MEASUREMENT AND CONTROL OF GREENHOUSE GAS EMISSIONS

FROM BEEF CATTLE FEEDLOTS

by

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B.S., Universidad Tecnológica de Panamá, 1993
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AN ABSTRACT OF A DISSERTATION

submitted in partial fulfillment of the requirements for the degree

DOCTOR OF PHILOSOPHY

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Abstract

Emission of greenhouse gases (GHGs), including nitrous oxide (N_2O), methane (CH_4), and carbon dioxide (CO_2), from open beef cattle feedlots is becoming an environmental concern; however, scientific information on emissions and abatement measures for feedlots is limited. This research was conducted to quantify GHG emissions from feedlots and evaluate abatement measures for mitigating emissions. Specific objectives were to: (1) measure N_2O emissions from the pens in a commercial cattle feedlot; (2) evaluate the effectiveness of surface amendments in mitigating GHG emissions from feedlot manure; (3) evaluate the effects of water application on GHG emissions from feedlot manure; and (4) compare the photo-acoustic infrared multi-gas analyzer (PIMA) and gas chromatograph (GC) in measuring concentrations of N_2O and CO_2 emitted from feedlot manure.

Field measurements on a commercial beef cattle feedlot using static flux chambers combined with GC indicated that N_2O emission fluxes varied significantly with pen surface condition. The moist/muddy surface had the largest median emission flux; the dry and compacted, dry and loose, and flooded surfaces had significantly lower median emission fluxes.

Pen surface amendments (i.e., organic residues, biochar, and activated carbon) were applied on feedlot manure samples in glass containers and evaluated for their effectiveness in mitigating GHG emissions. Emission fluxes were measured with the PIMA. For dry manure, all amendments showed significant reduction in N_2O and CO_2 emission fluxes compared with the control (i.e., no amendment). For moist manure, biochar significantly reduced GHG emissions at days 10 and 15 after application; the other amendments had limited effects on GHG emissions.

The effect of water application on GHG emissions from feedlot manure was evaluated. Manure samples (with and without water application) were placed in glass containers and analyzed for GHG emission using a PIMA. For the dry manure, GHG emissions were negligible. Application of water on the manure samples resulted in short-term peaks of GHG emissions a few minutes after water application.

Comparison of the GC and PIMA showed that they were significantly correlated but differed in measured concentrations of N_2O and CO_2. The PIMA showed generally lower N_2O concentrations and higher CO_2 concentrations than the GC.

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Nomenclature

A	Surface area (m^2)
AFOs	Animal feeding operations
C	Total carbon (%)
C:N	Carbon to nitrogen ratio
C_0	Gas concentration at time zero (ppm)
C_{15}	Gas concentration at 15 min (ppm)
C_{30}	Gas concentration at 30 min (ppm)
CI	Confidence interval
C_m	Mass-based concentration ($\mu g\ m^{-3}$)
C_{ppm}	Volume-based concentration (ppm)
CRDS	Cavity ring-down spectroscopy
CRLAS	Cavity ring-down laser absorption spectroscopy
EAC	Extruded activated carbon
EC	Eddy covariance
ECD	Electron capture detector
F	Emission flux ($mg\ m^{-2}\ h^{-1}$)
GC	Gas chromatograph
GHGs	Greenhouse gases
GWP	Global warming potential
IFARHU	Institute for the Formation and Development of Human Resources in Panama
IHF	Integrated horizontal flux
IPCC	Intergovernmental Panel on Climate Change
IR	Infrared
k	Conversion factor for gas concentration from ppm to $\mu g\ m^{-3}$
LMB	Loose manure biochar

MW	Molecular weight (g/gmol)
N	Total nitrogen (%)
NIFA	National Institute of Food and Agriculture
NRC	National Research Council
OP-FTIR	Open-path Fourier-transform infrared
OP-TDLAS	Open-path tunable diode laser absorption spectroscopy
P	Atmospheric pressure (mm Hg)
p	p-value
PAC	Powder activated carbon
PG	Prairie Grass
PGB	Prairie grass biochar
PIMA	Photo-acoustic infrared multi-gas analyzer
PM	Particular matter
PMB	Pellet manure biochar
R	Ideal gas constant
r	Pearson correlation coefficient
R^2	Coefficient of determination
REA	Relaxed eddy accumulation
Redox	Reduction/oxidation reaction
S	Slope of the least squares regression line between concentration and time (ppm/min)
SENACYT	National Bureau of Science and Technology of Panama
SFC	Static flux chamber
SS	Sorghum straw
SSB	Sorghum straw biochar
T	Temperature (K)
TCD	Thermal conductivity detector
UHP	Ultra high purity gas

US EPA   United States Environmental Protection Agency

USDA   United States Department of Agriculture

V Volume of air within the static flux chamber (L)

VOCs   Volatile organic compounds

WC   Woodchip

WCB   Woochip biochar

α   Level of significance in the statistical test (%)

$\varDelta C$ Gas concentration difference (ppm)

$\varDelta t$ Sampling interval (h)

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Dedication

I want to dedicate this work to my wife Hedda for her love, confidence, understanding, and for the sacrifice she made, leaving everything back, to come here with me, supporting me to pursue a Ph.D.

To my two kids, Orlando and Alexis, for their unconditional love and those moments of family fun.

I also dedicate this work to my father Rufino for his love and wise counsels, my two mothers Esther and Chela for their love and prayers, and my brothers Wilfredo, Walter, and Rufo, as well as my sisters Maribel, Carmen, and Marlin, for their support and good wishes.

Chapter 1 - Introduction

Animal feeding operations (AFOs) emit various air pollutants, including ammonia (NH_3), volatile organic compounds (VOCs), particulate matter (PM), and odor. In addition, AFOs are considered key sources of anthropogenic greenhouse gases (GHGs) (Mosier et al., 1998). Over the past several decades, research had been conducted on agricultural impacts on nitrous oxide (N_2O) emission fluxes and control measures, including application of nitrification inhibitors for agricultural soils and grasslands (Bronson et al., 1992; Di and Cameron, 2002; Malla et al., 2005; McTaggart et al., 1997; Menéndez et al., 2006; Parkin and Kaspar, 2006; Weiske et al., 2001a; Weiske et al., 2001b). The generation of enteric GHGs from beef cattle has also been documented (Boadi et al., 2004; McGinn et al., 2009). Further, N_2O emissions associated with manure composting have been reported as due to both nitrification and denitrification processes (Ma et al., 2008; Maeda et al., 2010).

