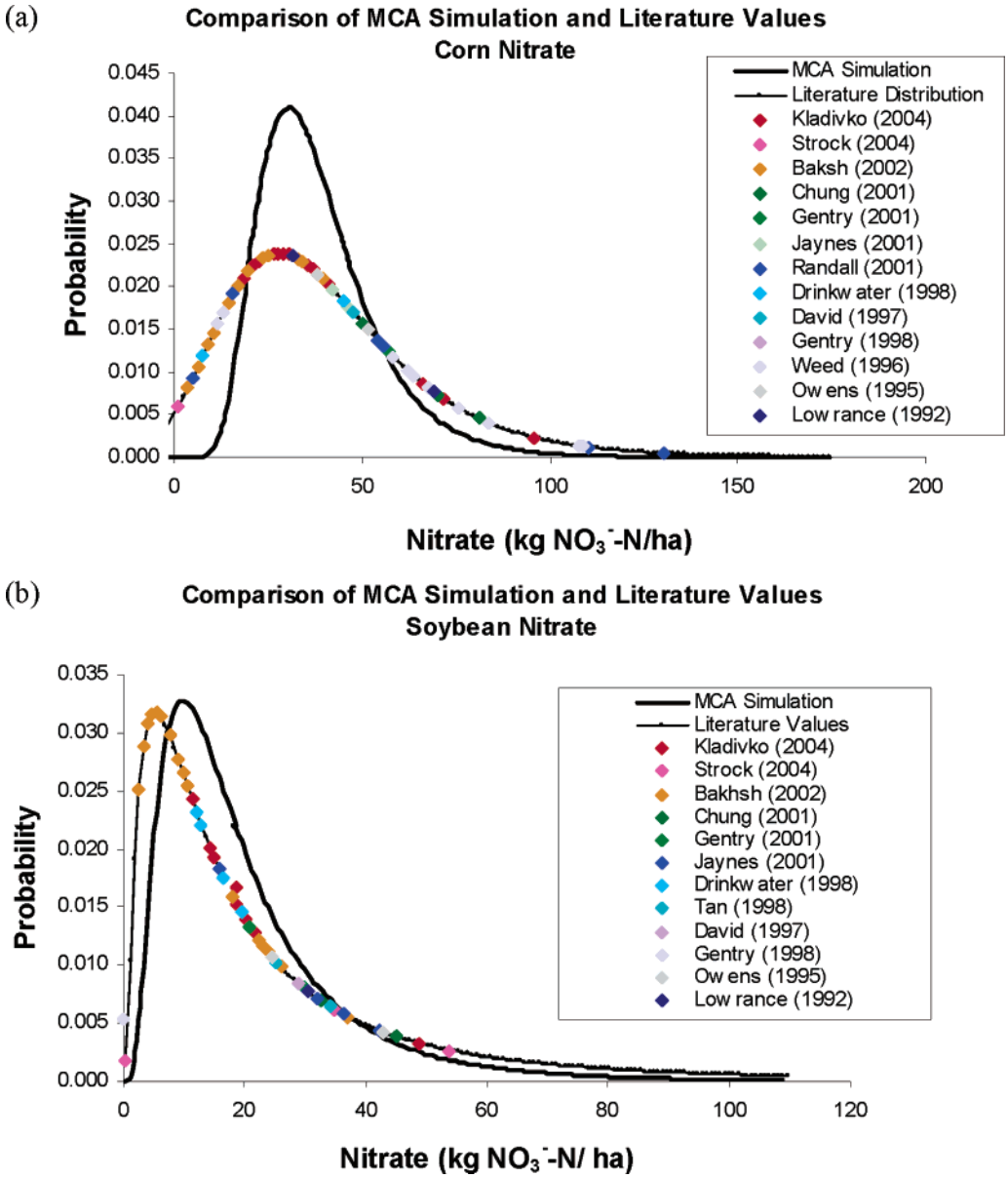


FIGURE 2. Comparison of literature values and model simulation regressions for nitrate runoff. Monte Carlo distribution of model data shown in black; distribution of literature values shown with specific data points: (a) nitrate emissions from corn fields; (b) nitrate emissions from soybean fields. (Data from refs *28, 41–45*).

Results and Discussion

Nutrient Cycle. Using the assigned parameter distributions, simulation forecasts are generated for biological nitrogen fixation, grain and residue nitrogen contents, N_2O and NO_x derived via nitrification and denitrification reactions, nitrate leaching, and volatilization of NH_3.

