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## Air, Soil and Water Research

## Nitrous Oxide Fluxes from a Commercial Beef Cattle Feedlot in Kansas

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**ABSTRACT:** Emission of greenhouse gases, including nitrous oxide ( $N_2O$ ), from open beef cattle feedlots is becoming an environmental concern; however, research measuring emission rates of  $N_2O$  from open beef cattle feedlots has been limited. This study was conducted to quantify  $N_2O$  emission fluxes as affected by pen surface conditions, in a commercial beef cattle feedlot in the state of Kansas, USA, from July 2010 through September 2011. The measurement period represented typical feedlot conditions, with air temperatures ranging from -24 to 39°C. Static flux chambers were used to collect gas samples from pen surfaces at 0, 15, and 30 minutes. Gas samples were analyzed with a gas chromatograph and from the measured concentrations,  $N_2O$  fluxes were calculated. Median emission flux from the moist/muddy surface condition was 2.03 mg m<sup>-2</sup> hour<sup>-1</sup>, which was about 20 times larger than the  $N_2O$  fluxes from the other pen surface conditions. In addition,  $N_2O$  peaks from the moist/muddy pen surface condition were six times larger than emission peaks previously reported for agricultural soils.

KEYWORDS: feedlot surface emissions, greenhouse gases, nitrous oxide flux, static flux chambers

CITATION: Aguilar et al. Nitrous Oxide Fluxes from a Commercial Beef Cattle Feedlot in Kansas. *Air, Soil and Water Research* 2014:7 35–45 doi:10.4137/ASWR.S12841. RECEIVED: July 22, 2013. RESUBMITTED: November 18, 2013. ACCEPTED FOR PUBLICATION: November 20, 2013.

ACADEMIC EDITOR: Carlos Alberto Martinez-Huitle, Editor in Chief

TYPE: Original Research

FUNDING: This study was supported in part by the government of the Republic of Panama through SENACYT/IFARHU/Technological University of Panama, USDA-NIFA Special Research Grant "Air Quality: Reducing Air Emissions from Cattle Feedlots and Dairies (TX and KS)," through the Texas AgriLife Research, and Kansas Agricultural Experiment Station (contribution number 13-150-J).

COMPETING INTERESTS: Authors disclose no potential conflicts of interest.

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## Introduction

Emission of greenhouse gases (GHGs) such as carbon dioxide (CO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), and methane (CH<sub>4</sub>) are contributing to global warming.<sup>1</sup> The 100 year linear trend (1906 through 2005) of the earth's climate system shows an increase of 0.74°C in air temperature.<sup>2,3</sup> Nitrous oxide has a global warming potential (GWP) 296 times greater than that of CO<sub>2</sub> and an atmospheric lifetime of approximately 120 years,<sup>4</sup> yet it is often one of the least known GHGs in terms of source material. Animal agriculture and N-enriched soils from fertilization are considered key sources of anthropogenic N<sub>2</sub>O emissions.<sup>5</sup> Total nitrogen (N) retained by the animal and animal products (ie, meat, milk, etc.) is estimated to be only 5–20% of the total N intake for animals, with the rest associated with either excreted feces or urine.<sup>5</sup> The total inventory of cattle and calves in the United States was 100 million head in 2011,<sup>6</sup> with approximately 34% of those animals concentrated in large open feedlots.<sup>7</sup> In open beef cattle feedlots, urine containing over 50% of intake N from animal diets<sup>5</sup> is deposited on the pen surface, available for microbial decomposition, which may result in high emissions of N<sub>2</sub>O. Significant increase in N<sub>2</sub>O emissions up to 14 days after urine application has been reported.<sup>8</sup> Nitrous oxide is primarily produced biologically by nitrification and denitrification processes.<sup>9–11</sup> In general, nitrification is the aerobic microbial oxidation of ammonia into nitrate (NO<sub>3</sub><sup>-</sup>), while denitrification is the anaerobic microbial reduction of NO<sub>3</sub><sup>-</sup> to NO, N<sub>2</sub>O, and N<sub>2</sub>. These processes result in N<sub>2</sub>O emissions as an intermediate by-product; however, activation of these processes is highly variable in

time and space, because they depend on soil water content, temperature, organic matter content,  $NO_3^-$  content, ammonium ( $NH_4^+$ ) content, microbial community, <sup>9–11</sup> as well as soil pH, bulk density, solid/liquid/gas phase percentages, C to N ratio, inorganic N/C/P, exchangeable cations, and electrical conductivity.

Knowledge on the effects of soil  $N_2O$  emissions from tillage operations is extensive,<sup>12</sup> and ruminant digestive systems have also been documented to some extent.<sup>13</sup> However, little information is available on the levels of  $N_2O$  emission from commercial beef cattle feedlots.<sup>14</sup> The main purpose of this study was to examine emission rates of  $N_2O$  from commercial beef cattle feedlots as affected by pen surface characteristics and environmental conditions. This research is expected to contribute to the limited published data on GHG emissions from beef cattle feedlots. Nitrous oxide emissions varied with pen surface condition and season, with  $N_2O$  emission fluxes from moist pen surface conditions more than six times larger than reported  $N_2O$  emissions from cultivated soils.

### Materials and Methods

Feedlot description. This study was conducted at an open beef cattle feedlot in the state of Kansas, USA, from June 2010 through September 2011. During the measurement period, in the feedlot area, air temperature ranged from -24 to 39°C and total rainfall was 352 mm, with the highest total seasonal rainfall of 134 mm in summer 2010 and the lowest rainfall amount of 20 mm in winter 2010-2011. The prevailing wind direction in the area was south/southwest. The feedlot had a total pen surface area of approximately 59 ha with a capacity of 30,000 head. The terrain was level to gently sloping with average slope less than 5%, and the feedlot was surrounded by agricultural lands. Each pen was scraped two to three times per year, and manure was removed at least once per year. Air temperature, total rainfall amount, and wind direction were measured with a meteorological station deployed in the field.

