DETERMINING GREENHOUSE GAS EMISSIONS AND NITROGEN DYNAMICS OF SOLID BEEF MANURE APPLIED TO FARGO-CLAY SOIL OF THE RED RIVER VALLEY

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The Supervisory Committee certifies that this ***disquisition*** complies with North Dakota State University's regulations and meets the accepted standards for the degree of

DOCTOR OF PHILOSOPHY

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ABSTRACT

Land application of solid beef manure may prompt greenhouse gases (GHGs) - nitrous oxide (N_2O), methane (CH_4), and carbon dioxide (CO_2) emissions. Nitrogen (N) in manure can also be lost through ammonia volatilization (NH_3), leaching (NO_3^-), denitrification, and erosion. The objectives of this research were to assess the effects of (i) land application of solid beef manure (SM) on emission of GHGs, NH_3 volatilization, and corn (*Zea mays* L.) yield, (ii) soil moisture [(30, 60, and 90% water-holding capacity (WHC)] on GHGs and NH_3 emissions from urea and manure application, and (iii) soil temperature (5, 10, 15, and 25°C) on GHGs and NH_3 emissions from urea and manure amended Fargo-Ryan silty clay soil of the RRV. The two-year growing season cumulative N_2O emission (cN_2O) ranged from 0.3 (non-fertilized, NF) to 1.2 (urea only, UO) kg N ha^{-1}. The UO reduced cumulative carbon dioxide (cCO_2) by 42% compared to manure N sources. The cumulative CH_4 (cCH_4) emission ranged from -0.03 to 0.23 kg CH_4-C ha^{-1} CH_4-C ha^{-1}, with the highest emission from manure with straw bedding (BM). Manure reduced cNH_3 by ~11% compared to UO. Cumulative soil N in 2017 were significantly greater by 11%, respectively, compared to 2016. Nitrogen source did not show any difference in grain yield and grain N uptake in field study. In the laboratory, across WHC levels, 1.01% of the total applied N was lost as N_2O at 60% WHC from urea treated soil. Soil CO_2 from manure was up to two times the emission from CF treated soils. The cumulative NH_3 volatilization loss from soil ranged from 29.4 to 1250.5 µg NH_3-N kg^{-1} soil, with the highest loss from CF amended soils at 30% WHC. In addition, laboratory study showed cumulative GHGs and NH_3 emission generally increased with increase in temperature, with the highest emission observed at 25 °C. The results highlight the challenge of meeting crop nutrients demand while reducing GHG emissions by selection of an N source.

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DEDICATION

This work is dedicated to my dear parents Mr. Durga Prasad Niraula and Mrs. Hema Kumari Niraula, my brother Santosh Niraula, my sister Sirjana Niraula, and my lovely wife Sabina Dangol.

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GENERAL INTRODUCTION

There are over 39 million acres of farmland in North Dakota. The state has been ranked as a leading state in the nation in the production of many agricultural commodities including spring wheat (1st), corn (9th), soybeans (7th), and cattle and calves (16th) (USDA-NASS, 2017a). In 2016 alone, 3.5 million acres of land was planted with corn in ND. About 1.8 million ha of soils in the Red River Valley (RRV) of the North Dakota and northern Minnesota are high clay and potentially highly productive (USDA-NRCS, 2014). However, the soils of this region are vulnerable to leaching, NH_3 and/or N_2O emission losses due to extensive use of conventional urea fertilizer (Thapa et al., 2015). In terms of livestock production in North Dakota, as of January 2017, the beef cow population increased 6% from 2016 to 954,000 heads (USDA-NASS, 2017a). Increased livestock production poses challenges, especially regarding proper treatment and disposal of the increased volume of manure. In addition, bedding livestock is a common practice that cattle producers use to provide comfort to the animals and absorb moisture. Most producers use locally available by-products of cereal grain production for bedding, such as corn stover, soybean stover, wheat straw, or corn cobs (Doran et al., 2010). Land application of solid beef manure is one strategy to manure management, however, the environmental and economic impact of manure application needs further investigation.

Manure can supply macronutrients namely nitrogen (N), phosphorus (P), potassium (K), as well as micronutrients, while improving soil health and fertility (Khaleel et al., 1981; Schroder, 2005). However, the land application effects of solid manure and manure with bedding materials on GHG emissions and N dynamics are less clear; possibly due to the interaction of abiotic factors such as soil texture, pH, CEC, clay and organic matter content, and soil management (Adviento-Borbe et al., 2010; Jantalia et al., 2012; Sommer et al., 2004). Manure application could affect manure nutrient levels by influencing gaseous emissions of carbon dioxide (CO_2), ammonia (NH_3), nitrous oxide (N_2O), and methane (CH_4) and exposure to runoff and leaching. Therefore manure application has repercussions for air (Tenuta et al., 2000) and water (Eghball and Gilley, 1999) quality as well as crop nutrient supply (Miller et al., 2009; Paul and Beauchamp, 1993). Research on the effects of manure on poorly drained soils of the RRV are limited, therefore, this project examined N transformations in soil and gaseous emissions from manure with and without bedding.

1. LITERATURE REVIEW

1.1. Overview of Greenhouse Gases

According to the U.S. Energy Information Administration (2004), greenhouse gases (GHGs) are the compounds that absorb the infrared radiation and trap heat in the atmosphere. The vast majority of GHGs are in the form of carbon dioxide (CO_2), followed by methane (CH_4) and nitrous oxide (N_2O) that contribute to the warming effect known as Global Warming Potential (GWP) (IPCC, 2013). The GWP of CO_2 is one, by definition, and is used as the reference while CH_4 and N_2O have the GWP of 21-36 and 265-310 times that of CO_2, respectively for a 100-year timescale (IPCC, 2007; Johnson et al., 2007).

In 2010, estimated net worldwide GHG emissions from human activities totaled nearly 46 billion metric tons of GHG, expressed as carbon dioxide equivalents (CO_2e), a 35% increase from 1990 (USEPA, 2017). Carbon dioxide accounted for about 75% of total global GHG emissions and during 1990 and 2010, net emissions of CO_2 increased by 42% and average surface temperature increased by 0.15°F per decade (USEPA, 2017). During the same period, N_2O emissions increased by 9% and CH_4 emission increased by 15%. By 2014, U.S. GHG emissions totaled 6,870 million metric tons (15.1 trillion pounds) of CO_2e, 7% increase since 1990 (USEPA, 2017). The global temperature is likely to increase 2.0–4.9 °C by year 2100 with median 3.2 °C and over 95% chance that it will be more than 2 °C (Raftery et al., 2017). The projected increase in global temperature is likely due to increases in population, economic growth, and C use. Many of the major GHGs are persistent and stay in the Earth's atmosphere for many years after being released and their warming effects on the climate continue over a long time.

1.2. Agriculture Sector as Source of Greenhouse Gases

As of 2014, the U.S. agriculture sector contributed to approximately 9% of the total GHGs emissions with CO_2, CH_4, and N_2O accounting for about 81, 11, and 6%, respectively, of all U.S. greenhouse gas emissions (USEPA, 2016). Most agricultural emissions originate from soil management, enteric fermentation, energy use, and manure management. As crops grow, photosynthesis removes CO_2 from the atmosphere and stores it in the plants and soils. Soil and plant respiration add CO_2 back to the atmosphere when microbes or plants break down molecules to produce energy (Extension, 2016).

Methane emission is attributed to natural sources such as wetlands, as well as human activities such as natural gas leakages and livestock operations. Methane emissions from enteric fermentation and manure management represent 25% and 10% of total CH_4 emissions from anthropogenic activities, respectively (USEPA, 2017). Of all domestic animal types, beef and dairy cattle were by far the largest emitters of CH_4. Both, CH_4 and CO_2 are also produced by enteric fermentation and manure management activities that include anaerobic storage of liquid manure, slurry, and solid manure, open pit system, composting, and aerobically digested slurry pits (IPCC, 2007). However, CO_2 and enteric CH_4 emission from concentrated animal feeding operations (CAFOs) are not currently regulated by USEPA. In addition to CO_2 and CH_4 emissions, N_2O emission is driven by the agriculture, transportation, and industrial activities with agricultural soil management as the largest source (75%) in the United States (USEPA, 2017). Farming practices such as the addition of N fertilizers induce N_2O emissions from agricultural soils. Nitrous oxide is also produced during the breakdown of N in livestock manure and urine, which contributed to 5% of N_2O emissions in 2015.

1.3. Nutrient Uptake in Corn

Corn plant development stages include vegetative (V) and reproductive (R) stages (Hanway, 1966). The subdivisions of V stages starts at emergence (VE) and goes towards V1 through V(n), where (n) represents the last leaf stage before tasselling (VT). Similarly, six subdivisions of R stages are labeled numerically with their common names (R1–R6) in Table 1.

Table 1: Vegetative (V) and reproductive (R) stages of a corn plant (Hanway, 1966).

Vegetative Stages	**Reproductive Stages**
VE emergence	R1 silking
V1 first leaf	R2 blister
V2 Second leaf	R3 milk
V3 third leaf	R4 dough
.	R5 dent
.	R6 physical maturity
V(n) nth leaf	
VT tasselling	

Most of the dry weight of the plant consists of organic carbonaceous materials resulting from photosynthesis and subsequent processes. At least 12 nutrient elements must be taken up for the corn plant to grow and develop normally. An adequate supply of each nutrient at each stage is essential for optimum growth at all stages. The seasonal pattern of nutrient accumulation is similar to dry matter accumulation. However, nutrient uptake begins even before the plant emerges from the soil. The amounts of nutrients taken up early in the growing season are small, but nutrient concentrations in the soil surrounding the roots of the small plant at that stage often must be high (Hanway, 1966). The soluble fraction of nutrients that are present in soil solution and are not held on the soil fractions flow to the root as water is taken up via mass flow. Nutrients such as nitrate-N, calcium, and sulfur are normally supplied by mass flow (Barber et al., 1963).

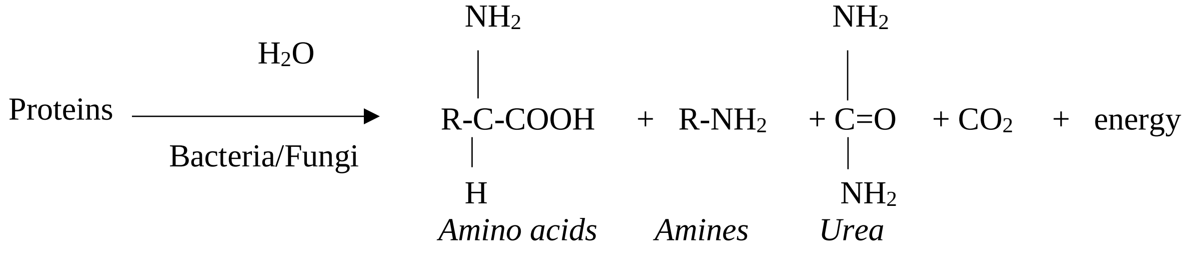
Uptake of potassium (K) is completed soon after silking, but uptake of other essential nutrients such as nitrogen and phosphorus continues until near maturity. Much nitrogen and phosphorus and some other nutrients are translocated from vegetative plant parts to the developing grain later in the season. This translocation can result in nutrient deficiencies in the leaves unless adequate nutrients are available to the plant during that period. A large portion of the N and P taken up by the plant is removed in the grain that is harvested. But most of the K is returned to the soil in the leaves, stalks, and other plant residues, unless the plant parts are removed for silage or other forms of feed (Hanway, 1966).

1.4. Nitrogen Transformations

1.4.1. Nitrogen Mineralization

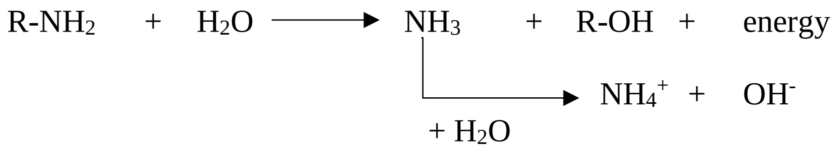
Nitrogen mineralization is the conversion of organic N to NH_4^+ through two reactions, *aminization* and *ammonification* (Halvin et al., 2013):

Step 1. *Aminization*



$$\text{Proteins} \xrightarrow[\text{Bacteria/Fungi}]{H_2O} \underset{\textit{Amino acids}}{R\text{-}\overset{NH_2}{\underset{H}{C}}\text{-}COOH} + \underset{\textit{Amines}}{R\text{-}NH_2} + \underset{\textit{Urea}}{\overset{NH_2}{\underset{NH_2}{C}}{=}O} + CO_2 + \text{energy}$$

Step 2. *Ammonification*



$$R\text{-}NH_2 + H_2O \longrightarrow NH_3 + R\text{-}OH + \text{energy}$$

$$NH_3 \xrightarrow[+\,H_2O]{} NH_4^+ + OH^-$$

Mineralization occurs through the activity of heterotrophic microorganisms that require organic C for energy. Heterotrophic bacteria dominate the breakdown of proteins in neutral and alkaline soils, while fungi predominate in acid soils. Aminization converts proteins in residues to amino acids, amines, and urea (step 1). These are organic N compounds that are further converted to NH_4^+ by ammonification (step 2). A diverse population of aerobic and anaerobic bacteria, fungi, and actinomycetes are capable of converting the products of aminization to NH_4^+ (Ren et al., 2014; Rochette et al., 2000). The NH_4^+ thus produced can be:

- Converted to NO_2^- and NO_3^- (nitrification)
- Absorbed directly by plants (N uptake)
- Used by heterotrophic bacteria to decompose residues (immobilization)
- Fixed as biologically unavailable N in the lattice of certain clay minerals (NH_4^+ fixation), or
- Converted to NH_3 and released back to the atmosphere (volatilization).

Soil moisture content regulates the proportions of aerobic and anaerobic microbial activity. Maximum aerobic activity and N mineralization occur between 50 and 70% water-filled pore space (Halvin et al., 2013; Linn and Doran, 1984). Soil temperature also influences microbial activity where optimum temperature ranges between 25 and 35 °C.

1.4.2. Nitrogen Immobilization

N immobilization is the conversion of reactive N (NH_4^+ and NO_3^-) to organic N. If decomposing residue contains low N, microorganisms will immobilize NH_4^+ and NO_3^- in the soil solution (Eghball et al., 2002; Ren et al., 2014). Microbes need a C:N ratio of ~8:1; therefore, inorganic soil N is utilized by the rapidly growing population, reducing NH_4^+ and NO_3^- to very low levels (Halvin et al., 2013). Microorganisms outcompete plants for NH_4^+ and NO_3^- during immobilization and plants can readily become N deficient. In most cropping systems, sufficient N is applied to compensate for N immobilization by microbes and to facilitate crop N uptake. If the added organic material contains high N, immobilization will not proceed because the residue contains sufficient N to meet microbial demands, and inorganic N in the soil will increase from mineralization of organic N in the residue.

1.4.3. Nitrification

Nitrification is a process which converts NH_4^+ produced from mineralization to NO_2^- and NO_3^- by nitrifying bacteria such as *Nitrosomonas* and *Nitrobacter*. *Nitrosomonas* converts ammonium into NO_2^- whereas *Nitrobacter* converts NO_2^- to NO_3^- (Oertel et al., 2016). Oxidation of NH_4^+ to NO_3^- is represented by:

Step 1:

$$2NH_4^+ + 3O_2 \xrightarrow{\textit{nitrosomonas}} 2NO_2^- + 2H_2O + 4H^+$$

$$(-3) \xrightarrow[\textit{increasing oxidation of N}]{} (+3)$$

Step 2:

$$2NO_2^- + O_2 \xrightarrow{\textit{nitrobactor}} 2NO_3^-$$

$$(-3) \xrightarrow[\textit{increasing oxidation of N}]{} (+5)$$

Net reaction: $NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$

Because nitrification is a microbial process, soil environment influence nitrification rates. Factors that affect nitrification are, supply of NH_4^+ (higher the rate of mineralization, better the nitrification), population of nitrifying soil organisms, soil pH (5-9, optimum range), soil aeration (adequate), soil moisture (<60% WFPS is better), and soil temperature (25-35 °C optimum) (Davidson et al., 1998; Halvin et al., 2013; Oertel et al., 2016).

Crops utilize both, NO_3^- and NH_4^+ forms of reactive N, with much preference towards NH_4^+, since this form is easily metabolized and less energy intensive for crops (Cambouris et al., 2016). However, the preference for NO_3^- or NH_4^+ differ between crops, and crop uptake of NO_3^- as primary N source is mainly due to rapid oxidation of NH_4^+ to NO_3^-. Plant uptake of N may influence the soil inorganic N dynamics. Generally, for corn, soil NO_3^- gradually increases until the plant is 12" tall, followed by a gradual decrease through tasselling to harvest (Tisdale et al., 1985). However, corn N accumulation generally increases throughout the growing season. It is well documented that nitrification can also produce N_2O, a potent GHG. Under anaerobic conditions, the concentration of NO_2^-, which is a toxic compost, increases in the soil, and it may be alternatively used by the nitrifying microorganisms as an electron acceptor, resulting in N_2O and NO during nitrification (Halvin et al., 2013; Oertel et al., 2016):

$$\begin{tikzcd} NH_4^+ \arrow[r] & NO_2^- \arrow[r] \arrow[d] & NO_3 & \\ & NO \arrow[r] & N_2O \arrow[r] & N_2 \end{tikzcd}$$

In addition, NO_3^- is very soluble and mobile in water and subject to runoffs, erosion, and leaching losses. Therefore, nitrification comes with both, benefits and losses.

1.4.4. Gaseous Losses of Nitrogen

The major losses of N from the soil are due to crop removal and leaching; however, under certain conditions, inorganic N can be converted to gases and lost to the atmosphere (Maharjan et al., 2014). The primary pathways of gaseous N losses are by denitrification and NH_3 volatilization. The most probable biochemical pathway for denitrification is:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O\ (g) \rightarrow N_2\ (g)$$

In this reaction, NO_3^- decreases as NO_2^- increases, then NO_2^- is replaced by N_2O, which is ultimately converted to N_2. Some anaerobic organisms in soil obtain their O_2 from NO_2^- and NO_3^- with the accompanying release of N_2O and N_2. Nitrous oxide and N_2 losses are highly variable because of fluctuation in environmental conditions between years, between seasons, and within a given field. N_2 loss predominates, sometimes accounting for >90% of the total denitrification, while N_2O loss is greater under less-reduced conditions (Halvin et al., 2013; Tisdale et al., 1985). The most important factors that affect the denitrification rate are (i) waterlogged or anaerobic environment, (ii) presence of NO_3^- in the anaerobic zones, and (iii) presence of decomposable or soluble C. If each of these parameters are high and occur together, denitrification potential and quantity of N losses are high (Halvin et al., 2013; Luo et al., 2012; Oertel et al., 2016).

Ammonia (NH_3) is a natural product of N mineralization of which only small amounts are volatilized compared to NH_3 volatilization from surface-applied N fertilizers and manure. The reversible reaction is:

$$NH_4^+ \rightleftarrows NH_3(g) + H^+$$

Urea and other amines are products of N mineralization from soil organic matter (SOM) and could be subject to NH_3 volatilization. The biological hydrolysis of urea requires the enzyme *urease*, which is abundant in soils (Huijsmans et al., 2003; Sommer and Hutchings, 2001). Urease activity is greatest in the rhizosphere where microbial activity is high. Although temperatures up to 37 °C favor urease activity, urea hydrolysis can occur at temperatures of <2 °C (Halvin et al., 2013). As a result, a portion of fall-applied or early winter-applied urea may be converted to NH_3 or NH_4^+ before the spring. While NH_3 volatilization is generally low in native unmanaged systems, adding fertilizer or manure N sources to soils can greatly increase N losses by volatilization. Understanding soil, environmental and N management factors influencing volatilization reactions is essential to minimize NH_3 losses.

1.5. Nitrogen Fate of Land Applied Manure

Livestock fecal matter, urine combined with waste feed, bedding material and wastewater in the animal confinement is commonly referred to as manure (Spellman, 2007). Nitrogen is often the yield-limiting nutrient in crop production and is used in large amounts by the growing plants as well as lost via various physical, chemical and environmental processes (Gregorich et al., 1998; Ma et al., 1999). Nitrogen mineralization rates are highly variable based on the manure types and characteristics (Van Kessel et al., 2000). Availability factors for P and K can be in the range of 80–90% because these nutrients have minimal loss potential with volatilization or leaching (as compared to N), and they remain relatively stable in the soil (Shaffer, 2015).

Manure N mineralization generally starts at a slow rate initially, which is indicative of a lag period but this is followed by a quick increase in rate and a subsequent slow N release rate (Chae and Tabatabai, 1986). Studies have reported anywhere between 11–21% manure N mineralization from composted and non-composted manure (Eghball, 2000), 25% from dairy cattle manure (Sanderson and Jones, 1997), 37-45 % from chicken manures amendments, and 41-52% from alfalfa pellets (Agehara and Warncke, 2005), and 56 % from beef feedlot manure (Chang and Janzen, 1996). Li and Li (2014) reported an average of 21, 19, and 13% added organic N from chicken manure, pig manure and cattle manure mineralized, respectively during 161 d of incubation. Furthermore, Eghball et al. (2002) reported 21 % organic N mineralized in dairy manure, of which 32% were available in the first year and 14% in the second year. In the same study, N mineralization was at 55% for poultry (hens) with 90% available in the first year and 2% the second year after application indicating that mineral composition of manures varies with size and species of animals, housing, and rearing management, feed ration, manure storage, and climate (Eghball et al., 2002).

1.5.1. Manure Application Rates and Handling

Manure used for crop production are generally applied on an N-basis. Manure application rate depends on the crop N requirement, understandings of manure history in the field, N content of the manure, and any fertilizer N that may be applied. Manure may be applied to provide N requirements of the crop based on the N availability in the first year. Manure contains nitrogen (N), phosphorus (P), potassium (K) and essential secondary and micronutrients needed for crop production and has been used as a substitute for inorganic fertilizers (Eghball and Power, 1994; Franke et al., 2008). For beef manure, incorporated within 12h of application, the first and second-year N availability assumption is approximately 60% and 25%, respectively (Hernandez and Schmitt, 2012). If beef manure is applied to provide 200 kg N ha^{-1} to a corn crop, then the total amount of N applied would be 333 kg ha^{-1}, since only 60% of N is available in the year of application.

Agriculture and grassland are the major land covers in the Great Plains of the United States and there is an abundant base for land application of different types of cattle manure where its application to soil can be effectively accomplished. However, manure handling depends on the characteristics, composition, consistency, amount and types of solids present in manure (Lorimor et al., 2004). Liquid manure consists of up to 4% solids content while slurry, semi-solid, and solid manures consist of 4–10%, 10–20%, and >20 % solids respectively. The chemical interaction of the organic and inorganic components of the manure such as cellulose, hemi-cellulose, fat, protein, and volatile materials under specific environmental condition may result in GHG emissions, NO_3^- leaching, NH_3 volatilization losses, and loss of crop yield (Kerr et al., 2006). While manures can be surface applied into the soil, incorporating manure below the soil surface may help lessen odor, reduce volatilization loss, prevent runoffs, and preserve nutrients for crops (Eghball and Power, 1994; Lorimor et al., 2004).

The GHG emissions and uptake of manure nutrients by crops depend on several variables - the application timing, manure types, application rates, soil properties, application methods, and other environmental variables such as temperature, and precipitation (Agnew et al., 2010; Hernandez and Schmitt, 2012). All of these variables play an important role in manure N transformation when applied to soil.

1.5.2. Land Application and NH_3 Volatilization

Ammonia (NH_3) volatilization is the major pathway of N loss after fertilizer application with agricultural activities representing 20–80% of NH_3–N emissions worldwide from sources that include cattle manures and inorganic fertilizers (Aneja et al., 2008; Misselbrook et al., 2000; Zhang et al., 2010). In the U.S., manures are the most important source of NH_3 emission as well. NH_3 fluxes from U.S. animal husbandry are approximately 2.4 Tg yr^{-1} with the majority coming from livestock manure exposed to the atmosphere in barns, during storage, and through field application (USEPA, 2011, 2004).

The partial pressure between the soil and the air is the primary driving force for NH_3 volatilization. Some conditions that favor NH_3 volatilization include high crop residue, temperature greater than 13°C, a drying soil surface, neutral or alkaline soil pH, and low soil cation exchange capacity (CEC) (Jantalia et al., 2012; Mkhabela et al., 2006; Pelster et al., 2012). Mkhabela et al. (2006) reported with pH increase NH_3 emissions increases because of the shift in the the equilibrium reaction [NH_4^+ (soil) = NH_3 (soil) = NH_3 (gas)] that pushes more NH_4^+ towards NH_3 form. Similarly, temperature effect on NH_3 emission as reported by Clay et al.

(1990) showed a linear increase in NH_3 volatilization with increasing temperature in moist soil. Further studies showed high NH_3 loss upon soil drying conditions (Alkanani et al., 1991). Higher NH_3 volatilization loss was also observed in soils with low CEC since these soils cannot retain much of NH_4^+ compared to that of soils with high CEC (Francisco et al., 2011). In contrast, with an increase in organic matter and clay content, the CEC of the soil increases thereby reducing NH_3 emissions (Alkanani et al., 1991; Pelster et al., 2012).

The process of NH_3 volatilization from urea is categorized into two steps. The first step is the hydrolysis of urea by urease to ammonium (NH_4^+) that can remain in the soil solution or be retained by the soil (Jones et al., 2013). The second step is the chemical change from NH_4^+ in the soil solution to aqueous NH_3 [NH_3 (aq)], which in turn can diffuse from the soil solution to the atmosphere giving rise to NH_3 volatilization (Jones et al., 2013).

In manure, the majority of the NH_3 originates from the labile N component of urine, mostly urea, and the rate and degree to which resulting NH_3 emissions occur will depend on several chemical and physical factors (Misselbrook and Powell, 2005). Thus suggesting that interactions between deposited urine and bedding materials may influence the emissions from livestock housing and following land application. For example, if the urine is protected from air turbulence by a physical bedding layer that has greater absorption capacity, NH_3 emissions will be reduced by increasing the resistance to gaseous transport (Misselbrook and Powell, 2005). The pH and CEC of the bedding materials may influence the extent to which NH_4^+ ions are held by the bedding (Freney et al., 1983), and the addition of C source in the bedding material may promote rapid immobilization of ammoniacal N (Chantigny et al., 2001).

Ammonia emission post-application of manure is affected by several factors that include: (i) Manure properties (DM, pH, NH_4-N), (ii) application management (incorporation, timing),

(iii) soil properties, and (iv) environmental factors (temperature, wind speed, rainfall) (Agnew et al., 2010; Bussink and Oenema, 1998; Meisinger and Jokela, 2000). Ammonia emissions typically are high within a few hours of manure application. Thompson and Meisinger (2004) reported that NH_3 loss represented 71% of slurry ammoniacal N 8 days after surface application of which 58 % of total NH_3 loss occurred within 6h after application, 67 % within 12h, and 72 % within 24h. The high initial NH_3 loss after the manure application is attributed to the availability of ammoniacal N concentration in manure (Sherlock et al., 2002). Ammonia emission can lead to negative impacts on human health and in the acidification and eutrophication of natural ecosystems (Davison and Cape, 2003).

At the feedlot level, NH_3 loss mitigation strategies from manure mainly focus on N excretion reduction in the manure, urease inhibitors, feces and urine separation, manure pH reduction during collection and storage, and land application techniques (Ndegwa et al., 2008; Sun et al., 2014). Minimal NH_3 losses can be achieved by immediate incorporation or injection of manure with the soil (Bittman et al., 2005). Studies show up to 90% reduction in NH_3 volatilization loss with immediate incorporation (within 24 hour) of manure to soil (Agnew et al., 2010; Huijsmans et al., 2003). In addition, preferably manure application during cool, calm weather and in the early morning or evening have shown to reduce NH_3 losses up to 50% (Lupis et al., 2012).

1.5.3. Land Application and GHG Emissions

1.5.3.1. Nitrous oxide (N_2O)

The concentration of N_2O in the atmosphere which was in the 180–260 ppb range during the preindustrial era, has gone up to 328 ppb in 2015 (IPCC Working Group 1 et al., 2013). As of

2016, agricultural soil management activities such as fertilizer application and cropping practices accounted for approximately 75% of the U.S. N_2O emissions.

Nitrous oxide production in soil is carried out through microbial processes, namely nitrification and denitrification, controlled by soil aeration, soil density, temperature, moisture, pH, organic matter, available N, C/N ratio, texture and soil management (Bremner, 1997; Brentrup et al., 2000; Snyder et al., 2009). The N_2O emission of from nitrification are mainly influenced by soil temperature and soil density (Davidson and Swank, 1986; Signor and Cerri, 2013) and from denitrification are mainly influenced by the amount of water filled pores space (Awale and Chatterjee, 2015; Linn and Doran, 1984). Nitrification is the aerobic oxidation of NH_4^+ to NO_3^- triggered by chemoautotrophic bacteria in two stages: *nitritation*, in which the NH_4^+ is oxidized to NO_2^- and *nitratation*, in which the NO_2^- is further oxidized to NO_3^- (Paul, 2007). Bremner (1997) summarized results from several researchers that N_2O from nitrification increased with increase in soil pH and organic matter, soil moisture and temperature and by the addition of manures and plant residues. Denitrification, on the other hand, involves the reduction of NO_3^- to atmospheric N_2 gas, facilitated by facultative anaerobic bacteria, which correspond to 0.1-5.0% of the total bacteria biomass in the soil (Butterbach-Bahl et al., 2013). Complete denitrification results in N_2, and incomplete denitrification can lead to a variable fraction of N emitted as NO and N_2O. Higher levels of organic C content in soils can also increase the N_2O emissions because it can stimulate microbial growth and activity that increases the consumption of O_2 and generates anaerobic conditions necessary for denitrification (Brentrup et al., 2000). However, the effect of organic matter depends on the degree of anaerobic conditions created by microbial metabolism (Stevens and Laughlin, 1998).

N_2O emissions following the land application of different types of manure have been studied in laboratory, plot, and field scale studies (Chadwick et al., 2000; Chang et al., 1998; Dittert et al., 2005). Loro et al. (1997) conducted a solid vs liquid manure study and showed immediate and intense denitrification in liquid manure while denitrification was more prolonged and less intense in solid manure. Tenuta et al. (2000) reported solid manures with bedding provide “more sustained release” of available C, as the bedding material decompose, promoting denitrification enzyme activity for longer periods. Furthermore, anaerobic conditions during storage of liquid manure result in C decomposition and N mineralization promoting higher emissions (Rochette et al., 2008). However, measuring manure-induced N_2O emissions over several years following application of solid manure may help understand the effects of solid vs liquid manure application fully. In fact, a 30-yr study (Mogge, 1999) with repeated application of solid manure reported higher emissions from soils applied with solid manure with a conclusion that nitrification was the major contributor to N_2O emissions. Gregorich et al. (2005) reported a linear increase in N_2O flux with fertilizer application rate. However, other studies that measured cumulative N losses over extended periods found non-linear relationship between overall N_2O fluxes and manure application rate (Hansen et al., 1993; Lessard et al., 1996). In addition, Wulf et al. (2002) reported that the flux pattern of different manure application techniques (injection and incorporation) varied, but cumulative emissions showed manure injection increased overall emissions because of the anaerobic conditions and diffusion constraints. Thus, there is a need to quantify N_2O emissions based on local and regional weather conditions and management practices to add emission information to national emission database.

1.5.3.2. Carbon dioxide (CO_2)

Carbon dioxide emission from soil is a result of soil respiration that includes biological and non-biological processes (Rey, 2015). The biological process includes microbial respiration, root respiration and faunal respiration at the soil surface where crop residue is present while non-biological processes (chemical oxidation) occur at higher temperatures (Bunt and Rovira, 1954; Rey, 2015). Several studies have shown that factors such as soil texture, temperature, moisture, pH, available C and N content of the soil influence CO_2 production and emission from the soil (Johnson et al. 2007; Agnew et al. 2010). Other studies reported soils to act as a sink for CO_2 and other GHGs (Paustian, 1997). Carbon dioxide emission is also affected by external factors (atmospheric pressure) and soil conditions such as tillage, irrigation, crop type, fertilizer and manure application (Rastogi et al., 2002).

Temperature and soil moisture affects soil respiration and hence CO_2 evolution. Wiant (1967) observed a logarithmic increase in soil CO_2 emissions when the temperature was between 20 and 40°C, but no emission at 10 ºC and rapid decline past 50 °C. In contrast, Bunt & Rovira (1954) had reported increased in CO_2 past 50°C and attributed to increased root activity and OM decomposition at a higher temperature. In addition to temperature, high soil water content generally would lead to more CO_2 evolution up to an optimum level, and then it would reduce from there (Rastogi et al., 2002). Periodic cycles of soil drying and wetting have a distinct influence on CO_2 progression. Casals (2000) reported a large CO_2 flux resulting from rewetting of a dry soil at high temperatures. Borken et al. (1999) observed reduced soil respiration under drought condition, while rewetting increased it by 48% to 144%. Moore & Dalva (1993), in a laboratory study to determine the influence of temperature and water-table position, found soil CO_2 emission 2.4 times more at 23°C than at 10°C showing a positive and linear relationship with temperature and soil moisture content. Bajracharya et al. (2000) also observed a significant correlation of CO_2 flux with soil temperature ($R^2 = 0.8$) and air temperature ($R^2 = 0.8$), but not with soil moisture.

Soil texture greatly influences the water infiltration and gas diffusion rates and thereby CO_2 formation and emission. A study conducted on clay loam soil and sandy soil (Kowalenko et al., 1978) found that CO_2 evolution was larger from clay loam soil (6.2 kg CO_2 ha^{-1} d^{-1}) than sandy soil (3.3 kg CO_2 ha^{-1} d^{-1}). Kowalenko et al. (1978) also reported an increase in CO_2 flux with an increase in soil pH. However, in another study (Rao and Pathak, 1996) soil pH beyond 7.0 showed low CO_2 emission, up to 18% reduction at pH 8.7 compared to that at neutral pH and further reduction of 83% when the pH was raised to 10.

Application of organic manure in the soil can also increase CO_2 emission (Rao and Pathak, 1996). Rochette and Gregorich (1998) observed increased soil respiration with manure application along with the increase in the levels of soluble organic carbon (SOC) and microbial biomass C by a factor of 2 to 3 compared with the control, whereas the inorganic N fertilizer had little effect on any parameter. Another study (Gregorich et al., 1998) on dairy cattle manure application at variable rates found that increasing the application rate increased both the CO_2 emissions and the SOC levels by 2 to 3 times than that of the control.

1.5.3.3. Methane (CH_4)

In 2014, total CH_4 emissions from enteric fermentation and manure management in the United States were at 22.5 and 8.4% of total CH_4 emissions, respectively (USEPA, 2016). Methane emission comes primarily from rice cultivation and from ruminant livestock and can be captured from manure using anaerobic digesters, anaerobic manure lagoons, and reduced by livestock diet modification (Snyder et al., 2009). Manure has biodegradable C, often in anaerobic conditions, which support methanogenesis and CH_4 emission (Chadwick et al., 1999). Methane production from manure depends on ultimately on composition and digestibility of the animal diet (Cornejo and Wilkie, 2010). Optimal conditions for CH_4 production include an anaerobic, water-based environment, a high level of nutrients for bacterial growth, a neutral pH (close to 7.0), and warm temperatures (Cornejo and Wilkie, 2010). Methane formation is a complex biological process that requires acidogenesis, acetogenesis, and methanation stages (Chandra et al., 2012). Methanogenic archaea utilize H_2 with CO_2, formate, methanol, and acetate as substrates for methanogenesis (Chandra et al., 2012). The optimal environmental requirements for biomethanation process are presented in Table 2 adapted from Deublein & Steinhauser (2008).

Table 2: Optimal environment requirements for biomethanation process.

Parameter	Hydrolysis/Acidogenesiss	Methane formation
Temperature	25–35 °C	Mesophilic: 32–42 °C thermophilic: 50–58 °C
pH value	5.2–6.3	6.7–7.5
C:N ratio	10:1–45:1	20:1–30:1
DM content	<40% DM	<30% DM
Redox potential	+400 to −300 mV	<−250 mV

Methane consumption may occur in non-rice agricultural soils and these soils are a sink for atmospheric CH_4 (Bowden et al., 2000). Studies show N fertilization also reduces soil CH_4 oxidation and that soils can be a source or a sink based on factors that include soil type, aeration, and nitrogen availability (Steudler et al. 1989; A.S. Chan & Parkin 2001; Chan & Parkin 2001). Manure application techniques such as subsurface injection reduce NH_3 and CH_4 emissions but can result in increased N_2O emissions (Hristov et al., 2013). In addition, use of bedding materials have been shown to favor reduction of CH_4, however, it may also favor the nitrification reaction leading to more N_2O emissions (Chadwick et al., 2011).

1.5.4. Land Application and Nitrate (NO_3^-) Leaching

Nitrogen loss as NO_3^- from agricultural fields can contaminate both surface and ground water while adversely affecting the environment and the crop yield (Angle et al., 1993; Drury et al., 2009). When cattle manure is applied as a N source, a large amount of plant available reactive N may be lost via NO_3^- leaching below the root zone (Roth and Fox, 1990). Nitrate is the primary form of leached N from the soil because it is weakly held by soil and is highly water-soluble. Ammonium (NH_4^+) is one of the major forms of plant available N, but it does not move far in soil (De Boer, 2017). Nitrate leaching is source independent meaning any NO_3^- available for plant uptake is susceptible to leaching loss.

The organic N fraction of manure mineralizes and becomes gradually plant available (Magdoff, 1978; van Es et al., 2006). If manure is effectively incorporated, most of the urea and NH_4^+ are converted to NO_3^-, thus making it plant available or subject to leaching or denitrification losses. However, the rate of N mineralization is strongly affected by variations in soil, weather, manure composition, and management factors. For instance, Magdoff (1978) estimated that manure N mineralization rates on a poorly drained clay soil were about half compared to a well-drained loam. Furthermore, the NO_3^- leaching loss may be greater from organic N sources than that from inorganic sources due to rapid mineralization that occurs continuously in organic fertilizers, even when there is no crop uptake (King, 1990). However, in a field study comparing manure composts and mineral NPK using lysimeters, Leclerc et al. (1995) demonstrated reduction of nitrate leaching from manure application during a 5-year rotation.

There have been several studies on soil NO_3^- dynamics as affected by different tillage practices and N sources (Angle et al., 1993; Constantin et al., 2010; Dou et al., 1995). Tyler and Thomas (1977) studied salt and water movement using lysimeters in the field under corn and found higher concentrations of NO_3^- under a no-tillage system. Another study (Elmi et al., 2003) on a sandy loam underlain by a clay layer found that tillage system had no effect on NO_3 losses. Conversely, some studies have shown reduced NO_3^- losses under no-till systems compared to the conventional systems either due to increase N mineralization under conventional tillage or greater denitrification under no-till systems (Angle et al., 1993; Mkhabela et al., 2008). Understanding the impact of tillage and N source on soil NO_3^- dynamics under various conditions is essential for refining N strategies. The use of N source and tillage preference need a further review of site specific research to understand the NO_3^- leaching because it may come with unintended environmental tradeoffs, including increased NH_3 and N_2O emissions.

1.6. Nitrogen Management Strategy

Fine textured and poorly drained soils such as that of the RRV calls for targeted N management strategies (Asgedom et al., 2014). National Pollutant Discharge Elimination System permits, the National Conservation Practice Standard 590, and associated state permit and standard practices all dictate responsible manure application practices that include estimates of available nutrients and aerial losses. Management of N application using solid beef manure may reduce the potential nutrient losses and GHGs from the agrosystem when compared to commercial fertilizers.

