THESIS

METHANE AND NITROUS OXIDE FLUXES FROM CATTLE EXCREMENT ON C3 PASTURE AND C4 NATIVE RANGELAND OF THE SHORTGRASS STEPPE

Submitted by

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ABSTRACT

METHANE AND NITROUS OXIDE FLUXES FROM CATTLE EXCREMENT ON C3 PASTURE AND C4 NATIVE RANGELAND OF THE SHORTGRASS STEPPE

Grazers play a major role in nutrient cycling of grassland ecosystems through the removal of biomass and the deposition of excrement in the forms of liquid, urine and solid feces. We studied the effects of cattle excrement patches on methane (CH_4) and nitrous oxide (N_2O) fluxes using semi-static chambers on cool-season (C3), Bozoisky-select pasture, and warm-season (C4-dominated) native rangeland on the shortgrass steppe. Trace gas measurements were conducted over a 2 year period from cattle urine (43 g N m^{-2}) and feces (94 g N m^{-2}) patches within replicated exclosures on each plant community. Cumulative N_2O emissions for the 2 year experimental period, on a per area basis, were 55% greater from feces relative to urine patches on native rangeland (1.81 and 1.17 kg N_2O-N ha^{-1}) and 25% greater on Bozoisky-select pasture (1.66 and 1.25 kg N_2O-N ha^{-1}). While the cumulative N_2O emissions were similar within treatments across plant communities, the magnitude of seasonal fluxes were different. Emissions from the excrement treatments were greater on the Bozoisky-select pasture the summer following treatment application, while emissions were greater on the native rangeland the following fall and spring. The emission factors for urine and feces did not differ for urine and feces on native rangeland (0.13 and 0.13%) and Bozoisky-select pasture (0.14 and 0.11%), but these emission factors were substantially less than the IPCC Tier 1 default factor (2%) for manure deposited on pasture, indicating that N_2O emissions from these plant communities are currently overestimated. These findings suggest that the IPCC Tier 1 Default N_2O emission

factor of 2% for manure deposited on pasture is not representative of N_2O emissions from cattle excrement on shortgrass steppe. Nitrous oxide emissions from the control plots on native rangeland and Bozoisky-select pasture were similar, 0.61 and 0.65 kg ha^{-1}, respectively. Methane uptake was significantly less from cattle excrement compared to control plots for both plant communities. Cumulative net CH_4 uptake rates were 68% greater for urine compared to feces patches on native rangeland (-2.73 and -0.88 kg CH_4-C ha^{-1}) and 86% greater on Bozoisky-select pasture (-2.16 and -0.30 kg CH_4-C ha^{-1}). Methane uptake rates were also 14% less for the control plots on Bozoisky-select pasture (-3.15 kg CH_4 ha^{-1}) compared to native rangeland (-3.60 kg CH_4 ha^{-1}). Future research should focus on CH_4 and N_2O fluxes from pasture 'hotspots', where nitrogen loading and soil compaction are commonly present.

We tested the capacity of the biogeochemical model DAYCENT to simulate N_2O and CH_4 fluxes from control plots and cattle excrement amended soils of the shortgrass steppe for both plant communities. Cumulative N_2O emissions from the urine treatment were overestimated using the DAYCENT model by a factor of 4 for native rangeland and by a factor of 5 for the Bozoisky-select pasture. While the measured and modeled cumulative emissions agreed reasonably well for the feces, water, and blank plots, the model did not accurately simulate the magnitude of seasonal N_2O emissions from these plots, overestimating emissions during periods of high fluxes during the growing season and underestimating during periods of low fluxes such as the winter. The cause for the poor agreement between measured and modeled N_2O emissions may be attributed to an overestimation of total system N, an overestimation of the proportion of nitrified-N emitted as N_2O, and the possibility that a substantial amount (> 20%) of the urine-N was rapidly volatilized as NH_3 due to the extremely dry conditions at the time of treatment application. Additional model validation for shortgrass steppe soils is needed using

data sets that include extensive soil N data to accompany the trace gas data to determine if the model is accurately simulating nitrification rates, the proportion of nitrified-N emitted as N_2O, and the proportion of N immobilized in microbial biomass. The model strongly overestimated CH_4 uptake rates for the control plots by a factor of 3 for native rangeland and 2 for Bozoisky-select, while the excrement plots were overestimated by a factor of 2 for both plant communities. The model underestimated the optimum water content for maximum CH_4 uptake by approximately 5%, which led to an overestimation of CH_4 uptake by a factor of 2 to 4 during periods of biological limitation when soils were extremely dry. The agriculture reduction factor, which accounts for fertilization and cultivation events, reduced CH_4 uptake from the urine and feces plots, but the uptake rates were still overestimated by a factor of 2 since the modeled failed to capture reduced uptake rates under low soil water content (< 0.15 volumetric water content). The overestimation of CH_4 uptake may partly be resolved by increasing the optimum water content at which maximum CH_4 uptake occurs, allowing the model to capture biological limitation on CH_4 uptake.

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TABLE OF CONTENTS

CHAPTER 1

INTRODUCTION

Rising atmospheric concentrations of greenhouse gases (GHG), methane (CH_4) and nitrous oxide (N_2O) are of substantial environmental concern due to their capacity to absorb infrared radiation and contribute to global climate change. Atmospheric concentrations of CH_4 and N_2O have fluctuated with time, however, the rate of increase since the Industrial Revolution has been unprecedented. Even though CH_4 and N_2O make up a relatively small proportion of the atmosphere compared to carbon dioxide (CO_2), they have much greater global warming potentials (GWP), 25 and 298 times (for a 100 year time horizon), respectively (Khan *et al.*, 2011; Dijkstra *et al.*, 2013). Atmospheric CH_4 is the second most important GHG following CO_2, accounting for 15-20% of global warming (Chen *et al.*, 2010). The GWP of a particular gas molecule is based on the lifetime that it resides in the atmosphere and its capacity to absorb infrared radiation. Nitrous oxide accounts for approximately 6% of the anthropogenic greenhouse effect (Barneze *et al.*, 2014). In addition to a high GWP, N_2O also contributes to stratospheric ozone depletion (Rochette *et al.*, 2014).

Primarily dependent on abiotic factors, terrestrial ecosystems can serve as a sink or a source of atmospheric CH_4. Natural and managed wetlands, termites, enteric fermentation, and animal wastes are major sources of CH_4. Methanogenesis, or CH_4 production, is exclusively carried out by archaea (i.e., group of single cell prokaryotic microorganisms) in anaerobic conditions when the redox potential is $\leq$ -100 mV. When the redox potential is low enough, the rate of CH_4 production is controlled by the amount of labile carbon (C) and temperature. Arable soils serve as a significant CH_4 sink, consuming roughly 30 Tg CH_4-C yr^{-1}, which accounts for 6

to 10% of the total atmospheric CH_4 sink (Sylvia, 2005; Chen *et al.*, 2010). Methane oxidation is primarily conducted by methanotrophs, but may also be carried out by nitrifying bacteria due to the similarity in mass and configuration of NH_3 and CH_4 molecules (Sylvia, 2005). Likewise, methanotrophs are also able to oxidize NH_3. Therefore, when NH_4^+ concentrations are high, CH_4 uptake rates tend to be less due to the competition between NH_3 and CH_4 for binding to the enzyme's active site. Anaerobic environments may exist within microsites in the soil profile; in these instances, methanogenesis and methanotrophy can occur simultaneously. In systems that do not produce significant amounts of CH_4, methanotrophs depend on gas diffusion of CH_4 from the atmosphere (1.8 ppm) into the soil profile. Methane oxidation is limited by slow gas diffusion during periods of high water-filled pore space (WFPS) and reduced microbial activity when soils are extremely dry (Sylvia, 2005).

Agricultural soils account for approximately one-third of the global annual N_2O emission budget (Flechard *et al.*, 2005; Liu *et al.*, 2012). The primary mechanisms of N_2O emissions from soils are nitrification and denitrification. During the aerobic nitrification pathway, ammonia oxidizing bacteria (AOB) use ammonium (NH_4^+) as an energy substrate; the completion of the pathway leads to the production of nitrate (NO_3^-). Under low soil oxygen concentration levels (approximately 1%), nitrification is only partially carried out and a proportion of the nitrogen (N) is lost as N_2O (Baily *et al.*, 2012; Schils *et al.*, 2013); this phenomenon is known as the 'leaky pipe' (Davidson and Firestone, 1988). Factors controlling the rate of nitrification include NH_4^+ availability and WFPS. While the rate of nitrification decreases as soil oxygen concentration levels decrease, the proportion of N_2O produced increases; this phenomenon is known as the 'leaky pipe' (Davidson and Firestone, 1988). The ratio of N_2O:NO_3^- produced during nitrification is greatest between WFPS values of 30-60%. Coarse-textured soils are typically

well-aerated and therefore nitrification tends to be the primary N_2O production mechanism for this soil texture (Singurindy *et al.*, 2006). As WFPS surpasses 60%, nitrification decreases and denitrification becomes more prevalent. Under anaerobic conditions (WFPS > 60%), denitrifying microorganisms use NO_3^- as an electron acceptor and labile C as an energy source with dinitrogen (N_2) as the end product (Figure 1). The holes in the "leaky pipe" are often larger during denitrification compared to nitrification. During both, nitrification and denitrification, N_2O production is highest at oxygen levels around 1% (Sylvia, 2005). While nitrification has been found to account for the majority of N_2O emissions from SGS soils, denitrification may be more prevalent following freeze-thaw events in late winter/early spring when WFPS is relatively high (Parton *et al.*, 1988; Mosier *et al.*, 2008).

Cattle are an integral part of the N cycle of grassland ecosystems. They redistribute up to 80% of consumed forage-N through highly N-concentrated excrement, urine and feces. Cattle urine and feces N deposition rates are highly variable and are dependent on the diet quality and water consumption, with values ranging from 20-80 g N m^{-2} and 50-200 g N m^{-2}, from urine and feces patches, respectively. Urea, the primary form of N in urine, is hydrolyzed to NH_3 (gas) and NH_4^+ within days of patch establishment (Schimel *et al.*, 1986; Oenema *et al.*, 1997; Wachendorf *et al.*, 2008). Hippuric acid, a constituent of urine, has been found to inhibit microbial activity and reduce N_2O emissions. Urine also contains organic C, which enhances microbial immobilization of urine-N (Kool *et al.*, 2006b). On the contrary, fecal matter is composed primarily of organic N, such as microbial biomass and undigested plant material, which are gradually mineralized to plant available forms over time (Wachendorf *et al.*, 2008). Only 20-25% of the N present in feces is water soluble (Oenema *et al.*, 1997). Therefore, soil mineral N concentrations are relatively low in soils under feces compared to urine patches. In addition to

N-loading, dependent on soil texture and water content, cattle trampling may also lead to soil compaction, resulting in reduced porosity and increased soil water-filled pore space (WFPS) presenting optimal conditions for denitrification (Simek *et al.*, 2006).

The conversion of shortgrass steppe (SGS) native rangeland, which are dominated by C4 photosynthetic pathway grasses, to cool-season (C3 photosynthetic pathway plants) Bozoisky-select pasture for early spring and late fall grazing increases beef production by 2-4 times compared to grazing native rangeland during the summer grazing season (mid-May to early October) alone (Derner and Hart, 2010). Bozoisky-select pasture undergoes vegetative growth earlier in the spring and later in the fall compared to native rangeland, thus the grazing season is extended when complementing native rangeland grazing with Bozoisky-select pasture. Cultivation and N fertilization of native grassland soils significantly reduces CH_4 uptake and increases N_2O emissions (Mosier *et al.*, 1996; Mosier *et al.*, 1997). Changes in soil-atmosphere gas exchange are attributed to diminished soil structure, increased decomposition of soil organic matter, and increased N concentration. Therefore, economic benefits for livestock producers by converting native shortgrass steppe to cool-season pastures may be partially or entirely offset by negative environmental impacts of increased fluxes of GHGs.

Grasslands occupy approximately 40% of the global terrestrial land surface area. Nearly 100% of uncultivated grasslands are grazed by large mammals (McSherry and Ritchie, 2013). Oenema et al. (1997) estimated that grazing cattle accounted for more than 10% of the global N_2O budget. While livestock (cattle, buffalo, sheep, goats, pigs, and poultry) account for 18% of the global GHG budget, emissions from livestock production accounts for a smaller proportion (3%) of annual emissions in the United States (Pitesky *et al.*, 2009; Capper, 2011). The cattle population is expected to increase from 1.5 billion in 2000 to 2.6 billion in 2050 to meet the food

demand of the steadily increasing human population (Baral *et al.*, 2014). Therefore grassland management practices are likely to have a significant impact on the global atmospheric GHG budget.

The focus of this research was to conduct field-based measurements of CH_4 and N_2O fluxes from cattle excrement (urine and feces) on native rangeland and cool-season, Bozoisky-select pasture and use the resulting data to validate the DAYCENT model, because:

- Long-lived trace gases, CH_4 and N_2O, are potent GHGs
- Data are limited on trace gas fluxes from cattle excrement
- Grassland management practices are likely to have a significant impact on the global GHG budget due to the large area covered by this land type
- Once validated, the DAYCENT model can predict GHG emissions for semi-arid grassland systems such as the shortgrass steppe ecosystems based on various grazing management scenarios

The DAYCENT model simulates C and N cycling through the soil, vegetation, and atmosphere pools. Nitrous oxide emissions from nitrification and denitrification are controlled by soil NH_4^+ and NO_3^- concentrations, water content, temperature, soil texture, and the concentration of labile C substrate (Del Grosso *et al.*, 2008). The DAYCENT model's capacity to simulate N_2O emissions has been tested with measured data from various systems including corn fields, turfgrass, and urine patches on a New Zealand pasture (Stehfest and Muller, 2004; Del Grosso *et al.*, 2008; Zhang *et al.*, 2013). The CH_4 oxidation sub model was tested extensively for various ecosystems during model development, but model validations have been lacking since (Del Grosso *et al.*, 2000b). Methane oxidation or uptake is driven by soil texture, WFPS, and soil temperature.

Field-based GHG measurements provide valuable knowledge on the small spatial scale. However, such experiments are very costly and time consuming and therefore are not economically feasible to conduct over large landscapes. Measurements of soil C and N, net primary production, N_2O emissions, and CH_4 uptake, among other ecosystem variables, are essential when validating process-based biogeochemical models such as DAYCENT for particular ecosystems and management practices. Validated models can be valuable tools for estimating GHGs on regional, national, and global scales.

Currently, most of the research on soil-atmosphere gas exchange of GHGs from cattle excrement patches on grasslands has been conducted using synthetic urine solutions over a single growing season (Wolf *et al.*, 2010). Measuring GHG emissions from 'real' urine patches would provide a better representation of field-based GHG emissions. Conducting GHG measurements over multiple growing seasons from feces patches allows adequate time for mineralization of feces organic-N, capturing GHG fluxes during the N transformation process that results in a more accurate estimation of cumulative emissions. Testing the DAYCENT model with extensive GHG datasets will help identify the model's strengths and areas where improvement is needed. A better understanding of GHG dynamics from SGS native rangeland and Bozoisky-select pasture will also provide policy makers and land managers with information to develop and implement sustainable grazing management policies that minimize GHG emissions.

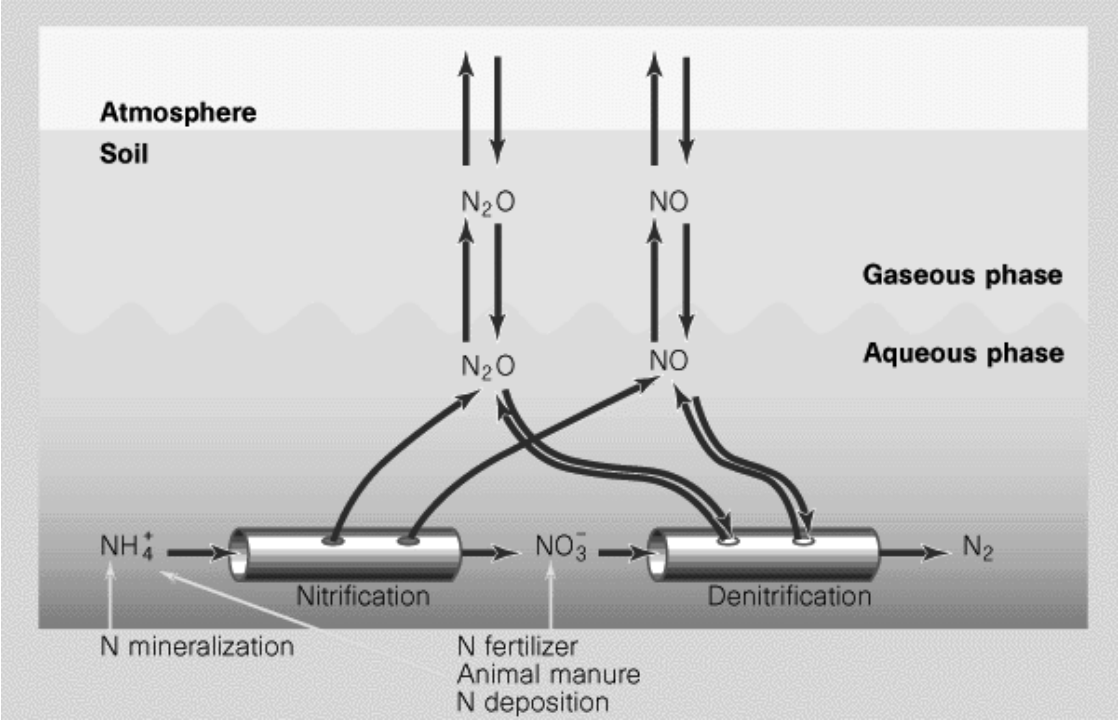


Figure 1. 'Hole-in-the-pipe' model for the nitrous oxide (N_2O) producing pathways, nitrification and denitrification (Bouwman, 1998).

CHAPTER 2

NITROUS OXIDE AND METHANE FLUXES FROM CATTLE EXCREMENT ON C3 PASTURE AND C4 NATIVE RANGELAND OF THE SHORTGRASS STEPPE

1. Introduction

Grazers play a significant role in the nitrogen (N) cycle of grassland ecosystems by redistributing up to 80% of consumed N through their excrement (Milchunas *et al.*, 1988; Wachendorf *et al.*, 2008). High concentrations of N in excrement of cattle greatly exceeds demands of surrounding plant communities, thereby subjecting excrement-N deposits to losses through nitrification, denitrification, ammonia (NH_3) volatilization, and leaching (Williams *et al.*, 1999; de Klein *et al.*, 2003; Maljanen *et al.*, 2007; Wachendorf *et al.*, 2008). Leaching is thought to be minimal in the shortgrass steppe (SGS) because potential evapotranspiration (PET) is substantially larger than the amount of precipitation received and hence water movement below the rooting zone rarely occurs (Schimel *et al.*, 1986; Augustine *et al.*, 2013). Direct N_2O emissions from urine and feces patches on grazed land ranges from 0.1-3.8% and 0.05-0.7% of total excrement N applied, respectively (Milchunas *et al.*, 1988; Oenema *et al.*, 1997; Follett, 2008; Yao *et al.*, 2010; van der Weerden *et al.*, 2011; Hoeft *et al.*, 2012). The IPCC Tier 1 Default Emission Factor (EF) for manure deposited on pasture is 2% (IPCC, 2006). While most of the N_2O emissions from urine treated soils occurs soon after patch establishment, elevated N_2O emissions have been reported to persist for 6-15 years following a simulated urine event at the SGS (Mosier *et al.*, 1998; Carter, 2007).

Most of the current knowledge on GHG emissions from urine patches is based on studies that measured GHG emissions from synthetic urine solutions, which according to Kool et al. (2006a) may over estimate N_2O emissions by up to 50%. Even though urea is the primary form of N in urine, it is also important to include hippuric acid when formulating a synthetic urine solution (Kool *et al.*, 2006a). Benzoic acid, a by-product of hippuric acid, has been shown to inhibit enzymatic and microbial activity (Fenner *et al.*, 2005), which alters N turnover and hence N_2O emissions. 'Real' urine also contains organic C, which promotes microbial immobilization of mineral N (Kool *et al.*, 2006a). In addition, high rates of N turnover have also been implicated to inhibit CH_4 uptake (Epstein *et al.*, 1998b). Mosier et al. (1998) found that a simulated urine (45 g N m^{-2} $CO(NH_2)_2$-N) event decreased CH_4 uptake rates in coarse textured soils of the SGS.

Currently, information on multi-year effects of feces patches on GHG fluxes is lacking. Short-term studies, encompassing a single growing season, may underestimate cumulative N_2O emissions from feces patches since organic N makes up the majority of N in feces. Feces-N takes more than a single growing season to mineralize and mineralization rates depend on environmental conditions, feces composition, and microbial community composition (Wachendorf *et al.*, 2008). Wachendorf et al. (2005) found that a year after feces patch establishment on a sandy soil in Germany, 70% of the cattle feces-N remained in the soil, accounting for 15% of the soil organic-N. Therefore, when studying cumulative GHG fluxes from feces patches, it is important to conduct measurements for multiple years (minimum of 2 years) to allow adequate time for mineralization of feces organic N.

Conversion of native rangeland (NR) in the SGS to Bozoisky-select (BS) pasture has been proven to be economically beneficial for ranchers (Derner and Hart, 2010), but currently

knowledge on GHG emissions from this plant community is lacking. Past research has shown that conversion of NR to cropland increases N_2O emissions and decreases CH_4 uptake (Mosier *et al.*, 1997). A study by Mosier et al. (1997) found that CH_4 uptake and N_2O emissions were 35% less and 25-50% greater, respectively, from NR that had been tilled 3 years prior compared to undisturbed NR. Following tillage of SGS NR, it takes 8-50 years for CH_4 and N_2O soil-atmosphere gas exchange rates to return to that of undisturbed NR (Mosier *et al.*, 1997). The difference in soil-atmosphere gas exchange between disturbed and undisturbed sites is suspected to be due to soil properties such as, diminished soil structure, soil mineral N concentration, surface soil moisture, and C availability.

Researchers have found the magnitude of intraseasonal GHG fluxes to vary between plant community types. Epstein et al. (1998b) observed significant differences in the magnitude of CH_4 uptake and N_2O emissions between C3 and C4 systems on a sandy clay loam soil when moisture and temperature were not limited. C3 plants actively acquire N during the cool-seasons, spring and fall; while C4 plants take up N during the warm summer months (Epstein *et al.*, 1998a). Ammonium (NH_4^+) availability to microbes may be limited during periods when plants are actively acquiring N, leaving low N quality (high C:N ratio) plant organic matter inputs from root exudates and leaf litter as the main N source for microbes. When NH_4^+ substrate is limited, immobilization increases and mineralization and nitrification decreases (Sylvia, 2005). Lower CH_4 uptake rates from soils of C3 relative to C4 plant communities have been attributed to greater N turnover (Mosier *et al.*, 1991).

The primary goal of this study was to evaluate effects of cattle excreta patches on CH_4 and N_2O flux rates over a 2 year period on NR and BS pasture of the SGS. We tested the following hypotheses for each plant community: (1) a greater proportion of the urine-N will be

emitted as N_2O compared to feces-N, (2) N_2O emissions will be greater from feces compared to the urine and control plots following the spring freeze-thaw cycle, and (3) CH_4 uptake rates will be less for urine and feces compared to control plots.

2. Materials and methods

2.1. Study site

The study was conducted at the USDA– Agricultural Research Service Central Plains Experimental Range (CPER), which is part of the semi-arid SGS on the northwestern corner of the Pawnee National Grasslands (PNG) located about 12 km northeast of Nunn, in north-central Colorado (40.841801,-104.70621; 1,650 m above sea level). This project focused on 2 plant communities, NR and BS pasture. Both plant communities had been grazed annually leading up to the experiment, with the exception of 2007 and 2008 on the BS pasture. The dominant vegetation of the NR is blue grama (*Bouteloua gracilis*). Other common plants found in this region include fringed sagebrush (*Artemisia frigida*), buffalo grass (*Bouteloua dactyloides*), and plains prickly pear (*Opuntia polyacantha*). Based on long-term data (1939-1990), the average NR forage production is 750 kg ha^{-1} (Milchunas *et al.*, 1994). The BS pasture was plowed and seeded in 1994. Prior to seeding, the pasture vegetation was classified as 'go-back' and was last cultivated in the 1930s and 1950s with winter wheat. 'Go-back' refers to abandoned cropland that is allowed to naturally revegetate. The BS and NR experimental plots are directly adjacent to one another, with the BS system directly south of the NR. The NR is typically grazed from mid-May to late-October, while the BS pasture is grazed in the spring (mid-April to mid-May) and fall (late-October to early-December). The mean annual precipitation (1939-2012) for the

region is 341 mm yr^{-1}, with 80% of the precipitation occurring between May-September. The mean annual temperature (MAT) for the region is 8.6 °C, with the coldest and warmest months being January (mean temperature -1.5 °C) and July (mean temperature 22.2 °C), respectively. Precipitation data were obtained from a weather station located due east from the CPER headquarters. The soil series for the experimental site is an Ascalon fine sandy loam (Fine-loamy, mixed, superactive, mesic Ardic Argiustolls).

Bozoisky-select is an improved cultivar of *Psathyrostachys juncea*, released by the USDA in 1984 that was selected for improved seedling vigor. It is a winter hardy, drought-resistant, bunch grass that is adapted to semi-arid grasslands. The species is a long-lived perennial with early season productivity and high forage quality. Roots of BS are capable of penetrating deep into the soil profile, 8-10 feet, and dispersing 4-5 feet horizontally from the basal portion of the plant, making it a good competitor with weeds once established (Jawson *et al.*, 2005). Bozoisky-select is high in crude protein and has high protein retention after maturity. It has been documented to contain over 20% crude protein in the spring, approximately 15% in the summer and fall, and 5-7% through the winter months (Murray, 1984; Gillen and Berg, 2005). The production of BS is highly dependent on spring moisture. Under optimal spring moisture, the aboveground production of BS is typically 2-3 times that of native rangeland plant species.

2.2. Experimental Design

In the spring of 2012, we established a randomized block design on each plant community, NR and BS. Each plant community contained 4 blocks, or replicates, with treatments of urine (U), feces (F), distilled water (Cw), and blank receiving no amendment (Cb). Each treatment was randomly assigned a plot within each block using the R software package

agricolae (R Development Core Team, 2010). Exclosures were constructed around each block using cattle panels (7.3 m x 7.3 m) in order to keep cattle off the experimental plots during grazing periods. By doing so, disturbance from cattle was avoided such as soil compaction and deposition of additional urine and feces. To simulate grazing, vegetation within the exclosures was periodically clipped by hand to an approximately height of 5 centimeters (cm) and removed from the study area. Due to extremely dry conditions and low plant biomass production in 2012, vegetation within the exclosures was only clipped once for each plant community. Vegetation removed was kept for C and N analysis.

Excrement applications were conducted on the morning of 19 June (DOY 170) in 2012. Treatment plots were clearly marked with hub survey flags for plot identification. Permanent rectangular aluminum anchors (80.5 cm x 43 cm x 10 cm) were installed to a depth of 10 cm over representative areas of 0.312 m^2 of grass. Each anchor served as a base to seat a trace gas chamber onto, creating an airtight seal while limiting soil disturbance. During trace gas sampling, chambers are seated onto anchors to create an airtight seal. Each treatment was applied to the entire area within the respective GHG anchor. Urine and distilled water treatments were applied using a treatment specific watering pitcher, 1.7 liters per plot (5.4 l m^{-2}). Each liquid treatment had its own designated watering pitcher to avoid cross contamination. Liquids were slowly poured from an approximate height of 1 foot above the soil surface in effort to allow infiltration with minimal pooling while achieving homogenous coverage of the entire surface area within treatment anchors. Each feces treatment plot received an addition of 6 kg (19.2 kg m^{-2}) of wet feces (76% water). Feces was evenly spread across the soil surface within the treatment anchor's area to an approximate thickness of 2.5-3.8 cm using a trowel. Based on the mass and volume applied per area, each feces plot was equivalent to 4-6 patches and each urine

plot was equivalent to approximately 1 urine patch (Yamulki *et al.*, 1998). The N application rates were as follows, 430 kg N ha^{-1} (13.4 g N $plot^{-1}$) for urine and 940 kg N ha^{-1} (29 g N $plot^{-1}$) for feces. The N rates in this study fall within the range reported for grazing cattle (Oenema *et al.*, 1997; Wachendorf *et al.*, 2008; van der Weerden *et al.*, 2011).

