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MEASURED AND DAYCENT- SIMULATED NITROUS OXIDE EMISSIONS FROM SOIL PLANTED TO CORN IN DAIRY CROPPING SYSTEMS

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ABSTRACT

Crop rotations, organic nutrient amendments, reduced tillage practices, and integration of cover crops are practices that have the potential to increase the sustainability of crop production, yet they also impact nitrous oxide (N_2O) emissions. Agricultural soil management has been estimated to contribute 79% of the total N_2O emissions in the U.S., and inorganic nitrogen (N) fertilization is one of the main contributors. Nitrous oxide is a potent greenhouse gas that has a global warming potential which is approximately 298 times that of carbon dioxide (CO_2) over a 100-year period and is currently the dominant ozone-depleting substance. Few studies have assessed the effects of organic N amendments on direct N_2O within the context of a typical dairy forage cropping system. Most research has been limited to studying the effects of one or two sources of N inputs on N_2O emissions; however, dairy forage cropping systems often apply manure and have more than two N sources that likely both contribute to N_2O emissions. This study investigated how different dairy cropping practices that include differences in crop residues, N inputs (dairy manure and inorganic fertilizer), timing of N amendment applications and environmental conditions influenced N_2O emissions from no-till soil planted to corn (*Zea mays* L.). A two-year field study was carried out as part of the Pennsylvania State Sustainable Dairy Cropping Systems Experiment, where corn was planted following annual grain crops, perennial forages, and a green manure legume crop; all were amended with dairy manure. In the corn-soybean *(Glycine max (L.) Merr.)* rotation, N sources (dairy manure and inorganic fertilizer) and two methods of manure application (broadcasted and injected) were also compared.

Chapter 1 reviews the scientific literature; describing the biotic and abiotic processes of N_2O production in soils, summarizing current research on N_2O emissions in agricultural systems, and emphasizing the main management and environmental drivers contributing to the emissions. This chapter reviews methods for matching N supply with crop demand, coupling N flow cycles, using advanced fertilizer techniques, and optimizing tillage management. Also, the applicability and limitations of current research to effectively reduce N_2O emissions in a variety of regions are discussed.

Chapter 2 analyzes the effect of corn production management practices and environmental conditions contributing to N_2O in the Pennsylvania State Sustainable Dairy Cropping Systems Experiment. Significantly higher N_2O emissions were observed 15-42 days

after manure injection and 1-4 days after mid-season UAN application. Manure injection had 2-3 times greater potential for N_2O emissions compared to broadcast manure during this time period. Integration of legumes and grasses in the cropping system reduced inorganic fertilizer use compared to soybean with manure or UAN, however, direct N_2O emissions were not reduced. The Random Forest method was used to identify and rank the predictor variables for N_2O emissions. The most important variables driving N_2O emissions were: time after manure application, time after previous crop termination, soil nitrate, and moisture. These field research results support earlier recommendations for reducing N losses including timing N inputs close to crop uptake, and avoiding N applications when there is a high chance of precipitation to reduce nitrate accumulation in the soil and potential N losses from denitrification.

Chapter 3 reports the comparison of N_2O fluxes predicted with the biogeochemical model DAYCENT compared to measured data from the two-year dairy cropping systems study. Daily N_2O emissions simulated by DAYCENT had between 41% and 76% agreement with measured daily N_2O emissions in 2015 and 2016. DAYCENT overestimated the residual inorganic N fertilizer impact on N_2O emissions in the corn following soybean with inorganic fertilizer and broadcast manure. Comparisons between DAYCENT simulated and measured N_2O fluxes indicate that DAYCENT did not represent well organic N amendments from crop residues of perennials and legume cover crops, or manure application in no-till dairy systems. DAYCENT was generally able to reproduce temporal patterns of soil temperature, but volumetric soil water contents (VSWC) predicted by DAYCENT were generally lower than measured values. After precipitation events, DAYCENT predicted that VSWC tended to rapidly decrease and drain to deeper layers. Both the simulated and measured soil inorganic N increased with N fertilizer addition; however, the model tended to underestimate soil inorganic N concentration in the 0-5 cm layer. Our results suggest that DAYCENT overestimated the residual N impact of inorganic fertilizer on N_2O emissions and mineralization of organic residues and nitrification happened faster than DAYCENT predicted.

Chapter 4 highlights the impact of manure injection and the importance of timing organic N amendments from manures and/or crop residue with crop N uptake to mitigate N_2O emissions. More research is needed to better understand the tradeoffs of these strategies in no till dairy cropping systems to help farmers in their operational management decisions. Improving the parametrization of DAYCENT for dairy cropping systems in no-till systems with high surface legume crop residues from perennials and cover crops, will make the model a more useful tool for testing different mitigation scenarios for farmers' and policy-designer decision making.

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Chapter 1

Nitrous oxide emissions from agricultural systems

Introduction

Greater nitrogen (N) inputs will be required to meet increasing world-wide demand for food. However, the use of large amounts of N inputs in intensive agricultural systems has environmental impacts (Gastal et al., 2015). In 2014, agricultural soil management was estimated to contribute 949 Gg of nitrous oxide (N_2O) (318 Tg CO2 Eq.), which represents 79% of the total N_2O emissions in the U.S. (US EPA, 2016). Mineralization and asymbiotic fixation were the main sources and contributed 360 Gg of N_2O, which represents 38% of the total US N_2O emissions. Nitrogen fertilization contributed 181 Gg of N_2O, which represents 19% of the total US N_2O emissions (US EPA, 2016).

Nitrous oxide is primarily produced in soils by the microbial processes of nitrification and denitrification. It is a potent greenhouse gas which has a global warming potential that is 298 times that of carbon dioxide (CO_2) over a 100-year period (US EPA, 2016) and currently is the dominant ozone-depleting substance (Ravishankara et al., 2009). The N_2O concentration in the atmosphere has increased by 14% from 286ppb (1950) to 327ppb (2015) (US EPA, 2016).

Because about 25-50% of the N fertilizer added to soils is typically lost from the plant-soil system, there is potential to reduce N_2O emissions with improved management (Del Grosso and Parton, 2011). Mosier et al. (1998) estimated that global emissions of N_2O could be reduced by 0.68 Tg N_2O y^{-1} through matching N supply with crop demand (0.24 Tg N_2O y^{-1}), coupling N flow cycles (0.14 Tg N_2O y^{-1}), using advanced fertilizer techniques (0.15Tg N_2O y^{-1}), and optimizing tillage management and drainage (0.15 Tg N_2O y^{-1}). This chapter describes the processes and management practices that influence N_2O emissions from agricultural systems.

Nitrogen in the soil

Because N is very mobile in the soil and transforms very easily it is susceptible to losses. Losses can occur through runoff, erosion, leaching, volatilization, and denitrification. Many of the N transformations are mediated by microbes. Nitrogen primarily enters the soil biological pool through N fixing bacteria. This process is called biological fixation and is the dominant natural process by which N enters the soil. Other transformations occur in the soil: N mineralization, which is the conversion of organic N to inorganic forms; N immobilization, which is the uptake or assimilation of inorganic forms of N by microbes, other soil heterotrophs and plants; nitrification, which is the conversion of ammonium (NH_4^+) to nitrite (NO_2^-) and nitrate (NO_3^-); and denitrification, which is the conversion of NO_3^- to N_2O and then dinitrogen gas (N_2) (Robertson and Groffman, 2007).

Nitrous oxide

Nitrous oxide is produced through biotic processes which include nitrification, nitrifier denitrification, nitrification-coupled denitrification, denitrification, hydroxylamine oxidation and abiotic process of hydroxylamine decomposition and chemodenitrification. In dry, well-aerated soil, the oxidative process of nitrification is the primary source of N_2O and the more oxidized gas, nitric oxide (NO), is the most common N oxide emitted from soil (Davidson et al, 2000). Chemoautotrophic bacteria mediate this process. These bacteria also mediate the processes of nitrifier denitrification and nitrification-coupled denitrification (Kool et al., 2011). In soils that are periodically wet, where gas diffusivity is low and aeration is poor, the process of denitrification is the primary source of N_2O and N_2 (Conrad, 1996; Davidson et al., 2000; Khalil et al., 2004). Facultative anaerobic bacteria mediate this process and oxidize organic carbon (C) from soil organic matter using oxidized forms of N (NO_2^- and NO_3^-) as respiratory electron acceptors in place of oxygen (O_2) when it is depleted. Oxidized forms of N are reduced by enzymes that conserve energy in reductive steps by electron transport phosphorylation (Tiedje, 1982); N_2O is released in this pathway. Nitrous oxide is also produced by hydroxylamine oxidation to NO_3^-. Hydroxylamine decomposition can occur via hydroxylamine oxidation by oxidized iron (Fe^{3+}) or manganese (Mn^{4+}) and the reaction is more thermodynamically favorable with manganese (Zhu-

Barker et al., 2015). Chemodenitrification occurs under anoxia conditions when the reduction of NO_3^-, NO_2^- or NO is coupled to the oxidation of iron (Fe^{2+}) (Zhu-Barker et al., 2015).

Processes that control N_2O emissions

The rate of formation and emission of N_2O that control microbial denitrification varies over time with changes in the following abiotic variables: moisture content, porosity, temperature, O_2 concentration, N content of the soil and available C (Robertson and Groffman, 2007). The size, composition, and activity of the microbial population are main biotic factors influencing N_2O production via denitrification (Rich and Myrold, 2004; Tiedje, 1988) although this will not be studied in this chapter.

- Soil moisture, porosity and temperature

The soil water content, expressed as water filled pore space (WFPS), is one of the major influences on denitrification and, therefore, on N_2O emissions (Linn and Doran, 1984). Water filled pore space is a useful measure that characterizes moisture's influence on soil biological activity (Robertson and Groffman, 2007). Denitrification typically begins when gas diffusion is limited by conditions leading to high soil water content (WFPS ≥60%), such as intense rainfall, impeded drainage, shallow groundwater, or soil compaction (Robertson and Groffman 2007; Bouwman et al., 2002). Temperature is another main factor controlling N_2O emissions; as temperatures increase N_2O emission rates also increase, but typically at a non-linear (exponential) rate (Burzaco et al., 2013). When moisture and temperature are favorable, large inputs of organic matter lead to high rates of microbial activity with the potential for high rates of N mineralization and immobilization (Robertson and Groffman, 2007).

- Available carbon, inorganic nitrogen

Available C is highly correlated with microbial respiration and denitrification (Weier et al., 1993). High soil organic C concentration is associated with increased N_2O emissions because it promotes microbial O_2 consumption, which creates anaerobic microsites in the soil causing denitrifying microbes to switch to denitrification from aerobic respiration (Bouwman et al., 2002, Del Grosso et al., 2006). Similarly, spatial variability of N in the soil influences the magnitude of N_2O emissions. For example, within a grazed pasture, the uneven deposition of urine patches in 1.1% of the field area contributed to 55% of the total estimated N_2O (Cowan et al., 2015). Sehy et al. (2003) observed the influence of site-specific fertilizer additions on N_2O fluxes, showing that a 16% reduction in fertilizer addition to low yielding areas located in a shoulder position resulted in a 34% reduction in N_2O emissions (2.3 Kg N_2O ha^{-1}), while crop yield remained the same. Conversely, a 16% increase in fertilizer addition to high yielding areas located in a foot slope position did not significantly affect N_2O emissions or yields.

Emissions of N_2O also depend on the quantity and quality of the decomposing plant residue. Patten et al. (1980) demonstrated that the rate of denitrification was dependent on the quantity of organic C that can be readily utilized by denitrifying microorganisms and that the organic C in various pools is not completely available to microorganisms. Heal et al. (1997) explained that substrates with a C:N ratio $<$ 20 decompose rapidly and N is released through mineralization. Materials with C:N ratios of 25-75 can also decompose quickly, but net N mineralization is often reduced by increased microbial immobilization as well as protein complexation by polyphenols when the cells lyse. For residues with C:N $>$75, the authors stated that these substrates are more difficult to break down and are generally characterized by greater amounts of structural woody materials such as lignin.

Management practices that influence N_2O emissions

The following management practices may impact the processes in ways that could potentially increase or reduce N_2O emissions.

Nitrogen fertilization

i. Nitrogen rate

Numerous studies have shown that increasing the amount of N added to soil increases N_2O emissions (Millar et al., 2010), and when fertilizer application coincided with high rainfall, the favorable conditions for denitrification stimulated the production of N_2O (Mitchell et al., 2003). A global meta-analysis suggests that the N_2O emission response to increasing N input is exponential rather than linear (Shcherbak et al., 2014). To reduce N_2O emissions, N fertilizer rates can be reduced to economically optimum levels by using a maximum return to N (MRTN) approach (Millar et al., 2010). Venterea et al. (2012) noted an emerging approach, variable-rate N application (VRNA) which adjusts N rate to meet real-time crop demand or prior-season yield variations within a given field and can improve N management.

ii. Nitrogen amendment type

Readily soluble N fertilizers such as urea, anhydrous ammonia, urea ammonium nitrate, ammonium nitrate and ammonium sulfate are the most commonly used synthetic fertilizers in row-crop agriculture (Millar et al., 2010). The fundamental challenge in reducing N losses from agricultural soils in general is to optimize crop N-use efficiency (NUE) (Venterea et al., 2012). Enhanced efficiency fertilizers (EEF) have been developed to increase NUE by providing better synchronization between crop N demand and N supply. According to the Association of American Plant Food Control Officials (AAPFCO), there are two subcategories of EEF: stabilized fertilizer and slow or controlled- released fertilizer. The stabilized fertilizers reduce the transformation rate of fertilizer compound by extending the time of nutrient availability to plant, while the slow-released fertilizers convert and/or release nutrients that are in the plant available form at a slower rate relative to a "reference soluble" product. A study carried out by Halvorson and Del Grosso (2012) in irrigated no-till corn (*Zea maize* L.) in Colorado comparing commercially available controlled-release and inhibitor treated N fertilizers to conventionally used granular urea and urea ammonium nitrate (UAN) showed that UAN+AgrotainPlus (AgrotainPlus contains nitrification and urease inhibitors) had the lowest level of N_2O emissions with no yield lost. In contrast, N_2O emissions were not reduced from the same EEF in a rain fed system in Iowa (Parkin and Hatfield, 2014) or Pennsylvania (Dell et al., 2014), where rainfall events limited the effectiveness of the EEF.

Composition of manure at the time of field application also influences N_2O emissions. Chadwick et al. (2000) reported higher N_2O emissions from liquid manure applied to the surface of grasslands compared to solid manure. The higher emissions were associated with the easily mineralizable C and N present in the liquid manure. On the other hand when manure was incorporated, Rochette et al. (2008) found no significant effect of manure form. An alternative approach for manure management is use of compost, which can be less detrimental to the environment with relatively lower emissions of CO_2 (Gil et al., 2008) and N_2O (Li et al., 2016).

iii. N amendment placement

Bowman (1996) found that nitrate-based fertilizers typically lead to greater emissions of N_2O compared to ammonia-based fertilizers. However, he found that anhydrous ammonia induced the highest N_2O fluxes. This was explained not by the source of N fertilizer but by its placement. For his experiment, anhydrous ammonia was injected, and, therefore this created highly alkaline zones of high NH_4^+ concentration that led to N_2O production (Bouwman, 1996). Liu et al. (2006) evaluated the impact of N placement on N_2O emissions, and found that injection of liquid UAN at 10 and 15 cm below the surface resulted in lower emission of N_2O as compared to shallow injection (0 and 5 cm). Similarly, manure placement affects the magnitude of N_2O emissions. Research has shown that N_2O emissions from manure injected are higher than from surface application (Duncan et al., 2017; Flessa and Beese 2000; Velthol et al., 2003, Velthof et al., 2011). This is explained because manure injection creates conditions that may favor denitrification by creating an anaerobic environment abundant in inorganic N and readily oxidizable C (Comfort et al., 1990).

iv. Nitrogen amendment timing

Fertilizer application in periods when the crop is actively taking up N can reduce N losses through denitrification and leaching (Mosier, 1993). Applying N at corn V6 growth state instead of at planting has been shown to be an effective strategy to reduce N_2O emissions without affecting corn yield (Roy et al., 2014). Rochette et al., (2004) assessed the timing of pig slurry application and found that emissions of N_2O were lower when manure was applied in the fall compared to the spring. The authors explained that this happened because in the fall, wet and cool conditions limited net nitrification, which resulted in little NO_3-N accumulation and limited the potential for denitrification. In contrast, the soil was warm and well aerated in the spring and this favored the processes of nitrification and denitrification after rainfall events. Manure-based fertilization typically increased N_2O emissions compared to inorganic N fertilization (Adviento-Borbe et al., 2010, Clayton et al., 1997). In temperate climates, it was observed that tilled soils that received manure had significant N_2O emissions during the thaw period, when WFPS was between 40 and 70% (Singurindy et al., 2009). However, soils managed as no-till have been found to significantly reduced N_2O emissions during thaw (80% of total reduction) compared to conventional tillage by reducing soil freezing due to the insulating effects of snow cover plus crop residue (Wagner- Riddle et al., 2007).

v. Cover crops

Research suggests that the magnitude of N_2O emissions with cover crops depends on the quantity and quality of the crop residue (Gomes et al., 2009). A meta-analysis carried out to assess the effect of cover crop on N_2O emissions (Basche et al., 2014) showed that incorporating cover crop residues increased N_2O emissions compared to when residues where left on the surface. This was attributed to an increase in N mineralization rate, and therefore, NO_3^- availability and denitrification. The study of Baggs et al. (2003) found the highest emissions of N_2O from conventionally tilled beans (*Vicia faba*) (1.0 kg N_2O-N ha^{-1} emitted over 65 days) and no-tilled rye (*Secale cereale* L.) cover crop (3.5 Kg N_2O ha^{-1}over 65 days). The authors explained that this was attributed to rapid release of N following incorporation of bean residues in the conventionally tilled treatments, and availability of readily degradable C from the rye in the presence of anaerobic conditions under the mulch in the zero tilled treatments.

In no-till cover crop based rotations in Brazil, Gomes et al. (2009) found higher N_2O emissions with corn planted after three different legume crops -pigeon pea (*Cajanus cajan* L. Millsp.), lablab (*Dolichos lablab*) and cowpea (*Vigna unguiculata* L.Walp)- compared to corn planted after oats cover crop (*Avena sativa* L.). They explained that this could have happened because: 1) the fast mineralization of N from legume residue increased the soil mineral N, providing substrate for denitrification: and 2) the increased consumption of O_2 during mineralization of N increased the occurrence of anaerobic microsites that enhanced denitrification. A laboratory incubation carried out by Huang et al. (2004) showed that soil N_2O emissions tended to be greater when the incorporated crop residue had a low C:N ratio compared to the control. Also, the content of N and lignin in the plant had an effect on N_2O emissions; low lignin:N ratio increased N_2O emissions relative to high lignin: N ratio (Millar and Baggs, 2004).

The use of overwintering crops can capture end-of season available NO_3^- and reduce N_2O emissions. A study carried out in Michigan, by McSwiney et al. (2010) showed that planting winter annual crops, cereal rye and wheat (*Triticum aestivum* L.) used as a cover crop, decreased mineral N availability for N_2O production. In Iowa, Mitchell et al. (2013) also found that the corn planted after rye cover, without fertilizer, decreased soil NO_3^- concentration and N_2O emissions compared to a treatment with no cover crop or fertilizer.

Tillage

Research has shown a positive long term effect of no-tillage on N_2O emissions. A three decade corn-soybean tillage experiment in west-central Indiana showed that N_2O emissions under no-till were about 40% lower relative to moldboard plowing and 57% lower relative to chisel plowing, but no significant differences among treatments were found (Omonde et al., 20011). The authors suggested that higher N_2O emission under moldboard plowing and chisel plowing could have been driven by soil organic C decomposition associated with higher levels of soil–residue mixing and higher soil temperatures.

Similarly, in corn-soybean systems in Iowa, Parkin and Kaspar (2006) found no significant differences in N_2O fluxes among no –till and conventional till systems, but cumulative N_2O emissions under no-till were 29% lower relative to conventional tillage. The authors suggested that this could have happened because the no-till treatment was stablished 8-9 years ago and it was not long enough to elucidate the differences. Six et al. (2004) reported that in humid climates, after 20 years of no till adoption, a significant reduction in N_2O and global warming potential was observed compared to conventional tillage, likely due to an increase in NUE.

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Chapter 2

Factors contributing to nitrous oxide emissions from no-till corn fields in dairy systems

Abstract

Crop rotations, organic nutrient amendments, reduced tillage practices, and the integration of cover crops have the potential to increase the sustainability of crop production, yet they also impact greenhouse gas emissions. We investigated how different cropping system practices that include differences in crop residues, nitrogen (N) inputs (dairy manure and inorganic fertilizer), and timing of N amendment applications, influenced direct nitrous oxide (N_2O) emissions in dairy systems. In 2015 and 2016, N_2O fluxes were measured from April to December using closed chambers in the Pennsylvania State Sustainable Dairy Cropping Systems Experiment. Gas was sampled from soils planted to corn following annual grain crops, perennial forages, and a green manure legume crop; all were amended with dairy manure. In the corn-soybean rotation we also compared N sources and two methods of manure application: i. urea ammonium nitrate, ii. manure surface broadcasted and iii. injected manure. Integration of perennials and a cover crop legume that amended soil N reduced inorganic fertilizer use; however compared to inorganic fertilizer application after soybean, N_2O emissions were not reduced. Emissions were higher between 15 and 45 days after manure was injected following soybeans compared to treatments where manure was broadcasted after legumes and grasses were terminated. In these no-till dairy corn systems about 0.4 to 1.8% of N added was lost as N_2O. The most important variables driving N_2O emissions identified with Random Forest analysis were: time after manure application, time after previous crop termination, soil nitrate, and moisture. These results suggest that timing N inputs close to crop uptake, and avoiding N applications when there is a high chance of heavy precipitation can reduce nitrate accumulation in the soil and potential N_2O losses.

Introduction

Traditional corn (*Zea maize* L.) and soybean (*Glycine max* L. Merr.) production systems rely heavily on nitrogen (N) inputs from inorganic fertilizers, and account for the highest nitrous oxide (N_2O) emissions among major cropping systems in the US (Del Grosso et al., 2005). Numerous studies have shown that increasing the amount of N added to soil can increase N_2O emissions (Millar et al., 2010), especially in response to N additions that exceed crop N needs (McSwiney and Robertson, 2005; Hoben et al., 2011). To replace inorganic fertilizer use, manure can be applied. In the U.S., applying manure to corn production is a significant nutrient source (11.9%) (MacDonald, 2009); but efficient management is critical to improve the economic benefits of manure use and protect water quality (Jokela, 1992). In dairy cropping systems, N use efficiency from manure/fertilizers varies from 16 to 77% (Powell et al., 2010). Strategies to increase manure N fertilizer value include adjusting manure application rates, timing, and placement to coincide with crop uptake (Schröder, 2005). Davidson (2009) estimated that 2.0% of manure and 2.5% of fertilizer N applied to soils was converted to N_2O between 1860 and 2005; therefore, manure soil application is an important opportunity to reduce anthropogenic gas emissions.

