SOIL TEXTURE AND SPRING PRECIPITATION CONTRIBUTE TO MAGNITUDE AND VARIABILITY IN N_2O EMISSIONS FROM CORN CROPPING SYSTEMS IN WISCONSIN

by

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Chapter 1: N_2O emissions from agriculture and estimating their magnitude

1 Introduction

Nitrous Oxide (N_2O) has been identified as a significant contributor to global anthropogenic climate change (IPCC, 2007). This contribution is due primarily to the 100 year global warming potential (GWP) of N_2O, which is approximately 300 times greater than that of carbon dioxide (CO_2). As a result, increases in the trace amounts of N_2O found in the atmosphere can have significant impacts on the radiative forcing of the atmosphere. These impacts are possibly already being realized as concentrations of atmospheric N_2O have increased from pre-industrial levels of 270ppb to 2005 levels of 319ppb (IPCC, 2007). This increase in N_2O has supported a 0.16 W m^{-2} increase in the radiative forcing of the atmosphere, which is approximately 14% of the total increase in radiative forcing caused by increases in CO_2, CH_4, and N_2O over pre-industrial levels (IPCC, 2007). As contributor of 58% of the anthropogenic emissions of N_2O, agriculture is the primary driver of the increase in the concentration of atmospheric N_2O (Smith et al., 2007). Gross calculations of the sum and effect of agricultural N_2O emissions in the atmosphere have identified agriculturally derived N_2O as a greenhouse gas species of concern. However, the management of agriculture, and subsequently agricultural N_2O emissions, occurs at the field-scale. In order to study N_2O emissions and potential mitigation strategies at the field-scale, several methods have been developed to estimate N_2O flux from specific instances in space and time.

Emissions of N_2O can be estimated by directly measuring N_2O flux from specific agricultural fields, through empirical relationships, or with complex process-based models. Direct measurements are often used to develop our understanding of the processes through which N_2O is produced in the agricultural environment. A better understanding of those processes can help to develop robust relationships between environmental variables and N_2O emissions. Those relationships can be used to

construct complex biogeochemical models that simulate the complex and interactive processes of agroecosystems. These tools can be used to compare the relative contributions of N_2O flux from different agricultural systems and regions and to develop and inform policies and greenhouse gas inventories. The purpose of this review is to describe the contribution of N_2O to the radiative forcing of the atmosphere, the processes through which N_2O is produced in the agricultural environments, and methods for estimating N_2O emissions from agricultural fields.

2 Nitrous Oxide in the Atmosphere

The contribution of N_2O to global climate change is directly related to two factors which determine global warming potential, radiative forcing potential and the lifespan of N_2O in the atmosphere. These two characteristics of atmospheric substances provide a metric for determining the relative potential of substances to affect the radiative and absorptive capacities of the atmosphere.

2.1 Radiative Forcing Potential

Radiative forcing is defined as 'the change in net (down minus up) irradiance (solar plus longwave; in W m^{-2}) at the tropopause after allowing for stratospheric temperatures to readjust to radiative equilibrium, but with surface and tropospheric temperatures and state held fixed at the unperturbed values' (Ramaswamy et al., 2001). In the context of climate change, radiative forcing is the potential for aa substance in the atmosphere to increase net irradiation at the planet's surface. Radiative forcing is calculated in reference to a percent change in global mean temperature from a time 0 (t0) to time X (tX) in conjunction with the change in the relative atmospheric concentration of a substance. The time frame used for this calculation most often begins at a pre-industrial time of 1750 CE (t0) and ends at present day (tx).

The radiative forcing potential (RFp) of different atmospheric components can be calculated by comparing the relative change in each component since pre-industrial levels (1750 CE) with the relative change in global mean temperature since 1750 CE, which returns a value in W m^{-2}. The current RFp of N_2O is 0.16 W m^{-2} with a 95% CI of 0.02 (Forster et al., 2007), meaning that the increase in atmospheric N_2O from pre-industrial levels is responsible for an increase in net irradiance at the equatorial surface of 0.16 W m^{-2}. It is also important to note that the RFp for N_2O increased 11% between the International Panel on Climate Change's (IPCC) Third Assessment Report (IPCC, 2001) and the Fourth Assessment report (IPCC, 2007) . Forster et al. (2007) explain this as a result of increasing concentrations (0.26% yr^{-1}) of N_2O in the atmosphere. If global average concentrations of N_2O continue to rise, the RFp for N_2O will increase relative to previous calculations.

2.2 Radiative Efficiency

The radiative forcing potential (RFp) can be translated into a radiative efficiency (RE) for atmospheric greenhouse gases. Radiative forcing potential and radiative efficiency are often used interchangeably to describe the impact of N_2O on the radiative forcing of the atmosphere; however, in the calculation of GWP, it is necessary to use radiative efficiency. The radiative forcing potential of N_2O is reported as the total amount of net irradiance increase caused by the percent increase of N_2O in the atmosphere. Radiative efficiency describes the increase in net irradiance in relation to the discrete increase in atmospheric N_2O. Radiative efficiency is simply the RFp divided by the actual increase in an atmospheric substance over the time frame used to calculate its RFp. For three major greenhouse gases, the radiative efficiencies as calculated by Forster et al. (2007) are:

$$CO_2 = 1.4 \times 10^{-5} \text{ W m}^{-2} \text{ ppb}^{-1}$$

$$CH_4 = 3.7 \times 10^{-4} \text{ W m}^{-2} \text{ ppb}^{-1}$$

$$N_2O = 3.03x10^{-3} \text{ W m}^{-2} \text{ ppb}^{-1}$$

The comparison of these three greenhouse gases shows that N_2O is two orders of magnitude more efficient than CO_2 in its ability to increase the net irradiance at the equatorial surface per unit increase in parts per billion. This relatively high RE contributes to the concern given N_2O, a relatively minor component of the atmosphere by volume.

2.3 Lifespan of N_2O in the atmosphere

A substance's lifespan in the atmosphere is the second major factor taken into consideration in the calculation of GWP. Knowing the lifespan of a greenhouse gas in the atmosphere makes it possible to integrate the impact of the substance over the time of its persistence in the atmosphere. Several studies have used various methodologies to determine the lifespan of N_2O in the atmosphere and have determined it to be approximately 120 years (Volk et al., 1997; Minschwaner and Carver, 1998; Forster et al., 2007). This is much longer than the other significant greenhouse gases CO_2 and CH_4. The lifespan of CH_4 is approximately 12 years and it is difficult to determine the lifespan of CO_2 as its persistence in the atmosphere is highly variable as a result of global photosynthetic and convective cycles. The relatively long lifespan of N_2O adds to the concern over its GWP as potential negative contributions to climate change may take much longer to reverse as compared with CH_4 and CO_2.

2.4 Global Warming Potential (GWP)

Global warming potential is a dimensionless, integrated metric for determining the relative potential of an atmospheric substance to contribute to the radiative forcing of the atmosphere over time. It is generally calculated for time frames of 20, 100, or 500 years, while the most widely cited and used timeframe for calculating GWP is 100 years. GWP is a relative term calculated against the time-

integrated radiative forcing potential of 1 kg pulse of CO_2 into the atmosphere. The equation for the GWP of substance (x) is:

$$GWP(x) = \frac{\int_0^{TH} a_x * [x(t)]dt}{\int_0^{TH} a_r * [r(t)]dt}$$

Where TH is the timeframe for the calculation (20, 100, or 500 years), a_x is the radiative efficiency of a 1kg pulse addition of a substance to the atmosphere, x_t is the time dependent decay for the instantaneous release of the substance, and the denominator is a calculation for the reference substance (CO_2). The 100 year GWPs for three major greenhouse gases as calculated by Forster et al. (2007) are:

CO_2 = 1

CH_4 = 25

N_2O = 298

Though GWPs have needed to be adjusted in conjunction with updates in RFp and RE for each gas, N_2O continues to stand out as having a significant ability to increase radiative forcing in the atmosphere. When the lifespan of N_2O is taken into consideration, the difficulty of reversing potential damage done by excessive N_2O emissions becomes a major concern for efforts regarding climate change mitigation.

3 Agricultural contributions of N_2O to the atmosphere

The production of N_2O in agricultural fields is primarily the byproduct of nitrification and denitrification in the soil profile and at the soil surface (Hénault et al., 2012). Nitrification and denitrification are processes in the greater nitrogen cycle, which is the path and series of

transformations that nitrogen species experience in the agroecosystem. These two processes work together, with denitrifiers often using the products of nitrification to complete the reduction of N species in the soil solution to the inert gas N_2.

3.1 The nitrification process in agroecosystems

The process of nitrification is a microbially mediated transformation of ammonium (NH_4+)to nitrate (NO_3-)This process is critical for the creation of plant available N, as the anion nitrate is much more mobile in the soil solution than ammonium. Although some nitrate enters the field through acid rain and certain forms of fertilizer, nitrification provides the bulk of plant available N in an agroecosystem (Robertson and Groffman, 2007).

The process of nitrification begins with the microbial oxidation of ammonium (NH_4+)to ammonia (NH_3) in aqueous solution represented by the reaction:

$$\mathrm{NH_4^+(aq) \leftrightarrow NH_3(aq) + H^+(aq)}$$

This reaction can occur through several pathways and is mediated by either autotrophic or heterotrophic respiration. The autotrophic bacteria gain significant energy from this process on the order of 444kJ of energy per mole of NH_3 when NO_3- is the end product (Robertson and Groffman, 2007). In the reduction of ammonium to nitrate, the dominant microbial nitrifiers are aerobic autotrophs and derive their C from CO_2 or carbonates, not organic matter. The subsequent autotrophic reduction of occurs in two stages, performed by ammonia oxidizers and nitrite oxidizers. The following equations represent the oxidation of ammonia and nitrite, respectively:

$$NH_3 + 1\,½\,O_2 \rightarrow NO_2^- + H^+ + H_2O$$

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$$

Nitrification can also be mediated by heterotrophs through pathways similar to the autotrophic nitrifiers. There may also be an organic nitrification pathway limited to fungi which is not linked to ATP and produces no energy (Robertson and Groffman, 2007).

The primary limiting factor for nitrification in the agroecosystem is the availability of NH_4+for reduction. At times when decomposition or plant uptake of NH_4+ is high, nitrification will generally be limited. Nitrification will generally increase with the increase of available, unless limited by some other factor. However, these increases in nitrification will usually only occur when NH_4+ availability exceeds plant demand, indicating that nitrifiers are poor competitors for NH_4+. In agricultural soils, nitrification is typically low after the addition of residue with a high C:N ratio.

The availability of O_2 is also an important limiting factor on the process of nitrification. Nitrifiers are obligate aerobes and O_2 must be present if complete nitrification is to occur. Some nitrifiers can substitute NO_2- as an electron acceptor in the place of O_2; however, O_2 is still necessary for the first step in the oxidation of ammonia. Soil texture and moisture are also important limiting factors on nitrification; however these factors are mostly indirect as their limitation on nitrification is mainly associated with the effect that texture and moisture have on O_2 availability within the soil solution. Temperature also has an indirect effect on nitrification by influencing soil microbial activity. The microbial species present in a soil solution can also have an impact on nitrification, as it is recognized that autotrophic species are the dominant nitrifiers in the system.

3.2 Contribution of nitrification to N_2O flux from agroecosystems

It is generally accepted that nitrification plays an important role in the production of N_2O in agroecosystems, where it has been shown to be the dominant process in N_2O production in soil conditions of 35-60% water filled pore space (WFPS) (Bateman and Baggs, 2005). However, there is still

considerable uncertainty regarding how and at what rate N_2O is produced during nitrification. These are both important issues to resolve if accurate estimations are to be made, as both of these factors inform process based models, which are important tools in the study of N_2O flux from agroecosystems. A more accurate understanding of the process of N_2O production during nitrification can inform intervention strategies designed to limit the potential for N_2O production and identifying the rate of N_2O production during nitrification will better inform estimates.

During nitrification, it has been suggested that N_2O can be produced through at least two distinct mechanisms, 'chemodenitrification' and 'nitrifier denitrification' (Wrage et al., 2001). During the reduction of NH_3 to NO_2^- , chemodenitrification and the production of N_2O can result from the decomposition of NO_2^- or the intermediate product NH_2OH. This process can be mediated either by microbial species or by processes of chemical decomposition (Bremner, 1997). Bremner (1997) also finds that the N_2O produced by chemical decomposition during nitrification is negligible when compared with N_2O produced through biological processes.

There is considerably more uncertainty surrounding the process of nitrifier denitrification where nitrifiers reduce NO_2^- to the gases NO, N_2O, and N_2, an ability that has long been recognized (Hooper, 1968). However, speculation over the process of and the purpose for this pathway has generated several theories. Poth and Focht (1985) showed that N_2O can derive from NO_2^- produced from within the cell, which was later confirmed by Remde and Conrad (1990), and suggested that this was a response to the toxic accumulation of NO_2^- within the cell body. It is important to consider the process and conditions under which nitrifier denitrification occurs as it has been identified as a significant contributor to total N_2O flux from soils (Wrage et al., 2001). In 2011, Kool et al. used a novel multi-isotope tracing approach to identify a distinct pathway for nitrifier denitrification, and confirmed the significance of nitrifier denitrification in the production of N_2O, especially in moisture conditions sub-optimal for denitrification. This is an important development in the estimation of N_2O flux from

agroecosystems as the contribution of nitrifier denitrification to total N_2O flux may have been previously underestimated.

The rate at which nitrified N is converted to N_2O is still an area of uncertainty, possibly because of the multiple pathways that N_2O as a product of nitrification might take. This is especially problematic when models are developed to predict N_2O production from nitrification, many of which use various and fixed percentages to estimate rates of N_2O production from nitrification which can vary from 0.06 - 2% (Mathieu et al., 2006). However, the availability of O_2 in the soil solution not only impacts the rate of nitrification, as mentioned above, but also the rates of N_2O production. Khalil et al. (2004) found that the percent of nitrified N converted to N_2O increased from 0.16 % to 1.48% when O_2 partial pressure fell from 20.4kPa to 0.76kPa. Mathieu et al. (2006) similarly found that while nitrification rates remained consistent under soil water-unsaturated and water-saturated conditions, the proportion of nitrified N emitted as N_2O increased from 0.13% (unsaturated) to 2.32% (saturated). Though there seems to be a clear effect of water-saturation and O_2 availability on the rate of N_2O production during nitrification, several current process-based models incorporate only a fixed percentage (0.02) to determine N_2O produced from nitrification.

3.3 The denitrification process in agroecosystems

Denitrification in agricultural fields is the microbially mediated reduction of nitrate (NO_3- to the gases NO, N_2O, and N_2. Denitrification is carried out by heterotrophic bacteria using NO_3- as a terminal electron acceptor instead of O_2 in respiration. This process mostly takes place under conditions limited by O_2 availability, typically at a WFPS of 60% or higher. These conditions are typically found in saturated fields and after rainfall or irrigation events, particularly in poorly drained soils. Denitrification plays a particularly important role in the agroecological and global N cycle as it is the only point where N_2 gas is produced. Without this production, N fixers would quickly deplete atmospheric N reserves and the N cycle would cease.

Each step in the pathway for denitrification is mediated by individual enzymes. The eventual product is N_2 gas; however the intermediate products can be exchanged within the soil environment. The following equation represents the pathway for denitrification:

$$\begin{array}{cccccc} & & & \uparrow & \uparrow & \uparrow \\ 2NO_3^- & \rightarrow & 2NO_2^- & \rightarrow 2NO & \rightarrow N_2O & \rightarrow N_2 \end{array}$$

Denitrification is a significant source of NO_2- and nitrogen gas species. Each of the gas species (NO, N_2O, and N_2) can be released into the atmosphere during denitrification. Organisms denitrify to gain energy and typically constitute 0.1-5% of the total culturable soil population and 20% of microbial biomass (Tiedje, 1988).

The factors governing denitrification are similar to those governing nitrification. The dominant control on denitrification is O_2 availability with denitrifiers being obligate anaerobes and typically flourishing in O_2 limited conditions. These conditions are more likely in agricultural soils with high water holding capacities, poorly drained soils, and after rainfall or irrigation events. Denitrification can also occur at anoxic microsites created by decomposition or as a result of soil texture (Tiedje, 1988). The effect of soil texture on gas diffusivity, and subsequently O_2 availability, is a function of porosity which is determined by the relative surface area and particle size of soil components (Del Grosso et al., 2000). Thus, while O_2 availability is considered the dominant control on denitrification, soil properties play a large and indirect role in the facilitation of favorable denitrification conditions.

The availability of nitrate (NO_3-)is also a major limitation on denitrification, though it is considered secondary to O_2 availability. In the agricultural environment, the availability of NO_3- is strongly regulated by plant uptake where high rates can substantially reduce rates of denitrification

(Tiedje, 1988). This indicates that denitrifying anaerobes are poor competitors for NO_3- . Soil moisture also has an indirect effect on NO_3- availability, as NO_3- is highly mobile in the soil solution and easily transported by water movement. The availability of labile C is also a constraint on denitrification. Labile C acts as an electron donor for NO_3- reduction and though denitrifying heterotrophs are a small percentage of the microbial population, when in an O_2 limited environment they are able to outcompete the nonfunctioning obligate aerobes for labile C.

3.4 Contribution of denitrification to N_2O flux from agroecosystems

Denitrification has been identified as the major source of atmospheric N_2O from agricultural soils. Denitrification produces N_2O as an intermediate product in the reduction of NO_3- to inert N_2. When denitrification is incomplete, N_2O is not reduced to N_2 and is emitted to the atmosphere. At a long term ecological research (LTER) site in Southwest Michigan, denitrification was identified as producing 87% of N_2O flux from agricultural fields under management for corn and soybean (Opdyke et al., 2009). Bateman and Baggs (2005) found that denitrification was the predominant producer of N_2O during soil conditions of <20% WFPS and >70% WFPS, although denitrification was observed in the intermediate WFPS values. The occurrence of anoxic microsites within the soil solution allow for denitrification to occur at WFPS values that are generally favorable to nitrification (Del Grosso et al., 2000). These microsites can be created as a result of soil texture, where small particle size and high surface area to volume ratios increase water holding capacity and heterogeneous particle distribution creates microsites of greater than average WFPS. Oxygen limitation and NH_3 and labile C availability are also necessary for denitrification to occur in these microsites, all of which can usually be found in the rhizosphere which creates another location for potential denitrification (Robertson and Groffman, 2007).

The rate at which denitrification produces N_2O is most often expressed as a ratio between N_2 and N_2O, where a higher ratio represents more complete denitrification and less emission of N_2O. The reason for the incomplete denitrification of N is the availability of O_2 as an electron acceptor. Thus, the general relationship is that as O_2 availability decreases, the N_2:N_2O ratio increases and less N_2O is produced from denitrification. Maag and Vinther (1996) confirmed this relationship in a study examining the effect of field capacity (FC) on the N_2:N_2O ratio where they found the ratio to increase from 1.7 at 75% FC to 15.9 at 175% FC. Process based models are most often used in the estimation of N_2O as a function of the N_2:N_2O ratio and employ functions to determine the ratio based upon O_2 availability (Parton et al., 2001).