The excrement was collected during the last week of May in 2012 in the metabolism barn at Colorado State University's (CSU) Agricultural Research, Development and Education Center (ARDEC). All sampling techniques, animal use, and handling were pre-approved by the CSU Animal Care and Use Committee. Total urine and feces were collected over a 24 hour period from nine, 800 weight cross-bred commercial steers that were retained in stalls equipped with stanchions during the collection process. The steers were fed a mixed ration that consisted of whole corn, silage, and hay rather than grazing the steers on NR and BS pastures for a period of time due to the difficulty of transporting steers to and from the housing the facility at ARDEC to CPER pastures. Homogenized samples of the mixed ration feed were taken and oven dried (55 °C) for C and N concentration analysis. Urine collection from each steer was accomplished using a urine collection harness and aspirated into a polypropylene jug under vacuum. Fifty ml of 6 *N* hydrochloric acid (HCl) was added to each carboy prior to urine collection in order to prevent NH_3 volatilization during the collection process. Feces were collected from the barn floor and stored in sealed, 18.9-liter buckets. At the end of the 24 hr holding period, the excrement was compiled, weighed, and frozen (-4 °C). Prior to freezing, a subsample of urine was collected in order to analyze the C and N content of the urine. Excrement was immediately transported back to the USDA Plains Area Agricultural Research Service, Soil-Plant Nutrient Research (SPNR) Unit for storage in a walk-in freezer (-4 °C).

One week prior to treatment application, excrement was moved from the walk-in freezer (-4 °C) to a walk-in cooler (10 °C) to allow gradual thawing. Once thawed, the feces was homogenized, subsampled for C and N concentration analysis on a mass spectrometer (20-20 Stable Isotope Analyzer, Europa Scientific, Chesire, UK), and partitioned by wet weight (2 kg) into 3.78 l sealable plastic bags for application. Subsamples of the feces were oven dried (55 °C) to calculate gravimetric moisture content, ground using a Wretch grinder, and analyzed for C and N concentration. Urine was homogenized and pH adjusted to approximately 8 by adding 300 ml of 6 *N* NaOH the morning of treatment application. Once the urine was homogenized and pH adjusted, subsamples were again taken to analyze C and N contents to verify that the addition of NaOH did not change the N content. Liquid urine subsamples were added to LECO dry prior to analysis on a LECO Tru-SPEC elemental analyzer (Leco Corp., St. Joseph, MI) located at the EcoCore Laboratory at Colorado State University. LECO dry is an inorganic compound used to dehydrate liquid samples for dry combustion. Mixed ration, feces, NR and BS vegetation clipping samples were analyzed on a Europa Scientific automated N and C analyzer (ANCA/NT) with a Solid/Liquid Preparation Module (Dumas combustion sample preparation system) coupled to a Europa 20-20 Stable isotope analyzer continuous flow isotope ratio mass spectrometer (Europa Scientific Ltd., Crewe, England). Table 1 shows the percent C and N of dry weight for urine, feces, mixed ration, Bozoisky-select, and native rangeland grass species.

2.3. Soil analyses

Due to the extreme drought in 2012, baseline soil samples were not taken until after significant rainfall was received with sampling of duplicate cores (3.5 cm core diameter) in control (Cb) plots to 30 cm occurring on 26 July 2012, and 2 August 2012, for the BS and NR

plant communities, respectively. Soil cores were separated into increments according to GRACEnet (2010) protocol (0-5, 5-10, 10-20, 20-30 cm). Gravimetric soil water content was determined on soils from each increment by oven-drying (110 °C) the soils for a minimum of 24 hours. Soils were transported to the USDA, ARS SPNR laboratory where they were air-dried and passed through a 2 mm sieve to remove the roots and rocks greater than 2 mm. Roots smaller than 2 mm were removed using an electrostatic wand. Air-dried picked soils were analyzed for total soil C and N. Soil inorganic C concentrations were determined by conducting a soil acidifications using 1.0 N Phosphoric acid (Follett *et al.*, 1997). Soil samples were analyzed for total C and N and inorganic C on the same instrument used for plant and feces analysis. The mean bulk densities (0-10 cm) for soils on the NR and BS sites were 1.27 and 1.45 g cm^{-3}, respectively. Bulk densities were determined by using the soil core method and a particle density of 2.65 g cm^{-3}. The average bulk density was taken for the 0-5 and 5-10 cm depths. Table 2 lists the soil properties.

2.4. CH_4 and N_2O measurements

Soil-atmosphere CH_4 and N_2O gas exchange was measured using the static chamber methodology outlined in Mosier et al. (2006). Baseline GHG measurements began on 22 May 2012 and were taken 1-3 times a week for a month prior to treatment application. Following treatment application on 19 June 2012, sampling frequency intensified. Sampling occasions took place 1, 4, and 8 hrs following treatment application and then once per day for the next 3 days. The sampling frequency for the first year of the study was as follows: 3 times a week during the growing season (May to September), 2 times a week during the fall (October to mid-November), 2-4 times a month during the winter (mid-November to March), and 1 time a week during the

spring (March-June). The sampling frequency during the second year of the study was reduced to 1 time per week over the growing season and then was further reduced to twice a month starting in November and was maintained at this frequency until the following spring when samplings were then increased to once per week. Due to the importance of soil moisture on GHG emissions, sampling frequencies increased following significant precipitation (25 mm) and freeze-thaw events in order to capture the resulting GHG dynamics. Van der Weerden et al. (2013) found that gas sampling urine patches 3 times a week between the times of 10:00 -12:00 h resulted in zero bias when compared to sampling every 2 h over 28 days. When sampling twice a week, with increased sampling frequency following significant rainfall events, an average bias of +4% resulted. Therefore, in order to approximate an average flux for each sampling occasion and avoid diurnal variation, samples were collected between 9:00-12:00 h (Mosier *et al.*, 1981; van der Weerden *et al.*, 2013). During chamber deployment, each chamber was seated in the water-filled track on top of an anchor, creating an airtight seal. Samples were taken from the chamber headspace at 0, 15, and 30 minutes after chamber placement and then the chambers were removed. Air temperature was recorded at time 0 and 30 minutes. Decagon Devices EC-TM soil moisture and temperature probes were installed in 2 of the 4 replicates for all treatments on each plant community. Soil water content and temperature (5-10 cm) was recorded during each sampling occasion using a handheld datalogger (Decagon Devices Inc., Pullman, WA). Gas samples were collected using 35 ml polypropylene syringes. Upon completion of sample collection, 25 ml of each sample was immediately transferred to a corresponding 12 ml evacuated-glass exetainer fitted with a screw cap and rubber butyl septa (Exetainer vial from Labco Limited, High Wycombe, Buckinghamshire, UK) for storage until analysis by gas chromatography (Laughlin and Stevens, 2003). The exetainers were over pressurized to avoid

sample contamination from ambient gases leaking into the exetainers. Five ml of each sample was analyzed on an automated gas chromatograph (Varian model 3800, Varian Inc., Palo Alto, CA) equipped with an electron capture detector and a flame ionization detector for N_2O and CH_4 analysis, respectively. Samples were analyzed within a month from the collection date, which has been found to be an appropriate time frame when using the described methodology (Laughlin and Stevens, 2003).

2.5. Statistical Analysis

Because N_2O and CH_4 concentrations were typically low from our field site, the linear equation method was used to calculate fluxes in order to avoid over estimation. Parkin et al. (2012) found that linear regression had the lowest detection limit, and was least sensitive to analytical precision and chamber deployment time when compared to the Hutchinson/Mosier, revised Hutchinson/Mosier, and quadratic methods (Hutchinson and Mosier, 1981). A correction factor was calculated for each gas molecule, CH_4 and N_2O, that adjusted for air temperature, number of moles of the gas molecule, atmospheric pressure (640 mm Hg), and chamber volume to surface area ratio (32 l: 0.312 m^2). Treatment flux rates for each sampling occasion were determined by taking the average of the 4 replicates. Flux estimates for non-sampling days were calculated by linear interpolation. Cumulative N_2O emissions were then calculated by taking the sum of measured and interpolated values (Hoeft *et al.*, 2012). Volume of the chamber headspace for feces plots was adjusted by subtracting 1.9 cm from the chamber height to account for thickness of the feces layer.

Treatment (U, F, Cw, & Cb) effects on the daily average, seasonal cumulative, and total cumulative CH_4 and N_2O fluxes were determined using the MIXED procedure of SAS (SAS

Institute, 2013). Nitrous oxide and CH_4 flux data were non-normal so the data were normalized by log transformation prior to analysis. Means were compared using LSMEANS with Tukey's HSD test for multiple comparisons ($p < 0.10$). Treatments were the fixed effect in the model. A Spearman's correlation analysis was conducted in SAS to determine if there were significant relationships ($\alpha = 0.10$) between water-filled pore space (WFPS) and soil temperature and CH_4 and N_2O flux from each treatment. Because the plant communities, NR and BS, were not randomized and replicated, inferences from this study comparing soil-atmosphere gas exchange between the 2 plant communities are limited.

The EF, or percentage of excrement-N emitted as N_2O, was calculated for U and F treatments by subtracting total emissions of the Cb treatment (M_C) from total emissions of each excreta treatment (M_T), U and F, dividing by the rate of urine-N or feces-N applied, and multiplying by 100 (van der Weerden *et al.*, 2011). The equation follows:

$$EF = \frac{M_T - M_C}{\text{Treatment N applied}} \times 100$$

3. Results

3.1. Environmental conditions

Extremely dry conditions occurred at the onset of this experiment. Spring precipitation during 2012 (40 mm) was 27% of the 74 year seasonal average (146 mm), making it the driest spring season in the last 58 years (Figure 1). In addition, air temperatures were also quite hot (>30 °C) during the early part of the experiment (Figure 2). Total precipitation for 2012 was 206 mm, well below the 74 year annual average of 340 mm. Total precipitation in 2012 was dominated by a few large rain events in July and September. Roughly 25% (51 mm) of the

annual precipitation occurred on July 7th and 8th. Another 50 mm of rainfall was received over 5 days in September. Overall trends in precipitation during 2013 and the first half of 2014 were close to average, with exception of a monsoonal rain event in September 2013 (Figure 1). Soil temperatures and WFPS values during trace gas samplings are displayed in Figure 3.

3.2. N_2O emissions

Differences between cumulative N_2O emissions (kg N_2O-N ha^{-1}) from excrement plots, U and F, and the control plots, Cw and Cb, were strongly significant ($\alpha = 0.10$) from soils of both plant communities. While the cumulative N_2O emissions from the F plots were greater than those from the U plots on a per area basis, the differences were only marginally significant (P = 0.07 and 0.06 for NR and BS, respectively). However, a greater N rate was applied for the F compared to the U treatment. Cumulative emissions from the control plots, Cw and Cb, did not differ (Table 3 and Figure 4). The *p-values* for treatment cumulative emission comparisons are provided in Table 4. By the fall of 2013, N_2O emission rates from the excrement plots (U and F) were not significantly different from the Cb plots, even though substantial rainfall was received during this period (79 mm) (Figure 5). There was not a significant difference in EFs, the proportion of excrement-N lost as N_2O, between U and F treatments for either plant community. EFs for excrement treatments were, 0.14% vs. 0.11% on the BS (P = 0.26) and 0.13% vs. 0.13% on the NR (P = 0.82) for U and F, respectively (Table 5).

Fluxes of N_2O tended to follow substantial precipitation events. Relatively large fluxes of N_2O from the U and F plots followed precipitation events during early summer and fall of 2012 from soils of both plant communities. Significant N_2O fluxes from the excrement plots were again observed during the spring and summer of 2013 (Figures 5 and 6). Similar trends in

N_2O emissions following precipitation events were observed from the Cw and Cb plots, but of a smaller magnitude. Nitrous oxide emissions from the U and F plots were greater on BS pasture compared to NR during the summer of 2012, while N_2O emissions from the F plots were greater on NR relative to BS pasture the following fall, spring, and summer (Figures 5 and 6).

N_2O emission rates from F peaked following a substantial rain event 23 days (7-8 July 2012) after treatment application. Emissions during this period were 74 and 262 μg N_2O-N m^{-2} hr^{-1} on NR and BS, respectively. Trace gas samples were collected 1, 2, 3, and 5 days following this precipitation event. N_2O flux rates increased from day 1 to day 3 with declines by day 5. Peak N_2O emissions from U were delayed compared to the F treatment and occurred on July 18, 2012, at 35 and 49 μg N_2O-N m^{-2} hr^{-1} for NR and BS soils, respectively. N_2O emissions from excrement plots remained above baseline levels until the end of July, when the soil WFPS dropped below 30% (Figure 3 and 6). In the fall of 2012, significant N_2O fluxes were observed from the U and F plots following precipitation events.

Soil WFPS and temperature were significant drivers of N_2O emissions from the U and F plots. Positive correlations between WFPS and N_2O flux from the F plots (r = 0.35 and 0.47 for NR and BS, respectively) were highly significant ($P < .0001$) from soils of both plant communities. Positive correlations were also observed between WFPS and N_2O flux for U on both plant communities (r = 0.13, P = 0.06 for NR; r = 0.23, P = 0.0007 for BS) and NR-Cw (r = 0.15, P =0.04). The negative correlation between WFPS and N_2O emissions from the BS-Cw plots was marginally significant (r = -0.11, P = 0.12). The majority of N_2O emissions occurred when WFPS was between 25-50% and 35-55% on NR and BS, respectively (Figure 7). Significant positive correlations between soil temperature and N_2O emissions were observed for excrement plots (BS-F r = 0.29, $P < .0001$; NR- F r = 0.19, P = 0.006; BS-U r = 0.17, P =0.02).

Correlations from the control plots tended to be negative (NR-Cw r = -0.19, P = 0.009; NR-Cb r = -0.11, P = 0.09). While significant, the aforementioned correlations were low and therefore not very robust. Table 6 and Figure 7 provide more detail on the relationships between soil temperature and WFPS and N_2O emissions.

3.3. CH_4 Uptake/Emissions

Cumulative CH_4 uptake (kg CH_4-C ha^{-1}) from F plots was significantly (α = 0.10) less than all other treatment plots from soils of both plant communities. Cumulative CH_4 uptake was also significantly less from the U plots compared to the control plots, Cw and Cb, on both plant communities with the exception of Cw-U (P = 0.14) on the BS pasture (Figure 8). After nearly 2 years (708 days), all plots were a CH_4 sink. Cumulative CH_4 uptake rates from NR-F, BS-F, and BS-U plots were still significantly less than control during the final season (spring 2014) of the experiment (Figure 9).

For nearly a week following treatment application (19 June 2012), a substantial amount of CH_4 production was observed from the F plots from soils of both plant communities (Figure 10). Methane production from F plots peaked at 4 and 8 hours following treatment application on BS and NR, respectively. Methane production from the F treatment of both plant communities continued for approximately 6 days following treatment application. From this point forward, F plots resumed CH_4 uptake (with the exception of 18 & 25 July 2012 on both plant communities), but at a rate significantly less than the other treatments. Net methane production from U plots occurred only once on each system (0.47 ± 1.28 on 15 August 2012 and 0.97 ± 3.33 μg CH_4-C m^{-2} hr^{-1} on 4 January 2013 NR and BS, respectively) for the duration of the study. Methane uptake rates tended to be the highest when WFPS was between 20-40% on

both plant communities (Figure 11), which occurred as the soil dried following significant precipitation events.

Methane uptake rates corresponded to soil wetting and drying cycles (Figures 11). Immediately following the large precipitation event on 7-8 July 2012, CH_4 uptake rates were near 0 μg CH_4-C m^{-2} hr^{-1} from all treatments. As soils dried, CH_4 uptake rates increased until the third week of July when uptake rates peaked from control plots at 35-40 and 30 μg CH_4-C m^{-2} hr^{-1} on the NR and BS, respectively. August was an extremely dry month (9 mm), 34 mm below the 74-year average (43 mm); as a result the soil became extremely dry during this time. As the soils dried out to WFPS levels below 20%, CH_4 uptake rates continued to decrease until mid-September (Figures 10 and 11). The coldest soil temperature during trace gas sampling, an average of -6.7 C (n=16), was observed on 4 January 2013. As the soil slowly began to warm during the end of winter and beginning of spring, CH_4 uptake rates increased until soil rewetted from snow events in April. Trends in CH_4 fluxes during the second year were similar to those observed during the first year. The cumulative CH_4 uptake (kg CH_4-C ha^{-1}) by season is provided in Figure 9. Average fluxes from sampling occasions are displayed in Figure 10. Trends in CH_4 fluxes were similar between the 2 plant communities, but total CH_4 uptake was less on the BS pasture compared to NR for each treatment (Table 3).

The optimum water content for CH_4 uptake was when WFPS was between 23-35% and 25-40% for NR and BS, respectively. Lower CH_4 uptake rates were observed when WFPS was above and below these ranges likely due to limited soil gas diffusion and microbial activity. Low negative correlations were found (BS-F $r = 0.23$, $P = 0.0008$; NR-F $r = 0.12$, $P = 0.09$) between WFPS and CH_4 uptake, a decrease in CH_4 uptake with increasing WFPS, for the F treatment on both plant communities. A significant positive correlation was observed between

WFPS and CH_4 uptake from the NR-Cw treatment (r = -0.19, P = 0.008). The relationship between CH_4 uptake and WFPS tended to be curvilinear, with the greatest uptake rates occurring at intermediate WFPS levels (25-40%) (Figure 11). While most correlations between soil temperature and CH_4 uptake were positive, an increase in CH_4 uptake with increasing soil temperature, there was a highly significant negative correlation (r = 0.30, P = <.0001) detected for the BS-F plots. Significant positive correlations were observed between soil temperature and CH_4 uptake from the Cb plots of each plant community and the U and F plots on NR (Table 6).

4. Discussion

4.1. N_2O

Our findings did not support the hypothesis that N_2O emissions would be greater from U compared to F plots. There was not a significant difference in N_2O EFs between treatments, U and F, from soils of either plant community. On the BS pasture, 0.14% of the urine-N and 0.11% of the feces-N was emitted as N_2O and on the NR system, 0.13% of the urine-N and 0.13% of the feces-N was emitted as N_2O. These EFs observed in this study were on the lower end reported in the literature. In a review by Oenema et al. (1997), EFs for urine and feces ranged from 0.1-3.8% and 0.1-0.7%, respectively. Hoeft et al. (2012) reported EFs for feces and urine of 0.05% and 0.4%, respectively, for an upland grassland in Germany. Mosier et al. (1998) determined that 0.5-1% of a synthetic urine solution (45 g N m^{-2}) was emitted as N_2O from SGS soil. The IPCC default Tier 1 EF is 2%, with a range of 0.5-3.0%, for manure deposited on pasture and rangeland (IPCC, 2006). Using the IPCC default Tier 1 EF for calculating N_2O emissions for urine and feces emitted from shortgrass steppe native rangeland and cool-season pasture would result in a significant overestimation of N_2O emissions.

Extremely dry conditions in 2012 likely contributed to the low EFs reported in this study. Over the past 74 years, 2012 was the 6th driest year on record, receiving 167 mm (60% of the 74 year average, 340 mm) (Figure 1). The dry soil conditions, likely reduced nitrifier activity in the upper soil profile due to limited substrate and water availability (Sylvia, 2005). Also, a large proportion of the urine-N may have been volatilized as NH_3 following urea hydrolysis due to the hot, dry conditions. The air temperature at the time of treatment application was above 30 °C (Figure 2). Ball and Ryden (1984) found that on average 28% of urine-N was volatilized as NH_3, but during warm, dry conditions NH_3 volatilization accounted for 66% of urine-N loss on a New Zealand pasture. Ammonia volatilization rates from feces patches are typically much less than those from urine patches due to the surface crust and lower pH of the feces, amongst other chemical, physical, and biological properties (Mulvaney *et al.*, 2008; Laubach *et al.*, 2013). In addition, when WFPS in the top 10 centimeters dropped below 30%, which was the case for most of June and August, a greater proportion of the emitted urine-N during nitrification could have been lost as nitric oxide (NO) (Sylvia, 2005). Yao et al. (2010) found that maximum NO emissions from an upland SGS soil were observed when WFPS was between 25-29% when incubating soil cores in a laboratory, which is in the range of our soils' moisture content during the summer. Martin et al. (1998) found maximum NO_x emissions from the SGS to occur from a coarse textured soil during the summer when WFPS was in the range of 32-35%. Mosier et al. (1998) found NO_x emissions were 10-20 times greater than N_2O emissions from a coarse textured N amended soil at the SGS.

On a per area basis, N_2O emissions from the F treatment were significantly greater than those from the U plots on both plant communities. Over a day, a single cow's urine covers approximately 6 times the area as feces. On average, cattle defecate 11-12 times per day and

urinate 8-11 times per day with a coverage area of 0.05 and 0.4 m^2 per defecation and urination, respectively (Oenema *et al.*, 1997). Using these values, we conservatively estimated the area covered by feces and urine from a single cow per day to be 0.55 and 3.2 m^2 day^{-1}, respectively. Scaling up, a single cow grazing for one day in June under drought conditions at the SGS would result in 217 and 59 mg N_2O-N yr^{-1} from urine and feces patches on NR, respectively, and 236 and 54 mg N_2O-N yr^{-1} from urine and feces patches on BS pasture, respectively. In order to calculate cumulative N_2O emissions for an entire grazing season, future studies are needed to evaluate temporal effects of urine and feces patch establishment on N_2O emissions.

Nitrous oxide emissions from excrement patches established on NR and BS soils of the SGS during periods of greater WFPS need further investigation. Emissions resulting from excrement patches during years of average or above average precipitation are needed to determine the difference in N_2O emissions from excrement patches under dry and wet soil conditions. Hartmann et al. (2012) found that N_2O emissions from simulated cattle urine patches were reduced by a magnitude of 1 to 2 from a Switzerland pasture when implementing drought conditions (25-30% reduction in precipitation) using rain exclusion roofs. Soil WFPS may also be greater in areas of the pasture where animals congregate such as fence corners and the perimeter around water tanks due to greater bulk density and less soil porosity. In addition to increased WFPS, these areas also experience N-loading from the high concentration of excrement patches, forming 'hotspots' (Augustine *et al.*, 2013). The combination of reduced air pore space and high nitrogen concentration provides ideal conditions for nitrification and denitrification to occur (Oenema *et al.*, 1997). Therefore, even though 'hotspots' occupy a small proportion of the total pasture area, these areas likely account for a significant proportion of N_2O emissions from these plant communities.

Our hypothesis that N_2O emissions would be greater from F plots relative to U and control plots following the freeze-thaw cycle in the spring of 2013 was partially supported. On a per area basis, N_2O emissions from F plots were significantly greater than the U plots on the NR during the spring, but not on the BS system. This result may have been due to greater plant uptake of F mineralized-N on the C3, BS pasture, during the spring relative to the predominately C4 NR, leaving less mineral-N to the microbial processes of nitrification and denitrification. Epstein et al. (1998a) found that following a wet and cool spring, C3 plants accumulated 2.7 times more N during the month of May than C4 plants. Precipitation received during April 2013 was 64 mm, which was 2 times the 74 year average (32 mm). The combination of the high soil moisture and the suspected high levels of soil mineral-N under F patches during the spring likely provided ideal conditions for biomass production on the BS pasture. During the spring on the NR, plant-microbial competition was likely minimal since the dominant warm-season grasses typically do not initiate substantial growth until mid to late May, subjecting the F mineral-N pool to microbial-mediated processes such as nitrification and denitrification.

Nitrification was likely the primary mechanism driving N_2O emissions since the high N_2O fluxes occurred when WFPS was between 30-60% (Sylvia, 2005). The WFPS taken during trace gas sampling occasions over the course of this experiment never exceeded 60%. These findings are supported by research conducted by Parton et al. (1996), who found that nitrification accounted for 60-80% of the N_2O emissions from SGS soils. In addition, Baral et al. (2014) determined that nitrification was the primary pathway for N_2O emissions from urine patches on a sandy soil in Denmark. However, denitrification may have occurred in the feces patches following a substantial rain event (51 mm) on 7-8 July, 2012, due to the presumably high concentration of labile C and WFPS in the feces patches and in anaerobic microsites in the

underlying soil. This period accounted for the largest N_2O flux from the F plots on the BS soil and one of the largest on the NR.

While cumulative N_2O emissions were similar between plant communities, the magnitude of seasonal fluxes varied. This phenomenon is likely due to differences in the plant phenology between the 2 plant communities. The productivity of C3 grasses at the SGS is highly dependent on spring precipitation (April-June) (Derner *et al.*, 2008). The extreme drought conditions during the spring of 2012 resulted in severely inhibited vegetative growth. Due to the lack of aboveground production, the BS plots were clipped once in the spring (not analyzed for C and N) prior to treatment application and the NR plots clipped once towards the end of July following a large rainfall event. Aboveground biomass sampling was not conducted on the BS pasture during 2012; the biomass production for the NR was 358 kg ha^{-1}, which is approximately half of the average biomass production for this system. The N concentrations of the NR grasses (clipped on 30 July, 2012) from the excrement plots were greater than those from the control plots (Figure 12). Thus the smaller magnitude of N_2O emissions from the excrement plots on the NR following the large rain event in July could have been an artifact of greater plant N uptake from the predominately C4 NR species compared to the C3 BS pasture. In addition to reduced plant N uptake from the BS pasture during the summer of 2012, there is also more bare ground interspace on the BS pasture compared to the NR, which might have contributed to the greater N_2O emissions from the BS treatment shortly after treatment application.

Over the 2 year experimental period, winter (December 21 – March 19) N_2O emissions from the Cb plots accounted for 26% and 30% of the total cumulative emissions from NR and BS, respectively, which is in accordance to the findings of Mosier et al. (1996). However, the relative proportion of total emissions occurring during the winter from the excrement plots was

only 19% and 10% on NR and 15% and 10% on BS, for U and F, respectively. A fall application of U and F might result in a greater relative proportion of the annual N_2O emissions occurring during the winter.

4.2. CH_4

Our hypothesis that the addition of U and F would reduce the rate of CH_4 uptake was supported. Cumulative CH_4 uptake (kg CH_4-C ha^{-1}) from the U and F plots was significantly less than that of the control plots, Cw and Cb, on both plant communities. This observation was likely the result of increased mineral-N turnover in the soils under the N-amended plots. High concentrations of mineral-N have been shown to inhibit CH_4 uptake through the competition of NH_3 and CH_4 for the active binding site of methanotrophs (Epstein *et al.*, 1998b; Sylvia, 2005). Even when excluding the CH_4 flux data for the first week following F application when CH_4 production occurred, average CH_4 uptake rates from the F plots (14.36 and 9.94 μg CH_4-C m^{-2} h^{-1} for NR and BS, respectively) were still significantly less ($\alpha = 0.10$) than the Cw (20.43 and 17.98 μg CH_4-C m^{-2} h^{-1} for NR and BS, respectively) and Cb (22.38 and 18.89 μg CH_4-C m^{-2} h^{-1} for NR and BS, respectively) plots on both plant communities. Reduced CH_4 uptake from F patches may also be a result of the presence of a surface crust, which forms as the patch dries. The surface crust inhibits gas diffusion. Due to the hot, dry conditions during the time of F application, the surface crust likely formed faster than it would have during an average precipitation year. The dry conditions also likely minimized the period of time when anaerobic conditions were present in the F patch resulting in less CH_4 production. (Yamulki *et al.*, 1999).

