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# A Rapid Method for Measuring Feces Ammonia-Nitrogen and Carbon Dioxide-Carbon Emissions and Decomposition Rate Constants

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## A Rapid Method for Measuring Feces Ammonia-Nitrogen and Carbon Dioxide-Carbon Emissions and Decomposition Rate Constants

Jiyul Chang, David E. Clay,\* Sharon A. Clay, Alexander J. Smart, and Michelle K. Ohrtman

#### **ABSTRACT**

A rapid approach is needed for determining the effectiveness of precision conservation on soil health as evaluated using  $CO<sub>2</sub>$ and  $NH<sub>3</sub>$  emissions. This study demonstrated an approach for calculating  $CO_2$ –C and NH<sub>3</sub>–N emissions and associated rate constants when feces were applied to bare soil or soil + vegetation. In addition, point  $CO<sub>2</sub>-C$  emission measurements were compared with near continuous measurements. The  $CO<sub>2</sub>-C$ emissions were measured at 2 h intervals over 20 d, whereas ammonia volatilization was measured three times daily for 7 d. Total CO<sub>2</sub>–C emissions over 20 d were 5% lower [186 g CO<sub>2</sub>–C  $(m^2 \times 20 \text{ d})$  <sup>-1</sup>] than point measurement collected at 1100 h every day (197 g CO<sub>2</sub>–C (m<sup>2</sup> × 20 d)<sup>-1</sup>), and about 10% lower than if collected every 2 d [206 g CO<sub>2</sub>–C (m<sup>2</sup> × 20 d)<sup>–1</sup>]. A Fast Fourier transformation (FFT) showed that temperature and  $NH_{3}-N$  and  $CO_{2}-C$  emissions followed diurnal cycles and that they were in-phase with each other. Over 7 d, 20% of feces  $NH<sub>A</sub>$ –N was volatilized and that this loss was similar when feces were applied over vegetation or mixed into the soil. Feces additions increased the amplitude of the  $CO<sub>2</sub>-C$  diurnal cycle, and the fecal-C first-order rate degradation constants were higher when mixed with soil  $[0.0109 \pm 0.0043 \text{ g(gxd})^{-1}, p = 0.1]$  than applied over vegetation  $[0.00454 \pm 0.00336 \text{ g(gxd})^{-1}, p = 0.1]$ .

#### **Core Ideas**

- • Carbon storage and ammonia volatilization from feces can be quantified using techniques described in this article.
- Carbon dioxide and  $NH<sub>3</sub>$  emission follow diurnal cycles and it is difficult to accurately predict  $CO<sub>2</sub>$  loss and ammonia volatilization based on point measurements.
- Conducting rapid assessments that produce definitive findings helps build trust between scientists and and on-farm producer collaborators.

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OLLABORATIVE PROJECTS between farmers/ranchers and scientists can be very rewarding, as well as produce lasting positive impacts on the environment (Smart et al., 2015). However, success requires the development of trust between the farmer and the scientists, and ability to use shortterm field experiments to produce results that can be communicated to the farming community in a timely manner. In projects addressing soil health, this may involve conducting demonstration or targeted experiments focused on one or two questions. This project is focused on the question, what is the fate of the C and N in cattle feces?

Carbon and N budgets are based on accurate measurements of the C and N additions and losses. Additions represent the C or N that is added through photosynthesis or fertilizer or manure applications, whereas losses represent leaching, erosion, and gaseous emissions. Research has shown that management, soils, and climatic conditions interact to influence both additions and losses in ecological systems. To accurately measure nutrient additions and losses, sampling approaches must be tested and modified for each unique problem (Clay et al., 1996, 2006; Chang et al., 2016b).

Three basic approaches have been used to determine  $CO<sub>2</sub>$ emissions in grassland systems (Fynn et al., 2009). The first approach measures  $CO_2$ –C or  $NH_3$  emission in the laboratory (Murwira et al., 1990; Van Kessel et al., 2000; Kyvsgaard et al., 2000; Powell et al., 2006; Ayadi et al., 2015). Laboratory experiment are most useful for measuring mineralization potential (Franzluebbers et al., 2000; Van Kessel et al., 2000), evaluating responses mechanisms (Adu and Oades, 1978), or determining the impact of a specific treatment on many factors including biological activity (Clay et al., 1990). However, the removal of the samples from the field or drying and grinding the samples can change the soils physical and biological characteristics (De Nobili et al., 2006).