The validity of this approach can be measured by the degree of conformance of the simulations to independently measured data. Figure 2 shows model distributions of exported nitrate for corn and soybean growing seasons and literature data for comparative purposes. The probability shown on the *y*-axis is the probability of an individual emission value; the area under the curve is the cumulative probability. Field studies conducted within the Corn Belt from independent literature sources encompassing a range of climates and agricultural practices are compiled into distributions using best-fit regression for comparison with model simulations. Fifteen field-scale studies are used, reporting 57 measurements for nitrate leaching during soybean years and 107 values for corn years. Best-fit regressions of the literature data result in an extreme value distribution for corn with a mean value of 39.8 ± 26.6 kg NO_3^- N /ha, as compared with model results that were log-normally distributed with a mean of 38.5 ± 15.9 kg NO_3^- N /ha. The soybean literature distribution was log-normal with a mean of 21.9 ± 13.4 kg NO_3^- N /ha, with the model simulation resulting in a log-normal distribution with a mean of 20.8 ± 16.5 kg NO_3^- N /ha. The simulation of leaching during corn years is log-normally distributed, while the collected data conform to an extreme value distribution. Although the type of distributions and peak heights are not identical, mean values for both the observed and simulated corn distributions fall within 1 kg/ha, and the ranges of emissions are similar. This indicates that the model equations and assigned distributions appropriately characterize nitrate emissions from corn–soybean agricultural systems in a large geographic region. The literature distributions show extreme variability with large standard deviations, underscoring the need for this type of analysis instead of using average values.

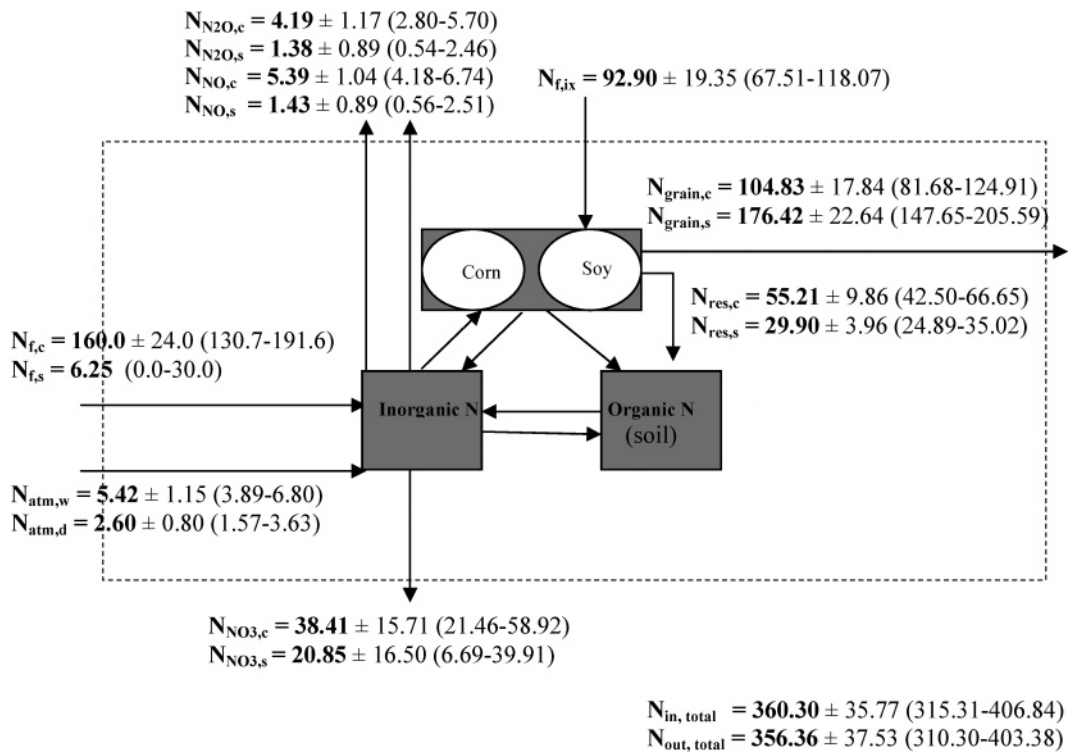


FIGURE 3. Modeled nitrogen fluxes. All data are reported as kg N/ha. Values in parentheses indicate 10−90% data range.

Supporting literature data and MCA distributions for the other reactive nitrogen fractions generated by the model can be found in the Supporting Information. The means, standard deviations, and 10−90% range of each calculated export distribution are reported in Figure 3.

Uncertainty and Variability. The goal of this study is to incorporate system and data variability into life cycle assessments. Typically, LCA studies use average values for inventory data to describe the components of a system. While this practice may be acceptable in industrial systems where variability is limited and uncertainties may be characterized, caution must be used in systems where average data do not depict the range of probable scenarios. Not only will the inventory outcomes vary considerably, but the potential impacts may be highly dependent on this variability.

It is important to draw the distinction between the natural variability and uncertainty associated with data collection. Variability pertains to naturally occurring fluctuations which may include differences in geographic and climatic factors (e.g., crop yields, soil type), or changes in agricultural practices (e.g., till vs no-till farming). Uncertainty is characterized by the lack of confidence in a given parameter (*34*). Parameter distributions in this model are a measure of both naturally occurring variability and uncertainty in the distributions. The output distributions from the model show the range of emissions from the system, and how the emissions can change depending on a variety of factors, as defined in the sensitivity analysis.

