NITROUS OXIDE EMISSIONS: MEASUREMENTS IN CORN AND SIMULATIONS AT FIELD AND REGIONAL SCALE

by

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B.S., National University of Colombia-Palmira, 2003
M.S., University of Puerto Rico-Mayagüez, 2007

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Abstract

Nitrogen is critical for plant growth and is a major cost of inputs in production agriculture. Too much nitrogen (N) is also an environmental concern. Agricultural soils account for 85% of anthropogenic N_2O which is a major greenhouse gas. Management strategies for N fertilization and tillage are necessary for enhancing N use efficiency and reducing negative impacts of N to the environment. The different management practices induce changes in substrate availability for microbial activity that may result in increasing or reducing net N_2O emitted from soils. The objectives of this research were to (1) integrate results from field studies to evaluate the effect of different management strategies on N_2O emissions using a meta-analysis, (2) quantify N_2O-N emissions under no-tillage (NT) and tilled (T) agricultural systems and the effect of different N source and placements, (3) perform sensitivity analysis, calibration and validation of the Denitrification Decomposition (DNDC) model for N_2O emissions, and (4) analyze future scenarios of precipitation and temperature to evaluate the potential effects of climate change on N_2O emissions from agro-ecosystems in Kansas.

Based on the meta-analysis there was no significant effect of broadcast and banded N placement. Synthetic N fertilizer usually had higher N_2O emission than organic N fertilizer. Crops with high N inputs as well as clay soils had higher N_2O fluxes. No-till and conventional till did not have significant differences regarding N_2O emissions. In the field study, N_2O-N emissions were not significantly different between tillage systems and N source. The banded N application generally had higher emissions than broadcasted N. Slow release N fertilizer as well as split N applications reduced N_2O flux without affecting yield. Simulations of N_2O emissions were more sensitive to changes in soil parameters such as pH, soil organic carbon (SOC), field capacity (FIELD) and bulk density (BD), with pH and SOC as the most sensitive parameters. The N_2O simulations performed using Denitrification Decomposition model on till (Urea) had higher model efficiency followed by no-till (compost), no-till (urea) and till (compost). At the regional level, changes in climate (precipitation and temperature) increased N_2O emission from agricultural soils in Kansas. The conversion from T to NT reduced N_2O emissions in crops under present conditions as well as under future climatic conditions.

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Dedication

In memory of Miguel and Gladys

Chapter 1 - Introduction

It have been estimated that the global population will increase to 9-10 billion by the middle of the 21st century (Smith et al., 2013). This increased population will increase pressure on the food production system. It is imperative to optimize cropping systems. One important question is how we can increase food production with no or reduced damage to the environment. Linquist et al. (2012) mentioned two options for cereal production. First, agriculture can be expanded to new areas that are not currently used for food production. Second, intensification of existing agricultural land can occur by achieving higher yield per unit of land. These two options have negative environmental impacts such as losing biodiversity and increasing greenhouse gas emissions.

Among the most important trace gases produced from agricultural practices that affect the atmosphere due to chemical or radiative effects are methane (CH_4), nitrous oxide (N_2O), nitric oxide (NO) and ammonia (NH_3) (Li, 2000). Soil is a major source of those trace gases and anthropogenic activities (tillage, fertilization, irrigation, etc.) that affect soil gas emission and, hence, play an important role in the atmospheric balance of the trace gases (Li, 2000).

Increasing concentrations of N_2O in the atmosphere are contributing both to the global warming and catalytic destruction of ozone in the stratosphere due to the photolysis of N_2O (Smith and Arah, 1992; Kim and Craig, 1993; Cliff and Thiemens, 1997; Rahn and Wahlen, 1997).

Agriculture accounts for 10-12% of the total global anthropogenic emissions of greenhouse gases (GHG) from which about 60-84% are associated with N_2O emissions (Robertson, 2004; Smith et al.,2007; Smith et al., 2008; Linquist et al., 2012). Of the global annual N_2O emissions 24% are produced by the application of synthetic N fertilizer (Bouwman, 1996; Ma et al., 2010).

The potential to offset greenhouse gases (GHG) emission from energy and industry sources has been based on documenting the CO_2 mitigation potential of no-till (NT) system, and consequently some planned emission trading between industry and producers are based on uptake CO_2 from the atmosphere and the subsequent soil storage of C adopting NT (Six et al., 2004).

According to Robertson (2004) NT does not change N availability, but the effect of no-till cultivation on N_2O emissions are widely variable, and most likely reflect site-specific response to simultaneous changes in soil aggregate structure, water-filled pore space and carbon availability. The net effects of reduced till or no till are inconsistent and not-well quantified globally. In some environments reduced till could promote N_2O emissions, while in other environments reduced till could reduce emissions or have no impact at all (Smith et al., 2008). Taking in account the effect of N_2O on the net GHG balance, it is important to have additional considerations in terms of the benefit of NT in reducing GHG additional to carbon sequestration.

Nitrogen cycling in the agro-ecosystems

Nitrogen, one of the most important nutrients in the living systems, cycles through plants, soil, water, and air in the agroecosystems. Plants require availability of mineral nitrogen (ammonium and nitrate) in the root zone. This available nitrogen comes from internal cycling and external inputs. Nitrogen mineralization during decomposition of soil organic matter generates ammonium which is then converted to NO_3^-; where both processes are microbially mediated. Fertilization, nitrogen fixation, and atmospheric decomposition comprise the external inputs. Leaching and runoff of dissolved nitrogen, erosional loss, gaseous losses from ammonia volatilization and denitrification, and removal of nitrogen in plant tissues at harvest represent losses from the ecosystem. Through N-immobilization, soil microbes compete with the plants for available nitrogen in the soil (Li et al., 2001).

Processes related to N_2O emissions

N_2O and NO are produced in soil mainly by two contrasting processes: nitrification of ammonium, NH_4^+, to nitrite, NO_2^- and then to nitrate, NO_3^- and denitrification of NO_3-N to N_2O and ultimately to molecular nitrogen, N_2 (Smith et al., 2003).

Nitrification is an aerobic process, but when the supply of O_2 is limited by diffusional constrains the nitrifying bacteria can use nitrite as an electron acceptor and reduce it to NO and N_2O (Li et al., 2001).

Denitrification occurs when anaerobic conditions develop, whether in entire horizons, as occurs in flooded soils, or in microsites. In all cases this condition is brought about when the demand of oxygen exceeds the supply, which is primarily controlled by diffusion. Anaerobic microsites above the water table may occur at the centers of the soil aggregates or in small saturated regions within a structureless soil, or wherever the O_2 demand is high (so called ‘hotspots’) (Smith and Arah, 1992; Sierra and Renault, 1996; Petersen et al., 2008). An increase in temperature leads to an increase the size of the zone causing large gradients of O_2 concentration rendering a larger soil volume O_2-free which leads to an increase in denitrification (Smith et al., 2003).

The fraction of the total gaseous products of denitrification depends of the structure and soil water content. If an N_2O molecule can readily diffuse from the site of production into an oxygenated pore it is likely to be emitted to the atmosphere rather than being reduced to N_2. On the other hand, N_2O produce well below the surface of saturated soil is much more likely to be reduced to N_2 (Smith et al., 2003).

Where denitrification is a dominant source of N_2O in very wet soils, and even where it is a minor source of N_2O in moderately moist soils, readily available organic-C is needed as a substrate for denitrifying bacteria and for all heterotrophic bacteria that contribute to O_2 consumption (Davidson, 1992). The ratio of $N_2O:NO_2^-$ produced by NH_4 oxidizing bacteria increases as pO_2 decreases. Pulses of N_2O and especially NO following wetting periods may also be related to accumulation of NO_2^- in dry soil.

Andersen and Petersen (2009) treating the soil with glucose at two water-potentials (-15 and -30 hPa) gave rise to short-live high N_2O evolution rate, presumably because soil respiration lead to a depletion of O_2 that induce N_2O production. High N_2O evolution in the treatments with glucose and a combination of glucose and ammonium suggest that heterotrophic denitrification was the major source of N_2O.

Coupled nitrification-denitrification can take place in soil where favorable conditions for both nitrification and denitrification are present in neighboring microhabitats (Wrage et al., 2001). The term coupled nitrification-denitrification is used to highlight that NO_2^- or NO_3^- produced during nitrification can be utilized by denitrifiers (Wrage et al., 2001). A study carried out by Khdyer and Cho (1983) found that N_2O was mainly produced at the aerobic-anaerobic interface where it could diffuse to the soil surface after addition of urea uniformly mixed throughout soil columns under steady-state O_2 gradients.

Nitrifier denitrification has been proposed as an important source of N_2O (Davidson, 1992; Wrage et al., 2001) which combines nitrification and denitrification. In nitrifier denitrification, the oxidation of NH_3 to NO_2^- is followed by a reduction of NO_2^- to N_2O. This reaction is carried out by a group of microorganisms namely autotrophic NH_3-oxidizers. The first part of nitrifier denitrification (oxidation of NH_3 to NO_2^-) has been attributed to nitrification (NH_3 oxidation), whereas the reduction of NO_2^- is regarded as denitrification. NO_2^- is reduced via NO to N_2O and further to N_2 as denitrification (Wrage et al., 2001). Consumption of O_2 by heterotrophs caused by increased available-C would affect nitrifier denitrification (Davidson, 1992).

Only nitrifiers carry out nitrifier denitrification, whereas nitrifiers and denitrifiers are involved in coupled nitrification-denitrification. Furthermore, NO_3^- is not produced in nitrifier denitrification, but it may be formed as an intermediate in coupled nitrification-denitrification (Wrage et al., 2001).

Management strategies for reducing N_2O emissions

Interaction among environmental drivers of nitrification and denitrification is the basis for accomplishing the aim of reducing N_2O emissions from agricultural soils. Soil water content, N and C status, pH, and temperature are the principle environmental drivers of nitrification and denitrification. Weier et al. (1993) found that a single factor may not be enough to trigger the denitrification process in soils, such as the case when adding glucose to soil greatly increased denitrification of NO_3-N, while the addition of N alone had a little effect. The effect of available C for denitrification is due to the fact that microorganisms require readily decomposable substrate before reduction of added NO_3^- can occur (Weier et al., 1993). Many of the environmental factors can be manipulated through management practices such as tillage, irrigation, N fertilizer source, timing and placement, or site-specific prescription of N fertilizer that accounts for differences in crop N demand (Adviento-Borbe et al., 2007).

Six et al. (2004) modeling GHG emissions found that in humid climates, the conversion from conventional tillage to no-till changed N_2O fluxes from a source to a sink after 20 years. The N_2O fluxes in no till systems evaluated by Petersen et al. (2008) are consistent with Six et al.(2004) findings. The shift from a source to a sink could be a result of better protection of organic N in the absence of soil disturbance (Oorts et al., 2007) or soil compaction could increase the efficiency the N_2O reduction to N_2 over time by reducing gas diffusivity (Ball et al., 1999).

Six et al. (2004) concluded that due to the high radiative forcing (or warming potential) of N_2O, greater N_2O fluxes offsets the benefits resulting from C sequestration and CH_4 uptake, leading to increase in the net global warming potential (GWP) during the first 5 to 10 years of adopting NT in both humid and dry climates. The net GWP is negative after 20 years of NT adoption. The GWP for both humid and dry climates have a large degree of uncertainty because N_2O fluxes have a disproportionate impact in the calculation and the high uncertainties associated with N_2O fluxes.

Enhanced efficiency fertilizers, such as those containing nitrification inhibitors (NIs) and urease inhibitors (UIs), and slow-release fertilizers (polymer-coated fertilizers, sulfur-coated fertilizers, isobutilidene diurea) have been developed to increase N-use efficiency fertilizer (Akiyama et al., 2009). They can be effective in increasing N-use efficiency and have other benefits such as reducing labor and fuel costs, decreasing N leaching, reducing N_2O and NO emissions while maintaining crop yields (Akiyama et al., 2009). The IPCC Fourth Assessment Report considered nutrient management had a mitigation potential of reducing N_2O as 0.07 tCO_2-eq ha^{-1} yr^{-1} (Smith et al., 2007).

N placement and timing is also considered an option for N_2O reduction without affecting crop production. Several studies comparing different methods of N application such as sidedress, banding, and deep placement have found contrasting results. Ma et al. (2010) showed the primary risk of increased N_2O emissions was due to large dose of fertilizer application more than the time of N application. Sidedress application often results in improved N use efficiency and the crop requires less N fertilizers to achieve the same or greater grain yields (Ma et al., 2010).

Adviento-Borbe et al. (2007) implied that optimizing N management practices such as deep placement of sidedress fertilizer, and the adoption of high yield hybrids with the proper population densities could reduce N_2O loses. On the other hand, several studies reported increasing N_2O emission of banded and deeper N applications (Thornton et al., 1996; Fujinuma et al., 2011; Gagnon et al., 2011; Halvorson and Del Grosso, 2013).

Zebarth et al. (2008) studied the effect of rate and timing of fertilizer N application to corn on N_2O emission in eastern Canadian soils. They found that while the delay of fertilizer application to sidedress and reduction of N fertilizer application reduced the availability of N in the soil, the emissions of N_2O were not affected.

Soil N_2O emission simulation by process-based models

Process-oriented models have been developed over the last several years with the objective of simulating terrestrial ecosystem carbon and nitrogen biogeochemistry and nitrogen trace gas emissions (Li et al., 2001). Generally process-based models are focused on the processes that mediate the movement and transformation of matter and energy. Soil organisms are mainly implicit in the model formulations, and organism components, if present, tend to represent a generic soil biomass, i.e. an undifferentiated mass of organisms in the soil. In many models, the soil microbial biomass is treated as an active (and often measurable) pool of soil organic matter (Smith et al., 1998).

According to Li et al. (2001) empirical and process-based models are the general approaches to estimate direct N_2O flux from soils. The empirical model estimates N_2O flux based on quantifiable factors which ignore some important details in the nitrogen cycle e.g. volatilization, nitrification and denitrification. Processes-oriented models attempt to simulate many or all of the components of the N cycle. At the fundamental level, processed oriented models carry out processes based on either experimental data or basic chemical and physical laws. By this way the main drivers of the processes-oriented models are moisture, pH, redox potential, and other basic environmental factors that are not usually applied to strict empirical models.

Elucidation of mechanisms that control the soil-atmosphere interchange of NO and N_2O is required in order to establish parameters for process-based models, and will also assist development of management strategies for mitigating impacts of N losses from intensively fertilizer systems (Rodney et al., 2000).

Process-based models have been proposed which describe NO and/or N_2O emissions rates as a function of N substrate levels, gross N mineralization, denitrification and/or nitrification rate systems (Rodney et al., 2000). Many of these models are specific formulations of the conceptual ‘hole-in-the-pipe’ model , which proposed that a proportion of the N which flows through the nitrification and/or denitrification processes leaks out in the form of gaseous N oxides systems (Rodney et al., 2000).

Denitrification Decomposition (DNDC) model

DNDC predicts N_2O emissions mimicking the N cycle which is represented in several sub-models (Li et al., 1992; Li et al., 1994; Li, 2000; Li, 2007) (Fig. 1.1). A soil climate sub-model uses daily meteorological data to predict soil temperature and moisture profiles, soil water flow and soil water uptake by plants for every hour of the simulation. A crop vegetation/growth sub-model simulates the growth of various crops from planting to harvest predicting biomass and N-content of grain, stalk and root. Crop growth is limited by nitrogen and water availability in the root zone. Transpiration water losses are calculated from crop growth and a crop growth water-use-efficiency parameter.

A decomposition sub-model has four soil carbon pools – litter, labile humus, passive humus, and microbial biomass. Each pool has a fixed decomposition rate and a fixed C:N ratio. Decomposition rates are influenced by soil texture, soil temperature and moisture, and potentially by nitrogen limitations.

The hourly time-step denitrification sub-model in DNDC is activated by three conditions which increase soil moisture and/or decrease soil oxygen availability: rain events, flooding (as in irrigated rice agriculture), and freezing temperatures. Air temperatures below -5°C are assumed to freeze the soil and thus inhibit oxygen diffusion into the soil. For any initiation of denitrification the initial status of the available NO_3^- and soluble carbon pools is provided by decomposition sub-model.

The rates for each step in denitrification reduction sequence ($NO_3^- \rightarrow NO_2^- \rightarrow N_2O \rightarrow N_2$) are a function of soluble carbon, soil temperature (or Eh for frozen soils), soil pH, N-substrate availability, and denitrifier biomass. The denitrification sub-model predicts the consumption of nitrate and generates soil fluxes of NO, N_2O and N_2. DNDC predicts nitrification rate by tracking nitrifier activity and NH_4^+ concentration. The growth and death rates of NH_4^+ oxidizers are calculated based on dissolved organic carbon (DOC) concentration, temperature, and moisture (Li, 2000).

Advantages of DNDC are that it has been extensively tested and has shown reasonable agreement between modeled and measured results for many different ecosystems such as grassland, cropland and forest. The model has a reasonable data requirement and it is suitable for simulation and appropriate temporal and spatial scales (Abdalla et al., 2010).

Objectives

- To conduct a meta-analysis to evaluate the effect of different management strategies on N_2O emissions.
- To determine the effect of N management strategies on N_2O emissions on tillage systems.
- To conduct sensitivity analysis of input parameters to calibrate and validate DNDC model.
- To determine climate change effect on N_2O emissions in Kansas agro-ecosystems.

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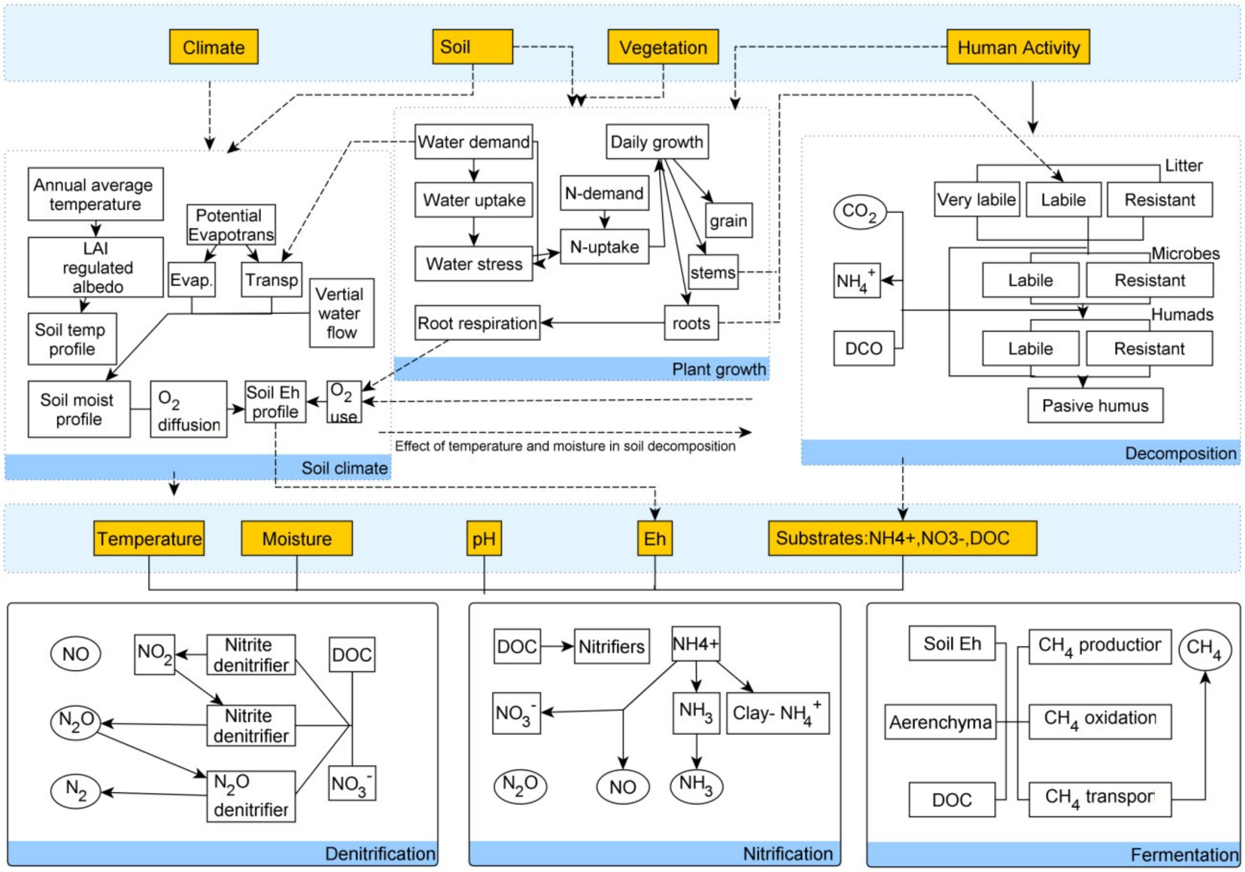

Figure 1.1. Diagram describing the interaction among ecological drivers, soil environmental factors and biochemical processes in DNDC model (Li, 2000)

Chapter 2 - Agricultural land management for N_2O emissions reduction: Meta-analysis

Abstract

In the global prospective, N_2O emissions have increased since the intensive use of synthetic N fertilizer. They have reached a level where ~50% of the emissions from agriculture sector come from agricultural soils. Thus there are opportunities for improving management strategies for N_2O reduction from cropping systems that have been tested in various scenarios. We performed a meta-analysis to test the hypothesis that in fact the agricultural N_2O emissions can be mitigated using various N management strategies under several soil type and crop systems. We estimated the fraction of N fertilizer lost as N_2O emission (NLost) and fertilizer-derived emission factor (EF) for several cropping systems, soils, N management, tillage, and the relationship of N rate with N_2O emission. We found that N placement in band or broadcast did not have significant differences but a trend of higher N lost with banded N placement. Ammonium nitrate, anhydrous ammonia and urea are major N sources that had higher percentage of overall N lost. Enhanced-efficiency fertilizer, organic fertilizer, as well as the combination of synthetic and organic N fertilizer had an overall lower percentage of N lost. High N demanding crops such as sugarcane and potato had the highest N lost. The majority of cropping systems had EF values between 1 and 2%. Clay, silt-loam and silt-clay soils had the highest N lost. There were no significant differences between tillage and no-tillage systems. The relationship between N inputs and N_2O emission followed a non-linear trend. Even though the factors influencing those reductions increased the uncertainty of the N losses, the compiled results from many research locations summarized in this work allowed us to conclude that the N management strategies have a positive impact on reducing N_2O emissions from agricultural soils.

Introduction

N_2O emissions have increased since 1950 with the intensive use of synthetic N fertilizer. The global N consumption increased from about 10 in 1950 to 100 Tg N in 2008 (Millar et al., 2010). The emission of N_2O attributed to human activity is approximately 7.68 Tg N ha^{-1} with a global concentration of 320 ppm in the atmosphere which is considerable higher than the pre-industrial concentration of 270 ppm (Mosier et al., 1998; Forster et al., 2007).

At the global scale, agriculture is responsible for about 4-5 Tg N_2O–N of the contemporary annual anthropogenic emissions (Hoben et al., 2011). Increasing concentrations of N_2O in the atmosphere are contributing both to the global warming and depletion of the stratospheric ozone layer (Smith and Arah, 1992). Significant contributions of N_2O emissions come from denitrification, and nitrification (Smith and Arah, 1992).

Soil N_2O emissions depend on the interaction of environment and management that influences the balance and rate of microbial nitrification and denitrification processes and the transport of N_2O (Adviento-Borbe et al., 2007). Temperature , moisture, pH, osmotic stress caused by soluble salts, supply of C and N compounds, and competition for mineral N by other sinks such as crops are key drivers of soil N_2O fluxes (Adviento-Borbe et al., 2007). Many of those factors can be manipulated through management practices such as tillage, irrigation, N fertilizer source, timing and placement, or site-specific prescription of N fertilizer that accounts for differences in crop N demand (Adviento-Borbe et al., 2007). Asgedon and Kebreab (2011) ranked the management practices according to importance. Application of the N fertilizers at the right rate is given the highest priority whereas proper selection of N source was ranked second and placement at the right position as well as timing of application were recommended for further studies to mitigate greenhouse gases (GHG) emissions.

The effect of climate, soils, tillage, crops, N management has been tested independently, with some few exceptions. Bouwman et al. (2002) summarized N_2O emission from 139 studies based on climate, crop type, fertilizer type, application rate, mode and timing of application, soil organic-C, soil N content, pH, texture and drainage, measurement technique and frequency, and length of measurement period. The N_2O emissions were expressed as total emissions during the measurement. Residual maximum likelihood (REML) procedure was used for data analysis in which the "research paper" was the random factor and a linear combination of controlling factors of N_2O were the fixed effect. Akiyama et al. (2006) compiled information from Japanese agricultural fields (36 sites) and calculated the mean effect of upland, tea and rice paddy fields on N_2O emissions as well as the emission factor for the upland category. Soil drainage was categorized as well-drained and poorly-drained in upland soils. Rochette (2008) summarized results from 25 field studies that had direct comparison between conventional tillage and no tillage and the influence of soils aeration on N_2O emissions. Akiyama et al. (2009) combined results from 35 studies with different managements to evaluate the overall effectiveness of enhanced-efficiency fertilizers on N_2O and NO emission using the response ration between treatment and control. Kim et al. (2012) collected information from 11 independent studies encompassing 27 datasets with the aim of examine the dependency of both direct and N_2O EF on N input. Linear, exponential and hyperbola response were tested in each dataset. Linquist et al. (2012) focused on GHG emissions, yield and yield-scale global warming potential (GWP) from rice, wheat and maize systems from 57 studies. The previous meta-analysis also included different N rates. For rice flooded and drained treatments were compared as well. Our study include most of the important factors that affect N_2O emissions such as N management practices, type of soil, crops and N application rate.

With the aim of explore the effect of agricultural management practices on N_2O emissions from different locations the objectives of this work were to perform a meta-analysis of the effect of N source, N placement, crops, soil type and tillage on percent of N_2O-N emitted from total N input (Nlost, %) and fertilizer-induced N_2O emission or EF (%), and to analyze the relationship between N rate and total N_2O emissions (kg N ha^{-1} $season^{-1}$).

Materials and methods

Data collection

Systematic literature review is a fundamental scientific activity (Mulrow, 1994; Crombie and Davies, 2009; Moher et al., 2009; Philibert et al., 2012) and is the first step in our meta-analysis (Fig. 2.1). In this study the primary literature research was conducted with Web of Science (ISI, Philadelphia, PA), Google Scholar (Google Inc, Mountain View CA, USA) and through studies included in the references. The systematic search of the keywords included “greenhouse gas”, “nitrous oxide”, “nitrogen management practices”, “cropping systems” and “tillage systems”. Studies under managed grassland and organic soils were excluded. Strategies evaluated were: N placement and timing, N source, cropping systems, soil texture, tillage and the rate of N fertilizer.

Data analysis

Description of database

The meta-analysis included 36 independent studies encompassing 43 datasets. Studies with multiple growing seasons were averaged across the seasons when they included the same treatments. In location 17 and 18 the N_2O emissions from three chamber locations in the experimental unit were averaged (ridge, compacted and un-compacted areas) (Table 2.1). Many studies included data from several strategies which resulted in a total of 212 observations. More than half of the experiments were carried out in North America (Table 2.1).

The data were grouped in different factors. The levels in each factor were constructed based on data availability. Several treatments did not have enough sample size so several treatments were the result of grouping several treatments reported in the research papers. The first factor, N placement and timing, was clustered as broadcasted (BC) and banded (B) in single and split application (SP). The second factor, N source, was clustered as U (urea), anhydrous ammonia (AA), ammonium nitrate (AN), urea and any additional synthetic fertilizer (U+F: urea and ammonium polyphosphate, urea ammonium nitrate, calcium ammonia nitrate, diammonium phosphate and ammonium sulfate), enhanced efficiency N fertilizer (EEF, which included polymer coated urea, Dicyandiamide, Controlled-release fertilizer-L30- , polyphenol-coated urea, S-benzylisothiuronium butanoate, S-benzylisothiuronium furoate), organic fertilizer (untreated pig slurry, digested pig slurry, municipal solid waste, composted crop residuals, dairy manure) and combination of synthetic and organic fertilizer (F+O). The third factor, crops, included: wheat (W), sugar cane (SC), rice (R), rice-winter wheat (R-W), potato (P), continuous corn (C), corn-winter wheat (C-W), soybean (S),corn-soybean (C-S), and barley (B). The fourth factor, soils, included different textural classes. The complete set of textural classes were: clay, clay loam, fine loamy, loam clay, loamy, loamy sand, sandy clay loam, sandy loam, silt, silt clay, silt clay loam and silt loam, and the fifth factor was tillage (conventional till (CT) and no-till (NT)).

Cumulative N_2O-N emissions (kg N ha^{-1} y^{-1}) for the growing season per treatment were recorded from each study. The effect of N placement and timing, N source, crops, soils, and tillage on N_2O emissions were estimated based on N lost as a percent of the applied N fertilizer (Nlost) and the fertilizer-induced N_2O emission (EF).

The percentage N lost (Nlost) was calculated based on the total N_2O-N emissions and the total N input.

$$Nlost(\%) = \frac{N_2O - N}{Total\,N\,Input} * 100$$

From the studies reporting a control treatment (No nitrogen added [19 studies, 108 observations]) the fertilizer-induced emission or emission factor was calculated following the Tier I methodology from IPCC approach (IPCC, 2006):

$$EF(\%) = \frac{[N_2O - N_{Applied}] - [N_2O - N_{Control}]}{Total\,N\,Input} * 100$$

where N_2O-$N_{Applied}$ is the emission recorded in a N treatment and N_2O-$N_{Control}$ is the emission recorded in a no-N treatment.

The effect of N rate was estimated base on the cumulative N_2O-N (kg N $ha^{-1}yr^{-1}$) values observed in each study.

Statistical analysis

Effect of N placement and timing, N source, crops, soils and tillage

Linear mixed model REML estimation methodology was used for analyzing the effect of N source, N placement and timing, crops, soils, and tillage on Nlost (%) and EF (%). The REML procedure is appropriate for analysis of unbalance data set with missing values (Bouwman et al., 2002). Due to data limitation a complete model including all factor and interactions was not fitted. Instead one-way mixed model was fit per each factor.

$$Y_{ij} = u + b_j + B_i + e_{ij}$$

where Y_{ij} is Nlost or EF for *ith* level of a given factor and *j* location; μ is the overall mean; B can be any of the fixed effect such as crops, placement, N source, tillage, and soils; *b* and *e* are the random terms corresponding to the location and the residual error of the model assumed to be normally distributed. The mean estimate of Nlost and EF, and their corresponded bias-corrected 95% confidence interval (CI) were calculated using a bootstrapping procedure (5000 iterations). The analysis was performed using proc mixed and jackboot macro from SAS (SAS Institute, 2010). Figures were constructed using the library ggplot2 (R Core Team, 2012).

Effect of N rate

A linear and non-linear functions were fit to interpret the relationship between N input and cumulative N_2O-N (kg N ha^{-1} yr^{-1}). Mixed model with non-linear function was selected based on Akaike information criterion (AIC) and Bayesian information criterion (BIC) as final approach for data analysis (Table 2.2).

The cumulative N_2O-N (kg N ha^{-1} y^{-1}) emission was evaluated using a non-linear mixed model. A non-linear response of N_2O to N rates has been found in several studies (McSwiney and Robertson, 2005; Hoben et al., 2011; Kim et al., 2012). In this study, the following non-linear mixed model was fitted based on Hoben et al. (2011) and Miguez et al. (2008) methodology.

$$Y_{ij} = \exp\left[\phi_{0i} + \phi_{1i} * N_{ij}\right] + e_{ij}$$

$$\phi_{0i} = \beta_0 + b_{0i}, \phi_{1i} = \beta_1 + b_{1i}$$

where Y_{ij} is the cumulative flux (kg N_2O-N $ha^{-1}y^{-1}$) in each ith location and jth N rate. ϕ_i represents the parameter vector that is allow to vary with location. β_0 and β_1 represent the average value of the intercept and slope, respectively. b_0 and b_1 are the random coefficients representing the deviations of ϕ_i from their population average and are assumed to be independent for different locations and multivariate normal distributed. A general positive-definite matrix was used to represent the random-effect variance-covariance structure. e_{ij} is assumed to be normally distributed with different variances at different N rates to account for unequal variances across different N rates.

A null model was fitted with random coefficient in the first parameter vector, $\phi_{0i,}$ and fixed second parameter vector, ϕ_{1i}. The next step was to include the crops, N source, soil and tillage as covariates in the model to explain the intercept site-to-site variations (complete model). Finally, a reduced model was selected with just the significant factor or factors detected in the previous step. Due to the lack of observations a complete model with all the covariates with interactions was not fitted, instead the following model were assessed:

$$\phi_{0i} = \beta_0 + A_1C_1 + A_2C_2 + A_3C_3 + A_4C_4 + b_{0i}$$

where A represent the coefficients of the covariates C (C1: N source, C2: crops, C3: soils, and C4: tillage) and b_{0i} represents the random coefficient assumed to be normally distributed.

The models were compared using likelihood ratio-based R^2-values, AIC and BIC criteria. The analysis were carried out using the libraries nlme and ggplot2 from R (R Core Team, 2012).

Results

Strategies to reduce N_2O emissions

The overall values of Nlost were up to 50% higher than EF values. The percentage of N lost by N_2O emissions (Nlost) ranged between 0.12 % to about 11.48% of the total N applied (Table 2.1). The direct N_2O emission factor (EF) was between -0.01 up to 10.9% (Table 2.1). The -0.01% was estimated from a nitrification inhibitor treatment evaluated in location 9 (Table 2.1).

Change in fertilizer placement and timing

There was no significant reductions of N_2O emissions in terms of N lost (Nlost) regarding the placement type and timing (Fig. 2.2a). However, banded (B) application of fertilizer increased the estimated mean Nlost in both single (1.51%) and split application (1.89%) compared to broadcast N application (1.28 and 1.22 for single and split application, respectively). Banded application had the highest EF (%) than BC (Fig. 2.2b). Single application of N in BC (0.65%) had the lowest N_2O emissions, however this was not significant from the single banded N application (1.33%) due to overlapped 95%CI (Fig. 2.1b).

Change in fertilizer N source

The N source had a significant impact on Nlost and EF values. AA (2.25%), U (2%) and U+F (2.17%) had significantly higher Nlost than EEF (0.74%). However, there were no significant differences among AA (2.25%), AN (2.34%), Organics (1.73%), U (1.97%) and U+F (2.17%). EEF and the combination of synthetic+ organic fertilizers (F+O, 1.38%) seemed promising treatments reducing N_2O-N emissions (Fig. 2.3a).

In terms of emission factor (EF) the estimated 95% CI for EEF (-2.8, 2.6%), AA (-1.5, 0.8%) and F+O (-1.47, 0.78) revealed high uncertainty. The average estimated EF for EEF (-0.1%), AA (0.13%) and F+O (-0.34%) were not significantly different from zero. AN (3.27 %), U+F (1.87 %), Organic (2.24%) and U (1.83%) were significant different from F+O (Fig. 2.3b).

Crop, soils and tillage

Sugarcane had the highest %N lost (3.86%) which was not significantly different than potato (P, 3.38%) but significantly different from all the other crops (Fig. 2.4a). Due to the high 95% CI found for potato the estimated Nlost value was not significantly different from the other crops. There was no clear evidence on the potential effect of multi-cropping systems in reducing N_2O emissions. For example C did not have a significantly higher Nlost value than C-S or C-W. However, there were significant differences between R-W (0.67%) and C-W (0.73%). Crops such as R, R-W, B, S and W had Nlost values less than 1.5 % (Fig. 2.4a).

In terms of emission factor (EF) there were detected significant differences among the crops. However, most of the crops had EF values between 1-2% except B (0.13%), R-W (0.34%) and C-W (0.68%) which had significantly low EF values. SC and C-S were the crops with highest %EF (1.73% and 1.57%, respectively) potato was not included in this analysis due to lack of sufficient data (Fig. 2.4b).

Overall in terms of Nlost, pair-wise differences were found in clay soil (2.66%) vs. clay loam (0.91%), fine-loamy (2.51%) vs. loamy soil (1.49%) and silt clay loam (2.16%) vs. silt soils (Fig. 2.5a). The emission factor (EF) values followed the same trend than Nlost values even though more contrasting values were found. Clay soils (3.26%) vs. clay loam (0.23%), silt-loam (4.07%) and silt-clay (2.1%) vs. silt soils (0.4%) were significantly different. Overall, most of the soils had EF values below 2% (Fig. 2.5b)

No significant differences in terms of tillage systems regarding Nlost and EF were found. Overall, the Nlost was 1.98% for CT and 1.68% for NT (Fig. 2.6a). The values of EF were 1.14% and 1.18% for CT and NT, respectively (Fig. 2.6b).

Reduce fertilizer N application rate

Overall, the null model, which did not include effect of variables such as soil, N source, crops, tillage predicted well a non-linear relationship between N_2O emissions and N input (AIC:742.9, BIC:763.1) (Table 2.2). The null model is useful to explain the potential of the non-linear relationship between N input and N_2O emissions. The complete model fit better the observe data than the null model (AIC, BIC and R^2 were 668.1, 801.8 and 49.5, respectively) (Table 2.2). Tillage was the only non-significant parameter in the complete model (Table 2.2, p-value=0.072). The reduced model excluded the tillage factor as a predictor (AIC, BIC and R^2

were 660.3, 794.5 and 0.51) (Table 2.2). Several locations were simulated using the null and reduce model (Fig. 2.7 and Fig. 2.8). The model with only fixed parameters (population average) resulted in similar simulation for each location (solid black line) (Fig 2.7). The mixed model with fixed plus random effect (dashed-red line, location-specific) fit better the observed emissions (Fig. 2.7). It seems that a mixed model with the random coefficient (Fig 2.7, dashed-line) explained the variability of N_2O emissions across the locations. The effect of crops, soils and N source were significant predictors due to their close relationship with N_2O emissions and it is depicted in Fig. 2.8.

Predictions of N_2O emissions based on the reduced model were performed for corn and corn-soybean rotation under clay and loam soil type and four fertilizer types to illustrate crops , N source and soil effects (Fig. 2.9 and 2.10). Urea (U) tended to have higher emissions at the same N rate as ammonium nitrate (AN), enhanced efficiency fertilizer (EEF) and anhydrous ammonia (AA). The differences in N_2O emissions were much higher at high N rates especially in clay soils (Fig. 2.9). Under loam soils, the predictions of N_2O were lower in all crops and N sources as expected (Fig. 2.10). These results suggest that single values to estimate N_2O losses from agricultural soils solely based on N input potentially under or overestimates the actual N_2O emissions. It is an assumption that does not take into account the uncertainty associated with N_2O emission, which depends on N source, crops, soils, management, and climate. In the non-linear mixed model we evaluated directly the effect of N source, crops, soils and tillage which explained about 50% of the variability. Including temperature and precipitation at each location as predictors explained up to 65% variability.

Discussion

Our results comparing banded and broadcast N application did not show significant differences. Adviento-Borbe et al. (2007) implied that optimizing N management practices such as deep placement of sidedress fertilizer, and the adoption of high yield hybrids with the proper population densities resulted in greater N uptake thus reducing N_2O losses. Generally N_2O emissions from subsurface applied or injected N fertilizers is higher than broadcast synthetic fertilizers and animal manure (Bowman et al., 2002).

Overall, split N application did not significantly reduce N_2O emissions relative to single or preplant application even thought site-specific studies such as Ma et al. (2010) reported that there were likely greater cumulative N_2O emissions for sidedress than for preplant fertilization. Zebarth et al. (2008) found that while delaying the fertilizer application to sidedress and reducing N fertilizer application the availability of N in the soil was reduced without affecting the emissions of N_2O in eastern Canadian soils. It seems that timing and placement N practices may have positive impact reducing N_2O emissions when integrated with additional managements such as tillage, N source and N rate. Robertson et al. (2000) suggested that the N_2O flux from cropping systems was related more to N availability than fertilizer *per se* and tillage.

Contrasting results about the effect of split application of N fertilizer have been found, including no effect (Ciarlo et al., 2008), reduced N_2O emissions (Burton et al., 2008) and higher N_2O emissions (Weier, 1999). Bowman et al. (2002) suggested that the confounding results on N_2O emissions of split N fertilizer application were due to unclear separation of contributing factors including local climate, fertilization rate, fertilization mode and measurement period. Inter-annual variability in split fertilizer effects has been associated with timing of application during growing season, in combination with rainfall events (Allen et al., 2010; Yan et al., 2001; Burton et al., 2008). In sugarcane, Allen et al. (2010) found that split application of fertilizer had no measurable effect on N_2O emissions at 100 kg N ha^{-1} rate, possibly because N uptake by sugarcane kept mineral N levels at similar concentrations in both methods of application single and split. However, at 200 kg N ha^{-1} the split application significant reduced N_2O emissions more than 50% compared to the single application. Weier (1999) showed that split application of urea at 160 kg N ha^{-1} to a sugarcane crop initially resulted in lower N_2O emissions but resulted in greater N_2O emissions later when soil moisture was higher.

The wide range in Nlost and EF estimates could be as a result of variation in biophysical settings and experimental methods (Asgedom and Kebreab, 2011). For some fertilizers using global aggregated data, Stehfest and Bouwman (2006) found a wide range of N_2O-N emissions (kg N ha^{-1}): 0-30 for ammonium nitrate (AN) , 0.05-19 for anhydrous ammonia (AA), 0.01- 46 for urea (U) and 0.08-0.1 for ammonium sulfate (AS). Our results showed that AA in corn had an estimated EF of 1.08% which is in the range estimated by Eichner (1990).

Ammonium nitrate (AN) had the highest EF followed by U and anhydrous ammonia (AA) regardless of soil, crop, location, and N management. Harrison and Webb (2001) proposed a relative emission assessment scheme that suggested N_2O emissions from urea under warm, wet conditions may exceed those of NH_4-based sources. Relative N_2O emissions from NO_3-based sources may exceed those from NH_4-based sources, and differences may increase with increasing wetness. Using balanced median values, Stehfest and Bouwman (2006) found that ammonium phosphate had the lowest emissions and calcium ammonium nitrate the highest.

The estimate for slow-release N fertilizer in our study was the lowest for EF and Nlost, indicating the potential of those products reducing N_2O emissions from soils. However, the high uncertainty on the mean response could be related to the specificity of the response given certain condition such as soil, crops and climate. Enhanced efficiency fertilizers, such as those containing nitrification inhibitors (NIs) and urease inhibitors (UIs), and slow-release fertilizers have been developed to increase the efficiency of fertilizer use by crops (Akiyama et al., 2009). NIs are compounds that delay bacterial oxidation of NH_4^+ by depressing the activities of nitrifiers in soil, whereas UIs are compounds that delay the hydrolysis of urea. Slow-release fertilizers slow the rate of nutrient release through coating or chemical modification of the fertilizers. NIs, UIs, and slow-release fertilizers have been studied intensively, and finding indicate that they can be effective in increasing nitrogen-use efficiency and have other benefits such as reducing labor and fuel costs and decreasing nitrogen leaching (Akiyama et al., 2009). The IPCC Fourth Assessment Report (Smith et al., 2007) considered nutrient management including NIs and slow-release fertilizers as a mitigation option, with a mean mitigation potential estimated to be 0.07 tCO_2-eq ha^{-1} yr^{-1}.

NIs are the most widely tested mitigation option for N_2O emission from agricultural soils. Among slow release fertilizers, the effectiveness of polymer-coated fertilizers (PCFs) on N_2O emissions have been tested in several studies (Cheng et al., 2002; Halvorson et al., 2010; Hyatt et al., 2010), while few studies have tested sulfur-coated fertilizers or chemically altered slow-release fertilizer such as isobutilidene diurea (Akiyama et al., 2009).

A meta-analysis carried out by Akiyama et al. (2009) on field experimental data and literature reviews (Snyder et al., 2009; Motavalli et al., 2008) showed that NIs, urease inhibitors, PCFs and stabilized N source could reduce N_2O emissions from agricultural soils while maintaining crop yields.

The organic fertilizers tested in our meta-analysis tended to have low estimates of Nlost and EF which were statistically similar to enhanced efficiency fertilizers. However, the combination of organic and synthetic fertilizer (O+F) had the lowest estimated EF. The positive effect of organic amendments on reducing N_2O emissions may be due to a more effective reduction of N_2O to N_2 during denitrification in the presence of more readily soluble C (Yao et al., 2010). However the reduction depends of C:N ratio of the crop residues or organic material applied (Yao et al., 2010). In general, the emissions would be lower after incorporation of residues with high C:N ratios, but would be comparatively large after incorporation of materials with low C:N ratios due to the promotion of mineralization and the subsequent availability of substrate for nitrification and denitrification (Kaiser et al., 1998; Baggs et al., 2000; Millar and Baggs, 2004; Baggs et al., 2006; Sanchez-Martin et al., 2010; Yao et al., 2010). Baggs et al. (2003) concluded that combining synthetic fertilizers and residuals either had no interactive effect on N_2O emissions, or slightly positive or negative which depended on the residue type and tillage.

Cropping systems such as sugar cane and potato, which tend to demand more N than many other crops such as cereals showed higher EF and Nlost values. Including a legume such as soybean in the rotation may enhance emissions as observed for corn and corn-soybean rotation.

Stehfest and Bouwman (2006) found that wetland rice, cereals and grass had lower values compared with legumes. Wetland rice, cereals and grass significantly differ from all the crop types and among each other. Linquist et al. (2012) reported a low percent of N lost by N_2O in rice, wheat and corn between 0.68 and 1.21 %. The EFs in this meta-analysis for those three crops were between 1.02 and 1.12%, respectively which were among the lowest and slightly higher than the suggested 1% used by the IPCC (IPCC, 2006).

Overall the soil effect was significant for Nlost and EF when two soils were compared simultaneously. The trend towards higher percentage of N_2O lost was detected in soil with high clay content (Fig. 2.5a, 2.5b). Stehfest and Bouwman (2006) found a significant influence of soil texture on N_2O emissions. The mean values of N_2O fluxes were significantly higher for fine textured soils that the coarser or medium textures. Fine-textured soils have more capillary pores within aggregates than do sandy soils, thereby holding water more tightly. Anaerobic conditions may be more easily attained and maintained for longer periods in fine-textured soils than in coarse-textured soils (Stehfest and Bouwman, 2006).

Since N often is the most limiting nutrient in intensive crop production the strategies to reduce N inputs in those systems should not compromise the productivity and economic return. Hoben et al. (2011) concluded that the agronomic optimum N rate had lower emissions than the maximum rate. Excessive N fertilization leads to increased N_2O loss without economic gain in yield suggesting a non-linear response between N rate and N_2O emissions. In our study a non-linear function best described the relationship between N rate and N_2O emission from various agricultural systems. The location as well as cropping systems, soil, N source had a significant impact on the response to N fertilizer.

A meta-analysis carried out by Van Groenigen et al. (2010) concluded that the total emissions remained essentially stable between 1 and 2 kg N_2O-N ha^{-1} up to a fertilizer application rate of 187 kg N ha^{-1}, which sharply increased to a mean value of 5.8 kg N_2O-N ha^{-1} for corn, barley, onion, rice wheat, potato and canola. Our results, using the average response of crops, soils and N source showed a similar pattern to Van Groenigen et al. (2010) up to ~200 kg N. However, an exponential response was observed after ~300 kg N. Similar results were reported by Grant et al.(2006) in Canada where N_2O emissions increased progressively with increasing N fertilizer once the N input exceeded crop N demand. Nitrous oxide emissions expressed as a percentage of applied anhydrous NH_3 fertilizer increased from 0.1% at 30 kg N ha^{-1} to 1.8% at 300 kg N ha^{-1}. Bouwman et al. (2002) reported a largely stable N_2O emission of approximately 1 kg N_2O-N ha^{-1} at application rates of 25-150 kg N ha^{-1}. At application of 200 kg N ha^{-1}, significant increases of N_2O emissions were observed. The effect of increasing N_2O emissions when more N was applied than was taken up by the crop may be due to several mechanisms. First, a large N surplus more mineral N was available for denitrification. Moreover, when the concentration of soil NO_3^- was high , the N_2O:N_2 ratio of denitrification increases (Van Groenigen et al., 2010). Van Groenigen et al. (2010) found that the amount of N_2O emitted per unit of above-ground N uptake decreased from 12.1 to 7.1 g N_2O-N kg^{-1} N uptake when N use efficiency increased from 19 to 75% suggesting that the best management options are the ones that maximize the crop uptake of N.

According West and Marland (2002) the ratio of CO_2 released for N produced is equal to 0.814 g C g^{-1} N . There is no doubt that reducing synthetic N use where available N exceeds plant requirements can reduce not only N_2O emissions from croplands but also CO_2 emissions from fertilizer production (Huang and Tang, 2010).

Conclusions

N lost measured as a fraction of the N fertilizer applied (Nlost) as well as fertilizer-induce N_2O emission (EF) are potential indicators of efficiency of N management practices for N_2O reduction. Even though the magnitude of those values can differ by 50% in many treatments, it was possible to reach similar conclusions. In the case of scaling-up emissions at the national level the former values could potentially overestimate the total emissions. These indicators can be used to calibrate and validate process-based models with the aim of extrapolating emissions at regional levels. The Tier I methodology that recommends 1% of fertilizer lost as N_2O could in many cases underestimate or overestimate the actual observations in various cropping systems.