Sampling and measurement. Emission fluxes of N<sub>2</sub>O from the pen surface were measured using 30 cm diameter static flux chambers (SFCs) with internal forced air circulation, following the procedure that has been used for soils.<sup>13,15-19</sup> The SFCs were designed with an average headspace volume and height of 13 L and 18 cm, respectively. Each SFC had the following components (Fig. 1): cylindrical body, metal ring, cap, and peripheral accessories (ie, sampling port, small blower, pressure equalizer, soil/manure and air temperature sensors, and data logger). The body was made from 30 cm diameter PVC pipe. The metal ring was made of 18 ga stainless steel and was tightly connected with the chamber body. The cap was a low-density polyethylene pipe cap with a diameter of 30 cm (Alliance Plastics, Little Rock, AR) and was covered with reflective adhesive tape to minimize internal heating by solar radiation.9,16 The



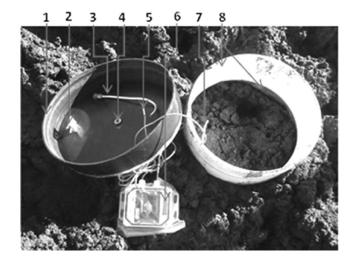


Figure 1. Photograph of the static flux chamber showing the major components: (1) chamber cap, (2) small blower, (3) pressure equalizer, (4) sampling port, (5) air temperature sensor, (6) data logger, (7) soil/ manure temperature sensor, and (8) body with the stainless steel ring.

sampling port was fitted with a rubber septum for syringe sampling. The pressure equalizer consisted of a vent tube made from aluminum pipe with a diameter of 0.6 cm and length of 22 cm.<sup>16</sup> A small blower, a single-phase, 6-pole brushless DC motor with dimensions of  $30 \times 30 \times 3$  mm (Newark Company, Chicago, IL) with a rated volumetric flow rate of 7.5 L minute<sup>-1</sup> was used for internal forced air circulation. This low flow rate was designed to prevent internal pen surface disturbance and the consequent effect on gas flux measurement. Soil/manure temperature and air temperature sensors were HOBO TMC6-HD sensors (-40-100°C  $\pm$  0.25°C, resolution 0.03°C) and were connected to a data logger (HOBO U12-008, Onset Computer Corp., Bourne, MA). Soil/manure volumetric water content was measured with a moisture sensor (model EC-5, Decagon Devices Inc., Pullman, WA). Gas samples were analyzed in the laboratory for N<sub>2</sub>O concentrations using a GC (model GC14A, Shimadzu, Kyoto, Japan). Each of the gas samples was injected manually to the GC. The GC was fitted with a Porapak-Q (80/100 mesh) stainless steel column (0.318 cm diameter by 74.5 cm long) and an electron-capture detector (ECD). The GC carrier gas was Ar/CH<sub>4</sub> (95:5 ratio). The column (oven), injector, and ECD were set up at 85, 100, and 320°C, respectively.

Soil/manure temperature through the first 10 cm below the surface and air temperature in the SFC headspace were measured every 60 seconds during sampling. Volumetric soil/ manure water content (5 cm, 0.3 L measurement volume) was measured before capping the chamber. During each field sampling campaign, once the last gas sample was collected, a 10 cm soil/manure core was collected from the inside of each SFC for each pen. In addition, in one of the pens, a deeper 15 cm core was collected immediately below the first 10 cm core in each chamber. Those 15 cm cores were collected from



the same pen. The cores were analyzed following standard procedures at the Kansas State University Soil Testing Laboratory (Manhattan, KS) for pH (soil:water 1:1 method),  $NH_4^+$ , and  $NO_3^-$  (KCI extraction method), total N (dry combustion method), and total C contents (salicylic-sulfuric acid digestion method).<sup>20,21</sup>

In addition to the required seal between the coupled elements of the SFC, the complete chamber must be adequately sealed to the pen surface at the deployment time; hence, the metal ring was tightly inserted into the soil/manure layer to limit subsurface gas movement in the vertical direction.<sup>17,22</sup> Rochette and Eriksen-Hamel<sup>18</sup> stated that "leakage or contamination can occur by lateral diffusion of N<sub>2</sub>O beneath the base in response to deformation of the vertical N<sub>2</sub>O concentration gradient in the soil." Previous studies inserted the chambers 2–7.5 cm deep into the soil.<sup>1,11–13,19,23,24</sup> Based on the procedure suggested for Rochette and Eriksen-Hamel,<sup>18</sup> SFCs in this research were inserted at least 6 cm deep for 30 minutes deployment time.

To calculate emission flux, the change in gas concentration with time  $(\Delta C / \Delta t)$  must be determined, and gas samples must be collected in the shortest possible time.<sup>18</sup> Preliminary tests were performed with a deployment time of 60 minutes, collecting chamber headspace samples each five minutes; results showed relatively constant concentration gradient during the first 30 minutes (Fig. 2). As such, for this study, the sampling protocol involved sampling at 0, 15, and 30 minutes once the chambers were capped. This agreed with protocols that have been developed for soils. Gas samples were collected with 20 mL disposable plastic monoject syringes with detachable 25GX 1.5 in. needles and injected into previously flushed and evacuated 12 mL glass vials. Overpressure in the syringes was intended to prevent sample contamination with atmospheric gases<sup>24</sup> and to have sufficient sample for multiple analyses in the GC. In addition, as a reference of the ambient N2O concentration (background), one gas sample was collected at 1 m height just before and after the sampling period in each pen.