The F plots were a significant source of CH_4 over the first week following treatment application due to the high concentration of C and anaerobic conditions within the feces patches

(75% WC). These findings were in accordance with Yamulki et al. (1999) who found CH_4 production to occur at similar rates and duration of time following fecal patch establishment on a silty clay loam soil in England. In contrast to our experiment, Yamulki et al. (1999) found CH_4 uptake rates from fecal patches on perennial ryegrass pasture to reach that of baseline levels 15 days after treatment application. In the present study, once the fecal patches were desiccated, CH_4 uptake resumed, but at a significantly lesser rate than the control plots. Reduced CH_4 uptake from the excrement plots was observed for a year and half following treatment application. When excluding the first week of CH_4 flux data following treatment application, there was no difference in average CH_4 uptake rates between the U and F plots over the course of the experiment.

We could not identify the driving factors of CH_4 emissions that occurred in mid to late July from the F patches on both plant communities. The pulse of CH_4 production on 18 July coincided with a substantial temperature increase, roughly an 8 °C increase from 17 July to 18 July, as well as 3.6 mm of precipitation on the morning of 17 July. On the other hand, CH_4 production on 25 July did not immediately follow a precipitation event or temperature shift. In addition to the warm and moist conditions, noticeable dung beetle activity was documented on F plots during the first half of July, which could have affected the CH_4 flux dynamics. While the limited amount of research on effects of dung beetle activity on GHG emissions suggests that presence of dung beetles reduces rates of CH_4 production and increases N_2O emissions through aeration of fecal patches (Penttila *et al.*, 2013), additional research is needed to better understand the influence that dung beetles have on GHG emissions under various environmental and fecal patch conditions.

The highest rates of CH_4 uptake for all the treatments observed in the present study occurred when WFPS was between 23-35% and 25-40% on NR and BS, respectively. Methane uptake rates approached zero when soils were near field capacity and the wilting point. These results do not correspond to the findings of Mosier et al. (1996) and Chen et al. (2010) who found that maximum CH_4 uptake rates occurred when WFPS levels were between 13-23%. The discrepancy may be due to differences in sampling methodologies. In the present study WFPS was calculated using soil VWC values for the 5-10 cm depth that were obtained from soil TDR probes. Mosier et al. (1996) on the other hand, conducted gravimetric analysis of soil water content for the 0-15 cm depth for each trace gas sampling. Chen et al. (2010) also used TDR probes to measure soil VWC, but the measurements were for the 0-6 cm depth. Another possible cause for the discrepancy is that bulk density, which is difficult to calculate for sandy soils, is used to calculate WFPS and therefore could be a source of error. In addition, cumulative CH_4 uptake was less for all treatments on the BS pasture compared to the NR. This phenomenon may have been due to increased N turnover on the BS pasture due to the more labile vegetation, lower C:N ratio (Table 1), relative to the NR or the diminished soil structure on the BS pasture as a result of plowing in 1997 (Mosier *et al.*, 1997; Gillen and Berg, 2005; Sylvia, 2005).

4.3. Limitations

While we attempted to simulate natural grazing conditions during the course of the experiment, there were limitations worth mentioning. First, the urine and feces used in this study was obtained from cattle that were fed a mixed ration (whole grain corn, corn silage, and alfalfa hay) rather than NR species and BS grass and therefore the C and N content of the excrement may have been different from cattle that were fed a diet composed of NR or BS species.

Secondly, cattle are typically transferred from the BS pasture to the NR by late-May; we did not apply our treatments to the experimental plots until Mid-June. In addition, the excrement was applied to the entire surface area (0.312 m^2) within the trace gas sampling anchors, which is approximately the size of a single urine patch and equivalent to 4-6 feces patches. The permanent trace gas anchors likely inhibited horizontal movement of soil water and chemical components of the excrement. Lastly, the exclosures acted as a snow fence, collecting snow during the extremely windy winter conditions at the SGS. The collection of snow might have caused greater soil moisture contents than what would have ordinarily occurred following freeze thaw events.

5. Conclusion

There was not a significant difference between the EFs for cattle urine and feces from soils of either plant community. The relatively low EFs observed in this study are likely attributed to the well-aerated soils studied in this experiment, extreme drought conditions during the onset of the experiment, and the use of real urine, which has chemical constituents that have been found to inhibit microbial activity. In accordance to previous findings, the IPCC default Tier 1 N_2O EF of 2% for manure deposited on pasture does not appear to adequately represent the proportion of urine- and feces-N emitted as N_2O on native rangeland and cool-season pasture of the SGS (van der Weerden *et al.*, 2011; Rochette *et al.*, 2014). Consideration should be given to implementing an EF less than the IPCC default Tier 1 N_2O EF of 2% for urine and feces deposited on semi-arid grazed land. Future research at SGS should focus on N_2O emissions from urine and feces patches deposited on pasture 'hotspots', highly congregated areas of the pasture where N-loading and soil compaction are common.

While trends in the timing of N_2O emissions from excrement plots were similar between plant communities, the magnitude of the emissions were not. Intraseasonal differences in N_2O emissions between the predominately C4 NR and the C3 BS pasture are likely due to differences in the phenology of each plant community type and the timing of nutrient acquisition. Therefore, to elicit accurate estimates of cumulative N_2O emissions for an entire grazing season at the SGS, future research is needed to determine the effects of the seasonality of patch establishment on N_2O EFs for urine and feces patches on each plant community.

Decreased CH_4 uptake rates from the urine and feces patches were observed over the entire 2 year study. The reduction was likely due to increased N turnover in the soil under the excrement patches as well as surface crust formation on the feces patches, inhibiting gas diffusion. In addition, CH_4 uptake from the BS pasture tended to be less than the same treatments on the NR system, which may have been an artifact of cultivation 20 years prior or plant community type. These results suggest that converting NR to BS pasture for complementary grazing at the SGS could significantly reduce the CH_4 sink. Future research on CH_4 uptake from native rangeland and Bozoisky-select pasture soils should incorporate randomized replication of each plant community in order to draw inferences to a larger geographic area on the implications of converting native rangeland to cool-season pasture on CH_4 uptake.

Table 1. Percent C and N of dry weight and C:N ratios for urine, feces, mixed ration, native rangeland, and Bozoisky-select.

	%N	%C	C:N
Urine	0.78	1.12	1.44
Feces	2.05	42.93	20.90
Mixed Ration	1.64	44.22	27.04
Native Rangeland[1]	1.94	45.73	23.57
Bozoisky-select[2]	2.99	48.32	16.16

1 Analysis included all plant species from within GHG anchor with the exception of plains prickly pear cactus. Percent C and N values were an average from 3 sampling occasions (Samples were collected on 7/30/12, 6/7/13, and 7/25/13; each sampling occasion consisted of 4 replicates).
2 Analysis included all plant species from within GHG anchor, predominately Bozoisky-select. Percent C and N values were an average from 2 sampling occasions (Samples were collected on 5/21/13 and 9/30/13; each sampling occasion consisted of 4 replicates).

Table 2. Soil properties (texture n=2; bulk density and total N and C n=16) for the 0-10 cm depth of plant communities, native rangeland (NR) and Bozoisky-select (BS) pasture.

Site	Sand (% ± SE)	Clay (% ± SE)	Bulk Density (g cm^{-3} ± SE)	Total N (Avg. % ± SE)	Total C (Avg. % ± SE)
Native Rangeland	68 ± 3.98	10 ± 0.51	1.27 ± 0.03	0.09 ± 0.01	1.00 ± 0.11
Bozoisky-select	83 ± 0.44	5 ± 0.54	1.45 ± 0.02	0.07 ± 0.01	0.65 ± 0.08

Table 3. N_2O and CH_4 cumulative fluxes and standard error (kg ha^{-1}; 736 days from 5/22/12-5/27/14) for treatment urine (U), feces (F), water (Cw), and blank (Cb) for soils of each plant community, native rangeland and Bozoisky-select.

	Cumulative Flux	
	N_2O (kg N_2O-N ha^{-1}) ± SE	CH_4 (kg CH_4-C ha^{-1}) ± SE
C4 – Native Rangeland		
U	1.17 ± 0.15^{a}	-2.73 ± 0.14^{a}
F	1.81 ± 0.39^{b}	-0.88 ± 0.15^{b}
Cw	0.55 ± 0.03^{c}	-3.34 ± 0.18^{c}
Cb	0.61 ± 0.07^{c}	-3.60 ± 0.13^{c}
C3 – Bozoisky-select		
U	1.25 ± 0.15^{a}	-2.16 ± 0.17^{a}
F	1.66 ± 0.15^{b}	-0.30 ± 0.21^{b}
Cw	0.61 ± 0.08^{c}	-2.95 ± 0.18^{ac}
Cb	0.65 ± 0.02^{c}	-3.15 ± 0.37^{c}

Cumulative values are an average of 4 replicates for each treatment. Cumulative values with different letters indicates a significant difference (ANOVA with Tukey's HSD adjustment, $\alpha = 0.10$).

Table 4. Pairwise treatment comparison of cumulative nitrous oxide and methane flux comparison for urine (U), feces (F), water (Cw), and blank (Cb) plots from soils of each plant community, native rangeland (NR) and Bozoisky-select (BS) pasture.

Cumulative Flux Comparison				
	Treatment		N_2O	CH_4
			----------P-value----------	
C4 - Native Rangeland				
	Cb	Cw	0.57	0.22
	Cb	F	<.0001*	<.0001*
	Cb	U	0.001*	0.002*
	Cw	F	<.0001*	<.0001*
	Cw	U	0.0004*	0.02*
	F	U	0.07*	0.0004*
C3 - Bozoisky-select				
	Cb	Cw	0.64	0.41
	Cb	F	0.0001*	0.0004*
	Cb	U	0.006*	0.03*
	Cw	F	<.0001*	0.002*
	Cw	U	0.002*	0.14
	F	U	0.06*	0.03*

ANOVA with Tukey's HSD adjustment.
*Indicates significant difference, $\alpha = 0.10$.

Table 5. Emission factors (EF) for urine (U) and feces (F) on native rangeland (NR) and Bozoisky-select (BS) pasture. EFs were calculated using total cumulative emissions for U and F plots over entire study (June 19, 2012 – May 27, 2014).

Plant Community	Treatment	Emission Factor (%)
Native Rangeland		
	Urine	0.13
	Feces	0.13
Bozoisky-select		
	Urine	0.14
	Feces	0.11

Table 6. Spearman's correlation coefficients (*r*) with p-values for the relationship between water-filled pore space (WFPS) and soil temperature (°C) to N_2O and CH_4 flux from native rangeland (NR) and Bozoisky-select (BS) pasture (7/9/2012-5/27/2014).

Greenhouse Gas	Plant Community/ Treatment	WFPS (%)	Soil Temperature (°C)
		----------r (p-value)----------	
N_2O			
	Native Rangeland		
	Urine	0.13 (0.06)*	0.08 (0.29)
	Feces	0.35 (<.0001)*	0.19 (0.006)*
	Water	0.15 (0.04)*	-0.19 (0.009)*
	Blank	0.005 (0.95)	-0.12 (0.09)*
	Bozoisky-select		
	Urine	0.23 (0.0007)*	0.17 (0.02)*
	Feces	0.47 (<.0001)*	0.29 (<.0001)*
	Water	-0.11 (0.12)	0.05 (0.52)
	Blank	0.08 (0.25)	-0.09 (0.23)
CH_4			
	Native Rangeland		
	Urine	0.08 (0.27)	-0.19 (0.006)*
	Feces	0.12 (0.09)*	-0.19 (0.008)*
	Water	-0.19 (0.008)*	-0.06 (0.41)
	Blank	0.03 (0.66)	-0.13 (0.08)*
	Bozoisky-select		
	Urine	0.07 (0.30)	-0.09 (0.19)
	Feces	0.23 (0.0008)*	0.30 (<.0001)*
	Water	0.004 (0.95)	-0.10 (0.16)
	Blank	0.02 (0.82)	-0.23 (0.0007)

*Indicates a significant difference ($\alpha = 0.10$).

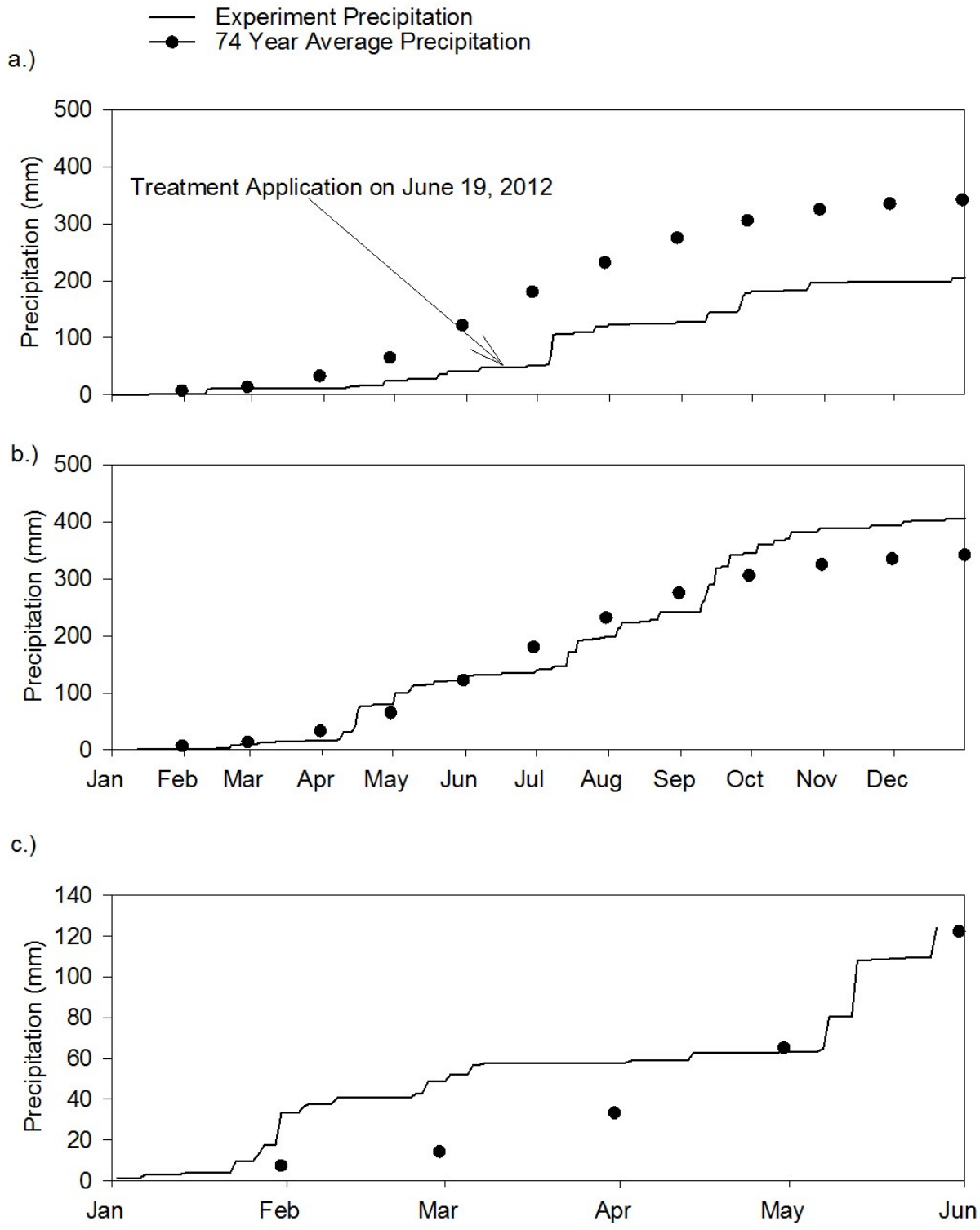


Figure 1. Average precipitation (n = 74) and precipitation received during a.) 2012, b.) 2013, and c.) 2014.

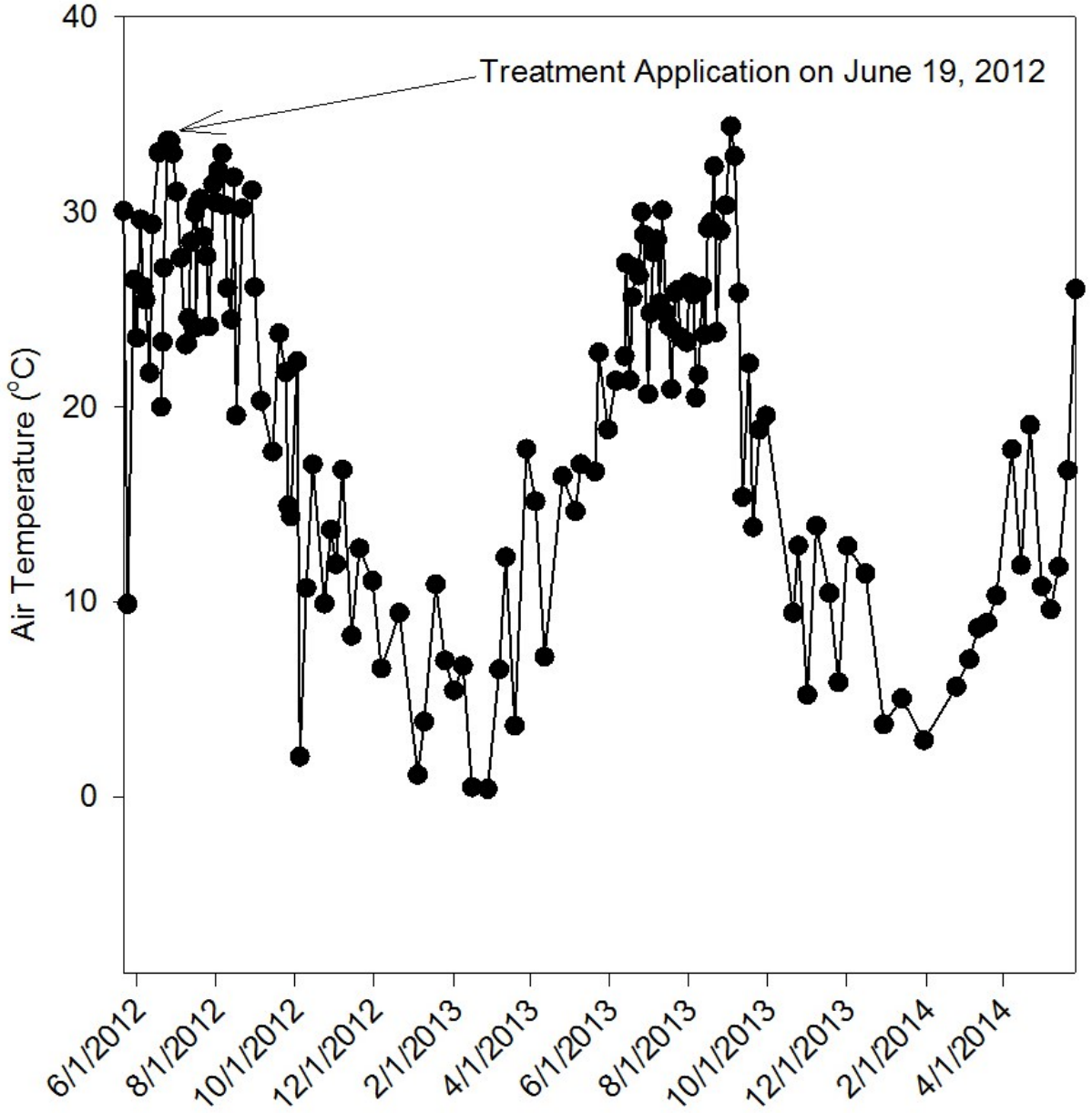


Figure 2. Air Temperature at approximately 10 cm above soil surface at the time of trace gas sampling.

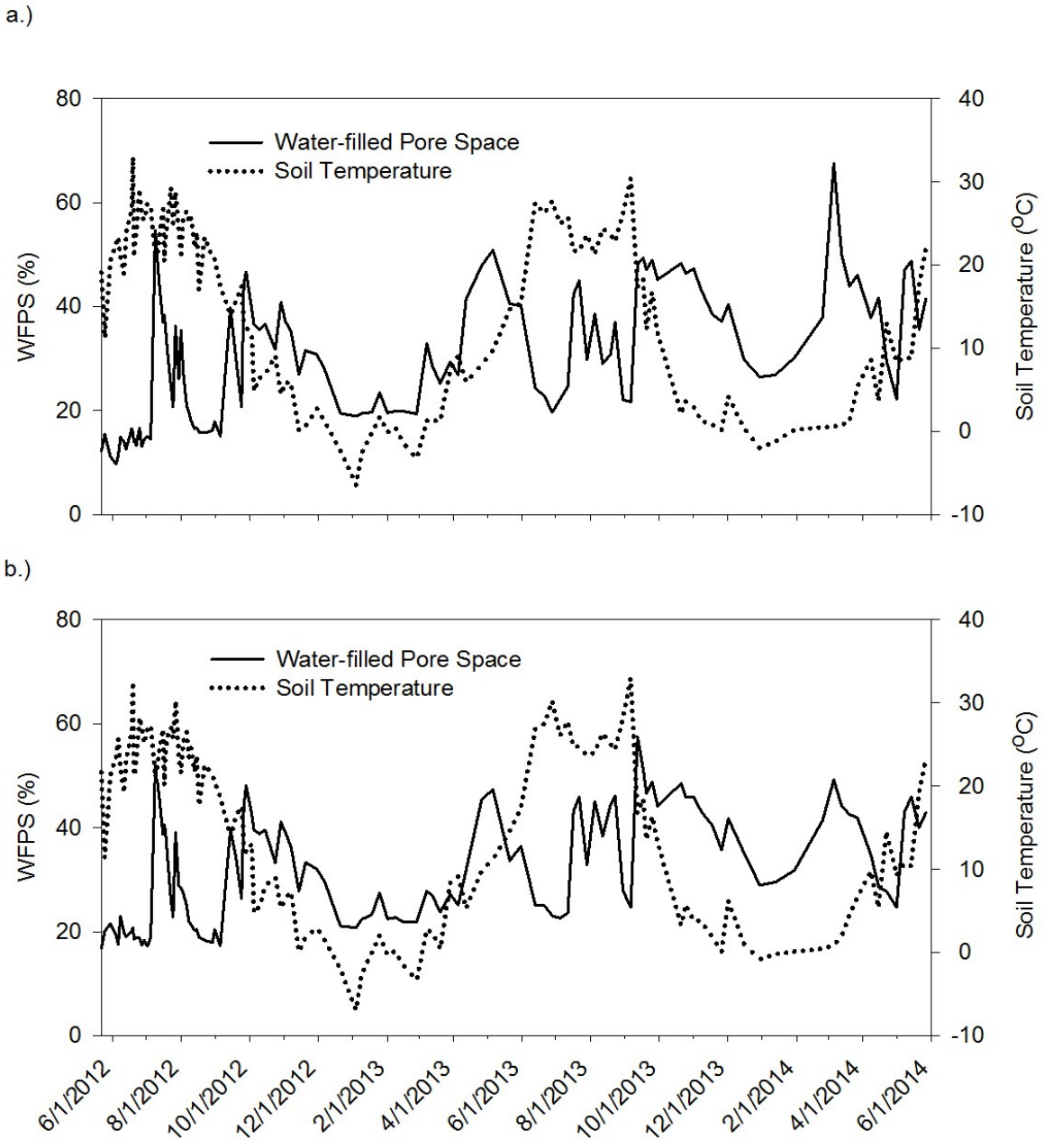


Figure 3. Mean (n=2) water-filled pore space (%) and soil temperature (°C) for the 5-10 cm depth from soils of both plant communities, a.) native rangeland (NR) and b.) Bozoisky-select (BS), for days that GHG sampling occurred between 5/22/12 – 5/27/14.

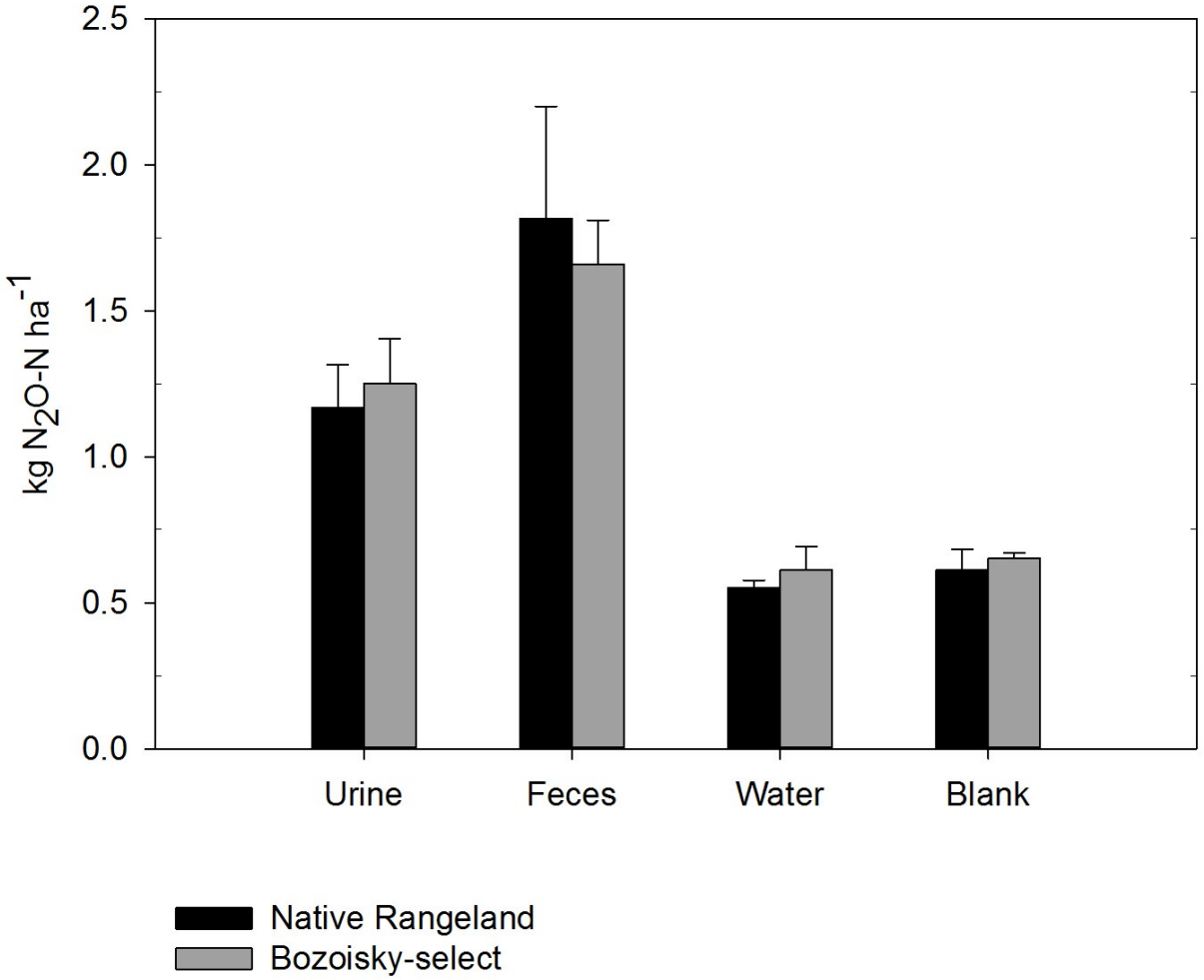


Figure 4. Cumulative nitrous oxide (N_2O) emissions from urine (U), feces (F), water (Cw), and blank (Cb) treatment soils on native rangeland (NR) and Bozoisky-select (BS) pasture.