In AFOs, meat and milk, among other animal products, generally contain 5 to 20% of the total nitrogen (N) present in the animal diet; the remainder is excreted as manure (Mosier et al., 1998). The manure is deposited on pen surfaces and available for microbiological decomposition, resulting in GHG emissions. In cattle feedlots and other AFOs, in which animal intake of N is high, more than half of the N intake is excreted as urine (Mosier et al., 1998). Urine application on soil samples significantly increased N_2O emission rates up to 14 days after application (Klein and Logtestijn, 1994). Respiration, nitrification, denitrification, and methanogenesis are microbial-related processes that result in emissions of CO_2, N_2O, and CH_4, respectively (IPCC, 1996; Li, 2007; Paul, 2007). Activation of these processes is highly variable in time and space because they are regulated by interactions among soil redox potential, pH, carbon (C) content, temperature, water content, oxidants (i.e., oxygen (O_2), nitrate (NO_3^-), manganese (Mn^{4+}), iron (Fe^{3+}), sulfate (SO_4^{2-}), CO_2), organic matter content, and microbial community (Hou et al., 2000; Li et al., 2012; Segers, 1998).

Beef cattle feedlots and other AFOs are important contributors to the U.S. economy and rural communities. In 2011, the economic impact of the beef industry in the U.S. was $44 billion in farm gate receipts (National Cattlemen's Beef Association, 2011). The total inventory of cattle and calves in the U.S. as of July 1, 2011, totaled 100 million head (USDA, 2011a). As of December 2011, more than 75% of the total "cattle on feed" in large feedlots, those with capacity

of 1,000 or more head (USDA, 2009), were located in the High Plains states of TX, NE, KS, and CO (USDA, 2011b). According to the 2007 Census of Agriculture, approximately 34% of them are produced on large feedlots (USDA, 2009). Moreover, some feedlots have capacities larger than 30,000 head. Unfortunately, beef cattle feedlots could affect air quality through emissions of pollutants such as NH_3, VOCs, PM, and GHGs. Greenhouse gas emissions from beef cattle feedlots may also be an important component of the national air emissions inventory. Despite this, limited scientific information is available on emission rates of GHGs from pen surfaces in beef cattle feedlots (Woodbury et al., 2001), as well as on control measures to minimize those emissions. As such, it is expected that in the near future there will be a growing effort to quantify and reduce air pollutant emissions from beef cattle feedlots.

Static flux chambers (SFCs) have been widely used in measuring emission fluxes of several trace gases from soil surfaces (Conen and Smith, 2000; Greatorex, 2000; Hutchinson and Livingston, 2001; Hutchinson et al., 2000; Kroon et al., 2008; Livingston et al., 2006; Venterea, 2010), due to their simplicity, ease of fabrication (De Klein et al., 1999; Reichman and Rolston, 2002), low cost, and ease of operation (Healy et al., 1996). The SFCs are commonly used in combination with gas chromatographs (GCs) for the analysis of gas samples. Using GC does not allow for direct gas readings in the field (Predotova et al., 2011). Moreover, this method is expensive, time-consuming (Spencer et al., 2001), and results are obtained several days after field sampling. As an alternative to sample collection and analysis with the GC, portable gas analyzers are being used for continuous measurement of gas concentrations. The photo-acoustic infrared multi-gas analyzer (PIMA) is a portable and accurate gas monitor commonly used to measure concentrations in air and stack emissions of almost any gas that absorbs infrared radiation (California Analytical Instruments, 2012). The use of PIMA directly connected to SFC might overcome the disadvantage of using GC for the analysis of gas samples collected with SFCs in the field. The portability of PIMA as well as the rapid and easy measurement, linearity of gas concentrations and its capacity of measuring up to five gases simultaneously *in situ*, are significant advantages over the GC technique (Ambus and Robertson, 1998; De Klein et al., 1999; Iqbal et al., 2012; Predotova et al., 2011; Yamulki and Jarvis, 1999).

1.1. Rationale

Concerns on the increased anthropogenic emissions of GHGs (i.e., CO_2, N_2O, and CH_4), the current role of animal agriculture in climate change, and the limited scientific information on GHG processes and emissions from beef cattle feedlots provided the impetus for this study. It is important to understand the processes and factors that affect GHG emissions from feedlots as well as to identify abatement measures for minimizing GHG emissions because: (i) anthropogenic emissions of GHGs have driven global warming during the last century (Li, 2007; Montzka et al., 2011), (ii) agricultural operations ranked fourth with 13.5 % in total anthropogenic GHG emissions (IPCC, 2007; Marinho et al., 2004), (iii) AFOs are key sources of anthropogenic GHGs (Mosier et al., 1998), and (iv) beef cattle feedlots are important contributors to the nation's economy and rural communities of the U.S. (National Cattlemen's Beef Association, 2011). Therefore, understanding the processes of GHG emissions from feedlots and identifying abatement measures to minimize those emissions are critical to the economic and environmental sustainability of this important agricultural activity as well as to contribute in reducing environmental pollution at local, regional and global scales.

This work provides scientific and technical information that can contribute to better understanding of the emissions of GHGs from beef cattle feedlots, as well as on the abatement measures to minimize those emissions. Because gas and other pollutants emitted from cattle feedlots may affect air quality at local, regional and global scales, this research will also contribute to the same scales. At the local scale, neighboring and rural communities that are economically and environmentally influenced by large commercial feedlots might benefit from this work because it provides information on GHG emission fluxes that can be expected. Once abatement measures for GHG emissions are implemented, it is expected that neighboring communities will be exposed to less pollutants. Feedlot operators will benefit because once the emission process of GHGs are well understood, mitigating measures can be implemented. At the regional and global scales, information from this work might be useful as preliminary step to understand and better estimate N_2O emissions from commercial beef cattle feedlots. New and more appropriate emission standards or guidelines might be developed to appropriately estimate N_2O emissions as well as to implement new air regulations to the sector.