Even with the uncertainty associated with field experimentations in N_2O emissions, the compiled results from many research locations summarized in this work allowed us to conclude that the N management strategies have a positive impact on reducing N_2O emissions from soils and reduction in N fertilizer applied also reduces manufacture of N fertilizer providing an additional benefit on reducing GHG. Soil and crops are key part of the equation for assessing N_2O emissions local and regional level. The managements that have been proposed through recent research findings has to be linked with environmental factors in order to assess the potentialities and applicability in reducing N_2O emissions. More information has to be gather in order to estimate possible interactions among factors related to N fluxes.

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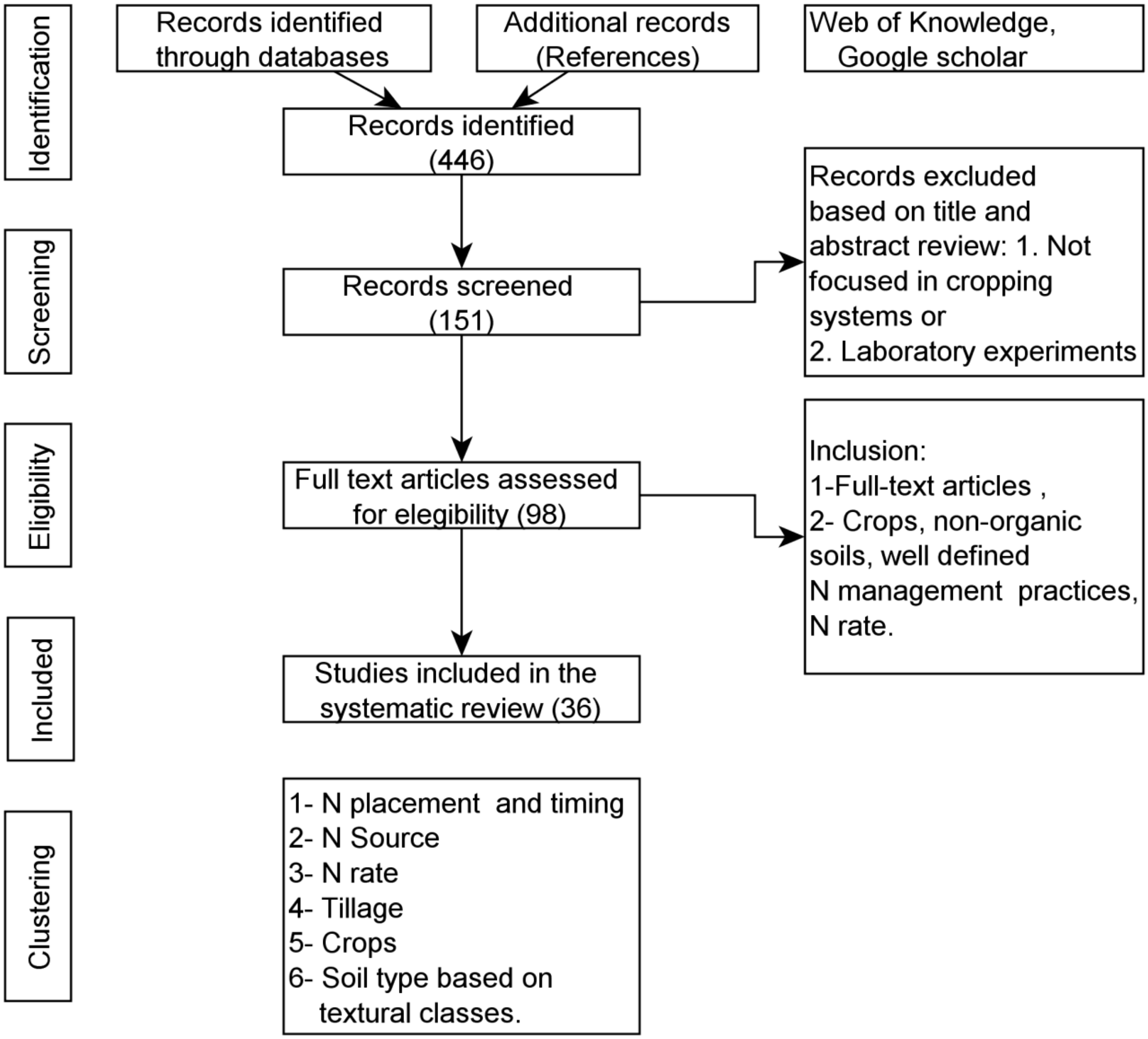

Figure 2.1 Main steps for developing a systematic literature review or meta-analysis. In parenthesis are the number of papers found in each step (Adapted from Moher et al., 2009)

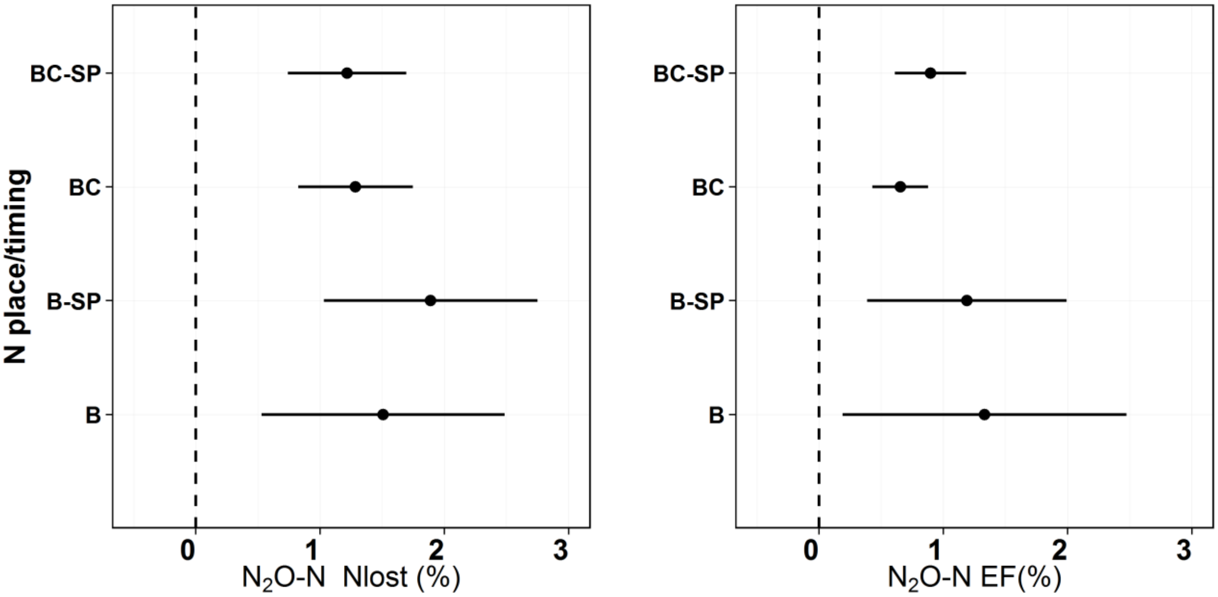

Figure 2.2 N lost by fertilizer placement and timing as management strategies for reducing N_2O fluxes in terms of Nlost (Left) and emission factor (%EF) (Right). 95%CI and means for broadcasted and split N application (BC-SP), broadcast N application (BC), banded and split N application (B-SP), band application of N (B).

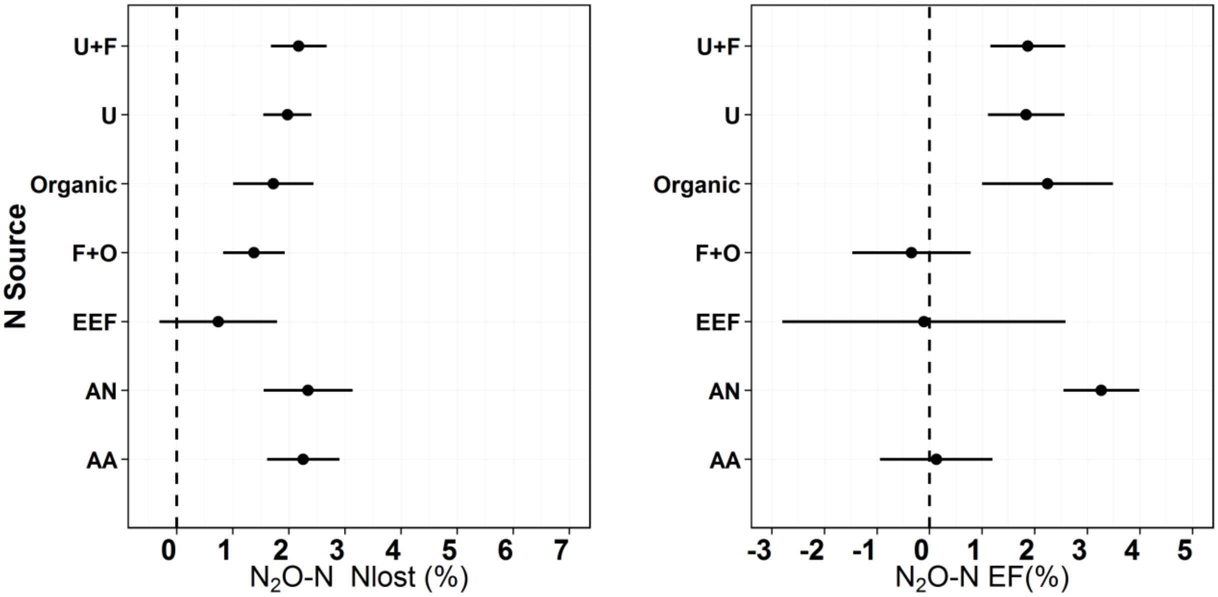

Figure 2.3 Effect of fertilizer types on N_2O emissions, shown as Nlost (Left) and percentage of N lost based on emission factor (EF). Mean effect and 95% CI are shown. U, Urea. U+F is referred as U plus any other chemical N fertilizer such as AN, AP, DAP and NPK. EEF, included Nitrification and Urease inhibitors, and coated-urea. Organic, stands for manure and compost treatments. F+O included chemical fertilizer above mentioned + organic amendments. AN, Ammonium Nitrate. AA, Anhydrous ammonia.

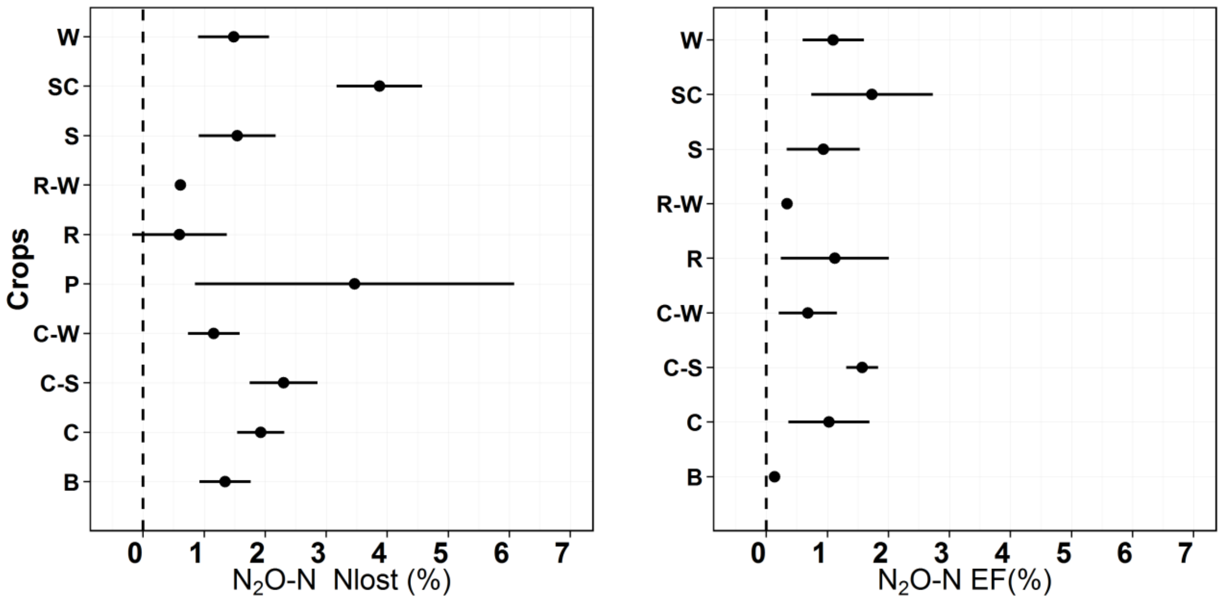

Figure 2.4 Crop effect on N lost by total % N lost (Left) and percentage of N lost using emission factor methodology (%EF). 95%CI and mean values for winter-wheat (W), sugar cane (SC), soybean (S), rice-winter wheat rotation (R-W), rice (R), potato (P); corn (C), corn-winter wheat rotation (C-W), corn-soybean rotation (C-S) and barley (B).

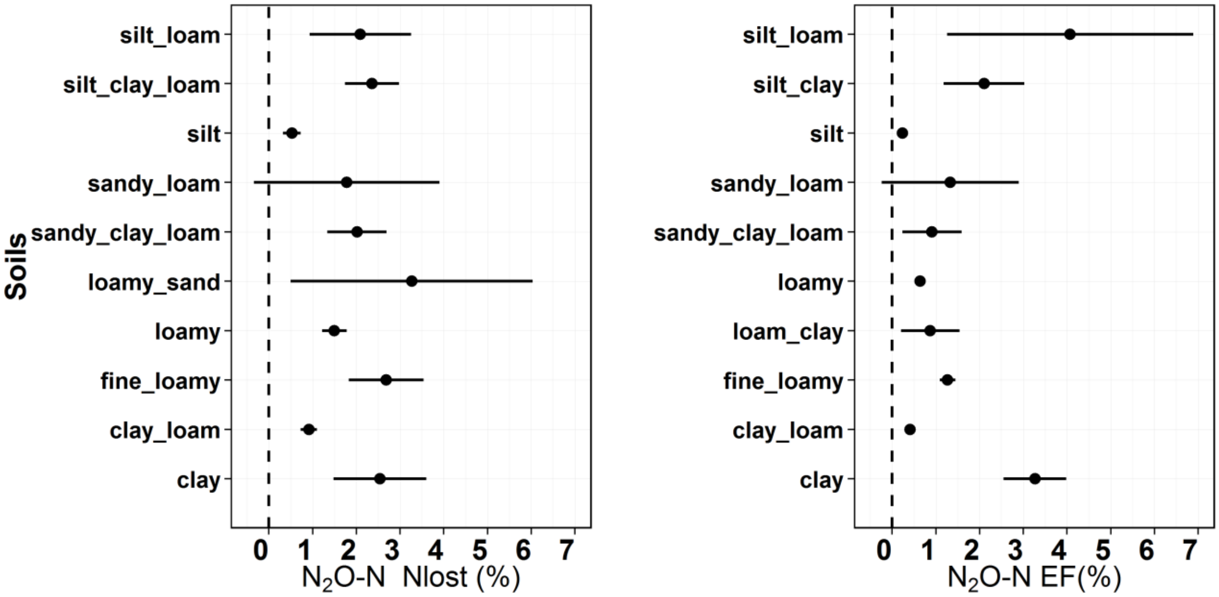

Figure 2.5 Effect of soil types on N lost by total percentage Nlost (left) and percentage of N lost using the emission factor methodology (%EF). Fifteen soil types were analyzed for %N lost and soil types for emission factor approach.

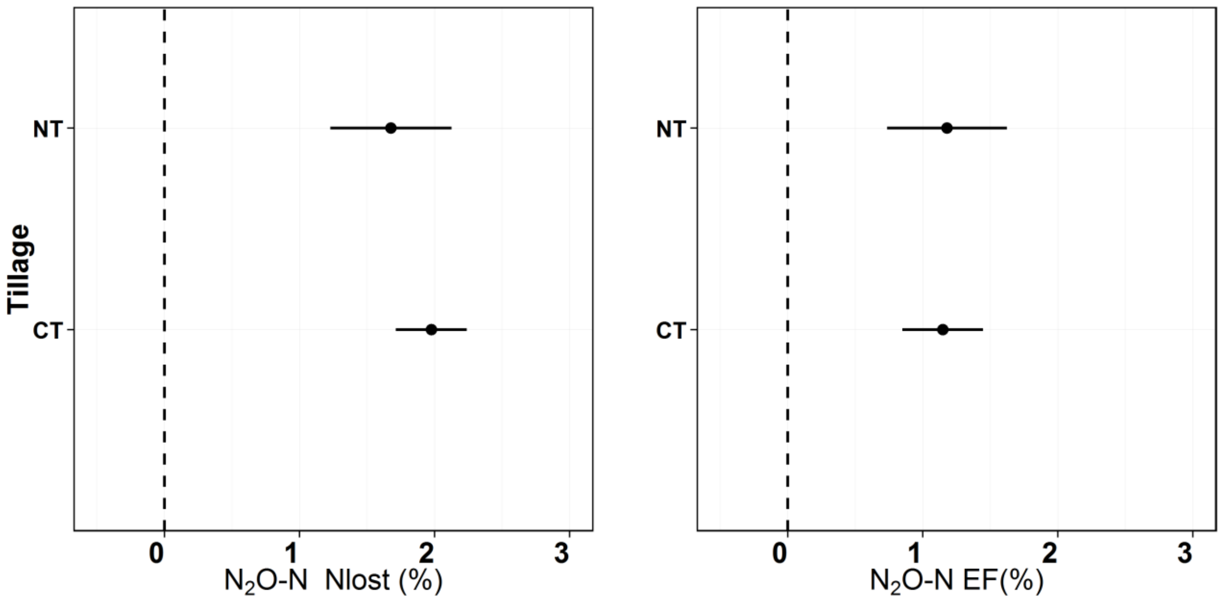

Figure 2.6 N lost by N_2O emissions in till (CT) and no-till (NT) systems, shown as % N lost (right) and emission factor approach (%EF) (left).

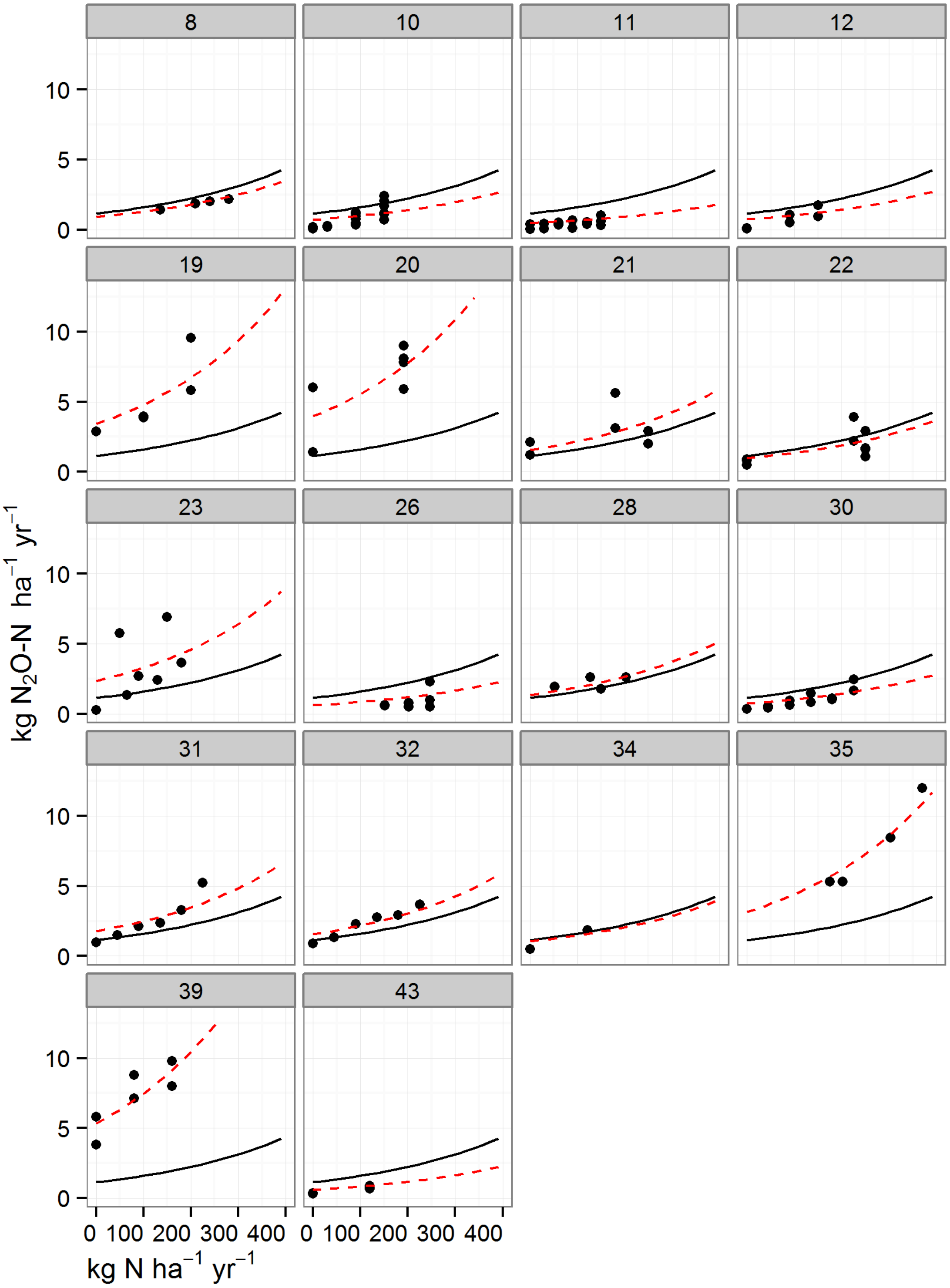

Figure 2.7. Site-specific (location, dashed line) and the population average (fixed, solid line) predicted N_2O obtained from null model. Dashed-red line represents the. Numbers in each panel represents the location number in Table 2.1.

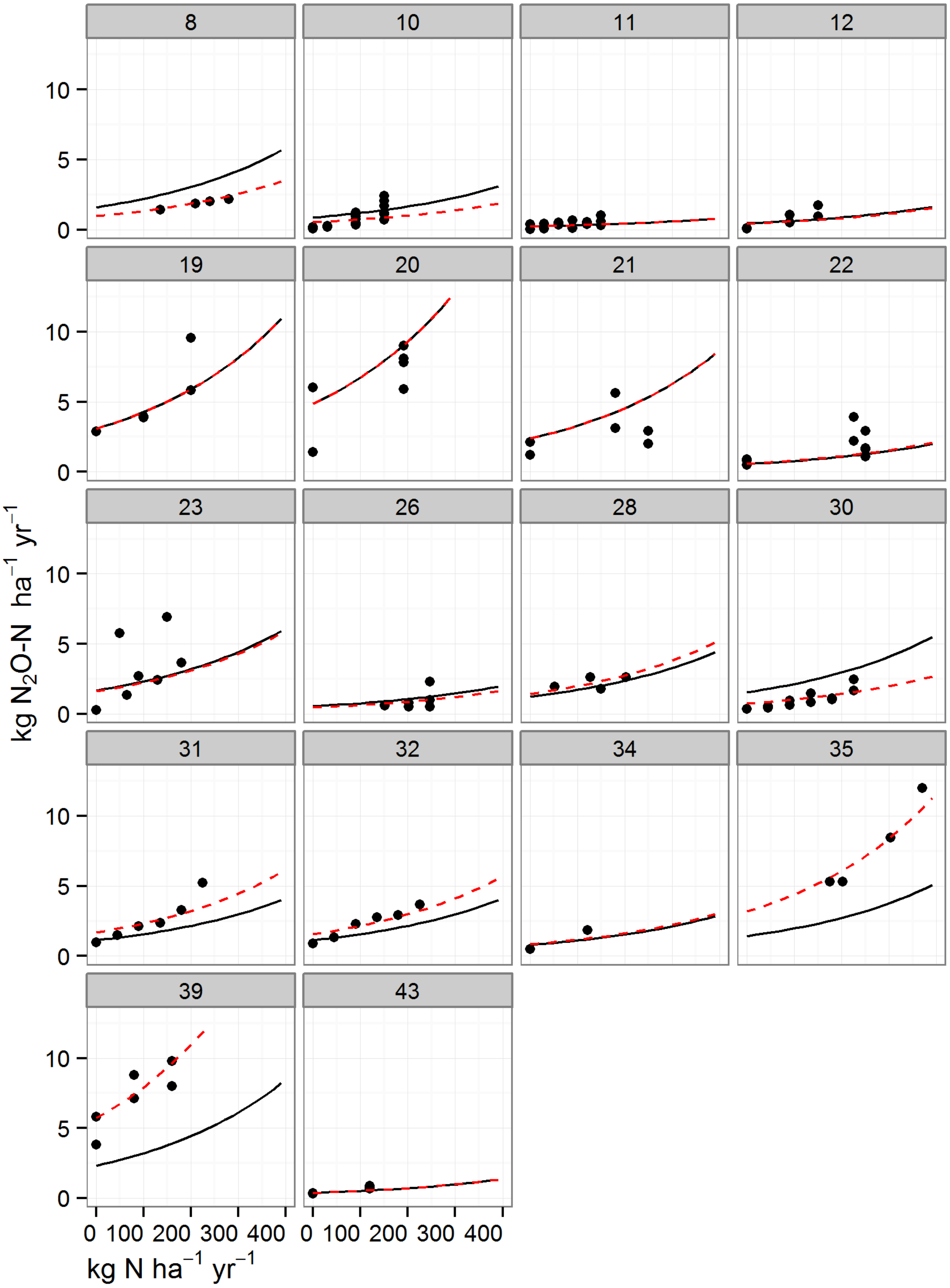

Figure 2.8. Prediction of cumulative N_2O-N per location from the complete model: Site-specific (dashed line) , and population average (solid line). This figure reflects the effect of crops, soils and N-source. Numbers in each panel represents the location number in Table 2.1.

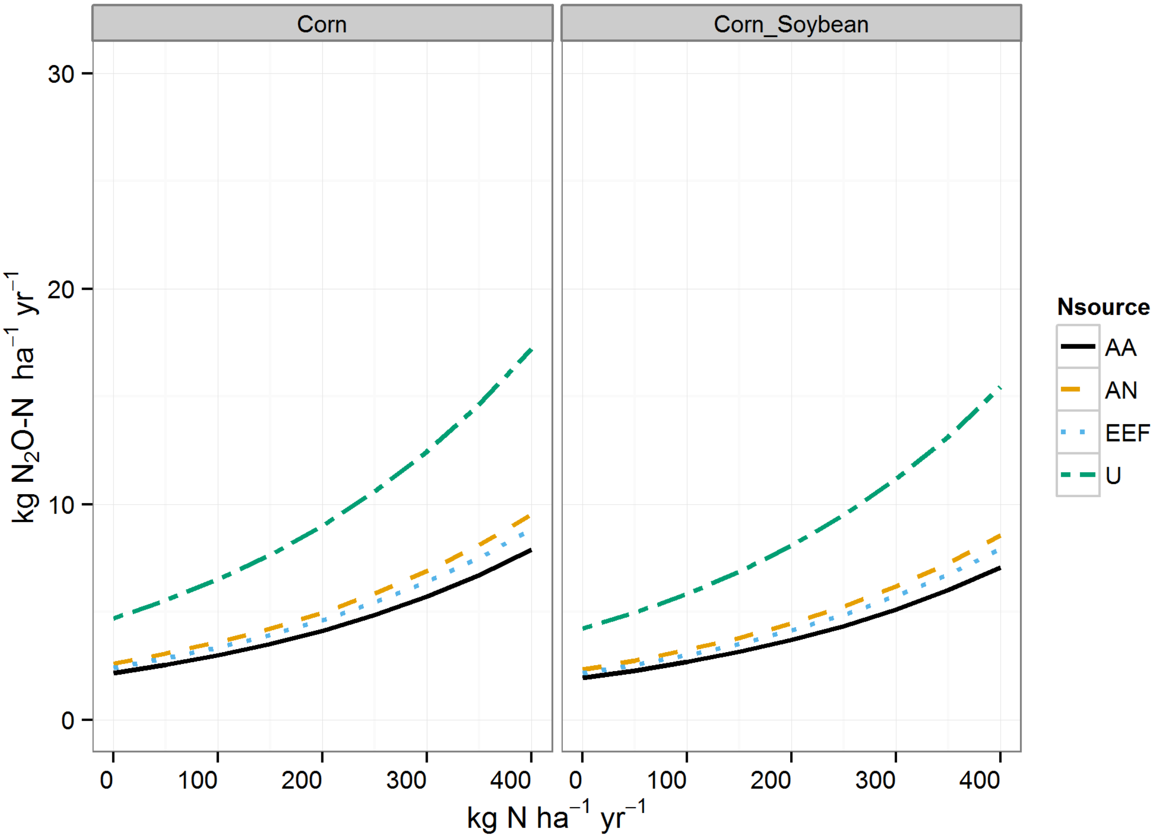

Figure 2.9 Effect of different N source (Anhydrous ammonia -AA-, Ammonium nitrate -AN-, efficient enhanced N fertilizer -EEF-) on N_2O emission under clay soil type in corn and corn-soybean rotation.

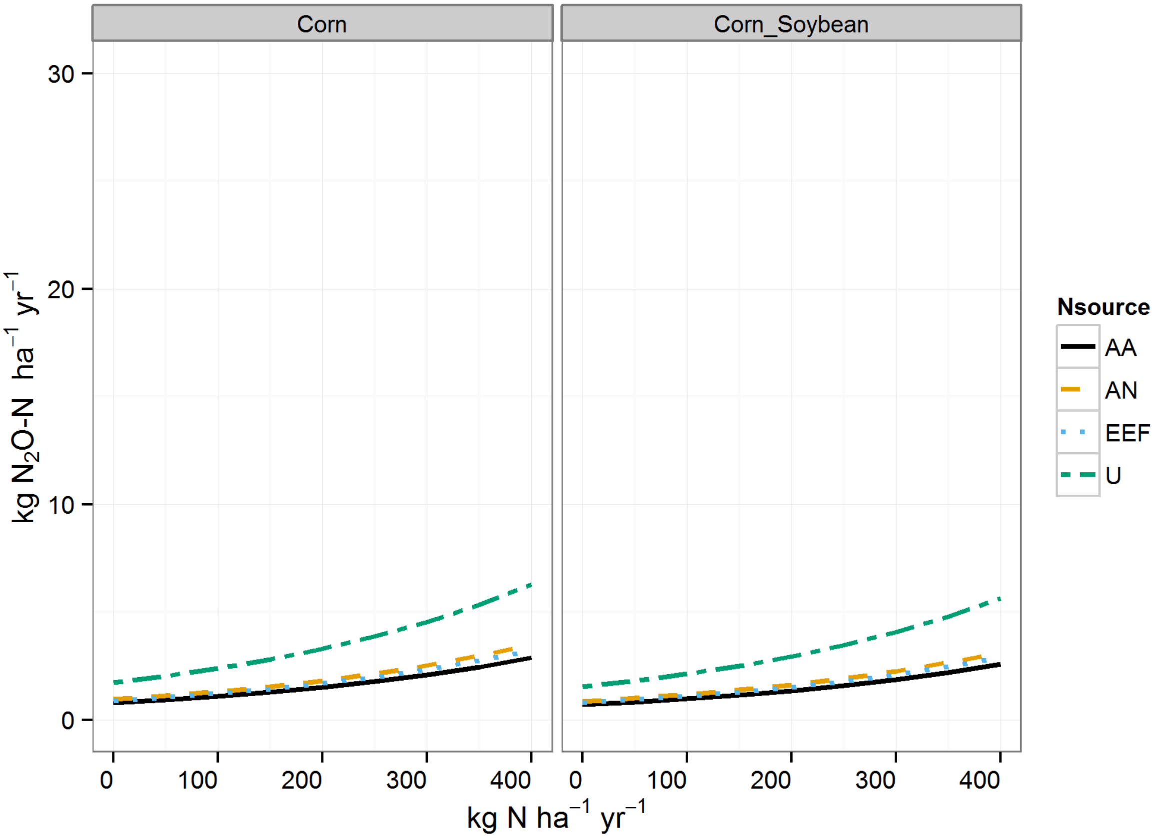

Figure 2.10. Effect of different N source (Anhydrous ammonia -AA-, Ammonium nitrate -AN-, efficient enhanced N fertilizer -EEF-) on N_2O emission under loam soil type in corn and corn-soybean rotation.

Table 2.1 Studies used in the meta-analysis.

Location	Loc. No.	Texture	Crop†	Till ‡	N source §	Placement ¶	N input	N_2O-N#	References
							kg N ha^{-1}	kg $ha^{-1}yr^{-1}$	
Nebraska , USA	1	silty_clay_loam	CC	.	AN/DA/M/C	.	151	1.4	(Ginting et al., 2003)
Iowa, USA	2	loam	CC/Rye/S	T/NT	AP+U	.	215	4.405-10.75	(Parkin and Kaspar, 2006)
Ohio, USA	3	fine_silty	CC/CS/CSW-V	T/NT/RT	AA/U/AN/C/GM	.	130-180	1.5-2.26	(Jacinthe and Dick, 1997)
Tsukuba,Japan	4	Andisol	Ch-C	.	NF/U/L/SRNF	.	0-250	0.12-.853	(Cheng et al., 2002)
	5								(Elder and Lal, 2008)
Boigneville, France	6	silt_loam	C-WW	CT/NT	AN	BC	158-169	0.8-1.32	(Oorts et al., 2007)
Ohio, USA	7	silt_loam	CC	CT/NT	NPK+AA	.	200	0.94-1.96	(Ussiri et al., 2009)
Nebraska, USA	8	silty_clay_loam	CC	CT	AN	BC/B-SP	135-240	1.42-1.87	(Adviento-Borbe et al., 2007)
Kalimantan, Indonesia	9	sandy_loam	CC	CT	NF/U/IN/SRNF	.	0-90	0.2-6.92	(Hadi et al., 2008)
Ottawa, Canada	10	loam	W-C/S/W/	CT	NF/U/U+AN	BC/BC-SP	0-150	0.11-2.42	(Ma et al., 2010)
Ontario, Canada	11	silt	WW-C/C	CT	NF/U/U+AN	BC/BC-SP	0-150	0.02-1.03	(Ma et al., 2010)
Quebec, Canada	12	clay_loam	S/CC	CT	NF/CAN+DAP/U+AN	BC/B-SP	0-150	0.09-1.75	(Ma et al., 2010)
Michigan, USA	13	fine_loamy	C-S-W	CT/NT	AA+AN	BC	179	1.175-1.27	(Robertson et al., 2000)
Quebec, Canada	14	heavy_clay/gravelly_loam	B	CT/NT	AN	BC	51.25	1-3.27	(Rochette et al., 2008)
Goiás, Brazil	15	clayey	R-Br	OFF/DMS	AS/U	.	114	0.031-0.035	(Metay et al., 2007)
Madagascar	16	clayey	C-S	DMC/CT	NPK+U+M	B-SP	57.2	0.263-0.259	(Chapuis-Lardy et al., 2009)
Munich, Germany	17	fine_loamy	P	CT	.	.	74	0.63-1.61	(Flessa et al., 2002)

Munich, Germany	18	fine_loamy	P	CT	.	.	37	2-2.5	(Flessa et al., 2002)
Brisbane, Australia	19	sandy_clay_loam	SC	CT	NF/U/U+AN	B/B-SP	0-200	2.86-9.56	(Allen et al., 2010)
Suzhou, China	20	silt_clay	W	CT	C+NPK+U/NPK+U/NF	.	191	6-9	(Yao et al., 2010)
Suzhou, China	20	silt_clay	R	CT	C+U/U/NF	.	191	1.4-7.8	(Yao et al., 2010)
Wuxi, China	21	loam_clay	R	CT	U+WS/NF	.	250	1.2-2.9	(Yao et al., 2010)
Wuxi, China	21	loam_clay	W	CT	NPK+U/NF	.	180	2.1-5.6	(Yao et al., 2010)
Jiangdu, China	22	sandy_loam	R	CT	NPK+WS+U/NPK+U/NF	.	250	0.5-1.6	(Yao et al., 2010)
Jiangdu, China	22	sandy_loam	W	CT	NPK+U/NF	.	225	0.9-2.2	(Yao et al., 2010)
Jiangdu, China	22	sandy_loam	R	CT	NPK+WS/NPK+U/NF	.	250	0.8-2.9	(Yao et al., 2010)
Munich, Germany	23	silt_loam	P/W/C/CTR	CT	U/NF	.	0-180	0.292-6.932	(Ruser et al., 2001)
Shanxi, China	24	silty_clay_loam	CTT	CT	U	.	66.3	2.6	(Liu et al., 2010)
Minnesota, USA	25	sand	P	CT	DAP+U+AN/SRNF	BC-SP/BC	270	0.83-1.36	(Hyatt et al., 2010)
Colorado, USA	26	clay_loam	C/C-DB/C-B	CT/NT	SRNF/U/IN	.	151-246	0.525-2.3	(Halvorson et al., 2010)
Tsukuba, Japan	27	clay_loam	C	CT	NF/SRNF/U	B/B-SP/BC-SP	0-250	0.125-.544	(Yan et al., 2001)
Fredericton,Canada	28	silt_loam	C	CT	AN	BC/B-SP/B/BC-SP	52	1.95	(Zebarth et al., 2008)
Maulde, Belgium	29	clay	C-WW	CT/RT/NT	AN+U+M	.	24.7-150	2.3-2.8	(Boeckx et al., 2011)
Michigan, USA	30-32	loamy/fine_loamy	C	CT	U	BC	0-225	0.348-5.21	(Hoben et al., 2011)
Shanxi, China	33	clay_loam	C-WW	CT	U	.	0-850	1.5-5.57	(Liu et al., 2012)
Costa Rica	34	loam	C	NT	NPK+U	.	0-122	0.51-1.83	(Crill et al., 2000)
Iowa, USA	35	silty_clay_loam	C	CT	M+UAN	.	175-370	5.29-12	(Jarecki et al., 2009)
Jokioinen, Findlandia	36	clay/loamy_sand	B	CT	AN	.	100	3.4-7.5	(Syväsalo et al., 2004)
Saskatchewan, Canada	37	sandy_clay_loam	B	NT	U	B	0-120	0.02-0.23	(Malhi et al., 2006)
Madrid, Spain	38	clay_loam	B	CT	Organic	BC	125	0.27-0.35	(Meijide et al., 2009)
Québec, Canada	39	clay	C-S	CT/NT	AN	B-SP	0-160	5.8-9.8	(Pelster et al., 2011)
Vihti, Finlandia	40	clay	B	CT	AN+Slurry/AN/Slurry	B/B-SP/BC/BC-SP	100-157	0.29-11	(Perälä et al., 2006)
Denmark	41	loamy_sand	B	CT/NT	AN	BC	100-117	0.29-0.89	(Chatskikh and Olesen, 2007)

Woodlseen, Canada	42	clay_loam	C	CT/NT	U/SRNF	.	152	1.19-9.19	(Drury et al., 2012)
New Delhi, India	43	loam	R-WW	CT/NT	SRNF	SP	0-120	0.31-0.87	(Bhatia et al., 2010)

† CC, Continues corn; CS, Corn soybean; CSW-V, Corn-soybean/wheat-hairy vetch; ChC, Chinese cabbage;C-WW, Corn-Winter Wheat; W-C, Wheat-Corn; C-S-W, Corn soybean wheat rotation; B, Barley; R-Br, Rice-brachiaria rotation; P, Potato; SC, sugar cane; CTT, cotton; R, Rice; R-WW, Rice-winter wheat; W, wheat; CTR, control (grass);C-DB, corn-dry beans rotation; C-B, corn-barley rotation.

‡ NT, No-till; CT, Conventional till; RT, reduced till; DMC, Direct seedling mulch-cover crop.

§ AN, Ammonium Nitrate; C, Compost; M, Manure; GM, green manure; AP, Ammonium Poliphosphate; U, Urea; AA, Anhydrous Ammonia; NF, No-fertilizer; IN, Urease or nitrification inhibitors; SRNF, Slow-release N fertilizer; CAN, Calcium ammonia nitrate; DA, Diammonium; DAP, Diammonium phosphate; AS, Ammonium sulfate; NPK, compound fertilizer; WS, wheat straw, UAN, Urea and ammonium nitrate solution.

¶ BC, broadcast; BC-SP, broadcasted and split application of N; B-SP, banded and split application of N.

Total N_2O-N lost during the growing season

Table 2.2 ANOVA table of the exponential regression models evaluating the relation N input (kg ha^{-1}) N_2O-N emissions (kg ha^{-1}yr^{-1})

Model	Factor	numDF	denDF	F-value	p-value	AIC	BIC	logLik	N	R^2
Linear	β_0	1	171	11.83677	<0.001	781.383	752.395	-386.691	212	
	β_1	1	171	64.08538	<0.0001					
Null	β_0	1	171	0.84278	0.3599	742.966	763.1055	-365.483	212	
	β_1	1	171	74.59807	<.0001					
Complete	β_0.(Intercept)	1	133	0.05836	0.8095	668.1495	801.8429	-294.0748	209	0.495
	β_0.Nsource	7	133	3.28443	0.003					
	β_0.crop	14	133	5.91106	<.0001					
	β_0.soil	14	133	2.5117	0.0033					
	β_0.till	1	133	3.28863	0.072					
	β_1	1	133	62.83589	<.0001					
Reduced	β_0.(Intercept)	1	136	0.46506	0.4964	660.2643	794.5278	-290.1322	212	0.509
	β_0.Nsource	7	136	5.458	<.0001					
	β_0.crop	14	136	6.26448	<.0001					
	β_0.soil	14	136	2.80052	0.0011					
	β_1	1	136	51.62133	<.0001					

Chapter 3 - Impact of N management strategies on N_2O emissions on tillage systems.

Abstract

Over 85% of anthropogenic N_2O emissions are associated with N enrichment of agricultural soils. There are opportunities for improved management strategies for reducing N_2O emissions in agricultural systems. The objective of this study was to assess N_2O emissions from different N management strategies under long-term and short-term tillage systems. N_2O emissions were evaluated since summer of 2008 on a Kennebec silt loam soil (fine-silty, mixed, superactive, mesic Cumulic Hapludolls). Four management strategies were evaluated: a) Tillage: till and no-till; b) Fertilizer type: Compost, Urea, and coated-urea; c) N placements: broadcast, and banded at three depths (0, 5 and 10 cm, respectively), and d) Timing: Split application of Urea. Short-term and long-term no tillage had similar N_2O emissions. Differences in no-tillage could be attributed to differences in inorganic N content and surface residues rather than the time under no-till. Overall, conventional till and no-till were not significantly different. Banded application of N increased the overall N_2O emissions by 30% compared with broadcast N application. In general synthetic N fertilizers increased N_2O emissions more than organic fertilizers, but changes in organic fertilizers characteristics such as C:N ratio could increase N_2O emissions. Enhanced efficient N fertilizer such as slow-release N-fertilizer and split application of N reduced N_2O emissions without affecting yield and N uptake.

Introduction

Nitrogen, one of the most important nutrients in the living systems, cycles through plants, soil, water, and atmosphere in agroecosystems. Plants require availability of mineral N (NH_4^+ and NO_3^-) in the root zone. Available N comes from internal N cycling and external inputs. Nitrogen mineralization during decomposition of soil organic matter generates NH_4^+, and microbially-mediated nitrification converts NH_4^+ to NO_3^-. Fertilization, N fixation, and atmospheric decomposition comprise external inputs. Leaching and runoff of dissolved nitrogen, erosional loss, gaseous losses from NH_3 volatilization and denitrification, and removal of N in plant tissues at harvest represents losses. Through N immobilization, soil microbes compete with the plants for available nitrogen in the soil (Li et al., 2001).

The N lost by N_2O emissions has a great importance in agriculture as it affects N use efficiency and impacts the environment. No-till adoption has been an important practice for C sequestration but its benefits can be offset by increased N_2O emissions (Six et al., 2002). The effect of long-term no-tillage on N_2O emissions may vary considerably with soil type, climate, management practices and their effect on litter accumulation and soil bulk density (Grandy et al., 2006).

Six et al. (2004) modeling greenhouse gases emissions found that in humid climates, the conversion from conventional tillage to no-till changed N_2O emissions by 3.8, 1.1 and -4.2 kg ha^{-1} day^{-1} after 5, 10, and 20 years. The N_2O emissions in no-till systems evaluated by Petersen et al. (2008) are consistent with Six et al. (2004). The shift from a N_2O source to sink could result from protection of organic N in absence of soil disturbance (Oorts et al., 2007a) or soil compaction that enhances the reduction of N_2O to N_2 by reducing gas diffusivity (Ball et al., 1999). At early stage of no-till implementation litter C accumulation at the soil surface could increase N immobilization or promote N_2O emissions (Baggs et al., 2003; Grandy et al., 2006). After 11 years of N_2O measurements, Grandy et al. (2006) did not find evidence of increasing N_2O production after no-till conversion. Several studies suggest that N_2O emissions were increased following no-till conversion on fine-textured soils (Aulakh et al., 1984; MacKenzie et al., 1997; MacKenzie et al., 1998; Ball et al., 1999; McConkey et al., 2008; Baggs et al., 2003). Rochette (2008) concluded that there would be greater probability of higher N_2O emissions in no-till than conventional tillage on poorly-aerated soils in humid climates. Well-drained soil tend to have lower N_2O emissions. No significant N_2O emission were found between no-till and till on a sandy-loam soils by Elmi et al. (2003). Bavin et al. (2009) did not find significant differences between short-term no-till and till until the N was applied in which NT had lower emissions than till. Bavin et al. (2009) conclude that N fertilization was the primary factor regulating N_2O fluxes in till and no-till treatments.

Six et al. (2004) concluded that due to the high radiative forcing (or warming potential) of N_2O, greater N_2O fluxes could offset the benefits of C sequestration and CH_4 uptake, during the first 5 to 10 years of adopting NT in both humid and dry climates. However after 20 y, the net GWP was negative.

Soil structure is one of the primary drivers on N_2O emissions. Six et al. (2004) and Grandy et al (2006) emphasized the improvement of soil structure (soil aggregation and associated soil physical properties) with time after conversion to no-till.

Understanding the interaction of tillage, N fertilization practices, soil, crops and climate is critical when investigating the impact of management practices on N_2O emissions. The objective of this work was to evaluate the effect of tillage and N management strategies on N_2O emissions in a long-term and short-term tillage experiments.

Methodology

Study site

Three experiments were conducted in a long-term and a short-term tillage-N experiment in corn (*Zea mays*) at the Kansas State University Agronomy North Farm (39°11'30"N, 96°35'30"W; elevation 325 m). Annual mean precipitation is 843mm yr^{-1}, annual mean temperature is 12.9°C, and the soil is a well-drained Kennebec silt loam (fine-silty, mixed, superactive, mesic Cumulic Hapludolls). Soil characteristics are described in Table 3.1.

Experiment I

N_2O-N emissions were measured from corn growing seasons 2009 to 2011. The treatments evaluated in the long-term experiment (established in 1990) were no-till (NT) and till (T) systems with two different types of fertilization (composted farmyard residues (C) and urea (F, 46%N)) at a rate of 168 kg N ha^{-1}. The T system included fall chisel plow and spring offset disk (Table 3.2).

Experiment II

Different N managements were evaluated during 2009 -2011 growing seasons. A polymer-coated urea (CU, 44%N), surface banded urea (SB), subsurface banded urea (SUB[5 cm depth]), and split application of Urea (SP) were evaluated under the long-term till and no-till systems. In season 2011, a sub-surface banded application of urea was evaluated (SUB [10 cm depth]) (Table 3.2). In the SU treatment 50% (84 kg N ha^{-1}) was applied 10 days after planting and 50% 47 days after planting.

Experiment III

A newly established no-till corn field was established on the same soil adjacent to the long-term study. These two sites bracket 18-20 and 2-3 yr no till environments.

Four fertilizer managements and a control (No Nitrogen) were evaluated during 2008: Broadcast (BC), surface (SB), and sub-surface urea application (SUB [5cm depth]). An additional treatment (slow-release N fertilizer [CU, 44%N]) was tested in 2009. In 2010, treatments evaluated were broadcast (BC), surface banded (SB), split-urea (SP) and a control treatment (Table 3.1). The SP was applied at the same rate and time as applied in experiment II.

Nitrous oxide flux measurements

The N_2O-N fluxes were calculated following the method of Hutchinson and Mosier. (1981), Ginting et al. (2003) and Bremer (2006). Briefly, the flux measurements were taken by placing vented chambers on polyvinylchloride (PVC) tubing (20 cm diam. x 10 cm height) inserted ~5cm into the soil and collecting gas samples after 0, 15, and 30 min (C_0,C_1 and C_2, respectively) during midmorning of each sampling day (Fig. 3.1). Air samples were collected weekly or after rainfall events during the growing season. The 20 mL gas samples were transported to the laboratory in 12-mL evacuated tubes sealed with butyl rubber septa (Exetainer vial, Labco Ltd). Concentrations were determined by gas chromatography (Model GC 14A; Shimadzu, Kyoto, Japan) equipped with a ^{63}Ni electron capture detector and a stainless steel column (0.318-cm dia. by 74.5 cm long) with Poropak Q (80-100 mesh, Shimadzu, Kyoto, Japan).