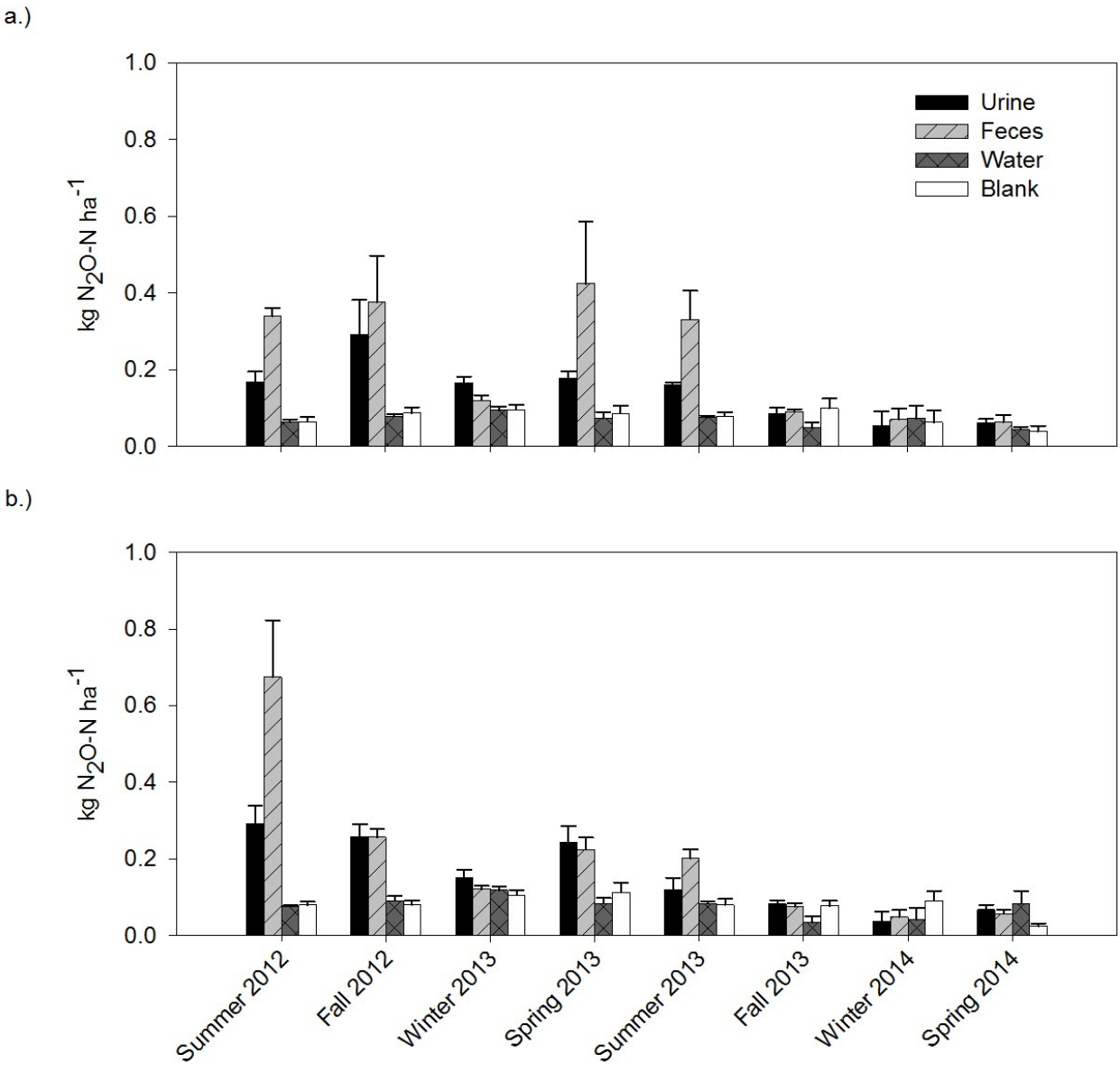
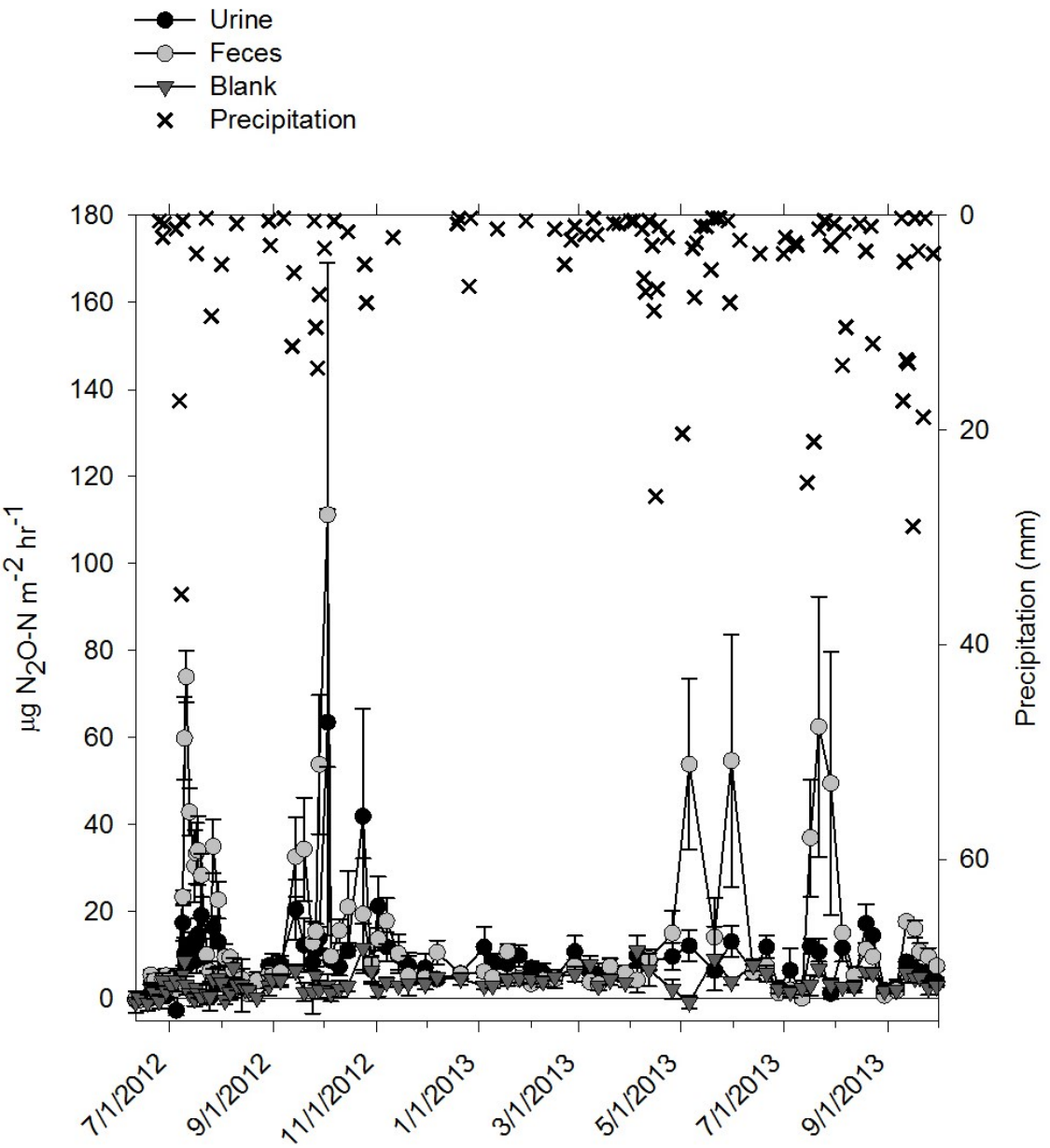


Figure 5. Cumulative seasonal N_2O fluxes (kg N_2O-N ha^{-1}) with standard deviations by treatment (urine, feces, control water, and control blank) for plant communities a.) native rangeland (NR) and b.) Bozoisky-select pasture.

a.)


Urine
Feces
Blank
Precipitation
µg N2O-N m-2 hr-1
Precipitation (mm)
180
160
140
120
100
80
60
40
20
0
0
20
40
60
7/1/2012
9/1/2012
11/1/2012
1/1/2013
3/1/2013
5/1/2013
7/1/2013
9/1/2013

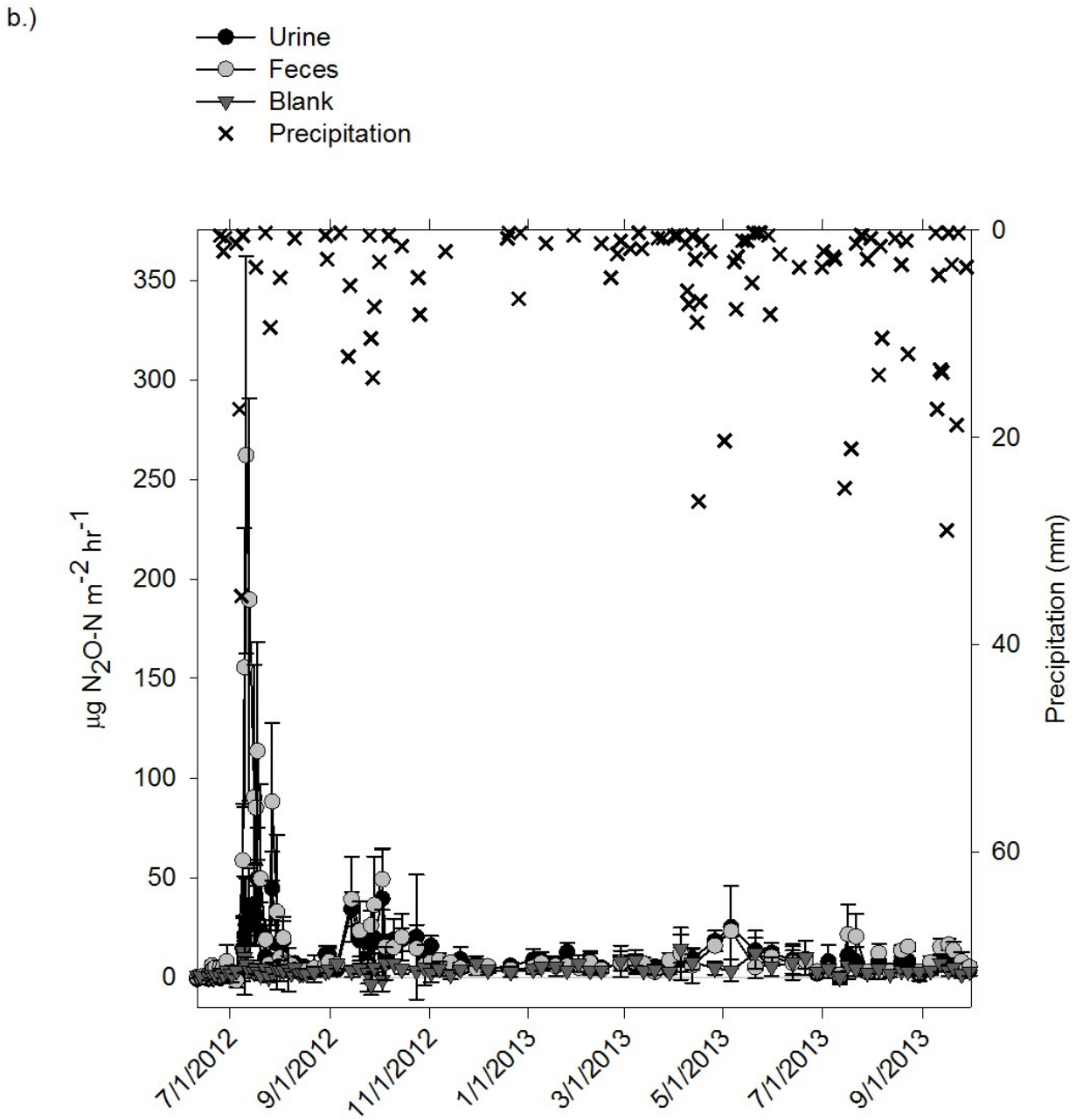


Figure 6. Average nitrous oxide (N_2O; µg N_2O-N m^{-2} hr^{-1}) fluxes ± standard errors (n = 4) for each treatment (urine, feces, control water, and control blank) from a.) native rangeland (NR) and b.) Bozoisky-select (BS) pasture soils and precipitation (mm) from 5/22/2012 to 9/30/2014.

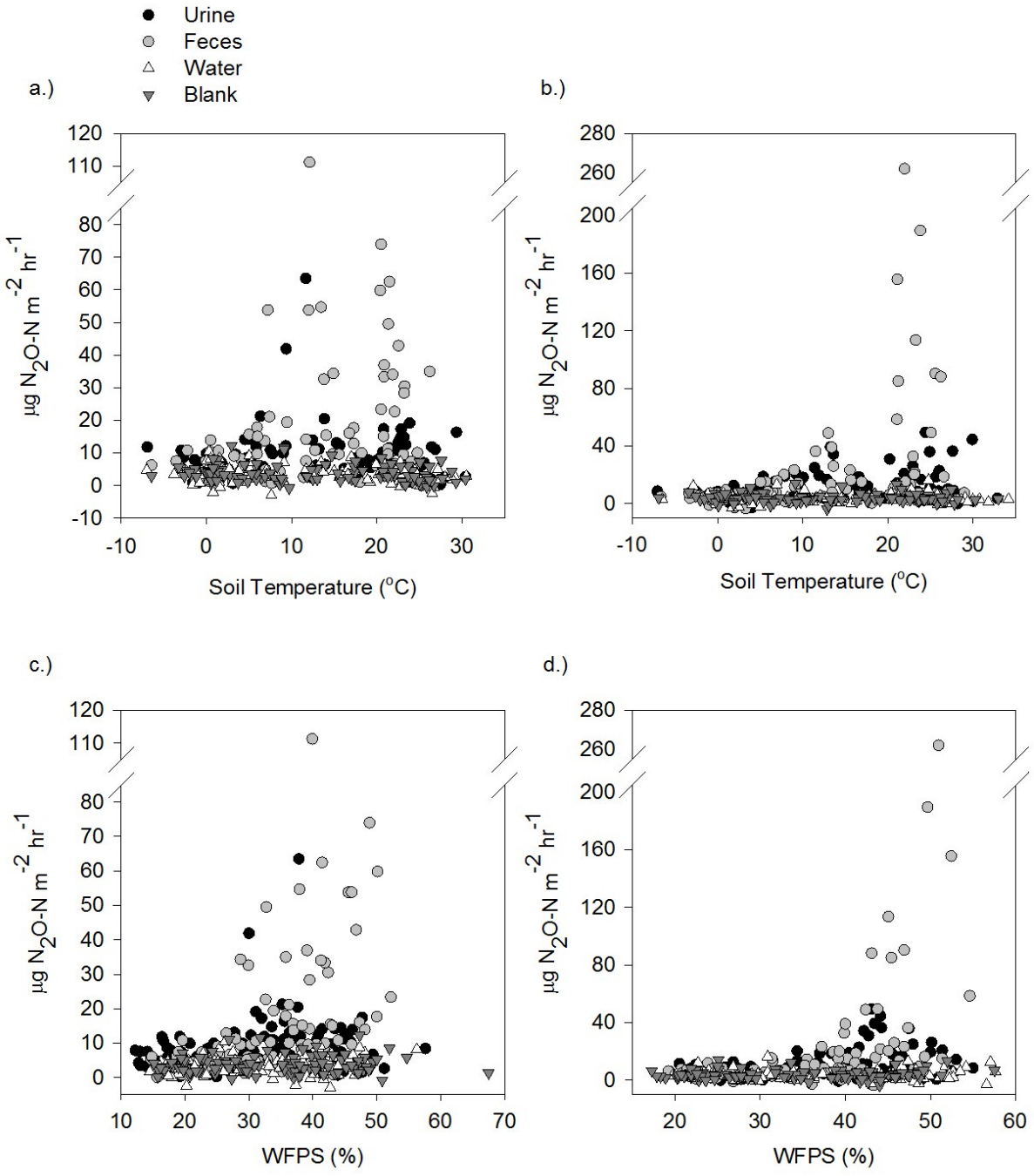


Figure 7. Nitrous oxide (N_2O) fluxes as a function of soil temperature (°C) water-filled pore space (WFPS) for urine (U), feces (F), control water (Cw), and control blank (Cb) on a.) and c.) native rangeland (NR) and b.) and d.) Bozoisky-select (BS) pasture.

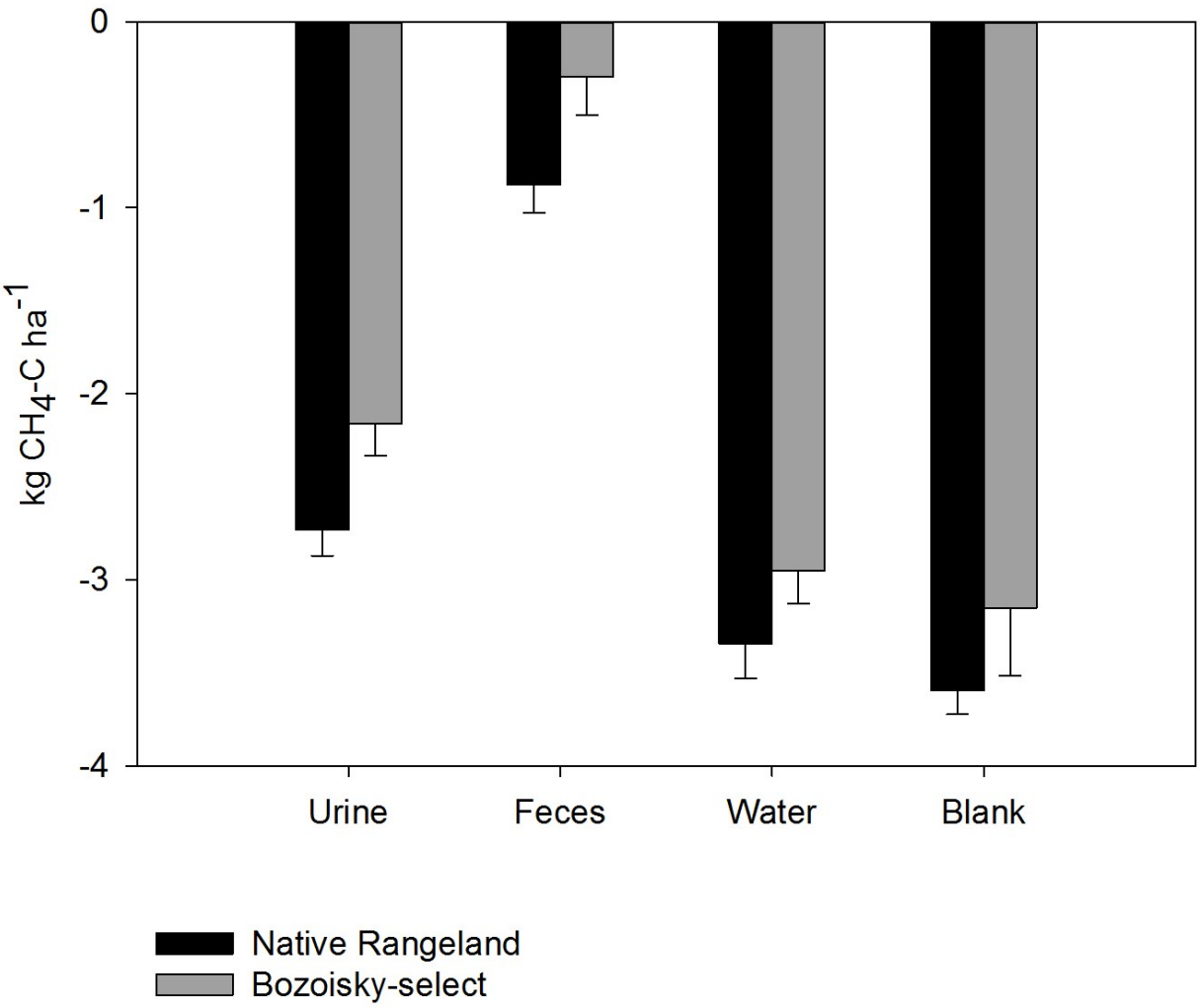


Figure 8.Cumulative methane (CH_4) emissions from urine (U), feces (F), water (Cw), and blank (Cb) treatment soils on native rangeland (NR) and Bozoisky-select (BS) pasture.

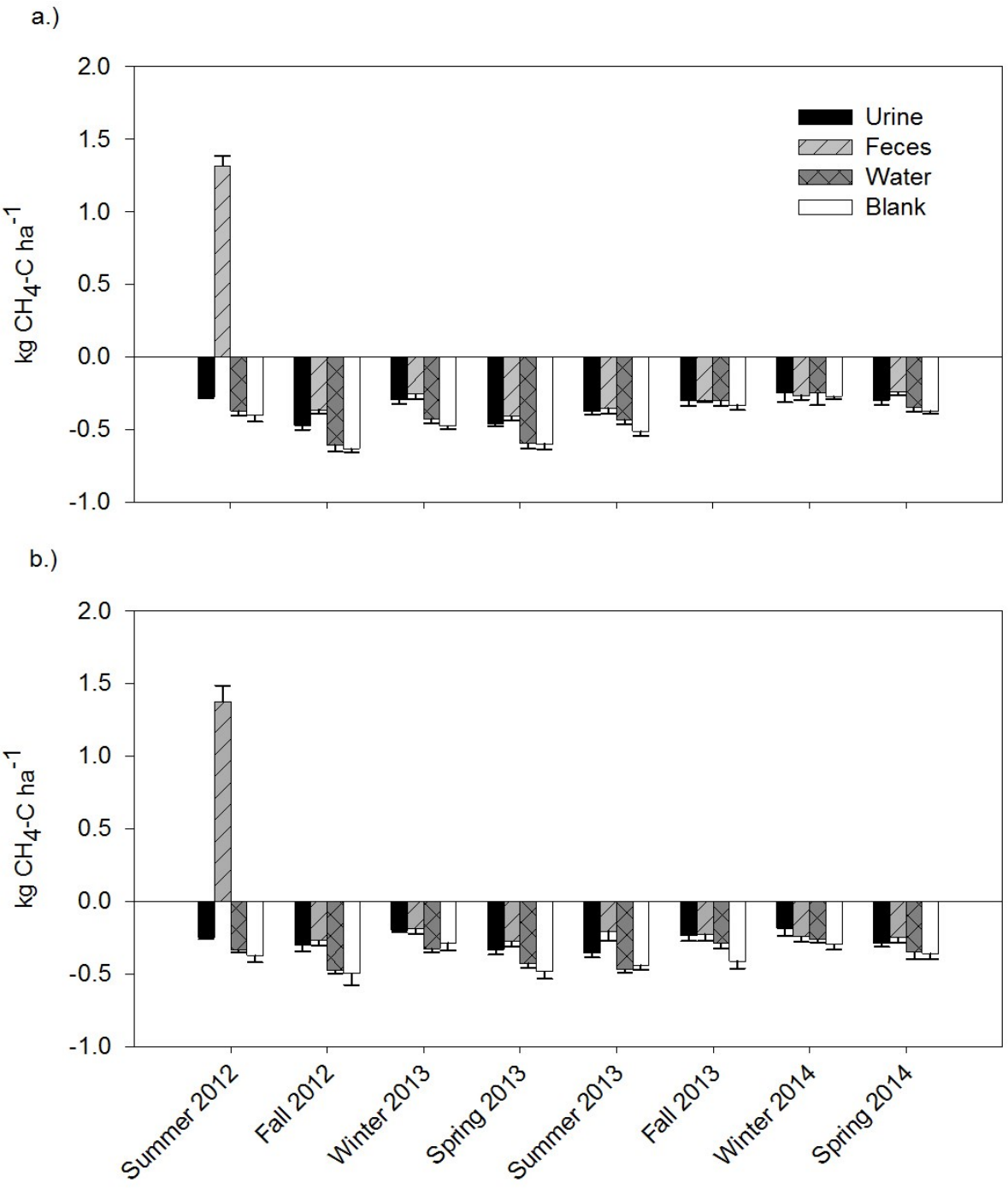


Figure 9. Cumulative seasonal methane (CH_4) fluxes (mg CH_4-C m^{-2}) with standard deviations by treatment (urine, feces, control water, and control blank) for plant communities a) native rangeland (NR) and b) Bozoisky-select pasture.

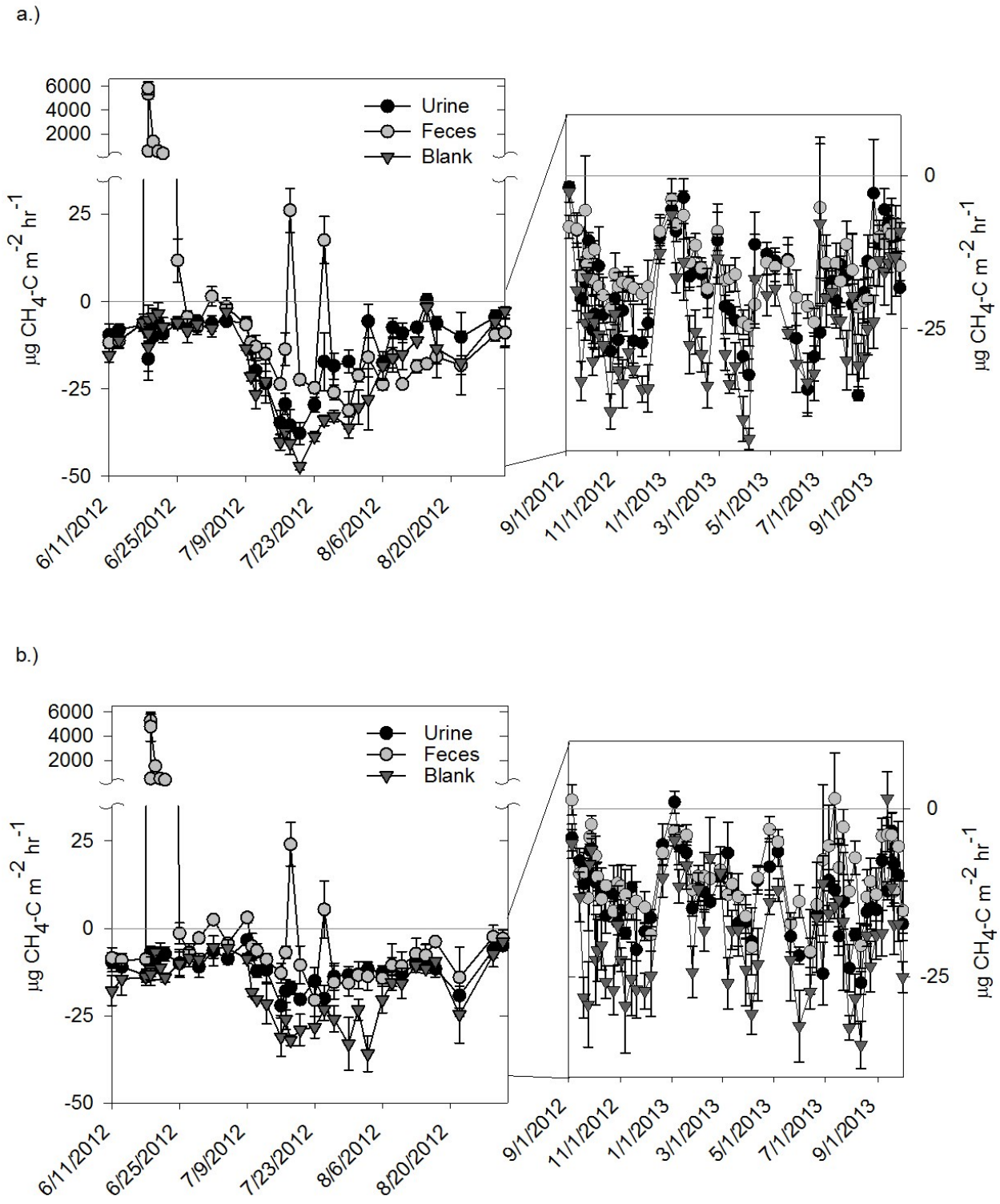


Figure 10. Average methane (CH_4) fluxes (µg CH_4-C m^{-2} hr^{-1}) ± standard errors (n = 4) for urine (U), feces (F), control water (Cw), and control blank (Cb) on a) native rangeland (NR) and b) Bozoisky-select (BS) pasture from 6/11/2012 to 9/30/2013.