1.2. Objectives

The main objective of this research was to quantify GHG emissions from feedlots and evaluate abatement measures for mitigating emissions. Specific objectives were as follows:

1. Measure the N_2O emission fluxes from pen surfaces in a commercial open-lot beef cattle feedlot, as affected by pen surface characteristics and weather conditions.
2. Evaluate the effectiveness of surface amendments in mitigating GHG emissions from feedlot manure.
3. Evaluate the effects of water application on GHG emissions from feedlot manure.
4. Compare the photo-acoustic infrared multi-gas analyzer (PIMA) and gas chromatograph (GC) in measuring the concentrations of N_2O and CO_2 emitted from feedlot manure.

1.3. References

Ambus, P., and G. P. Robertson. 1998. Automated near-continuous measurement of carbon dioxide and nitrous oxide fluxes from soil. *Soil Science Society of America Journal* 62(2): 394–400.

Boadi, D. A., K. M. Wittenberg, S. L. Scott, D. Burton, K. Buckley, J. A. Small, and K. H. Ominski. 2004. Effect of low and high forage diet on enteric and manure pack greenhouse gas emissions from a feedlot. *Canadian Journal of Animal Science* 84: 445–453.

Bronson, K. F., A. R. Mosier, and S. R. Bishnoi. 1992. Nitrous oxide emissions in irrigated corn as affected by nitrification inhibitors. *Soil Science Society of America Journal* 56: 161–165.

California Analytical Instruments, Inc. 2012. Photoacoustic multi-gas analyzer, Model 1312. Worthington, OH: I.E. Monitoring Instruments. Available at: www.ierents.com/ProductInfo.aspx?productid=RCAI1312. Accessed 14 September 2012.

Conen, F., and K.A. Smith. 2000. An explanation of linear increases in gas concentration under closed chambers used to measure gas exchange between soil and the atmosphere. *European Journal of Soil Science* 51: 111–117.

De Klein, C. A., P. McTaggart, K. A. Smith, R. J. Stevens, R. Harrison, and R. J. Laughlin. 1999. Measurement of nitrous oxide emissions from grassland soil using photo-acoustic infra-red spectroscopy, long-path infra-red spectroscopy, gas chromatography, and continuous flow isotope-ratio mass spectrometry. *Communications in Soil Science and Plant Analysis* 30(9-10): 1463–1477.

Di, H.J., and K.C. Cameron. 2002. The use of a nitrification inhibitor, dicyandiamide (DCD), to decrease nitrate leaching and nitrous oxide emissions in a simulated grazed and irrigated grassland. *Soil Use and Management* 18:395–403.

Greatorex, J. M. 2000. A review of methods for measuring methane, nitrous oxide and odour emissions from animal production activities. JTI-rapport, Lantbruk & Industri, Nr 274. JTI – Institutet för jordbruks- och miljöteknik. Uppsala.

Healy, R.W., R.G. Striegl, T.F. Russel, G.L. Hutchinson, and G.P. Livingston. 1996. Numerical evaluation of static-chamber measurements of soil-atmosphere gas exchange-identification of physical processes. *Soil Science Society of America Journal* 60: 740–747.

Hou, A. X., G. X. Chen, Z. P. Wang, O. Van Cleemput, and W. H. Patrick, Jr. 2000. Methane and nitrous oxide emissions from a rice field in relation to soil redox and microbiological processes. *Soil Science Society of America Journal* 64: 2180–2186.

Hutchinson, G. L., and G. P. Livingston. 2001. Vents and seals in non-steady-state chambers used for measuring gas exchange between soil and the atmosphere. *European Journal of Soil Science* 52: 675–682.

Hutchinson, G.L., G.P. Livingston, R.W. Healy, and R.G. Striegl. 2000. Chamber measurement of surface-atmosphere traces gas exchange: numerical evaluation of dependence on soil, interfacial layer and source/sink properties. *Journal of Geophysical Research* 105: 8865–8875.

IPCC. 1996. Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories, Chapter 4, Agriculture. NGGIP Publications. Intergovernmental Panel on Climate Change. Available at: www.ipcc-nggip.iges.or.jp/public/gl/invs6c.html. Accessed 9 October 2010.

IPCC. 2007. Working Group II Report: Impacts, Adaption and Vulnerability. IPCC Fourth Assessment Report: Climate Change 2007. Intergovernmental Panel on Climate Change. Available at: www.ipcc.ch/publications_and_data/ar4/wg2/en/contents.html. Accessed 7 October 2010.

Iqbal, J., M. J. Castellano, and T. B. Parkin. 2012. Evaluation of photoacoustic infrared spectroscopy for simultaneous measurement of N_2O and CO_2 gas concentrations and fluxes at the soil surface. *Global Change Biology* n/a-n/a. doi: 10.1111/gcb. 12021.

Klein, C. A. M., and R. S. P. Logtestijn. 1994. Denitrification and N_2O emission from urine-affected grassland soil. *Plant and Soil* 163(2): 235–241.

Kroon, P. S., A. Hensen, W. C. M. van den Bulk, P. A. C. Jongejan, and A. T. Vermeulen. 2008. The importance of reducing the systematic error due to non-linearity in N_2O flux measurements by static chambers. *Nutrient Cycling in Agro-ecosystems* 82:175–186.

Li, C. 2007. Quantifying greenhouse gas emissions from soils: Scientific basis and modeling approach. *Soil Science and Plant Nutrition* 53(4): 344–352.

Li, C., W. Salas, R. Zhang, C. Krauter, A. Rotz, and F. Mitloehner. 2012. Manure-DNDC: a biogeochemical process model for quantifying greenhouse gas and ammonia emissions from livestock manure systems. *Nutrient Cycling in Agroecosystems* 93(2): 163–200.

Livingston, G. P., G. L. Hutchinson, and K. Spartalian. 2006. Trace gas emission in chambers: a non-steady-state diffusion model. *Soil Science Society of America Journal* 70: 1459–1469.

Ma, W. K., R. E. Farrel, and S. D. Siciliano. 2008. Soil formate regulates the fungal nitrous oxide emission pathway. *Applied and Environmental Microbiology* 74(21): 6690–6696.