In the feedlot, cattle grouped by age were normally assigned pens based on availability. Therefore, as there were no special criteria to assign cattle to the pens, three pens were randomly selected to perform the measurement campaigns. In general, each pen included a part of the mound (highly compacted surface located at the center of the pen), dry and loose surfaces, as well as muddy and flooded spots. From preliminary work, four main pen surface conditions were identified (Fig. 3): I - moist/muddy, II - dry and loose, III - dry and compacted, and IV - flooded. Their respective average dry bulk densities were 0.86, 1.06, 1.03, and 0.82 g cm<sup>-3</sup>. In the pen, surface condition I corresponds to the condition that appears relatively moist or muddy on the surface and wet/muddy at least 5 cm underneath. On sampling days, the different surface conditions were randomly selected in the pen to deploy the SFCs. The presence and locations of the surface conditions changed with time. During two sampling days in March 2011, the relative sizes (%) of the surface conditions were estimated. Mean areas  $(\%) \pm$  standard deviations (%) as a percent of the total pen area were  $14 \pm 10$ ,  $47 \pm 27$ ,  $24 \pm 2$ , and  $15 \pm 20$  for surface conditions I (moist/muddy), II (dry and loose), III (dry and compacted), and IV (flooded), respectively.

During the GHG measurement period (June 2010 through September 2011), three pens were randomly selected and 10 field sampling campaigns with a total of 23 sampling days were conducted. During three days in July 2010, within 1 m<sup>2</sup>, paired SFCs were installed in three different surface conditions in a pen. Gas samples were taken from the chamber headspaces four times a day, twice in the morning (from 08:00 to 12:30 hours) and twice in the afternoon (from 12:30 to 21:00 hours). From the paired SFCs, N<sub>2</sub>O fluxes were averaged and reported as the flux from the respective surface condition during that particular sampling time. Results indicated that the N<sub>2</sub>O fluxes among the morning

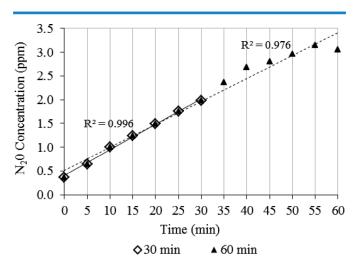


Figure 2. Concentration gradient in the chamber headspace during the preliminary one hour gas sampling tests.

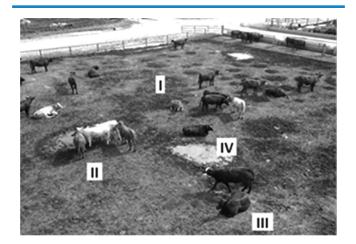


Figure 3. Photograph of a pen showing the different studied pen surface conditions (I – moist/muddy, II – dry and loose, III – dry and compacted, and IV – flooded).

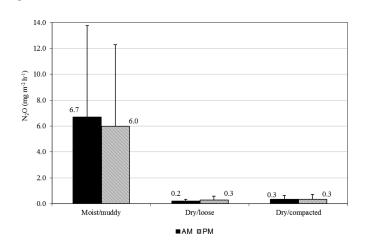


Figure 4. N<sub>2</sub>O emissions behavior between morning and afternoon sampling periods.

sampling events were not significantly different. Fluxes from the two afternoon sampling events were also not significantly different. Therefore, during sampling from September through November 2010, SFCs were deployed in the pens, with each available surface condition covered by one SFC. Gas samples were collected twice a day (morning and afternoon). Analysis of the data indicated that the N2O fluxes were not significantly different (P = 0.894) between the morning and afternoon sampling periods (Fig. 4). As such, in succeeding sampling campaigns (ie, February through September 2011), during sampling, each available surface condition was covered by a SFC in each pen and sampled only once a day. During a few sampling campaigns, as a result of weather conditions, animal behavior, and feedlot maintenance practices, the flooded and the moist/muddy surface conditions were not present; as such, the numbers of samples were unbalanced.

#### Calculation of N<sub>2</sub>O Emission Fluxes

Emission fluxes were computed from the change in N<sub>2</sub>O concentration with time, as described by Hutchinson and Mosier,<sup>16</sup> Ginting et al,<sup>23</sup> and Anthony et al<sup>25</sup>:

$$F = \left[ \left( \frac{V}{A} \right) \left( \frac{\Delta C}{\Delta t} \right) \right] \tag{1}$$

where F is the gas emission rate ( $\mu g m^{-2} hour^{-1}$ ); V is volume of air within the chamber (m<sup>3</sup>), which was determined for each sampling event based on the chamber's internal height; A is the surface area of soil/manure within the chamber (m<sup>2</sup>); and  $(\Delta C/\Delta t)$  is the concentration gradient with time, in which,  $\Delta C$ is the N2O concentration difference (ppm) between two sampling times and  $\Delta t$  is the respective sampling interval (hours). The gas concentration was converted from parts per million to micrograms per cubic meter assuming ideal gas behavior.