4 Estimating N_2O emissions from agroecosystems

Estimating field scale agricultural emissions is useful for the study of N dynamics and biophysical processes contributing to the production of N_2O as well as developing local and regional estimates of N_2O emissions. Several methods have been developed to estimate field scale N_2O emissions with each method reflecting the intended application of the data. This section will focus on three common methods for estimating field scale emissions with an emphasis on their respective applications. The first method is the site specific and direct measurement of N_2O flux from an agricultural field. This method is useful for characterizing specific fields or cropping systems and provides the most accurate information for estimating total N_2O flux for a single field. The second method is the empirical modeling of N_2O where some known variable, often N fertilization rate, is associated with N_2O flux through an empirical relationship. For instance, the IPCC proposes that anthropogenic N_2O emissions can be calculated as percentage of applied N fertilizer (IPCC, 2006). Empirical modeling is particularly useful when available data is limited, and it is the most common method used for making estimates at national and global scales. The third method is the use of a process based model to simulate N_2O flux within an

agroecosystem. These complex models are built from known biophysical and biogeochemical relationships and can provide a means to study the dynamics of N_2O flux at field scales where site-specific measurements are impractical and empirical models insufficient.

4.1 Site-specific measurements of N_2O from agroecosystems

Chamber techniques for measuring N_2O flux have been used for over 8 decades and are still the most common approach for studying N_2O flux in agroecosystems (Rochette and Bertrand, 2008). Chambers allow for measurements of very small fluxes and can be implemented in a variety of conditions and locales, which makes them ideal for studying diverse agroecosystems. The design for chambers and sampling is outlined thoroughly by Rochette and Bertrand (2008). Chamber techniques can be divided into two categories, steady-state (SS) and nonsteady-state (NSS). The SS chamber has the advantage of automated continuous monitoring of N_2O flux and provides data closest to the ambient flux of N_2O from the surrounding field. While SS chambers offer the most accurate estimations of N_2O flux, they are less common than NSS due to their prohibitive expense. An example of a typical SS chamber study was conducted by Jarecki et al. (2008) where a corn field was monitored for one year with samples collected every 6 minutes and the objective was to evaluate the performance of the process-based model DAYCENT. It is common for site-specific measurements of N_2O to both inform the development and evaluate the performance of process-based models.

. The non-steady state methodology is similar to that of steady-state in structural design, with the exception of measurement frequency. NSS chambers are sampled manually at time 0 (t0) and time x (tx), usually a 20-60 minute differential, and use laboratory gas chromatography to determine N_2O concentrations at t0 and tx. The resulting differential is used to calculate the interim flux of N_2O. A major disadvantage to NSS chambers is the necessary assumption that the rate of N_2O flux during the

measurement period is consistent for the interim period between measurements. The closed headspace of the NSS chamber can alter gas fluxes relative to undisturbed values (Rochette and Hutchinson, 2005). Gas accumulation within the closed chamber alters the concentration gradient, which can suppress gas diffusion and lower estimations of gas flux. Duran and Kucharik (2013) found that the suppression of gas flux can increase as measurement periods exceed 20 minutes. Although it is generally accepted that more frequent measurements return more accurate characterizations of interim flux, Smith and Dobbie (2001) found that estimations calculated from an interval of 14 days ranged from an acceptable -66 to +58% of the estimates calculated from 8 hour intervals.

The particular economic advantage of NSS chambers has resulted in their use for a variety of objectives and over a variety of time frames in the estimation of agricultural N_2O emissions. Similar to Jarecki et al. (2008) several uses of NSS chambers have been to evaluate the performance of process-based models. For example, Abdalla et al. (2010) compared NSS chamber measurements with the performance of the two process-based models DAYCENT and DNDC over one year on Irish grasslands. Another important use for NSS chambers is to generate data for the calibration of a process-based model to represent a particular agroecosystem as Mosier et al. (2006) did for 3 growing seasons across several corn-soybean cropping systems. NSS chambers have also been used to study the effect of environmental variables such as soil texture and organic matter content on N_2O flux (Harrison-Kirk et al., 2013). The effects of management and potential mitigation strategies can also be studied with NSS chambers, specifically in the context of the effects of nitrogen fertilizer management (Ma et al., 2010; Hoben et al., 2011) on N_2O flux. However, despite the extensive use of NSS chambers in the evaluation of N_2O emissions, the disadvantages described by Rochette and Hutchinson (2005) and Duran and Kucharik (2013) may indicate that new methods are needed to accurately measure cumulative N_2O fluxes.

4.2 Empirical modeling of N_2O from agroecosystems

Empirical models using N fertilization rates to estimate N_2O emissions have been used to single site studies (Bremer et al., 2011) as well as for national-scale inventories (Dalgaard et al., 2011), and have been proven relatively reliable for estimating average N_2O fluxes (IPCC, 2007). A common empirical model for the estimation of field-scale agricultural N_2O emissions was developed for the Intergovernmental Panel on Climate Change (IPCC). The IPCC uses a methodology built upon an 'emission factor' (EF), which is a dimensionless figure that represents a proportion of applied nitrogen that is assumed to be emitted as N_2O (IPCC, 2007). The IPCC EF methodology is divided into two 'Tiers' where Tier I is a standard EF of 0.01 and Tier II requires the development of a nationally or regionally derived EF. Tier I assumes that 1% of all applied nitrogen (organic and chemical) will be converted into N_2O, and has been shown to be useful for rough estimates of global and national scale N_2O emissions (Del Grosso et al., 2008). However, many studies have also shown the Tier I methodology to be less accurate when applied to smaller regional and farm-field scales (Brown et al., 2002; Del Grosso et al., 2008; Hoben et al., 2011). The development of regionally specific emission factors (Tier II methodology) can help to capture some landscape variation in N_2O emissions, as shown by Wang et al. (2011) in their assessment of greenhouse gas emissions from agriculture in the United Kingdom. However, EF methodology incorrectly calculates a linear response of N_2O emissions to increases in N fertilization rate.

Several studies have observed a nonlinear response of N_2O flux to an increase in the rate of nitrogen fertilization, which contradicts the linear estimates associated with an EF methodology. Hoben et al. (2011) found that as the level of synthetic N application increased, there was an exponential response in the rate of increase for the flux of N_2O. In fact, in this study the EF was found to vary between 0.006 and 0.015, compared to the constant IPCC EF of 0.01. Jarecki et al. (2009) also found a

significant nonlinear response of N_2O to rate of organic N fertilization in the form of manure, though timing, form, and presence of cover crops were also influential. These nonlinear responses are most likely due to the inability of plants to increase their uptake of nitrogen, leading to an excess of substrates in the system becoming available to populations of nitrifiers and denitrifiers. However, although it seems apparent that a constant EF becomes problematic at the field scale, Philibert et al, (2012) suggest that the information required to determine nonlinear responses at the national scale may be prohibitively complicated and difficult to gather.

The most appropriate use for Tier I and Tier II EF methodology appears to be for evaluations at national scales and particularly for evaluating future climate change scenarios. Dalgaard et al. (2011) estimated the combined effect of Danish agriculture on GHG emissions using EF methodology to evaluate the relative contributions of individual greenhouse gases and mitigation scenarios. Wang et al. (2011) have incorporated EF methodology into a versatile framework for evaluating agriculture in the United Kingdom. These methods can be particularly useful in identifying and evaluating potential focal points for national efforts at GHG mitigation, as Kim et al. (2013) found that potential reductions in N_2O emissions from land use change and nitrogen fertilizer reduction in Irish grasslands could be negated by future climate change scenarios. The use of empirical models for estimating N_2O flux from agricultural fields can be extremely useful when used to calculate regional averages, but are less capable of evaluating variation in N_2O emissions at the regional and field scales.

4.3 Process-based modeling of N_2O from agroecosystems

The complexity of biological systems, where combinations of multiple components interact simultaneously in non-linear and seemingly chaotic ways, makes predicting system outcomes equally complex and difficult (Jones and Luyten, 1998). This can be especially true for estimating N_2O flux where the understanding of contributing processes and interactions is still developing. However, the

established and developing mathematical representations (models) of these systems can still provide insight into the processes contributing to the production of N_2O in agroecosystems. These models are identified as 'process-based' because they mathematically represent the biological and biophysical processes that mediate the flows of energy, matter, and nutrients in biological systems. Models can be used to examine the hierarchies embedded in biological systems where, for example, the effects of stomatal conductance at a lower level of organization can be observed at higher levels like plant productivity. These models are particularly useful in investigating questions that would, in real world circumstances, be impractical, if not impossible to evaluate.

There have been several process-based agroecosystem models either developed to simulate or capable of simulating the production of N_2O in agricultural fields (Chen et al., 2008). DAYCENT (Parton et al., 1996, 1998, 2001; Del Grosso et al., 2000) is the daily time-step version of the CENTURY model (Parton et al., 1994) and capable of simulating trace N_2O flux from agroecosystems. DAYCENT is run on input data for daily weather (maximum air temperature, minimum air temperature, daily precipitation totals, solar radiation (optional), relative humidity (optional), wind speed (optional)), soil properties (bulk density and percent sand, silt and clay), site location (latitude and longitude) and current and historical land use. DAYCENT uses submodels for nitrification and denitrification to simulate the production of N_2O. In the United States, DAYCENT has been shown to accurately estimate annual cumulative N_2O emissions, while less accurately predicting daily N_2O flux (Del Grosso et al., 2000, 2006; Parton et al., 2001). The DNDC (DeNitrification-DeComposition) model was specifically developed to predict daily N_2O fluxes through nitrification and denitrification (Li et al., 1996). One advantage of the DNDC model is that it is capable of simulating denitrification on an hourly time-step.

These models are capable of evaluating how climate change scenarios might affect particular fields and also how management impacts the flux of N_2O from an agroecosystem (Grant et al., 2004).

The IPCC created a Tier III methodology which specifically requires the use of process based models and recognizes their advantage over empirical models in estimating GHG emissions (IPCC, 2007). While these models are useful for evaluating particular fields, they can also be employed in national inventories to refine and strengthen aggregate estimates of agricultural N_2O emissions (Del Grosso et al., 2006; USEPA, 2012). However, the invaluability of these models is tempered by their limitations which include an inability to account for every factor occurring in real agroecosystems as well as inaccurate embedded empiricisms. This requires that models often be calibrated to individual fields or instances to ensure the best performance of the model. While research and increased data collection informs the continuous improvement of models (Del Grosso et al., 2008), the use of SS and NSS chambers to compare site-specific N_2O emissions with model predictions is still an advised and common practice (Del Grosso et al., 2008; Jarecki et al., 2008; Abdalla et al., 2010; De Gryze et al., 2010).

5 Conclusion

It has been well documented that the production of N_2O from agriculture is exerting an influence on the radiative forcing of the atmosphere (Ramaswamy et al., 2001; Forster et al., 2007; IPCC, 2007). This review has described the current impacts of N_2O emissions in the atmosphere, the processes through which N_2O is produced in the agricultural field, and current methods for estimating field-scale N_2O emissions. While the increase in atmospheric N_2O concentration has contributed only 14% to the total net radiative forcing of the atmosphere due to the greenhouse gases CO_2, CH_4, and N_2O, the radiative efficiency and lifespan of N_2O make it a gas species of particular concern. Due to its atmospheric longevity, present day efforts to reduce concentrations of atmospheric N_2O may take more than a century to be realized. As principle contributor of anthropogenic N_2O, agriculture is an area that may provide an opportunity to make significant reductions in annual anthropogenic emissions of N_2O.

Reducing agricultural N_2O emissions requires an understanding of the processes contributing to its production in the agricultural field. The processes of nitrification and denitrification are known to be to dominate the production of N_2O; however the relative contribution of each to total N_2O flux is still an area where more study is needed. Several laboratory experiments have indicated that the effect of soil texture and water filled pore space are important regulators of the two processes and total N_2O flux (Maag and Vinther, 1996; Khalil et al., 2004; Bateman and Baggs, 2005) and Opdyke et al. (2009) found that denitrification dominates in one temperate agricultural soil in Michigan. However, the extrapolation of these results to all temperate agricultural soils is difficult without further research. Agricultural soils in temperate regions are diverse in texture, and continued research can offer insight into the influence that soil texture exerts on N_2O emissions on a range of soil textures.

The methods for studying N_2O emissions from agricultural soils each provide particular challenges and capabilities. Direct measurements using chamber methodology are one of the most common methods for sampling agricultural N_2O emissions. Chamber sampling offers the advantage of collecting physical measurements and can be used to investigate relationships between environmental variables and N_2O emissions. However, the accuracy of chamber measurements may be influenced by several methodological choices, including chamber type, design, and sampling interval. For example, Duran and Kucharik (2013) found that extended sampling periods can suppress gas flux within the chamber, leading to an underestimation of total N_2O flux. Empirical methods for estimating N_2O flux are useful where data is limited and in cases where aggregate estimates of regional emissions are desired. While empirical estimation tools, such as the IPCC's emission factor methodology (IPCC, 2006), may be useful for estimating mean flux, they are less able to explain the high degree of spatial and temporal variability observed in N_2O flux from agricultural fields. The use of process-based models has the advantage of simulating the influence environmental variables exert on N_2O flux and can extend predictive capabilities across the landscape with a higher degree of confidence than empirical methods.

However, model performance and confidence is limited by the number of relationships and interactions they are comprised of. Limited understanding of ecosystem processes also limits model performance, which is also limited by the accuracy of the mathematical relationships used to construct the model. Process-based modeling is an iterative process in a constant state of validation, calibration, revision, and construction. While results from model simulations should be interpreted with consideration for the difficulty involved in simulating complex agroecosystems, they are powerful tools capable of extending our current understanding of ecosystem processes across the landscape in ways that may otherwise be impractical to address with traditional field experiments. Current understanding of N_2O flux from agroecosystems is limited by the number of field and laboratory studies available for N_2O emissions from agricultural soils. Due to the diverse nature of agroecosystems, it may also be difficult to establish field experiments to study environmental variables, such as soil texture, that influence N_2O emissions from agricultural fields. However, the impact that agricultural N_2O emissions exert upon the radiative forcing of the atmosphere has increased interest in the study of factors influencing N_2O flux. In the development of accurate emissions estimates and potential mitigation strategies, process-based models are playing an increasingly important role. While models may need continuous improvement and revision, they are currently a powerful tool useful in the extension of limited field studies and the study of potential scenarios for the reduction of agricultural N_2O emissions.

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Chapter 2: Soil N_2O emissions from corn and soybean agriculture in Wisconsin: simulated causes of spatial and temporal variability

1. Introduction

In the Midwest region of the United States, N_2O emissions constitute the majority (64%)of greenhouse gas emissions from agriculture (Larsen et al., 2007) and are driven predominately by the application of nitrogen fertilizer in row cropping systems (Grace et al., 2011). In 2013, row-crop agriculture of corn and soybeans constituted 55.7% of total planted acres in the state of Wisconsin (USDA NASS, 2013). Interest in refining estimates and mitigating emissions of N_2O from agriculture has led to several studies investigating the sources of variation in N_2O emissions (Stehfest and Bouwman, 2006; Mathieu et al., 2006; Hénault et al., 2012). Previous studies have calculated N_2O emissions from Midwest agriculture using the IPCC Tier I emission factor methodology (Larsen et al., 2007; Grace et al., 2011), which estimates N_2O-N emissions as 1 percent (emission factor) of total N applied to the agroecosystem in chemical and organic forms (IPCC, 2006). However, emission factor methodologies are only able to account for variation in N_2O emissions due to variable rates of N fertilizer application. Studies have shown that cumulative N_2O emissions from Midwest corn agriculture can range from <2 kg N_2O-N ha^{-1} at an N application rate of 225 kg N ha^{-1} (Hoben et al., 2011) to 10.2 kg N_2O-N ha^{-1} at an N application rate of 202 kg N ha^{-1} (Parkin and Kaspar, 2006). The discrepancy in emission factors calculated from the results of these two studies (<0.01 vs. 0.05) indicates that other factors are contributing to variability in N_2O emissions in the Midwest.

Spatial variability in N_2O emissions is partly linked to soil textural properties (Henault et al., 1998), which influence the dominant physical processes that produce N_2O in agricultural fields, microbial nitrification and denitrification (Groffman, 1991; Conrad, 1996). One of the primary controls on nitrification and denitrification is the availability of O_2 in the soil solution (Robertson and Groffman,

2007). Soil texture exerts an indirect influence on O_2 availability where decreasing particle size is associated with higher field capacity and lower saturated conductivity (Saxton and Rawls, 2006). Additionally, N_2O production from denitrification is more likely in finer textured soils where increased water content and smaller particle size increase the likelihood of anoxic denitrification microsites (Tiedje, 1988; Del Grosso et al., 2000). Several laboratory experiments have examined the effects of soil texture on the production of N_2O (Maag and Vinther, 1996; Khalil et al., 2004; Bateman and Baggs, 2005), yet few have examined the relationship between soil texture and total N_2O flux at the field scale.

Variation in N_2O emissions has also been linked to the effect rainfall patterns exert on soil moisture conditions (Dobbie et al., 1999; Gagnon et al., 2011). Specifically, Dobbie et al. (1999) found that heavy rainfall events following the application of inorganic N fertilizer increased soil N_2O flux. As chemical N fertilizer applications are commonly made in the early growing season, interannual variability in rainfall during this time may help to explain the high temporal variability observed in N_2O emissions. In the state of Wisconsin, several climatic trends have been observed by Kucharik et al. (2010), including a significant increase of 14mm in Spring precipitation in the South Central region of the state. The potential impact of precipitation events and trends on N_2O emissions from agricultural fields has yet to be studied and could inform future estimations of N_2O emissions the evaluations of climate change scenarios.

Accurately quantifying and estimating N_2O emissions from agricultural fields is still a major challenge in the Midwest. Several studies have collected N_2O flux measurements in the region (Goodroad et al., 1984; Cates and Keeney, 1987; McSwiney and Robertson, 2005; Parkin and Kaspar, 2006; Jarecki et al., 2008; Hoben et al., 2011; Burzaco et al., 2013, Osterholz et al., in press), but diversity in agroecosystems makes extrapolation of these results to the entire region difficult. Additionally, drivers of spatial and temporal variability in N_2O flux are difficult to assess from a limited number of field

studies. However, the development of process-based models capable of simulating N_2O flux has provided a method for extending results from field and laboratory experiments and evaluating N_2O emissions over time and across the landscape. The DAYCENT agroecosystem model (Del Grosso et al., 2001; Parton et al., 2001) has been frequently validated and used to estimate field, regional, and national scale agricultural N_2O emissions (Parton et al., 1998; Del Grosso et al., 2006, 2008; Jarecki et al., 2008; Abdalla et al., 2010; Chamberlain et al., 2011). DAYCENT inputs include soil texture and daily cumulative precipitation, and the model is capable of simulating the response of N_2O flux to changes in those variables. Using DAYCENT we were able to assess the influence of 19 years of variation in precipitation and 35 different soil textures on cumulative N_2O emissions from corn and corn-soybean agroecosystems in Wisconsin. Validating the model with N_2O flux data collected in Wisconsin and developing simulations to represent a range of agricultural scenarios can increase confidence in predictions of N_2O emissions across the state and our understanding of the drivers of variation in N_2O emissions.