1.6.1. Solid Beef Manure

Solid beef manure applied to the soil as a part of manure management strategy can partially or completely meet crop N demand. A three-year study (Evans et al., 1977) comparing the effects of heavy applications of solid beef, liquid beef, and liquid hog manure showed no significant differences in corn yield from the inorganic N treatment. Another study (Sutton et al., 1986) on liquid and solid dairy manure application over 5-yr reported maximum corn yields that were 1% higher than commercial fertilizer. Furthermore, Ferguson et al. (2005) reported the high average silage yield and crop nutrient removal with N-based manure treatments, intermediate with P-based manure treatments, and least with inorganic N fertilizer. However, cattle manure and other forms of organic wastes including municipal wastes and their composts, may promote more emissions of NH_3, CH_4, CO_2 and N_2O than inorganic fertilizers (Ding et al., 2007; Johnson et al., 2007) and promote NO_3^- leaching below root zone when applied at higher rate (Evans et al., 1977). Rochette et al. (2008) suggested that dairy cattle manure N application to silage corn could result in greater or equal N_2O emissions than synthetic N application. This indicates that other factors such as additional C substrates and enhanced soil respiration resulting in greater denitrification and gaseous emission (Rochette et al., 2008).

The manure and commercial fertilizer use in combination (Hou et al., 2012) may increase crop yield and nitrogen (N) content of the crop. Magdoff and Amadon (1980) also determined that applications of both dairy manure and inorganic N were necessary to obtain maximum yields of continuous corn (*Zea mays* L.) silage on a relative low producing clay soil. These variations in yield response are often attributed to manure composition, application rates, and climatic conditions.

1.6.2. Solid Beef Manure with Bedding

Manure bedding provided comfort for cattle and helps with manure management (Ayadi et al., 2015). Because of the extreme weather, low run-off risks, and/or high land price in the Northern Great Plains, beef cattle are raised in confined housing, such as hoop and monoslope barns (Ayadi et al., 2015). Most commonly used bedding materials in these confined housings are those that are available locally, such as corn stover, soybean stover, wheat straw, or corn cobs (Doran et al., 2010). These bedding materials are usually applied in every 7-14 days in order to properly manage manure and moisture and for the comfort of cattle (Doran et al., 2010).

Bedding materials, organic or inorganic, differ in their physical and chemical composition. For instance, wood chips contain higher lignin content; hence, they degrade much slower than straw (Bollen and Lu, 1957; Saliling et al., 2007). Use of bedding materials in feedlot manure may help improve certain soil properties, increase the rate of N mineralization and produce better yields (Ferguson et al., 2005; Miller et al., 2014). Miller et al. (2014) monitored clay loam soil properties following long-term application of stockpiled feedlot manure containing straw or wood-chip bedding under barley silage production and their results show soil C, C:N ratio, and water-soluble total N (WSTN) had the most consistent and significant ($P \leq 0.05$) bedding effects. Total organic C and C:N ratio were generally greater for wood-chips than straw bedding, and the reverse trend for WSTN. In another study with wood-chip bedding and straw, stockpile bedding with wood-chip bedding had greater C, and C:N ratio while straw bedding had greater pH, NO_3-N, and NH_4-N (Miller et al., 2014).

Ayadi et al. (2015) studied a simulated beef cattle bedded pack and suggested that NH_3 volatilization and GHGs (N_2O, CO_2, and CH_4) concentration are expected to increase from corn stover bedding compared with soybean stubble during warmer weather. The differences between bedding material was due to rapid urea hydrolysis, with some contributions attributed to rapid protein hydrolysis and higher moisture content in corn stover (Ayadi et al., 2015). However, N_2O concentration were not affected by bedding material. In another simulated beef cattle bedded pack study (Spiehs et al., 2014) using different wood-based bedding materials, pine chips and corn stover had higher NH_3 and CO_2 concentrations than for green and dry cedar chips, whereas CH_4 was the highest with green cedar chips bedding and there was no change in N_2O concentration for all bedding types. The differences in NH_3 and CH_4 was attributed to pH levels of the bedding materials, whereas low CO_2 in cedar bedding was likely due to its antimicrobial properties (Spiehs et al., 2014). For N_2O, Baggs et al. (2003) reported that straw with high C:N ratio on the soil surface may increase the immobilization of the N fertilizer applied and thus decrease the denitrification reactions and N_2O emissions.

Most studies on livestock manure and emission focus on liquid dairy manure management (Comfort et al., 1990; Pfluke et al., 2011; Rotz and Oenema, 2006) or open feedlot manure (Borhan et al. 2011; Hristov et al. 2013; Miller et al. 2014) or in-barn emissions (Cortus et al., 2014; Joo et al., 2014). There is a limited information on how land application of solid beef manure and bedded beef manure practices influences overall nitrogen dynamics and GHG emissions.

1.6.3. Inorganic Fertilizer

Various form of synthetic N fertilizers include (i) NH_4^+ or NH_4^+ forming sources [(*e.g.*, urea, UAN, anhydrous NH_3, ammonium nitrate (NH_4NO_3)], (ii) controlled and slow release fertilizers (*e.g.*, ESN, polymer-coated CRFs), and (iii) urease and nitrification inhibitors (*e.g.*, NBPT, Nitrapyrin). Since the decline of fertilizer prices in 2010, the U.S. intake of commercial fertilizers was at 21 million tons, and increased to 22 million tons in 2011, primarily due to N intake increase (USDA, 2012). The increase is more rapid for N fertilizer compared to P and K due to the development of seed varieties that favor yield responses to N fertilizers (USDA, 2012). Urea ($CO(NH_2)_2$), a white crystalline solid containing 46% nitrogen (46-0-0), is extensively used as an animal feed additive and fertilizer (Overdahl et al., 2017). From 1960 to

2011, use of solid urea (46-0-0), which has the most percent of N by weight among solid N fertilizers, increased from 2 percent to 22 percent replacing anhydrous ammonia that was the dominant N fertilizer for many years (USDA, 2012).

Corn crops account for approximately 40% of the U.S. fertilizer consumption (USDA, 2012). In order to achieve high quality yield, grain corn requires substantial amounts of fertilizer N (Gagnon et al., 2011). Excess application of inorganic N is susceptible to N losses via N_2O emissions (McSwiney and Robertson, 2005), NH_3 volatilization (Rochette et al., 2009) and NO_3^- leaching (Liang et al., 2011). The portion of N lost as NH_3 not affected by the rate of N applied, have also been reported (Guang-Ming et al., 1998). These results suggest that it is difficult to accurately assess the mineralization of inorganic N from soil organic matter; since it depends on factors such as precipitation and temperature (Dinnes et al., 2002). It is due to the variability in mineralization rates, plant biomass recovery of applied N have been reported to be low (<50%) (Cassman et al., 2002; Chien et al., 2009; Ladha et al., 2005). Adding urea to soils also lead to the loss of CO_2 fixed during the industrial production process as urea is converted into ammonium (NH_4^+), hydroxyl ion (OH^-), and bicarbonate (HCO_3^-), in the presence of water and urease enzymes (IPCC, 2006). Bicarbonate then evolves into CO_2 and water. Furthermore, the NH_4^+ produced dissociates into gaseous NH_3 by combining with the hydroxyl ion (OH^-), formed from the reaction of HCO_3^- with water (Zerpa and Fox, 2011). The chemical reaction is as follows:

$$CO(NH_2)_2 + 2H_2O + \text{urease} \rightarrow (NH_4)_2CO_3 + H^+ \rightarrow 2NH_4^+ + HCO_3^-$$

$$NH_4^+ \rightarrow NH_{3(g)} + H^+$$

Ammonia (NH_3) volatilization is one of the major N loss pathways associated with the use of surface applied urea with agricultural activities accounting for nearly 81% of the anthropogenic NH_3 emissions in the U.S. (Aneja et al. 2008).

In the northern Great Plains of the U.S., livestock is an important contributor to the agricultural economy, and many livestock farms are located near water bodies. With the increased concentration of livestock, there are many confined-animal feeding operations (CAFOs) and associated manure stocks. Agricultural producers who focus on making economic management decisions regarding manure utilization in their production systems are often in conflict with environmental interests (Moshia et al., 2014). Livestock farmers have recycled manure on the land where it was produced primarily because of high transportation costs to offsite areas. The study on the use manure to replace inorganic fertilizer to poorly drained soils is limited. Therefore, research is needed to evaluate if the N fertilizer management practices can increase crop production while reducing the potential of N loss, GHG emission from poorly drained soils in the RRV.

1.6.4. Objectives

The objectives of this study were as follows:

i. To evaluate the daily and seasonal emissions/uptake rates of N_2O, CO_2, CH_4, and NH_3 in corn cropping systems,

ii. To evaluate soil N and leachate NO_3 levels under different N sources in corn cropping systems.

iii. To evaluate the effects of manure N management on crop yield

iv. To evaluate effects of soil moisture and temperature on GHGs and N dynamics from the soils of the RRV.

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2. FIELD MEASUREMENT OF GREENHOUSE GAS EMISSIONS AND NITROGEN DYNAMICS FROM SOLID BEEF MANURE APPLIED IN FARGO-CLAY SOIL

2.1. Abstract

Land application of manure is causing nutrient losses and environmental concerns. The fate of nutrients in beef cattle (*Bos taurus*) manure from the land application is influenced by the interaction of manure and soil properties with environmental variables. A 2-yr field study was conducted to examine the influence of land application of solid beef manure (SM) and solid beef manure with straw bedding (BM) on the emission of greenhouse gases (GHGs)-nitrous oxide (N_2O), methane (CH_4), and carbon dioxide (CO_2). Nitrogen (N) losses and/or gains of manure as ammonia (NH_3) volatilization, nitrate (NO_3^-) leachate below root-zone, residual soil N, corn (*Zea mays* L.) plant tissue N, and corn yield were determined. In addition to SM and BM, the influence of urea (UO) and no-fertilizer (NF) treatments were also examined and compared with manure treatments. Treatments were applied to Fargo silty clay soil of the Red River Valley (RRV) to meet the corn N demand and yield goal of >10,760 kg ha^{-1} (>160 bushel/acre). The two-year growing season cumulative N_2O emission (cN_2O) ranged from 0.3 (NF) to 1.2 (UO) kg N ha^{-1} with the highest emission from UO for both years. The UO treatment reduced cumulative CO_2 (cCO_2) by 42% compared to manure treatments over two growing seasons. The cumulative CH_4 (cCH_4) emission ranged from -0.04 to 0.21 kg CH_4-C ha^{-1}, with the highest emission from BM treatment. When comparing manure (SM and BM) versus UO sources of N, manure reduced cumulative NH_3 (cNH_3) by ~11%. Cumulative soil NH_4^+ plus NO_3^- in 2017 were significantly greater by 11% compared to 2016. Grain yield and grain N uptake were not affected by the N source. The variable effects are likely due to the composition inconsistency of the manure N as

well as from interactions with the soil environment. The results highlight the challenge of meeting crop demand while reducing GHG emissions by selection of manure as the N source.

2.2. Introduction

Agricultural practices such as the use of N fertilizer are estimated to contribute up to 70, 20, and 27% of the global anthropogenic N_2O, CO_2 and CH_4 emissions, respectively (Hernandez-Ramirez et al., 2009; IPCC, 2013). Soil N_2O emission from fertilizer application is a result of nitrification and denitrification processes and is influenced by fertilizer type and properties (inorganic vs. organic), soil N availability, soil C, temperature, soil moisture, and soil organic matter (Dobbie and Smith, 2003; Khalil et al., 2005). Agricultural soils act as a source of CO_2 primarily due to biological oxidation as root respiration and as microbial soil respiration of plant residue and soil organic matter (Raich and Schlesinger, 1992). Methane emission in anaerobic soil occurs via CO_2 reduction and/or acetate fermentation pathways (Avery et al., 2003). In contrast, CH_4 consumption in soil (as oxidation to CO_2) may be catalyzed by methanotrophs and NH_4^+ oxidizing bacteria (Henckel et al., 2000). In addition to soil GHGs, ammonia (NH_3) emission from soil contribute to acidification and eutrophication of ecosystem on its deposition (Aneja et al., 2008).

Compared to commercial N fertilizers (*e.g.*, urea), land application of animal manures can supply soluble C and N for microbial respiration as well as phosphorus (P) and potassium (K) for plant growth (Eghball and Power, 1999). However, the quantity of manure N available for plant uptake is affected by factors such as application timing, manure type and quality, manure bedding type, soil properties, and weather. Loecke et al. (2004) reported the nitrogen use efficiency on corn yield in the range of 11% for spring-applied manure to 35% for fall-applied composted manure. In a long-term (9-yr) study, Miller et al. (2009) found no difference in fresh and composted beef cattle manure to inorganic fertilizer (NH_4NO_3) on barley dry matter yield and N uptake. However, the variable influence of straw and wood bedding on N uptake were observed on a year-to-year basis in other studies (Miller et al., 2009). The quantity of manure nutrients available for plant uptake can be lost as GHG and NH_3 volatilization. Moreover, nitrate-N (NO_3-N) is one of the primary sources of N to most crops and is susceptible to runoff and leaching losses from below the root-zone and can add to NO_3^- concentrations in groundwater above acceptable human health standards (Basso and Ritchie, 2005).

In North Dakota, the number of beef cows increased 6% from 2016 to 954,000 head as of January 01, 2017 (USDA-NASS, 2017a). The increase in cattle number directly increases the production of manure and the challenges to managing it with better manure management practices. There is limited information on how the land application of solid beef manure and bedded beef manure practices influence overall gaseous emissions. Most cattle manure and cattle emission studies focus on managing liquid dairy manure (Rotz and Oenema, 2006) or manure in open feedlots (Borhan et al., 2011), and in barn-emissions (Spiehs et al., 2010). The use of straw bedding during winter to mitigate cold stress on the animals could alter the nutrient availability of manure. However, the field research on GHG emissions and fate of nitrogen in soil from cattle manure with and without bedding is limited, even though emissions may be more significant than those from slurry or liquid manure (Dustan, 2002).

The ongoing integration of beef cattle manure and crop production means that the impact of management decisions need to be understood and be sustainable at multiple levels. Furthermore, to understand the full extent of manure contributions to anthropogenic GHG emissions and the mitigation potential from management modifications on crop production needs to be comparatively assessed with commercial fertilizer, such as urea. Thus, the objectives of this study were:

i. To estimate daily and seasonal:
    - Emission/uptake rates of CO_2, CH_4, N_2O, and NH_3;
    - Soil N and NO_3 leachate levels under different N sources in corn cropping system.
ii. To identify soil and weather control variables for gaseous emissions and,
iii. To assess the effects of different N management on corn yield and grain quality.

2.3. Materials and Methods

2.3.1. Site Description and Experimental Setup

A two-year field experiment was conducted during 2016 and 2017 corn (*Zea mays* L.) growing seasons at the North Dakota State University (NDSU) research farm in Fargo, ND (46° 55' 15" N, 96° 51' 31" W; 272.3 m above sea level), USA. The soil is poorly drained Fargo-Ryan silty clay with 0 to 1 percent slope, and classified as fine, smectitic, frigid Typic Epiaquerts (Fargo) and fine, smectitic, frigid Typic Natraquerts (Ryan) (Soil Survey Staff, 2017). During the 2015 growing season, the field was chisel plowed and corn was grown.

The experimental plots (each 3.3 m by 9.1 m excluding alleys) were established in August 2015 as a randomized complete block design with four blocks (n=4) (Figure 1). Treatments were applied to the same plot areas both years and consisted of a nonfertilized (NF) control plus three management systems:

i. Solid beef cattle manure (SM) applied at 34 Mg ha^{-1} and 20.2 Mg ha^{-1} on October 15, 2015 and October 19, 2016, respectively.
ii. Solid beef cattle manure with wheat straw bedding (BM) applied at 67.3 Mg ha^{-1} and 43 Mg ha^{-1} on October 15, 2015 and October 19, 2016, respectively.

iii. Urea only (UO) (46-0-0) at 220 kg ha^{-1} applied on May 04, 2016 and May 09, 2017, respectively. In addition, 117 kg P ha^{-1} in 2016 and 88 kg P ha^{-1} in 2017 was applied to UO plots to meet the corn P demand. Phosphorus was supplied with Triple Superphosphate (TSP, 0-45-0).

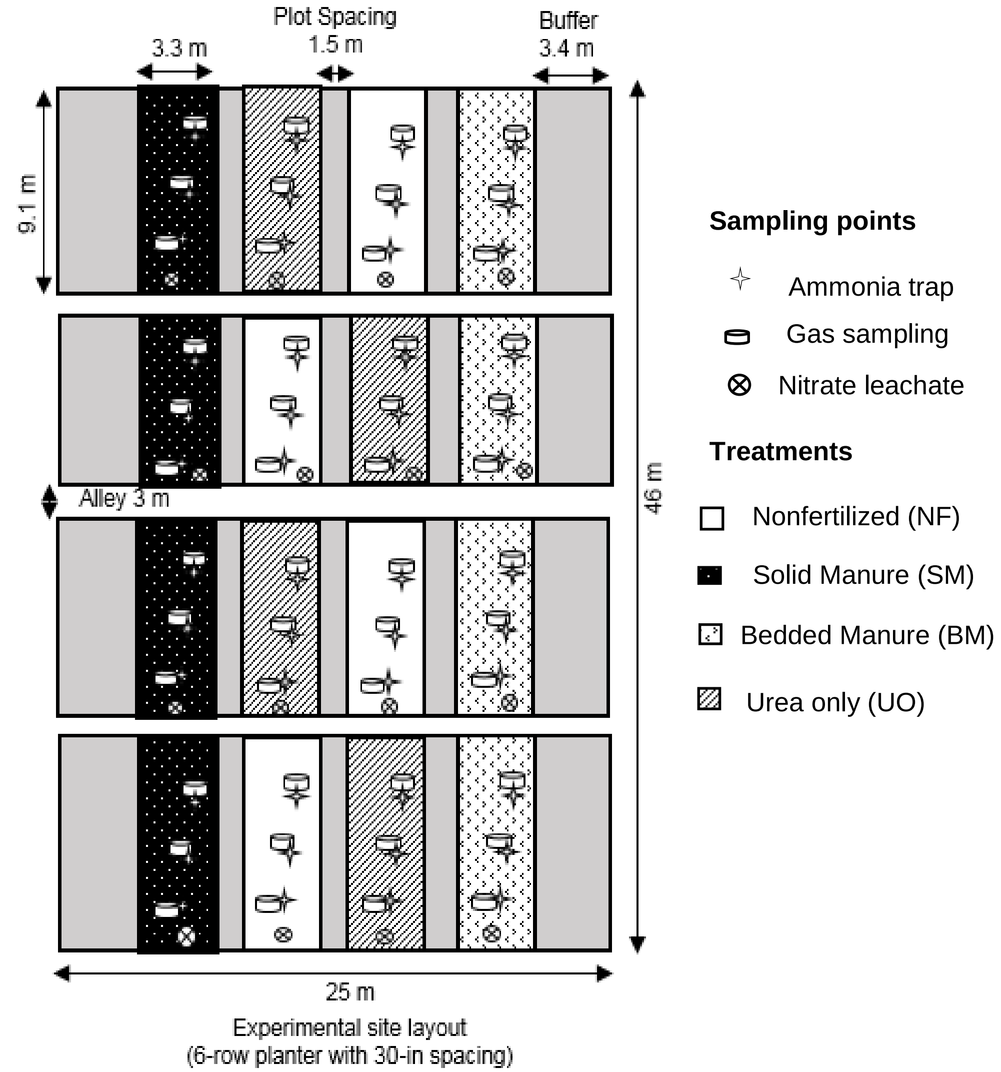


Figure 1: Layout of the experimental site at the North Dakota State University Research Farm.

Fertilizer treatments were applied at 100% of the recommended N rate for Eastern North Dakota high clay soil for corn (220 kg ha^{-1}). Recommended N was determined based on soil nitrate test at 2-feet depth, soil type, soil OM concentration and yield goal of >10,760 kg ha^{-1}

(>160 bushel/acre) using the North Dakota Soil Fertility Recommendations for Corn (Franzen, 2015). In addition, manure application rates for each growing season were calculated based on manure testing for nutrient concentrations and nutrient availability factors. In 2015, nutrient availability factors of 0.95 and 0.5 were used for NH_4-N and organic N respectively and these values were adapted from the NDSU Manure Application Calculator for Corn (NDSU, 2015). Similarly, in 2016, manure application rates were calculated based on the assumption that 25% of organic N is available from the manure applied in the previous year.

Manure (SM and BM) was applied using the manure spreader in fall of 2015 (15 Oct.) and were uniformly broadcasted by hand in 2016 (19 Oct.). Manures were incorporated immediately to a depth of 0.2 m with a field cultivator. Fall application of manure allows sufficient time for the freshly tilled soil to settle and give microbes time to decompose the manure–making nutrients more available to crops and preventing germination concerns in spring (Lewandowski, 1995). Manures were applied in between 0900 to 1200 local hours. The average air temperature and average wind speed on the application day were 7.7 °C and 4.6 ms^{-1} in 2015 and 7.2 °C and 2.9 ms^{-1} in 2016, respectively. Urea and TSP fertilizers were uniformly broadcasted on UO plots by hand in the springs of 2016 (04 May) and 2017 (09 May), just before planting, and incorporated immediately with a field cultivator. Field corn (VT Double Pro Corn, 86-day relative maturity) was planted on May 04 in 2016 and on May 09 in 2017 with a 1010 John Deere seed planter (John Deere, Moline IL). The seeds were placed 0.05 m deep into the soil with 0.15 m in-row (seed-to-seed) spacing and 0.76 m between-rows (row-to-row) spacing. Corn was grown under the rainfed condition without any irrigation water inputs. Experimental plots were sprayed with roundup herbicide and corn silk adjuvant on week 4 and week 12 from planting. Buffer alley was rotter tilled during the same week of herbicide application. Corn plots were machine harvested with a forage harvester on 21 Sept. 2016 and with a 3-row header combine harvester (ALMACO, IA) on 18 Oct. 2017. Corn grain yields were determined at 15% moisture content.

2.3.2. Soil and Manure Analysis

Soil cores – at depth intervals of 0-0.15, 0.15-0.30, and 0.30-0.60 m - were collected using a truck-mounted probe (0.036 m internal diameter, Giddings Machine Company Inc., Windsor, CO). Additionally, three soil cores with depth intervals of 0-0.15 and 0.15-0.30 m were collected from each block during the first soil sampling event in 2015 and 2016 to determine bulk density (Blake and Hartge, 1986). Gravimetric soil moisture content (SMC) was determined by collecting soil at 0-0.15 and 0.15-0.30 m depth from each plot using soil probe and drying sub-samples at 105 °C for 24 h. The average bulk density and SMC were then used to calculate the water filled pore space (WFPS) in soil.

$$\%\mathrm{WFPS} = \frac{\mathrm{SMC} \times \mathrm{BD}}{\left[1-\left(\frac{\mathrm{BD}}{\mathrm{PD}}\right)\right]} \times 100$$

where, SMC is the soil moisture content, BD is the bulk density (1.08 g cm^{-3}), and PD is the particle density of the soil (assumed to be 2.65 g cm^{-3}).

Soil pH and electrical conductivity (EC) were determined electrometrically in 1:2.5 soil/water extract (Thomas, 1996) using Accumet AB pH meter (Fisher Scientific, Hampton, NH); soil texture by hydrometer method (Elliott et al., 1999); soil organic matter (OM) by loss on ignition method (Combs and Nathan, 1988); CEC by sodium acetate method (Chapman, 1965); soil NO_3^- and NH_4^+ concentration by KCL extract method (Maynard et al., 2008); Olsen-P by sodium bicarbonate method (Frank et al., 1998); and total carbon and nitrogen results were obtained from the NDSU Soil Testing Laboratory, Fargo, North Dakota. Soil samples were also sent to a commercial laboratory (AGVISE Laboratories, Northwood, North Dakota) for N, P, and

K analyses.Samples of SM and BM were collected from stockpiles at NDSU Beef Cattle Research Complex facility, Fargo, ND. Ten random shovel-samples of manure were taken from each stockpile, combined, mixed thoroughly, and then a subsample was taken from the composite pile for chemical analysis.

2.3.3. Weather Data

Daily precipitation during the fall of 2015 and 2016 (post-application of manure) and growing seasons 2016 and 2017 were obtained from the nearest North Dakota Agricultural Weather Network (NDAWN) station, Fargo, which is within 2 km from the research site (Figure 2). Mean air temperature and wind speed were also obtained from NDAWN station (Figure 3).

2.3.4. Grain Yield and Plant Analysis

At physiological maturity, corn ears were hand harvested from the middle two rows of each plot in 2016. In 2017, a three-row header combine harvester was used to collect harvested grain. Grain was dried for one week at 65 °C, shelled and weighed to obtain dry matter (DM) yield. Grain moisture was determined using a moisture meter (DICKEY John GAC 500 XT Grain Moisture Tester). The grain N uptake (kg N ha^{-1}) was determined by multiplying DM grain yield by the N concentration in grain (% N) (Murrell, 2008).

Apparent Nitrogen Recovery (ANR) in grain was determined by subtracting the mean aboveground grain N uptake in the control treatment from grain N uptake of fertilized treatments divided by N application rate. During 2016 and 2017 growing seasons, corn leaves for tissue analysis were collected in a clean and dry brown kraft paper bags at V6 (vegetative stage of six leaves with visible collars), VT (vegetative stage of tasselling), and R6 (reproductive stage of physiological maturity) stages of corn development. At V6 stage, eight-first fully developed leaf from top (first leaf below whorl) was cut at its base where it joins sheath. At VT stage, 25 leaves from the outer rows below and opposite ear was cut and collected at its base where it joins sheath. At R6 stage, 25 leaves below and opposite ear were cut and collected. Leaves collected at each stage were then dried at 55 °C oven for one week and grounded in a Thomas Wiley mill to pass a 2-mm screen. Subsamples of dried corn grain and leaves were sent to AGVISE Laboratories, Northwood, North Dakota for Inductively Coupled Plasma (ICP) analysis.

2.3.5. Measurement of Soil Inorganic N Content

Soil samples from the upper 0.30 m soil profile - with 0.15 m increments - were collected throughout the growing season using a hand soil probe (0.02 m internal diameter) for the analysis of inorganic soil N (NH_4^+ and NO_3^-) contents. Three soil cores from each plot were composited, transferred to the laboratory at 5°C, and stored at -18°C until analysis within a week. After thawing and homogenizing the field soil, gravimetric soil moisture content (SMC) was determined by weighing approximately 10 g of field moist soil in an aluminum cup followed by overnight drying in an oven set to 105 ºC. In addition, for analysis of extractable soil N, approximately 6.5 g of field-moist soil (W_m) were collected in a 50-mL polypropylene vial and was extracted with 25 mL of 2 M KCl solution (1:5 soil/extractant ratio), after shaking for 30 min in a reciprocal shaker (Maynard et al., 2008). The soil suspension was then centrifuged for 5 min and filtered through Whatman no. 2 filter paper. The KCl extracts were analyzed for NO_3^- and NH_4^+ using Timberline TL2800 Ammonia Analyzer (Timberline Instruments, Boulder, CO). The results determined in mg NO_3^- kg^{-1} and mg NH_4^+ kg^{-1} soil (dry basis) were calculated as described in the following steps:

$$\text{Step 1: Oven-dried soil weight (g) } (W_d) = \frac{W_m \times (100\% - \text{SMC})}{100\%}$$

$$\text{Step 2: Moisture factor (MF) } = \frac{W_m}{W_d}$$

Where, Wd, SMC, and Wm, and MF are the weight of oven dried soil, soil moisture content, weight of moist soil (~6.5 g), and moisture factor, respectively.

$$\text{Step 3: } NO_3^- \text{ in moist soil (mg kg}^{-1}\text{)} = \frac{[NO_3\text{-N in extract } (\mu g\ mL^{-1}) \times \text{extractant (25 mL)}]}{[\text{Weight of moist soil } (W_m)(g)]}$$

$$\text{Step 4: } NO_3\text{-N in oven-dried soil (mg kg}^{-1}\text{)} = NO_3\text{-N in moist soil (mg kg}^{-1}\text{)} \times MF$$

Soil NH_4^+ concentration was calculated following the same procedure (step 1-4) using the values for NH_4^+-N in extract (µg mL^{-1}) in step 3 and NH_4^+-N in moist soil (mg kg^{-1}) in step 4. Soil NH_4^+ and NO_3^- were determined separately for the two sampling depths and summed to represent the 0-to-30 m. Finally, both the NH_4^+ and NO_3^- contents were added together to obtain total inorganic N contents for 0-0.30 m soil depth. Soil N intensity (g N kg^{-1} soil) was determined by trapezoidal integration of daily soil inorganic N concentrations over the growing season (Burton et al., 2008) separately for NH_4^+ and NO_3^- and for sum of NH_4^+ and NO_3^-.

2.3.6. Measurement of Leachate NO_3^-

Leachate samples at 0.60 m soil depth were collected from each plot using ceramic suction cup lysimeters (1.20 m in length and 22 mm diameter, Irrometer Company, Inc., CA, USA) during the 2016 and 2017 growing seasons. Before the installation, the ceramic end of the lysimeters were soaked in deionized water for 24 h at a constant vacuum of -70 kPa. For lysimeter installation, a 0.6-m deep soil hole was bored using a probe (36 mm inner diameter) on each plot. A lysimeter was inserted into the hole and the gap around the lysimeter was re-filled with silica slurry along with excavated soil. The ceramic suction cup lysimeters were installed on 09 May in 2016 (5d after planting) and on 18 May in 2016 (9d after planting) and were allowed to equilibrate for a week such that the first water sample collected was discarded and not used for data analysis. Then onward samples, if any, were collected during every sampling event. Using a hand pump, a vacuum of -70 kPa was applied and maintained until the next sampling day. Water samples inside the lysimeters were extracted using a 50-mL polypropylene syringe and then frozen at -18 °C until analysis. In the laboratory, NO_3^- concentrations in the leachate samples were analyzed using the Automated Timberline TL2800 Ammonia Analyzer. The lysimeters were devoid of water samples in all plots for over 90% of the sampling period.

2.3.7. Measurement of GHGs

Nitrous oxide (N_2O), carbon dioxide (CO_2), and methane (CH_4) fluxes from the soil surface were measured using static chambers constructed of polyvinyl chloride (PVC) as recommended in the GRACEnet project protocol (Parkin and Venterea, 2010). Three PVC anchor rings (0.25 m internal diameter and 0.10 m height) were inserted at 0.05 m depth in each plot such that each anchor spaced at an approximately equal distance from the center. The germinating crops, if any, inside the PVC rings were removed out at the time of anchor installation. Anchors were installed 24 h before sampling for the first time to minimize soil microclimate effects. Thereafter, anchors were left in the field for the rest of the sampling period. Headspace air sampling was done during 0900 to 1200 local hours, because during this time, surface soil temperature is near to its daily average (Maharjan et al., 2014). On each sampling day, insulated, vented, and reflective PVC chamber tops were placed above the anchors. The PVC chamber tops had an additional opening fitted with septum used as a port for air sample withdrawal. Headspace air samples were collected at 0, 0.5, and 1 h after chamber placement using 30 mL graduated polypropylene syringe and transferred to 12 mL pre-evacuated glass vials sealed with butyl rubber septa. Headspace air samples were collected on an average 7 d interval throughout 2016 and 2017 growing seasons with more frequent sampling a few weeks after planting. Headspace air samples were analyzed for N_2O, CO_2, and CH_4 within two days using a master SHS headspace autosampler (DANI Instruments, Milan, Italy) connected to a DGA-42 Master Gas Chromatograph (DANI Instruments, Milan, Italy). The Gas Chromatograph (GC) was fitted with a ^{63}Ni electron capture detector (ECD) for N_2O (carrier gas: 10% CH_4 and 90% Ar), thermal conductivity detector (TCD) for CO_2 (carrier gas: He), and flame ionization detector (FID) for CH_4 (carrier gas: He) quantitation. The GC columns in an oven was operated at 80 °C. Analytical gas standards (0, 1, 2, 5, and 10 ppm for N_2O; 0, 500, 1000, 3000, and 5000 ppm for CO_2; and 0, 4, 10, 30, and 100 ppm for CH_4; Scotty Specialty Gases) were included after every twenty samples to construct standard calibration curves.

The average of eight ambient air concentration of the research field was used as 0-hr (T_0) samples for each sampling day. The daily GHG flux ($\mu L\ L^{-1}\ h^{-1}$) from each of the three sampling points within a plot were determined from concentrations relative to elapsed time using the following procedure: (1) flux calculations were not performed if (a) the time 0.5-hr ($T_{0.5}$) and/or time 1-hr (T_1) concentration(s) were less than [(1- error) × ambient concentration (T_0)], (b) the quadratic curve through the three data points was concave down and [T_1 × (1+error)] was less than [$T_{0.5}$ × (1-error)], or (c) the quadratic curve through the three data points was concave up and a linear slope fit through the three points was not significantly different than zero; (2) if the quadratic curve through the three points was concave down, the first order coefficient of the quadratic equation fit through the three data points was considered the flux; and (3) if the quadratic curve through the three points was concave up, but the linear slope through the three points was significantly different than zero, the slope was considered the flux. The allowable error (proportional to concentration) was set at 20%.

Evaluated fluxes of GHGs were then converted from volumetric basis to mass basis (μg m^{-2} h^{-1}) using the modified Ideal Gas Law equation (Adviento-Borbe et al., 2010; Parkin and Venterea, 2010):

$$F=\frac{\Delta C}{\Delta t}\times\frac{V}{A}\times\frac{P\times k\times MW}{R\times(273+T)}$$

where *F* is the gas flux rates of N_2O (μg N_2O-N m^{-2} h^{-1}), CO_2 (mg CO_2-C m^{-2} h^{-1}), or CH_4 (μg CH_4-C m^{-2} h^{-1}), $\Delta C/\Delta t$ denotes the increase/decrease of gas concentration in the chamber, *V* is the chamber volume (cm^3), *A* is the chamber surface area (506.7 cm^2), *P* is the atmospheric pressure (0.9678 atm), *R* is the gas law constant (0.08206 L atm Mol^{-1} K^{-1}), *T* is the temperature (°C), *k* is the unit conversion, and *MW* is the molecular weight of nitrogen and carbon (28, 12, and 12 $g.mol^{-1}$ for N_2O-N, CO_2-C, and CH_4-C, respectively).

The resulted fluxes of N_2O and CO_2 were corrected with soil properties (bulk density, clay fraction, pH, moisture content, and soil temperature) using the theoretical flux underestimation (TFU) method as described by Venterea (2010). Soil temperature and volumetric soil water content at the 0.06 m depth were measured with a GS3 soil moisture-temperature sensor (Decagon Devices, Inc., Pullman, WA 99163) by inserting its probe within 1 m from the PVC anchors. Venterea (2010) suggested that the TFU method is based on the theory that does not account for gas consumption, such as biogenic trace gas CH_4 that are known to undergo substantial uptake in the soil profile. Therefore, for this study, the TFU flux correction method was not used to correct for CH_4 and are reported 'as is' using the modified Ideal Gas Law equation. The flux for each plot was estimated using the mean flux of the three chambers within a plot. The minimum detectable flux of gas chromatograph was estimated by sampling ambient air samples from the experimental site and was at 0.1, 10, and 0.1 ppm for N_2O, CO_2, and CH_4 respectively. Daily fluxes and cumulative emissions were calculated as N_2O-N, CO_2-C, and CH_4-C, however for simplicity flux is herein referred to as N_2O, CO_2, and CH_4, respectively.

Growing season cumulative area-scaled GHG emissions/consumption (cN_2O, cCO_2, and cCH_4) for each plot was calculated using trapezoidal integration of daily measured flux versus time, which in effect assumes that fluxes changed linearly between measurement dates. Fertilizer-induced cumulative N_2O emission (fN_2O) was determined by subtracting cN_2O in the nonfertilized (NF) plots from cN_2O in N-amended soil (SM, BM, and UO). The fertilizer-induced N_2O emission factor (EF) was determined by dividing fN_2O by the N application rate. Yield-scaled N_2O emissions (yN_2O) and grain N scale N_2O emissions (gN_2O) were calculated by dividing cN_2O by grain yield and grain N uptake, respectively (Venterea et al., 2011).

2.3.8. Measurement of NH_3 Volatilization Loss

Ammonia volatilization losses from each plot were measured using semi-static open chamber (trap) following the procedure described by Jantalia et al. (2012). This trap uses a 2-L polyethylene terephthalate (PET) bottle (covering 0.0079 m^2 surface area of soil) and polyfoam strips (0.25 m long by 0.040 m wide by 0.005 m thick) as NH_3 traps. The chambers were secured in an upright position on the soil surface using wire stakes, surrounded by rubber bands. On the day of measurement, polyfoam strips were rinsed thoroughly with deionized water; excess water removed, and then rinsed with 0.5 M phosphoric acid (H_3PO_4) solution, finally the excess solution was removed. A single polyfoam strip was then hung from the bottle lid inside each chamber using a wire hook. The lower end of the polyfoam strip was dipped into 30 mL H_3PO_4 solution inside a 60-mL plastic cup suspended from the wire hook. Three chambers were installed in each plot within 0.6 m of the GHG anchors.

Strip foam and H_3PO_4 solution from inside each chamber were collected on the same day following GHG sampling during fall 2015, spring 2016, fall 2016, and spring 2017 with 34 sampling dates across all seasons. At the end of each sampling period, ammonia trap polyfoam strip and the acid solution in the plastic cup were collected in 125 mL of 2 M KCl. Fresh polyfoam strips and 30 mL H_3PO_4 solution were added inside the chambers to facilitate NH_3 trapping until next sampling day. The solution containing NH_3 traps were transferred to the laboratory and maintained at 5°C until analysis within 2 days. In the laboratory, the solution was filtered through Whatman filter paper and the filtrate was brought to 250 mL by further rinsing the strips with KCl solution. Fifty milliliters of this solution was then sealed and frozen at -18°C in polypropylene vials, until analysis within 2 days using Automated Timberline TL2800 Ammonia Analyzer. Ammonia loss during consecutive sampling dates (kg NH_3 ha^{-1}) was obtained by multiplying NH_3 concentration (µg mL^{-1}) by the total volume of solution (250 mL), divided by the surface area of the soil covered by the respective chamber (0.0079 m^2). The final NH_3 volatilization loss from each plot was estimated as the average loss of the three chambers. Cumulative NH_3 volatilization losses (kg N ha^{-1}) in 2016 and 2017 growing seasons were determined by summing the amount of NH_3 volatilized during each sampling period.

2.3.9. Statistical Analysis

Data were considered significantly different at $p = 0.05$ significance level using the MIXED procedure of SAS (SAS Institute, 2014). Repeated measures analyses were conducted on daily mean samples using the PROC GLIMMIX procedure of SAS with time (day of sample collection) as the repeated measure variable. N management system and year were considered as fixed effects, and time, block (replication) and the interactions with time and block were considered random effects. Residuals were evaluated for homogeneity of variance and normality using Q-Q plots and the requirements were met for all dependent variables except soil NO_3 leachate. A lognormal distribution improved the Q-Q plot of soil NO_3 leachate data set. Covariance structures tested were – Compound Symmetry (CS), Autoregressive AR(1), Heterogeneous Autoregressive ARH(1), Variance Components (VC), Toeplitz (TOEP), Heterogeneous Toeplitz (HTOEP), and Heterogeneous Compound Symmetry (CSH). The covariance structure resulting in the smallest Akaike information criterion (AIC) was considered most appropriate for analysis. For post hoc test, Tukey's Honest Significant Difference (HSD) was used. Relationships of soil and environmental variables with gas fluxes were assessed by performing regression on means using PROC REG in SAS to obtain correlation coefficient (R^2). When appropriate, data were log transformed and back-transformed means are presented here. Additionally, 'manure treatment' in data analysis herein refers to the average of both, SM and BM.