The concentration gradient with time ( $\Delta C / \Delta t$ ), was calculated based on three general cases<sup>23</sup>:

#### **Statistical Analysis**

Emission flux data and soil/manure chemical and physical characteristics were first analyzed for normality using the univariate procedure in SAS.27 Normality for each individual factor was analyzed based on the complete dataset, then classified by pen, season, and pen surface condition. Soil/manure characteristics, including water content, temperature, pH, total N content, total C content, and chamber air temperature were normally distributed. As N2O fluxes were highly episodic<sup>28</sup> and dependent on soil/manure conditions, which results in large spatial variability,<sup>8,12,14</sup> N<sub>2</sub>O as well as the soil/manure  $NH_4^+$  content and  $NO_3^-$  content were not normally distributed at the 5% level. The N2O emission flux data showed positively skewed distribution; as such, log transformation was performed.<sup>29,30</sup> The logtransformed data were normally distributed and then analyzed for unequal variances using the MIXED procedure in SAS.<sup>31</sup> P-values and confidence intervals were adjusted

Case  $1 - \Delta C_1 \ge \Delta C_2$  and  $C_0 \le C_{15} \le C_{30}$  (steadily increasing concentrations) or  $C_0 > C_{15} > C_{30}$  (steadily decreasing concentrations)

$$\frac{\Delta C}{\Delta t} = \left[ \frac{\left(\Delta C_1\right)^2}{\Delta t \left(2C_{15} - C_{30} - C_0\right)} \ln\left(\frac{\Delta C_1}{\Delta C_2}\right) \right] \tag{2}$$

Case 2 –  $\Delta C_1 \leq \Delta C_2$  and  $C_0 \leq C_{15} \leq C_{30}$  (steadily increasing concentrations) or  $C_0 > C_{15} > C_{30}$  (steadily decreasing concentrations)

$$\frac{\Delta C}{\Delta t} = \left[\frac{\Delta C_1 + \Delta C_2}{2\Delta t}\right] \tag{3}$$

Case 3 –  $\Delta C_1 \leq \Delta C_2$  and  $C_0 < C_{15} > C_{30}$  or  $C_0 > C_{15} < C_{30}$ (fluctuating concentrations with sampling time)

$$\frac{\Delta C}{\Delta t} = \left[\frac{\Delta C_1}{2\Delta t} + \frac{\Delta C_3}{4\Delta t}\right] \tag{4}$$

where  $\Delta C_1 = (C_{15} - C_0); \ \Delta C_2 = (C_{30} - C_{15}); \ \Delta C_3 = (C_{30} - C_0);$  $C_0$ ,  $C_{15}$ , and  $C_{30}$  are the measured N<sub>2</sub>O concentrations (ppm) within the SFC at sampling times of 0, 15, and 30 minutes, respectively, and  $\Delta t = 0.25$  hours. Case 1 is based on the diffusion approach considering the SFC N<sub>2</sub>O saturation with time.<sup>16,23,25</sup> Case 2 is based on the average of the two slopes between concentrations when there is no N<sub>2</sub>O saturation; that is, the gas concentration gradient is linear over time.<sup>23,27</sup> Case 3 is based on the average of the slopes between the first and second and between the first and third N2O concentrations, respectively.<sup>23</sup>



#### Table 1. Measured N<sub>2</sub>O concentrations inside the SFCs.

SURFACE CONDITION		SAMPLING TIME (MINUTES)		
	MEASUREMENT	0	15	30
I – Moist/muddy	Number of data points	39	39	39
	Average concentration (ppm)	0.53	4.49	7.75
	Standard deviation (ppm)	0.31	8.94	17.06
	Minimum concentration (ppm)	0.29	0.41	0.54
	Soil water content (cm <sup>3</sup> cm <sup>-3</sup> )	0.493	0.512	0.592
	Soil temperature (°C)	19.6	1.7	25.6
	Maximum concentration (ppm)	1.89	42.9	78.3
	Soil water content (cm <sup>3</sup> cm <sup>-3</sup> )	0.422	0.422	0.422
	Soil temperature (°C)	19.2	19.2	19.2
II – Dry and loose	Number of data points	54	54	54
	Average concentration (ppm)	0.42	0.60	0.75
	Standard deviation (ppm)	0.13	0.28	0.45
	Minimum concentration (ppm)	0.31	0.33	0.32
	Soil water content (cm <sup>3</sup> cm <sup>-3</sup> )	0.293	0.293	0.223
	Soil temperature (°C)	22.6	22.6	30.0
	Maximum concentration (ppm)	0.94	1.71	2.46
	Soil water content (cm <sup>3</sup> cm <sup>-3</sup> )	0.20	0.20	0.244
	Soil temperature (°C)	22.5	22.5	20.4
	Number of data points	51	51	51
	Average concentration (ppm)	0.38	0.55	0.64
III – Dry and compacted	Standard deviation (ppm)	0.07	0.28	0.32
	Minimum concentration (ppm)	0.26	0.32	0.34
	Soil water content (cm <sup>3</sup> cm <sup>-3</sup> )	0.07	0.18	0.18
	Soil temperature (°C)	33.5	29.7	29.7
	Maximum concentration (ppm)	0.70	1.78	1.69
	Soil water content (cm <sup>3</sup> cm <sup>-3</sup> )	0.155	0.104	0.13
	Soil temperature (°C)	23.5	24.1	27.2
IV – Flooded	Number of data points	32	32	32
	Average concentration (ppm)	0.47	0.59	0.70
	Standard deviation (ppm)	0.17	0.22	0.34
	Minimum concentration (ppm)	0.32	0.37	0.41
	Soil water content (cm <sup>3</sup> cm <sup>-3</sup> )	0.60	0.60	0.58
	Soil temperature (°C)	25.3	26.1	35.0
	Maximum concentration (ppm)	1.07	1.26	1.93
	Soil water content (cm <sup>3</sup> cm <sup>-3</sup> )	0.60	0.60	0.60
	Soil temperature (°C)	20.3	20.3	22.3

for Bonferroni.<sup>32</sup> In addition, the median of the N<sub>2</sub>O emission fluxes and the confidence interval for the median were reported rather than the mean and standard deviation.<sup>29</sup> Regression analyses between N<sub>2</sub>O emission flux and soil/manure physical and chemical properties for the complete dataset as well as segregated analysis by pen surface condition were performed using the stepwise procedure of SAS. Predictor factors were assessed for multicollinearity based on the variance inflation factor.<sup>33</sup>