Maeda, K., S. Toyoda, R. Shimojima, T. Osada, D. Hanajima, R. Morioka, and N. Yoshida. 2010. Source of nitrous oxide emissions during the cow manure composting process as revealed by isotopomer analysis of and amoA abundance in betaproteobacterial ammonia-oxidizing bacteria. *Applied and Environmental Microbiology* 76(5): 1555–1562.

Malla, G., A. Bhatia, H. Pathak, S. Prasad, N. Jain, and J. Singh. 2005. Mitigating nitrous oxide and methane emissions from soils in rice-wheat system of the Indo-Gangetic plain with nitrification and urease inhibitors. *Chemosphere* 58(2): 141–147.

Marinho, E. V. A., R. D. Delaune, and C. W. Lindau. 2004. Nitrous oxide flux from soybeans grown on Mississippi alluvial soil. *Communications in Soil Science and Plant Analysis* 35(1): 1–8.

McGinn, S. M., and K. A. Beauchemin, T. K. Flesch, and T. Coates. 2009. Performance of a dispersion model to estimate methane loss from cattle in pens. *Journal of Environmental Quality* 38: 1796–1802.

McTaggart, I. P., H. Clayton, J. Parker, L. Swan, and K.A. Smith. 1997. Nitrous oxide emissions from grassland and spring barley, following N fertilizer application with and without nitrification inhibitors. *Biology and Fertility of Soils Journal* 25: 261–268.

Menéndez, S., P. Merino, M. Pinto, C. Gonzalez-Murua, and J. M. Estavillo. 2006. 3,4-Dimethylpyrazol phosphate effect on nitrous oxide, nitric oxide, ammonia, and carbon dioxide emissions from grasslands. *Journal of Environmental Quality* 35: 973–981.

Montzka, S. A., E. J. Dlugokencky, and J. H. Butler. 2011. Non-CO_2 greenhouse gases and climate change. *Nature* 476(7358): 43–50.

Mosier, A., C. Kroeze, C. Nevison, O. Oenema, S. Seitzinger, and O. van Cleemput. 1998. Closing the global N_2O budget: nitrous oxide emissions through the agricultural nitrogen cycle. *Nutrient Cycling in Agro-ecosystems* 52: 225–248.

National Cattlemen's Beef Association (NCBA). 2011. Beef industry statistics. Available at: www.beefusa.org/beefindustrystatistics.aspx. Accessed 28 December 2011.

Parkin, T. B., and T. C. Kaspar. 2006. Nitrous oxide emissions from corn-soybean systems in the Midwest. *Journal of Environmental Quality* 35: 1496–1506.

Paul, E.A. 2007. *Soil Microbiology, Ecology, and Biochemistry*. 3rd ed. Burlington, MA: Academic Press.

Predotova, M., R. Kretschmann, J. Gebauer, and A. Buerkert. 2011. Effects of cuvette surface material on ammonia-, nitrous oxide-, carbon dioxide-, and methane-concentration measurements. *Journal of Plant Nutrition and Soil Science* 174(3): 347–349.

Reichman, R., and D. Rolston. 2002. Design and performance of a dynamic gas flux chamber. *Journal of Environmental Quality* 31:1774–1781.

Segers, R. 1998. Methane production and methane consumption: a review of processes underlying wetland methane fluxes. *Biogeochemistry* 41: 23–51.

Spencer, L. A., T. B. Parkin, J. W. Doran, B. Eghball, and A. R. Mosier. 2001. Automated gas sampling system for laboratory analysis of CH_4 and N_2O. *Communications in Soil and Science Plant Analysis* 32: 2795–2807.

USDA. 2009. Census of agriculture 2007, U.S. Summary and State Report, Vol. 1, Chapter 2, Table 11. The Census of Agriculture. Washington, D.C.: USDA National Agricultural Statistics Service. Available at: www.agcensus.usda.gov/. Accessed 9 October 2010.

USDA. 2011a. Cattle 2011, Economics, Statistics and Market Information System, Washington, D.C.: USDA National Agricultural Statistics Service. Available at: http://usda01.library.cornell.edu/usda/nass/Catt// 2010s/2011/Catt-07-22-2011.pdf. Accessed 28 December 2011.

USDA. 2011b. Cattle on feed, 2011, Economics, Statistics and Market Information System, Washington, D.C.: USDA National Agricultural Statistics Service. Available at: http://usda01.library.cornell.edu/usda/current/ CattOnFe/CattOnFe-12-16-2011.pdf. Accessed 28 December 2011.

Venterea, R.T. 2010. Simplified method for quantifying theoretical underestimation of chamber-based trace gas fluxes. *Journal of Environmental Quality* 39:126–135.

Weiske, A., G. Benckiser, and J. C. G. Ottow. 2001a. Effect of the new nitrification inhibitor DMPP in comparison to DCD on nitrous oxide (N_2O) emissions and methane (CH_4) oxidation during 3years of repeated applications in field experiments. *Nutrient Cycling in Agroecosystems* 60: 57–64.

Weiske, A., G. Benckiser, T. Herbert, and J. C. G. Ottow. 2001b. Influence of the nitrification inhibitor 3,4-dimethylpyrazole phosphate (DMPP) in comparison to dicyandiamide (DCD) on nitrous oxide emissions, carbon dioxide fluxes and methane oxidation during 3 years of repeated application in field experiments. *Biology and Fertility of Soils Journal* 34: 109–117.

Woodbury, B. L., D. N. Miller, J. A. Nienaber, and R. A. Eigenberg. 2001. Seasonal and spatial variations of denitrifying enzyme activity in feedlot soil. *Transactions of the ASAE* 44(6): 1635–1642.

Yamulki, S., and S. C. Jarvis. 1999. Automated chamber technique for gaseous flux measurements: Evaluation of a photoacoustic infrared spectrometer-trace gas analyzer. *Journal of Geophysical Research* 104(d5): 5463–5469.