Farmers in the Northeastern US are under pressure due to regulations and policies to reduce nutrient losses, especially in Pennsylvania where excess N application causes air pollution and contributes to water pollution. Pennsylvania is the 5th largest producer of dairy in the US (USDA ERS, 2015) and dairy milk sales were the highest value agricultural commodity (USDA NASS, 2014). No-till dairy farms in Pennsylvania broadcast dairy manure onto corn fields to supply nutrients, often after perennial alfalfa is harvested. Manure injection with a shallow disk injector has been shown to be an alternative no-till manure application strategy to conserve nutrients and reduce ammonia volatilization, but with potential for increased N loss via leaching (Dell et al., 2011) and denitrification (Duncan et al., 2017). The use of a nutrient management plan can also help improve manure use efficiency (Aillery et al., 2006). Some of the strategies to improve manure management include soil testing for N, manure testing, calibrating application equipment, and accounting for residual legume N to reduce manure application rates (Beegle et al., 2008).

Additional N inputs on dairy farms are often provided by fertilizer or fixation by legume (Powell et al., 2010). In eastern Canada, Wagner-Riddle et al. (2007) found that N_2O emissions were reduced in no-till soils when fertilizer application rate matched timing of corn needs. However, depending on weather conditions, applying fertilizer to coincide with periods of high crop N demand does not necessarily reduce and may increase N_2O emissions. Venterea et al. (2015) reported an increase in N_2O emissions when sidedress N application coincided with a heavy rainfall. In forage production land, clover provides forage and fixed N (Velthof et al., 1998). The use of alfalfa (*Medicago sativa* L.) in cropping systems is often recommended to reduce or eliminate nitrate pollution (Randall and Mulla, 2001; Peterson and Russelle, 1991). While contributing fixed N to the soil, alfalfa reduces the need for N applications on corn planted after alfalfa (Fox et al., 1988) or after manure application.

Research has shown that including cover crops in cropping systems can reduce inorganic fertilizer use. However, this management practice influences carbon (C) and N dynamics in the soil (Dabney et al., 2007; Sainju et al., 2005), and some can contribute to increasing N_2O emissions. A meta-analysis carried out by Basche et al. (2014) indicated that 40% percent of the cover crop treatments decreased N_2O emissions compared to treatments with no cover crops, while 60% increased N_2O emissions. The crop management practices that reduce direct N_2O emissions from the soil surface included incorporating residues into the soil and using non-legume cover crop species. Their analysis indicated that geographies with higher total precipitation and variability in precipitation tended to produce higher N_2O emissions with cover crops. Gomes et al. (2009) monitored N_2O emissions in Southern Brazil in long-term no-till systems (19 and 21 years) and found higher emissions in corn planted after three different crops - pigeon pea (*Cajanus cajan* L. Millsp.), lablab (*Dolichos lablab*), and cowpea (*Vigna unguiculata* L.Walp)- compared to corn planted after oats cover crop (*Avena sativa* L.). They attributed the higher N_2O emissions to: i) fast mineralization of N from legume residue that increased the soil mineral N, providing substrate for denitrification, and ii) increased consumption of oxygen during mineralization of N that created anaerobic microsites enhancing denitrification.

Most research has typically been limited to studying the effects of one or two sources of N inputs on N_2O emissions; however, dairy cropping systems often apply manure and have more than two N sources that likely contribute to N_2O emissions. Few studies have assessed the effects of organic N amendments on direct N_2O emissions within the context of a typical dairy crop system. This study investigates how different cropping practices that include differences in crop residue types, N inputs (dairy manure and inorganic fertilizer), fallow period, and timing of N amendment applications influence N_2O emissions from no-till soil planted to corn. Since the mineralization of organic N inputs depend on weather conditions, matching N supply from these sources applied prior to corn planting with crop N demand is challenging and can result in increasing N_2O emissions. Applying inorganic fertilizer to coincide with periods of high crop N demand can reduce N_2O emissions if it does not coincide with a heavy rainfall. We hypothesized that treatments receiving organic N amendments prior to corn planting would have higher potential for N_2O emissions compared to the treatment receiving only inorganic fertilizer. Based on prior studies on methods of manure applications, we hypothesized that when manure is injected, emissions would be greater than when it is broadcasted without incorporation.

Materials and Methods

Soil N_2O emissions were measured in the Northeastern Sustainable Agriculture Research and Education Dairy Cropping Systems (NESARE DCS) project at the Pennsylvania State University Russell E Larson Agronomy Research Farm, Pennsylvania, USA (Latitude 40^{o}43’12”; Longitude 77^{o}56’02”; Elevation 366m). This project was initiated in 2010 and aims to sustainably produce the forage, feed, and fuel for a 65 cow, 97 ha dairy farm in Pennsylvania, at 1/20th of the scale on 4.85 ha of land. The soil at the site is primarily a Murrill channery silt loam (fine-loamy, mixed, semiactive, mesic Typic Hapludults) with small areas of Buchanan channery silt loam (fine-loamy, mixed, semiactive, mesic Aquic Fraguidults).

In this study, two of the NESARE DCS crop rotations were compared: a dairy forage rotation and a corn-soybean (C-S) rotation (Fig 2.1). The 6-year dairy forage rotation consisted of a 2-yr alfalfa and orchardgrass (*Dactylis glomerata* L.) forage crop, followed by corn grown for grain (2015) - interseeded with a mixture of cover crop species dominated by annual rye gras (*Lolium multiflorums* L.) and forage radish (*Raphanus sativus* L.) - or corn grown for silage (2016). Then corn for grain or silage was followed by cereal rye (*Secale cereale* L.) grown for silage, followed by crimson clover (*Trifolium incarnatum* L.) or red clover (*Trifolium pretense* L.), corn grown for silage (2015) or grain (2016), followed by oats cover crop. Two green manure crops (crimson and red clover) were compared within split-split plots (27 x 9 m) of the dairy forage rotation. In the 2-year C-S rotation, broadcast manure application and shallow disk manure injection were compared to inorganic-fertilizer within split-split plots (27 x 9 m). The crop rotations were randomized in complete block design with 4 blocks and, within each rotation; each crop entry point was randomized and planted each year.

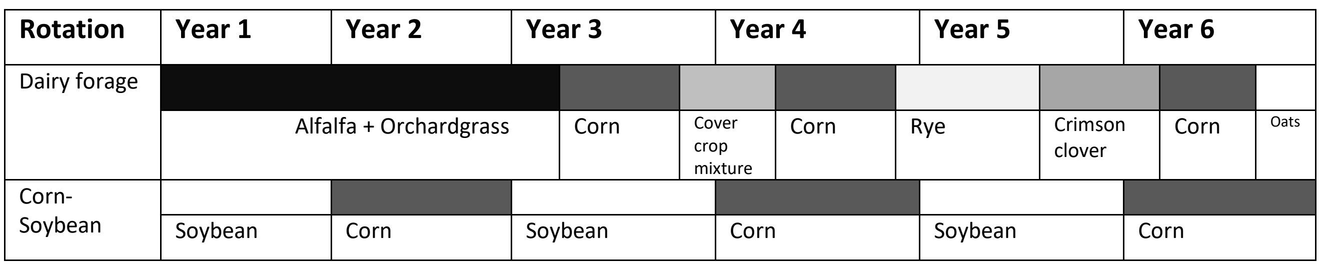

Fig 2. 1 Dairy forage rotation and corn-soybean rotations in the Northeastern Sustainable Agriculture Research and Education Dairy Cropping Systems project at the Pennsylvania State University

From the dairy forage rotation, we sampled two corn entries that received broadcasted manure (BM) and were planted after: i. alfalfa and orchardgrass (AO) and ii. crimson clover (CC). From the C-S rotation, we also sampled three nutrient management treatments of corn with: iii. broadcast manure (S-BM), iv. injected manure with a shallow disk injector (10 cm depth) (S-IM), and v. with liquid urea ammonium nitrate (S-UAN) fertilization. Since 2010, the S-BM and S-IM treatments received manure once in the spring before corn planting every other year. However, the corn sampled in the S-BM treatment in 2016 did not receive manure in 2012 and 2014. We reported results for gas samples taken in 2015 and 2016 in three blocks of the experiment. In 2015, corn planted after crimson clover was measured from only two blocks because in the third block, samples were accidentally taken from corn planted after red clover instead of crimson clover.

All crop rotations have been managed under no-till, and previous perennial and legume crops were planted with a Great Plains 1005 solid-stand no-till drill (Great Plains Manufacturing, Inc., Salina, KS). ‘6422Q’ Alfalfa (NexGrow Genetics, Fort Dodge, IA) and ‘Extend’ orchardgrass (SEED WAY, Hall, NY) were planted at a rate of 9,900 and 24,700 kg ha^{-1}, respectively, in 19-cm rows on 24 Apr. 2013 and 14 Apr. 2014. 'Dixie' crimson clover (King Agriseed's, Ronks, PA) was planted at 49,420 kg ha^{-1} in 19- cm rows on 12 Sept. 2014 and 29 Aug. 2015. Alfalfa and orchardgrass and crimson clover were terminated with glyphosate [N-(phosphonomethyl) glycine] and 2,4D [(2,4-dichlorophenoxy)acetic acid] on 8 May 2015 and 27 Apr. 2016. Growmark 'HS32A90' soybean (Growmark, Inc., Bloomington, IL) were planted at a rate of 494, 000 seeds ha^{-1} in 38-cm rows on 2 June 2014 and 22 May 2015 and harvested with a Massey Ferguson 550 plot combine (AGCO Corporation, Duluth, GA) on 27 Oct. 2014 and 8 Oct. 2015.

Corn was planted in 76-cm wide rows with a no-till planter (John Deere 1780, Deere & Company, Moline, IL) between 14 May and 19 May in 2015 and 2016. Corn for grain (TA566-31, T.A. Seeds, Jersey Shore, PA; 105 RDM and MC5663 Kings Agri Seeds, Ronks, PA in 2016; 106 RDM) was planted in the C-S rotation and in the forage rotation (TA566-18, T.A. Seeds, Jersey Shore, PA in 2015, 105 RDM and MC5661, Kings Agri Seeds, Ronks, PA in 2016, 106 RDM) at a rate of 79,070 seeds ha^{-1}. Corn for silage (TA089-00, T.A. Seeds, Jersey Shore, PA, in 2015 and TA290-18, T.A. Seeds, Jersey Shore, PA in 2016; both 89 RDM) was planted in the forage rotation at a rate of 86,500 seeds ha^{-1}. Corn grain was harvested mechanically with an Almaco SPC -40 small plot- combine (Almaco, Nevada, IA) on 5 Nov. 2015 and 28 Oct. 2016. Corn silage was harvested on 8 Sept. 2015 and 16 Sept. 2016 in the center of each split-split plot. The corn silage yield was adjusted to 65% moisture, and the corn grain yield to 15% moisture. The rest of the corn plot was harvested by a local farmer using field-scale equipment (Kempler Champion C1200, Champion Danmark A/S Chrisitnafeld 6070, Denmark).

Starter fertilizer was applied to corn after crimson clover at 9 kg ha^{-1} N as 7-21-7 and after alfalfa and orchardgrass and in the C-S treatments at 22 kg ha^{-1} N as 12-40-0. Liquid dairy manure was surface broadcast applied or shallow disk injected prior to corn planting in 2015 at 44 Mg ha^{-1} and in 2016 at 42 Mg ha^{-1}. Manure was injected to approximately 10 cm with a shallow disk injector (Avenger, Yetter Manufacturing, Inc., Colchester, IL). To calculate the amount of N and other nutrients added, manure samples were analyzed by The Pennsylvania State University's Agricultural Analytical Services Laboratory.

Pre-sidress nitrate test (PSNT) is a soil test developed by Magdoff (1991), conducted to determine the amount of nitrate (NO_3^-) available to corn just before the period of major N demand. The test was done at V6 corn growth stage, and inorganic N was applied when NO_3^- levels where lower than 21 ppm to achieve yield goals (Beegle et al., 1999). Based on the PSNT tests in 2015 and 2016, CC-BM, AO-BM and S-IM did not require supplemental N to achieve the corn crop yield goals. The S-BM and S-UAN treatments needed supplemental application of inorganic fertilizer later in the season and were side-dressed with liquid UAN at 53 kg ha^{-1} N and 129 kg ha^{-1} N in 2015 and 100 kg ha^{-1} N and 122 kg ha^{-1} N in 2016, respectively.

Crop Residue sampling

Aboveground biomass was determined for crimson clover, and alfalfa and orchardgrass through destructive harvest of two 0.25 m^2 quadrats per plot before crop termination. Prior to drying, aboveground biomass was sorted into legume vs non-legume plant types. A sub-sample of the biomass was ground following drying, and total C and N were determined by combustion analysis (Elemental Vario Max N/C; Horneck and Miller, 1998). The ratio of C to N was calculated for the random forest analysis to account for the influence of aboveground residue decomposition rate on N_2O emissions.

N_2O measurements

Gas samples were collected in 2015 from 15 April to 7 December and in 2016 from 12 April to 9 September. Nitrous oxide fluxes were measured from each treatment plot with vented static chambers (78.5 cm x 40.5 cm) (Parkin and Venterea, 2011). Chamber frames were placed perpendicularly between two corn rows in two locations in each plot, for a total of 30 frames (5 treatments x 3 blocks x 2 frames). Measurements were taken prior to and during the period of anticipated N_2O fluxes to capture profile of gas emissions during the entire growing season. We sampled two times a week for approximately 60 days after cover crops were terminated and manure was applied. After the 60 days, N_2O fluxes measured were usually low, so we sampled every 7 to 31 days. Fluxes were measured between 9:00 to 12:00 h to minimize diurnal variation in the flux pattern. Samples were collected at approximately 10, 20, and 30 minutes after placing the cover over the frame. Ambient air samples were taken outside of the chamber and used as the time 0 measurement. Emission rate was determined by linear regression of change in N_2O concentration versus time since chamber deployment. Gas samples were analyzed using a Varian

3800 gas chromatograph (Scion Instruments, West Lothian, UK) with an electron capture detector and an automated sample injection system. The chromatograph oven and injector were maintained at 50°C and the detector at 285°C. Dinitrogen was the carrier gas. Cumulative N_2O emissions were calculated by linear extrapolation between sampling dates. The need to assume a linear change in emission rate between sampling dates likely leads to estimation error. However, since gas samples were taken in all treatments on the same sampling date, the cumulative emission estimates were a useful tool for comparison among treatments. Nitrous oxide emissions per unit grain yield were calculated by dividing cumulative N_2O emissions during the corn growing season by the dry grain yield.

Estimated available N

In all treatments, estimated available N was calculated by summing residual N contribution from legumes, the N added in the manure, and the inorganic fertilizer. We used Penn State Agronomy Guide (2015) estimates for the residual legume N to account for the N contribution of the above and below- ground biomass. The N contribution from the soybean was estimated by multiplying soybean grain yields (kg ha^{-1}) by 56 kg N kg^{-1} soybean (Penn State, 2015). Crimson clover was estimated to contribute 45 kg N ha^{-1} and alfalfa 90 kg N ha^{-1} (Penn State, 2015). Manure N available for corn was calculated by multiplying the total amount of N added with the manure by the crop N availability factors estimated in the Penn State Agronomy guide (Penn State, 2015). When manure was broadcasted without incorporation, total manure N was multiplied by 0.2 to estimate available N. When manure was injected, total manure N was multiplied by 0.5. Cumulative N_2O emissions per unit of N applied were calculated by dividing cumulative N_2O emissions during corn growing season by the estimated available N.

Soil measurements

Soil temperature (Model HI 145, Hanna Instruments) and volumetric soil water content (VSWC) (Model ML3 ThetaProbe, Delta-T Devices) were measured from the 0-10 cm soil depth every time N_2O gas samples were collected. Three random soil samples (2.5cm diameter cores $plot^{-1}$) were collected in each treatment-plot, except for the S-IM treatment, once a week from the surface layer (0-5cm) and analyzed for ammonium (NH_4^+) and NO_3^-. For S-IM, we followed the soil N sampling protocol developed by Meinen et al. (2015). Five soil samples were collected 15.2 cm apart across the 76 cm injection band. Inorganic N was extracted with 2 M KCl following the method of Mulvaney (1996), with NH_4^+ and NO_3^- in extracts determined by a flow injection analyzer (Lachat Instruments 2001 and 2003).

Weather data

Daily air temperature and precipitation data were obtained from the NRCS-ARS SCAN site at Rock Springs, Pennsylvania (http://wcc.sc.egov.usda.gov/reportGenerator). The weather station was located less than 0.5 km from the experimental site.

Statistical Analysis

To test the effect of management among treatments, we performed an analysis of variance (ANOVA) with repeated measures using PROC MIXED of SAS software v. 9.4 (SAS Institute Inc., 2012) on the soil moisture, soil temperature, N_2O, NO_3^- and NH_4^+ in the soil with cropping system treatment as a fixed effect, block as a random effect, and sampling date as a repeated fixed effect. Based on the Akaike Information Criterion (AIC) and due to unequally spaced sampling events, covariance was modeled using the spatial power law structure [SP(POW)]. Kenward-Roger method was used to approximate denominator degrees of freedom. The SLICE option of the LSMEANS subcommand was used to test differences among treatment means by day. When there were differences among treatment means, the LSMEANS with Tukey–Kramer adjustments for the p-values option was used to separate means. Treatments were considered statistically different at $P \leq 0.05$.

Differences among treatments in spring legume biomass, cumulative N_2O emissions, yields, and cumulative N_2O emissions per unit grain yield and per unit of N applied, were analyzed by ANOVA using SAS PROC MIXED with cropping system treatment as a fixed effect and blocks as a random effect. The cumulative N_2O emissions per unit grain yield and per unit of N applied were log transformed to improve normality. The LSMEANS with Tukey–Kramer adjustments for the p-values option was used to test differences among treatment means. Treatments were considered statistically different at $P \leq 0.05$. A two-sided F test was performed with residual values to compare variances among 2015 and 2016. Since variances were significantly different, treatments were analyzed within each year.

In order to identify the main environmental and management drivers of N_2O emissions from all five cropping systems, we used Random Forests (RF), a multivariate analysis technique that uses a recursive partitioning method for classification and regression. The response variable is successively divided into groups containing observations with similar values (Strobl et al., 2009). In recent years, ecologists have used RF because of its simple interpretation, high classification accuracy, and ability to characterize complex interactions among variables (Cutler et al., 2007). Also, data do not need to be rescaled, transformed, or modified.

The most widely known recursive partitioning method is the classification and regression tree (CART), which generates a binary tree containing a series of splits based on the factor that best splits a group of observations into two groups with similar response variables (Breiman et al., 1984). Random Forests is an extension of the tree approach where a set of trees are each constructed from bootstrapped samples of observations using a limited number of randomly selected predictor variables (Breiman, 2001). The trees are constructed from two thirds of the data (called the "in-bag"), and the one third of the data not selected is referred to as "out-of-bag" data (OOB). Tree growth ends when the number of observations in the terminal nodes reaches one for classification trees and five or less for regression trees (Liaw and Wiener, 2002). When RF is used for classification, the results generated are obtained by using a voting mechanism among the trees involved. For regression, the trees are averaged at the end for the prediction. Since each tree is constructed by bootstrapping the input data and by using randomly sampled input variables, RF does not over-fit as more trees are added (Aulia et al., 2014). Random forests also provide information on a measure of the importance of the predictor variable. For this, OOB data for a given variable is permuted while all others are left unchanged and then passed down on each tree in the forest to obtain new predictions. The relevant variables used in this RF analysis include a suite of environmental and management predictors expected to influence N_2O emission and are shown in Table 2.1. We implemented the RF algorithm in R statistical software (R Development Core Team 2013) using the "Random Forest" package.

Table 2. 1 Response variable and the 18 input variables evaluated across five corn cropping systems with Random Forest analysis in 2015 and 2016.

Name	Type[1]	Description
N_2O	Q	Nitrous oxide emission (g N ha^{-1} d^{-1})
Treatment	C	Cropping system in study
Crop residue type	C	Grass/Legume/Mixture/No
Days after previous crop termination	Q	Julian days
Days after manure application	Q	Julian days
Nitrate	Q	Soil nitrate on the day of observation at 5 cm depth (mg N kg^{-1})
Ammonium	Q	Soil ammonium on the day of observation at 5 cm depth (mg N kg^{-1})
Soil moisture	Q	Soil volumetric water content on the day of observation at 10 cm depth.
Precipitation 1	Q	Precipitation one day prior the observation (mm)
Precipitation 2	Q	Precipitation two days prior the observation (mm)
Precipitation 3	Q	Precipitation three days prior the observation (mm)
Soil temperature	Q	Average soil temperature (°C) on the day of observation at 10 cm depth.
Maximum air temperature	Q	Maximum air temperature on the day of the observation (°C)
Minimum air temperature	Q	Minimum air temperature on the day of the observation (°C)
N legume	Q	N contribution from the legume crops (N Kg^{-1})
C:N	Q	C:N ratio of aboveground spring legume biomass
Fertilizer	Q	N application rate (Kg N ha^{-1})
Season of manure application	C	Spring/No
Manure placement	C	Broadcast/Injected

[1]Q=quantitative variable, C= categorical variable

Results and Discussion

Environmental factors

Soil temperature, soil moisture, and precipitation during the 2015 and 2016 sampling periods are shown in Figs 2.2&2.3. Soil temperatures and soil moisture differed significantly across sampling dates ($P<0.0001$), but were not affected by crop management on individual sampling dates. In 2015, the soil in S-BM was warmer than other treatments on 7 May ($P=0.0018$). In both years, soils were cooler in April (avg. temperature of 9 °C) and warmer in

June (20 °C). On 5 May and 15 May 2015, the soil moisture in S-BM was significantly higher than the other treatments. Precipitation during the growing season varied widely between 2015 and 2016. May was a drier month in 2015 (64 mm) compared to 2016 (86 mm), and the amount of precipitation was higher in June and July of 2015 (294 mm) compared to 2016 (164 mm).

