# Evaluation of DeNitrification DeComposition Model for Estimating Ammonia Fluxes from Chemical Fertilizer Application

Srinidhi Balasubramanian[1], Andrew Nelson[1,2], Sotiria Koloutsou-Vakakis[1, *], Jie Lin[1], Mark J. Rood[1], LaToya Myles[3] and Carl Bernacchi[4,5]

[1] *Department of Civil and Environmental Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, 61801, USA*

[2] *U.S. Army Corps of Engineers, Engineer Research and Development Center, Construction Engineering Research Laboratory, 2902 Newmark Dr., Champaign, IL, 61822, USA*

[3]*National Oceanic and Atmospheric Administration, Air Resources Laboratory, Atmospheric Turbulence and Diffusion Division, Oak Ridge, TN 37831-2456, USA*

[4]*Department of Plant Biology and the Energy Biosciences Institute, University of Illinois at Urbana−Champaign, 1206 West Gregory Drive, Urbana, Illinois 61801, USA*

[5]*USDA-ARS Global Change and Photosynthesis Research Unit, Urbana, IL 61801, USA*

* Corresponding Author: S. Koloutsou-Vakakis, sotiriak@illinois.edu

# Abstract

DeNitrification DeComposition (DNDC) model predictions of $NH_3$ fluxes following chemical fertilizer application were evaluated by comparison to relaxed eddy accumulation (REA) measurements, in Central Illinois, United States, over the 2014 growing season of corn. Practical issues for evaluating closure were addressed by accounting for fluxes outside the measurement site and differences in temporal resolution. DNDC modeled $NH_3$ fluxes showed no significant differences in magnitude (at $p=0.05$) compared to measurements and replicated trends satisfactorily ($r_a^2 > 0.74$), during the initial 33 days after fertilizer application, when measured fluxes were to the atmosphere, compared to later time periods when depositional fluxes were measured ($r_a^2 < 0.52$). Among the model input parameters, $NH_3$ fluxes were most sensitive to air temperature, precipitation, soil organic carbon, field capacity, pH, and fertilizer application rate, timing, and depth. By constraining these inputs for conditions in Central Illinois, uncertainty in daily $NH_3$ fluxes was estimated to vary from 0% to 70% on a daily basis, during the corn growing season, with the highest uncertainty values estimated for the period of highest positive $NH_3$ fluxes. These results can guide future improvements in DNDC, which is a valuable tool to assist (1) in the development of $NH_3$ emission inventories with high spatial (constrained by the spatial resolution of input parameters) and temporal resolution (daily) and (2) in upscaling emissions from the site (farm) to the regional scale.

**Keywords**

DNDC, REA, ammonia emissions, fertilizer, sensitivity analysis, uncertainty analysis

## 1. Introduction

Application of chemical nitrogen fertilizers has supported increases in crop productivity to meet global food demands (Smil, 2002). However, the introduction of excess nitrogen into the environment has simultaneously resulted in adverse multi-scale, multi-environmental media impacts (Galloway et al., 2003). Ammonia ($NH_3$) is one of the gaseous species emitted to the atmosphere following application of chemical fertilizers. $NH_3$ is a precursor to secondary ambient particulate matter (PM) (Dentener and Crutzen, 1994) that is regulated for impacts on human health and visibility (US EPA, 2016). Atmospheric deposition of $NH_3$ and other nitrogenous compounds can also alter the structure and diversity of plant communities (Krupa, 2003) and exacerbate surface water eutrophication and soil acidification (Erisman et al., 2013). Volatilization of applied nitrogen as $NH_3$ is influenced by fertilizer type (Bouwman et al., 2002), rate and mode of application, and local weather and soil conditions (Sommer et al., 2004). Characterizing spatial and temporal heterogeneity associated with $NH_3$ fluxes from chemical fertilizer application under various environmental conditions is essential for development of representative emissions inventories for air quality modeling (Appel et al., 2011). While flux measurements can support such efforts, the high reactivity of $NH_3$ and simultaneous presence of atmospheric gaseous $NH_3$ and ammonium ($NH_4^+$) in PM (Norman et al., 2009) make such measurements resource intensive and technically challenging. Given that $NH_3$ is not a criteria air pollutant in the United States (US), measurement studies are spatially sparse and limited to short time periods (SAB, US EPA, 2011).

Several modeling techniques have been developed to characterize variability in $NH_3$ fluxes from chemical fertilizer application, which need to be evaluated by field measurements. Current estimates, reported in the National Emissions Inventory for the US, use an emission factor approach (US EPA, 2015). Spatial distribution of $NH_3$ emissions has been obtained empirically based on crop acreages at coarse (county level) (Goebes et al., 2003) and fine scales (4 km x 4 km) (Balasubramanian et al., 2015) and inversion of wet deposition fluxes of $NH_4^+$ at 36 km x 36 km (Gilliland et al., 2006) and 0.5° x 0.5° (Paulot et al., 2014). Temporal variability of $NH_3$ fluxes has been characterized using approximations based on crop planting and harvesting schedules, and seasonal nitrogen management data that identify percentages of nitrogen applied before, during and after planting and post-harvest (Goebes et al., 2003); empirical relationships using hourly temperature and wind speed (Gyldenkærne et al., 2005); inverse modeling techniques (Gilliland et al., 2006; Paulot et al., 2014); and implementation of semi-empirical models such as Environmental Policy Integrated Climate (EPIC) (Cooter et al., 2012) and process models such as DeNitrification DeComposition (DNDC) (Balasubramanian et al., 2015). Process-based models are particularly advantageous as they account for complex physico-chemical and ecological processes in the soil and soil-atmosphere interactions. Such models can be employed under a wide range of environmental conditions and nutrient management practices (Cuddington et al., 2013) and for scaling fluxes from site to regional scales (Olander et al., 2011). An example of process-based model is Volt'Air that simulates $NH_3$ fluxes following slurry application by accounting for the transfer and equilibria of nitrogen in the soil and between soil and atmosphere (Génermont and Cellier, 1997). Other models such as AGRIN (Beuning et al., 2008) and DNDC (Li et al., 1992) additionally simulate biological processes of decomposition, nitrification and denitrification.

Originally developed to simulate $N_2O$ and $N_2$ fluxes from the soil following rain events (Li et al., 1992), DNDC was later modified to additionally simulate fluxes of trace gases, including $NH_3$ (Li, 2000). DNDC has been widely employed to simulate magnitude and timing of trace gas fluxes based on site-specific inputs describing climate, crop growth and nutrient management practices (Gilhespy et al., 2014). For example, at the site scale, DNDC has been employed to study impact of crop-rotation and tillage on crop yields (Farahbakhshazad et al., 2008), greenhouse gas fluxes (Gopalakrishnan et al., 2012), $NH_3$ fluxes from fertilized cropland (Balasubramanian et al., 2015), and nitrate leaching into water bodies (David et al., 2009). While DNDC model performance has been evaluated in many studies for prediction of greenhouse gases (for example Giltrap et al., 2010; Hastings et al., 2010; and review by Gilhespy et al., 2014), evaluation for prediction of $NH_3$ fluxes is limited. DNDC performance including $NH_3$ fluxes was initially evaluated, in China, during nine days following application of urea and ammonium bicarbonate in a rice field (Li, 2000) and more recently, for a wheat-corn rotation system, for an 11 day period following urea application (Cui et al., 2014). Further, Manure-DNDC was recently evaluated for its performance to predict $NH_3$ fluxes following field application of livestock waste manure (Deng et al., 2015; Li et al., 2012), and for modeling fluxes following swine-slurry application for Canada (Congreves et al., 2016).

Since, models such as DNDC parameterize pathways of evolution for different trace gas fluxes with different degrees of detail, it is important to evaluate the model for each of its trace gas outputs under different environmental conditions, crops and management practices in different localities (Bennett et al., 2013). The objectives of this study are: (1) evaluation of closure between modeled $NH_3$ fluxes with measurements over a corn canopy in Central Illinois (located in Midwest US), for an entire growing season; (2) evaluation of model sensitivity to identify impact of different environmental and nutrient management inputs on modeled $NH_3$ fluxes; and (3) estimation of uncertainty in modeled $NH_3$ fluxes at the measurement site. Results from this study respond to the need of evaluating DNDC for $NH_3$, at a location within the socalled US ‘Corn Belt’. Such results are important to guide future efforts to (1) further improve DNDC predictions; (2) facilitate quantitative estimates of $NH_3$ fluxes and associated uncertainties for use in emission inventories, and (3) test the model as a tool for upscaling $NH_3$ emissions from the site to the regional scale.

# 2. Methods

## 2.1 Measurement Site

The measurement site is located at the Energy Farm in Urbana, Illinois, part of the Energy Biosciences Institute at the University of Illinois (40° 3' 46.209" N, 88° 11' 46.0212" W, 220 m above sea level) (Zeri et al., 2011) (Figure 1). The rationale for selection of this site is described by *Nelson et al.* (2016). Plots were planted with corn (plot 1), miscanthus (*Miscanthus x giganteus*, plot 2), switchgrass (*Panicum virgatum* L., plot 3); and a mix of 28 native prairie species (plot 4) during the 2014 growing season. Privately owned corn (plot 5) fields were located to the south and southwest and alfalfa (plot 6) fields were located south southeast of the Energy Farm. Environmental and average climatic parameters for the site are shown in Tables 1 and S1 (Supplementary Information) as baseline, for year 2014.

The experimental field campaign was conducted at the Energy Farm corn plot (plot 1) that was fertilized with 168 kg-N $ha^{-1}$ of 28% nitrogen solution, on May 6th 2014. $NH_3$ fluxes were measured during the 2014 corn-growing season (Day of Year (DOY) 115-272) using the relaxed eddy accumulation (REA) method. Briefly, REA is a micrometeorological method, introduced by Businger and Oncley (1990) that involves conditional measurement of trace gas concentrations, at a constant sample flow rate, by accumulating samples in separate reservoirs during atmospheric updrafts and downdrafts, as determined by measurement of vertical wind speed with a three-dimensional sonic anemometer. Field sample blanks were also obtained during all REA sampling and included in sample analysis. In this experimental setup, annular glass denuders coated with phosphoric acid were used to capture $NH_3$ in the sampled ambient air stream. Following sampling, denuders were extracted in deionized water and $NH_4^+$ in the extract solution was quantified by flow injection analysis. Experimental methods, including quality assurance and quality control procedures, and measurement results are described in detail in Nelson et al. (2016). Flux footprints for the measurement campaign were calculated using the EddyPro software package (Version 5.1.1, LI-COR, Lincoln, NE), according to the methods by (Kljun et al., 2004; and Kormann and Meixner, 2001).