Data Interpretation. To generate a better picture of the system and related nitrogen fluxes, Figure 3 depicts the fluxes calculated within the system, showing the average and standard deviation, as well as the values contained within the 10−90% range. The 10−90% range describes the range of values that represent 80% of the probable scenarios. The results of the nitrogen balance are consistent with numerous field-scale and large watershed calculations, although the individual parameters used to calculate nitrogen balances vary (*35*). For this system, only external inputs to the system are shown and not internal fluxes such as mineralized nitrogen. Similarly, nitrogen in crop residue is considered a system input, since it is usually reincorporated into the soil matrix (*36*). It would be considered an export if crop residue were used as a coproduct for cellulosic energy production. It is commonly assumed that net soil mineralization is zero in established agricultural soils, where any mineralized nitrogen is offset by immobilization (*37*).

As shown in Figure 3, the modeled system is generally balanced, which strengthens the assertion that current agricultural soils are at steady state, with no net nitrogen loss or accumulation. If crop residues, which account for 85.11 kg N/ha, become useful as a feedstock for commodity goods, this may disrupt soil nitrogen balances, causing net soil mineralization loss. It should also be noted that the values of the balance may change if additional system parameters are included, such as complete interactions of N_2, crop senescence to NH_3, or nitrogen attached to eroded soils.

Integration into LCA. The nitrogen model in this study calculates nitrogen emissions on a kg/ha basis for easy comparison with published values. The LCA process requires inventories of material fluxes on the basis of the utility of a product, which can be accomplished by multiplying the various emission estimates by crop yield. This assumes all nitrogen exports from an individual growing season are allocated to the crop grown that year. Distributions describing crop yield information from 1993 to 2002 are compiled to show the impact yield has on the emission distributions (*39*, *40*). Figure 4 shows the emissions associated with corn and soybean production on a mass of emissions per mass of product basis. These data can be further manipulated to reflect the emissions associated with a commodity product. It should be noted that there is a 75% probability of zero ammonia emissions in soybean fields, since ammonia volatilization depends on fertilizer application, which occurs on only 25% of soybean crops.

Once emissions are calculated on a product basis, some interesting relationships are revealed. On an absolute basis, corn agriculture is responsible for greater nitrate emissions than soybeans, as well as greater NH_3, NO_x, and N_2O emissions, and nitrogen residue content. Because soybean