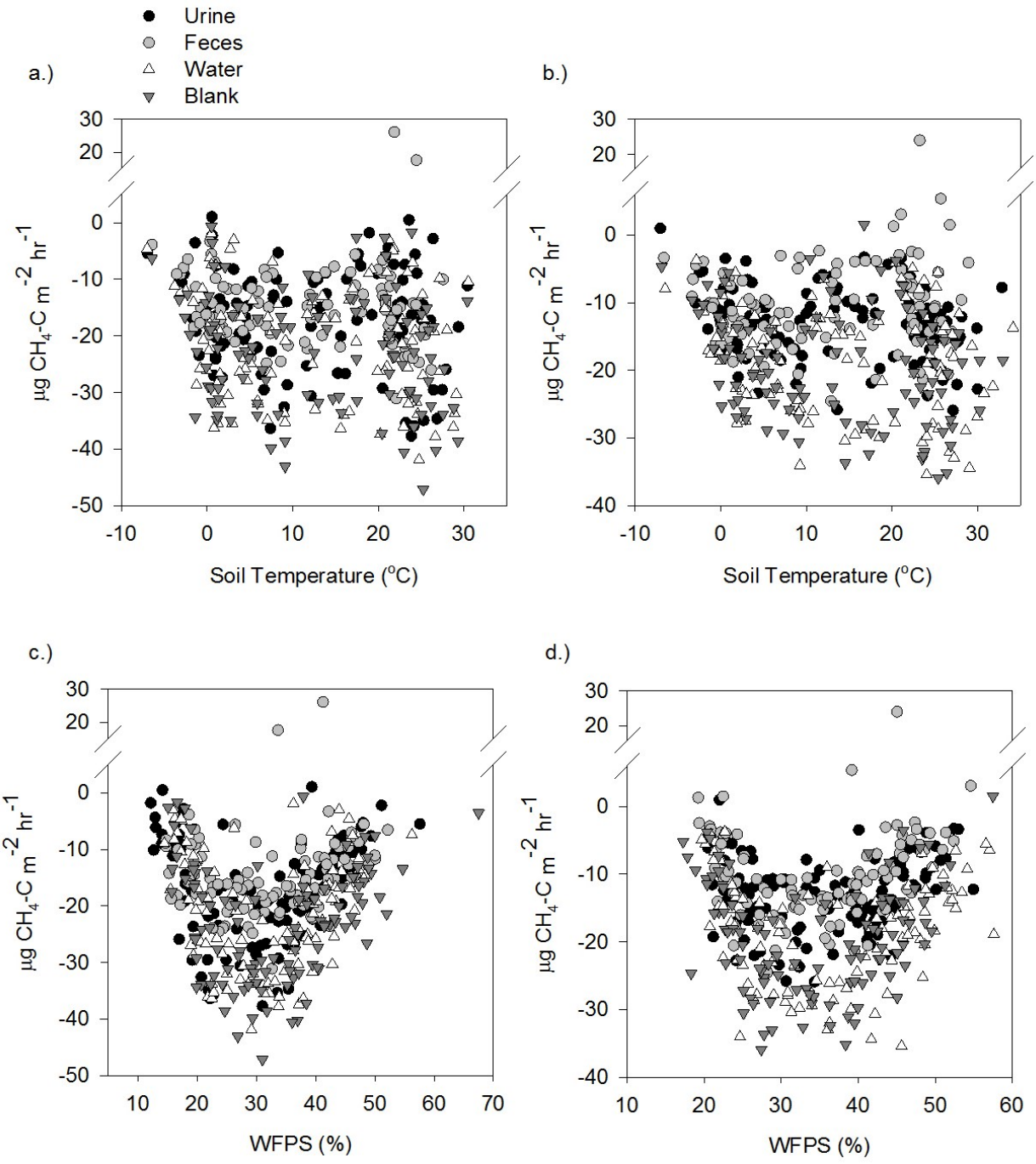


Figure 11. Methane (CH_4) fluxes as a function of soil temperature (°C) water-filled pore space (WFPS) for urine (U), feces (F), control water (Cw), and control blank (Cb) on a.) and c.) native rangeland (NR) and b.) and d.) Bozoisky-select (BS) pasture.

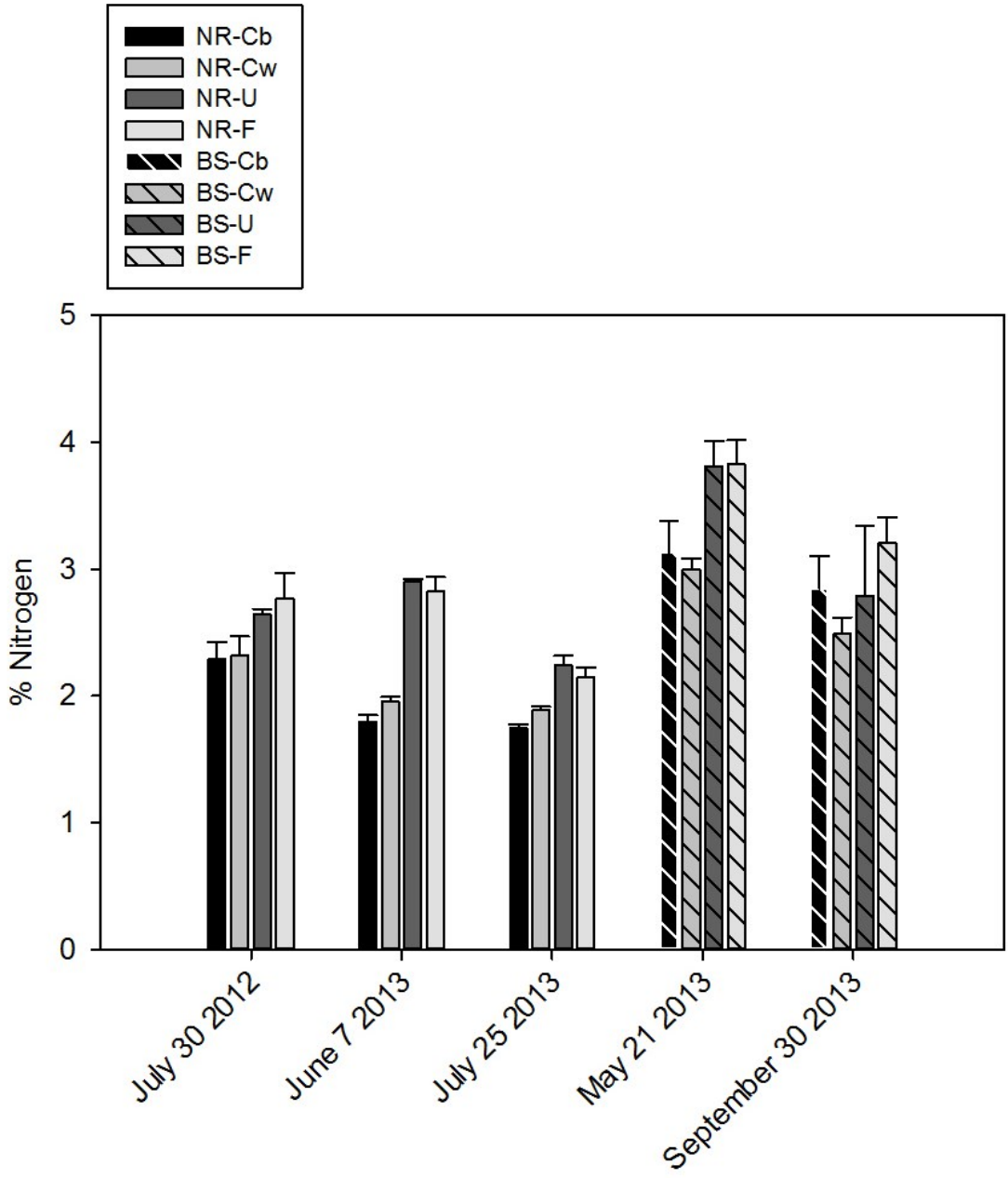


Figure 12. Nitrogen content (%) of aboveground biomass from grass clippings taken from blank (Cb), water (Cw), urine (U), and feces (F) plots during different times of the year from each plant community, native rangeland (NR) and Bozoisky-select (BS).

CHAPTER 3

TESTING DAYCENT MODEL SIMULATIONS OF GREENHOUSE GAS FLUXES FROM CATTLE EXCREMENT ON C3 PASTURE AND C4 NATIVE RANGELAND OF THE SHORTGRASS STEPPE

1. Introduction

Since the industrial revolution, atmospheric concentrations of the greenhouse gases (GHGs) methane (CH_4) and nitrous oxide (N_2O) have drastically increased. In 2013, the mean global atmospheric CH_4 concentration was 1814.1 ppb, with an approximate growth rate of 6 ppb yr^{-1} since 2007 (Arndt *et al.*, 2014). Meanwhile, the mean global concentration of N_2O was 325.9 ppb yr^{-1} in 2013 and increased at a rate of 0.92 ppb yr^{-1} from 2010 to 2013 (Arndt *et al.*, 2014). The primary contributors to the increase in atmospheric GHGs are the burning of fossil fuels, agriculture, deforestation, and land use change (Braun *et al.*, 2013). Greenhouse gases are of great environmental concern due to the molecules capacity to absorb and reemit infrared radiation and ultimately contribute to global climate change. In addition, N_2O causes the depletion of stratospheric ozone (Liu *et al.*, 2012).

Even though CH_4 and N_2O make up a relatively small proportion of the atmosphere compared to CO_2, they have much greater global warming potentials (GWP)(over a 100 year time horizon), 25 and 298 times, respectively (IPCC, 2006). Atmospheric CH_4 is the second most important long-lived GHG, accounting for 15-20% of anthropogenic GHG warming (Chen *et al.*, 2010; Cheng *et al.*, 2013). Wetlands, termites, and animal wastes are major sources of CH_4, while atmospheric hydroxyl radicals and upland soils serve as a significant CH_4 sinks.

Upland soils consume roughly 30 Tg CH_4-C yr^{-1}, which accounts for 6 to 10% of the total atmospheric CH_4 sink (Sylvia, 2005; Chen *et al.*, 2010). Agricultural soils are the primary source of N_2O, accounting for approximately one-third of the annual global N_2O budget, while grazing animals contribute >10% (Flessa *et al.*, 1996; Oenema *et al.*, 1997; Flechard *et al.*, 2005; Liu *et al.*, 2012). .

Soils can serve as a source or sink for GHGs driven by complex interactions between soil characteristics, such as water-filled pore space (WFPS) and the carbon (C) and nitrogen (N) supply, and the plant and microbial community. Under aerobic conditions, which typically occur in shortgrass steppe (SGS) soils, methanotrophs oxidize CH_4 as their sole energy source. Nitrous oxide is an intermediate by-product of the microbial-mediated processes, denitrification and nitrification, which occur under anaerobic and aerobic soil conditions, respectively. Nitrification is the dominant contributor to N_2O emissions from arable soils such as those of the SGS. Under aerobic conditions, nitrifying bacteria convert NH_4^+ to NO_3^-, with a greater ratio of N_2O:NO_3^- produced as the concentration of O_2 decreases (Sylvia, 2005).

Grazers are an integral part of the N cycle of grassland ecosystems, returning up to 80% of the N consumed through forage via excrement, urine and feces (Wachendorf *et al.*, 2008). The high concentration of N in excrement patches greatly exceeds the N demands of the affected plant community, creating potential for N_2O emissions via nitrification and denitrification. In addition to the large N returns, grazers also indirectly affect the soil temperature and moisture through the removal of vegetation and soil trampling, in turn altering the rates of nitrification and denitrification (Oenema *et al.*, 1997; Liu *et al.*, 2007; Wolf *et al.*, 2010). Grassland ecosystems occupy approximately 40% of the terrestrial land surface area globally; therefore grazing management practices are likely to have a significant impact on the global GHG budget (Kang *et*

al., 2013). Cool-season pastures are grazed in the spring and fall to complement grazing of native rangeland in semi-arid grasslands.

The Intergovernmental Panel on Climate Change (IPCC) provides guidelines for a simple approach, also known as Tier 1, for calculating cumulative N_2O emissions from various ecosystems. Default emission factors (EF) for various N inputs are calculated based on findings from research conducted at the field level. The current IPCC default EF for manure (defined as urine and feces) deposited on pasture is 2% (IPCC, 2006). Recently, researchers have suggested the need for separate EFs for urine and feces, since the proportion of feces-N emitted as N_2O tends to be less than the proportion from urine-N (van der Weerden *et al.*, 2011; Rochette *et al.*, 2014). In addition, Rochette et al. (2014) found soil texture to have a profound effect on the amount of excrement-N emitted as N_2O, highlighting the need to incorporate soil texture when determining an appropriate EF.

While the DAYCENT model's capacity to estimate N_2O fluxes from agricultural soils has been validated for many ecosystems and management practices, ranging from cropping systems to native rangeland; model validation studies are lacking for urine and feces amended grassland soils (Stehfest and Muller, 2004; Del Grosso *et al.*, 2008; Abdalla *et al.*, 2010; Zhang *et al.*, 2013; Campbell *et al.*, 2014) Stehfest et al. (2004) found a previous version of the DAYCENT model to overestimate N_2O emissions from a urine-treated New Zealand pasture soil by a factor of 3. The researchers partially attributed the overestimation to the DAYCENT assumption that a fixed proportion (2%) of nitrified-N is emitted as N_2O, since observations from urine-amended soils have provided insight that substantial nitrification rates can take place with minimal N_2O emissions. Carter et al. (2007) determined that 0.3% of nitrified urine-N was emitted as N_2O, while even lesser proportions were observed from water-amended grassland

soils. Del Grosso et al. (2008) found that model fit for N_2O from an irrigated tillage cropping system in northeastern Colorado was improved by decreasing the amount of nitrified-N emitted as N_2O from 2 to 1%. In addition, after adjusting the proportion of nitrified-N emitted as N_2O to 1%, DAYCENT simulated N_2O emissions more accurately than those calculated using the IPCC default emission factor (EF) of 2%.

The CH_4 oxidation sub-model was rigorously tested during model building, using CH_4 uptake data from various ecosystems such as the grasslands, deciduous and tropical forests, and agriculture fields. The model performed well (r^2=0.73) when comparing measured versus modeled CH_4 uptake data for the above mentioned systems (Del Grosso *et al.*, 2000b). Since the development of the CH_4 oxidation sub-model, model validation studies have been lacking. While the CH_4 oxidation sub-model has been tested using CH_4 uptake data for synthetic urine patches on native rangeland, it has not been tested with data from cool-season pasture and feces patches at the SGS.

The combination of field-based GHG measurements and biogeochemical models, such as DAYCENT, are invaluable in estimating GHG fluxes on large spatial scales. Field-based measurements provide GHG dynamics at a fine spatial scale, but are too costly to conduct continuously over a large spatial scale. Therefore, by validating the DAYCENT model with field-based N_2O and CH_4 measurements for urine and feces amended SGS soils, the model may be used to extrapolate estimates of GHG fluxes on regional, national, or even global scales for SGS soils. In addition, model testing has the potential to identify weaknesses in the model and areas where improvement is needed. Our objectives were to evaluate DAYCENT's ability to simulate N_2O and CH_4 fluxes and soil volumetric water content (VWC) and temperature from native rangeland (NR) and Bozoisky-select (BS) pasture soils treated with cattle urine (U), feces

(F), distilled water (Cw), and soils receiving no amendment (Cb) in the semi-arid Shortgrass steppe ecosystem.

2. Materials and Methods

2.1. DAYCENT Model Overview

The DAYCENT model is a daily time scale version of the CENTURY model that is of intermediate complexity, which includes site specific input parameters for soils, vegetation, weather, and land management practices. It is a biogeochemical model composed of sub-models to simulate ecosystem processes such as organic matter decomposition, biomass production, nitrate leaching, and GHG fluxes. The land surface sub-model has been shown to accurately simulate soil water and temperature dynamics in many systems, which are controlling factors on many ecosystem processes (Parton *et al.*, 1998). Once the DAYCENT model has been parameterized and validated for a particular ecosystem, estimates for ecosystem processes over a long-term time scale may be conjectured for climate and management scenarios (Cheng *et al.*, 2013; Zhang *et al.*, 2013).

The general CH_4 oxidation sub-model is primarily driven by soil volumetric water content (VWC), temperature, porosity, and field capacity (FC) in the top 15 cm of the soil profile (Del Grosso *et al.*, 2000b). When VWC is high, CH_4 oxidation, from here on referred to as uptake, is limited by gas diffusion. Under low VWC, biological activity is the limiting factor. The estimated optimum soil volumetric water content (W_{opt}) for maximum CH_4 uptake increases with FC. The maximum CH_4 uptake (CH_{4max}) rate is a function of the soil gas diffusivity coefficient (D_{opt}), which is determined based on soil bulk density (BD) and FC. Modeled CH_4 uptake is more sensitive to soil temperature when soil gas diffusivity is not limiting. A reduction

factor is also incorporated in the sub-model to account for the reduction in CH_4 uptake as a result of cultivation and fertilization. The magnitude in the reduction of CH_4 uptake is correlated to the D_{opt}, the greater the D_{opt} the greater the reduction in CH_4 uptake. The assumption that the soil-atmosphere CH_4 concentration gradient is constant is incorporated in the model. Greater detail regarding the general CH_4 oxidation model are provided in Del Grosso et al. (2000b).

The DAYCENT model accounts for both, nitrification and denitrification. Important soil variables for each of these pathways include soil texture, mineral N, VWC, pH, and temperature (Parton *et al.*, 1996). The DDCentEVI version of the DAYCENT model includes a nitrification adjustment factor that allocates a determined percentage of nitrified-N to be emitted as N_2O. The default value for this parameter is 0.6, which equals 1.2% of nitrified-N. In addition to VWC, the concentration of soil labile C is another control on denitrification rates (Del Grosso *et al.*, 2000a) and is estimated by heterotrophic respiration. Ammonium is immobile and the model assumes that it is limited to the top 15 cm of the soil profile. Conversely, NO_3^- is mobile and assumed to leach into the soil profile during DAYCENT model simulations. The movement of NO_3^- is dependent on soil water flow and plant N uptake (Del Grosso *et al.*, 2008).

2.2. Experimental Data

Data used for model testing was obtained from a SGS field experiment at the Central Plains Experimental Range (CPER) located approximately 12 km north of Nunn, Colorado (lat 40°50'N, long 104°43'W). The climate of the region is semi-arid, on average receiving 340 mm of precipitation yr^{-1}. The soils are classified as an Ascalon fine-sandy loam. Soil characteristics of the experimental site are provided in Table 1. The dominant grasses of the native rangeland include blue grama (*Bouteloua gracilis*) and buffalo grass (*B. dactyloides*). Scarlet globemallow

(*Sphaeralcea coccina*) is the most prevalent forb on the SGS. A pasture east of the CPER headquarters was seeded with an improved cultivar of Russian wildrye 'Bozoisky-select' in the fall of 1994 to complement grazing of native rangeland in the spring (April-June) and fall (October-December).

Research plots were established in a randomized block design on representative patches of native rangeland (NR) and Bozoisky-select (BS) pasture during the spring of 2012 and described in detail in Nichols (Chapter 2, this thesis). Briefly, four blocks were implemented on each plant community (NR or BS), each encompassed by an exclosure. On 19 June, 2012, steer urine (43 g N m^{-2}), steer feces (94 g N m^{-2}), and distilled water were applied to the corresponding treatment plots. Trace gas measurements began 1 hr after treatment application with subsequent samplings occurring 4 and 8 hours after application. For the remainder of the first week following treatment application, trace gas samplings were conducted daily between 9-11:00 AM. During the 2012 growing season trace gas samples were collected 3 times per week with increased sampling frequency following precipitation events. Following the 2012 growing season, trace gas measurements were conducted for an additional year and a half with sampling frequency ranging from 2-8 times per month depending on the season and climatic conditions. The grass within the research plots was periodically clipped in order to mimic grazing. Soil temperature (°C) and moisture readings (m^3 m^{-3}) for the 5-10 cm depth were recorded at the time of each trace gas sampling. Weather data was obtained from the weather station located at the CPER Headquarters. For detailed information on the trace gas sampling methodology, see Mosier et al. (2006).

2.3. DAYCENT Simulations

The rates of many ecosystem processes, such as denitrification, nitrification, and CH_4 oxidation, are affected by the levels of soil organic carbon (SOC) and mineral N, NH_4 and NO_3, in the soil. In order to initialize SOC and mineral N conditions, historical model simulations were conducted and the output files saved for initializing soil conditions for the period of interest (Del Grosso *et al.*, 2008). The native rangeland system was initialized by simulating bison grazing until 1850 and then domestic livestock grazing from 1850 to 2011. The Bozoisky-select system was initialized similarly with the exception of winter wheat cultivation from 1932 to 1955 and planting of Bozoisky-select in 1996. The resulting model output was used as initial conditions for the treatment simulations, U, F, Cw, and Cb, on Bozoisky-select pasture and native rangeland for 2012 and 2013. A CH_4 reduction function was implemented on the day of treatment application for the U and F plots to account for the effect of added N, suppressing CH_4 uptake. In order to mimic the grass clipping events, a harvest event removing 80% of the aboveground biomass was scheduled for the days that clipping occurred.

The U treatment was scheduled as a urea fertilizer application, along with an addition of 0.5 cm of water. The F addition was divided into 2 organic matter additions to account for the labile (25%) and recalcitrant (75%) C fractions. To account for the moisture (75%) in fresh feces, 1.9 cm of water was added at the time of organic matter addition. Model outputs for biomass, soil VWC and temperature (5-10 cm), and N_2O and CH_4 flux for both plant communities were saved for comparison to measured values. Since the DAYCENT model does not account for methanogenesis, measured and modeled CH_4 uptake comparison for the F plots began on 27 June, 2012, when CH_4 uptake resumed for the F plots during the field experiment. Since, the model currently does not simulate NH_3 volatilization, the IPCC (IPCC, 2006) default EF for

ammonia volatilization (20%) was subtracted from the total N applied for U and F plots, resulting in N additions of 34 g N m^{-2} and 75 g N m^{-2}, respectively. Simulations were also conducted without accounting for NH_3 volatilization in which case the total amount of N was applied 43 g N m^{-2} and 94 g N m^{-2} for treatments U and F, respectively. In addition, the simulated and measured N_2O flux data were compared to flux estimates calculated using the IPCC (IPCC, 2006) N_2O emission default (2%) for livestock manure.

3. Results and Discussion

Overall, the model did well simulating VWC (5-10 cm; r^2 = 0.55 and 0.63 for BS and NR, respectively) and soil temperature (5-10 cm; r^2 = 0.89 and 0.87 for BS and NR, respectively) (Figures 1 and 2). During April of 2013, the model overestimated VWC following a snowmelt event, specifically for the BS system. Soil temperatures were below freezing during the week prior to the overestimated VWC. In addition, the model simulated 3 cm of snow melted over this time span with 0.3 cm of runoff for each plant community. For the BS, the modeled VWC for this period was nearly double that of the measured 0.20 m^3 m^{-3}; while the modeled VWC for the NR was only slightly greater than the measured, 0.23 m^3 m^{-3}. A greater proportion of the water from the snowmelt remained in the 0-5 cm portion of the profile on the NR due to the lower sand content in the upper depths compared to the BS soil (Table 1). Snow accumulation and the resulting snowmelt are difficult to model since snow typically does not accumulate homogenously across the landscape due to redistribution by wind and variability in vegetation. While the model was able to accurately simulate peaks in VWC following precipitation events, the model predicted more rapid drainage from the soils of both plant communities than was observed.

The model significantly overestimated cumulative CH_4 uptake for all treatments from soils of both plant communities, in particular the Cw and Cb on NR (Figure 3). The DAYCENT model simulated CH_4 uptake rates under high VWC (>0.15 m^3 m^{-3}) relatively well, but significantly overestimated CH_4 uptake when VWC was low (<0.15 m^3 m^{-3}). It appears that the modeled value for W_{opt} was too low, resulting in a linear relationship between modeled VWC and CH_4 uptake. The measured CH_4 uptake and VWC data provided a bell-shaped curve for both the NR and BS systems, this relationship has been well-documented for grassland soils (Mosier *et al.*, 1996; Chen *et al.*, 2010; Dijkstra *et al.*, 2013). The measured and modeled W_{opt} values for CH_4 uptake were approximately 0.15 and 0.10 m^3 m^{-3} for both plant communities (Figures 4 and 5). Suppressed methanotroph activity has been documented from SGS soils as WFPS drops from 38 to 15% (von Fischer *et al.*, 2009). Due to the underestimated W_{opt}, the modeled output did not capture the reduction in CH_4 uptake attributed to limited biological activity from water stress when VWC was less than 0.15 m^3 m^{-3}.

The overestimation of CH_4 uptake was exacerbated when soil temperatures were relatively hot, as the modeled output was more sensitive to soil temperature than the measured data (Figures 6 and 7). The coarse-textured soils of the experimental site and the extremely dry soil conditions in 2012 likely provided maximum soil gas diffusivity, thus increasing the model's sensitivity to soil temperature (Del Grosso *et al.*, 2000b). Soils were also dry during the winter and soil temperatures were much lower. Therefore, the magnitude of the overestimation of CH_4 uptake was not as great when compared to summer months (Figures 8 and 9). As a result, the model fit was much better during the winter (December – March) (NR Cb: r^2=0.19, BS Cb: r^2=0.30) compared to the summer (June-September) (NR Cb: r^2=0.02, BS Cb: r^2=0.10). In addition, the modeled CH_{4max} for the soils of both plant communities were approximately 50%

greater than the measured rates, 16.95 g C ha^{-1} compared to 11.31 g C ha^{-1} for NR Cb and 12.34 g C ha^{-1} compared to 8.62 g C ha^{-1} for BS Cb. The modeled CH_{4max} was greater from the NR compared to the BS soils due to the greater estimated diffusivity of the NR soils. Modeled CH_{4max} occurred during periods when the soil was the hottest and driest, when biological activity was likely inhibited (Figures 4-7). The average measured and modeled CH_4 uptake rates for NR Cb were 5.2 and 13.2 g C ha^{-1} d^{-1}, while the average uptake rates for BS Cb were 4.4 and 8.9 g C ha^{-1} d^{-1}, respectively. Average CH_4 uptake rates for temperate grasslands have been found to range between 5 and 10 g C ha^{-1} d^{-1} (Mosier *et al.*, 1996; Chen *et al.*, 2010). Since the model output for CH_4 uptake is based on soil temperature and VWC dynamics in the top 0-15 cm, future field studies should incorporate higher resolution soil temperature and moisture measurements in addition to CH_4 flux data to allow for a better measured to modeled comparison.

The addition of U and F reduced CH_4 uptake in the modeled output, as was observed with the measured data (Figure 3). Reduction in CH_4 uptake was greater on the NR compared to BS system as a result of greater D_{opt} on the NR system. The model assumes that CH_4 uptake is more affected by fertilization and cultivation events in soils with high gas diffusivities (Del Grosso *et al.*, 2000b). Modeled cumulative CH_4 uptake estimates for U and F plots were 39 and 45% less than Cb from NR soil and 18 and 27% less than Cb from BS soil, respectively. While the modeled magnitude of reduction for CH_4 uptake from the U and F plots adequately represented the measured data for BS soils, the model overestimated the magnitude of reduction by a factor of approximately 3 for the NR soils.

Measured and modeled cumulative N_2O emissions (kg N_2O-N ha^{-1}) agreed reasonably well from the F, Cw, and Cb plots from soils of both plant communities, NR and BS (Figure 10).

The model overestimated N_2O emissions from the U treatment plots by a magnitude of 4 and 5 for NR and BS soils, respectively. Despite the model overestimate when compared to the measured fluxes, the EFs calculated from the DAYCENT model output were a better representation of the measured data than the IPCC Tier 1 (IPCC, 2006) default EF (2%) for cattle manure on grazed pasture (Table 2). Cumulative N_2O emissions based on the IPCC 2% EF resulted in an overestimation by a factor of 8 and 12 for U and F, respectively. Insignificant reductions in cumulative N_2O emissions from the U and F treatment plots were observed in the model output after accounting for the IPCC default (20%) for NH_3 volatilization. Due to the hot, dry conditions during the time of treatment application, more than 20% of the excrement N may have been volatilized as NH_3 (Ball and Ryden, 1984).