## 2.2 Implementation of the DNDC Model to Estimate $NH_3$ Fluxes

DNDC (version 9.5, downloaded January 2014) models variations in trace gas fluxes at site scale (perceived as the scale of a single farm) as a function of weather, soil, crop growth and management inputs (Li, 2000). These inputs are used to model the evolution of soil climate, crop growth, plant decomposition, and trace gases fluxes. $NH_3$ fluxes are estimated within the decomposition sub-model and are regulated by soil ammonium concentration that is generated by the turnover of soil organic matter, soil pH and ambient temperature that govern the partitioning of $NH_3$ between liquid phase in soil and gaseous phase in the soil pores. Volatilization of $NH_3$ to the atmosphere from the soil pores is controlled by diffusion as a function of porosity and clay content (Li, 2000). $NH_3$ deposition is modeled based on atmospheric $NH_3$ concentrations and deposition velocity adjusted for leaf area index, crop nitrogen and leaf surface moisture (Li, 2000).

### *2.2.1 Modeling Scheme and Input Data*

For the measurement-model comparison study, the 90% footprint of the REA tower, at the measurement site was considered. The footprint describes the probability of an area source emitting a passive scalar (such as $NH_3$) to contribute to the turbulent flux at the receptor location (Kljun et al., 2004). The 90% footprint, calculated as distance, represents the radius of the area that contributes 90% to the flux measured at the REA tower. For the cases when the 90% REA footprint extended beyond the boundary of plot 1, and depending on the dominant wind direction, contributions from the surrounding crops (plots 2-6) were also estimated by running DNDC with the parameters of the respective ‘sites’.

For each crop plot, input data were first obtained from field records or where unavailable, from regional databases or literature. Baseline inputs were obtained as follows: Daily ambient temperature, wind speed, precipitation, solar radiation and humidity were obtained from the Illinois Climate Network (ICN) site located at Bondville (15 km west of plot 1), for years 1999-2014 (Illinois State Water Survey, 2015). Local site measurements of temperature and wind speed, substituted the ICN data, when available (April to October 2014). Ambient $NH_3$ concentration (National Atmospheric Deposition Program, 2015a) and $NH_4^+$ wet deposition data were obtained from observations at Bondville (National Atmospheric Deposition Program, 2015b). Soil pH, bulk density and soil organic carbon (SOC) were obtained from Energy Farm records (communication with Energy Farm manager Timothy Mies and field research specialist Michael Masters). These data resulted from analysis of bulk soil, with 5 cores taken at each plot, in April 2014 at depths of 0-10 cm and 10-30 cm. Soil texture (loam), clay content and porosity were obtained from the Web Soil Survey (USDA, 2015a). Saturation field capacity (water filled porosity at saturation field capacity, henceforth referred to as field capacity) and wilting point were obtained from measurements reported by the ICN for the Bondville site (Illinois State

Water Survey, 2015).

In terms of crop parameters, default values from DNDC's crop library were considered for corn and soybeans, except for growing degree days which were obtained for the Bondville site (Illinois State Water Survey, 2015). Crop parameters for switchgrass and miscanthus were added to the DNDC crop library based on *Heaton et al.* (2008). Harvest for these two crops was assumed to occur the year after planting. Default values from DNDC's crop library were used for prairie grass and alfalfa. A corn-soybean rotation was considered for years 1999-2005 and fertilizer management practices were developed following seasonal nitrogen management data (Balasubramanian et al., 2015). Turnover of cropland to establish the Energy Farm in years 2006-2007 was modeled as fallow land. For years 2008-2014, planting and harvest dates, fertilizer type, application amount and timing and tillage dates were obtained from Energy Farm records for all plots (personal communication with Energy Farm manager, Timothy Mies). These baseline inputs (Supplementary information, Section S1), were used to initialize independent DNDC model runs for crop plots 1-6 to model daily $NH_3$ fluxes for the year 2014. To minimize impact of initial conditions, a spin up period of 15 years was used, that lies within the literature recommended range of 10-20 years (Fumoto et al., 2008; Perlman et al., 2013).

### *2.2.2 Methods for Closure Evaluation*

In order to make modeled and measured $NH_3$ fluxes comparable, methods were developed to account for fluxes from surrounding crops for time periods when the REA footprint extended outside the measurement site and for the difference in the time resolution between model predictions (daily) and measurements (4 hr). The 90% REA footprint was first calculated for each measurement period. If the 90% footprint was less than 100 m (minimum distance from REA tower to edge of plot 1), measured $NH_3$ flux was assumed to include contributions only from plot 1; otherwise, fluxes from plots 2-6 were also accounted. For measurement periods with 90% REA footprints exceeding 100 m, the 30%, 50% and 70% footprints were additionally calculated and interpolation was performed to identify the percentage of REA footprint at 100 m. Prevailing wind direction was then determined using wind roses for each measurement period. Wind direction was used to identify which contributing plots to consider. Frequency of wind from identified directions was used to adjust the modeled flux at the measurement site by weighing the contributing fluxes relative to the REA footprints. Sample calculation is provided in supplementary information (Section S2).

Differences in temporal scales between modeled and measured $NH_3$ fluxes were bridged using concurrent continuous $NH_3$ flux measurements from a flux gradient system operated at the measurement site that used cavity ring-down spectroscopy (CRDS) [Meyers and Baldocchi, 2005; NOAA/ATDD, 2016]. The aggregated $NH_3$ flux profile over the measurement period as a function of time is presented in supplementary information (Section S3). Using the CRDS data, the hourly percent flux was first calculated for each day. Then, the mean and standard deviation of these hourly percent fluxes were calculated for the entire measurement period that the flux gradient system was operated (DOY 129-269, in year 2014). The resulting mean hourly temporal profile was applied to scale the modeled $NH_3$ fluxes from the daily to the hourly scale and aggregated over the hours corresponding to REA measurements.

Four scenarios were considered to obtain $NH_3$ flux outputs from DNDC: (a) ‘baseline’, only fluxes from plot 1 were considered, (b) ‘baseline_spatial’, baseline $NH_3$ fluxes from plot 1 were adjusted for $NH_3$ fluxes outside plot 1 with REA footprint correction, (c) ‘baseline_temporal’, baseline $NH_3$ fluxes from plot 1 were scaled from day to the hour scale, and (d) ‘baseline_spatial_temporal’, baseline $NH_3$ fluxes from plot 1 adjusted using both REA footprint and temporal scale corrections.

### *2.2.3 Statistical Evaluation of Closure between Modeled and Measured $NH_3$ Fluxes*

Closure was evaluated using analysis of association and analysis of coincidence. Analysis of association indicates how well trends in modeled and measured $NH_3$ fluxes are replicated while the analysis of coincidence estimates the differences in magnitude of modeled and measured $NH_3$ fluxes (Smith and Smith, 2007). Association was analyzed using the sample correlation coefficient ($r_a$, Equation 1a) where $r_a = 1$ indicates positive association of trends between measured and modeled values, while $r_a = -1$ indicates negative association. $r_a^2$ value of 0.8 or higher is typically identified as significant association (Smith and Smith, 2007).

$$r_a = \frac{\sum_{i=1}^{i=n}\left(O_i - \overline{O}\right)\left(P_i - \overline{P}\right)}{\sum_{i=1}^{i=n}\left(O_i - \overline{O}\right)^2 \sum_{i=1}^{i=n}\left(P_i - \overline{P}\right)^2} \quad \text{... Equation 1a}$$

Coincidence was analyzed using the root mean square error (RMSE, Equation 1b) and Student's t-test statistic (t, Equation 1c) to identify if differences in modeled and measured fluxes were statistically significant at 5% significance level (Smith and Smith, 2007).

$$\mathrm{RMSE}\ (\%) = \frac{100}{\overline{O}} \times \sqrt{\frac{\sum_{i=1}^{i=n}\left(O_i - P_i\right)^2}{n}} \quad \text{… Equation 1b}$$

$$t = \frac{\dfrac{\sum_{i=1}^{i=n}(O_i - P_i)}{n} \times \sqrt{n}}{\sqrt{\dfrac{\sum_{i=1}^{i=n}\left((O_i - P_i) - \left(\sum_{i=1}^{i=n}\dfrac{O_i - P_i}{n}\right)\right)^2}{n-1}}} \quad \text{… Equation 1c}$$

where, $O_i$ = i$^{th}$ observation, $\bar{O}$ = mean of i observations, $P_i$ = i$^{th}$ prediction, $\bar{P}$ = mean of i predictions, $n$ = number of samples.

### 2.3 Sensitivity to Inputs and Uncertainty in Modeled $NH_3$ Fluxes

As previously mentioned, DNDC inputs were obtained from site measurement records and regional databases for Central Illinois. There are underlying uncertainties in these inputs, either from natural variability (e.g. inputs such as soil moisture or soil organic carbon) or from uncertainties in knowledge of farm management practices in neighboring plots. The latter is important in this study because in order to make modeling results comparable to measurements, we considered the extend of the REA method footprint, which depending on wind speed and direction was occasionally extending outside of a single plot, where farm management parameters were different. To estimate the resulting uncertainty in modeled $NH_3$ fluxes, from both natural variability and management practices of adjacent plots, a model sensitivity analysis was performed followed by uncertainty analysis. Sensitivity analysis was first performed to identify input parameters that have the most influence on the modeled $NH_3$ fluxes, using the built-in Monte Carlo function in DNDC (Li et al., 2004), by changing one parameter at a time. Then, the range of the identified most influential inputs was constrained for conditions in Central Illinois, and used as input to DNDC to estimate uncertainty in $NH_3$ fluxes. Choosing the one parameter at a time approach for sensitivity analysis of DNDC is appropriate to help us identify the most influential parameters because any single change in the primary drivers (e.g., climate, soil, vegetation or anthropogenic activity) alters one or more of the environmental factors (e.g., radiation, temperature, moisture, Eh, pH and substrate concentration gradient); and these changes can affect the biochemical or geochemical reactions, which finally determine the transport and transformation of C and N in the ecosystem (Li, 2011).

In the literature, we have identified one previous DNDC sensitivity analysis study for $NH_3$ fluxes that assessed inputs related to alternate nutrient management practices (Cui et al., 2014). In this study, we have included a larger number of inputs, assessing 26 input variables related to weather, soil, crop growth and management practices using Monte Carlo simulations. For this purpose, inputs for plot 1 for the year 2014 were considered (baseline_montecarlo, Table S1). Inputs were varied, one at a time, over 3000 iterations, keeping other inputs constant at baseline_montecarlo values. Since wind speed was unavailable within the built-in Monte Carlo function, it was evaluated separately by changing daily wind speed in increments of 0.5 m/s over a range of ± 10 m/s (excluding negative values).