## **Results and Discussion**

Nitrous oxide emission fluxes. Measured concentrations of N<sub>2</sub>O inside the SFCs at sampling times of 0, 15, and 30 minutes are summarized in Table 1. In general, N<sub>2</sub>O concentrations inside the SFCs increased steadily (ie,  $C_0 < C_{15} < C_{30}$ ). Based on the concentration gradients, 41% of 176 samples followed case 1 (ie,  $\Delta C_1 > \Delta C_2$  and  $C_0 < C_{15} < C_{30}$ ), 40% followed case 2 (ie,  $\Delta C_1 \leq \Delta C_2$  and  $C_0 < C_{15} < C_{30}$ ), and the remaining 19% followed case 3 (ie,  $\Delta C_1 \leq \Delta C_2$  and  $C_0 < C_{15} > C_{30}$  or  $C_0 > C_{15} < C_{30}$ ).



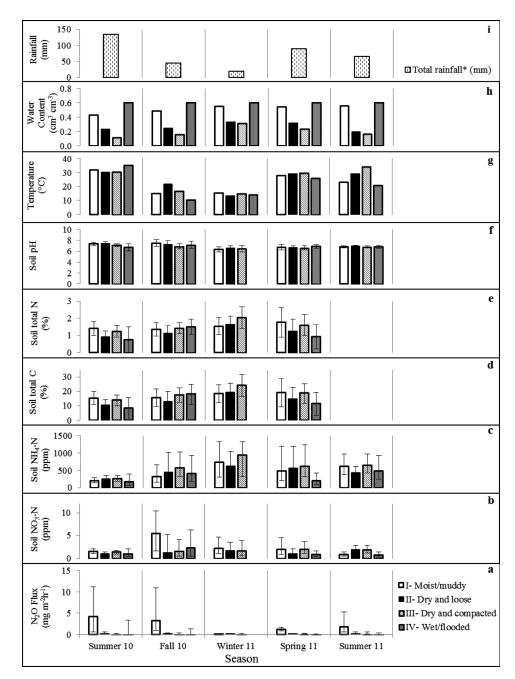


Figure 5. N<sub>2</sub>O emission fluxes and related factors as affected by pen surface conditions and season: (a) median N<sub>2</sub>O flux, (b) median nitrate content, (c) median ammonium, (d) median total carbon, (e) median total nitrogen, (f) median pH, (g) median soil/manure temperature, (h) water content, and (i) median rainfall. Error bars represent 95% CI.

Emission fluxes of  $N_2O$  for each pen surface condition and season during the study period are shown in Figure 5a. The fluxes, particularly those for surface condition I (moist/ muddy), showed considerable temporal variability, as indicated by the large confidence intervals. The largest seasonal fluxes were observed in summer 2010 and fall 2010. In summer 2010, total rainfall amount (Fig. 5i) and soil/manure temperature (Fig. 5g), during the study period were also the highest. In contrast, the total rainfall during summer 2011 was less than half the amount during summer 2010, which also corresponds with the lower  $N_2O$  fluxes observed during summer 2011. In summer 2010, during the July sampling campaign, large fluxes (15–28 mg m<sup>-2</sup> hour<sup>-1</sup>) were observed in one of the studied pens, three days after a heavy rainfall event. During that period, air temperatures, greater than 40°C, resulted in some areas in the pen that were partially dry on the surface, but moist 5–10 cm deeper underneath. The areas, identified as moist/muddy (surface condition I), accounted for the largest fluxes reported during that sampling campaign. On the other hand, in fall 2010 (October), large N<sub>2</sub>O fluxes were also observed in the second studied pen (39–42 mg m<sup>-2</sup> hour<sup>-1</sup>). In that pen, there was a large surface area that most of the



time remained flooded; however, after two dry summer months with a total combined precipitation of only 14 mm, that flooded area became moist/muddy (surface condition I), which resulted in the large measured N<sub>2</sub>O fluxes. Large N<sub>2</sub>O emission fluxes were also measured in the same pen during the summer 2011 (July), with peak fluxes of 22 mg m<sup>-2</sup> hour<sup>-1</sup>.

As N<sub>2</sub>O is primarily produced biologically by both nitrification and denitrification processes,<sup>9,11,14</sup> and because denitrification is activated by high water content in the field,<sup>10</sup> the particular under-surface higher moisture in surface condition I may explain its highest N<sub>2</sub>O emission rate several days after a rainfall event. The level of the soil microorganism activity has also been associated with seasonality and NO<sub>3</sub><sup>-</sup> availability.<sup>34</sup> The increased N<sub>2</sub>O emission rate after rainfall events, shown in this study, was consistent with general observations in both agricultural soils<sup>10,12,24</sup> and turfgrass soils.<sup>9</sup> These findings confirm that N<sub>2</sub>O emissions from cattle feedlots are episodic and related to rainfall events and warm temperatures, as noted by Von Essen and Auvermann.<sup>35</sup>