The goals of this study were to: (i) validate the ability of the DAYCENT agroecosystem model to simulate N_2O emissions from a continuous corn and corn-soybean row cropping system in Wisconsin; (ii) identify ranges for N_2O emissions from different soil textures in the state of Wisconsin; (iii) demonstrate the influence soil texture exerts on spatial variability in N_2O emissions; and (iv) investigate the influence of Spring cumulative precipitation on temporal variability in cumulative annual N_2O emissions.

2 Methods and Materials

2.1 DAYCENT model description

DAYCENT is a biogeochemical model that has been extensively tested for the modeling of N_2O flux from agroecosystems (Del Grosso et al., 2005, 2006; Jarecki et al., 2008; Abdalla et al., 2010).

DAYCENT uses a daily time step to simulate the short term effects of environmental variables on the production of nitrogen gases in ecosystems (Frolking et al., 1998; Martin et al., 1998). The production of N_2O in DAYCENT is the result of the processes of nitrification and denitrification modeled in the soil and at the soil surface. Simulations of daily N_2O emissions are driven by soil water content, temperature, , , and respiration (Parton et al., 2001). Total rates of nitrification and denitrification are calculated and a ratio function of NO_x to N_2O is used to calculate individual gas species emissions.

Denitrification Submodel

Denitrification in DAYCENT (Parton et al., 1996, 2001) is controlled by the availability of substrate, , labile carbon (C), and O_2. Increasing substrate availability contributes to increased denitrification (Figure 1). Simulated heterotrophic respiration is used as a surrogate for labile C availability. Increased respiration contributes to an increase in denitrification before asymptotically reaching a maximum level of denitrification (Figure 2). Simulated water filled pore space (WFPS) is used as a surrogate for O_2 availability. There is an exponential relationship between WFPS and denitrification (Figure 3) that is controlled by soil texture. The DAYCENT denitrification submodel assumes the denitrification process is controlled by the most limiting of these three factors.

A maximum denitrification rate is calculated from the relationship between substrate availability (as e^- acceptor) and respiration (CO_2 as e^- donor). It is assumed that denitrification will not occur when WFPS is less than 55%. The rate of denitrification increases exponentially from 55-90% WFPS, where the rate of denitrification levels off at the point of soil saturation. An attenuated multiplier is applied to the maximum nitrification rate based upon O_2 availability, which controls the magnitude of the exponential relationship between WFPS and denitrification. This multiplier is calculated as a function of soil gas diffusivity, where soils with textures limiting diffusivity will tend to generate anoxic microsites and allow for denitrification to occur at lower WFPS. The total daily amount of denitrified N is apportioned to the

N gas species N_2 and N_2O through a calculated N_2 to N_2O ratio, which is function of O_2 availability in the soil (Figure 4).

Nitrification Submodel

The nitrification submodel (Parton et al., 1996, 2001) assumes that nitrification rates are controlled by soil concentration, water content, temperature, and pH. Daily net mineralization is calculated from soil organic matter decomposition and a constant fraction (0.2) is assumed to be nitrified. The maximum fraction (0.1) of available for nitrification is limited by WFPS, temperature, and pH. Total daily nitrification is the sum of nitrification from SOM decomposition and nitrification from available . Produced N_2O is calculated as a constant fraction (0.02) of total nitrified N (Parton et al., 2001).

Model Drivers

Inputs used to drive the DAYCENT model are soil physical and chemical properties, weather, latitude, longitude, and management. The model requires information on soil bulk density, pH, and percentages of sand, silt, and clay. DAYCENT can be run using weather data consisting of daily minimum temperature, maximum temperature, and total precipitation. Latitude and longitude are used to calculate day length and the accumulation of growing degree-days, the latter of which is used to simulate plant development and growth. The manipulation of management in the DAYCENT model consists of scheduling 'events' for specific days and can include crop type, planting month, harvest date, first month of growth, last month of growth, senescence month, fertilization, cultivation, organic matter addition, irrigation, grazing, erosion, fire, tree type, tree removal, first month of forest growth, and last month of forest growth. DAYCENT is capable of simulating annual, perennial, forest, and savannah ecosystems and the selected management options determine the type of system to be simulated.

2.2 DAYCENT Validation

A series of model runs were used to evaluate DAYCENT's ability to predict corn and soybean yields from 1993-2011, soil organic carbon changes between 1989 and 2009, and N_2O emissions for two years (2010 – 2011) at an agricultural research site in southern Wisconsin. DAYCENT monthly and yearly output was compared with data collected at the Wisconsin Integrated Cropping Systems Trial (WICST), which is an ongoing long-term agricultural experiment designed to evaluate the impact of varied management and cropping systems on crop production and soil carbon (Posner et al., 2008; Sanford et al., 2012).

Two WICST cropping systems were used for model validation, a continuous corn rotation (CS1) and a reduced tillage corn-soybean rotation (CS2), which represent important historical and current agricultural systems in Wisconsin and Midwestern USA. In 2012, corn and soybean accounted for over 6 million planted acres and 40% of farmed acres in the state (USDA NASS, 2014). Management practices at WICST were used to parameterize DAYCENT for each simulated system (Table 1). Corn for both CS1 and CS2 was conventionally managed with inorganic nitrogen fertilizer and chisel plowed with no mechanical cultivation. No-till soybean management was simulated with no pre-plant tillage, no mechanical cultivation, and no nitrogen fertilizer addition. For CS2, two simulations were used to ensure that both corn and soybean crops were represented in each simulated year. In total, three cropping system scenarios were simulated for 1993-2011: continuous corn (C-C), corn-soybean (C-Sb), and soybean-corn (Sb-C). Results from both of the CS2 rotations were aggregated for comparison with CS1.

Our model validation exercise first required an initialization and spin-up procedure for 1000 years prior to the year 1989 that represented the historical land cover/land use change in the southern Wisconsin region (Table 2). This procedure was necessary to allow soil carbon and nitrogen pools to increase and reach an equilibrium state that was reflective of long-term land cover and management

change in the Arlington, Wisconsin region. DAYCENT was driven from the year 1932 to 2011 with minimum and maximum daily temperatures and daily total precipitation available from the University of Wisconsin-Madison Arlington agricultural research station (UWEX, 2014). The 80-year time sequence was repeated, backwards in time, to year -1000 to drive the model spin-up and initialization. For years -1000 to 1830, prairie grass was grown to simulate native vegetation in the Arlington Wisconsin area, which was part of the former Empire Prairie. Starting in 1830, a three year rotation of wheat-wheat-fallow was simulated until year 1860. In 1861, land was converted to pasture and grazed continuously under low intensity through 1969. In 1970, the pasture was converted to a four year dairy cropping rotation of corn-alfalfa-alfalfa-alfalfa, and was simulated through 1989. Simulated values of SOC present in 1989 to a depth of 15cm were compared with soil samples collected at WICST in 1989 (Sanford et al., 2012).

The second stage of model validation used simulations of the CS1 and CS2 WISCT management systems for the 1990-2011 time period. Model output for these years was compared with crop yield data (Posner et al., 2008), soil organic carbon at 0-15cm (Sanford et al., 2012) and soil N_2O emissions (***Osterholz et al., under review***). Yield data was available for each year 1993-2011, soil organic carbon was available for the initiation of the WICST experiment (1989) and again in 2009, and weekly to bi-weekly soil N_2O flux data was available for the 2010 and 2011 growing seasons.

DAYCENT Experimental Simulations

DAYCENT was used as an experimental modeling tool to more fully examine the relationships between weather variability, soil productivity, N-fertilizer management and N_2O emissions for common continuous corn and corn-soybean management systems in Wisconsin, such as those studied and used for DAYCENT validation (e.g., CS1 and CS2 at the Arlington Agricultural Research Station). To cover a range of soil types and climate regimes (e.g., agro-climatic regions) that could contribute to a large

range of N_2O emissions in corn and soybean systems, four Wisconsin counties were selected as representative of major Wisconsin ecotypes (Figure 5) including the Northern Highlands (Marathon County), Central Plains (Waushara County), Eastern Ridges and Lowlands (Columbia County), and Western Uplands (Grant County). Wisconsin is a geographically diverse state and corn and corn-soybean agriculture is practiced in each of these four major regions. The representative counties were also chosen because they are home to an agricultural research station managed by the University of Wisconsin system, and have consistent, long-term weather data available (UWEX, 2014) to drive DAYCENT.

From the four counties of interest, a collection of 35 soil series (Table 3) were used for model simulations, with their selection based upon two criteria: (1) the soil series was designated as either 'prime farmland' or 'farmland of statewide importance' by the United States Department of Agriculture (USDA), which limited the simulations to soils that are best suited for growing corn and soybeans; (2) one slope rating for the series covered at least 5000 acres within the county. For example, the soil series of 'Plano silt loam' has several variants that differ by slope and erosion rating. If one of these variants covered at least 5000 acres, the soil series was included as part of the simulation. DAYCENT is a point-based model and does not differentiate between slopes. For each soil, an addition of N fertilizer (157 kg ha^{-1}) was simulated before corn planting. The combinations of the variables soil series, and cropping system yielded a total of 105 separate simulations (Figure 6). Each of the 35 soils was designated with a soil textural classification using the USDA soil texture triangle (Fig. 7). Soil textural classifications fell within one of three classifications, loamy sand (LSa), sandy loam (SaL), and silt loam (SL).

2.3 Analysis of N_2O emissions

DAYCENT output for N_2O emissions were simulated as N_2O-N from nitrification and N_2O-N from denitrification. Total cumulative emissions were calculated as the sum of N_2O-N emissions from

nitrification and denitrification. To calculate an emission factor for each simulation year, a null simulation without a simulated addition of N fertilizer was run for each soil series and cropping system. The N_2O-N emitted from the null simulation is assumed to be 'background' emission. The difference between the null and N-fertilized simulation is assumed to be a direct result of the addition of N fertilizer. The emission factor is calculated as the percentage of applied N fertilizer that is converted to N_2O-N. Emission factors were not calculated for soybean years, as no nitrogen additions were made. The IPCC (IPCC, 2006) recommendations suggest that an EF be calculated as:

N_2O emission factor =

((N_2O-N emitted from fertilized plot)-(N_2O-N emitted from unfertilized plot))/(N applied to plot)

A calculation for yield-scaled emissions was also made for each simulation year. Yield-scaled emissions represent the greenhouse gas intensity of a product where each unit of product (Mg grain) is allocated an associated cost (kg N_2O-N). The simple, mass-based calculation is represented as:

Greenhouse gas intensity = kg N_2O-N/Mg grain

2.4 Weather variability

Previous studies have identified that increases in precipitation can have an effect on N_2O emissions (Dobbie et al., 1999) and emission factors (Lesschen et al., 2011). Nitrous oxide emissions from soils are also particularly sensitive to rainfall events preceding and following the application of N fertilizer (Dobbie et al., 1999; Gagnon et al., 2011). Preliminary analysis from N_2O data collected at WICST showed that up to 73.5% of N_2O emissions accumulated in the two months following N fertilizer application (May and June). We investigated the effects of early growing season (April-June) cumulative precipitation on N_2O flux by comparing the deviation from mean precipitation with deviations from mean N_2O flux. Temperature has also been shown to be an important determinant of denitrification

rates in soils (Maag and Vinther, 1996; Liang and Mackenzie, 1997). To assess the impacts of interannual variability in temperature on denitrification rates during months of peak N_2O production from denitrification, we compared deviation from mean May and June air temperatures with deviations from mean N_2O flux from denitrification.

2.5 Statistics

All statistics were run in R using the 'lattice' and 'stats' packages (R Core Team, 2013). Model output was organized by cropping system (CS1, CS2), crop (corn, soybean), and soil texture (loamy sand, sandy loam, silt loam) to determine means and standard deviations for N_2O emissions, emission factors, and yield-scaled emissions. Variables were compared with an ANOVA to determine significant differences in means. Linear and logarithmic models were fit to relationships between variables and model selection was based upon adjusted R^2.

3 Results

3.1 DAYCENT Validation

3.1.1. Soil carbon and yields

Simulated soil carbon (0-15cm) for the Plano silt loam soil in the Arlington, WI region at the beginning of WICST (1989) was 5% lower than the observed value (86.3 Mg C ha^{-1}). For the CS1 and CS2 management systems, the 2009 simulated 0-15cm soil carbon (SOC) was 4% and 1% higher, respectively, than the observed values (76.5 Mg C ha^{-1} and 71.3 Mg C ha^{-1}, respectively) (Figure 7). Although, the observed declines in SOC were not significant (Sanford et al., 2012), DAYCENT captured the direction of change in SOC loss. The observed decline in SOC on WICST was 11% (9.81 Mg C ha^{-1}) for CS1 and 17% (15.02 Mg C ha^{-1}) for CS2. DAYCENT simulated declines in SOC of 3% (2.39 Mg C ha^{-1}) for CS1 and 12%

(9.92 Mg C ha^{-1}) for CS2. DAYCENT also simulated a higher rate of SOC loss for CS2 than for CS1, which was also observed by Sanford et al. (2012), indicating that the model captured the effect on SOC of introducing soybeans into a corn rotation at WICST. DAYCENT was able to capture average yield (1993-2011) within one standard deviation for both CS1 and CS2 (Table 4). Mean observed and simulated yields in Mg of corn grain ha^{-1} for CS1 were 10.91 and 10.98, respectively, a difference of 0.68%. For corn in CS2, mean observed and simulated yields were 11.47 and 9.95 Mg grain ha^{-1}, respectively, a difference of 13%. Mean observed and simulated grain yields for soybeans grown in CS2 were, respectively, 3.39 and 3.62 MG grain ha^{-1}, a difference of 7%. The linear regression between annual observed and simulated yields was significant ($P < 0.001$) for CS1, but not for the CS2 corn or soybean phases.

3.1.2. Soil N_2O emissions

For CS1 during the 2010 and 2011 growing seasons, the relationship between simulated and observed daily N_2O flux was positive and significant in both years (R^2=0.7 and R^2=0.29, respectively; $P < 0.001$ and $P < 0.01$, respectively; Fig. 8a,b) with a high residual standard error (S=17.38 and 27.5, respectively). For the CS2 corn phase during the 2010 and 2011 growing seasons, the relationship between simulated and observed daily N_2O flux was poor ($R^2 = 0.08$ and $R^2 = -0.04$, respectively) and not significant in either year (Fig. 8c,d). For the CS2 soybean phase in the 2010 growing season, the relationship between simulated and observed daily N_2O flux was poor and not significant (Fig. 8e). For CS2 soybean during the 2011 growing season, the relationship between simulated and observed daily N_2O flux was positive ($R^2 = 0.27$) and significant ($P < 0.01$; Fig. 8f) with a residual standard error of S=2.292. High residual standard error for the years with significant relationships indicates that DAYCENT over-predicted high daily flux values and under-predicted low daily flux values.

DAYCENT simulated annual cumulative N_2O flux within one standard deviation of observations at WICST for each phase of both CS1 and CS2 during 2010-2011 (Figure 9). Rainfall for the 2010 growing season (April–September) was 36% above average, which likely resulted in the greater variability in sampling times and subsequently larger variability in fluxes observed by Osterholz et al. (under review). In 2010 and 2011, simulated cumulative N_2O flux for CS1 was 12% (0.8 kg N_2O N ha^{-1}) and 4% (0.11 kg N_2O N ha^{-1}) lower, respectively, than the observed cumulative values of 6.73 and 3.06 kg N_2O N ha^{-1}, respectively (Fig. 10a,b). In 2010 and 2011, simulated cumulative N_2O flux for CS2 corn was 38% (1.49 kg N_2O N ha^{-1}) and 9% (0.18 kg N_2O N ha^{-1}) higher, respectively, than the observed cumulative values of 3.94 and 2.04 kg N_2O N ha^{-1}, respectively (Fig. 10c,d). In 2010, DAYCENT did not capture the difference in observed mean cumulative N_2O emissions from corn in CS2 (3.94 kg N_2O-N ha^{-1}) and corn in CS1 (6.73 kg N_2O N ha^{-1}). However, due to high variability in measured values, the observed difference was not significant. Simulated cumulative N_2O flux for CS2 soybean was 16.5% higher (0.22 kg N_2O N ha^{-1}) than the observed value of 1.33 kg N_2O N ha^{-1} in 2010 (Fig. 10e), and in 2011 was 30.6% lower (0.46 kg N_2O N ha^{-1}) than the observed value of 1.49 kg N_2O N ha^{-1} (Fig. 10f).

DAYCENT was able to capture the difference in magnitude between 2010 and 2011 N_2O emissions from corn phases in CS1 and CS2. For CS1, the observed and simulated 2011 growing season accumulations of N_2O-N were, respectively, 55% (3.67 kg N_2O-N ha^{-1}) and 50% (2.98 kg N_2O-N ha^{-1}) less than growing season accumulations for 2010. For CS2, the observed and simulated 2011 growing season accumulations of N_2O-N were, respectively, 49% (1.91 kg N_2O-N ha^{-1}) and 59% (3.22 kg N_2O-N ha^{-1}) less than growing season accumulations for 2010. DAYCENT was also able to capture the pattern of N_2O accumulation from CS1 and CS2. For corn phases, accumulations of N_2O from May – July constituted the bulk of total growing season accumulations (Fig. 10a-d). For CS1, May-July observed and simulated N_2O emissions were, respectively, 86% and 75% of total emissions for 2010, and 77% and 84% for 2011. For CS2, May-July observed and simulated N_2O emissions were, respectively, 82% and 73% of total

emissions for 2010, and 46% and 53% for 2011. Emissions accumulated more rapidly for CS2 corn in 2011 (Fig. 10c), though total simulated accumulation was within one standard deviation of the observed value. DAYCENT was also able to simulate the consistent rates of N_2O accumulation observed throughout the growing seasons of CS2 soybean phases in 2010 and 2011.

Observations from WICST showed that N_2O emissions from the months of May and June contributed between 40-74% of total cumulative emissions from corn in 2010 and 2011. For corn in CS1, emissions from May and June totaled 74% (4.94 kg N_2O N ha^{-1}) of emissions for 2010, and 70% (2.13 kg N_2O N ha^{-1}) for 2011. For corn in CS2, emissions from May and June totaled 48% (1.37 kg N_2O N ha^{-1}) of emissions for 2010, and 45% (0.73 kg N_2O N ha^{-1}) for 2011.