Chapter 2 - Review of Literature

2.1. Greenhouse Gas Formation

2.1.1. Mechanisms of greenhouse gas formation in soils

In most soils, microorganisms play an important role in the production or consumption of greenhouse gases (GHGs), including nitrous oxide (N_2O), methane (CH_4), and carbon dioxide (CO_2). The soil microbiological processes responsible for these GHGs are nitrification, denitrification, methanogenesis, and respiration. Those processes are regulated by interactions among soil reduction-oxidation (redox) potential, pH, carbon (C) content, temperature, water content, and oxidants, including oxygen (O_2), nitrate (NO_3^-), manganese (Mn^{4+}), iron (Fe^{3+}), sulfate (SO_4^{2-}), CO_2, and hydrogen (H_2) (Hou et al., 2000; Li et al., 2012; Li, 2007). To survive, grow, and reproduce, most soil microorganisms need a source of C as basic building block for new cells; they obtain energy by catalyzing redox reactions, in which inorganic compounds accept electrons (electron acceptors), allowing the complete oxidation of organic substrates (electron donors) (NRC, 1993a). To accomplish this process, electrons are transferred from the organic C substrate to an electron acceptor. Under aerobic conditions, most soil microbial cells use O_2 as electron acceptor, releasing CO_2 into the atmosphere (Li, 2007). When the O_2 concentration within the soil decreases, the activity of aerobic microorganisms is depressed, but a special group of microorganisms, capable of using NO_3^- as an electron acceptor, can be activated. Further reductions of NO_3^- might result in a net emission of N_2O (Hofstra and Bouwman, 2005; Li, 2007). If conditions within the soil become anaerobic for several days, methanogen cells are activated using H_2 as electron acceptor, which results in CH_4 as byproduct from the microbial respiration (Li, 2007). In addition to H_2, methanogens can also use as electron acceptors CO_2, methanol, methylamines, and acetate; these compounds may result from fermentation in anaerobic processes (Paul, 2007). There are two main groups of CH_4 producer microorganisms: chemolithotrophic and chemoorganotrophic; the first group produces CH_4 from the reduction of $H_2 + CO_2$, while the second group produces CH_4 from methanol, methylamines, or acetate (Paul, 2007).

Nitrous oxide is produced biologically by nitrification and denitrification processes (Kanako et al., 2006; Lee et al., 2008). The first step in the generation process of N_2O in the pen

surfaces of a cattle feedlot is mineralization. Once cattle feces and urine are deposited on the pen surface, the organic N is mineralized into ammonium ions (NH_4^+) (NRC, 1993b; Taghizadeh-Toosi et al., 2011), which are then released into the manure pack and stay relatively immobile (NRC, 1993b). The second step involves nitrification, if the manure conditions are appropriate. Nitrification is the microbial oxidation of NH_4^+ to nitrite (NO_2^-), followed by oxidation into NO_3^- when conditions are aerobic with adequate water content (relatively dry), temperature above 9°C, and under oxidizing conditions in the manure (Mosier et al., 1998; NRC, 1993b). Nitrates that are not absorbed by plants or microorganisms or otherwise immobilized may readily move with percolating water and may leach through the soil to groundwater (NRC, 1993b). The third step is denitrification. It is a microbial facultative anaerobic respiratory process that reduces oxidized forms of N such as NO_3^- and/or NO_2^- in response to the oxidation of organic matter wherein NO_3^- and/or NO_2^- act as electron acceptors (Hofstra and Bouwman, 2005; Mosier et al., 1998; NRC, 1993b). The final product of denitrification is N_2 gas with N_2O released as by-product (Mosier et al., 1998). Mineralization, nitrification, and denitrification are interactive processes that can simultaneously coexist in close proximity in the same setting.

2.1.2. Factors affecting GHG emissions

2.1.2.1. Chemical and physical factors

Activation of the microbiological processes described above (i.e., nitrification, denitrification, methanogenesis, and respiration) is highly variable in time and space because those processes are regulated by interactions of many factors, including soil redox potential, pH, C content, NH_4^+ content, water content, temperature, oxidants, and microbial community (Bremer, 2006; Hou et al., 2000; Li et al., 2012). Under aerobic conditions, most soil microbial cells use O_2 as electron acceptor, releasing CO_2 into the atmosphere as its main respiratory product (Li, 2007). Under anaerobic conditions, organic soils have high denitrification rates due to their high organic C content (Hofstra and Bouwman, 2005), which results in emission of N_2O. Dry soil conditions combined with high soil temperatures result in low N_2O emission fluxes (Kanako et al., 2002). Limited N_2O emission flux in soil with temperatures higher than 35°C has been reported (Lee et al., 2008). Nevertheless, as the soil conditions (i.e., water content, temperature, and NO_3^-) become favorable for microorganism activity, the rate of denitrification increases (Groffman et al., 1993; Kanako et al., 2006; Lee et al., 2008). From a review of 336

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measurements of denitrification in agricultural soils, Hofstra and Bouwman (2005) reported that soil pH was the only soil property with a significant influence on denitrification, with slightly alkaline conditions favoring it. They also reported that all other factors related to soil and climate conditions did not significantly influence denitrification. A pH around 7 is favorable for N_2O and CH_4 emissions (Hou et al., 2000).

If conditions within the soil remain anaerobic for several days, soil redox potential decreases (Johnson-Beebout et al., 2008; Li, 2007). Delaune and Reddy (2005) reported that in soil sediments, anaerobic condition was reached at redox potential below +400 mV. They also indicated that the approximate range of denitrification activity was between +400 to +300 mV and that the reduction of CO_2, which yields CH_4 (Paul, 2007; Segers, 1998), was below -200 mV. Soil redox potential values lower than -200 mV have been reported in flooded fields fertilized with manure (Hou et al., 2000). Research on a rice paddy soil (Hou et al., 2000) and in a rice paddy greenhouse (Johnson-Beebout et al., 2008) reported that significant N_2O emissions only occurred at redox potentials above +200 mV and significant CH_4 emission occurred below -200 mV. Therefore, in flooded agricultural soils, high emissions of both N_2O and CH_4 do not occur simultaneously.

As described previously, the type of microorganisms that are activated in the soil depends on the presence or absence of O_2. Water content might be a major factor in controlling the O_2 content in the soil, and therefore, GHG emissions. After water application (i.e., rainfall, water sprinkling), the O_2 in the top soil surface is displaced by water (NRC, 1993b) and the O_2 left in the soil might be quickly consumed by the aerobic microorganism present in the soil (Li, 2007). Therefore, reduced conditions may dominate temporarily (NRC, 1993b).