Emissions of GHGs and NH_3 were calculated from (i) daily mean soil to atmosphere fluxes for 1st year (fall 2015 and spring/summer 2016) and 2nd year (fall 2016 and spring/summer 2017) combined, and (ii) cumulative growing season emission for 2016 (May 2016–September 2016) and 2017 (May 2017–September 2017) combined. The cumulative emission comparison on growing seasons were made because the activity of the crop during these periods would alter the response of trace gas emissions to the environmental variables (Pelster et al., 2012).

2.4. Results

2.4.1. Weather, Soil and Manure Conditions

The laboratory results of the soil tests prior to fertilizer application in 2016 and 2017 are presented in Table 3. Manure samples were sent to a commercial laboratory (AGVISE

Laboratories, Northwood, North Dakota) for nutrient analysis prior to application each year (Table 4).

Table 3: Soil properties at the beginning and prior to manure application of the field experiment in 2015 and 2016.

Soil Properties	pH	EC	NO_3-N	P	K	CEC	Silt[a]	Clay	OM	Total C	Total N	C:N
		dS m^{-1}	-----------mg kg^{-1}---------			cmolc kg^{-1}	-------------------------%---------------------					
Soil depth (m)						***2015***						
0 - 0.15 m	8.05	1.4	5.7	2.3	380.5	39.6	44.3	52.1	6.8	3.1	0.23	13.5
0.15 - 0.30 m	8.1	1.2	3.0							2.6	0.2	13.0
0.30 - 0.60 m	7.6	2.3	3.4							2.5	0.2	12.5
						2016 [b]						
						Solid manure (SM) applied plots						
0 - 0.15 m	8.0	0.7	16.1	20.0	562.5	41.3	43.7	52.5	7.7	2.9	0.4	7.3
0.15 - 0.30 m	8.0	0.7	6.4	2.5	306.8					2.4	0.2	12.0
0.30 - 0.60 m	8.2	0.7	2.6	2.3	296.0					2.5	0.2	12.5
						Bedded manure (BM) applied plots						
0 - 0.15 m	8.1	0.7	9.3	9.8	439.0	41.6	43.7	52.5	7.4	2.8	0.3	9.3
0.15 - 0.30 m	8.1	1.2	6.5	2.3	301.3					2.4	0.3	8.0
0.30 - 0.60 m	8.2	1.4	3.4	2.0	291.5					2.6	0.3	8.7
						Urea only (UO) applied plots						
0 - 0.15 m	8.0	0.8	23.6	8.0	351.5	40.4	43.7	52.5	6.8	2.4	0.2	12.0
0.15 - 0.30 m	8.0	1.1	22.3	2.3	293.8					2.4	0.3	8.0
0.30 - 0.60 m	8.3	1.4	8.9	2.3	280.0					2.6	0.2	13.0
						No Fertilizer (NF) plots						
0 - 0.15 m	8.1	0.7	8.5	6.5	351.3	36.2	43.7	52.5	6.6	2.1	0.2	10.5
0.15 - 0.30 m	8.1	1.0	8.1	2.3	316.8					2.3	0.2	11.5
0.30 - 0.60 m	8.1	1.2	3.9	3.3	309.8					2.5	0.2	12.5

[a] Soil texture was determined for 0-0.15 m depth soil and values of No Fertilizer (NF) plots used in 2016.

[b] Post-harvest soil test results from treatment plots were used to determine application rates for 2017 growing season.

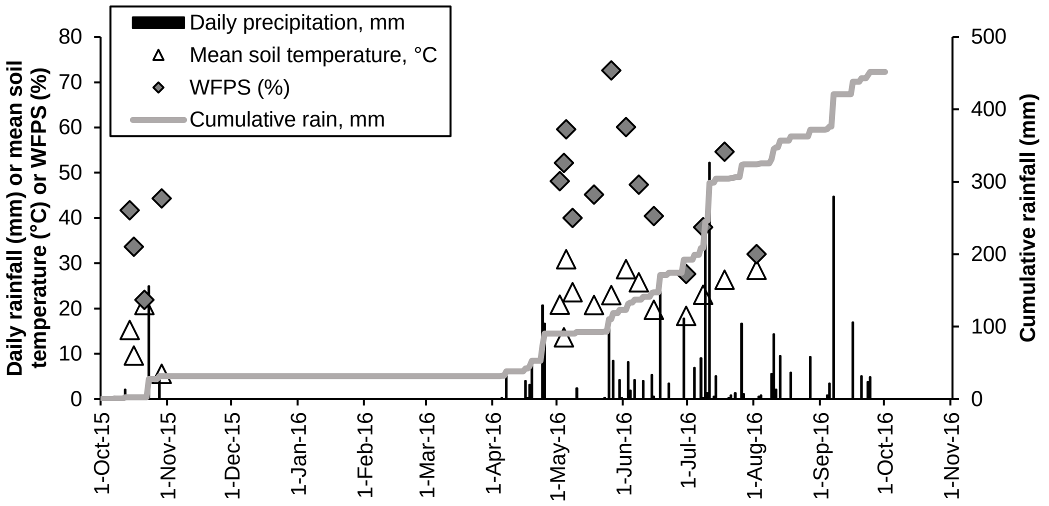
Table 4: Manure properties used in the experiment at the beginning and prior to field experiment in the fall of 2015 and 2016.

Manure Properties	**2015**		**2016**	
	SM[a]	BM[b]	SM	BM
pH	8.4	9.1	8.5	9.0
Inorganic N (g kg^{-1})	0.5	0.4	0.3	0.3
Organic N (g kg^{-1})	12.6	5.9	7.9	3.8
Total C (g kg^{-1})	205.0	249.0	134.0	161.5
Total N (g kg^{-1})	13.1	6.3	8.2	4.0
C:N	15.7	35.6	16.3	40.3
Moisture (%)	40.0	42.0	38.0	53.0
Dry matter (%)	60.0	38.0	62.0	36.0
Zn (g kg^{-1})	0.1	0.0	0.1	0.0
S (g kg^{-1})	0.9	0.7	1.2	1.3
P_2O_5 (g kg^{-1})	7.5	2.8	3.1	2.3
K_2O (g kg^{-1})	18.5	12.0	9.5	13.0
Application Rate (Mg ha^{-1})	34	67.3	20.2	43

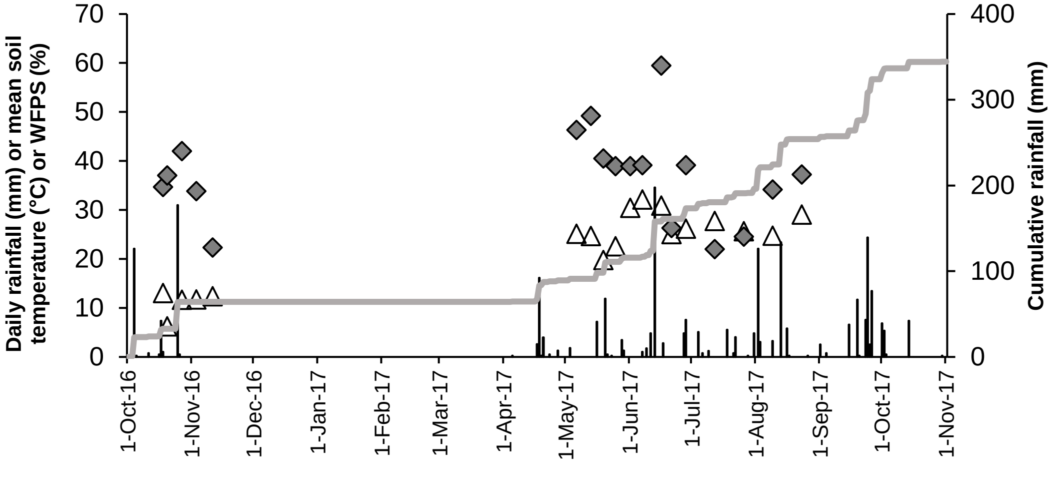
[a] SM = Solid beef manure, [b] BM = Solid beef manure with wheat straw as bedding.

Daily and cumulative precipitation, mean soil temperature, and mean WFPS (%; 0-0.15 m depth) during the 1st and 2nd year of the research study are presented in Figure 2. In addition, daily mean air temperature and mean wind speed are presented in Figure 3. Daily mean air temperature (8.1 °C) and wind speed (3.3 ms^{-1}) during 1st year (01 Oct. 2015–30 Sep. 2016) were greater than the mean air temperature (7.6 °C) and lower than the wind speed (3.5 ms^{-1}) recorded during 2nd year (01 Oct. 2016–30 Sep. 2017). Total precipitation during May through September was higher in 2016 (361.5 mm) compared to 2017 (241.5 mm) and lower than the long-term (1991-2017) mean annual precipitation (477.4 mm). In 2016 growing season (May–September), 65% of precipitation occurred in May, June, and July (combined), compared to 44% in 2017. In 2016, a dry period occurred in May, during which 33 mm of rainfall was recorded, and the average soil moisture content at 0-0.15 m was at 0.31 m^3m^{-3} (Decagon Devices, Inc., Pullman, WA 99163). In 2017, a dry period occurred in July, during which 23 mm of rainfall was recorded and the average soil moisture content at 0-0.15 m soil depth was 0.14 m^3m^{-3}. Averaged across the growing season, soil moisture contents were 0.28 and 0.22 m^3m^{-3} in 2016 and 2017, respectively. The average soil temperature during 2016 (23 °C) was lower than the 2017 growing season average (26.5 °C).

In 2016, the average growing season soil WFPS was at 47%. Comparatively, 2017 growing season was drier with drought conditions across the State and WFPS at 36%. For both growing seasons, the soil WFPS reflected the precipitation pattern (Figure 2).

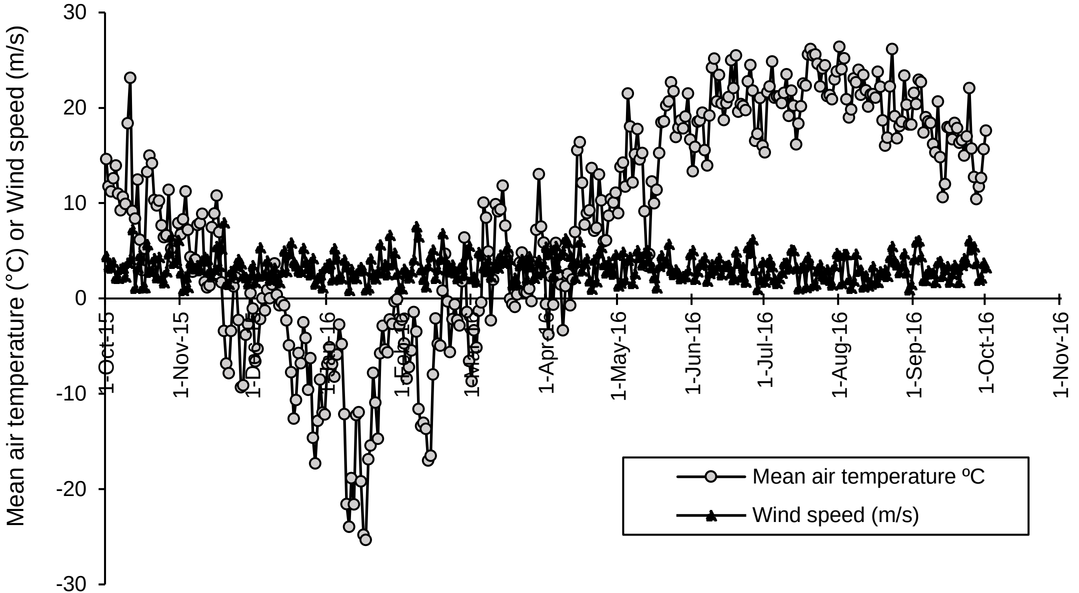


(a) Year 1 (01 Oct. 2015 - 01 Nov. 2016)

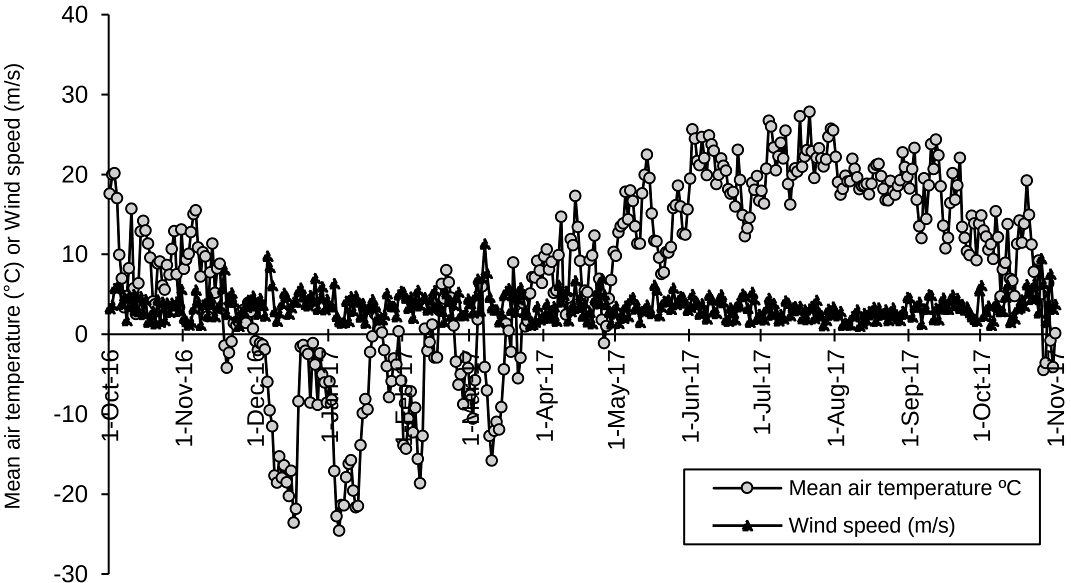


(b) Year 2 (Oct 01. 2016 - Nov 01. 2017)

Figure 2: Daily precipitation, mean soil temperature, mean water filled pore space (WFPS), and cumulative precipitation for (a) Year 1, and (b) Year 2 at the research site.



(a) Year 1 (01 Oct. 2015 - 01 Oct. 2016)



(b) Year 2 (Oct 01. 2016 - Nov 01. 2017)

Figure 3: Daily mean air temperature and mean wind speed for (a) Year 1, and (2) Year 2 at the research sites.

2.4.2. Crop Response

Corn grain yield over two growing seasons averaged approximately 8.1 Mg ha^{-1} with a maximum yield of 9.8 Mg ha^{-1} measured in 2016 from UO treatment (Figure 4). Averaged across growing seasons, year and N management significantly affected corn grain yield and grain N uptake (Table 5). There was no significant year × treatment effect on grain yield, grain N content, grain N uptake, and grain ANR. Corn grain yield and grain N uptake were significantly greater in 2016 than in 2017 by 24 and 18%, respectively. Within N management, there was no difference in grain yield and grain N uptake between treatments receiving N fertilizer. In addition, NF treatment had 21% lower corn grain yield and 30% lower grain N uptake compared to UO treatment. Manure treatments showed no significant influence on grain yield and grain N uptake compared to NF. Average grain N content across growing seasons were in the range of 13.1 (NF) to 14.6 g kg^{-1} (UO) and did not vary by year ($P = 0.17$), N management system ($P = 0.22$), and N source ($P = 0.16$) (Table 5). Averaged across two growing seasons, ANR in grain did not vary by year and N management system, however, there was a trend of UO>BM>SM ($P = 0.06$).

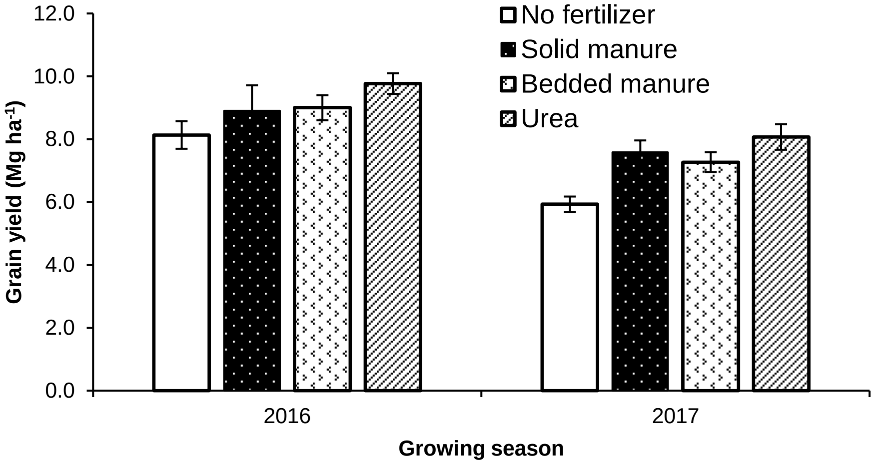


Figure 4: Corn grain yield for 2016 and 2017 growing seasons as affected by N management systems. Vertical bars are standard errors.

Table 5: Mean ± standard error of grain yield, grain N content, grain N uptake and grain ANR during 2016 and 2017 growing seasons as influenced by year, N management, and N source.

	Grain yield	Grain N content	Grain N uptake	Grain ANR[a]
	Mg ha^{-1}	g kg^{-1}	kg N ha^{-1}	%
		year		
2016	8.95±0.28[b]	13.36±0.37	119.59±5.0	9.48±2.78
2017	7.21±0.26	14.04±0.34	101.53±4.72	13.67±2.55
Pr > F	***<0.0001***[c]	*0.1735*	***0.0006***	*0.4328*
		N management		
No fertilizer	7.03±0.48 b	13.08±0.42 a	91.46±5.84 b	-
Solid manure	8.24±0.34 ab	13.06±0.57 a	107.49±6.0 ab	7.29±3.71 a
Bedded manure	8.13±0.53 ab	14.08±0.51 a	113.45±6.0 ab	10.00±2.96 a
Urea	8.92±0.40 a	14.58±0.38 a	129.83±6.0 a	17.44±2.25 a
Pr > F	***0.0033***	*0.2224*	***0.0037***	*0.0572*
		N source		
Manure	8.19±0.40	13.57±0.37	110.47±5.0	8.64±3.01
Urea	8.92±0.40	14.58±0.38	129.83±6.03	17.44±6.38
Pr > F	*0.0875*	*0.1589*	***0.0054***	***0.015***

[a] ANR refers to Apparent Nitrogen Recovery.
[b] Means within a column followed by the same letter are not significantly different at $P<0.05$ level.
[c] Significant *F* values ($P \leq 0.05$) for fixed sources of variation are shown in bold.

When comparing differences in N sources (manure vs. urea) across two growing seasons, grain N uptake and grain ANR were significantly affected by the type of N source used. Manure reduced grain N uptake (by 15%) and grain ANR (by 50%) compared to UO as N source.

2.4.3. Leaf Tissue N Response

Corn leaf tissue N content over two growing seasons were in the range of 12.3 (R6 stage in 2016) to 32.7 g kg^{-1} (V6 stage in 2016). Averaged across 2-growing seasons, there was a significant growth stage×year interaction with 10% higher leaf N content in 2016 compared to

2017 (*P* = 0.012) (Table 6). Treatment and interaction effects of treatment×growth stage, treatment×year, and treatment×growth stage×year did not affect leaf N content (*P* > 0.25).

Table 6: Mean ± standard error of plant leaf N concentration at V6, VT, and R6 growth stages during 2016 and 2017 growing season.

Treatment	Leaf N
Growth stage - Year	g N kg^{-1}
V6 - 2016	32.70±0.53 a [a]
VT - 2016	29.14±0.42 b
R6 - 2016	12.32±0.42 d
V6 - 2017	30.25±0.73 b
VT - 2017	23.96±0.63 c
R6 - 2017	13.03±0.77 d
Year	
2016	24.71±1.32 a
2017	22.41±1.11 b
Main effects	
Treatment (T)	0.4023
Growth stage (G)	**<0.0001[b]**
Year (Y)	**0.0117**
Interaction effects	
T × G	0.2458
T × Y	0.4089
G × Y	**<0.0001**
T × G ×Y	0.2728

[a] Means within a column followed by the same letter are not significantly different at P<0.05 level.

[b] Significant *F* values (P ≤ 0.05) for fixed sources of variation are shown in bold.

Leaf N concentration was higher at earlier stages of plant growth and gradually decreased over the rest of the growing season. Within each growing season, V6 growth stage had the highest leaf N content followed by VT and R6 (V6>VT>R6). From V6 to R6, there was 62%

decrease in leaf N content at the end of 2016 and 57% decrease at the end of 2017. Leaf N content at all three stages of plant growth positively correlated with soil inorganic N (NH_4^+ + NO_3^-) at 0–0.3m and explained about 31.5% of the overall variation in leaf N across three growth stages under this study (Figure 5).

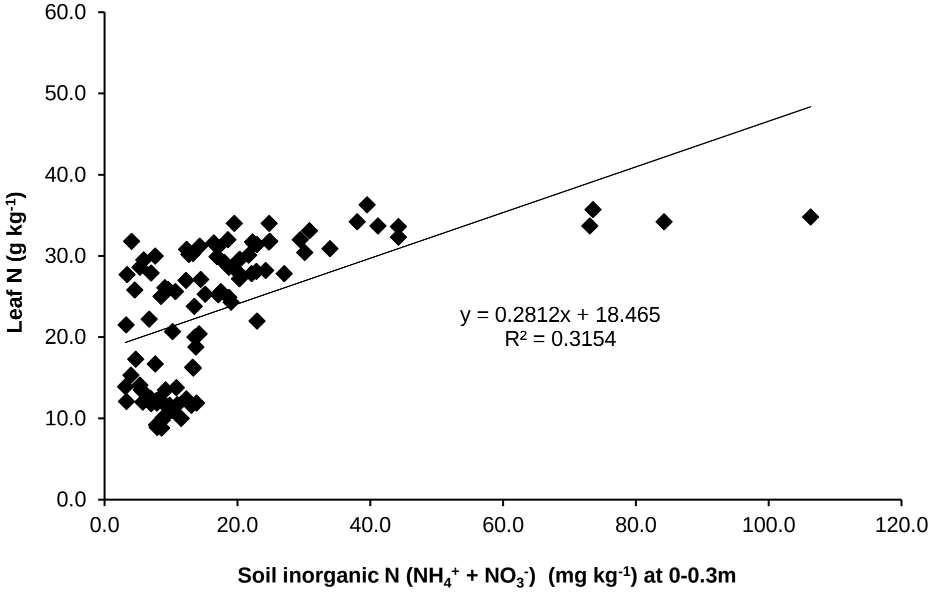


Figure 5: Relationship between soil inorganic N (NH_4^+ + NO_3^-) (0–0.30 m deep) and Leaf N concentration at V6, VT, and R6 stages over two growing seasons. Soil inorganic N was measured following plant sampling at V6, VT, and R6 stages.

2.4.4. Soil CO_2 Flux and Cumulative CO_2 Emission

Daily mean fluxes of CO_2 measured throughout the entire sampling period (excluding winter months) exhibited patterns of increased flux after manure application, spring tillage, and rise in soil temperature (Figure 6).

The average fluxes of CO_2 following the fall application of manure (SM and BM) was greater by over two-folds under manure treatment compared to NF during fall of 2015 and 2016. Averaged across all sampling dates, year and year×N management did not affect the mean annual CO_2 flux ($P > 0.5$). The mean CO_2 flux across all sampling dates ranged from 34.6 (NF) to 73.5 (BM) mg CO_2-C m^{-2} hr^{-1} with significantly higher fluxes from SM (by 90%) and BM (by

83%) compared to UO. There was no manure-type difference in the mean annual CO_2 flux. In addition, the mean annual CO_2 flux from UO (45.1 mg CO_2-C m^{-2} hr^{-1}) was higher than NF (34.6 mg CO_2-C m^{-2} hr^{-1}), however, the difference was not significant. In both growing seasons, CO_2 fluxes gradually increased from May along with increasing temperature and corn growth. On the 34 dates across two years where soil CO_2 flux and soil temperature were measured on the same day, soil CO_2 flux from N fertilized plots were positively correlated with soil temperature (R^2 = 0.23–0.37) (Figure 7). There were also positive correlations between soil CO_2 flux from N-treated soil and WFPS, but in all cases R^2 values were <0.05.

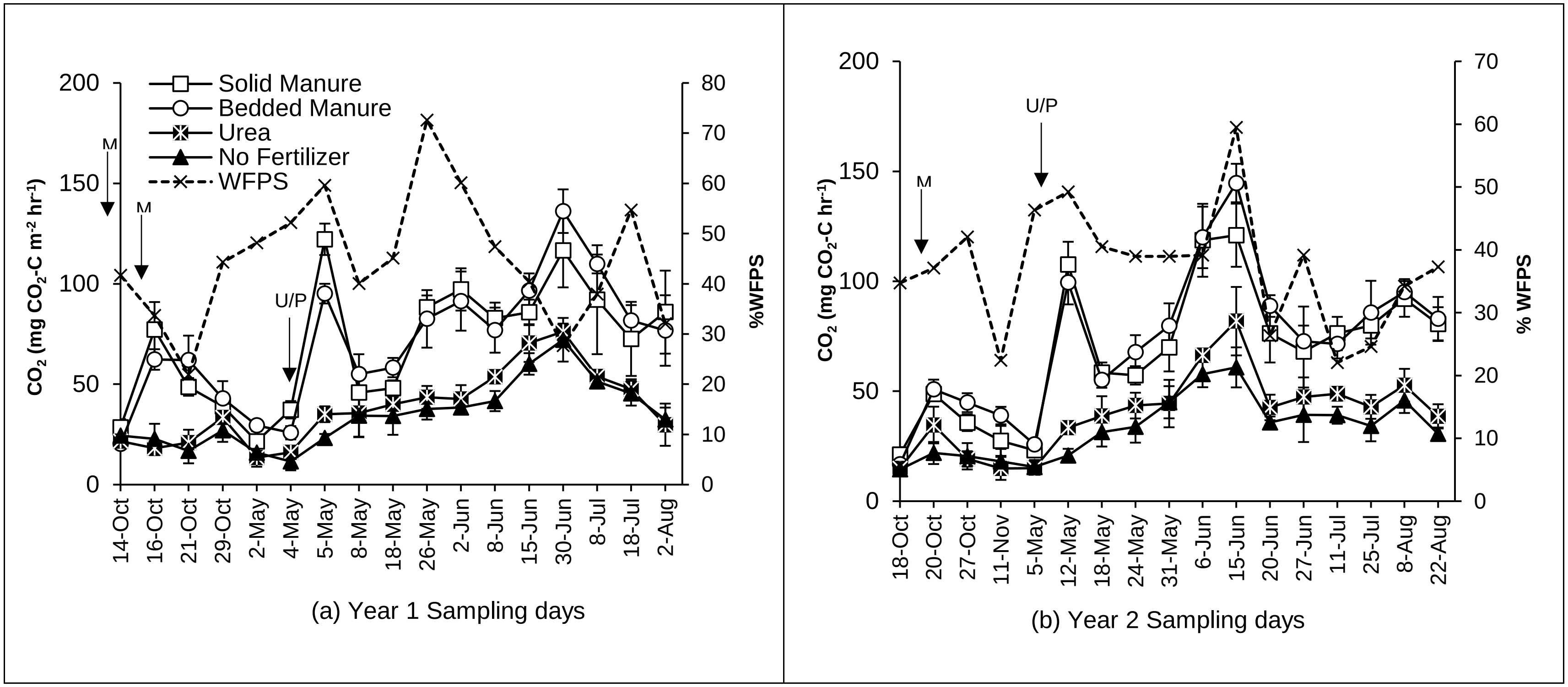


Figure 6: Carbon dioxide (CO_2) fluxes measured on each sampling date under different N sources: solid beef manure, bedded manure, urea, and no fertilizer during (a) year 1 and (b) year 2. Dotted line represents the soil water filled pore space (WFPS) at measured during each sampling event. Downward pointing arrows indicate the date of manure application (M), urea application (U) and planting (P). Vertical bars represent standard errors (n=4).

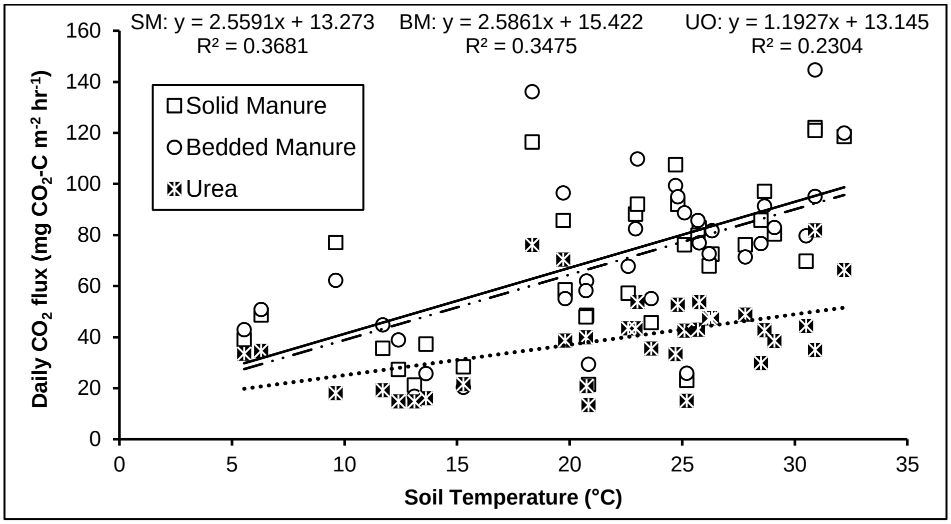
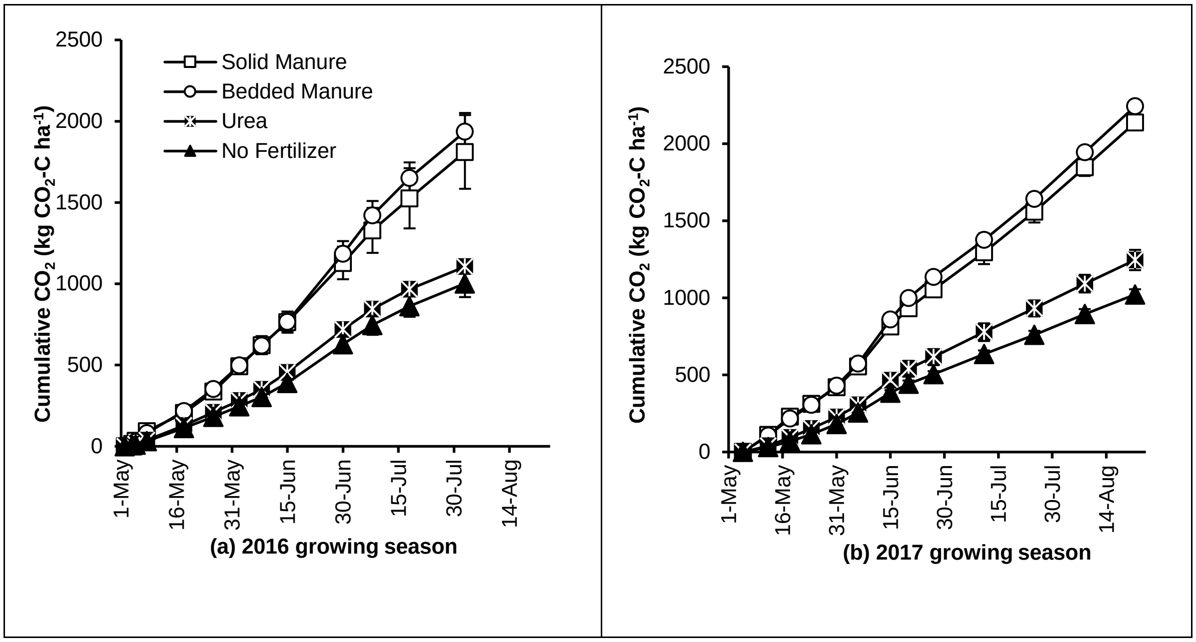


Figure 7: Relationship between soil temperature (°C) and mean CO_2 fluxes under different N sources: solid beef manure (SM), solid beef manure with bedding (BM), urea (UO), and no fertilizer (NF) determined from all 34 dates where soil CO_2 flux and soil temperature were measured on the same day.

Year, N management, and N source affected the growing season *c*CO_2 with ~14% higher emission in 2017 than in 2016 (Table 7). Both 2016 and 2017 growing season *c*CO_2 followed the order BM=SM>UO=NF (Figure 8) and there was no significant year×N management effects on *c*CO_2 ($P = 0.31$). Cumulative CO_2 emissions in SM and BM averaged across all growing seasons were 1.97 and 2.09 Mg CO_2-C ha^{-1}, respectively; and the difference was not significant ($P = 0.72$). The UO treatment reduced *c*CO_2 by 42% compared to manure source (SM and BM) over two growing seasons (Table 7).



(a) 2016 growing season

(b) 2017 growing season

Figure 8: Cumulative CO_2 emission measured across sampling dates under different N sources: solid beef manure, bedded manure, urea, and no fertilizer during (a) 2016 and (b) 2017 corn growing seasons. Vertical bars represent standard errors (n=4).

Table 7: Cumulative emissions of CO_2 (Mg ha^{-1}) and CH_4 (kg ha^{-1}) across 2016 and 2017 corn growing seasons as influenced by year, N management, and N source.

	Cumulative CO_2	Cumulative CH_4
	Mg CO_2-C ha^{-1}	kg CH_4-C ha^{-1}
	By year	
2016	1.46±0.12	0.09±0.04
2017	1.66±0.14	0.09±0.03
Pr > F	***0.0087*** [a]	*0.9904*
	By N management	
No fertilizer	1.01±0.04 b [b]	-0.04±0.03 b
Solid manure	1.97±0.12 a	0.18±0.03 a
Bedded manure	2.09±0.08 a	0.21±0.03 a
Urea	1.18±0.04 b	-0.01±0.02 b
Pr > F	***<.0001***	***<.0001***
	By N source	
Manure	2.03±0.10	0.20±0.02
Urea	1.18±0.04	-0.01±0.02
Pr > F	***0.0002***	***<.0001***

[a] Significant *F* values ($P \leq 0.05$) for fixed sources of variation are shown in bold.

[b] Values are means ± standard errors. Means within a column followed by the same letter are not significantly different at $P<0.05$ level.

2.4.5. Soil CH_4 Flux and Cumulative CH_4 Emission

Daily mean soil surface CH_4 fluxes were highly variable with episodes of redox events throughout the measurement period (Figure 9) and ranged from -1.2 (NF) to 7.7 (BM) µg CH_4-C m^{-2} hr^{-1}. Following manure application and rain events, CH_4 fluxes exhibited higher peaks. Average CH_4 fluxes following the fall application of manure (SM and BM) was >5 folds higher in manure applied plots than NF plots. The two-day average CH_4 flux from manure applied plots measured after ~17 mm rain (May 26th and June 30th) during 2016 growing season accounted for >6-folds higher flux (38.6 µg CH_4-C m^{-2} hr^{-1}) than average manure flux average for the entire measurement days of 1st year. The highest CH_4 flux during 2017 growing season was observed following major rain events (Figures 2 and 9). However, across 34 sampling dates, there was a weak but positive correlation between daily mean CH_4 flux with soil temperature and WFPS with $R^2 < 0.05$. Averaged across all sampling dates, year and year×N management did not affect the mean annual CH_4 flux ($P > 0.5$). The sampling period mean CH_4 flux from SM and BM were significantly higher than UO and NF plots and no manure-type difference was found.

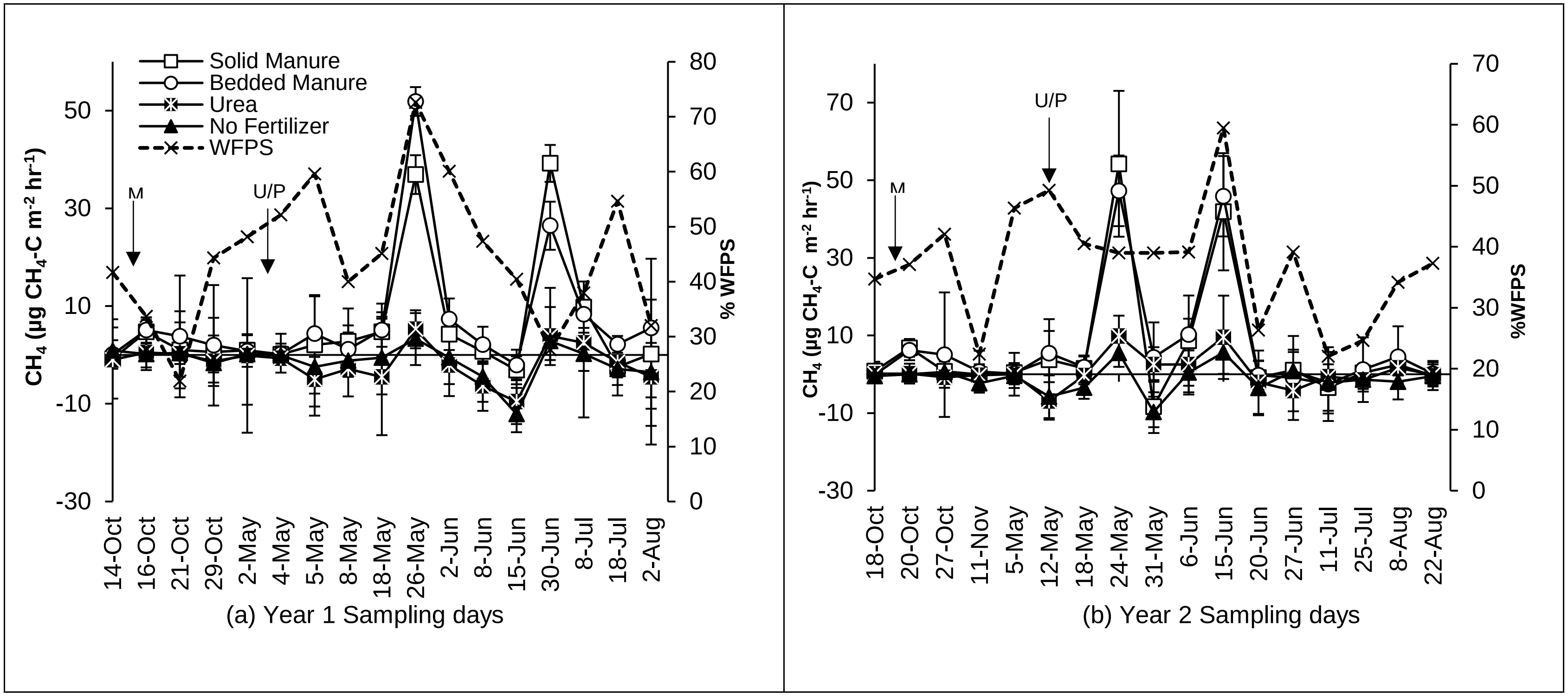
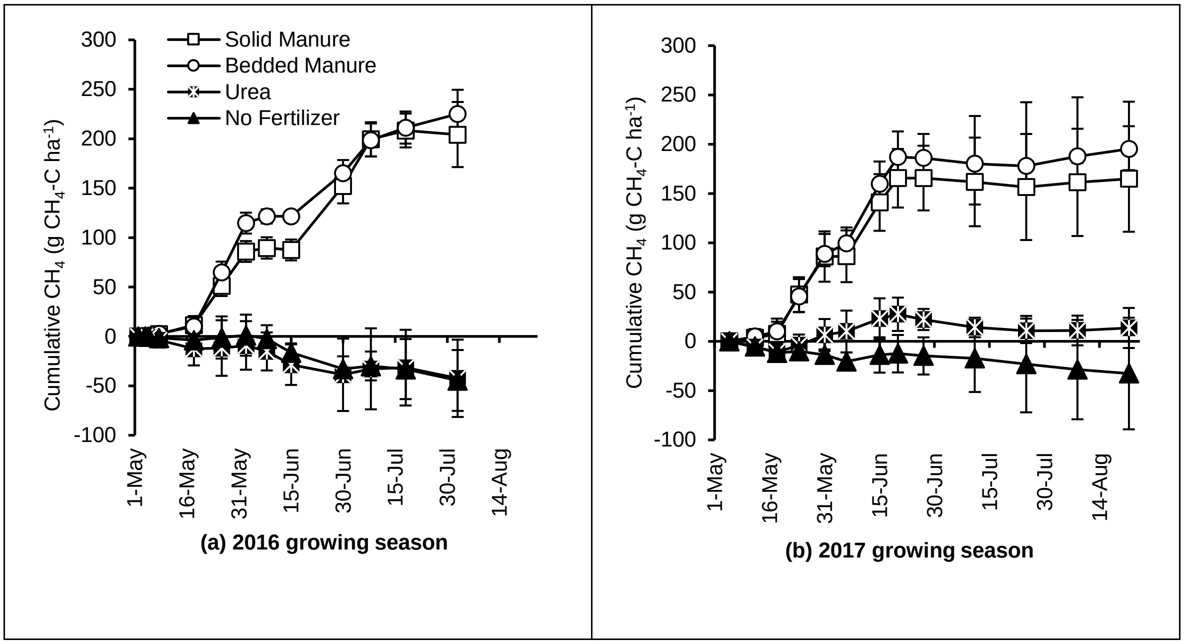


Figure 9: Methane (CH$_4$) fluxes measured on each sampling date under different N sources: solid beef manure, bedded manure, urea, and no fertilizer during (a) year 1 and (b) year 2. Dotted line represents the soil water filled pore space (WFPS) at measured during each sampling event. Downward pointing arrows indicate the date of manure application (M), urea application (U) and planting (P). Vertical bars represent standard errors (n=4).