The relative deviation ratio (RDR, Equation 2a) was used to identify inputs to which modeled $NH_3$ fluxes were most sensitive (Hamby, 1994). RDR > 1 indicates high sensitivity to the input, since the uncertainty propagated through the model is increased due to the formulation of the model. An RDR = 1 indicates that all input uncertainty is passed through the model and appears as output uncertainty, while RDR < 1 indicates that the model is less sensitive to the parameter, thereby the parameter is contributing to output uncertainty to a lesser degree (Hamby, 1994). The sensitivity index (SI, Equation 2b) was used to evaluate qualitative inputs of fertilizer and tillage timing (Hamby, 1994). Higher SI implies higher sensitivity of model outputs to the input parameter. For this study, inputs with RDR > 0.2 or SI > 0.2 were identified as "key inputs", meaning that they contribute most to the modeled $NH_3$ flux uncertainty.

$$\mathrm{RDR} = \frac{\overline{O} \times \sqrt{\sum_{i=1}^{i=n} \left(P_i - \overline{P}\right)^2}}{\overline{P} \times \sqrt{\sum_{i=1}^{i=n} \left(O_i - \overline{O}\right)^2}} \qquad \text{… Equation 2a}$$

$$\mathrm{SI} = (P_{max} - P_{min}) / P_{max} \qquad \text{… Equation 2b}$$

where, $P_{max}$ = maximum of all $P_i$, $P_{min}$ = minimum of all $P_i$

Once the influential inputs were identified for the DNDC modeled $NH_3$ fluxes, variabilities of these inputs were used to estimate uncertainty in modeled fluxes. Observed ranges in values of key inputs for Central Illinois were constrained using measurement site records and regional databases (Table 1). Minimum and maximum input values were considered in the modeling scheme provided in Section 2.2.1 for the corn in plot 1 and plot 5. While inputs for biofuel crops (plots 2, 3, 4, 6) were not varied due to the small contributions of their fluxes, their flux contributions were accounted by making the spatial adjustments described in Section 2.2.2. The total uncertainty band was estimated by considering the maximum and minimum modeled $NH_3$ fluxes resulting from this approach.

**Table 1**: Range of input values observed in Central Illinois. For each input parameter, the minimum and maximum values were used in the modeling scheme provided in Section 2.2.1 to characterize uncertainty in modeled $NH_3$ fluxes at the measurement site for the year 2014.

| Parameter | Baseline | Minimum-maximum values observed in Central Illinois |
|---|---|---|
| Air temperature (°C) (annual average) | 9.44 | Comparing measurements at the Energy Farm and Bondville and Willard weather stations[a] |
| Precipitation (cm) (annual average of daily precipitation) | 0.3 | Comparing measurements at the Energy Farm and Bondville and Willard weather stations[a] |
| Field capacity | 0.36 | 0.33[b] - 0.44[a] |
| pH | 5.16 | 4.42[c] – 6.7[d] |
| Soil organic carbon (kg-C/kg-soil) | 0.035 | 0.015[e] – 0.045[d] |
| Tilling date | 5th May | 4th May – 6th May |
| Tilling depth (cm) | 10 | 10[f] – 15[g] |
| Fertilizer application date | 5th May | 21st April[h] – 23rd May[h] |
| Fertilizer application depth (cm) | 15 | 10[f] – 15[g] |

| **Parameter** | **Baseline** | **Minimum-maximum values observed in Central Illinois** |
|---|---|---|
| Fertilizer application amount (kg-N ha$^{-1}$) | 168 | 160[i] – 220[i] |

[a] *Illinois State Water Survey* [2015]; [b] *Hollinger* [1995]; [c] Energy Farm records; [d] *USDA* [2015b]; [e] *Gopalakrishnan et al.* [2012]; [f] DNDC default value for chisel tillage; [g] *Simmons and Nafziger* [2014]; [h] *USDA* [2010]; [i] Observed values (1999-2014) (USDA, 2015b).

# 3.0 Results and Discussion

## 3.1 Evaluation of Predictive Capability of DNDC

### *3.1.1 Modeled $NH_3$ Fluxes at the REA Measurement Site*

Ambient temperature and modeled $NH_3$ fluxes for crops in plots 1-6 are shown in Figures 2a and 2b respectively, for the year 2014. Largest modeled $NH_3$ fluxes occurred after fertilizer application for corn in plot 1 (7.13 kg-N $ha^{-1}yr^{-1}$) and plot 5 (9.22 kg-N $ha^{-1}yr^{-1}$). In contrast, $NH_3$ fluxes from miscanthus (plot 2, 0.79 kg-N $ha^{-1}yr^{-1}$) and switchgrass (plot 3, 0.57 kg-N $ha^{-1}yr^{-1}$) were considerably lower, while modeled $NH_3$ fluxes were zero for prairie grass (plot 4) and alfalfa (plot 6). These differences are attributed to the differences in amount, timing and type of fertilizer application.

Plot 1 was planted and fertilized on May 6th with 28% urea ammonium nitrate (UAN), while plot 5 was fertilized on March 26th with 28% UAN (33 kg-N $ha^{-1}$) and 82% anhydrous ammonia (168 kg-N $ha^{-1}$) and planted on April 23rd (personal communication with EBI Energy Farm manager, Timothy Mies). Use of anhydrous ammonia in plot 5, resulted in a spike in fluxes within a day that is consistent with previous observations (Sommer and Christensen, 1992; Sommer et al., 2004) and $NH_3$ fluxes continued for a period of 55 days. Similarly, $NH_3$ peak fluxes in plot 1 were observed shortly after application but they continued over a shorter period of 35 days. These results are consistent with previous measurement studies that indicate largest initial $NH_3$ fluxes were correlated with higher temperatures on and following the day of application (Fenn and Hossner, 1985; Sharpe and Harper, 1995). The fluxes following UAN application in plot 1 are of the same order of magnitude and display similar temporal trends to those reported by *Jantalia et al.* (2012), with peak fluxes observed 6-10 days following application.

### *3.1.2 Evaluating Closure between Modeled and Measured $NH_3$ Fluxes*

Comparison of modeled $NH_3$ fluxes under four scenarios with REA measurements is shown in Figure 3. DNDC overall underestimated $NH_3$ fluxes compared to measurements, except for the baseline case (Table 2). Modeled fluxes after DOY 178 were zero for all cases. However, measurements indicated fluxes of smaller magnitudes (under 0.20 µg $m^{-2}s^{-1}$) in the same time period. No negative fluxes were captured by DNDC during the entire measurement period, indicating a limitation of the model in capturing depositional fluxes for the year 2014. Modeled $NH_3$ fluxes were evaluated for closure using coincidence and association statistics (Table 2) over two time frames: (1) for the entire time period for which REA measurements were available (DOY 115-272, 36 samples) and (2) a shorter time period characterized by highest positive fluxes recorded by REA measurements in plot 1 (DOY 126-158, 14 samples) (Nelson et al., 2016).

RMSE for the baseline case was higher for the entire measurement period (168.8%) compared to DOY 126-159, characterized by higher measured positive fluxes (114.6%). RMSE also reduced from 168.8% to a lowest value of 123.8% for the entire measurement period and from 114.6% to lowest value of 58.1% for DOY 126-159, when considering alternative scenarios. A two-tailed t-test (Table 2), showed no significant differences between modeled and measured $NH_3$ fluxes for DOY 126-159, while two scenarios (baseline_temporal and baseline_spatial_temporal) resulted in significant differences when considering the entire measurement period. Association statistics ($r_a^2$ = 0.38-0.52) indicated poor correlation between measurements and modeled results for the entire growing season. However, $r_a^2$ values were considerably higher (0.74-0.83), for DOY 126-159, while $r_a^2$ values improved when external flux contributions were accounted (baseline_spatial) and when the day to hour conversion was applied (baseline_temporal and baseline_spatial_temporal).

**Table 2**: Coincidence and association statistics for evaluating closure between modeled and measured $NH_3$ fluxes. Two time frames were considered for analysis: entire measurement period (DOY=115-272) and days characterized by high positive $NH_3$ fluxes following fertilizer application in plot 1 (DOY= 126-159).

| **Scenario** | **Coincidence statistics** | | | **Association statistics** | | |
|---|---|---|---|---|---|---|
| | | DOY 115-272 (n=36) | DOY 126-159 (n=14) | | DOY 115-272 (n=36) | DOY 126-159 (n=14) |
| baseline | **RMSE (%)** | 168.8 | 114.6 | | | |
| | **t** | 0.86 | 1.04 | **$r_a^2$** | 0.38 | 0.74 |
| | **p** | {0.40} | {0.32} | | | |
| baseline_spatial | **RMSE (%)** | 123.8 | 58.1 | | | |
| | **t** | 0.36 | 0.09 | **$r_a^2$** | 0.47 | 0.74 |
| | **p** | {0.72} | {0.93} | | | |
| baseline_temporal | **RMSE (%)** | 145.7 | 76.6 | | | |
| | **t** | 2.56 | 1.33 | **$r_a^2$** | 0.42 | 0.83 |
| | **p** | {0.01}$^{+}$ | {0.20} | | | |
| baseline_spatial_temporal | **RMSE (%)** | 156.1 | 102.3 | | | |
| | **t** | 2.91 | 1.45 | **$r_a^2$** | 0.52 | 0.83 |
| | **p** | {0.01}$^{+}$ | {0.17} | | | |

$^{+}$ indicates significant difference at 5% significance level

These results suggest that DNDC has poorer agreement with the REA measurements when there are depositional fluxes to the corn canopy. Estimated RMSE's for all four modeled cases and time frames were higher compared to RMSE reported by *Cui et al.* (2014) (77.4%) and *Li* (2000) (39%). These studies considered shorter time scales (< 11 days) compared to the time scales of analysis in this study. This could be one reason for the higher RMSE's observed in our study. Improved RMSE for DOY 126-159, for all four modeled cases, indicate that modeled $NH_3$ fluxes were more representative of the physico-chemical processes governing soil-atmosphere exchange of $NH_3$ as compared to the entire time period of DOY 115-272. Since, REA measurements indicate higher depositional fluxes after DOY 159, this is indicative of possible limitations of the DNDC depositional algorithm for $NH_3$. Addition of flux contributions from adjacent fields when the REA footprint was exceeding the 90% footprint limit, and adjustment to match the measurement and simulation time scales resulted in improved model-measurement agreement for the time period when fluxes were to the atmosphere.

## 3.2 Assessing DNDC Model Uncertainty

### *3.2.1 Results of Sensitivity Analysis using Monte Carlo simulations for $NH_3$ Predictions*

Results from sensitivity analysis using Monte Carlo simulations are presented in Table 3. DNDC modeled $NH_3$ fluxes were most sensitive ($RDR > 0.2$ or $SI > 0.2$) to changes in daily air temperature, precipitation, soil properties of field capacity, pH and SOC content and nutrient management practices of tillage date and fertilizer amount, timing and depth of placement. Changes in soil porosity resulted in a smaller but measurable ($RDR > 0.1$) impact on $NH_3$ fluxes. Crop parameter inputs and wind speed had little ($RDR < 0.1$) impact; while average annual atmospheric nitrogen concentrations and wet deposition had no detectable impact on DNDC modeled $NH_3$ fluxes.