3.2 DAYCENT experimental simulations

3.2.1. Simulated cumulative N_2O emissions

Simulated total N_2O emissions differed by cropping system and crop type (Table 5). Emissions for the continuous corn rotation (CS1) were 4.20 kg N_2O-N ha^{-1} yr^{-1} and differed significantly ($p<0.001$) from the corn-soybean rotation (CS2) emission of 3.05 kg N_2O-N ha^{-1} yr^{-1} (Fig. 10). This was due to the inclusion of soybeans which had a significantly lower annual contribution of 1.63 kg N_2O-N ha^{-1} yr^{-1} than corn (4.34 kg N_2O-N ha^{-1} yr^{-1}) (Fig. 11). Mean N_2O emissions for CS2 corn were 0.27 kg N_2O-N ha^{-1} yr^{-1} higher than CS1 corn, but not significantly different ($p=0.122$).

Mean emissions also differed by soil texture (Table 5). Mean emissions from loamy sands (LSa) (1.70 kg N_2O-N ha^{-1} yr^{-1}) were significantly ($p=0.038$) lower than emissions from sandy loams (SaL) (1.91 kg N_2O-N ha^{-1} yr^{-1}), and emissions from silt loams (SL) (4.5 kg N_2O-N ha^{-1} yr^{-1}) were significantly ($p<0.001$) higher than emissions from sandy loams (Fig. 12). Significant differences between loamy sand (LSa) and

sandy loam (SaL) were only found when the data was aggregated by soil texture across all systems and crop phases and when CS1 and CS2 corn phases were analyzed together (Table 5).

The relative contributions of nitrification and denitrification to total N_2O flux explained the differences in mean N_2O emissions between soil textures (Fig. 13) and crop (Fig.15). The contribution of nitrification to total N_2O emissions for loamy sand, sandy loam, and silt loam was, respectively, 1.15, 1.27, and 1.44 kg N_2O-N ha^{-1} yr^{-1}. The contribution of denitrification to total N_2O emissions for loamy sand, sandy loam, and silt loam was, respectively, 0.55, 0.64, and 3.06 kg N_2O-N ha^{-1} yr^{-1}. The difference between mean N_2O flux from loamy sand and sandy loam soils (Table 5) was explained by a significant ($p<0.001$) difference in the contribution of nitrification to total N_2O flux (Fig. 13). The contribution of denitrification to total N_2O flux in silt loam soils (3.06 kg N_2O-N ha^{-1} yr^{-1}) was significantly higher than total N_2O flux in both loamy sand and sandy loam soils. The difference in the annual contribution of denitrification to total N_2O flux was best explained by a logarithmic function between denitrification and sand content (Fig. 14). Increasing sand content of a soil was negatively correlated (adjusted $R^2=0.40$) with N_2O flux from denitrification. The difference between mean N_2O emissions in the corn phases of CS1 and CS2 was likely driven by a significant increase ($p<0.001$) in the contribution of nitrification to total N_2O flux in CS2 corn (1.69 kg nitrified N_2O-N ha^{-1} yr^{-1}) over CS1 corn (1.39 kg nitrified N_2O-N ha^{-1} yr^{-1}) (Fig. 15). N_2O from denitrification in CS1 corn (2.81 kg N_2O-N ha^{-1} yr^{-1}) and CS2 corn (2.78 kg N_2O-N ha^{-1} yr^{-1}) was not significantly different ($p=0.896$).

3.2.2. Variation in N_2O flux

Variability in the magnitude of N_2O flux was best explained by the contribution of denitrification to total N_2O flux (Fig. 16). The contribution of denitrification to annual N_2O flux was able to explain 98% of the variation in annual N_2O flux, which suggests that variation in denitrification rate is the strongest predictor of annual N_2O flux across all soil textures, cropping systems, and crop phases. When soil

textures were isolated, denitrification was the strongest predictor of total N_2O flux for loamy sands (adjusted R^2=0.91), sandy loams (adjusted R^2=0.91), and silt loams (adjusted R^2=0.99) (Fig. 17b,d,f). When total N_2O emissions were limited to values within the 2nd and 3rd quartiles for each soil texture, nitrification became the strongest predictor of annual N_2O flux for loamy sands (adjusted R^2= 0.55) and sandy loams (adjusted R^2=0.36)(Fig. 18a,c). For silt loam soils, denitrification was the strongest predictor (adjusted R^2=0.93) of total N_2O flux (Fig. 17f). For crop phases, denitrification was the strongest predictor of total N_2O flux for both corn (adjusted R^2=0.99) (Fig. 19b) and soybeans (adjusted R^2=0.97) (Fig. 19d). When total N_2O emissions for crop phases were limited to values within the 2nd and 3rd quartile for each crop, denitrification was the strongest predictor of total N_2O flux for corn (adjusted R^2=0.93) (Fig. 20b). For total N_2O flux within the 2nd and 3rd quartiles for soybean phases, denitrification (adjusted R^2=0.38) was a slightly better predictor of total N_2O flux than nitrification (adjusted R^2=0.38) (Fig. 20c,d).

3.2.3. Weather variability

The impact of spring precipitation on N_2O from denitrification varied by crop type and cropping system. In corn from CS1, annual deviations from mean April-June precipitation had a significant ($p<0.001$) linear correlation (adjusted R^2=0.13) with deviations from mean N_2O flux from denitrification (Fig. 28a). Mean cumulative precipitation for April-June from 1993-2011 was 28.72 cm. For CS1 corn, a deviation of 1cm (3.5%) from mean April-June cumulative precipitation was positively correlated with a deviation of 0.09 kg N_2O-N ha^{-1} from denitrification. The relationship simulated in CS1 corn was present, though weaker, in CS2 corn following soybeans. For CS2 corn, deviation from mean April-June precipitation had a significant ($p<0.001$) linear correlation (adjusted R^2=0.05) with deviations from mean N_2O flux from denitrification (Fig. 28b). A deviation of 1cm from mean April-June cumulative precipitation was positively correlated with a deviation of 0.05 kg N_2O-N ha^{-1} from denitrification in CS2

corn. Correlation between variation in cumulative April-June precipitation and N_2O from denitrification was significant ($p<0.01$) with a positive linear correlation (adjusted $R^2= 0.02$). Emission factors for corn phases were weakly correlated with increases in April-June precipitation in both CS1 (adjusted $R^2=0.02$) and CS2 (adjusted $R^2= 0.03$)(Fig 29a,b; respectively). The effect of deviation from mean April-June precipitation on yield-scaled emissions was similar to the effects on N_2O from denitrification, where the strongest correlation (adjusted $R^2=0.18$) was with yield-scaled emissions in CS1 corn (Fig. 30a). Correlation was weak (adjusted $R^2=0.03$) for CS2 corn (Fig. 30b) and not significant ($p=0.43$) for soybeans (Fig. 30c). Temperature had very little effect on the interannual variability of N_2O flux from denitrification. Across all soil textures and cropping systems, correlation between deviation from mean temperatures for May (Fig. 31a) and June (Fig. 31b) had significant ($p <0.001$)but low correlation with deviation from mean N_2O flux from denitrification (adjusted $R^2= 0.04, 0.01$; respectively). The relationship was not improved by isolating soil textures, crop phases, or by comparison with total N_2O flux from nitrification and denitrification.

3.2.4. Emission Factors

Emission factors differed significantly ($p<0.001$) by cropping system with mean emission factors of 0.142 and 0.285 for corn from CS1 and CS2, respectively (Fig. 21). The response of emission factor to soil texture simulated by DAYCENT was similar to total N_2O emissions. Mean emission factors for loamy sands and sandy loams were 0.0091 and 0.0104, respectively and not significantly different ($p=0.678$). The mean emission factor for silt loam soils was 0.029 and significantly higher ($p<0.001$) than mean emission factors for loamy sands and sandy loams. The range and variability of emission factors for silt loams was also greater than for the sandier soil textures (Fig. 22). Soil sand content best explained the difference in emission factors across soil textures. Increasing sand content was correlated (adjusted $R^2=0.36$) logarithmically with a decrease in emission factor (Fig. 23). Variation in emission factors for CS1

and CS2 within soil textures was best explained by N_2O flux from denitrification with descriptive capability differing by cropping system (Fig. 24). For CS1, N_2O from denitrification explained 27, 31, and 61% of the variation in emission factor for loamy sands, sandy loams, and silt loams, respectively. For CS2, N_2O flux from denitrification explained 95% of the variation in emission factor for each soil texture (Fig. 24b,d,f).

3.2.5. Yield-scaled emissions

Yield-scaled emissions differed by crop across soil textures (Fig. 25). Mean yield-scaled emissions for the corn phases of CS1 and CS2 were 0.71 and 0.68 kg N_2O-N/Mg grain, respectively, and not significantly different ($p=0.291$). For soybean phases of CS2, mean yield-scaled emissions were 0.63 kg N_2O-N/Mg grain, and significantly ($p=0.014$) different from corn phases of CS1 and CS2. When isolated by soil texture, differences in yield-scaled emissions depended upon crop (Fig. 26). There was no significant difference ($p=0.416$) in yield-scaled emissions for soybeans between the soil textures. Mean yield-scaled emissions for corn in loamy sands and sandy loams were 0.51 and 0.54 kg N_2O-N/Mg grain, respectively, and not significantly different ($p=0.462$). Mean yield-scaled emissions from silt loams were 0.80 kg N_2O-N/Mg grain and significantly ($p<0.001$) different from the sandier soils. Variation in yield-scaled emissions was explained by N_2O from denitrification across soil texture and crop (Fig. 27). A linear model significantly ($p<0.001$) fit the relationship between yield-scaled emissions and N_2O from denitrification for corn on loamy sands (adjusted $R^2=0.66$), sandy loams (adjusted $R^2=0.66$), and silt loams (adjusted $R^2=0.6$) (Fig. 27a,c,e; respectively). A linear model also significantly ($p<0.001$) fit the relationship between yield-scaled emissions and N_2O from denitrification for soybeans on loamy sands (adjusted $R^2=0.54$), sandy loams (adjusted $R^2=0.63$), and silt loams (adjusted $R^2=0.81$) (Fig. 27b, d,f; respectively).

4 Discussion

4.1. DAYCENT accurately simulates cumulative N_2O flux

The performance of DAYCENT with respect to simulated N_2O fluxes was comparable with previous studies evaluating the model for similar agricultural systems. Parton et al. (2001) found low correlation (R^2= 0.02-0.19) between simulated and observed daily N_2O flux, but good agreement with cumulative annual flux. Similarly, our results showed that DAYCENT was capable of simulating cumulative N_2O fluxes within 8-38% of observed means. Daily N_2O flux correlation coefficients (R^2) from Parton et al. (2001) ranged from 0.02 to 0.19, whereas this study reported a range of adjusted R^2 values from 0.698 to -0.035 with significant correlations found for the continuous corn rotation in CS1. Our results for daily N_2O flux also agreed with the findings of Jarecki et al. (2008), who found that DAYCENT has a tendency to overpredict N_2O fluxes for high observed flux values, and under-predict for low observed flux values. DAYCENT was able to simulate the effects of weather variability by capturing the difference in the magnitude of emissions from corn phases for 2010 and 2011. In 2010, accumulated precipitation at the Arlington research station for the growing season (April-September) was 86.22 (cm) compared with 44.68 (cm) for 2011. We would expect that a very wet year would increase soil water content thus limiting O_2 availability and increasing denitrification, supporting an increase in N_2O fluxes. DAYCENT also simulated greater cumulative N_2O flux in 2010 for soybeans, though the magnitude was less than that seen in corn phases. Parkin & Kaspar (2006) found similar results for a corn-soybean rotation in Iowa, where an increase in rainfall increased N_2O flux from soybean plots. Interestingly, flux measurements for soybeans at WICST showed higher flux in 2011 than in 2010. Variability in measurements on WICST was high in 2010, which could indicate that the true mean for N_2O flux was greater than the 1.33 kg N_2O-N recorded.

Our results for cumulative N_2O flux were comparable with several other studies conducted in the Upper Midwest (Table 6). DAYCENT accurately simulated the seasonal pattern of N_2O flux accumulation where flux is expected to be highest during the months of May-July (Cates and Keeney, 1987; Parkin and Kaspar, 2006; Jarecki et al., 2009). The range of average cumulative N_2O flux we observed on our simulated soil series (Table 5) was similar to ranges reported by field studies on similar cropping systems under similar management (Goodroad et al., 1984; Cates and Keeney, 1987; Parkin and Kaspar, 2006; Jarecki et al., 2008; Hoben et al., 2011; Burzaco et al., 2013). This suggests that DAYCENT was simulating reasonable values and that validation at the Arlington site was sufficient to parameterize the model for Wisconsin.

While DAYCENT is able to capture mean cumulative N_2O flux from specific crops and some interannual variation due to weather variability, the model may be less able to capture variation within the agricultural field. DAYCENT is a point-based model and is unable to account for the lateral movement of soil water within the agroecosystem. However, slope and topography have been shown to regulate spatial variation in N_2O emissions from agricultural fields by influencing the effect of soil hydrological process on water-filled pore space (Vilain et al., 2010; Gu et al., 2011). Because DAYCENT cannot account for these effects, simulated results from DAYCENT are likely most accurate where slope has little to no effect on soil hydrology. The Plano silt loam from which validation data was collected was on slopes of 0-2%, and it is possible that the strong agreement between observed and simulated values was facilitated by the minimal slope found at the validation site. While the ability of DAYCENT to simulate N_2O flux at specific points on the landscape may be influenced by soil slope, past validation of the model (Parton et al., 1998; Del Grosso et al., 2008; Jarecki et al., 2008; De Gryze et al., 2010; Chamberlain et al., 2011) indicates that DAYCENT is capable of simulating N_2O flux typical of particular soil textures and cropping systems. Additionally, soil concentrations of water soluble forms of nitrogen are likely to be influenced by the effect of topography on soil hydrology. Castellano et al. (2013) found

that as sampling sites progressed down a hillslope gradient on two silty Ultisols and one sandy Entisol from the Chesapeake Bay in Maryland, NO_3 concentrations increased and NO_3-N retention decreased in the soil profile. At points in agricultural fields where topography increases soil water content and NO_3 concentrations, there is likely to also be some impact on soil emissions of N_2O. DAYCENT is capable of simulating the short term effects of soil water and NO_3 concentrations on soil N_2O emissions, and the coupling of DAYCENT with a soil hydrological model capable of simulating the lateral flow of soil water maybe increase the accuracy of DAYCENT simulations for agricultural fields with topography significantly effecting soil hydrology. The results from the experimental simulations in the current study likely represent typical values for soil textures and cropping systems where there is little impact of slope on soil hydrology. Future research should investigate the degree to which the inability of DAYCENT to account for slope effects regional estimations of N_2O emissions by comparing simulated N_2O flux between various topographies.

4.2. Soil texture, crop selection, and denitrification influence variability in N_2O emissions

Our results indicate that soil texture exerts an influence on the mean and range for cumulative N_2O emissions from corn and corn-soybean systems in Wisconsin. We expected that the coarser textured soils with high sand content (loamy sand, sandy loam) would have lower cumulative emissions than the silt loam soils(Stehfest and Bouwman, 2006). We found that the difference in cumulative N_2O emissions between soil textures was related to the relative proportions of N_2O produced by nitrification and denitrification. While Opdyke et al. (2009) found that denitrification was the dominant contributor to cumulative N_2O flux on a mesic, fine-loamy, Typic Hapludalf in Southwestern Michigan, we conclude that those results cannot be extrapolated to all temperate agricultural soils in the Midwest. Nitrification produced approximately 65% of total N_2O flux from the loamy sand and sandy loam soils in our study, which are designated as prime and important farmland in Wisconsin (USDA-NRCS, 2014). The greater

contribution of nitrification to total N_2O flux in coarser soils is, partly, an artifact of DAYCENT model processes. Denitrification is regulated in DAYCENT simulations by O_2 availability and by a multiplier which decreases the likelihood of denitrification as soil texture becomes more coarse (Parton et al., 1996, 2001; Del Grosso et al., 2000). Results from Bollmann and Conrad (1998) confirm the response of denitrification to increasing soil particle size simulated by DAYCENT and we expect that our results accurately represent N_2O flux from loamy sands and sandy loams in Wisconsin. Our results (Table 5) for sandy soils were higher than values reported by van Groenigen et al. (2004) of 0.24 kg N_2O-N ha^{-1} from a sandy soil in the Netherlands cultivated for corn silage and fertilized with 150 kg N ha^{-1}. However, to our knowledge, values for N_2O flux from sandy soils in the Upper Midwest have not been reported, and further study is needed in the region to determine the accuracy of simulations. In silt loam soils, we found that N_2O from denitrification was the dominant contributor to total N_2O flux. There was a significant increase in the contribution of nitrification to total flux in silt loam soils over the loamy sand and sandy loam, but the six fold increase in N_2O from denitrification accounted for the increase in magnitude of total emissions. The increase in N_2O from denitrification in the silt loam soils can be explained as a function of O_2 availability. Finer textured soils have higher field capacities, where water is held in in the soil at higher volumes and for longer after saturation. This creates the potential for anoxic microsites to form and denitrification to take place (Del Grosso et al., 2000; Parton et al., 2001).

Interannual variability in N_2O flux was influenced by N_2O from nitrification and denitrification and depended on soil texture. Across all soil textures and crop types, N_2O from denitrification explained 98.4% of the variation in annual cumulative flux (Fig. 16b). This relationship persisted when soil textures were isolated (Fig. 17), though denitrification explained slightly less variation in the loamy sand and sandy loam soils than in silt loams. In the sandier soils, it appeared that several extreme values for N_2O from denitrification were driving the relationship. When the interquartile range for N_2O flux was analyzed separately, N_2O flux from nitrification was a more significant predictor of cumulative flux in

sandy and silt loam soils, which indicates that for years with average N_2O flux, nitrification is best predictor of interannual variability. These results also indicate that extreme N_2O flux in Wisconsin loamy sands and sandy loams is driven by above average rates of denitrification. In silt loam soils, N_2O from denitrification was the best predictor of total N_2O flux for the complete data set and the interquartile range. This is likely due to the consistent and dominant contribution of denitrification to N_2O flux in finer textured soils. Average cumulative N_2O flux appears to be associated with the interannual variability of the process dominating total flux, while extreme fluxes are a result of above average rates of denitrification.