2.1.2.2. Water application

Several studies (Kanako et al., 2008; Marinho et al., 2004; Scholes, 1997) reported increased N_2O emission rates after rainfall events or watering processes in agricultural soils. Peaks as much as 22 times larger than normal emission fluxes (Kanako et al., 2006) were observed at different times (i.e., from several minutes to several days after the watering event). Kanako et al. (2002, 2006) reported that nitrification activity is enhanced by the presence of NH_4^+ and that it is activated under low water soil conditions, which produces NO_3^-. They also suggested that denitrification is enhanced by the presence of high amount of NO_3^- and that it is activated under high soil water content.

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Few other studies (Davidson, 1992; Scholes, 1997) reported that N_2O emissions began and markedly increased within minutes after adding water to dry soil. Nitrifying and denitrifying microorganisms appear to be well adapted to surviving several days of dry conditions and extreme high and low temperatures simultaneously. They become active within minutes after dry soil/manure becomes wet (Davidson, 1992).

Davidson (1992) and Saggar et al. (2004) reported that when soil water content was below field capacity, the N_2O emission was inhibited by the addition of acetylene (C_2H_2), suggesting that below field capacity, nitrification accounted for the emission of N_2O and that denitrification was the dominant process above field capacity. Rates of N_2O were up to 5 times higher when soil water content was above field capacity, indicating the formation of anaerobic sites following watering (Saggar et al., 2004), compared to rates observed below field capacity (Davidson, 1992). Mikha et al. (2005) indicated that after watering dry soil, there was a quick release of readily degradable organic compounds from dead cells, such as amino acids, NH_4^+ compounds, and glycerol, which may be utilized by alive microorganisms, increasing their activity after a watering event, resulting in a pulse of CO_2 emission after watering.

2.2. Greenhouse Gas Sampling and Measurement Techniques

Quantifying GHG emissions from soils and/or pen surfaces is challenging because the conditions of open and large surfaces, wide surface heterogeneity and the large temporal and spatial variability of the emissions (Marinho et al., 2004; Parkin and Kaspar, 2006). Several methods to quantify gas fluxes have been proposed: mass balance, reverse dispersion modeling, micrometeorological techniques, and flux chambers. Each of these methods is described briefly below.

2.2.1. Mass balance

Some studies have used mass balance to quantify total N emissions from feedlots (Adams et al., 2004; Farran et al., 2006); however, this approach does not distinguish among several N species. Mass balance requires detailed information on feedlot configuration and operational parameters such as pen sizes, stocking densities, animal diet (i.e., N intake, animal live weight, dry matter intake, and gross energy), feed refusals, manure characteristics (i.e., total mass, chemical and physical composition, and C:N ratio), runoff from the pens, and N retention for the animals (Adams et al., 2004; Farran et al., 2006). Several equations are used to compute N

intake, N of feed refusal, net protein and net energy, N excreted, N retention, manure N, runoff N, and total N lost per animal.

2.2.2. Reverse dispersion modeling

Reverse dispersion modeling is a non-intrusive approach for determining GHG emissions from the whole feedlot (McGinn et al., 2009). McGinn and Beauchemin (2012) and McGinn et al. (2009) used reverse dispersion modeling to estimate CH_4 emissions from a dairy farm and a cattle feedlot, respectively. The accuracy of reverse dispersion modeling depends on the model and the model input accuracies. In addition, this technique requires in situ weather information as well as GHG concentrations upwind and downwind of the source. This approach is not labor intensive and emissions can be calculated at short time intervals over a long period of time (McGinn et al., 2009). In addition, measuring from a group of animals negates the need to account for between- and within-animal variability when considering treatment differences for developing mitigation strategies (McGinn et al., 2009).

2.2.3. Micrometeorological techniques

Micrometeorological techniques are based on flux-gradient relationships, such as aerodynamic and Bowen ratio energy balance, eddy transfer theory, such as the eddy covariance and relaxed eddy accumulation (REA), or mass balance, such as integrated horizontal flux (IHF), and mass difference (McGinn et al., 2007). These techniques employ a combination of atmospheric turbulence theory and gas concentration measurements to estimate gas flux to or from a surface (McGinn et al., 2007). They are typically implemented by installing instrumentation on tower platforms (NRC, 2003). McGinn et al. (2007) explained the basic principles of the most common micrometeorological method - the eddy covariance technique, also called the eddy correlation or eddy flux. The technique accounts for the vertical transfer of a gas by monitoring the vertical movement of parcels of air, known as eddies. The emission rate is calculated as the product of the fluctuations in gas concentration and vertical wind speed over a short period. The REA, also called conditional sampling, separates the upward and downward moving air depending on the sign and magnitude of the vertical wind speed. The REA technique samples air at a constant rate to determine the difference in concentration. The standard deviation of the vertical wind speed during the sampling period is measured with an ultrasonic anemometer. Pattey et al. (2005a) demonstrated the viability of several micrometeorological

techniques to provide data on the spatial and temporal resolution to develop scaling-up models with regional and global capabilities. The use of several micrometeorological techniques has also been reported in McGinn et al. (2007): the aerodynamic technique was used to calculate the turbulent diffusivities for NH_3 emissions from a manure-holding facility and to estimate CH_4 emissions from grazing dairy cows in a field. The IHF has been used for monitoring CH_4 emissions from manure-holding facilities. The mass difference technique was used to measure CH_4 emissions from grazing cattle and feedlot cattle. Micrometeorological methods are commonly considered the most adequate for measuring emission fluxes from soils and AFOs because they do not interfere on the measurement being made and they are generally nonintrusive (McGinn et al., 2009; McGinn et al., 2007). However, because they require substantial experimental infrastructure, highly qualified personnel, and sophisticated and expensive equipment, such as fast-response sensors and recorders in the order of 10–20 Hz (McGinn et al., 2007), these methods are expensive. In addition, most micrometeorological methods require that the field has to be horizontal and homogeneous (McGinn et al., 2007). Additional considerations must also be taken due to air flow distortion caused by the tower and the instruments and sensors (NRC, 2003). In general, micrometeorological techniques are flexible in that they can be used to estimate gas emission from some point sources and most non-point sources (McGinn et al., 2007). They can also measure emissions from a single point source for 24 hours a day, 365 days a year and for several hectares at the same time (Delft University of Technology, 2010).