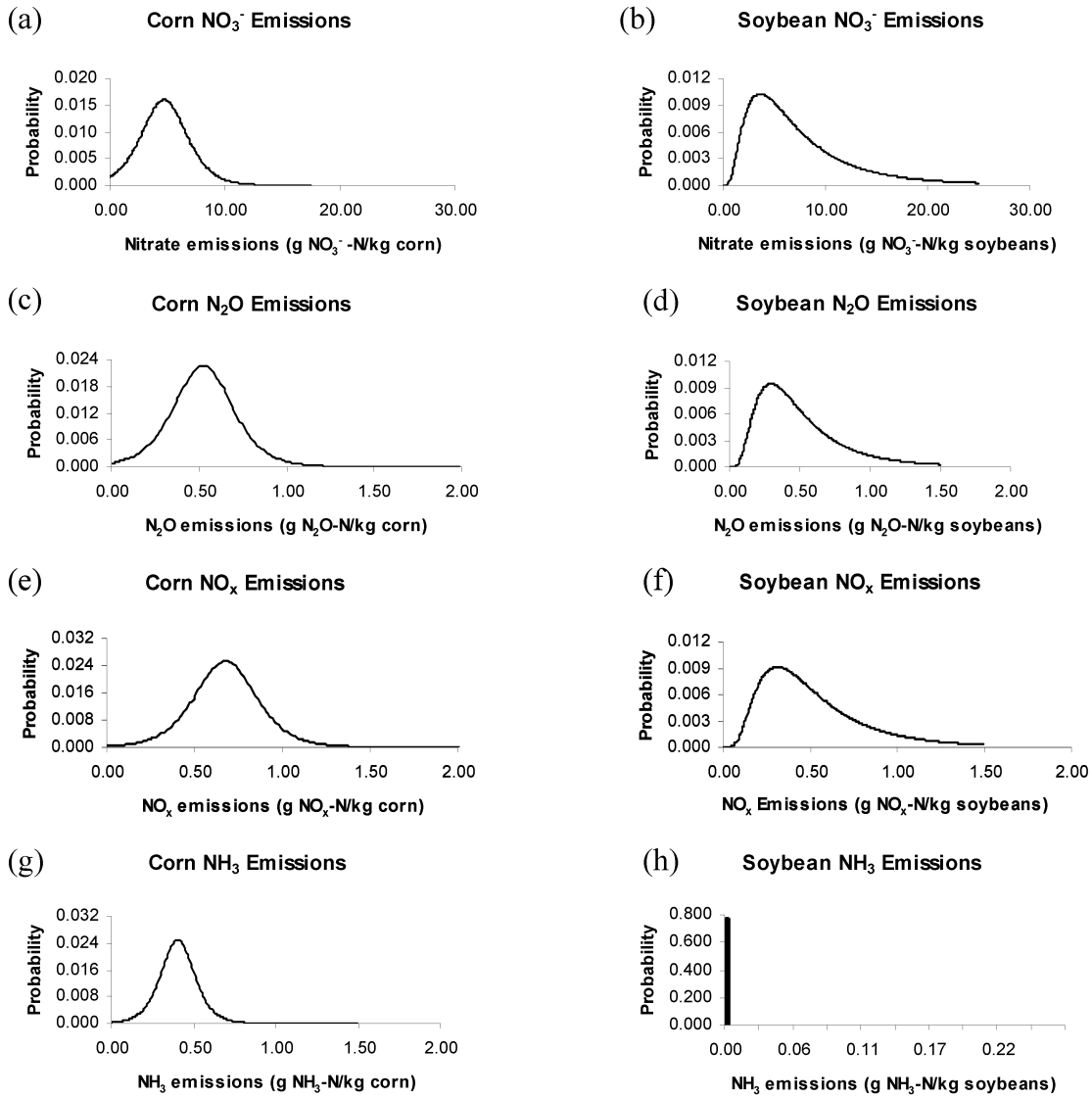


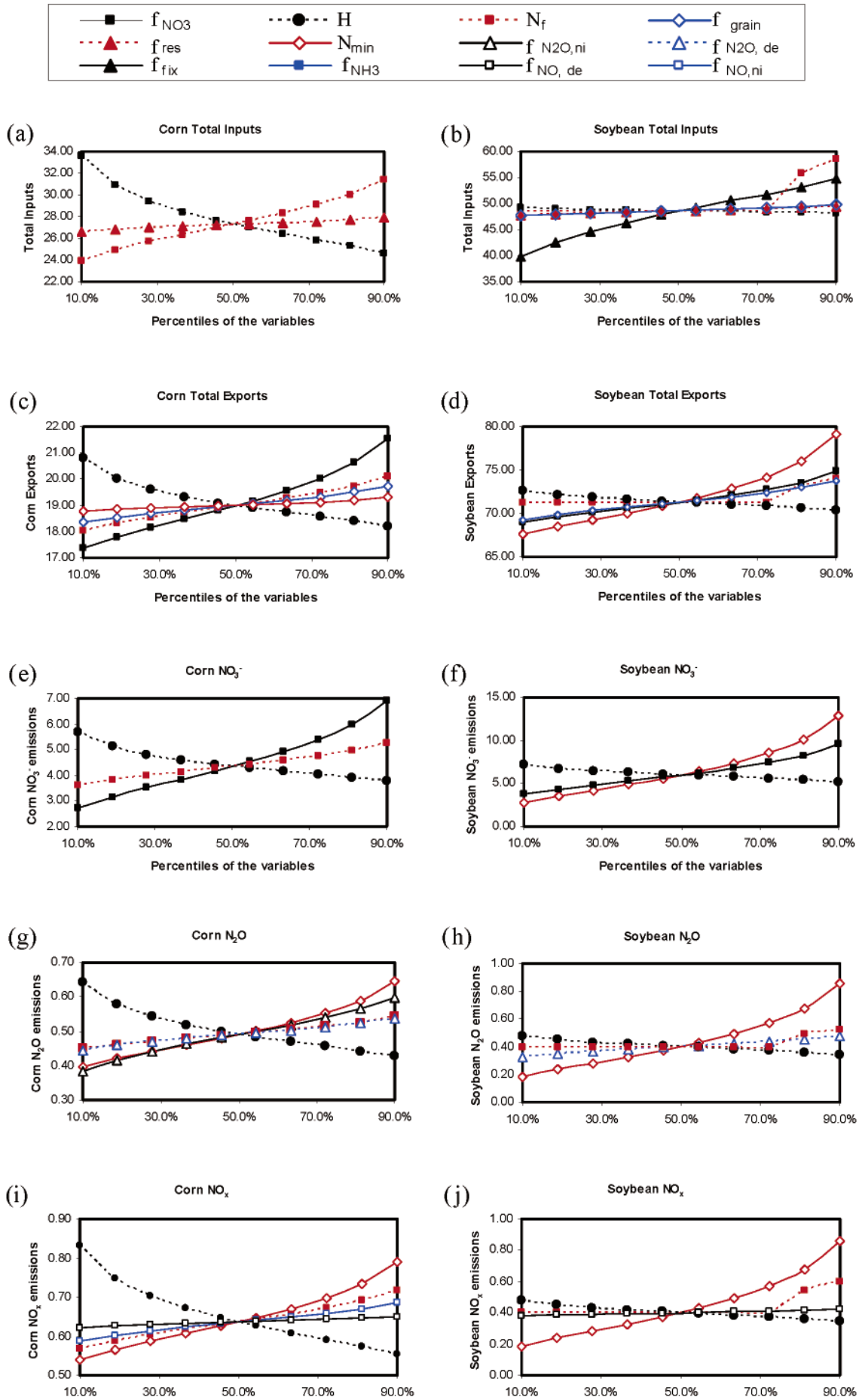
FIGURE 4. Monte Carlo distributions for major nitrogen exports calculated on a per product basis. All data are shown on a g N/kg product basis.

yields result in significantly less product per hectare, emissions calculated on a per mass-of-product basis show that soybeans are responsible for greater nitrate emissions than corn on a relative mass basis. While NH_3 emissions are still much lower due to the lack of synthetic fertilizer application, N_2O and NO_x emissions are comparable for both corn and soybeans on a product mass basis. The interesting implication in an LCA context is that even though corn is responsible for the bulk of emissions on an absolute basis, soybeans are responsible for the majority of nitrogen emissions on a per mass basis. Of course, soybeans also possess a much higher nitrogen content, which is important from a nutritional perspective.