In the second approach, soil organic carbon (SOC) losses are determined by difference. In this approach, changes in SOC and net aboveground and belowground productivity are measured at the beginning and completion of an experiment (Schuman et al., 1999; Franzluebbers et al., 2000; Tate et al., 2003; Chang et al., 2004, 2016b; Clay et al., 2005, 2006, 2015; Derner et al., 2006; Derner and Schuman, 2007; Smart et al., 2010a, 2010b; Dunn et

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Abbreviations: FFT, Fast Fourier transformation; SOC, soil organic carbon.

al., 2010). Increases or decreases in SOC with time are attributed to decreased or increased  $CO<sub>2</sub>$  emissions. Carbon budgets based on temporal changes in SOC have many complicating factors including: (i) the long period of time required to quantify SOC temporal changes (Clay et al., 2006, 2015); (ii) the difficulty with measuring belowground biomass and associated degradation rates (Chang et al., 2014, 2016b); (iii) the difficulty in quantifying dissolved organic C and inorganic N leaching (Clay et al., 1995) and erosional losses (Hoese et al., 2009); and (iv) that large errors can occur when data from small plots was extrapolated over landscapes. This approach is not well suited for short-term experiments conducted in farmers' fields.

In the third approach, the emissions of  $CO<sub>2</sub>$  or other gases are measured at targeted locations or times (Manley et al., 1995; Petersen et al., 1998; Cao et al., 2004; Parkin and Venterea, 2010; Gong et al., 2014). The collection of gas samples has been used to assess the fate of both N and C in a wide range of systems (Omonode et al., 2015; Chang et al., 2016a). However, collecting gas samples can bias gas emission values if the samples are collected prior to or after the average temperature (Parkin and Venterea, 2010; Chang et al., 2016a). This bias has been overcome by measuring gas emissions on a near continuous basis (Cao et al., 2004; Laubach et al., 2013; Macdonald et al., 2015; Fischer et al., 2016). However, due to high costs many of these continuous measurement experiments are not replicated. For example, Cao et al. (2004) measured  $CO<sub>2</sub>$ –C emissions every 2 h using closed chambers at two experimental sites with different temperatures, rainfall, vegetative surface coverage, and grazing intensities. Based on these data, total emissions were estimated at 5560 kg  $CO_2-C$ (ha  $\times$  year)<sup>-1</sup> in a lightly grazed (2.55 sheep ha<sup>-1</sup>) and 4170 kg CO<sub>2</sub>–C (ha  $\times$  year)<sup>-1</sup> in a heavily grazed (5.35 sheep ha<sup>-1</sup>) system. In this experiment, the importance of feces-C was not determined. If a protocol could be developed, this basic approach may be suitable for on-farm studies.

Because little fertilizer is applied to rangeland systems, longterm productivity and plant and soil health assessments may require estimates of N losses through denitrification, leaching, or volatilization (Clay et al., 1990, 1996; Smart et al., 2013; Chang et al., 2016a). However, many rangeland studies do not measure C and N cycling in the field which can result in large errors in C footprint or regional assessments (Ryden et al., 1987). For example, little information is available about the fate of feces in rangeland systems. For cattle, feces contain almost all of the organic C and about half of the excreted N. The rest of the N is contained in urine, which is composed of between 60 and 80% urea. Nitrogen losses from urine can be as high as 50% (Petersen et al., 1998; Laubach et al., 2013). To calculate fecal C and N additions and losses, the amount of fecal C and N added to the system is required. Based on the definition of forage digestibility (Minson, 2012), feces can be estimated using the following equation:

$$
Feces = \text{Consumed forage} \times \left[ 1 - \frac{\text{digestibility}\left(g\,\text{kg}^{-1}\right)}{1000} \right] \quad [1]
$$

Following deposition, the ammonia can be volatilized, nitrified, and used by the surrounding plants, whereas the C containing compounds can be mineralized into  $CO<sub>2</sub>$  or integrated into the SOC (Clay et al., 2005, 2006, 2012, 2015).

The above discussion highlights the importance and potential impacts in working with farmers and ranchers in collaborative projects. However, maintaining these collaborations requires active communication and the timely reporting of findings to the farmer collaborators. In addition, many of experimental approaches designed for long-term projects may not be suitable for on-farm studies. This study demonstrated a short-term approach for calculating total NH<sub>3</sub>–N and  $CO_2$ –C emissions and associated rate constants when feces were applied to bare soil or soil + vegetation. In addition, total  $CO<sub>2</sub>-C$  emissions were compared with point measurements at a specific time. Due to the limited number of chambers that can be physically connected to a single analyzer, it was not feasible for experiments to contain true replications. We overcame this hurdle by repeating the experiment in four different environments.

#### **Materials and Methods Carbon Dioxide–Carbon Emissions and Ammonia Volatilization**

The experimental design was a randomized complete block. Each blocks represented 20 d experiments that were initiated on 12 June, 2 July, 26 July, and 19 August in 2013. Each block was conducted at a new site, where fresh feces were applied. During each experiment,  $CO<sub>2</sub>-C$  emissions were measured every 2 h, and in a linked experiment, ammonia volatilization was measured three times daily for 7 d starting on the first day of each  $CO<sub>2</sub>$  study. In this study, near continuous  $CO<sub>2</sub>$  emissions over 20 d were compared with point measurements collected at 1100 h every day, every second day, and every third day. These point measurements were contained within in the continuous data set. Each block contained each of the following treatments:

- 1. Lightly mixed soil,
- 2. Vegetation that was clipped to 2 cm,
- 3. Lightly mixed soil plus suspended fecal material,
- 4. Simulating trampling that lightly mixes the fecal material with the surface soil,
- 5. Fresh fecal material that was suspended above the vegetation, and
- 6. Fresh fecal material applied over clipped vegetation.