Crop selection was also an important factor in characterizing the interannual variability of cumulative N_2O flux. Similar to soil texture, N_2O from denitrification appeared to exert the dominant control on total flux for both corn and soybeans (Fig. 19). However, when the interquartile ranges were analyzed (Fig. 20), N_2O from nitrification had no influence on total flux from corn and an approximately equal influence with denitrification in soybeans. This may be a result of increased substrate for denitrification due to N fertilization in the corn phases and DAYCENT's simulation of NO_3 availability as limiting denitrification (Del Grosso et al., 2000). Additionally, we might expect this to occur on the landscape, as the presence of high NO_3 concentrations in the soil has been shown to inhibit the reduction of N_2O to N_2 (Weier et al., 1993), which would result in greater emissions of N_2O. A significant increase in denitrification in corn phases could conceal the influence of nitrification observed in soybeans.

4.3 Emission factors differed by cropping system and soil texture

The results of this study indicate that soil texture and can be used to further refine estimates of emission factors in Wisconsin. Emission factors are useful in estimating emissions of nitrous oxide from agriculture due to the simplicity of their implementation, where only the amount of applied

nitrogen fertilizer is required. However, they have also been shown to be exceedingly variable at the regional (Leip et al., 2011) and field scale (McSwiney and Robertson, 2005). Some attempts at quantifying this variability have been made by assessing the impact of environmental factors such as water filled pore space (Dobbie and Smith, 2003), precipitation (Lesschen et al., 2011), and nitrogen fertilization rate (Mosier et al., 2006b) on emission factors. The IPCC Tier II methodology for estimating greenhouse gases from agriculture requires that a regionally specific emission factor be used in calculations. Mechanistic models, like DAYCENT, have been used to evaluate emission factors where physical data collection is impractical. Leip et al. (2011) used the DNDC-Europe model to construct spatially stratified emission factors for Europe and found a high degree of spatial variability, but confirmed that variability did not translate into uncertainty for national or global scale emission factors. Similar validation of DAYCENT's ability to simulate field scale emission factors more accurate than IPCC Tier I methodology(Delgrosso et al., 2005) indicates that mechanistic models can be used to accurately simulate emission factors for specific environmental conditions.

The range of emission factors simulated by DAYCENT (0.004-0.0454) were comparable to the range of emission factors, 0.02-0.07, from corn systems in the Upper Midwest reported by McSwiney and Robertson (2005). The mean simulated emission factors for loamy sands and sandy loams (0.0091 and 0.0104, respectively) were similar to the IPCC recommended default emission factor of 0.01 (Smith et al., 2007). In silt loam soils, a simulated mean emission factor of 0.029 was nearly three times greater than the Tier I IPCC recommendation. The difference in mean emission factors between the soil textures was best explained by the sand content of the soil (Fig. 26), which was similar to findings for emission factors previously simulated by DAYCENT (Del Grosso et al., 2006). The source of the difference in emission factors between CS1 and CS2 was unclear. However, higher emission factors (Fig. 24) and mean N_2O flux (Table 5) from CS2 could indicate that soil N pools were higher for corn following

soybeans than for corn following corn. The increase in cumulative emissions without an increase in N fertilization would account for the higher emission factors.

4.4 Yield-scaled emissions differed by soil texture and crop selection

Yield-scaled emissions do little to inform total volumetric estimates of agriculture's contribution of N_2O to the atmosphere. However, it is an interesting metric in the consideration of process and land use efficiency. Van Groenigen et al. (2010) suggest that growing global food demand and increasing greenhouse gas emissions are issues of equal concern and, because yield-scaled emissions represent the maximization of food production and minimization of greenhouse gas emissions, it is the only metric capable of addressing current challenges. For yield-scaled emissions analysis in this study, results were segregated by crop. The range of yield-scaled emissions for conventionally managed corn simulated by DAYCENT (0.154-3.72 kg N_2O-N Mg^{-1}) was greater than the ranges reported by Venterea et al. (2011) (0.046-0.1 kg N_2O-N Mg^{-1}) on a similar silt loam soil in Minnesota, and by Johnson et al. (2012)(0.536-0.995 kg N_2O-N Mg^{-1}) on loams and clay loams in Minnesota. However, simulated mean yield-scaled emissions for corn (0.69 ± 0.499 kg N_2O-N Mg^{-1}) were similar to values from Johnson et al. (2012). Our results for yield-scaled emissions were an order of magnitude larger than those reported by Venterea et al. (2011), which was most likely due to an order of magnitude lower cumulative N_2O emissions reported by Venterea et al. (2011). The range of simulated yield-scaled emissions from soybeans (0.198-4.06 kg N_2O-N Mg^{-1}) was greater than the range (0.623-0.716 kg N_2O-N Mg^{-1}) and simulated mean (0.621 kg N_2O-N Mg^{-1}) similar to values reported by Johnson et al. (2012).

Several studies have shown that residual surplus N can be a key factor in the increase of yield-scaled emissions (Van Groenigen et al., 2010; Venterea et al., 2011; Burzaco et al., 2013). However, our results indicate that extreme N_2O flux from denitrification was the best predictor of above average values for yield-scaled emissions. For both corn (Fig. 33a,b,c) and soybeans (Fig. 32a,b,c) correlation

between yield-scaled emissions and N_2O from denitrification was driven by extreme values, which indicates that years and soils subject to high rates of denitrification are at risk for greater N_2O emissions per unit grain yield. The relationship between soil texture and yield-scaled emissions was similar to relationships between soil texture and cumulative N_2O flux. Given the correlation between denitrification and yield-scaled emissions (Figs. 32, 33) and differences between mean contributions of denitrification to total N_2O flux between the soil textures (Fig. 13), we conclude that N_2O produced from denitrification was the main driver of differences in mean yield-scaled emissions between the soil textures.

4.5 Spring precipitation influences N_2O emissions differently by crop and cropping system

Our results showed a strong influence of N_2O produced from denitrification on total N_2O emissions, emission factor and yield-scaled emissions. We also found that soil texture exerts and influence on the proportion and magnitude of N_2O flux produced from denitrification. In silt loam soils, where the contribution of denitrification to total N_2O flux was highest, we evaluated the effects of changes in spring precipitation and temperature on N_2O produced from denitrification. We found that April-June precipitation was a stronger predictor of interannual variability in N_2O flux from denitrification in CS1 corn, than in either crop phase of CS2 . The stronger correlation in corn phases was not surprising, as we would expect levels of soil NO_3 to be higher in N fertilized corn. Dobbie et al. (1999) found that increased precipitation was correlated with increases in denitrification, especially at times when soil NO_3 was abundant. The literature suggests that increased precipitation drives increases in WFPS which, in turn, increases the production of N_2O from denitrification (Khalil et al., 2004; Bateman and Baggs, 2005). The relationship between WFPS and denitrification simulated by DAYCENT (Parton et al., 1996) and described by Davidson (1993), suggests that N_2O produced from denitrification reaches a maximum at 60% WFPS and declines as soil approaches saturation. If increased precipitation has a direct

effect on increased WFPS, we would expect that N_2O produced from denitrification would begin to decline after reaching some maximum. While a linear model best fit the data, we did find that maximum rates of N_2O produced from denitrification in CS1 corn were at intermediate increases of10-20 cm(34.83-69.66%) in April-June precipitation (Fig. 28a). This may indicate that while increases in spring precipitation do lead to increases in N_2O flux, a linear model may not be the best predictor of the relationship. Future studies should evaluate the impact of spring precipitation patterns on WFPS, which may provide a more consistent predictor of the effect of precipitation on N_2O flux produced from denitrification.

Interestingly, the relationship between increased spring precipitation and N_2O produced from denitrification was not as strong in either crop phase of CS2, as in corn from CS1. This may indicate that the inclusion of soybeans in a corn rotation mediates the effect of increases in spring precipitation on N_2O produced from denitrification. Additionally, total N_2O flux from CS2 corn tended to be higher than flux from CS1 corn (Table 5), and we suspect that higher residual soil N following soybeans increased total emissions. Denitrification is also limited by levels of NO_3 in the soil (Parton et al., 1996; Robertson and Groffman, 2007), and the reduced impact of variation in April-June precipitation in CS2 corn may indicate that soil N levels were more influential than precipitation in this system. While Burzaco et al. (2013) found that, over two years, WFPS was the most consistent predictor of total N_2O fluxes (Spearman correlation coefficient = 0.39) , for one of those years, soil NO_3 was the best predictor of total N_2O flux (Spearman correlation coefficient = 0.71). Results from the soybean phases of CS2 also showed maximum N_2O production from denitrification occurred within increases of 10-20 cm over mean April-June precipitation. The weak relationship in unfertilized soybeans (Fig. 28c) indicates that the effect of increasing precipitation on N_2O produced from denitrification in corn is likely the result of an interaction between the application of N fertilizer and increased precipitation. An interaction between soil NO_3 and precipitation was observed by Dobbie et al. (1999), and our results also indicate that soil NO_3 levels may

mediate the effect of changes in spring precipitation on N_2O flux from denitrification. Although our study did not evaluate the effects of soil NO_3 on denitrification or N_2O flux, our results indicate that, over time, the effect of crop rotation on soil NO_3 levels may play an important role in mediating the effect of increasing spring precipitation on N_2O flux from denitrification.

Surprisingly, emission factors were not strongly correlated with deviations from mean April-June precipitation. Evidence from the literature suggests that increases in emission factors are associated with increases in WFPS (Dobbie and Smith, 2003; Ruser et al., 2006) and precipitation (Lesschen et al., 2011). Given the strong association between N_2O produced from denitrification and emission factor in silt loam soils (Fig. 24), we expected that increases in April-June precipitation would increase WFPS and lead to subsequent increases in emission factor. However, while we did find significant linear correlations between increased precipitation and increased emission factor (Fig. 29a,b), the strength of the relationships lead us to conclude that April-June precipitation is weak predictor of interannual variability in emission factor. Similar to N_2O flux from denitrification, we expect that an inclusion of soil NO_3 levels in the analysis would have provided a better explanation of interannual variability in emission factor.

Our analysis of deviation from mean temperatures in May and June did not produce strong relationships with N_2O flux from denitrification (Fig. 31a, b). DAYCENT simulates an indirect effect of temperature on N_2O produced from denitrification (Parton et al., 1996) where increases in temperature increase soil respiration and effects the ratio of N_2:N_2O produced from denitrification (Fig. 2). Given this relationship, we would expect to see decreases in N_2O produced from denitrification as temperature increases. Maag and Vinther (1996) reported similar findings from sandy, loamy sand, and sandy loam soils. We found a downward trend in N_2O produced from denitrification in silt loam soils as temperatures increased in May and June (Fig. 31a,b; respectively).

The impact of temporal variability in climate on N_2O emissions from silt loam soils in Wisconsin is still uncertain. Our results show a significant correlation between increasing spring precipitation and increased N_2O flux; however, the magnitude of the response seems to be dependent upon cropping system and crop selection. It appears that the inclusion of soybeans into a corn rotation mediate the effect of temporal variability in precipitation, though higher mean emissions from corn in CS2 may indicate that mediation does not equate with emission reductions between the corn phases of CS1 and CS2. We suspect that system differences are driven by higher residual soil N following soybeans and propose that future analysis include an evaluation of the interaction between soil N levels and precipitation on N_2O produced from denitrification. While increases in temperature are likely to decrease N_2O produced from denitrification in silt loam soils, weak correlation between temperature and N_2O flux from denitrification suggest that the net effect on N_2O emissions may be minimal. The effects of climate parameters on the temporal variability of N_2O emissions are important for evaluating the impacts of future climate change scenarios. Between the years of 1950 and 2006, Kucharik et al. (2010) reported a +14.9mm statewide trend in springtime precipitation for Wisconsin and a significant trend toward warmer temperatures in spring and summer. While precipitation trends were significant only for a small section of southern Wisconsin, it is an area in which silt loam soils represent a significant portion of the landscape. The results of the current study indicate that there may be a net balancing effect of the trends observed by Kucharik et al. (2010) on N_2O flux from denitrification and future simulations should evaluate the relative impacts of precipitation and temperature trends on N_2O emissions.

5 Conclusions

We found that soil texture is an important determinant of both total N_2O emissions and emission factors from agricultural soils under corn and corn-soybean management in Wisconsin.

DAYCENT simulated mean cumulative emissions of 1.70, 1.91, and 4.5 kg N_2O-N ha^{-1} yr^{-1} for loamy sand, sandy loam, and silt loam soils, respectively. Mean emission factors for loamy sands and sandy loams were 0.0091 and 0.0104, respectively, and similar to the IPCC tier I default emission factor of 0.01, while the mean emission factor for silt loam soils was 0.029. Millar et al. (2010) have recommended an N_2O reduction protocol for the US Midwest that suggests reductions in N fertilizer application can reduce N_2O emissions without significant losses in corn yields. Our study raises the question of whether soil texture may also be an important consideration when estimating N_2O emission reduction potential. While the current study did not address the relationship between N application rate and N_2O emissions, others have found a nonlinear relationship between increases in N fertilizer and increases in N_2O emissions (McSwiney and Robertson, 2005; Hoben et al., 2011). Future research should consider whether soil texture has the potential to influence the response of N_2O to N fertilization.

Denitrification proved to be the most important factor in explaining variability in N_2O emissions across all soil textures. . Temporal variability in N_2O emissions was strongly correlated with the contribution of denitrification to total N_2O flux in both corn (adjusted R^2=98.9) and soybeans (adjusted R^2=97.2). Nitrification inhibitors have been shown to have important implications for nitrogen management and loss in the cropping systems of the Midwest (Wolt, 2004). However, with regard to reductions in cumulative annual N_2O emissions, the literature provides conflicting results. Some studies have shown between 29-50% reductions in N_2O-N emissions from nitrification inhibitors (Halvorson et al., 2010; Halvorson and Del Grosso, 2012), whereas others have reported no significant effect on N_2O emissions (Parkin and Hatfield, 2010; Burzaco et al., 2013). Our results indicate the discrepancy may be related to the contribution of denitrification to total N_2O flux. Denitrification contributed 67% of the total N_2O flux for silt loam soils, with little variation in the annual contributions of nitrification to total flux. While, in some cases, nitrification inhibitors may be successful in reducing total N_2O emissions,

estimates of reductions and effectiveness should consider the potential contribution of denitrification to N_2O flux from specific soils.

Managing soils to limit denitrification potential may be a difficult task. Increases in N use efficiency can limit nitrate available to denitrifying microbes, but environmental factors play an important role in determining denitrification rates. Our study shows a significant relationship between increases in spring precipitation and increases in N_2O produced from denitrification. We expect this relationship is directly related to the influence of WFPS on denitrification described by Davidson (1993). However, our experimental design was not able to evaluate the effect of spring precipitation patterns on WFPS and denitrification. While it appears that cumulative precipitation is useful in describing interannual variability in N_2O produced from denitrification, further refinement may be necessary in order to describe this relationship more accurately. Patterns of climate change in Wisconsin indicate an increase in cumulative spring precipitation (Kucharik et al., 2010), but further study of the effects of climate change on spring precipitation periodicity and intensity are necessary.

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Figures

Figure 1. The effect of soil NO_3^- on total denitrification and equation used by DAYCENT (Parton et al., 1996)

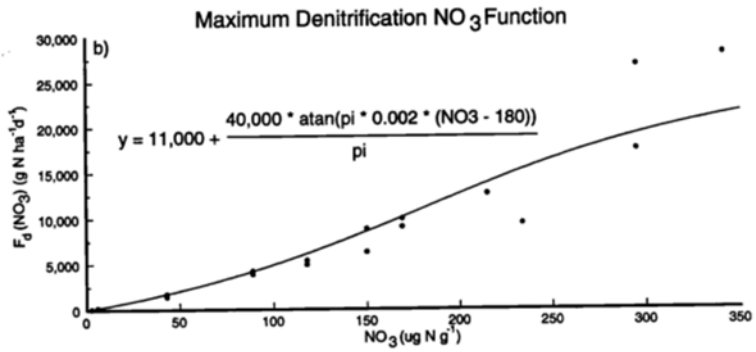


Figure 2. The effect of soil respiration on total denitrification (Parton et al., 1996)

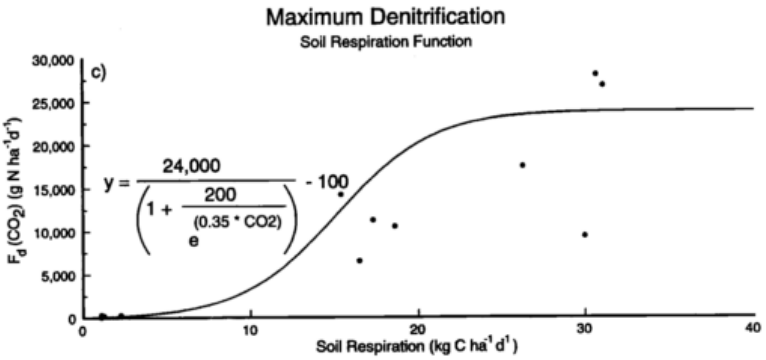


Figure 3. The effect of WFPS on total denitrification (Parton et al., 1996)

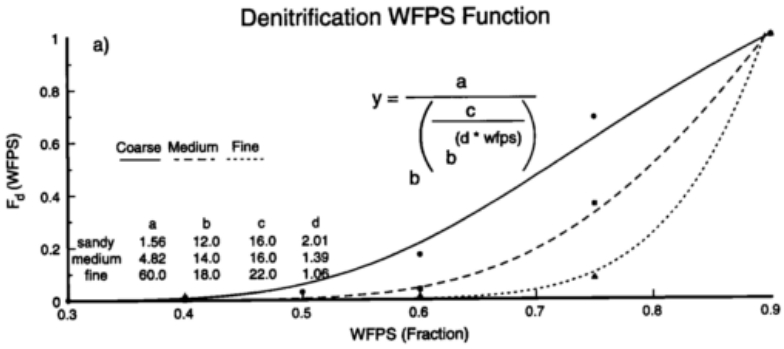


Figure 4. The effect of WFPS on the ratio of N_2 to N_2O produced from denitrification (Parton et al., 1996)

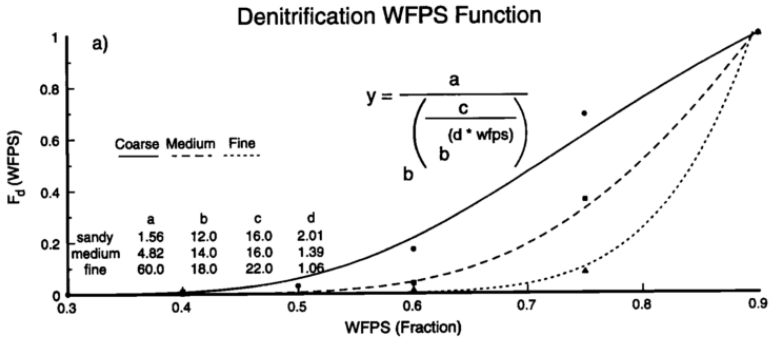


Figure 5. Representation of 4 major ecotypes in Wisconsin and their geographic locations

Figure 6. USDA soil textural triangle

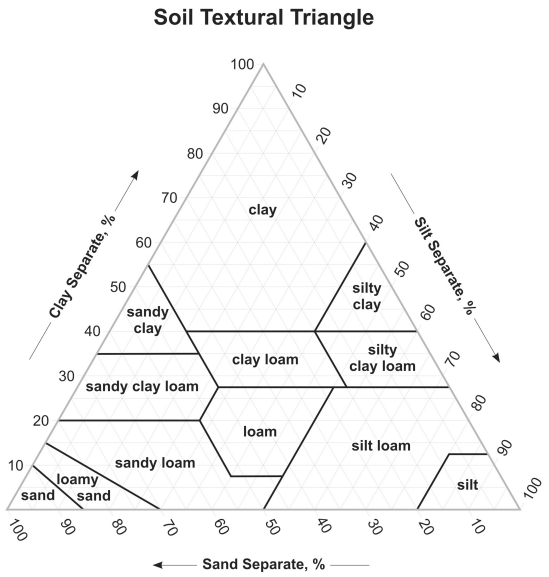


Figure 7. Soil organic carbon levels (0-15cm) and standard deviation for CS1 and CS2 as observed at WICST and simulated by DAYCENT for years 1989 and 2009.