If the gas concentration inside the chamber steadily increased or decreased with time ($C_0<C_1<C_2$ or $C_0>C_1>C_2$) in a non linear trend the flux was calculated following Hutchinson and Mosier (1981) equation:

$$f_0 = kd\left(\frac{273}{T}\right)\frac{V(C_1-C_0)^2}{At_1(2C_1-C_2-C_0)}\ln\left(\frac{C_1-C_0}{C_2-C_1}\right), \text{ if } \ln\left(\frac{C_1-C_0}{C_2-C_1}\right)>1$$

where *fo* is the flux rate (g ha^{-1} day^{-1}), k is the unit of conversion that is equal to 144000, and d is gas density at 273.15 K and 0.101 MPa pressure equal to 1.25 $x10^{-3}$ g cm^{-3}, T is the air temperature (K), V is the volume within the chamber (cm^3). A is the area occupied by the chamber (cm^2), C is the gas concentration in ppm [v/v]. Gas density was calculated based on the assumption that 1M of air occupied 22.414 L-volume at 273.15K and 0.101 MPa.

If the gas concentration increased or decreased with time and the ratio $\ln\left(\frac{C_1 - C_0}{C_2 - C_1}\right) \leq 1$, then the flux was calculated following Ginting et al (2003) approach:

$$f_0 = kd\left(\frac{273}{T}\right)\frac{V}{A}\left[\frac{\Delta C}{\Delta t}\right]$$

where $\frac{\Delta C}{\Delta t}$ is the average rate of the change of concentration between C_1-C_0 and C_2-C_1.

When gas concentrations fluctuated with time ($C_0<C_1>C_2$ or $C_0>C_1<C_2$), this indicated that the flux within 30 minutes was inconsistent (emission followed by uptake or vice versa). So that $\frac{\Delta C}{\Delta t}$ is the average rate of change of concentration C_1-C_0 and C_2-C_0.

A weighed-area function was used to calculate the fluxes from banded N applications. For the banded treatments in 2008 the control treatment was used for the off-band N_2O emissions. For banded treatments in 2009 and 2010 a second ring in each experimental unit was used for the off-band N_2O emission (Fig. 3.1). The final daily flux on banded treatments was calculated based on the following equation.

$$f_0 = 0.21R_{on-band} + 0.79R_{off-band}$$

where $R_{on-band}$ refers to the N_2O emissions from fertilized band and $R_{off-band}$ refers to N_2O emissions determined outside fertilized band. The constants 0.21 and 0.79 refer to the proportion of the area occupied by the ring on the fertilizer band and the remaining non fertilized area, respectively in a total area of 0.15 m^2 (0.75 m [between rows distance] x 0.2 m [diameter of ring])

Cumulative nitrous oxide flux calculations

Once the flux was calculated for each plot and sampling time, linear integration was used to estimate the total N_2O emitted during the study period for each treatment.

$$Cumulative\, N_2O(g\ N\ ha^{-1}) = \sum_{i}^{n} \frac{(X_i + X_{i+1})}{2}(t_{i+1} - t_i)$$

where, X_i was the initial N_2O-N flux (g $ha^{-1}day^{-1}$) reading, and X_{i+1} was the next reading at times t_i and t_{i+1}, respectively; n was the last N_2O-N flux estimated during the study period.

Ancillary measurements

Throughout the growing season several soil samples (0-5 cm) were collected for determination of NO_3-N and NH_4-N concentrations. Daily precipitation and average air and soil temperatures were collected at a nearby meteorological station. Soil temperature (5 cm) was measured at the time of gas sampling using a digital soil temperature probe. Surface water content (0-5 cm) was also measured at the time of gas flux measurement.

Grain yield and Nitrogen uptake

Grain and stover yields were estimated by counting and harvesting two rows (3.05 m each) in the center of each sampling plot. The grain yield is reported in terms of grain weight at 155g kg^{-1} water content, and stover yield was expressed on dry weight basis. Grain and stover N concentration were determined by dry combustion using a C-N Elementar Analyzer (Flash EA1112, Carlo Erba Instruments, Milano, Italy).

Experimental Design

The experimental design for the experiment I and II (2009 and 2010) was a split-plot design with whole-plots randomly assigned into each of four blocks and repeated measurements in time. The mixed model used to analyze the daily N_2O-N, NO_3-N and NH_4-N data sets with repeated measures from experiment I and II (season 2009 and 2010) was:

$$y_{ijkl} = u + b_i + T_j + N_k + T*N_{jk} + p_{ij} + t_l + T*t_{jl} + N*T_{kl} + T*N*t_{jkl} + \varepsilon_{ijkl}$$

where y_{ijkl} is the daily N_2O-N emissions (g N $ha^{-1}d^{-1}$), NO_3-N or NH_4-N concentrations (µg N g^{-1}); u the intercept; b the block, ; T_j tillage effect; N_k the N management effect; $T*N_{ij}$ the tillage and N management interaction; p_{ij} is the main plot effect within block; t_l the time effect (Day of year, DOY); $T*t_{jl}$ is the tillage and time interaction; $N*t_{kl}$ the N management and time interaction; $T*N*t_{jlk}$ the interaction tillage, N management and time; and ε_{ijkl} the random experimental error.

The mixed model used to analyze the seasonal N_2O-N, yield, grain and stover N content (kg N ha^{-1}), data sets from experiment I and II (season 2009 and 2010) was:

$$y_{ijk} = u + b_i + T_j + N_k + T*N_{jk} + p_{ij} + \varepsilon_{ijk}$$

where y_{ijk} is the total N_2O-N emissions (kg N ha^{-1}), yield (kg ha^{-1}), grain and stover N (kg N ha^{-1}); μ the intercept; b the block ; T_j tillage effect; N_k the N management effect; $T*N_{jk}$ the tillage and N management interaction; p_{ij} is the main plot effect within block; and ε_{ijk} the random experimental error.

Experiment II (2011 season) and experiment III were randomized complete block designs with repeated measures in time and four replications (blocks). The mixed model used to analyze the daily N_2O-N, NO_3-N and NH_4-N data sets with repeated measures from experiment II (season2011) and experiment III was:

$$y_{ijk} = u + b_i + N_j + t_k + N*t_{jk} + \varepsilon_{ij}$$

where y_{ijk} is the daily N_2O-N emissions (g N $ha^{-1}d^{-1}$), NO_3-N and NH_4-N concentrations (µg N g^{-1}); μ the intercept; b the block; N_j the N management effect; t_k the time effect; $N*t_{jk}$ the N management and time interaction; and ε_{ijk} the random experimental error.

The mixed model used to analyze the seasonal N_2O-N, yield, grain and stover N concentrations, data sets from experiment II (2011) and III was

Experiment II (2011): $y_{ij} = u + b_i + T_j + \varepsilon_{ij}$

Experiment III: $y_{ik} = u + b_i + N_k + \varepsilon_{ik}$

where y_{ij} and y_{ik} is the total N_2O-N emissions (kg N ha^{-1}), yield (kg ha^{-1}); μ the intercept; b the block ; T_j tillage effect; N_k the N management effect; and ε_{ij} the random experimental error for Experiment II (2011); and ε_{ik} the random experimental error for Experiment III.

Measurements taken on the same plot over time were assumed to be correlated. A set of covariance structures were used which included the first order autoregressive, first order autoregressive with heterogeneous variances and unstructured. The final analysis was reported based on the covariance structure that minimized Akaike information criterion (AIC) and Bayesian information criterion (BIC).

The analysis of variance (ANOVA) was performed using proc Mixed from SAS 9.2 (SAS Institute, 2010). For all the tests, $P \leq 0.05$ was consider to indicate a statistically significant difference, unless otherwise stated.

Results

Environmental factors

Total precipitation during growing seasons (May-October) 2008, 2009, 2010 and 2011 was 870 mm, 588 mm, 551 mm and 457 mm, respectively. Soil temperature during early growing season (May) was around 20°C, middle of the season (June-July) soil temperature registered around 24-26°C, and end of seasons (August- Sep) around 16-25°C.

Experiment I: Tillage, Urea and Compost effects

N_2O emissions

The N_2O emissions were sensitive to the interaction of soil inorganic N and soil moisture, represented by fertilization and precipitation events (Fig. 3.2) in which N application and precipitation events were the main N_2O emission drivers. In the season 2009 there was a significant interaction between tillage type and N source. In terms of the seasonal estimated mean daily fluxes T-F had the highest daily N_2O-N flux (24.3 g N_2O-N ha^{-1} day^{-1}±5.3) which was not significantly different than NT-F (12.7 g N_2O-N ha^{-1} day^{-1}±3.1), marginally significant (p-value=0.06) from NT-C (10.3 g N_2O-N ha^{-1}day^{-1}±2.3) and significantly different from T-C (8.5 g N_2O-N ha^{-1} day^{-1}±1.9). Urea (F) had higher averaged daily N_2O-N emissions than organic fertilizer (C) that accounted for 18.5±3 and 9.4 ±1.5 g N_2O-N ha^{-1} day^{-1}, respectively. The first significant N_2O flux came at Day of Year (DOY) 123 (27.5± g N_2O-N ha^{-1} day^{-1}) after application of N (compost [DOY107] and urea [DOY119]) and two main precipitation events at DOY116 (76.2 mm) and DOY120 (21.8 mm) (Fig. 3.2 and Fig. 3.3) where WFPS reached almost 80%. The highest mean value of N_2O emission was on the DOY 155 (81±16 g N_2O-N ha^{-1} day^{-1}) which was not significantly different from DOY161 (71.8±19 g N_2O-N ha^{-1} day^{-1}) and DOY 168 (69±22 g N_2O-N ha^{-1} day^{-1}) (Fig.3.3). Several precipitation events between DOY150 and DOY168 accounted for 126 mm (Fig. 3.2).

The cumulative N_2O-N emissions showed that overall T-F treatment had the highest total emissions during the season accounting for 3.8±0.5 kg N_2O-N ha^{-1} followed by NT-F (1.8±0.5), NT-C (1.7±0.5) and T-C (1.4±0.5) (Fig.3.6). There were no significant differences detected between tillage type (p-value=0.22) nor fertility (p-value=0.0796) (Fig. 3.6).

A significant interaction of N source x DOY was detected in the growing season 2010. Two significant N_2O emissions were detected. The first started to increase significantly in the mineral fertilizer treatments (F) from DOY121 (12.3±2.4 g N_2O-N ha^{-1} day^{-1}) up to DOY141 (231 ±61 g N_2O-N ha^{-1} day^{-1}) after fertilizer was applied (urea [DOY119]), and the second one started on DOY153 (9.5±2 g N_2O-N ha^{-1} day^{-1}) and reached the maximum at DOY159 (212.1±57.8 g N_2O-N ha^{-1} day^{-1}) (Fig. 3.3). Besides fertilization events, rainfall events drove the first emission since the total precipitation accounted for 117 mm between DOY112 and DOY141 (Fig. 3.2 and Fig. 3.3). The second N_2O peak was triggered by a single precipitation event at DOY158 of 20.8 mm (Fig. 3.2 and Fig. 3.3). There were no significant emissions detected after compost application (DOY116). The highest N_2O emission in the compost treatment (C) was detected at DOY159 (102±58 g N_2O-N ha^{-1} day^{-1}) (Fig. 3.3). The cumulative N_2O showed a significant effect of N source (p=0.0079) but no an effect of tillage (p=0.79). Overall, the mineral fertilizer or urea (F) treatment had a total emission of 4.7±0.6 kg N ha^{-1} which was statistically significant than compost treatment (1.3±0.6 kg N ha^{-1}) (Fig. 3.6).

Season 2011 had the highest daily N_2O emissions among all growing seasons. Initial peaks were observed after N application (DOY119) (Fig. 3.3). High N_2O emissions were observed at DOY119 in compost treatments (107±34 and 115 g N_2O-N ha^{-1} day^{-1} for NT and T, respectively) (Fig. 3.3).

Precipitation events were registered at DOY125 (2 mm), DOY126 (5 mm) and DOY127 (9 mm) (Fig. 3.2). Those events plus recently fertilization may have triggered a N_2O emission of 200±78.2 g N_2O-N ha^{-1} day^{-1} from the no-till fertilized treatment (NT-F) and a emission of

537±78.2 g N_2O-N ha^{-1} day^{-1} from NT-C on DOY128 (Fig. 3.3). No significant differences between those two daily emissions were found. The WFPS around those days was maintained near 60% due to those consecutive precipitation vents (Fig. 3.2). During the following days (DOY128 to DOY137) the WFPS dropped below 40%, as result the emissions decreased significantly for NT-F and NT-C (Fig. 3.2).

The third event with high emissions occurred on DOY141 and DOY150 (Fig.3.3). Four precipitation events at DOY139 (14.2 mm), DOY140 (15.2 mm), DOY144 (30.2 mm) and DOY145 (34.5 mm) kept the WFPS between 60-80% (Fig. 3.2). A final N_2O emission (111±9.6 g N_2O-N $ha^{-1}day^{-1}$) was detected at DOY188 due to a precipitation event DOY188 (27.2 mm) (Fig. 3.3).

The cumulative emissions were significantly different between tillage treatments (8.1 ±0.8 kg ha^{-1}, and 4 ± 0.8 kg N ha^{-1} for no-tillage and tillage, respectively) and N treatments (8.6±0.8 kg N ha^{-1} and 3.5±0.8 kg N ha^{-1} for Compost [C] and urea [F], respectively) but there was no interaction between tillage and N treatments regarding total N_2O-N emission (Table 3.3).

Soil Inorganic N

A significant interaction between tillage and DOY was found during the growing season 2009 for NO_3-N. The NO_3-N concentrations were similar in T and NT after fertilization until DOY162 (Fig. 3.8a). From DOY177 NO_3-N concentration decreased until DOY 274. Ammonium (NH_4-N) concentration had a significant DOY effect in which the concentration significantly decreased during the growing season (Fig. 3.8b).

During the 2010 season, the concentration of NO_3-N in soil decreased from 86.8±11.5 µg N g^{-1} (urea [F]) and 80.4 ± 11.5 µg N g^{-1} (compost [C]) to 32.4±3.1 µg N g^{-1} (C) and 23.7±3.1 µg N g^{-1} (F) (Fig. 3.8a). Ammonium (NH_4-N) did not have any significant trend during the growing season. Overall, higher concentration of NH_4-N were found in C (2.1 ± 0.1 µg N g^{-1}) than F (1.6± 0.1µg N g^{-1}), and higher in NT (2.1±0.1 µg N g^{-1}) than T (1.5±0.1 µg N g^{-1}) (Fig. 3.8b).

In growing season 2011, NO_3-N concentration from the urea (F) treatment was higher (66.1±5.8 µg N g^{-1}) after N fertilizer application and lower concentration after harvesting DOY298 (18.7±6.3 µg N g^{-1}) (Fig. 3.8a). For the compost (C) treatments the trend was similar until DOY178, with a value of NO_3-N concentration after fertilization of 94.6±7 µg N g^{-1} and reaching a minimum of 30±3.8 μg N g^{-1} at the end of the season (Fig. 3.8a). No significant effect of tillage, N source and DOY was observed on NH_4-N soil concentrations.

Experiment II: N management and tillage effect

N_2O emissions

The daily emissions did not have significant interactions among tillage, N placement and sampling time (DOY). There were no differences between tillage (T and NT) and N placement treatments of surface (SB, 0 cm) and subsurface N application (SUB, 5 cm) during the first year of study (2009) (Fig. 3.4). The daily emissions of N_2O were significant among the sampling dates (DOY) which were clearly related to precipitation events at DOY166 (44.9mm) and DOY167 (14.5 mm) (Fig. 3.2 and Fig. 3.4). All treatments had the highest emissions at DOY 168 (13 days after N fertilization) (Fig. 3.4). In terms of cumulative emissions a marginal difference of $P<0.1$ were found between SUB and SB where the cumulative N_2O-N emissions were 2.5±0.5 and 1.8±0.5 kg N ha^{-1}, respectively (Fig. 3.6).

In the growing season 2010, several treatments were evaluated in order to minimize the N_2O emissions from corn. From previous findings (season 2009) we concluded that the banded application of N either at 0 cm or 5 cm depth had the same effect on N_2O emissions, and no tillage effect. In this second year of this study several management N strategies were evaluated: a surface banded N fertilizer (SB), a polymer-coated urea product (CU) and a split application of urea (SP). The treatments had a similar response in the till systems evaluated (T and NT) (No significant interaction among tillage, treatment and sampling day [DOY]). The interaction treatment and sampling day (DOY) was significant. The initial N_2O-N emissions were between 10 and 30 g N_2O-N ha^{-1} d^{-1} (Fig. 3.4). The first significant emission was detected after a precipitation of 6 mm (DOY145) at DOY146 in SB (50.5±22.4 g N_2O-N ha^{-1} d^{-1}) and SP (112±34 g N_2O-N ha^{-1} d^{-1}) but not in CU (19±4.5 g N_2O-N ha^{-1} d^{-1}) (Fig. 3.4). The second event of N_2O emission occurred at DOY160 and remained high until sampling day DOY167 in the three treatments (CU, SB and SP) (Fig. 3.4). Several precipitation events accounted for 112 mm. The highest peaks during that time frame belonged to SB (677±233 g N_2O-N ha^{-1} d^{-1}) and SP (406±145 g N_2O-N ha^{-1} d^{-1}) significant different from CU (121±34 g N_2O-N ha^{-1} d^{-1}) (Fig. 3.4). At DOY173 emissions from SB (184± g N_2O-N $ha^{-1}d^{-1}$) and SP (129± g N_2O-N $ha^{-1}d^{-1}$) were significantly reduced, while emissions from CU treatment (129±56 g N_2O-N ha^{-1} d^{-1}) did not change significantly (Fig. 3.4). The second application of urea (DOY173) in split N treatment (SP) followed by 60.5 mm of rain in DOY184 and DOY185 triggered a pulse of 88±22 g N_2O-N $ha^{-1}d^{-1}$ at DOY188 (Fig. 3.2 and Fig. 3.4).

Despite the high differences in magnitude among the treatments, the cumulative values of each treatment were not significant (p-value=0.05). SB had the highest annual emissions in T and NT (12.6±2.9 and 5.8±2.9 kg N ha^{-1}, respectively), followed by SP (7.6±2.9 and 4.8±2.9 kg N $ha^{-1}day^{-1}$ for T and NT, respectively) and CU (4.0±2.9 and 3.4±2.9 kg N ha^{-1}day) (Fig. 3.6).

To test if deeper application of N would reduce the high fluxes observed under surface application, a sub-surface banded (SUB [10cm]) application of N was evaluated during the third growing season (2011).

The 2011 season sub-surface (SUB) application of urea was evaluated at 10 cm depth in NT and T systems (Fig. 3.4). No significant interaction between tillage and DOY was found. High N_2O emissions were found between DOY141 (185±60 g N ha^{-1} day^{-1}) and DOY154 (277±60 g N $ha^{-1}day^{-1}$) after 100 mm of rain (DOY151-DOY153) (Fig. 3.2). The average daily N_2O-N flux was higher in T-SUB (81±22 g N ha^{-1} day^{-1}) than NT-SUB (31±6 g N ha^{-1} day^{-1}). The cumulative emission was not significantly different between treatments (Fig. 3.6).

Soil inorganic N

Concentrations of NO_3-N and NH_4-N were not significantly affected by treatments in 2009 season. High concentrations of NO_3-N appeared at DOY177 (176±23 µg g^{-1}) once the treatments were applied. Before fertilizations the concentration was 20±2.4 µg N g^{-1}. At the end of the season the concentration of NO_3-N was 22.5±1.3 µg N g^{-1}. NH_4-N concentrations increased with fertilizer application (2.7±0.1 µg g^{-1}), remained statistically similar until the end of growing season (3.4±0.4 µg g^{-1}) (Fig. 3.9a). During 2010, the NO_3-N concentrations had a significant interaction between treatment and sampling day (DOY). SB (289±41.2 µg N g^{-1}) and SP (179.5±41.2 µg N g^{-1}) had similar concentrations of NO_3-N which were significantly different than CU (112.8±41.2 µg N g^{-1}) after fertilizer application. At the end of the season the NO_3-N concentrations from CU (22.1±3.1 µg N g^{-1}), SP (21±3.1 µg N g^{-1}) and SB (17.5±3.1 µg N g^{-1}) had significantly decreased (Fig. 3.9a). No significant changes were detected for NH_4-N concentrations (Fig. 3.9b).

A significant interaction between tillage and sampling day was found in growing season 2011. NO_3-N concentrations increased up to 138.1±49 µg N g^{-1} in no-tillage (DOY158) and up to 108±46 µg N g^{-1} in till treatment (DOY172) after fertilizer application. At the end of season the concentration of NO_3-N were 9.6±1.6 µg N g^{-1} and 14.6±1.6 µg N g^{-1} for no-tillage and tillage, respectively (Fig. 3.9a). NH_4-N concentrations were not significant different throughout the season (Fig. 3.9b).

Experiment III: Effect of short-term no-tillage management on N_2O emissions

N_2O emissions

Significant daily emissions were found during 2008 growing season where the highest emissions occurred at DOY201 for SUB and SB treatments (205±52 and 195±52 g N ha^{-1} day^{-1}) which were significantly different from the broadcast (BC) and control (C) treatments (34±52.3 g N $ha^{-1}day^{-1}$ and <0 g N ha^{-1} day^{-1}, respectively). The control and BC treatments did not have significant temporal changes throughout the season with average emissions of 3.2±6.4 g N ha^{-1} day^{-1} and 4.7±6.4 g N ha^{-1} day^{-1}, respectively (Fig. 3.5).

Cumulative N_2O-N emissions had significant treatment effect in which SB (1.9±0.3 kg N ha^{-1}) and SUB (2±0.3 kg N ha^{-1}) were significantly different than the C (0.5±0.3 kg N ha^{-1}) and BC (0.5±0.3 kg N ha^{-1}) (Fig. 3.7).

During season 2009 there was a significant interaction between treatment and sampling time. The highest emissions were detected in DOY168 in treatments BC, SUB and SB with N fluxes of 376±167, 167±80 and 90±46 g N ha^{-1} day^{-1}. Slow-release N fertilizer (CU) and control (C) had average emissions of 10.4±2.3 and 1.6±0.5 g N ha^{-1} day^{-1}, respectively (Fig. 3.5). Significant treatment effect was found for cumulative N_2O-N emissions were BC (3.7 ±0.6 kg N ha^{-1}) had the highest N_2O-N emission followed by SUB (1.7±0.6 kg N ha^{-1}), SB (1.4±0.6 kg N ha^{-1}), CU (0.9±0.6 kg N ha^{-1}) and C (0.2±0.6 kg N ha^{-1}) (Fig. 3.7).

Several pulses of N_2O-N emissions were observed during the growing season 2010 influenced primarily by precipitation events as observed in previous experiments. The highest daily emissions were produced on DOY169 for most treatments following several days of rain (DOY162 [19.5mm], DOY163 [44.4 mm], and DOY166 [4.06 mm]) (Fig. 3.2 and Fig. 3.5). No significant differences among the treatments were found for that sampling day. Initial growing season emissions increased significantly in treatment BC on DOY148 and in treatments CU, BC and SB on DOY 169. SP emissions were similar in magnitude throughout the growing season, there was no detected a significant pulse after application of the second half of fertilizer in DOY174 (Fig. 3.5). The cumulative N_2O-N emissions were significantly different between the N management treatments (CU, SP, BC, and SB) and the control (C). The cumulative emissions from CU, SP, BC, SB and C were 2±0.2, 2±0.2, 1.4±0.2, 1.1±0.2, and 0.2±0.2 kg N ha^{-1}, respectively (Fig. 3.7).

Inorganic Nitrogen

The highest concentrations of NO_3-N were reached after fertilization in all years (Fig. 3.10a). In 2009 high concentrations of inorganic N in BC, SB, SUB and CU were not significantly different from each other. In 2010, higher concentrations of NO_3-N were observed after fertilization events and a second higher concentration for SP after the second application of urea (Fig. 3.10a).

Grain yield, N uptake and N_2O emissions as a function of yield and N uptake

In all the experiments a reduction in precipitation in 2010 and 2011 reduced yields and overall N uptake (Table 3.3, 3.4, 3.5). Tillage and N management did not significantly affect yield and N uptake in the long-term tillage study (Experiment I, Table 3.3). N_2O-N emissions as a function of yield and grain N uptake had significant differences in growing season 2011 between compost (C) and urea (F) (Table 3.3) due to the increased N_2O emissions and reduction in yield during 2011 growing season. In the experiment II, where several N management practices were tested (Table 3.2) no significant differences were detected in any agronomical variables described in Table 3.4. The practices proposed for N_2O-N reduction from agricultural system did not affect the yield and N uptake. Reduction in precipitation during the growing season reduced yield, but did not reduce N_2O emissions.

In the short-term no-tillage experiment (experiment III) the yield decrease from 2008 to 2011 was due to reduction in precipitation. The N management did not have a significant effect on yield in 2008 and on yield and N uptake in 2009 (Table 3.5). Cumulative emissions in 2009 from BC were significantly higher. In 2010 the cumulative emissions did not differ among treatments but the yield and N uptake was significantly higher in split-urea (SP) and polymer-coated urea (CU) treatments (Table 3.5).

Discussion

N_2O-N emissions responded to N inputs and precipitations events. Overall, the first pulse of N_2O came between 4 and 18 days after fertilization which depended on the wetness of the soil at the moment of fertilizer application. For example, in the long-term experiment (Experiment I 2011, Fig.3. 3) the first flux appeared 9 days after urea application, while in the experiment II (2011, Fig. 3.4) the first N_2O flux appeared 18 days after urea application. The cumulative precipitation of five days before N application was 12.7 mm in experiment I, and no precipitation events were recorded in experiment II.

It is known that denitrification and N_2O production increase with increasing WFPS, reaching maximum N_2O emission at WFPS values between 60 and 75% and maximum denitrification occurs at saturation (Davidson et al., 1986; Almaraz et al., 2009) (Fig. 3.2). It is possible that the high pulses of N_2O-N observed after precipitation events were associated with denitrification, however the development of anaerobic micro-sites permits both nitrification and denitrification occurs simultaneously (Davidson et al., 1986). The highest rates of N_2O production should occur under microaerophilic conditions, when N_2O reduction in the nitrification process is inhibited by O_2 and when the nitrifiers, limited in their use of O_2 as electron acceptor, also form N_2O (Klemedtsson et al., 1988).

No significant N_2O emissions between T and NT were found in seasons 2009 and 2010 (Experiment I) and 2011 (Experiment II), however drier soils in 2011 (Experiment I) had an overall effect on tillage, where no-till had higher N_2O emissions that conventional till (T) during the high emission period (Fig. 3.3). Several studies had found similar results where the magnitude of N_2O emissions in till and no-till systems were governed by the soil water content (Drury et al., 2006; Almaraz et al., 2009; Boeckx et al., 2011). However, the impact of no-till on N_2O emissions can have a positive or negative response based on mainly in the soil texture and climate conditions (Rochette et al., 2008).

Besides the type of fertilizer used, the distribution of precipitation played a key role on N_2O emissions (Jacinthe and Dick, 1997; Almaraz et al., 2009). For example, in the long-term tillage experiment (Experiment I), the compost fertilizer in 2009 season had similar results to the 2010 season, but the emissions were contrasting to the season 2011. The emissions in compost in 2011 were higher than 2009. Both years had similar fertilizer application dates and N rate but the cumulative precipitation between the application date and the first pulse of N_2O-N was different. In 2009 the cumulative precipitation accounted for 107.7 mm while in 2011 was 59.2 mm.

A complete denitrification process might have taken place during 2009 (Experiment I) due high WFPS (~ 80%) due to precipitation after compost application (high N_2:N_2O ratio). Above 80% WFPS, O_2 becomes limited and restriction to gas diffusion are high that N_2O is fully reduced to N_2 before escaping the soil (Davidson et al., 1986; Almaraz et al., 2009; Boeckx et al., 2011; Gagnon et al., 2011). In 2011 high precipitation events were not observed prior first N_2O-N flux, although two events were recorded at DOY112 (21.3mm) and DOY 115 (12.7 mm). Following those precipitation events high N_2O emissions were observed at DOY119 and DOY128 (Fig. 3.3). It is possible that incomplete denitrification process might have taken place (low N_2:N_2O ratio). A similar pattern was found by Drury et al. (2006) in which the degree and frequency of wet soil conditions prior to N application explained the differences in N_2O emission between two growing seasons. Bateman and Baggs (2005) found that increasing the WFPS between 60 and 70% resulted in significant increasing in N_2O emissions under laboratory conditions.

In addition to soil water status, the difference in N_2O emissions between seasons may be related to the organic fertilizer composition as well. The compost used in 2011 had higher total N and C content (1.77% and 12%, respectively) than the compost used in 2009 (0.9% and 5.62%, respectively) and 2010 (1.1% and 8.4%, respectively). More available carbon from organic fertilizer decomposition can enhance N losses through denitrification (Drury et al., 2006). Soil denitrification is strongly influenced by the supply of water-soluble or readily decomposable organic matter or available carbon (Miller et al., 2012). The low emissions from compost treatments in 2009 and 2010 (Experiment I) may be due to lower water-soluble C, available C or readily decomposable organic C in the compost.

In 2011 the NO_3-N concentration in soils from the compost treatments (C) was higher that urea treatment (F) after harvest. The NO_3-N concentration remained high but no N_2O emissions were detected due to low WFPS (Fig. 3.2). Boeckx et al. (2011) attributed the lack of N_2O emissions when the NO_3 concentrations were high to a low WFPS and becoming sub-optimal for denitrification in a silt loam soil.

N_2O emissions from the long-term tillage (Experiment II, 2010) and the short-term no-tillage (Experiment III, 2010) were different in magnitude despite similarities in weather condition, soil type and N management. One possible explanation was the contrasting amount of residues found in each experiment prior to fertilization. Higher amounts of residues in experiment III were observed than experiment II during 2010, which could affect the proper contact of fertilizer and soil enhancing N losses after heavy rain (66 mm of rainfall during the next five days after N application). On the other hand, high amount of residues from previous year and high soil moisture content (WFPS~80%) following N application could have triggered denitrification process and higher N_2:N_2O ratio in experiment III than experiment II.

Overall, soil inorganic N in experiment II during 2010 was higher than experiment III after N application (Fig. 3.7, 3.8). This could help to explain the contrasting results regarding N_2O emissions. The yield and N uptake values were similar between experiments (Table 3.4 and 3.5).

A significant difference (p-value<0.1) was found in 2009 between cumulative N_2O emission of SUB and SB in experiments II and III. It seemed that denitrification was more important as N_2O source at deeper N application in our study. It may be possible that O_2 availability decreased with depth (Breitenbeck and Bremner, 1986; Drury et al., 2006). Our results contrast with results from Fujinuma et al. (2011) where shallower N application may have stimulated nitrification-derived N_2O production in soils fertilized with anhydrous ammonia. In Fujinuma et al. (2011) WFPS during the period of greatest N_2O emissions were generally below 50%, while in our study WFPS was >60% (Fig. 3.2). The magnitude of N_2O emission in BC from the long-term experiment (Experiment I and II) was lower than surface banded (SB) or sub-surface banded (SUB) treatments. Surface N application tended to reduce total N_2O-N emissions without affecting crop productivity. In the short-term no-till experiment (Experiment III), BC had lower emissions than banded in 2008, higher emission in 2010, and no significant emission in 2011. Beside soil water content influencing the high fluxes, there was high inorganic N in the BC treatment in 2010 that could have enhanced emissions (Fig. 3.10).

High N_2O emissions in the banded zones have been attributed to high concentrations of NH_4 and elevated pH after application of Anhydrous Ammonia (AA) (Fujinuma et al., 2011; Gagnon et al., 2011a). Urea hydrolysis also increases pH and may increase NH_3, which is toxic to many microorganism, especially nitrite (NO_2^-)-oxidizing bacteria that carry out the second step of nitrification (Fujinuma et al., 2011). Under our conditions N_2O could have been produced by nitrifier denitrification (Wrage et al., 2001; Bateman and Baggs, 2005) or /and by coupled nitrification-denitrification processes (Wrage et al., 2001). In wetter soils, the amount of N_2O derived from nitrifier denitrification was less than 3% (Wrage et al., 2001). Wetter conditions during the high emission period with high NO_3-N could support the second pathway. However, nitrification, denitrification, and nitrifier denitrification may occur simultaneously in different microsites of the same soil but there is uncertainty associated with which process predominates in a particular soil (Davidson et al., 1986; Bateman and Baggs, 2005). Applying urea at broadcast reduces the concentration of N per area since the prills are distributed over approximately 10 times the area compared with banded application of AA (Fujinuma et al., 2011). Burton et al. (2008) did not find differences between banded urea and AA, which we could infer that banded urea could have the same effect of AA localizing high concentration of NH_4 . However, urea requires dissolution and hydrolysis before NH_4/NH_3 is released to the soil (Fujinuma et al., 2011).

The use of slow-release N fertilizer such as polymer-coated urea (experiment II, 2010 and experiment III, 2010) or Nitamin (experiment III season 2009) and split application of urea seemed to be promising practices for reduction of N_2O without affecting significantly the agronomic variables (yield and N uptake, Table 3.3,3.4,3.5). Halvorson and Del Grosso, (2013) stressed that the small differences in yield comparing enhanced-efficient N fertilizer or additional practices such as split application of urea to traditional source and methods of fertilization may be limited by economic constraints unless producers are compensated for using them based on the environmental benefit. Taking into account that corn is an important crop in Kansas agriculture, the appropriate selection of N source and methods of placement could significantly reduce the impact of N_2O emissions.

Conclusions

Cumulative N_2O emissions in the short-term no-till and long-term no tillage experiments were not different when similar treatments were evaluated in both systems, opposite as reported in some studies (Ball et al., 1999; Baggs et al., 2003; Six et al., 2004; Petersen et al., 2008).

Conventional till and no-till were not significantly different in most of the growing seasons. Banded application of N tended to enhance N_2O emissions.

In general synthetic N fertilizers increased the N_2O emissions more than organic fertilizers, but changes in characteristics of the organic fertilizers could increase N_2O emissions.

Enhanced efficient N fertilizer or slow-release N-fertilizer and split application of N reduced the N_2O emissions without affecting yield and N uptake.

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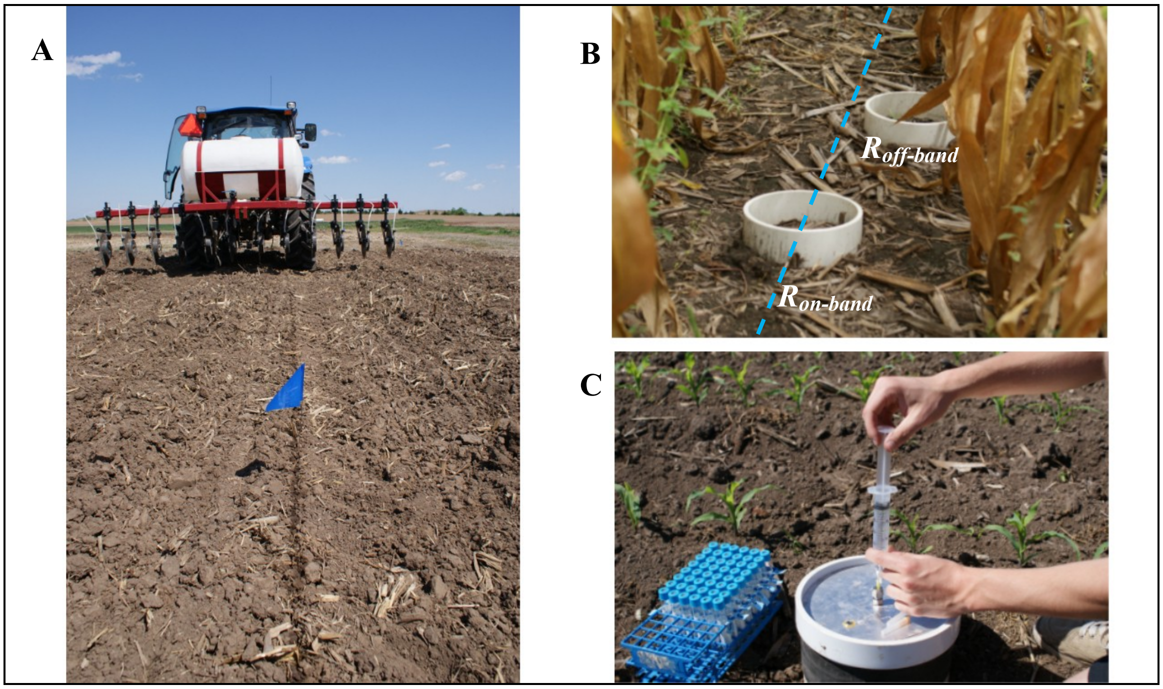


Figure 3.1. (A) Banded N application, (B) Location of rings in surface banded fertilization treatments. $R_{on\text{-}band}$ rings placed on fertilizer bands and $R_{off\text{-}band}$ refers to rings placed outside fertilizer band, and (C) Chamber-base technique for gas sampling.

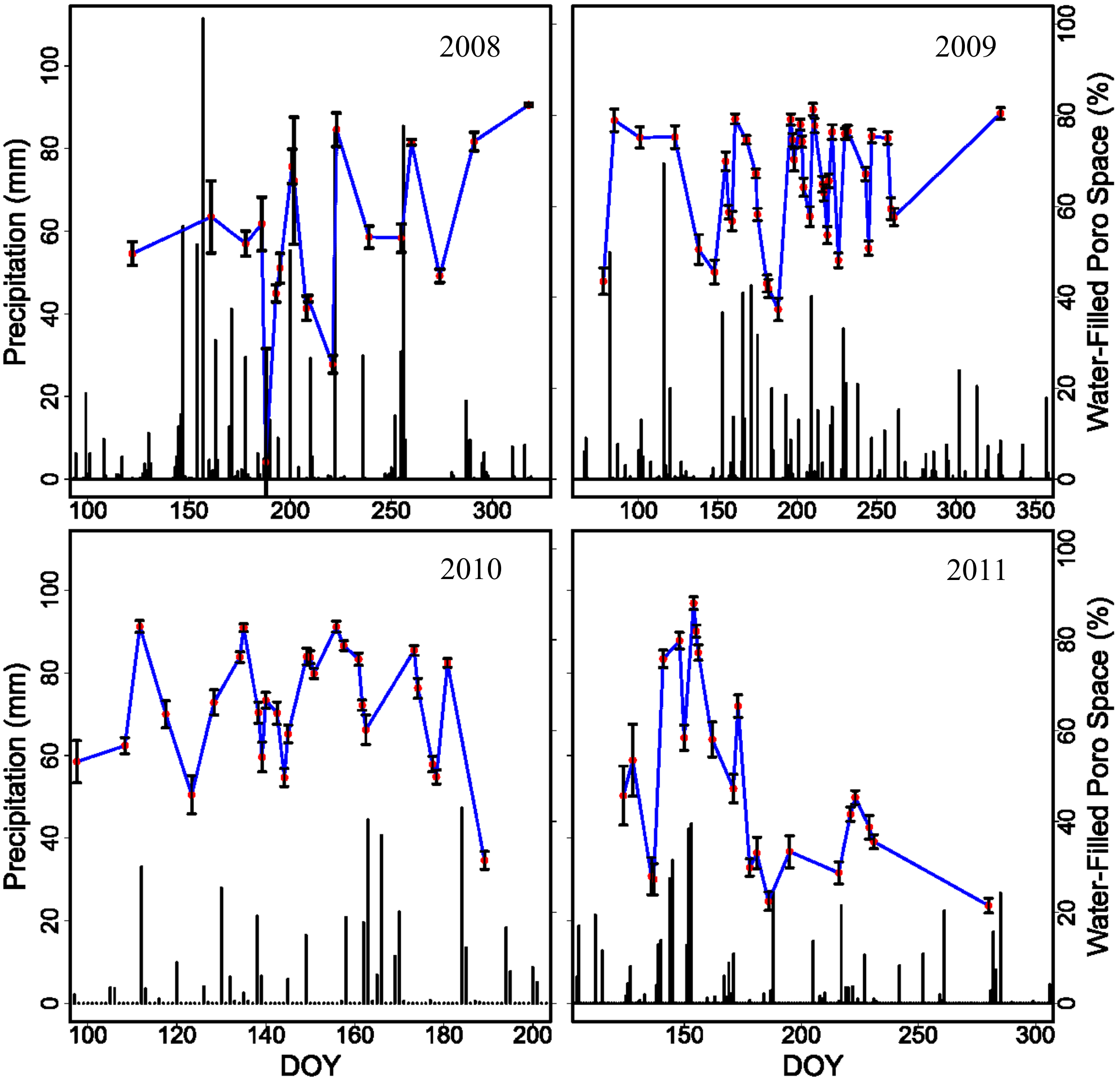


Figure 3.2. Precipitation (mm) and water-filled pore space (%) recorded during the period of study

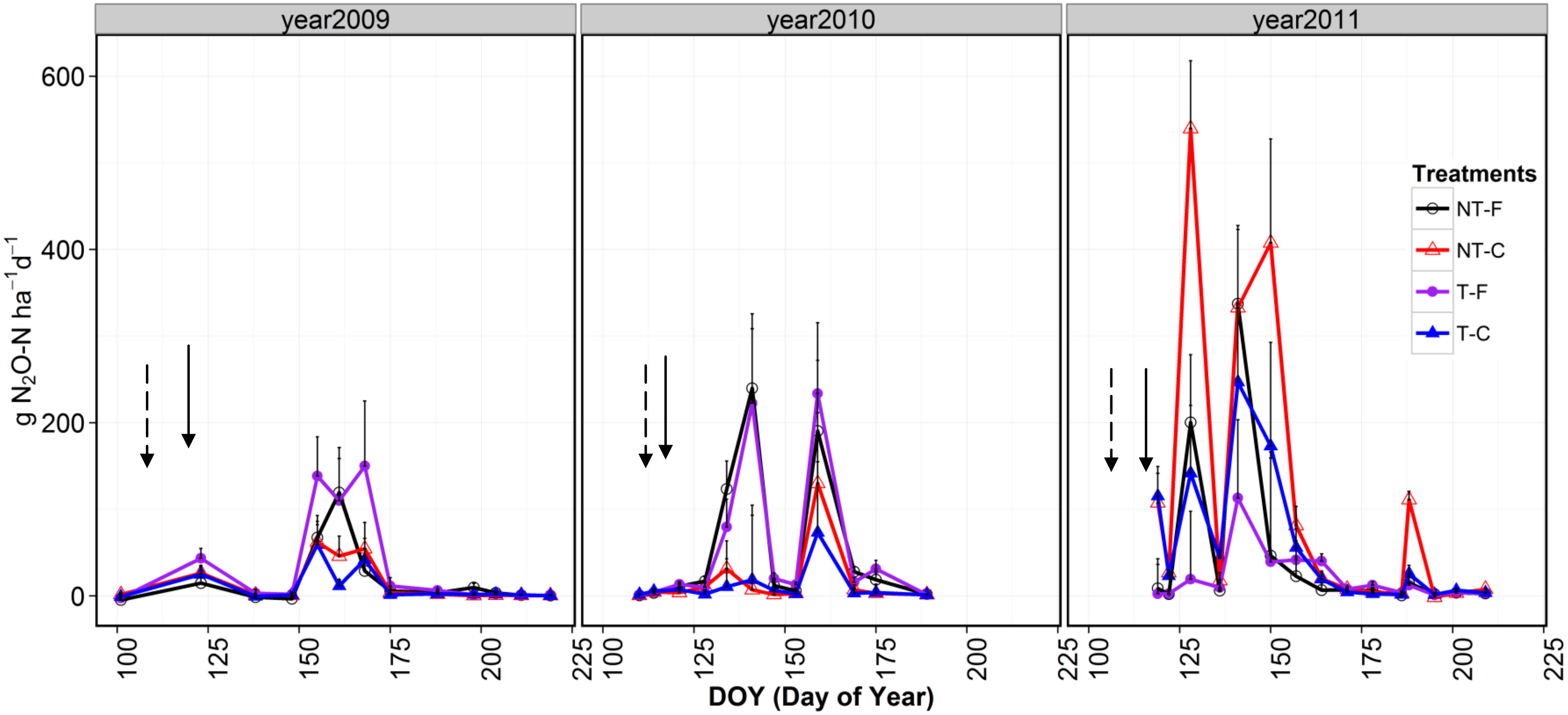


Figure 3.3. Daily N_2O emissions from T and NT systems under compost (C) and Urea (F) (Experiment I). Arrows indicate management operations. Dashed: Application of compost, Solid: Application of urea

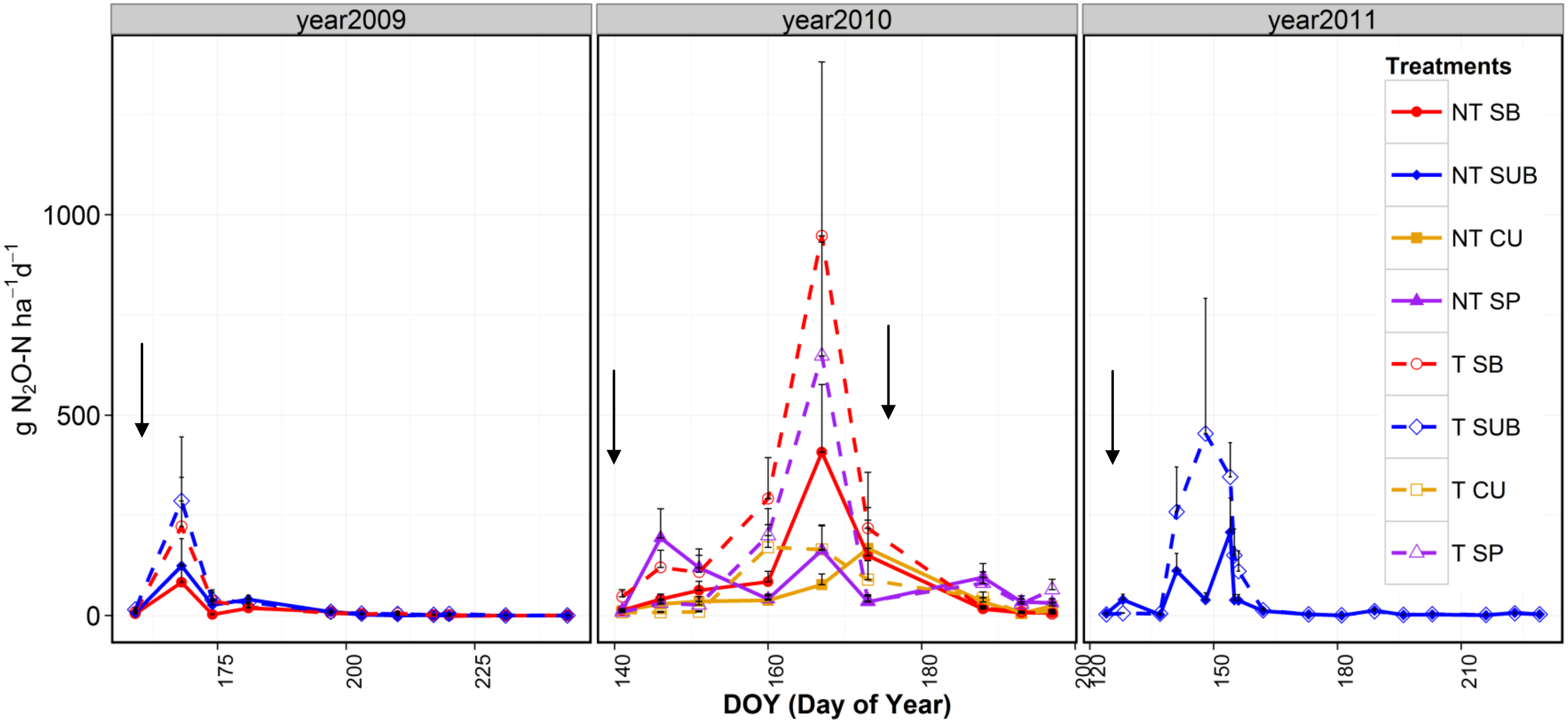


Figure 3.4. Daily N_2O-N emissions from experiment II. Tillage represented by dashed lines and No-tillage represented by solid lines. Different colors represent the treatments as follows: Red circle is the surface banded (SB), blue rectangle is the sub-surface application of N at 5cm depth (SUB) except 2011 which was applied at10cm depth, orange square is the polymer-coated urea and purple triangle is the split application of N (SP).