The experiment contained two types of controls. The first control was that feces were not applied to the soil (Treatment 1) or the soil plus vegetation (Treatment 2), whereas in the second control, the feces were physically separated from the soil (Treatment 3) or the soil plus vegetation (Treatment 5).

The treatments were selected to allow for  $CO<sub>2</sub>-C$  and  $NH<sub>3</sub>–N$  emissions from the soil and feces to be calculated by difference. In Treatments 2, 5, and 6 the vegetation was mowed to a height of 2 cm prior to the start of each replication. This height was selected to simulate very heavy grazing intensity (90% of aboveground biomass; Hart, 2001), and to prevent vegetation interference with the  $CO<sub>2</sub>$  automated sampling system. In Treatments 4 the feces were lightly mixed into the surface 7.5 cm with a trowel to simulate cattle trampling. For Treatments 3 and 5, fresh fecal materials were deposited on 14-cm diam. plastic plates that were placed on a platform suspended 2.5 cm above the soil. The plates did not interfere with automated  $CO<sub>2</sub>$ 

measurements. Treatments 1, 2, 3, and 5 were used to examine  $CO<sub>2</sub>-C$  emissions from soil, vegetation, and the fecal materials.

At the beginning of each block (experiment), composite soil samples consisting of eight soil cores from the 0- to 7.5-cm depth were collected from the area where the chambers were installed. These samples were not located within the areas occupied by the chambers. At the completion of each block, four soil cores from the 0- to 7.5-cm soil depth were collected from each treatment. The samples were analyzed for bulk density, ammonium N, nitrate N, total N, and total C (Clay et al., 2015).

#### **Site Characteristics**

This experiment was conducted on a Barnes clay loam (fineloamy, mixed, frigid Udic Haploboroll), that was located near Brookings, SD. The coordinates of the site were  $44^{\circ}20'6''$  N, –96°48¢28² W. The slope was between 0 and 2%. The climatic conditions were characterized by cold winters and hot summers, a growing season from April to October, a frost-free period that ranges from 120 to 160 d, and an average annual temperature of 6.5°C (Chang et al., 2016b). According to the Köppen classification it is characterized as Dfa. The soil texture in the surface 7.5 cm was a clay loam with a pH (water) of 7.0 and a bulk density of 1.29  $\rm g\,cm^{-3}$ . In addition, following combustion (1000 $^{\circ}$ C) and analysis, the soil was found to contain 5.3 g N kg soil<sup>-1</sup> and 44.1 g C kg soil<sup>-1</sup> (Clay et al., 2015). In the study area, the pasture botanical composition was 5% smooth bromegrass (*Bromus inermis* L.), 20% Kentucky bluegrass (*Poa pratensis* L.), 70% quackgrass [*Elytrigia repens* (L.) Desv. ex Nevski], and 5% birdsfoot trefoil (*Lotus corniculatus* L.). Prior to the study the site had been managed similarity for at least 5 yr.

#### **Climatic Conditions**

Precipitation from 1 Jan. to 31 Dec. 2013 was approximately 64 cm, which was similar to the long-term rainfall average of 62 cm. Rainfall in June, July, and August was 14.9, 9.2, and 3.9 cm, respectively, and the average volumetric soil moisture contents [(begin $n$ ning + final)/2] were 0.38, 0.31, 0.33, and 0.22 g water cm<sup>-3</sup> for the 12 June, 2 July, 26 July, and 19 August experiments, respectively. These moisture contents were measured with a commercial sensor. The average air temperatures during each experimental replication were 21.2, 23.5, 17.8, and 23.6°C for the 12 June, 2 July, 26 July, and 19 August experiments, respectively.

#### **Fecal Collection and Characterization**

Fecal materials were collected from four adult cows grazing a pasture when the experiments were initiated in June 2013. As standard in the region, the livestock diets were augmented with an appropriate feed supplement containing Ca, P, Na, Cl, Mg, K, Cu, Se, Zn, and Vitamins A, D3, and E. Based on forage analysis, the grazed forage had a digestibility of between 600 and 700 g kg<sup>-1</sup> and it contained 180 g crude protein kg<sup>-1</sup>, 530 g neutral detergent fiber (NDF)  $kg^{-1}$ , 290 g acid detergent fiber  $(ADF)$  kg<sup>-1</sup>, and 91 g ash kg<sup>-1</sup>. The fecal materials were collected in a bucket before it reached the soil. After collection, the materials were mixed, stored in sealed containers, and cooled to 5°C. The average fecal pH and moisture content (MC) were 7.5 and  $85\%$  [MC =  $100 \times$  (wet-dry)/wet weight], respectively. The same fecal material was used in all experimental blocks. Dried fecal material contained 18.2 g total N kg $^{-1}$  and 38.5 g total C kg $^{-1}$ ,

which was determined on a ratio mass spectrometer after combustion at 1000°C. The  $\delta$  <sup>13</sup>C value was –28.62 ‰, which indicated that the excreted materials were primarily derived from  $C_3$ plants (Kim et al., 2008). Inorganic N was extracted from fresh fecal materials with 1M KCl and analyzed on a spectrometer to determine fecal NH<sub>4</sub>–N, which averaged 370 mg NH<sub>4</sub>–N (kg dry fecal material)  $^{-1}$  (Kim et al., 2008).