Wind speed was not identified as an influential input. Sharpe and Harper (1995) reported that $NH_3$ fluxes increase under higher wind speeds due to rapid transport of $NH_3$ away from the soil surface. *Gyldenkærne et al.* (2005) also assumed wind speed as an influential input and developed an empirical model using hourly wind speed data to estimate temporal variations in $NH_3$ fluxes. However, other studies have reported wind speed as an influential factor only in the presence of high $NH_3$ fluxes over a relatively short period of time (Sommer et al., 2004). Such results suggest that the temporal resolution of the REA method (4 hr) may not be sufficient to resolve the impact of wind speed on $NH_3$ flux. Similarly, DNDC exhibited no sensitivity to background $NH_3$ concentrations. Since $NH_3$ is bi-directionally exchanged between the crop canopy

**Table 3**: Baseline and range of input parameters chosen for sensitivity analysis to identify most influential input parameters for predicted $NH_3$ fluxes. Influential inputs, highlighted in grey, are considered when RDR > 0.2 and SI > 0.2.

| Parameter | | Baseline | Range | RDR | SI |
|---|---|---|---|---|---|
| **Climate** | Wind speed (m/s)$^{+}$ | 2.69 | ± 10 | 0.004 | |
| | Air temperature (°C) | 9.44 | ± 4 | 0.48 | |
| | Precipitation (cm) | 0.3 | ± 75% | 0.55 | |
| | Atm. $CO_2$ concentration ($ppm_v$) | 380 | ± 20% | 0.02 | |
| | Atm. $NH_3$ concentration ($ppm_v$) | 1.28 | ± 100% | 0.00 | |
| | Atm. N deposition (mg-N $ha^{-1}$) | 1.39 | ± 100% | 0.00 | |
| **Soil** | Soil clay $^{++}$ | 0.22 | ± 20% | 0.06 | |
| | Bulk density ($g/cm^3$) | 1.36 | ± 40% | 0.00 | |
| | Hydro conductivity (m/hr) | 0.02502 | ± 40% | 0.03 | |
| | Field capacity $^{++}$ | 0.36 | ± 50% | 0.57 | |
| | Wilting point $^{++}$ | 0.14 | ± 40% | 0.00 | |
| | Porosity $^{++}$ | 0.451 | ± 40% | 0.14 | |
| | pH | 5.16 | ± 75% | 0.98 | |
| | Soil organic carbon (kg-C/kg-soil) | 0.035 | ± 75% | 0.57 | |
| | Initial [$NO_3^-$] in soil (mg-N/kg-soil) | 0.5 | ± 75% | 0.00 | |
| | Initial [$NH_4^+$] in soil (mg-N/kg-soil) | 0.05 | ± 75% | 0.00 | |
| **Crop** | Maximum yield (kg-C $ha^{-1}$) | 4123.6 | ± 30% | 0.06 | |
| | Plant C/N ratio | 50 | ± 30% | 0.06 | |
| | Water requirement (kg-water/kg-dry matter) | 150 | ± 50% | 0.06 | |
| | Growing degree days (°C) | 3150 | ± 50% | 0.07 | |
| **Nutrient management** | Crop residue $^{++}$ | 0.3325 | ± 35% | 0.00 | |
| | Tilling date | 5 May | ± 15 days | | 0.38 |
| | Tilling depth (cm) | 10 | ± 100% | 0.03 | |
| | Fertilizer application date | 5 May | ± 15 days | | 0.93 |
| | Fertilizer application depth (cm) | 15 | ± 100% | 0.33 | |
| | Fertilizer application amount (kg-N $ha^{-1}$) | 168 | ± 100% | 1.39 | |

$^{+}$Wind speed is not an input option within the Monte Carlo function in DNDC. Sensitivity to wind speed was estimated by varying wind speed within a range of ±10 m/s in increments of ±0.5 m/s (no negative values) in repeated DNDC runs. $^{++}$ Reported as a fraction (0-1).

and the atmosphere, higher background $NH_3$ concentrations could potentially enhance nitrogen deposition to the crop (Sutton et al., 1995). The lack of sensitivity to background $NH_3$ concentrations could be due to either much higher fluxes to the atmosphere resulting from fertilizer application or the current representation of $NH_3$ deposition to the crop within DNDC.

Response in modeled $NH_3$ fluxes (% change with respect to baseline_motecarlo) with changes in influential input parameters (% change of input with respect to baseline_montecarlo) is presented in Figure 4. To estimate trace gas fluxes and nitrogen pools in the soil, DNDC uses empirical "climate reduction factors" to model impact of air temperature and water content on nitrification and denitrification rates (Li et al., 1992). Results (Figure 4a) were consistent with observations of enhanced $NH_3$ volatilization due to higher ambient temperatures (Sharpe and Harper, 1995) but reduced microbial activity in presence of higher soil temperatures (Fenn and Hossner, 1985). Inhibition of $NH_3$ fluxes in during higher precipitation (Figure 4b) was consistent with observations, since a rain event would typically enhance urea dissolution and infiltration into the soil (Black et al., 1987; Sommer et al., 2004).

Field capacity refers to the amount of water held by the soil before draining and is typically estimated using soil moisture data (Richards and Weaver, 1944). Increasing field capacity values lowered $NH_3$ fluxes (Figure 4c); since higher moisture content lowered ammoniacal nitrogen concentration and reduced $NH_3$ volatilization (Haynes and Sherlock, 1982). Soil pH plays an important role in $NH_3$ volatilization. Modeled trends (Figure 4d) were consistent with enhanced $NH_3$ fluxes from alkaline soils with pH > 7 (Sommer et al., 2004). Soil organic carbon (Figure 4e) is linked to the potential for denitrification (Sommer et al., 2004) and influences the amount of $NH_4^+$ available in soil water after decomposition processes are accounted for (Li, 2000).

Modeled $NH_3$ fluxes are highly sensitive to tillage and fertilizer practices as indicated in Table 3. The impact of changing tillage dates (Figure 4f) should be interpreted in conjunction with the fertilizer application date. As indicated in Figure 4f, tilling before fertilizer application (indicated by negative date on the x-axis) has virtually no impact on $NH_3$ fluxes, since very little nitrogen is available in the soil water to volatilize. *Cui et al.* (2014) modeled trace gas fluxes by considering tillage one day after fertilizer application, to ensure DNDC can model this process. When the tillage occurs 1-10 days after fertilizer application, $NH_3$ volatilization is reduced, possibly due to the incorporation of applied nitrogen in the soil (Fernández et al., 2014). While $NH_3$ fluxes were not sensitive to tillage depth within DNDC, depth of fertilizer application is an influential input. From Figure 4g, it is evident that increasing depth of fertilizer incorporation (negative depths) reduces $NH_3$ volatilization. However, it is unclear why DNDC Monte Carlo simulation resulted in highest $NH_3$ fluxes at baseline of 15 cm depth compared to surface application (100% increase with respect to baseline_montecarlo). This point is important to examine during future investigations of DNDC. Studies indicate that surface application of fertilizers enhances $NH_3$ fluxes in comparison with injection (Nyord et al., 2008; Sommer et al., 2004) while injection of fertilizers especially urea deeper than 7.5 cm in the soil reduces $NH_3$ fluxes (Liu et al., 2015; Rochette et al., 2013). Response of modeled $NH_3$ fluxes to nitrogen loading (Figure 4h) was consistent with several studies (Haynes and Sherlock, 1982; Sommer et al., 2004). The influence of change in fertilizer application date (Figure 4i) could be linked to two factors; change in temperature with time and the lag between fertilizer application and planting date. Applying fertilizers ahead of planting increases $NH_3$ fluxes since the time for nitrification and loss to the atmosphere before crop uptake is increased (Fernández et al., 2014).

### *3.2.2 Estimating Uncertainty in DNDC Modeled $NH_3$ Fluxes*

Uncertainty in modeled $NH_3$ fluxes for plot 1 is presented in Figure 5, for the varying range of input conditions characteristic of Central Illinois (Table 1). Only input parameters that were most influential on the sensitivity of modeled $NH_3$ fluxes are included in Figure 5. The typical nitrogen loading rates ranged from 160 kg-N $ha^{-1}$ (USDA, 2015b) to 220 kg-N $ha^{-1}$ (Fernández et al., 2014), the resulting uncertainty in modeled $NH_3$ fluxes was estimated as –14% to 42%. Uncertainty from UAN injection depth (baseline value of 15 cm and 10 cm as reported by Simmons and Nafziger (2014)) was -11%. Similarly, if fertilizer application date was varied between the earliest and latest reported planting dates of corn (USDA, 2010), uncertainty in modeled $NH_3$ fluxes were as high as 28%. Tillage was varied to occur either on or a day after fertilizer application as recommended by *Cui et al.* (2014), resulting in a smaller variability of 8% in modeled $NH_3$ fluxes.

Variations in reported values of soil field capacity and pH resulted in variabilities in $NH_3$ fluxes between -16% to 7% and 6% to -1%, respectively, while varying soil organic carbon resulted in a larger variability (-50% to 7%) in $NH_3$ fluxes. By varying daily minimum and maximum air temperature, uncertainty in $NH_3$ fluxes was estimated in the range of -9 to -13%. Similarly, varying daily precipitation introduced uncertainty in the range of -7% to 23%. These results support that among the influential parameters fertilizer application rate and timing, field capacity, SOC and precipitation are the ones that most contribute to the uncertainty of DNDC predicted $NH_3$ fluxes.

The overall uncertainty in modeled $NH_3$ fluxes based on variability of aforementioned influential inputs are presented on a daily scale, as a grey band, in Figure 6 that also includes the results from the REA measurements. At the daily scale, the uncertainty varied between 0% and 70% with highest uncertainty between DOY 88-116. REA measurements on DOY 115-116 and after DOY 159 lay outside the uncertainty band in modeled $NH_3$ fluxes. Since, plot 1 was fertilized only on DOY 126, fluxes on DOY 115-116 were spatially accounted from corn plot south of plot 1 (plot 5).

## 4.0 Summary and Conclusions

DNDC is widely used to predict fluxes of greenhouse and trace gases such as $NH_3$ to the atmosphere. While the model's performance for predicting greenhouse gas fluxes has been evaluated in many studies, assessment of $NH_3$ fluxes following chemical fertilizer application is reported only in two studies in China, for periods of a few days ( Li, 2000; Cui et al., 2014). In this study, DNDC's ability to model $NH_3$ fluxes following fertilizer application at a typical US Corn Belt site over an entire corn growing season was evaluated. Modeled $NH_3$ fluxes were compared with measurements obtained using the relaxed eddy accumulation (REA) method, at a measurement site in Central Illinois, Midwest US, in year 2014. Practical issues in evaluating closure were also addressed.

In DNDC, a field site is conceptualized with uniform nutrient management and environmental parameters. Similarly, REA towers are ideally capturing fluxes from uniform environments. However, such ideal conditions are rarely realizable first because of high natural variability of environmental parameters and second because of farmer decisions. To make model-measurement inter comparison possible, we considered all of REA measurements regardless of the REA footprint and devised a method to account for spatial heterogeneity by apportioning fluxes to plots surrounding the measurement plot. We also devised an approach to scale down the daily DNDC predictions to the 4-hr duration of the REA measurements. Thus, to evaluate closure between modeled and measured fluxes, we developed a four scenario approach, where different scenarios accounted for spatial heterogeneity and temporal resolution differences. Overall, for this study, DNDC fluxes were less than measured ones for all scenarios and DNDC fluxes were in better agreement with REA measured fluxes during periods of high positive fluxes rather than periods of observed negative fluxes, indicating possible need for improvement of the $NH_3$ deposition algorithm of the model. Comparison of uni-directional to bi-directional parameterization of dry deposition have been found to account for up to 50% differences, at the site scale (Dennis et al., 2013).