An LCA documents not just nitrogen, but all material and energy fluxes in a system, therefore, a complete analysis would track energy and material use, in addition to nitrogen. Such studies exist, but acknowledge the need for supplemental nitrogen data (*5*, *7*). The data presented in this model are necessary contributions to a comprehensive assessment of biocommodities.

Sensitivity Analysis. Due to the naturally occurring variability found in agricultural systems, some of the output parameter ranges are rather large. The degree of variability is impacted to a large extent by key assumptions. For any analysis of this type, it is important to determine the sources of variability and the impact that parameters and their embedded assumptions have on the results. Sensitivity analysis allows a better understanding of the controlling variables in a system.

A sensitivity analysis was conducted on the system using parametric analysis, also called "one-at-a-time perturbation". This technique measures the effect of each parameter on the output distribution by successively altering each of an equation's variables, while the others are held constant at their medians. Figure 5 shows sensitivity diagrams for each of the export variables. Each line represents the amount to which the output was affected by a given parameter. A line with a steep slope indicates that the output variable is extremely sensitive to assumptions regarding that parameter, while flatter slopes indicate low sensitivity to the parameter. High sensitivities may be caused by a very close relationship to the parameter, or indicate a large variability contained within the parameter distribution. Positive slopes indicate the output increases directly with the parameter, while negative slopes signify inverse relationships. Only parameters that account for greater than a 1% deviation from the median are displayed for clarity. For instance, atmospheric deposition is used to calculate total system inputs, however, variations


f NO3
H
Nf
f grain
f res
Nmin
f N2O,ni
f N2O, de
f fix
fNH3
f NO, de
f NO,ni
(a)
Corn Total Inputs
Total Inputs
Percentiles of the variables
(b)
Soybean Total Inputs
Total Inputs
Percentiles of the variables
(c)
Corn Total Exports
Corn Exports
Percentiles of the variables
(d)
Soybean Total Exports
Soybean Exports
Percentiles of the variables
(e)
Corn NO3-
Corn NO3- emissions
Percentiles of the variables
(f)
Soybean NO3-
Soybean NO3- emissions
Percentiles of the variables
(g)
Corn N2O
Corn N2O emissions
(h)
Soybean N2O
Soybean N2O emissions
(i)
Corn NOx
Corn NOx emissions
(j)
Soybean NOx
Soybean NOx emissions
10.0%
30.0%
50.0%
70.0%
90.0%