#### **Quantifying Carbon Dioxide-Carbon and Ammonia-Nitrogen Emissions**

In the  $CO<sub>2</sub>-C$  emission experiment, one fecal pile (500 g wet weight equivalent to 75.4 g dry material or 29 g C) was placed in the center of a  $314 \text{ cm}^2$  chamber. This deposition rate was equivalent to 15.9 kg wet fecal material m<sup>-2</sup> (2.4 kg dry fecal material m<sup>-2</sup> or 920 g C m<sup>-2</sup>). The feces size was selected to ensure that  $CO<sub>2</sub>-C$  that was derived from soil, plants, and feces could be accurately measured. The  $CO<sub>2</sub>-C$  gas flux from each treatment was measured every 2 h over 20 d by an 8100A Automated Soil  $CO<sub>2</sub>$  Flux System (LI-COR, Lincoln, NE) that was connected to six gas chambers. Soil surface temperatures were measured continuously with thermocouples.

In the ammonia volatilization experiment, the fecal deposition rate was 1.72 kg dry fecal  $m^{-2}$  which contained 636 mg  $NH_4$ –N m<sup>–2</sup>. The fecal material and soil were open to the atmosphere between collection periods and covered to make a closed gas sampling chamber when gas samples were collected. The collection chambers had width, length, and height dimensions of 22 by 30 by 21 cm with an effective air volume (total volume – pump volume) was  $11.9$  L. The NH<sub>3</sub>–N gas was captured three times a day (700, 1400, 1900 h) for 7 d using an electric pump placed above the soil within the chamber to push air at the rate of 57.6 L h<sup>-1</sup> for 20 min through a glass bottle containing 20 mL of boric acid (0.32 M  $H_3BO_3$ ). The total amount of trapped  $NH<sub>3</sub>$  gas was determined by titration with 0.0025 M  $H_2SO_4$  (Clay et al., 1990). The sampling protocols were selected based on the expected air temperatures (Clay et al., 1990). The  $NH<sub>3</sub>–N$  trapping efficiency was calculated to be 69.5 $\pm$ 11.9% by placing a known about of NH<sub>3</sub> on an impervious surface, followed by  $NH<sub>3</sub>$  collection and analysis as described above. The efficiency was calculated with the equation, % trapped =  $100 \times$  (applied NH<sub>3</sub>–trapped NH<sub>3</sub>)/applied NH<sub>3</sub>). The efficiency value was used to correct the measured  $NH<sub>3</sub>-N$  losses.

The percentage of the  $NH<sub>3</sub>$  loss from feces after 7 d was calculated using the equation, % feces N loss =  $\{100 \times$  [(treated-control)]/(total mg NH<sub>4</sub> m<sup>-2</sup> added)}. For example, [100×[(483 mg  $NH_4-N/m^2 - 364$  mg  $NH_4-N/m^2$ ]/(370 mg  $NH_4-N/kg$ feces×1.72kg feces/m<sup>2</sup>) = 18.7%]. In this equation, the control is the ammonia loss in Treatments 1 and 2, and the treatments are the losses in Treatments 3 through 6.

#### **Determining Carbon Dioxide and Ammonia Cycles and Phase Shift**

The FFT of the air temperatures,  $NH_3-N$ , and  $CO_2-C$  emissions were used to convert the temporal data to the frequency domain (Chang et al., 2016a). This analysis was conducted using Microsoft Excel using a method reported by Klingenberg (2005). This analysis is used to determine patterns and phase shifts in temporal data sets (Fig. 1). The FFT analysis can be used to identify

the different cycles that occur within the data set, and if two data sets are in or not in phase with each other. For example, it can be used to determine the temperature phase shift with increasing soil depth. Over longer periods of time, this approach can be used to separate daily and seasonal cycles from each other (Thoning et al., 1989). Figure 1 shows that the FFT analysis could be used to characterize the phase shift in the  $CO<sub>2</sub>-C$ . Two data sets consist of an original data set and one that was off-set 6 h. Both data sets had near identical frequency distributions, however analysis of phase angle showed that the two cycles were offset 6 h.

A FFT of the  $CO_2$ –C and temperature data showed that the temperature and  $CO<sub>2</sub>-C$  cycle phase shift was 19 h. Chang et al. (2016a) had similar results. It is important to point out that not all biological systems follow identical patterns and phase shifts. For example, Clay et al. (1990) reported that soil water and soil temperature both followed diurnal cycles, however they were 12 h out of phase with each other, and that the amplitude of the diurnal cycle was reduced by covering the soil with residue.