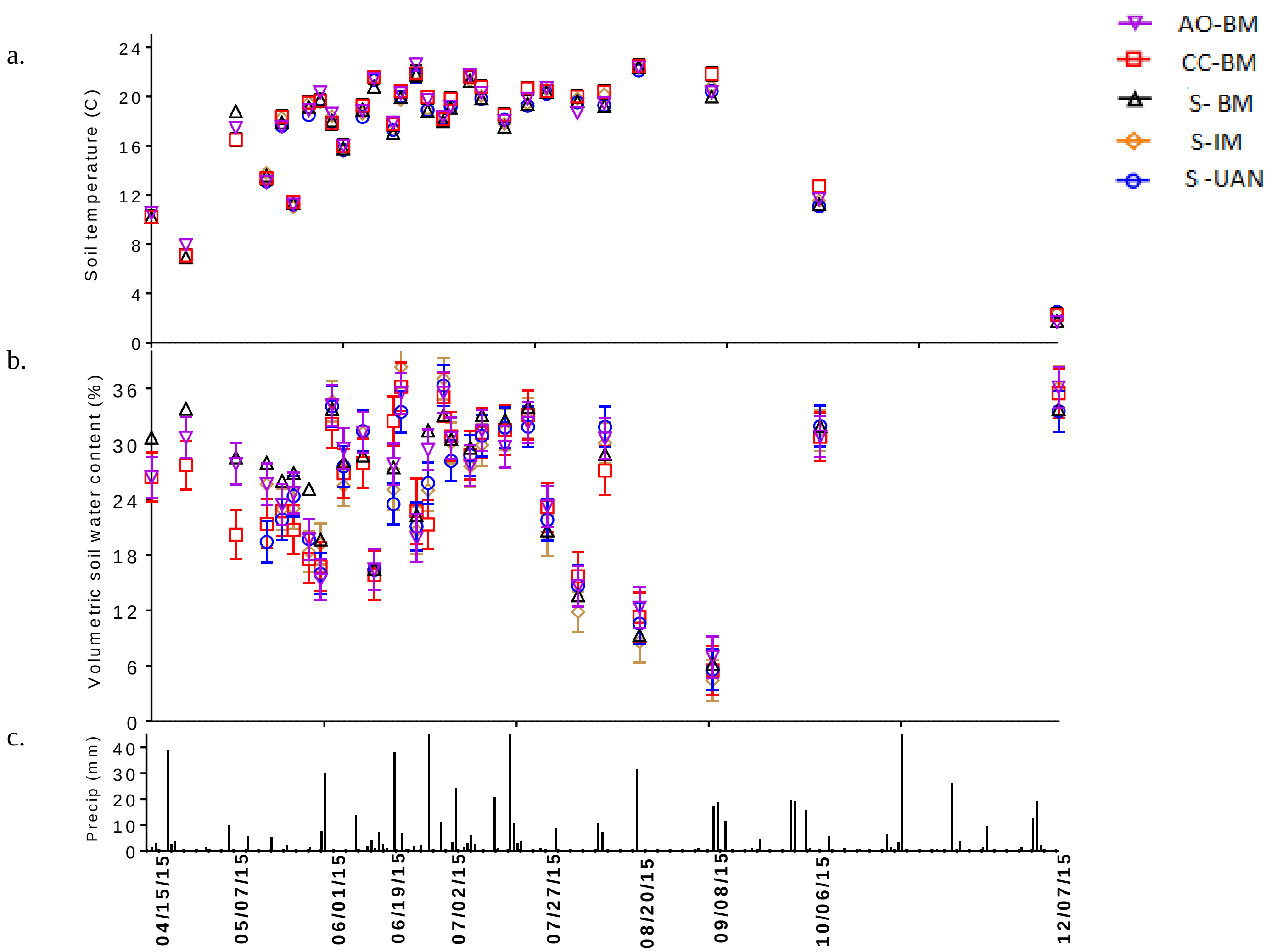

Fig 2. 2 2015 (a), soil temperature (10 cm depth) (b), volumetric soil water content (10 cm depth) and (c), precipitation during soil gas measurements in the corn following: alfalfa and orchardgrass with broadcast manure (AO-BM), crimson clover with broadcast manure (CC-BM), soybean with broadcast manure (S-BM), soybean with inorganic fertilizer (S-UAN), and soybean with injected manure (S-IM).

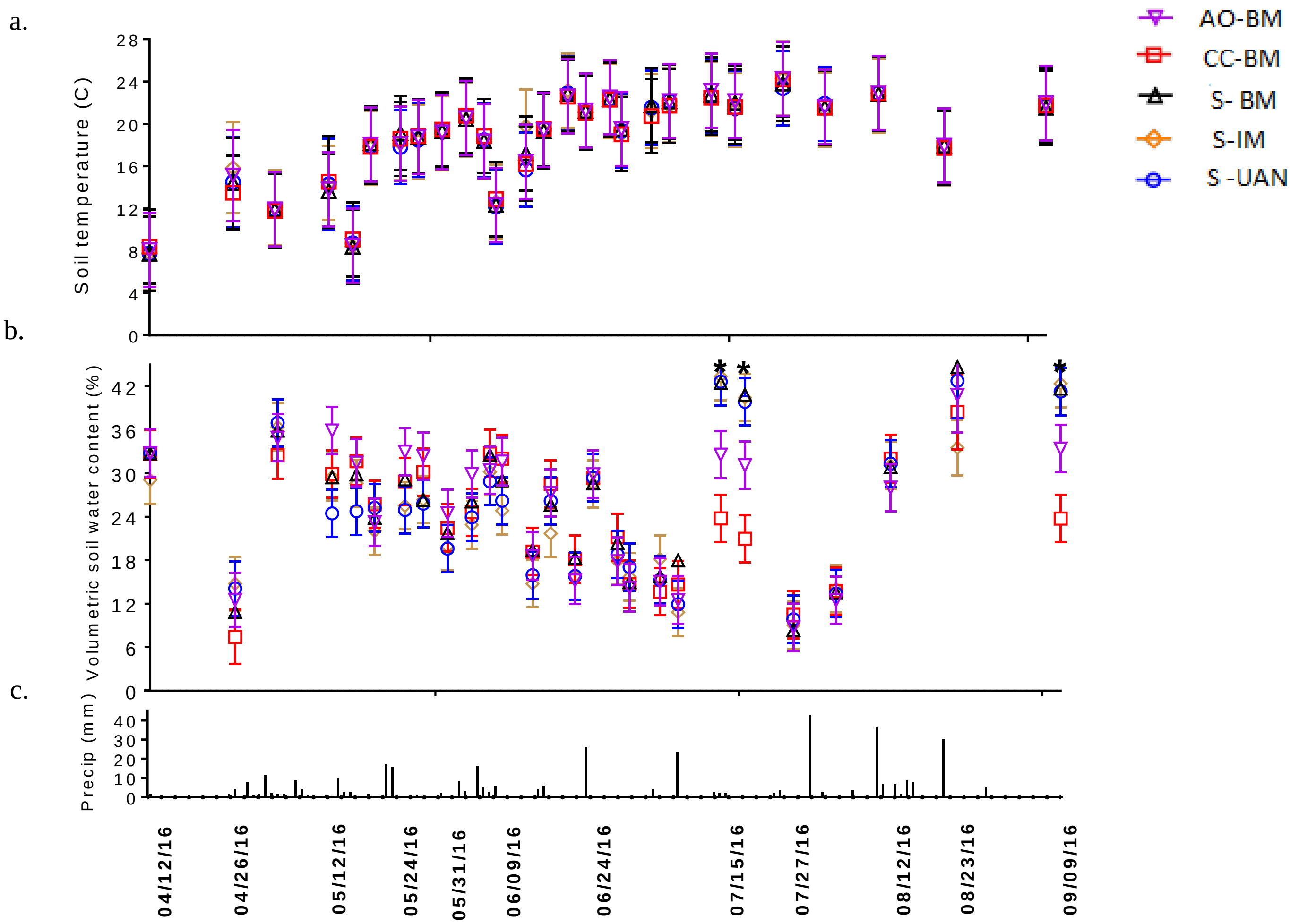

Fig 2. 3 2016 (a), soil temperature (10 cm depth) (b), volumetric soil water content (10 cm depth) and (c), precipitation during soil gas measurements in the corn following: alfalfa and orchardgrass with broadcast manure (AO-BM), crimson clover with broadcast manure (CC-BM), soybean with broadcast manure (S-BM), soybean with inorganic fertilizer (S-UAN), and soybean with injected manure (S-IM). * Significant difference among treatments at p value <0.01.

Spring crop aboveground biomass

Spring crop aboveground biomass differed by year but not by crop management. The alfalfa and orchardgrass biomass was 1.08 Mg ha^{-1} in 2015 and 2.75 Mg ha^{-1} in 2016. The C:N ratio of the alfalfa and orchardgrass aboveground biomass was 11.6 in 2015 and 11.5 in 2016. Crimson clover aboveground biomass was 1.56 Mg ha^{-1} in 2015 and 1.80 Mg ha^{-1}in 2016. The C:N ratio of the crimson clover aboveground biomass was 12.1 in 2015 and 11.0 in 2016. The C-S treatments had no living crop biomass in the spring only the residue from the soybeans that were harvested the previous autumn. Soybean average grain yields were 3.60 Mg ha^{-1}.

Soil inorganic nitrogen

In 2015 and 2016, NO_3^- -N and NH_4^+ -N soil concentrations in the upper 5 cm differed significantly across sampling dates ($P<0.0001$). The main effect of cropping system treatment was not significant, but the interaction between the cropping system treatment and sampling date was significant in both years ($P<0.0001$). The NO_3^- -N soil concentrations in CC-BM and S-IM were approximately 2 times greater compared to S-UAN on 25 May 2015 ($p= 0.0034$), and the NH_4^+-N in S-IM were 4 times greater than the other treatments on 27 May 2016 ($p= 0.0224$), approximately 20 days after manure application (Figs 2.4&2.5). In 2015, soil inorganic N significantly increased immediately after side-dress N application in S-BM (176 mg NH_4^+-N kg $soil^{-1}$ and 145 mg NO_3^- -N kg $soil^{-1}$) and was approximately 3 times greater than S-UAN (54 mg NH_4^+-N kg $soil^{-1}$ and 58 NO_3^- -N kg $soil^{-1}$) and 6 to 14 greater than the AO-BM and CC-BM treatments that did not receive inorganic fertilizer. Eight days after side-dress N application in 2015, soil inorganic N was not significantly different among treatment (Fig. 2.4). Precipitation events after fertilizer application likely moved soil NO_3^- to deeper layers or facilitated denitrification. However in 2016, the NO_3^--N concentrations were elevated for 4 weeks after side-dressing (>58 mg N kg $soil^{-1}$) in S-BM and S-UAN, and NH_4^+-N was elevated for 3 weeks in S-BM (49 mg N kg $soil^{-1}$) (Fig. 2.5).

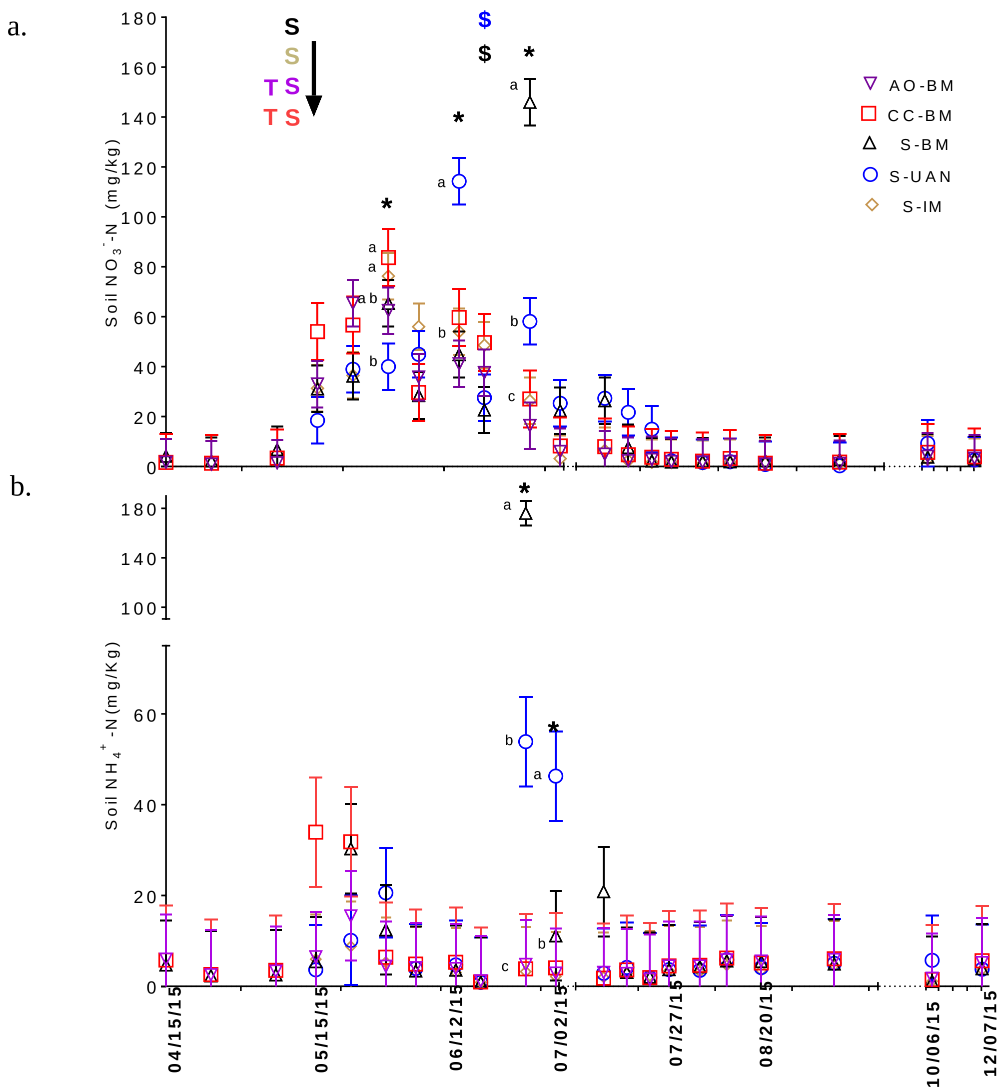

Fig 2. 4 2015(a), nitrate and (b) ammonium levels in the soil (0-5cm) during soil gas measurements in the corn following: alfalfa and orchardgrass with broadcast manure (AO-BM), crimson clover with broadcast manure (CC-BM) , soybean with broadcast manure (S-BM), soybean with inorganic fertilizer (S-UAN), and soybean with injected manure (S-IM). T indicates when the crop prior to corn was terminated; S indicates when manure was applied,↓ indicates when corn was planted, $ indicates when side-dress N was applied. * significant difference among treatments at p value <0.05. Different letters (a, b, c) indicate a statistical significance at P < 0.05

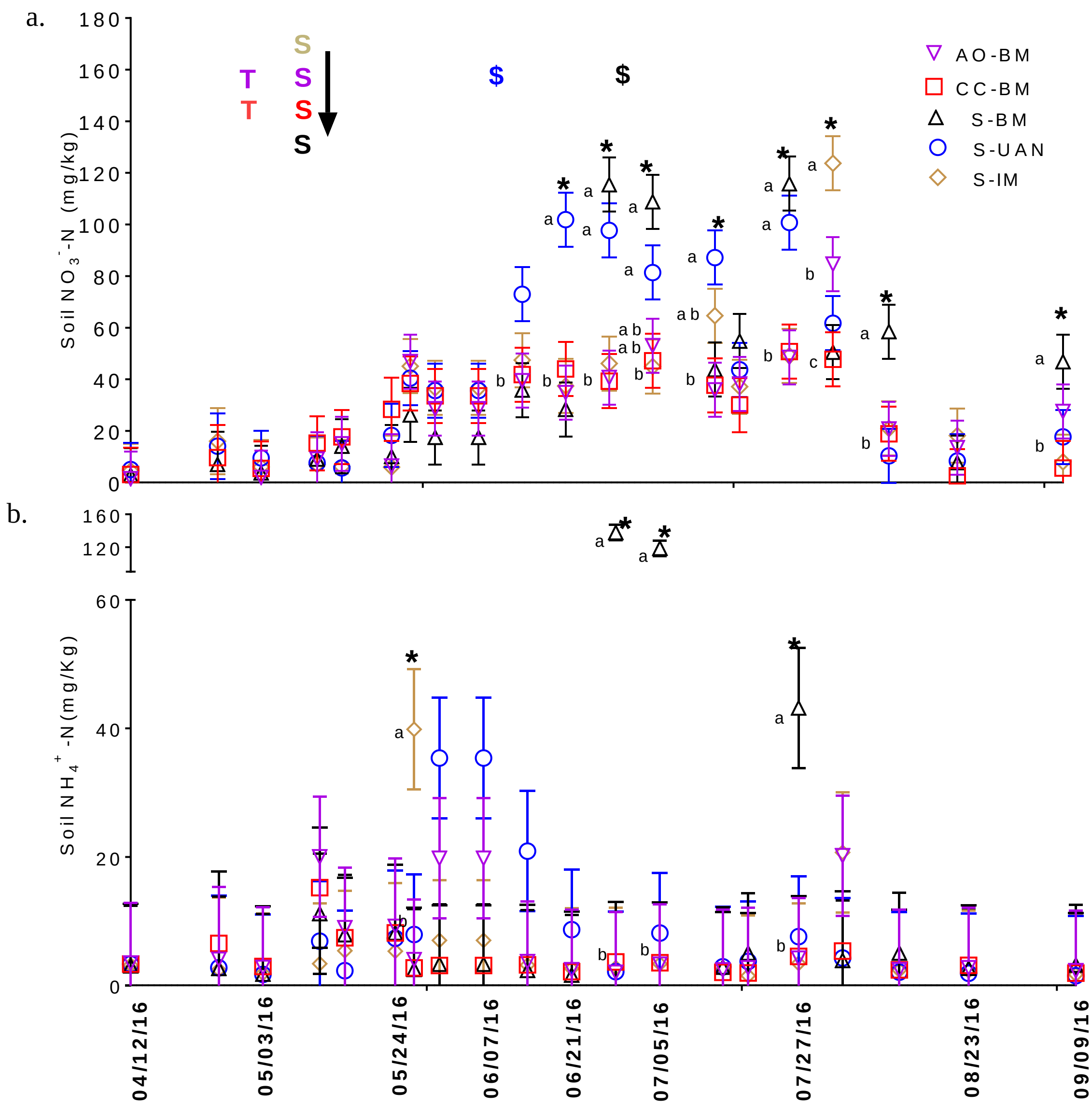

Fig 2. 5 2016 (a), nitrate and (b) ammonium levels in the soil (0-5cm) during soil gas measurements in the corn following: alfalfa and orchardgass with broadcast manure (AO-BM), crimson clover with broadcast manure (CC-BM) , soybean with broadcast manure (S-BM), soybean with inorganic fertilizer (S-UAN), and soybean with injected manure (S-IM). T indicates when the crop prior to corn was terminated; S indicates when manure was applied,↓ indicates when corn was planted, $ indicates when side-dress N was applied. * significant difference among treatments at p value <0.05. Different letters (a, b, c) indicate a statistical significance at P < 0.05

Nitrous oxide emissions

In 2015 and 2016, there were significant differences in N_2O emissions among cropping system treatments ($P=0.0005$ in 2015 and $P<0.0001$ in 2016) and sampling date ($P<0.0001$ for both years), and there were significant interactions between sampling date and cropping system treatment ($P<0.0001$ for both years). Emissions were significantly different among treatments in May and June after manure and inorganic fertilizer application, but not in July. In both years, N_2O emissions dropped in July likely because corn was actively growing and taking up the available N (Figs. 2.6&2.7).

In 2015 and 2016, N_2O emissions from S-IM were significantly higher compared to S-BM and S-UAN approximately 20 days after manure application ($P<0.0001$), with emissions of 421 kg $N\text{-}N_2O$ ha^{-1} d^{-1} and 122 kg $N\text{-}N_2O$ ha^{-1} d^{-1} respectively. By contrast in 2015, N_2O emissions from S-BM were 66 kg $N\text{-}N_2O$ ha^{-1} d^{-1} 20 days after manure application; and in 2016, N_2O emissions were lower after manure application, varying from 7 to 16 kg $N\text{-}N_2O$ ha^{-1} d^{-1}. In both years, emissions from S-IM were higher compared to S-BM and S-UAN. The higher emissions from S-IM were likely due to 10 cm deep manure band of concentrated N with high moisture and organic matter, which likely favored denitrification. Similarly, in a study conducted in an adjacent field, Duncan et al. (2017) found higher N_2O emissions from injected manure compared to unincorporated broadcast manure with emissions significantly increasing 7 to 10 days after manure application. These results are also consistent with others' findings that N_2O emissions from manure injection are higher than from surface application (Flessa and Beese, 2000; Velthof et al., 2003; Velthof et al., 2011). Despite the higher N_2O emission associated with shallow disk injection, the negative impact of N_2O increase must be weighed against value of other benefits; especially reducing ammonia emissions (Dell et al., 2012; Morken and Sakshaug, 1998), odor (Jacobson et al., 1999), and potentially increasing profits (Rotz et al., 2011).

Four days after side-dress inorganic fertilizer application in 2015, N_2O emissions in S-BM and S-UAN were significantly higher ($P=0.001$) compared to S-IM, likely promoted by precipitation events that created conditions favorable for denitrification (Fig. 2.6). In contrast, emissions in S-BM were low after side-dress N fertilizer application in 2016 (Fig. 2.7). Emissions in response to inorganic fertilizer application in S-BM varied between the years, probably because the side-dress inorganic fertilizer application coincided with a heavy rainfall in 2015, but not in 2016. In Canada, Mackenzie et al. (2000) also found higher N_2O emission fluxes when the soil was moist in June after side-dressing corn plots with ammonium nitrate. Similarly in Canada, Ma et al. (2010) reported that rainfall and favorable soil temperatures (> 15 °C) also stimulated N_2O emissions after side-dress fertilization in July.

In 2015, daily mean N_2O fluxes in AO-BM and CC-BM tended to increase 15 days after the previous crops were terminated and spring manure was applied, 51 kg N-N_2O ha^{-1} d^{-1} and 101 kg N-N_2O ha^{-1} d^{-1}, respectively (Fig 2.6). By 45 days after previous crops were terminated and manure was applied, the emissions were lower, varying in AO-BM from 0 to 7 kg N-N_2O ha^{-1} d^{-1} and in CC-BM from 0 to 6 kg N-N_2O ha^{-1} d^{-1}. As in 2015, N_2O emissions in 2016 were elevated 15 days after spring legume crops were terminated and manure was applied (72 kg N-N_2O $ha^{-1}d^{-1}$ and 70 kg N-N_2O ha^{-1} d^{-1}, respectively (Fig. 2.7)) and were significantly higher than the C-S treatments with the exception of S-IM. In 2016, N_2O emissions were elevated in May shortly after large precipitation events. Mineralized N from recently terminated legumes, manure application, and wet weather conditions favored denitrification early in the season. Also, higher N_2O emissions from AO-BM, compared to the C-S treatments with no spring residue, may be in part the result of higher soil labile C levels, as observed in a study in New York (Tan et al., 2009). In a study also conducted at Rock Springs, PA, Adviento-Borbe et al. (2010) found that N_2O fluxes were higher with corn following alfalfa with spring manure than with synthetically fertilized continuous corn. Contrary to our systems, in their study alfalfa residue was incorporated into soil prior to corn planting. They explained that the higher emissions could have happened because: 1) the organic N amendments increased C and N availability, leading to changes in microbial communities that increased N_2O emissions; and 2) perennial crops and manure application altered soil structure and aggregation, which influenced gas exchange. Perennial kura clover (*Trifolium ambiguum* M. Bieb.) in Minnesota also did not reduce N_2O emissions when integrated into a C-S rotation; even though N application rate was reduced by 43% compared to a conventional C-S system (Turner et al., 2016). In that field experiment, manure was not applied but mid-season fertilizer was applied to both systems. On the other hand, in a system in Canada where manure was not applied, Mackenzie et al. (2000) found that emissions of N_2O were higher in continuous corn than with corn planted after soybean or alfalfa. According to the authors, this was largely related to increased NO_3^- levels from the inorganic N fertilizer applications in the continuous corn that could have stimulated N_2O production.