Measurements as well as model outputs include uncertainties. Measurement uncertainty is not easy to quantify for a micrometeorological method because there is no standard method to compare to. Reliability of REA measurements is established based on theoretical validity, comparison with other measurement methods, and by following strict quality control and quality assurance protocols. With regard to DNDC, uncertainty is introduced either due to the representation of physico-chemical and biological processes that influence $NH_3$ fluxes or from variability of the input parameters. Uncertainty due to model formulation was identified by the consistent underprediction of fluxes, especially in the time period with higher depositional (negative) fluxes. Uncertainties were also introduced due to the inherent variability of inputs such as soil properties or because of inputs that are typically reported within a range, such as fertilizer application loading, depth and timing. In this study, we quantified the resulting uncertainty from variability in inputs that DNDC modeled $NH_3$ fluxes were most sensitive to. Sensitivity analysis indicated that for the case we examined, DNDC modeled $NH_3$ fluxes were most sensitive to the environmental inputs of ambient air temperature, precipitation, soil organic carbon, pH and field capacity and nutrient management practices of tillage date, fertilizer application depth and fertilizer loading. By constraining the range of these inputs excluding fertilizer application rate and timing (that were well defined for our measurement site), an uncertainty band was estimated around modeled fluxes that enabled us to qualitatively evaluate if the measurement values fall within or outside the uncertainty band. Consideration of the uncertainty band further supported model limitations in capturing depositional flux magnitudes and an overall underprediction of fluxes.

Accurate spatial and temporal variations in $NH_3$ emissions are needed as inputs to air quality models, for accurate estimates of nitrogen loss in the environment and quantification of nitrogen deposition fluxes to sensitive and intensively managed ecosystems. This study is the first to evaluate the predictive capability of DNDC to model $NH_3$ fluxes over an entire growing season and estimate associated uncertainty. Our results have important implications for three reasons. First, they demonstrate that DNDC is able to capture timing of $NH_3$ emission peaks following chemical fertilizer application. Second, they identify key influential parameters that resulted in highest model output uncertainty. Third, they highlight practical issues when examining closure between model predictions and measurements due to underlying assumptions of homogeneous spatial unit and differences in temporal resolution between model and measurements. In a broader perspective, while measurements provide valuable site-level data, models are advantageously used to estimate trace gas fluxes at regional and global scales. Therefore, it is important that the most commonly used models are evaluated for the application used and their limitations are well understood. With this is mind, in the case of using DNDC for obtaining $NH_3$ fluxes following fertilizer application, our results point to the following areas for future improvements: a) improvement of the $NH_3$ deposition algorithm to include detailed parameterization describing the bi-directionality of the $NH_3$ fluxes (Nemitz et al., 2001); b) flux output at time scales relevant to air quality models (hourly); c) further evaluation/closure studies at the site mode; and d) investigations of DNDC use for upscaling fluxes from the site to the regional scale. A regional mode of DNDC is available and implemented widely (Neufeldt et al., 2006; Pathak et al., 2005). However, while multiple crops can be represented using the regional scale version of DNDC, it does not allow accounting for detailed site specific inputs and modeled fluxes are obtained at the annual level, for the sake of computational efficiency (Perlman et al., 2013). Therefore, large discrepancies between the use of site and regional modes have been highlighted by *Perlman et al.* (2013). In the absence of a clear distinction between the descriptions of site and regional models (Perlman et al., 2013), comparisons of modeled results to predictions, as presented in this study can help constrain model uncertainties and assist in future model improvements.

## Acknowledgements

This study was funded by the National Science Foundation, Award Numbers AGS 12-36814 and 12-33458 with an accompanying research experience for undergraduates (REU). Srinidhi Balasubramanian acknowledges the Faculty for the Future Fellowship from the Schlumberger Foundation. The views reported here do not necessarily represent the views of these funding agencies. The authors gratefully acknowledge the Energy Biosciences Institute and Timothy Mies and Collin Reeser for facilitating the use of the Energy Farm for the field campaign. Michael Masters from the University of Illinois, Plant Biology Department, is thanked for providing local soil data and Mark Heuer of ORAU assigned to the NOAA Atmospheric Turbulence and Diffusion Division for providing the continuous flux gradient

$NH_3$ data. Requests for data can be addressed to the corresponding author (sotiriak@illinois.edu).

## References

Appel, K.W., Foley, K.M., Bash, J.O., Pinder, R.W., Dennis, R.L., Allen, D.J., Pickering, K., 2011. A multi-resolution assessment of the Community Multiscale Air Quality (CMAQ) model v4.7 wet deposition estimates for 2002-2006. Geosci. Model Dev. 4, 357–371. doi:10.5194/gmd-4-357-2011.

Balasubramanian, S., Koloutsou-Vakakis, S., McFarland, D.M., Rood, M.J., 2015. Reconsidering emissions of ammonia from chemical fertilizer usage in Midwest USA. J. Geophys. Res.  Atmos. 120, 1–15. doi:10.1002/2015JD023219.

Bennett, N.D., Croke, B.F.W., Guariso, G., Guillaume, J.H. a, Hamilton, S.H., Jakeman, A.J., Marsili-Libelli, S., Newham, L.T.H., Norton, J.P., Perrin, C., Pierce, S. A., Robson, B., Seppelt, R., Voinov, A. A., Fath, B.D., Andreassian, V., 2013. Characterising performance of environmental models. Environ. Model. Softw. 40, 1–20. doi:10.1016/j.envsoft.2012.09.011.

Beuning, J.D., Pattey, E., Edwards, G., Van Heyst, B.J., 2008. Improved temporal resolution in process-based modelling of agricultural soil ammonia emissions. Atmos. Environ. 42, 3253–3265. doi:10.1016/j.atmosenv.2007.04.057.

Black, A.S., Sherlock, R.R., Smith, N.P., 1987. Effect of timing of simulated rainfall on ammonia volatilization from urea, applied to soil of varying moisture content. J. Soil Sci. 38, 679–687. doi:DOI: 10.1111/j.1365-2389.1987.tb02165.x.

Bouwman, A.F., Boumans, L.J.M., Batjes, N.H., 2002. Estimation of global $NH_3$ volatilization loss from synthetic fertilizers and animal manure applied to arable lands and grasslands. Global Biogeochem. Cycles 16, 8–1--8–11. doi:10.1029/2000GB001389.

Businger, J., and Oncley, S.P., 1990. Flux measurement and conditional sampling. J. Atmos. Ocean Tech. 7, 349-352. doi: http://dx.doi.org/10.1175/1520-0426(1990)007<0349:FMWCS>2.0.CO;2.

Congreves, K.A., Grant, B.B., Dutta, B., Smith, W.N., Chantigny, M.H., Rochette, P., Desjardins, R.L., 2016. Predicting ammonia volatilization after field application of swine slurry: DNDC model development. Agric. Ecosyst. Environ. 219, 179–189. doi:10.1016/j.agee.2015.10.028.

Cooter, E.J., Bash, J.O., Benson, V., Ran, L., 2012. Linking agricultural crop management and air quality models for regional to national-scale nitrogen assessments. Biogeosciences 9, 4023–4035. doi:10.5194/bg-9-4023-2012.

Cuddington, K., Fortin, M.-J., Gerber, L.R., Hastings, A., Liebhold, A., O'Connor, M., Ray, C., 2013. Process-based models are required to manage ecological systems in a changing world. Ecosphere 4, 1–20. doi:10.1890/ES12-00178.1.

Cui, F., Zheng, X., Liu, C., Wang, K., Zhou, Z., Deng, J., 2014. Assessing biogeochemical effects and best management practice for a wheat-maize cropping system using the DNDC model. Biogeosciences 11, 91–107. doi:10.5194/bg-11-91-2014.

David, M.B., Del Grosso, S.J., Hu, X., Marshall, E.P., McIsaac, G.F., Parton, W.J., Tonitto, C., Youssef, M.A., 2009. Modeling denitrification in a tile-drained, corn and soybean agroecosystem of Illinois, USA. Biogeochemistry 93, 7–30. doi:10.1007/s10533-008-9273-9.

Deng, J., Li, C., Wang, Y., 2015. Modeling ammonia emissions from dairy production systems in the United States. Atmos. Environ. 114, 8–18. doi:10.1016/j.atmosenv.2015.05.018

Dennis, R.L., Schwede, D.B., Bash, J.O., Pleim, J.E., Walker, J.T., Foley, K.M., 2013. Sensitivity of continental United States atmospheric budgets of oxidized and reduced nitrogen to dry deposition parametrizations. Philos. Trans. R. Soc. B Biol. Sci. 368:201301.

Dentener, F.J., Crutzen, P.J., 1994. A three-dimensional model of the global ammonia cycle. J. Atmos. Chem. 19, 331–369. doi:10.1007/BF00694492.

Erisman, J.W., Galloway, J.N., Seitzinger, S., Bleeker, A., Dise, N.B., Petrescu, A.M.R., Leach, A.M., de Vries, W., 2013. Consequences of human modification of the global nitrogen cycle. Philos. Trans. R. Soc. Lond. B. Biol. Sci. 368, 1–10. doi:10.1098/rstb.2013.0116.

Farahbakhshazad, N., Dinnes, D.L., Li, C., Jaynes, D.B., Salas, W., 2008. Modeling biogeochemical impacts of alternative management practices for a row-crop field in Iowa. Agric. Ecosyst. Environ. 123, 30–48. doi:10.1016/j.agee.2007.04.004.

Fenn, L.B., Hossner, L.R., 1985. Ammonia Volatilization from Ammonium or Ammonium-Forming Nitrogen Fertilizers, in: Stewart, B.A. (Ed.), Advances in Soil Science. Springer New York, pp. 123–169. doi:10.1007/978-1-4612-5046-3_4.

Fernández, F.G., Nafziger, E.D., Ebelhar, S.A., Hoeft, R.G., 2014. Managing Nitrogen, in: Illinois Agronomy Handbook. University of Illinois at Urbana-Champaign, College of

Agriculture, Cooperative Extension Service, Champaign, Illinois, pp. 113–132.

Fumoto, T., Kobayashi, K., Li, C., Yagi, K., Hasegawa, T., 2008. Revising a process-based biogeochemistry model (DNDC) to simulate methane emission from rice paddy fields under various residue management and fertilizer regimes. Glob. Chang. Biol. 14, 382–402. doi:10.1111/j.1365-2486.2007.01475.x.