Median N<sub>2</sub>O emission fluxes, soil/manure temperature, air temperature, and soil/manure water content for the different pen surface conditions are summarized in Table 2. Surface condition I (moist/muddy) had a median emission flux that was over 20 times greater and significantly higher than those for the other surface conditions. Whalen<sup>19</sup> reported 0.356 mg-N<sub>2</sub>O m<sup>-2</sup> hour<sup>-1</sup> among the largest N<sub>2</sub>O fluxes from agricultural soils; median N<sub>2</sub>O flux reported from the moist/muddy surface condition (2.03 mg-N<sub>2</sub>O m<sup>-2</sup> hour<sup>-1</sup>) is six times larger than that. On the other hand, emission fluxes from surface conditions II (dry and loose), III (dry and compacted), and IV (flooded) were comparable to those of Boadi et al,<sup>13</sup> who reported mean N<sub>2</sub>O emission rate of 0.134 mg-N<sub>2</sub>O m<sup>-2</sup> hour<sup>-1</sup> in a manure pack. Surface conditions II, III, and IV did not differ significantly in N2O median emission flux.

Surface condition I (moist/muddy) could be considered "hot spots", which are localized micro-sites with physical and chemical conditions favoring intense microbial activity.<sup>14</sup> Surface condition II (dry and loose) was dry on the surface and below it, and had smaller N<sub>2</sub>O emission fluxes. In the same way, surface condition III (dry and compacted), which represented the pen mound, also showed small N<sub>2</sub>O emission fluxes. In this case, even if the subsurface might be relatively moist, the dry and highly compacted top surface condition might have minimized gas diffusion from the wetter subsurface to the surface. Surface condition IV (flooded) had the smallest N<sub>2</sub>O emission flux.

The large variability of  $N_2O$  flux among pen surface conditions (Fig. 5a) was consistent with observations for agricultural soils. Parkin and Kaspar<sup>12</sup> reported large emission fluxes related to positional differences in chamber placement in the field. The reported spatial variability may also be explained by the activation of nitrification and denitrification processes. The activation of these processes varies in time and space

because of factors such as temperature,  $NO_3^{-}$ ,  $NH_4^{+}$ , water, and organic matter contents.<sup>9,10,36</sup> Woodbury et al<sup>37</sup> reported that emissions of  $NH_3$ , VOC, and  $CO_2$  were highly variable at short distances within pens in a cattle feedlot.

## Relationship Between N<sub>2</sub>O Emission Flux and Soil/Manure Properties

Pen surface conditions differed significantly in water content and temperature (Table 2). Figures 5g and h show mean values of pen surface temperature and soil water content by season and surface condition. Mean values of volumetric water content during the experimental period were 0.52, 0.26, 0.19, and 0.60 cm<sup>3</sup> cm<sup>-3</sup> for surface conditions I, II, III, and IV, respectively. Mean soil/manure temperatures were 20.9, 24.9, 25.0, and 19.5°C for surface conditions I, II, III, and IV, respectively. In general, soil/manure temperature significantly decreased as soil/manure water content increased (P = 0.0025), as shown in Figure 6. In surface conditions II and III, soil/manure temperature and water content were significantly correlated (P = 0.0002). Moreover, because of their high water content (>0.40 cm<sup>3</sup> cm<sup>-3</sup>), surface conditions I and IV did not show significant correlation between soil/manure temperature and water content. Rather, surface conditions I and IV showed large changes in soil/manure temperature with small to constant changes in soil/manure water content.

The largest difference in soil/manure temperature within a pen during the same sampling period was 9.6°C; it was observed in spring 2011 between surface conditions III (34.7°C) and IV (25.1°C). A second large soil temperature difference (6.3°C) was observed in another pen during winter 2011, among surface conditions I (2.2°C) and III (8.5°C). Surface condition I, because of its higher soil water content (0.53 cm<sup>3</sup> cm<sup>-3</sup>), remained colder than the drier surface condition III (0.30 cm<sup>3</sup> cm<sup>-3</sup>). During the experimental period, differences in soil/manure temperature such as 2–5°C were commonly observed within the same pen in different surface conditions.

As reported by Groffman et al,<sup>34</sup> rates of denitrification are correlated with high water content and  $NO_3^-$  content. Therefore, in surface condition I, the higher  $N_2O$  emission rate is most likely because of the combination of high soil/manure water content, moderate soil/manure temperature, and high  $NO_3^-$  concentrations in that surface condition compared to the other surface conditions (Table 2). Moreover, during the winter 2011 sampling campaign, even though soil water content of surface condition I was favorable for  $N_2O$  production, its lower temperature resulted in an unusually lower  $N_2O$  flux compared with surface condition III.

Kanako et al<sup>1</sup> reported that dry soil conditions combined with high soil temperatures resulted in low N<sub>2</sub>O emission fluxes; therefore, low soil/manure water content combined with soil/manure temperatures greater than 35°C,<sup>11</sup> in surface conditions II and III, may explain in part their consistently lower N<sub>2</sub>O emission fluxes, similar to what has been seen in soils as they dry.<sup>38,39</sup> Surface condition IV had the lowest soil/manure a.

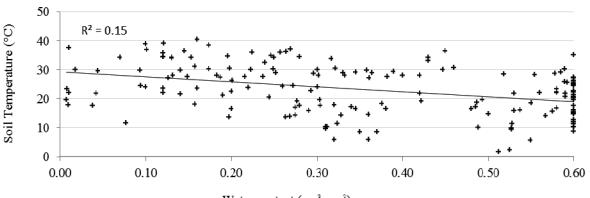


 Table 2. Data summary for the experimental period.