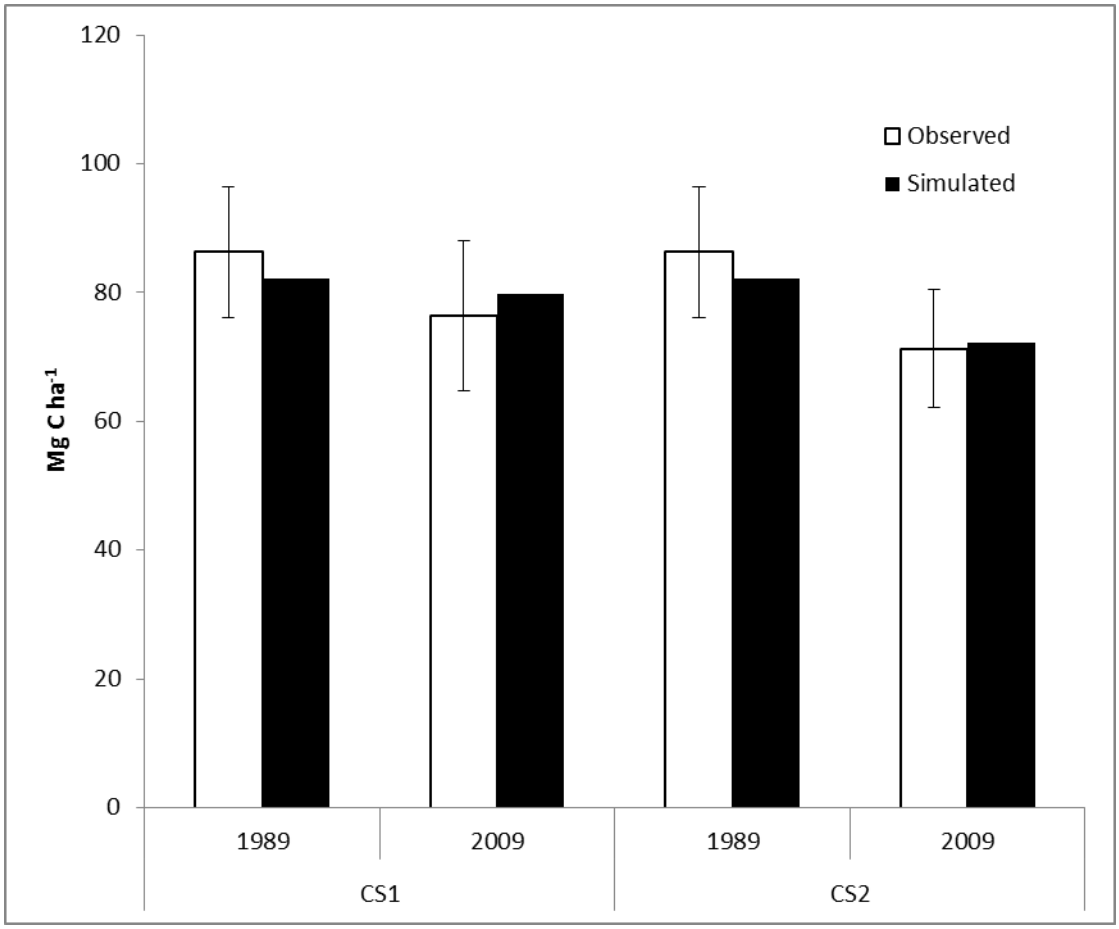


Figure 8. Correlation between daily soil N_2O flux observed at WICST and simulated by DAYCENT for cropping systems by phase: (a) 2010 CS1 corn phase; (b) 2011 CS1 corn phase; (c) 2010 CS2 corn phase; (d) 2011 CS2 corn phase; (e) 2010 CS2 soybean phase; (f) 2011 CS2 Soybean phase.

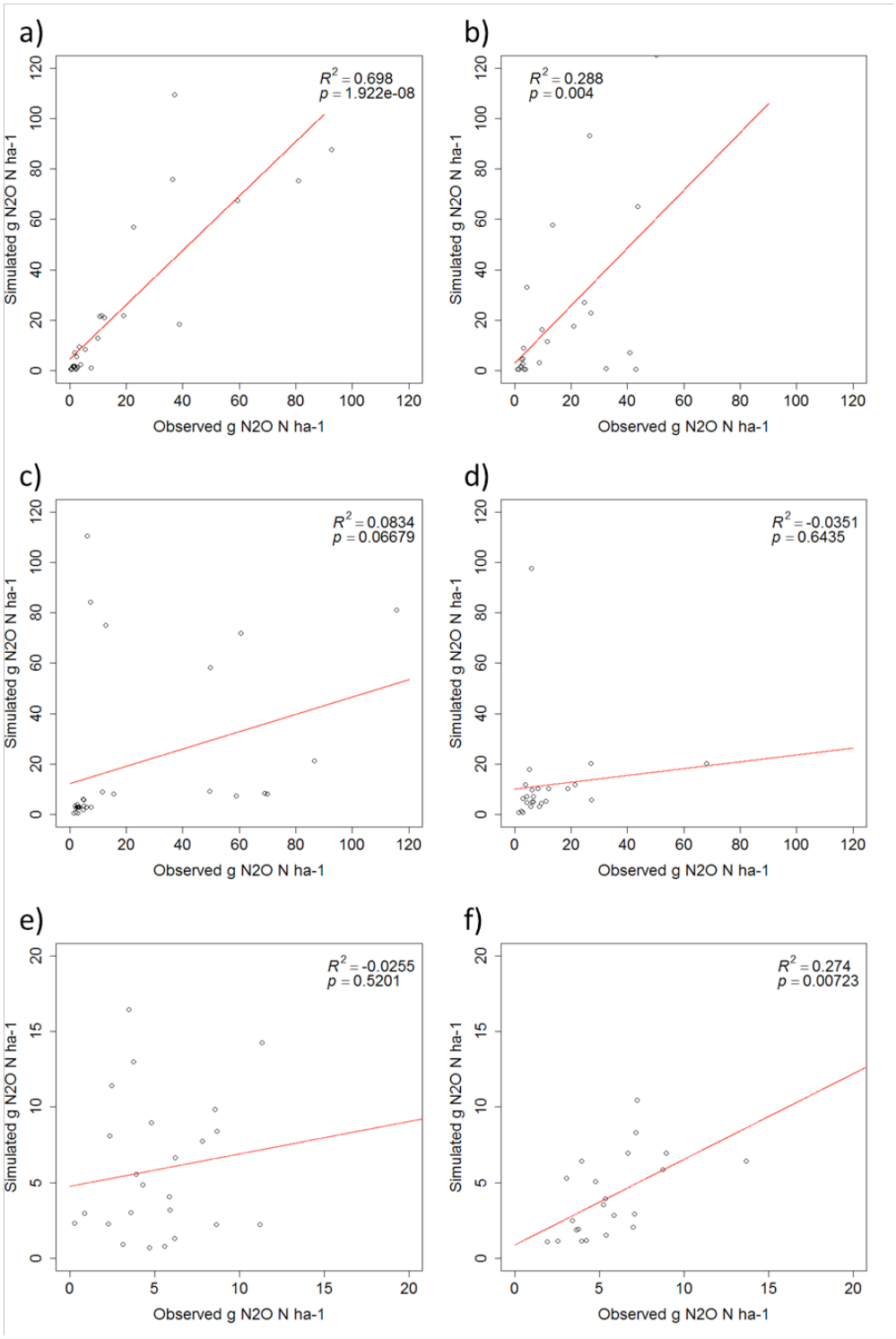


Figure 9. Accumulation of observed and simulated soil N_2O flux at WICST for; (a) CS1 2010; (b) CS1 2011; (c) CS2 corn 2010; (d) CS2 corn 2011; (e) CS2 soybean 2010; (f) CS2 soybean 2011

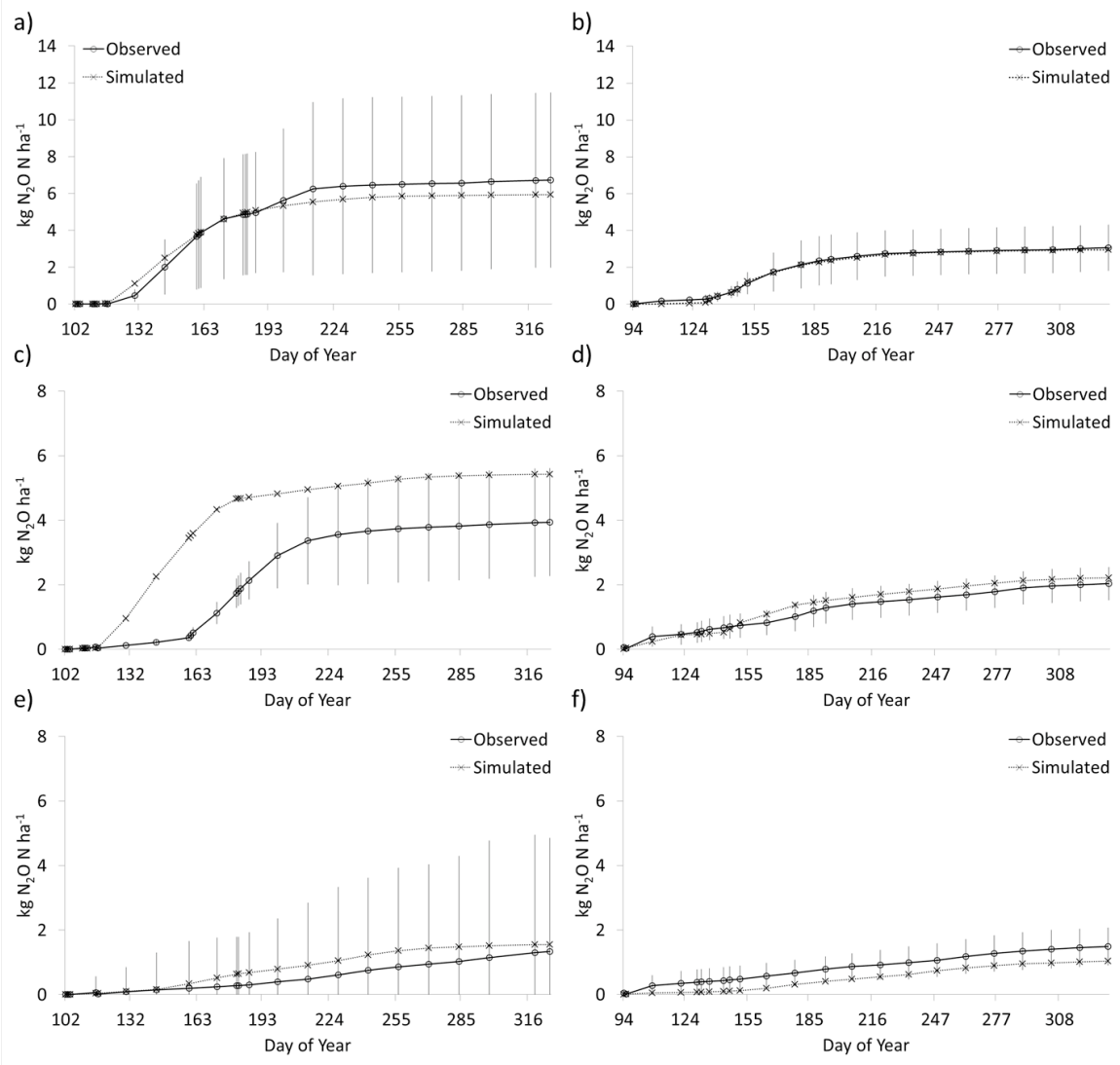


Figure 10. Ranges of soil N_2O flux by cropping system.

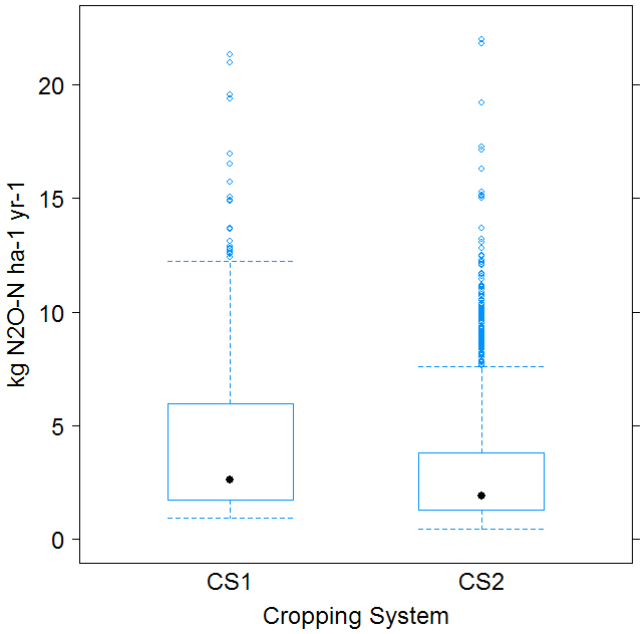


Figure 11. Ranges of soil N_2O flux by crop

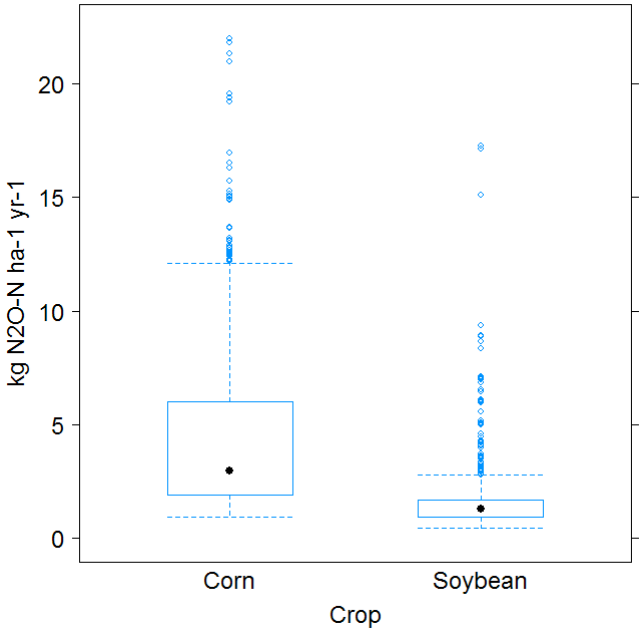


Figure 12. Ranges of soil N_2O flux by the soil textures of loamy sand (LSa), sandy loam (SaL), and silt loam (SL).

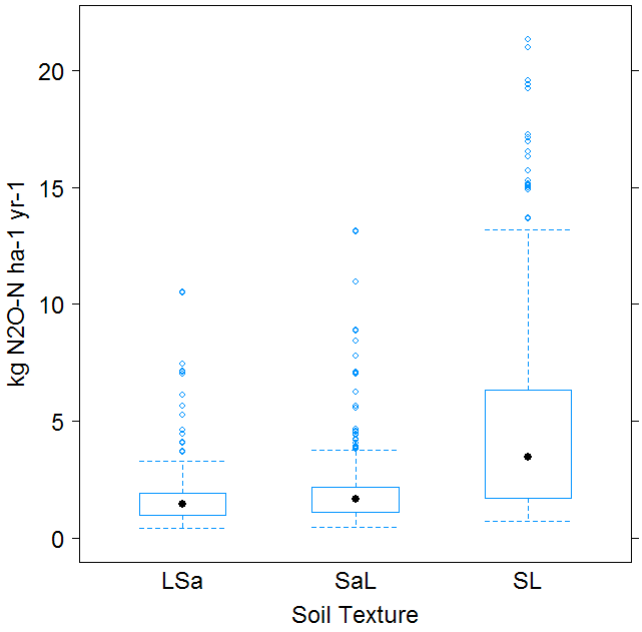


Figure 13. Relative contributions of nitrification and denitrification to total soil N_2O flux by the soil textures of loamy sand (LSa), sandy loam (SaL), and silt loam (SL). Values are averaged across crop (corn, soybean) and cropping system (CS1, CS2). Rates of soil N2O flux that are not connected by the same letter across textural types denote significant differences ($p < 0.05$).

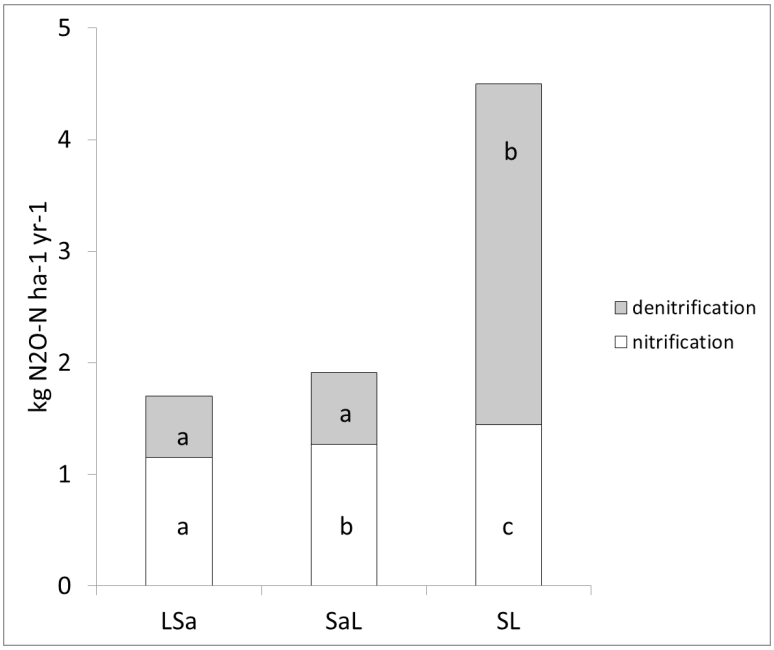


Figure 14. Correlation between sand content and soil N_2O derived from denitrification.