The growing season cumulative CH_4 (cCH_4) emission for 2016 and 2017 ranged from -0.04 to 0.23 kg CH_4-C ha^{-1} and -0.03 to 0.20 kg CH_4-C ha^{-1}, respectively, with the highest emission from BM for both years. The growing season cCH_4 trends showed SM and BM above the baseline (Figure 10). Over two years, cCH_4 was significantly affected by the N management system. Cumulative CH_4 emissions in SM and BM averaged across growing seasons were 0.18 and 0.21 kg CH_4-C ha^{-1}, respectively; however, the difference was not significant (Table 7). The UO treatment had reduced cCH_4 approximately by over 95% compared to manure treatments. There was no significant year and year×treatment effects on cCH_4 emission.



(a) 2016 growing season

(b) 2017 growing season

Figure 10: Cumulative CH_4 emission measured across sampling dates under different N sources: solid beef manure, bedded manure, urea, and no fertilizer during (a) 2016 and (b) 2017 corn growing seasons. Vertical bars represent standard errors (n=4).

2.4.6. Soil N_2O flux, Cumulative N_2O Emission, and N_2O Emission Factor (EF)

The daily mean N_2O fluxes ranged from 2.2 (NF) to 191 (UO) μg N m^{-2} hr^{-1}, with episodic increases observed after N-fertilizer application, tillage operation and precipitation events (Figure 11). Average soil surface N_2O flux was 80-85% higher in the manured soil compared to NF soil on day 1 following the fall application of manure. Averaged across sampling dates, no difference in daily mean N_2O flux between N-fertilized treatments was observed, however, all N-fertilized soils were statistically significant and 3-4 folds higher than NF soils. There was no significant year×treatment interaction effects on daily mean N_2O flux.

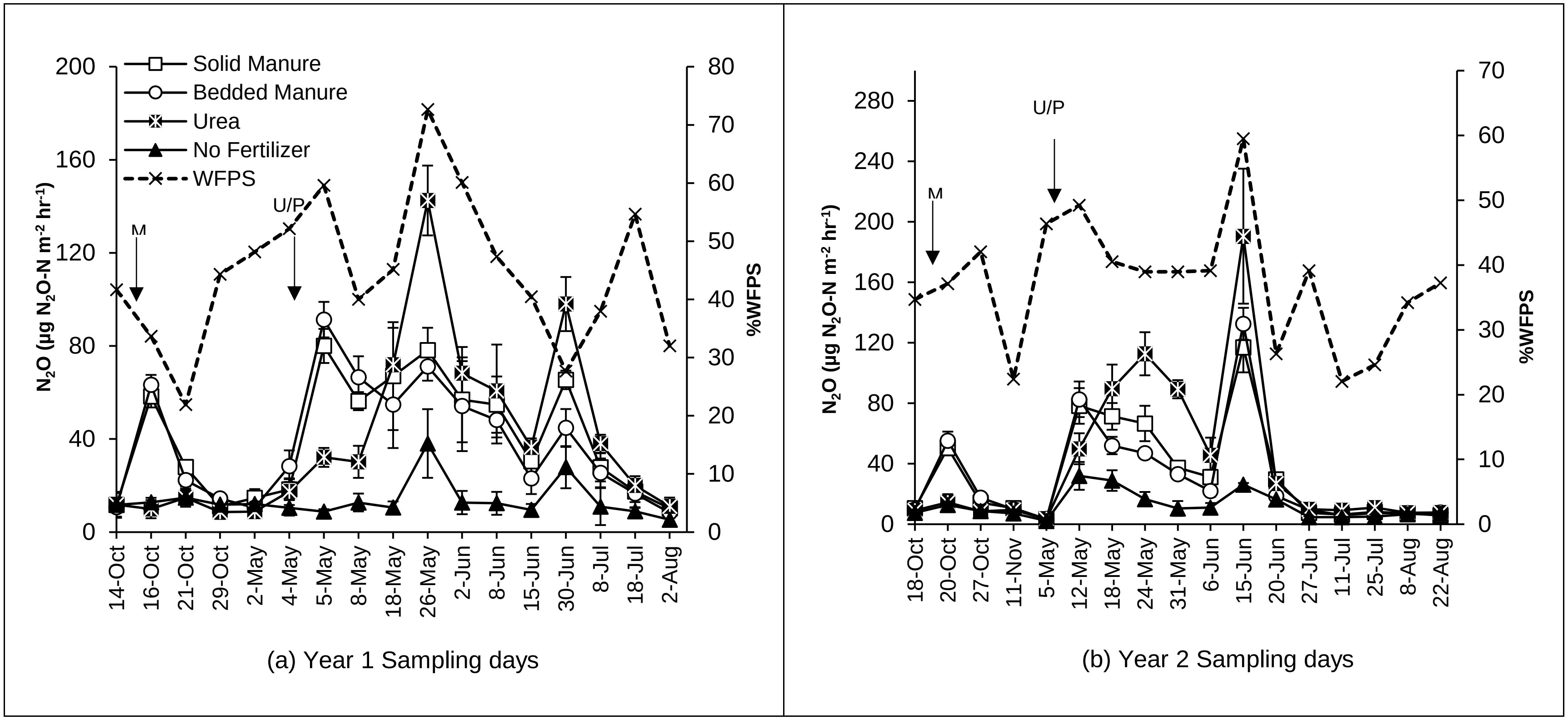


Figure 11: Nitrous oxide (N_2O) fluxes measured on each sampling date under different N sources: solid beef manure, bedded manure, urea, and no fertilizer during (a) year 1 and (b) year 2. Dotted line represents the soil water filled pore space (WFPS) at measured during each sampling event. Downward pointing arrows indicate the date of manure application (M), urea application (U) and planting (P). Vertical bars represent standard errors (n=4).

Peaks of daily N_2O fluxes closely matched with soil WFPS (Figure 11). The daily mean N_2O flux in all N-fertilized soil was positively correlated with WFPS (R^2 = 0.22–0.30, P <0.001). Peak fluxes of 142.5 and 190.5 μg N m^{-2} hr^{-1} were observed from the UO applied plots on 21d after corn planting in 2016 and on 37d in 2017, respectively. Flux of N_2O in manure plots also occurred during the same peak period as in the UO plots, however, the rates of emission were comparatively lower in manure plots. During growing seasons of 2016 and 2017, the highest N_2O flux from manured plots was observed immediately following the spring tillage and planting (83–91 μg N m^{-2} hr^{-1}). After planting, the occurrence of higher flux coincided with larger rain events. However, rain events later in the growing season did not induce peak N_2O fluxes.

The growing season cumulative N_2O emission (cN_2O) for 2016 and 2017 ranged from 0.3 (NF) to 1.2 (UO) kg N ha^{-1} and 0.3 (NF) to 1.1 (UO) kg N ha^{-1}, respectively, with the highest emission from UO applied plots for both years (Figure 12). Averaged across two years, N management practices influenced all the N_2O response indices (Table 8). Cumulative N_2O emission was not significantly affected by year (2016 vs 2017), but there was a trend (P = 0.08) of higher emission in 2016 (0.85 kg N ha^{-1}) than in 2017 (0.73 kg N ha^{-1}). All soils receiving N fertilizer had greater cN_2O than no fertilizer plots. Cumulative N_2O emissions in SM and BM averaged across two growing seasons were 0.89 and 0.80 kg N ha^{-1}, respectively; however, the difference was not significant. In addition, manure-type (SM vs. BM) did not show any significant differences in the fertilizer-induced N_2O (fN_2O), yield-scale N_2O (yN_2O), grain N scale N_2O (gN_2O), and N_2O emission factor (EF). In fact, manure treated soil had reduced cN_2O (by 23% in SM and 31% in BM), fN_2O (by 32% in SM and 42% in BM), and EF (by 35% in SM and 47% in BM) compared with the UO treated soil (Table 8). There was no significant year×treatment interaction effects on cN_2O. The pattern of significant differences in N-fertilizer treatments did not change when emissions were expressed per unit of yN_2O and gN_2O.

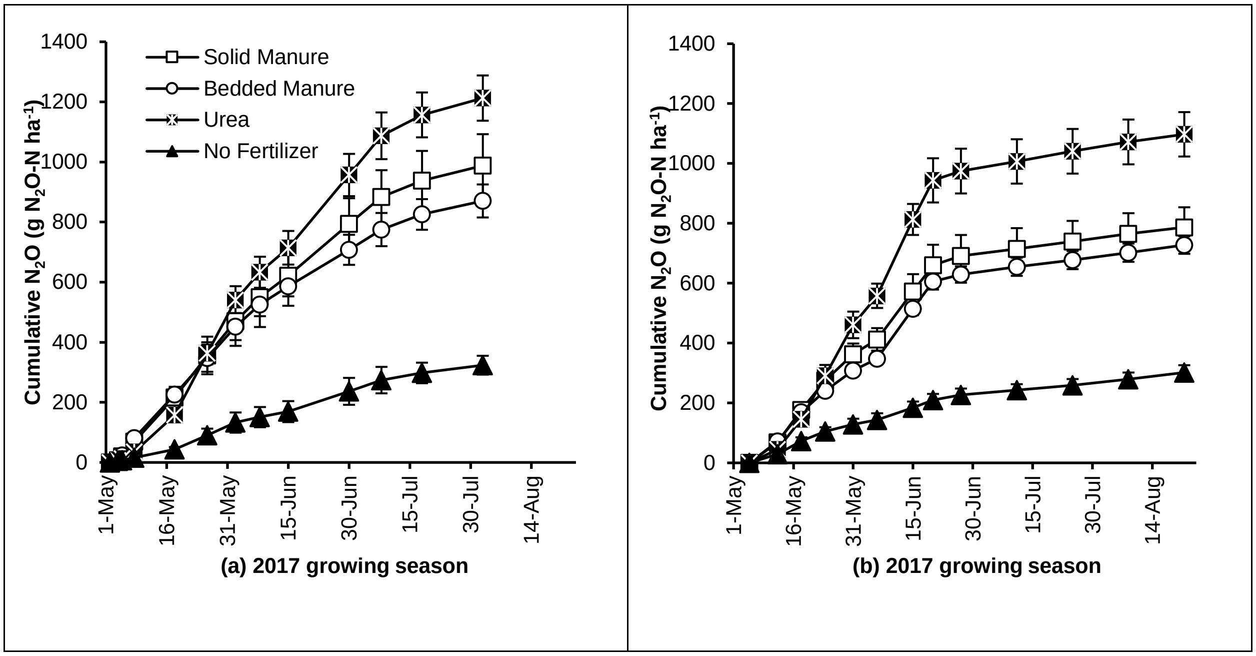


Figure 12: Cumulative N_2O emission measured across sampling dates under different N sources: solid beef manure, bedded manure, urea, and no fertilizer during (a) 2016 and (b) 2017 corn growing seasons. Vertical bars represent standard errors (n=4).

Table 8: Cumulative emissions and related indices of N_2O across 2016 and 2017 corn-growing seasons as influenced by year, N management, and N source.

	Cumulative N_2O (cN_2O)	Fertilizer-induced (fN_2O)	Yield-scale N_2O (yN_2O)	Grain N scale (gN_2O)	Emission Factor (EF)
	----------- kg N ha^{-1}------------		g N Mg^{-1}	g N kg^{-1}	%
			year		
2016	0.85±0.09	0.70±0.06	94.75±10.3	7.11±0.78	0.32±0.03
2017	0.73±0.08	0.57±0.06	97.99±8.3	6.97±0.58	0.50±0.06
Pr > F	*0.0838*	*0.1206*	*0.7348*	*0.8317*	***0.0125*** [a]
			N management		
No fertilizer	0.31±0.02 c [b]	-	45.65±3.7 b	3.50±0.27 b	-
Solid manure	0.89±0.07 b	0.57±0.06 b	108.70±9.2 a	8.52±0.94 a	0.37±0.04 b
Bedded manure	0.80±0.04 b	0.49±0.03 b	100.40±7.2 a	7.17±0.54 a	0.30±0.02 b
Urea	1.16±0.05 a	0.84±0.06 a	130.71±6.8 a	8.97±0.42 a	0.57±0.08 a
Pr > F	***<0.0001***	***0.0048***	***0.0002***	***0.00052***	***0.0024***
			N source		
Manure	0.84±0.05 a	0.53±0.04 a	104.55±7.6	7.85±0.70	0.33±0.03 a
Urea	1.16±0.05 b	0.84±0.06 b	130.73±6.8	8.97±0.42	0.57±0.08 b
Pr > F	***0.0094***	***0.0107***	*0.1042*	*0.2324*	***0.0078***

[a] Significant *F* values ($P \leq 0.05$) for fixed sources of variation are shown in bold.

[b] Values are means ± standard errors. Means within a column followed by the same letter are not significantly different at $P<0.05$ level.

2.4.7. Soil NH_3 Volatilization Loss

The daily mean NH_3 volatilization loss increased immediately after the fall application of manure and showed episodic increases following spring tillage and soil drying periods after rain events (Figure 13).

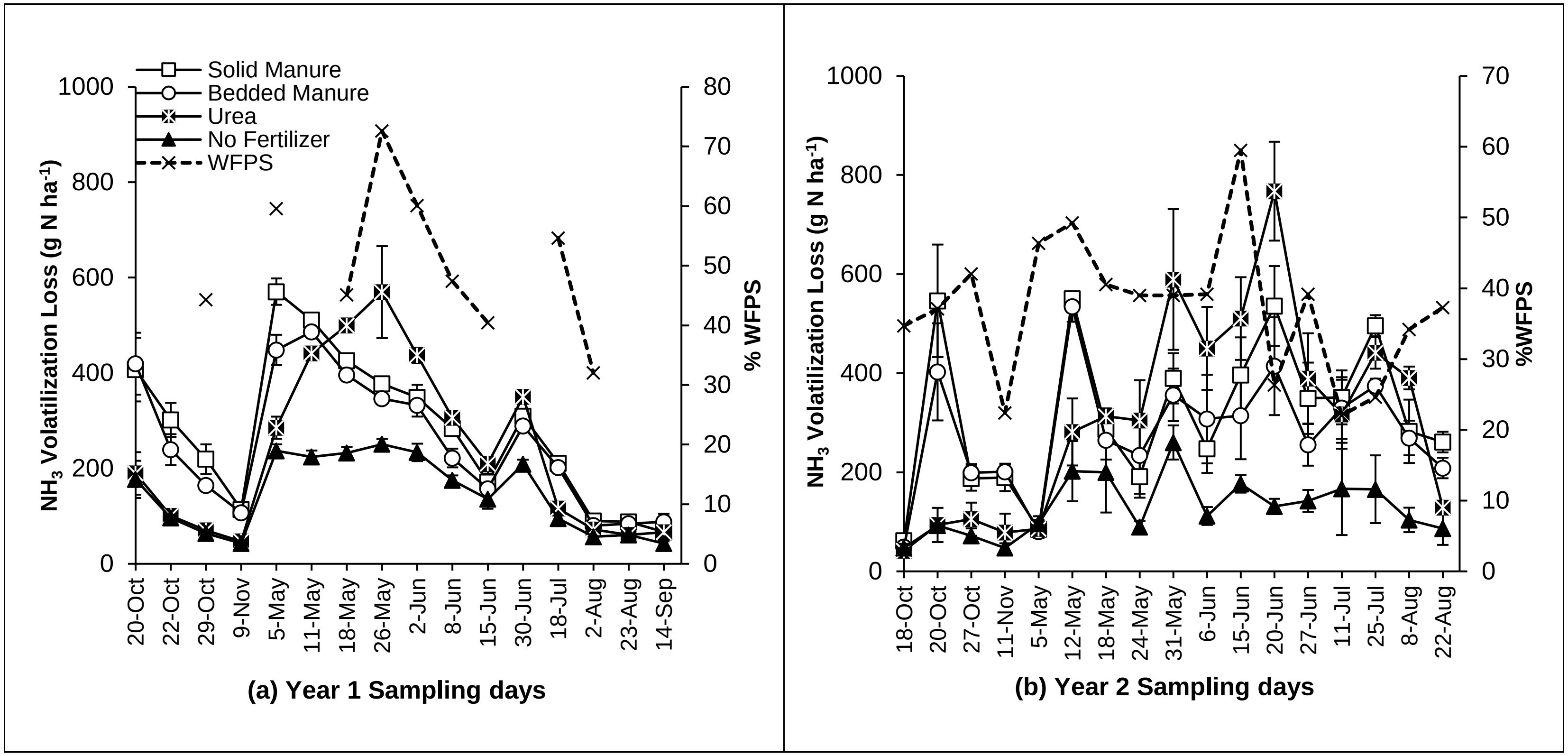


Figure 13: Ammonia (NH$_3$) volatilization loss measured on each sampling date under different N sources: solid beef manure, bedded manure, urea, and no fertilizer during (a) year 1 and (b) year 2. Dotted line represents the soil water filled pore space (WFPS) at measured during each sampling event. Vertical bars represent standard errors (n=4).

Daily mean NH_3 volatilization loss across all sampling dates ranged from 42.5 to 767.5 g N ha^{-1}, with the highest emission from UO applied plots. Averaged across sampling dates, no difference in daily mean NH_3 volatilization loss among N-treatments was observed (*P*=0.05–0.64), however, all N-treatments were statistically significant and up to two-folds higher than NF soils. There was no significant year (*P* = 0.43) and year×treatment (*P* = 0.08) effects on daily mean NH_3 volatilization loss.

During 2016 and 2017 growing seasons, the first peak of NH_3 emission from UO occurred after ~2 weeks from planting and its application. There was a significant year×treatment interaction effect on cumulative NH_3 volatilization loss (cNH$_3$) ($P<0.01$) (Figure 14). Growing season cNH$_3$ was significantly affected by year, N management, and N source with ~25% higher cNH$_3$ in 2017 than in 2016 (Table 9). All N-treatments had significantly greater cNH$_3$ than the NF. Across growing seasons cNH$_3$ in SM and BM were 3.9 and 3.5 kg N ha^{-1}, respectively; however, the difference was not significant. Within 2016 growing season, cNH$_3$ from treatments followed the decreasing order of UO>SM>BM>NF, however, all treatments receiving N fertilizer showed no significant differences (Figure 14). In contrast, within 2017 growing season, BM significantly reduced the NH_3 emission (by 21%) compared to UO applied soil (*P* = 0.003). Moreover, when comparing manure (SM and BM) versus UO sources of N, manure reduced cNH$_3$ by ~11% (*P* = 0.02). In addition to cNH$_3$, the emission factor (EF) was also significantly affected by year, N management systems and N source, which were >3-folds higher in 2017 than in 2016 growing season (Table 9). Manure with bedding (BM) significantly reduced EF compared to UO plots. However, across two growing seasons, manure (SM and BM) reduced the EF by 27% compared to EF from UO treatment.

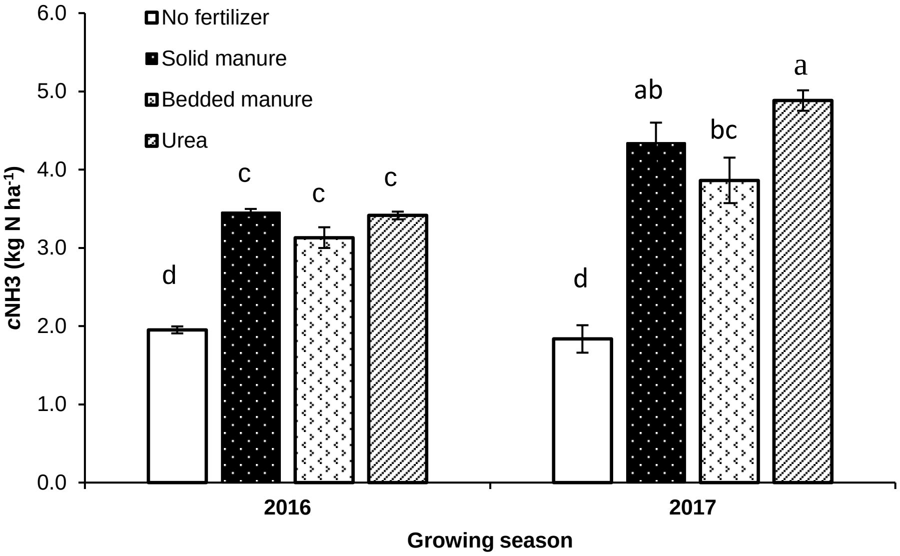


Figure 14: Cumulative NH_3 volatilization at the end of 2016 and 2017 growing seasons under different N sources: solid beef manure, bedded manure, urea, and no fertilizer. Means with same letter are not significantly different at P<0.05 level. Vertical bars represent standard errors (n=4).

Table 9: Cumulative NH_3 volatilization loss and emission factor between 2016 and 2017 corn-growing seasons as influenced by year, N management, and N source

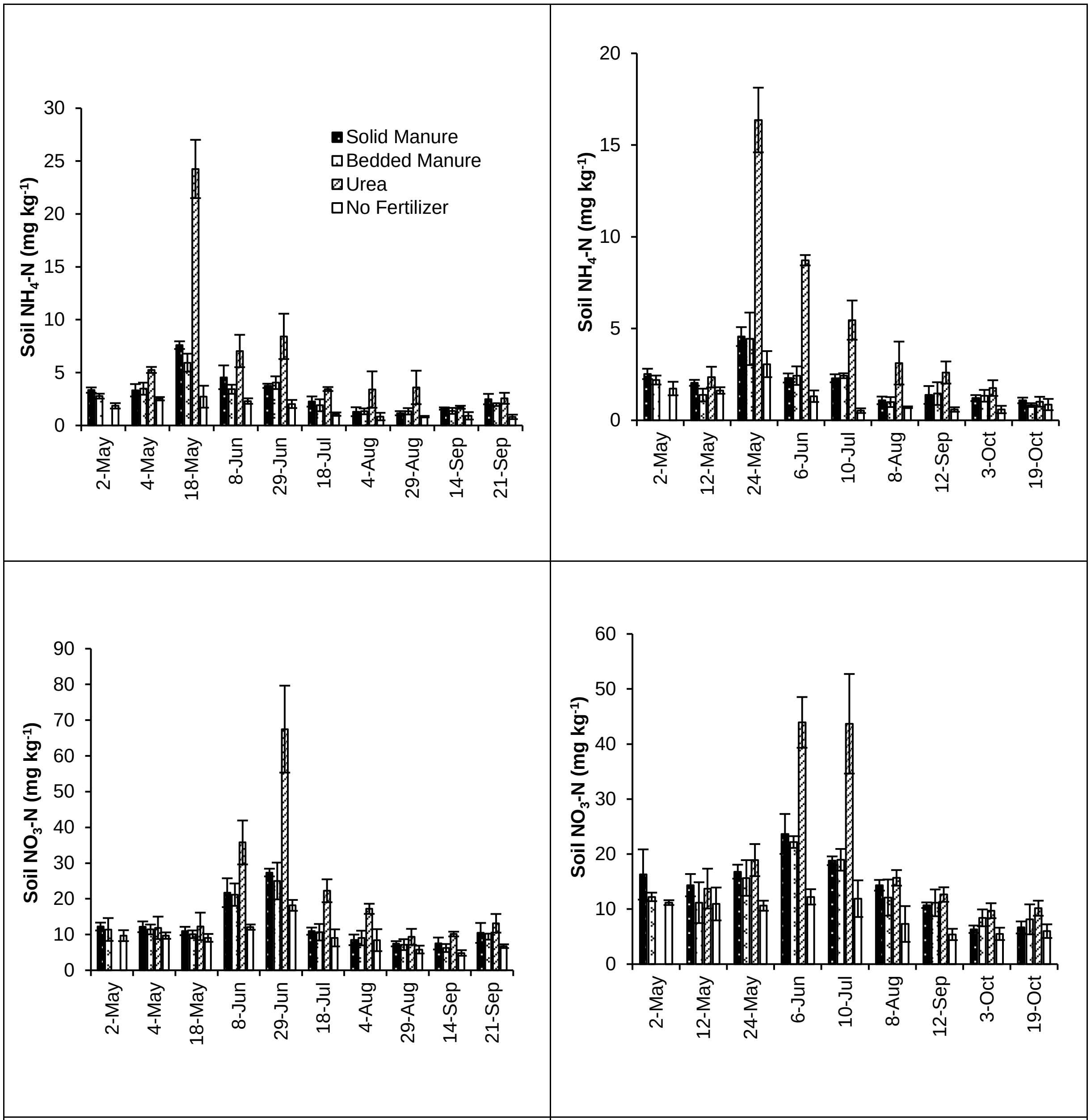
	Cumulative NH_3	Emission Factor (EF)
	kg N ha^{-1}	%
	By year	
2016	2.99±0.16	0.63±0.04
2017	3.73±0.31	2.22±0.18
Pr > F	***0.0029***[a]	***0.0001***
	By N management	
No fertilizer	1.89±0.07 c[b]	-
Solid manure	3.89±0.19 ab	1.45±0.30 a
Bedded manure	3.49±0.19 b	1.09±0.23 b
Urea	4.15±0.31 a	1.73±0.43 a
Pr > F	***<0.0001***	***0.0013***
	By N source	
Manure	3.70±0.17	1.27±0.26
Urea	4.15±0.31	1.73±0.43
Pr > F	***0.0194***	***0.0095***

[a] Significant *F* values ($P \leq 0.05$) for fixed sources of variation are shown in bold.

[b] Values are means ± standard errors. Means within a column followed by the same letter are not significantly different at *P*<0.05 level.

2.4.8. Soil N Dynamics and Intensity

Soil NH_4^+ and NO_3^- concentrations at 0.30 m soil depth increased above the baseline levels over the period of two growing seasons (Figure 15). Sampling period mean NH_4^+ ranged from 0.81 to 24.2 mg N kg^{-1} in 2016 and from 0.53 to 16.4 mg N kg^{-1} in 2017. Sampling period mean NO_3^- ranged from 4.9 to 67.5 mg N kg^{-1} in 2016 and from 5.4 to 44.0 mg N kg^{-1} in 2017. All three soil N indices (NH_4^+, NO_3^-, and NH_4^+ plus NO_3^-) showed a greater response to fertilizer addition resulting in greater concentrations of soil inorganic N compared to the NF. In general, soil NH_4^+ peaked after two weeks from UO application and planting and then declined gradually to below 5.0 mg N kg^{-1} from July until harvest. The disappearance of NH_4^+ from N-fertilized soils coincided well with the accumulation of NO_3^- in soils (Figure 15). Soil NO_3^- was generally higher after 3-4 weeks of plant emergence (VE stage) and until the V6 plant stage (vegetative growth stage). For the rest of the growing season and from the V8 stage of corn development to tasselling (VT) stage, soil NO_3^- declined to pre-fertilizer levels. Averaged across sampling dates, UO applied soil had significantly higher sampling period mean NH_4^+ (5.9 mg N kg^{-1}), NO_3^- (21.6 mg N kg^{-1}) and total soil inorganic N (26.1 mg N kg^{-1}) than SM, BM, and NF plots. However, there was no significant differences in year and treatment×year interaction on 2-year sampling period mean ($P>0.05$).



(a) 2016 growing season

(b) 2017 growing season

Figure 15: Temporal soil ammonium (NH_4^+) and nitrate (NO_3^-) dynamics at 0-0.3 m soil depth for N treatments over (a) 2016 and (b) 2017 corn growing seasons. Vertical bars represent standard errors (n=4).

Growing season cumulative soil inorganic N (NH_4^+ plus NO_3^-) were affected by year, N management, and N source (Table 10). Averaged across two growing seasons cumulative soil NH_4^+ plus NO_3^- in 2017 were greater by 11% compared to 2016. All plots receiving N-treatments had greater soil N indices than NF plots. The UO treatment increased NH_4^+ (by 139–

158%), NO_3^- (by 68–76%), and NH_4^+ plus NO_3^- (by 78–87%) compared to SM and BM. The soil N intensity in manure treatments averaged across two growing seasons showed a higher concentration of all three indices in SM (by up to 7.2% in NH_4^+, 4.5% in NO_3^-, 5.2% in NH_4^+ plus NO_3^-) compared to BM treatment, however, the difference was not significant ($P > 0.05$). All three soil N indices were positively correlated with cN_2O ($P < 0.01$) and explained 50 to 66% of the overall variation in cN_2O across all treatments (Figure 16). In addition, soil NH_4^+ positively correlated with the soil cNH_3 volatilization loss ($P < 0.01$) and explained 23% of the overall variation in cNH_3 across all treatments (Figure 16).

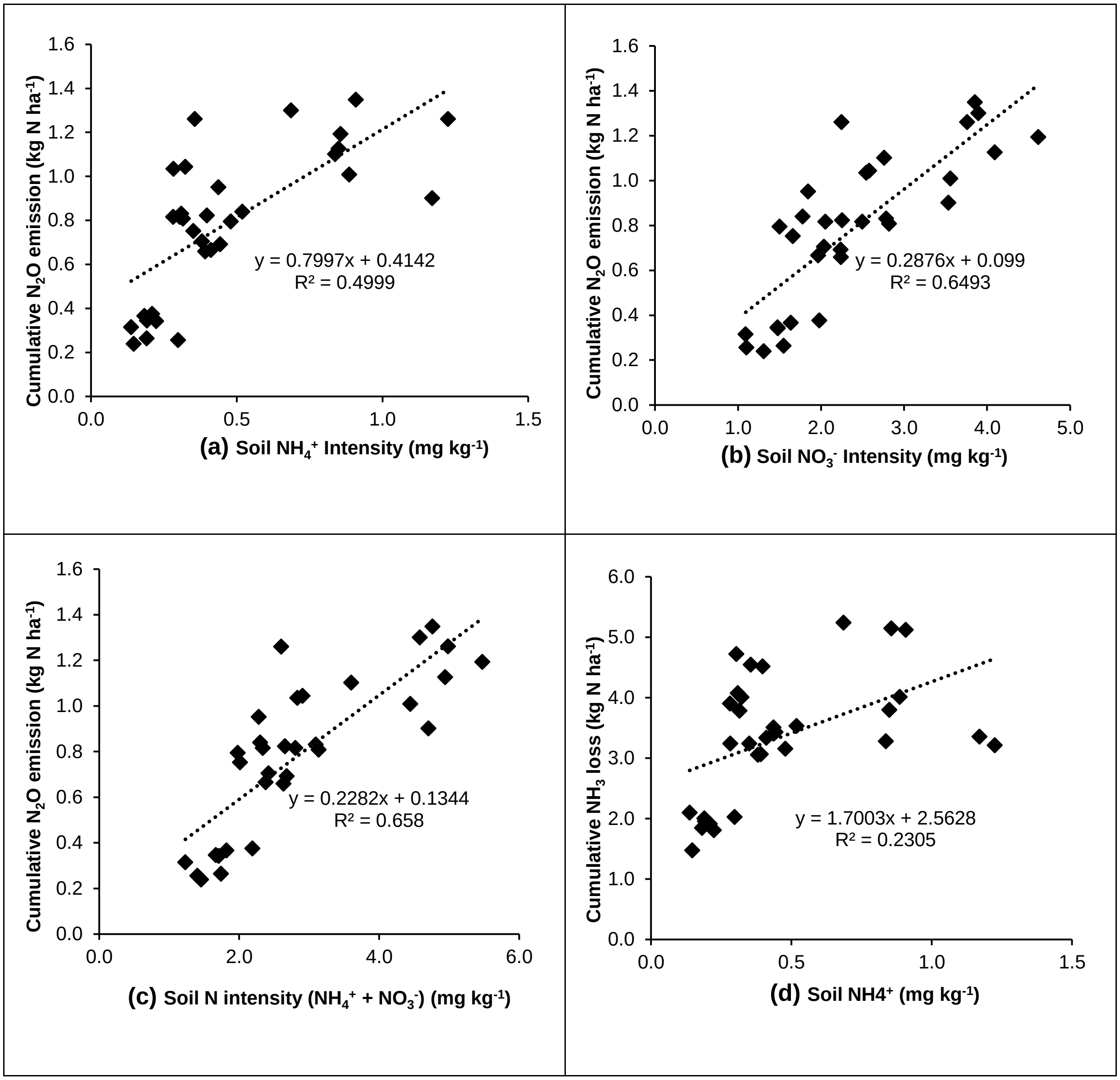


Figure 16: Relationship between two-year growing season (a) cumulative N_2O emissions and soil NH_4^+ intensity, (b) cumulative N_2O emissions and soil NO_3^- intensity, (c) cumulative N_2O emissions and soil N intensity (NH_4^+ + NO_3^-), and (d) cumulative NH_3 loss and soil NH_4^+ across all N management system. Soil NH_4^+ and NO_3^- intensities were determined from the surface soil (0–0.30 m deep) over the growing season.

Table 10: Cumulative soil N indices at top 0.30 m depth across 2016 and 2017 corn-growing seasons as influenced by year, N management, and N source

Cumulative Soil N Intensity (0-0.3 m) (g kg^{-1})			
	NH_4	NO_3	NH_4+NO_3
		By year	
2016	0.52±0.08	2.19±0.22	2.71±0.30
2017	0.41±0.07	2.61±0.24	3.02±0.30
Pr > F	***0.0017*** [a]	***0.0031***	***0.0389***
		By N management	
No fertilizer	0.198±0.02 c[b]	1.45±0.10 c	1.65±0.10 c
Solid manure	0.388±0.03 b	2.24±0.13 b	2.63±0.10 b
Bedded manure	0.360±0.02 b	2.14±0.15 b	2.5±0.14 b
Urea	0.928±0.06 a	3.76±0.19 a	4.68±0.19 a
Pr > F	***<0.0001***	***<0.0001***	***<0.0001***
		By N source	
Manure	0.374±0.02	2.19±0.13	2.56±0.11
Urea	0.927±0.06	3.76±0.19	4.68±0.19
Pr > F	***<0.0001***	***<0.0001***	***<0.0001***

[a] Significant *F* values ($P \leq 0.05$) for fixed sources of variation are shown in bold.
[b] Values are means ± standard errors. Means within a column followed by the same letter are not significantly different at $P<0.05$ level.

2.4.9. Leachate NO_3^- Concentration

The NO_3^- concentration in leachate samples from each plot during 2016 and 2017 corn growing seasons were highly inconsistent with <1.0 mL-to-none collected during most lysimeter sampling dates. Across two growing seasons, only 6 days (out of 26 days) worth of leachate samples were obtained with lysimeter generally following precipitation events (Figure 17). Leachate NO_3^- concentration (mg L^{-1}) measured at 0.60 m soil over growing seasons ranged from 12.8 to 53.3 mg L^{-1} with highest mean NO_3^- concentration from SM treatment followed by UO, BM and NF, respectively. Averaged across sampling dates, there was a significant treatment and year×treatment effect on daily mean leachate NO_3^- concentration ($P < 0.05$) with SM significant and 43% greater than BM (Table 11). In contrast, there was no significant differences in UO and manure applied soils. Generally, NO_3^- concentrations from SM plots were higher during 2016 and from UO plots during 2017 growing seasons. However, there was no significant effect of year on daily mean leachate NO_3^- concentration. Interestingly, two sampling events during 2017 (31st May and 8th August) showed higher NO_3^- concentrations in NF plots than that of BM plots, possibly due to immobilization.

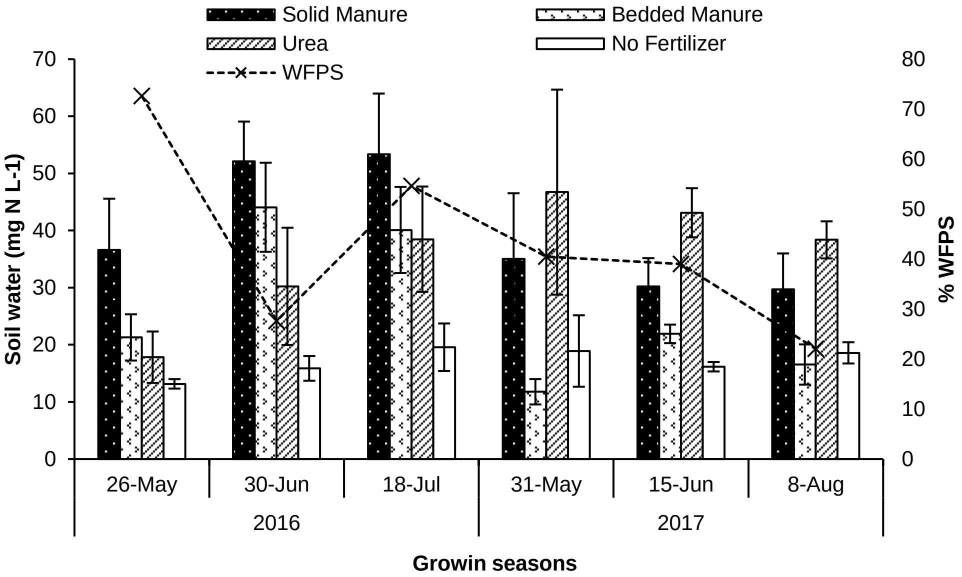


Figure 17: Temporal soil leachate (NO_3^-) dynamics for N treatments at 0.30 m soil depth over 2016 and 2017 corn growing seasons. Dotted line represents the soil water filled pore space (WFPS) at measured during each sampling event. Vertical bars represent standard errors.