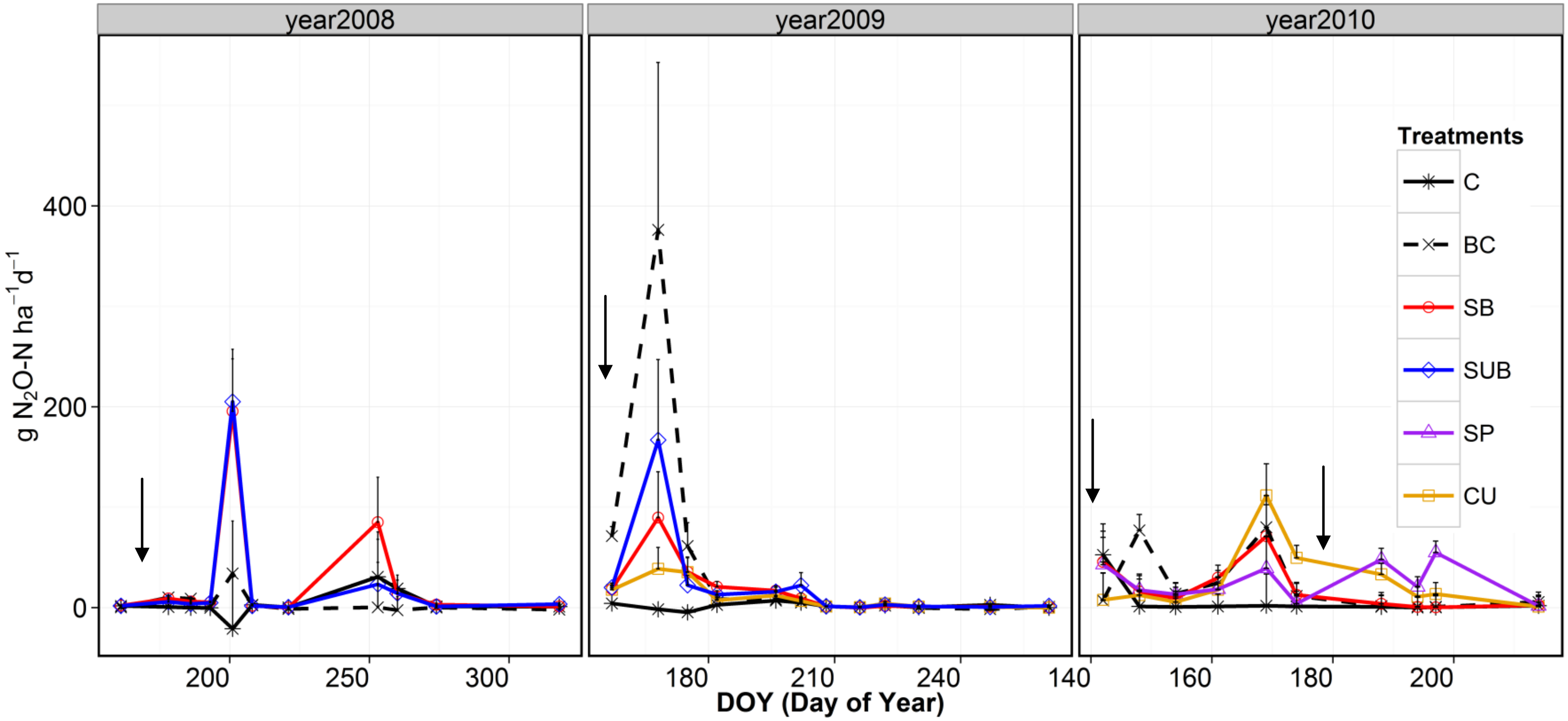


Figure 3.5. Daily N_2O-N emissions from the short-term no-tillage experiment under different management strategies (Experiment III). BC: Broadcast N application, C: Control (No fertilizer), SB: Surface banded N application, SUB: Sub-surface N application (5cm), CU: Nitamin in 2009 and polymer-coated urea in 2010

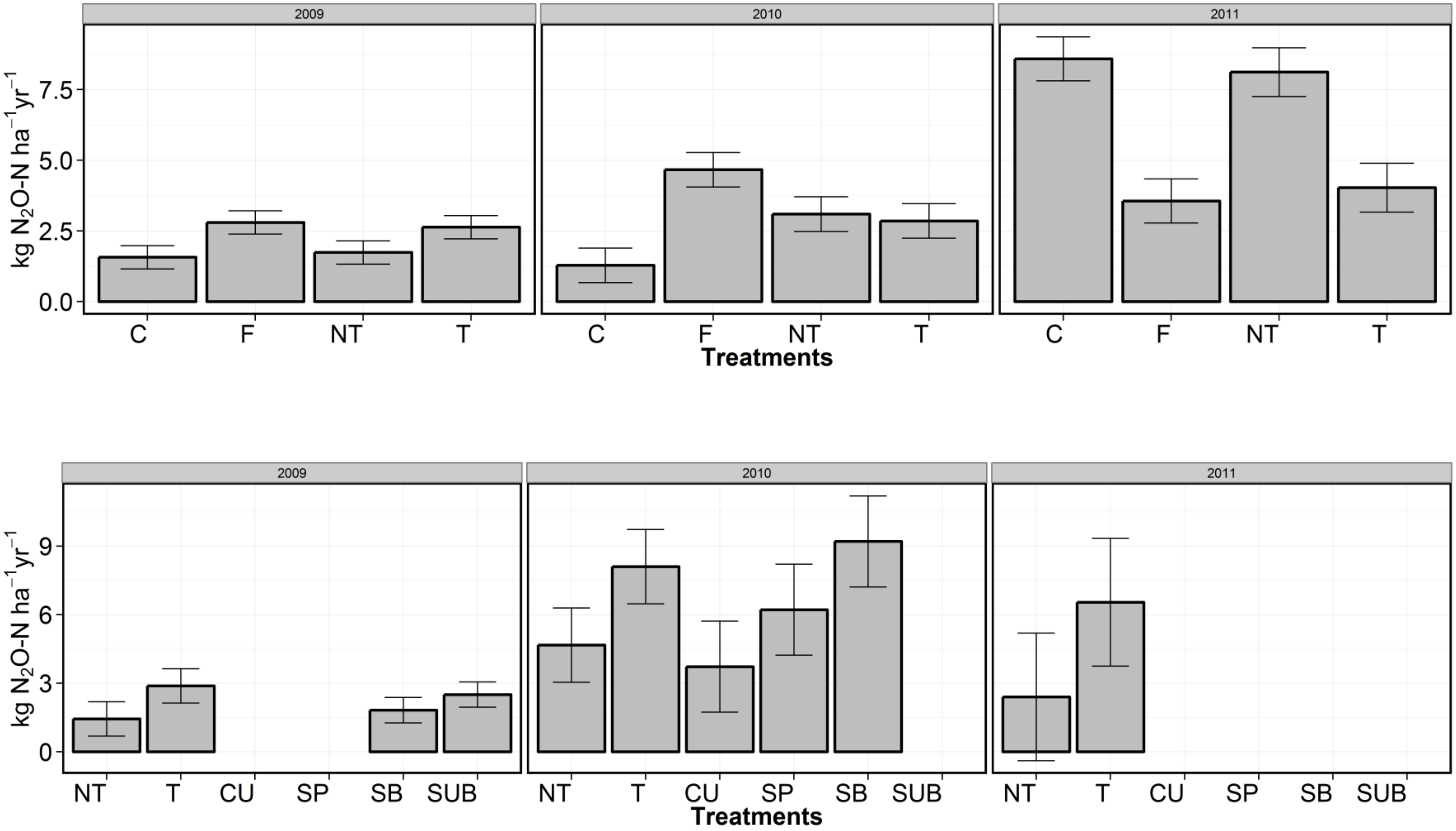


Figure 3.6. Cumulative N_2O-N emissions –Long-term no-tillage experiment I (upper panel) and II (lower panel). Growing season 2009, 2010, and 2011.

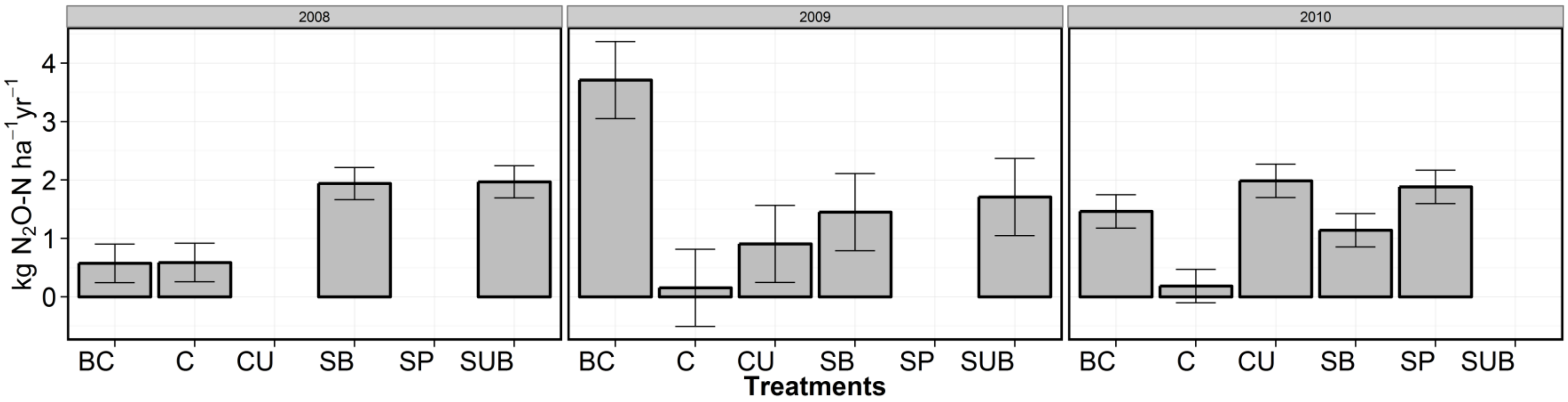
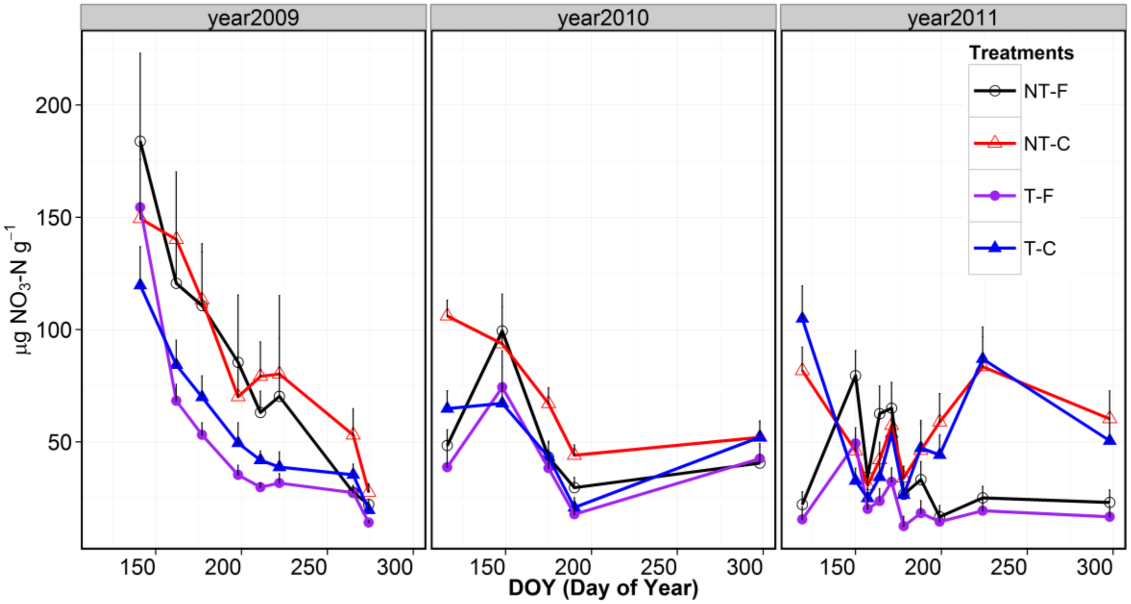


Figure 3.7. Cumulative N_2O-N emission in the short-term no-till experiment –Experiment III. Growing season 2008, 2009, and 2010.

a)



b)

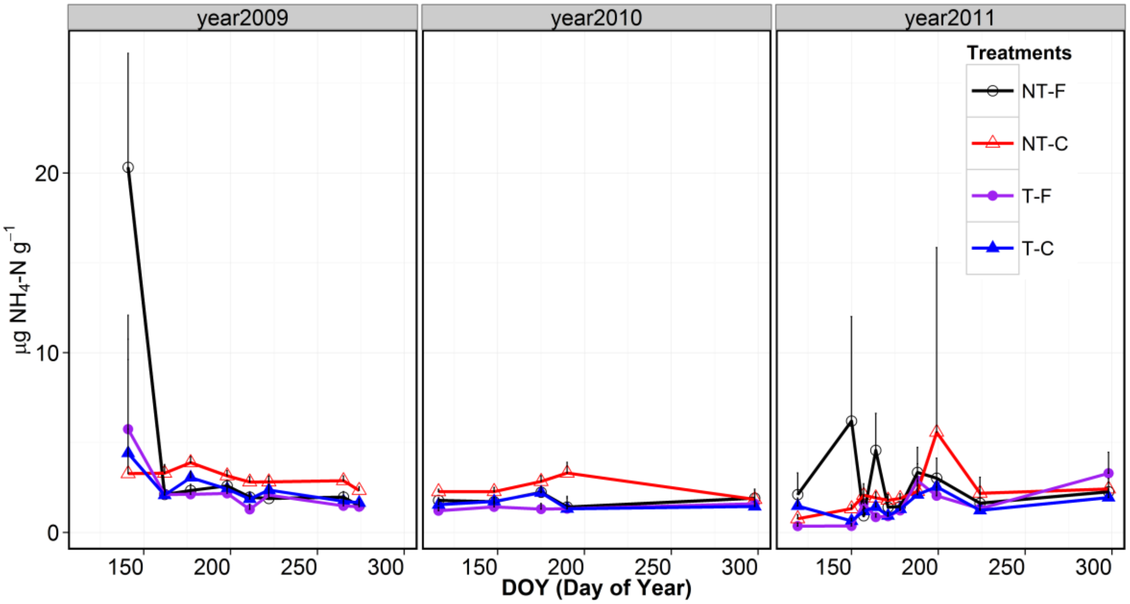


Figure 3.8. a) NO_3-N and b) NH_4-N content in soil during growing season in the long-term tillage experiment (Experiment I).

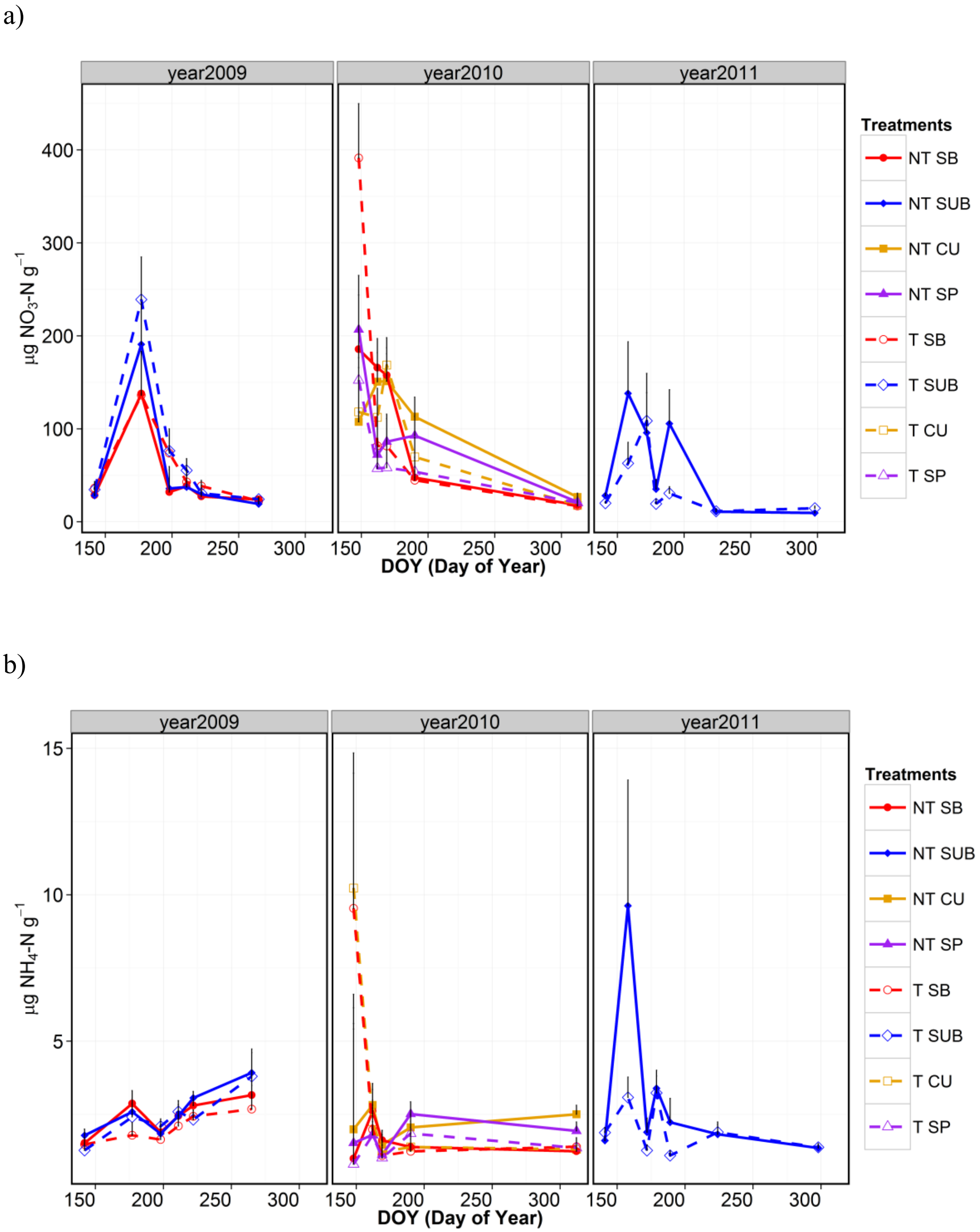


Figure 3.9. a) NO_3-N and b) NH_4-N content in soil during growing season in the long-term tillage experiment (Experiment II).

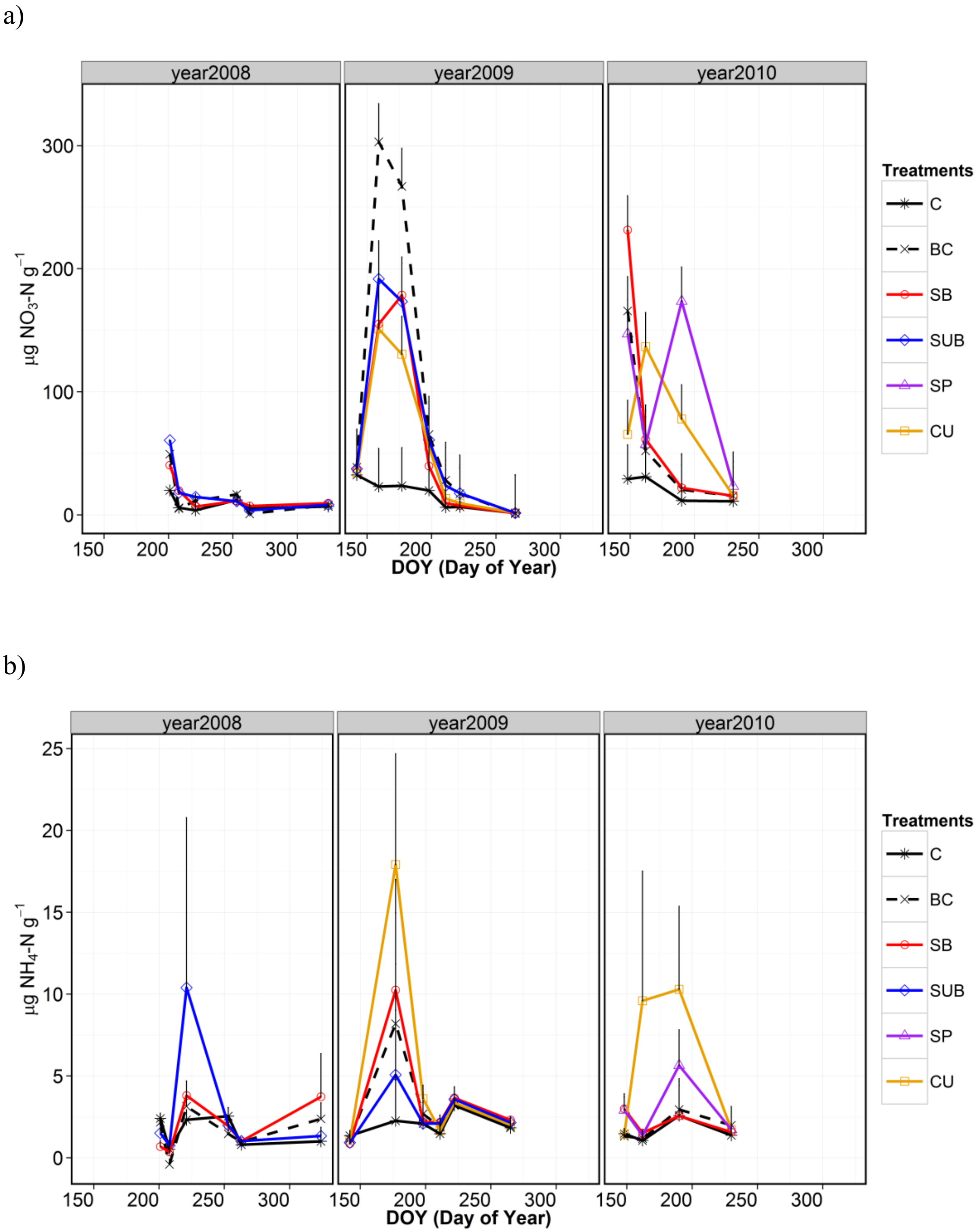


Figure 3.10. a) NO_3-N and b) NH_4-N content in soil during growing season in the short-term tillage experiment (Experiment III).

Table 3.1. **Soil chemical characteristics at 0-5cm depth**

Soil Type	pH	Mehlich-P mg kg^{-1}	CEC† cmol(+)kg^{-1}	Sand† (%)	Silt† (%)	Clay† (%)
Mollisol						
Till	7.2	286	17.1	10	70	20
No-till	6.9	356	18.4	12	68	20

† Adapted from Fabrizzi et al. (2009)

Table 3.2. **Management practices for evaluation N_2O-N emissions in corn**

Experiment	Description	Year	Tillage	Nitrogen management		
				N source	N placement	No. of fertilizer applications
Experiment I	Long-term tillage experiment	2009	Till, No-till	F, C	BC	1
		2010	Till, No-till	F, C	BC	1
		2011	Till, No-till	F, C	BC	1
Experiment II*	Long-term tillage experiment	2009	Till, No-till	F	SB, SUB	1
		2010	Till, No-till	F, CU	SB	2-SP
		2011	Till, No-till	F	SUB†	1
Experiment III	Short-term no-till experiment	2008	No-till	F	BC,SB,SUB	1
		2009	No-till	F, CU‡, C§	BC, SB, SUB	1
		2010	No-till	F, CU,C§	BC, SB	2-SP

F: Urea, **C**: Compost, **CU**: polymer-coated urea, ‡ **CU**: Nitiamin, **BC**: Broadcast, **SB**: Surface, **SUB**: Subsurface 5 cm depth, † **SUB**: Subsurface application 10cm depth, § **C**: Control, **SP**: split applications of urea, two applications of N fertilizer (50% after planting and 50% at the growing stage V6 of corn).

Table 3.3. Effect of tillage and N-management on cumulative N_2O-N emissions, grain yield, N uptake, and N_2O emission per unit of biomass N uptake in experiment I.

								N2O-N emissions		
Year	Tillage	N manage-ment	Total N_2O-emissions	Grain yield	Grain N uptake	Residue N uptake	Total N uptake	per unit of grain	per unit grain N uptake	per unit total N uptake
			g N ha^{-1}	kg ha^{-1}	kg N ha^{-1}			g N Mg^{-1}	g N kg^{-1}	
2009	NT		1740 a†	9001 a	72.1	75.6	147.6	195.5	23.5	12.3
2009	T		2630 a	8566 a	74.8	61.1	135.9	399.3	53	26.8
2009		F	2803 a	8077 a	66.2	57.7	123.8	421.7	55.4	28.7
2009		C	1572 a	9494 a	80.7	78.9	159.6	173	21.1	10.3
2010	NT		3096 a	4190 a	49.9	32.5	82.4	712.2	63	37.9
2010	T		2855 a	5009 a	50.1	34.4	84.6	897.5	87.6	45.9
2010		F	4667 a	4783 a	51.2	34.1	85.3	1302.2	123.6	67.9
2010		C	1284 b	4416 a	48.9	32.8	81.6	307.5	26.9	15.9
2011	NT		8119 a	4538 b	49.4	46.2	95.6	2338.9	211.1	87
2011	T		4031 b	4830 a	57.7	69	126.7	1749.7	139.9	34.4
2011		F	3562 b	4986 a	56.6	46.4	103	973.4 b	86.3 b	43.1
2011		C	8589 a	4382 a	50.5	68.8	119.3	3115.2 a	264.7 a	78.4

† Different letters represent significant differences at probability level of 5%

Table 3.4. Effect of tillage and N-management on cumulative N_2O-N emissions, grain yield, N uptake, and N_2O emission per unit of biomass N uptake in experiment II (No detected significant differences at probability level of 5%).

								N_2O-N emissions		
Year	Tillage	N manage ment	Total N_2O-N emissions	Grain yield	Grain N uptake	Residual N uptake	Total N uptake	per unit of grain	per unit grain N uptake	per unit total N uptake
			g N ha^{-1}	kg ha^{-1}		kg N ha^{-1}		g N Mg^{-1}		g N kg^{-1}
2009	NT		1437	7438	50.6	71.7	110.7	191.8	7.7	4.4
	T		2886	6623	79.0	59.0	135.2	619.3	52.1	26.9
		SB	1820	6104	74.9	74.3	146.7	443.9	34.8	16.5
		SUB	2504	7957	54.7	56.5	99.2	367.2	24.9	14.8
2010	NT		4667	3991	51.5	28.0	79.8	1265.7	92.3	56.8
	T		8099	5014	50.3	26.4	76.6	2132.9	227.9	110.8
		CU	3725	3495	39.7	28.3	68.4	1736.1	165.1	58.0
		SB	9207	5802	65.2	27.4	92.7	1522.3	143.4	97.5
		SP	6217	4210	47.8	25.8	73.6	1839.5	171.7	95.9
2011	NT	SUB	2401	5245	51.6	23.4	75.0	465.3	45.9	32.6
	T	SUB	6542	5746	60.9	26.5	87.5	1015.2	95.0	62.9

Table 3.5. Effect of tillage and N-management on cumulative N_2O-N emissions, grain yield, N uptake, and N_2O emission per unit of biomass N uptake in experiment III.

												N_2O-N emissions			
Year	N Management	Total N_2O-N		Grain yield		Grain N uptake		Residual N uptake		Total N uptake		per unit grain yield		per unit grain N uptake	per unit total N uptake
		g N ha^{-1}		kg ha^{-1}		kg N ha^{-1}						g N Mg^{-1}		g N kg^{-1}	
2008	BC	574	b†	8291	a	ND ‡		ND		ND		76.1	b	ND	ND
	C	588	b	3802	b	ND		ND		ND		104.7	b	ND	ND
	SB	1939	a	8502	a	ND		ND		ND		230.0	a	ND	ND
	SUB	1969	a	7911	a	ND		ND		ND		243.6	a	ND	ND
2009	BC	3712	a	11195		110.5		115.7		220.5		334.2		36.1	17.5
	C	154	b	7762		69.2		51.2		148.0		11.3		10.1	4.5
	SB	1450	b	8382		85.0		78.5		175.5		178.0		29.0	13.9
	SRNF	906	b	8523		82.8		63.5		166.0		143.0		21.4	12.0
	SUB	1709	ab	8704		75.9		77.4		167.0		193.0		29.0	13.6
2010	BC	1464	a	3846	bc	33.3	ab	19.8	bc	53.0	ab	445.6		56.4	38.0
	C	186	b	500	d	2.0	c	14.2	c	19.7	c	657.7		15.4	2.2
	CU	1986	a	4772	ab	44.4	a	27.7	ab	72.1	ab	416.3		43.7	27.4
	SB	1140	a	3163	c	24.2	b	22.7	ab	46.9	bc	398.9		53.1	24.2
	SP	1884	a	5089	a	46.8	a	29.7	a	76.5	a	376.3		41.8	24.6

† Different letters represent significant differences at probability level of 5%

‡ No determined

Chapter 4 - Sensitivity analysis, calibration and validation in modeling N_2O: Application to DNDC for corn production

Abstract

When time scales differ between measurements (e.g., biweekly) and model simulations (e.g., daily), the results are compared through aggregating to a common time scale. However the variation in model results are not clearly documented for different aggregation methods. This study attempts to document the variation in modeling results using three methods of aggregation in sensitivity analysis (SA), calibration, and validation of modeled N_2O emissions for combinations of fertilization and management. Daily N_2O emissions were modeled using the Denitrification–Decomposition (DNDC) model, and values were compared with measurements available at biweekly time scale. Although the DNDC model is used as an example, the techniques described can be applied to many modeling problems in different locations at multiple time scales. The three aggregation methods used in this study were two parametric methods (mean [MN] and cumulative [CM]) and third a nonparametric method (median [MD]). Further, sensitivity analysis of all the 38 parameters was carried out using three methods (two graphical and one sensitivity index). Soil pH, temperature, clay fraction, soil organic carbon, bulk density, NO_3 and NH_4 in Rainfall, maximum yield, filed capacity, and thermal degree days were found to be the sensitive parameters in the study. The model efficiency (ME) and R^2 in the calibration and validation steps were higher using the MN approach specially for the conventional tillage and urea treatments.

Introduction

The atmospheric concentration of N_2O has increased by 18% since 1750, from a pre-industrial value of about 270 ppb to 319 ppb in 2005, a concentration that has not been exceeded during the last thousand years (Forster et al., 2007). Agricultural soil management such as N application and other cropping practices produced approximately 69% of N_2O in the United States in 2009 (USEPA, 2011). Direct measurement of N_2O emissions for inventory purposes is impractical because many measurements would be required over large areas and for long periods of time (Stange et al., 2000; Giltrap et al., 2010). Quantification of these emissions from soil is needed for global modeling studies in the context of ecosystem modification and climate change (Li et al., 1997; Pathak et al., 2005); therefore, process-based modeling of N_2O is necessary (Du et al., 2011). Some models couple decomposition and denitrification processes as influenced by the soil environment to predict emissions from agricultural soils and help better understand and quantify soil sources of N_2O (Li et al., 1992a).

Past direct measurements are at a coarser time scale than the modeled N_2O emissions, which causes a mismatch in time scales that introduces a source of uncertainty. This study uses a case study to address the uncertainties while performing model sensitivity analysis (SA), calibration, and validation. An N_2O simulation model is used here as an example, but the techniques described can be applied to many different modeling problems.

Sensitivity analysis (SA) is important in process-based ecosystem models because these models contain complex nonlinear mathematical equations, and it is a research needed in many terrestrial ecosystem models that address C and N cycling (Larocque et al., 2008). A large number of methods are used to perform SA and can be broadly divided into two main categories: local sensitivity methods (e.g., parameter perturbation method, differential analysis) and global sensitivity analysis (e.g., Fourier amplitude sensitivity test, regional sensitivity analysis, adjoint sensitivity method, Monte Carlo analysis) (Yongtai and Lei, 2008). Most studies in SA assume parameter independence and explore the individual impacts of each parameter on each system response taken one at a time (Bastidas et al., 1999). Although SA is important, very few studies have addressed it in modeling N_2O in general and the Denitrification–Decomposition (DNDC) model in particular (Table 4.2).

The DNDC model was originally developed to simulate N_2O emissions from cropped soils in the U.S. (Li et al., 1992a; Li et al., 1992b; Li et al., 2000; Li et al., 2004; Li et al., 2011). It has since been used and expanded by many research groups covering a range of countries and production systems (Giltrap et al., 2010). The parameters in the model can be broadly classified into four categories: climate, soil, crop, and management (Table 4.1). SA of all the parameters is computationally challenging and is a lengthy process. The details of the studies that have addressed SA for the DNDC model for soils under both agriculture and forest conditions are given in Table 4.2, and the parameters are briefly discussed below. Earlier studies have focused on sensitivity of (1) a few climate parameters such as temperature, precipitation, CO_2 concentration in the atmosphere, and N deposition (Li et al., 1996; Zhang et al., 2002; Abdalla et al., 2009; Li et al., 2010; Du et al., 2011); (2) soil parameters such as soil organic C (SOC), pH, bulk density (BD), and initial soil inorganic N (Xu et al., 2003b; Li et al., 2004; Beheydt et al., 2007; Abdalla et al., 2009; Li et al., 2010; Du et al., 2011); (3) management parameters such as tillage, drainage, and fertilization (date, depth, amount of N) (Li et al., 1994; Li et al., 1996; Li et al., 2004; Pathak et al., 2005; Abdalla et al., 2009; Li et al., 2010) and (4) crop parameter such as cultivar type (Zhang et al., 2002). Some of the studies focused on SA of the DNDC model in forest systems (Stange et al., 2000; Lamers et al., 2007a; Lamers et al., 2007b). To our knowledge, no studies have carried out complete SA of all input parameters in the DNDC model.

The objectives of this paper were threefold. First, we performed complete SA of all input parameters in the DNDC model using two SA approaches (graphical approach and sensitivity index) and on all the climate, soil, and crop parameters in the DNDC model for various management options for a corn crop. Through these methods we can determine which of the parameters give rise to variations, determine the nature of the variations, select the behavioral range of the parameters, and classify the sensitivity of the parameters into some order of relative importance for different corn cropping systems. Second, we calibrated and validated N_2O emissions using the DNDC model by comparing the simulated N_2O emissions with measurements. Third, we address the uncertainties while performing SA, calibration, and validation when the direct measurements are at a coarser time scale than the modeled N_2O emissions.

Methods

The DNDC model

The DNDC (Version 9.4) model has been developed for almost 20 years; its initial aim was to model N_2O emission from cropped soils in the U.S. (Giltrap et al., 2010). Information on the mathematics and the concept of the model can be found in Li et al. (1992a) and Li et al. (2000).

The DNDC model simulates biochemical and geochemical reactions common in agroecosystems, which include mainly carbon (C) and nitrogen (N) transport and transformation in plant-soil-climate systems (Li et al., 2011). The model consists of six submodels: thermal-hydraulic, aerobic decomposition, nitrification, denitrification, fermentation, and plant growth.

The thermal-hydraulic submodel calculates soil temperature and moisture profiles based on soil physical properties, daily weather, and plant water use. The aerobic decomposition simulates production of soil organic matter driven by soil microbial respiration. The nitrification submodel calculates growth of nitrifiers and oxidation of ammonium to nitrate. The denitrification submodel simulates denitrification and the production of nitric oxide, nitrous oxide, and dinitrogen at an hourly time step. The fermentation submodel simulates methane production and oxidation under anaerobic condition. Plant growth is modeled with the DNDC daily crop growth curve (Giltrap et al., 2010).

Sensitivity Analysis

The parameter perturbation method used in this study is the "one at a time (OAT)" approach (Fig. 4.1). The DNDC model has 'k' parameters $\boldsymbol{p} = \{p_1, p_2, \ldots. p_k\}$, which influence the time (t_j, for j time steps) evolution behavior of several different modeled variables. In the present study, a single modeled response ($V(\boldsymbol{p}, t_j)$; N_2O) for DNDC is studied for 38 parameters (k = 38). The value of j will depend on the number of observations ($j = 1, \ldots, n$). Feasible parameter space (a range in which a parameter can possibly vary) is defined for each of the 38 model parameters considered in our study. The value of number of samples of each parameter depends on the feasible limits of the parameter; in our study, it was set to 20 ($m = m_1, m_2, ..m_{20}$). The variations in the model response ($V(p, t_j)$) reflect the sensitivity of the solution to the varied parameter while holding all other parameters constant.

In the first graphical approach, the plot of the variation of modeled response (N_2O) for 'm' values of a parameter in its feasible range is used to classify the variables as sensitive and not sensitive.

For the second graphical approach, first a single criterion for the model response is defined as $f(p_k, m)$ that measures the distance between the modeled response and some benchmark response. The benchmark response in our study is based on a set of measurements of N_2O emissions made at a study site. The mathematical form of the criteria adopted in our study is the commonly used Nash–Sutcliffe model efficiency (ME, equation 1). The single criterion vector of ME values ($F(p_k) = \{f(p_{k,1}), f(p_{k,2}), \ldots. f(p_{k,m})\}$) is estimated for a parameter where 'm' is the number of times a parameter is sampled. Second, a plot of the $F(p_k)$ for a parameter is used to classify the feasible range of a parameter into "behavioral" and "non-behavioral" regions (results shown in next section). The negative ME values of the parameters are chosen as the non-behavioral range. The values of the parameters with ME between 1 and 0 are chosen as the behavioral range and were further used in model calibration. The Nash–Sutcliffe model efficiency [ME] ranges between -∞ to 1. An ME equal to 1 corresponds to an ideal fit, and the positive ME value indicates that the model prediction is better than the mean of observations.

$$ME = 1 - \frac{\sum_{j=1}^{n}(M_j - O_j)^2}{\sum_{j=1}^{n}(O_j - \bar{O})^2} \tag{1}$$

where O, $\bar{O}$, M and n stand for observed, mean, modeled, and total number of observation values, respectively. In the graphical approaches, the modeled N_2O for the various parameters perturbed in the feasible range were plotted to determine the nature of the variations in the modeled N_2O emission.

The other objective was to classify the sensitivity of the parameters into an order of relative importance using the sensitivity index (B, equation (2)) following Deng et al. (2011):

$$B = \frac{(M_{p_{kmx}} - M_{p_{kmn}})/\overline{M}_{p_k}}{(p_{kmx} - p_{kmn})/\overline{p}_k} \tag{2}$$

where $\overline{M}_{p_k} = (M_{p_{mx}} + M_{p_{mn}})/2$ and $\overline{p}_k = (p_{k_{mx}} + p_{k_{mn}})/2$, p_{kmx}, and p_{kmn} represent maximum and minimum value for the parameter *k*, respectively. M_{pkmx} and M_{pkmn} are the corresponding model N_2O fluxes. The results of SA are subject to the criterion function, ‘m’ uniform samples used, benchmark response and method of estimating the sensitivity index.

Model calibration and validation

Site description and N_2O emission measurements

The N_2O emissions in the present article are based on measurements from a long-term tillage-N experiment in corn at the Kansas State University Agronomy North Farm (39°11’30”N, 96°35’30”W, 325 masl). Annual precipitation is 843mm yr^{-1}, average temperature is 12.9°C, and the soil type is a fine-silty, mixed, superactive, mesic Cumulic Hapludolls. N_2O emissions have been evaluated since summer of 2008. The treatments evaluated in the long-term experiment (established in 1990) were no-till (NT) and till (T) systems with two different types of fertilization (composted farmyard residuals (M) and urea (F)) at a rate of 168 kg N ha^{-1}. The T system included fall chisel plow and spring offset disk.

The flux measurements were performed by placing vented chambers on polyvinyl rings (PVC) and collecting gas samples once a week and after rainfall events during the growing season. Concentrations were determined by gas chromatography (Model GC 14A; Shimadzu, Kyoto, Japan) equipped with a ^{63}Ni electron capture detector and a stainless steel column (0.318 cm dia. by 74.5 cm long) with Poropak Q (80-100 mesh, Shimadzu). N_2O emission were calculated following Hutchinson and Mosier (1981) approach. Three years of data from 2009 to 2011 were used in this study. The experimental design for the field experiment was a split-plot design with whole-plots randomly assigned into each of four blocks and repeated measurements in time. Tillage treatment was the whole-plot and the type of fertilization was the subplot.

Measurements taken on the same plot over time were assumed to be correlated. The final analysis was reported based on the unstructured covariance structure. The mixed model used was analyzed with proc mixed from SAS 9.3 (SAS Institute, 2010).

Linear integration was used to estimate the total N_2O emitted during the study period for each treatment. The accumulated N_2O emissions were analyzed under the split-plot design.

Estimates of N_2O emissions from field experiments are listed in Appendix A.1 and A.2.

Calibration

An important aim of SA is to reduce the number of parameters that must be estimated and the parameter space, thereby reducing computational time required for model calibration and validation. For calibration the set of the most sensitive parameters was selected (Table 4.4) and the model performance was calculated per parameter value. The model performance measures the distance between the modeled response and some benchmark response (N_2O measurements from 2009 season) mathematically using ME, equation (1))(Deng et al., 2011). The parameter value, "m", having the maximum ME was selected (Table 4.4).

Validation

For model validation, the N_2O emissions measured in seasons 2010 and 2011 were used. The simulated N_2O emission from 2010 and 2011 were obtained running DNDC with the optimum parameters found in the calibration. The model performance was evaluated using ME and the coefficient of determination (R^2, equation 3). The coefficient of determination examines the correlation between model predictions and field measurements (Deng et al., 2011)

$$R^2 = \left(\frac{\sum_{J=1}^{n} (O_j - \overline{O})(M_j - \overline{M})}{\sqrt{\sum_{j=1}^{n} (O_j - \overline{O})^2 \sum_{j=1}^{n} (M_j - \overline{M})^2}} \right)^2, \qquad (3)$$

where O, $\bar{O}$, M, and n stand for observed, mean, modeled, and number of observation values, respectively.

Uncertainty Analysis

Very few studies have carried out measurements of N_2O emissions at a daily timescale, [e.g., Flessa et al. (2002); Barton et al. (2011)], so there is a difference in timescale between modeled N_2O (daily) and its measurements (e.g., monthly, bi-weekly). In such situations, while evaluating the model performance, the modeled response (N_2O at daily timescale) can be aggregated in a number of ways (parametric and non-parametric) to match the timescale of the measurements (benchmark response) before they can be compared. To determine the subjectivity in the aggregations, we conducted the SA, calibration, and validation of the parameters for 3 types of aggregation of modeled N_2O namely (1) the bi-monthly mean (MN, parametric), (2) the bi-monthly median (MD, non-parametric), and (3) the cumulative (CM, parametric) for the time period. For SA we used 38 parameters, and for model calibration and validation we used the sensitive parameters (Table 4.1).

Results

In this section, the results of graphical approaches and sensitivity index methods for SA of parameters (listed in Table 4.1) for two management practices (NT and T), systems with two different types of fertilization, (C and F) and three modeled N_2O aggregation methods (MN, MD, CM) are presented. The combinations of management practices and types of fertilization are represented as NT-C, NT-F, T-C, T-F.

Sensitivity analysis (SA)

Representative plots in Fig. 4.2 for MN (first row) and MD (second row) aggregation methods are used to (1) show the changes in the nature of the variations of the parameters with the type of aggregation, management, and fertilization; and (2) determine the nature of the variations in SA of DNDC model for N_2O emissions in cropland which no studies have previously shown. The parameters, soil organic C (SOC), bulk density (BD), temperature (TEMP), and NO_3 and NH_4 in rainfall (NDEP) showed a linear increase in the modeled N_2O when the parameters were modified, whereas the parameter maximum yield (MAXYIELD) showed a linear decrease in the modeled N_2O. Some parameters such as soil pH, field capacity (FIELD), and thermal degree days (TDD) showed a non-linear relation between modeled N_2O and parameter value. The rest of the parameters showed negligible change in the modeled N_2O for changes in the parameters. Some sensitive parameters and one non-sensitive parameter are shown in Fig. 4.2.

The variations in the behavioral and non-behavioral regions of the parameters to the type of aggregation, management, and fertilization can be observed from the values of the parameters in Table 4.4. Further the differences in the behavioral and non-behavioral regions of the parameters for combinations of management, and fertilization for an aggregation method (MN) are brought out using representative plots in Fig. 4.3. For instance the behavioral range for pH in all treatments were between 5.5 and 7.1 and the non-behavioral range in higher pH values (pH>7.1). The flux values using the CM approach are the total N_2O-N lost during the year, so those values are in kg yr^{-1}; however, MD and MN fluxes are given in terms of N_2O-N lost per day (Table 4.4). With the CM aggregation method, NT-C and T-C had the most negative ME values in all parameters evaluated, which made this approach least suitable for evaluation of those treatments (Data not shown). The behavioral parameter range obtained from the MN approach shows higher simulated N_2O-N emission than the MD approach. Among the type of aggregation and combinations of management, and fertilization, significant differences were detected in the T-C between CM and MD approaches.

The order of relative importance of the parameters classified using sensitivity index also varied with the type of aggregation, management and fertilization. We calculated the mean sensitive index for the three aggregation methods to classify the parameters as sensitive (S) and non-sensitive (NS) parameters (Table 4.1) for different management practices in Manhattan, Kansas. The mean sensitivity index and the standard error to represent the variations in aggregation method are shown in Fig. 4.4. Higher standard error in the Fig. 4.4 indicates higher variability among the three aggregation methods. Based on the mean value, soil pH had the highest sensitivity followed by TEMP, Clay fraction (CLAY), SOC, BD, NDEP, MAXYIELD, FIELD, and TDD. In this study, an index close to zero (~0 ± 0.5) was used to classify parameters as not sensitive.

Model calibration and validation

Calibration of the DNDC model was carried out for the sensitive parameters in the behavioral range to select the optimum parameter. The NDEP and TEMP were set to the values observed in the area of study, and soil microbial index (SMI) was set to the default value in the model.

The model performance measures (ME and R^2) for the optimum parameter values estimated and the value itself were different for the type of aggregations, management, and fertilization. The MN approach presented the highest ME among the treatments followed by CM and MD approaches. Optimum parameter values estimated using the MN approach did not differ significantly with CM approach, but differed from the MD approach. We detected no differences among approaches in NT-F, NT-C, and T-F. The T-F presented the highest ME (0.33) followed by T-C (0.044), NT-C (-0.038) and NT-F (-0.49) (Fig. 4.5). For the model performance measure (R^2), the T-F treatment presented the highest R^2 (0.62) followed by NT-F (0.18), NT-C (0.17), and T-C (0.14) (Fig. 4.6). The variations across years (2009, 2010 and 2011) can be observed in Fig 4.7-4.9. In general, observed N_2O flux from the tillage treatments was better simulated for DNDC than the no-tillage treatments, and in terms of N source, mineral fertilized soils performed better that the organic fertilizer simulation.

Discussion

Sensitive parameters

This study brings out the SA of all 38 climate, crop, and soil parameters in the DNDC model for different management practices using two graphical approaches and sensitivity index methods. The management practices evaluated were NT and T systems with two types of fertilization (M and F). Because one SA method does not stand out as being universally accepted as "correct," a composite of three methods was used to better understand the changes in model outputs for changes in inputs and the uncertainty associated with SA. Each SA method had its strengths; one was useful in determining the nature of the variations in the modeled N_2O, the others in classifying the parameter space into behavioral and non-behavioral regions or ranking the parameters in order of importance. Because of the nature of these sensitivity tests (graphical and sensitivity index), their results are not compared quantitatively. We found pH, CLAY, SOC, BD, FIELD, SMI, TDD, MAXYIELD, NDEP, and TEMP as the sensitive parameters for Manhattan, Kansas, conditions.

Soil pH was a sensitive parameter in DNDC. Our results are consistent for NT and T treatments with other studies in agricultural soils (Du et al., 2011) and forest soils (Stange et al., 2000; Kiese et al., 2005; Werner et al., 2007). Small changes in the pH range 7–7.5 had a significant effect in the rate of N_2O released (Fig. 4.2), because soil pH is a key factor affecting nitrogen transformations such as nitrite reduction to ammonia (Li, 2000; Du et al., 2011), denitrification, and nitrification (Li et al., 2000); however, acidic conditions produce more N_2O in all treatments evaluated (T and NT). Simek et al. (2002) reported that 55% more of N_2O was released from acidic soils than from neutral soils, and extreme high or low pH could stimulate N_2O emissions. Simek et al. (2000) reported that denitrification rates were less in acidic than in neutral or slightly alkaline soils, but our results differ from those of Zhang et al. (2010), who found that pH had a minor effect on N_2O emissions where more N_2O was produced from soils with low pH than from alkaline soils. The lower initial values of SOC (0.0025 kg C kg^{-1} soil), lower precipitation (520 mm), no fertilizer added, and the type of agricultural system (grassland) may explain why pH was not sensitive.

Another sensitive parameter was SOC. Higher values of SOC increased N_2O production (Fig. 4.2). The model's sensitivity to SOC has been noted by several authors (Li et al., 1996; Xu et al., 2003a; Xu et al., 2003b; Kiese et al., 2005; Abdalla et al., 2009; Li et al., 2010; Zhang et al., 2010). One of the main reason is that the organic matter pools correlate with microbial activity (Abdalla et al., 2009). Beheydt et al. (2007) varied the SOC by 15% from the baseline and found that higher SOC (+15%) increases the baseline and the magnitude of the N_2O peaks, but the overall pattern did not change. Abdalla et al. (2009) found that increasing the baseline SOC value by 20% increased the annual N_2O flux by 65% in a spring barley field under conventional till. Under Kansas conditions, we found an increase in annual N_2O flux of 12 to 26%, respectively, in the NT and T compost treatments when the initial SOC was increased by 18%. However, the N_2O flux in the treatment T-F decreased slightly (1%) with increasing SOC. The differences between our study and Abdalla et al. (2009) could be related to the differences in cropping systems (spring barley vs. corn), BD (1.4 vs. 0.84 g cm^{-3}), fertilizer type (calcium ammonium nitrate vs. urea), and fertilization rate (140 vs. 168 kg N ha^{-1}). Li et al. (2010) tested several natural factors and indicated that SOC showed the greatest impact under a irrigated tillage wheat-corn rotation system. When the SOC increased from 0.25% to 2%, the annual N_2O emission rate increased from <1 to 22 kg N ha^{-1}, so higher SOC produced more DOC and inorganic N (i.e., ammonium and nitrate) through decomposition that lead to higher rates of nitrification and denitrification (Li et al., 2010).