The integration of alfalfa and orchardgrass and crimson clover in this no-till experiment was likely beneficial, because in the fall, winter and spring, these crops could have immobilized N that would otherwise have been available for N_2O production during the thaw period (Wagner-Riddle et al., 1998). Wagner-Riddle et al. (2007) reported that in eastern Canada, no-till systems contributed to reducing N_2O emissions compared to conventional tillage during the thaw period by 80%. The authors attributed this reduction to the insulating effects of the larger snow cover plus crop residue reducing soil freezing. Also, replacing winter fallow with perennial legumes and grasses can reduce N leaching that could indirectly contribute to N_2O emissions.

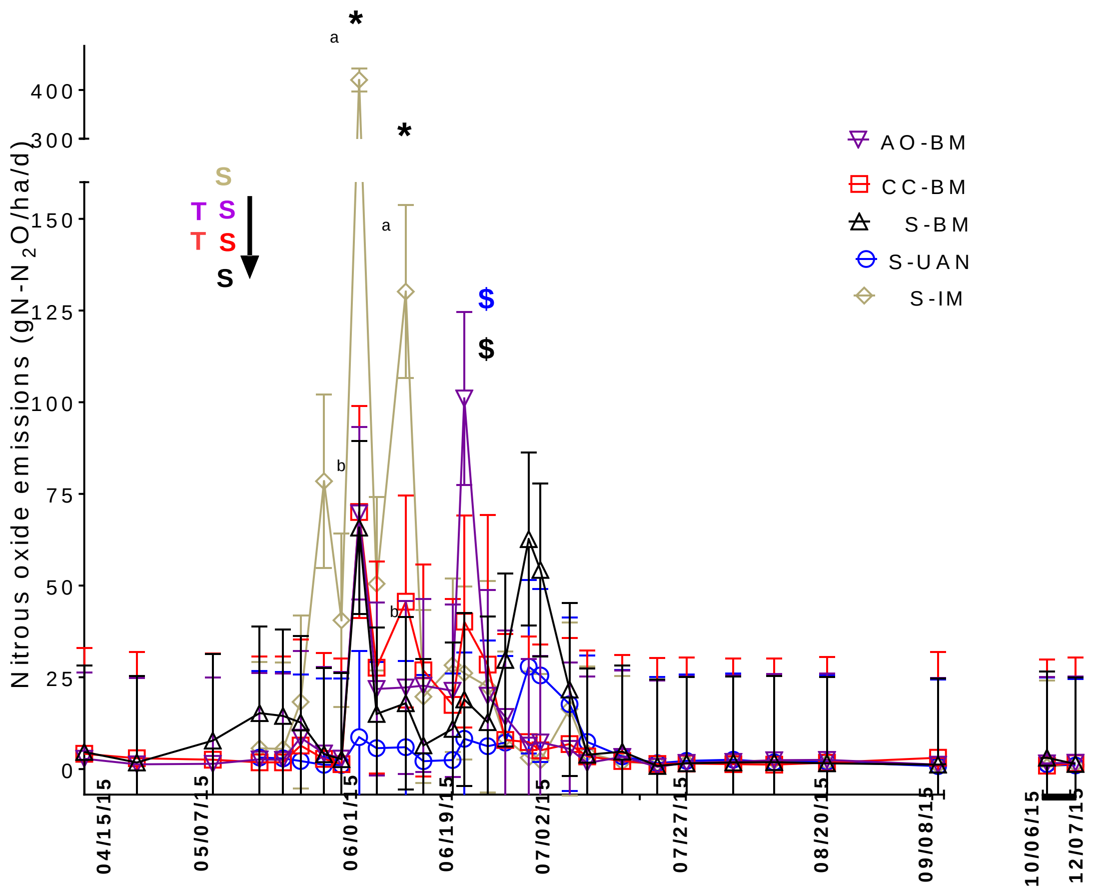

Fig 2. 6 2015 Nitrous oxide emissions from soil planted to corn after different crops and N amendments. T indicates when the crop prior to corn was terminated; S indicates when manure was applied,↓ indicates when corn was planted, $ indicates when side-dress N was applied * significant difference among treatments at p value <0.05. Different letters (a, b) indicate a statistical significance at P < 0.05.

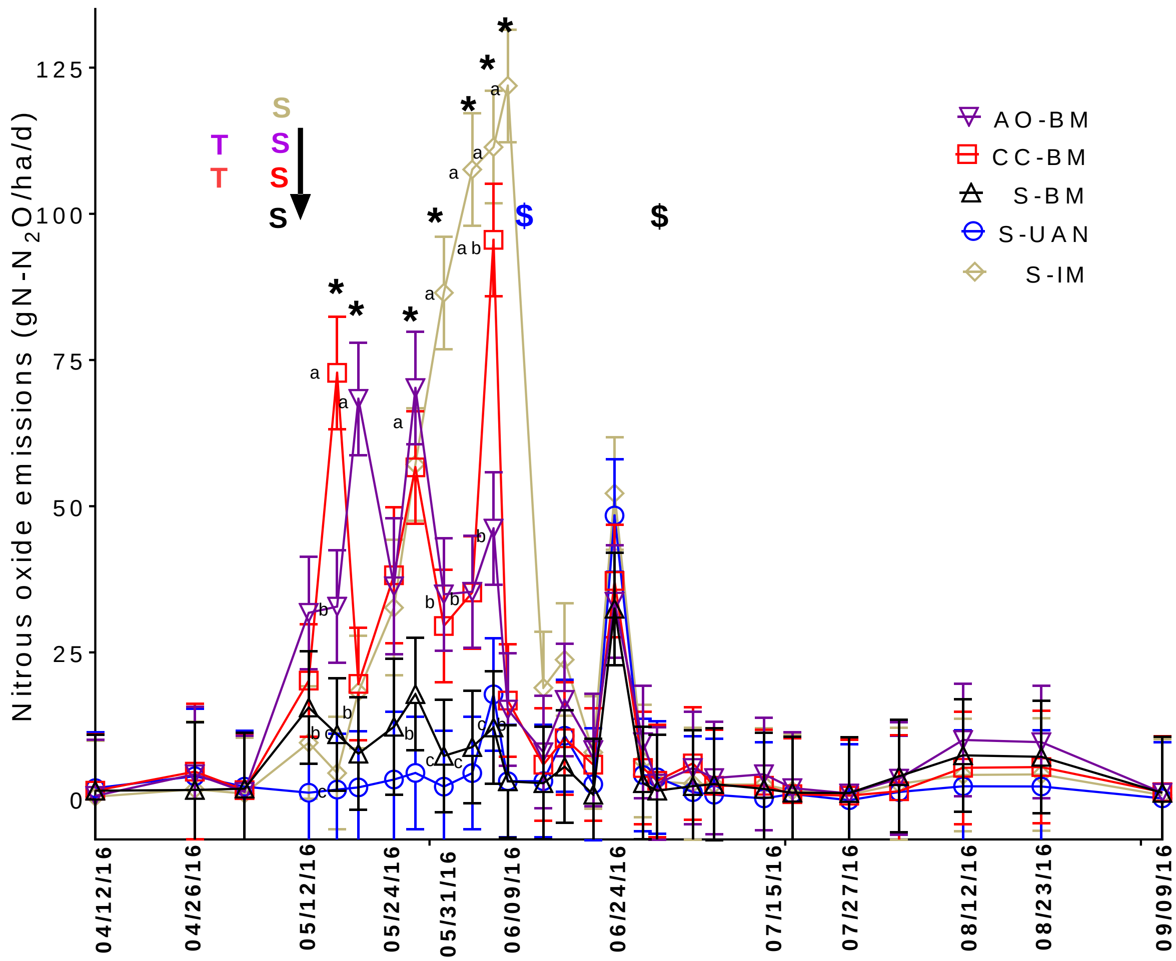

Fig 2. 7 2016 Nitrous oxide emissions from soil planted to corn after different crops and N amendments. T indicates when the crop prior to corn was terminated; S indicates when manure was applied,↓ indicates when corn was planted, $ indicates when side-dress N was applied * significant difference among treatments at p value <0.05. Different letters (a, b, c) indicate a statistical significance at P < 0.05

Cumulative N_2O emissions and N_2O emissions per unit available N applied

In 2015 and 2016, there were significant differences in cumulative N_2O emissions among cropping system treatments (P= 0.0292 and P=0.0088, respectively). In both years, S-IM had approximately 7 times greater N_2O emissions than S-UAN (Table 2.2). In 2015, AO-BM and CC-BM were not significantly different from the other treatments, but in 2016, AO-BM and CC-BM had higher N_2O emissions than S-UAN. The wet spring in 2016 likely contributed to the higher N_2O emissions in AO-BM and CC-BM relative to S-UAN than in 2015, which was a drier spring. The lower cumulative emissions of S-UAN relative to S-BM probably occurred because the UAN application allowed for a better synchronization between corn N uptake and N supply, which reduced excess inorganic N and potential N_2O losses relative to the manure that was applied prior to corn planting. With the exception of S-UAN in 2016, cumulative N_2O emissions in our study are within the range of total annual N_2O emissions reported from cropping systems in the central and eastern US, 400 to 19,300 g N_2O-N ha^{-1} y^{-1} (Cavigelli and Parkin, 2012). In a study in Kentucky, Sistani et al. (2010) also found no significant differences in N_2O emissions between UAN or manure surface- applied in no-till corn fields over 2 years. Similar to our systems with broadcast manure and UAN, but in tilled continuous corn in Indiana, Hernandez-Ramirez et al. (2009) found that cumulative N_2O emissions did not differ when UAN was applied at sidedress or when manure was applied in the spring. Cumulative N_2O emissions from their treatments varied from 5.93 to 9.55 kg ha^{-1} yr^{-1}. The higher cumulative N_2O emissions in their study are likely because the soils were under tillage for 8-9 years.

Previous studies have reported lower emissions in no-till soils after long-term adoption compared to tilled soils. For instance, a three decade corn-soybean tillage experiment in west-central Indiana showed that N_2O emissions under no-till were about 40% lower relative to moldboard plowing, and 57% lower relative to chisel plowing, but treatments did not differ significantly (Omonde et al., 2009). The authors suggested that N_2O emission tended to be higher under moldboard plowing and chisel plowing likely because soil organic C decomposition is associated with higher levels of soil–residue mixing and higher soil temperatures. In corn-soybean systems in Iowa, Parkin and Kaspar (2006) found that N_2O fluxes from no-till tended to be 29% lower than conventional till systems, but were not significantly different.

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Table 2. 2 Cumulative corn growing season N_2O emissions, estimated available N, N_2O -N emissions per unit available N applied, grain yield and N_2O -N emissions per unit grain yield from corn after the following crops and amendedments: alfalfa and orchardgrass with broadcast manure (AO-BM), crimson clover with broadcast manure (CC-BM), soybean with broadcast manure (S-BM), soybean with inorganic fertilizer (S-UAN) and soybean with injected manure (S-IM)

Year	Treatment	Corn growing season N_2O emissions (g N ha^{-1})		Estimated available N (kg N ha^{-1})	N_2O-N emissions per unit available N applied (%)		Grain yield (Mg ha^{-1})		N_2O-N emissions per unit grain yield (g N Mg^{-1} $grain^{-1}$)	
2015	S-IM	3050±196	a	179	1.8±0.1	a	8.9±1.2	a	322.8±50.2	a
	S-BM	1420±196	ab	179	0.9±0.1	ab	8.9±1.2	a	158.5±50.2	ab
	AO-BM	1262±196	ab	132	0.9±0.1	ab	10.2±1.2	a	124.9±50.2	ab
	CC-BM *	1194±232	ab	101	1.2±0.2	ab	NA		NA	
	S-UAN	436±196	b	226	0.4±0.1	b	11.4±1.2	a	55.1±50.2	b
2016	S-IM	2460±450	a	175	1.4±0.4	a	10±0.8	a	246.6±29.5	a
	S-BM	742±450	bc	179	0.3±0.4	ab	11.1±0.8	a	67.2±29.5	ab
	AO-BM *	1915±450	ab	143	1.4±0.4	a	NA		NA	
	CC-BM	1770±450	ab	102	1.7±0.4	a	11.7±0.8	a	146.9±29.5	ab
	S-UAN	370±450	cd	225	0.2±0.4	b	11.1±0.8	a	31.3±29.5	b

Mean ± standard error. Different letters (a, b, c, d) indicate a statistical significance at $P < 0.05$ within a year.
* Corn silage (89 RDM) was grown instead of corn grain (105 or 106 RDM) in the other treatments. Corn silage yield in 2015 was 46.7 Mg ha^{-1} and 43 Mg ha^{-1} in 2016.

In 2015, cumulative N_2O emissions per unit available N applied from AO-BM and CC-BM were not significantly different from the other treatments. In 2016, AO-BM and CC-BM only had higher emissions per unit of N applied than S-UAN (Table 2.2). Our results, on N_2O-N per N applied basis, are within the range of other studies in the central and eastern US, 0.13 to 17.9 % (Cavigelli and Parkin, 2012). Despite the small amount of N that was lost as N_2O in this study (0.4 to 1.8% of total applied N), the N_2O global warming potential is 298 times that of carbon dioxide (CO_2) over a 100-year period (US EPA, 2016) and it is currently the dominant ozone-depleting substance (Ravishankara et al., 2009).

While N_2O emissions were not reduced with alfalfa and crimson clover in the rotation, life cycle analysis is likely to show these systems can help reduce global warming potential by reducing greenhouse gas (GHG) emissions associated with the production of the inorganic N fertilizers and by increasing soil C sequestration. Camargo et al. (2013), using the Farm Energy Analysis Tool (FEAT), estimated that using no-till and legume cover crops in rotation prior to corn relative to no-till with synthetic fertilizer reduced GHG by 8% by replacing the use of synthetic fertilizer. Chianese et al. (2009) used IFSM, a process-based whole-farm model, and estimated that reducing the use of inorganic fertilizer by adding a mulch cover crop of rye to corn reduced N_2O emission by 34% and all GHG by 7%.

Grain yield and yield-scaled N_2O emissions

In 2015, average corn grain yield was 9.85 Mg ha^{-1} and was not significantly different among the treatments that received organic N inputs from manure and/or crop residues (Table 2.2). Similarly, in 2016, grain yields averaged 10.98 Mg ha^{-1} and the effect of cropping system treatment was not significant. In a study carried out in Maryland, corn grain yield in a 6-year organic rotation that included corn-soybean, winter wheat, and 3yrs of alfalfa, was on average 30% greater than in a 2-year rotation that included only summer annual cash crops (Cavigelli et al., 2013). The authors explained that this happened as a result of increased N availability and decreased weed competition as crop rotation length and complexity increased. Contrary to their cropping system management, in this experiment inorganic N was applied in all treatments that needed supplemental N to meet corn yield goals, which may explain why the effect of diverse rotations on yield was not observed in 2016.

In 2015 and 2016, the cropping system treatment had a significant effect on N_2O emissions per unit of grain yield, P=0.023 and P=0.01., respectively. In 2015 and 2016, S-UAN had lower N_2O cumulative emission per unit grain yield than S-IM (Table 2.2). Integration of perennial and cover crop legumes in the cropping system did not reduce N_2O emissions per unit of grain yield relative to S-UAN. As in our study, Osterholz et al. (2014) found that cropping system treatment did not significantly affect yield-based emissions in grain and forage-based productions systems in Wisconsin. Additionally, they found that corn that received dairy slurry in the spring and followed two years of alfalfa had greater yield-scaled N_2O emissions compared to corn following soybean fertilized with UAN.

Main drivers contributing to N_2O fluxes

Random forest analysis explained 48% of variation in N_2O emissions measured in 2015 and 2016. Days after manure application was identified as the most important variable, followed by days after previous crop termination, soil NO_3^- levels, and soil moisture (Fig 2.8). Figs. 2.6 &2.7 show the highest emissions after manure application and previous crop termination which likely coincided with mineralization of these organic N amendments prior to rapid corn N uptake. By contrast, later in the season after inorganic N fertilizer application, emissions were low. These results suggest that synchronizing manure application and crop residue termination with crop N uptake is critical to reduce N_2O emissions from these no-till dairy-cropping systems.

A study carried out by Fernández et al. (2016), also showed that timing inorganic fertilizer application close to crop N uptake reduced emissions. They compared a split application to a single application in drained and undrained soils, and emissions were reduced with a split application in both drainage systems. These results also suggest that reducing inorganic fertilizer additions to the lowest levels that still ensure optimal corn yield and, therefore reducing NO_3^- accumulation in the soil, can reduce N_2O emissions. The PSNT test allowed for informed N fertilizer management and reduced excess NO_3^- that could be lost as N_2O. As in our study, previous studies have shown that soil NO_3^- was one of the main factors driving N_2O emissions (Gomes et al., 2009). Research has also shown that higher NO_3^- concentrations inhibits N_2O reductase activity, which converts N_2O to N_2, resulting in higher N_2O emissions (Weier et al., 1993).

As identified before, soil moisture content was one of the major influences on denitrification and, N_2O emissions (Linn and Doran, 1984; Clayton et al., 1997) as gas diffusivity is low and aeration is poor (Davidson et al., 2000). In our study, a mulch of crop residue accumulated on the soil surface with no-till soil management and likely contributed to reduced evaporation and increased soil moisture content. Also in a system that was under no-till management for less than 10 years, higher denitrification losses were reported compared to conventional tillage, due to higher soil moisture contents (MacKenzie, et al. 2010). As in our study, previous studies also found that, when fertilizer application coincided with high rainfall, favorable conditions for denitrification stimulated the production of N_2O (Mitchell et al., 2013).

Understanding which management variables influence N_2O emissions can help improve effective N management without decreasing yield goals. Management of combinations of organic

N sources associated with N_2O emissions in dairy cropping systems should be assessed in future studies to evaluate the potential of using cover crop legumes, perennials and manure for increasing both the agronomic and environmental efficiency of dairy cropping systems.

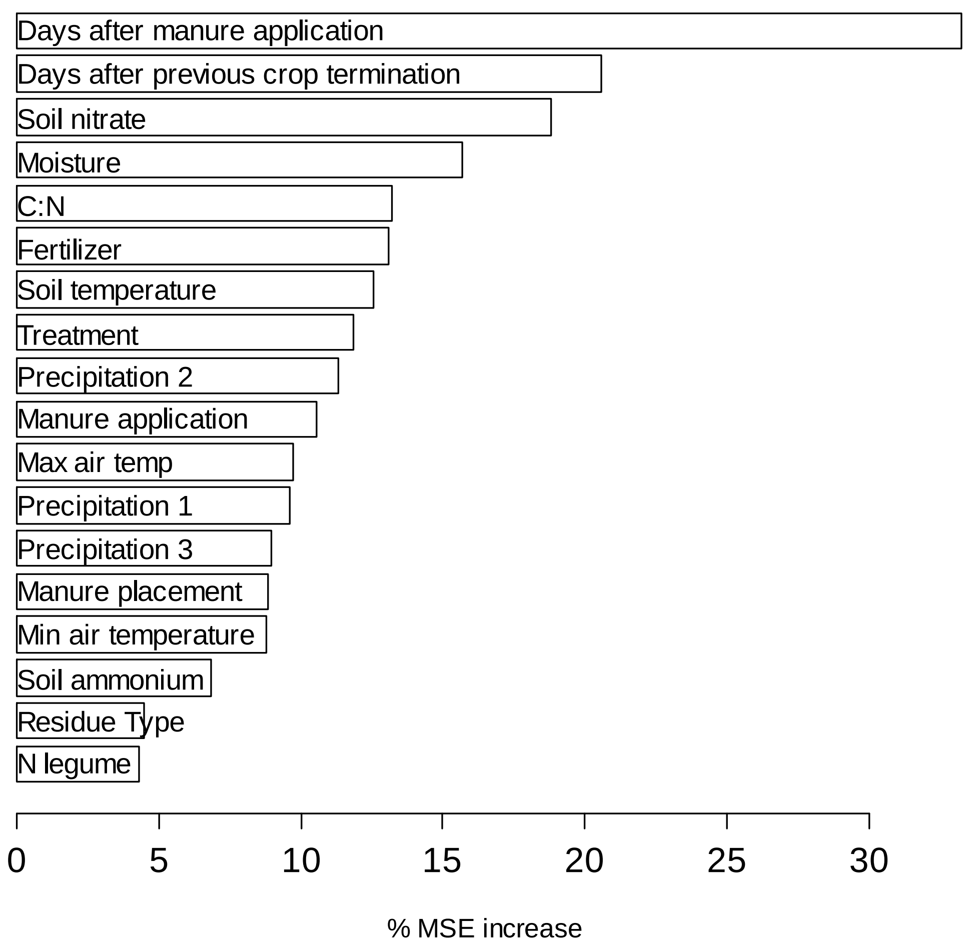

Fig 2. 8 Variable importance plots for predictor variables from random forests (RF)

Conclusion

Diversification of crop rotations, greater use of organic nutrient amendments, reduced tillage, and the integration of cover crops provide the potential to increase the sustainability of crop production, yet these practices can also impact greenhouse gas emissions. Integration of perennial and cover crop legumes and dairy manure in this study contributed to meeting yield goals with reduced use of inorganic fertilizer; but did not reduce direct cumulative N_2O emissions compared to corn following soybean with manure or UAN. Elevated soil N_2O emissions were observed between 15 and 42 days after spring crop termination and manure application. Although manure injection has many benefits, including reducing NH_4^+ volatilization and supplemental inorganic fertilizer use, when manure was injected in corn after soybean higher N_2O emissions were observed compared to when manure was broadcasted in one out of two years and compared to UAN in both years. The higher N availability, C, and moisture concentration in the 10 cm injection band likely favored N_2O production by denitrification.

The management and environmental variables included in the Random Forest analysis explained about 48% of the variability in the N_2O emissions. Time after manure application, days after previous crop residue termination, soil nitrate, and moisture were identified as the main variables driving N_2O emissions. These results suggest that practices to reduce N_2O emissions should include synchronizing N application events with plant N demand, and avoiding application of N when there is a high chance of heavy precipitation.