Table 11: Growing season mean soil leachate NO_3^- measured at 0.60 m soil depth 2016 and 2017 corn-growing seasons as influenced by N management and year.

Treatment (T) [a]	Soil leachate NO_3^- (mg L^{-1})
SM	40.8±4.0 a[b]
BM	28.6±3.8 bc
UO	35.9±3.9 ab
NF	17.3±1.3 c
Treatment-year (Y)	
SM-2016	48.0±5.5 a
SM-2017	31.8±4.5 ab
BM-2016	35.6±4.8 ab
BM-2017	16.7±2.5 ab
UO-2016	31.1±5.6 ab
UO-2017	42.1±4.4 ab
NF-2016	16.6±1.8 b
NF-2017	17.9±1.9 ab
Effects	***Pr > F***
T	**0.0004**[c]
Y	0.6085
T×Y	**0.0116**

[a] SM, BM, UO, and NF refers to solid beef manure, solid beef manure with bedding, urea, and no fertilizer, respectively.

[b] Values are means ± standard errors. Means within a column followed by the same letter are not significantly different at $P<0.05$ level.

[c] Significant F values ($P \leq 0.05$) for fixed sources of variation are shown in bold.

2.5. Discussion

2.5.1. Crop Response

Our study showed higher grain yield and grain N uptake in 2016 compared to 2017 and were most likely influenced by greater precipitation (102 mm) during early vegetative stages (VE to V6) in 2016. In contrast, the cumulative precipitation during VE to V6 stages was at 89.2 mm in 2017. The average temperature during VE to V6 stages was at 18 °C for both years. Moreover, high total precipitation during May–September (361.5 mm) in 2016 compared to the same period in 2017 (241.5 mm) likely stimulated greater N mineralization and the crop N uptake. Reduced crop N uptake in 2017 was also likely responsible for greater soil N intensities in 2017. The combined effects of the warm enough temperature and soil water availability probably influence the corn yields differently (Runge and Odell, 1960). The U.S. corn production in 2016 was at a record-high in 2016 (11% higher than 2015) with average yield of 11 Mg ha^{-1} (175 bushels acre^{-1}) mostly attributed to ample rain and moderate temperatures across the Nation's mid-section (USDA-NASS, 2017b).

In this study, corn yield and grain N uptake across years were higher than NF in UO and did not vary among N-sources and the similar results were reported by others (Eghball and Power, 1999a; Ma et al., 1999; Miller et al., 2009). These results suggest the necessity of N application regardless of N source in order to optimize crop yields. The lack of yield differences among N-treatments further suggests that supplemental inorganic fertilizer may not be required for manure amendments to maintain yields similar to inorganic N sources. No differences in grain yield and grain N uptake among N treatments may have been partially due to the relative amount of N supplied from soil N mineralization (Miller et al., 2009). Contrary to our findings, some studies have reported greater crop yields for inorganic fertilizer compared with beef cattle manure (Eghball and Power, 1999b; Paul and Beauchamp, 1993), and others have reported the opposite results (Zvomuya et al., 2006). The differences in the results may be attributed to management practices. For instance, Paul and Beauchamp (1993) had applied solid and composted manure in the spring while manure was applied in the fall in our study. Fall application of manure in this study probably allowed sufficient time for the freshly tilled soil to settle and give microbes time to decompose the manure–making nutrients more available to crops and preventing germination concerns in the spring (Lewandowski, 1995). In addition, the differences in crop yields between Zvomuya et al. (2006) with our study was most likely because Zvomuya et al. (2006) manure application was P based and we followed N based manure application. Other studies have found that crop yields for manure (dairy and beef) and fertilizer treatments were dependent on site location, soil type, or year (Gagnon et al., 1997).

The grain ANR in UO was up to 2-folds greater than manure treatments and could be due to the combined effects of slow manure N mineralization and/or N immobilization. Our grain ANR result was consistent with the previous findings of greater N use efficiency for fertilizer than beef manure (Eghball and Power, 1999a; Paul and Beauchamp, 1993), various livestock manures (Gagnon et al., 1997), or dairy manure (Ma et al., 1999). Greater grain ANR in previous studies were attributed to the loss of inorganic N in manure to NH_3 volatilization and potential N immobilization.

Weather condition, especially precipitation during the growing season most likely affected the leaf N concentration (Asghari and Hanson, 1984). For example, 45 mm of precipitation was received 2-weeks prior to V6 stage leaf sampling in 2016, whereas only 14.7 mm of precipitation was received 2-weeks prior to V6 stage leaf sampling in 2017. Low rainfall can lead to low nutrient availability because nutrients are not available unless they are in solution form (Cunningham et al., 1999).

2.5.2. N_2O Response

In this study, the contrasts between the N-fertilized (SM, BM, and UO) and unfertilized plots (NF) on silty clay soil suggested a trend toward greater emission (by 2-4 folds) from N-fertilized plots in terms of both, mean N_2O flux across all sampling events and *c*N_2O across two growing seasons. The greater microbial N_2O emissions from the N fertilized plots may have been related to the physical and chemical properties of fertilizer, soil, N substrate availability, and their interaction (Table 8) with environmental condition (temperature and rainfall). Nitrous oxide is produced in soils primarily via microbial processes of nitrification and denitrification and can be affected by the addition of chemical fertilizer or organic amendments (Ma et al., 2012).

A significant rise in N_2O flux after manure application and again after spring tillage might be due to simultaneous production of N_2O through nitrification and denitrification. Emissions of N_2O during nitrification of N fertilizers was probably dominant under marginal O_2 levels and when NH_4^+ from manure was available for microbes to use as energy source. Also, enhanced denitrification of soil NO_3^- by the addition of degradable organic substrates have been reported in previous studies (Chadwick et al., 2000a; Velthof et al., 2003). However, the dominant process depends on the availability and type of substrates and the soil oxygen and moisture levels (Khalil et al., 2002; Kowalenko et al., 1978). Velthof et al. (2003) and Chadwick et al. (2000c) also reported higher flux of N_2O on d1 after manure application and attributed results to microbial breakdown of volatile fatty acids in manure. In contrast, Asgedom et al. (2014a) reported no appreciable N_2O flux following the fall application of manure. This difference in response could be due environmental conditions at the time of manure application.

Air and soil temperature declined to near 0°C during Asgedom et al. (2014a) compared to our study where average air and soil temperature were 5 and 8°C, respectively. The mean N_2O flux for the entire sampling events under this study followed the order of UO>SM>BM>NF, however, there was no significant differences in mean fluxes of N-applied plots which may be linked to the timing of fertilizer application. Urea was applied in the springs of 2016 and 2017 whereas manures were applied in the fall of 2015 and 2016. In addition, during early spring of 2016 and 2017, N_2O fluxes from manured plots were higher than the UO plots (Figure 11). After spring tillage for corn planting, when the soils were dry and well aerated, nitrification in manure, probably became increasingly important due to the availability of NH_4^+ (Asgedom et al., 2014a). Moreover, denitrification can also occur in aerated soils, presumably in anaerobic microsites or aggregates, where O_2 diffusion is slow (Halvin et al., 2013).

In the current and previous studies, daily N_2O fluxes following the addition of synthetic N fertilizer and manure early in the season were linked to rainfall events (Gao et al., 2014; Venterea et al., 2011). In this study, rainfall during the growing season probably restricted gaseous diffusion in the poorly drained silty clay soil, thereby stimulating denitrification during which anaerobic microbes convert NO_3^- to N_2, releasing N_2O as an intermediate product. A gradual decrease in N_2O fluxes from all N fertilized soil towards the end of the growing season, was likely due to the active crop N uptake and N losses via NO_3^- leaching, and NH_3 volatilization. Soil WFPS measured at 0–0.15m during each sampling event positively correlated ($R^2 = 0.22–0.30$) to fluxes of N_2O suggesting that the anaerobic microbes rely mostly on high soil moisture levels to induce N_2O emission. In general, denitrification are lower at <60% WFPS, increases slowly between 60–80% WFPS, and then increases more rapidly above 80% WFPS (Linn and Doran, 1984). The 2017 growing season was a dry season (Figure 2), with highest daily precipitation of 35 mm received on 12-June for the growing season. In contrast, the highest precipitation received during 2016 growing season was 56 mm on 11-July. Therefore, low rainfall in 2017 could have reduced large peaks in N_2O following rainfall events.

The growing season cN_2O emission observed across N sources in the current study were in the same range (0.8 to 1.2 kg N ha^{-1}) as those observed in previous studies (Asgedom et al., 2014a; Venterea et al., 2016) and lower than others (Burton et al., 2008; Glenn et al., 2012) where manure and/or synthetic fertilizer was applied. Lower gas diffusivity and high CEC in Fargo silty clay soil may have limited N_2O production in this study. Moreover, literature comparing the effects of manure types versus mineral fertilizers on N_2O emissions tend to be inconsistent. Some studies note greater emissions from mineral N applications (Chantigny et al., 2010; Hernandez-Ramirez et al., 2009) and others note the opposite results (Chantigny et al., 2007; Rochette et al., 2000; Van Groenigen et al., 2010) or no difference between the various N source (López-Fernández et al., 2007). In the present study, cN_2O from fine-textured silty clay over the period of two growing seasons suggested a trend towards higher emissions from UO (1.16 kg N ha^{-1}) than SM (0.89 kg N ha^{-1}) and BM (0.80 kg N ha^{-}1). Higher emission from UO applied plots may have been due to greater availability of NH_4^+ content (compared to SM and BM) and lower soil C:N ratio that may have favored the rate of mineralization. Generally, organic matter with C:N < 20:1 release mineral N early in the decomposition process (Halvin et al., 2013). In contrast, manure treatments in this study had higher C:N ratio and probably reduced the release or availability of manure organic N for nitrification and denitrification processes. The SM increased the cN_2O emission by 11% compared to the soil amended with BM; however, the difference was not significant. Solid manure (SM) used in this study had higher inorganic N (year 1), organic N, and dry matter content (Table 4) compared to BM, all of which are known to positively induce N_2O emission. Bedded manure, on the other hand, had higher C:N (>35) and are known to produce a varying effect on denitrification rate and nitrification processes (Dustan, 2002; Miller et al., 2014). Khalil et al. (2002) also reported increased N_2O emission with a decrease in C:N ratio of different organic matter. The annual mean N_2O fluxes and overall growing season *c*N_2O in this study were thus influenced by the variation in manure characteristics, straw bedding, soil properties (texture, soil N, soil moisture, and C:N ratio), and weather conditions (mostly rainfall).

2.5.3. Area- and Yield-scaled N_2O Emission Factor

The mean fraction of applied inorganic N (UO) lost as N_2O [N_2O emission factor (EF)] from the silty clay over two growing season was 0.6%, which is significantly less than the default IPCC value of 1% (IPCC, 2007) and also less than several published values of 3 to 8% (MacKenzie et al., 1997; Mukumbuta et al., 2017). However, our EF was similar to those reported in the range of 0.1 to 3% (Cai et al., 2013; Ding et al., 2007a). Manure N_2O EFs from SM and BM applied plots were 0.37 and 0.30%, respectively and are similar to those reported by Akiyama et al. (2004) (0.01–1.6%) and greater than Collins et al. (2010) (0.05–0.1%). Low emission factors in this study could be due to the low soil NO_3^- concentration. Year, N management and N sources, all affected the EF in this study, with EF under UO significantly higher than manure applied plots. The net impact of N application on N_2O flux in a given situation depends on N source, soil temperature and moisture, C availability, and climatic conditions (Venterea et al., 2016). Our study indicated that the different EFs of applied fertilizer as N_2O primarily resulted from the types of fertilizer applied. Therefore, the recommended default EF of fertilizer nitrogen by IPCC might overestimate N_2O emissions from the silty-clay under urea and manure in the RRV.

The reports on yield-scaled N_2O emission (yN_2O) in grain production systems are limited and have varying values. Our yN_2O were in the range of 45.7 (NF) to 130.7 (UO) g N Mg^{-1} (Table 8), which is similar to the range reported by Venterea et al. (2011) (46–100 g N Mg^{-1}) on fertilizer source and tillage study in Minnesota. Our values are on average 41% higher than the values reported by Halvorson et al. (2010) (31–67 g N Mg^{-1}) in a controlled release fertilizers (CRFs) study in irrigated corn in Colorado. Interestingly, our values are more than 10 times less than values (1.3–2.0 kg N Mg^{-1}) reported by Gagnon et al. (2011a) in a clay soil receiving sidedress N applications for rainfed corn in eastern Canada. Studies on N_2O emissions per unit grain N uptake (gN_2O) are even fewer. The range of gN_2O found here are (3.5–9.0 g N kg^{-1} N) similar to the range reported by Venterea et al. (2011) (4–11 g N kg^{-1} N) and about 10 times less than the range reported by Wei et al. (2010) (50–150 g N kg^{-1} N) in a rainfed wheat system in China. The differences in the literature occurred due to at least one of the N treatments having significantly higher emission factor within or between years. Expressing N_2O emissions on yield-scaled basis provided additional information for evaluating overall GHG impacts. For example, based on the current findings, if the same amount of grain were produced using beef manure (SM and BM averaged) and UO, then the manure would emit 26% more N_2O compared to UO under the same fertilizer regime and would require the additional land area to produce the same amount of grain. The same considerations would apply to the practices of tillage that could potentially affect yields and N_2O emissions. For example, Venterea et al. (2011) noted 53% more N_2O emission from no-till system compared to conventional till under the same fertilizer regime, given both systems produced the same amount of corn grain.

2.5.4. Soil Inorganic N and its Relation to N_2O and NH_3

Soil inorganic N concentration is driven by microbial activity and is influenced by several factors, including temperature, soil properties, manure and bedding characteristics (Eghball et al., 2002). In our study, there was a slight decrease in soil inorganic N immediately after plowing and planting. This decrease may be due to nitrification/denitrification loss as N_2O and potential NH_3 volatilization loss of N after the plots were tilled for planting. The increase in soil NO_3^- with the decrease in NH_4^+ content was likely due to nitrification that may have converted most of the NH_4^+ to NO_3^- (Halvin et al., 2013). Higher rates of urea hydrolysis in UO may have contributed to more cumulative NH_4-N in UO compared to SM and BM across two growing seasons. Once applied to the soil, urea is rapidly hydrolyzed by urease enzymes in the soil and organic material to yield two NH_4^+ per $CO(NH_2)_2$ (Sherlock and Goh, 1984). Miller et al. (2010) reported that bedding effects on soil NO_3-N (0-0.60 m) varied with application rate or year. In contrast, our result showed that immediate incorporation of land applied solid beef manure with or without straw bedding could provide similar N availability to corn in silty clay soils of the RRV. Cumulative soil N was significantly higher in UO compared to manure sources and NF, which is consistent with the previous research on manure and inorganic N source fertilizers (Paul and Beauchamp, 1993). Higher concentrations of soil inorganic N for 2017 despite low precipitation compared to 2016 growing season could be due to reduced crop N uptake in 2017.

Literature report both, linear and non-linear relationship of one or many soil inorganic N indices with cumulative N_2O and NH_3 emissions (Burton et al., 2008; Engel et al., 2010; Gagnon et al., 2011b; Maharjan et al., 2014). Our results suggest a strong positive correlation of cN_2O with all three soil inorganic N indices (R^2 = 0.50–0.66) across the N-fertilized treatments. The correlation between N_2O and soil inorganic N does not necessarily indicate denitrification as the source of N_2O. However, the high correlation of N_2O emission with NH_4^+ may also reflect nitrification-derived N_2O. There was a positive but a weak correlation of soil NH_4^+ with cNH_3 ($R^2 = 0.23$) which could be due to greater NO_3^- content in the soil compared to NH_4^+ as the growing season progressed.

2.5.5. CO_2 and CH_4 Response

Immediate increase in CO_2-C flux after manure application in the fall and planting in the spring may be linked to tillage and aeration. Soil was plowed using a field cultivator after the manure application; therefore, tillage-induced disturbance may have increased aeration within the top soil, inducing microbial decomposition of organic matter (Rastogi et al., 2002; Reicosky et al., 1997). Six et al. (2006) reported that the upper 5-cm soil layer is the most susceptible to the effects of tillage and retains less microbial organic matter when tilled. In our study, tillage also most likely allowed the release of trapped CO_2 from the soil to the atmosphere by breaking the upper layer of soil. The seasonal pattern was governed by soil temperature which explained between 23-37% of the variation in CO_2 flux in our study. Other studies have reported >50% of the variation in soil CO_2 explained by soil temperature (Rochette and Gregorich, 1998) and attributed results to confounding factors such as soil texture, pH, atmospheric pressure, and moisture. Daily emission pattern showed increased flux with the presence of corn crop, most likely due to increased root respiration. The decline of CO_2 emissions in all treatments approximately at late VT (tasselling) stage could be due to low rainfall and depleted labile C substrate.

High sampling period mean and cumulative growing season emission of CO_2 from manure amended soil (SM and BM) compared to UO in this study was most likely due to differences in the amount of C input as indicated by the total C and C:N ratio of manure in Table 2. Higher *c*CO_2 emission in 2017 may be attributed to the increased availability of substrates from microbial decomposition of leftover plant residues. Several studies have also shown addition of straw or organic manure to soil can result in substantial increases in the soil respiration rate (Ding et al., 2007a; Mapanda et al., 2011). Therefore, manure and straw bedded manure applications in our study may have greatly increased the amount of substrate for soil microorganisms, subsequently accelerating SOM decomposition further aided by the temperature effects. The low CO_2 emission in UO applied soil may be due to the suppression of the respiration of native soil organic C. In fact, high N levels in soils are known to repress the synthesis and activity of certain enzymes (Carreiro et al., 2000). Our results show that addition of manure could substantially increase the CO_2 emission in the high clay soils of the RRV.

The initial CH_4 emission immediately following manure application (Figure 9) was most likely due to trapped CH_4 produced during manure storage being released after land application (Rodhe et al., 2006; Sommer et al., 1996). The rapid decline in emissions thereafter was probably because CH_4 production ceased due to the sensitivity of methanogens to oxygen (Dave Chadwick et al., 2011; van der Weerden et al., 2014). The immediate release of CH_4 after manure application was also observed by Chadwick et al. (2000b), with > 90% of the total loss occurring in the first 24h. The observed increase in methane flux following the rain events was expected due to an increase in anaerobic sites mostly.

The ability of soils to consume (act as a sink) or produce CH_4 have been discussed in many previous studies (Bowden et al., 1998; Hutsch, 2001; Whalen and Reeburgh, 1996). Methanogens, under anaerobic condition, degrade hydrocarbons in SOM to produce CH_4 and CO_2. In contrast, the consumption of CH_4 occurs under aerobic conditions, where CH_4 is oxidized to CO_2 by methanotrophs (Topp and Pattey, 1997). Moller et al. (2004) showed an increase in volumetric as well as livestock-based methane production from the use of straw bedded manure due to higher volatile solids (VS) content of straw-bedded manure. Total emissions are also found to be driven by the fermentation-related parameters and the quality, quantity, and type of animal feed.

Application of inorganic fertilizer N has been shown to inhibit CH_4 oxidation in soil and non-amended soil to act as a sink of CH_4 (Flessa et al., 1995; Sherlock et al., 2002b). In our study, seasonal mean flux rates and growing season cumulative CH_4 emission in UO showed no clear trend that an inorganic N application decreased CH_4 uptake by soil. Our result suggests that N fertilized silty clay soil of the RRV may not induce CH_4 production, however, its production from manure application is affected by C availability, physical and biological factors. Low emission of CH_4 in our study can be attributed to the manure (solid vs liquid) type. In addition, CH_4 emission from manure is mostly produced under anaerobic conditions during storage (Hristov et al., 2013). Therefore, opportunities to reduce CH_4 emission are centered on preventing anaerobic conditions during storage or capturing and transforming the CH_4 that is produced.

2.5.6. NH_3 Volatilization

Our results suggest increased NH_3 volatilization losses with N application over the unfertilized soil due to greater availability of N in the fertilized plots (Khalil et al., 2005). Ammonia volatilization loss from the soil increased from the baseline level immediately after manure application during fall. This is partly due to the conversion of NH_4^+ present in the surface mixture of soil and manure and partly due to rise in pH in the surface of freshly spread solid manure. The NH_3 volatilization from land applied N fertilizers and manure follow the reversible reaction of $NH_4^+ \rightleftarrows NH_3 + H^+$ as a result, H^+ is consumed (increase in pH) and $NH_4^+ \rightleftarrows NH_3$ equilibrium shifts to the right to favor NH_3 volatilization (Halvin et al., 2013). Manure used in this study had higher dry matter contents (Table 2) which would reduce its infiltration into the soil, thereby increasing its susceptibility to NH_3 emissions (Pain et al., 1989; Sommer and Olesen, 1991a). Ammonia volatilization following UO application in spring showed few distinct peaks, especially during the drying period followed by rain events. It is likely that during wet conditions, soil moisture diluted Total Ammoniacal Nitrogen (TAN) in the NH_3 form (because the pKa of $NH_4^+ = NH_3 + H^+$ changes with temperature) and decreased the equilibrium portion of NH_3 in air relative to soil, thereby reducing the NH_3 emission rate (Kissel et al., 2008). Lower NH_3 emission towards the end of the growing season was most likely due to the combined effects of crop uptake and canopy that potentially minimized the air turbulence and moisture loss at the soil level.

The cumulative volatilization rate also varied between the two study years (Figure 14), with higher rates in 2017. During 2016 growing season, higher rain events may have caused fertilizer to dissolve more into soil solution compared to dry growing season of 2017. Therefore, the longer periods of drying conditions followed by rain events during 2017 growing season most likely triggered higher cNH_3 in soils receiving N-fertilizer. Jones et al. (2013) also reported largest losses (30-44%) of applied N when urea was applied to a moist soil surface, followed by a period of slow drying condition with little or no precipitation. In our study, during 2017 growing season, BM reduced the cNH_3 by 21% compared to UO applied plots. The BM treatment also reduced the cNH_3 compared to SM (by 11%); however, the difference was not significant. The studies on land applied manure with bedding are limited and the studies based on group-housing system for sows or in controlled environments show bedded manure to typically reduce the NH_3 volatilization loss (Andersson, 1996; Groenestein et al., 2006). Chambers et al. (2003) reported NH_3 emissions to be 30% lower from a straw-bedded, deep litter cattle housing system than from a slurry-based (i.e., free-stall) system. In contrast, Misselbrook and Powell (2005) attributed the higher NH_3 emission rates from chopped straw, chopped corn stalks, and chopped newspaper to the open structure of these bedding materials, which increased the surface area coated by urine from which NH_3 emissions occurred. In our study, low NH_3 emission from the BM treatment could be due to added C source that may have promoted immobilization of ammoniacal N. The most significant point of this data is the increasing capture or sequestration of N, which will increase the value of manure as fertilizer while reducing potential pollution by NH_3 and runoff.

Cumulative NH_3 volatilization loss observed here are (3.0–3.7 kg N ha^{-1}) <3% of the fertilizer N applied. Paramasivam et al. (2009) reported cumulative NH_3 volatilization loss over 19 days, in the range of 4 to 27% and 14 to 32% of total N applied as poultry litter and swine manure, respectively. Low NH_3 volatilization loss in this experiment may be linked to application techniques, soil and manure properties, and weather patterns (Huijsmans et al., 2003). Approximately 60-90% reduction in total losses can be achieved with immediate incorporation due to increase in volume of soil to retain NH_4^+ (Adviento-Borbe et al., 2010; Agnew et al., 2010; Huijsmans, 2003). In addition, with the incorporation of N fertilizers, NH_3 formed must diffuse over greater distance before reaching the atmosphere. Manure application during cool, calm weather and in the early morning or evening have shown to reduce NH_3 losses up to 50% (Lupis et al., 2012). In the current study, both manure and urea were applied during early morning hours. Moreover, the silty clay soil in this study had high soil buffering capacity as indicated by the high CEC and organic matter content (Table 3). Subsequent NH_3 loss are less in soil with high buffering capacity because of increased adsorption of NH_4^+ (Pelster et al., 2012). Better manure management practices (immediate incorporation, manure testing, and application time) have potential to reduce NH_3 volatilization loss from fine-textured soils.

2.5.7. Leachate NO_3^- Concentration

Soil water NO_3^- concentrations were strongly affected by soil type and the magnitude of this difference was affected by precipitation patterns. In agreement with Magdoff (1978), our results show that manure N mineralization rates are further induced by the high organic matter content of the soil of the RRV. In general, NO_3^- concentration was greater in SM compared to UO and BM treatments. Solid manures with bedding may have reduced NO_3^- leaching due to immobilization of N with the addition of the straw. The manure in this study were effectively incorporated in fall, which possibly increased the water percolation as well. In contrast, van Es et al. (2006) reported lower NO_3^- concentrations from manure treatments than for the fertilizer-only treatment and was mostly attributed to a higher application rate of N fertilizer-only treatment. In the annual cropping system of this study, nitrate leaching also occurred in the non-fertilized plots suggesting that NO_3^- leaching can be reduced by management but not eliminated.

2.6. Conclusion

The data collected during this 2-yr field experiment showed that higher corn yield and grain N uptake in 2016 than 2017 was associated with the soil dry-wet condition with moist conditions more favorable for higher corn yield. Our results imply that manure application practices can reduce N_2O emission and have potential to also maintain corn yield comparable to urea application practices. The N_2O emissions from the silty clay appeared to be limited not only by the soil dry-wet cycle, but also soil C:N and composition of N-treatments because the addition of manure with high C:N decreased N_2O emissions. The presence of crop during the growing season contributed to higher CO_2 fluxes but did not have a significant effect on N_2O fluxes. This study showed that addition of manure to soil with high OM and high clay content could substantially increase the CO_2 fluxes. Fluxes of CH_4 from N fertilized silty clay soil of the RRV are most affected by the wet soil condition and C availability that favors the reduction of CO_2 gas.

Inherent N mineralization appears to be an important factor controlling inorganic N indices and its relationship to N_2O flux and with cumulative NH_3 volatilization losses. Therefore, assessment of soil mineral N during crop growing period is important to improve our knowledge on N availability for crops. The higher cumulative NH_3 volatilization loss in 2017 could be attributed to long dry periods following major precipitation events that could cause fertilizer to dissolve into soil solution more rapidly. Moreover, results showed that silty clay soils of the RRV with high soil pH, high CEC, and high OM content could limit the overall NH_3 losses from N-fertilizer application. Controllable factors, such as type of manure, time of application, and management of crops, could be key factors to reducing GHG emissions and NH_3 losses in RRV area. The findings from this study could be useful in considering manure application as an alternative to conventional urea application. These results further advance understanding of the impact of long-term N application from a variety of sources (manure with and without bedding and synthetic fertilizer) on gas emissions, crop response and soil N dynamics, and provide information for assessing the sustainability of corn-based crop in the RRV. With contrasting weather patterns during 2016 and 2017 growing seasons, our study emphasized the need for long-term study to fully understand the emission ‘trend’ because individual year may not fully account for variabilities in soil N indices and weather of the long-term. Additionally, laboratory simulation study at different soil WHC and soil temperature might also further add to understand the emission trend.

2.7. References

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3. RELEASE OF AMMONIA AND GREENHOUSE GASES ALONG MOISTURE GRADIENT FROM MANURE AND UREA TREATED FARGO SILTY CLAY SOIL[1]

3.1. Abstract

Greenhouse gas (GHG) [nitrous oxide (N_2O), carbon dioxide (CO_2), and methane (CH_4)] emission and ammonia (NH_3) volatilization from organic and commercial fertilizers are likely related to soil moisture levels. Effect of soil moisture [(30, 60, and 90% water-holding capacity (WHC)] on emissions from urea and manure treated (215 kg ha^{-1}) Fargo-Ryan silty clay soil was studied under laboratory conditions. Soils (250 g) amended with solid beef manure (SM), straw-bedded solid beef manure (BM), urea (CF), and control (NF) were incubated for 28 days at 22±1 ºC, to determine GHGs (N_2O, CO_2, and CH_4) emission and NH_3 volatilization loss. The cumulative emission of N_2O-N, CO_2-C, and CH_4-C ranged from 27 to 4402 µg N_2O-N kg^{-1}, 272 to 2030 mg CO_2-C kg^{-1}, and 10.1 to 1389 µg CH_4-C kg^{-1} soil, respectively. The daily fluxes and cumulative emissions of N_2O and CO_2 generally followed the decreasing order of 30% < 90% < 60% of WHC. At 60% WHC, 1.01% of the total applied N was lost as N_2O from urea treated soil. Carbon dioxide emission from manure treated soil (SM and BM) was up to two times the emission from CF treated soils. The Fargo clay soils showed higher CH_4 emission at near saturation level. The cumulative NH_3 volatilization loss from soil ranged from 29.4 to 1250.5 µg NH_3-N kg^{-1}, with the highest loss from CF amended soils at 30% WHC. These results suggest that gaseous emissions from manure and urea application are influenced by moisture levels of Fargo-Ryan silty clay soil.

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[1] The material in this chapter was co-authored by Suresh Niraula, Shafiqur Rahman, and Amitava Chatterjee. Suresh Niraula had primary responsibility for the collection and analyses of samples, and was the primary developer of the conclusions that are advanced here. Shafiqur Rahman and Amitava Chatterjee served as proofreader and checked the math in the statistical analysis conducted by Suresh Niraula. This chapter has been accepted with major revision and further review is underway in the Applied Engineering in Agriculture Journal.

3.2. Introduction

Nitrogen (N) input from manure or synthetic fertilizer *(e.g.*, urea) applications are known to increase gaseous emissions from soil. The U.S. Environmental Protection Agency (USEPA, 2016) estimates agricultural activities in 2014 accounted for 8.3% of the total U.S. greenhouse gas (GHG) emissions through components of the livestock and agricultural production system. The main three GHGs linked with agriculture are nitrous oxide (N_2O), carbon dioxide (CO_2), and methane (CH_4), with global warming potentials (GWP) of CH_4 and N_2O, 21-25 and 298-310 times higher than CO_2, respectively (Borhan et al., 2011; Chan and Parkin, 2001; USEPA, 2016). Annually, 1 to 1.25% of the total N fertilizer applied to arable soils is lost as N_2O (IPCC, 2006); however, 3–5% has also been reported (Crutzen et al., 2007). In addition to N_2O, ammonia (NH_3) volatilization is also a major pathway of N loss after fertilizer application, with agricultural activities representing 20–80% of NH_3–N emissions worldwide from sources that include manure and inorganic N fertilizers (Aneja et al., 2008; Misselbrook et al., 2000; Zhang et al., 2010). Ammonia released to environment contributes to acidification and eutrophication of ecosystems on its deposition, leading to detrimental effects on aquatic and human health (Aneja et al., 2008).

Soil moisture is regarded as a major determining factor for gaseous emissions since it controls microbial activity, root respiration, and chemical decay process (Oertel et al., 2016). The loss of fertilizer N as N_2O is mostly driven by denitrification (NO_3^- reduction to N_2O and N_2) under anaerobic conditions, and also via nitrification (oxidation of NH_4^+ to NO_3^- via NO_2^-) under aerobic conditions (Linn and Doran, 1984). Studies have shown an increase in N_2O flux rates in response to precipitation events due to denitrification when water-filled pore space (WFPS) ≥ 60% (Awale and Chatterjee, 2015; Linn and Doran, 1984; Signor and Cerri, 2013).

Many literature reviews have suggested that the abundance of soil denitrifier population and activity are primary factors that influence denitrification rates, nevertheless the decline in N_2O emissions under wettest soil conditions have also been reported, possibly owing to the strict anaerobic conditions, resulting in the formation of N_2 rather than N_2O (Butterbach-Bahl et al., 2013; Flessa et al., 1995). For instance, Flessa et al. (1995) found no strong relationship between N_2O emission rates and soil moisture (R^2=0.08-0.27) in a manure application study and attributed the result to soil physical and chemical properties that may induce N_2O production differently. Furthermore, the influence of soil water on infiltration and gas diffusion rates vary with soil texture and substrate addition. For instance, Kowalenko et al. (1978) observed larger CO_2 emissions from clay loam soil (6.2 kg CO_2 ha^{-1} d^{-1}) than sandy soil (3.3 kg CO_2 ha^{-1} d^{-1}). Contrary to N_2O and CO_2, soils are generally net sinks to CH_4 under aerobic conditions; however, anaerobic conditions, including wetlands, rice paddies, saturated soils, and flooded areas, soils can be a net source of CH_4 (Chan and Parkin, 2001; Gao et al., 2014). Similarly, high NH_3 volatilization has been reported under conditions that include soil drying (Al-Kanani et al., 1991) and high soil water content near saturation due to greater accumulation of NH_4^+ with O_2 limitation (Singh et al., 2012). The impact of fertilizer use on soil health and N cycle needs to be accurately assessed to attain high soil fertility, while mitigating GHG emissions (Zhang et al., 2016). Therefore, use of manure and inorganic fertilizers to meet the crop N demand without compromising economic yields or increasing gaseous emissions require careful consideration about physical and chemical properties of the soil and substrates added to soil as an N source.

Most studies on livestock manure and emission focus on liquid dairy manure management (Comfort et al., 1990; Leytem et al., 2011; Rotz and Oenema, 2006) or open feedlot manure (Borhan et al., 2011; Hristov et al., 2013) or in-barn emissions (Joo et al., 2014;

Kaharabata et al., 2000). Land application of several types of manure and GHG emissions have been reported in laboratory, plot, and field scale studies (Chadwick et al., 2000; Chang et al., 1998; Sherlock et al., 2002). Loro et al. (1997) found that liquid manure showed immediate and intense denitrification while denitrification was more prolonged and less intense with solid manure. On the contrary, Mogge et al. (1999) showed the repeated application of solid manure induced higher N_2O emissions with nitrification as the major contributor. Manure bedding is another factor that complicates the estimation of nutrient availability from solid manure given the range of bedding types, application and incorporation timing, and climatic factors (Petersen et al., 2007).

Studies on the effects of soil moisture regimes on manure-N application to fine textured and poorly drained soils in the Red River Valley (RRV) are limited. In North Dakota, the number of beef cattle increased by 6% from 2016 to 2017 (total of 954,000 animals as of January 01, 2017) (USDA, 2017). This increase in cattle directly affects the production of manure, which then calls for better manure management practices to mitigate environmental risks. There is limited information on how land application of solid beef manure and bedded beef manure practices influence overall gaseous emissions. This research gap suggests a need to quantify GHG emissions and NH_3 volatilization, specifically under different soil moisture conditions and in high clay soils. The objectives of this study were to assess the effects of (i) soil moisture regimes and (ii) urea and solid beef manure, with and without straw bedding, on emissions of N_2O, CO_2, CH_4, and NH_3 from Fargo-Ryan silty clay soil. We hypothesize that addition of solid beef manure in clay soils with high organic matter (OM) content would act as a source of GHG and NH_3 with higher emissions at higher moisture levels.

3.3. Materials and Methods

3.3.1. Soil Collection and Preparation

Soils for the laboratory incubation study were collected from the North Dakota State University (NDSU) research field in Fargo, ND (46° 55' 15" N, 96° 51' 31" W; 272.3 m above mean sea level). The soil was poorly drained Fargo-Ryan silty clay with 0 to 1 percent slope, and classified as fine, smectitic, frigid TypicEpiaquerts (Fargo) and fine, smectitic, frigid TypicNatraquerts (Ryan) (Soil Survey Staff, 2014).

A composite sample of the top 0.15 m (0-15 cm) soil were collected from the 5 spots from a previously cultivated surface. Soil was then air-dried, thoroughly mixed, and finely ground down to ~2 mm size using an oscillating stainless-steel sieve in a Wiley mill mechanical grinder (Thomas Scientific, Swedesboro, NJ). The main properties of air-dried soil are presented in Table 12. The WHC of the sieved soil was determined by saturating 10 g of soil with deionized water inside a funnel. Then, the soil was drained for 4 h and WHC was determined gravimetrically by drying soil at 105°C to a constant weight (Bowden et al., 1998). Laboratory incubation was set up in a 1-L clear glass mason jar of 0.00466 m^2 (area=46.6 cm^2), each filled with 250 g of sieved soil mixed with the N-fertilizer (both organic and inorganic) amendments, following the procedure described by (Mukome et al., 2013). Bulk density of the soil was 1.1 g cm^{-3} and was determined by soil core collection and gravimetric method (Blake and Hartge, 1986). The soil put inside mason jars were compacted to the height of 0.049 m (4.9 cm) to achieve the field bulk density of 1.1 g cm^{-3}.

Table 12: Physical and chemical properties of soil at 0.15 m (0-15 cm), Solid beef manure (SM) and Bedded manure (BM) used in the study.

Properties	Soil	SM	BM
pH [a]	8.2	8.4	9.4
EC (dSm^{-1}) [a]	1.32		
NO_3-N (mg kg^{-1}) [b]	14.9		
NH_4-N (mg kg^{-1}) [b]	1.6	460	355
Sand (%) [c]	3.7		
Silt (%) [c]	44.3		
Clay (%) [c]	52.1		
CEC ($cmol_c$ kg^{-1}) [d]	41.4		
OM (%) [e]	6.8		
Total C (%) [f]	3.29	20.5	24.9
Total N (%) [f]	0.26	1.3	0.63
C:N	12.5	15.7	35.6
Dry matter (%) [f]		60	58

[a] pH and Electrical conductivity (EC) determined in 1:2.5 soil/water extractant (Thomas, 1996).

[b] Inorganic soil N (NH_4^+ and NO_3^-) determined using 2M KCl extractant (Maynard et al., 2008).

[c] % sand, silt and clay determined by hydrometer method (Elliott et al., 1999).

[d] Cation Exchange Capacity (CEC) determined by sodium acetate method (Chapman, 1965).

[e] Organic matter (OM) determined using loss-on-ignition method (Combs and Nathan, 1988).

[f] Total C, Total N, and Dry matter content obtained from NDSU Soil Testing Lab., Fargo, North Dakota.

3.3.2. Manure Collection and Preparation

Representative samples of both solid beef manure (SM) and wheat straw-bedded solid beef manure (BM) were collected from a year-old manure stockpile outside the NDSU Beef Cattle Research Complex located in Fargo, ND. Average temperature and wind speed at the time of manure sample collection were 6.1 °C and 4.5 ms^{-1}. The manure stockpile remained uncovered and exposed to weather conditions prior to sample collection. Five subsamples from different depth (avoiding surface crust) were placed in a 10-gallon bucket and mixed thoroughly. Then, manure samples were air-dried, finely ground down to ~2 mm, and mixed thoroughly before use. The EC and pH of the manure were measured at 1:2.5 manure to water suspension using Accumet AB pH meter (Fisher Scientific, Hampton, NH). The main properties of the organic amendments used in this study are presented in Table 12.

3.3.3. Experimental Approach

A completely randomized design (CRD) in a split-plot arrangement with four replications was used in this study. The whole-plot were three soil moisture regimes (30, 60 and 90% WHC) and the subplot treatments were four N fertilizer treatments (SM, BM, CF, and NF) with four replications (16 jars at each WHC level, total of 48 jars). The N application rates in the glass mason jars were established based on the typical N application rate (215 kg N ha^{-1}) for a corn (*Zea mays* L.) as recommended for Eastern North Dakota, except for NF where no fertilizer was added. Application rates were at 11 g of SM, 22 g of BM, and 218 mg of CF (0-46-0) per 250 g soil (equivalent to 215 kg N ha^{-1} on an area basis), incorporated using a glass rod stirrer. Deionized water (71, 141, and 212 mL) was added evenly over the surface with a pipette to bring the moisture content to 30, 60, and 90% WHC, respectively. Each mason jar was weighed soon after the setup and the water lost through evaporation was replaced by adding deionized water during sampling days. The mason jars were sealed with airtight lids, fitted with gas sampling ports (butyl rubber septum), and incubated at 22 ± 1 °C for 28 days.