Galloway, J.N., Aber, J.D., Erisman, J.W., Seitzinger, S.P., Howarth, R.W., Cowling, E.B., Cosby, B.J., 2003. The Nitrogen Cascade. Am. Inst. Biol. Sci. 53, 341. doi:10.1641/0006-3568(2003)053[0341:TNC]2.0.CO;2.

Génermont, S., Cellier, P., 1997. A mechanistic model for estimating ammonia volatilization from slurry applied to bare soil. Agric. For. Meteorol. 88, 145–167. doi:10.1016/S0168-1923(97)00044-0.

Gilhespy, S.L., Anthony, S., Cardenas, L., Chadwick, D., del Prado, A., Li, C., Misselbrook, T., Rees, R.M., Salas, W., Sanz-Cobena, A., Smith, P., Tilston, E.L., Topp, C.F.E., Vetter, S., Yeluripati, J.B., 2014. First 20 years of DNDC (DeNitrification DeComposition): Model evolution. Ecol. Modell. 292, 51–62. doi:10.1016/j.ecolmodel.2014.09.004.

Gilliland, A.B., Wyat Appel, K., Pinder, R.W., Dennis, R.L., 2006. Seasonal NH3 emissions for the continental united states: Inverse model estimation and evaluation. Atmos. Environ. 40, 4986–4998. doi:10.1016/j.atmosenv.2005.12.066.

Giltrap, D.L., Li, C., Saggar, S., 2010. DNDC: A process-based model of greenhouse gas fluxes from agricultural soils. Agric. Ecosyst. Environ. 136, 292–300. doi:10.1016/j.agee.2009.06.014.

Goebes, M.D., Strader, R., Davidson, C., 2003. An ammonia emission inventory for fertilizer application in the United States. Atmos. Environ. 37, 2539–2550. doi:10.1016/S1352-2310(03)00129-8.

Gopalakrishnan, G., Cristina Negri, M., Salas, W., 2012. Modeling biogeochemical impacts of bioenergy buffers with perennial grasses for a row-crop field in Illinois. GCB Bioenergy 4, 739–750. doi:10.1111/j.1757-1707.2011.01145.x.

Gyldenkærne, S., Skjøth, C.A., Hertel, O., Ellermann, T., 2005. A dynamical ammonia emission parameterization for use in air pollution models. J. Geophys. Res. Atmos. 110, 1–14. doi:10.1029/2004JD005459.

Hamby, D.M., 1994. A review of techniques for parameter sensitivity analysis of environmental models. Environ. Monit. Assess. 32, 135–154. doi:10.1007/BF00547132.

Hastings, A.F., Wattenbach, M., Eugster, W., Li, C., Buchmann, N., Smith, P., 2010. Uncertainty propagation in soil greenhouse gas emission models: An experiment using the DNDC model and at the Oensingen cropland site. Agric. Ecosyst. Environ. 136, 97–110. doi:10.1016/j.agee.2009.11.016.

Haynes, R.J., Sherlock, R.R., 1982. Gaseous Losses of Nitrogen, in: Haynes, R.J. (Ed.), Mineral Nitrogen in the Plant–Soil System. ACADEMIC PRESS, INC., Orlando, Florida, pp. 242–302. doi:10.1016/B978-0-12-334910-1.50009-1.

Heaton, E.A., Dohleman, F.G., Long, S.P., 2008. Meeting US biofuel goals with less land: The potential of Miscanthus. Glob. Chang. Biol. 14, 1–15. doi:10.1111/j.1365-2486.2008.01662.x.

Hollinger, S.E., 1995. Midwestern climate center soils atlas and database, Circular 179. Champaign, Illinois.

Illinois State Water Survey, 2015. Water and Atmospheric Resources Monitoring Program [WWW Document]. Illinois Clim. Netw. URL. http://www.isws.illinois.edu/warm/datatype.asp (accessed 10.1.16).

Jantalia, C.P., Halvorson, A.D., Follett, R.F., Alves, B.J.R., Polidoro, J.C., Urquiaga, S., 2012. Nitrogen Source Effects on Ammonia Volatilization as Measured with Semi-Static Chambers. Agron. J. 104, 1595–1603. doi:10.2134/agronj2012.0210.

Kljun, N., Calanca, P., Rotach, M.W., Schmid, H.P., 2004. A simple parameterisation for flux footprint predictions. Boundary-Layer Meteorol. 112, 503–523. doi:10.1023/B:BOUN.0000030653.71031.96.

Kormann, R., Meixner, F.X., 2001. An analytical footprint model for non-neutral stratification. Boundary-Layer Meteorol. 99, 207–224. doi:10.1023/A:1018991015119.

Krupa, S.V., 2003. Effects of atmospheric ammonia (NH3) on terrestrial vegetation: a review. Environ. Pollut. 124, 179–221. doi:10.1016/S0269-7491(02)00434-7.

Li, C., Frolking, S., Frolking, T.A., 1992. A model of nitrous oxide from soil driven by rainfall events: 1. Model structure and sensitivity. J. Geophys. Res. 97, 9759–9776. doi:10.1029/92JD00509.

Li, C., Mosier, A., Wassmann, R., Cai, Z., Zheng, X., Huang, Y., Tsuruta, H., Boonjawat, J., Lantin, R., 2004. Modeling greenhouse gas emissions from rice-based production systems: Sensitivity and upscaling. Global Biogeochem. Cycles 18, 1–19. doi:10.1029/2003GB002045.

Li C., 2011, Mitigating Greenhouse Gas Emissions from Agroecosystems: Scientific Basis and Modeling Approach. In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.; ACS Symposium Series; American Chemical Society: Washington, DC, 2011. doi: 10.1021/bk-2011-1072.ch016.

Li, C., Salas, W., Mitloehner, F., Zhang, R., Krauter, C., Rotz, A., Mitloehner, F., 2012. Manure-DNDC: A biogeochemical process model for quantifying greenhouse gas and ammonia emissions from livestock manure systems. Nutr. Cycl. Agroecosystems 93, 163–200. doi:10.1007/s10705-012-9507-z.

Li, C.S., 2000. Modeling trace gas emissions from agricultural ecosystems. Nutr. Cycl. Agroecosystems 58, 259–276.

Liu, T.Q., Fan, D.J., Zhang, X.X., Chen, J., Li, C.F., Cao, C.G., 2015. Deep placement of nitrogen fertilizers reduces ammonia volatilization and increases nitrogen utilization efficiency in no-tillage paddy fields in central China. F. Crop. Res. 184, 80–90. doi:10.1016/j.fcr.2015.09.011.

Meyers, T. P. and Baldocchi, D.D., 2005. Current Micrometeorological Flux Methodologies with Applications in Agriculture, *Micrometeorology in Agricultural Systems* Agronomy Monograph no. 47, 381-396.

National Atmospheric Deposition Program, 2015a. Ammonia Monitoring Network (AMoN) [WWW Document]. URL http://nadp.sws.uiuc.edu/amon/ (accessed 5.20.16).

National Atmospheric Deposition Program, 2015b. National Trends Network (NTN) [WWW Document]. NRPS-3. URL http://nadp.sws.uiuc.edu/NTN/ (accessed 5.20.16).

Nelson, A.J., Koloutsou-Vakakis, S., Rood, M.J., Myles, L., Lehmann, C., Bernacchi, C., Balasubramanian, S., Joo, E., Heuer, M., Vieira-Filho, M., Lin, J., 2016. Ammonia Flux Above Fertilized Corn in Central Illinois, USA, Using Relaxed Eddy Accumulation. Agric. For. Meteorol. submitted, 1–35.

Nemitz, E.; Milford, C.; Sutton, M. A., A two-layer canopy compensation point model for describing bi-directional biosphere-atmosphere exchange of ammonia. Q. J. R. Meteorol. Soc 2001, 127, 815-833. doi:10.1002/qj.49712757306.

Neufeldt, H., Scha, M., Angenendt, E., Li, C., Kaltschmitt, M., Zeddies, J., 2006.

Disaggregated greenhouse gas emission inventories from agriculture via a coupled economic-ecosystem model. Agric. Ecosyst. Environ. 112, 233–240. doi:10.1016/j.agee.2005.08.024.

NOAA/ATDD, 2016. Unpublished data.

Norman, M., Spirig, C., Wolff, V., Trebs, I., Flechard, C., Wisthaler, A., Schnitzhofer, R., Hansel, A., Neftel, A., 2009. Intercomparison of ammonia measurement techniques at an intensively managed grassland site (Oensingen, Switzerland). Atmos. Chem. Phys. 9, 2635–2645. doi:10.5194/acpd-8-19791-2008.

Nyord, T., Søgaard, H.T., Hansen, M.N., Jensen, L.S., 2008. Injection methods to reduce ammonia emission from volatile liquid fertilisers applied to growing crops. Biosyst. Eng. 100, 235–244. doi:10.1016/j.biosystemseng.2008.01.013.

Olander, L.P., Haugen-Kozyra, K., Del Grosso, S., 2011. Using biogeochemical process models to quantify greenhouse gas mitigation from agricultural management, echnical working group on agricultural greenhouse gases (T-AGG) Supplemental report Nicholas Institute for Environmental Policy Solutions. Duke University, North Carolina.

Pathak, H., Li, C., Wassmann, R., 2005. Greenhouse gas emissions from Indian rice fields: calibration and upscaling using the DNDC model. Biogeosciences Discuss. 2, 77–102. doi:10.5194/bgd-2-77-2005.

Paulot, F., Jacob, D.J., Pinder, R.W., Bash, J.O., Travis, K., Henze, D.K., 2014. Ammonia emissions in the United States , European Union, and China derived by high-resolution inversion of ammonium wet deposition data : Interpretation with a new agricultural emissions inventory (MASAGE_NH3). J. Geophys. Res. Atmos. 4343–4364. doi:10.1002/2013JD021130.

Perlman, J., Hijmans, R.J., Horwath, W.R., 2013. Modelling agricultural nitrous oxide emissions for large regions. Environ. Model. Softw. 48, 183–192. doi:10.1016/j.envsoft.2013.07.002.

Richards, L.A., Weaver, L.R., 1944. Moisture Retention by Some Irrigated Soils as related to Soil-Moisture Tension. J. Agric. Res. 69, 215–235.

Rochette, P., Angers, D.A., Chantigny, M.H., Gasser, M.-O., MacDonald, J.D., Pelster, D.E., Bertrand, N., 2013. Ammonia Volatilization and Nitrogen Retention: How Deep to Incorporate Urea? J. Environ. Qual. 42, 1635–1642. doi:10.2134/jeq2013.05.0192.

SAB, US EPA, 2011. Reactive nitrogen in the United States: an analysis of input, flows, consequences and management options. EPA-SAB-11-013. [WWW Document]. URL http://yosemite.epa.gov/sab/sabproduct.nsf/WebBOARD/INCSupplemental. (accessed 6.1.15).

Sharpe, R.R., Harper, L.A., 1995. Soil, plant and atmospheric conditions as they relate to ammonia volatilization. Fertil. Res. 42, 149–158. doi:10.1007/BF00750509.