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Chapter 3

Simulation of nitrous oxide emissions in dairy cropping systems

Abstract

Dairy farms account for the highest agricultural sales in Pennsylvania ((USDA NASS, 2014) and are major contributors to the northeastern US economy In dairy cropping systems, legume cover crops and perennials, and the use of dairy manure offer alternatives to inorganic nitrogen (N) fertilizer, yet they impact nitrous oxide (N_2O) production. The purpose of this study was to compare N_2O fluxes predicted by the DAYCENT model to two growing seasons of measured N_2O fluxes from corn in a no-till conservation dairy cropping system in central Pennsylvania and a corn-soybean rotation without a cover crop. The cropping systems were initiated in 2010 and include corn treatments with or without crops growing the prior winter with manure applied; and treatments without prior winter cover with or without manure. Soil temperature, volumetric soil water content (VSWC), and inorganic N, simulated by DAYCENT, were also compared to field-measured values. We observed that in general DAYCENT accurately predicted soil temperature in summer; but in spring, DAYCENT-predicted soil temperatures tended to be lower than measured values. VSWC predicted by DAYCENT were generally lower than measured. After precipitation events, DAYCENT predicted that VSWC tended to rapidly decrease and drain to deeper layers. Soil inorganic N was underestimated in all of the treatments except for ammonium in corn following soybean with inorganic fertilizer in both years. In general, N_2O emissions were overestimated for the corn following soybean with inorganic fertilizer and broadcast manure. On the other hand, simulated N_2O emissions were underestimated compared to measured fluxes for the corn following alfalfa and orchardgrass in both years and crimson clover in one out of two years. Daily N_2O emissions simulated by DAYCENT had between 41% and 76% agreement with measured daily fluxes in 2015 and 2016.The mean absolute error and root mean square error were low for all treatments in both years, ranging from 1.22 to 1.86 g N_2O-N d^{-1} and 1.65 to 3.6 g N_2O-N d^{-1}, respectively. Elevated N_2O emissions in July, August and September were simulated, but not observed, and followed a temporal pattern of simulated VSWC, suggesting that conditions were favorable for denitrification. Our results suggest that DAYCENT overestimated the residual

inorganic N fertilizer impact on N_2O emissions in the corn following soybean with inorganic fertilizer and broadcast manure. Comparisons between DAYCENT-simulated and measured N_2O fluxes suggest that DAYCENT does not simulate effects of organic N inputs from perennials and legume cover crop residues and manure application in no-till dairy systems well. In these systems mineralization of organic residues and nitrification likely happened faster than DAYCENT predicted.

Introduction

Nitrous oxide (N_2O) is a potent greenhouse gas (GHG) which has a global warming potential that is 298 times that of carbon dioxide (CO_2) over a 100-year period (US EPA, 2016). Since 1950, N_2O concentration in the atmosphere has increased by 14% and reached 327 ppb in 2015 (US EPA, 2016). Agricultural soils in the U.S, particularly croplands, are the main source of N_2O contributing 185 MMT CO_2 Eq., while grasslands contribute 76 MMT CO_2 Eq. (US EPA, 2016). Nitrous oxide is produced in soils, primarily by the microbial processes of nitrification and denitrification. Management practices such as application of N fertilizers, crop type, and tillage influence soil conditions and the extent of N_2O production. Emission rates of N_2O from soils vary with changes in moisture content, porosity, temperature, oxygen (O_2) concentration, nitrogen (N) content of the soil and available carbon (C) (Robertson and Groffman, 2007). In the eastern U.S, denitrification is generally considered to be the dominant source of N_2O emissions from moist soils (Cavigelli et al., 2012); however, if soils receive ammonical fertilizers, nitrification may be the dominant source (Venterea, 2007).

In Pennsylvania dairy cropping systems, heavily fertilized crops (e.g. corn) have been estimated to be the greatest contributor of N_2O emissions with 485 kg N-N_2O ha^{-1}, followed by manure storage with 197 kg N-N_2O ha^{-1} (Chianese et al., 2009). Most of the N_2O emissions resulting from manure are from manure-amended soils compared to manure storage (Montes et al., 2013). Animal manures are likely to increase soil N_2O emission compared to inorganic fertilizer because manure provides C, which stimulates heterotrophic respiration and depletes O_2 concentration, favoring denitrification (Cavigelli and Parkin, 2012). However, as noted by Cavigelli and Parkin (2012), N_2O emissions from manures can be reduced by increasing C:NO_3^-

ratio. Some studies found no significant difference in N_2O emission between inorganic fertilizer or manure applied in spring to corn (*Zea mays* L.) in tilled (Hernandez-Ramirez et al., 2009) or no-till soils (Sistani et al., 2010). However, in soils with a long-term history of manure application, residual C and N likely contributed to increased N_2O production (Spargo et al., 2011; Chang et al., 1998).

In the northeastern US, cover crops are often grown from late fall until early spring. The effect of cover crops on N_2O emissions has been found to depend on whether the crop is a legume or grass, cover crop residue management and weather conditions. A meta-analysis conducted by Basche et al. (2014) on the effect of cover crops on N_2O emissions indicated that emissions tended to be greater with legume cover crops compared to grasses. A meta-analysis conducted by Chen et al. (2013) on the effect of the C:N ratio of crop residues on N_2O emissions showed that emissions were not reduced until C:N ratios were above 45 and that the most N_2O production occurred when soil water-filled pore space was between 60 and 90%. Their analysis suggested that crop residue not only supplies N for N_2O but also stimulates microbial respiration and O_2 depletion, and therefore, promotes anaerobic conditions for denitrification. In Pennsylvania, synthetically fertilized continuous corn under conventional tillage resulted in lower N_2O emissions than corn following alfalfa (*Medicago sativa* L.) (Adviento-Borbe et al., 2010). The authors explained that the higher emissions after alfalfa could be due to higher labile C and N availability leading to changes in microbial communities that increased N_2O emissions. Additionally, the perennial crop altered soil structure and aggregation which influenced gas exchange and N_2O diffusivity. By contrast, overwintering crops can capture nitrate (NO_3^-) available at the end of the season, and reduce N_2O emissions. In Michigan, McSwiney et al. (2010) found that planting winter annual crops, cereal rye (*Secale cereale* L.), and wheat (*Triticum aestivum* L.) as a cover crop, decreased mineral N availability for N_2O production compared to a treatment with no cover crop. In Iowa, Mitchell et al. (2013) also found that the corn planted after rye cover, without fertilizer, decreased soil NO_3^- concentration and N_2O emissions compared to a treatment with no cover crop or fertilizer.

Models that simulate N_2O fluxes from agricultural soils are needed to better assess human activities that contribute to soil N budgets (Parton et al., 2001). Models offer an alternative to direct measurement, which traditionally has done using field-based chambers. The application of models can allow prediction of responses to climate changes and soil and crop management practices that may influence N_2O emissions (Jarecki et al., 2008). The finer time-scale resolution of models enables simulation of N gas emission from soils (Del Grosso et al., 2011a). The DAYCENT model is the daily time step version of the Century model, and it has been widely-used to simulate GHG emissions at a national scale (Del Grosso et al., 2006), regional level (Del Grosso et al., 2005), and field-scale (Jarecki et al., 2008; Abdalla et al., 2010; Gaillard et al., 2016, Field et al., 2016; Scheer et al., 2014; Ryals et al., 2015). DAYCENT simulates N cycling in a daily time step as a function of organic matter decomposition rates and environmental variables such as soil water and temperature. After mineralization, N from manure amendments and legumes provides substrates for nitrification and denitrification, as well as for plant growth (Del Grosso et al., 2011a). On the other hand, inorganic fertilizer application directly increases the pool of mineral N available for plant growth and microbial processes that can result in trace gas production (Del Grosso et al., 2011a). A sensitivity analysis showed that simulated N_2O emissions increase with N application rate and as soil texture becomes finer (Del Grosso et al., 2006).

In Pennsylvania, dairy farms typically produce corn-alfalfa rotations though some farmers integrate rye cover crops. Most of the land is managed with no-till or conservation tillage practices rather than conventional tillage (USDA NASS, 2014). Few studies (Adviento-Borbe et al. 2010, Duncan et al. 2017) have evaluated the impact of two or more sources of N inputs on N_2O emissions in dairy cropping systems in the Northeastern US. Comparisons of DAYCENT simulated N_2O fluxes for major cropping systems in the US have shown that simulated N_2O fluxes typically compared well with measured values (Del Grosso et al., 2006). However, to our knowledge DAYCENT has not been calibrated for no-till dairy cropping systems with larger crop residue inputs from perennials and/or legume cover crops. The objective of this study was to test how well the DAYCENT model predicted N_2O fluxes from an experimental no-till corn field that received manure and/or inorganic fertilizer without crop residues; or with crop residues from perennial legume/grass forages or a legume cover crop and manure. DAYCENT- simulated soil temperature, volumetric soil water content (VSWC), NO_3^- and ammonium (NH_4^+) levels were compared to measured values.

Materials and Methods

Experimental data

The DAYCENT model was evaluated against field measurements, collected in 2015 and 2016, quantifying N_2O emissions, soil temperature, VSWC, and soil NH_4^+ and NO_3^- concentrations. The cropping systems sampled are part of the NESARE Dairy Cropping Systems experiment at the PSU Russell E Larson Agronomy Research Farm, PA, USA (Latitude 40^o43’12”; Longitude 77^o56’02”; Elevation 366m). The dairy cropping systems were designed to produce the feed required to maintain a dairy herd of 65 cows on the farm using 1/20th scale of 100 ha of land. In the systems, corn was grown for both silage and for grain. The corn entries (previous crop-N amendment) selected for this study were: alfalfa and orchardgrass (*Dactylis glomerata* L.) with broadcast manure (AO-BM), crimson clover (*Trifolium incarnatum* L.) with broadcast manure (CC-BM), soybean (*Glycine max* L. Merr.) with broadcast manure (S-BM), and soybean with liquid urea ammonium nitrate fertilization (S-UAN). Nitrous oxide fluxes were measured from each treatment plot throughout the corn-growing season using closed chambers (78.5 cm x 40.5 cm). The chamber design followed the static-chamber methodology for measuring trace gas fluxes (Parkin and Ventera, 2011). Chamber frames were placed perpendicularly between two corn rows in two locations in each treatment plot within three experimental blocks. Gas samples were collected at 10, 20, and 30 minutes after placing the cover over the frame. Ambient air samples were used as the time 0 measurement. Emission rate was calculated by linear regression of change in N_2O concentration versus time since chamber deployment. Gas samples were analyzed using a Varian 3800 (Varian Inc., USA) gas chromatograph with an electron capture detector and an automated computer that controlled the sample injection system. Soil temperature (Model HI 145, Hanna Instruments) and VSWC (Model ML3 ThetaProbe, Delta-T Devices) were measured from the 0-10 cm soil depth every time N_2O gas samples were collected. Soil samples were collected weekly for the 0- 5 cm depth and analyzed for NH_4^+ and NO_3^-. A detailed description of the study site and measurements can be found in Chapter 2.

DAYCENT model

The DAYCENT model is an ecosystem model that simulates terrestrial C, N, P, and S dynamics and includes sub-models for land surface processes, plant productivity, soil organic matter decomposition, and trace gas fluxes (Parton et al., 2001). Soil temperature and moisture are the key factors controlling plant growth, decomposition and denitrification. The plant productivity sub-model simulates growth of various crops from planting to harvest. Carbon and N content of above and below-ground plant components are modeled. The model assumes that C decomposition flows are associated with microbial activity and that microbial respiration occurs for each of these flows. Plant residue and organic matter additions are partitioned into structural and metabolic pools based on the lignin:N ratio. The metabolic pool consists of easily decomposable materials and the structural pool contains material with lower decomposition rates including all of the plant lignin. Soil organic matter is divided into three pools based on turnover rates: active (0.5 to 1 year turnover), slow (10 to 50 year turnover), and passive (1000 to 5000 year turnover). Each pool has a fixed C:N ratio and decomposition rate is influenced by soil clay content, soil moisture, and temperature. DAYCENT simulates N cycling as a function of organic matter decompositions rates and environmental variables. Nitrogen mineralization, N fixation, N fertilization and N deposition supply the available N pool (Parton et al., 2001).

DAYCENT simulates N_2O emissions through the processes of nitrification and denitrification. To calculate N_2O emissions from nitrification, a function of soil NH_4^+ concentration, water filled pore space (WFPS), temperature, pH and texture is used (Parton et al, 2001). To calculate N_2O emissions from denitrification, a function of soil NO_3^- concentration, heterotrophic CO_2 respiration rate, soil bulk density, soil texture, and volumetric field capacity (cm^3 H_2O cm^{-3} soil) is used (Parton et al, 2001). The model assumes that the process is controlled by the input that is most limiting. Soil heterotrophic CO_2 respiration is used as a proxy for labile C availability. The model assumes that N_2O fluxes from denitrification occur after intense rainfall and during snow melt (Parton et al., 1998), when WFPS values are in the interval ~55% <WFPS<~90% (Parton et al., 2001). Nitrous oxide emissions are calculated from N_2 + N_2O gas emissions and with an N_2:N_2O ratio function (Parton et al 2001). The N_2:N_2O ratio of gases emitted increases as the NO_3^-:labile C ratio decreases and as soil gas diffusivity and O_2 availability decrease (Del Grosso et al., 2000).

DAYCENT simulation

The DAYCENT simulation was performed using daily local air minimum and maximum temperature, daily precipitation, solar radiation, wind speed, and relative humidity. The majority of the data was from a weather station located near the field experiment, but when the weather station mal-functioned, additional weather data was used from a weather station located less than 0.5 km from the experiment (http://wcc.sc.egov.usda.gov/reportGenerator).

For simulation purposes, soil textural properties for a silt loam soil were used (23% clay, 62% silt, 15% sand) (NRCS, 2016). The saturated hydraulic conductivity used was also based on a silt loam soil texture (4.23 µm sec^{-1}). Soil organic matter content was measured in 2014 from soil samples collected randomly across plots. Average organic matter content in each soil layer was calculated for each treatment and was used in this model. Average measured soil pH input in the model was 6.9. Field capacity of the soil was assumed to be 0.33 cm^3 water cm^{-3} soil, and the permanent wilting point was assumed to be 0.13 cm^3 water cm^{-3} soil.

To initialize the C and N pools five sets of simulations were run. Data about these management practices were collected from the Agronomy Research Farm Manager, Scott Harkcom (personal communication, 2016). From 1 BC to 1920 AD, the sampled fields were under native forest vegetation. The crop rotation from 1921 to 1940 was corn, oats/wheat, hay, and potatoes without inorganic fertilizer application and with conventional tillage. From 1941 to 1983, the crop rotation was corn, oats/wheat, hay, and potatoes with inorganic fertilizer application and conventional tillage. From 1984 to 2009, the rotation was corn, soybean, and wheat with inorganic fertilizer application managed with no tillage. From 2010 to 2016, the current agricultural practices were used. The first four crop history simulations initialized the soil organic matter pools in the model to provide native baseline to compare with those from agriculture. The simulations assumed conventional tillage cultivation, gradual improvement of cultivars, and gradual increases in synthetic fertilizer. The model has the ability to generate long-term statistical weather data based on the present limited weather data.

The DAYCENT files that schedule agricultural practices were based on records of when these management events were actually implemented. The no-till effect was simulated with the worms (*W*) subcommand in the cultivation parameters. This parameter specifies that 0.5 of the surface litter is transferred to the top soil layer. Liquid dairy slurry was analyzed for C, N, and lignin content and these values were added to the structural and metabolic pool using the omadtyp(1) subcommand for the simulations in 2015 and 2016.

Initial simulations used default model parameters; however, this resulted in underestimated N_2O emissions from treatments that received organic amendments. This was likely due to a limit on the C for denitrification. Therefore, the respiration constraint was turned off approximately 28 days after organic N application and approximately 6 days after inorganic fertilizer application. To simulate rapid accumulation of early-season N_2O emissions after N application, another DAYCENT simulation study found that turning off the respiration constraint produced favorable simulations of N_2O emissions (Gaillard et al., 2016).

Corn grain growth was simulated with a harvest index of 0.6 and a coefficient for calculating potential aboveground production (prdx(1)) as a function of solar radiation of 1.1. Corn silage was simulated with 0.9 aboveground biomass removed. To reduce sensitivity to moisture stress, the relative water content of the wettest soil layer in the rooting zone used was reduced from 0.38 to 0.2. Another simulation study in Kansas and Oklahoma with non-irrigated switchgrass cultivation reported that modifying this parameter allowed for better simulation of plant growth (Field et al., 2016). The default parameters for the soybean planted before corn was used in the simulation, and the crimson clover crop was simulated with the parameters of a temperate clover pasture. The alfalfa and orchardgrass mixture was simulated using alfalfa default parameters and the N fixing factor was reduced based on the ratio of alfalfa to total biomass (0.6 and 0.5 in 2015 and 2016, respectively), from 0.07 to 0.045 in 2015 and to 0.035 in 2016.

Statistical analysis

The statistical measures used to assess the accuracy of model predictions were the mean absolute error (MAE), the root mean square error (RMSE) as recommended for DAYCENT simulations studies (Del Grosso et al., 2011b), and an index of agreement (IA) (Willmott, 1981) in R statistical software (R Development Core Team 2013) using the “hydroGOF” package. The MAE gives equal weight to all errors, while RMSE gives extra weight to large errors. As with these indices, the IA is related to the size of the differences between observed and simulated variates (Willmott 1981). The correlation between observed and simulated data was also calculated.

Preliminary analysis of measured and simulated N_2O fluxes failed Levene’s test for equal variances ($p<0.05$) and normality; therefore N_2O data was log transformed. The NO_3^- and NH_4^- data did not satisfy the assumption of normality after transformation, and therefore untransformed data was assessed. Since we had large enough sample sizes (> 100), the violation of the normality assumption for our data should not cause major problems (Ghasemi and Zahedias, 2012). According to the central limit theorem, in large samples (> 30 or 40), the sampling distribution tends to be normal, regardless of the shape of the data (Ghasemi and Zahedias, 2012). The assumptions of normality and constant variance were met for the other variables in the study.

Mean Absolute Error $=\sum_1^n |M - O|/n$

Root Mean Square Error = $\left(\sum_1^n (M - O)^2/n\right)^{1/2}$

$$\text{Index of Agreement} = 1 - \left[\frac{\sum_1^n (O - M)^2}{\sum_1^n \left(|M - \overline{O}| + |O - \overline{O}| \right)^2} \right]$$

Where *n* is the number of data observations, *M* is modelled data, and *O* is observed data.

Results and Discussion

Environmental factors

Precipitation during the growing season varied widely between 2015 and 2016. May was a drier month in 2015 (64 mm) compared to 2016 (86 mm), and the amount of precipitation was higher in June and July of 2015 (294 mm) compared to 2016 (164 mm). In both years, soil temperatures were cooler in April (avg. temperature of 9 °C) and warmer in June (20 °C). A detailed description and figures can be found in Chapter 2.

Nitrous oxide fluxes from corn following soybean with inorganic fertilizer or broadcast manure (S-UAN and S-BM)

Results for the measured N_2O emissions are shown at each sampling date and simulated N_2O fluxes are shown in a daily time step through the sampling period (Figs. 3.1 & 3.2). In both years, mean daily simulated N_2O fluxes for S-UAN were higher than the measured fluxes, by 63% in 2015 and 78% in 2016 with mean values of 9.2 ±1.6 g N-N_2O ha^{-1} and 8.9±1.6 g N-N_2O ha^{-1} (Tables 3.1 & 3.2). Similarly, in both years, simulated cumulative N_2O emissions in S-UAN was higher than cumulative measured fluxes by 46% in 2015 and 82% in 2016 (Table 3.4).

In S-UAN, the measured N_2O fluxes increased as much as 4 to 6 fold four days after UAN was applied in 2015, and 3 to 5 fold after application in 2016. These elevated emissions, however, were not simulated by the model (Figs. 3.1a & 3.2a). Conversely, DAYCENT simulated elevated N_2O emissions later in the season which could be attributed to a residual effect of the UAN application; however, we did not observe elevated emissions later in the field. This could also be because rapid N uptake by corn later in the season was not predicted well. Due to the time delay of the simulated N_2O emissions in both years with S-UAN, in 2015 the correlation was 0.53 and in 2016 the correlation was 0.55. The MAE was lower for 2016 than for 2015 (0.71 g N-N_2O ha^{-1} vs 1.66 g N-N_2O ha^{-1}, Table 3.3). Also, the RMSE was lower in 2016 compared to 2015 (1.28 vs 3.42 g N-N_2O ha^{-1}, Table 3.3). The higher errors in 2015 likely resulted from high spatial variation in the N_2O measurements.

In 2015, mean daily simulated N_2O fluxes for S-BM were similar to the measured fluxes; simulated values were only 4% higher with mean values of 14.1 ± 3.3 g N-N_2O ha^{-1} (Tables 3.1). In 2016, mean simulated fluxes were higher than the measured fluxes by 34%, with mean values of 8.6±1.8 g N-N_2O ha^{-1} (Table 3.2). In both years, simulated cumulative N_2O emissions in S-BM were similar to the cumulative measured fluxes only lower by 7% in 2015, and 13% lower in 2016 (Table 3.4). For S-BM, the higher measured and simulated elevated emission happened approximately 14 days after manure was applied (Figs. 3.1b & 3.2b). The S-BM treatment had a better correlation and IA in 2015 compared to 2016. In 2015, 76 % of the simulated N_2O fluxes agreed with the measured fluxes, however in 2016 only 59 % were in agreement (Table 3.3). In 2015, MAE and RMSE were lower compared to 2016 (Table 3.3). The lower correlation and IA in 2016 is likely because the model was not able to simulate the high peak one day after side-dress N was applied. The simulations in the S-BM treatment were better correlated compared to the S-UAN treatment in 2015; 0.58 vs. 0.53. Contrarily in 2016, the S-UAN treatment was better correlated compared to the S-BM treatment; 0.55 vs. 0.3.

The correlation of measured and simulated emissions in our study was consistent with those of other researchers. A similar correlation coefficient, r=0.37, was obtained by Jarecki et al. (2008) for a chisel plowed corn/soybean field in Iowa, where soils were planted to corn fertilized with anhydrous ammonia. As in their study, we observed a mismatch between the observed and simulated N_2O emissions after inorganic fertilizer application. The correlation was also low (r=0.4) for a study in Lusignan, France where conventionally tilled soils were planted to corn with inorganic fertilizer (Senapati et al., 2006). As in their study, DAYCENT simulated elevated N_2O emissions (>10 g N_2O-N) after the first fertilization event in early May, but no such emission was measured. Other simulations, carried out in a humid pasture in Ireland with perennial ryegrass (*Lolium perenne* L.) and white clover (*Trifoliuim repens* L.) that received inorganic fertilizer, showed that DAYCENT overestimated the influence of added N fertilizer, producing a small emission immediately after inorganic fertilizer application and a larger one approximately 4 months after application (Abdalla et al., 2010). As in their study, we did not observe N_2O emissions in the field late in the season that DAYCENT predicted after inorganic fertilizer application.

Nitrous oxide fluxes from the spring terminated legume treatments (AO-BM and CC-BM)

In both years, mean daily simulated N_2O fluxes for the AO-BM treatment were lower than the measured fluxes, by 12% in 2015 and 35% in 2016 with mean values of 10.4 ±1.7 g N-N_2O ha^{-1} and 18.14 ± 3.9 g N-N_2O ha^{-1}, respectively (Tables 3.1 & 3.2). In both years, simulated cumulative N_2O emissions in AO-BM were lower than cumulative measured fluxes by 43% in 2015 and 47% in 2016 (Table 3.4). In both years, simulated and measured N_2O emissions increased after alfalfa and orchardgrass were terminated and manure was applied. However, elevated emissions were measured on June 19, 2015 and May 19 and May 27 in 2016 and the model did not simulate those (Figs. 3.1c & 3.2c). The correlation and IA were higher in 2016, compared to 2015 and the MAE and RMSE were also favorable for 2016 (Table 3.3). In all treatments, elevated emissions (>10 g N_2O-N) were simulated during July and September, but were not measured in the field.