3.3.4. Measurement and Analysis of Greenhouse Gases

Headspace air samples (25 mL) were collected from the mason jars (on days 1, 2, 4, 5, 7, 10, 15, 18, 21, and 28 after incubation), following the described procedure (Awale & Chatterjee, 2015; Mukome et al., 2013). Headspace gas sampling was done by inserting a gas tight luer lock syringe into the jar, and immediately transferred it into a pre-evacuated 12 mL gas serum vials. After sampling, jars were left open for an hour for aeration. Vials were analyzed for N_2O, CO_2, and CH_4 within 24 h using gas chromatograph (GC) (Model: DGS-42 Master, Dani Instruments, Milan, Italy) paired with an auto sampler (Master SHS, Dani Instruments, Milan, Italy). The GC was fitted with a ^{63}Ni electron capture detector (ECD) for N_2O (carrier gas 10% CH_4 and 90% Ar), thermal conductivity detector (TCD) for CO_2 (carrier gas He), and flame ionization detector (FID) for CH_4 (carrier gas He). The GC oven was operated at 80 °C and auto sampler oven at 70 °C. Analytical gas standards (0, 1, 5, 50, 100, 500, and 1000 ppm for N_2O; 0, 500, 1000, 3000, 5000 ppm for CO_2; and 0, 4, 10, 30, 100 ppm for CH_4; Scotty Specialty Gases) were included after every twenty samples to construct standard curves during each analysis event. Background gas concentrations were subtracted from the measurements prior to data analysis. The N_2O, CO_2, and CH_4 concentrations were converted into mass units assuming ideal gas relations and expressed as micrograms N_2O-N, milligrams CO_2-C, and micrograms CH_4-C produced between sampling dates per kilogram of soil, respectively. The headspace concentration of gas samples measured between the sampling dates were divided by the elapsed time to obtain daily N_2O (μg N_2O-N kg^{-1} moist soil d^{-1}), CH_4-C (μg CH_4-C kg^{-1} moist soil d^{-1}), and CO_2 fluxes (mg CO_2–C kg^{-1} moist soil d^{-1}) using the following equation:

$$Flux = \frac{P \times Ct(Vh + Vw) \times M}{R \times T \times W \times t} \times 1000$$

Where C_t is the gas concentration in the gas phase (μL gas L^{-1}), V_h is the volume of the headspace (mL), V_w is the volume of water in the soil (mL); M is the atomic weight of C or N (g mol^{-1}), P is the standard atmospheric pressure (101.325 kPa), R is the universal gas constant (8.31451 L kPa mol^{-1} K^{-1}), T is the temperature in Kelvin (295.15°K), W is the oven dry mass of soil (g), and t is the time between the 1st and 2nd sample collection.

Cumulative μg N_2O-N, mg CO_2-C, or μg CH_4-C emission per kg^{-1} soil during the incubation period was calculated by summing the gas emissions during each sampling period.

Emissions were calculated as N_2O-N, CO_2-C, and CH_4-C, however, for simplicity flux is herein referred to as N_2O, CO_2, and CH_4, respectively.

3.3.5. Measurement and Analysis of Soil Inorganic N

At the end of the incubation, 6.5 g of field-moist soil samples from each treatment (total of 48 soil samples) were extracted with 25 mL of 2 M potassium chloride (KCl) solution (1:5 soil/extractant ratio), after shaking for 30 min in a reciprocal shaker (Maynard et al., 2007). The soil suspension was then centrifuged for 5 min and filtered through a Whatman no. 2 filter paper. The KCl extracts were analyzed for soil inorganic N (NH_4^+ + NO_3^-) using the Timberline TL2800 Ammonia Analyzer (Timberline Instruments, Boulder, CO). Gravimetric soil water content was used to express soil inorganic N contents on a dry-mass basis.

3.3.6. Measurement and Analysis of NH_3 Volatilization

Ammonia (NH_3) volatilization losses from each experimental jar were measured using the phosphoric acid (H_3PO_4) traps placed inside the headspace of the screw-top Mason jar (Khan et al., 2001). In order to facilitate the capture of NH_3, 20 mL of 0.5 M H_3PO_4 was placed inside a 50 mL cup and hung above the soil surface using a metal wire from the lid. Following gas sampling, acid traps were collected and replaced with freshly prepared 20 mL H_3PO_4 solution to facilitate NH_3 trapping until the next sampling day. The traps were extracted with 50 mL of 2M KCl, sealed and frozen at -18°C in polypropylene vials, until analysis within 2 d using the Automated Timberline TL2800 Ammonia Analyzer (Timberline Instruments, Boulder, CO). Daily NH_3 volatilization loss (μg NH_3–N kg^{-1} soil d^{-1}) were calculated by dividing the NH_3-N emitted between the sampling dates by the elapsed time. In addition, NH_3 volatilization losses during each sampling periods were summed to obtain the cumulative NH_3-N losses (μg NH_3–N kg^{-1}) of entire incubation period. The final ammonia volatilization loss between sampling dates at each WHC was estimated using the mean loss from the replicated jars. Cumulative NH_3 volatilization loss (µg NH_3 kg^{-1}) over the entire sampling period was calculated by summing the amount of NH_3 volatilized during each sampling event.

3.3.7. Measurement of Emission Factors

The fertilizer-induced emission factor (%EF) emitted as N_2O-N or NH_3-N from the applied N treatments was calculated using the following equation:

$$\%EF=\frac{C_{fert}-C_{control}}{N_{applied}}\times 100$$

where C_{fert} and $C_{control}$ are the cumulative N_2O or NH_3 emissions from fertilized N treatments and control, respectively (Gagnon et al., 2011).

3.3.8. Data Analysis

The effect of soil WHC and N fertilizers on daily and cumulative GHG emissions (N_2O, CO_2, and CH_4), NH_3 volatilization, and soil inorganic N were analyzed using the PROC MIXED procedure of SAS. Residuals were evaluated for normality using scatter plots of residuals versus predicted values using the UNIVARIATE procedure of SAS (SAS Institute, 2014). The covariance structure resulting in the smallest Akaike and Schwarz Bayesian criteria was considered most appropriate for analysis. Analysis of variance with a test of Tukey-Kramer Method at p-value ≤ 0.05 was used to determine significant differences of means across WHC levels. Relationships of N treatment and moisture variables with gas fluxes were assessed using Pearson correlation analysis. Correlation coefficients (R^2) were obtained using linear regression analysis with PROC CORR in SAS ($P \leq 0.05$).

3.4. Results and Discussion

3.4.1. Effect of Soil Moisture on N_2O Emissions

The daily mean N_2O emissions at 30, 60, and 90% WHC, ranged from 0 to 83, 0 to 949, and 0 to 1443 μg N_2O-N kg^{-1} d^{-1}, respectively, with the highest daily emission from CF amended soil at all moisture levels (Figure 18). The daily and cumulative N_2O emission from N treatments followed the decreasing order of 30% < 90% < 60% WHC, indicating that both, very dry and very wet soil conditions favor lower N_2O emission. Low microbial activity at 30% WHC and more N_2 production than N_2O at 90% WHC possibly reduced N_2O emissions at both extremes. At 90% WHC, an anaerobic condition most likely favored the denitrification of NO_3^- to N_2. Anaerobic organisms are known to utilize NO_2^- and NO_3^- as an electron acceptor under O_2 limiting condition and release N_2 and N_2O, with N_2 about 90% of the total denitrification release under reduced condition (Halvin et al., 2013). Our results are in agreement with Smith et al. (1998), where they reported the decrease in N_2O emission at WFPS greater than 90% in clay loam soil due to the reduction of N_2O to N_2.

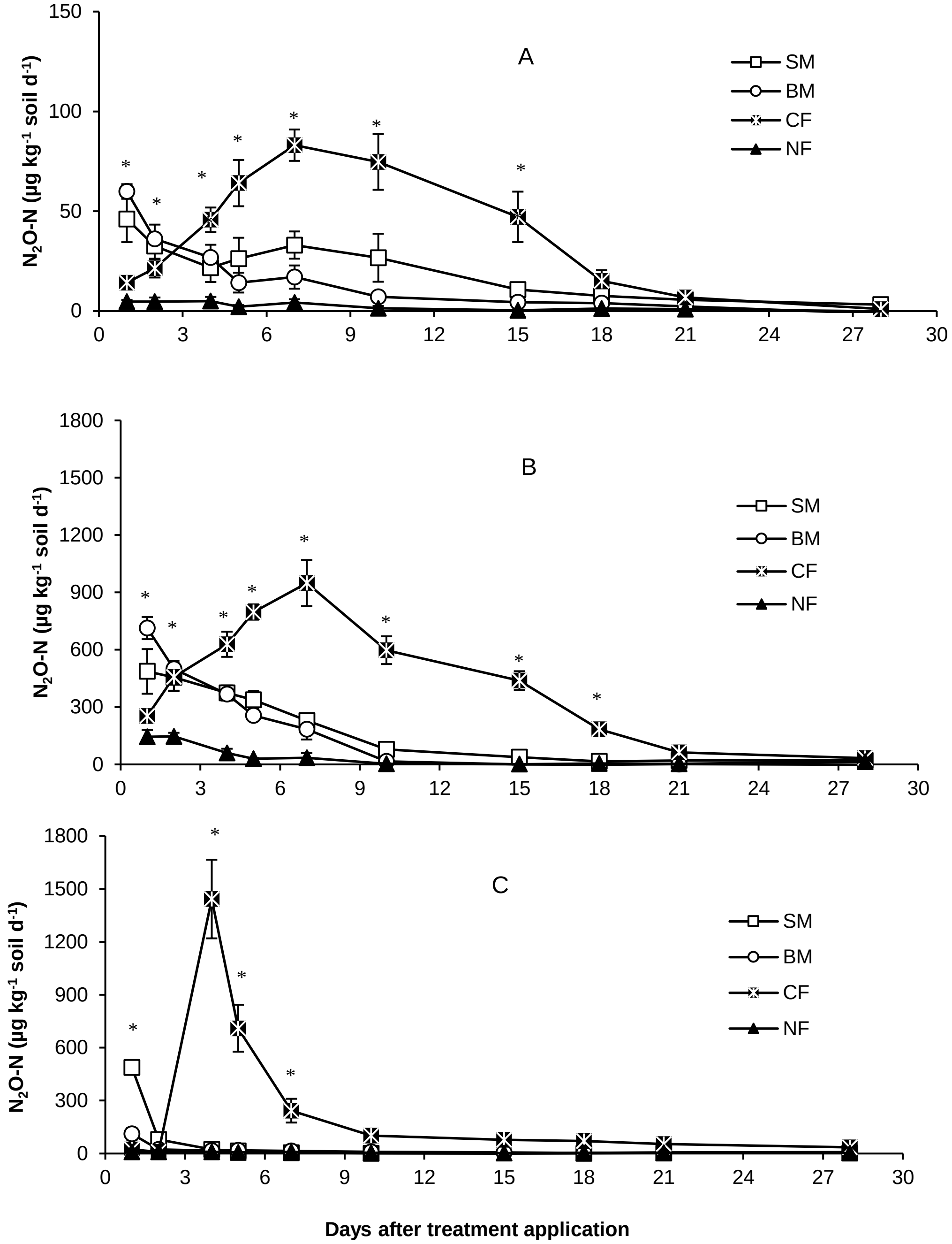

Figure 18: Daily soil N_2O fluxes after N fertilizers [solid beef manure (SM), straw-bedded solid beef manure (BM), urea (CF), and control (NF)] application on silty clay soils at (A) 30% WHC, (B) 60% WHC, and (C) 90% WHC over 28 d of incubation. Vertical bars are standard errors (n=4). *Indicates any significant ($P \leq 0.05$) differences between treatments for the day. Please note the large differences in y-axis scaling.

Nitrogen (urea or manure-N) treated soil produced significantly higher N_2O emission than NF at all WHC levels ($P \leq 0.05$), throughout the incubation period (Table 13). Increased availability of N substrate from urea-N and manure-N application may have intensified N_2O emissions, also explained in a study by Khalil et al. (2005). When comparing N treatments and moisture level, cumulative N_2O emissions from 60% WHC were 9.5-16 and 1.5-9.5 times greater than emissions from 30% and 90% WHC treated soils, respectively. Across all N treatments and WHC levels, approximately 0.53% of the total applied N was lost in the form of N_2O-N. The highest N_2O emission at 60% WHC (1.01% EF of total applied N) was likely due to both, nitrification and denitrification processes occurring simultaneously, with possible denitrification at soil anaerobic microsites. At or near field capacity (~60% WFPS), nitrification and denitrification occur simultaneously, and nitrification is comparable to denitrification as a source of N_2O (Davidson, 1991; Linn and Doran, 1984). Similarly, in aerated soils, denitrification presumably occurs in anaerobic microsites or aggregates, where oxygen diffusion is slow (Bateman and Baggs, 2005; Halvin et al., 2013). Low N_2O emissions at 30% WHC, in this study, may have been dominated by nitrification that has a much lower N_2O emission potential than denitrification, which also supports the findings of Jiang & Bakken (1999) and Morkved et al. (2007).

Table 13: Cumulative N_2O emissions from soil treated with N sources (manure and urea) over 28 days of incubation at 30, 60, and 90% WHC.

N fertilizer source	Cumulative N_2O Emissions (μg N_2O-N kg^{-1} soil) [a]		
	30% WHC	60% WHC	90% WHC
Control (NF)	27 ± 4.9 cA	448 ± 58.7 cB	63 ± 7.9 dC
Solid beef manure (SM)	216 ± 35.2 aA	2060 ± 275.5 aB	621 ± 47.4 bC
Bedded manure (BM)	173 ± 8.5 aA	2039 ± 107.4 aB	220 ± 37.2 aA
Urea (CF)	375 ± 14.2 bA	4402 ± 199.2 bB	2771 ± 364.3 cC

[a] Values are means ± standard errors (n=4). Different lowercase letters within a column and different uppercase letters within a row indicate significant differences at 0.05 significance level.

Our study also showed soil moisture control on daily N_2O release pattern. At the beginning, emissions from manure amended soil showed a sharp peak (Figure 18); possibly due to higher nitrification of manure NH_4^+ and dentrification soil NO_3^-. Greater and relatively short-lived N_2O emissions immediately after manure application was also observed by Dutta & Stehouwer (2010). At 30, 60, and 90% WHCs, the cumulative N_2O emission from SM amended soil was higher by 20%, 1%, and 64% compared to BM amended soil, respectively. The majority of the inorganic N present in SM and BM was in the form of NH_4-N, with SM ~30% higher than BM (Table 12). The presence of high NH_4-N in SM may have favored higher nitrification in SM amended soil thus producing higher NO_3^-, a source of N for denitrification. Other studies have reported a similar or higher levels of NH_4-N present in slurry and fresh solid manures (Chadwick et al., 2000; Sommer et al., 1992). Conversely, Zhang et al. (2005) reported little or no N_2O emissions from systems that do not use bedding. This difference in response could be related to the difference in management systems and manure types. Zhang et al. (2005) quantified emissions from livestock buildings where the slurry/feces/urine mostly remained in anaerobic state with little opportunity for the NH_4^+ to be nitrified. However, in our study, we applied dried and ground SM and BM under laboratory conditions. In addition to the differences in NH_4-N of manures, the C:N ratio of SM and BM were 15.7 and 35.6, respectively, and this might have led to higher N_2O emissions from SM treated soil. Soil N mineralization is most favorable at the C:N ratio ≤ 20, and the substrate with lower C:N ratio release mineral N early in the decomposition process (Halvin et al., 2013). The measured residual inorganic N, presented in table 14, at the end of the incubation was higher in SM than BM amended soil by 1.3, 17.9, and 39.1% at 30, 60, and 90% WHC, respectively, however, our results did not show significant differences in residual N between manure type ($p>0.05$).

Table 14: Soil residual inorganic N content measured at the end of 28 d incubation as influenced by N fertilizer sources at 30, 60, and 90% WHC.

	Soil residual inorganic N (mg kg^{-1} soil) [a]		
N fertilizer source	30% WHC	60% WHC	90% WHC
Control (NF)	82.2 ± 9.9 cA	32.6 ± 6.1 cB	53.8 ± 7.0 cA
Solid beef manure (SM)	199.9 ± 29.7 aA	71.8 ± 8.1 aB	167.1 ± 47.4 abA
Bedded manure (BM)	197.4 ± 11.6 aA	60.9 ± 14.4 aB	120.1 ± 36 aB
Urea (CF)	374.8 ± 48.2 bA	162.7 ± 6.8 bB	207.8 ± 29.8 bC

[a] Values are means ± standard errors (n=4). Different lowercase letters within a column and different uppercase letters within a row indicate significant differences at 0.05 significance level.

When comparing manure vs. urea across moisture levels, our results show a 62% reduction of N_2O emissions from manure (SM+BM) amended soil compared to CF. The highest cumulative N_2O emission was observed for CF amended soil at 60% WHC (4402 μg N_2O-N kg^{-1}). Rapid hydrolysis of CF to NH_4^+ most likely influenced the higher emission. The hydrolysis of CF in the range of 83-90% have been reported in several studies (Halvin et al., 2013; Macleant and McRae, 1987; Tomar and Soper, 1981), whereas organic amendment mineralization are reported a range of 16-53% (Chae and Tabatabai, 1986; Li and Mahler, 1995; Morvan et al., 2006). Greater emissions from mineral N application compared to manure N have been reported in previous studies (Chantigny et al., 2010; Hernandez-Ramirez et al., 2009). However, studies on the emission of N_2O in fine-textured, high clay and OM in the Red River Valley are limited (Asgedom et al., 2014). Our findings suggest that use of manure amendments with wheat straw bedding is promising in reducing N_2O emissions from silty clay soil, and thus the results can be useful in devising manure management decisions for crop production and in reducing GHG contribution from land application.

3.4.2. Effect of Soil Moisture on CO_2 Emissions

The daily mean CO_2 emission at 30, 60, and 90% WHC, ranged from 14 to 271, 12 to 560, and 0.7 to 432 mg CO_2-C kg^{-1} d^{-1} (Figure 19), respectively, and SM amended soil had the highest cumulative CO_2 emission at all moisture levels (Table 15). Cumulative CO_2 emission followed a similar decreasing order as N_2O emission, with 30% WHC < 90% WHC < 60% WHC, indicating that both, very dry and very wet soil conditions favored lower CO_2 emissions. Under almost saturated soil, soil CO_2 is restricted because substantial portion of the soil pores are filled with water, but not as much as when water is a limiting factor (Bowden et al., 1998; Franzluebbers, 1999; Gulledge and Schimel, 2000; Sänger et al., 2011). The effect of soil water content on CO_2 emission has been described by numerous equations, including linear, logarithmic, quadratic, and parabolic functions. The soil water equations were expressed as matric potential, gravimetric water content, volumetric water content, WHC, WFPS, precipitation indices, or depth to water table (Epron et al., 1999; Linn and Doran, 1984; Orchard and Cook, 1983; Qi and Xu, 2001). In this study, the WHC expressed as a quadratic function that resulted in the R^2=1 was superior to other functions used for fitting the respiration and moisture relationship for all soils, suggesting the effect of moisture on CO_2 emission depend on the range of moisture. Differences in results with other studies can be attributed to the variable temperature effects on CO_2, soil drying effects on microorganisms, and crop respiration effects. This study was conducted at a constant room temperature, on air-dried soils and in absence of vegetation, while others have included the variable effects.

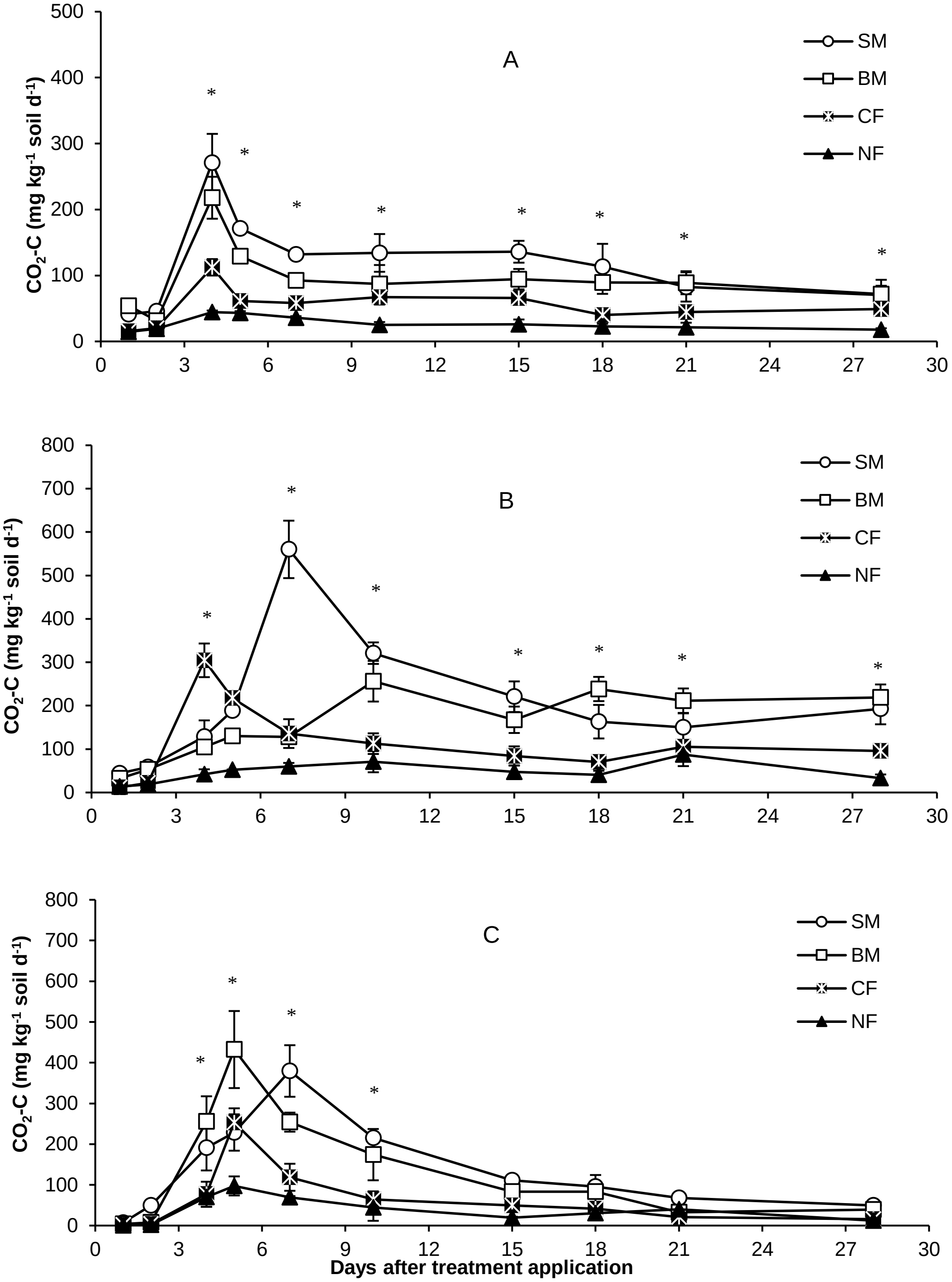

Figure 19: Daily soil CO_2 fluxes after N fertilizers [solid beef manure (SM), straw-bedded solid beef manure (BM), urea (CF), and control (NF)] application on silty clay soils at (A) 30% WHC, (B) 60% WHC, and (C) 90% WHC over 28 days of incubation. Vertical bars are standard errors (n=4). *Indicates any significant ($P \leq 0.05$) differences between treatments for the day. Please note the large differences in y-axis scaling.

Table 15: Cumulative CO_2 emissions from N fertilizers over 28 days of incubation at 30, 60, and 90% WHC.

N fertilizer source	Cumulative CO_2 Emissions (mg CO_2-C kg^{-1} soil) [a]		
	30% WHC	60% WHC	90% WHC
Control (NF)	272 ± 7.6 dA	468 ± 46.8 dB	388 ± 27.6 cB
Solid beef manure (SM)	1201 ± 41.5 aA	2030 ± 128 aB	1398 ± 30.6 aA
Bedded manure (BM)	959 ± 37 bA	1543 ± 85.1 bB	1368 ± 58.5 aB
Urea (CF)	537 ± 28.3 cA	1163 ± 76.6 cB	648 ± 69.4 bA

[a] Values are means ± standard errors (n=4). Different lowercase letters within a column and different uppercase letters within a row indicate significant differences at 0.05 significance level.

The daily mean CO_2 emissions from NF soil, at all WHC levels, remained below 100 mg CO_2-C kg^{-1} and was consistently lower than SM, BM, and CF (Figure 19). Furthermore, the cumulative CO_2 emission from NF soil was significantly lower at all moisture levels ($P \leq 0.05$), indicating the influence of substrate limitation on CO_2 emission (Khalil et al., 2005). The highest CO_2 emission from all N treatments, at all moisture levels, was observed during the first 4-7 days. These results suggest that rapid decomposition of manure and total C increases the number of heterotrophic organisms and CO_2 emission, as discussed in previous studies as well (Ding et al., 2007; Gagnon et al., 2016; Sainju et al., 2012).

When comparing manure treatments (SM vs. BM) within a moisture level, SM amended soils had significantly higher CO_2 than BM amended soils at ≤ 60% WHC ($P \leq 0.05$). Furthermore, CO_2 emission from manure amended soil (SM and BM) was significant and up to two times higher than the emission from CF treated soils at all moisture levels. These differences in CO_2 emissions from CF and manure-N sources were most likely due to differences in the amount of carbon input as indicated by the higher C and C:N ratio of manure in Table 12. Gagnon et al. (2016), in an incubation study with 5 different inorganic N-fertilizers, also reported decreased CO_2 emission from inorganic N forms applied to soil that had decreased microbial respiration rates. Our findings suggest that soil treated with inorganic fertilizers may help limit

CO_2 emission compared to manure treated soil, especially from the Fargo silty clay soil of the RRV. Furthermore, while reliable predictions can be made on the effect of moisture levels on soil treated with inorganic and organic forms of N; further studies that incorporate other possible confounding variables, such as temperature and environmental conditions are important to better understand the dynamics of CO_2 emission.

3.4.3. Effect of Soil Moisture on CH_4 Emissions

The daily mean CH_4 emission from all N treatments at 30, 60, and 90% WHC ranged from -0.5 to 2.8, -0.50 to 2.9, and 0.60 to 680.2 μg CH_4-C $kg^{-1}d^{-1}$, respectively, where negative emission indicates consumption of CH_4, and positive emission indicates the net CH_4 production from the soil. Few CH_4 oxidation events were observed during the individual sampling dates, especially for soils at $\leq$ 60% WHC. The ability of soils to consume (act as a sink) or produce CH_4 have been discussed in many previous studies (Bowden et al., 1998; Hutsch, 2001; van den Pol-van Dasselaar et al., 1998; Whalen and Reeburgh, 1996). Methanogens, under anaerobic condition, degrade hydrocarbons in soil organic matter to produce CH_4 and CO_2. In contrast, the consumption of CH_4 occurs under aerobic conditions, where CH_4 is oxidized to CO_2 by methanotrophs (Topp and Pattey, 1997). The cumulative CH_4 emission ranged between 8.8 μg CH_4-C kg^{-1} from BM at 60% WHC and 1389 μg CH_4-C kg^{-1} from SM at 90% WHC (Table 16), indicating that soil amended with N treatments at all moisture levels, were the net emitter of the CH_4 gas.

Table 16: Cumulative CH_4 emissions from N fertilizers over 28 days of incubation at 30, 60, and 90% WHC.

N fertilizer source	Cumulative CH_4 Emissions (μg CH_4-C kg^{-1} soil) [a]		
	30% WHC	60% WHC	90% WHC
Control (NF)	13.9 ± 0.9aA	15.9 ± 1.3 aA	33.9 ± 1.1 cB
Solid beef manure (SM)	13.7 ± 0.5aA	14.2 ± 1.2 aA	1389 ± 193.3 aB
Bedded manure (BM)	10.1 ± 0.7aA	8.8 ± 1.4 bA	495.3 ± 86.2 bB
Urea (CF)	15 ± 0.2aA	18.5 ± 1.8 aA	23.5 ± 1.4 cA

[a] Values are means ± standard errors (n=4). Different lowercase letters within a column and different uppercase letters within a row indicate significant differences at 0.05 significance level.

Our results suggest that CH_4 emission is strongly correlated (R^2=0.75-0.98) to soil moisture levels, indicating higher emission at near saturation level. At 90% WHC, slow diffusion of CH_4 and O_2 gas through water most likely created a water-based anaerobic environment, condition known to support methanogenic archaeal growth (Chadwick et al., 1999). The addition of manure further added C, N, and microbes involved in methanogenesis. When comparing CF with the manure-N treatments, manure amended soil at 90% WHC had significantly higher CH_4 emission, up to 59 fold higher, most likely due to higher anaerobic decomposition of manure by methanogens. Furthermore, at near 90% WHC level, soils treated with SM had 2-3 folds higher cumulative CH_4 emission compared to soils treated with BM. This result was possibly due to slow degradation of lignin, a complex heteropolymer, in wheat straw, as well as due to lower inorganic N in the form of NH_4-N in BM (Table 12). In farmland, NH_4^+ in substrate added to agricultural soil can inhibit CH_4 oxidation, meaning more CH_4 emission (Hütsch et al., 2001; King and Schnell, 1994). Manure contains high concentrations of organic matter that can be mineralized into NH_4^+ and soluble C and this most likely influenced intensity and rate of CH_4 emission from incubated soils in this study. However, in terms of NH_4^+, some studies indicate that NH_4^+ in substrate added to agricultural soil can stimulate CH_4 oxidation and reduce CH_4 emissions (Bender and Conrad, 1995; Bodelier et al., 2000). Therefore, the role of NH_4^+ in CH_4 oxidation is not well-understood and further research is needed (Bodelier et al., 2000; De

Visscher and Van Cleemput, 2003). Our findings suggest that significant reduction in CH_4 emission is possible with proper management practices, including maintaining optimal field moisture level and aeration, irrespective of the choice of N source.

3.4.4. Effect of Soil Moisture on NH_3 Volatilization

The daily mean NH_3 volatilization loss at 30, 60, and 90% WHC ranged from 1.0 to 704.3 , 0.46 to 365.5, and 0.75 to 98.0 µg NH_3-N kg^{-1} soil, respectively (Figure 20). The cumulative soil NH_3 volatilization loss ranged from 29.4 to 1250.5 µg NH_3-N kg^{-1} soil, with the highest loss from CF amended soils at 30% WHC, and the lowest from NF soils at 90% WHC (Table 17). Ammonia volatilization loss showed a strong linear decrease (R^2=0.88-0.99) with increasing moisture levels (90% < 60% < 30% WHC), signifying the dominant effect of soil moisture on NH_3 volatilization. The decrease in NH_3 volatilization loss from soils under high moisture condition have been discussed in many previous studies (Liu et al., 2007; Yan et al., 2016). Yan et al., (2016) showed over 70% cumulative NH_3 emission decrease in intermediate (50%) and high (70%) soil moisture content as compared to low (30%) soil moisture. In the present study, soil receiving N amendments had significantly higher NH_3 volatilization compared to NF soil across all moisture levels ($P \leq 0.05$), which is most likely due to the addition of NH_4^+ containing substrate that increased the soil pH during hydrolysis. The soil used in this study had an initial pH of 8.2, and when NH_4^+ containing fertilizers were added, the $NH_4^+ \rightleftarrows NH_3$ equilibrium during hydrolysis reaction may have shifted to the right due to consumption of H^+, thus favoring more NH_3 volatilization from N amended soils (Al-Kanani et al., 1991; Overrein and Moe, 1967; Rochette et al., 2009).

Table 17: Cumulative NH_3 volatilization loss from N fertilizers over 28 days of incubation at 30, 60, and 90% WHC.

N fertilizer source	Cumulative NH_3 Emissions (µg NH_3-N kg^{-1} soil) [a]		
	30% WHC	60% WHC	90% WHC
Control (NF)	71.8 ± 12.5 cA	37.6 ± 8.2 cA	29.4 ± 3.9 aB
Solid beef manure (SM)	567.0 ± 19.1 aA	331.7 ± 59.8 aB	80.9 ± 5.6 aC
Bedded manure (BM)	552.7 ± 102.1 aA	224.1 ± 34.3 aB	57.8 ± 8.6 aC
Urea (CF)	1250.5 ± 112.1 bA	782.4 ± 138.4 bA	208.9 ± 37.6 bB

[a] Values are means ± standard errors (n=4). Different lowercase letters within a column and different uppercase letters within a row indicate significant differences at 0.05 significance level.

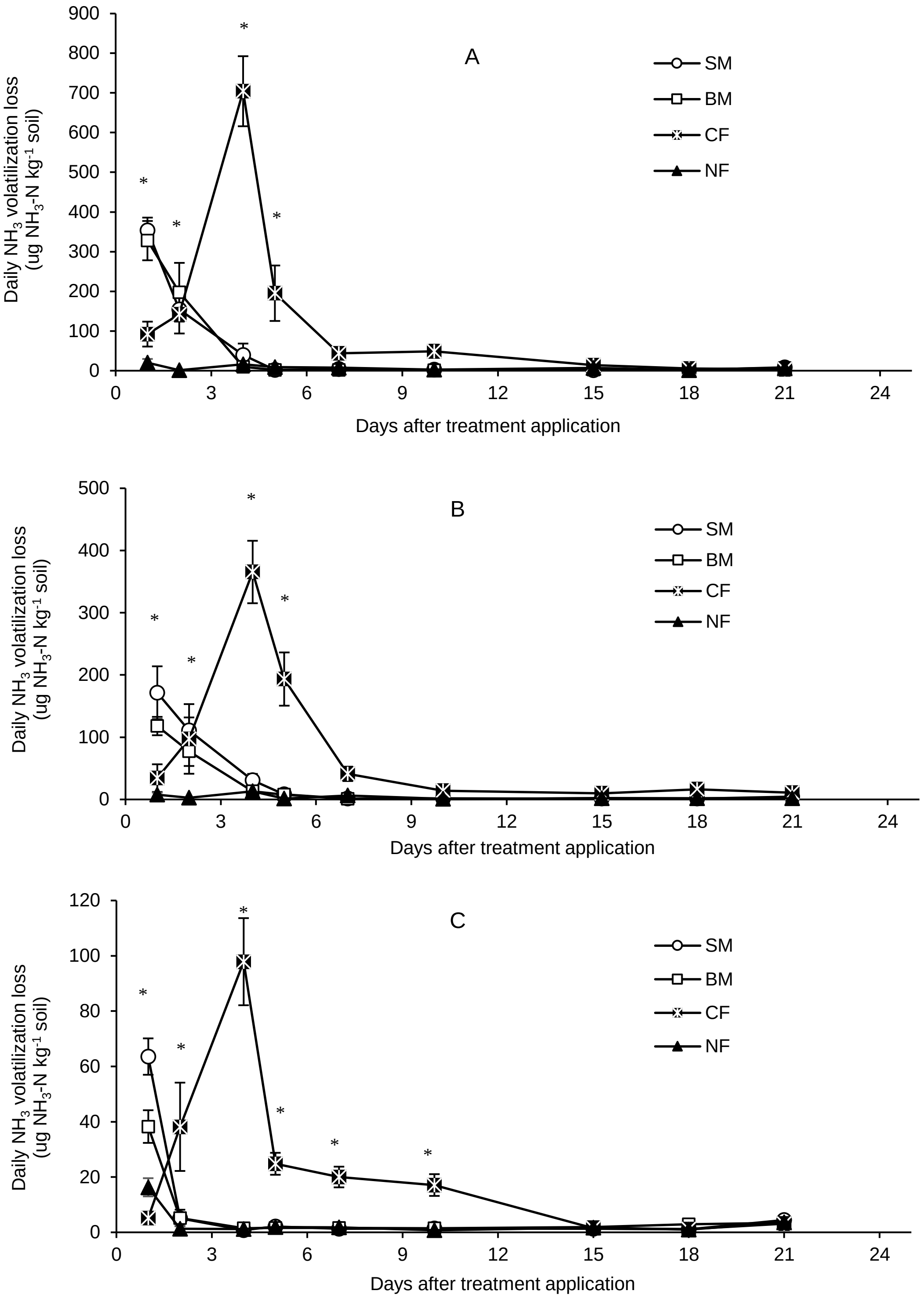

Figure 20: Daily soil NH_3 volatilization loss after N fertilizers [solid beef manure (SM), straw-bedded solid beef manure (BM), urea (CF), and control (NF)] application on silty clay soils at (A) 30% WHC, (B) 60% WHC, and (C) 90% WHC over 28 days of incubation. Vertical bars are standard errors (n=4). *Indicates any significant ($P \leq 0.05$) differences between treatments for the day. Please note the large differences in *y* axis scaling.

The NH_3 volatilization immediately following SM and BM application accounted for over 60% of the cumulative loss from SM and BM amended soil, respectively. Within a particular soil moisture level, NH_3 volatilization loss was not influenced by the manure type ($P>0.05$). Both manure types had higher pH and dry matter contents, both of which would reduce infiltration into the soil, thereby increasing susceptibility to NH_3 loss emissions (Pain et al., 1989; Sommer and Olesen, 1991). The cumulative NH_3 volatilization loss from CF amended soil was significantly higher than manure amended soils across all moisture levels and accounted for 44-55% of the cumulative NH_3 loss. The volatilization loss from CF amended soil occurred mostly during the first 5 day after N application, and accounted for up to 56% of the total loss from CF. The high cumulative NH_3 loss from CF amended soil at all WHC was possibly due to the immediate hydrolysis NH_4^+ near the dissolving urea granule (Halvin et al., 2013).

Across N treatments and WHC levels, NH_3 volatilization loss was less than 1% of the total applied N with highest EF from CF treated soil at 30% WHC. Our EF values are less than what others have reported (Awale and Chatterjee, 2017; Cameron et al., 2013; Paramasivam et al., 2009). Paramasivam et al (2009) reported the cumulative NH_3 volatilization loss over 19 days, in the range of 4 to 27% and 14 to 32% of total N applied as poultry litter and swine manure, respectively. Treatments in our study were mostly under anaerobic condition except for the time 1 hr of aeration following sample collection. Denitrification and subsequent loss of N as N_2O or N_2 is most prominent under anaerobic conditions and may have influenced emission of NH_3 differently. Low cumulative NH_3 volatilization loss during the present study period was possibly because of immediate incorporation of N-fertilizers to soil, which may have increased the volume of soil to retain NH_4^+ (Adviento-Borbe et al., 2010; Agnew et al., 2010; Huijsmans et al., 2003). Most other studies have shown a maximum potential NH_3 loss, either during slow drying periods of the moist soil or from light-textured soil (Al-Kanani et al., 1991; Clay et al., 1990). In contrast, our study was set up at room temperature of 22±1ºC, constant humidity, fine-textured silty clay soil, and three different constantly maintained moisture levels. Furthermore, silty clay soil with fine texture and addition of organic matter possibly increased the CEC of soil, thereby reducing NH_3 volatilization (Al-Kanani et al., 1991; Awale and Chatterjee, 2017; Pelster et al., 2012). In addition, manure application during cool, calm weather and in the early morning or evening are known to reduce NH_3 loss up to 50% (Lupis et al., 2010). Both manure types and urea were applied to soil in the laboratory settings that may have further favored low NH_3 volatilization during this study. Our results show the relative importance of maintaining soil moisture, the timing of fertilizer application, and the benefits of N-fertilizer incorporation in reducing potential NH_3 volatilization loss from fine-textured soils.