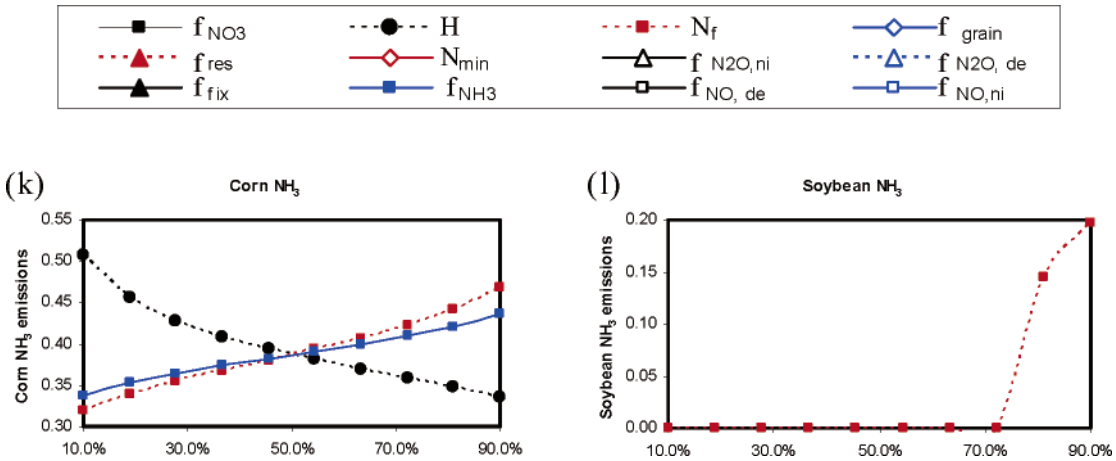


FIGURE 5. Sensitivity plots for emission estimates. All emissions are reported as g emission/kg crop basis. (f_{NO_3} = fraction of fertilizer leached as NO_3^-; H = crop harvested; N_f = rate of fertilizer application; f_{grain} = nitrogen fraction of harvested grain; f_{res} = nitrogen fraction of residue; N_{min} = mineralized nitrogen from soil and crop residue; $f_{N_2O,ni}$ = fraction of applied fertilizer nitrified to N_2O; f_{NH_3} = fraction of applied fertilizer volatilized to NH_3; $N_{atm,w}$ = wet atmospheric deposition as either ammonium or nitrate; $N_{atm,d}$ = dry atmospheric deposition; N_{fix} = nitrogen fixed via biological nitrogen fixation; $f_{NO,de}$ = fraction of mineralized nitrogen denitrified to NO; $f_{NO,ni}$ = fraction of applied fertilizer nitrified to NO)

in their values do not significantly impact the overall value, and are not displayed in Figure 5a and b.

As can be seen from Figure 5, all of the emissions are directly related to nitrogen input and fractionation parameters, and inversely related to crop yield. Crop yield is a predominant factor for each of the corn emissions calculations, but is generally not as significant for the soybean distributions. In addition to being larger in magnitude than soybean yields, corn yields historically demonstrate greater annual and geographic variability which are reflected in the parameter distribution. The predominant controlling factor in the soybean distributions is mineralized nitrogen. Its prevalence in the soybean equations results from lack of fertilizer inputs and the relatively small variability ranges associated with other parameters. It is interesting to note the soybean fertilizer contribution in the sensitivity graphs for soybean emissions. The assigned parameter distribution indicates that only 25% of soybeans receive fertilizer, therefore, the sensitivity to fertilizer is only seen at the high end of the distribution.

Sensitivity analysis of the total nitrogen exports shows that the system is dominated by the nitrate fractionation parameter (f_{NO_3}) for corn, and the nitrogen grain fraction ($f_{grain,s}$) for soybeans. The total nitrogen flux from the system is much less sensitive to the other controlling variables. The sensitivity to nitrate fractionation (f_{NO_3}) is the major controlling factor for nitrate emissions in corn agriculture, but less so for soybeans potentially due to the large amount of nitrogen exported in the soybean harvest. Meanwhile, mineralization rates (f_{min}) control NO_3^- emissions in soybean fields more than the nitrate fractionation parameter. This highlights the importance of understanding nitrate fractionation in agricultural soils to achieve better management practices.

In summary, the findings indicate that the fractionation model is able to describe the inherent variability observed in agricultural systems, as reflected by the agreement between model and literature data. These data can be used in conjunction with transport models to better understand nitrogen fluxes into the MRB and lead to better management practices. These data can be incorporated into LCAs, where quantitative nutrient information is lacking.

Acknowledgments

We thank Dr. Susan Powers of Clarkson University and Mr. Lowell Gentry of the University of Illinois at Urbana-Champaign for their guidance and helpful suggestions. Support for this research was provided by the National Science Foundation's PREMISE (DMI 225912 and DMI 400277) and IGERT (DGE 9720779) programs, the U.S. EPA's TSE program (RD 83152101), and Alcoa, Inc.

Supporting Information Available

Documentation includes data used to construct probability distributions for the fractionation model, as well as emission distributions generated on a kg N/ha basis. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Fixen, P. E.; West, F. B. Nitrogen fertilizers: Meeting contemporary challenges. *AMBIO* **2002**, *31*, 169−176.
(2) Galloway, J. N. The global nitrogen cycle: Changes and consequences. *Environ. Pollut.* **1998**, *102*, 15−24.
(3) Galloway, J. N.; Aber, J. D.; Erisman, J. W.; Seitzinger, S. P.; Howarth, R. W.; Cowling, E. B.; Cosby, B. J. The nitrogen cascade. *BioScience* **2003**, *53*, 341−356.
(4) Wolfe, A. H.; Patz, J. A. Reactive nitrogen and human health: Acute and long-term implications. *AMBIO* **2002**, *31*, 120−125.
(5) Sheehan, J.; Camobreco, V.; Duffield, J.; Graboski, M.; Shapouri, H. *Life Cycle Inventory of Biodiesel and Petroleum Diesel for Use in an Urban Bus*; NREL/SR-580-24089; National Renewable Energy Laboratory: Golden, CO, 1998.
(6) Shapouri, H.; Duffield, J. A.; Wang, M. *The Energy Balance of Corn Ethanol: An Update*; Agricultural Economic Report 813; U.S. Department of Agriculture, Economic Research Service: Washington, DC, 2002.
(7) Wang, M. *GREET-Greenhouse gases, Regulated Emissions, and Energy use in Transportation*; Argonne National Laboratory: Argonne, IL, 1999.
(8) Patel, M.; Bastioli, C.; Marini, L.; Wurdinger, E. In *Biopolymers*; Steinbuchel, A., Ed.; Wiley-VCH: Weinheim, 2002; Vol. 10, pp 409−452.
(9) Brentrup, F. Life cycle assessment to evaluate the environmental impact of arable crop production. *Int. J. Life Cycle Assess.* **2003**, *8*, 156.
(10) Goolsby, D. A.; Battaglin, W. A.; Aulenbach, B. T.; Hooper, R. P. Nitrogen flux and sources in the Mississippi River Basin. *Sci. Total Environ.* **2000**, *248*, 75−86.
(11) Scavia, D.; Rabalais, N. N.; Turner, R. E. Predicting the response of Gulf of Mexico hypoxia to variations in Mississippi River nitrogen load. *Limnol. Oceanogr.* **2003**, *48*, 951−956.
(12) Dale, B. E.; Kim, S. Greenhouse Gas Emission Profile of Ethanol Production under Various Cropping Systems. Proceedings of the AIChE Conference. In American Institute of Chemical Engineers: San Francisco, CA, 2003.
(13) Williams, J. R.; Dyke, P. T.; Jones, C. A. EPIC - Erosion Productivity Impact Calculator. USDA ARS: Temple, TX, 1997.