PARAMETER	SURFACE CONDITION					
	I – MOIST/MUDDY	II – DRY AND LOOSE	III – DRY AND COMPACTED	IV – FLOODED		
$N_2O$ emission flux (mg m <sup>-2</sup> hour <sup>-1</sup> )						
Median	2.03ª	0.16 <sup>b</sup>	0.13 <sup><i>b</i></sup>	0.10 <sup>b</sup>		
95% CI	1.24–3.33	0.11-0.24	0.09-0.20	0.06-0.17		
Minimum/maximum	0.07/41.4	0.01/1.24	0.0/1.17	0.0/0.66		
Sample size	39	54	51	32		
Chamber air temperature (°C)						
Mean $\pm$ standard dev.	26.6 ± 9.2 <sup>a</sup>	$29.3\pm7.8^{\text{a}}$	$28.5\pm8.6^{a}$	$26.0\pm8.6^{a}$		
Minimum/maximum	5.3/41.5	10.7/42.1	5.3/40.5	5.2/41.5		
Sample size	39	54	51	32		
Soil/manure temperature (°C)						
Mean $\pm$ standard dev.	20.9 ± 8.6 <sup>a</sup>	24.9 ± 8.2 <sup>b</sup>	$25.0\pm9.0^b$	19.5 ± 6.4°		
Minimum/maximum	1.7/36.5	5.9/40.5	5.9/39.1	8.7/35.0		
Sample size	39	54	51	32		
Soil/manure water content (cm <sup>3</sup> cm <sup>-3</sup> )						
Mean ± standard dev.	0.52 ± 0.06ª	0.26 ± 0.09 <sup>b</sup>	0.19 ± 0.10°	0.60 ± 0.0 <sup>d</sup>		
Minimum/maximum	0.40/0.58	0.1/0.5	0.01/0.39	0.60/0.60		
Sample size	39	54	51	32		
Soil/manure NO₃ <sup>-</sup> content (ppm)						
Median	1.9ª	1.3ª	1.6ª	1.1ª		
95% CI	1.3–2.7	1.0–1.8	1.2–2.2	0.7–1.6		
Minimum/maximum	0.4/79.3	0.7/5.3	0.9/15.0	0.5/6.8		
Sample size	20	26	27	12		
Soil/manure NH4 <sup>+</sup> content (ppm)						
Median	359.9ª	416.7ª	505.4ª	275.6ª		
95% CI	257.0-503.8	317.4-546.9	387.0-660.1	184.6-411.3		
Minimum/maximum	148.4/1332.3	154.5/1043.8	163.9/1407.9	27.6/1001.0		
Sample size	20	26	27	12		
Soil/manure total carbon content (%)						
Mean ± standard dev.	16.7 ± 4.2 <sup>a</sup>	13.6 ± 6.1ª	17.1 ± 5.3ª	13.6 ± 7.1ª		
Minimum/maximum	9.7/24.4	1.7/23.4	9.1/26.4	5.0/26.8		
Sample size	14	16	19	7		
Soil/manure total nitrogen content (%	<b>b</b> )					
Mean ± standard dev.	1.5 ± 0.4 <sup>a</sup>	1.2 ± 0.5ª	1.5 ± 0.4ª	1.1 ± 0.6ª		
Minimum/maximum	1.0/2.0	0.2/2.0	0.8/2.1	0.4/2.1		
Sample size	14	16	19	7		
Soil/manure pH						
Mean ± standard dev.	7.0 ± 0.5 <sup>a</sup>	7.0 ± 0.5ª	6.8±0.4ª	6.9±0.6ª		
Minimum/maximum	6.1/7.7	6.0/8.1	6.1/7.7	6.2/8.1		
Sample size	21	26	27	13		

Means/medians followed by the same letter are not significantly different at 5% level.





Water content (cm<sup>3</sup> cm<sup>-3</sup>)

Figure 6. Soil/manure surface conditions vs. season (a) soil/manure water content, (b) soil/manure temperature, and (c) soil/manure temperature vs. soil/manure water content.

temperature, and because of its flooded condition, its redox potential must have been reduced considerably. Hou et al<sup>40</sup> reported that redox potential less than -200 mV in flooded fields fertilized with organic manure had significant reduction in N<sub>2</sub>O emission fluxes; this holds true for other soils with low soil redox potential.<sup>41</sup> Therefore, reduced redox potential may explain in part the lowest N<sub>2</sub>O emission in surface condition IV. In addition, because of its flooded condition, gas diffusion through the soil would be lower, corresponding to low N<sub>2</sub>O emission flux.

In addition, the highly compacted top layer of surface condition III retarded water movement and limited oxygen diffusion to the underneath moist layer; thereby, reduced redox potential might also be present in the deeper layers, as suggested by the strong darker coloration<sup>14,42</sup> and smooth/homogeneous texture observed in its subsurface (Fig. 7). Therefore, reduced redox potential in the subsurface may explain in part the lower  $N_2O$  fluxes in surface condition III; moreover, because of its highly compacted top surface condition, gas diffusion from

the subsurface may also be limited, consequently decreasing the  $N_2O$  emission flux.

No significant relationship was observed between  $N_2O$  emission flux and soil/manure water content and temperature (Fig. 8). This might be a consequence of the large temporal and spatial variability in  $N_2O$  emission fluxes among the different surface conditions within pens and seasons. Contrary to results in this study, Kanako et al<sup>1</sup> reported significant relationship between soil temperature and  $N_2O$  emission flux in cultivated soil. In surface condition I, as water content increased over 0.50 cm<sup>3</sup> cm<sup>-3</sup>, the soil/manure became closer to saturation, decreasing the soil air-filled porosity, which may reduce gas diffusion through the soil. Lee et al<sup>11</sup> reported limited  $N_2O$  emission flux in extremely wet soil conditions as well as in soils with temperatures higher than 35°C.