The DAYCENT model accurately simulated trends in N_2O emissions following precipitation events for all treatments, but the magnitude of the modeled emissions were significantly highly than measured emissions (Figures 11 and 12). The magnitude of the modeled output was typically 2 to 4 times greater than the measured emissions for the Cb and Cw treatments following significant precipitation events for BS and NR soils, respectively. For example, the modeled N_2O emissions from the U treatment following a substantial precipitation event (53 mm) in early July of 2012 were overestimated by a factor of 9 and 16 for BS and NR, respectively. The timing and magnitude of N_2O emissions from F plots were represented relatively well with the exception of the model underestimating N_2O emissions following precipitation events in July and September for BS and NR, respectively. The model tended to overestimate N_2O emissions during periods of relatively high VWC (>10 and 15% for NR and BS, respectively) for Cb, Cw, and U treatment plots (Figures 13 and 14). Due to the governing importance of WFPS on nitrification rates, the overestimation of VWC following a snowmelt

event during April of 2013, led to an overestimation of N_2O emissions from all the treatments on both plant communities even though the soil temperatures were slightly above 0 °C (Figures 15 and 16). While the F treatment measured and modeled comparison of N_2O emissions as a function of soil temperature and VWC agreed reasonably well, a portion of the emissions are likely a result of processes occurring within the feces patch itself and not the underlying soil. Therefore decent model results may have been obtained for the wrong reasons.

The concentration of soil NH_4^+ is another primary driver of nitrification rates. While this study lacked substantial soil mineral-N data, a measured versus modeled comparison of the baseline average soil mineral-N data from the NR Cb plots (n=8, 23 July 2013), illustrates that the model overestimated soil NH_4^+ and NO_3^- concentrations in the top 0-15 and 5-20 cm depths for both plant communities, respectively (Figure 17). In addition, the model also overestimated (0.77 g N m^{-2}) the N content in the aboveground plant biomass for NR vegetation when compared to measured values (avg. = 0.27 g N m^{-2}; n = 4) from plant clippings taken from the NR Cb plots in July 2013. Simulated N contents of aboveground biomass for the U and F plots on NR were overestimated by approximately a factor of 2 (Simulated: U = 1.17 g N m^{-2} and F = 1.30 g N m^{-2}; Measured: U = 0.61 g N m^{-2} and F 0.53 g N m^{-2}). Over a 21-year span (1992-2012), the model consistently overestimated total aboveground biomass production from the native rangeland (Figure 18). The overestimation of N in the soil mineral-N pool and aboveground plant biomass may be due to the model underestimating the N fraction immobilized in microbial biomass (Bontti *et al.*, 2011). Naturally occurring N-inputs at the SGS through NH_3 deposition and N-fixation are highly uncertain and therefore the model may have also overestimated (0.8 g N m^{-2} yr^{-1}) this source of N, resulting in a greater estimate of total system N. In order to better understand N turnover, in particular nitrification rates, from SGS soils future

field studies should include several soil mineral-N samplings to accompany trace gas measurements for model validation purposes.

Essentially all of the model output N_2O emissions were attributed to nitrification (99.8%). We were not able to elucidate the actual driving mechanism of the observed N_2O emissions due to a lack of soil mineral-N and oxygen concentration data during the periods of great N_2O flux activity. Although, it appears that N_2O emissions were primarily due to nitrification since the measured WFPS never exceeded 60% during the time of trace gas samplings (Sylvia, 2005). Through laboratory experiments using C_2H_2 to inhibit nitrifier activity, Parton et al. (1988) found nitrification to be the primary pathway contributing to N_2O emissions at the SGS, accounting for 60-80% of annual emissions. Kool et al. (2006a) found that using an artificial urine solution that does not contain hippuric acid, a constituent of urine, could lead to an overestimation of N_2O emissions up to 50%. Model simulations did not account for inhibited microbial activity for the U treatment; therefore this could have also been a source for the overestimation of N_2O emissions.

A previous DAYCENT model validation study found that the model underestimated nitrification rates, while overestimating the proportion (2%) of nitrified-N emitted as N_2O from urine amended soils (Stehfest and Muller, 2004). It has been documented that significant rates of nitrification can take place with minimal N_2O production, 0.01-0.02% and 0.29% moles of N_2O lost to moles of NO_3^- produced, for grassland soils amended with water and cattle urine, respectively (Stehfest and Muller, 2004; Carter, 2007). Therefore the default setting of 1.2% for the proportion of nitrified-N emitted as N_2O used in the present study may be an overestimation for this particular system. As a result of the well aerated-coarse soils and dry conditions, it is likely that the nitrification pathway was carried out to near completion, converting the majority

of nitrified-N to NO_3^- with minimal N_2O emissions. Thus, the overestimation of N_2O emissions observed in this model validation study may be partially attributed to the assumption that 1.2% of nitrified-N is emitted as N_2O.

The ratio of N_2O-N:NO-N produced during nitrification did not appear to be a factor in the overestimation of N_2O emissions, as the ratio was toward the lower end of the range that is reported in the literature. Previous research has shown that the N_2O-N:NO-N ratio is relatively high (>120) immediately following urine application, but the ratio decreases within days to values around 1. The magnitude of the decrease in the ratio is dependent on variables such as urine-N concentration, climate, and soil conditions (Clough *et al.*, 2003; Khan *et al.*, 2014). The model estimated ratio from all the treatments over the course of the experiment varied from 0.08 to 0.47, while the highest ratios were from the U and F plots on BS pasture. We presume that NO_x emissions were relatively high during the course of the field experiment due to the coarse-textured soils, prolonged periods of drought, and high soil temperatures; therefore these ratios appear reasonable (Martin *et al.*, 1998; Mosier *et al.*, 2008).

4. Conclusions

The DAYCENT model did well simulating soil temperature and VWC with the exception of significantly overestimating the VWC following a snowmelt event in April of 2013. A better simulation of VWC following snowmelt events is needed in order to accurately model CH_4 and N_2O fluxes during freeze-thaw events. While the model performed well simulating trends in reduced CH_4 uptake when diffusion was limited during periods of high VWC, it did poorly under low VWC when biological activity was limited. The model overestimated maximum CH_4 uptake rates and the magnitude of the reduction in CH_4 uptake resulting from U and F additions on NR.

Simulation of maximum CH_4 uptake rates may be improved by increasing the model's sensitivity to biological limitation under water stress soil conditions. While the N_2O EFs for U and F calculated from the DAYCENT model output represented the measured EFs better than the IPCC default of 2%, the modeled output may be improved by assigning a lower nitrification adjustment factor for model simulations of urine amended SGS soils. Multiple soil mineral-N measurements from urine and feces patches on SGS soils are needed in order to verify that the model is accurately simulating rates of nitrification. Furthermore, model fit for N_2O emissions and aboveground biomass may be improved by lowering the amount of background N present in the soil mineral-N pool.

Table 1. Soil characteristics for the Bozoisky-select (BS) pasture and native rangeland (NR) for the top 20 cm.

Site	Depth	Sand	Silt	Clay	Bulk density
	cm	----------*%*----------			*g cm^{-3}*
Bozoisky-select					
	0-5	83	12	5	1.46
	5-10	83	12	5	1.45
	10-20	84	11	5	1.43
Native Rangeland					
	0-5	63	28	9	1.16
	5-10	72	18	10	1.37
	10-20	76	14	10	1.34

Table 2. Nitrous oxide (N_2O) emission factors (EF) for IPCC default, DAYCENT model output, and measured data.

		Emission Factor	
Site	Method	Urine	Feces
		----------*%*--------	
Bozoisky-select			
	IPCC	2	2
	DAYCENT	1.06	0.08
	Measured	0.14	0.11
Native Rangeland			
	IPCC	2	2
	DAYCENT	0.79	0.07
	Measured	0.13	0.13

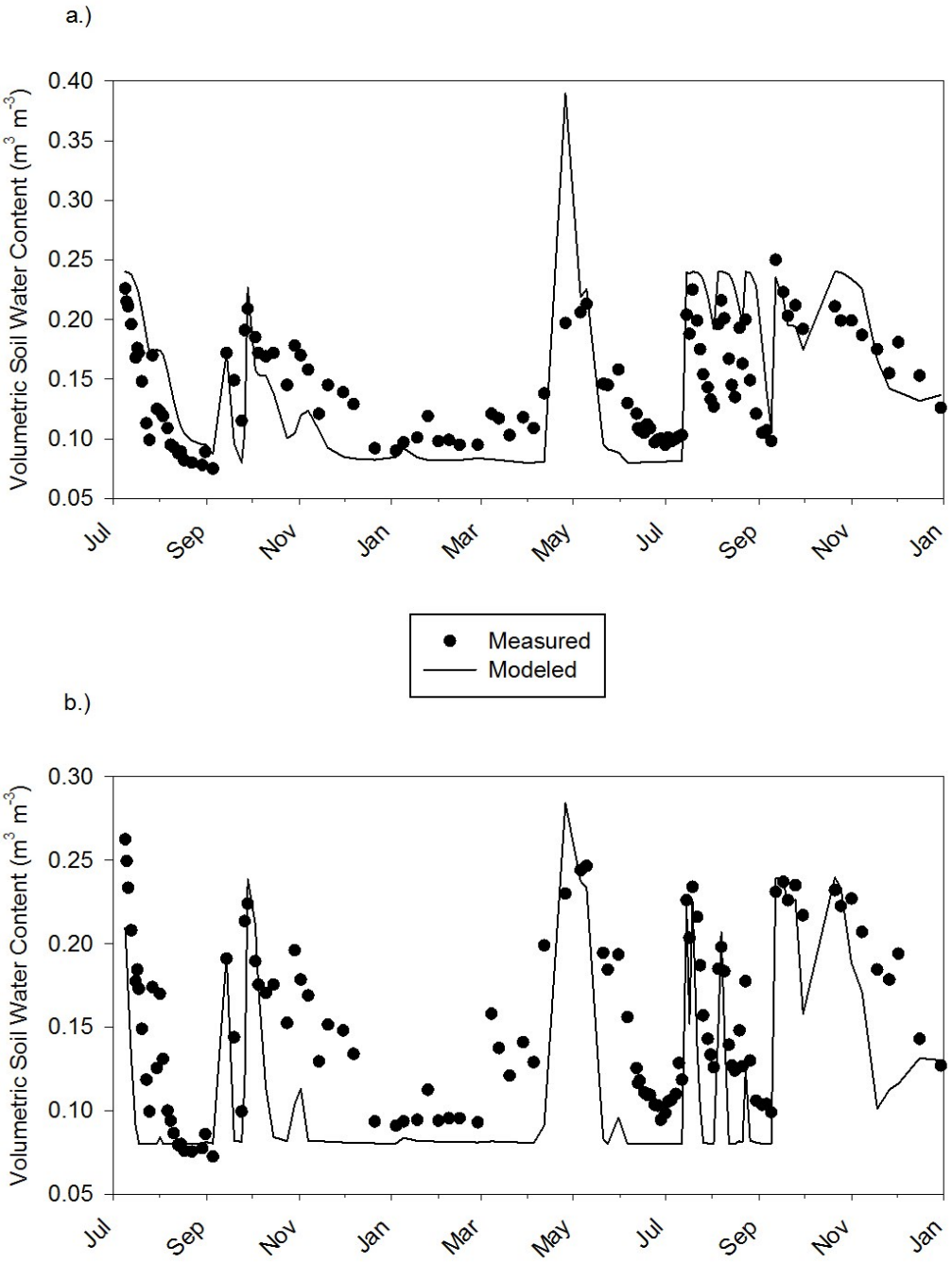


Figure 1. Measured versus modeled volumetric soil water content (m^3 m^{-3}; 5-10 cm) for a.) Bozoisky-select (BS) and b.) native rangeland (NR) from 9 July, 2012 - 31 December, 2013.

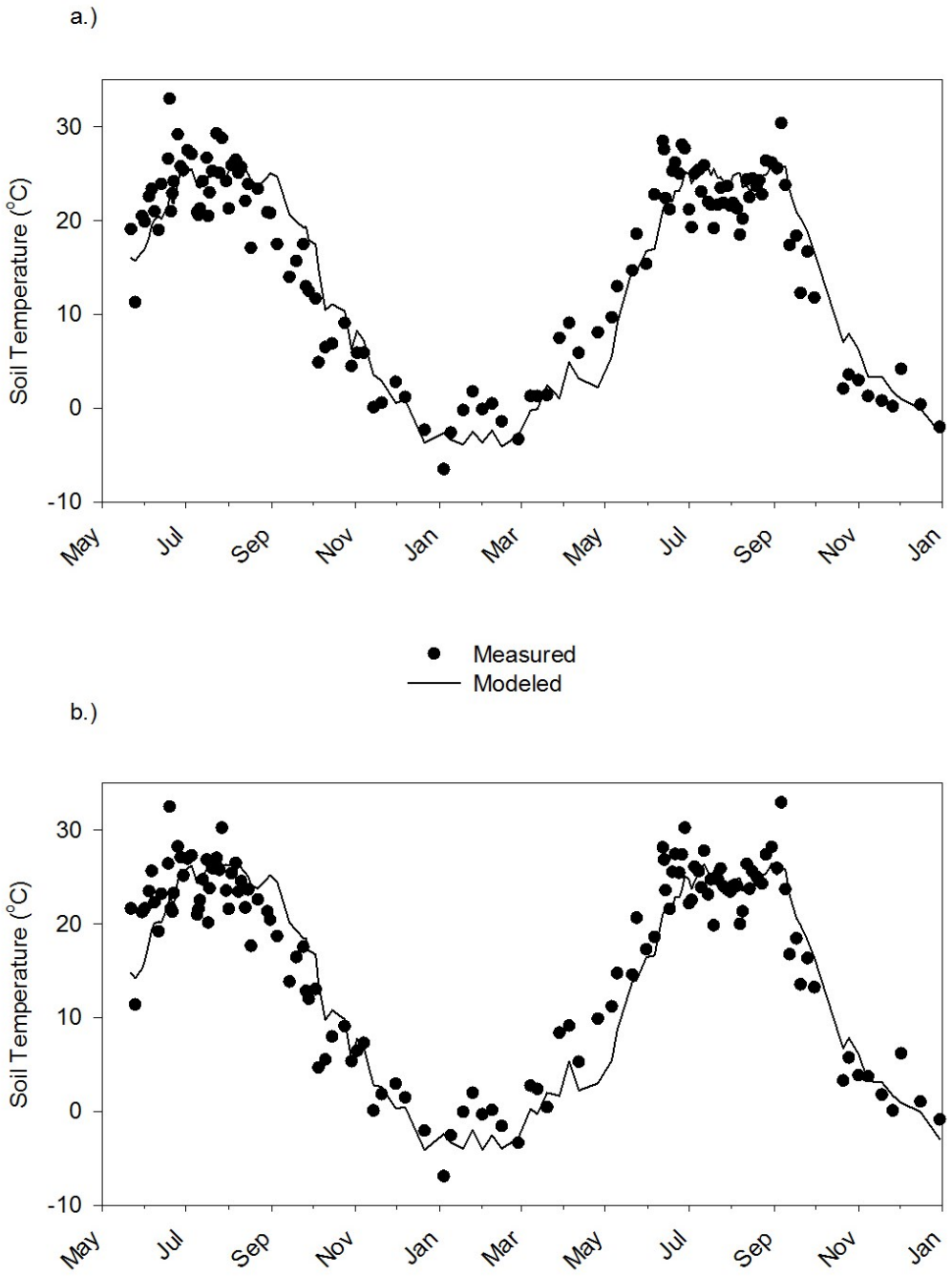


Figure 2. Measured versus modeled soil temperature (°C; 5-10 cm) for a.) Bozoisky-select (BS) and b.) native rangeland (NR).

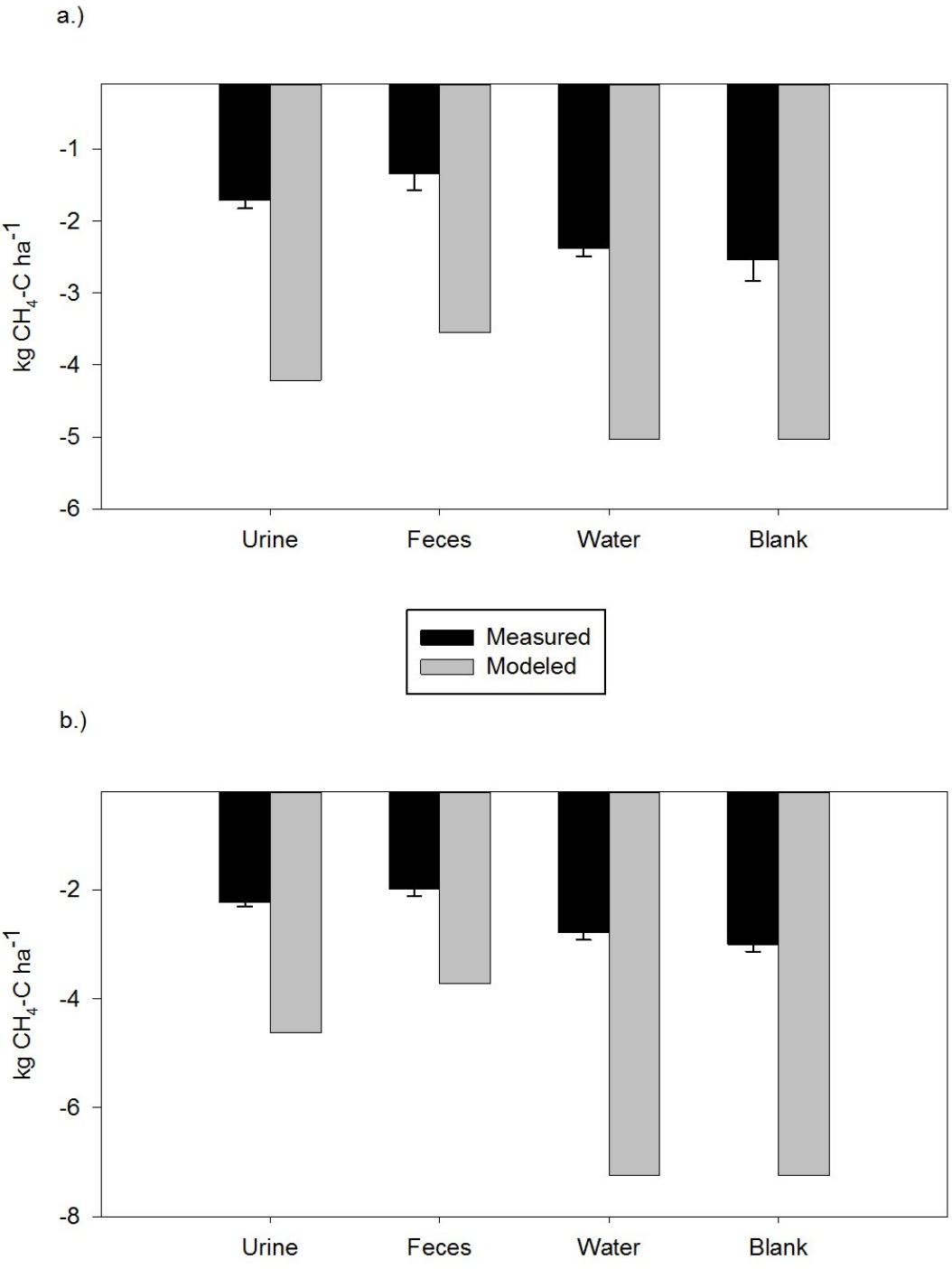


Figure 3. Measured and modeled cumulative methane (CH_4) uptake (kg C ha^{-1}) for urine (U), feces (F), water (Cw), and blank (Cb) plots and standard error for Bozoisky-select (BS) pasture (a) and native rangeland (NR) (b). Cumulative CH_4 uptake for U, Cw, and Cb plots were calculated from 6/19/2012 to 12/31/2013; while emissions for the F treatment was calculated from 6/27/2012 to 12/31/2013 in order to omit periods of methogenesis since the DAYCENT model does not have a CH_4 production sub-model.

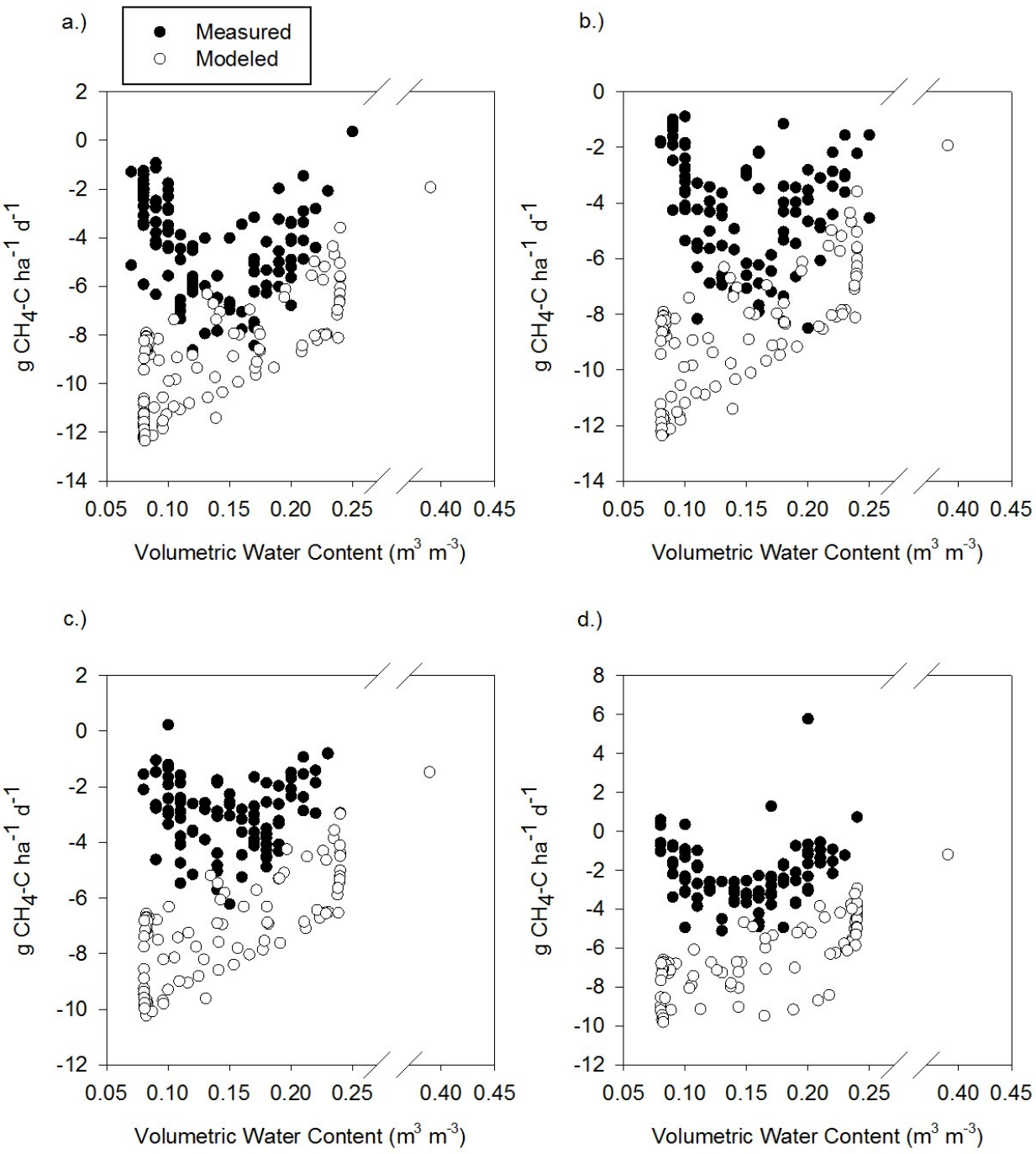


Figure 4. Measured and modeled methane (CH_4) uptake as a function of volumetric water content (m^3 m^{-3}) for a.) blank (Cb), b.) water (Cw), c.) urine (U), and d.) feces (F) plots on Bozoisky-select (BS) pasture.

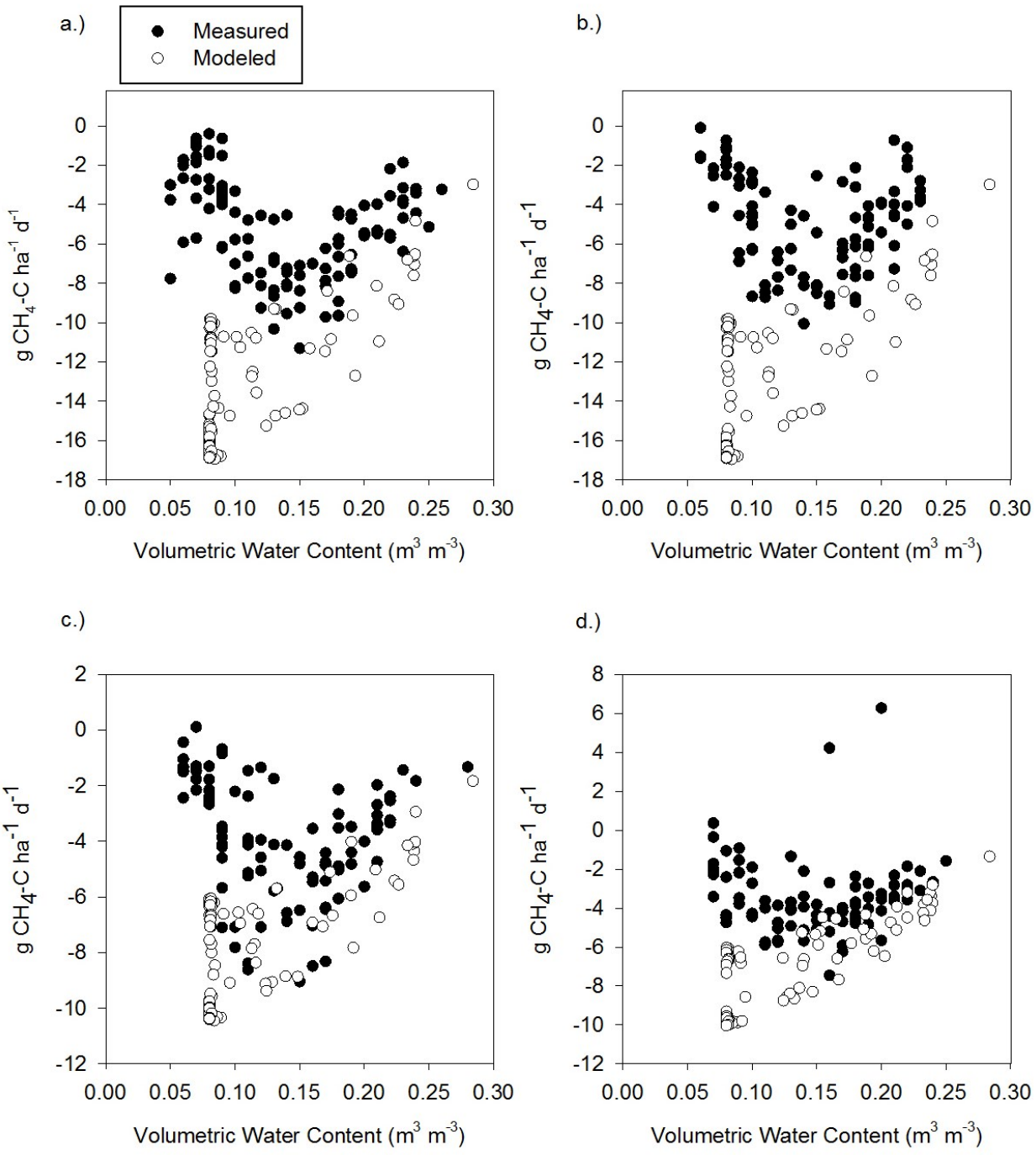


Figure 5. Measured and modeled methane (CH_4) uptake as a function of volumetric water content (m^3 m^{-3}) for a.) blank (Cb), b.) water (Cw), c.) urine (U), and d.) feces (F) plots on native rangeland (NR) pasture.