In 2015, mean daily simulated N_2O emission for the CC-BM treatment was higher than measured fluxes by 15 % (Fig. 3.1d, Table 3.1), however in 2016, simulated fluxes were 87% lower (Fig.3.2d,Table 3.2). In both years, simulated cumulative N_2O emissions in CC-BM were lower than cumulative measured fluxes by 29% in 2015 and 88% in 2016 (Table 3.4). In 2015, measured and simulated N_2O emissions tended to increase after crimson clover was terminated and manure was broadcast applied; however in 2016, simulated N_2O emissions were low in contrast to the field measurements (Figs. 3.1 &3.2). Slightly higher correlation and IA were observed in 2016 compared to 2015 (Table 3.3). This could be due to different weather conditions after N amendment application that influenced mineralization and nitrification (wet spring and dry summer in 2015; dry spring and wet summer in 2016). Crimson clover had not been simulated in previous studies, and better parametrization of this crop could help predict its effect on N_2O emissions. Contrarily, the ability to simulate N_2O fluxes has been much more tested for corn following soybeans (Del Grosso et al. 2005, Stehfest et al. 2007) compared to crimson clover or a mixture of alfalfa and orchardgrass, which to our knowledge has not been evaluated with field observations.

As in our study, previous studies have found that daily N_2O measured fluxes are not always well correlated with simulated N_2O emissions. At a short grass steppe site in northeast Colorado, measured versus simulated daily N_2O emissions yielded regression coefficients (r^2) between 0.02 and 0.19 (Parton et al., 2001). The study site included a fertilized (ammonium nitrate) and unfertilized pasture with a sandy loam texture, a fertilized (urea) and unfertilized sandy clay loam site, and a clay loam site. Del Grosso et al. (2002) observed similar findings when no-till and conventional till systems were used for winter wheat/fallow cropping in Nebraska, with an r^2 of 0.04 between measured and DAYCENT- predicted fluxes. However, in both studies, DAYCENT accurately predicted average annual N_2O emissions.

The MAE and RMSE were low for all the treatments in both years, ranging from 1.22 to 1.86 g N_2O-N d^{-1} and 1.65 to 3.6 g N_2O-N d^{-1}, respectively. Values of RMSE were higher than MAE in all cases, since RMSE gives extra weight to large N_2O errors (Table 3.3).

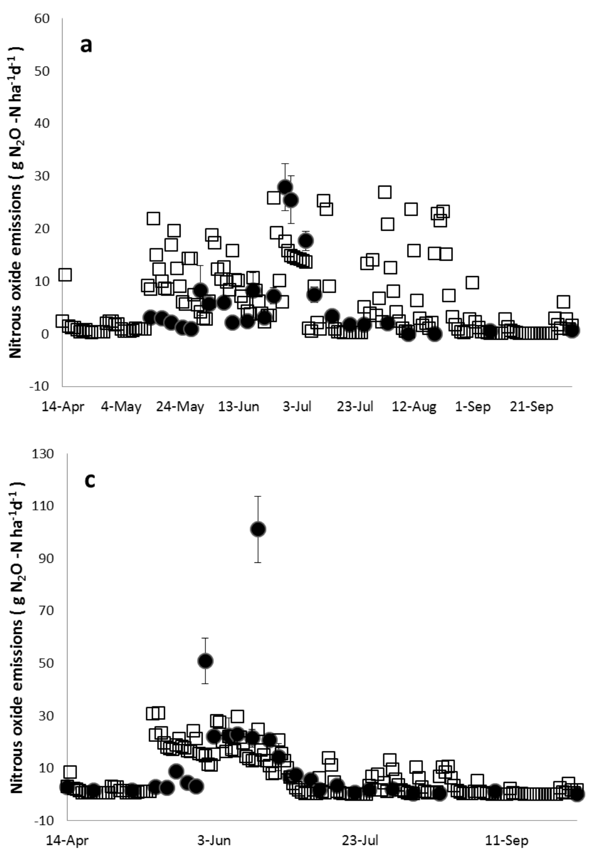

Fig. 3. 1 2015 comparisons of DAYCENT simulated (□) and field measured (●) N_2O fluxes from corn planted after the following crops and amendedments: (a) soybean with inorganic fertilizer (S-UAN), (b) soybean with broadcast manure (S-BM), (c) alfalfa and orchardgrass with broadcast manure (AO-BM), and (d) crimson clover with broadcast manure (CC-BM). Error bars for measured values are ±standard error.

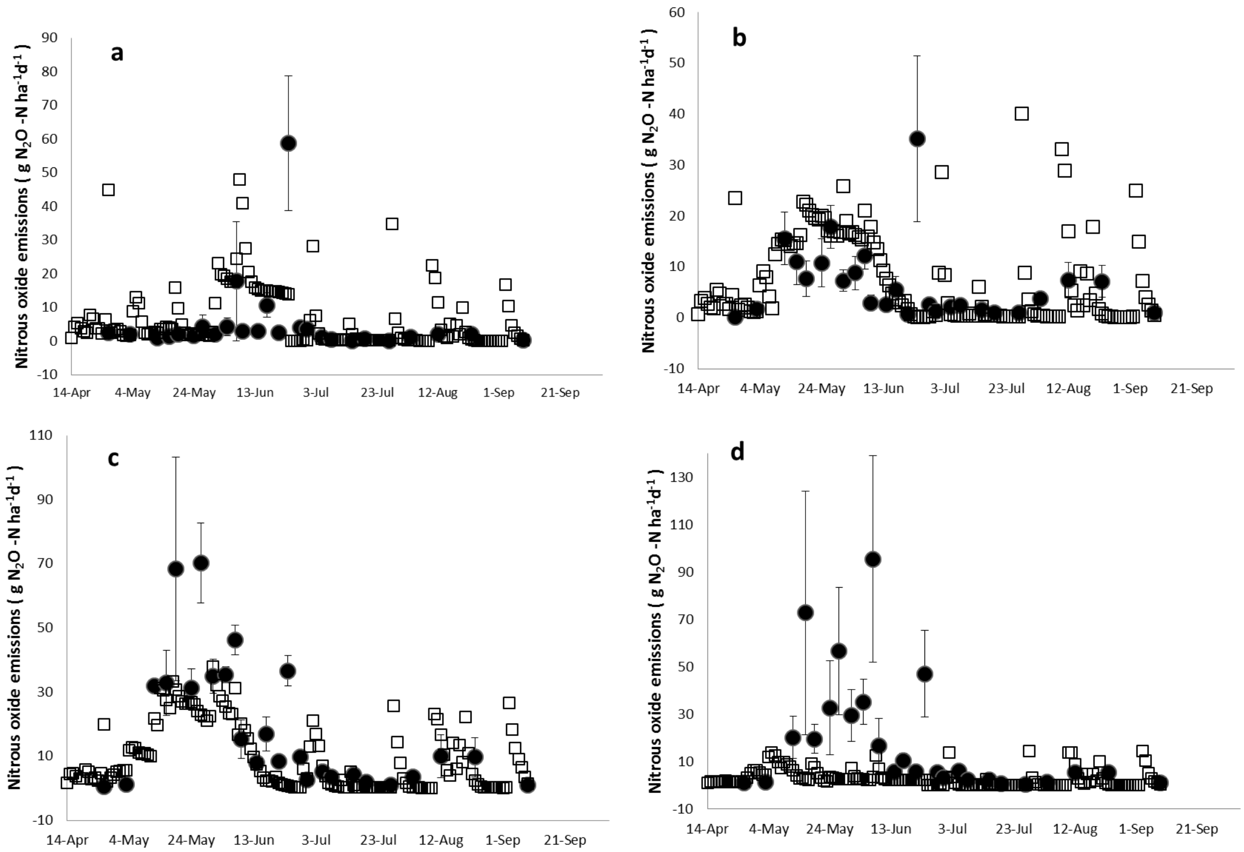

Fig. 3. 2 2016 comparisons of DAYCENT simulated (□ and field measured (● N_2O fluxes from corn planted after the following crops and amendedments: (a) soybean with inorganic fertilizer (S-UAN), (b) soybean with broadcast manure (S-BM), (c) alfalfa and orchardgrass with broadcast manure (AO-BM), and (d) crimson clover with broadcast manure (CC-BM). Error bars for measured values are ±standard error.

Table 3. 1 2015 Mean, standard error and range of field measured and simulated N_2O emissions, soil temperature, soil moisture, and soil inorganic N during the corn growing season for the four cropping systems in the study

	S-UAN		S-BM		AO-BM		CC-BM	
	Measured	Simulated	Measured	Simulated	Measured	Simulated	Measured	Simulated
N_2O loss (g N ha^{-1}) [a]	5.66±1.5	9.22±1.6	13.6± 3.4	14.1 ± 3.3	11.8±3.9	10.4±1.7	10.6±2.8	12.5±2.1
Range	0-27.9	0.2-28.4	0-62.7	0.1-68.1	0-101.1	0.1-29.5	0-51.2	0.1-41.1
Soil temperature (°C)	18.4±0.6	18.5±0.5	17.7±0.7	16.9±1	18.0±0.7	17.8±0.5	18.1±0.7	17.9±0.8
Range	11-1-22.1	11.7-21.9	6.9-22.4	7.3-22.4	7.9-22.4	10.4-22.1	7.1-22.5	7.7-23
Soil moisture (%)	23.7±0.9	20.7±2	24±1.1	20.5±1.4	25.1±1.4	22.6±1.9	23.9±0.9	23.4±1.8
Range	19.4-31.4	9.5-30	10.3-31	9.9-31.9	9.4-31.3	10-32.2	19.4-28.8	10.1-31.4
Soil nitrate (mg N-$NO_3^-$$kg^{-1}$)	20.1±4.3	9.5±1.2	16.6±0.1	1.7±0.4	16.2±4.8	0.4±0.1	16.6±4.9	0.7±0.1
Range	0.6-46.0	1.9-17.1	1.8-65.4	0.2-6.8	1-65.5	0.1-1.0	0.9-59.2	0.1-1.2
Soil ammonium (mg N-$H_4^+$$kg^{-1}$)	11±4	15.2±2.5	6.7±1.7	4.5±0.7	4.5±0.7	2.9±0.4	6.9±2.1	3.5±0.2
Range	0.8-53.8	2.2-35.3	0.8-30.3	0.0-12.0	1.2-15.5	0.8-9.3	1-33.9	2.2-5.5

[a] Mean emission rate and standard error

Table 3. 2 2016 Mean, standard error and range of field measured and simulated N_2O emissions, soil temperature, soil moisture, and soil inorganic N during the corn growing season for the four cropping systems in the study

	S-UAN		S-BM		AO-BM		CC-BM	
	Measured	Simulated	Measured	Simulated	Measured	Simulated	Measured	Simulated
N_2O loss (g N ha^{-1}) [a]	5.0±1.6	8.9±1.6	6.4±1.5	8.6±1.8	18.1±3.9	11.8±2.4	18±4.7	2.4±0.56
Range	0-58.8	0.3-45	0.2-35.2	0.1-25.8	0.5-70.19	0.2-37.8	0.5-95.54	0.1-11.3
Soil temperature (°C)	18.6±0.8	18±0.8	18.6±0.8	17.3±0.8	18.7±0.9	19.4±0.9	18.5±0.8	17.5±0.8
Range	7.8-24.4	7.5-23.7	8.1-24.1	5.8-23.3	7.8-24.1	8.8-25.2	7.6-23.3	6.2-23.5
Soil moisture (%)	21.5±1.5	18.4±1.3	24.1±1.5	20.5±1.6	25.5±1.7	19.7±1.3	21±1.6	15±1.1
Range	9.9-32.8	9.9-31.9	8.4-35.9	9.4-32	8.7-35.9	9.7-31.5	9.1-33.5	8.2-28.7
Soil nitrate (mg N-$NO_3^-$$kg^{-1}$)	41.5±7.6	1.9±0.3	41.3±8.7	1.5±0.5	29.2±4.3	0.8±0.1	27.4±3.7	0.3±0.05
Range	5.3-116.3	0.2-5.5	1.6-130.9	0.1-9.1	1.4-69.9	0.05-1.2	2.6-50.8	0.03-0.8
Soil ammonium (mg N-$H_4^+$$kg^{-1}$)	7.1±1.9	7.7±1.6	19.2±9.3	7.1±1.7	6.9±1.5	3.6±0.3	4.4±0.7	2.4±0.3
Range	1.5-35.4	1.1-29.2	1.5-166.3	1.7-31.4	2-20.2	1.9-8.44	1.9-15.2	0.5-5.2

[a] Mean emission rate and standard error

Table 3. 3 Model performance measures comparing simulated against measured data for N_2O emissions, soil temperature, soil moisture and soil inorganic N for the four cropping systems in the study.

	2015				2016			
	S-UAN	**S-BM**	**AO-BM**	**CC-BM**	**S-UAN**	**S-BM**	**AO-BM**	**CC-BM**
N_2O loss (g N ha^{-1})								
Correlation	0.53	0.58	0.28	0.53	0.55	0.3	0.54	0.58
Index of Agreement (IA)	0.5	0.76	0.41	0.54	0.71	0.59	0.73	0.56
Mean Absolute error (MAE)	1.66	1.17	1.82	1.63	1.28	1.25	1.22	2
Root mean square error (RMSE)	3.42	1.67	3.6	2.07	1.54	1.8	1.65	2.29
Soil temperature (°C)								
Correlation	0.61	0.69	0.72	0.75	0.7	0.73	0.68	0.7
Index of Agreement (IA)	0.75	0.81	0.82	0.86	0.83	0.83	0.81	0.82
Mean Absolute error (MAE)	1.83	2.7	2.17	2.24	2.4	2.57	2.74	2.71
Root mean square error (RMSE)	2.32	3.58	2.58	2.77	3.3	3.41	3.43	3.41
Soil moisture (%)								
Correlation	0.19	0.59	0.41	0.19	0.06	0.62	0.4	0.6
Index of Agreement (IA)	0.49	0.7	0.59	0.47	0.43	0.73	0.59	0.61
Mean Absolute error (MAE)	6.2	4.9	6.63	4.6	7.93	5.78	7.5	7.1
Root mean square error (RMSE)	7.6	6.3	7.87	7.2	9.27	7.27	10	9.28
Soil nitrate (mg N-NO_3^- kg^{-1})								
Correlation	-0.15	0.41	0.7	-0.2	0.1	0.1	0.59	-0.18
Index of Agreement (IA)	0.25	0.07	0.02	0.01	0.04	0.04	0.01	0
Mean Absolute error (MAE)	16.79	14.87	15.87	15.9	3956	39.8	28.4	27.1
Root mean square error (RMSE)	20.73	23.14	26.17	26.5	51	54.76	33.9	31.5
Soil ammonium(mg N-NH_4^+ kg^{-1})								
Correlation	0.62	0.5	0.44	0.75	-0.24	0.05	0.13	0.5
Index of Agreement (IA)	0.74	0.5	0.59	0.22	0.15	0.07	0.17	0.52
Mean Absolute error (MAE)	10.39	4.05	2.1	4.2	7.68	16.62	3.97	2.17
Root mean square error (RMSE)	12.8	6.63	3.1	9.1	11.66	42.4	7.49	3.34

Table 3. 4 Cumulative N_2O emissions during the corn growing season for the four cropping systems in the study.

Year	Treatment	Corn growing season N_2O emissions (g N ha^{-1})	
		Measured	Simulated
2015	S-UAN	436	637
	S-BM	1420	1325
	AO-BM	1262	715
	CC-BM	1194	850
2016	S-UAN	370	674
	S-BM	742	649
	AO-BM	1915	1025
	CC-BM	1770	211

Soil temperature

The comparison of simulated versus observed soil temperature data at 10 cm depth indicates that DAYCENT estimates compared favorably with soil measurements (Table 3.3). Average predicted values differed from the observed data by less than 5% in 2015 and less than 8% in 2016 during the sampling period. The soil temperature simulated by DAYCENT had between 75% and 86% agreement with measured soil temperature in 2015 and 2016 (Table 3.3). Lower measured soil temperatures early in the season, from treatments that received manure or had crop residues, are likely associated with the mulch cover creating cooler soil compared to DAYCENT simulations (Figs. 3.3 and 3.4). In both years of our study, the IA and correlation were favorable, ranging from 0.75 to 0.86 and 0.61 to 0.75 respectively. Similarly, in Irish grasslands, Abdalla et al. (2010) found that soil temperature simulated by DAYCENT compared favorably with measurements (r^2=0.79). Parton et al. (2001) also found that DAYCENT provided favorable predictions for soil temperature (r^2=0.79) in grassland soils across a range of soil textures and fertility levels during the growing season.

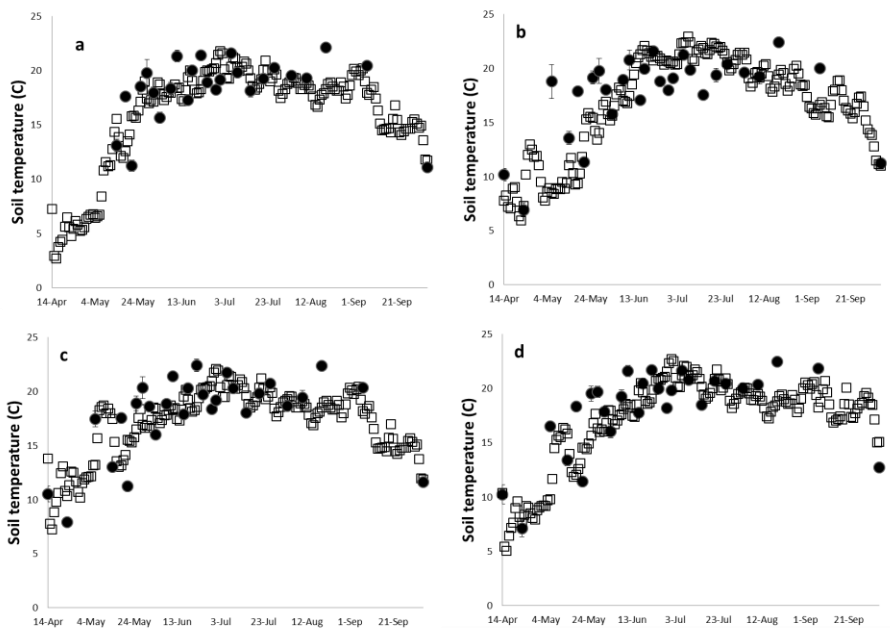

Fig. 3.3 2015 comparisons of DAYCENT simulated (□) and field measured (●) soil temperature from corn planted after the following crops and amendedments: (a) soybean with inorganic fertilizer (S-UAN), (b) soybean with broadcast manure (S-BM), (c) alfalfa and orchardgrass with broadcast manure (AO-BM), and (d) crimson clover with broadcast manure (CC-BM). Error bars for measured values are ±standard error.. Error bars for measured values are ±standard error.

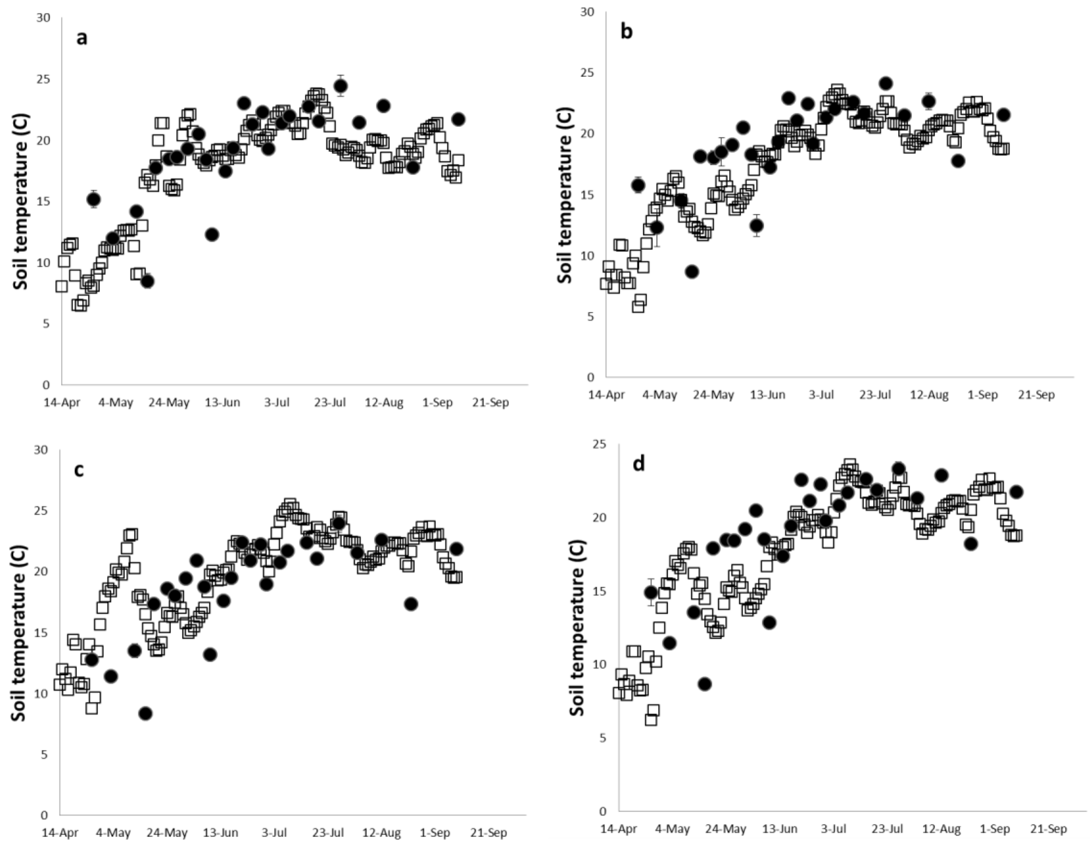

Fig. 3. 4 2016 comparisons of DAYCENT simulated (□) and field measured (●) soil temperature from corn planted after the following crops and amendedments: (a) soybean with inorganic fertilizer (S-UAN), (b) soybean with broadcast manure (S-BM), (c) alfalfa and orchardgrass with broadcast manure (AO-BM), and (d) crimson clover with broadcast manure (CC-BM). Error bars for measured values are ±standard error.. Error bars for measured values are ±standard error.