In simulations of corn on both loamy sand and loamy soils, Li et al. (1994) found that annual N_2O emissions increased in both soils with fertilizer additions. The depth of fertilizer application affected the annual N_2O emissions; annual N_2O emissions decreased on both soils with deeper N application. Annual N_2O emissions were sensitive to the timing of the fertilizer application, which depend mainly on rainfall patterns around fertilizer application time. Similar to our results, Li et al. (1996) found sensitivity to NDEP with the difference that the sensitivity to NDEP presented a linear increasing at higher deposition rates over the range studied specially in the NT treatments.

Under corn in Iowa with an initial SOC of 0.041 kg C kg^{-1}, CLAY fraction of 0.22, and BD of 1.3g cm^{-3}, Zhang et al. (2002) found contrasting sensitivities depending on the year of analysis; i.e., in 1997 N_2O emissions increased around 20%, increasing the temperature by 2°C and doubling the CO_2 (650 ppm), but in 1998 with the same parameter values, N_2O emissions decreased around 11%. Abdalla et al. (2009) found that increasing the average daily temperature 1.5°C resulted an increasing of 62% in the annual N_2O emission. Li et al. (1996) detected sensitivity to temperature in a simulation of loam soil in Iowa corn whereby the influence of increasing the temperature was nonlinear with N mineralization rates and N_2O emissions increased more rapidly with higher temperatures. In our study, increasing the temperature 2°C decreased the annual flux by 9% in the conventional T treatment (T-F). The only treatment that showed an increase in N_2O flux (59%) was NT-F due to a temperature increase of 2°C. The DNDC model was not sensitive to changes in atmospheric CO_2.

Increasing the soil BD from 1.4 to 1.8 g cm^{-3} resulted in an increase of 29% of annual N_2O emissions in a spring barley crop (Abdalla et al., 2009). In our study under continuous corn, the increment varied depending on the treatment. NT-F had the highest increment in N_2O emissions switching the BD from 1.4 to 1.8 g cm^{-3} followed by NT-C, T-C, and T-F with increasing values of 28, 24, 22, and 1% in N_2O emissions, respectively. Xu-Ri et al. (2003b) found that N_2O simulations performed with DNDC were sensitive to available SOC and BD in semi-arid grasslands with average precipitation and temperature of around 400 mm and -1.3°C, respectively. The model was not sensitive to initial inorganic N pools. SA performed in paddy rice ecosystems in China for N_2O emissions using DNDC by Li et al.(2004) found that water management showed the greatest sensitivity followed by SOC and temperature. Increasing frequency of midseason drainage increased N_2O fluxes due to elevated soil redox potential during the drainage period (Li et al., 2004). Increasing SOC or temperature resulted in higher fluxes (Li et al., 2004).

Sensitivity to clay content and leaf C:N ratio has been found by Stange et al. (2000) and Kiese et al. (2005) in forest systems. We did not find sensitivity to those parameters under the agricultural soil conditions studied in Kansas.

Abdalla et al. (2009) found that changes in rainfall of ± 20% resulted in changes in annual N_2O emission of 10–15%. Under Kansas conditions, the treatments that showed increasing N_2O emissions due to incremental rainfall were NT-F and NT-C, with 34 and 2% increments on N_2O emissions, respectively. DNDC was not sensitive to changes in precipitation in T-F and T-C treatments. Similar results have been found in simulations carried out by Li et al. (1996). For the M treatment, the sensitivity was generally higher than F treatment for both T and NT tillage systems. In the agricultural practices simulated by Li et al. (1994) and Li et al. (1996), compost applications had the most pronounced effect on N_2O emissions. The emissions were generally lower after incorporation of residues with high C:N ratios but would be comparatively large after incorporation of materials with lower C:N ratios due to the promotion of mineralization and the subsequent availability of substrate for nitrification and denitrification (Kaiser et al., 1998; Baggs et al., 2000; Baggs et al., 2006; Sanchez-Martin et al., 2010; Yao et al., 2010).

Abdalla et al. (2009) reported sensitivity of DNDC to changes in fertilizer type. Switching the fertilizer type from CAN to urea or ammonium sulfate resulted in increasing annual N_2O emissions of around 50 and 55%, respectively. In our study, switching from mineral fertilizer (urea) to compost did not have a significant effect in terms of total N_2O emitted in 2009 and 2010 when the C:N ratio of the compost was around 15 (neither simulated nor observed data).

Calibration and validation

The validated model was able to capture some important events that drive denitrification, which are rainfall and fertilizer application; however, the model did not capture the observed high fluxes, especially under manure treatments (NT-C, T-C), resulting in low coefficient of determination (0.24 and 0.013, respectively). Rainfall events increased soil moisture, thus enhancing the diffusion of NO_3^--N and soluble C to micro-sites of denitrification (Xu et al., 2003b); consequently, the transport process of N and soluble C from the compost to those micro-sites or hot-spots may not be well represented in the model.

The N_2O emission simulated was underestimated in our study, especially in the compost treatments (NT-C, T-C), where the deviations in cumulative values were around -72 and -80%, respectively (data not shown). Deviations found for Smith et al. (2008) were around -25 and 52 for pig slurry and NH_4NO_3 application, respectively. Despite changing the C:N ratio of the manure in 2011, underestimates persisted in those treatments. According to Smith et al. (2002), one of the factors contributing to the under- or over-predictions was the difficulty of the model in predicting the proper timing of events. Although the seasonal magnitudes were well predicted, the field measurements of N_2O emissions may misrepresent the detailed shape of the N_2O pulse (Wang et al., 2012), and may depend of the type of fertilizer used. Du et al. (2011) concluded that the DNDC model worked better for ecosystems with high N_2O emissions rates, which usually have high SOC content and humid climate. Smith et al. (2002) found that the DNDC model often predicted the correct seasonal magnitude of N_2O emission but had difficulties predicting the proper timing of events, which may be the cause of low ME in some of the treatments evaluated. Results of SA, model calibration, and validation for some studies are provided in Tables 4.2 and 4.3.

According to Wang et al. (2012), the discrepancies between modeled and observed values using UK-DNDC (DNDC customized for ecosystems in United Kingdom) may be because the complexity of soil structures such as pore size and tortuosity were not represented in the model. Small changes in moisture can change the associated rate coefficients by an order of magnitude because they are sensitive to fine-scale structure, which may affect directly the soil microbial activity within soil aggregates (Wang et al., 2012). Besides the soil microbial processes carried out by the model, the model does not take into account the highly heterogeneous microbial distribution that can vary depending of the soil structure, moisture, and substrate availability (Wang et al., 2012). The horizontal transports of water and substrates were not represented in the model (Zhang et al., 2002; Wang et al., 2012).

Direct measurements of N_2O emissions are generally at a coarser time scale than modeled N_2O emissions. So studies aggregate them to a common time scale to compare results using an aggregation method (e.g. mean). However there is no documentation which brings out the variations in the model results to different aggregation methods. This study attempts to fill this gap by documenting the variation in the sensitivity analysis (SA), calibration, and validation of modeled N_2O for combinations of fertilization and management using three aggregation methods namely: two parametric methods (mean [MN] and cumulative [CM]) and third a nonparametric method (median [MD]). Daily N_2O was modeled for Manhattan, Kansas, using the Denitrification–Decomposition (DNDC) model, and values were compared with measurements available at biweekly time scale.

To document the uncertainty of aggregation methods in SA, three methods (two graphical and one sensitivity index) were used in all the user available 38 parameters in DNDC model. The uncertainty in the nature of variations and “behavioral” and “non-behavioral” range to the aggregation methods was studied using two graphical methods (change in parameter vs. modeled N_2O emissions and change in parameter vs. model performance measure[ME]), while the order of importance of sensitive parameters was studied using sensitivity index.

To document the uncertainty of aggregation methods in model calibration and validation we used two model performance measures (R^2 and ME) to select the optimum parameter values. The optimum parameter values selected during the calibration period also varied with the type of aggregation, management practices, and performance measure (R^2 and ME) used.

Conclusions

The list of sensitive parameters and the order of their importance vary with the aggregation method. For example pH, CLAY, and TDD were sensitive in MD aggregation but not in MN and CM aggregation. FIELD was sensitive in MN and CM but not in MD. We used the mean sensitivity index in three approaches to select the sensitive parameter to account for the uncertainty in the type of aggregation. Soil pH, temperature, clay fraction, soil organic carbon, bulk density, soil microbial index, NO_3 and NH_4 in rainfall, maximum yield, field capacity, and total degree days were found to be the sensitive parameters in the study.

The sensitivity analysis using graphical and numerical approaches (sensitivity index) were complementary since by using graphical approach was possible to evaluate the behavior of the model to parameter perturbation. The sensitivity index allowed us to rank the most influential parameters for N_2O modeling.

Results from calibration showed that using parametric approaches to determine optimum DNDC model parameters gave a better estimation of N_2O fluxes from field conditions, especially in the tillage treatments. Overall, the R^2 and ME were higher using the MN (parametric) approach than MD and CM approaches. The highest uncertainty associated with the model calibration is produced when the optimum parameters were selected using the MD approach. Similar to calibration, the uncertainty is observed to be associated with the four combinations; thus, the uncertainty in the model calibration and validation due to the type of aggregation is highlighted in this study. This uncertainty decreases when the differences in the aggregated mean, median, and cumulative values between the measurements and model simulations decrease. Although the DNDC model was used as an example, the techniques described can be applied to many modeling problems in different locations at multiple time scales.

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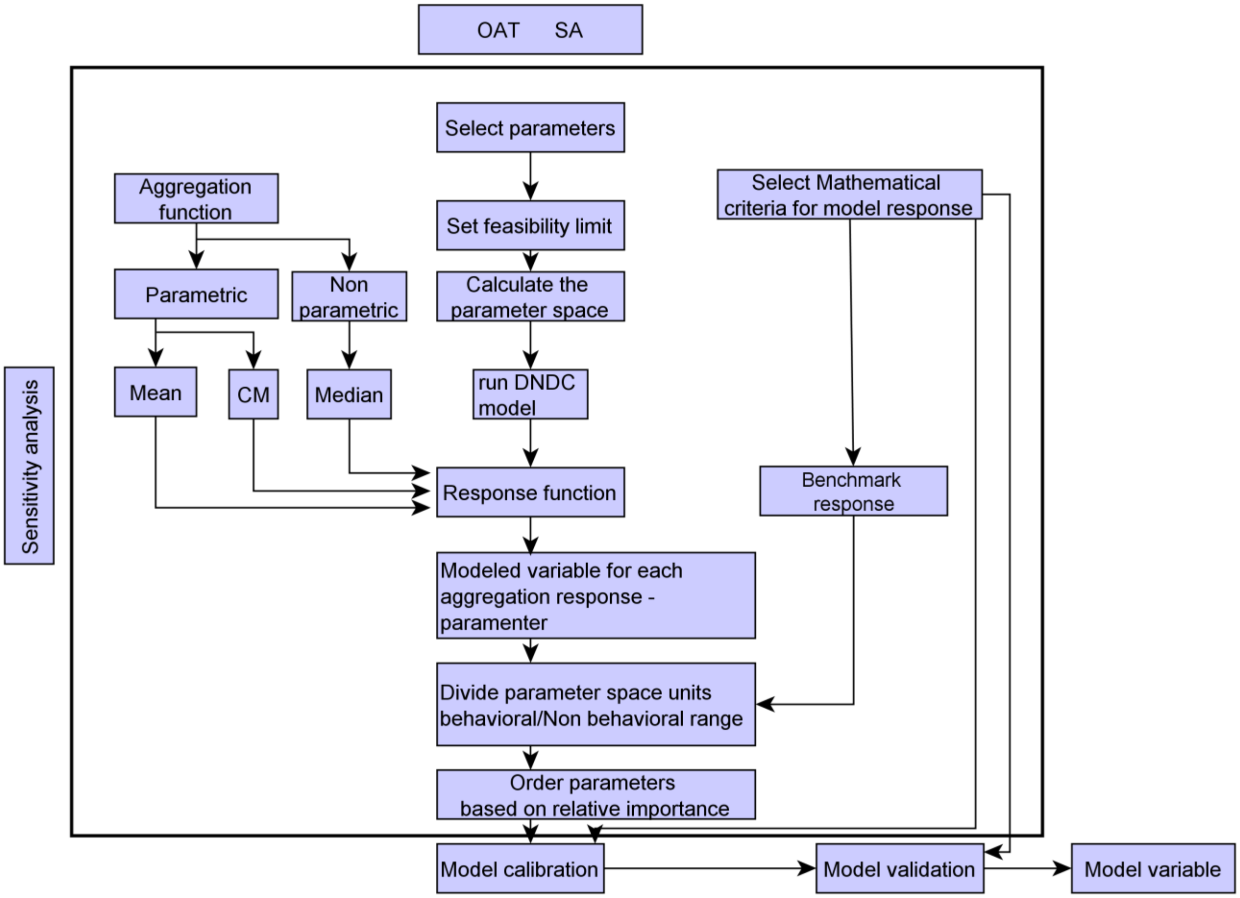

Figure 4.1. Flowchart describing the methodology for model sensitivity, calibration, and validation.

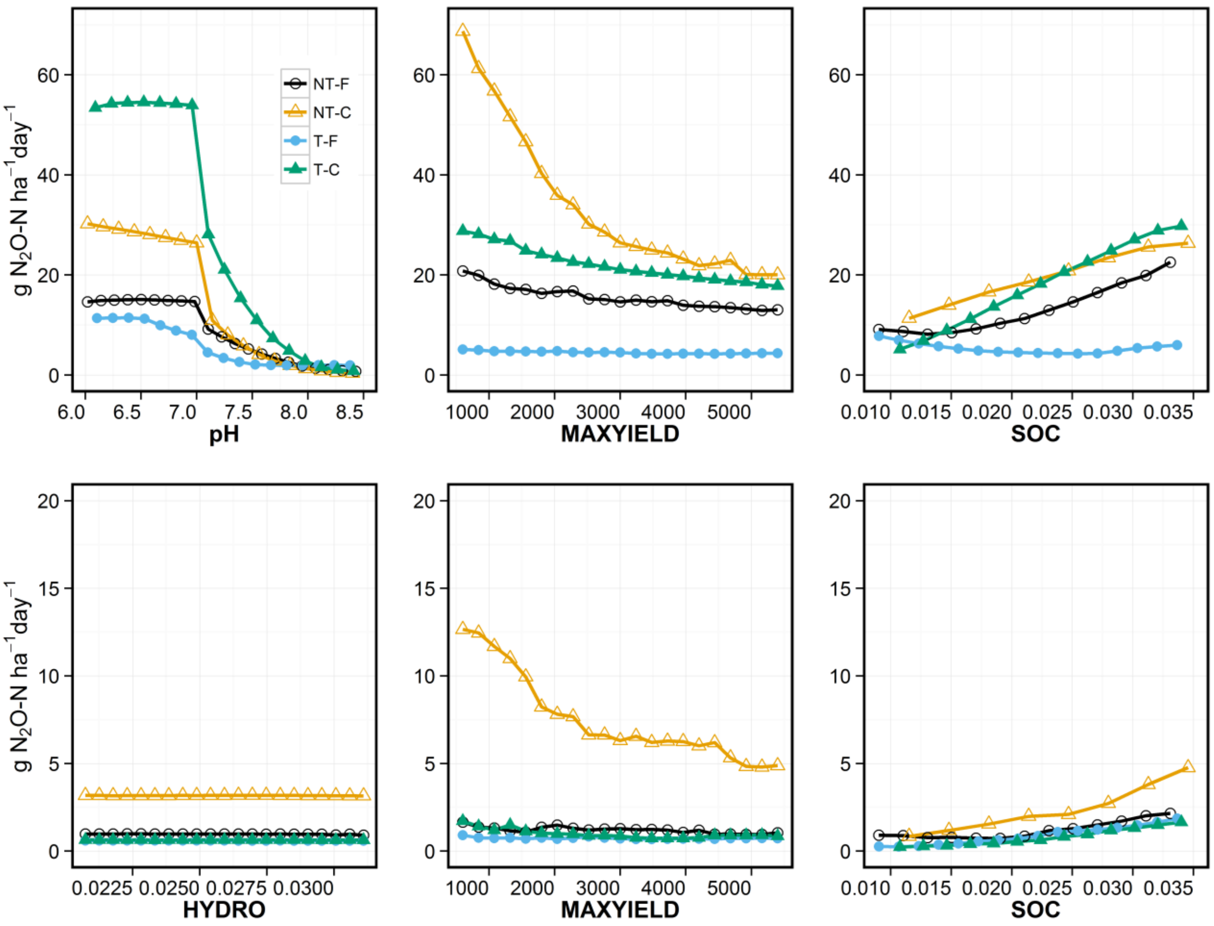

Figure 4.2. Patterns observed in SA using two aggregation methods. Mean (MN) and median (MD) aggregation figures are displayed at the upper and lower side, respectively. A non-sensitive parameter is included in the lower panel (HYDRO).

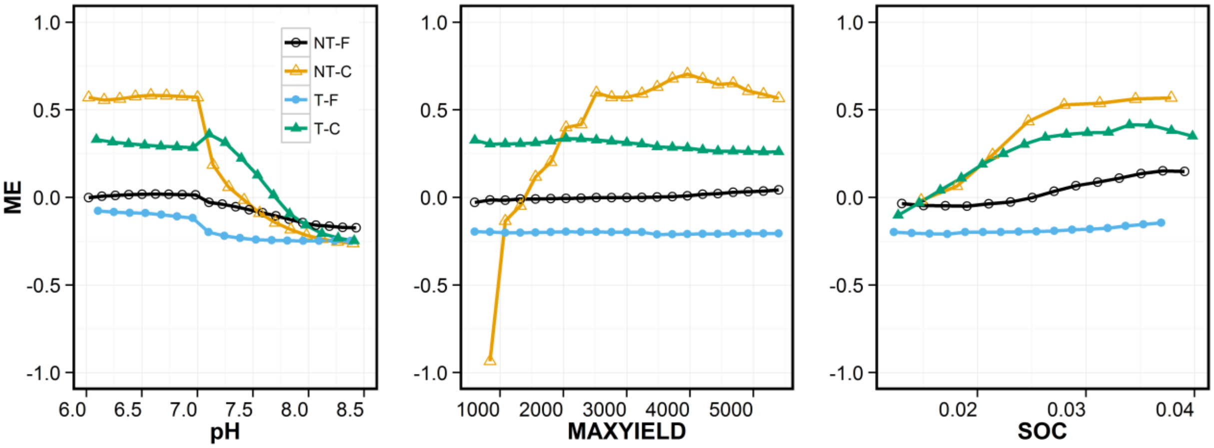

Figure 4.3. Nash-Sutcliffe Model Efficiently (ME) for N_2O based on mean (MN) approach.

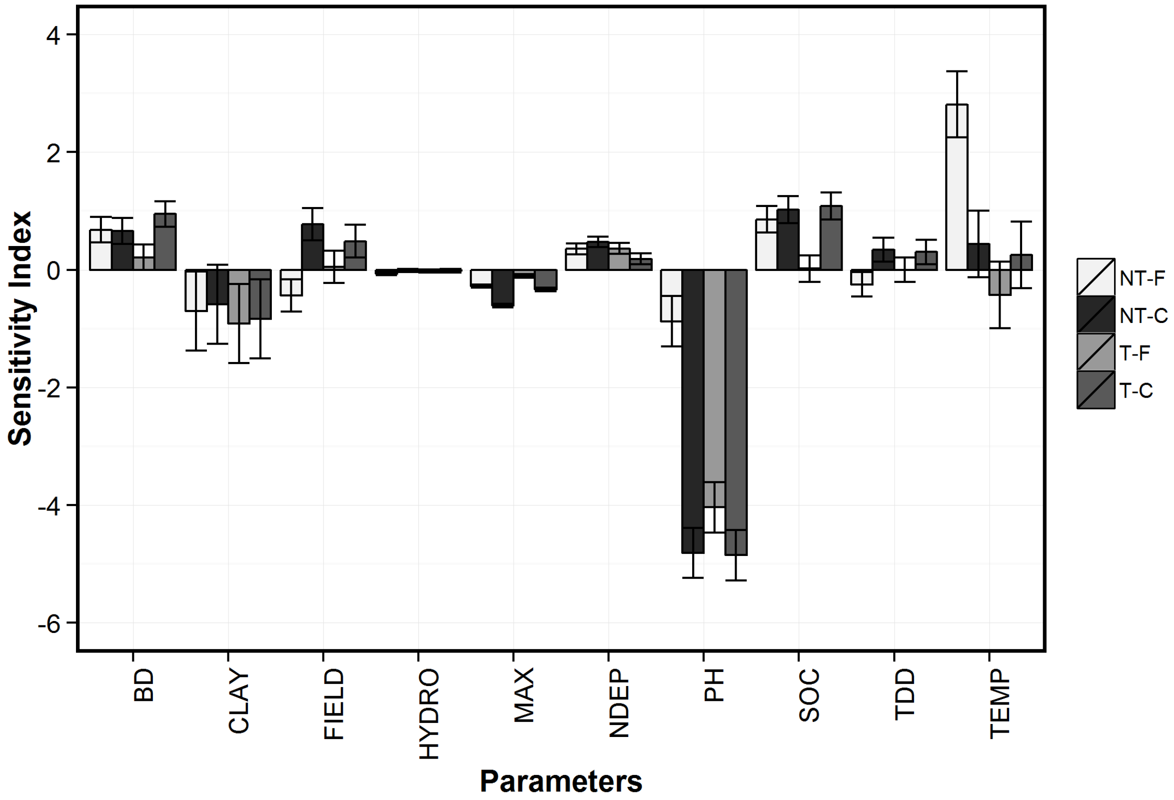

Figure 4.4. Mean sensitive index of the aggregation methods in each of the management practices and parameters. The sensitive parameters are shown except one non-sensitive parameter (HYDRO).

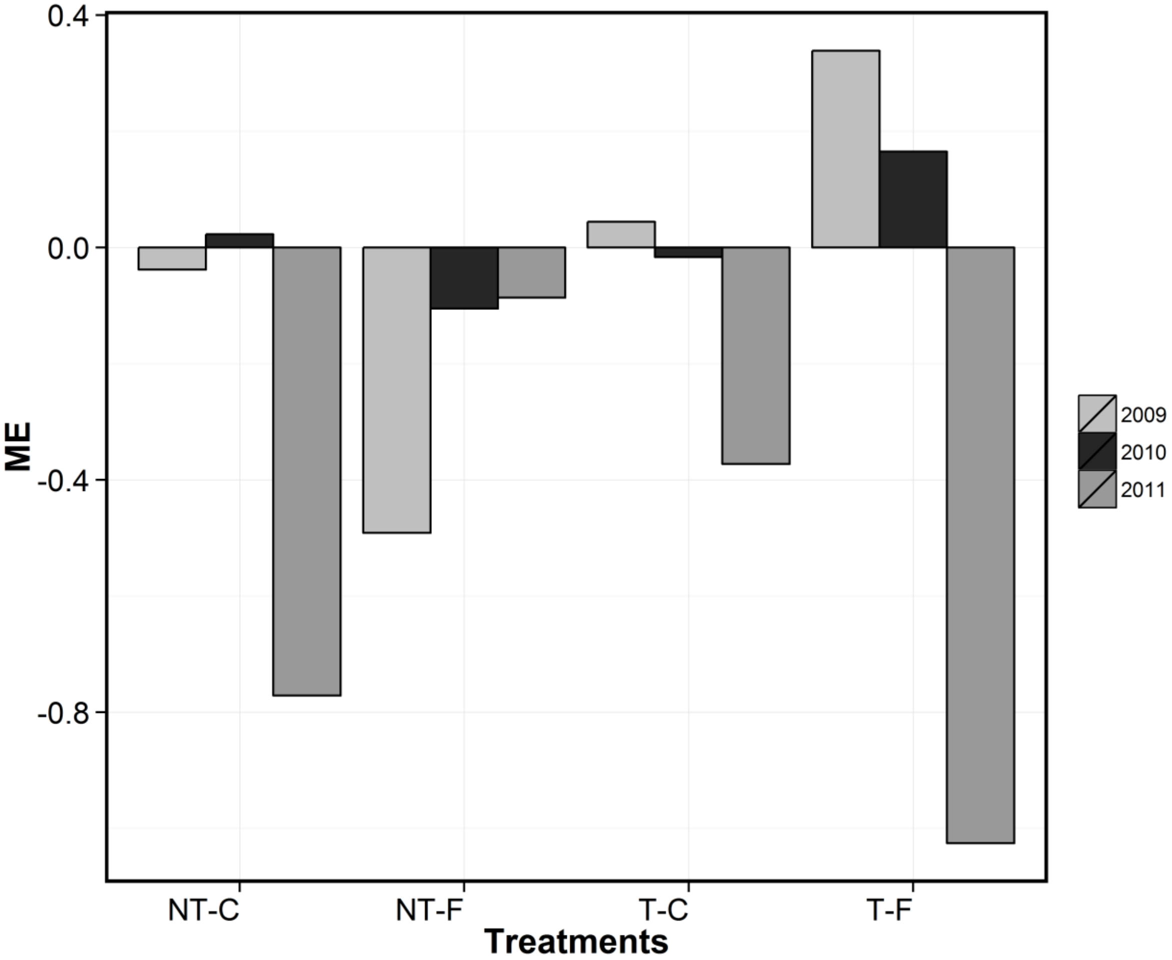

Figure 4.5. Model efficiency using mean (MN) aggregation approach for calibration (2009) and validation datasets (2010, 2011).

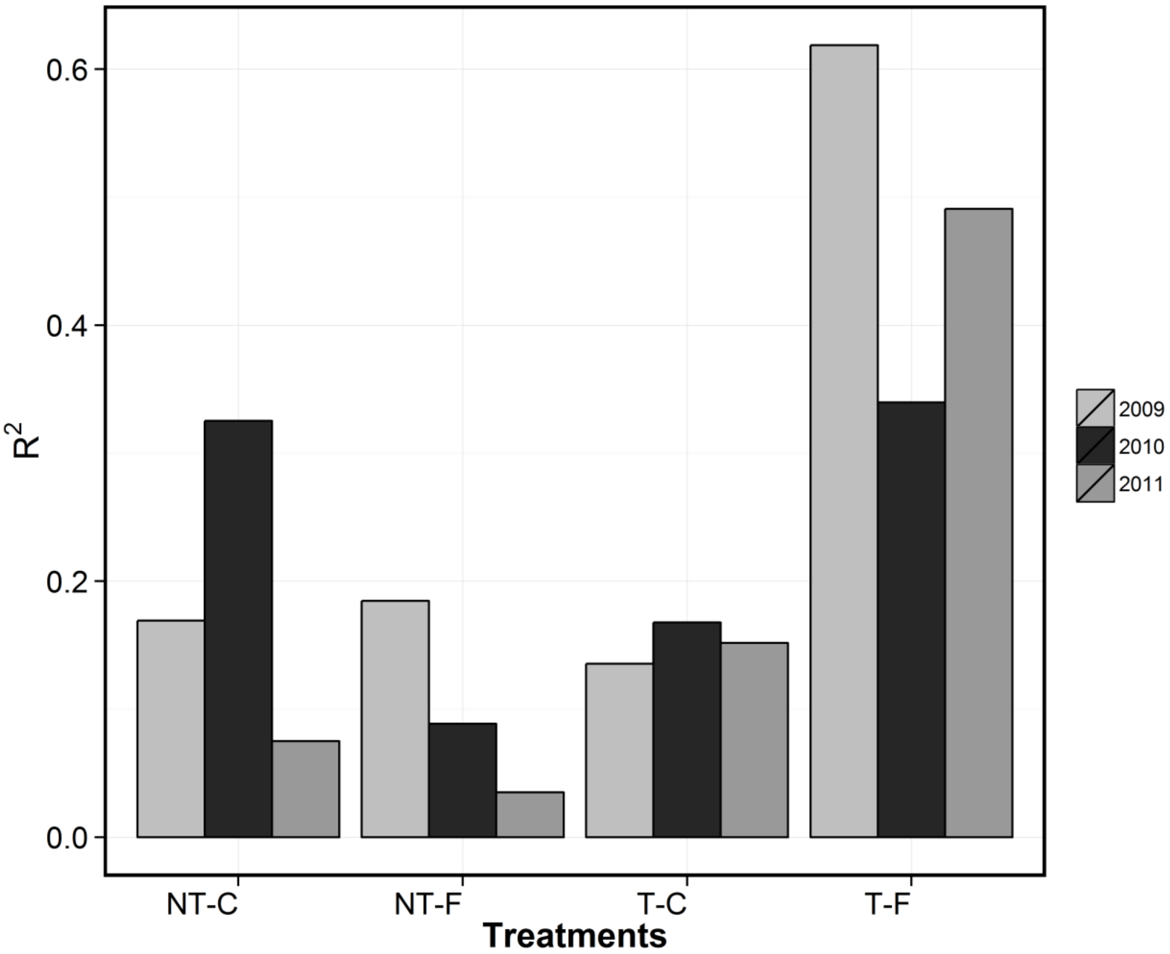

Figure 4.6. R^2 values for calibration and validation datasets using the mean aggregation method (MN).

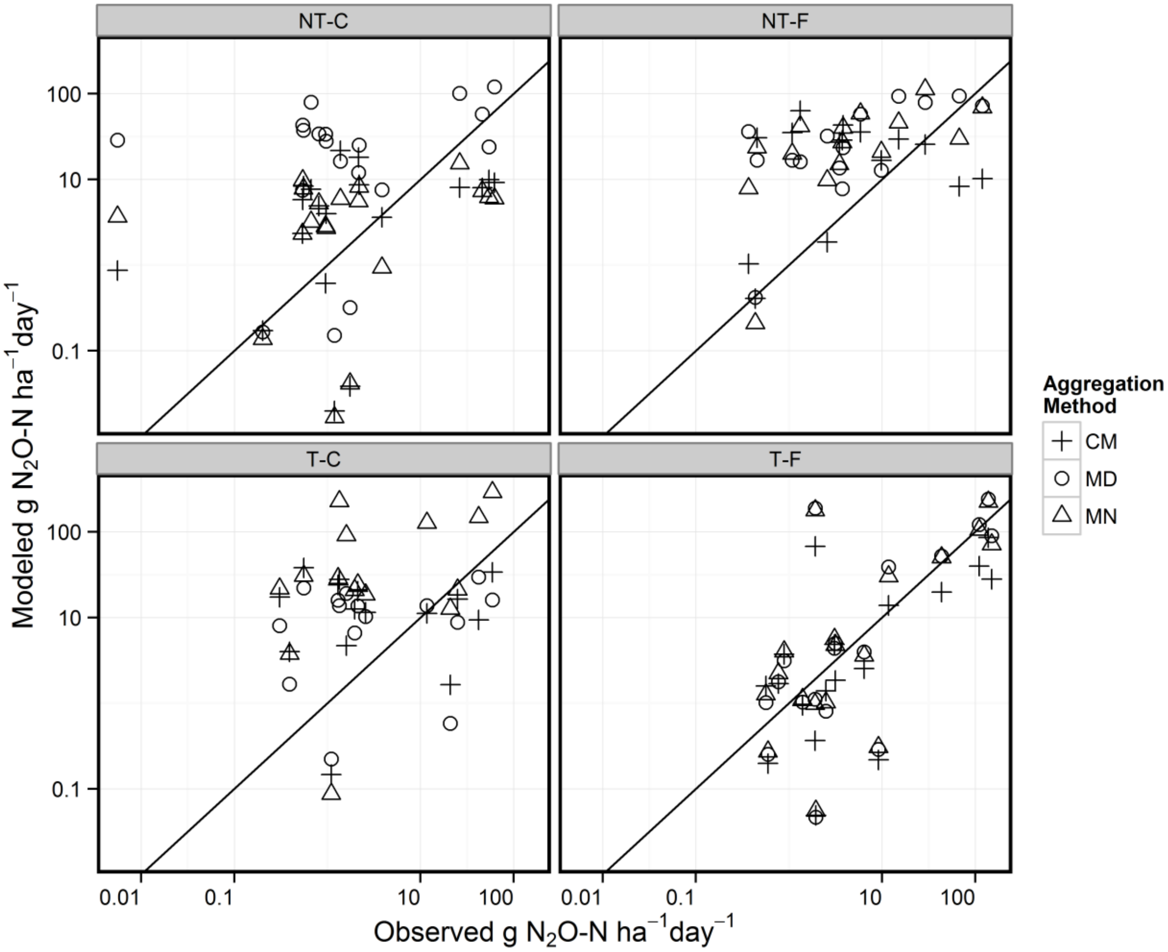

Figure 4.7. Modeling results using the different approaches compared with the daily observed N_2O-N emissions from 2009: median (MD [circles]), mean (MN [triangles]), and cumulative (CM [pluses]).

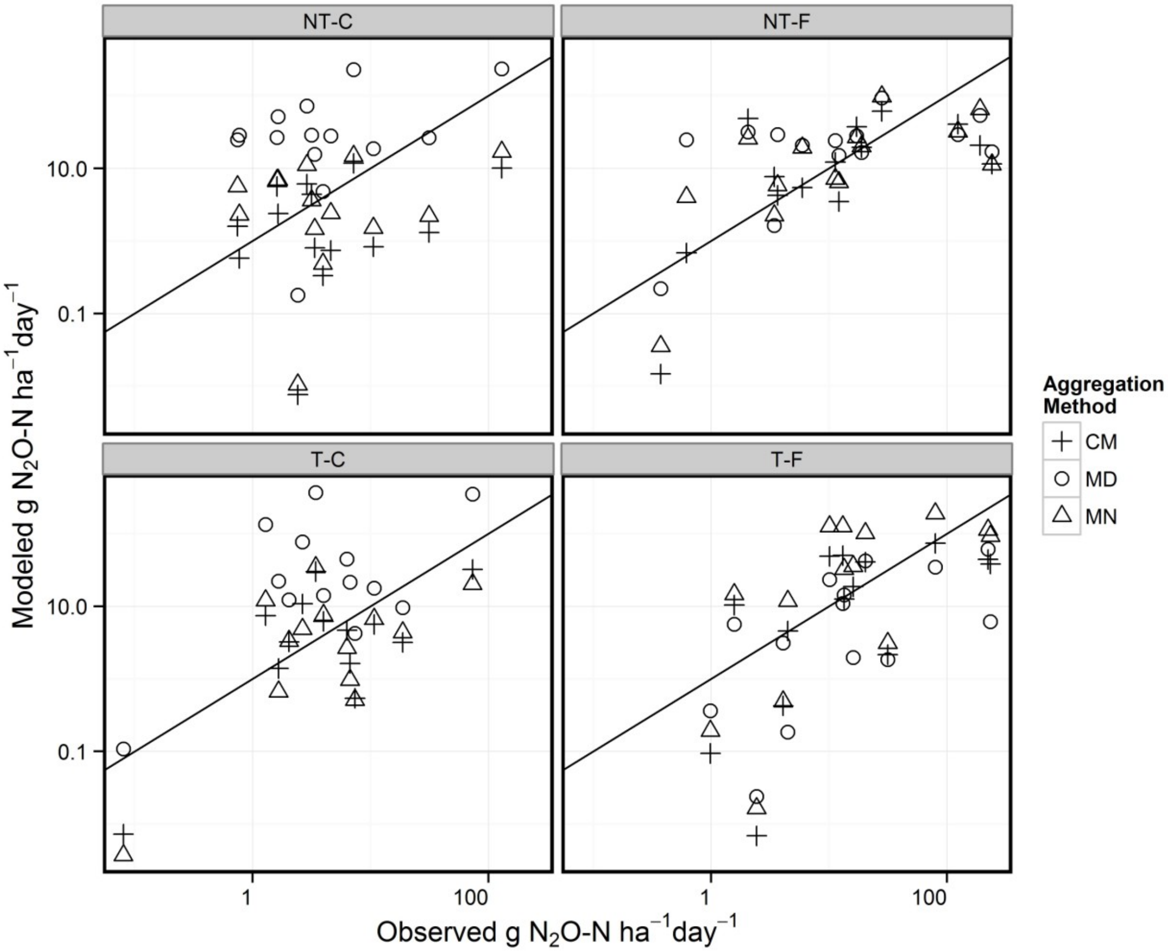

Figure 4.8. Modeling results using the different approaches compared with the daily observed N_2O-N emissions from 2010: median (MD [circles]), mean (MN [triangles]), and cumulative (CM [pluses]).

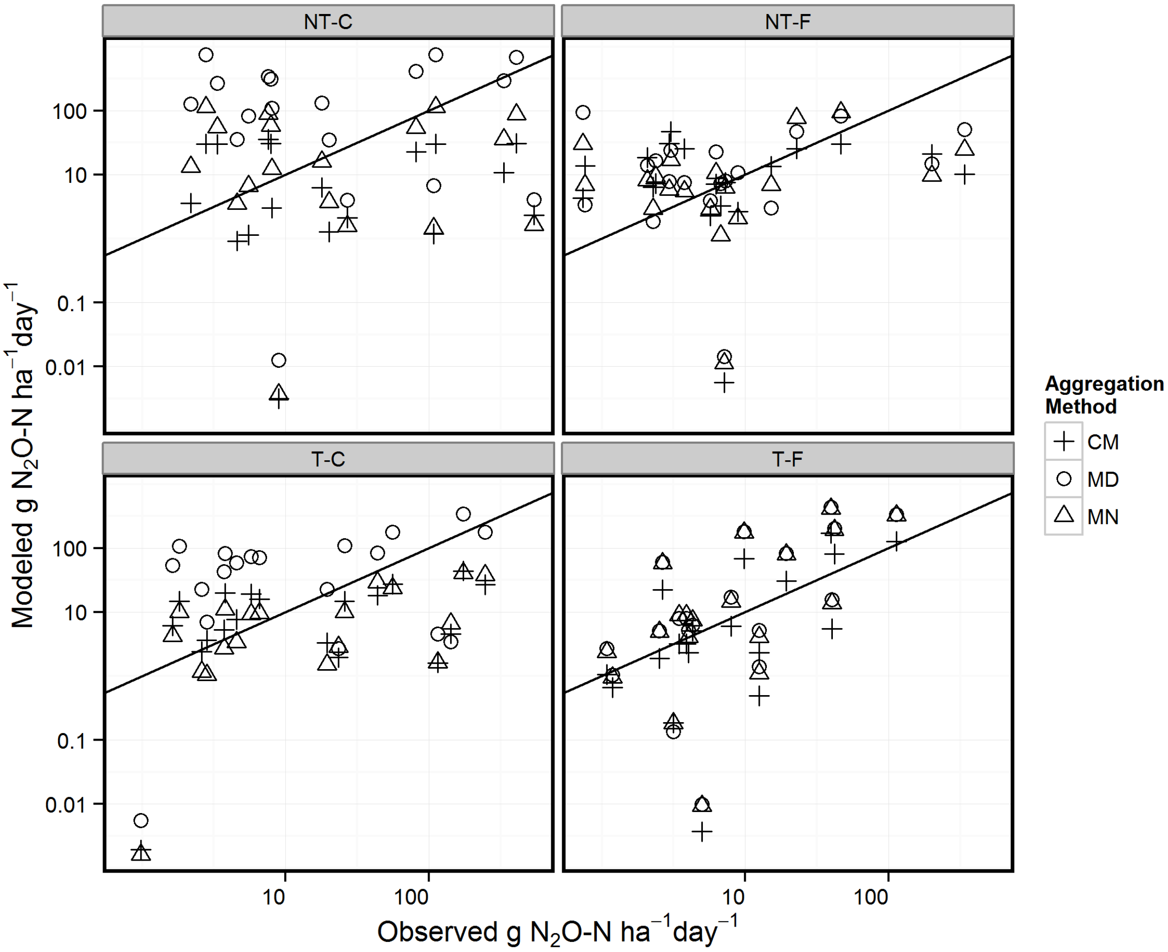

Figure 4.9. Modeling results using the different approaches compared with the daily observed N_2O-N emissions from 2011: median (MD [circles]), mean (MN [triangles]), and cumulative (CM [pluses]).

Table 4.1 Climate, soil, crop and management parameters in the Denitrification–Decomposition model

SL	Parameters	Abbreviation	Sensitivity†
	Climate:		
1	NO_3 and NH_4 in rainfall	NDEP	E(S)
2	NO_3 of atmosphere	NO3ATM	E(NS)
3	CO_2 of atmosphere	CO2	E(NS)
4	Temperature	TEMP	E(S)
5	Precipitation	PPTN	E(NS)
	Soil:		
6	Density	BD	E(S)
7	Soil pH	pH	E(S)
8	SOC at surface	SOC	E(S)
9	Clay fraction	CLAY	E(S)
10	Soil NO_3(-)(mgN/kg)	SOILNO3	E(NS)
11	Soil NH_4(+)(mgN/kg)	SOILNH4	E(NS)
12	Field capacity	FIELD	E(S)
13	Wilting point	WP	E(NS)
14	Hydro conductivity	HYDRO	E(NS)
15	Soil porosity	PORO	E(NS)
16	Thickness of uniform topsoil	DEPTHSOC	E(NS)
17	SOC decrease rate in profile	decsoc	E(NS)
18	Bypass flow	BF	E(NS)
19	Humads CN	HCN	E(NS)
20	Humads SOC fraction	HSOC	E(NS)
21	Humus CN	HmCN	E(NS)
22	Humus SOC fraction	HmSOC	E(NS)
23	Litter SOC fraction	LSOC	E(NS)
24	Soil microbial index	SMI	E(S)
	Crop:		

25	Maximum Yield	MAXYIELD	E(S)
26	Plant Carbon:Nitrogen	plant CN	E(NS)
27	Total Degree Days	TDD	E(S)
28	Water requirement	WR	E(NS)
29	N fixation	Nfix	NE
30	Maximum height	MaxH	NE
31	Grain CN	GCN	E(NS)
32	Grain Fraction	GF	E(NS)
33	Root CN	RCN	E(NS)
34	Shoot Fraction	SF	E(NS)
	Management:		
35	Crop residue incorporation	INC	E(NS)
36	Tillage date	TD	P
37	Tillage depth	Tdepth	P
38	Fertilizer depth	FD	P
39	Fertilizer amount	Fam	NE
40	Manuring date	MD	P
41	Manure C:N	MANCN	E
42	Manure amount	MANAM	NE

†S-sensitive, NS-not sensitive. A parameter is considered sensitive if the sensitivity was detected in at least one management practice.

Note: In Sensitivity column, "E" indicates the terms for which SA is carried out for the entire feasible range, "P" indicates the terms on which SA is carried out for selected values, and "NE" indicates the terms for which SA was not carried out because they were not appropriate for corn crop.

Table 4.2. Studies that performed sensitivity analysis and calibration of the Denitrification–Decomposition model for N_2O fluxes

Location	Model version	N_2O emission	System	Datasets	Parameters Evaluated	Behavioral Range	Model Performance						References
							CD	ME	RMSE	EV	SSR	Merr	
Ireland	DNDC 9.2	kg N /ha/yr	CT SB		BD, SOC, FT, R	0.67-2.65							Abdalla et al. (2009)
Germany	ForestDNDC37W		Forest	cold 2001-2002	N-dep,pH-FF, pH-MS,SOC		1.79	-0.45		22.56	2346		Lamers et al. (2007a)
				cold 2003-2004	N-dep,pH-FF, pH-MS,SOC		3.87	-0.3		6.5	338		
				opt 2001-2002	N-dep,pH-FF, pH-MS,SOC		1.4	0.28		11.16	1161		
				opt 2003-2004	SOC		0.78	-0.27		6.38	332		
Germany	Wetland-DNDC		Forest-Humid Gleysol	Cal-Cold	FC, Ks,WP, H, L		0.54	-1.24	13.6	183		4.92	Lamers et al.(2007b)
				Cal-Opt			2.53	-0.15	9.7	94.1		-2.05	
				Val-Cold			0.07	-15.1	11.4	129.1		9.5	
				Val-Opt			0.14	-6.6	7.8	60.7		6	
			Forest-Histic Gleysol	Cal-Cold	Ks, WP, H		2.23	-4.2	10.7	116.5		-5.41	
				Cal-Opt			2.54	0.1	8.65	74.9		-3.69	
				Val-Cold			1.43	-0.69	3.7	13.5		-1.34	
				Val-Opt			0.42	-1	4.04	16.1		0.35	
China	DNDC Modified	kg N/ha/yr	R-WC/RF		SOC, Clay, pH, BD	0.4-17							Li et al. (2004)
Thailand	DNDC Modified	kg N/ha/yr	R-WC/RF		SOC, Clay, pH, BD	15-46							
USA	DNDC Modified	kg N/ha/yr	R-WC/RF		SOC, Clay, pH, BD	9-20							
USA, Iowa		Kg N/ha/yr	Corn		T,P, N-dep	3.7-7.2							Li et al. (1996)
China and USA	Crop-DNDC	kgN/ha			T+2,2XCO2,Crop	3.25-6.6							Zhang et al. (2002)

Table 4.3. Validation studies comparing Denitrification–Decomposition model prediction and observed values (not all the studies below performed model calibration or sensitivity analysis)

Location	Model version	N_2O emission	System	Datasets	Modeled	Observed	Model Performance							References
							R2	ME	RMSE	ARE	CV (%)	SEE	MAE	
Belgium	DNDC8.3P	g N/ha/day	Crop+grass						98					Beheydt et al. (2007)
		kg N /ha/yr	Cropland				0.85							
		kg N /ha/yr	grassland				0.16							
Belgium	DNDC8.3P	kg N /ha	MT-C		2.18	5.27								Beheydt et al. (2008)
			MT-SO		3.5	3.64								
			CT-C		17.71	0.27								
Japan, China	DNDC 7.2		Cropland	Japan	3.14-11.26	0.17-15.93								Cai et al. (2003)
			Cropland	China	0.41-5.7	0.62-1.99								
Denmark	MoBilE-DNDC	g N/ha/day	C4-CC,O4-CC,O4+CC, O2+CC					-1.78 , -10.82						Chirinda et al. (2011)
USA	Wetland DNDC+MIKE SHE		Forest	1994			0.809							Cui et al. (2005)
Europe	MoBiLE-DecoNit-DNDC	g N/ha/day	Forest	NOFRETETE	0.1-18.3	0.1-18.2	0-0.72		0.1-17.7					de Bruijn et al. (2011)
China	DNDC	kg N/ha	Grassland	2004-2005	2.26-2.49	2.01-2.96	0.35-0.37							Du et al. (2011)
Multiples sites	DNDC?	kg N/ha	Rangeland	1991	1.4	0.11-0.15								Frolking et al. (1998)
			Grassland	1992	1.4-2.1	1.6-4								
			Grassland	1992	0.9-1	3-5.2								

			Cropland	1992-1993	3.1-5.3	9.4-16.8								
Ireland		kg/ha	HG		15.4	11.6								Hsieh et al. (2005)
India	Modified DNDC	g N/ha/day	R-W	Urea, NN,AS,GM	78.71	49.41	0.93		529.6				29.23	Babu et al. (2006)
		g N/ha	R-W	Urea, NN,AS,GM	0.22-14.1	0.24-15.4			2.09				0.98	
Canada	DNDC91	g N/ha/day	C-S-WW				0.02		2.4					Kariyapperuma et al. (2011)
Europe	PnET-N_DNDC	g/ha/day	Forest	NOFRETETE	0.2-15.7	0.1-18.2	0.0-0.69		0.3-13.8					Kesik et al. (2005)
Multiple sites	PnET-N-DNDC	g N/ha/day	TR	Several data sets	7.1	6.1	0.68	0.66						
Costa Rica	DNDC	kg/ha	C-Fertilized	1994-1995	1.17	1.25-1.4								Li (2000)
			C-Control		0.39	0.29-0.46								
Multiple sites	DNDC	kg N/ha	Crops, Pasture, Fa		0.252-137	0.143-165								Li et al. (1992b)
USA	DNDC	kg/ha/yr	Fa,G,SC	1979-1980	40.8-135.2	48.4-164.9								Li et al. (1994)
			Fa,G,SC	1980-1981	1.9-64.8	7.6-51.1								
China	DNDC	kg N/ha/yr	W-C		3.38	4.9	0.71							Li et al. (2010)
					1.28	2.3	0.6							
Germany	DNDC V4	g N/ha	L-WW		2210	2210								Ludwing et al. (2011)
India	Modified DNDC	kg N/ha	Rice		0.69	0.74								Pathak et al. (2005)
New Zealand	NZ-DNDC	g N/ha/day	Grassland	2001-2002	1.88-12.4	2-12†								Saggar et al. (2004)
New Zealand	NZ-DNDC	kg N/ha	Grassland	2003-2004	2.3	0.9-3.7								
Canada	DNDC7.1	kg N/ha	Maiz	1993	0.22-1.51	0.37-1.26				3	41	0.42		Smith et al.(2002)
				1994	0.56-2.43	0.78-1.57								
Canada			Can,W,Fa	1993						7	111	0.259		
			Can,W,Fa	1995						17	157	0.293		
Canada	DNDC89	kg /ha	Maiz	2007	0.738-	0.228-				-41,	142,	0.028,		

					2.04	3.08			224	435	0.121	
Canada	DNDC89	kg/ha	Maiz		0.86-0.965	0.916-1.03			-16, 5	305, 384	59, 66	
Germany	PnET-N-DNDC	g N/ha/day	Forest		0.6-12.8	0.1-13.4		0.08, 0.79				Stange et al. (2000)
UK	UK-DNDC		Grassland	Rowden Site			0.11-0.41					Wang et al. (2012)
China	Modified DNDC7.2	kg N/ha/yr	LC,GLC,SG, LC,SG	1995, 1998	0.125-0.185	0.211-0.612	0.5-0.66					Xu-Ri et al. (2003a)
China	DNDC7.2	g N/ha/day	LC,GLC,SG, GAF,CPM,AF,MM		0.41-1.92	0.35-1.23	0.054-0.68					Xu-Ri et al.(2003b)

Abbreviations Table 4.2 and 4.3

† Estimated based on Fig. 7 (Saggar et al., 2004), **2XCO2**:Atmospheric CO_2 doubling [650ppm], **AA**: Anhydrous ammonia, **AF**: Typical steppe area-no grazing, **AN**: Ammonium nitrate, **ARE**: Average Relative Error, **AS**: Ammonium sulfate, **BD**: Bulk density, **C**:Corn, **C4-CC**:Organic system without catch crop, **Can**: Canola, **Cal**: Calibration, **CD**: Coefficient of determination, **CM**: Cattle manure, **CmM**: Composted Manure, **Cold**: Using default model input, **CPM**: Meadow steppe area-cropped site, **Crop**: Crop adjustments, **C-S-WW**: Corn, Soybean and Winter wheat rotation, **CT**: Conventional tillage, **CT/RT**: Regular moldboard plough 25cm depth followed by seedbed preparation with a rotary arrow RT with shallow cultivation at 5-8 cm, **EV**: Error variance, **F**: Fertilizer type, **Fa**: fallow, **FC**: Field capacity, **G**: grassland, **GAF**: Typical steppe area-rotate grazing, **GLC**: Typical steppe area-free grazing, **GS**: Gas Chromatography, **H**: Humads, **HG**: Humid grassland, **Ks**: Hydrological Conductivity[cm min^{-1}], **L**: Litter , **LC**: Typical steppe area-*Leymus chinensis,* **L-WW**: Legumes-Winter wheat, **MAE**: mean absolute error, **ME**: Nash-Sutcliffe efficiency , **Merr:** Mean Error, **MI**: Microbial Index, **MM**: Meadow steppe area-Mowing, **MT**: Minimum tillage, **NA**: no value, **N-dep**: N-deposition (ppm), **NN**: No Nitrogen, **NOFRETETE**: Nitrogen Oxides Emissions from European Forest Ecosystems, **NR**: No Reported value, **NT**: No tillage, **O**: Onio, **O2+CC**:Organic with catch crop, **O4+CC**:Organic with catch crop, **O4-CC**:Organic system without catch crop, **Opt**: Optimized, **pH-FF**: pH-forest floor, **pH-MS**: pH-Mineral soil, **PS**: Pig Slurry, **R**: Rainfall**, Rdev**: Relative deviation % (*Abdala et al.,* 2009), **R-W**: Rice-Wheat cropping systems, **R-WC/RF**: Rice-winter cover crop/rice-fallow, **SB**: Spring-Barley, **SB**: Spring Barley, **SC**: Sugarcane, **SEE**: Standard error estimate, **SG**: Typical steppe area-*Stipa grandis*, **SL**: Sandy loam, **SO**: Summer oats, **SSR**: Sum of square residuals, **T+2**:Temperature +2°C, **TR**: Tropical rainforest, **Val**: Validation, **W-C**: Wheat-corn rotation, **WP**: Wilting Point, **ZT**: Zone tillage (reduce tillage scenario).