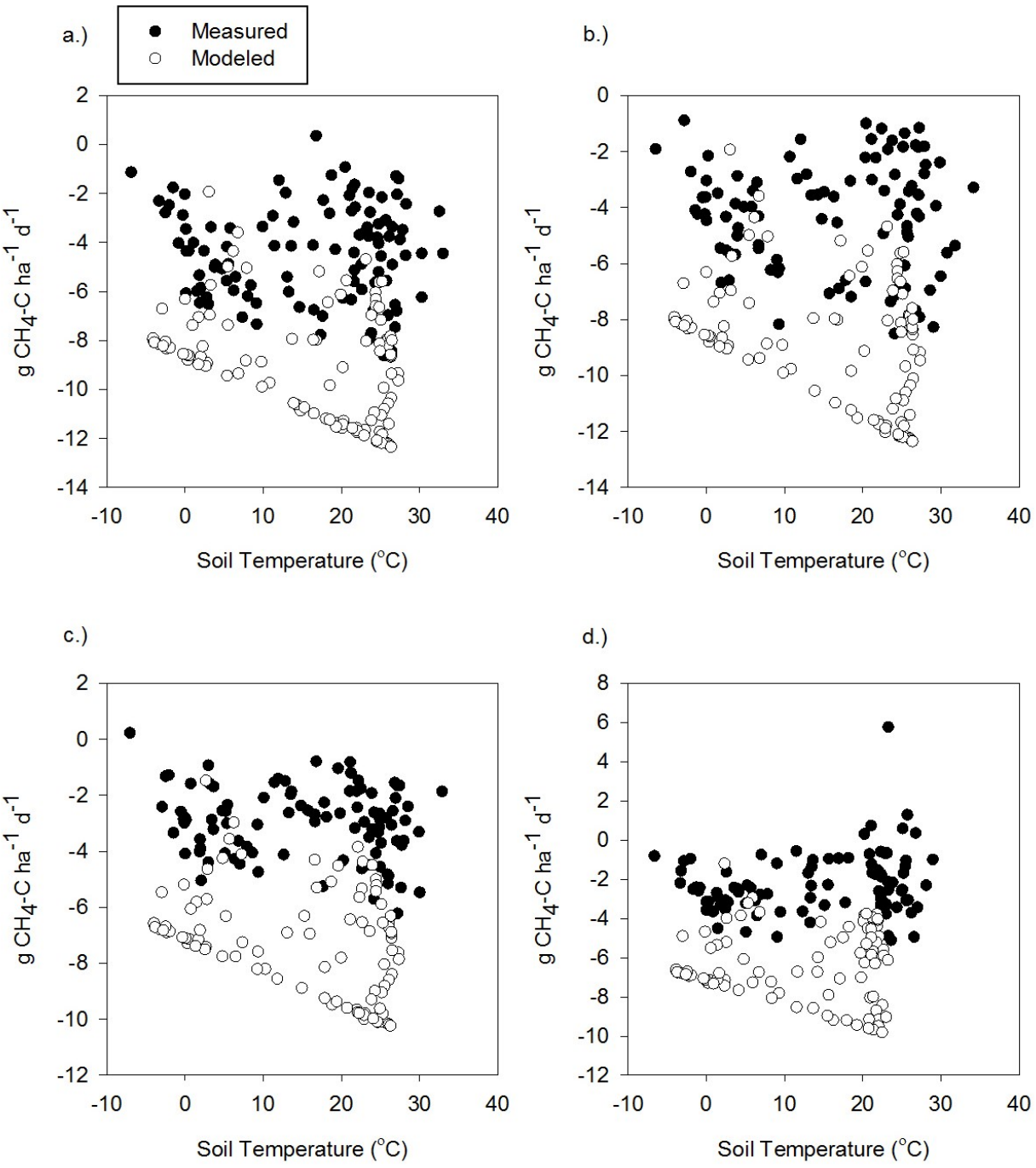


Figure 6. Measured and modeled methane (CH_4) uptake as a function of soil temperature (°C) for a.) blank (Cb), b.) water (Cw), c.) urine (U), and d.) feces (F) on Bozoisky-select (BS) pasture.

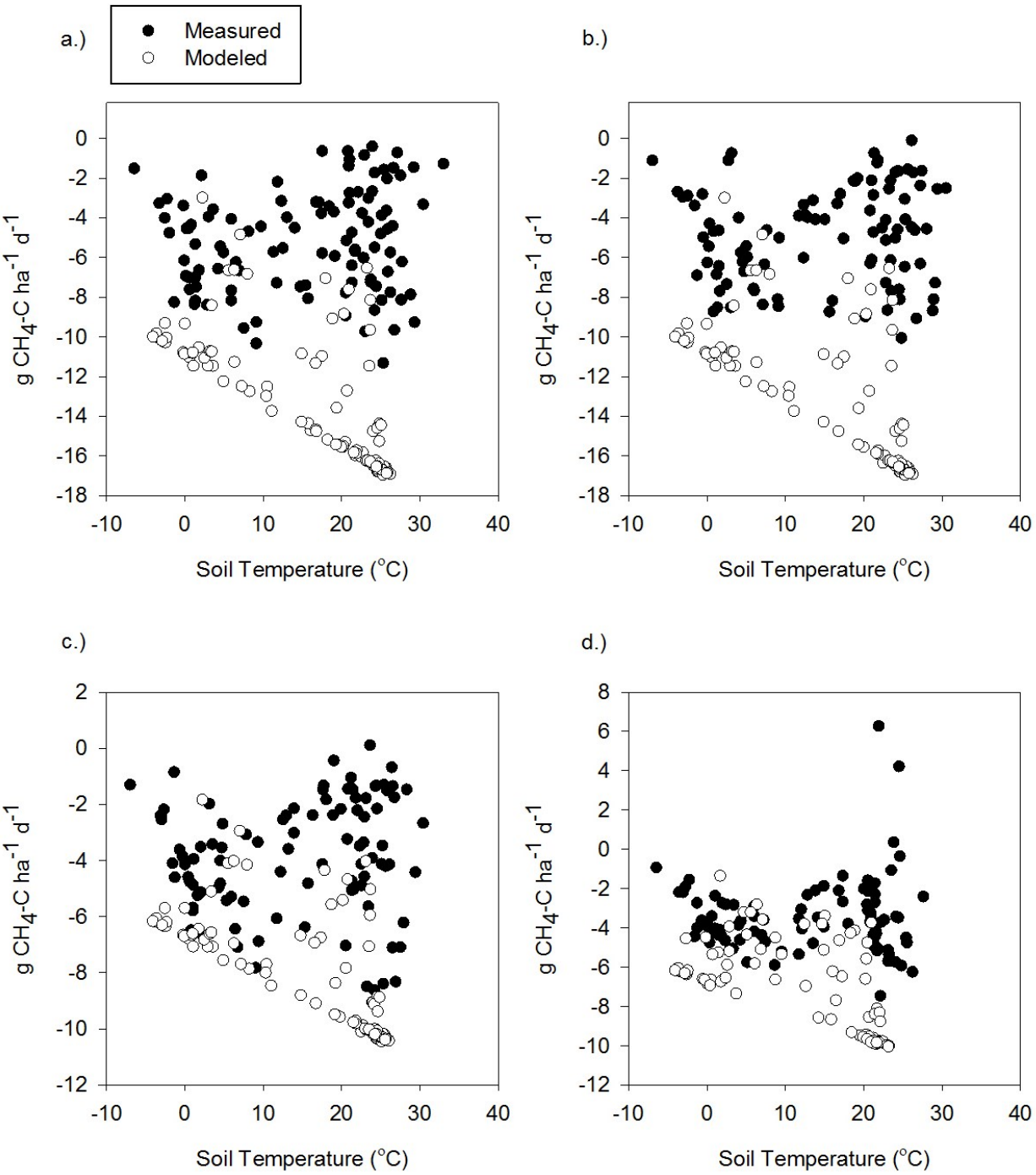


Figure 7. Measured and modeled methane (CH_4) uptake as a function of soil temperature (°C) for a.) blank (Cb), b.) water (Cw), c.) urine (U), and d.) feces (F) on native rangeland (NR).

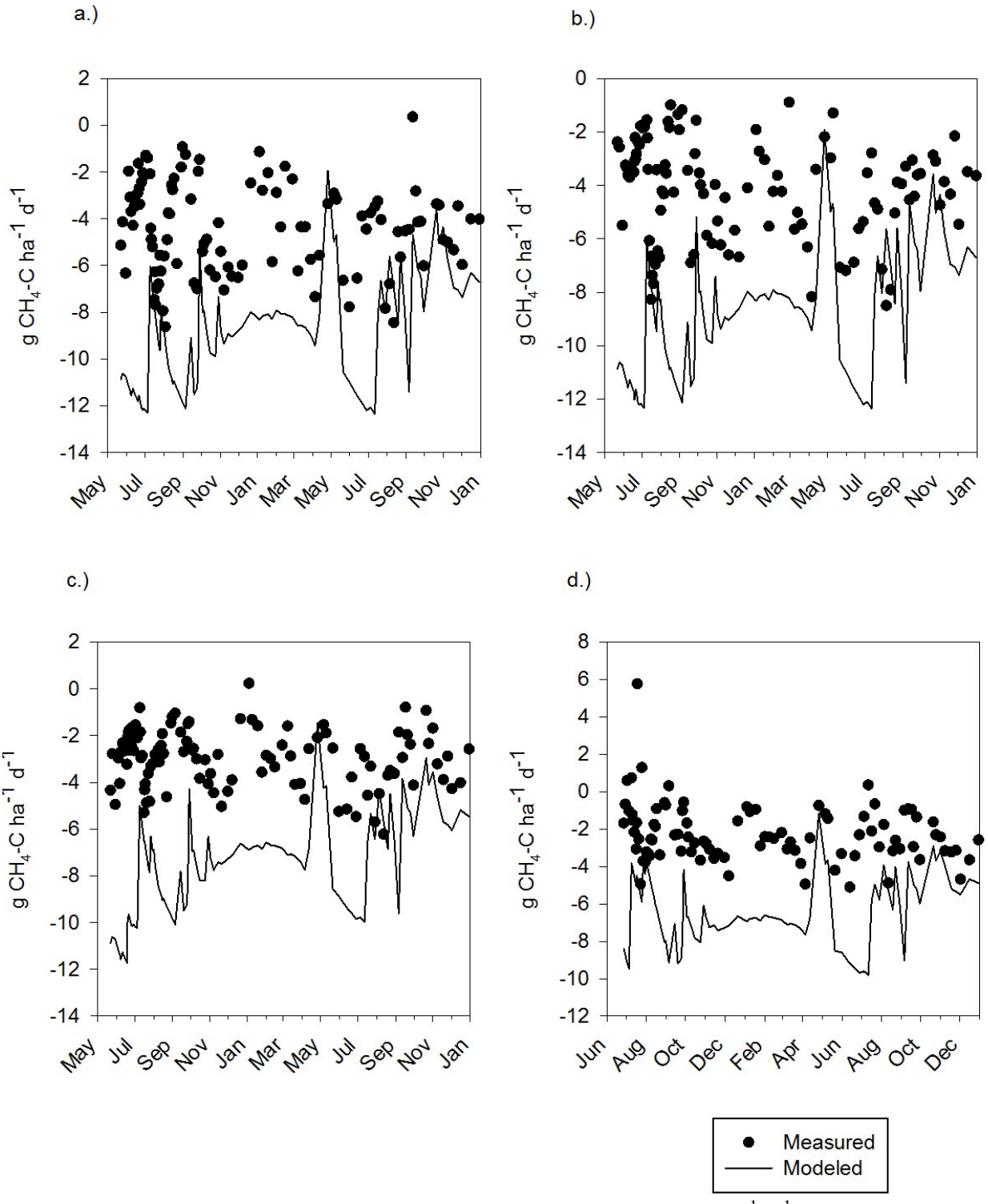


Figure 8. Measured versus modeled daily methane (CH_4) uptake (g C ha^{-1} d^{-1}) for a.) blank (Cb), b.) water (Cw), c.) steer urine (U), and d.) feces (F) on Bozoisky-select (BS) pasture.

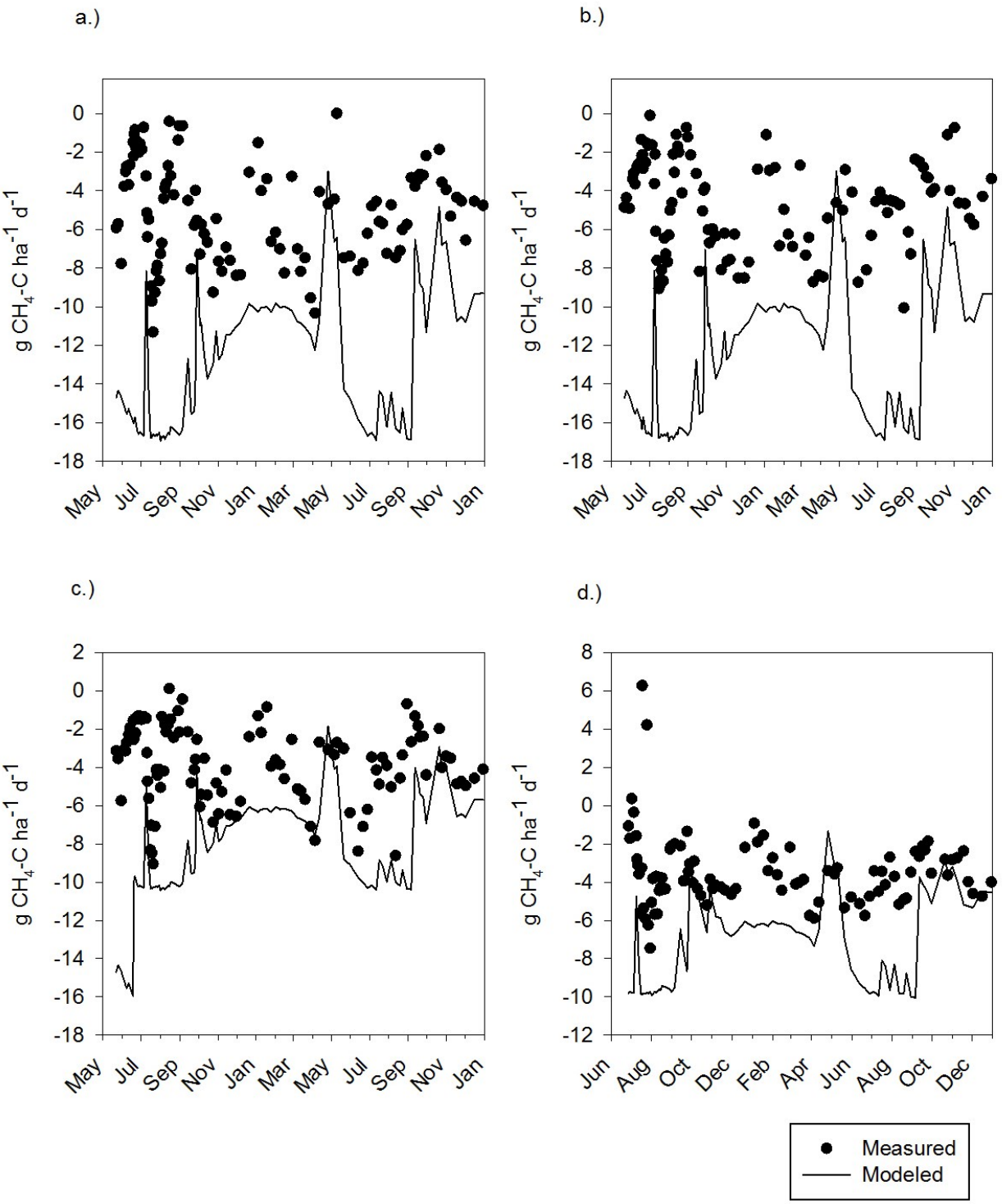


Figure 9. Measured versus modeled daily methane (CH_4) uptake (g C ha^{-1} d^{-1}) for a.) blank (Cb), b.) water (Cw), c.) steer urine (U), and d.) feces (F) on native rangeland (NR).

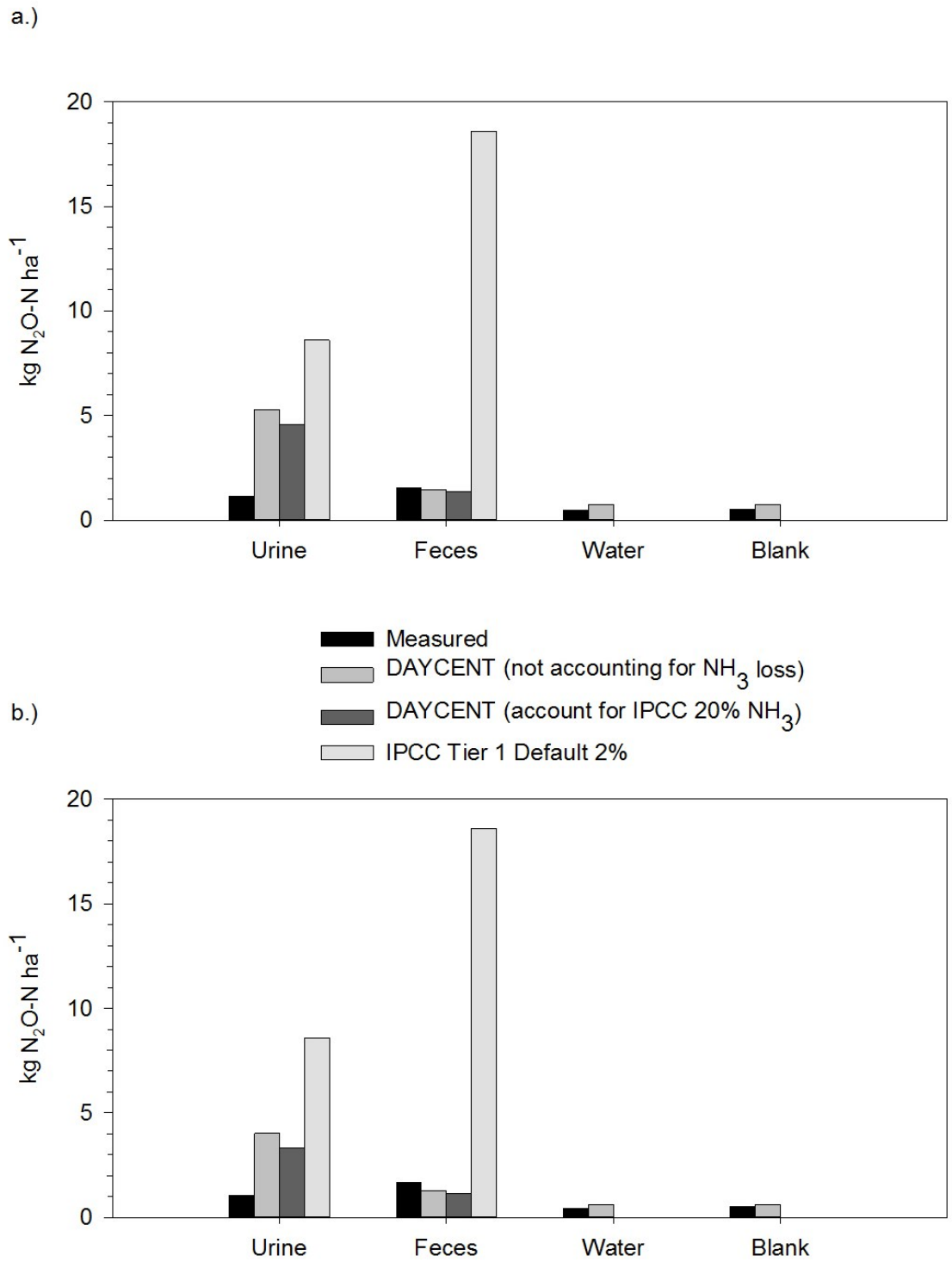


Figure 10. Cumulative nitrous oxide (N_2O) emissions (kg N ha^{-1}) (6/19/2012-12/31/13) for urine (U), feces (F), water (Cw), and blank (Cb) plots for measured (± standard error), DAYCENT without accounting for ammonia (NH_3) loss, DAYCENT (accounting for IPCC 20% default for NH_3 loss), and IPCC for (a) Bozoisky-select (BS) and (b) native rangeland (NR).

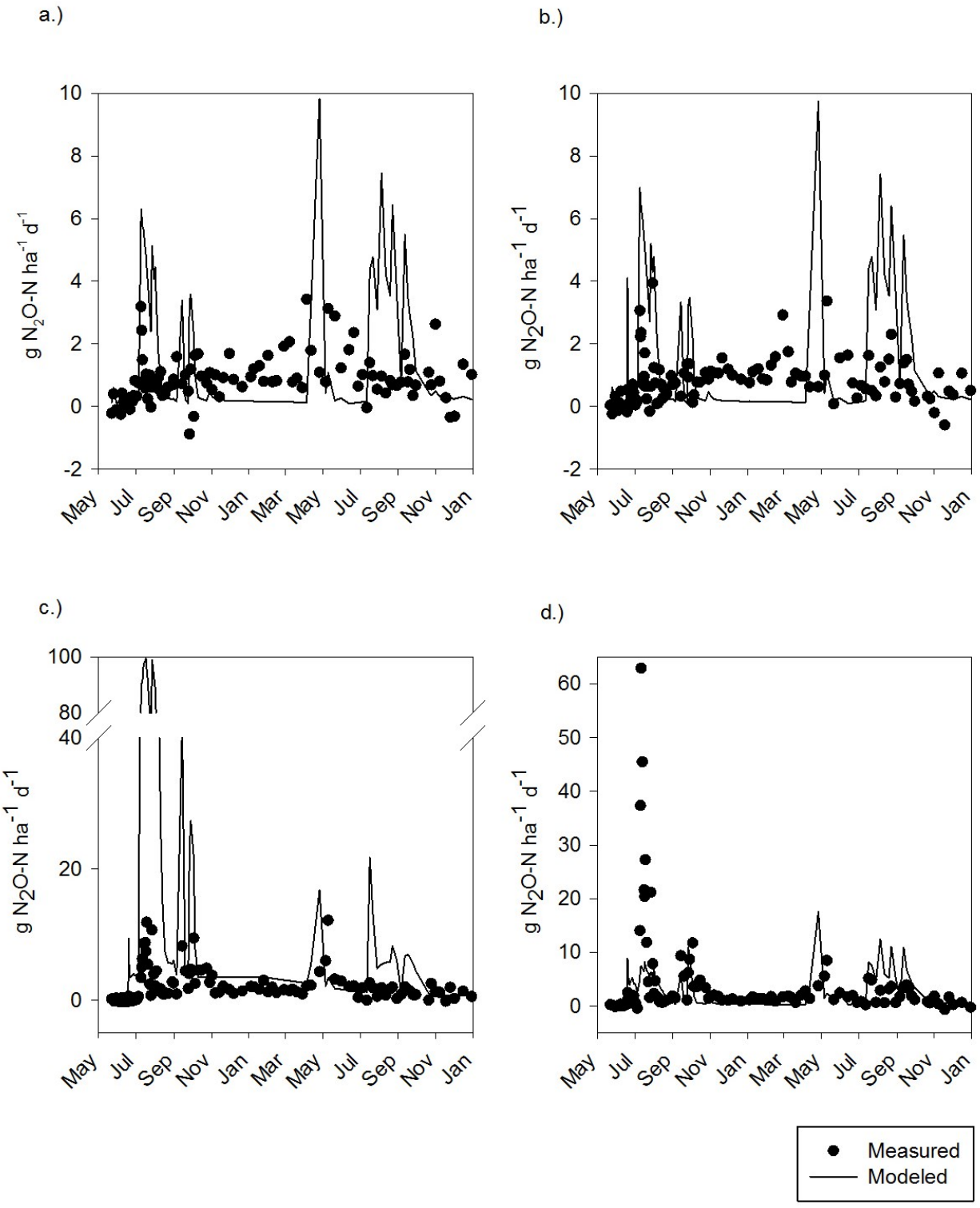


Figure 2. Nitrous oxide (N_2O) measured versus modeled emissions for a.) blank (Cb), b.) water (Cw), and cattle c.) urine (U) and d.) feces (F) plots on Bozoisky-select (BS).

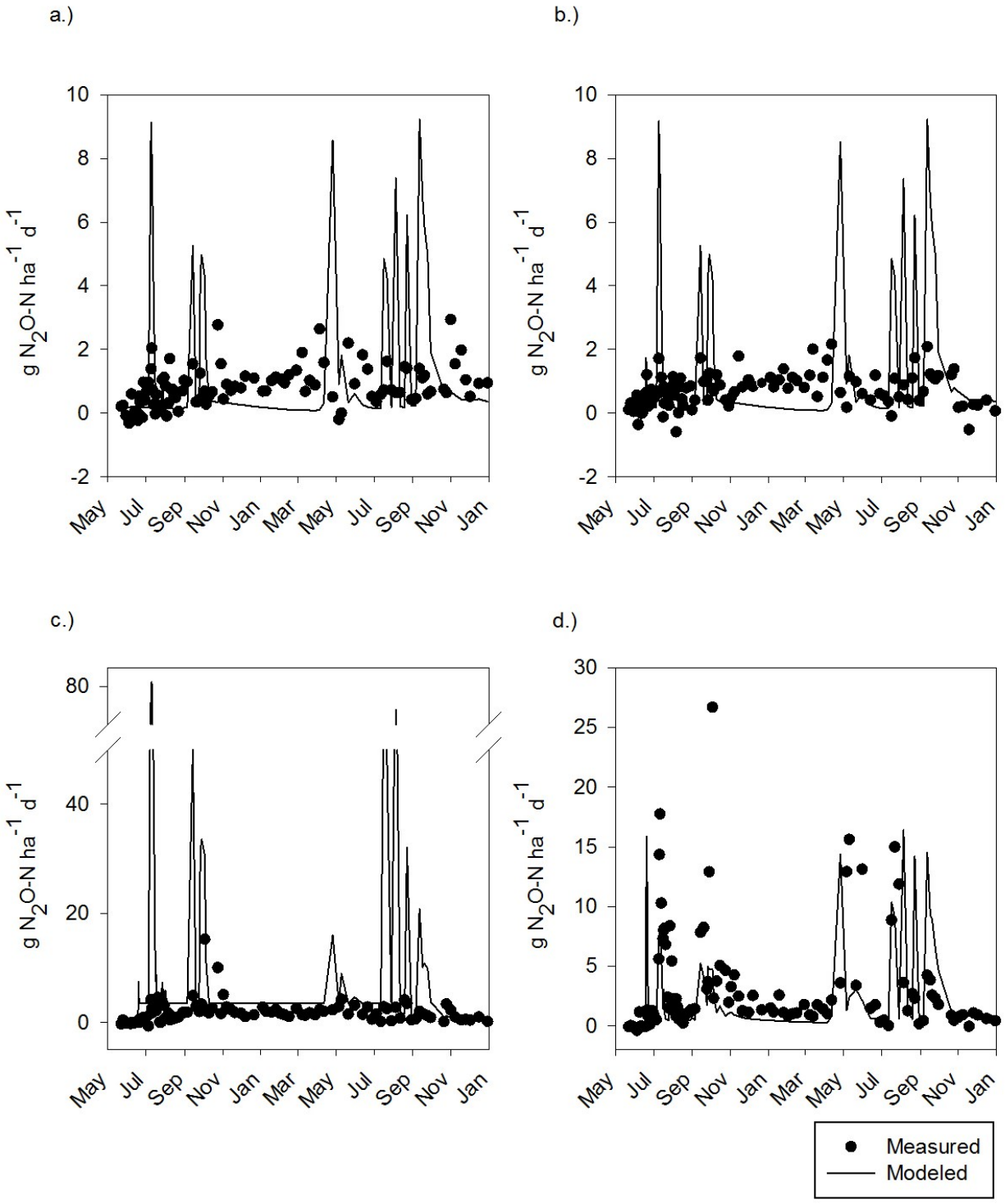


Figure 12. Nitrous oxide (N_2O) measured versus modeled emissions for a.) blank (Cb), b.) water (Cw), and cattle c.) urine (U) and d.) feces (F) plots on native rangeland (NR).