The application of micrometeorological techniques requires the measurement of gas concentrations in the air, the wind vertical and horizontal speed, as well as meteorological conditions. Some common instruments for measuring air concentrations of N_2O and CH_4 are described below.

1. Photo-acoustic infrared multi-gas analyzer is based on photo-acoustic infrared detection. The gas to be measured is irradiated by modulated light of a pre-selected wavelength. The gas molecules absorb some of the light energy and convert it into an acoustic signal, which is detected by a microphone.This technique can measure virtually any gas that absorbs radiation in the infrared spectrum. Gas selectivity is achieved through the use of optical filters, which provides means of detecting the gas of interest as well as compensation for interfering gases and water (LumaSense, 2012). The main limitation of

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this technique is the cross interference among gases and water vapor. Water vapor absorbs infrared radiation at most wavelengths so that, irrespective of which optical filter is used, water vapor will contribute to the total acoustic signal in the analysis cell. To compensate for water vapor's inteference, an optical filter is permanently installed to measure water vapor in the gas sample. Any other interfering gas can be compensated for in a similar fashion (LumaSense, 2012). This instrument can be equipped with several optical filters for measuring up to five gases plus water vapor. Among those gases NH_3, N_2O, CH_4, and CO_2 are commonly measured.

2. Open-path tunable diode laser absorption spectroscopy (OP-TDLAS) uses wavelength scanning, narrow line-width lasers to determine the path-integrated concentration of a gas (Thoma et al., 2005). A basic OP-TDLAS setup consists of a tunable diode laser source, drive electronics, receiving optics, detector, and micro-computer (Boreal Laser, 2012). The emission wavelength of the tunable diode laser is tuned over the characteristic absorption lines of the specie in the gas in the path of the laser beam. This causes a reduction of the measured signal intensity, which can be detected by a photodiode, and then used to determine the gas concentration and other properties such as the temperature, pressure, velocity, and mass flux of the gas under observation. This particular system does not need calibration as it contains a calibration cell with a known proportion of CH_4, through which the device frequently and automatically calibrates itself within a few seconds. McGinn and Beauchemin (2012) used the open-path CH_4 laser to measure the upwind CH_4 mixing ratio to compute CH_4 emissions from a dairy farm. McGinn et al. (2009) used a similar device to assess the performance of a dispersion model in evaluating the effect of diet on CH_4 emissions from a feedlot. The open-path laser has also been used to compute NH_3 and CH_4 from area sources (McGinn et al., 2007; Ro et al., 2007).

3. Open-path Fourier-transform infrared (OP-FTIR) spectroscopy is a technique for the identification and quantification of several dozen of atmospheric contaminants in real-time (Thoma, et al., 2005). A beam of light spanning a range of wavelengths in the near-IR portion of the electromagnetic spectrum (approximately 2 to 14 μm) is propagated from the transmitter. A retro-reflector is positioned to intercept this radiation and redirect it back to the receiver portion of the instrument. A spectrum in the optical frequency units

is obtained by performing a Fourier transform on the interferogram. Gases such as CH_4 are identified and quantified via comparison to the system's internal reference spectra library. Any other gaseous compound that absorbs in the IR region is a potential candidate for monitoring using this technology. Path-integrated concentrations are usually reported in units of ppm-meter (ppm-m). For an open-path FTIR spectrometer, the total contaminant is measured within the approximate cylinder defined by the cross-section of the light beam and the length of the beam itself. This contaminant burden is then normalized to a path length of 1 m. The advantage of open-path FTIR spectroscopy is that it covers a broad spectral range compared to laser systems. Additional advantages are real-time measurement results are available directly in-situ, speed and versatility, data quality, and no calibration is required. As disadvantages, OP-FTIR requires significant resources and highly trained users to ensure proper deployment, operation, and final data production (Thoma et al., 2005).

4. Cavity Ring-down spectroscopy (CRDS) or cavity ring-down laser absorption spectroscopy (CRLAS) is a laser-based absorption spectroscopy technique (Wheeler et al., 1998) that has been widely used to study gaseous samples that absorb light at specific wavelengths. A typical CRDS setup consists of a laser that is used to illuminate a high-finesse optical cavity, which in its simplest form consists of two highly reflective concave mirrors, typically 99.9% reflectivity over the wavelength range of interest (Wheeler et al., 1998). When the laser is in resonance with a cavity mode, intensity builds up in the cavity due to constructive interference. The laser is then turned off in order to allow the measurement of the exponentially decaying light intensity leaking from the cavity. During this decay, light is reflected back and forth thousands of times between the mirrors giving an effective path length on the order of up to tens of kilometers (Wheeler et al., 1998). If a gas that absorbs light is placed in the cavity, the amount of light decreases faster. A CRDS measures how long it takes for the light to decay to $1/e$ of its initial intensity, and this "ring-down time" can be used to calculate the concentration of the absorbing substance in the gas mixture in the cavity. Advantages of CRDS include high sensitivity due to the multi-pass nature of the detection, immune to shot-to-shot variations in the laser intensity, and high throughput (Stelmaszczyk et al., 2009; Wheeler et al., 1998). Disadvantages include the following: the spectra cannot be acquired quickly

due to the monochromatic laser source, analytes are limited both by the availability of tunable laser light at the appropriate wavelength and also the availability of high reflectance mirrors at those wavelengths, and it is more expensive than some alternative spectroscopic techniques as consequence of the laser systems and high reflectivity mirrors required (Stelmaszczyk et al., 2009).

2.2.4. Static flux chambers

The static flux chamber (SFC) technique has been used extensively to measure rates of trace gas exchange between soil surfaces and air, lagoons, and vegetation (NRC, 2003). As indicated by Hutchinson and Mosier (1981), Kanako et al. (2008), and Livingston et al. (2006), SFC is the technique that has contributed the most to the current knowledge of trace gas exchange rates. Additional advantages are the ability to conduct process-level tests of the factors that control emissions and the significantly less complex infrastructure required when compared to the micrometeorological techniques (NRC, 2003). Hutchinson and Mosier (1981) noted that SFC techniques to measure soil gas emissions offer the most useful approach; however, it is necessary to implement a good SFC design and to follow an adequate experimental protocol to overcome the potential errors that may be associated with this technique. Flux chamber techniques are also applicable in measuring gas emission rates from hazardous waste land treatment and land fill facilities, contaminated areas with organic volatile compounds due to spills and leakage from underground pipelines and storage tanks, and from surface impoundments (Kienbusch, 1986). As described by McGinn et al. (2007) and Delft university of Technology (2010), by making careful SFC measurements, it is possible to identify the main sources of gas emissions from the soil.