The FFT analysis of NH<sub>3</sub> volatilization and  $CO<sub>2</sub>$ –C emissions was based on 21  $NH<sub>3</sub>$  volatilization measurements over 7 d and 240  $CO<sub>2</sub>$ –C measurements over 20 d, respectively. Because the FFT analysis requires equal time between the samples, the observed relationship between temperature and measured  $NH<sub>3</sub>$ volatilization values were used to populate the data set. The



Fig. 1. Original and data shifted 6 h to the right in the top chart. Fourier transformation in bottom charts. These data indicate that the dominant frequency in the temporal data was one cycle per day. However, additional analysis showed that in a data set that was shifted 6 h, the calculated phase shift accounted for this shift.

amplitudes and phase shifts of the dominant frequency were determined using the equation,

$$
y_c(t) = A_c \left[ \cos \left( \frac{2\pi ct}{T} - \phi_c \right) \right]
$$
 [2]

where *T* is the interval,  $y_c(t)$  is the gas concentration at time t,  $A_c$ is amplitude of the cosine curve,  $\phi_c$  is phase angle of the cosine curve, and *c* is the frequency of wave cycles (Carr, 1995; Chang et al., 2016b). The amplitude  $(A_c)$  represents the height of  $CO_2-C$ 24 h emission peak, whereas the phase angle or shift represents the peak offset. The phase angle was the minimum value in the diurnal cycle, whereas the shift  $+1200$  h was the maximum value. In this experiment, *T* is 1 (a day in 24 h period) and *c* is 1 (a complete cycle).

The total amount of  $CO_2$ –C and NH<sub>3</sub> emissions after 7 and 20 d were calculated. Based on these values, the  $CO<sub>2</sub>-C$ or  $NH_3$ –N emissions from the soil, feces, and vegetation were determined based on following calculations:

- a. Soil  $CO_2$ –C or NH<sub>3</sub>–N emissions = Treatment 1,
- b. Soil + grass  $CO_2$ –C or NH<sub>3</sub>–N emissions = Treatment 2,
- c. Vegetation  $CO_2$ –C or NH<sub>3</sub>–N emissions = Treatment 2 Treatment 1,
- d. Suspended feces  $CO_2$ –C or NH<sub>3</sub>–N emissions over soil = Treatment 3 – Treatment 1,
- e. Soil-mixed feces  $CO_2$ –C or NH<sub>3</sub>–N emissions = Treatment 4 – Treatment 1,
- f. Suspended feces  $CO<sub>2</sub>-C$  or  $NH<sub>3</sub>-N$  emissions over vegetation = Treatment 5 – Treatment 2,
- g. Feces  $CO<sub>2</sub>$  or NH<sub>3</sub>–N emissions applied over vegetation = Treatment 6 – Treatment 2.

The statistical analysis of the cosine amplitudes and phase shifts, as well as  $CO_2$ –C and NH<sub>3</sub>–N emissions were conducted in PROC GLM in SAS (SAS Institute, 2008). In this analysis, blocks were random and the treatments were fixed. The *p* value for calculated confidence intervals was  $p = 0.10$ . Correlation coefficients between the measured parameters were calculated.



Fig. 2. The relationship between time and natural log (ln) fecal C remaining. In this chart the slope is the first order rate constant and has the units g  $(g \times day)^{-1}$ . The open circles are the grass + fecal material and the filled circles are the soil + fecal material treatment.

#### **Determining Feces-Carbon First-Order Mineralization Rate Constants**

The fecal-C first-order rate constants were the absolute value of the slope between the time in days (*x*) and the natural log of the fecal C remaining [fecal C at time zero – fecal-C  $CO<sub>2</sub>$ –C emissions] at 0, 7, and 20 d (Mamani-Pati et al., 2010; Chang et al., 2016a). The first-order rate constants for soil-mixed feces and feces applied over vegetation for each block were computed (Fig. 2). These rate constants were used to estimate the amount of fecal-C that remained using the equation,  $\text{focal}_{\text{remaining}} = \text{focal}_{\text{initial}} \times \exp^{-k_t \times \text{time}}$ .