3.5. Conclusion

The variation in GHG emissions under three soil moisture levels from silty clay soils amended with manure and urea exhibit the importance of N application at times of rainfall or spring thaw events. This study demonstrates that manure application to silty clay soils have potential to reduce gaseous release, especially N_2O-N and CH_4-C emissions, when management practices allow soil moisture levels to be $\leq$ 60% WHC. However, the CO_2-C emission is profound in manure amended soil at moisture levels $\leq$60% and is most likely related to high C:N ratio of manure. Between manure types, wheat straw bedded manure appears to favor lower emission of all three GHGs analyzed. This study show that NH_3 volatilization following fertilizer N application, especially from manured soil, are relatively short-lived. Furthermore, manure application has potential to significantly reduce N loss as NH_3 when incorporated immediately after application and under anaerobic conditions. The findings from this study could be useful in considering manure application as an alternative N management strategy to conventional urea application to minimize N losses in arable systems within the RRV. Further investigation into animal diet, composition of bedding materials, and emissions during stockpiling could add to the results of our findings. Long-term field experiments in cropped soils, to understand the complexity of confounding factors (temperature, weather variations, wind speed, radiation etc.) that govern gaseous emissions and N losses from solid manured amended soils deserve further research.

3.6. References

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4. TEMPERATURE RESPONSE ON AMMONIA AND GREENHOUSE GAS EMISSION FROM MANURE AMENDED SILTY CLAY SOIL[2]

4.1. Abstract

Soil temperature plays an important role in organic matter decomposition, thus likely to affect ammonia and gaseous emission from land application of manure. An incubation experiment was conducted to quantify ammonia and greenhouse gas (GHG) (N_2O, CO_2 and CH_4) emissions from manure and urea applied at 215 kg N ha^{-1} to Fargo-Ryan silty clay soil. Soil (250 g) amended with solid beef manure (SM), straw-bedded solid beef manure (BM), urea only (UO), and control (CT) were incubated at 5, 10, 15, and 25 °C for 31 days at constant 60% water holding capacity (WHC). The cumulative GHGs and NH_3 emission generally increased with temperature and highest emission observed at 25 °C. Across temperature levels, 0.11–1.3% and 0.1–0.7% of the total N was lost as N_2O and NH_3, respectively. Cumulative CO_2 emission from manure was higher than UO and CT at all temperatures ($P < 0.05$). Methane accounted for <0.1% of the total C ($CO_2 + CH_4$) emission across temperatures. The Q_{10} values (temperature sensitivity coefficient) derived from Arrhenius and exponential models ranged 1.5–3.7 for N_2O, 1.4–6.4 for CO_2, 1.6–5.8 for CH_4, and 1.4–5.0 for NH_3. Our results demonstrated that temperature significantly influences NH_3 and GHG emissions irrespective of soil amendment but the [2]magnitude of emission varied with soil nutrient availability and substrate quality. Overall, the highest temperature resulted in the highest emission of NH_3 and GHGs.

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[2] The material in this chapter was co-authored by Suresh Niraula, Shafiqur Rahman, and Amitava Chatterjee. Suresh Niraula had primary responsibility for the collection and analyses of samples, and was the primary developer of the conclusions that are advanced here. Shafiqur Rahman and Amitava Chatterjee served as proofreader and checked the math in the statistical analysis conducted by Suresh Niraula. This chapter has been published in the Acta Agriculturae Scandinavica, Section B - Soil & Plant Science online [April 05, 2018], Available online: https://doi.org/10.1080/09064710.2018.1459822

4.2. Introduction

It has been estimated that more than 13% of the global anthropogenic GHGs are associated with direct soil-derived GHGs from agricultural inputs (Lal 2004; Zhao et al. 2016). In addition to GHG emissions, NH_3 volatilization losses from soil contribute to acidification and eutrophication of ecosystems on its deposition and can adversely affect human health (Aneja et al. 2008). Soil temperature and its interaction with agricultural management practices such as addition of commercial (*e.g.,* urea) and organic (*e.g.,* livestock manure) N fertilizers, and soil characteristics [moisture, texture, cation exchange capacity (CEC), organic matter (OM), C:N etc.] have been reported to induce gaseous production from soils (Chadwick et al. 2011; Ren et al. 2017).

Organic matter decomposition has often been overlooked and considered as quantitatively negligible during winter period when soil temperature is close to or below 0°C (Chantigny et al. 2001). Nevertheless, significant levels of microbial activity have been reported in soils in a colder environment (Dorland & Beauchamp 1991; Singurindy et al. 2009). Dorland and Beauchamp (1991) further showed that denitrifiers could function at -2 °C in an unfrozen soil. Carbon and N dynamics are closely linked to decomposition of animal manure and that the significance and extent of decomposition across variable temperature ranges are still poorly understood (Petersen et al. 2013). Kirschbaum (1995) suggested that a 1°C increase in temperature could ultimately lead to a loss of over 10% of soil organic C in regions of the world with an annual mean temperature of 5°C whereas the same temperature increase would lead to a loss of only 3% of soil organic C for a soil at 30°C. These findings further highlight the temperature effects on soil respiration, N decomposition, nitrification and denitrification, and the subsequent production of CO_2 and N_2O.

The temperature sensitivity (Q_{10}) is a factor by which the rate of decomposition increases with a 10 °C rise in temperature and it has been widely used to depict the responses of soil gaseous emission rate to temperature changes (Davidson et al. 2006; Zhao et al. 2016). Since Q_{10} values of various agrosystems are not yet known, a default value of 2.0 has been used in exponential functions to simulate the effect of changing the temperature on gaseous emission rate (Li et al. 2015). A large variation in Q_{10} values of N_2O (2.01–3.48) (Li et al. 2013), CO_2 (1.9–18.2) (Chen et al. 2010), and CH_4 (1.3–28) (Van Hulzen et al. 1999) are reported in literature, suggesting apparent uncertainty of Q_{10} estimation. Attention has shifted to exponential and Arrhenius models to determine Q_{10} (Lloyd & Taylor 1994; Davidson et al. 2006), especially with laboratory incubation data. Furthermore, with Arrhenius equation, the decomposition rate and the temperature response of reactions are determined as activation energy (E_a), the minimum amount of energy required for the reaction to occur (Lloyd & Taylor 1994). The soil respiration rate increases with increases in temperature. However, the kinetic theory says that Q_{10} will be higher in soil organic matter that are resistant to decomposition (*e.g.,* cellulose), than those decompose easily (*e.g.,* glucose). In this study, we applied exponential and Arrhenius models to investigate gaseous emissions (N_2O, CO_2, CH_4, and NH_3), Q_{10}, and E_a from Fargo-clay soil of the RRV under incubation condition at four temperature levels.

Fargo Clay soils of North Dakota are productive soils with high organic matter content and undergoes cycles of cold winters to warm summers annually. Much of the attention in the Red River Valley (RRV) region has been given to the N_2O emissions from N-fertilizer application during the growing season (Asgedom et al. 2014; Thapa et al. 2015). However, the overall effect of manure as a source of organic-N on emissions of N_2O, CO_2, and CH_4 needs to be quantified to understand the overall GHG emissions from agrosystems in the region. In terms of manure management, recently, North Dakota beef cattle number increased by 6% from 2016 to 2017 (USDA 2017) and with this increase in beef cattle, the need for better manure management is essential. There is also limited information on the application of bedded manure to soils with high clay content. Use of manure bedding can influence the nutrient availability of solid manure given the range of bedding types, application and incorporation timing, and climatic factors (Petersen et al. 2007). In addition, the influence of temperature on gaseous emission from soils amended with N-fertilizers may vary with variations in climate and management practices (Bowden et al. 1998; Jenkins & Adams 2010). Our 2-year field studies showed the range of soil temperature between 5.5-32 ºC across fall and corn growing seasons that significantly influenced the variations on gaseous emissions.

Because climatic condition varies with agro-ecosystem, we conducted a lab incubation study on Fargo-clay soils of the RRV amended with urea and solid manure (with and without bedding) as N-fertilizer source. The objectives of this study were to (1) assess the effects of temperature variations (5, 10, 15, and 25°C) on N_2O, CO_2, CH_4, and NH_3 emissions from urea and manure amended soils and (2) investigate temperature sensitivity (Q_{10}) models using exponential and Arrhenius models.

4.3. Materials and Methods

4.3.1. Soil and Manure Preparation

Five composite samples of surface soil (0-15 cm) from different areas within the field were collected from the North Dakota State University (NDSU) research farm (46° 55' 15" N, 96° 51' 31" W) located in Fargo, North Dakota, USA. The soil is classified as Fargo-Ryan silty clay (fine, smectitic, frigid Typic Epiaquerts) with 0 to 1 percent slope (Soil Survey Staff 2016). Soils were then air-dried, ground down to pass a 2-mm sieve, and analyzed for their physical and chemical properties (Table 18). Soil pH and electrical conductivity (EC) were determined electrometrically in 1:2.5 soil/water extract (Thomas 1996) using Accumet AB pH meter (Fisher Scientific, Hampton, NH); soil texture (3.7% sand, 44.3% silt, and 52.1% clay) by hydrometer method (Elliott et al. 1999); soil organic matter (OM) by loss on ignition method (Combs & Nathan 1988); CEC by sodium acetate method (Chapman 1965); soil NO_3^--N and NH_4^+-N concentration by KCL extract method (Maynard et al. 2008); soil water holding capacity (WHC) was determined following the procedure of Bowden et al. (1998); and total carbon and nitrogen results were obtained from the NDSU Soil Testing Laboratory, Fargo, North Dakota.

Table 18: Physical and chemical properties of soil (0-15 cm) and manure used in the study.

Properties	Soil	Solid manure	Bedded manure
pH	8.1	8.3	8.7
EC (dSm^{-1})	0.82	5.9	4.8
NO_3-N (mg kg^{-1})	11.2		
NH_4-N (mg kg^{-1})	2.2	873.3	703.3
Sand (%)	3.6		
Silt (%)	43.8		
Clay (%)	52.6		
CEC (cmol$_c$ kg^{-1})	41.1		
OM (%)	6.3	25.8	23.2
Total C (%)	3.3	18.7	28.2
Total N (%)	0.28	1.1	0.72
C:N	11.8	17	39.2
Dry matter (%)		54	38
Bulk density (g cm^{-3})	1.1		

Manure used in this study consisted of solid beef manure (SM) and solid beef manure with wheat straw bedding (BM). Representative samples of SM and BM were collected from the manure stockpile at the NDSU Beef Cattle Research Complex in Fargo, ND. Manures were then air-dried, ground down to pass a 2-mm sieve, and analyzed for their physical and chemical properties (Table 18). Manure pH, EC, NH_4-N, total C, and total N were determined using the same procedure used to determine soil properties. Additionally, the NDSU Soil Testing Laboratory, Fargo, North Dakota, determined manure dry matter content (% DM) for this study.

4.3.2. Experimental Set-up

Emissions of N_2O, CO_2, CH_4, and NH_3 from manure N-sources as well as untreated urea (460 g N kg^{-1}) applied to Fargo silty clay soils were studied under controlled laboratory conditions. A set of 64 1-L clear glass canning jars (area=46.6 cm^2), each filled with 250 g of sieved soil were used to monitor gaseous emissions following the procedure described by Mukome et al. (2013) and Awale and Chatterjee (2017). Each of the canning jar lids were fitted with gas sampling port (butyl rubber septum) on the top surface. The bottom surface of each jar lids were attached to a metal wire and modified as a 50-mL cup-holder to capture NH_3 emission (discussed later).

The canning jars were placed in polystyrene boxes (to reduce temperature fluctuation) and 16 of the total 64 jars were then placed in each of four incubators set at 5, 10, 15, and 25 °C (±0.2 °C) and allowed to equilibrate and reactivate soil microorganisms for one week (Harrison-Kirk et al. 2013). Soil moisture inside each jar was maintained at 40% WHC during pre-incubation period. After one week of pre-incubation, 16 jars placed inside each incubator were assigned to four treatments and four replications. The four treatments used in this study included: (1) solid beef manure (SM), (2) solid beef manure with wheat straw bedding (BM), (3) urea only (UO), and (4) control (CT) with only the soil. The treatment assigned jars, except CT, were then amended by uniformly broadcasting 23 g of SM, 26 g of BM, and 218 mg of UO (equivalent to

215 kg N ha^{-1}) and incorporated immediately using a glass rod stirrer. The N application rates were determined based on the typical N application rate for a corn (*Zea mays* L.) as recommended for the Eastern North Dakota. The soil inside the jars was compacted to the height of 4.9 cm to achieve the field bulk density (determined by gravimetric method) of 1.1 g cm^{-3}. The WHC of the soil was maintained at 60% by uniformly adding additional water to achieve 117 mL of deionized water over the soil surface inside each jar. A set of 16 jars were then placed inside the respective incubators set at 5, 10, 15, and 25 °C and were removed for gas sample collection on days 1, 2, 3, 4, 7, 10, 14, 17, 21, 24, 28, and 31 after treatment additions. For rest of the 31-day incubation period, the soil moisture inside each jar was maintained to 60% WHC by weighing each jar on sampling days and adding deionized water as a fine spray to replace the lost weight, if needed.

4.3.3. Gas Sampling and Analysis

On each sampling day, the headspace air inside each jar was mixed by pumping a polypropylene syringe three times, and finally, a 30-mL headspace air sample was collected for N_2O, CO_2, and CH_4 analysis. Headspace air samples were collected by inserting gas tight Luer lock syringe into the jar through lid septum, and immediately transferring it into a pre-evacuated 20-mL gas serum vials. Prior to sampling, gas serum vials were over-pressurized to eliminate air diffusion into them and to facilitate the subsequent removal of gas samples for analysis.

The gas samples were analyzed for N_2O, CO_2, and CH_4 within 24 h of their collection using gas chromatograph (GC) (Model No. 8610C, SRI Instruments, Torrance, CA) paired with a 10-vial Autosampler (SRI part# 8690-0047, SRI Instruments, Torrance, CA). The GC oven was operated at 60 °C and was fitted with electron capture detector (ECD) for N_2O and flame ionization detector (FID) for CO_2 and CH_4 detection. The ECD and the FID were operated at 350

°C and 300 °C, respectively, and N_2 carrier gas was supplied at 20 PSI for the ECD whereas air and H_2 were supplied to FID/methanizer at 20 PSI. Compound peaks were recorded and analyzed with PeakSimple Chromatography Data System Software (Ver. 3.72; SRI Instruments, Torrance, CA, USA). A detailed description of the GHG measurement using SRI Instruments GC is described by Borhan et al. (2011). In addition, before each measurement, analytical gas standards (0, 1, 5, 50, 100, 500, and 1000 ppm for N_2O; 0, 500, 1000, 3000, 5000 ppm for CO_2; and 0, 4, 10, 30, 100 ppm for CH_4; Scotty Specialty Gases) were included to construct standard calibration curve. The gas concentrations were then analyzed following the procedure outlined by Mukome et al. (2013) and Awale and Chatterjee (2017). Briefly, the concentrations of N_2O, CO_2, and CH_4 were converted into mass units assuming ideal gas relations and expressed as micrograms N_2O-N, milligrams CO_2-C, and micrograms CH_4-C produced between sampling dates per kilogram of soil, respectively. Cumulative µg N_2O-N, mg CO_2-C, or µg CH_4-C emission per kg^{-1} soil was calculated by adding the gas emissions during each sampling period. Daily and cumulative emissions were calculated as N_2O-N, CO_2-C, and CH_4-C, however for simplicity flux is herein referred to as N_2O, CO_2, and CH_4, respectively.

Ammonia (NH_3) volatilization losses were measured immediately following the gas sampling using phosphoric acid (H_3PO_4) traps that were placed inside the headspace of the screw-top canning jars (Khan et al. 2001). Briefly, after treatment application, 50 mL clear plastic cup containing 15 mL of 0.5 M H_3PO_4 were placed in the cup-holder attached to the lid and the lid was then placed in the jar. After removal of NH_3 traps or after gas sampling the jars were kept open for ~1 h for aeration. The collected traps were extracted with 50 mL of 2 M KCL solution and jars were replaced with freshly prepared 15 mL H_3PO_4 solution to facilitate NH_3 trapping until the next sampling day. The extracts were then analyzed for NH_3 concentrations using an Automated Timberline TL2800 Ammonia Analyzer (Timberline Instruments, Boulder, CO). Daily NH_3 volatilization loss (μg NH_3–N kg^{-1} moist soil d^{-1}) were calculated by dividing the NH_3-N emitted between the sampling dates by the elapsed time. In addition, NH_3 volatilization losses during each sampling periods were summed to obtain the cumulative NH_3-N losses (μg NH_3–N kg^{-1}) during entire 31-day incubation.

The emission factor (%EF), percent of N emitted as N_2O-N or NH_3-N from the applied N treatments was calculated using the following equation:

$$\%EF = \frac{C_{fert} - C_{control}}{N_{applied}} \times 100$$

where C_{fert} and $C_{control}$ are the cumulative N_2O or NH_3 emissions from fertilized N treatments and control, respectively (Gagnon et al. 2011).

4.3.4. Statistical Analysis

A completely randomized design (CRD) in a split-plot arrangement with four replications was used in this study. The four temperature regime (5, 10, 15, and 25 °C) were the whole-plot treatments and the four N fertilizers (SM, BM, UO, and CT) were subplot treatments. The effects of soil temperature and N-fertilizers on daily and cumulative N_2O, CO_2, CH_4, and NH_3 emission were analyzed using the PROC MIXED procedure of SAS (SAS Institute 2014). Soil temperature and N-fertilizer were considered fixed effects, and replication and interaction with replication were considered random effects. Residuals were evaluated for homogeneity of variance and normality using the UNIVARIATE procedure of SAS. Analysis of variance with a test of Tukey-Kramer Method at $p\text{-value} \leq 0.05$ was used to determine the significant differences of means within and across temperature levels.

Regression analysis was conducted by fitting both, an exponential (ln soil flux vs. T) and Arrhenius functions (ln soil flux v. $1/T$) (Jenkins & Adams 2010). Equations are shown below for soil flux measures over four temperature levels.

$$\text{Exponential:} \quad F = ae^{bT}$$

Where F is the soil flux rate (µg N_2O-N kg^{-1} soil, mg CO_2-C kg^{-1} soil, µg CH_4-C kg^{-1} soil, and µg NH_3-N kg^{-1} soil), a and b are the rate constants, and T is the temperature in Kelvin (K).

$$\text{Arrhenius:} \qquad F = Ae^{-Ea/RT}$$

Where A is a constant, E_a is the activation energy of the process (kJ mol^{-1}), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the temperature in Kelvin (K). To determine E_a, natural logarithm (ln) of soil flux was plotted against $1/T$ to generate a slope ($-E_a/R$). The parameter E_a in the Arrhenius equation is directly related to the temperature sensitivity (Q_{10}) variation.

The Q_{10} was then calculated from the derived parameter for both exponential and modified Arrhenius function accordingly:

$$\text{Exponential:} \qquad Q_{10} = e^{10b}$$
$$\text{Arrhenius:} \qquad Q_{10} = e^{10Ea/RT(T+10)}$$

All fitted regressions were highly significant ($P<0.05$) and the r^2 values indicate the strong fit of both Arrhenius (r^2 =0.89–0.95) or exponential functions (r^2 =0.90–0.96).

4.4. Results and Discussion

4.4.1. Temperature effect on N_2O emissions

This study was focused on direct effects of variable temperature on soil N_2O emission in presence of either organic or inorganic N fertilizer. The daily mean N_2O emissions at 5, 10, 15, and 25 °C ranged from 1 to 76, 1 to 146, 1 to 217, and 1 to 704 μg N_2O-N kg^{-1} d^{-1}, respectively, with the highest daily emission from urea only (UO) amended soil at all temperature regimes. The analysis of treatment×day showed significant differences in N-treatments at all temperature levels for the first 6 days of incubation ($P<0.05$). Fluxes of N_2O during 1st day after soil application were up to 6-folds higher for the manured soil than for urea applied soil, across temperature gradient (Figure 21). Thereafter, fluxes from manured soils gradually decreased for rest of the incubation period. The sharp peak on 1st day is likely due to enhanced denitrification of soil NO_3^- by the addition of easily degradable organic substrates. Velthof et al. (2003) also reported a peak in N_2O emission on the first days after manure application. Moreover, volatile fatty acids from the manure are metabolized within a few days by soil bacteria, increasing denitrification and/or immobilization of N (Kirchmann & Lundvall 1993). In addition, the amount of manure applied to soil was over 100 times the amount of urea that was applied to the soil that likely created anaerobic microsites. It would also explain the relatively slow start of N_2O emission from urea.

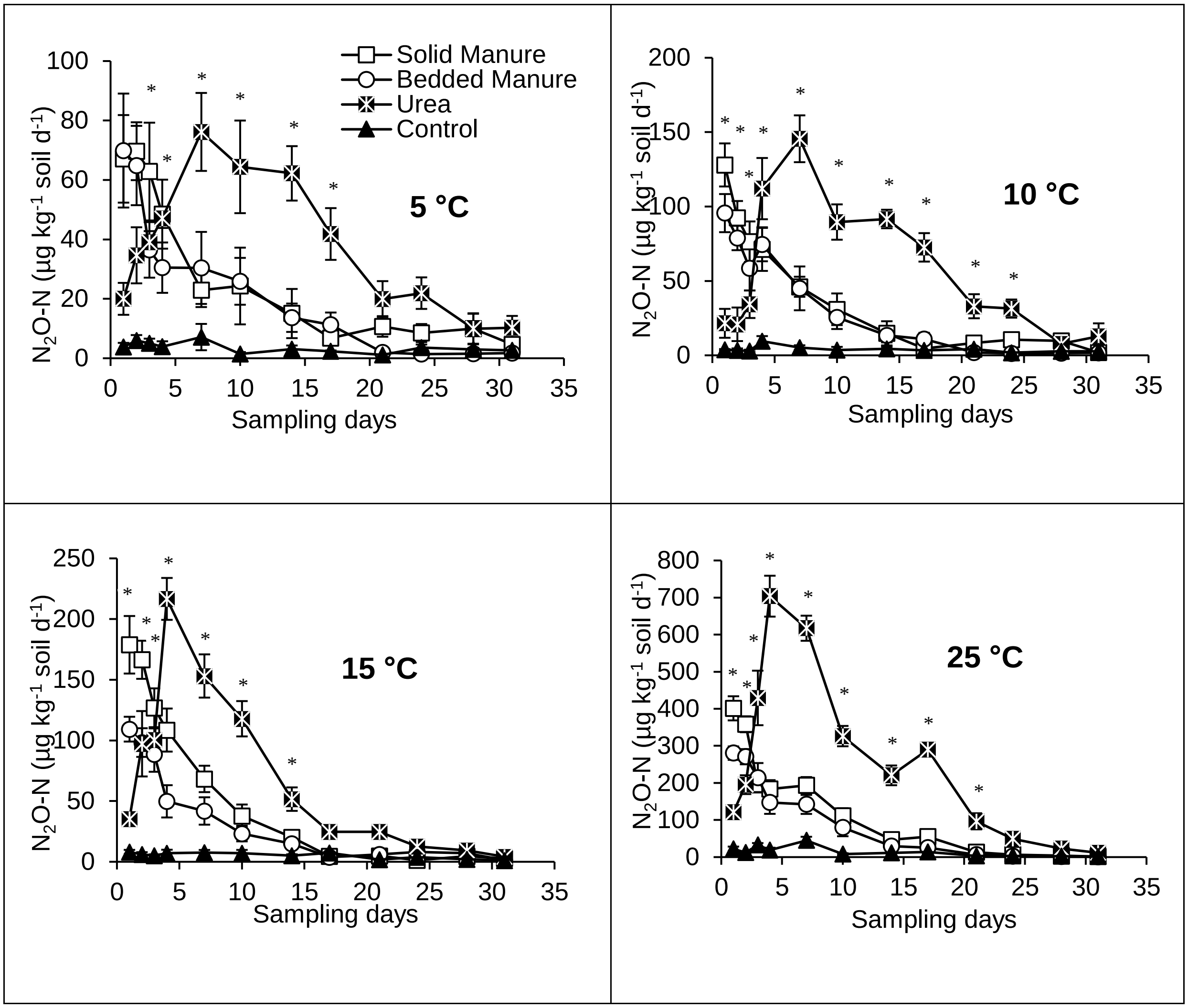

Figure 21: Daily soil N_2O fluxes after N fertilizers [SM (solid beef manure), straw-bedded solid beef manure (BM), urea only (UO), and control (CT)] application on silty clay soils at 5, 10, 15, and 25 °C incubation temperatures. Vertical bars are standard errors (n=4). *Indicates any significant ($P \leq 0.05$) differences between treatments at the day. Please note the large differences in y-axis scaling.

Contrary to the N_2O emission trend of manured soil, urea applied soils gradually increased to its peak level on day-7 for soils at 5 and 10 °C and on day-4 for soils at 15 and 25 °C (Figure 21). Of the total incubation time, the daily emission from urea-applied soils were higher for 58-83% of the time points compared to manured soils. A large portion of manure N in our study was in the organic form (Table 18) and organic-N requires mineralization followed by nitrification to form manure derived NO_3^- pool for denitrification (Chadwick et al. 2011).

Previous studies (Macleant & McRae 1987; Halvin et al. 2013) predicted the hydrolysis of urea in the range of 83-90% whereas organic substance mineralization rates are reported in the range of 16-53% (Hernandez-Ramirez et al. 2009). In this study, rapid hydrolysis of urea to NH_4^+ most likely influenced the higher N_2O emission across all temperature regimes with emission in the decreasing order of 25 >15> 10 > 5°C. In addition, manure induced NH_3 volatilization loss following the incorporation most likely reduced the pool of N available for N_2O emission.

The cumulative soil N_2O emission and the N_2O emission factors within and across all four temperature regimes and treatments are summarized in Table 19 and Table 20, respectively. Compared to CT, cumulative N_2O emissions from the SM, BM, and UO applied soils during the entire incubation period were significantly higher (all $P < 0.05$; Table 19, Figure 22) by up to 17 fold. Low availability of N substrate in control soil compared to fertilized soils most likely influenced N_2O emissions differently.

Table 19: Cumulative GHGs (N_2O, CO_2 and CH_4) emission and NH_3 volatilization loss from N fertilizers over 31 days of incubation at 5, 10, 15, and 25 °C.

	5 °C	10 °C	15°C	25°C
N fertilizer source	Cumulative N_2O-N (µg N_2O-N kg^{-1} soil)			
Control	43 ± 6 bA[†]	47 ± 5 cA	62 ± 4 cA	174 ± 9 cB
Solid beef manure	351 ± 31 aA	495 ± 23 abAB	725 ± 36 abB	1569 ± 81 aC
Bedded manure	289 ± 49 aA	409 ± 59 bAB	452 ± 20 bB	1199 ± 77 aC
Urea	447 ± 57 aA	673 ± 22 aAB	848 ± 38 aB	3083 ± 97 bC
	Cumulative CO_2-C (mg CO_2-C kg^{-1} soil)			
Control	141 ± 7 bA	206 ± 25 bA	316 ± 19 bB	1189 ± 95 bC
Solid beef manure	278 ± 27 aA	450 ± 30 aB	517 ± 29 aB	3260 ± 118 aC
Bedded manure	238 ± 11 aA	343 ± 9 aAB	462 ± 30 aB	2407 ± 60 aC
Urea	150 ± 15 bA	227 ± 20 bB	347 ± 14 bC	1377 ± 101 bD
	Cumulative CH_4-C (µg CH_4-C kg^{-1} soil)			
Control	1.4 ± 1 aA	2.7 ± 3 aA	5.0 ± 4 bAC	7.8 ± 11 bC
Solid beef manure	4.3 ± 2 aA	10.2 ± 1 aA	22.1 ± 2 aB	52.8 ± 3 aC
Bedded manure	6.5 ± 1 aA	10.7 ± 1 aA	27.2 ± 2 aB	61.5 ± 6 aC
Urea	2.2 ± 0 aA	3.2 ± 1aA	6.8 ± 2 bAC	11.1 ± 4 bC
	Cumulative NH_3-N (µg NH_3-N kg^{-1} soil)			
Control	92 ± 18 cA	100 ± 2 cA	224 ± 1 cB	498 ± 6 cC
Solid beef manure	272 ± 5 aB	319 ± 1 aAB	461 ± 16 aA	1039± 108 aC
Bedded manure	254 ± 5 aB	340 ± 20 aAB	442 ± 6 aA	977 ± 61 aC
Urea	397 ± 31 bA	494 ± 36 bA	1309 ± 123 bB	2193 ± 122 bC

[†] Values are means ± standard errors (n=4). Different lowercase letters within a column and different uppercase letters across a row indicate significant differences at 0.05 significance level.

Table 20: Emission factors (%) of N_2O and NH_3 from N fertilizers estimated from the cumulative emission of 31 days of incubation at 5, 10, 15, and 25 °C.

	5°C	10°C	15°C	25°C
N fertilizer source	N_2O Emission factor (EF, %)			
Solid beef manure	0.14	0.2	0.29	0.62
Bedded manure	0.11	0.16	0.17	0.46
Urea	0.18	0.28	0.35	1.29
	NH_3 Emission factor (EF, %)			
Solid beef manure	0.09	0.09	0.10	0.23
Bedded manure	0.07	0.10	0.09	0.20
Urea	0.13	0.17	0.46	0.69

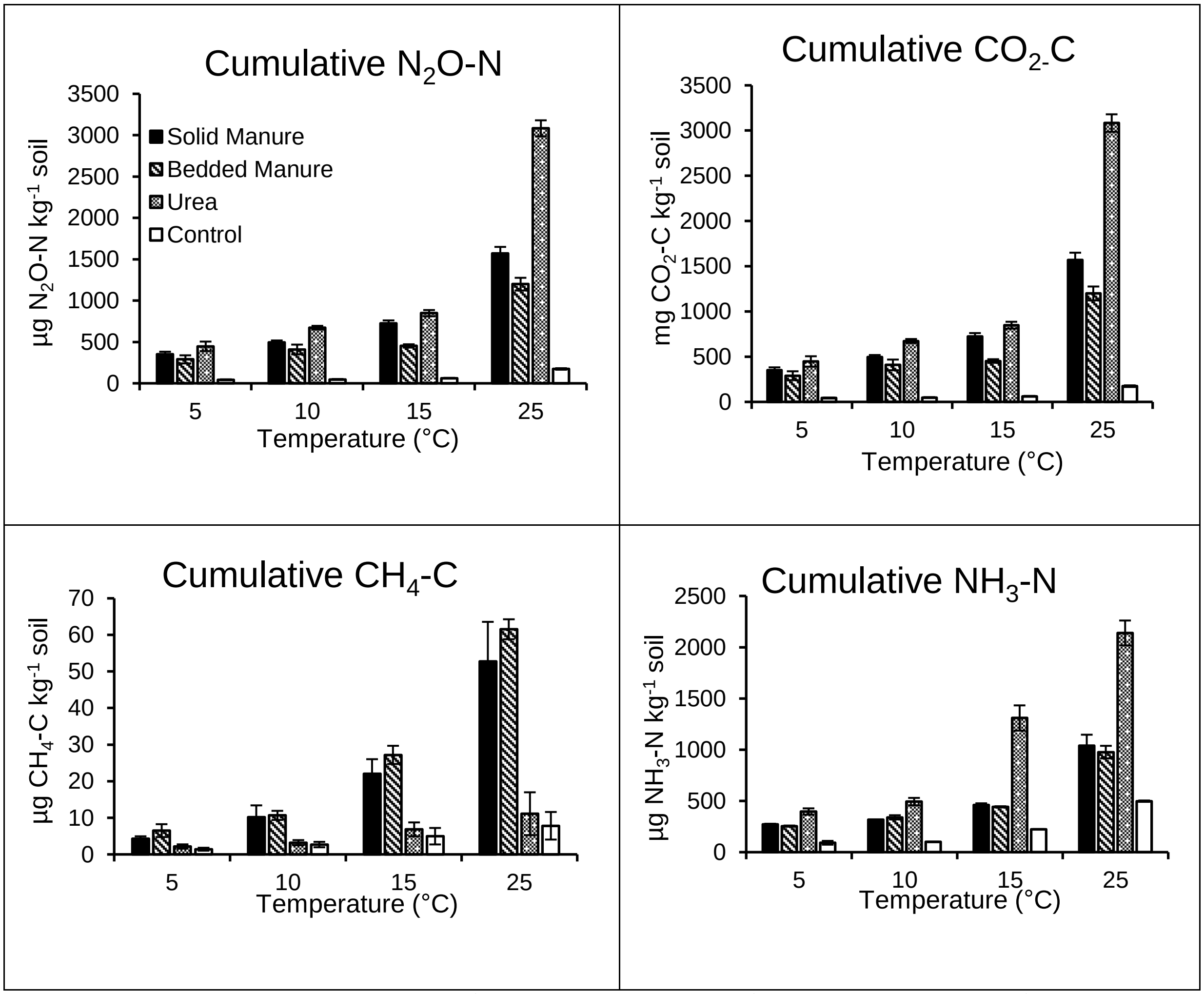

Figure 22: Cumulative N_2O-N (µg kg^{-1} soil), CO_2-C (mg kg^{-1} soil), CH_4-C (µg kg^{-1} soil), and NH_3-N (µg kg^{-1} soil) emission measured from 31-day incubation from soil amended with N fertilizers [SM (solid beef manure), straw-bedded solid beef manure (BM), urea only (UO), and control (CT)] at 5, 10, 15 and 25 °C incubation temperatures. Vertical bars are standard errors (n=4).

No difference in the total N_2O emission was observed between the three N-treated soils at 5 °C ($P>0.05$). A significant difference in cumulative N_2O emission from all soil was observed only at 25 °C where the highest emissions were observed for all treatments under study (Figure 22, Table 19). High temperature in moist soil can cause an increase in microbial activity increasing the activity of denitrifiers in soil. This was most likely the reason for the higher concentration of N_2O at 25 °C. Chantigny et al. (2001) reported similar result where maximum N_2O accumulations occurred when O_2 content fell below 6%, whereas the time of complete N_2O disappearance in the jars corresponded fairly well with the time of NO_3^- depletion.

When comparing manure-types, no significant differences were found on cumulative N_2O emission from SM and BM treated soils at all temperature regime. The presence of high and readily available NH_4-N in UO compared to manure may have favoured higher nitrification in UO amended soil thus producing higher NO_3^-, a source for denitrification. Moreover, soils were at 60% WHC and both nitrification and denitrification can occur simultaneously at ~60% WHC (Linn & Doran 1984; Uchida et al. 2013). Urea treated soil had significantly higher N_2O emission than BM at $T \geq 10$ °C by a factor of 1.5-2.6 across temperature regime while it was significantly higher than SM only at 25 °C. Because urease is an extracellular enzyme produced by microorganisms, high temperatures can increase microbial growth and urease production. Moyo et al. (1989) found that increasing temperature from 5 to 45 °C greatly increased urease activity. Furthermore, lower cumulative N_2O emission from manure amended soil compared to UO can be attributed to the higher C:N ratio in SM and BM, which may have promoted N immobilization and/or slow mineralization. The cumulative N_2O emission were negatively correlated with the C:N ratio in organic amendments in other studies (Baggs et al. 2000; Huang et al. 2004) as well. Thus, it can be concluded that at ~ 60% WHC levels, soil temperature was the main factor determining the N_2O emission from the N-treated soils and its effects are manifested with the increasing temperature regimes.

The values of EFs of N_2O were in the range of 0.11–1.29% (Table 20). Our results indicated that the EF values are proportional to the increase in temperature, with the highest value of 1.29% from UO applied soil at 25 °C. The low loss of fertilizer N (EF = 0.11-0.16) were expectedly observed at low temperatures (5-10 °C). Across all temperature regime, EF followed the decreasing trend of UO>SM>BM. The obtained values from our study agree with the annual EF values of the agricultural soils (0.1-7.3%) (Bouwman 1996; Dobbie & Smith 2003).

The relationship between soil N_2O emission and temperature were approximated by both Arrhenius and exponential functions (Table 21). Temperature response of N_2O production fitted to an Arrhenius function in the range 5-25 °C generated apparent activation energies (E_a) between 49.5 to 66.7 kJ mol^{-1} (Table 21). This value corresponds to a Q_{10} of ~2, which indicates that the reaction rates doubled for every 10 °C rise in temperature. Our temperature response for the 5-25 °C range are similar to those observed by others; the activation energy of NO_3^- disappearance by denitrification has been estimated to be 28-76 kJ mol^{-1} in a temperate soil (Holtan-Hartwig et al. 2002) to 47-89 kJ mol^{-1} for riparian soils (Maag et al. 1997). The reaction rate of the higher activation energy in treatments increased faster while undergoing the same extent of temperature rise. The Q_{10} derived from both Arrhenius and exponential equations were in the range of 1.94 to 2.74 (Table 22). Arrhenius model showed a slight decrease in Q_{10} with increasing temperature [calculated using Arrhenius equation (4) at 5, 10, 15, and 25 °C] (Figure 23, Table 22).

Table 21: Fitted parameters describing Arrhenius and two-parameter exponential function for soil GHG emission (N_2O-N, CO_2-C, and CH_4-C) and NH_3 volatilization loss measured over four-temperature regime.

	Arrhenius Equation			Two-parameter Exponential		
	N_2O-N					
Treatments	***A***	***E_a*** (kJ mol^{-1})	***r^2***	***a***	***b***	***r^2***
Control	$e^{25.4}$	50.5	0.89	4.6 x 10^{-7}	0.07	0.9
Solid beef manure	$e^{28.4}$	52.2	0.98	1.7 x 10^{-6}	0.08	0.98
Bedded manure	e^{27}	49.5	0.91	7.8 x 10^{-5}	0.07	0.91
Urea	$e^{34.8}$	66.7	0.95	1.0 x 10^{-8}	0.1	0.96
	CO_2-C					
Control	$e^{36.9}$	74.2	0.96	1.4 x 10^{-10}	0.11	0.97
Solid beef manure	$e^{41.8}$	84.2	0.91	1.4 x 10^{-12}	0.12	0.92
Bedded manure	$e^{39.9}$	80.2	0.93	2.3 x 10^{-12}	0.12	0.94
Urea	$e^{38.3}$	77.4	0.96	2.3 x 10^{-11}	0.11	0.96
	CH_4-C					
Control	$e^{23.2}$	53.0	0.51	1.7 x 10^{-2}	0.08	0.51
Solid beef manure	$e^{40.2}$	90.2	0.84	2.9 x 10^{-13}	0.13	0.83
Bedded manure	$e^{37.7}$	82.9	0.97	6.5 x 10^{-12}	0.12	0.96
Urea	$e^{23.6}$	53.1	0.62	4.2 x 10^{-3}	0.08	0.61
	NH_3-N					
Control	$e^{32.1}$	64.2	0.92	2.2 x 10^{-8}	0.09	0.93
Solid beef manure	$e^{25.8}$	47.1	0.96	2.1 x 10^{-5}	0.07	0.97
Bedded manure	$e^{25.5}$	46.3	0.98	5.7 x 10^{-6}	0.07	0.98
Urea	$e^{32.9}$	62.3	0.92	3.9 x 10^{-8}	0.09	0.92

Regression analysis was conducted using linearized data for both Arrhenius (soil NH_3 vs. $1/T$) and exponential functions (ln soil NH_3 vs. T) for all reported data. All regressions were significant at $P < 0.05$.