Simmons, F.W., Nafziger, E.D., 2014. Soil Management and Tillage, in: Illinois Agronomy Handbook. University of Illinois at Urbana-Champaign, College of Agriculture, Cooperative Extension Service, Champaign, Illinois, pp. 133–142.

Smil, V., 2002. Nitrogen and Food Production: Proteins for Human Diets. AMBIO A J. Hum. Environ. 31, 126–131. doi:10.1579/0044-7447-31.2.126.

Smith, J., Smith, P.W., 2007. How to evaluate a model, in: Introduction to Environmental Modeling. Oxford University Press, New York, USA, pp. 69–118.

Sommer, S.G., Christensen, B.T., 1992. Ammonia volatilization after injection of anydrous ammonia into arable soils of different mioisture levels. Plant Soil 142, 143–146. doi:10.1007/BF00010184.

Sommer, S.G., Schjoerring, J.K., Denmead, O.T., 2004. Ammonia Emission from Mineral Fertilizers and Fertilized Crops. Adv. Agron. 82, 557–622. doi:10.1016/S0065-2113(03)82008-4.

Sutton, M.A., Fowler, D., Burkhardt, J.K., Milford, C., 1995. Vegetation atmosphere exchange of ammonia: Canopy cycling and the impacts of elevated nitrogen inputs. Water Air Soil Pollut. 85, 2057–2063.

US EPA, 2015. 2011 National Emissions Inventory, version 2 Technical Support Document [WWW Document]. URL https://www.epa.gov/sites/production/files/2015-10/documents/nei2011v2_tsd_14aug2015.pdf (accessed 5.20.16).

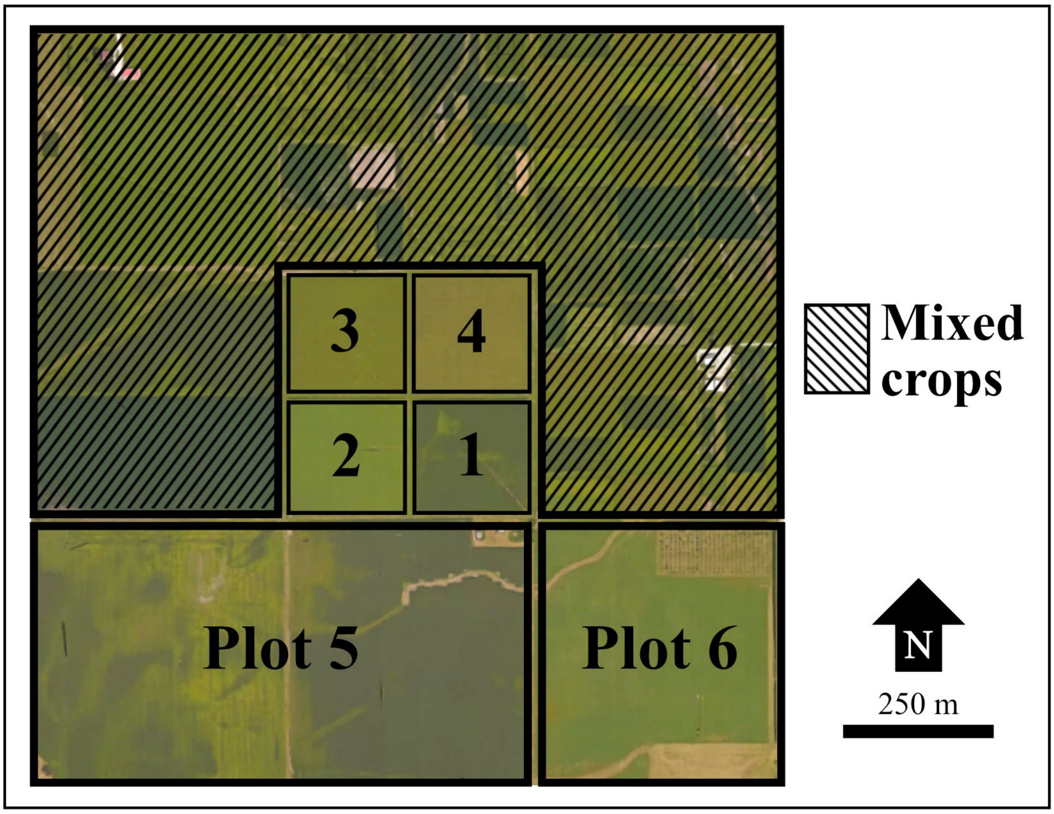
US EPA, 2016. National Ambient Air Quality Standards for Particulate Matter [WWW Document]. URL https://www.epa.gov/criteria-air-pollutants/naaqs-table (accessed 9.26.16).

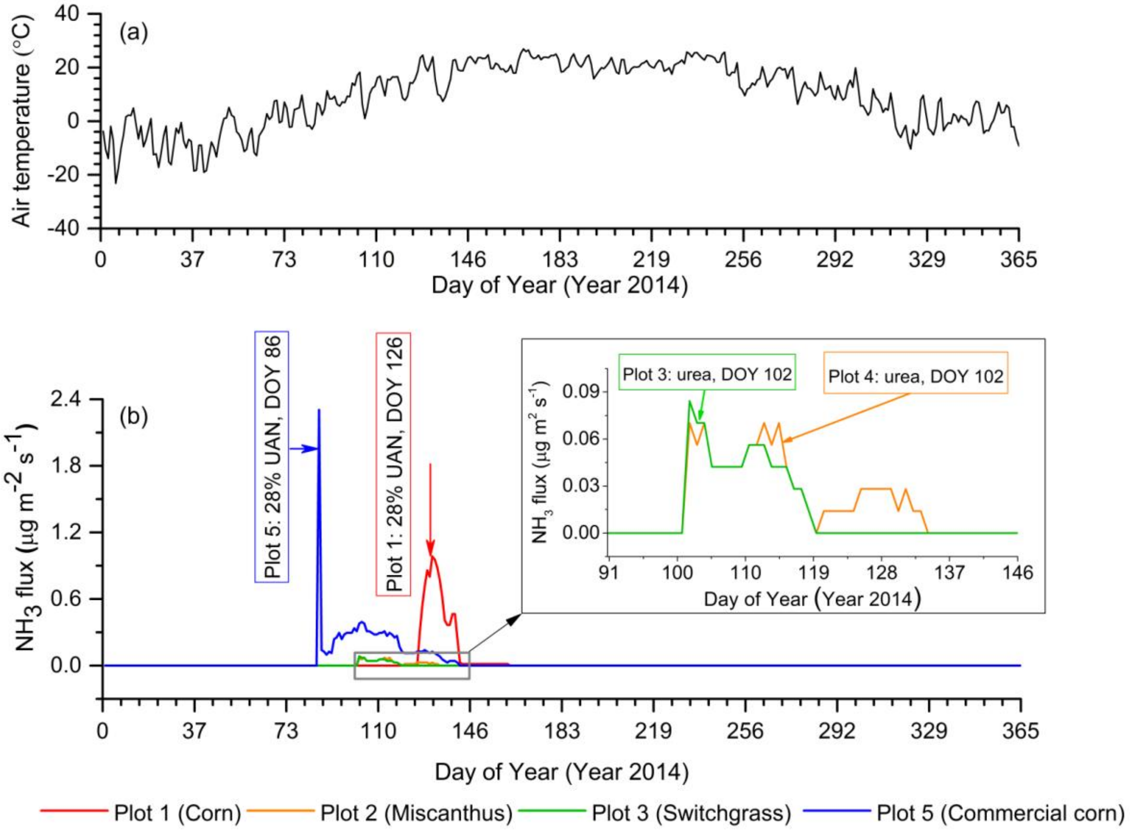
USDA, 2010. Field Crops Usual Planting and Harvesting Dates [WWW Document]. Agric. Handb. Number 628. URL http://usda.mannlib.cornell.edu/usda/current/planting/planting-10-29-2010.pdf (accessed 5.20.16).

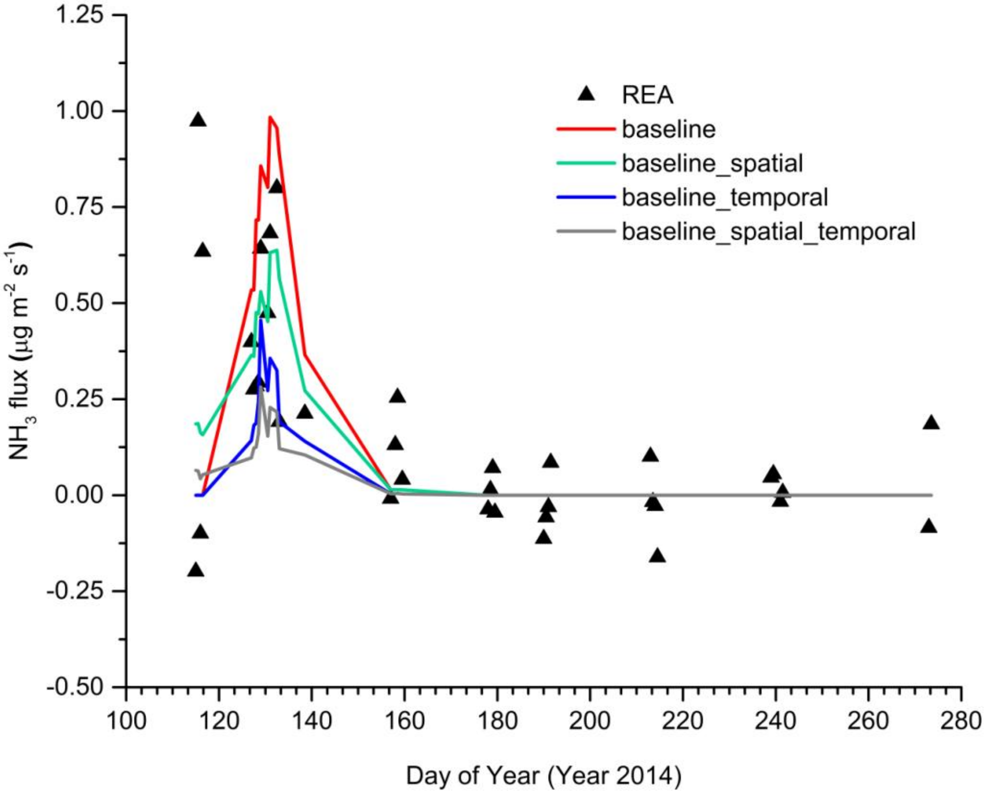
USDA, 2015a. Web Soil Survey [WWW Document]. Soil Surv. Staff. Nat. Resour. Conserv. Serv. URL http://websoilsurvey.nrcs.usda.gov/ (accessed 1.1.16).