Twenty day area adjusted  $CO<sub>2</sub>-C$  emissions were calculated for the treatments where feces were lightly mixed into the soil or applied over vegetation. For the feces that was lightly mixed with the soil, the 20 d area-corrected  $CO<sub>2</sub>$ –C emissions were calculated by combining  $CO<sub>2</sub>-C$  emissions from the soil (Treatment 1) and the soil + mixed feces (Treatment 4). The  $CO<sub>2</sub>$ –C losses from bare soil (Treatment 1) were calculated by combining the losses from Days 1 through 7 with Days 8 through 20. For example,  $kg C$  loss ha<sup>-1</sup> in bare soil treatment (Treatment 1) was equal to [7 d ×3.05 g (m<sup>2</sup> × day)<sup>-1</sup> + 13 d × 3.54 g (m<sup>2</sup> × day)<sup>-1</sup>] × 10,000 m<sup>2</sup> ha<sup>-1</sup> × kg 1000 g<sup>-1</sup> = 674 kg CO<sub>2</sub>-C ha<sup>-1</sup>. The CO<sub>2</sub> from areas where the feces was lightly mixed with the soil was based on an estimated fecal deposition. This value was based on a forage digestibility value of 560 g  $kg^{-1}$ , a livestock consumption rate of 1460 kg biomass (ha  $\times$  year)<sup>-1</sup> which resulted in an annual feces-C application rate of 270 kg feces-C ha<sup>-1</sup> (Ferebee et al., 1972; Larsen, 1996; Tate et al., 2003; Mortellaro-Brown, 2014). The amount of mineralized feces-C was calculated using the first order rate constants of 0.0109 ( $\pm$  0.0043) (g  $\times$  d)<sup>-1</sup> in the trampled soil treatments. For example, C mineralized from feces was 270  $[1 - \exp(-0.00454 \times 20d)] = 52.9$  kg feces-C ha<sup>-1</sup> mineralized. Total mineralization was  $727 \text{ kg} \text{ ha}^{-1}$  (53+674). For the feces applied over vegetation, similar calculations were conducted using data from Treatments 2 and 6.

#### **Results and Discussion Carbon Dioxide Emission**

Air temperatures and  $CO<sub>2</sub>$ –C emissions followed a diurnal cycle that had maximum values between 1500 and 1800 h of the day and minimum values between 300 and 600 h of the day (Table 1, Fig. 3). Similar  $CO<sub>2</sub>$ –C emissions and soil temperatures phase shifts were attributed to the impact of temperature on microbial activity and that  $CO<sub>2</sub>$  solubility decreases with increasing temperature (Chang et al., 2016a). During the first 7 d,  $CO<sub>2</sub>-C$  emissions were almost 50% less in the lightly mixed soil [3.05 g CO<sub>2</sub>–C (m<sup>2</sup>×d)<sup>-1</sup>] than the clipped vegetation [7.53 g CO<sub>2</sub>–C (m<sup>2</sup>×d)<sup>-1</sup>] treatment. Differences in the CO<sub>2</sub> emissions between the mixed soil and vegetation treatments were attributed to several factors including plant respiration and/ or that the plant stimulated soil organic matter mineralization (Phillips et al., 2010).

Similar fecal-C  $CO_2$ –C emissions were observed for the first 7 d when they were suspended over soil [9.6 g C (m<sup>2</sup>×d)<sup>-1</sup>] or vegetation [10.4 g C (m<sup>2</sup>×d)<sup>-1</sup>]. When the feces were applied and partially mixed into the soil,  $CO<sub>2</sub>$  emissions [Treatment 4 – Treatment 1] increased 59% when compared with the mixed soil without feces. This increase is attributed to the fecal materials stimulating heterotrophic respiration.

For the 8 to 20 d period, the relative  $CO<sub>2</sub>–C$  emissions per day were numerically lower than emissions that occurred during the first 7 d. Decreases in  $CO<sub>2</sub>-C$  emissions with time are consistent with first order kinetics (Mamani-Pati et al., 2010; Kyvsgaard et al., 2000), and they are similar to the findings of Ajwa and Tabatabai (1994).

When the feces were lightly mixed into the soil, the first-order rate constants were higher  $[0.0109 \pm 0.0043 \text{ g (g} \times \text{day})^{-1}]$  than when applied over vegetation  $(0.00454 \pm 0.00336 \text{ g} (\text{g} \times \text{day})^{-1}]$ . The soil-mixed feces first-order rate constants were correlated to the volumetric soil moisture content  $[k<sub>feces mixed</sub> = 0.03685 \times$ (water content) –  $0.00053$ ,  $p = 0.097$ ], but were not correlated to the average air temperature ( $p = 0.44$ ). The lack of correlation





† The same letters within a column are not significantly different (*p* = 0.10).

‡ ns: nonsignificant.



Fig. 3. Soil temperature,  $CO<sub>2</sub>-C$  emissions and  $NH<sub>3</sub>-N$ emissions in the soil lightly mixed and feces lightly mixed into soil. The mixing was used to simulated cattle traffic.

between the average temperatures and first-order rate constants is similar to the findings of Clay et al. (2010, 2012), and is attributed to soil temperature diurnal variability (Fig. 2). When the feces were applied over vegetation, the feces-C mineralization rate constants were not correlated to either soil water or air temperature. These results were attributed to the feces not being mixed into the soil. To assess the repeatability of the measurement system,  $CO<sub>2</sub>-C$  emissions of feces suspended over bare soil and vegetation were compared. For this time period, the  $CO<sub>2</sub>-C$ emission rates were similar and the difference between these two treatments represented 4.3% of the total  $CO<sub>2</sub>-C$  emitted.