(14) Parton, W. J.; Schimel, D. S.; Cole, C. V.; Ojima, D. S. 5th ed.; CENTURY Soil Organic Matter Model. National Renewable Energy Laboratory: Golden, CO, 1987.
(15) National Oceanic and Atmospheric Administration. *Hypoxia in the Gulf of Mexico: Progress towards the completion of an integrated assessment*; National Centers for Coastal Ocean Science, NOAA: Washington, DC, 2000.
(16) Smith, R. A.; Schwarz, G. E.; Alexander, R. B. Regional interpretation of water-quality monitoring data. *Water Resour. Res.* **1997**, *33*, 2781−2798.
(17) Alexander, R. B.; Smith, R. A.; Schwarz, G. E. Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico. *Nature* **2000**, *403*, 758−761.
(18) USDA. Crop Production, Report CrPr2−5(6-03); USDA National Agricultural Statistics Service, 2003.
(19) ERS. Crop production practices data, USDA, Economic Research Service, Agricultural Resource Management Survey, 2001.
(20) Huijbregts, M. A. J.; Norris, G. A.; Bretz, R.; Ciroth, A.; Maurice, B.; Bahr, B. v.; Weidema, B.; de Beaufort, A. S. H. Framework for modeling data uncertainty in life cycle inventories. *Int. J. Life Cycle Assess.* **2001**, *6*, 127−132.
(21) Huijbregts, M. A. J.; Gilijamse, W.; Ragas, A. M. J.; Reijnders, L. Evaluating uncertainty in environmental life-cycle assessment. A case study comparing two insulation options for a Dutch one-family dwelling. *Environ. Sci. Technol.* **2003**, *37*, 2600−2608.
(22) deVries, W.; Kros, J.; Oenema, O.; deKlein, J. Uncertainties in the fate of nitrogen II: A quantitative assessment of the uncertainties in major nitrogen fluxes in The Netherlands. *Nutr. Cycling Agroecosyst.* **2003**, *66*, 71−102.
(23) Schulz, K.; Beven, K.; Huwe, B. Equifinality and the problem of robust calibration in nitrogen budget simulations. *Soil Sci. Soc. Am. J.* **1999**, *63*, 1934−1941.
(24) *Decisioneering*; Crystal Ball 5.5, Decisioneering, Inc.: Denver, CO, 2001.
(25) Ma, B. L.; Dwyer, L. M. Nitrogen uptake and use of two contrasting maize hybrids differing in leaf senescence. *Plant Soil* **1998**, *199*, 283−291.
(26) Mertens, M.; Huwe, B. Fun-balance: A fuzzy balance approach for the calculation of nitrate leaching with incorporation of data imprecision. *Geoderma* **2002**, *109*, 269−287.
(27) Howarth, R. W.; Boyer, E. W.; Pabich, W. J.; Galloway, J. N. Nitrogen use in the United States from 1961 to 2000 and potential future trends. *AMBIO* **2002**, *31*, 88−96.
(28) Gentry, L. E.; David, M. B.; Smith, K. A.; Kovacic, D. A. Nitrogen cycling and tile drainage nitrate loss in a corn/soybean watershed. *Agric., Ecosyst. Environ.* **1998**, *68*, 85−97.
(29) Padgitt, M.; Newton, D.; Penn, R.; Sandretto, C. *Production practices for major crops in U.S. agriculture, 1990−97*; Statistical Bulletin No. 969; USDA, ERS: Washington, DC, 2000.
(30) Christensen, L. A. *Soil, nutrient, and water management systems used in U. S. corn production*; Agriculture Information Bulletin No. 774; USDA, ERS: Washington, DC, 2002.
(31) International Panel of Climate Change. *Revised 1996 IPCC guidelines for national greenhouse gas inventories*, UK Meteorological Office: Bracknell, U.K., 1996.
(32) Patni, N. K.; Masse, L.; Jui, P. Y. Tile effluent quality and chemical losses under conventional and no-tillage. Part I: Flow and nitrate. *Trans. ASAE* **1996**, *39*, 1665−1672.
(33) Klocke, N. L.; Watts, D. G.; Schneekloth, J. P.; Davison, D. R.; Todd, R. W.; Parkhurst, A. M. Nitrate leaching in irrigated corn and soybean in a semi-arid climate. *Trans. ASAE* **1999**, *42*, 1621−1630.
(34) SETAC. SETAC−Europe LCA working group "data availability and data quality". *Int. J. Life Cycle Assess.* **2001**, *6*, 127.