Table 4.4. Feasible range, optimum values and behavioral range of parameter values for N_2O simulations

Treatment	Parameters	Feasible range (optimum values)†	Behavioral Range‡	Behavioral Range§	
			CM	MN	MD
			kg N_2O-N ha^{-1} yr^{-1}	g N_2O-N ha^{-1} day^{-1}	
NT-F	BD	0.28-2.52(0.84,1.4**, 1.28)	1.42-4.12	0.55-2.89	7.72-25.43
	CLAY	0.198-0.242(0.23,0.20,0.24)	2.36-2.59	0.99-1.49	14.34-15.82
	FIELD	0.08-0.72(0.496,0.688,0.366)	2.33-9.62	0.7-3.3	13.74-60.89
	MAXYIELD	600-5400(5160,5400,2520)	2.16-3.33	0.95-1.66	12.94-20.83
	pH	4.816-7.224(5.06,6.22,5.54)	2.18-2.54	1.06-1.29	12.51-15.66
	SOC	0.0050-0.045(0.02,0.037,0.025)	1.49-7.19	0.49-4.01	8.17-45.25
	TDD	640-5760(1405,2170,3700)	2.03-3.28	1.06-4.83	11.58-20.06
	NDEP	1-6(5.39,5.39,5.39)	2.63-4.92	0.97-1.39	15.7-28.53
NT-C	BD	0.28-2.52(1.40,0.95,1.4)	3.06-8.32	1.61-12.66	18.68-39.48
	CLAY	0.198-0.242(0.22,0.198,0.231)	4.89-5.28	5.86-7.05	25.24-28.01
	FIELD	0.08-0.72(0.4,0.43,0.208)	3.03-8.5	0.72-9.08	14.03-48.18
	MANURECN	3-27(15*,15,15)	2.19-67.71	2.02-16.94	8.82-371.77
	MAXYIELD	600-5400(5400,3960,5400)	4.19-11.43	4.8-12.66	20.04-68.72
	pH	5.6-8.4(7.28,5.74,7.14)	3.47-5.68	4.82-6.76	15.2-30.53
	SOC	0.0082-0.074(0.00822,0.044,0.014)	1.52-12.7	0.67-17.49	8.86-59.64
	TDD	640-5760(1915,2680,2425)	4.26-9.08	4.49-10.16	19.59-53.81
	NDEP	1-6(5.39,5.39,5.39)	2.68-6.53	3.19-4.52	15.9-39.42
T-F	BD	0.28-2.52(0.84,1.4,0.84)	0.86-1.26	0.13-1.58	4.37-7.65
	CLAY	0.198-0.242(0.22,0.198,0.242)	0.87-0.9	0.59-1.03	4.49-4.66
	FIELD	0.08-0.72(0.4,0.4,0.4)**	0.86-1.69	0.13-1.7	4.05-11.06
	MAXYIELD	600-5400(5400,5400,5400)	0.84-0.98	0.68-0.91	4.24-5.13
	pH	5.68-8.52(7.1,5.8,6.5)	0.84-0.9	0.69-0.74	4.2-4.68
	SOC	0.0041-0.037(0.0041,0.004,0.0041)	0.87-2.45	0.26-2.18	4.29-16.37
	TDD	640-5760(2170,2170,2170)	0.84-0.96	0.67-0.99	4.09-4.97
	NDEP	1-6(5.39,5.39,5.39)	3.13-3.78	0.6-1.24	4.36-8.6
T-C	BD	0.28-2.52(0.616,1.4,0.616)	0.71-4.49	0.2-2.06	4.71-29.3
	CLAY	0.198-0.242(0.22,0.198,0.198)	3.08-3.1	0.66-1.12	21.03-21.3
	FIELD	0.08-0.72 (0.4,0.464,0.4)	1.39-3.17	0.46-2.25	8.4-21.46
	MANURECN	3-27(15*,15,15)	0.48-13.78	0.54-1.6	2.19-71.38
	MAXYIELD	600-5400(5400,2040,5400)	2.59-4.18	0.73-1.72	17.81-28.79
	pH	5.8-8.7(7.1,7.1,7.1)**	2.17-3.24	0.61-0.87	14.58-22.1
	SOC	0.0049-0.0437(0.0166,0.034,0.01)	0.42-5.54	0.23-3.15	2.46-34.94
	TDD	640-5760(1405,5230,1405)	1.22-3.92	0.77-2.42	6.61-27.16
	NDEP	1-6(5.39,5.39,5.39)	3.13-3.78	0.64-1	21.8-25.77

† Values corresponding to the optimum parameters for the aggregation methods CM, MD, and MN, respectively, are in parentheses.

‡ Behavioral range for CM approach.

§ Behavioral range for MD and MN approaches, respectively.

*The C:N manure ratio was set at 5 for 2011 simulations.

**Optimal values out of the range were set to the default values or a plausible value from the other aggregation methods.

Chapter 5 - Evaluation of climate change on N_2O emissions in Kansas agro-ecosystems

Abstract

Nitrous oxide (N_2O) emissions is one of the main greenhouse gases and it is important to understand how the agricultural soil management activities, such as tillage and other cropping practices contribute to the local and global N_2O emissions. Climate change impacts involve developing plausible future climate scenarios to be used in a process based N_2O model at the regional level. The objectives of this study were to analyze future climate scenarios of daily precipitation, maximum and minimum temperatures, and to evaluate potential effects of climate change on N_2O emissions from Kansas agroecosystems. Change Factor Methodology (CFM) was used to derive plausible future scenarios of precipitation and temperatures from Regional Climate Models (RCM). Two time periods -baseline (20C3M, 1968-2000) and future (A2, 2038-2070) - of daily weather simulations from multiple RCMs were obtained from North American Regional Climate Change Assessment Program (NARCCAP) and the observed weather data were obtained from 23 long-term weather stations in Kansas. The Denitrification and Decomposition (DNDC) model was used to simulate N_2O emissions at regional level. Results indicated an increase in temperature across the state and the rate of increase varied among the climate zones. In the case of precipitation, there was variability in the rate and direction of change across the state. As a result of changes in climate, N_2O emissions predicted from the DNDC model was highly variable due to changes in climate, soil conditions and agricultural management practices. Conversion from till to no-till had an overall reduction of N_2O emissions for corn, sorghum and soybean under non-irrigated systems (2.9-23.1%) and no effect on irrigated systems (-19.5-29%). In winter wheat the conversion to no-till increased the overall N_2O emissions, in both irrigated and non-irrigated systems for about 30%.

Introduction

There is strong evidence of climate change due to human activities such as burning fossil fuels, deforestation, and several agricultural practices and industrial processes. Those activities are increasing the concentration of CO_2 and other greenhouse gases. Changes in atmospheric composition induces changes in temperatures and precipitation which alters marine and terrestrial ecosystems (Walthall et al., 2012).

The primary tools to understand and project climate change due to increasing greenhouse gas concentrations are global circulation models (GCM) (Intergovernmental Panel on Climate Change, 2007) and a large body of theoretical and observational results (Walthall et al., 2012). GCM can simulate contrasting changes in future climate. Consequently, data from various GCMs are essential for uncertainty assessment on the impact of climate change (Lee et al., 2011).

Projections of the future global change have been generated as a result of many different emission scenarios (Nakicenovic et al., 2000) as part of the International Panel on Climate Change (IPCC) Fourth Assessment Report (AR4). Many studies evaluating impacts and mitigation strategies from agriculture have been focused on emission scenarios (Flynn et al., 2005; Avnery et al., 2011; Eckard and Cullen, 2011; Lee et al., 2011; Syp et al., 2011; Tao et al., 2011; Ko et al., 2012; Tatsumi and Yamashiki, 2012; Ye et al., 2013), mainly the IPCC SRES A2 scenario (Ducharne et al., 2007; Tadross et al., 2009; Sushama et al., 2010; Lee et al., 2011; Syp et al., 2011; Ramirez-Villegas et al., 2012; Moore and Ghahramani, 2013). The A2 scenario is the result of slow technological improvement, high growth rate of population, and lack of interest from individual, corporation and governments to limit emissions (Walthall et al., 2012). Under the A2 scenario, the CO_2 concentration is expected to increase exponentially from 352 ppmv in 1990 to 522 ppmv by 2050 and 836 ppmv until 2100 (Lee et al., 2011). At the end of the 21st century an increase in surface temperature between 2.0 and 5.4°C is projected compared with the period between 1980 and 1999 (Lee et al., 2011; Walthall et al., 2012).

Integrating emission scenarios with ecosystem models will not only improve estimates of emissions and impact assessments, but also identify and evaluate mitigation strategies (Pathak et al., 2005). Until now, most assessment studies have focused on the effect of climate change on crop production (Lee et al., 2011: Ko et al., 2012). Few studies have attempted to evaluate the effect of climate change on greenhouse emissions from soils (Flynn et al., 2005; Abdalla et al., 2010b; Syp et al., 2011; Abdalla et al., 2012) even though a substantial increase in N_2O emissions from agricultural soils is projected through to 2030 as a result of the expansion in crop and livestock production (Reay et al., 2012).

Nitrogen is an important nutrient for life processes on earth so too little or too much nitrogen can have a large impact on ecosystems. From the agricultural perspective the lack or excess of N represents limitation in food production or contaminations of water and air. Soil microbial processes are important in the N cycle so changes in temperature and precipitation can trigger events of higher emissions of gaseous N molecules. Nitrous oxide (N_2O) is one of the three major anthropogenic greenhouse gases (CO_2, CH_4 and N_2O), and in cultivated soils levels of N fertilizer have a major influence on N_2O emissions (Flynn et al., 2005; Delgado et al., 2013).

Understanding the effects of climate change on nitrous oxide (N_2O) emissions in agro-ecosystems is important because agricultural soil management activities, such as fertilizer application and other cropping practices play a major role in N_2O emissions. This involves developing plausible future climate scenarios which can then be used in process-based models for predictions of N_2O at regional level.

The objectives of this study were to create a future scenarios of daily precipitation, maximum and minimum temperature and to evaluate the potential effects of future climate and tillage on N_2O emissions from both irrigated and non-irrigated crops across Kansas

Methodology

Study area

The region of interest was the state of Kansas an energy-producing and agriculture-based state (Merriam, 2009), which is part of the central Great Plain region of United States, one of the largest agricultural areas for global economy and food security (Easterling et al., 1993). Winter wheat, corn, and sorghum and soybean are among the main cropping systems in Kansas. The state of Kansas covers an area of 213,096 km^2 (Institute for Policy & Social Research, 2011) and nine climate divisions (NCDC, 1994).

Data

The North American Regional Assessment Program (NARCCAP) provides dynamically downscaled GCMs output at a spatial resolution of 50 km. An area that covered the entire state of Kansas was selected (Fig. 5.1). NARCCAP uses different atmosphere-ocean circulation models (AOGCMs) to provide boundary conditions for different regional climate models (RCMs) which help to explore the uncertainties in regional climate model simulations and provide regionally resolved climate projections important for adaptation and mitigation studies (Mearns et al., 2012). NARCCAP is divided in two phases: Phase I, in which six RCMs use boundary conditions for the NCEP-DOE Reanalysis II (R2) for a 25-yr period (1980-2004), and phase II, in which the boundary conditions are provided by four AOGCMs for 30 years of current climate (1971-2000) and future climate for 30 years (2041-2070) for the Special Report on Emissions Scenarios (SRES) A2 emissions scenarios (Nakicenovic et al., 2000) .

In the current work, datasets from the phase II include a series of AOGCMs and RCMs combinations (Table 5.1). Briefly, six datasets were used as result of three RCMs and three AOGCMs. The three RCMs were: The Canadian RCM (CRCM) from OURANOS/UQAM, the Regional Climate Model version 3 (RCM3) from UC Santa Cruz and the Weather Research and Forecasting model (WRFG) from the Pacific Northwest National Lab. The three GCMs were: The Community Climate System Model (CCSM) from National Center for Atmospheric Research, the Third Generation Coupled Global Climate Model (CGCM3) from Canadian Center for Climate Modeling and the Geophysical Fluid Dynamics Laboratory GCM (GFDL). Due to differences in the coordinate systems, all models were re-gridded to an identical grid resolution using the function linint2_Wrap from NCL software (NCL, 2012). The total number of cells used in this analysis was 97 that cover the state of Kansas (Fig. 4.1).

The data used in this study was accessed on Sep/2012 (Mearns, 2007, upated 2012). The selected combinations of AOGCMs and RCMs, referring later as RCMs, had simulations of precipitation, maximum and minimum temperatures. Precipitation is at 3 hr resolution (kg m^{-2} s^{-1}) and maximum and minimum are at daily resolution (°K). The data is available via Earth System Grid data portal. The data format is in standard-compliant, GIS compatible Network Common Data Form (NetCDF).

Scenarios of precipitation and temperature

The change factor methodology was used to develop plausible climate change scenarios (CFM) or delta change factor following the methodology proposed by Anandhi et al. (2011) (Fig. 5.2). The CFM used in this study was categorized by its mathematical formulations (additive or multiplicative) as explained in Fig. 5.2. Briefly, the first step is to estimate the mean values of each combination of RCMs (Table 5.1) simulated baseline (current climate) and future climates (equations (1) and (2)) for the closest point to each long-term weather station.

$$\overline{RCMb} = \sum_{i=1}^{Nb} RCMb_i / Nb \tag{1}$$

$$\overline{RCMf} = \sum_{i=1}^{Nf} RCMf_i / Nf \tag{2}$$

$\overline{RCMb}$ and $\overline{RCMf}$ represents the mean values of precipitation or temperature in the temporal domain selected (month), in which $RCMb_i$ and $RCMf_i$ represent the daily values of precipitation and temperature representing the RCM baseline (20C3M) and RCM future climate scenario, respectively. Nb and Nf are the number of values in the temporal domain (e.g. 31x30 , representing the days of a specific month (31) and years of analysis (30)).

The second step was to calculate the additive and multiplicative change factors (CF_{add}, CF_{mul}, respectively) (Equations (3) and (4)).

$$CFadd = \overline{RCMf} - \overline{RCMb} \tag{3}$$

$$CFmul = \overline{RCMf} / \overline{RCMb} \tag{4}$$

The final step was to estimate the local scaled future values ($LSf_{mul,i}$ and $LSf_{add,i}$) by applying the CF_{add} and CF_{mul} (equation (5) and (6)).

$$LSf_{add,i} = LO_{bi} + CF_{add} \tag{5}$$

$$LSf_{mul,i} = LOb_i x CF_{mul} \tag{6}$$

where LOb_i were the observed precipitation and temperature values from the 23 long-term weather stations across Kansas (Fig. 4.1, Appendix B.1). $LSf_{add,i}$ and $LSf_{mul,i}$ are the values that represent future scenarios for temperature (maximum and minimum) and precipitation, respectively.

Scenarios of N_2O emissions

The Denitrification and Decomposition model (DNDC version 9.4) (Li et al., 1992b) was used for N_2O simulations. The soil (pH, soil organic carbon, clay content and bulk density), management (conventional tillage, no-tillage, irrigation and no-irrigation), crop (corn, sorghum, soybean and winter wheat) and weather (precipitation and temperature mainly) information were the main input parameters for DNDC. The construction of a GIS dataset was the first step towards N_2O simulation regionally.

GIS datasets for Nitrous Oxide simulations using DNDC

USGS level 14 hydrologic unit code boundaries (HUC14 watersheds) were used as the mapping unit for this model run (USGS, 2008). There were 2,052 watersheds averaging 10,387 ha. Crop area for each watershed was estimated using 2006 USDA National Agricultural Statistics Service Cropland Data Layer for Kansas. Crop areas (ha) were calculated for each watershed using the ArcGIS Spatial Analyst zonal sum command (ESRI, 2011).

The USDA NRCS Soil Survey Geographic Database (SSURGO) was used to estimate watershed-wide soil properties. For each map unit the top soil horizon was extracted along with the soil attributes shown in Table 5.2. SSURGO data were downloaded for each county in the study area. The DNDC model requires four soil attribute inputs at a minimum. The following SSURGO horizon attributes were extracted:

Total clay fraction (representative value) – a proxy for soil texture
Organic matter fraction (representative value) – a proxy for soil organic carbon
Bulk density at a water tension of 0.03 MPa (representative value)
Soil pH (representative value) – converted to ion concentration for spatial averaging

The map unit was the smallest explicitly mapped area in the SSURGO dataset. Soil attributes were stored by soil horizon; soil horizons were linked to soil components. Each map unit has one or more soil component of varying percentages. Therefore, soil attributes were averaged to the appropriate depth within horizons (from 0 to 10 cm), then averaged by percentage among components within a map unit. Map units with "no data" were also tracked.

For each HUC14 watershed a spatially weighted mean value for each soil attribute was calculated by converting map unit data to raster format and performing a zonal mean using ArcGIS Spatial Analyst. Soil clay, organic matter, pH and clay fraction are key soil environmental drivers that influence N_2O emissions. The spatial variability in soil clay fraction, organic matter content, pH and bulk density by HUC14 are illustrate in Fig 5.3.

N deposition was estimated using National Atmospheric Deposition Program National Trends Network sites data (National Atmospheric Deposition Program, 2012) (total wet deposition, kg/ha, year 2009). Sites were converted to a GIS format and converted to raster using the ArcGIS Spatial Analyst inverse distance weighted interpolation algorithm (ESRI, 2011).

Crop management practices such as planting and harvesting dates varied across the four agricultural zones (Fig. 5.4) and were based on the Kansas Crop Planting Guide (Kansas State University Experiment Station and Coopertive Extension Service, 1996) (KSU Extension publication L818) (Table 5.3). Date ranges for each agricultural zone were averaged to arrive at a single date.

Management practices

Different management strategies were tested regionally based on different crops, irrigations and tillage. Tillage dates were based on planting and harvesting dates. Plowing with moldboard at 20 cm during planting date and plowing with disk or chisel at 10cm after harvesting date were set in DNDC as conventional tillage management. Mulching in DNDC refers to no tillage management. Fertilizer application rates for corn (147 and 205 kg N ha^{-1} for non-irrigated and irrigated systems, respectively), soybean (0 kg N ha^{-1}) and winter wheat (60 and 128 kg N ha^{-1} for non-irrigated and irrigated systems, respectively) were based on USDA Economic Research Service Farm and Business and Household Survey Data, (USDA Economic Research Service, 2012). The fertilization rate for sorghum (91 and 140 kg N ha^{-1} for non-irrigated and irrigated systems, respectively) was based on the Grain Sorghum Production Handbook (Kansas State University Experiment Station and Coopertive Extension Service, 1998). For the management scenarios with irrigation, we set the irrigation index in DNDC to 1.0 and 0.0. In the first case the model assumes irrigation water is applied to meet agronomic demand and the second case the water is supplied by precipitation.

Uncertainty analysis

Precipitation and temperature scenarios

Different RCMs allowed calculation of uncertainty due to climatic variables. The uncertainties of CFs were calculated based on the 5 and 95 percentile in each one of the 23 long-weather stations per season. Analysis of variance was performed for detecting differences among RCMs, climatic zones and climate seasons using proc mixed (SAS Institute, 2010).
For maximum and minimum temperatures and precipitation the next statistical model was evaluated:

$$Y_{ijkl} = u + R_i + C_j + S_k + RC_{ij} + RS_{ik} + CS_{jk} + e_{ijkl} \qquad (7)$$

where Y_{ijkl} is the estimated change factor (CF) for temperature or precipitation in *ith* RCM, *jth* Climate zone, *kth* season and *lth* grid point, *u* is the overall mean, *R* is the effect of RCMs, *C* is the effect of climate zones, *S* is the effect of seasons, *RC* is the interaction RCMs x Climate zones, *RS* is the interaction RCMs x Seasons, *CS* is the interaction Climate zones x Seasons and *e* is the overall random error.

N_2O emissions

N_2O fluxes have skewed distribution in which a lognormal distribution is often recommended. The statistical analysis were performed using the proc mixed from SAS (SAS Institute, 2010), assuming log-normal distribution. A 2 x 2 x 4 x 7 factorial design was used involving two tillage practices (conventional tillage and no-tillage), two irrigation practices (irrigated and non-irrigated land), four crops (corn, sorghum, soybean and winter wheat) and seven sources of climate data (One local observed climate: Climatic observation from 23 long-term weather station across Kansas, and six local scaled future climate: based on six RCM climatic simulations-Table 5.1-).

For testing the effect of conversion of conventional tillage to no-till under irrigated or non-irrigated land, a 4 x 7 factorial design was used with four crops and seven climate datasets. The response variable is the difference between conventional till and no till in terms of N_2O-N fluxes (kg N ha^{-1} yr^{-1}) and the total emissions (area-weighted emissions) per watershed (Mg N yr^{-1}).

N_2O distribution analysis

The simulated N_2O from local observed climate conditions (Obs) and climate change scenarios (RCMs) where evaluated using probability density curves. If the probability density curves were significantly different, there was an effect of climate change on N_2O emissions. In addition to the visual plots, the statistic Kolmogorov-Smirnov (K-S) test was used to determine significant differences. The maximum absolute distance of cumulative distributions between N_2O simulations based on Obs and RCMs is the computed K-S test statistic. When the K-S test was smaller than the correspond critical value, both data distributions were significantly similar (Cheng et al., 2008). The analysis was performed using the function ks.test and the library ggplot2 (Wickham, 2009) from R (R Core Team, 2012).

Uncertainty due to soil conditions

The uncertainty analysis was performed using a Monte-Carlo routine in DNDC (Li et al., 2004). The observed range of each soil property in each cell was divided in eight intervals. DNDC selects randomly each interval of the properties selected to form a scenario. The process was repeated 4000 times. Since the method was computationally expensive in order to cover all of Kansas, the grid cell corresponding to the Manhattan area was selected. Several soil properties were selected: SOC (0.016-0.032 kg C kg^{-1}), pH (5.89-7.23), bulk density (1.14-1.32 g cm^{-3}) and clay content (19.27-28.52 %).

Results

Precipitation and temperature scenarios

Maximum Temperature

Based on the percentiles 5 and 95, the maximum variability in CFs among RCMs occurred during fall season (SON; September – October - November) (Fig. 5.6).

There was a significant interaction between GCM and climate zones. The CFs from model WRFG driven by ccsm (WRFGccsm) were statistically different from WRFGcgcm in all the climate zones (Fig. 5.7). The CFs from model RCM3cgcm was statistically different from RCM3gfdl in the climate zone north-east (NE). The only model that captured significant differences in change factors (CFs) among zones was WRFGcgcm in which the climate zones east-central (EC) and south-west (SW) had a marginal statistical difference (p=0.0561), and north-east (NE) and north-west (NW) and south-east (SE), and SE and SW had significant differences (p-value < 0.05). The higher CF occurred in the SW and NW, and no significant differences between zones SW and NW.

The season x RCMs interaction effect was significant. In all GCMs the change factors between DJF (D: December, J: January, F: February) and MAM (M: March, A: April, M: May) were not statistically different. In some RCMs (CRCMccsm, RCMgfdl and WRFGccsm) there were no significant differences between DJF and SON. In CRCMcgcm and RCM3cgcm the change factors in seasons JJA (J: Jun, J: July, A: August) and SON were not significantly different (Fig. 5.8). There were significant maximum temperature changes between winter (DJF) and summer (JJA), and between spring (MAM) and summer (JJA). The magnitude of change in temperature during summer was significantly higher. During the winter season the change factors in NW and SE, and SE and SW were statistically significant. The climate zones central (C), north-central (NC), south-central (SC), east-central (EC), west-central (WC) did not have a significant seasonal effect (Fig. 5.9).

Maximum CFs among most RCMs occurred during summer season (JJA; June-July-August) excepting WRFGcgcm3 which occurred during spring season (MAM; May-April-May). Among six RCMs, RCM3cgcm has highest CF (3.09±0.06°C) while WRFGccsm had the lowest CF (1.64 ±0.04°C). In terms of season effect, JJA had the highest CF in maximum temperature (3.51±0.04°C) while MAM had the lowest (1.94± 0.04°C).

Minimum Temperature

Maximum variability in CF among RCMs occurred during winter (DJF; December-January-February) and spring season (MAM) in most of the state of Kansas (Fig. 5.10).
The season x GCMs interaction was significant. Two models had a significantly higher CFs during summer (CRCMccsm, RCM3gfdl). CRCMcgcm and RCMcgcm had similar CF values in

summer (JJA) and fall (SON), WRFCcgcm had a higher CF on spring (MAM) and WRFGccsm had higher CF during winter. The models driven by the same GCM do not necessarily agree with seasonal changes factors for minimum temperature (Fig. 5.10).

Overall, the highest CFs occurred during summer season (JJA) (3.04 ±0.03°C) followed by SON (2.53 ±0.03°C) (Fig. 5.11). No significant differences were detected between DJF and MAM (2.31± 0.04 and 2.23± 0.03°C, respectively). Among the mean values of change factors (CF) in GCMs, the models WRFGccsm, CRCMccsm, and RCM3cgcm had the highest CF (2.79±0.03°C ,2.74 ±0.04 °C and 2.71±0.04°C, respectively) while WRFGcgcm had the lowest CF (1.96±0.04°C). RCM3gfdl had a CF of 2.4±0.05°C significantly different from all the other RCMs (Fig. 5.11).

No significant changes in CF were detected throughout the climatic zones.

Precipitation

Maximum variability in CF occurred mostly in winter season (DJF) at most weather stations (Fig. 5.12). Significant decreases in precipitation was detected by most of the RCMs evaluated during the summer season (JJA) (change factors values from CRCMcgcm, RCM3gfdl, CRCMccsm and WRFGccsm were -12±2%, -14 ±1.5%, -21 ±2.3%, -21± 1% , and -31± 2.3% , respectively) except the WRFGcgcm model where the precipitation increased 5%±2.4 (Fig. 5.13). RCM3cgcm, CRCMccsm and WRFGccsm detected increasing precipitation during the spring months (MAM) (11±1.5% , 16±1.3%, and 33±2% , respectively) while CRCMcgcm, RCM3gfdl and WRFGcgcm detected higher change in precipitation during winter months (15 ±2.8%,19±2.8% and 34±4%, respectively) (Fig. 5.13). Overall, increases in precipitation were similar in MAM and DJF seasons (14.2±0.6% and 12.5±1%, respectively) and significant than the SON season (4±1.2%). The season JJA had a significant reduction in precipitation of around 26±0.8%. RCMs driven by different OAGCMs resulted in significant change in precipitation.

Regional N_2O simulations

There were significant differences in the overall mean values and distribution of N_2O emissions due to (1) RCMs forced with two AOGCMs (Table 5.1) and (2) conversion from conventional till to no-till.

Changes in precipitation and temperature increased the N_2O emission rate (kg N ha^{-1} yr^{-1}) as well as total area-weighted emission per watershed (Mg N yr^{-1}). The simulations based on RCMs tended to produce higher emissions in all crops under till and no-till systems across the state.

Statewide N_2O emission rate on cropping systems

The N_2O fluxes from sorghum had a similar response to irrigation. In general, irrigation affected significantly the emissions in corn, soybean and winter wheat (Fig. 5.14a, 5.14b) where the emissions were significantly higher in non-irrigated corn than irrigated corn, the emissions under NT soybean switched from lower in non-irrigation to higher emissions under irrigation and the emission in winter wheat under irrigation where higher than in non-irrigation systems (Fig. 5.14a, 5.14b) .

The N_2O emissions in corn, sorghum, soybean and winter wheat increased under future conditions around 0.5 to 2.2 kg N_2O-N ha^{-1} yr^{-1} (Fig. 5.14a, b).

Tillage effect

The N_2O simulations using observed weather data (Obs) showed that the conversion from till to no-till under non-irrigated systems reduced (absolute values in parenthesis) N_2O emissions in Kansas for corn (0.71 kg N ha^{-1} yr^{-1}, 95%CI:0.65-0.77), sorghum (1.43 kg N ha^{-1} yr^{-1}, 95%CI:1.37-1.5) and soybean (0.12 kg N ha^{-1} yr^{-1}, 95%CI:0.06-0.18), but increased emissions for winter wheat (0.50 kg N ha^{-1} yr^{-1}, 95%CI:0.45, 0.55) (Fig. 5.15, and spatial distribution of N_2O changes Fig.5.18-5.21).

Overall, under current condition the reduction of N_2O emissions accounted for about 0.4 kg N ha^{-1} yr^{-1} (0.38-0.44) in non-irrigated cropping systems. Under irrigated systems that difference was 0.34 kg N ha^{-1} yr^{-1}(0.32-0.38). The effect of climate change on N_2O emissions follows the same trend as the observed dataset (Obs). Results using different RCMs as weather input for N_2O simulation resulted in higher reduction of N_2O emission than the observed weather (Fig. 5.15). On average, under future scenarios the reduction in N_2O emission was between 0.45 up to 0.95 kg N ha^{-1} yr^{-1} in non-irrigated systems and from 0.38 up to 0.88 kg N ha^{-1} yr^{-1} in irrigated systems.

It appears that the conversion from conventional tillage to no-tillage has an overall positive impact on reducing N_2O emissions under current conditions but the impact of reducing N_2O emissions was higher under changing climate conditions (temperature and precipitation).

Kolmogorov-Smirnov test was used to detect differences among the distributions of N_2O emissions based on RCMs and observed data sets (Fig. 5.16, 5.17). In all crops evaluated the data distributions of N_2O emissions were different among the RCMs, tillage and conversion to no-tillage.

The N_2O emission response to climate change and cropping systems did not have similar response across tillage and irrigation systems. For example, in soybean and winter wheat the distributions of predicted N_2O emissions using RCMs driven by different GCMs (CRCMccsm and CRCMcgcm) were similar in conventional till as well as in no-till system for emission rate (kg N_2O ha^{-1} yr^{-1}) and for area-weighted emissions (Mg N yr^{-1}) (p-value > 0.05, K-S test, Appendix B.2). On the other hand, in corn, sorghum and soybean the N_2O distributions under conventional till and no-till based on RCMs driven by different GCMs were significantly different (p-value<0.001, K-S test). In some cases the area-weighted emission values of N_2O (Mg N yr^{-1}) had similar distributions (p-value > 0.05 K-S test) while the emission rates had significantly different distributions. For instance, while the distributions of N_2O emission rates in irrigated corn, soybean and winter wheat were different between RCM3 models, the distribution of the area-weighted N_2O emissions were similar (See Appendix B.2, K-S results). It may not be appropriate to use a single RCM driven by several GCM for climate change studies because it may not provide enough evidence of climatic change affecting N_2O emissions.

The rate of N_2O emission distribution based on different datasets were significantly different in most of the crops and RCMs, except in soybean and winter wheat, where CRCM driven by two GCM models did not have significant differences (p-value>0.05 K-S test, Appendix B.2).

Conversion from conventional tillage to no-tillage had an overall positive effect on N_2O emission reduction. Conversion effect was detected using different RCM models in most of the crops evaluated (Fig. 5.18-5.20). The conversion in terms of area-weighted was not detected in non-irrigated and irrigated soybean when RCM3cgcm and RMC3gfdl model were used as climatic inputs (p-value>0.05, K-S test, Appendix B.3).

The uncertainty of N_2O emissions due to spatial distributions of crops and soil, in additions of climate change are shown in Fig 5.18-5.21. For instance, in corn the conversion from conventional tillage to no-till resulted in a reduction of N_2O emission (>7.04 Mg yr^{-1}) per HUC14 unit in the major growing areas (Fig. 5.18). Opposite results were observed for winter wheat (Fig. 5.21) where the increase in N_2O emissions were significant with the conversion from conventional tillage to no-till. Among the four crops evaluated winter wheat accounted for 54% of the cropping area. Even though the emission rate was significantly lower for corn and sorghum, the area-weighted emissions were higher.

Uncertainty associated with soil properties

The Monte Carlo simulations provide information of the frequency of distribution of the modeled N_2O emissions in a single watershed (where the experimental plots are located) (Fig. 5.22). Observations of N_2O emissions in corn (3.8±0.5 kg N_2O-N $ha^{-1}yr^{-1}$) fell inside the histogram of N_2O simulated for non-irrigated conventional tillage. No observations from sorghum, soybean and winter wheat were available for testing the accuracy of simulated N_2O emissions.

Discussion

Based on climate change factors using six RCMs we found positive temperature changes for all season which were significantly higher during summer season. Those results were in concordance with Walthall et al. (2012) for most of the regions of the United States where the annual mean temperatures for the next 40 yr will increase of 1°C to 2°C which reflect the accelerated rate of GHG concentration and temperature observed during the past decades. Walthall et al. (2012) found that much of the interior of the United States is likely to see increases of 2°C and 3°C. Brunsell et al. (2010) found a general trend of greater increase in temperature in the western portions of the state of Kansas for spring, summer and fall. In winter the eastern portion of the state had a higher temperature increase. Using change factor methodology we found the same trend for maximum temperature. Higher change in temperature in the western climate zones during spring, summer and fall and higher change in temperature for winter in the eastern climate zones. Increases in temperature will likely have an impact in the length of growing season reaching the scale of a month or two by the end of the 21th century (Walthall et al., 2012). Increases in temperature will negatively affect crop yield throughout the 21st century (Schlenker and Roberts, 2009; Hatfield et al., 2011; Lobell et al., 2011; Walthall et al., 2012).

For precipitation an increase change factor for winter, spring and fall in all climate zones and a decrease change factor for summer. Similarly, Brunsell et al. (2010) found increasing trends for spring (except in south western Kansas) and winter precipitation, but due to the large variance during the summer, the decreasing trend was only detected in the south western Kansas. Opposite results were found for the fall season. Our results exhibit a slight increase in the change factor, while Brunsell et al. (2010) reported a decreasing trend across the state. The differences between studies may be related with the resolution of the analysis. In our study we use RCMs driven by different GCMs for 90 grid cells across Kansas, while Brunsell et al. (2010) used GCMs results from 6 grid cells. According to Walthall et al. (2012) precipitation is likely to decrease during the summer and increase during the winter (for about 5-15% in most of the northern and central U.S over the next 30-40 years).

Decreasing precipitation during the summer accompanied by increasing in temperature will lead to a greater soil moisture deficit affecting agricultural production (Brunsell et al., 2010). Although there will be likely an overall increase in precipitation, it does not necessarily mean available water for agriculture when it is needed since the impact of high temperatures have both earlier melt and runoff of water store in snow cover, and increase evapotranspiration (Walthall et al., 2012). It is projected that an increase in precipitation intensity will lead to rapid runoff and less available water for ecosystems (Walthall et al., 2012).

Syp et al. (2011) performed simulation of N_2O for eastern Poland (using one location as representative of the region) where the highest temperature increases in January, and the mean annual precipitation decreased 1% for C2030 and 1.2% for C2050. Syp et al. (2011) found that the emissions decreased by 6 % and 10% compared with the baseline (C2000) for C2030 and C2050, respectively with no significant differences between scenarios. In a single location study carried out by Abdalla et al. (2012) found that future scenarios of temperature and precipitation reduced total N_2O emissions in a sandy loam soil under conventional tillage but increased N_2O emissions under reduced tillage coupled with cover crops in Ireland. Even though there is spatial variability, the changes in climatic conditions observed for Kansas, N_2O emissions were enhanced, and the differences between conventional tillage and no-till were significant for the crops evaluated. Similarly Flynn et al. (2005) reported changes in N_2O emissions in Scotland due to climate change from 0.50 kg N_2O-N ha^{-1} yr^{-1} to 0.80 kg N_2O-N ha^{-1} yr^{-1} using the emission factor methodology. Eckard and Cullen (2011) estimating the effect of climate change from Australian pasture-based dairy systems found an increase in N_2O emissions up to 40%. It seems that predicted warmer temperatures and wet soil conditions during cooler months resulted in an increase in N_2O emissions (Abdalla et al., 2012; Reay et al., 2012).

Syp et al. (2011) found significant differences between tillage and reduce tillage. Reduce tillage decreased the emissions for about 16-23% in all scenarios. Our results showed that under non- irrigated systems the reduction of N_2O emission rate due to the conversion to no-tillage was 21% for corn, 21% for sorghum and 11.4% for soybean under the future scenarios of climate change. For winter wheat the conversion to no-till increased N_2O-N emissions by 17%. The increased precipitation during spring and warmer winters in most climate scenarios (Fig.5.8, Fig.5.11 and Fig. 5.13) may increase N_2O emissions in no-till winter wheat more than in no-till summer crops. Syp et al. (2011) found increasing emission of N_2O due to conversion to reduced tillage of around 2.5% in winter wheat. The main differences between the two sites were the clay fraction and SOC content. In Kansas the clay fraction in a large part of the area ranges between 16 and 45% (Fig. 5.3). In eastern Poland the clay fraction was 9%. The SOC in the majority of Kansas area is higher than 0.02 kg C kg^{-1}, while in eastern Poland is around 0.01 kg C kg^{-1}.

In our study considering the area-weighted values of N_2O emission, the average reduction of N_2O emissions due to conversion to no-till was 2.1%. But that percentage could be higher if additional practices (such as crop rotation, fertilizer source, timing of N application, etc) are implemented for reduction of N_2O especially for winter wheat, since this crop alone accounted for about 50% of the total area-weighted N_2O emissions. Grand et al. (2004) found that change of management from conventional to no-tillage resulted in a reduction of N_2O emission of around 17% on a weighted average for Canada over 30 yr.

Conclusions

Although the emissions will likely increase due to increasing the temperature and changes in precipitation, our study shows that no-tillage in both irrigated and non-irrigated cropping systems (corn, sorghum and soybean) will reduce the N_2O emissions from soils at a statewide level and therefore contribute to mitigate the global warming.

The conversion from till to no-till under winter wheat may not be suitable for future mitigation of N_2O since the higher temperatures in cooler months as well as higher precipitation have direct effects particularly on denitrification and mineralization.

No-tillage coupled with practices that promote N-use efficiency such as the use of efficiency-enhanced N fertilizers, reducing N rates, optimizing N placement and timing will have a major impact reducing the overall N_2O emission from Kansas agriculture.

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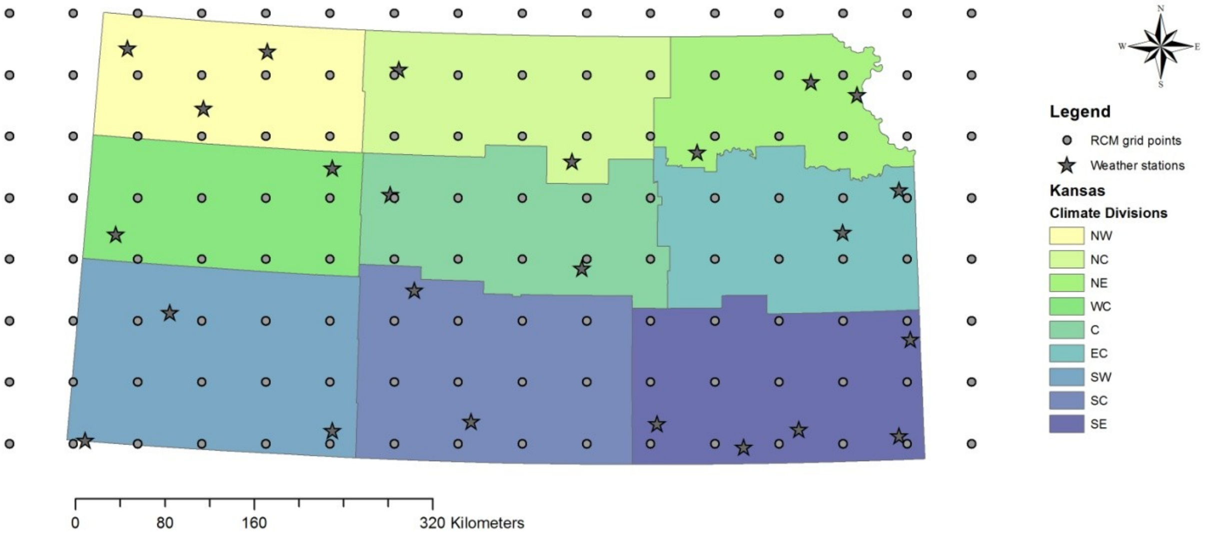


Figure 5.1. Grid points of the space domain (state of Kansas). The stars represent the locations of the 23 long-term weather stations across nine climate divisions.

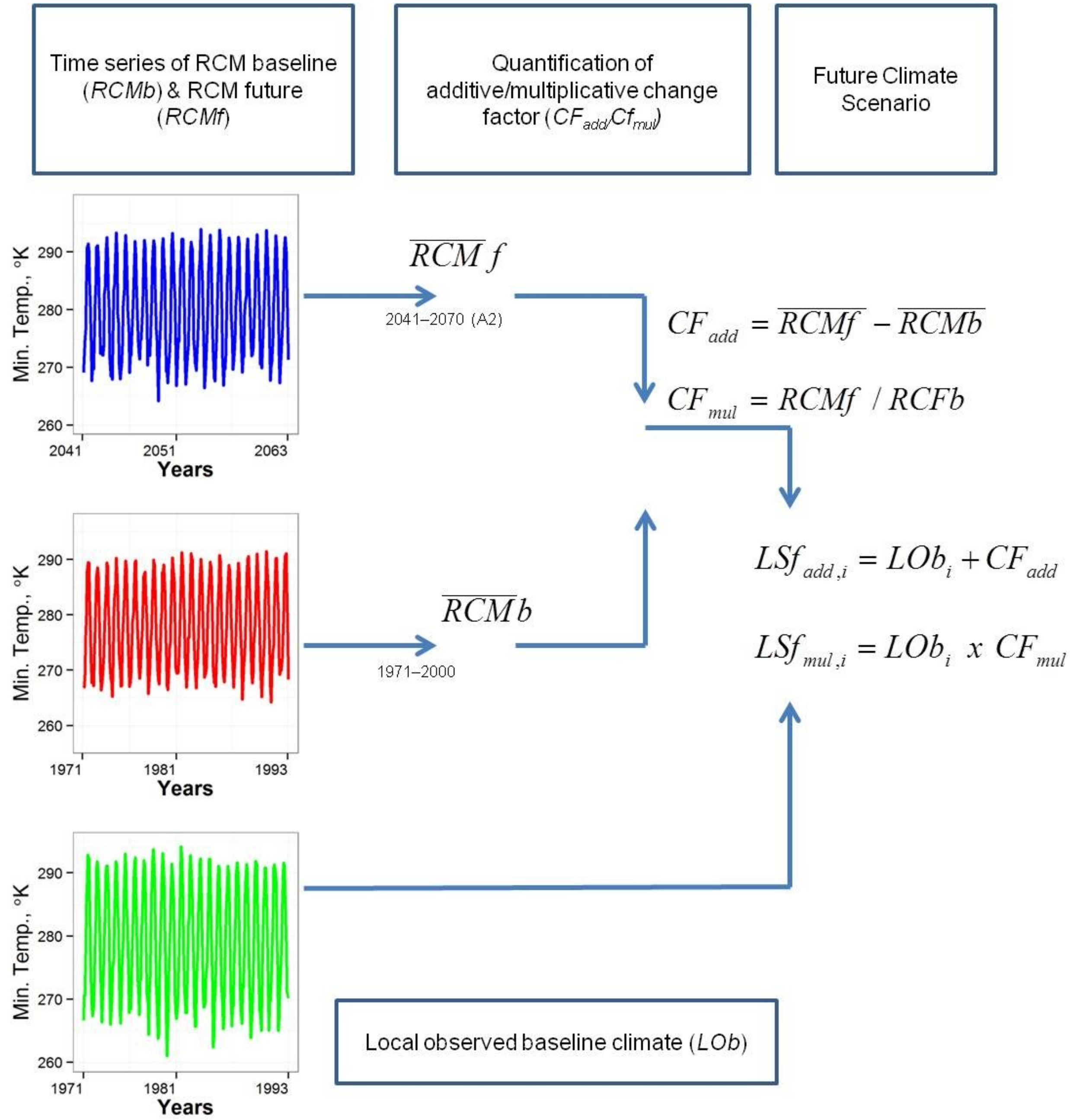


Figure 5.2. Change factor Methodology for calculating future changes in precipitation and temperature.