#### **Comparison Between Near Continuous and Point Carbon Dioxide-Carbon Emissions Measurements**

In this experiment, gas samples are collected and analyzed on near continuous basis. However, to reduce the cost associated gas sample collection and analysis, Parkin and Venterea (2010) recommend that the samples be collected at a time that corresponds to the average temperature and where possible these points should be as close together as possible. Based on these recommendations, numerous studies have been conducted where point greenhouse gas emissions are measured at regular time

intervals over the study. For example, Hamido et al. (2016) measured  $CO<sub>2</sub>-C$  emissions weekly from 1200 to 1400 h, whereas Nykanen et al. (1995) did not identify when the samples were collected. Generally, total emissions are determined by using linear interpolation across sampling times.

Based on the FFT, the peak temperatures occurred at about  $1600 h (1200 h + 400 h)$  phase sift). Based on the measured temperatures in Fig. 3, the average temperature occurred at 1019  $\pm$  0.93 h. A comparison between the CO<sub>2</sub>–C emissions at 1100 h and near continuous measurement showed that the two measurements were highly correlated  $(r^2 = 0.99^{**})$ , however they predicted different emissions. Point samples when collected daily at 1100 h, every 2 d, and every 3 d, when averaged across blocks and the four treatments (1, 2, 4, and 6) had emissions of 196, 206, and 200 g CO<sub>2</sub>–C (m<sup>2</sup> × 20 d)<sup>-1</sup>, respectively. In all cases, these values were 5 to 10% greater than the near continuous measurement of 186 g CO<sub>2</sub> (m<sup>2</sup> × 20 d)<sup>-1</sup>. In addition, sampling every 2 d had different results than sampling every day, and delaying sample collection from 1100 to 1300 h in the soil + manure treatment between Days 1 and 2 (Fig. 1) would have increased emission 62% [from 7.53 to 12.2 g CO<sub>2</sub>–C (m<sup>2</sup>  $\times$ hour) $-1$ ]. This assessment suggests that point measurement can be used to provide qualitative emissions. However, if the samples are not collected at the average temperature, they may not be accurate.

#### **Ammonia-Nitrogen Volatilization from Cow Fecal Materials**

In northern Great Plains rangeland systems, the primary sources of N are atmospheric deposition,  $N_2$  fixation by legumes, and feces-N and urine depositions from animals. Because little N fertilizer is applied to these systems, their long-term productivity relies on minimizing N losses (Vlassak et al., 1973; Reeder and Schuman, 2002; Köchy and Wilson, 2001; Fornara and Tilman, 2012; Keuter et al., 2014).

Ammonia loss from the feces followed a diurnal cycle with peak values occurring at 1400 h (Fig. 2). These results are in agreement with Sherlock and Goh (1985) and Clay et al. (1990) who reported that  $NH<sub>3</sub>$  peaks matched temperature peaks. This diurnal cycle was attributed to the temperature dependence of microbial activity and decreasing  $NH<sub>3</sub>$  solubility with increasing temperature. Decreased  $NH<sub>3</sub>$  volatilization when mixed with the soil was expected, and even though volatilization was numerically lower when mixed with the soil, it was not significant (Table 2).

The total amount of volatilized  $NH_3-N$  in the non-feces treatments (Treatments 1 and 2) for the first 7 d was 0.36 g  $NH_3-N$  m<sup>-2.</sup> When feces was applied (Treatments, 3, 4, 5, and 6), the total loss over 7 d was 0.49 g NH<sub>3</sub>–N m<sup>-2</sup> (Table 2). Based on the difference between the treated and untreated soil, approximately 20% of the fecal  $NH_4$ –N was volatilized. These values are higher than the 3.9% loss reported by Fischer et al. (2016). Differences between Fischer et al. (2016) and our results, are attributed to Fischer et al. (2016) making a comparison with total N, whereas we only considered  $NH<sub>3</sub>–N$  in the feces. Laubach et al. (2013) used a micrometeorotical technique to measure  $NH<sub>3</sub>$  volatilization above a small paddock containing both feces and urine patches. In Laubach et al. (2013), NH<sub>3</sub> volatilization was measured at 5 m heights above the soil surface.

Table 2. Total NH<sub>3</sub>–N loss (g NH<sub>3</sub>–N m<sup>-2</sup>) over 7 d and percentage of loss relative to the controls (Treatments 1 and 2) and initial amount of  $NH<sub>3</sub>$  contained in the feces.

	∍		
	<b>Treatments</b>	$NH3-N$ loss	Feces $NH2-N loss$
		$mg \, m^{-2}$	℅
	Lightly mixed soil	355b <sup>+</sup>	
2	Vegetation	364b	
3	Trampled soil + suspended feces	483a	19.4
4	Soil trampled with feces	475a	18.I
5	Veg.+ suspended feces	506a	23.0
6	Vegetation + feces	488a	20.9
	Þ	0.005	ns‡
	LSD(0.1)	0.072	

† The same letters in parentheses represents that they are not significantly different at the 10% level.