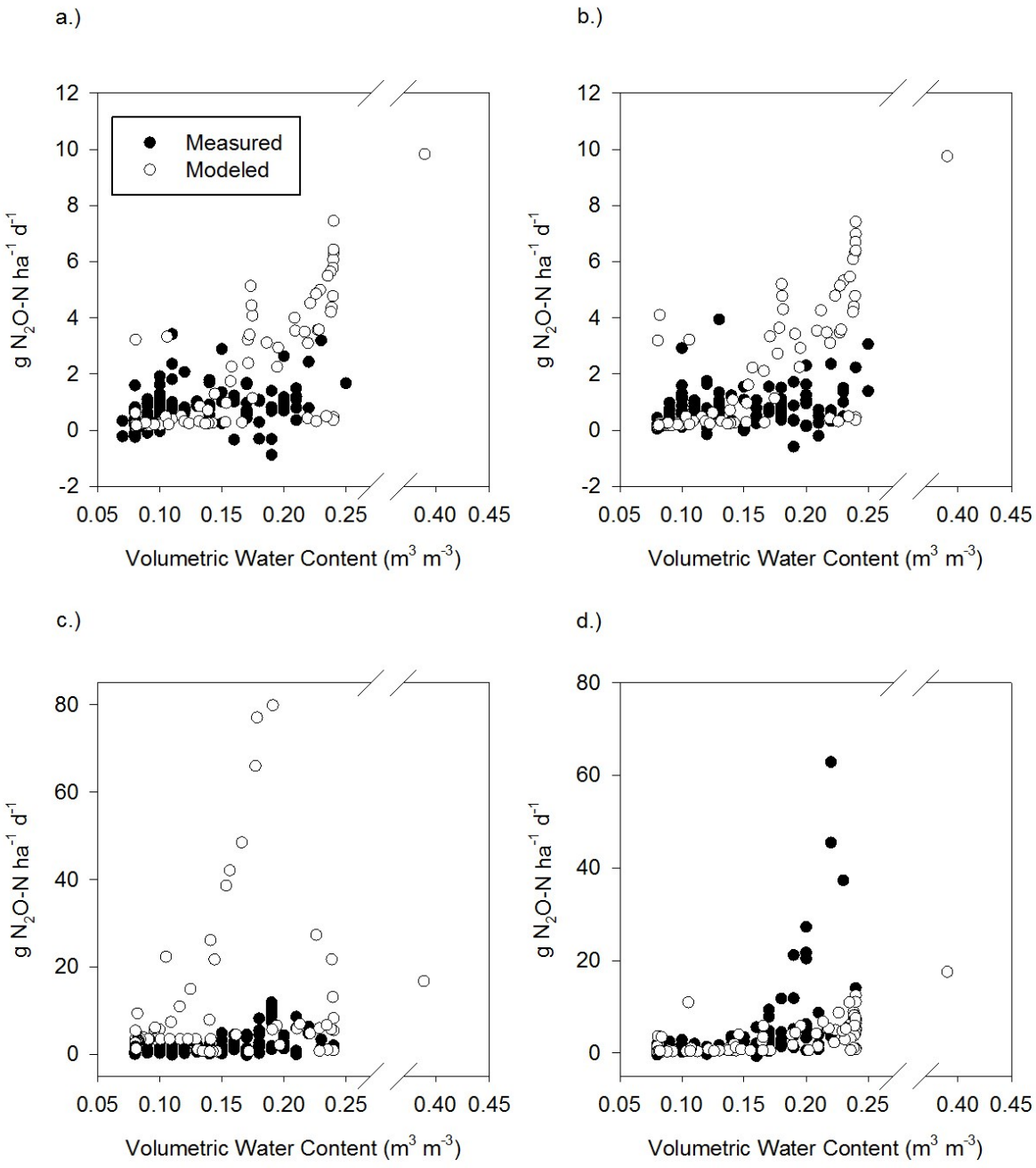


Figure 13. Measured and modeled nitrous oxide (N_2O) emissions as a function of volumetric water content (m^3 m^{-3}) for a.) blank (Cb), b.) water (Cw), and cattle c.) urine (U), and d.) feces (F) on Bozoisky-select (BS) pasture.

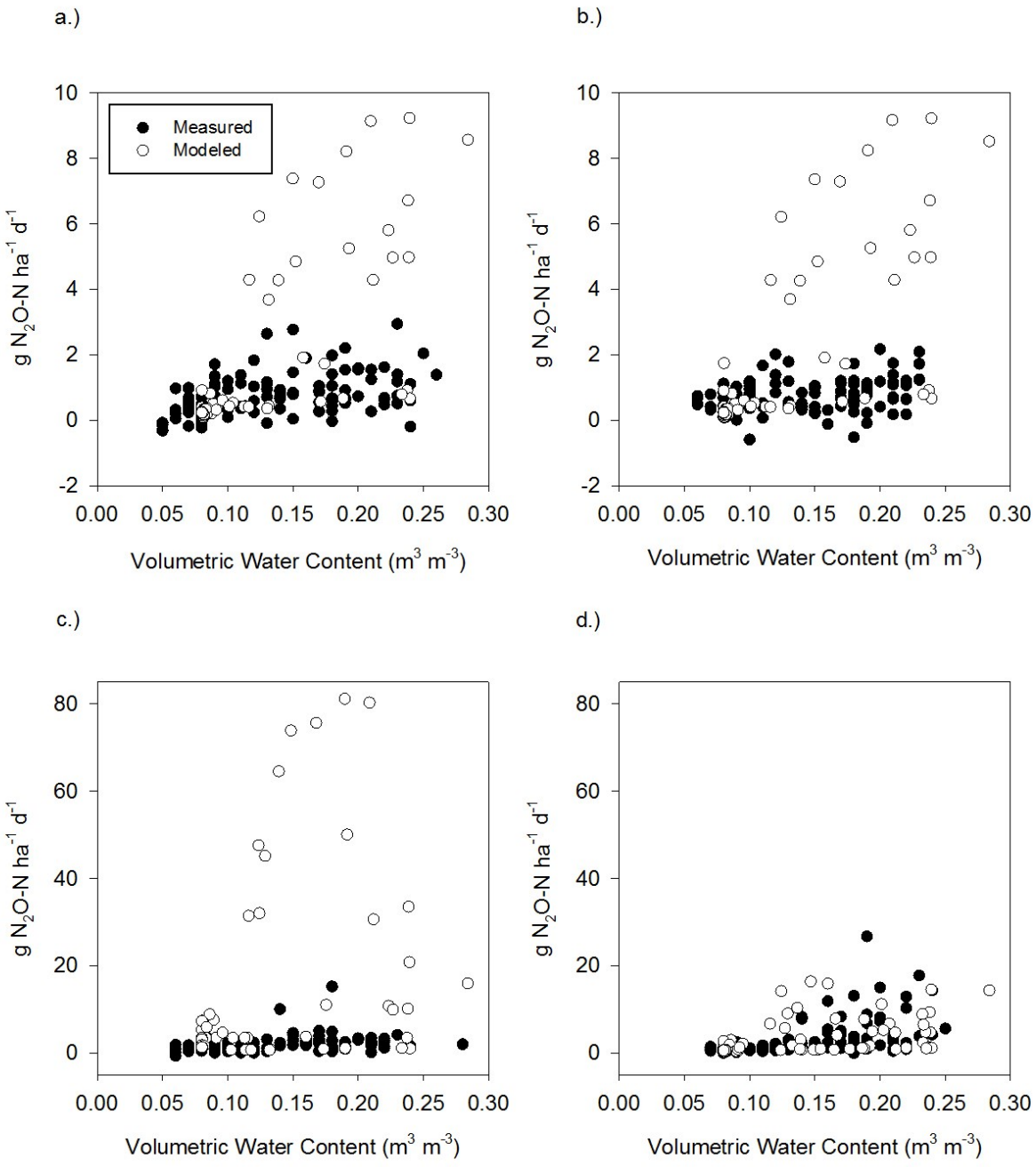


Figure 14. Measured and modeled nitrous oxide (N_2O) emissions as a function of volumetric water content (m^3 m^{-3}) for a.) blank (Cb), b.) water (Cw), and cattle c.) urine (U), and d.) feces (F) on native rangeland (NR).

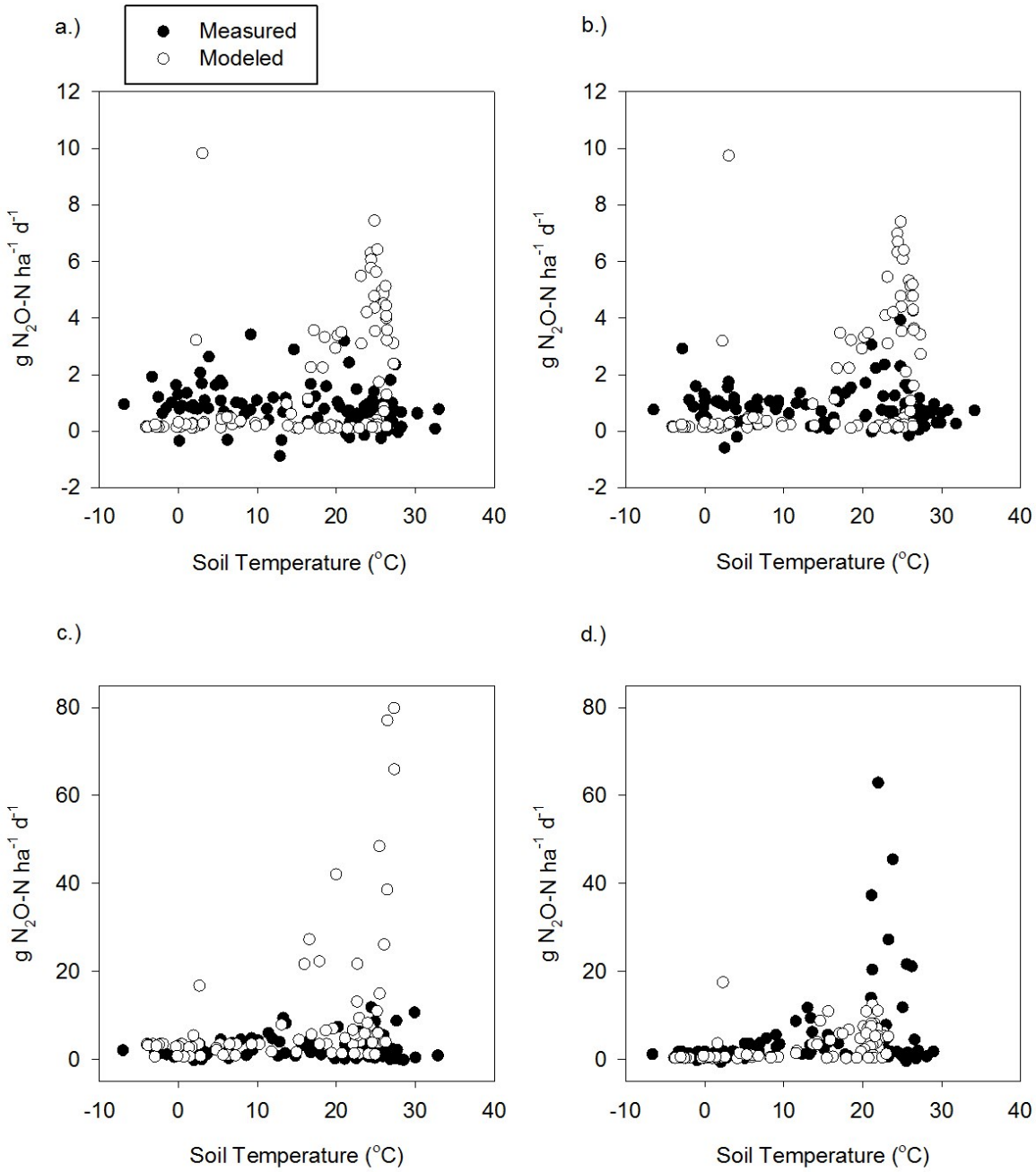


Figure 15. Measured and modeled nitrous oxide (N_2O) emissions as a function of soil temperature (°C) for a.) blank (Cb), b.) water (Cw), cattle c.) urine (U), and d.) feces (F) on Bozoisky-select (BS) pasture.

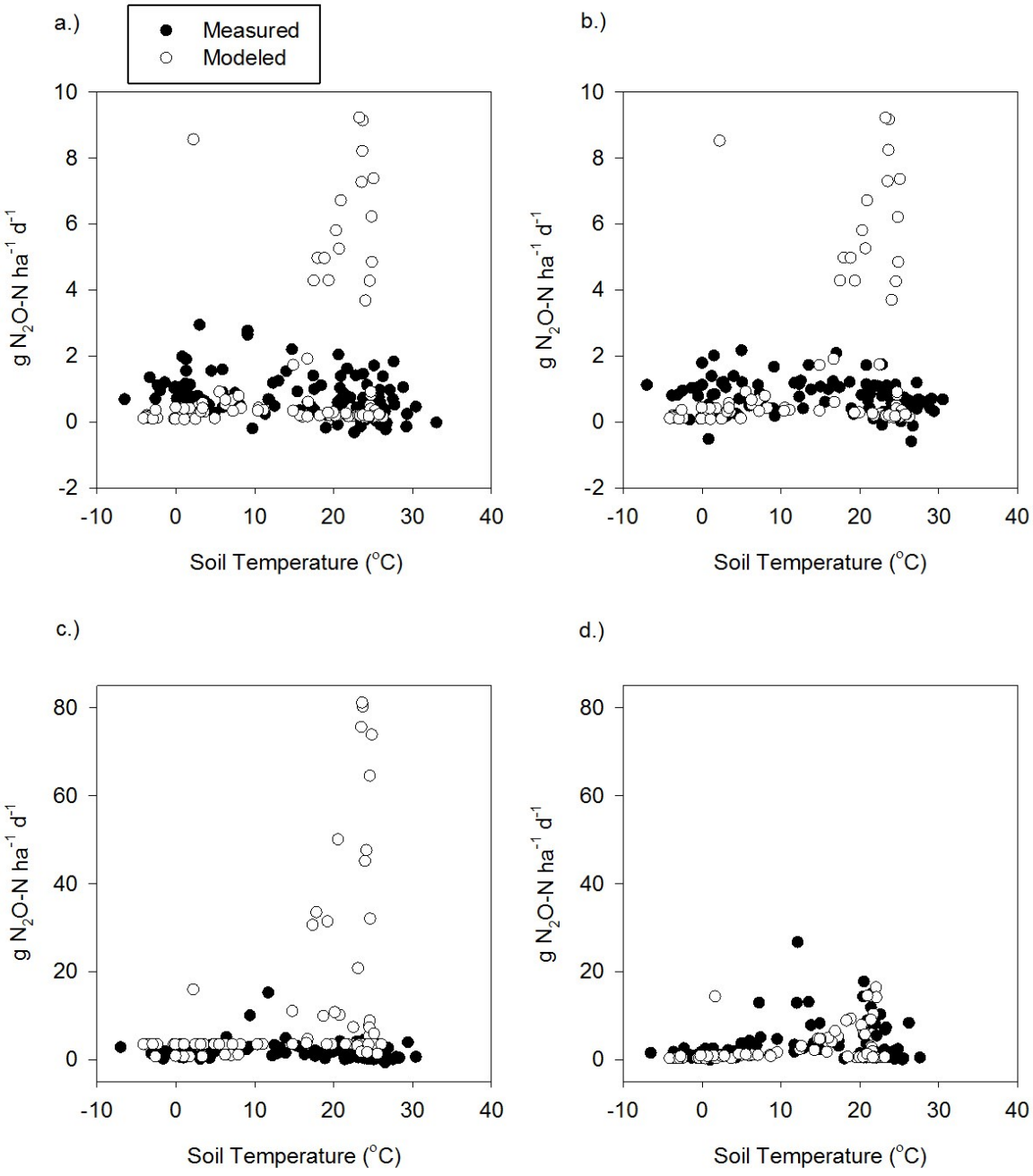


Figure 16. Measured and modeled nitrous oxide (N_2O) emissions as a function of soil temperature (°C) for a.) blank (Cb), b.) water (Cw), and cattle c.) urine (U) and d.) feces (F) on native rangeland (NR).

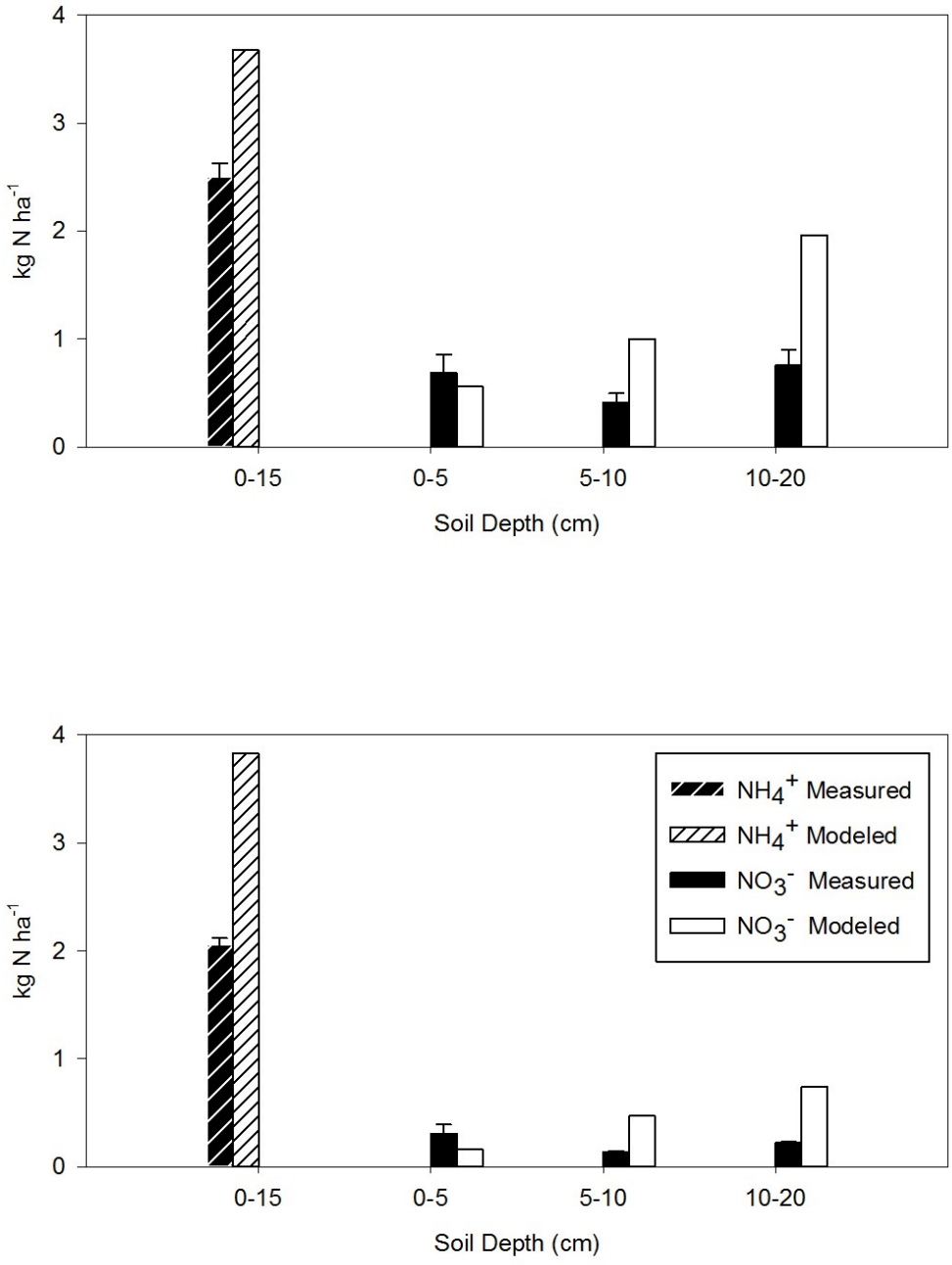


Figure 17. Mean measured (n=8; standard error) and modeled baseline soil mineral-N, ammonium (NH_4^+) and nitrate (NO_3^-), concentration (kg N ha^{-1}) to 20 cm depth for a.) Bozoisky-select pasture (BS) and b.) native rangeland (NR).

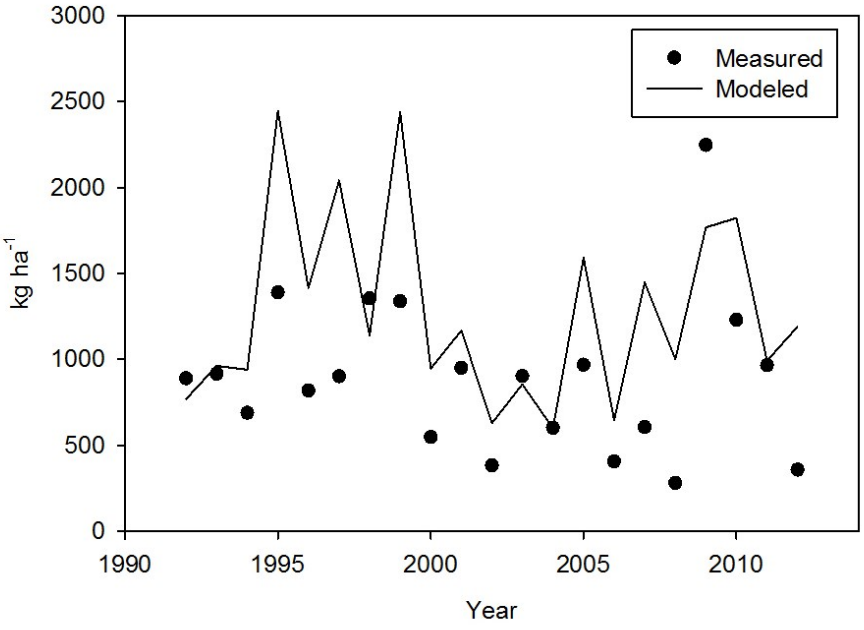


Figure 18. Measured and modeled biomass (kg ha^{-1}) for native rangeland (NR) from 1992-2012 (r =0.36).

CHAPTER 4

SUMMARY AND CONCLUSIONS

Static chambers were implemented to measure methane (CH_4) and nitrous oxide (N_2O) fluxes from cattle excrement, urine and feces, as well as controls, water and blank. In addition to the trace gas measurements, soil moisture and temperature and average air temperature were measured and recorded during each sampling occasion. Linear regression was used to calculate fluxes for each treatment replicate. A correction factor was implemented to adjust for the air temperature, moles of the gas molecule, atmospheric pressure, and chamber volume to surface area ratio. Treatment fluxes for CH_4 and N_2O were averaged over 4 replicates. Fluxes for non-sampling days were estimated using linear interpolation. Cumulative fluxes were calculated by taking the sum of the measured and interpolated values. Baseline soil samples were taken from each plant community and were analyzed for carbon and nitrogen as well as texture.

Cumulative N_2O emissions from the excrement, urine (U) and feces (F), plots were significantly greater than those from control plots, distilled water (Cw) and blank (Cb). On an area basis, cumulative N_2O emissions from the feces treatment were significantly greater than those from the urine treatment. The emission factors (EF), proportion of N emitted as N_2O, for the urine and feces plots were not significantly different and varied between 0.11-0.14%. The EFs for cattle urine and feces were on the lower end of the spectrum from what has been reported in the literature. The low EFs for the excrement plots were likely due to the high sand content and the extreme drought conditions during the experiment. Based on the soil water-filled pore space values during the periods of elevated N_2O emissions, it appears that nitrification was the prevalent N_2O producing pathway. Conditions for denitrification may have existed following

substantial precipitation and freeze thaw events. Cumulative N_2O emissions and trends in the timing of fluxes were similar between plant communities, but the magnitude of seasonal emissions varied. This phenomenon was likely due to phenology differences between the two plant community types, C4 native rangeland and C3 Bozoisky-select pasture.

Cumulative CH_4 uptake was significantly less from the urine and feces plots relative to the control plots, water and blank. The reduction in CH_4 uptake was likely due to greater N turnover in the soils treated with cattle excrement. The formation of a surface crust on the feces patches likely limited gas diffusion further inhibiting CH_4 uptake (Yamulki *et al.*, 1999). Methane uptake was less on Bozoisky-select pasture for all treatments compared to the same treatments on native rangeland. Reduced CH_4 uptake on the Bozoisky-select pasture may have been a result of diminished soil structure from historical cultivation events as the 0-15 cm depth of the soil profile contained greater sand and lesser organic carbon contents relative to the native rangeland soil (Mosier *et al.*, 1997).

For DAYCENT model validation, soil organic carbon and mineral N conditions were initialized by conducting simulations based on historical land management practices and climate. The resulting conditions were used as baseline conditions for the treatment simulations. Site specific input files containing soil properties, management practices, and vegetation type were implemented for each plant community and treatment. Urine patches were simulated by scheduling a urea fertilizer event, while the feces treatment was simulated by scheduling 2 organic matter additions to account for the labile and recalcitrant C fractions. Each excrement treatment also received a water addition to account for the moisture content of each treatment.

Overall, the DAYCENT model adequately simulated soil water content and temperature. While the model did well simulating the timing and magnitude of the peaks for soil water

content, it predicted more rapid soil drainage than was observed. The model also significantly overestimated the soil water content following a snowmelt event in the spring of 2013.

While the DAYCENT model captured trends of N_2O emissions following precipitation events, emissions during these periods were significantly overestimated for the urine, water, and blank plots. The overestimation may have been a result of the model predicting greater total system N as the model overestimated soil mineral N and aboveground plant N during July 2013. In addition, the model overestimated native rangeland aboveground plant biomass for 14 out of 21 growing seasons from 1992-2011. A possible explanation for the overestimate of total system N could be that the natural N inputs through ammonia (NH_3) deposition and N fixation, which are highly uncertain, were overestimated. Alternatively, the model assumption that 1.2% of nitrified-N emitted is N_2O may not be an accurate representation for cattle excrement patches at the SGS as researchers have found that nitrification from urine patches on a sandy soil can occur with minimal N_2O emissions (Carter, 2007). The model significantly underestimated N_2O emissions from the feces treatment during the first growing season following treatment application, but did well simulating emission trends for the remainder of the study.

The model significantly overestimated N_2O emissions from the Cb and Cw plots during periods of great flux activity following precipitation events, while periods of minimal N_2O production over the winter were underestimated. Therefore, cumulative N_2O emissions calculated from the DAYCENT model output represented the measured data well for the water and blank plots. Cumulative N_2O emissions and the magnitude of fluxes were simulated reasonably well for the F treatment. The model overestimated cumulative N_2O emissions for the urine treatment by a factor of 4 and 5 for native rangeland and Bozoisky-select, respectively. While the DAYCENT model did not simulate N_2O emissions for cattle urine and feces deposited

on SGS soils exceptionally well, it still represented the measured data better than estimated emissions based on the IPCC Tier 1 default EF (2%) (IPCC, 2006).

Cumulative CH_4 uptake was significantly overestimated for all treatments on both plant communities. The model accurately simulated reduced CH_4 uptake immediately following precipitation events when soil gas diffusion was limited. Since the model estimated the soils to drain more quickly than what was observed, maximum gas diffusion and CH_4 uptake rates resumed more quickly following precipitation events than what was observed with the measured data. The model failed to capture decreased CH_4 uptake when soil microbial activity was limited during extremely dry soil conditions. This was a result of the model underestimating the optimum soil water content for maximum CH_4 uptake. Therefore, the maximum CH_4 uptake rates were estimated to occur when soils were the driest and warmest. The reduction factor, which accounts for cultivation and fertilization events, adequately suppressed CH_4 uptake rates from the excrement plots, but the rates were still overestimated since the baseline rates were poorly represented.

During the present study, EFs for cattle excrement deposited on semi-arid SGS were substantially less than the IPCC Tier 1 default EF (2%). A significant overestimation of N_2O emissions would result from using the IPCC Tier 1 default EF for SGS soils. Soil texture and average climate for the area of interest should be taken into consideration when selecting an EF for cattle excrement. Future research on trace gas fluxes from SGS should focus on areas of the pasture where cattle congregate, such as fence corners and the perimeter of water tanks. These areas incur N-loading and soil compaction and thus there is potential for decreased CH_4 uptake and increased N_2O emissions. In addition, studies with randomized replication are needed to

determine the effects of converting native rangeland to Bozoisky-select pasture on the CH_4 sink potential of these landscapes.

Currently, the DAYCENT model does not accurately simulate CH_4 uptake and N_2O emissions from native rangeland and Bozoisky-select soils of the SGS. In order to elucidate areas where model improvement is needed, the DAYCENT model needs additional testing with extensive datasets that contain high temporal and spatial resolution of soil C and N, soil moisture and temperature, plant C and N, and trace gas fluxes from SGS native rangeland and Bozoisky-select.

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