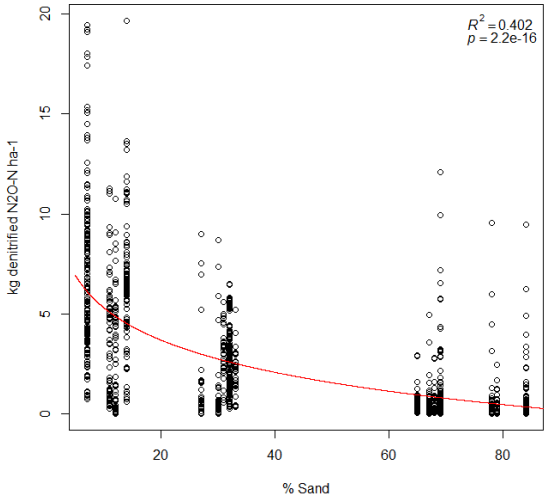


Figure 15. Relative contribution of nitrification and denitrification to total soil N_2O flux by cropping system corn phase. Rates of soil N2O flux that are not connected by the same letter across management systems denote significant differences at $P < 0.05$.

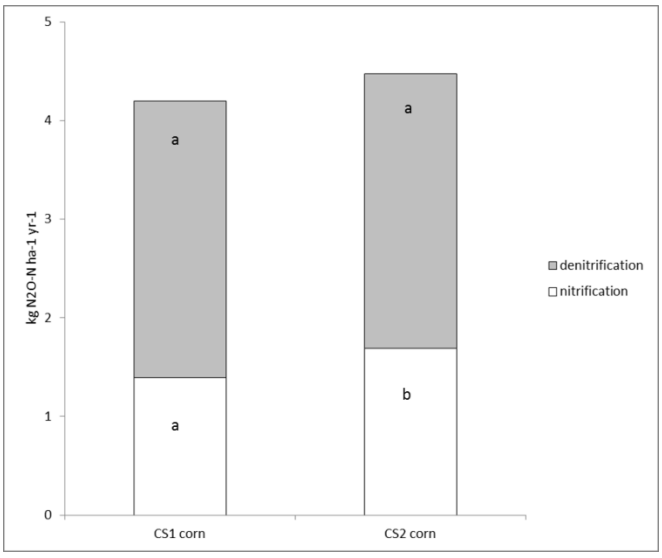


Figure 16. Correlation between total soil N_2O flux and the contribution of (a) nitrification and (b) denitrification to the total N_2O flux.

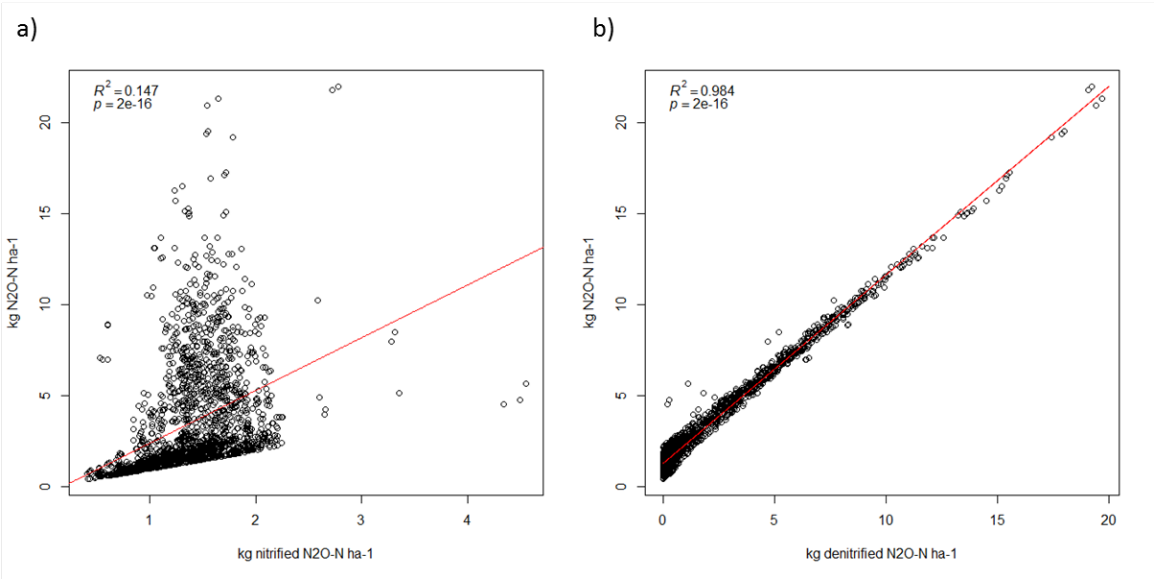


Figure 17. Correlation between total soil N_2O flux and (a) nitrification in loamy sands; (b) denitrification in loamy sands; (c) nitrification in sandy loams; (d) denitrification in sandy loams; (e) nitrification in silt loams; (f) denitrification in silt loams

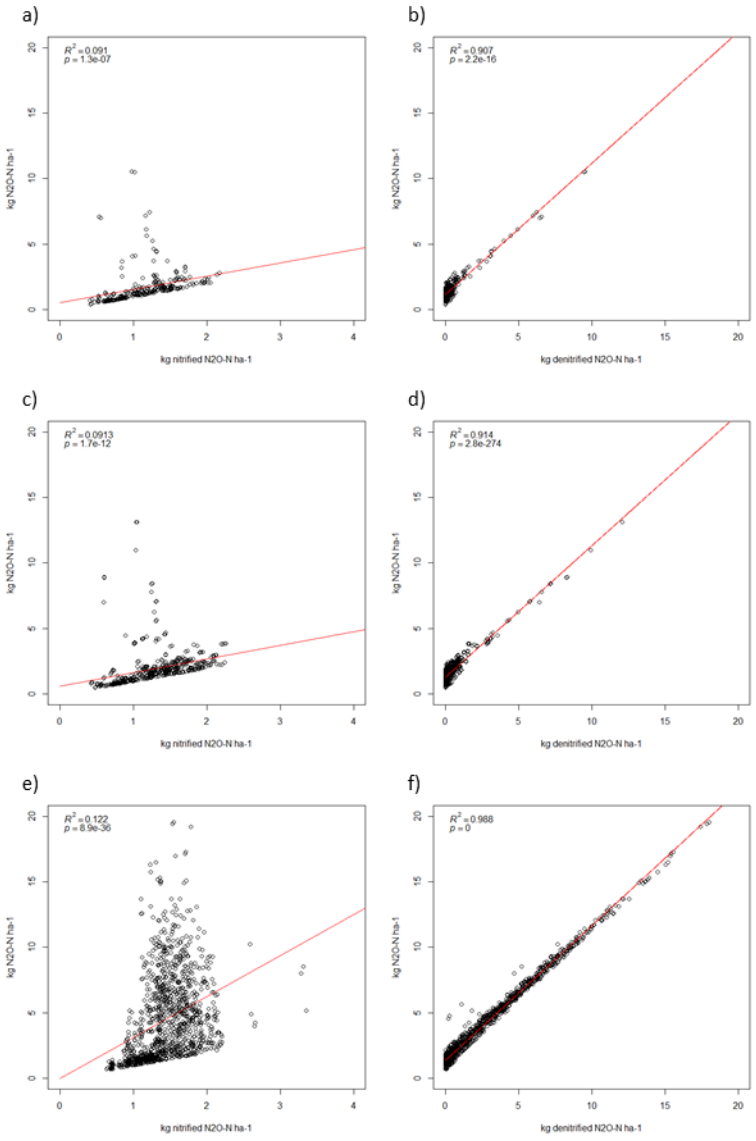


Figure 18. Correlation between values for total soil N_2O flux between the 1st and 3rd quartiles and (a) nitrification in loamy sands; (b) denitrification in loamy sands; (c) nitrification in sandy loams; (d) denitrification in sandy loams; (e) nitrification in silt loams; (f) denitrification in silt loams

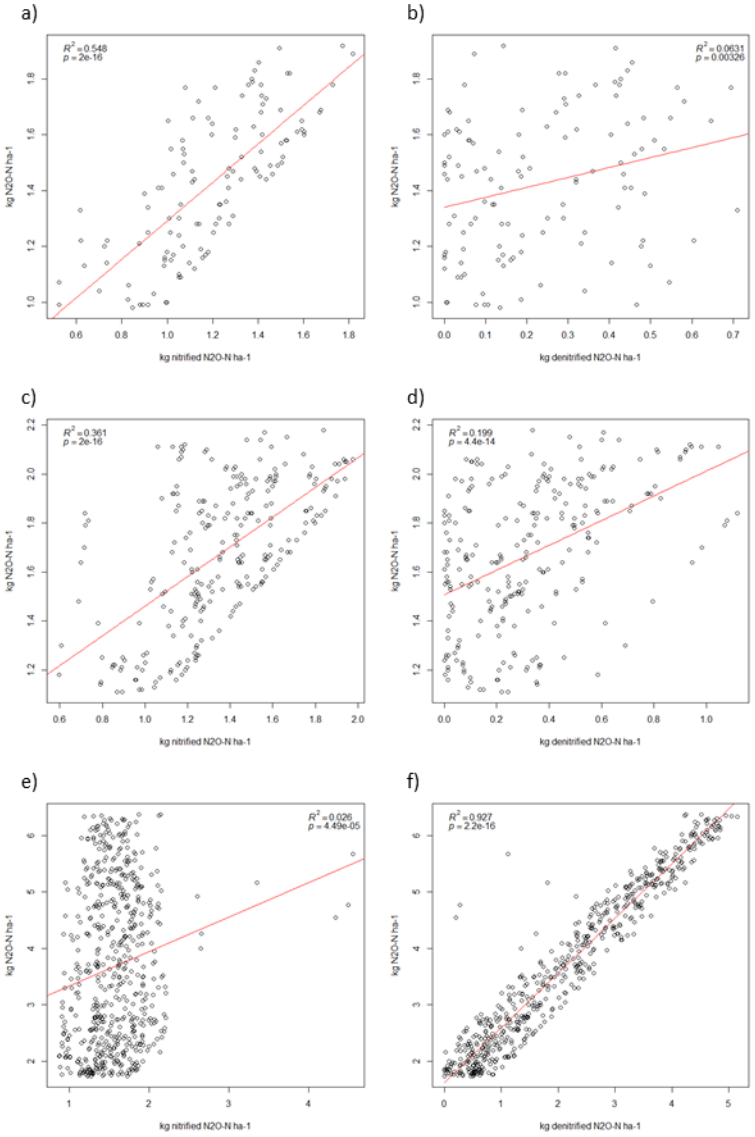


Figure 19. Correlation between total soil N_2O flux and (a) nitrification in corn; (b) denitrification in corn; (c) nitrification in soybeans; (d) denitrification in soybeans

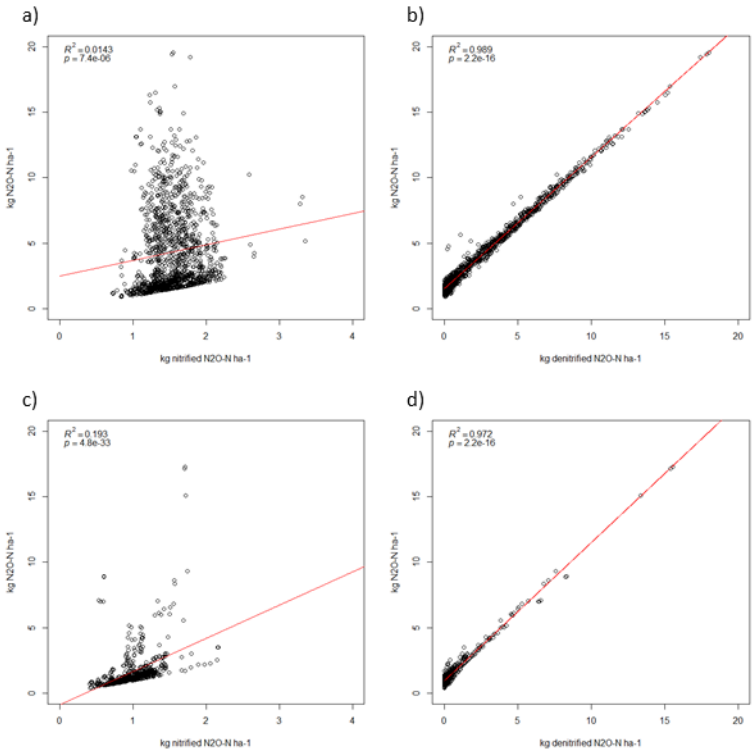


Figure 20. Correlation between values for total N_2O flux between the 1st and 3rd quartiles and (a) nitrification in corn; (b) denitrification in corn; (c) nitrification in soybeans; (d) denitrification in soybeans

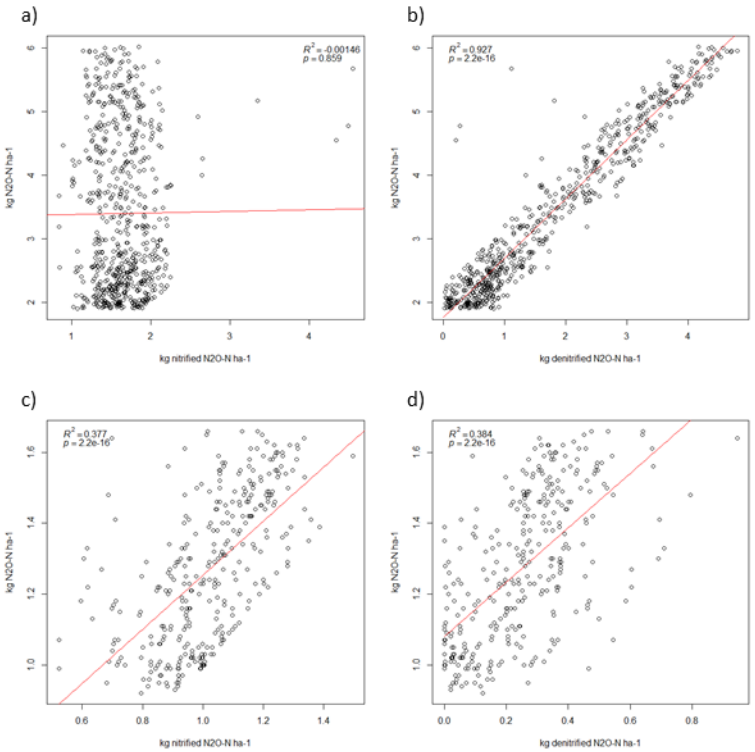


Figure 21. Ranges for emission factors (% of applied N fertilizer emitted as N_2O-N) associated with corn phases of CS1 and CS2

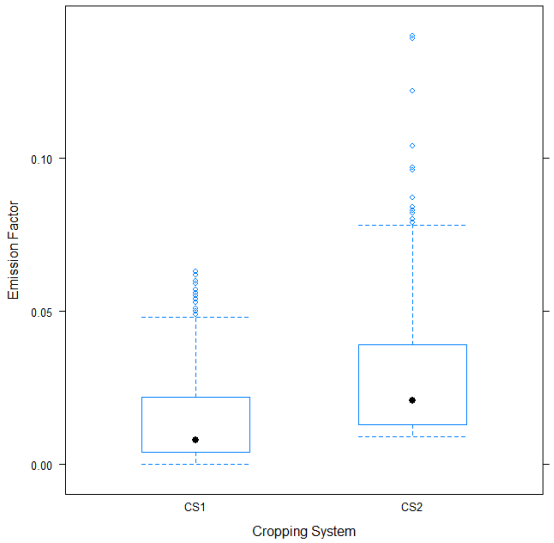


Figure 22. Ranges for emission factors (% of applied N fertilizer emitted as N_2O-N) associated with soil textures

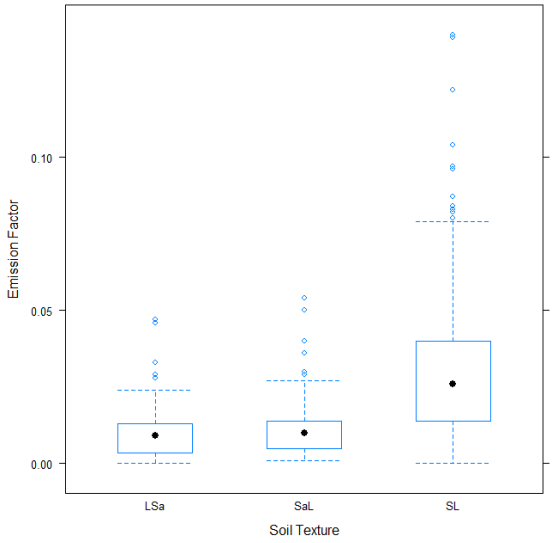


Figure 23. Correlation between soil sand content and emission factor (% of applied N fertilizer emitted as N_2O-N) .

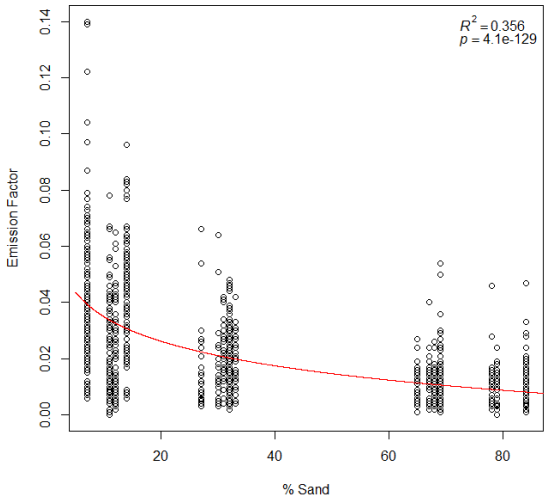


Figure 24. Correlation between emission factor and soil N_2O flux from denitrification for: (a) CS1 loamy sands; (b) CS2 loamy sands; (c) CS1 sandy loams; (d) CS2 sandy loams; (e) CS1 silt loams; (f) CS2 silt loams

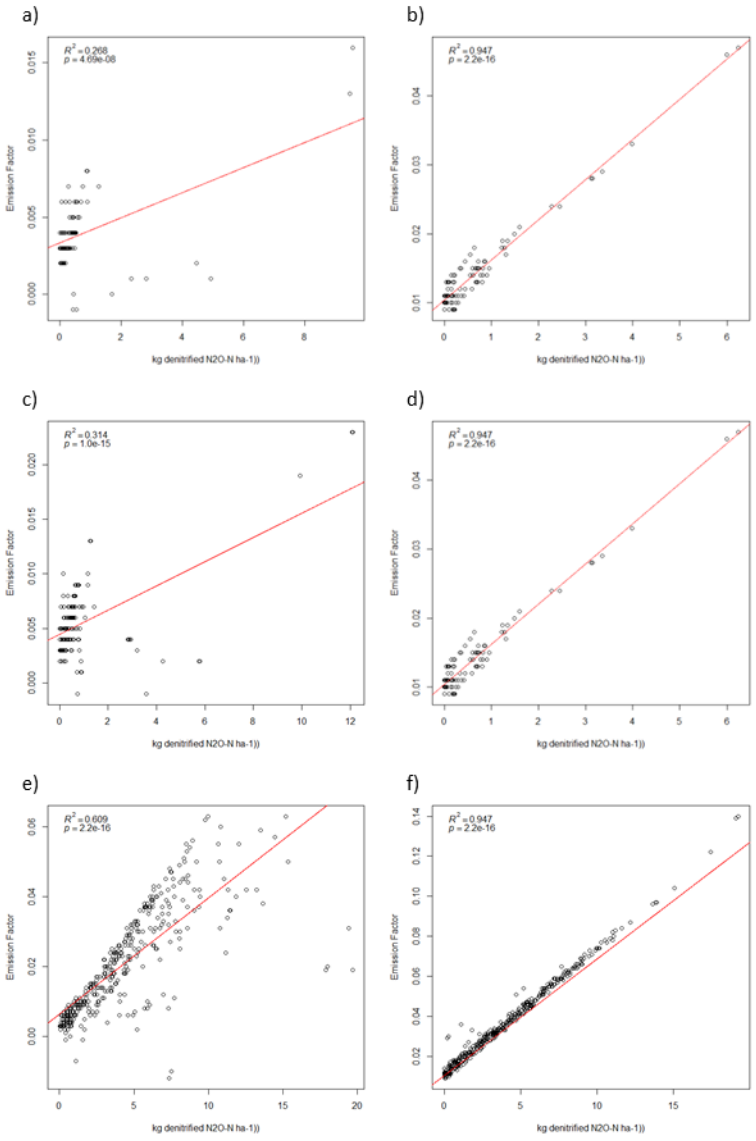


Figure 25. Yield-scaled soil N2O emissions associated with crop phase.