‡ ns: nonsignificant.

Based on temporal and spatial variability, they reported that 11.6% of the dung N was volatilized. However, they did not provide treatments where  $NH<sub>3</sub>$  from soil, feces, and urine could be separated and they did not report the efficiency of the collection system. Laubach et al. (2013) value of 11.6% was much higher than the 3.9% reported by Fischer et al. (2016). Similarly, Lee et al. (2011) in a laboratory study had slightly lower  $NH<sub>3</sub>$ volatilization which ranged from 1 to 13%. In our study, 20%  $NH_4$ –N volatilization loss is similar to the losses reported for urea (Clay et al., 1990) and simulated urine (Sherlock and Goh, 1985) and lower than the losses reported for surface-applied manure (Stevens and Laughlin, 1997; Lee et al., 2011; Hristov et al., 2011).

#### **Calculating the Potential Impact of Feces on Whole Paddock Carbon Dioxide Emissions**

Area corrected  $CO<sub>2</sub>-C$  emissions for the lightly mixed soil and for the lightly mixed soil plus feces were 674 and 727 kg  $CO_2$ –C ha<sup>–1</sup>, respectively. These calculations suggest that 52 kg feces-C ha<sup>-1</sup>, or 19% of the applied feces C was respired over 20 d, and that the feces deposition increased total  $CO_2-C$ emission 7.6%. The 90% confidence interval for mineralized feces C ranged between 33 and 71 kg C  $ha^{-1}$ .

When the feces were deposited over the clipped vegetation, slightly different results were observed. In the clipped vegetation, 9.3% of the feces-C was emitted and  $CO<sub>2</sub>-C$  emissions increased from 1711 kg  $CO_2$ –C ha<sup>-1</sup> in area without feces to 1736 kg CO<sub>2</sub>–C ha<sup>–1</sup> in areas with feces. By difference, the amount of feces-C emitted was 25 kg CO-C and the 90% confidence interval for the mineralized feces-C was between 6.3 and 39 kg C ha<sup>-1</sup>. The small differences between the grassland with and without feces may explain why previous studies have reported that grazing can produced a mixed impact on C sequestration (Conant and Paustian, 2002; Yuan and Hou, 2015). The area corrected 20 d  $CO<sub>2</sub>-C$  emissions from bare soil (676 kg  $CO_2$ –C ha<sup>–1</sup>) were much lower than areas with only vegetation  $(1711 \text{ kg CO}_2 - \text{Ca}^{-1}).$ 

#### **Summary**

In the northern Great Plains, farmers and ranchers are interested in conducting research on techniques to increase their soil C levels. This paper demonstrated an approach to assess precision conservation treatments at targeted locations. In addition, the research compared total  $CO<sub>2</sub>-C$  emissions over 20 d using near continuous measurements with point measurements collected at 1100 h every day, every 2 d, and every 3 d. This comparison showed that the two methods were highly correlated, however point measurements over estimated total emissions. These findings suggest that targeted point sampling for greenhouse gases can contain substantial uncertainty.

The temporal data was converted to the frequency domain using the FFT. This analysis confirmed that temperature, NH volatilization, and  $CO<sub>2</sub>$ –C emissions followed a diurnal cycle and that differences in the phases were not detected. If the measurements would have been collected over a several years, FFT could have been used to separate the seasonal and diurnal cycles.

In situ measurements of  $CO<sub>2</sub>$  emissions showed that management can influence  $CO_2-C$  emissions and that mixing feces with soils increased  $CO<sub>2</sub>$  emissions. The first-order fecal-C mineralization rate constants and 90% confidence intervals for the feces mixed with soil and for the feces applied over vegetation were  $0.0109 \pm 0.0043$  g (g×d)<sup>-1</sup> and  $0.00454 \pm 0.00336$  g  $(g \times d)^{-1}$ , respectively. The rate constants and digestibility values were used to calculate area corrected  $CO<sub>2</sub>-C$  emissions. The area corrected 20-d  $CO<sub>2</sub>-C$  emissions for the simulated trampled soil and for the feces that was simulated to be trampled into the soil were 674 and 726 kg  $CO_2$ –C ha<sup>-1</sup>, respectively. These values indicate that in bare soil, there was a 7% difference between the soil and soil plus feces treatment, and that of the 270 kg of feces-C added, the 90% confidence interval for mineralized feces-C ranged between 33 and 71 kg C ha<sup>-1</sup>. In range systems, highly trampled bare soil is often found near shade and food and water sources. In the vegetation treatment, there was a 1.4% difference between the vegetation (1711 kg  $CO_2$ –C ha<sup>-1</sup>) and vegetation plus feces (1736 kg  $CO_2$ –C ha<sup>-1</sup>). These calculations show that accurate accounting requires the measurement or estimation of the feces deposition rate. Once the locations and amounts are determined, techniques discussed in this paper can be used to calculate  $NH_3-N$  and  $CO_2-C$  emissions.

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