Table 22: Temperature dependence of soil GHG emission (N_2O-N, CO_2-C, and CH_4-C) and NH_3 volatilization loss across N fertilizer sources.

N fertilizer source	Arrhenius Equation (Q_{10})[‡]				Two-parameter Exponential Q_{10}
	5°C	10°C	15°C	25°C	
			N_2O-N		
Control	2.15 ± 0.2 aA[†]	2.09 ± 0.1aA	2.04 ± 0.1 aAB	1.95 ± 0.1 aB	2.1 ± 0.1 a
Solid beef manure	2.20 ± 0.1 abA	2.14 ± 0.1 abAB	2.09 ± 0.1 aB	1.99 ± 0.1 aC	2.14 ± 0.1 a
Bedded manure	2.15 ± 0.3 aA	2.09 ± 0.2 aAB	2.04 ± 0.2 aB	1.94 ± 0.2 aC	2.09 ± 0.2 a
Urea	2.74 ± 0.2 bA	2.65 ± 0.2 bB	2.56 ± 0.2 aC	2.4 ± 0.1 aD	2.65 ± 0.2 b
			CO_2-C		
Control	3.1 ± 0.2 aA	2.94 ± 0.2 aB	2.84 ± 0.1 aC	2.65 ± 0.1 aD	2.95 ± 0.1 a
Solid beef manure	3.55 ± 0.1 aA	3.40 ± 0.1 aB	3.26 ± 0.1 aC	3.02 ± 0.1 aB	3.41 ± 0.1 a
Bedded Manure	3.33 ± 0.1 aA	3.20 ± 0.1 aB	3.07 ± 0.1 aC	2.86 ± 0.0 aD	3.21 ± 0.1 a
Urea	3.21 ± 0.2 aA	3.09 ± 0.2 aB	2.97 ± 0.2 aC	2.77 ± 0.2 aD	3.09 ± 0.2 a
			CH_4-C		
Control	2.63 ± 0.8 aA	2.53 ± 0.8 aAB	2.44 ± 0.7 aAB	2.29 ± 0.7 aB	2.52 ± 0.8 a
Solid beef manure	3.97 ± 0.5 aA	3.78 ± 0.5 aAB	3.61 ± 0.4 aB	3.32 ± 0.4 aC	3.77 ± 0.5 a
Bedded manure	3.52 ± 0.4 aA	3.37 ± 0.3 aA	3.23 ± 0.3 aAB	2.99 ± 0.3 aC	3.35 ± 0.3 a
Urea	2.56 ± 0.8 aA	2.46 ± 0.7 aB	2.38 ± 0.7 aC	2.23 ± 0.6 aD	2.44 ± 0.7 a
			NH_3-N		
Control	2.65 ± 0.2 abA	2.56 ± 0.2 bB	2.48 ± 0.2 aC	2.33 ± 0.2 aD	2.56 ± 0.2 b
Solid beef manure	2.03 ± 0.1 aA	1.99 ± 0.1 acAB	1.94 ± 0.1 bB	1.86 ± 0.1 aC	1.99 ± 0.1 a
Bedded manure	2.01 ± 0.1 aA	1.96 ± 0.1 aAB	1.92 ± 0.1 bB	1.84 ± 0.1 aC	1.96 ± 0.1 a
Urea	2.56 ± 0.2 bA	2.48 ± 0.2 bcB	2.41 ± 0.2 abC	2.27 ± 0.2 aD	2.47 ± 0.2 b

[†] Values are means ± standard errors (n=4). Different lowercase letters within a column and different uppercase letters across a row indicate significant differences at 0.05 significance level.

[‡] Q_{10} calculated according to two-parameter exponential and for Arrhenius model.

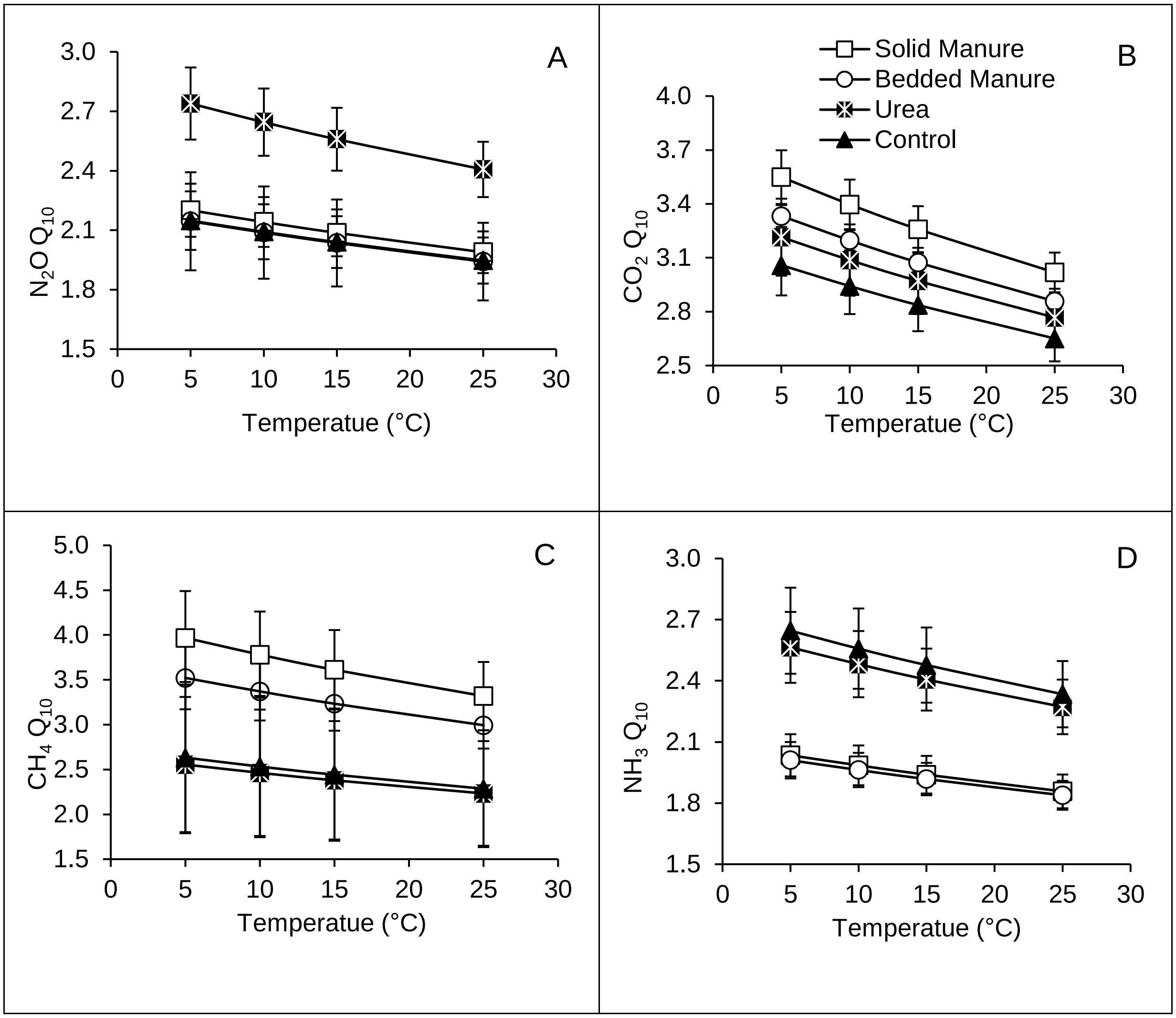

Figure 23: Temperature sensitivity (Q_{10}) calculated using Arrhenius model for (A) N_2O-N, (B) CO_2-C, (C) CH_4-C, and (D) NH_3-N across 5, 10, 15, and 25 °C incubation temperatures for soil amended with solid beef manure (SM), solid beef manure with wheat straw bedding (BM), urea only (UO), and control (CT). Vertical bars are standard errors (n=4).

The Q_{10} for N_2O production not only expressed the temperature effect but rather a combined effect of temperature and the development of anaerobic microsites in the soils under incubation. Our findings further illustrate that temperature regulates the soil denitrification both directly and indirectly, the latter by influencing the availability of O_2, NO_3^-, N_2O and C substrates.

In summary, both organic amendments (SM and BM) and UO appeared to stimulate microbial activity in warm as well as cold soils, indicating that C and N transformations can occur throughout the winter and summer period in soils. Our results suggest that if O_2 diffusion is markedly restricted in cold, NO_3^- might not accumulate during winter months. However, N_2O production can occur even at a temperature close to 5 °C in Fargo-clay soils.

4.4.2. Temperature Effects on CO_2 Emission

In general, rates of respiration increased across a temperature gradient from 5 °C to 25 °C throughout the incubation period (Figure 24). In agreement with previous studies (Brooks et al. 1997; Chantigny et al. 2001), soil respiration occurred at significant rates in our study even at low temperature (5 °C). The daily average CO_2 emission varied from 1.8-79.4, 2.8-104.6, 2.7-133.2, and 11.7-641.8 mg CO_2-C kg^{-1} soil d^{-1} at 5, 10, 15, and 25 °C, respectively. The CO_2 flux rate was large right after manure application, which was most likely due to rapid decomposition of labile and refractory organic carbon in manure. At low temperatures, the CO_2 fluxes have been linked to labile organic carbon because at higher temperature refractory organic carbon are likely to increases (Bais et al. 2006). However, we did not investigate the changes in soil organic matter over time in this study. In our study, 25 °C temperature significantly increased daily average CO_2 flux compared with treatments at temperatures <25 °C (Figure 24). A marked decrease in C mineralization rates was previously reported when amended soils change from aerobic to anaerobic condition (Chantigny et al. 2001). Our results suggest that soils slowly progressed towards anaerobic environment after the initial peak of CO_2 emission. The progressive decrease after the peak CO_2 emission from all soils was observed at all temperature regimes during the incubation, which was likely caused by a gradual shortage of easily available C from the amendments.

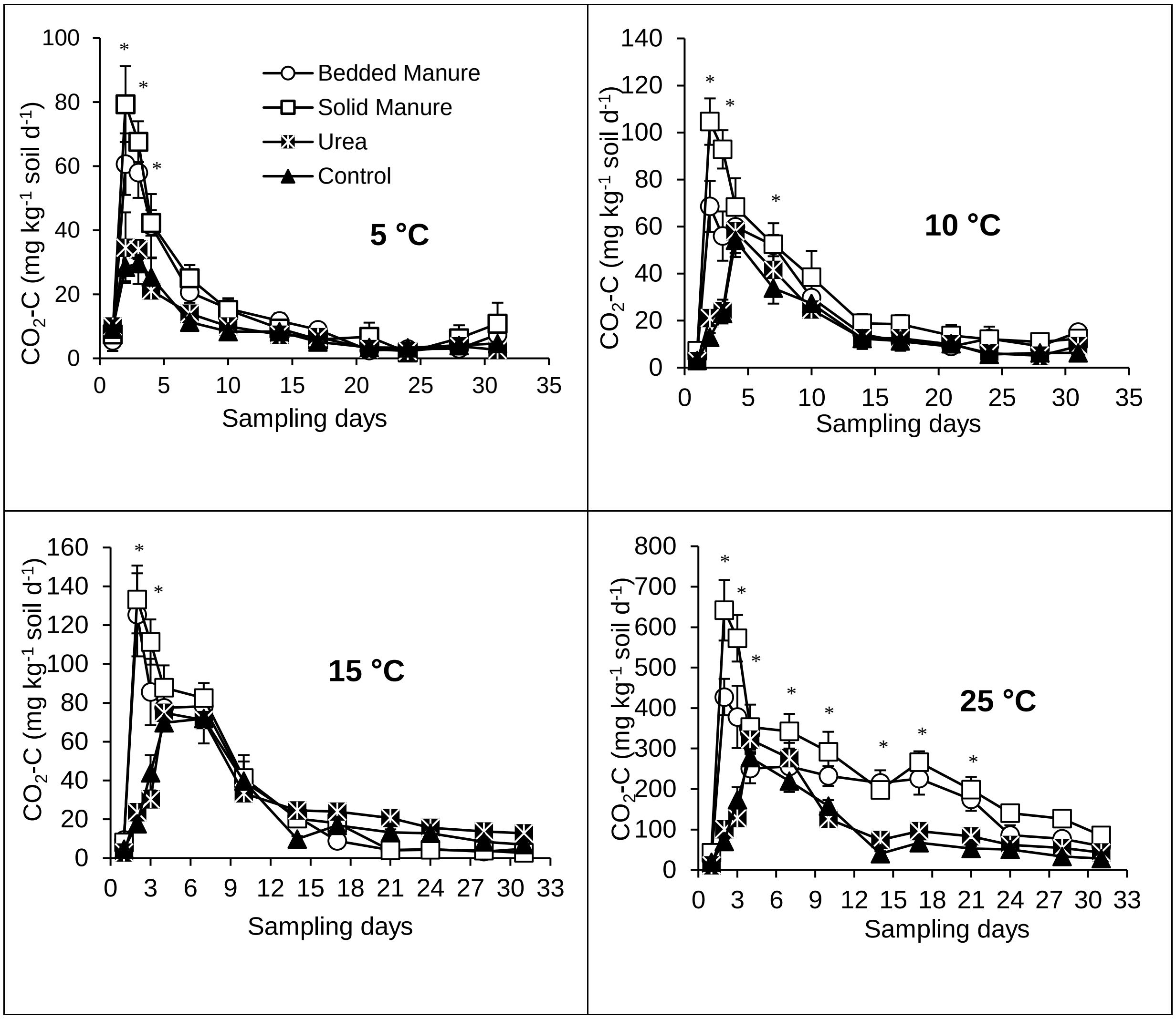

Figure 24: Daily soil CO_2 fluxes after N fertilizers [SM (solid beef manure), straw-bedded solid beef manure (BM), urea only (UO), and control (CT)] application on silty clay soils at 5, 10, 15, and 25 °C incubation temperatures. Vertical bars are standard errors (n=4). *Indicates any significant ($P \leq 0.05$) differences between treatments at the day. Please note the large differences in y-axis scaling.

The cumulative CO_2 emission followed the decreasing trend of 25 >15 >10 >5 °C, with the highest emission from SM followed by the BM treated soil at all temperature levels (Figure 22). Similarly, amendments at 25 °C resulted in significantly greater emissions than amendments at 5, 10, and 15 °C (Figure 22, Table 19). Moreover, cumulative CO_2 emission from SM and BM were significantly higher than that in UO and CT at all temperature regime, whereas there was no difference in the emission comparison between UO and CT only (Table 19). When comparing the manure-type, CO_2 emission from SM treated soil was 16.8, 31.2, 11.9, and 35.4% higher than BM treated soil at 5, 10, 15, and 25 °C, respectively, however no significant differences in cumulative CO_2 emission was observed.

The differences in cumulative CO_2 emission from UO and manure-N sources can be attributed to lower microbial activity in UO treated soil at low C:N ratio. Several studies showed a return of straw or addition of organic manure to soil can result in substantial increases in the soil respiration rate (Ding et al. 2007; Mapanda et al. 2011). Therefore, manure with and without straw bedding may have greatly increased the amount of substrates for soil microorganisms, subsequently increasing SOM decomposition, further aided by the increasing temperature levels. The low CO_2 emission in UO applied soil may also be due to the suppression of the respiration of native soil organic C. Several other possible mechanisms were suggested in literature. First, a decrease in pH caused by nitrification may inhibit microbial activity (Kuzyakov et al. 2000). Second, soil microbial population may have been adversely affected by the increase in solute concentration (DeForest et al. 2004). Third, high N levels in N-abundant soils repressed the synthesis and activity of certain enzymes (Carreiro et al. 2000). Our study showed the response of CO_2 emission to UO is most likely temporary; however, long-term study is suggested to investigate whether there exists differences in soil respiration between UO and CT soil on a long-term basis.

There are still uncertainties associated with modelling the strong temperature dependence of soil respiration. Some researchers (Lloyd & Taylor 1994; Thierron & Laudelout 1996) strongly recommended Arrhenius equation because it gives evenly distributed residual variances across temperature range. Buchmann (2000), however, found that an exponential equation could more accurately explain the observed relationships. In our study, Q_{10} values calculated based on the Arrhenius model (Figure 23) and exponential function ranged between 2.65–3.55 and 2.95–3.41, respectively (Table 22), and within the range of 2.0 to 3.9 generally given for bulk soil respiration (Raich & Schlesinger 1992; Ding et al. 2007). Moreover, our r^2 values from Arrhenius and exponential equations indicate that 92–97% of the variation in soil CO_2 emission under the current incubation conditions can be explained by the change in temperature (Table 21). Arrhenius equation further showed that Q_{10} of CO_2 emission was highest under cold temperatures suggesting temperature increase to have a larger impact on CO_2 emissions in cold areas (e.g. northern latitudes or mountain areas). Overall, this study showed that at 60% WHC level in Fargo-clay soil of the RRV flux-temperature relationships alone can be used to reasonably estimate CO_2 emission. Similarly, our data support the kinetic theory of activation energy and previous findings of low respiration and carbon concentration with increasing Q_{10} (Jenkins & Adams 2010).

The apparent activation energy for respiration (E_a) was at 84, 80, 77, and 74 kJ mol^{-1} in SM, BM, UO, and CT, respectively (Table 21). This suggests that the energy required for SOM decomposition is related to substrate quality and that higher E_a associated with the breakdown of recalcitrant substrates result in a greater Q_{10} at low temperatures. To a certain extent, E_a reflected soil substrate and soil microbial activity, and that higher energy is required to initiate a reaction in complex organic compounds. We found that the difference in the Q_{10} values as a result of the added substrate are not coincidental. Additionally, the significantly higher Q_{10} values for CO_2 than N_2O ($P<0.05$) might indicate that the impacts of global warming on the emission of CO_2 from soils were higher than on the emissions of N_2O in the silty clay soils of the RRV.

4.4.3. Temperature Effects on CH_4 Emissions

Daily variations of soil CH_4 emission and uptake for soils incubated at 5, 10, 15, and 25 °C are presented in Figure 25. During the 31-day soil incubation study, the average CH_4 emission ranged from -0.45 to 1.33, -0.21 to 2.20, -3.39 to 8.16, and -1.85 to 14.83 µg kg^{-1} soil d^{-1} at 5, 10, 15, and 25 °C, respectively, where negative values indicate CH_4 consumption and positive values indicate the net CH_4 emission from the soil under the current incubation condition. Previous studies (Hutsch 2001; Le Mer & Roger 2001) show CH_4 production in the anaerobic zones of submerged soils by methanogens and the oxidation into CO_2 by methanotrophs in the aerobic zones of wetland and upland soils. The significant differences in daily average CH_4 flux were most likely due to higher emission from manure treated soil, most noticeably observed with increasing temperature regime (Figure 25). Organic matter addition is one of the factors that favor CH_4 emission from soils (Le Mer & Roger 2001).

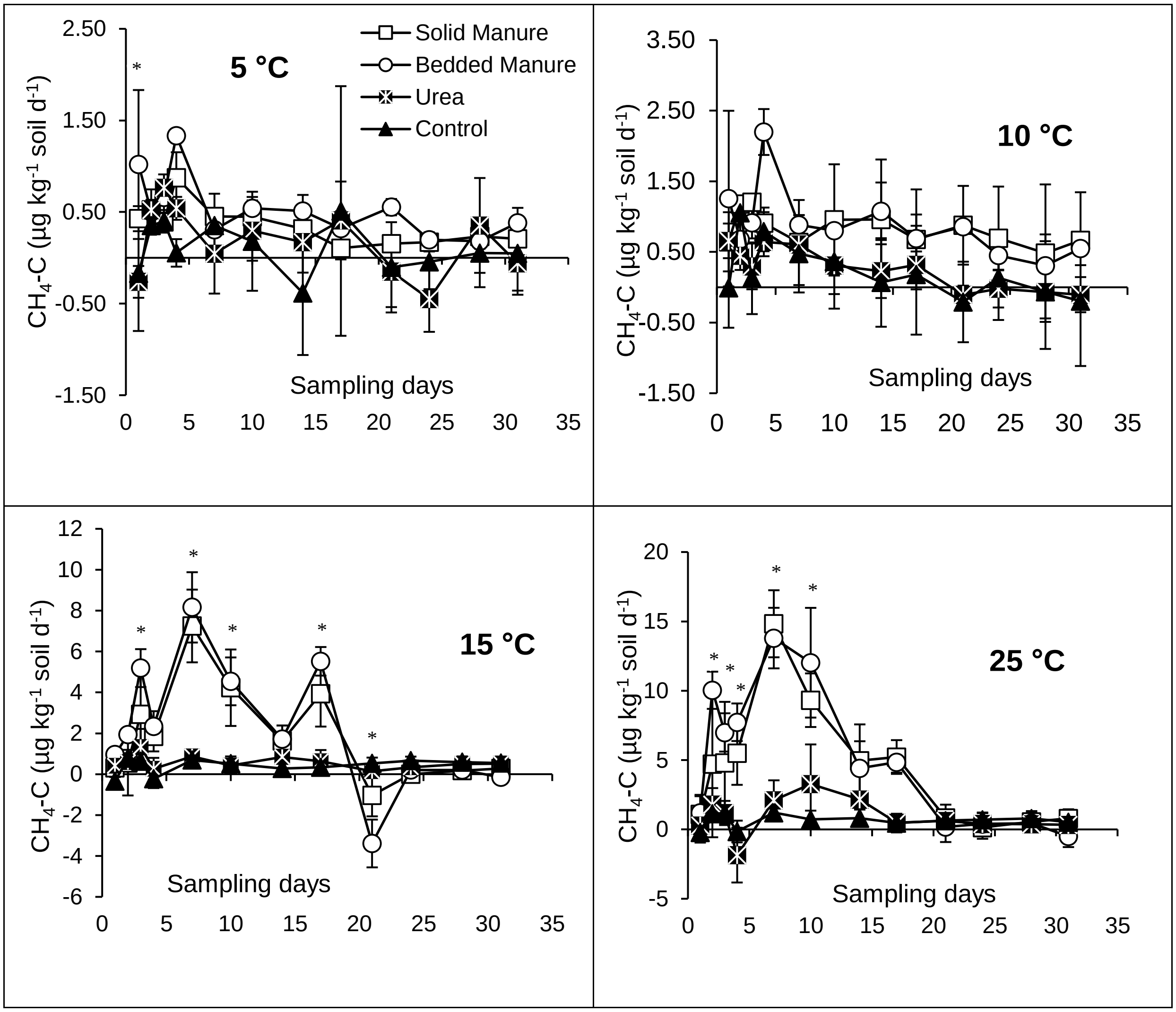

Figure 25: Daily soil CH_4 fluxes after N fertilizers [SM (solid beef manure), straw-bedded solid beef manure (BM), urea only (UO), and control (CT)] application on silty clay soils at 5, 10, 15, and 25 °C incubation temperatures. Vertical bars are standard errors (n=4). *Indicates any significant ($P \leq 0.05$) differences between treatments at the day. Please note the large differences in y-axis scaling.

The cumulative CH_4 emission across temperature regime was in the range of 1.4–61.5 µg CH_4-C kg^{-1}, with highest emission from BM treated soil at 25 °C (Table 19, Figure 22). Moller et al. (2004) also showed an increase in livestock-based CH_4 production from the use of straw bedded manure due to higher volatile solids (VS) content of straw-bedded manure. Combined across all temperature regime, manure treated soil had significantly higher emissions (P<0.05) compared to UO and CT soils. Further analysis of temperature×treatment showed no significant differences in CH_4 emission for treatments at 5 and 10 °C. Similarly, at 15°C, only BM treated soil showed significantly higher emission than CT soils while there were no significant differences between other treatments. The lack of significant differences at $T < 15°C$ even when the cumulative emission from UO and CT were on average 4-folds lower than manure treated soil was probably due to high variability in the CH_4 emission data. The literature on CH_4 emissions from soils as the consequence of CH_4 production, consumption and transport show large spatial variability (Bartlett & Harriss 1993; Van Den Pol-Van Dasselaar et al. 1999). However, at 25 °C, both SM and BM treated soils had greater CH_4 emission compared to UO treated and CT soils (Table 19).

In this study, CH_4 emission was weakly influenced by temperature with CH_4 accounting for less than 0.1% of the total C (CO_2 + CH_4) emission at all temperature regime and for all treatments. The major portion (83%) of the total CH_4 emission came from manure sources suggesting that CH_4 originated primarily from the decomposition of straw and manure rather than SOM sources.

The Q_{10} from Arrhenius equation ranged from 2.2 to 4.0, with highest Q_{10} from SM amended soil at 5 °C (Table 22, Figure 23). The decrease in Q_{10} values (higher Q_{10} at low temperature and vice-versa) from Arrhenius equation have been observed in many other studies (Lloyd & Taylor 1994; Schipper et al. 2014). Kirschbaum (1995) reported the Q_{10} of organic matter decomposition decrease with the increases in temperature (4.5 at 10°C and 2.5 at 20°C). The Q_{10} from two-parameter exponential equation were at 3.8, 3.4, 2.4, and 2.5 for SM, BM, UO, and CT respectively, and within the range of abovementioned studies.

The two parameter exponential functions and E_a calculated are summarized in Table 21. The values of E_a were at 90, 83, 53, and 53 kJ mol^{-1} in SM, BM, UO, and CT, respectively.

Apparent activation energy in this study comprised temperature response of both, CH_4 emitting and CH_4 oxidizing microbial communities present in the surface layers of the soil. Moreover, E_a also comprised the temperature response of the physical transport of CH_4 into the atmosphere. Thus, E_a of CH_4 emission measured the temperature response of the overall reaction suggesting that recalcitrant organic matter might have higher E_a for decomposition. Our initial prediction from this study is that soils of the RRV can be both the source or sink to CH_4 emission across all temperature regimes; however, the interaction of organic matter and factors such as moisture content needs further evaluation.

4.4.4. Temperature Effects on NH_3 Volatilization Loss

Daily NH_3 volatilization loss of N-fertilizer treatments from soils incubated at four different temperature levels are presented in Figure 26. The 31-day average NH_3 emission at 5, 10, 15, and 25 °C ranged from 7.7 to 33.1, 8.4 to 41.1, 18.7 to 109.1, and 41.5 to 178.25 µg NH_3 kg^{-1} soil d^{-1}, respectively, indicating an increase in NH_3 volatilization loss with the increase in temperatures across all treatments. Maximum ammonia loss rates did not develop until 10 days after urea application in 5 and 10°C in all soils, presumably due to delayed urea hydrolysis and lower temperature. A lower urease activity would be expected in soil incubated at 5 °C compared to 25 °C because of the decrease in general biological activity at low temperatures. Temperature effect on NH_3 emission reported by Clay et al. (1990) showed a linear increase in volatilization of NH_3 in soil with an increase in temperature. Soil warming at higher temperature possibly increased the turbulence in the soil surface inside the jar increasing the transport of NH_3 away from the surface and into the headspace inside the incubation jars. Soils in this study were maintained at 60% WHC by adding additional water to balance the lost water through evaporation; however, the drying (evaporation) rate was not measured. Temperature increases the rate of diffusion in the soil water and air, increasing the volatilization from the soil surface as shown in a number of studies (Freney et al. 1983; Harrison & Webb 2001; Halvin et al. 2013).

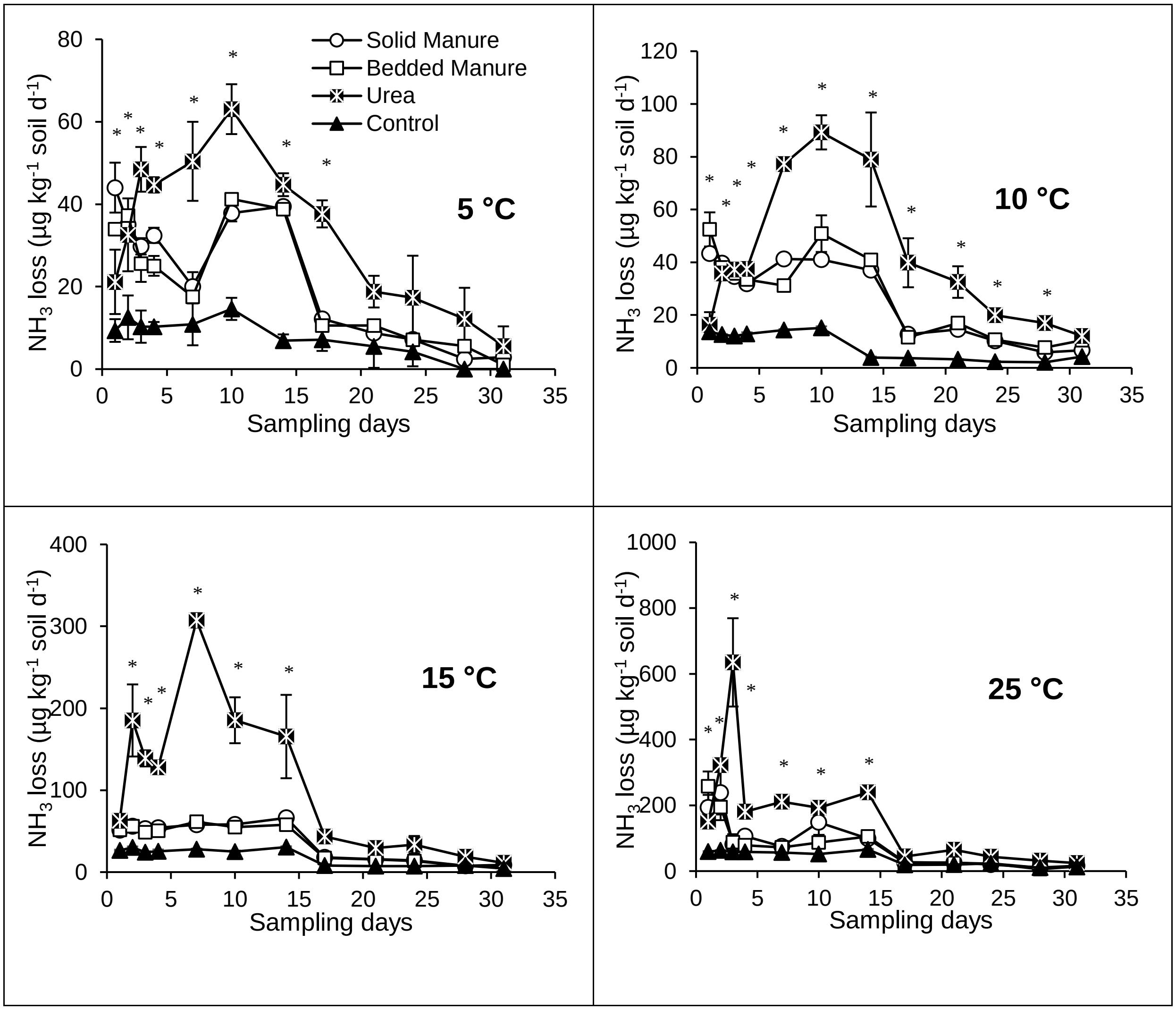

Figure 26: Daily soil NH_3 fluxes after N fertilizers [SM (solid beef manure), straw-bedded solid beef manure (BM), urea only (UO), and control (CT)] application on silty clay soils at 5, 10, 15, and 25 °C incubation temperatures. Vertical bars are standard errors (n=4). *Indicates any significant ($P \leq 0.05$) differences between treatments at the day. Please note the large differences in y-axis scaling.

The cumulative NH_3 volatilization loss ranged from 92 µg NH_3 kg^{-1} in CT soils at 5 °C to 2193 µg NH_3 kg^{-1} in UO amended soil at 25 °C (Table 19, Figure 22). Ammonia volatilization losses were influenced significantly by temperature×N-fertilizer with the highest cumulative NH_3 emission from UO treated soil at all temperature levels. The UO amended soil alone accounted for 39, 39, 54, and 46% of the total NH_3 volatilization loss at 5, 10, 15, and 25 °C, respectively. The increase in urea hydrolysis rate with increasing temperature most likely led to the more rapid formation of NH_4^+, pushing the equilibrium between NH_4^+ and NH_3 towards NH_3. In contrast, Sommer et al. (2004) suggested that volatilization continues for a longer period at low temperature compared to high temperature, consequently, total loss is most related to soil properties and other climatic variables.

When comparing manure-type differences (SM vs BM), NH_3 volatilization loss in SM was 7.1, 6.6, 4.3, and 6.7% higher than BM treated soil within 5, 10, 15, and 25 °C, respectively, however, the difference was not significant (within column, Table 19). Dry matter (DM) content in solid manure vary between 31 and 67% and higher dry matter content in manure are linked to increases the NH_3 volatilization potential of manure (Sommer & Hutchings 2001; Huijsmans et al. 2003). In our study, SM had 41% higher DM compared to BM (Table 18). The equilibrium between NH_4^+ and NH_3 in manure are also regulated by the pH levels, with higher pH (7–10) associated with the increase in the rate of reaction and subsequent formation of NH_3 (Rhoades et al. 2008). Rhoades et al. (2008) also reported an increase in NH_3 volatilization loss from the feedlot surface with increased ambient temperature from spring to summer. In the current study, SM and BM pH levels were at 8.3 and 8.7, respectively, which probably influenced similar emissions.

When comparing individual treatment across temperature levels (*e.g.* SM at 5, 10, 15, and 25°C), effects of temperature were more evident with increased temperature (Table 19, Figure 22). For soils with manure amendments, significantly higher NH_3 volatilization loss was observed only when the temperature difference was $\geq$ 10 °C (5 vs.15°C, 5 vs. 25°C, and 10 vs. 25°C). However, for CT and UO amended soils, only 5 vs 10 °C showed no significant difference in NH_3. These results suggest temperature as a major factor that can increase the rate of N loss through volatilization. High temperature not only increases urease activity and formation of NH_4^+ and OH^- in the soil solution (Lai & Tabatabai 1992) but also increases the conversion of NH_4^+ to NH_3 and the diffusion of NH_3 from aqueous phase to the air phase volatilization (Sander 1999). The influence on NH_3 volatilization loss from soils under variable soil moisture contents have been discussed in previous studies (Liu et al., 2007; Yan et al., 2016), however, it is to be noted that our study shows the effect of temperature at 60% WHC only.

Across N treatments and temperature levels, NH_3 volatilization loss was in the range of 0.1–0.7% of the total applied N with the most loss from UO treated soils at 25 °C (Table 20). Others (Jarecki et al. 2008; Cameron et al. 2013) have reported much higher NH_3 volatilization losses than what we observed. The combined effects of manure and soil properties (silty clay with fine texture, high organic matter and high CEC) most likely reduced the overall cumulative NH_3 volatilization loss from the current study. In addition, N-treatments used in this study were immediately incorporated into soil that likely increased the volume of soil to retain NH_4^+ and reduced the total NH_3 emission. Immediate incorporation of surface-applied N fertilizers have potential to reduce the total NH_3 volatilization loss by 60–90% (Huijsmans et al. 2003; Agnew et al. 2010).

Both, Arrhenius and exponential functions were used to approximate the relationship between soil NH_3 loss and temperature (Table 22). Moreover, Q_{10} of NH_3-N using Arrhenius model across 5, 10, 15, and 25 °C incubation temperatures for soil amendments are presented in Figure 23. All fitted regressions were highly significant ($P<0.05$) and the r^2 values indicate the strong fit of both, Arrhenius or exponential functions (r^2 =0.92–0.98). Temperature response of

NH_3 emission fitted to an Arrhenius function in the range 5-25 °C generated apparent activation energies (E_a) between 47.1 to 64.2 kJ mol^{-1}, suggesting variation in the minimum amount of energy required to ensure that the reaction will occur varies with temperature and N-source (Table 21). The variation in E_a values between different treatments indicate differences in NH_4^+ desorption potential of the N-amended soils and increased urease activity. In our study, the Q_{10} derived from Arrhenius and exponential function was in the range of 1.8 to 3.0 and 1.96 to 2.56, respectively. These results indicate that Q_{10} and E_a could be used as indices for N management for crop production to minimize NH_3 emissions.

4.5. Conclusion

This study examined the greenhouse gas and ammonia emissions response to variable temperature (5, 10, 15, and 25 °C) from soil amended with manure and urea under incubation. Our results demonstrated that cumulative emissions followed the decreasing trend of 25>15 >10 >5 °C, irrespective of the N-source used. However, the magnitude of emission varied with soil nutrient availability and substrate quality. Arrhenius and exponential functions were used to approximate the relationship between soil gaseous emissions (N_2O, CO_2, CH_4, and NH_3) and temperature. Soil temperature explained the seasonal variation in soil fluxes by 51–97% using Arrhenius and exponential models. The Q_{10}-values for the soils incubated at higher temperatures tended to be lower than those at lower temperatures, suggesting that the response of microbial respiration, nitrification and denitrification may differ due to the difference in the choice of N-fertilizer and climate. The findings from this study could be useful in developing alternative N management strategies to conventional urea application for mitigating N losses in arable systems within the RRV. Temperature can influence soil and manure properties such as OM, moisture, and C:N ratio. We recommend future studies to address these changes with destructive sampling and long-term field experiment as the rate and extent of emissions may differ from those with a shorter time scale because of the changes in microbial composition, substrate quality and quantity associated with changes in agro-environment.

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5. GENERAL CONCLUSION

General conclusions of this study are summarized below:

- The impact of manure application are dependent on soil properties, bedding materials, manure nutrient composition, and weather conditions.
- The lack of yield differences among N-treatments suggests that supplemental inorganic fertilizer may not be required for manure to maintain yields similar to inorganic N sources.
- Nitrous oxide emission from fine-textured silty clay over the period of two growing seasons suggested a trend towards higher emissions from UO. On the contrary, CO_2 and CH_4 emissions were significantly increased by manure. In addition to GHG emissions, NH_3 volatilization loss was significantly reduced with BM, however, SM and UO were not statistically significant.
- Compared to solid manure, straw bedding did not significantly influence corn yield, GHG emissions, NH_3 volatilization, soil N intensities and soil water NO_3^-.
- Moisture study showed the daily fluxes and cumulative emissions of N_2O and CO_2 generally followed the decreasing order of 30% < 90% < 60% of WHC suggesting that the soil moisture levels influences gaseous emissions from N-treated silty clay soil.
- Temperature study showed an increase in cumulative GHGs and NH_3 emission with an increase in temperature with the highest emission observed at 25 °C.

6. FUTURE SUGGESTIONS

The results obtained must be considered in the context of yields and other aspects of environmental quality. For example, a complete accounting of intrinsic C costs associated with all aspects of agricultural production (e.g., N fertilizer, grain drying, farm equipment, emission during hauling and stockpiling, winter soil gas emissions, and changes in soil organic C is required to fully assess life-cycle global warming potential of these N management systems. While many farmers apply manure at rates similar to those we tested, an alternative approach would use manure to meet P demand and supplemental fertilizers or legume cover crops to supply crop N requirements. Further research in the following area are recommended:

- Use the emission data to adapt and evaluate existing process-based farm level models to evaluate the environmental and economic impacts of full production systems.
- Use of real-time automated gas measurement chambers and compare the method with a static chamber method.
- Use of both manure and synthetic fertilizer in combination.
- Precision manure management across site-specific management zones.
- Manure pathogens and implications on land application.