Analyses on the effects of soil/manure properties such as  $NO_3^-$ ,  $NH_4^+$ , pH, total C, and total N contents on  $N_2O$  emission flux were performed for each pen surface condition. Figures 5b and c show that  $NO_3^-$  and  $NH_4^+$  contents for all



Figure 7. Photograph showing dark coloration underneath surface condition III (dry and compacted) suggesting reduced redox potential.



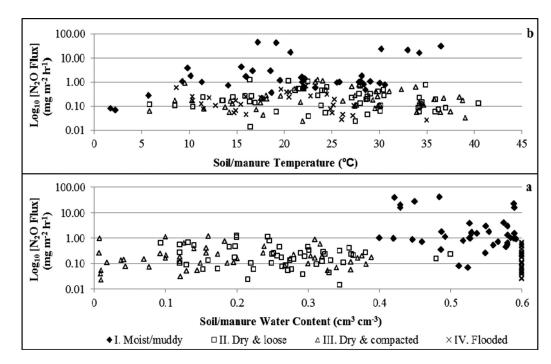


Figure 8. Nitrous oxide emission flux vs. (a) soil/manure water content and (b) soil/manure temperature.

surface conditions were inversely related, as might be expected in agricultural soils; however, in this case, the inverse relationships were not significant at the 5% level. Unlike agricultural soils, fresh manure and urine are constantly added to the pen surface. The urine, once mineralized into  $NH_4^+$ , becomes a constant source for nitrification; therefore, it is expected that at adequate physical conditions for microorganism activity, the rates of nitrification and denitrification in the top 10 cm soil/manure layer might not be significantly different. However, when the top 10 cm soil/manure layer was compared with the 15 cm layer underneath, the mean/median values of  $NO_3^{-}$ ,  $NH_{4}^{+}$ , total C (Fig. 5d), and total N (Fig. 5e) contents were significantly higher in the top layer. This result can be explained by the fact that the deeper the soil/manure layer, the lesser the availability of O2,43 which limits nitrification.44 In addition, O<sub>2</sub> limitation is a factor that promotes denitrification,<sup>45</sup> reducing even more the NO<sub>3</sub><sup>-</sup> as well as the total C and N contents in the deeper soil/manure layers.

Figures 5a, b, and c show that the lowest  $\rm NO_3^-$  and  $\rm NH_4^+$  contents correspond to seasons with the highest  $\rm N_2O$  fluxes. As the soil/manure conditions (ie, water content and temperature) become favorable for microorganism activity, the rate of denitrification increases.<sup>1,10,11,34</sup> Therefore, because the rate of supply of manure and urine to the pen surface is likely constant within season, a net result is the reduction of  $\rm NO_3^-$  and  $\rm NH_4^+$  contents with an increase in  $\rm N_2O$  emission flux. Hofstra and Bouwman<sup>45</sup> reported that organic soils have high denitrification rates because of their generally anaerobic condition and their high soil organic C content. In addition, the decrease in  $\rm NH_4^+$  to the air in  $\rm NH_4^+$  to the air in favor the loss of  $\rm NH_4^+$  to the air in

the form of  $\rm NH_3$ , as suggested by the observed inverse relationship between surface temperature and  $\rm NH_4^+$  content. From the analysis of the soil/manure chemical conditions, none of the factors (ie  $\rm NO_3^-$ ,  $\rm NH_4^+$ , total C, total N, and pH) were significantly different between surface conditions within each season.

### **Summary and Conclusion**

This study used SFCs and gas chromatograph to measure  $N_2O$  emission fluxes from pen surfaces in a large cattle feedlot in Kansas from July 2010 through September 2011 for a total of 23 sampling days. Emission fluxes varied with pen surface condition, with the moist/muddy surface condition having the largest median flux (2.03 mg m<sup>-2</sup> h<sup>-1</sup>), followed by the dry and compacted, dry and loose, and flooded surfaces with median fluxes of 0.16, 0.13, and 0.10 mg m<sup>-2</sup> hour<sup>-1</sup>, respectively. Fluxes varied seasonally as affected by rainfall events and soil temperature. Depending on the surface condition, emission fluxes were affected by one or more soil/manure properties, such as water content, temperature, and total C, pH, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> contents.

## Acknowledgements

Technical support by Miguel Arango, Edna Razote, Dr Li Guo, Henry Bonifacio, Curtis Leiker, Howell Gonzales, David Becker, and Darrell Oard is acknowledged. The cooperation of the feedlot operator and managers is greatly appreciated.

## **Author Contributions**

OAA and RM conceived and designed the experiments. OAA and RM analyzed the data. OAA wrote the first draft



of the manuscript. OAA, RM, and SLT contributed to the writing of the manuscript. OAA, RM, SLT, CWR, and LEE agree with manuscript results and conclusions. OAA and RM jointly developed the structure and arguments for the paper. OAA, RM, CWR, SLT, and LEE made critical revisions and approved final version. All authors reviewed and approved of the final manuscript.

#### DISCLOSURES AND ETHICS

As a requirement of publication the authors have provided signed confirmation of their compliance with ethical and legal obligations including but not limited to compliance with ICMJE authorship and competing interests guidelines, that the article is neither under consideration for publication nor published elsewhere, of their compliance with legal and ethical guidelines concerning human and animal research participants (if applicable), and that permission has been obtained for reproduction of any copy-righted material. This article was subject to blind, independent, expert peer review. The reviewers reported no competing interests.

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