Volumetric soil water content

The model underestimated the measured VSWC at 10 cm depth (Figs. 3.5 and 3.6). The predicted values were generally lower than measured values during most of the experimental period by less than 17 % in 2015 and less than 29% in 2016 (Tables 3.1 and 3.2). The VSWC simulated by DAYCENT had between 43% and 73% agreement with measured VSWC in 2015 and 2016, respectively. In both years, correlations were better for the S-BM treatment (r=0.59 and r=0.62 in 2015 and 2016 respectively) compared to the other treatments (Table 3.3). In all treatments, a high MAE was observed, ranging from 4.6 to 6.6 in 2015 and 5.78 to 7.9 in 2016. The RMSE was also high and ranged from 6.3 to 7.9 in 2015 and 9.3 to 10 in 2016. The large errors are likely associated with the simulated water drainage. In all treatments, after precipitation events, DAYCENT predicted that VSWC tended to rapidly decrease and drain to deeper layers. In our systems, higher measured VSWC values could be partly explained by differences in crop residues and no-till soil with higher soil C that can retain more water.

Our findings, in terms of correlation, were consistent with those of other researchers. In corn plots in Iowa, Jarecki et al. (2008) found that the correlation between measured and simulated soil water content was low ($r = 0.26$). The authors explained that following precipitation events, predicted soil water contents generally increased to levels approaching the measured values, but the model predicted faster decreases in soil water content than were observed after rainfall. As in our study, Abdalla et al. (2010) found that DAYCENT did not simulate the saturated conditions observed at their study site following heavy rainfall on freely draining sandy clay loam soils in Ireland. The authors noted that DAYCENT simulates soil moisture by adding rainfall and immediately draining before allowing any other processes to occur. This could explain why in some cases our measured VSWC values after precipitation events where higher than those simulated.

Similar to our simulations in the S-BM treatment, DAYCENT underestimated soil water content during the growing season by approximately 10% for a corn field fertilized with swine slurry in Quebec, CA and in a wheat-maize-soybean rotation in Ontario, CA (Smith et al., 2008). The authors explained that it is possible that water could be supplied through lateral flow or groundwater, and noted that DAYCENT did not account for this flow. Favorable coefficient of determination between measured and simulated fluxes were observed in no-till corn plots in Iowa that did not have cover crops and were fertilized with UAN (Necpálová et al., 2015). The VSWC simulations using the default DAYCENT parameters resulted in r^2 of 0.51 and IA of 0.7. When the model was calibrated using inverse modeling to improve simulations, r^2 was 0.47 and IA was 0.77. Similarly, favorable r^2 were also observed when the water flow sub-model was tested by comparing simulated model results with observed VSWC data from a dry grassland, wet managed grassland, and wet cropland systems, with r^2 values of 0.58, 0.65 and 0.87, respectively (Parton et al. 1998).

Although the model underestimated VSWC in our systems, measured and simulated VSWC help explain differences between measured and simulated N_2O fluxes; which tended to increase when VSWC increased. Simulated, but not observed, elevated N_2O emissions in July, August and September followed the temporal pattern of simulated VSWC, suggesting that conditions were favorable for denitrification of residual N.

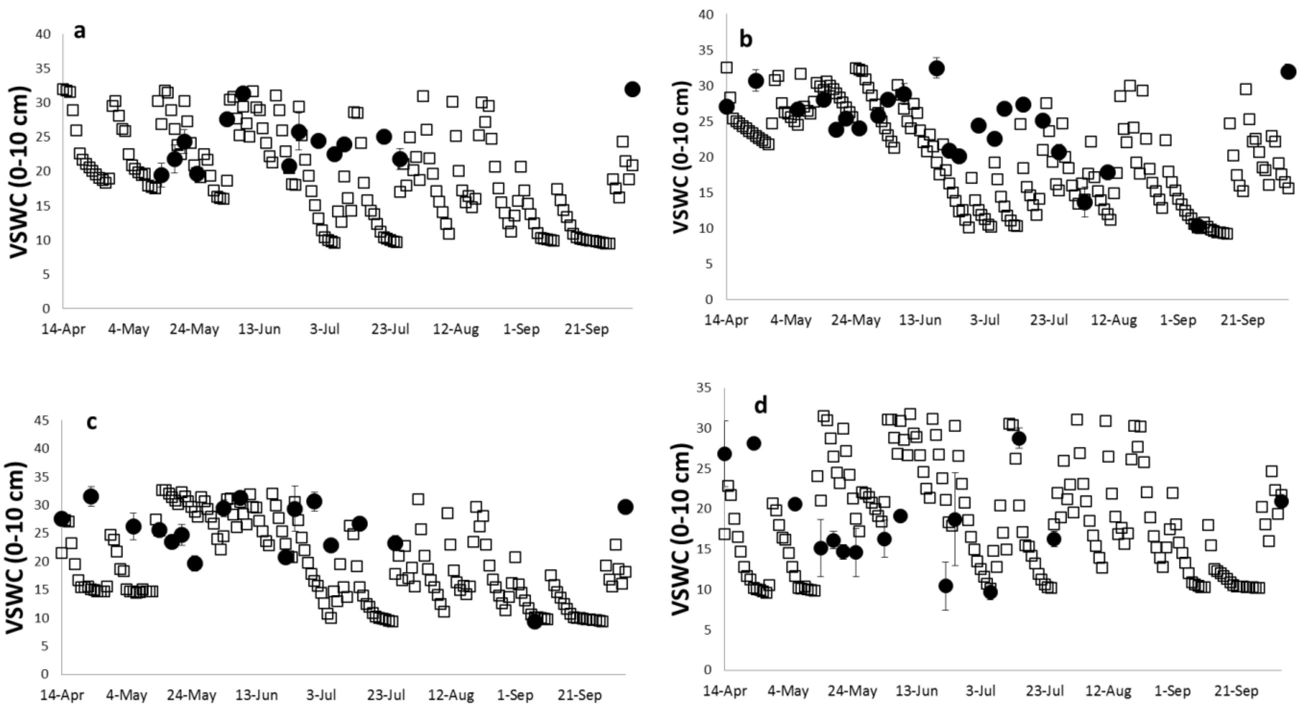

Fig. 3. 5 2015 comparisons of DAYCENT simulated (□) and field measured (●) soil volumetric soil water content (VSWC) from corn planted after the following crops and amendedments: (a) soybean with inorganic fertilizer (S-UAN), (b) soybean with broadcast manure (S-BM), (c) alfalfa and orchardgrass with broadcast manure (AO-BM), and (d) crimson clover with broadcast manure (CC-BM). Error bars for measured values are ±standard error.

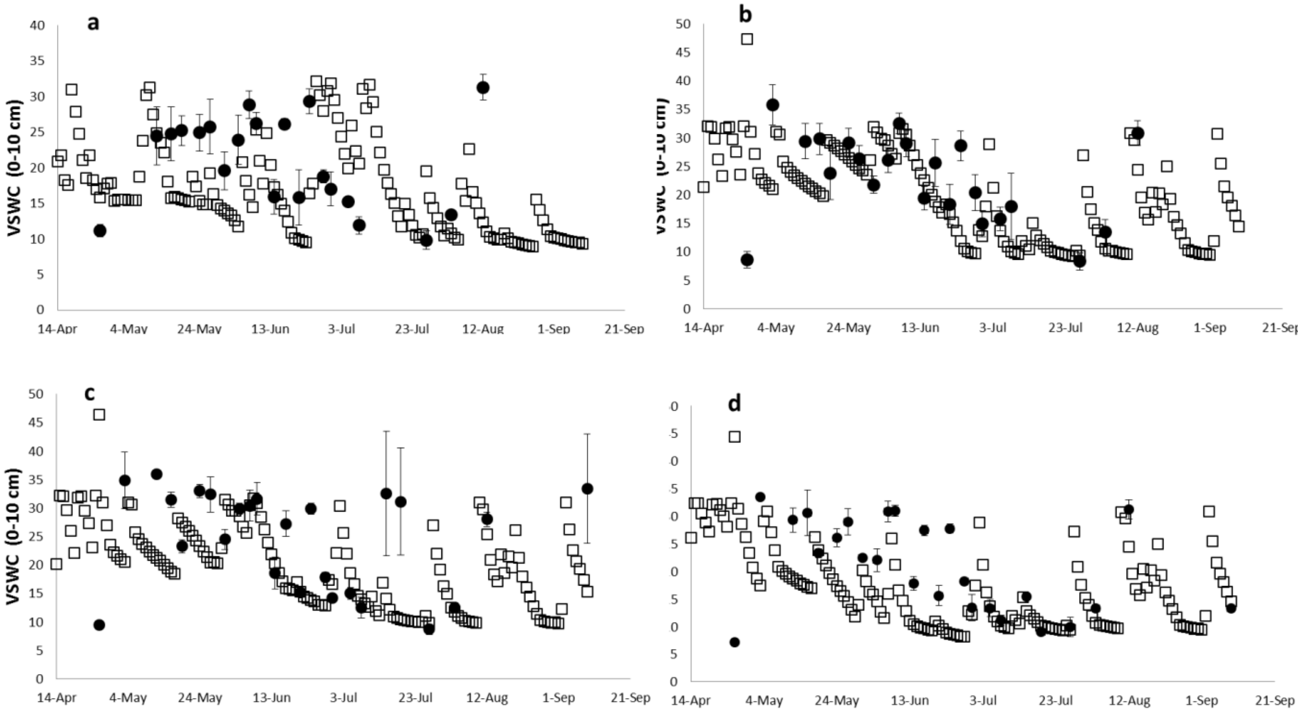

Fig. 3. 6 2016 comparisons of DAYCENT simulated (□) and field measured (●) soil volumetric soil water content (VSWC) from corn planted after the following crops and amendedments: (a) soybean with inorganic fertilizer (S-UAN), (b) soybean with broadcast manure (S-BM), (c) alfalfa and orchardgrass with broadcast manure (AO-BM), and (d) crimson clover with broadcast manure (CC-BM). Error bars for measured values are ±standard error. Error bars for measured values are ±standard error.

Soil inorganic N

The comparison of soil NH_4^+ and NO_3^- measured in the 0- to 5 -cm layer on 20 and 26 occasions in 2015 and 2016 to simulated values indicated that DAYCENT generally underestimated available N concentrations. Simulated and measured soil NH_4^+ concentration increased with N additions from crop residues, manure or inorganic fertilizer (Appendix B).

Soil inorganic N from corn following soybean with inorganic fertilizer or broadcast manure (S-UAN and S-BM)

In both years, mean daily simulated NO_3^- concentrations for the S-UAN treatment were lower than the measured values, by 53% in 2015 and 95% in 2016 with mean values of 9.5 ±1.2 mg N-NO_3^-kg^{-1} and 1.9±0.3 mg N-NO_3^-kg^{-1}, respectively (Tables 3.1 & 3.2). On the other hand, the mean simulated NH_4^+ for S-UAN were higher than the measured values by 38% in 2015, with mean values of 15.2 ± 2.5 mg NH_4^+ kg^{-1}. In 2016, simulated NH_4^+ was similar to the measured values; mean simulated NH_4^+ was only 8% higher with mean values of 7.7 ± 1.6 mg NH_4^+ kg^{-1}. Similarly, simulated NO_3^- for the S-BM treatment were lower than the measured values in both years, by 90% in 2015 and 96% in 2016 with mean values of 1.7 ±0.4 mg N-$NO_3^-$$kg^{-1}$ and 1.5±0.5 mg N-$NO_3^-$$kg^{-1}$, respectively (Tables 3.1 & 3.2). Contrarily to S-UAN, simulated NH_4^+ concentrations for S-BM were lower than measured values by 32% in 2015 and 63% in 2016, with mean values of 4.5 ± 0.7 mg NH_4^+ kg^{-1} and 7.1±1.7 mg NH_4^+ kg^{-1}, respectively. Overall, DAYCENT did not predict soil NH_4^+ or NO_3^- well. The simulated NO_3^- had a low correlation with field measurements ranging from -0.15 to 0.41, and NH_4^+ from -0.24 to 0.62 (Table 3.3). For S-UAN and S-BM, the IA was higher for NH_4^+ than for NO_3^- concentration in the 0-5 cm layer, ranging from 7 to 74% and 4 to 25%, respectively

Soil inorganic N from the spring terminated legume treatments (AO-BM and CC-BM)

In both years mean daily simulated NO_3^- for AO-BM were lower than the measured values, by 98% in 2015 and 48% in 2016 with mean values of 0.4 ±0.1 mg N-$NO_3^-$$kg^{-1}$ and 0.8±0.1 mg N-$NO_3^-$$kg^{-1}$, respectively (Tables 3.1 & 3.2). Also, in both years, the mean simulated NH_4^+ was lower than the measured values by 36% in 2015 and 48% in 2016 with mean values of 2.9±0.4 mg NH_4^+ kg^{-1} and 3.6± 0.3 mg NH_4^+ kg^{-1}, respectively. Similarly, mean daily simulated NO_3^- for CC-BM were lower than the measured values, by 96% in 2015 and 99% in 2016 with mean values of 0.7 ±0.1 mg N-$NO_3^-$$kg^{-1}$ and 0.3±0.1 mg N-$NO_3^-$$kg^{-1}$, respectively (Tables 3.1 & 3.2). In both years, the mean simulated NH_4^+ was lower than the mean of measured values by 49% in 2015 and 46% in 2016 with mean values of 3.5±0.2 mg NH_4^+ kg^{-1} and 2.4± 0.3 mg NH_4^+ kg^{-1}, respectively. In both years, the DAYCENT simulations for NO_3^- were better correlated for AO-BM compared to CC-BM (Table 3.3). On the other hand, DAYCENT simulations for NH_4^+ were better correlated for CC-BM compared to AO-GM.

The simulated NO_3^- concentrations in the top soil layer may have been lower than measured because NO_3^- leached faster than DAYCENT predicted or because nitrification happened faster than DAYCENT predicted. While NH_4^+ is immobile in DAYCENT and it is distributed in the top layers (0-10 cm), NO_3^- is mobile and distributed throughout the soil profile. The model estimates that NO_3^- leaching from a soil layer to the one below occurs when water infiltrates into the next layer; therefore, as the simulated VSWC increases, NO_3^- also moves faster to deeper layers. Simulated NO_3^- was highly concentrated from 5-20 cm. A sensitivity analysis modifying the parameters MINLCH , FLEACH(1), FLEACH(2), and FLEACH(3) could help to improve N transfer to the next layer. However, in our systems, preliminary simulations modifying these parameters did not improve soil inorganic N estimates. Instead of parametrizing the model through the traditional “trial and error” approach, the model could be calibrated by fitting the model to data with inverse modeling (Rafique et al., 2013). Necpálová et al. (2015) calibrated the model through inverse modeling and found the largest discrepancy between simulated and observed values was after UAN application in corn fields in Iowa. The authors reported that from 0-10 cm, soil NO_3^- was overestimated by 3.4%, and soil NH_4^+ was underestimated by 71%; they suggested that the model be improved to represent highly fertilized conditions.

Other studies have also noted that N transformation was not always in agreement with field observations. Del Grosso et al. (2008) found that DAYCENT underestimated soil inorganic N and explained that the nitrification rate estimate was low for their field site. Jarecki et al. (2008) also found that DAYCENT underestimated soil inorganic N in corn plots where anhydrous ammonia was injected, and they suggested the underestimate was because DAYCENT simulates N transformations as a function of depth, but does not take into account spatial variations in the soil surface.

The underestimated soil NO_3^- and NH_4^+ concentrations at 5 cm depth in all the treatments (except for NH_4^+ in S-UAN) could explain DAYCENT’s underestimate of N_2O emissions in AO-SM in both years, and in CC-BM in one out of two years. Similarly, the overestimated NH_4^+ in S-UAN could explain the overestimated N_2O simulated.

Conclusion

We observed that DAYCENT was generally able to reproduce temporal patterns of soil temperature and N_2O daily fluxes. In general, DAYCENT accurately predicted soil temperature in the summer; but in the spring, DAYCENT-simulated soil temperatures tended to be lower than measured values. The simulated N_2O flux and the measured data increased with N inputs and varied in response to changes in precipitation. In general, N_2O emissions were overestimated for corn following soybean with inorganic fertilizer and broadcast manure. On the other hand, simulated N_2O emissions were underestimated compared to measured fluxes for corn following alfalfa and orchardgrass in both years, and crimson clover in one out of two years. Similar index of agreement with measured values was observed from the corn following soybean with broadcast manure (76 % and 59%) and the corn with inorganic fertilizer (50% and 71%). Simulated N_2O emissions from the spring terminated perennial and cover crop legume treatments had an index of agreement with measured values that ranged from 41 to 56%, except for the alfalfa and orchardgrass with broadcast manure treatment that had an index of agreement of 73%.

While field measures of soil temperature and were generally reproduced by DAYCENT, VSWC and soil inorganic N were not. Volumetric soil water contents predicted by DAYCENT were generally lower than measured values. After precipitation events, DAYCENT predicted that VSWC tended to rapidly decrease and drain to deeper layers. Both the simulated and measured NH_4^+ and NO_3^- soil levels increased with N fertilizer addition. However, the model underestimated soil NH_4^+ and NO_3^- levels in the top layers for all the treatments except for the NH_4^+ levels in the corn following soybean with inorganic fertilizer. Improvements in the N leaching components of DAYCENT could improve simulations of nitrification rates and soil inorganic N. Mechanisms for on-site calibration using techniques such as inverse modeling would likely be useful in future applications of this model.

Our results suggest that DAYCENT overestimated the residual side-dress inorganic N fertilizer impact on N_2O emissions in the corn following soybean with inorganic fertilizer and broadcast manure. To achieve more reliable estimates of N_2O emissions, nitrification parameters could be modified to represent less accumulation of N_2O late in the season after side-dress inorganic fertilizer application, or crop N parameters could be modified to represent rapid N uptake late in the season. Also, further model refinement is needed to account for C and N inputs from crimson clover and alfalfa and orchardgrass residues. Improving the parametrization of DAYCENT for dairy cropping systems in no-till systems with high surface legume crop residues from perennials and cover crops will make the model a more useful tool for testing different mitigation scenarios for farmers' and policy making.

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Chapter 4

Conclusions and Future Research

Because of environmental concerns, manure management strategies that reduce nutrient losses are being promoted. While manure injection had 2-3 times higher nitrous oxide (N_2O) emissions compared to broadcast manure during the corn growing season, it has many benefits that include reducing the use of inorganic fertilizer, minimizing soil disturbance in no-till and conservation tillage cropping systems, and decreasing ammonia emissions by 91 to 99% compared to surface applied manure (Dell et al., 2011). A better understanding of the tradeoffs of this technology is needed to help farmers in their operational management decisions. Accounting for the energy use and greenhouse gas (GHG) emissions associated with applying inorganic fertilizer would better inform farmers about the impact of manure injection.

Incorporating perennial grasses and legumes into the cropping system with manure application reduced the use of inorganic fertilizer later in the season compared to corn following soybean with manure or UAN, but did not directly reduce N_2O emissions. However, a complete life-cycle analysis of GHG emissions that includes GHG emissions produced when manufacturing UAN and how perennials and cover crop residues increase C in the soil would help elucidate how these practices may impact direct and indirect GHG emissions. As demonstrated in this study, N_2O emissions from N fertilization depend on the timing of application. Emissions can be reduced when fertilizer is applied close to crop N uptake. However, in wet soils N_2O emissions can greatly increase.

Few studies have been done in the northeastern US that investigate the effect of no-till systems with high crop residues from no-till perennials and/or cover crops on N_2O emissions. These practices offer the potential to conserve N and reduce N losses, especially in the long-term. Understanding ways in which N can be retained in the soil is crucial to improving N management and reducing N_2O emissions in agricultural systems for sustainable crop production. Since soil microbes drive most of N transformations and are sensitive to weather conditions and soil properties, studying microbial communities can help provide a better understanding of N_2O

production. In addition, testing how crop N uptake may differ at various stages of growth from early season to later at side-dress application, may also improve simulations of soil N available for nitrification

Using modeling tools such as DAYCENT, can be helpful to test management practices that can mitigate N_2O emissions. In our study, we observed that simulated N_2O fluxes from corn in a no-till conservation dairy cropping system and a corn-soybean rotation without cover crop had between 41 and 76% agreement with measured daily N_2O fluxes in 2015 and 2016. DAYCENT generally predicted temporal patterns of soil temperature but not soil moisture or inorganic N. Volumetric water contents predicted by DAYCENT were generally lower than measured values. After precipitation events, DAYCENT predicted that VSWC tended to rapidly decrease and drain to deeper layers. Both the simulated and measured soil NH_4^+ and NO_3^- increased with N fertilizer addition, however, the model tended to underestimate soil inorganic N concentration in the top layers. To achieve more reliable estimates of N_2O emissions, nitrification parameters could be modified to represent rapid accumulation of N_2O right after inorganic fertilizer application or parameters that represent crop N uptake could be modified to represent rapid N uptake late in the season. Also, further model refinement is needed to account for C and N inputs from crimson clover and alfalfa and orchardgrass residues. Improvements in the N leaching component of DAYCENT could help represent better nitrification rates and soil inorganic N.

Improving the parametrization of DAYCENT for dairy cropping systems will make the model a more useful tool for testing different mitigation or adaptation scenarios for farmers and policy makers. For instance, timing crop residue termination and manure application with crop N uptake can help reduce N_2O emissions. When coupling cover crops with manure application, it is difficult to synchronize N availability with plant nutrient uptake. However, delaying cover crop termination in the spring close to the time when corn is planted can likely contribute to conserving more N and reducing N_2O losses. Since manure storage capacity is often limited to 6 months in Pennsylvania, strategies comparing the effect of fall and spring application on N_2O emissions would be of interest to farmers. Applying manure late in the fall to a rye cover crop could reduce N_2O emissions compared to when manure is applied early in the fall to a rye cover crop or than when it is split in two times (50% fall and 50% spring). Applying N close to rapid plant nutrient uptake has the potential to reduce inorganic N accumulation in the soil and potential losses from denitrification. Also, lower temperatures later in the fall would reduce the mineralization of manure and N_2O emissions.