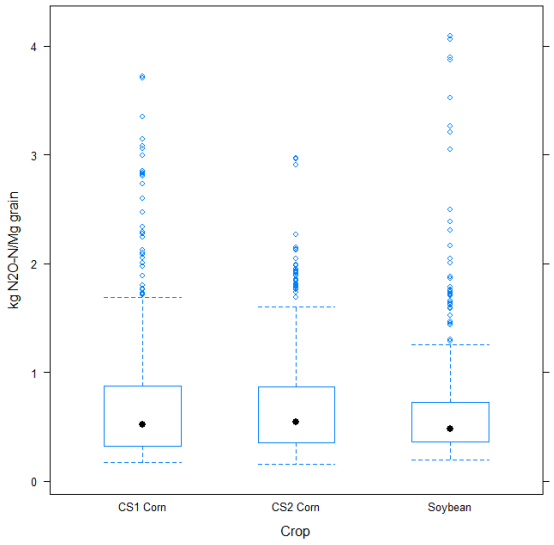


Figure 26. Yield-scaled soil N2O emissions associated with crop type and soil textures loamy sand (LSa), sandy loam (SaL), and silt loam (SL)..

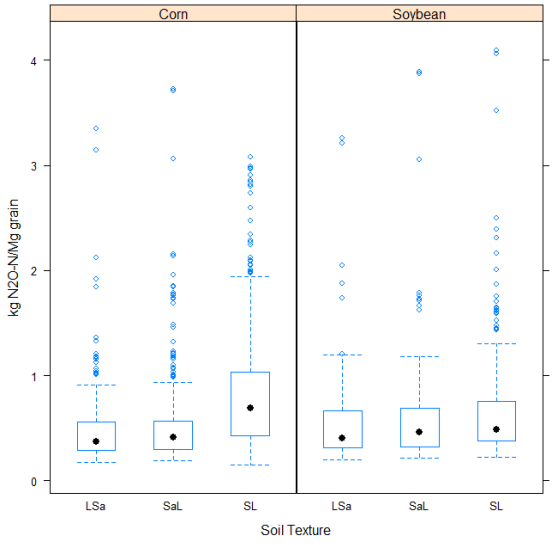


Figure 27. Correlation between yield-scaled emissions and soil N_2O emissions from denitrification in: (a) corn on loamy sands; (b) soybean on loamy sands; (c) corn on sandy loams; (d) soybean on sandy loams; (e) corn on silt loams; (f) soybean on silt loams

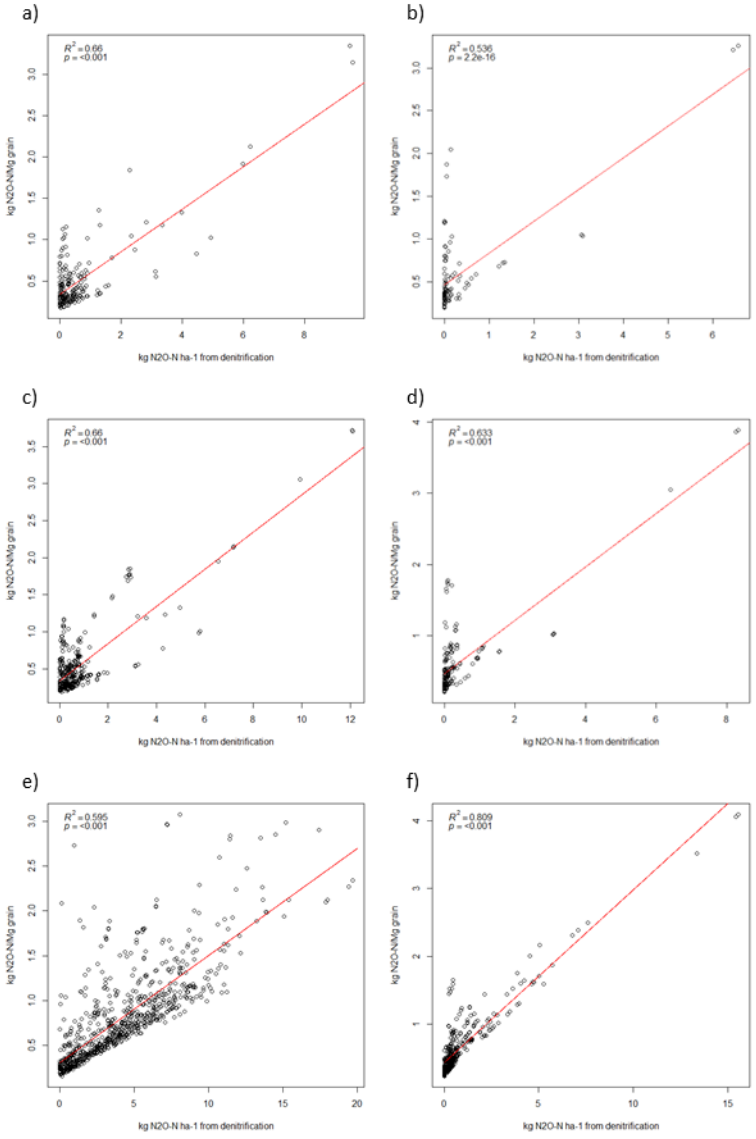


Figure 28. Correlation between deviation from mean April-June precipitation (1993-2011) and deviation from mean N_2O flux from denitrification on silt loam soils in: (a) CS1 corn; (b) CS2 corn; (c) CS2 soybean

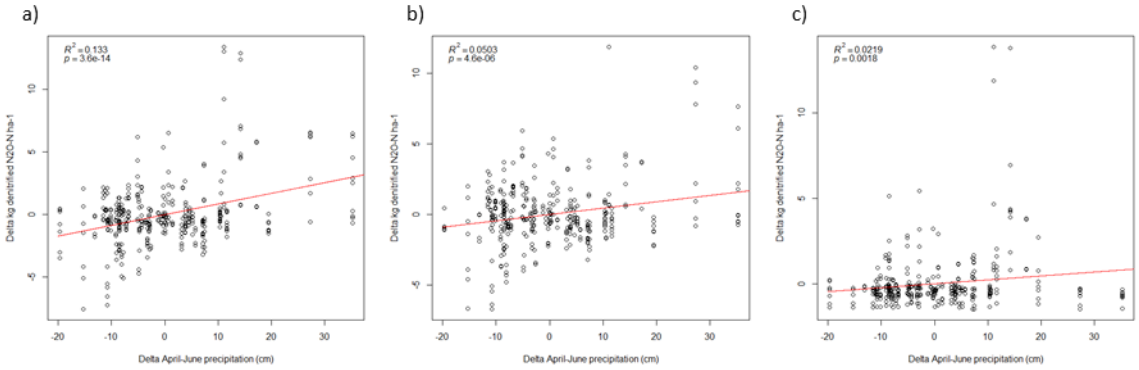


Figure 29. Correlation between annual deviation from mean April-June precipitation and deviation from mean N_2O emission factor on silt loam soils in: (a) CS1 corn; (b) CS2 corn

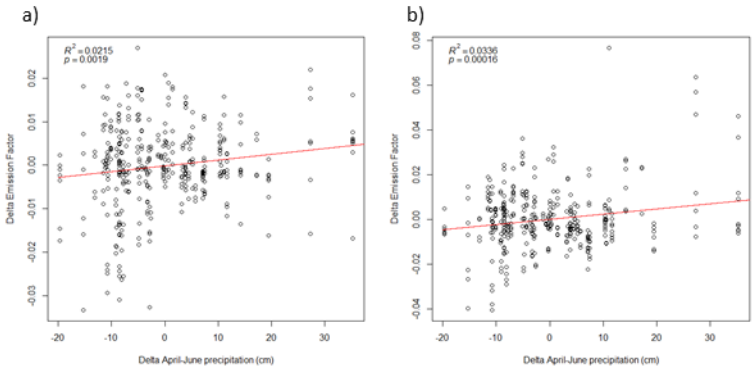


Figure 30. Correlation between annual deviation from mean April-June precipitation and deviation from mean yield-scaled emissions on silt loam soils in: (a) CS1 corn; (b) CS2 corn; (c) CS2 soybean

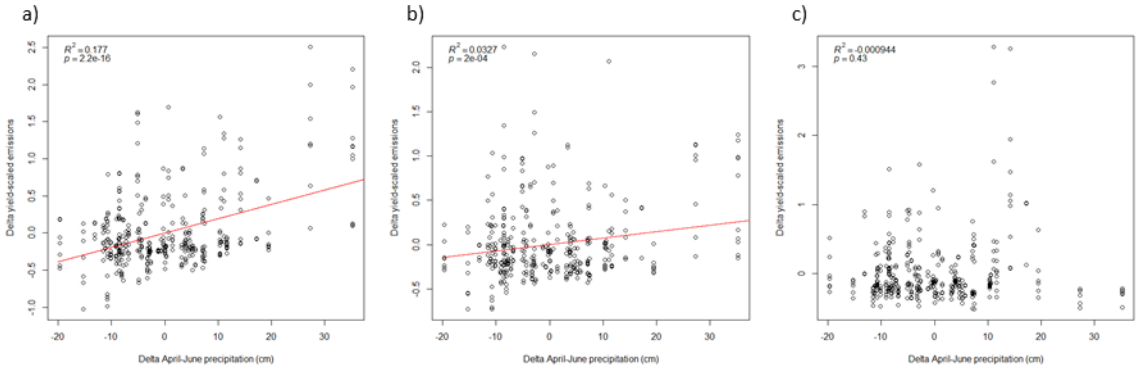
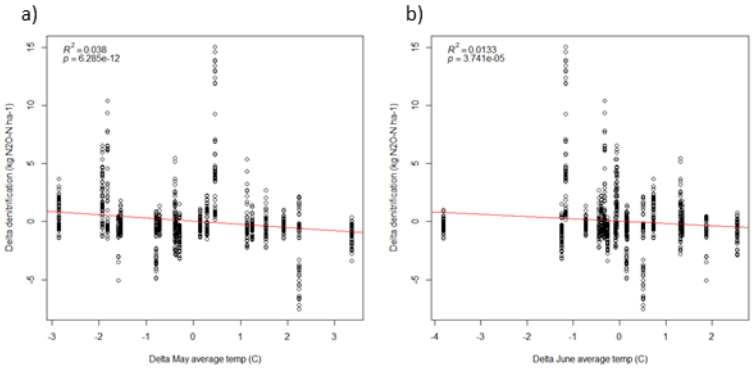


Figure 31. Correlation between deviation from mean N_2O flux from denitrification and deviation from mean average daily temperature in: (a) May; (b) June



Tables

Table 1. Summary of management practices for continuous corn (CS1) and corn-soybean (CS2) cropping systems at the Wisconsin integrated cropping systems trial (WICST) simulated by DAYCENT.

CS1 (Continuous Corn)

Year 1

Day of Year	Management Activity
29-Apr	Nitrogen Fertilizer Applied
1-May	Corn Planted
30-Oct	Corn Harvested
5-Nov	Field Cultivated

CS2 (Corn-Soybean)

Year 1

Day of Year	Management Activity
29-Apr	Nitrogen Fertilizer Applied
1-May	Corn Planted
30-Oct	Corn Harvested

Year 2

Day of Year	Management Activity
15-May	Soybean Planted
30-Oct	Soybean Harvested
5-Nov	Field Cultivated

Table 2. Description of spin-up scenario used to calibrate the DAYCENT model.

Spin Up Scenario Description		
Start Year	End Year	Description
-1000	1830	Native tallgrass prairie
1831	1832	Sod-busting
1833	1860	Wheat-Wheat-Fallow
1861	1969	Grazing of cool season grass pasture
1970	1989	Corn-alfalfa-alfalfa-alfalfa

Table 3. Description of representative soils and properties simulated by DAYCENT.

County	Soil	%Sand	%Silt	%Clay	BulkD	Ph	Acres	% County
Columbia								
	Dodge silt loam	14	71	15	1.45	6.45	9830	1.9
	Friesland sandy loam	69	22	9	1.55	6.05	7100	1.2
	Grellton sandy loam	69	22	9	1.55	6.2	10750	2.2
	Griswold silt loam	27	54	19	1.2	6.7	12350	2.4
	Joy silt loam	11	69	20	1.15	6.45	5100	1.3
	Lapeer fine sandy loam	69	22	9	1.35	6.05	55400	10.9
	McHenry silt loam	30	55	15	1.2	6.45	10050	1.9
	Okee loamy sand	84	10	6	1.625	6.45	7600	1.5
	Oshtemo loamy sand	78	16	6	1.475	5.8	8647	1.6
	Plano silt loam	7	70	23	1.2	6.7	43400	8.6
	St. Charles silt loam	7	70	23	1.225	6.45	26340	5.2
	Saybrook silt loam	7	70	23	1.2	6.45	8650	1.8
								40.5
Grant								
	Arenzville silt loam	14	72	14	1.375	6.7	38075	5
	Chaseburg silt loam	14	72	14	1.45	6.95	14003	1.8
	Downs silt loam	11	67	22	1.275	6.2	16011	2.1
	Dubuque silt loam	12	69	19	1.3	6.7	155375	20.4
	Fayette silt loam	7	67	26	1.4	6.2	165037	21.9
	Seaton silt loam	12	70	18	1.15	6.45	16908	2.2
	Tama silt loam	7	68	25	1.275	6.2	62970	8.6
								62
Marathon								
	Chetek sandy loam	69	24	7	1.5	6.2	17220	1.7
	Fenwood-Rozellville silt loam	32	56	12	1.375	5.5	81710	8.1
	Freeon silt loam	33	56	11	1.4	5.9	36699	3.6
	Kennan sandy loam	68	24	8	1.4	5.9	55550	5.4
	Loyal silt loam	32	56	12	1.45	5.9	85569	8.5
	Magnor silt loam	32	56	12	1.45	5.45	36649	3.6
	Marathon silt loam	31	56	13	1.425	5.9	21821	2.2
	Mosinee sandy loam	65	29	6	1.525	5.9	34740	3.4
	Mylrea silt loam	32	56	12	1.45	5.5	21111	2.1
	Rietbrock silt loam	32	56	12	1.4	5.9	73702	7.3
	Rosholt sandy loam	69	24	7	1.55	5.9	13996	1.3
								47.2
Waushara								
	Billett sandy loam	67	23	10	1.55	6.15	9249	2.3
	Boyer loamy sand	79	17	4	1.475	6.45	12544	3.1
	Hortonville sandy loam	69	22	9	1.45	6.7	7860	1.9
	Okee loamy sand	84	9	7	1.625	6.45	23517	5.8
	Richford loamy sand	84	9	7	1.5	6.45	63283	15.6
								28.7

Table 4. Average grain yields (1993-2011) observed at WICST and simulated by DAYCENT.

		Observed Mg grain ha^{-1}	Std. Dev.	Simulated Mg grain ha^{-1}	% Difference	adjusted R^2	p=
CS1							
	Corn	10.91	± 1.97	10.98	+ 0.68	0.46	< 0.001
CS2							
	Corn	11.47	± 1.71	9.95	- 13.25	0.03	0.24
	Soybean	3.39	± 0.58	3.62	+ 6.78	-0.05	0.80

Table 5. Average annual N_2O emissions (kg N_2O-N ha^{-1}) by cropping system, crop, and soil texture with standard deviations. Textural categories not connected by the same letter across columns are statistically significant ($p < 0.05$).

		LSa	SaL	SL	
CS1		1.79 (1.50)a	2.15 (1.62)a	5.65 (3.43)b	**4.2 (3.35)**
CS2		1.66 (1.20)a	1.80 (1.27)a	3.92 (3.27)b	**3.05 (2.86)**
Corn		2.02 (1.31)a	2.28 (1.40)b	5.77 (3.35)c	**4.34 (3.25)**
	CS1 Corn	1.79 (1.50)a	2.15 (1.63)a	5.65 (3.43)b	**4.20 (3.35)**
	CS2 Corn	2.26 (1.04)a	2.41 (1.11)a	5.89 (3.27)b	**4.47 (3.15)**
Soybean		1.07 (1.06)a	1.18 (1.11)a	1.96 (1.73)b	**1.63 (1.56)**
		1.70 (1.31)a	**1.91 (1.41)b**	**4.50 (3.42)c**	

Table 6. Review of soil N_2O fluxes occurring in agricultural landscapes of the upper Midwest USA.

Study	State	Management	Crop	Annual N2O flux (kg N2O N ha-1)
Goodroad et al. (1984)	Wisconsin	Reduced-tillage	corn	3.5 - 6.3
Cates and Keeney (1987)	Wisconsin	Conventional tillage	corn	3.6 - 5.2
Parkin and Kaspar (2006)	Iowa	Chisel Plow	corn	7.8 - 11.3
	Iowa	Chisel Plow	soybean	2.17 - 6.96
Jarecki et al. (2008)	Iowa	Chisel Plow	corn	4.26(1.11)
Hoben et al. (2011)	Michigan	Conventional tillage	corn	7.2 - 1.06
Burzaco et al. (2013)	Indiana	Conventional tillage	corn	3.52