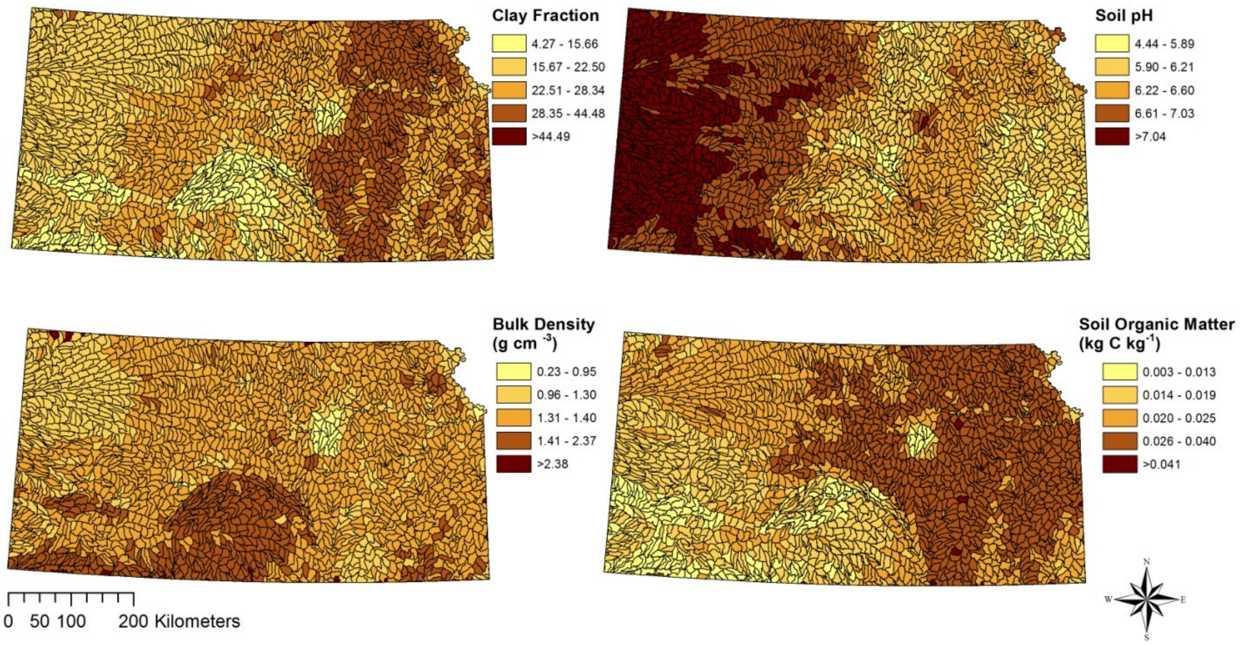


Figure 5.3. Spatial variability in soil environmental drivers

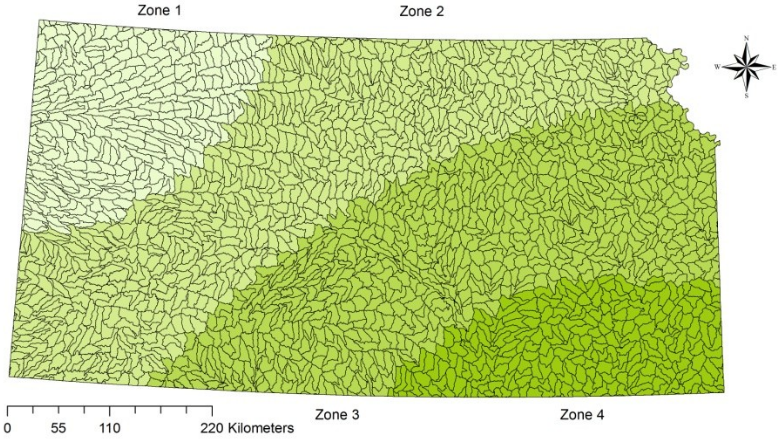


Figure 5.4. HUC14 watersheds (2052 watersheds) colored by agricultural zones

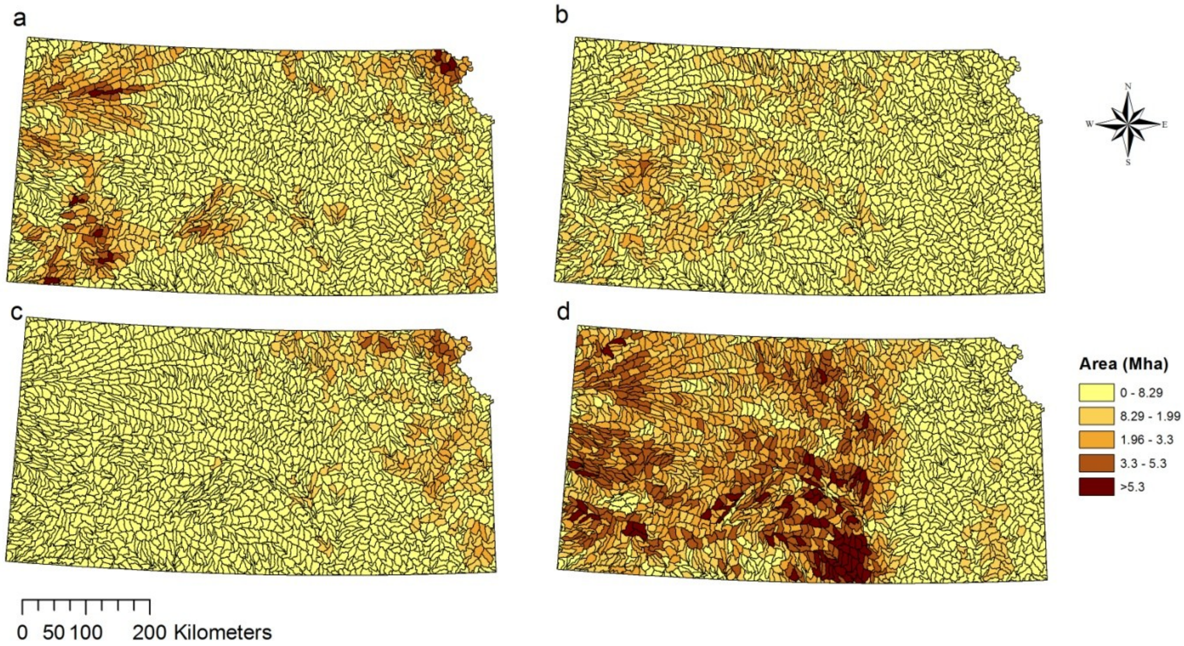


Figure 5.5. Crop distribution across Kansas per watershed in Mha (1 x 10^3 ha). a) Corn, b) Sorghum, c) Soybean and d) Winter wheat

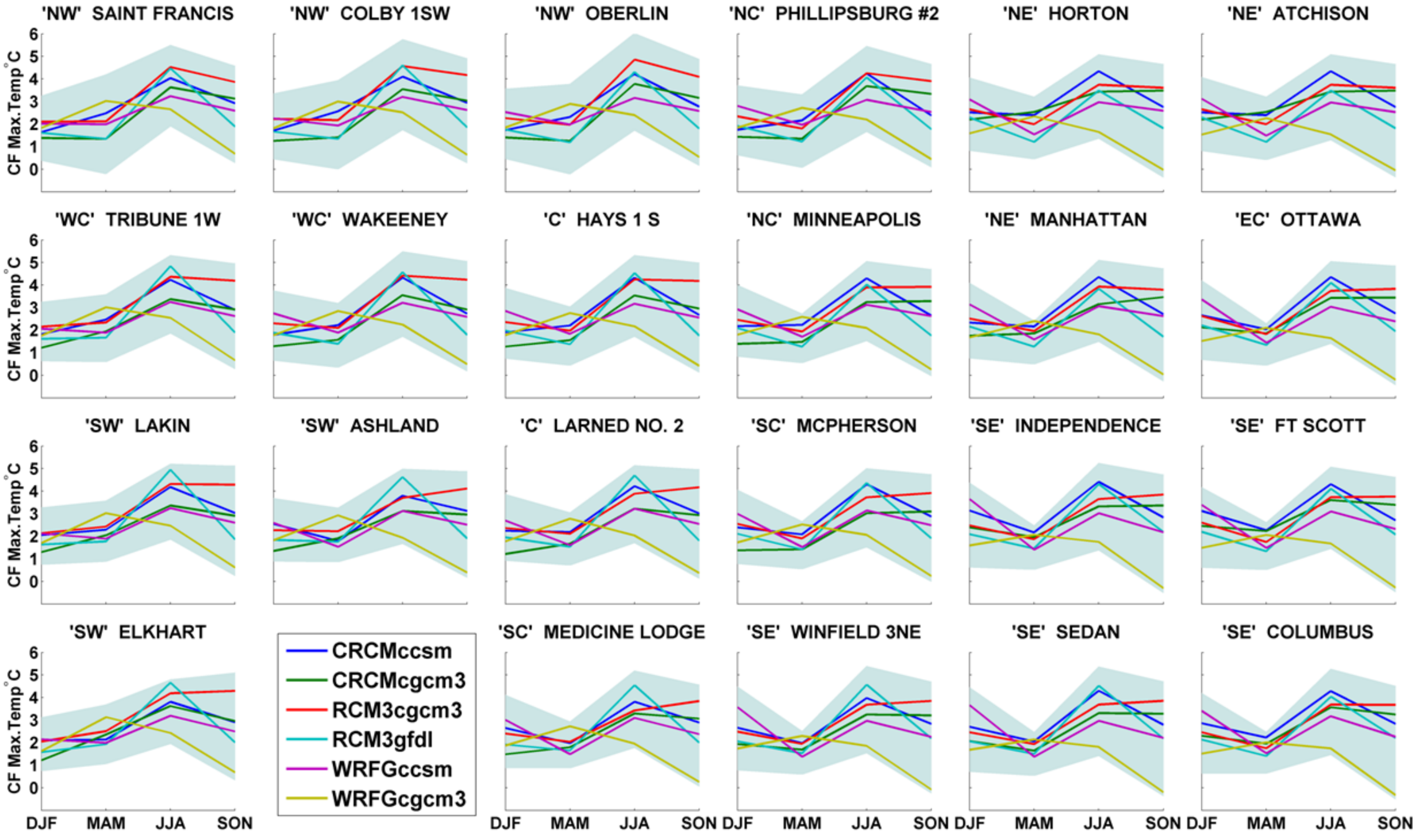


Figure 5.6 Change factor for maximum temperature. RCMs are represented by solid color lines. The blue area is the 5 and 95 percentile.

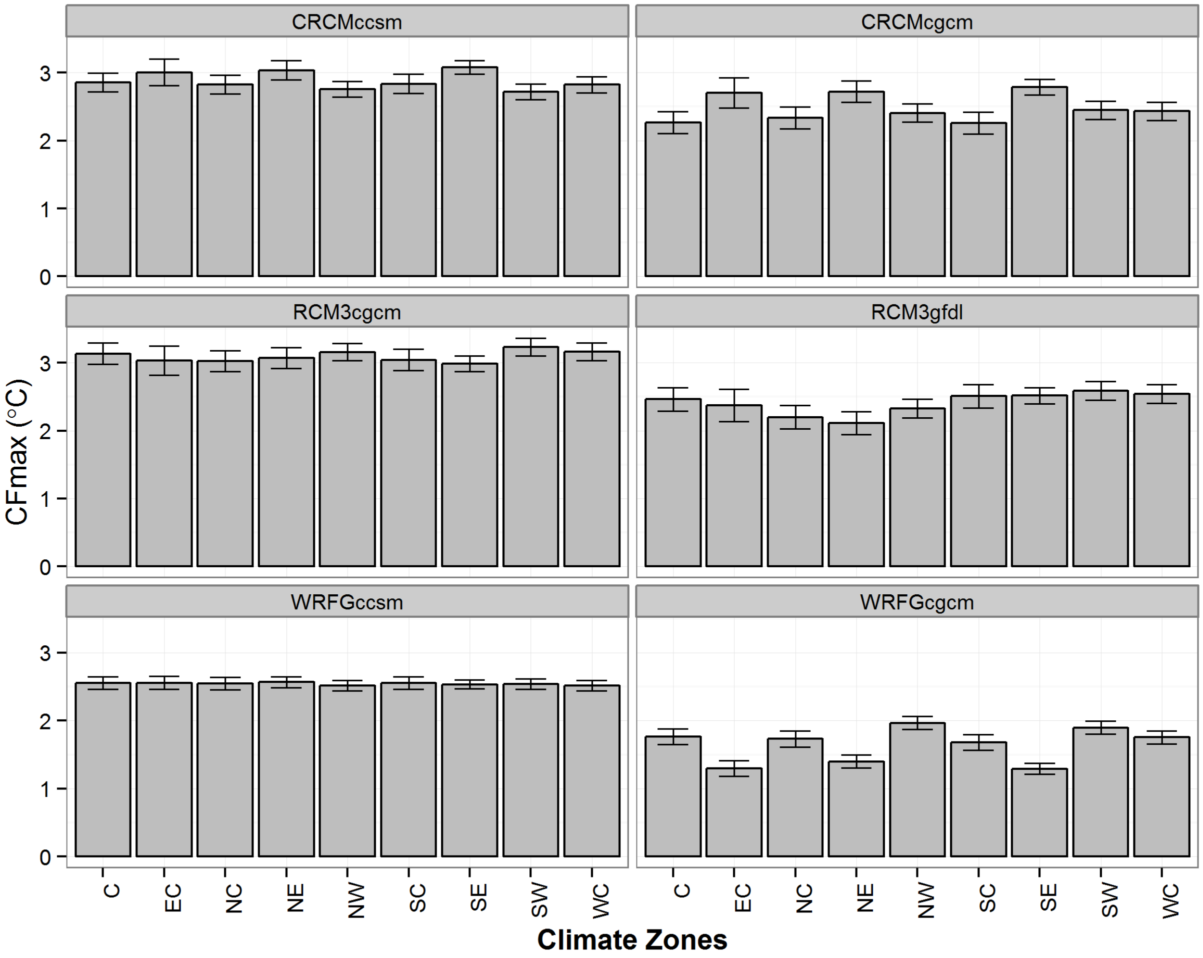


Figure 5.7. Interaction RCM x Climate zones for change factors of maximum temperature (CFmax).

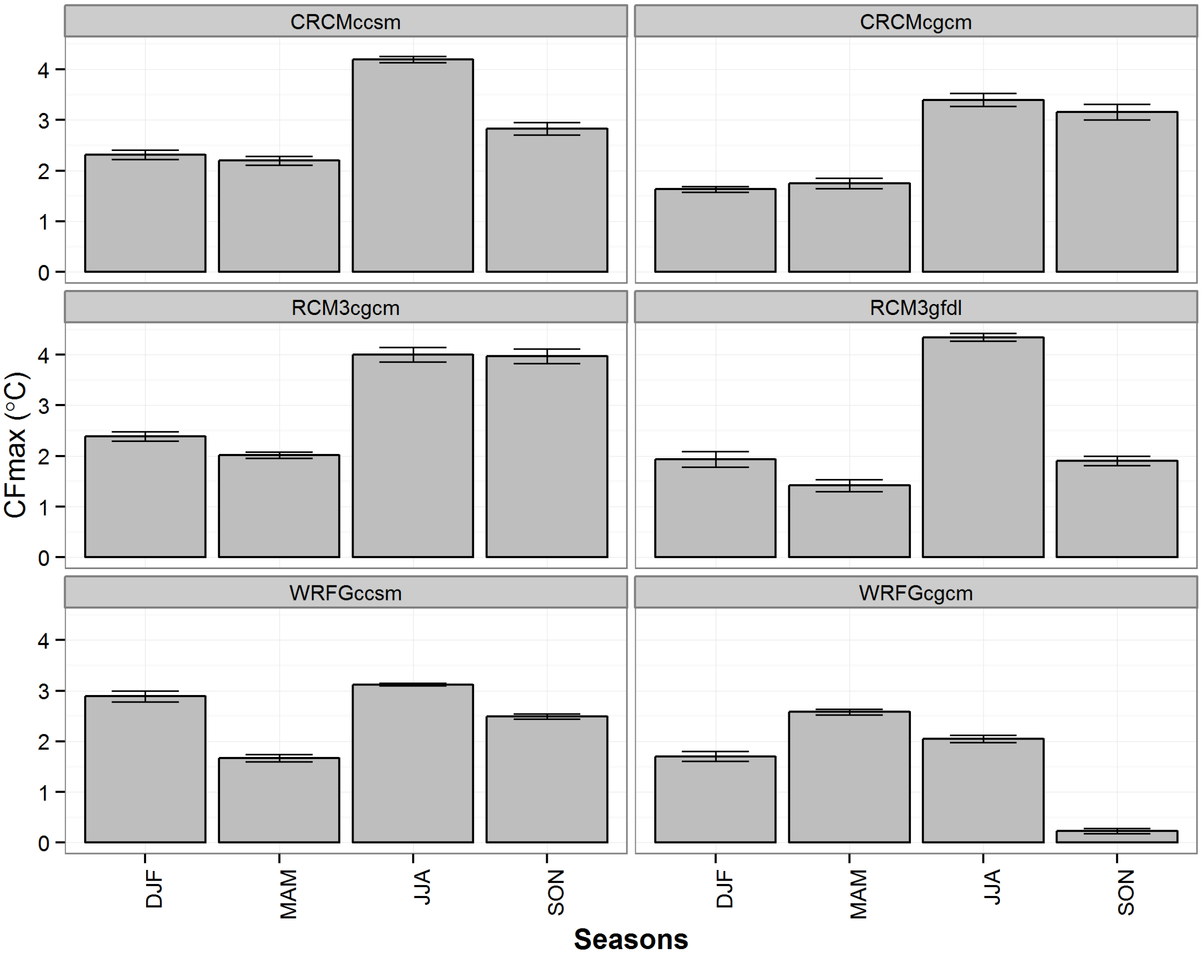


Figure 5.8. Interaction RCM x Season for change factor for maximum temperature (CFmax).

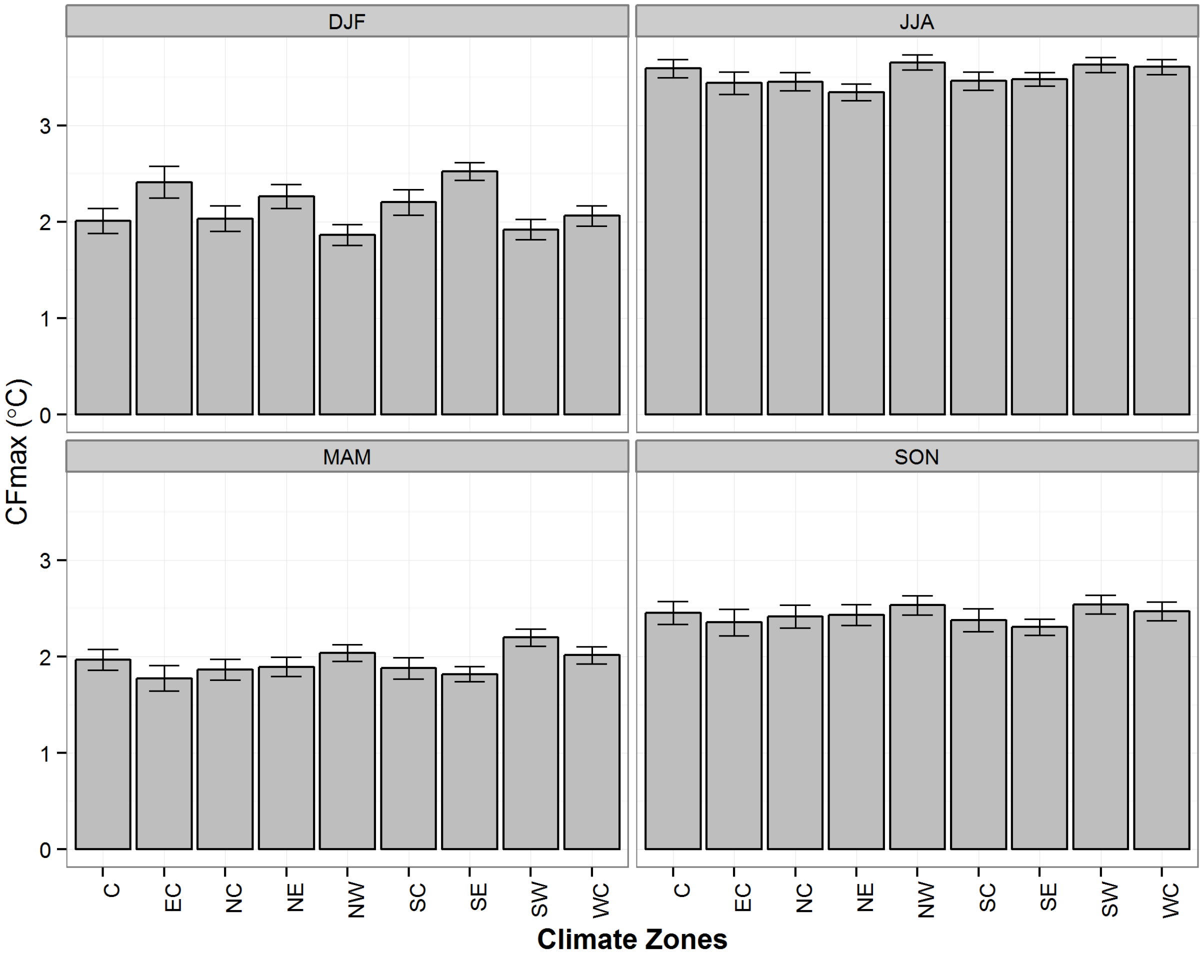


Figure 5.9. Interaction Climate Zones x Season for change factor of maximum temperature (CFmax).

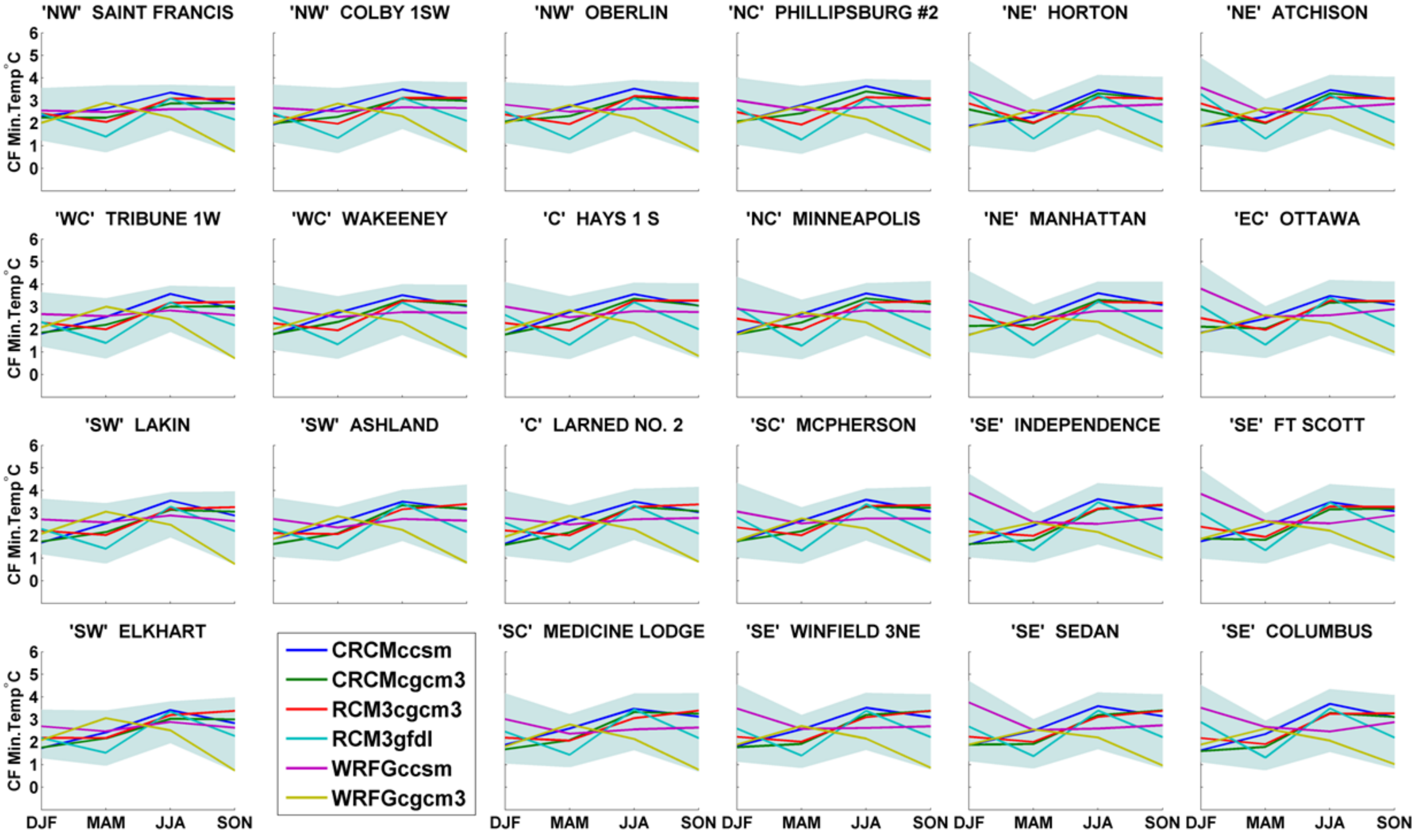


Figure 5.10. Change factor for minimum temperature. RCMs are represented by solid color lines. The blue area is the 5 and 95 percentile.

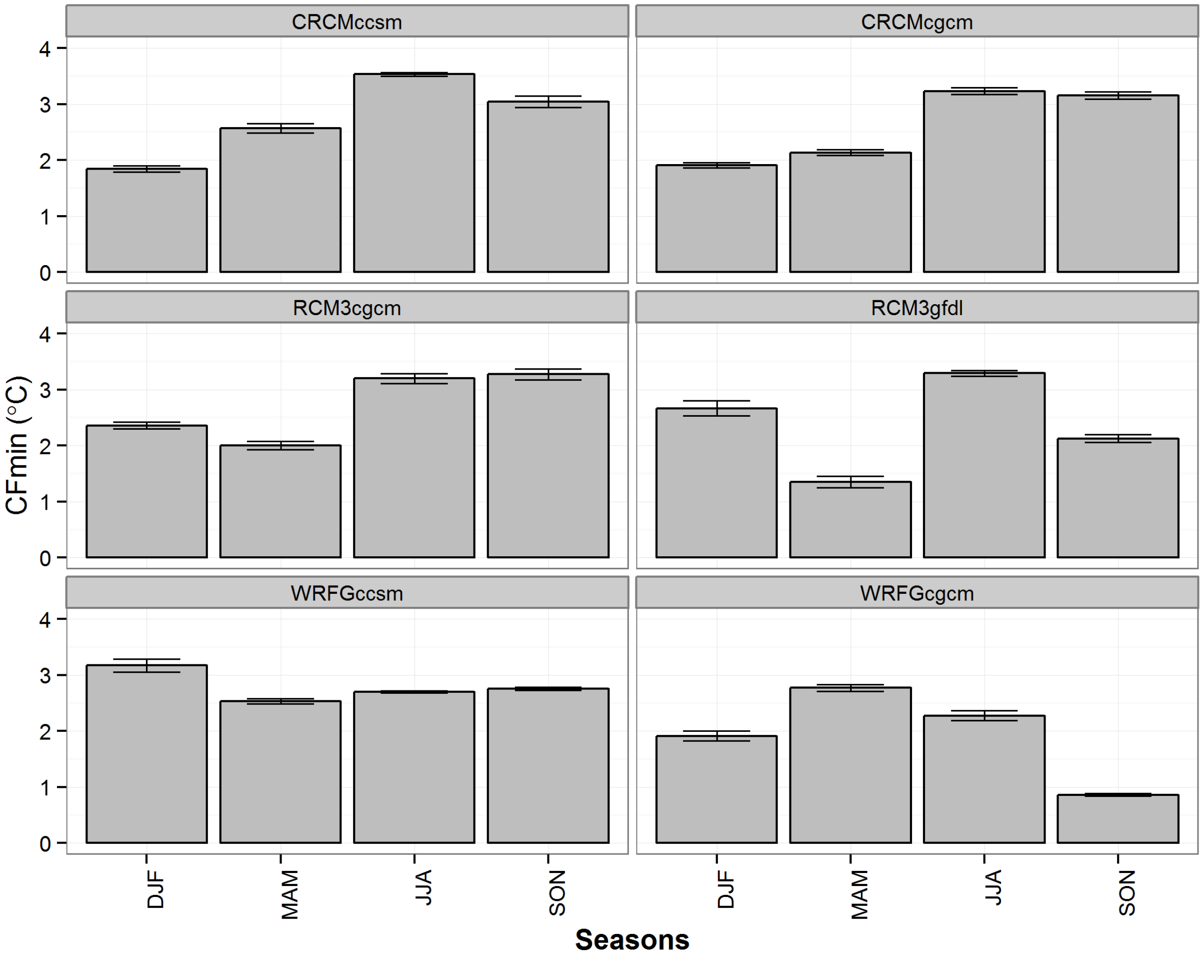


Figure 5.11. RCM x season for change factor of minimum temperature (CFmin)

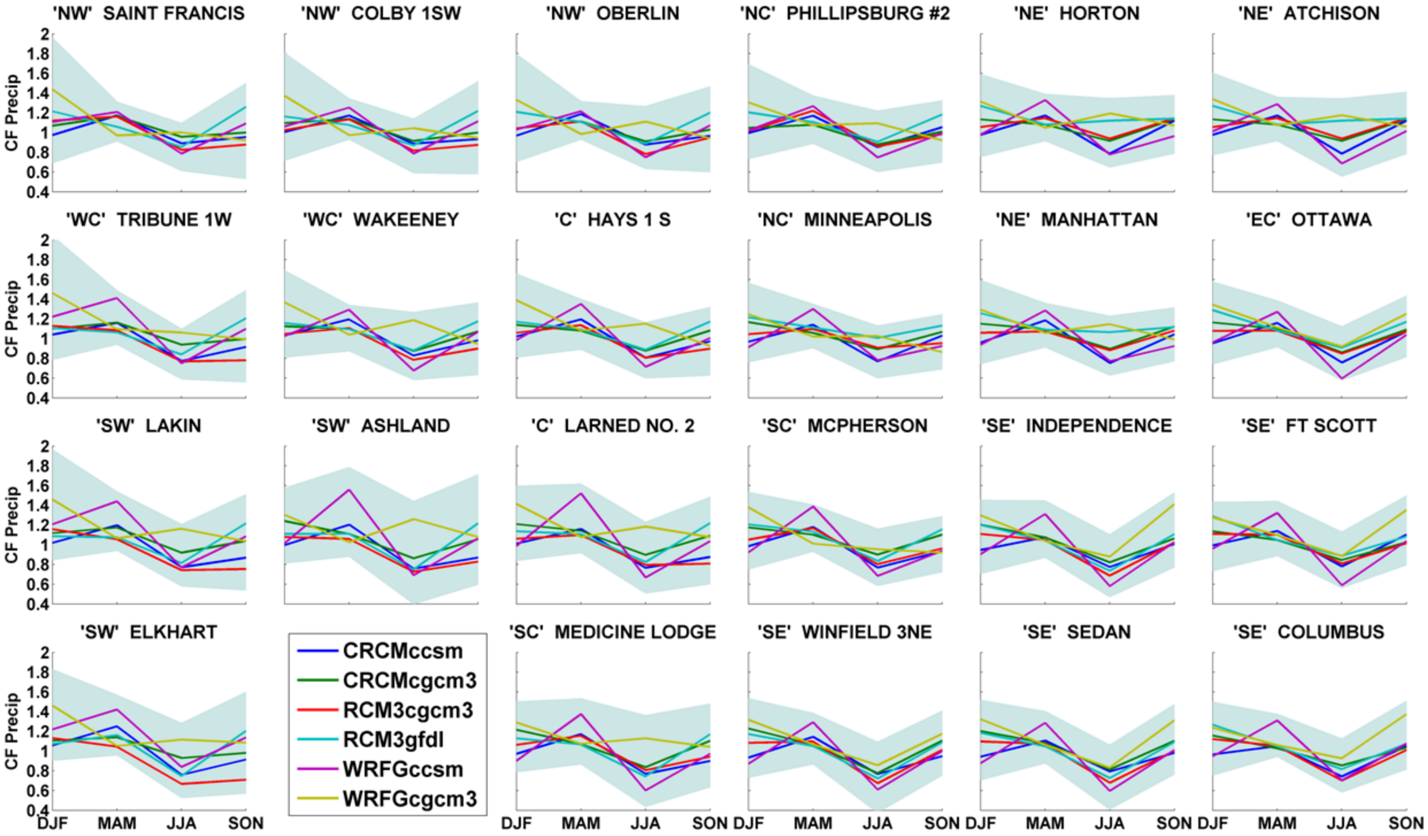


Figure 5.12.Change factor for precipitation. RCMs are represented by solid color lines. The blue area is the 5 and 95 percentile.

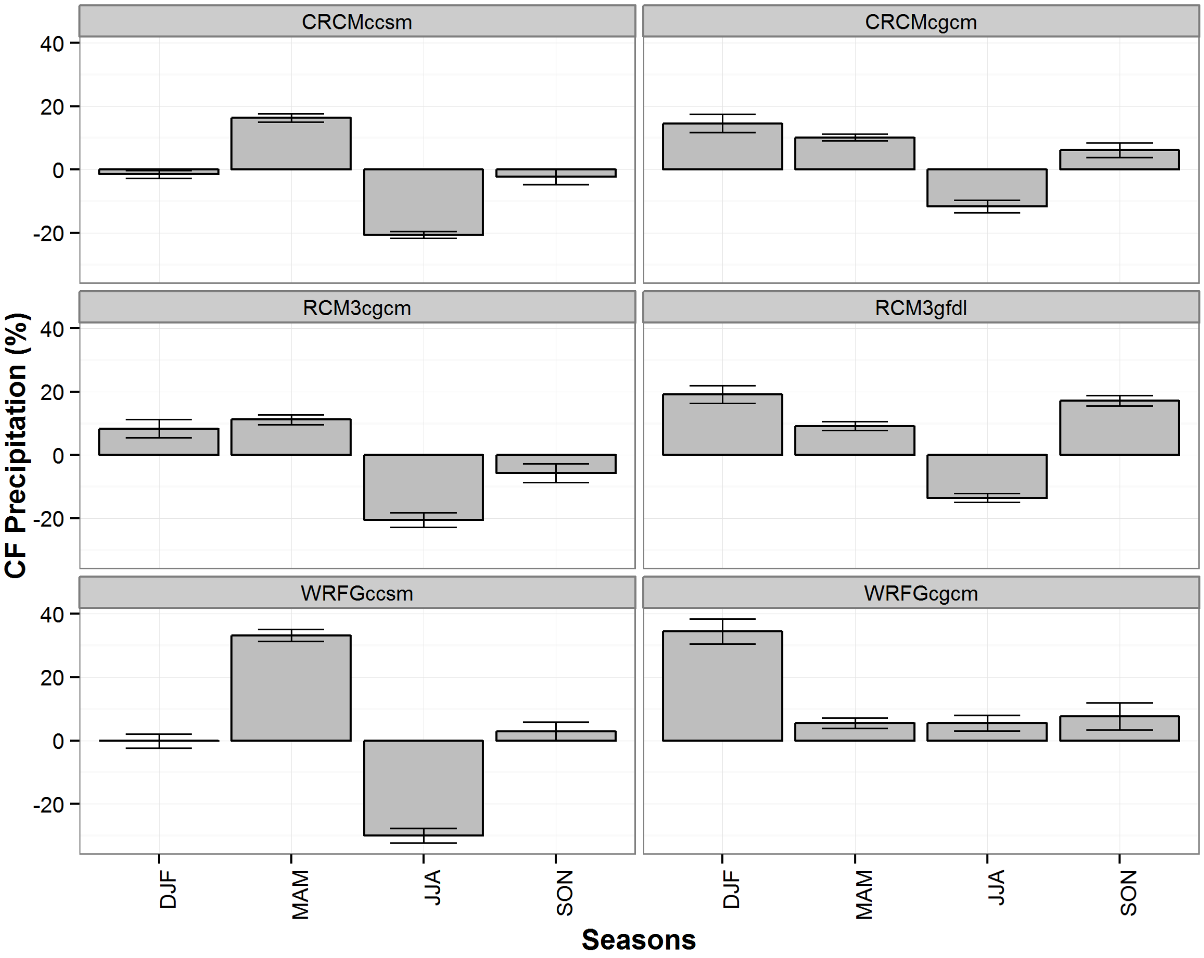
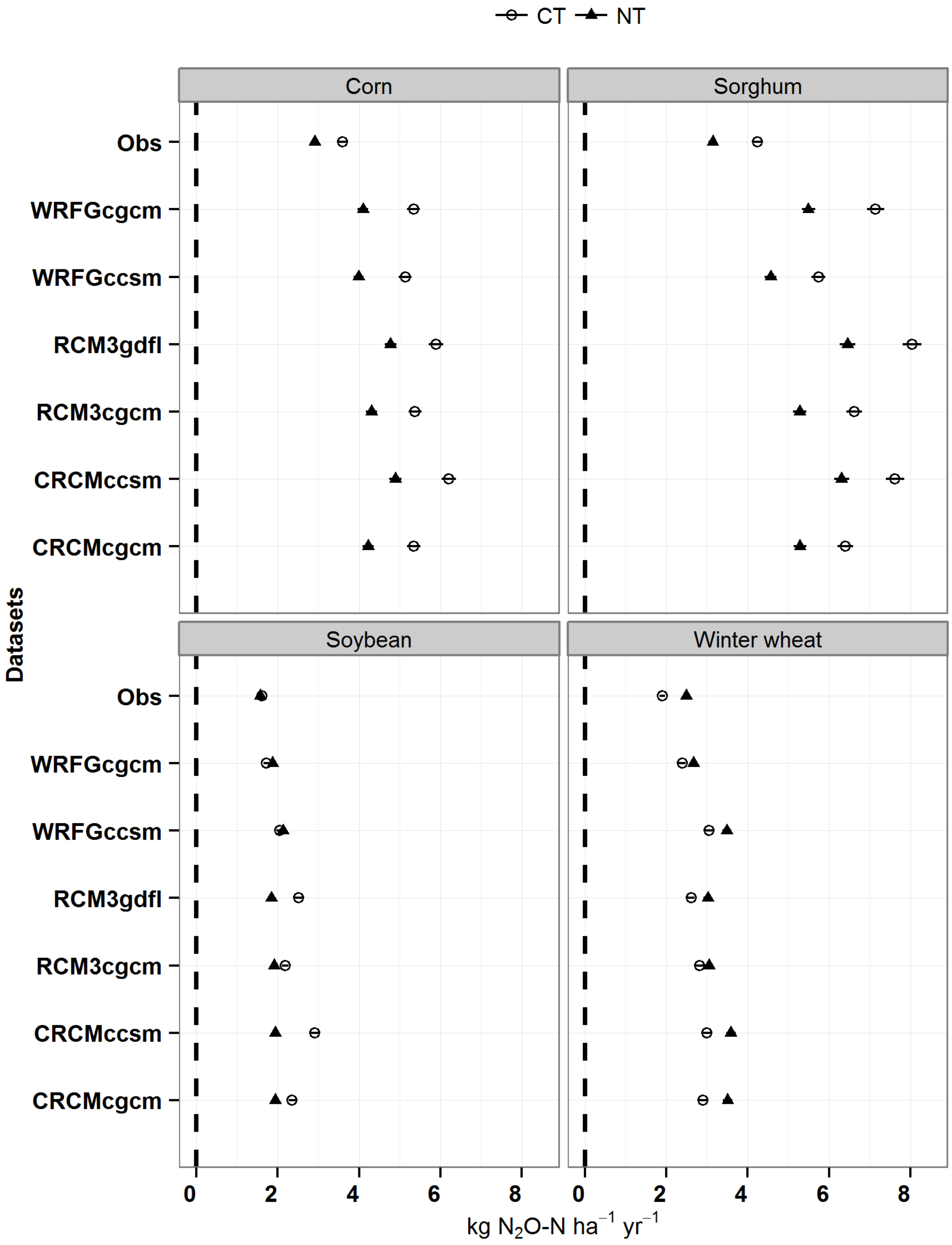


Figure 5.13. Precipitation change factors in term of percentage of change.

(a)


CT
NT
Corn
Sorghum
Soybean
Winter wheat
Datasets
Obs
WRFGcgcm
WRFGccsm
RCM3gdfl
RCM3cgcm
CRCMccsm
CRCMcgcm
0
2
4
6
8
kg N_2O-N ha^{-1} yr^{-1}

(b)

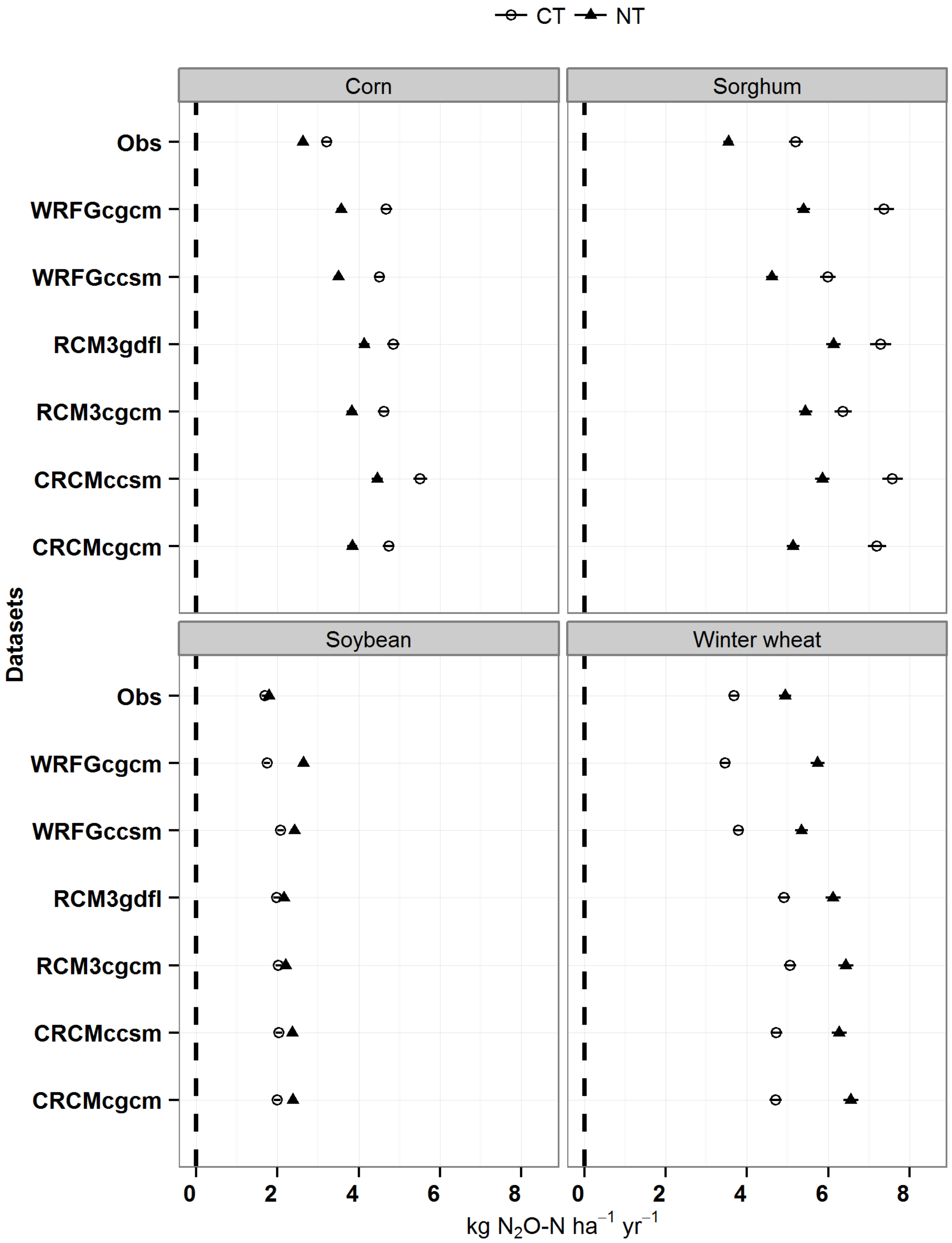


Figure 5.14 N$_2$O-N emissions (kg ha^{-1} yr^{-1}) under (a) non-irrigated and (b) irrigated till (CT) and no-till (NT) systems.

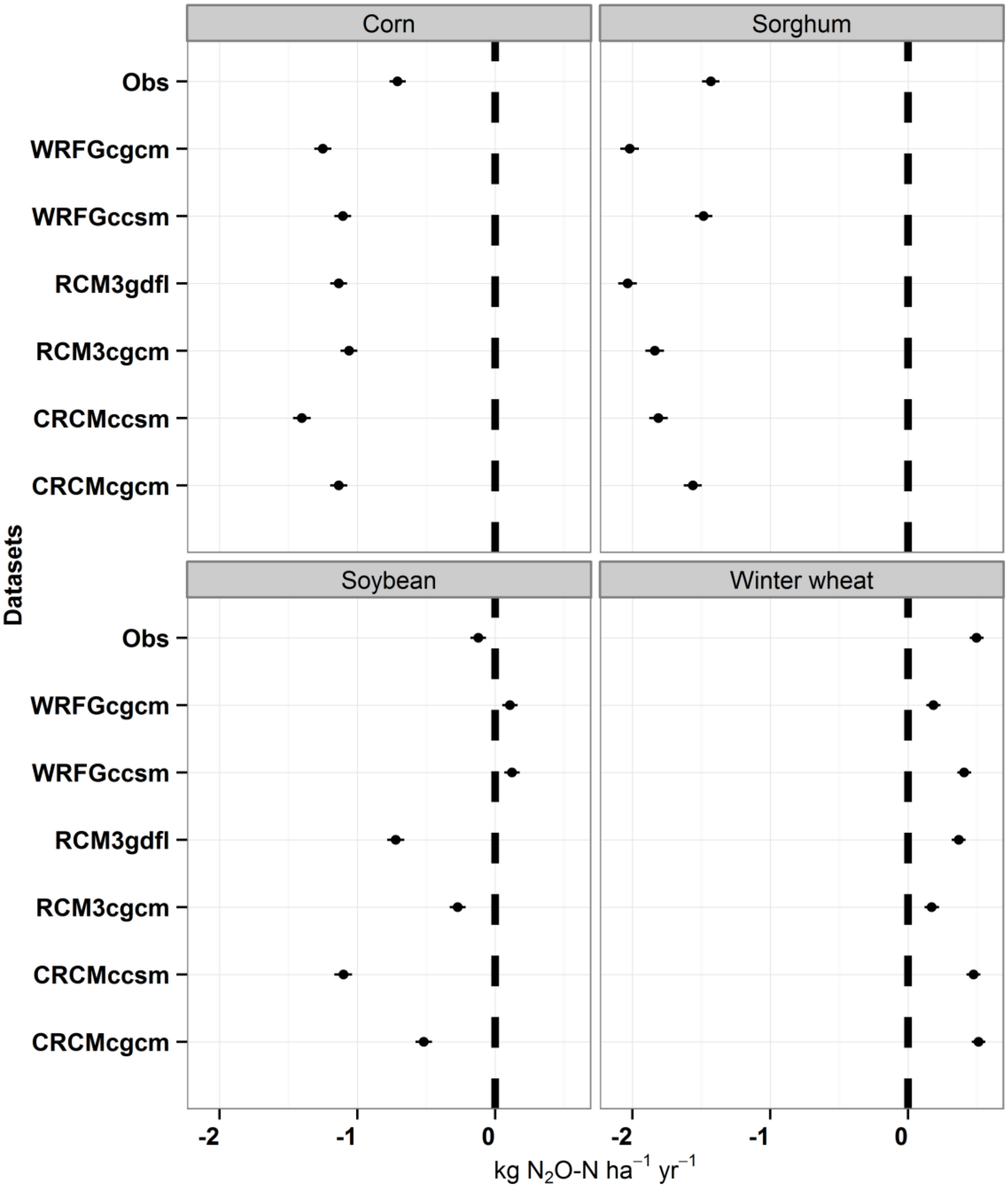


Figure 5.15. Change in N_2O emissions in non-irrigated cropping systems in Kansas due to conversion from conventional tillage to no-tillage. Mean and 95% confidence intervals. Values below zero represent reduction in N_2O emissions.

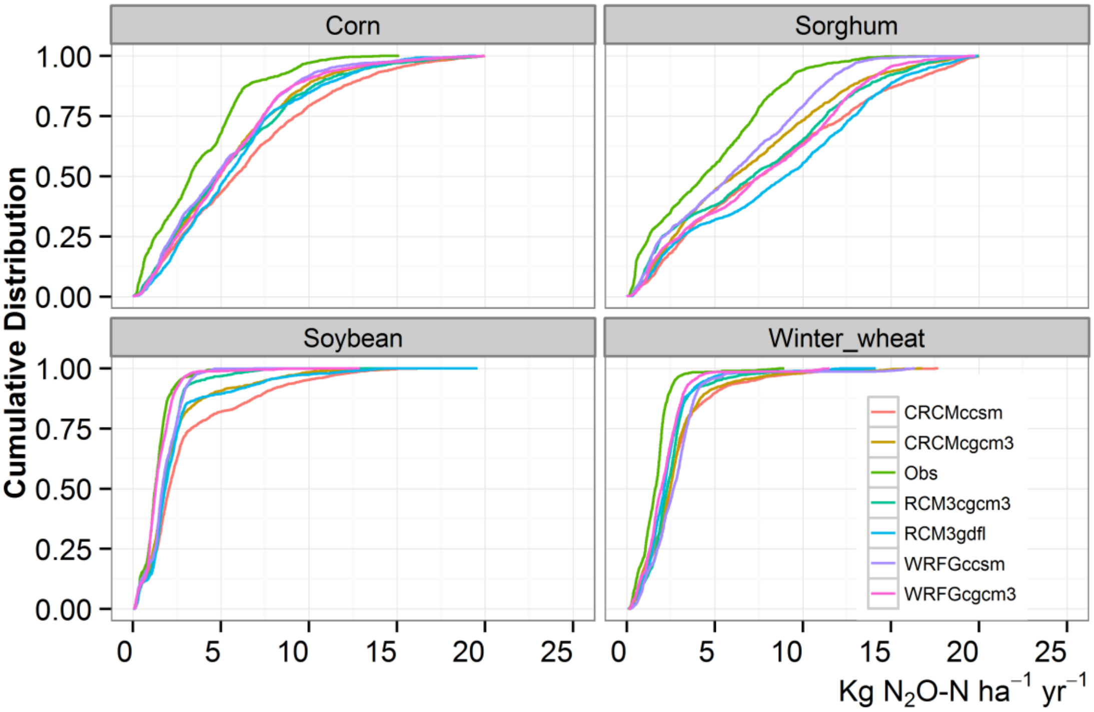


Figure 5.16. Cumulative distribution of N_2O emissions from observed and RCM datasets for non-irrigated conventional tillage.