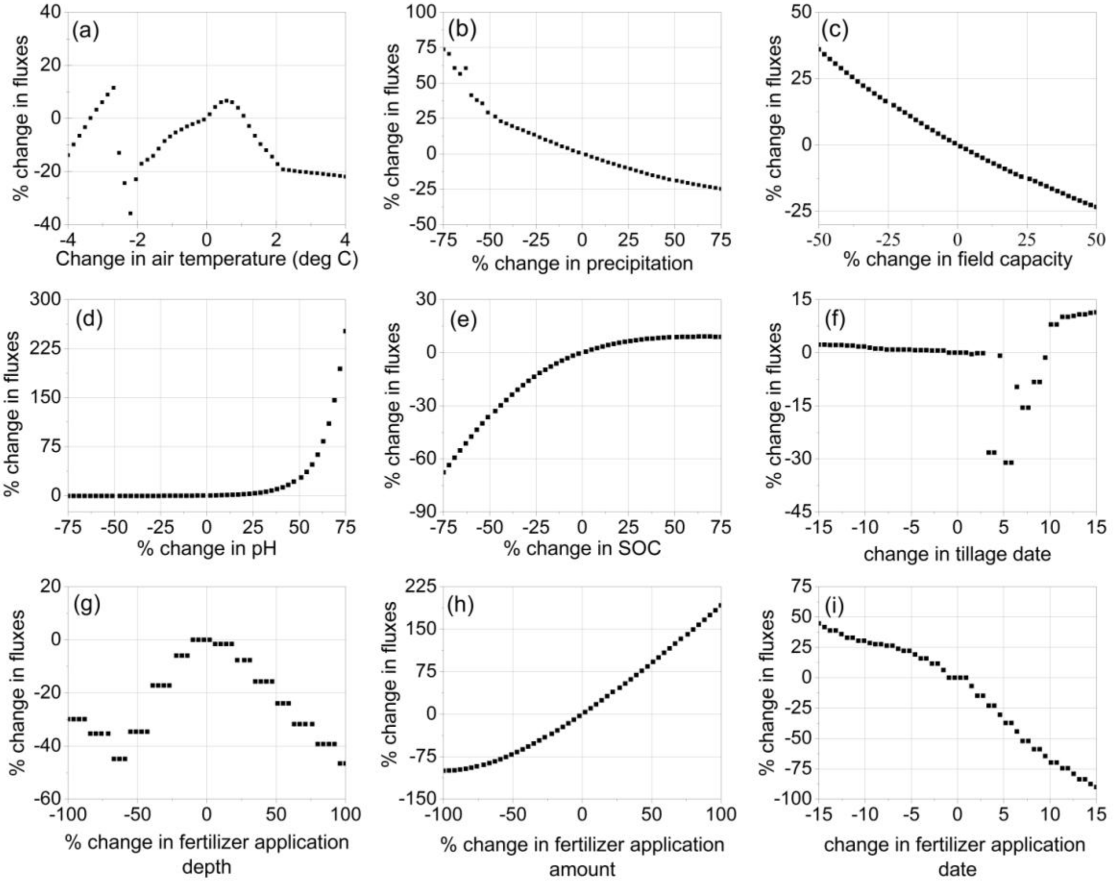
USDA, 2015b. Chemical Distribution Rate [WWW Document]. Quick Stats 2.0. URL http://www.nass.usda.gov/Quick_Stats/ (accessed 5.1.16).

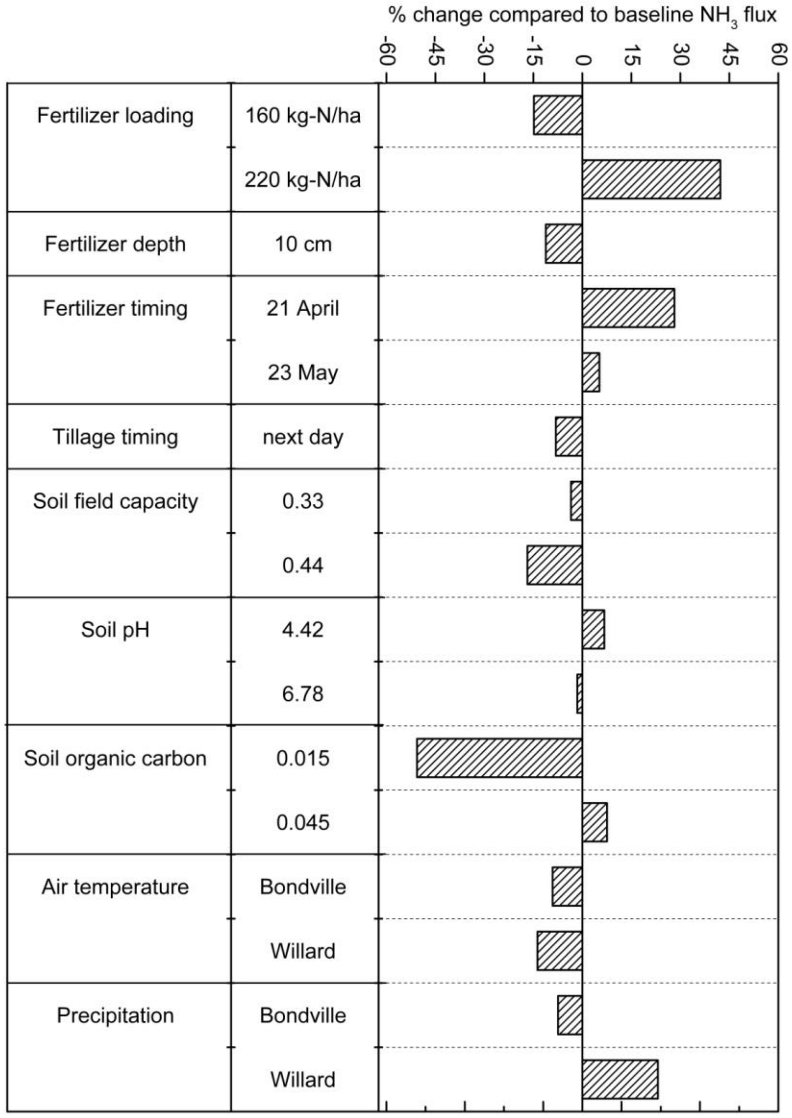
Zeri, M., Anderson-Teixeira, K., Hickman, G., Masters, M., DeLucia, E., Bernacchi, C.J., 2011. Carbon exchange by establishing biofuel crops in Central Illinois. Agric. Ecosyst. Environ. 144, 319–329. doi:10.1016/j.agee.2011.09.006.

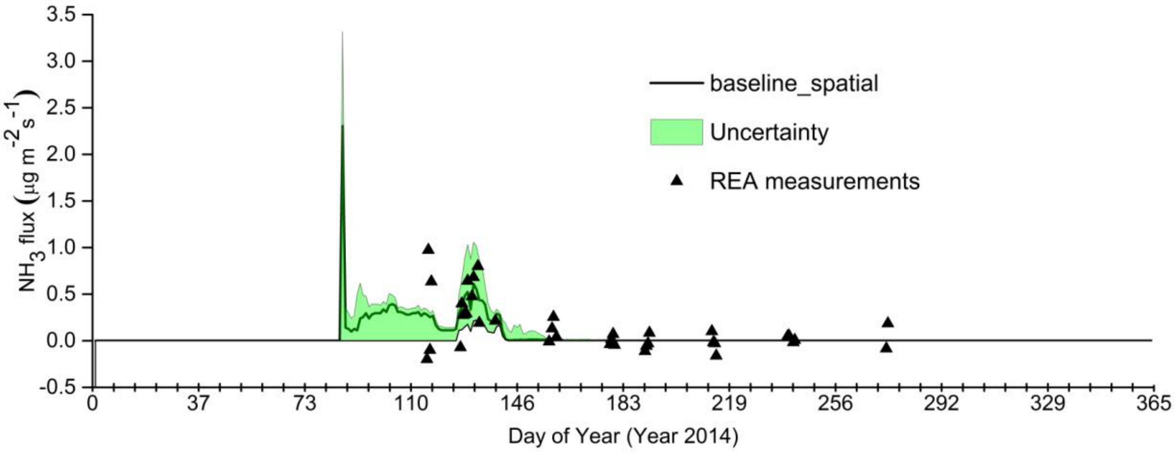

3
4
2
1
Mixed crops
Plot 5
Plot 6
N
250 m


(a)
Air temperature (°C)
40
20
0
-20
-40
0
37
73
110
146
183
219
256
292
329
365
Day of Year (Year 2014)
(b)
$NH_3$ flux ($\mu g\ m^{-2}\ s^{-1}$)
2.4
1.8
1.2
0.6
0.0
Plot 5: 28% UAN, DOY 86
Plot 1: 28% UAN, DOY 126
0
37
73
110
146
183
219
256
292
329
365
Day of Year (Year 2014)
Plot 3: urea, DOY 102
Plot 4: urea, DOY 102
$NH_3$ flux ($\mu g\ m^2\ s^{-1}$)
0.09
0.06
0.03
0.00
91
100
110
119
128
137
146
Day of Year (Year 2014)
Plot 1 (Corn)
Plot 2 (Miscanthus)
Plot 3 (Switchgrass)
Plot 5 (Commercial corn)


REA
baseline
baseline_spatial
baseline_temporal
baseline_spatial_temporal
$NH_3$ flux (μg $m^{-2}$ $s^{-1}$)
1.25
1.00
0.75
0.50
0.25
0.00
-0.25
-0.50
100
120
140
160
180
200
220
240
260
280
Day of Year (Year 2014)


(a)
% change in fluxes
Change in air temperature (deg C)
40
20
0
-20
-40
-4
-2
0
2
4
(b)
% change in fluxes
% change in precipitation
100
75
50
25
0
-25
-50
-75
-50
-25
0
25
50
75
(c)
% change in fluxes
% change in field capacity
50
25
0
-25
-50
-25
0
25
50
(d)
% change in fluxes
% change in pH
300
225
150
75
0
-75
-50
-25
0
25
50
75
(e)
% change in fluxes
% change in SOC
30
0
-30
-60
-90
-75
-50
-25
0
25
50
75
(f)
% change in fluxes
change in tillage date
15
0
-15
-30
-45
-15
-10
-5
0
5
10
15
(g)
% change in fluxes
% change in fertilizer application depth
20
0
-20
-40
-60
-100
-50
0
50
100
(h)
% change in fluxes
% change in fertilizer application amount
225
150
75
0
-75
-150
-100
-50
0
50
100
(i)
% change in fluxes
change in fertilizer application date
75
50
25
0
-25
-50
-75
-100
-15
-10
-5
0
5
10
15


% change compared to baseline $NH_3$ flux
-60
-45
-30
-15
0
15
30
45
60
Fertilizer loading
160 kg-N/ha
220 kg-N/ha
Fertilizer depth
10 cm
Fertilizer timing
21 April
23 May
Tillage timing
next day
Soil field capacity
0.33
0.44
Soil pH
4.42
6.78
Soil organic carbon
0.015
0.045
Air temperature
Bondville
Willard
Precipitation
Bondville
Willard


3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
NH$_3$ flux (µg m$^{-2}$ s$^{-1}$)
0
37
73
110
146
183
219
256
292
329
365
Day of Year (Year 2014)
baseline_spatial
Uncertainty
REA measurements