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Appendix A. Measured and DAYCENT- simulated soil nitrate and ammonium

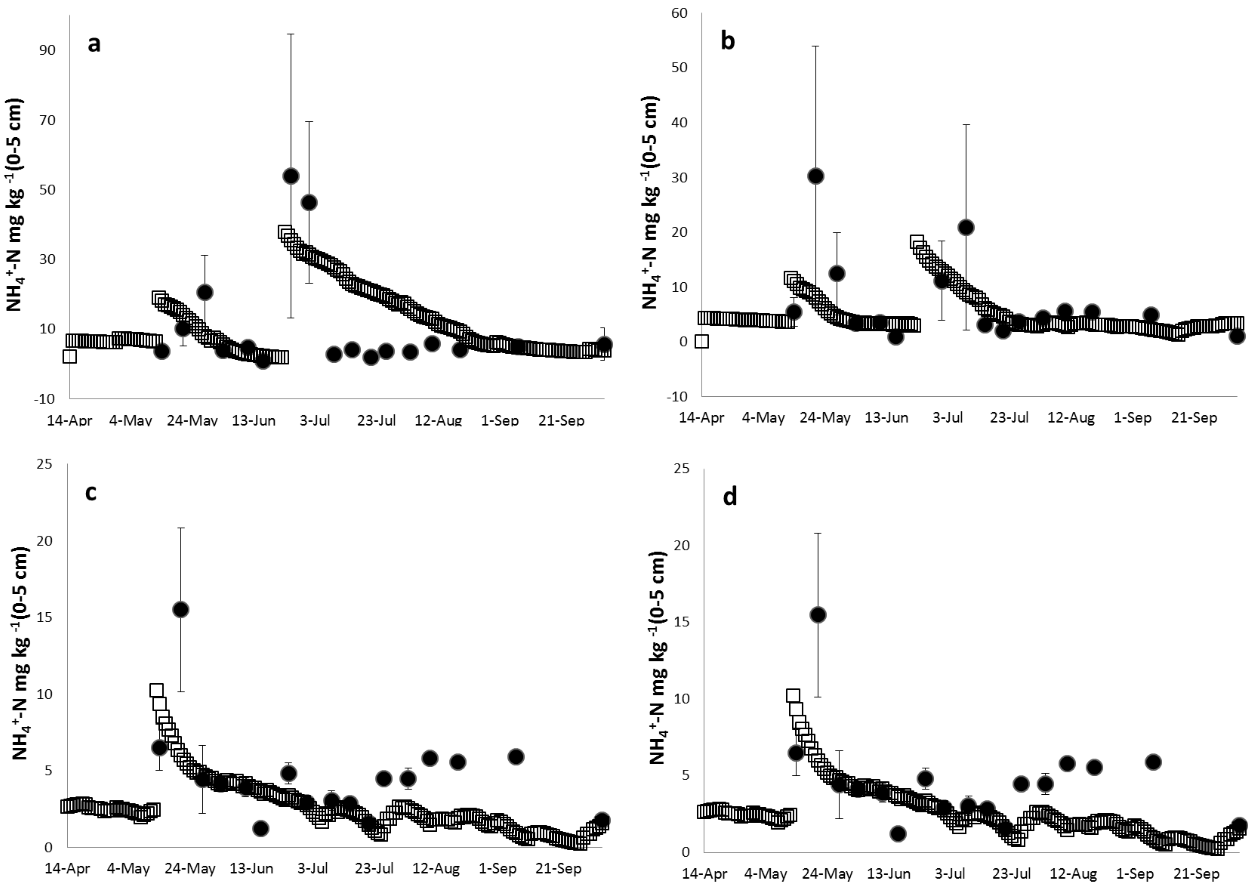

Fig. B. 1 2015 comparisons of DAYCENT simulated (□) and field measured (●) NH_4^+ from corn planted after the following crops and amendedments: (a) soybean with inorganic fertilizer (S-UAN), (b) soybean with broadcast manure (S-BM), (c) alfalfa and orchardgrass with broadcast manure (AO-BM), and (d) crimson clover with broadcast manure (CC-BM). Error bars for measured values are ±standard error.

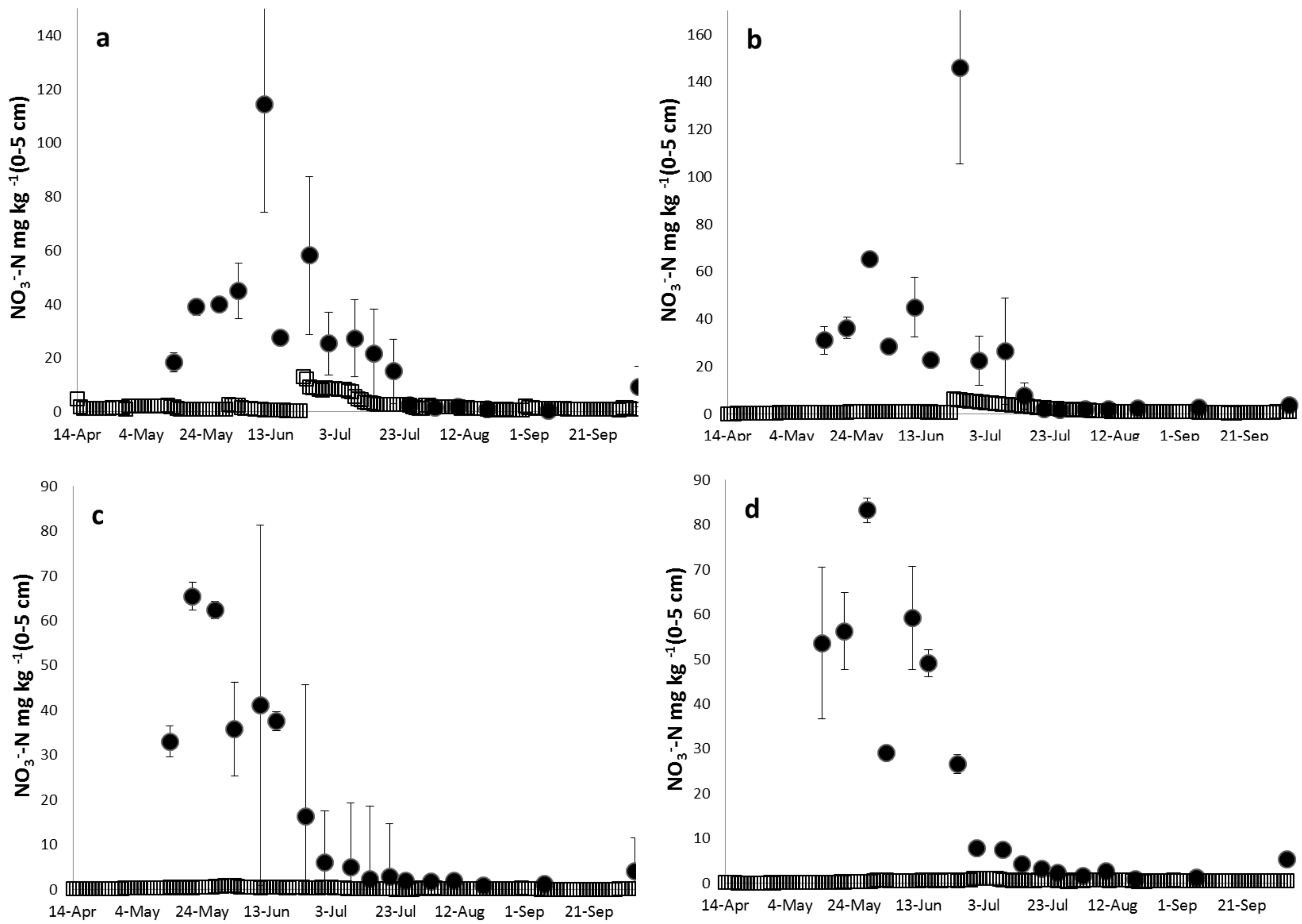

Fig. B. 4 2015 comparisons of DAYCENT simulated (□) and field measured (●) NO_3^- from corn planted after the following crops and amendedments(a) soybean with inorganic fertilizer (S-UAN), (b) soybean with broadcast manure (S-BM), (c) alfalfa and orchardgrass with broadcast manure (AO-BM), and (d) crimson clover with broadcast manure (CC-BM). Error bars for measured values are ±standard error.

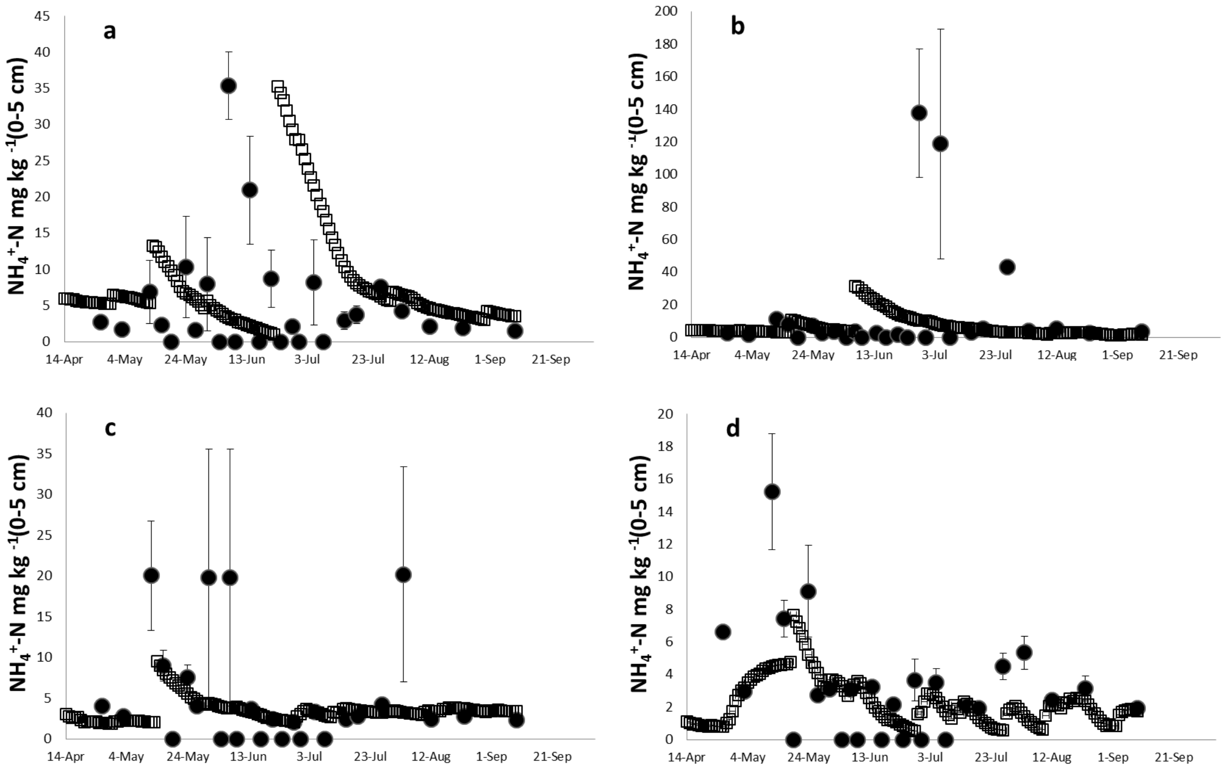

Fig. B. 3 2016 comparisons of DAYCENT simulated (□) and field measured (●) NH_4^+ from corn planted after the following crops and amendedments: (a) soybean with inorganic fertilizer (S-UAN), (b) soybean with broadcast manure (S-BM), (c) alfalfa and orchardgrass with broadcast manure (AO-BM), and (d) crimson clover with broadcast manure (CC-BM). Error bars for measured values are ±standard error.

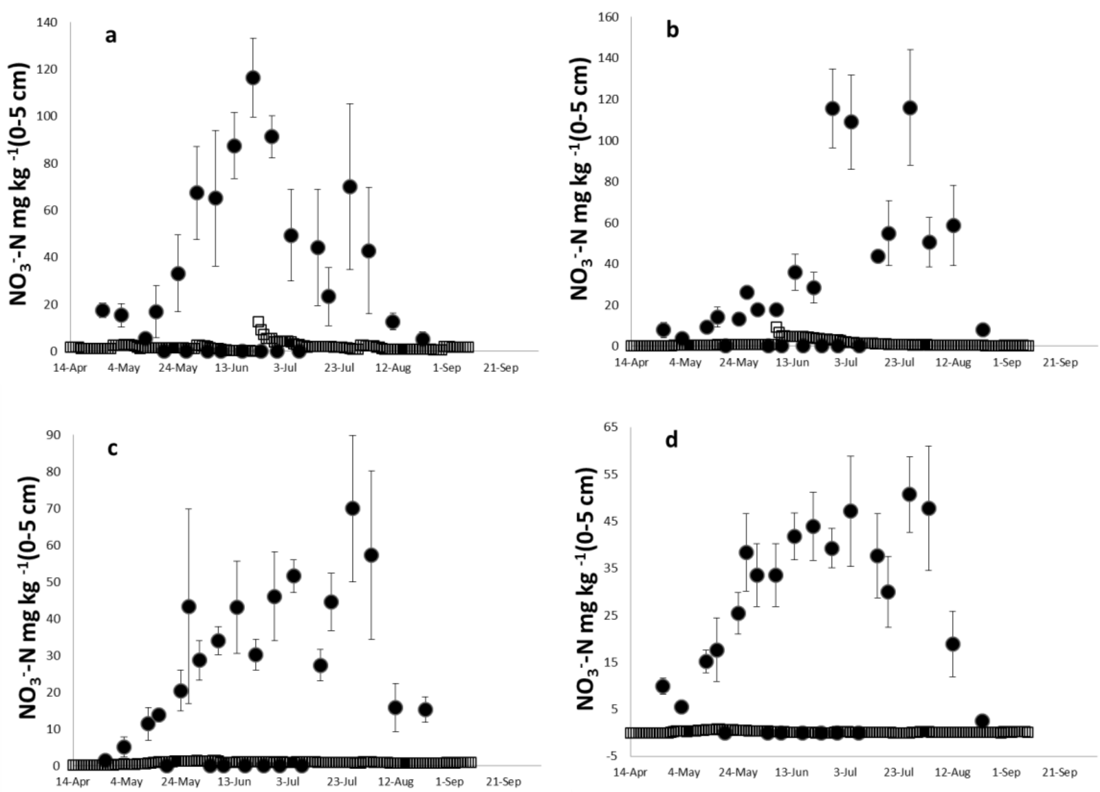

Fig. B. 4 2016 comparisons of DAYCENT simulated (□) and field measured (●) NO_3^- from corn planted after the following crops and amendedments: (a) soybean with inorganic fertilizer (S-UAN), (b) soybean with broadcast manure (S-BM), (c) alfalfa and orchardgrass with broadcast manure (AO-BM), and (d) crimson clover with broadcast manure (CC-BM). Error bars for measured values are ±standard error.

Appendix B. Nitrous oxide emissions from corn following rye cover crop

In addition to the gas samples taken in the corn-soybean and forage rotation in the Pennsylvania State Sustainable Dairy Cropping System experiment, gas samples were also taken in the grain rotation of the experiment (Fig. B1). The 6-year grain rotation consisted of a 2-yr alfalfa and orchardgrass (*Dactylis glomerata* L.) forage crop, followed by canola, rye (*Secale cereale* L.) cover crop, followed by soybean (*Glycine max* L. Merr), rye cover crop, then by corn silage and oats (*Avena sativa* L.) (Fig B.1). From the grain rotation, we sampled the corn entry that followed rye that received injected manure (RYE-IM).

In this section we reported results for gas samples taken in 2015 and 2016 in three blocks of the experiment in RYE-IM and S-BM. In RYE-IM manure was injected in the fall before rye was planted. Gas samples were only measured one year right after manure injection in the fall, and both years during the corn growing season. The amount of manure injected was 39 Mg ha^{-1}. Starter fertilizer was applied to corn after rye at 9 kg ha^{-1} N as 7-21-7. The corn after rye also needed supplemental application of inorganic fertilizer later in the season and was side-dressed with liquid UAN at 75 kg ha^{-1} N in 2015 and 72 ha^{-1} N in 2016.

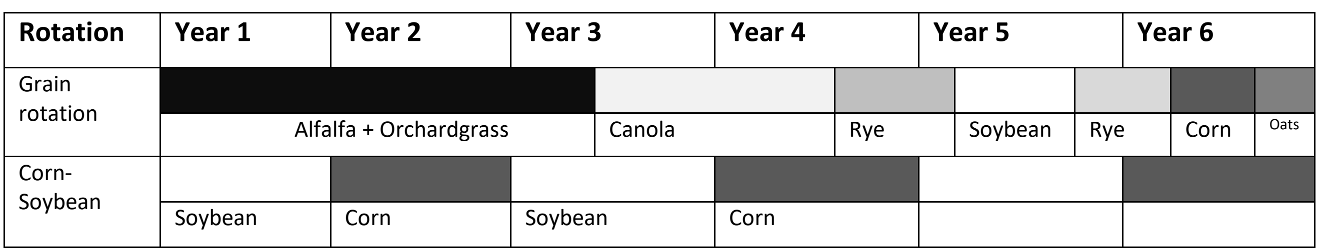

Fig. B1 Grain rotation and corn-soybean rotation in the Pennsylvania State Sustainable Dairy Cropping System experiment

Results and discussion

In both years N_2O emissions tended to increase after spring manure application in S-BM about 5 to 10 days after manure was applied (Figs. B2 & B3). It is likely that this happened because crop plant nitrogen demand was not high when nitrogen was available from the manure and previous crop residues, resulting in excess N that could be denitrified. In contrast, when manure was injected in the fall, emissions were low. It is likely that low temperatures limit the mineralization of organic N inputs and nitrification so there was less potential for N_2O production.

Later in the corn growing season when the side-dress fertilizer N was applied to S-BM and RYE-IM, N_2O emissions were low in both years except for S-BM in 2015. The lower emissions are likely partly because the fertilizer N was more rapidly taken up by the actively growing corn. In both years cumulative N_2O emissions during the sampling period were higher from S-BM compared to RYE-IM by 179% in 2015 and by 27% in 2016 (Figs. B2 & B3).

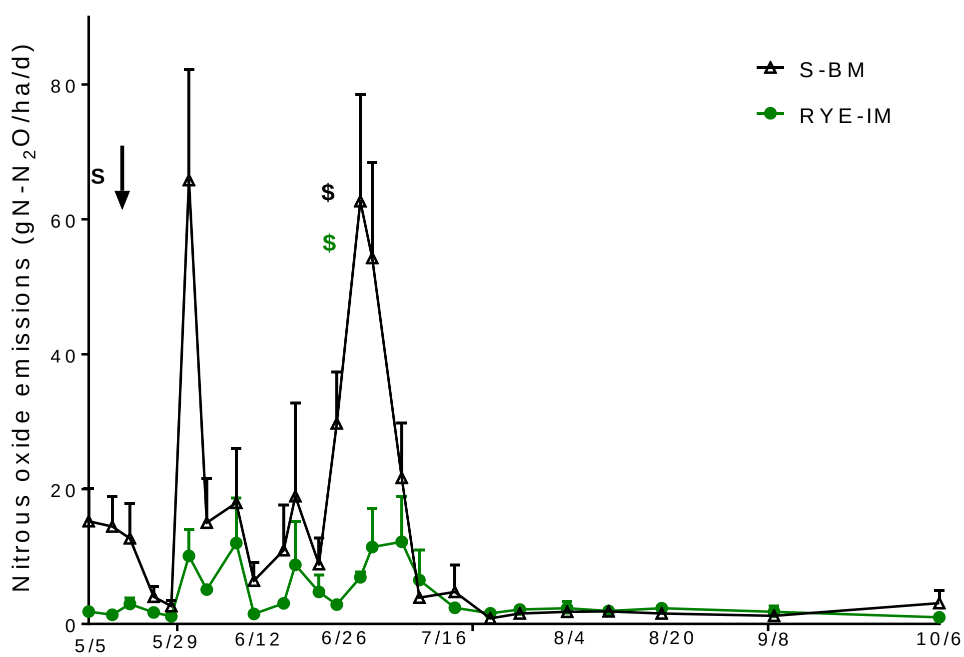

Fig. B2. 2015 Nitrous oxide emissions from soil planted to corn following rye with injected manure (RYE-IM) and soybean with broadcast manure (S-BM). S indicates when manure was applied,↓ indicates when corn was planted, $ indicates when side-dress N was applied

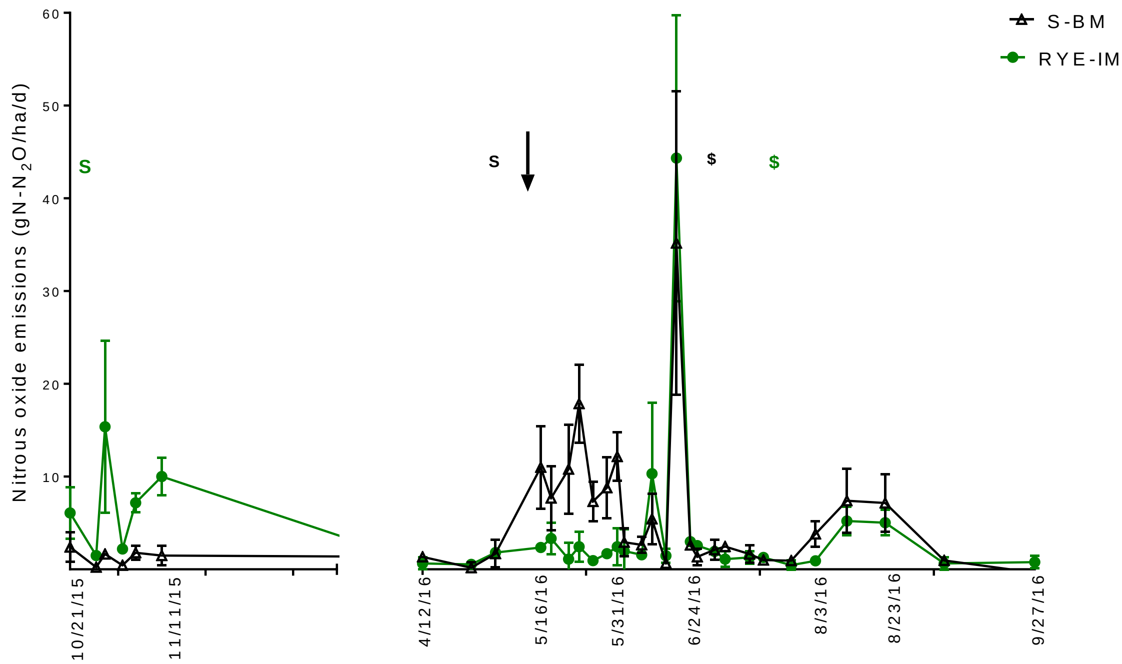

Fig. B3. 2016 Nitrous oxide emissions from soil planted to corn following rye with injected manure (RYE-IM) and soybean with broadcast manure (S-BM). S indicates when manure was applied,↓ indicates when corn was planted, $ indicates when side-dress N was applied

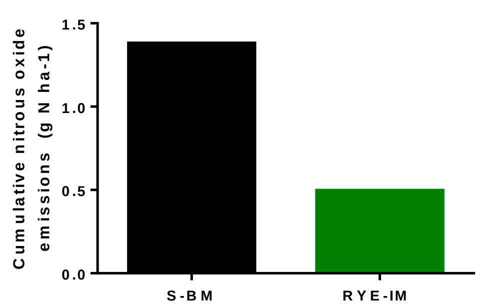

Fig. B4. 2015 Cumulative nitrous oxide emissions from soil planted to corn following rye with injected manure (RYE-IM) and soybean with broadcast manure (S-BM).

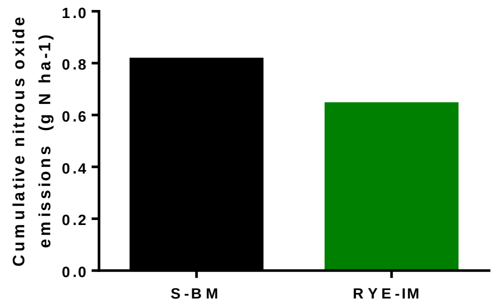

Fig. B5. 2016 Cumulative nitrous oxide emissions from soil planted to corn following rye with injected manure (RYE-IM) and soybean with broadcast manure (S-BM).