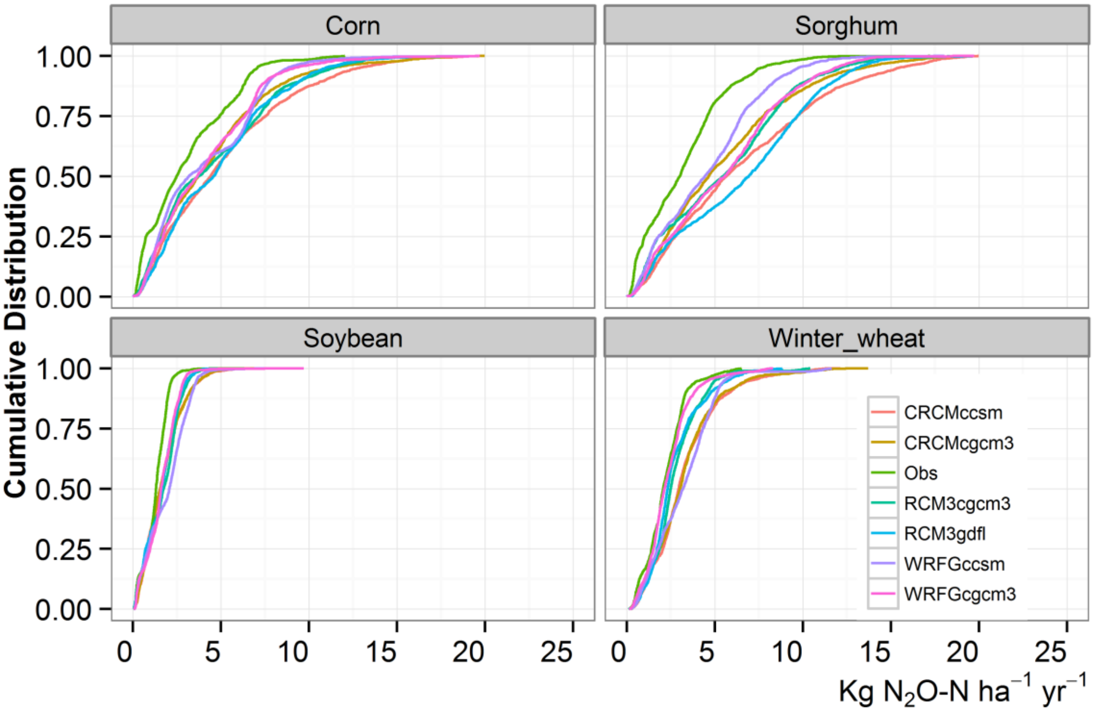


Figure 5.17. Cumulative distribution of N_2O-N emissions from observed (Obs) and different RCM datasets for non-irrigated no-tillage system.

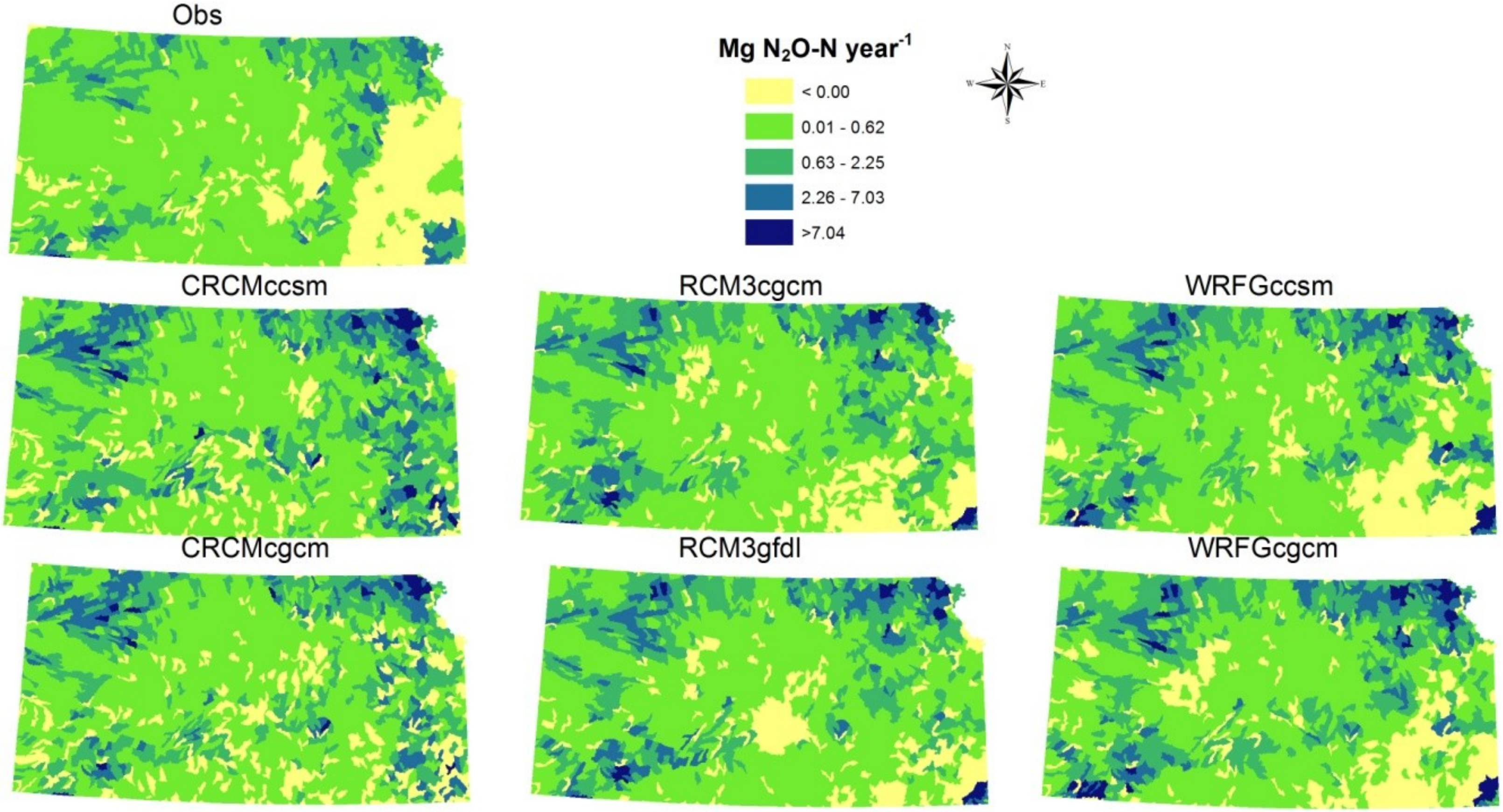


Figure 5.18. Changes in area-weighted N_2O emissions (Mg N_2O-N yr^{-1}) in non-irrigated corn in Kansas due to conversion from conventional tillage to no tillage. Observed (Obs) and RCM datasets.

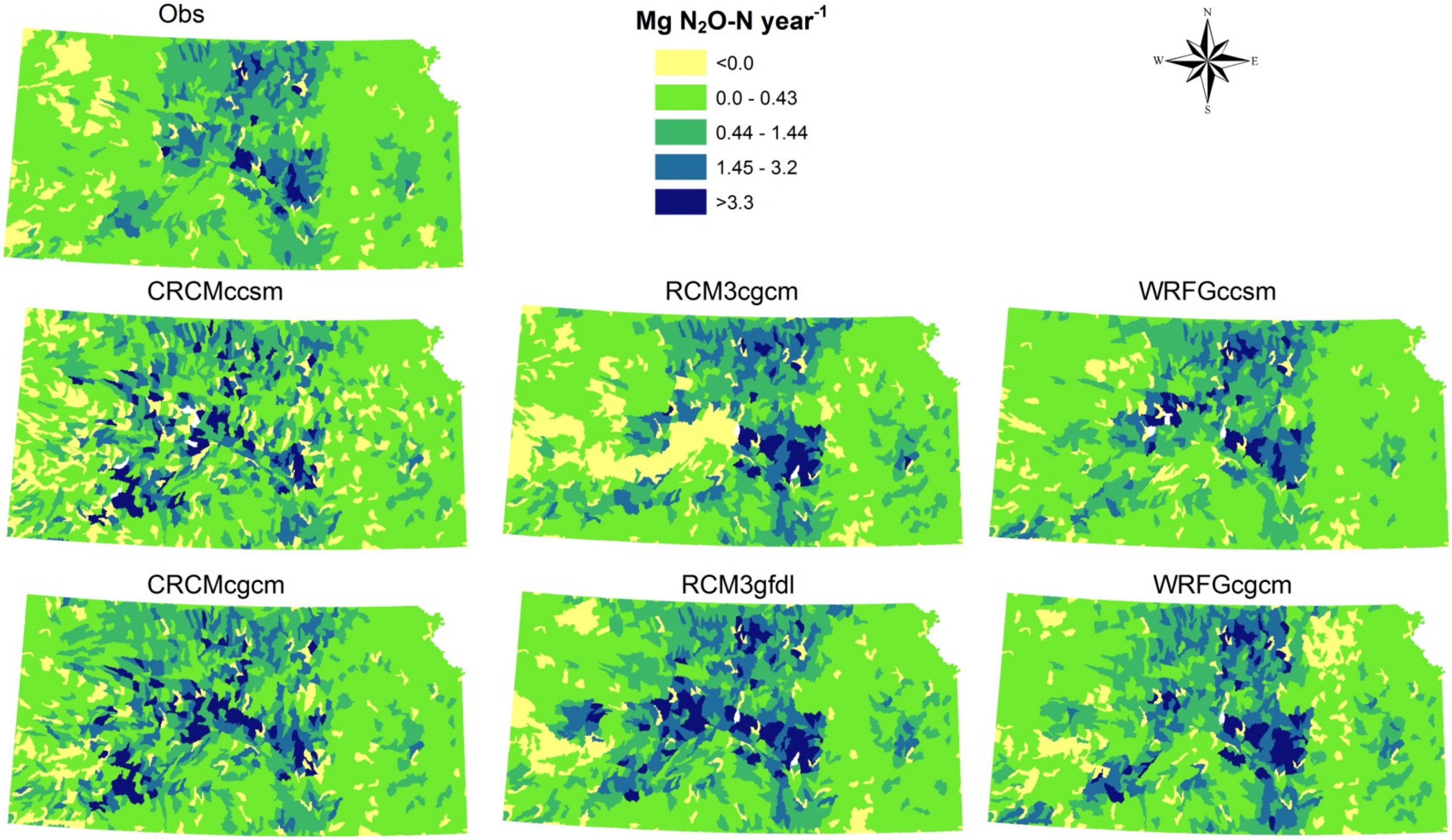


Figure 5.19. Changes in area-weighted N_2O emissions (Mg N_2O-N yr^{-1}) in non-irrigated sorghum in Kansas due to conversion from conventional tillage to no tillage. Observed (Obs) and RCM datasets.

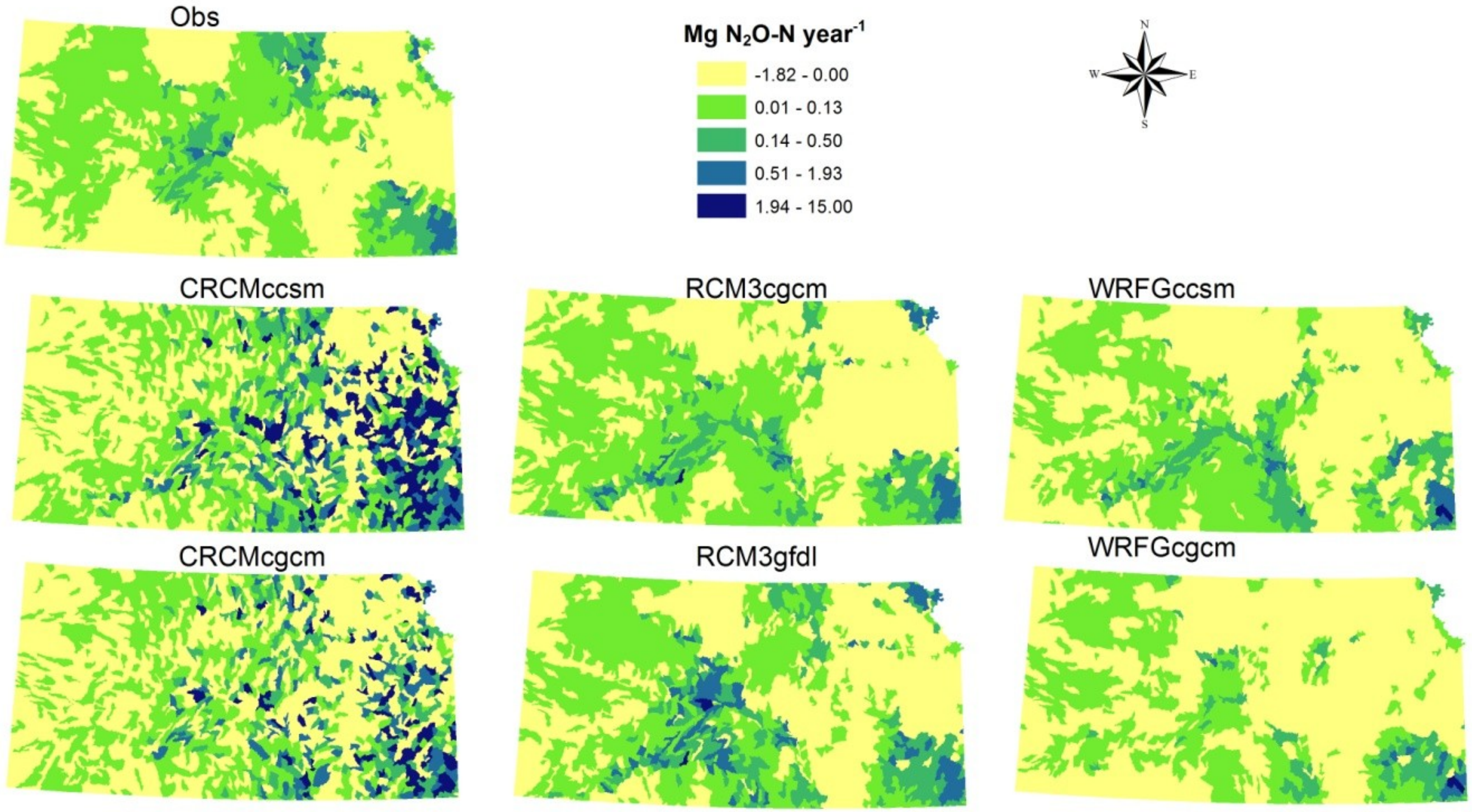


Figure 5.20. Changes in area-weighted N_2O emissions (Mg N_2O-N yr^{-1}) in non-irrigated soybean in Kansas due to conversion from conventional tillage to no tillage. Observed (Obs) and RCM datasets.

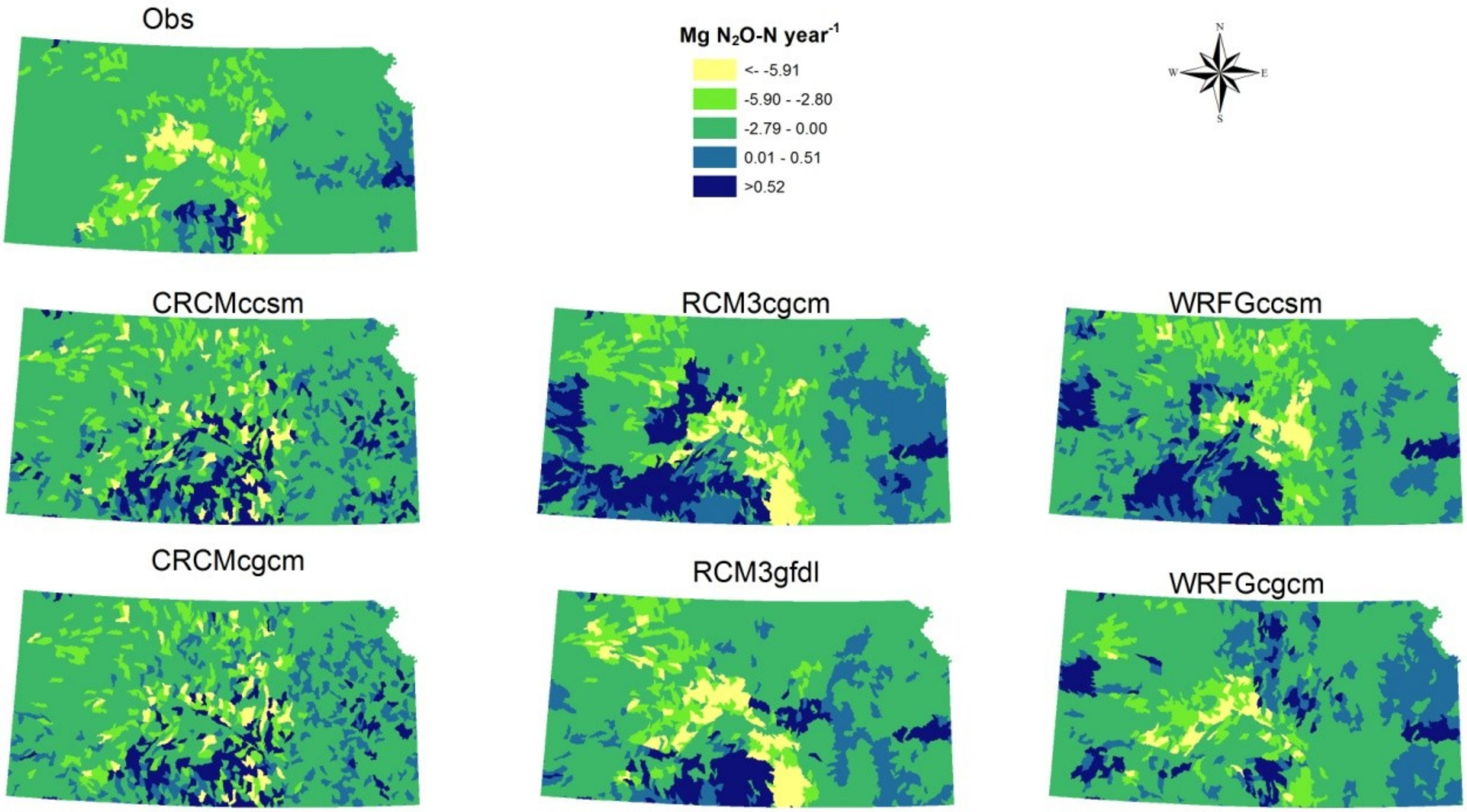


Figure 5.21. Changes in area-weighted N_2O emissions (Mg N_2O-N yr^{-1}) in non-irrigated winter wheat in Kansas due to conversion from conventional tillage to no tillage. Observed (Obs) and RCM datasets.

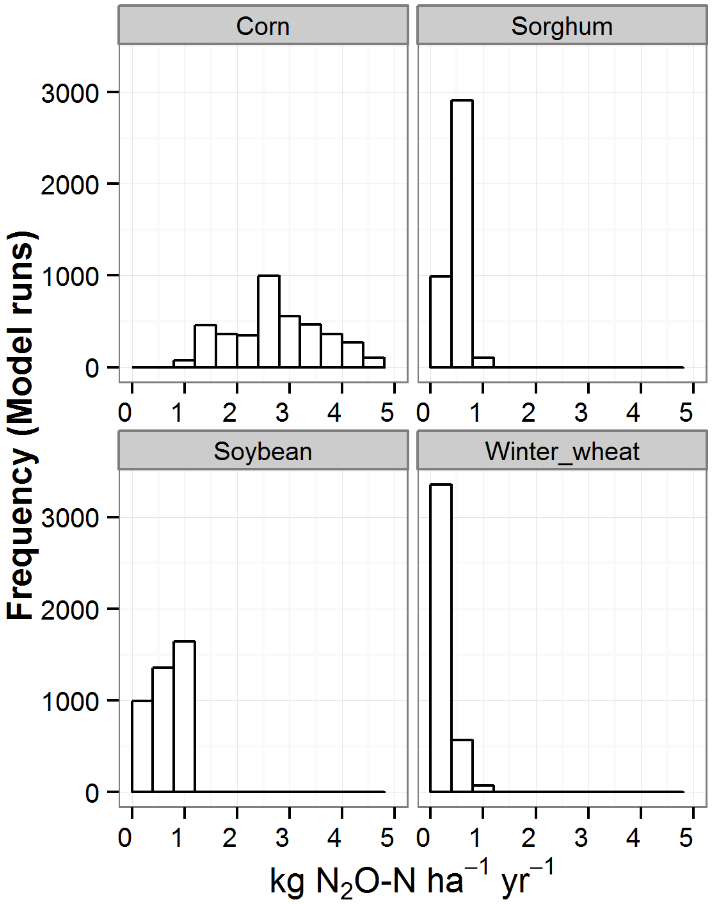


Figure 5.22. Frequencies of N_2O-N simulations with Monte Carlo approach.

Table 5.1. Climate model data available in NARCCAP used for N_2O regional simulations

		AOGCM		
		CCSM	**CGCM3**	**GFDL**
RCM	**CRCM**	X	X	
	RCM3		X	X
	WRFG	X	X	

Table 5.2. SSURGO Soil Attributes

SSURGO Attribute	**Definition**
Organic Matter (om)	The amount by weight of decomposed plant and animal residue expressed as a weight percentage of the less than 2 mm soil material
Clay (claytotal)	Mineral particles less than 0.002mm in equivalent diameter as a weight percentage of the less than 2.0mm fraction
pH (ph1to1h2o)	The negative logarithm to the base 10, of the hydrogen ion activity in the soil using the 1:1 soil-water ratio method. A numerical expression of the relative acidity or alkalinity of a soil sample.
Bulk Density (dbthirdbar)	The oven dry weight of the less than 2 mm soil material per unit volume of soil at a water tension of 1/3 bar

Table 5.3 Planting and harvest dates for corn, soybean, winter wheat and sorghum.

		Zone			
		1	**2**	**3**	**4**
Corn	*Planting(date/doy)*	5/5	5/2	4/20	4/9
		125	122	110	99
	Harvest	9/2	8/30	8/18	8/7
		245	242	230	219
Soybeans	*Planting*	5/21	5/23	5/21	6/8
		141	143	141	159
	Harvest	9/18	9/20	9/18	10/6
		261	263	261	279
Sorghum	*Planting*	5/28	6/2	6/2	5/28
		148	153	153	148
	Harvest	9/28	10/3	10/3	9/28
		271	276	276	271
Winter wheat	*Planting*	9/20	10/3	10/3	10/15
		263	276	276	288
	Harvest	6/25	7/8	7/8	7/20
		176	189	189	201

Chapter 6 - Summary

Non-CO_2 greenhouse gases have received attention of the scientific community in the recent years due to the net anthropogenic climate forcing and the low or negative abatement cost of the potential mitigation options (Reay et al., 2012). N_2O is one of those non-CO_2 greenhouse gases and one of the most important in which agriculture represents the major anthropogenic source. Agricultural soils account for 85% of anthropogenic N_2O. Management strategies for N fertilization and tillage are necessary for enhancing N use efficiency and reducing the negative impacts of N to the environment. Different management practices induce changes in substrate availability for microbial activity that may result in increases or reductions in the net N_2O emitted from soils. In order to understand and predict the effect of different management practices on greenhouse gas emissions under different climatic conditions a summary from field studies and from our own study as well as a modeling was employed. The objectives of this research were to (1) integrate results from field studies to evaluate the effect of different management strategies on N_2O emissions using a meta-analysis, (2) quantify N_2O-N emissions under no-tillage (NT) and tilled (T) agricultural systems and evaluate the effect of different N source and placements on N_2O-N emissions, (3) perform sensitivity analysis, calibration and validation of the Denitrification Decomposition (DNDC) model for N_2O emissions, and (4) analyze future scenarios of precipitation and temperature to evaluate the potential effects of climate change on N_2O emissions from agroecosystems in Kansas.

Systematic literature review was carried out in order to estimate the effect of management practices in different agroecosystems in terms of percentage of N lost by N_2O emissions as well as the relationship between N application rate and N_2O emissions. Several factors were evaluated: N placement and timing, N source, cropping systems, soil type and N application rate. Under field conditions N_2O emissions were evaluated since summer of 2008 on a Kennebec silt loam soil (Fine-silty, mixed, superactive, mesic Cumulic Hapludoll). Three management strategies were evaluated in Manhattan, Kansas: 1) Till (T) and no-till systems (NT), 2) Fertilizer type: compost (C), urea (F), and slow release N fertilizer (SRNF); 3) N placements: broadcast (BC), surface banded (SB) and subsurface banded (SUB), and 4) Split application of Urea (SU). The results were statistically analyzed using the MIXED procedure from SAS 9.3 (SAS Institute, 2010).

The Denitrification DeComposition (DNDC) model was tested against annual data sets (2009, 2010 and 2011) of N_2O flux from T and NT systems and C and F as the main N management practices. Bulk density (BD-g cm^3-), clay fraction (CLAY), field capacity (FIELDCAP), maximum C grain yield (MAXYIELD kg C yr^{-1}), plant C:N ratio (PLANTCN), pH, soil organic carbon (SOC –kg C kg^{-1} soil) and thermal degree days (TDD) were selected for calibration and validation. The performance of the model was evaluated calculating the Nash–Sutcliffe model efficiency. Scenarios of precipitation and temperature were analyzed following the change factor methodology (CF). Briefly, dataset of current and future prediction of precipitation and temperature were obtained from different regional circulation models (RCM). Current (1971-1999) and Future (2041-2070) dataset were used to estimate the uncertainty associated with future climate change. Observed weather datasets were available from 23 long-term weather stations across the state. For regional N_2O simulations the USGS level 14 hydrologic unit code boundaries (HUC14 watersheds) were used as the mapping unit and DNDC was used for N_2O simulation in various scenarios in corn, soybean, sorghum and winter wheat.

The overall estimation of N lost by N_2O-N emissions using an emission factor EF (%) and Nlost (%) estimates differed by up to 50%. In general using either EF or Nlost most of the time it was possible to reach the same conclusion. Based on the meta-analysis there was no significant effect of N placement (BC and B) in single and split applications. Among the N sources evaluated Ammonium Nitrate (AN) fertilizer had the highest percentage of N lost by N_2O-N emissions. Enhanced efficiency N fertilizer and F+O had the lowest percentage of N lost. The N_2O emission factors of different crops were statistically significant. The EF values ranged from 0.1% for barley up to 1.7% for sugar cane. For the crops typically found in Kansas (winter wheat, corn, soybean) the EFs ranged between 1 and 2 %. The type of soil had a significant effect on N_2O EFs and Nlost values. Clay, silt-loam and silt-clay had the highest emission factors (2.1 - 4%) and the lowest EF was detected in silt and clay loam soil (~0.3%). No-till and conventional till did not significantly affect N_2O emissions (1.18 and 1.14 %, respectively). A non-linear relationship was detected between N input rate and N_2O emissions. The non-linear mixed model explained around 65% of the variability found in the total N_2O emissions from agricultural systems when management factors such as N source, till, crops as well as environmental factors such as soil, precipitation and temperature were included in the model.

In the field study N_2O-N emissions were not significantly different between tillage systems and N source. The cumulative N values of N_2O-N were greater in the tilled (T) than the no-till (NT) system (2.7 kg N_2O-N ha^{-1} y^{-1} and 2.4 kg ha^{-1} y^{-1}). The cumulative emission of urea and compost were 3.7 and 1.4 kg N_2O-N $ha^{-1}y^{-1}$, respectively. Overall, there were no significant differences among the N placement treatments. SB had the highest N_2O-N cumulative emission (6.4 kg N_2O-N ha^{-1} y^{-1}) which was higher than the BC application of N (2.5 kg N_2O-N ha^{-1} y^{-1}, 3 y average). During 2010, slow-release N fertilizer had lower emissions than SB and SP.

During 2011 the N_2O emissions were significantly different with regard N source and tillage. Compost presented higher emissions which accounted for 8.5 kg N_2O-N ha^{-1} during the growing season whereas urea had 3.5 kg N_2O-N ha^{-1}. The high emissions from compost affected the overall emissions in NT systems. The cumulative value of NT and T systems were 8.1 and 4 kg N_2O-N ha^{-1}, respectively. Overall, there were no significant differences between SUB and BC; however SUB had higher cumulative N_2O-N emissions than BC, which were 4.4 and 3.8 kg N_2O-N ha^{-1}, respectively.

The N_2O simulations were more sensitive to changes in the soil parameters such as pH, SOC, FIELD and BD, being pH and SOC the most sensitive parameters. Till (Urea) had higher model efficiency followed by no-till (compost), no-till (urea) and till (compost). Most of the model efficiency values in till (urea) were positive which indicated that the model performed well in that situation. At the regional scale the change factors estimated from various RCM varied in space and time. Overall, most of the RCM predicted increasing trend in future regarding temperature (0.21 – 4.4°C). Change factors of precipitation were not uniform across the state (reduction in 15% or increasing in 34%). The changes in climate increased N_2O emission from agricultural soils in Kansas. The conversion from T to NT reduced the emission in crops under present conditions as well as future climatic conditions.

Despite of the high variability of N_2O emissions, it was possible to reproduce important findings regarding the effect of tillage and N management as well as the effect on agronomic variables. Results from field experiments regarding management practices for N_2O emission reduction corroborated other findings from around the world where there is an overall significant effect of mitigating N_2O by improving N management without affecting yields. It is imperative to point out that N management strategies have to be tuned according to the specific characteristics of any given location. Modeling approaches in this particular case emerged as an important tool for exploring alternative N managements in which scenarios of climate change are embed as well as intrinsic soil conditions. Increasing the temporal resolution from weekly to daily observations would provide more details about soils processes that can be integrated in a modeling approach. Remote sensing can be integrated to process-base models to enhance the regional prediction of GHG emissions from a broader range of agroecosystems and scenarios. So observed N_2O data from various agroecosystems would be desired in order to validate the modeling approach.

References

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Appendix A - Chapter 4

Table A.1 Data sets of observed daily N_2O emissions (kg N ha^{-1} day^{-1}) for DNDC calibration and validation

DOY	*Season*	*Tillage*	*Fertilizer*	*Emission*	*SE†*
				g N_2O-N ha^{-1} day^{-1}	
78	2009	NT	F	-1.47	1.28
85	2009	NT	F	2.57	3.39
101	2009	NT	F	-4.58	2.63
123	2009	NT	F	15.01	6.83
138	2009	NT	F	-1.23	1.65
148	2009	NT	F	-3.24	2.47
155	2009	NT	F	67.42	25.48
161	2009	NT	F	119.36	51.93
168	2009	NT	F	28.97	17.48
175	2009	NT	F	5.84	4.81
188	2009	NT	F	3.73	1.10
198	2009	NT	F	9.82	4.67
204	2009	NT	F	3.47	1.62
211	2009	NT	F	0.87	0.85
219	2009	NT	F	0.45	0.24
226	2009	NT	F	1.32	1.10
232	2009	NT	F	3.81	3.37
245	2009	NT	F	-0.12	0.45
259	2009	NT	F	0.37	0.86
328	2009	NT	F	0.43	0.78
78	2009	T	F	0.59	0.54
85	2009	T	F	9.13	8.20
101	2009	T	F	-2.26	2.06
123	2009	T	F	43.48	11.38
138	2009	T	F	3.14	4.63
148	2009	T	F	1.91	2.29
155	2009	T	F	138.55	45.26
161	2009	T	F	110.18	48.51
168	2009	T	F	150.13	75.06
175	2009	T	F	11.74	9.41
188	2009	T	F	6.40	1.21
198	2009	T	F	1.39	1.13
204	2009	T	F	2.49	1.38
211	2009	T	F	0.56	0.75

219	2009	T	F	0.77	0.58
226	2009	T	F	3.07	2.11
232	2009	T	F	0.88	1.40
245	2009	T	F	-0.32	0.61
259	2009	T	F	1.94	0.90
328	2009	T	F	1.90	2.03
78	2009	NT	C	-0.88	0.78
85	2009	NT	C	0.01	1.27
101	2009	NT	C	1.75	1.90
123	2009	NT	C	26.39	8.89
138	2009	NT	C	1.19	1.60
148	2009	NT	C	0.67	2.00
155	2009	NT	C	62.23	23.91
161	2009	NT	C	46.08	23.10
168	2009	NT	C	54.46	30.57
175	2009	NT	C	3.85	3.23
188	2009	NT	C	2.19	1.01
198	2009	NT	C	0.54	0.57
204	2009	NT	C	0.97	0.87
211	2009	NT	C	0.81	0.83
219	2009	NT	C	0.55	0.34
226	2009	NT	C	1.38	1.13
232	2009	NT	C	2.16	2.31
245	2009	NT	C	0.54	0.73
259	2009	NT	C	0.96	0.89
328	2009	NT	C	0.20	0.57
78	2009	T	C	-0.20	0.19
85	2009	T	C	20.89	16.25
101	2009	T	C	-0.77	1.50
123	2009	T	C	24.98	8.65
138	2009	T	C	-0.46	0.79
148	2009	T	C	1.34	2.18
155	2009	T	C	59.26	22.99
161	2009	T	C	11.71	7.20
168	2009	T	C	42.14	24.36
175	2009	T	C	1.60	1.39
188	2009	T	C	2.58	1.04
198	2009	T	C	1.96	1.45
204	2009	T	C	2.12	1.28
211	2009	T	C	1.30	0.96
219	2009	T	C	0.31	0.13
226	2009	T	C	0.56	0.56
232	2009	T	C	-0.33	0.94

245	2009	T	C	0.39	0.66
259	2009	T	C	-0.01	0.79
328	2009	T	C	1.10	1.35
97	2010	NT	F	0.37	0.72
110	2010	NT	F	0.62	0.57
114	2010	NT	F	3.65	2.74
121	2010	NT	F	11.27	3.40
128	2010	NT	F	17.14	5.13
134	2010	NT	F	123.58	32.26
141	2010	NT	F	239.80	86.05
147	2010	NT	F	12.10	6.29
153	2010	NT	F	5.92	2.76
159	2010	NT	F	190.40	81.65
169	2010	NT	F	28.01	5.43
175	2010	NT	F	18.84	9.79
189	2010	NT	F	2.05	0.49
97	2010	T	F	2.43	0.72
110	2010	T	F	0.98	0.57
114	2010	T	F	4.46	2.74
121	2010	T	F	13.41	3.40
128	2010	T	F	10.07	5.13
134	2010	T	F	79.65	32.26
141	2010	T	F	222.61	86.05
147	2010	T	F	20.28	6.29
153	2010	T	F	13.05	2.76
159	2010	T	F	233.75	81.65
169	2010	T	F	15.99	5.43
175	2010	T	F	31.40	9.79
189	2010	T	F	1.57	0.49
97	2010	NT	C	2.42	0.72
110	2010	NT	C	0.77	0.57
114	2010	NT	C	4.60	2.74
121	2010	NT	C	3.94	3.40
128	2010	NT	C	10.59	5.13
134	2010	NT	C	31.39	32.26
141	2010	NT	C	7.29	86.05
147	2010	NT	C	1.64	6.29
153	2010	NT	C	2.88	2.76
159	2010	NT	C	129.99	81.65
169	2010	NT	C	7.18	5.43
175	2010	NT	C	3.17	9.79
189	2010	NT	C	1.61	0.49
97	2010	T	C	0.08	0.72

110	2010	T	C	1.66	0.57
114	2010	T	C	5.51	2.74
121	2010	T	C	7.38	3.40
128	2010	T	C	2.04	5.13
134	2010	T	C	10.72	32.26
141	2010	T	C	18.73	86.05
147	2010	T	C	6.32	6.29
153	2010	T	C	2.65	2.76
159	2010	T	C	73.35	81.65
169	2010	T	C	3.44	5.43
175	2010	T	C	3.99	9.79
189	2010	T	C	1.29	0.49
119	2011	NT	F	8.90	33.97
122	2011	NT	F	2.07	2.88
128	2011	NT	F	200.36	78.27
136	2011	NT	F	6.23	9.09
141	2011	NT	F	337.45	90.23
150	2011	NT	F	46.54	119.78
157	2011	NT	F	22.81	22.14
164	2011	NT	F	6.75	8.46
171	2011	NT	F	7.28	2.33
178	2011	NT	F	5.71	4.06
186	2011	NT	F	0.76	1.43
188	2011	NT	F	15.17	9.61
195	2011	NT	F	2.28	1.50
201	2011	NT	F	3.77	1.98
209	2011	NT	F	2.94	1.12
221	2011	NT	F	3.03	0.67
231	2011	NT	F	2.37	0.63
280	2011	NT	F	0.74	0.75
119	2011	T	F	2.52	33.97
122	2011	T	F	2.65	2.88
128	2011	T	F	19.37	78.27
136	2011	T	F	9.80	9.09
141	2011	T	F	113.16	90.23
150	2011	T	F	39.44	119.78
157	2011	T	F	41.77	22.14
164	2011	T	F	40.21	8.46
171	2011	T	F	7.95	2.33
178	2011	T	F	12.49	4.06
186	2011	T	F	4.02	1.43
188	2011	T	F	12.52	9.61
195	2011	T	F	1.19	1.50

201	2011	T	F	3.87	1.98
209	2011	T	F	3.44	1.12
221	2011	T	F	4.30	0.67
231	2011	T	F	3.15	0.63
280	2011	T	F	1.09	0.75
119	2011	NT	C	107.50	33.97
122	2011	NT	C	27.00	2.88
128	2011	NT	C	539.60	78.27
136	2011	NT	C	17.85	9.09
141	2011	NT	C	332.75	90.23
150	2011	NT	C	407.70	119.78
157	2011	NT	C	81.29	22.14
164	2011	NT	C	20.06	8.46
171	2011	NT	C	8.00	2.33
178	2011	NT	C	4.60	4.06
186	2011	NT	C	2.79	1.43
188	2011	NT	C	111.16	9.61
195	2011	NT	C	-1.41	1.50
201	2011	NT	C	3.34	1.98
209	2011	NT	C	7.91	1.12
221	2011	NT	C	7.56	0.67
231	2011	NT	C	5.52	0.63
280	2011	NT	C	2.18	0.75
119	2011	T	C	115.39	33.97
122	2011	T	C	23.30	2.88
128	2011	T	C	141.77	78.27
136	2011	T	C	43.85	9.09
141	2011	T	C	246.97	90.23
150	2011	T	C	173.05	119.78
157	2011	T	C	55.86	22.14
164	2011	T	C	19.41	8.46
171	2011	T	C	4.55	2.33
178	2011	T	C	2.60	4.06
186	2011	T	C	1.82	1.43
188	2011	T	C	25.74	9.61
195	2011	T	C	1.63	1.50
201	2011	T	C	6.58	1.98
209	2011	T	C	3.79	1.12
221	2011	T	C	5.74	0.67
231	2011	T	C	2.82	0.63
280	2011	T	C	3.71	0.75

† Estimated mean and standard error values are based on the fitted mixed model

Table A.2 Data sets of observed cumulative N_2O emissions (kg N $ha^{-1}yr^{-1}$) for DNDC calibration and validation

Year	*Tillage*	*Fertilizer*	*Estimate*	*SE†*
			g N_2O-N $ha^{-1}yr^{-1}$	
2009	NT	F	1802.07	656.85
2009	NT	C	1677.86	656.85
2009	T	F	3803.06	656.85
2009	T	C	1465.76	656.85
2010	NT	F	4638.12	1013.49
2010	NT	C	1554.13	1013.49
2010	T	F	4695.51	1013.49
2010	T	C	1014.22	1013.49
2011	NT	F	4764.97	1620.92
2011	NT	C	11474	1620.92
2011	T	F	2358.13	1620.92
2011	T	C	5703.57	1620.92

† Estimated mean and Standard Error values are based on the fitted mixed model

Appendix B - Chapter 5

Table B.1 Long-term weather stations in the state of Kansas

STATION NAME	*ZONE*	*STATE*	*COUNTY*	*LAT*	*LONG*	*ELEVATION(ft)*
HAYS 1 S	C	KS	ELLIS	38.51	-99.2	2010
LARNED NO. 2	C	KS	PAWNEE	38.11	-99.05	2015
OLATHE 3E	EC	KS	JOHNSON	38.53	-94.45	1055
OTTAWA	EC	KS	FRANKLIN	38.36	-95.16	919
MINNEAPOLIS	NC	KS	OTTAWA	39.07	-97.42	1322
PHILLIPSBURG #2	NC	KS	PHILLIPS	39.44	-99.18	1889
ATCHISON	NE	KS	ATCHISON	39.34	-95.06	945
HORTON	NE	KS	BROWN	39.4	-95.31	1030
MANHATTAN	NE	KS	RILEY	39.11	-96.34	1065
COLBY 1SW	NW	KS	THOMAS	39.23	-101.04	3170
OBERLIN	NW	KS	DECATUR	39.49	-100.31	2610
SAINT FRANCIS	NW	KS	CHEYENNE	39.46	-101.48	3362
MCPHERSON	SC	KS	MCPHERSON	38.22	-97.36	1520
MEDICINE LODGE	SC	KS	BARBER	37.17	-98.33	1535
COLUMBUS	SE	KS	CHEROKEE	37.1	-94.5	905
FT SCOTT	SE	KS	BOURBON	37.5	-94.42	845
INDEPENDENCE	SE	KS	MONTGOMERY	37.14	-95.42	805
SEDAN	SE	KS	CHAUTAUQUA	37.07	-96.11	900
ASHLAND	SW	KS	CLARK	37.11	-99.45	1970
ELKHART	SW	KS	MORTON	37	-101.53	3599
LAKIN	SW	KS	KEARNY	37.56	-101.14	2998
TRIBUNE 1W	WC	KS	GREELEY	38.27	-101.46	3636
WAKEENEY	WC	KS	TREGO	39.01	-99.52	2460
WINFIELD 3NE	WC	KS	COWLEY	37.17	-96.56	1235

Table B.2 K-S test results for comparing same RCM driven by different GCMs

Dataset No.†	*Dataset No.*	*Dataset ‡*	*Corn*		*Sorghum*		*Soybean*		*Winter wheat*	
			D§	p¶	D	p	D	p	D	p
1	2	DMg_irr	0.08	0.00	0.06	0.00	0.09	0.00	0.07	0.00
1	2	DMg_nirr	0.07	0.00	0.09	0.00	0.11	0.00	0.03	0.37
1	2	MgNTirr	0.05	0.01	0.05	0.01	0.01	1.00	0.03	0.51
1	2	MgNTnirr	0.05	0.02	0.05	0.01	0.01	1.00	0.01	0.98
1	2	MgTirr	0.04	0.04	0.05	0.03	0.01	1.00	0.02	0.97
1	2	MgTnirr	0.05	0.03	0.06	0.00	0.05	0.01	0.02	0.80
1	2	NT_irr	0.09	0.00	0.09	0.00	0.04	0.15	0.06	0.00
1	2	NT_nirr	0.09	0.00	0.13	0.00	0.03	0.41	0.03	0.19
1	2	NT_T_Diff_irr	0.10	0.00	0.08	0.00	0.10	0.00	0.10	0.00
1	2	NT_T_Diff_nirr	0.09	0.00	0.11	0.00	0.13	0.00	0.03	0.41
1	2	T_irr	0.11	0.00	0.05	0.07	0.04	0.19	0.03	0.20
1	2	T_nirr	0.11	0.00	0.11	0.00	0.14	0.00	0.03	0.33
4	5	DMg_irr	0.03	0.34	0.11	0.00	0.07	0.00	0.05	0.01
4	5	DMg_nirr	0.03	0.27	0.11	0.00	0.08	0.00	0.15	0.00
4	5	MgNTirr	0.04	0.08	0.06	0.00	0.02	0.84	0.03	0.48
4	5	MgNTnirr	0.05	0.02	0.08	0.00	0.03	0.59	0.02	0.72
4	5	MgTirr	0.03	0.19	0.07	0.00	0.02	0.96	0.03	0.38
4	5	MgTnirr	0.04	0.04	0.08	0.00	0.04	0.22	0.03	0.23
4	5	NT_irr	0.07	0.00	0.08	0.00	0.06	0.00	0.15	0.00
4	5	NT_nirr	0.09	0.00	0.14	0.00	0.09	0.00	0.08	0.00
4	5	NT_T_Diff_irr	0.04	0.14	0.10	0.00	0.07	0.00	0.14	0.00
4	5	NT_T_Diff_nirr	0.07	0.00	0.12	0.00	0.11	0.00	0.17	0.00
4	5	T_irr	0.07	0.00	0.09	0.00	0.05	0.01	0.13	0.00
4	5	T_nirr	0.07	0.00	0.11	0.00	0.08	0.00	0.10	0.00
6	7	DMg_irr	0.03	0.42	0.17	0.00	0.23	0.00	0.16	0.00
6	7	DMg_nirr	0.04	0.10	0.09	0.00	0.11	0.00	0.07	0.00
6	7	MgNTirr	0.02	0.97	0.06	0.00	0.03	0.46	0.05	0.01
6	7	MgNTnirr	0.01	1.00	0.06	0.00	0.05	0.01	0.08	0.00
6	7	MgTirr	0.02	0.78	0.12	0.00	0.05	0.01	0.04	0.06
6	7	MgTnirr	0.02	0.82	0.07	0.00	0.06	0.00	0.09	0.00

6	7	NT_irr	0.05	0.01	0.11	0.00	0.08	0.00	0.07	0.00
6	7	NT_nirr	0.07	0.00	0.16	0.00	0.20	0.00	0.32	0.00
6	7	NT_T_Diff_irr	0.07	0.00	0.14	0.00	0.29	0.00	0.21	0.00
6	7	NT_T_Diff_nirr	0.08	0.00	0.16	0.00	0.11	0.00	0.19	0.00
6	7	T_irr	0.05	0.01	0.11	0.00	0.24	0.00	0.12	0.00
6	7	T_nirr	0.05	0.01	0.18	0.00	0.25	0.00	0.25	0.00

† 1: CRCMcgcm, 2: CRMCccsm, 4: RCM3cgcm, 5: RCM3gdfl, 6: WRFGccsm, 7: WRFGcgcm

‡ N_2O datasets from DNDC simulations:

NT_T_Diff : Differences between till (T) and no-till (NT) in terms of emissions rate (kg N_2O-N ha^{-1} yr^{-1}).

DMg: Difference between till and no-till in terms of area-weighted N_2O-N emission (Mg yr^{-1})

T/NT_irr, emission rate in irrigated till or no-till crops

T/NT_nirr, emission rate in non-irrigated till or no-till crops

§ Kolmogorov-Smirnov statistic

¶ p-values

Table B.3 K-S test for comparing T vs. NT area-weighted N_2O emissions (Mg N yr^{-1}) per dataset

Irrigated		*Dataset No.†*	*Corn*		*Sorghum*		*Soybean*		*Winter wheat*	
			D‡	p§	D	p	D	p	D	p
T	NT	1	0.07	0.00	0.13	0.00	0.05	0.02	0.10	0.00
		2	0.07	0.00	0.13	0.00	0.06	0.01	0.11	0.00
		3	0.08	0.00	0.14	0.00	0.02	0.75	0.09	0.00
		4	0.07	0.00	0.16	0.00	0.02	0.81	0.07	0.00
		5	0.06	0.00	0.17	0.00	0.03	0.46	0.07	0.00
		6	0.08	0.00	0.13	0.00	0.05	0.04	0.11	0.00
		7	0.07	0.00	0.17	0.00	0.08	0.00	0.18	0.00
Non-irrigated										
T	NT	1	0.07	0.00	0.06	0.00	0.10	0.00	0.08	0.00
		2	0.07	0.00	0.07	0.00	0.05	0.03	0.08	0.00
		3	0.07	0.00	0.09	0.00	0.02	0.79	0.10	0.00
		4	0.07	0.00	0.07	0.00	0.04	0.10	0.05	0.01
		5	0.07	0.00	0.07	0.00	0.07	0.00	0.07	0.00
		6	0.08	0.00	0.06	0.00	0.05	0.04	0.06	0.00
		7	0.08	0.00	0.08	0.00	0.05	0.03	0.13	0.00

† 1: CRCMcgcm, 2: CRMCccsm, 4: RCM3cgcm, 5: RCM3gdfl, 6: WRFGccsm, 7: WRFGcgcm

‡Kolmogorov-Smirnov statistics

§ p-values