(35) David, M. B.; McIsaac, G. F.; Royer, T. V.; Darmody, R. G.; Gentry, L. E. Estimated Historical and Current Nitrogen Balances for Illinois. In *The Scientific World*, **2001**, *1*, 597−604.
(36) McIsaac, G. F.; David, M. B.; Gertner, G. Z.; Goolsby, D. A. Relating net nitrogen input in the Mississippi River Basin to nitrate flux in the lower Mississippi River: A comparison of approaches. *J. Environ. Qual.* **2002**, *31*, 1610−1622.
(37) Barry, D. A. J.; Goorahoo, D.; Goss, M. J. Estimation of nitrate concentrations in groundwater using a whole farm nitrogen budget. *J. Environ. Qual.* **1993**, *22*, 767−775.
(38) Karlen, D. L.; Kramer, L. A.; Logsdon, S. D. Field-scale nitrogen balances associated with long-term continuous corn production. *Agron. J.* **1998**, *90*, 644−650.
(39) National Corn Growers Association. *Corn Production Trends*; National Corn Growers Association: St. Louis, MO, 2004.
(40) United Soybean Board. *Soybean Almanac 2002*; United Soybean Board: Chesterfield, MO, 2003.
(41) Lowrance, R. Nitrogen outputs from a field-size agricultural watershed. *J. Environ. Qual.* **1992**, *21*, 602−607.
(42) Tan, C. S.; Drury, C. F.; Soultani, M.; Van Wesenbeeck, I. J.; Ng, H. Y. F.; Gaynor, J. D.; Welacky, T. W. Effect of controlled drainage and tillage on soil structure and tile drainage nitrate loss at field scale. *Water Sci. Technol.* **1998**, *38*, 103−110.
(43) Owens, L. B.; Edwards, W. M.; Shipitalo, M. J. Nitrate leaching through lysimeters in a corn-soybean rotation. *Soil Sci. Soc. Am. J.* **1995**, *59*, 902−907.
(44) Gentry, L. E.; Below, F. E.; David, M. B.; Bergerou, J. A. Source of the soybean N credit in maize production. *Plant Soil* **2001**, *236*, 175−184.
(45) David, M. B.; Gentry, L. E.; Kovacic, D. A.; Smith, K. M. Nitrogen balance in and export from an agricultural watershed. *J. Environ. Qual.* **1997**, *26*, 1038−1048.
(46) Randall, G. W.; Mulla, D. J. Nitrate nitrogen in surface waters as influenced by climatic conditions and agricultural practices. *J. Environ. Qual.* **2001**, *30*, 337−344.
(47) Jaynes, D. B.; Colvin, T. S.; Karlen, D. L.; Cambardella, C. A. Nitrate loss in subsurface drainage as affected by nitrogen fertilizer rate. *J. Environ. Qual.* **2001**, *30*, 1305−1314.
(48) Chung, S. W.; Gassman, P. W.; Huggins, D. R.; Randall, G. W. EPIC tile flow and nitrate loss predictions for three Minnesota cropping systems. *J. Environ. Qual.* **2001**, *30*, 822−830.
(49) Bakhsh, A.; Kanwar, R. S.; Bailey, T. B.; Cambardella, C. A.; Karlen, D. L.; Colvin, T. S. Cropping system effects on NO_3^- N loss with subsurface drainage water. *Trans. ASAE* **2002**, *45*, 1789−1797.
(50) Strock, J. S.; Porter, P. M.; Russelle, M. P. Cover cropping to reduce nitrate loss through subsurface drainage in the northern U.S. Corn Belt. *J. Environ. Qual.* **2004**, *33*, 1010−1016.
(51) Kladivko, E. J.; Frankenberger, J. R.; Jaynes, D. B.; Meek, D. W.; Jenkinson, B. J.; Fausey, N. R. Nitrate leaching to subsurface drains as affected by drain spacing and changes in crop production system. *J. Environ. Qual.* **2004**, *33*, 1803−1813.
(52) Powers, S. E. *Quantifying cradle-to-farm gate life cycle impacts associated with fertilizer used for corn, soybean, and stover production*; TP-510-37500; DOE National Renewable Energy Laboratory, 2005.
(53) Mosier, A.; Kroeze, C.; Nevison, C.; Oenema, O.; Seitzinger, S. P.; van Cleemput, O. Closing the global N_2O budget: Nitrous oxide emissions through the agricultural nitrogen cycle. *Nutrition Cycling in Agroecosystems* **1998**, *52*, 225−248.

Received for review September 23, 2005. Revised manuscript received December 21, 2005. Accepted January 5, 2006.

ES0518878