Flux chambers represent an invasive technique because they can influence the micro-environmental conditions within the chamber (NRC, 2003). In SFC, the gas concentration gradient in the headspace tends to increase, but as gas accumulates, the gas concentration gradient decreases once equilibrium is reached (Hutchinson and Mosier, 1981). The main negative impact of this situation is presented whenever the chamber is deployed on the surface and utilized to perform gas sampling for several hours from the same enclosed space. The SFC technique overcomes that problem when chambers are utilized for periods less than 40 min continuously (Rochette and Eriksen-Hamel, 2008) and chambers are adequately sealed to the soil

surface (Hutchinson and Livingston, 2001). For continuous gas measurement, forced air flow-through chambers are recommended. However, for periodic and instantaneous gas sampling, non-flow-through chambers are recommended because lower fluxes can be measured and the presence of the vent maintains equal pressure outside and inside the chamber, reducing potential measurement errors (Hutchinson and Mosier, 1981).

The most common method to analyze gas samples obtained from SFCs is the gas chromatograph (GC). Using GC does not allow direct gas readings in the field (Predotova et al., 2011), is time-consuming, and the resulting fluxes are commonly obtained several days after field sampling. Another technique that is becoming more common involves use of real-time measuring instruments, including the photo-acoustic infrared multi-gas analyzer (PIMA). The PIMA is a portable and accurate gas monitor commonly used to measure concentrations in air and stack emissions of almost any gas that absorbs infrared radiation (California Analytical Instruments, 2012). Using a PIMA in combination with the SFC allows rapid collection of larger data sets of several gases simultaneously and their immediate analysis *in situ* (Predotova et al., 2011). The portability of PIMA as well as the rapid and ease of measurement, linearity of gas concentrations and its capacity of measuring up to five gases simultaneously are significant advantages over the GC (Ambus and Robertson, 1998; De Klein et al., 1999; Iqbal et al., 2012; Yamulki and Jarvis, 1999).

More researchers rely on the use of the PIMA technique for the measurement of gases both at laboratory and field applications. Cayuela et al. (2010a) evaluated the effect of organic animal by-product wastes and commercial mineral fertilizer as soil amendments on N_2O and CO_2 emissions from agricultural soils. Cayuela et al. (2010b) evaluated the impact of bioenergy by-products as soil amendments on GHG emissions. Predotova et al. (2011) assessed the effect of several materials used for static flux chamber construction on NH_3, CH_4, CO_2, and N_2O concentrations. Predotova et al. (2010) determined emissions of NH_3, N_2O, and CO_2 from urban gardens. Osada and Fukumoto (2001) assessed emissions of NH_3, CH_4, and N_2O from composting livestock wastes. In all of the above works, the PIMAs were set to compensate for water vapor and CO_2 cross-interferences according to the manufacturer's instructions.

Several researchers have compared PIMAs with GCs. Osada and Fukumoto (2001) reported that measured values of NH_3, CH_4, and N_2O obtained from the PIMA compared with the respective values obtained from conventional methods, such as sulfuric acid trap for NH_3 and

GC for CH_4 and N_2O, respectively. They observed a small difference when total emissions from composting swine waste were compared. Iqbal et al. (2012) reported that mean fluxes of N_2O and CO_2 measured with the PIMA and GC were less than 10% and 7% different for N_2O and CO_2, respectively. Ambus and Robertson (1998) also reported that N_2O and CO_2 fluxes based on gas concentrations measured with both methods were not significantly different. Akdeniz et al. (2009), on the other hand, reported significant differences between N_2O concentrations measured with the two methods.

There are two main approaches to compute emission fluxes of GHGs based on SFCs: linear and non-linear (diffusion) models (Anthony et al., 1995; Hossler and Bouchard, 2008; Rochette and Eriksen-Hamel, 2008). The linear model approach is used to correlate the observed SFC headspace gas concentrations and time. It is applicable only for short time intervals, in which gas concentration gradient is linear or nearly constant over time (Anthony et al., 1995; Hossler and Bouchard, 2008; Rochette and Eriksen-Hamel, 2008). The following equation is the linear approach to compute gas fluxes from the soil:

$$F = \left[\left(\frac{V}{A} \right) \left(\frac{\Delta C}{\Delta t} \right) \right] k \tag{2.1}$$

where F is gas emission rate ($\mu g \ m^{-2} \ h^{-1}$), V is volume of air within the chamber (m^3), A is the surface area of soil within the chamber (m^2), $\left(\frac{\Delta C}{\Delta t} \right)$ is the gas concentration gradient with time within the chamber (ppm h^{-1}), and k is a conversion factor for gas concentration from ppm to $\mu g \ m^{-3}$.

This approach offers many advantages but the validity of assuming a linear model depends on soil conditions, which might vary from one soil spot to another within the same sampling event (Anthony et al., 1995). As such, before adopting a linear regression approach, significant attention must be given to potential soil conditions with high emission rates. In such cases, sampling times should be short to avoid significant non-linearity (Anthony et al., 1995; Ginting et al., 2003; Hutchinson and Mosier, 1981; Rochette and Eriksen-Hamel, 2008).

As an alternative to the linear model, Hutchinson and Mosier (1981) proposed an exponential model based on diffusion theory to correct for the decreasing concentration gradient within the SFC headspace. This approach is valid only when the change in gas concentration is measured for two consecutive periods of equal time (Anthony et al., 1995), starting from time 0, just as soon as the chamber is installed on the surface. The main advantage of this non-linear

approach is that the computed fluxes are independent of the sampling time (Hutchinson and Mosier, 1981) and are therefore, not affected by soil conditions and the chamber headspace gas equilibrium. Its main limitations are that this approach does not account for measurement variability, it is highly sensitive to that variability when soil condition produces small fluxes, and finally, because only three gas concentrations can be used, its goodness of fit as well as the statistical significance of the flux based on those three data points cannot be tested (Anthony et al., 1995).

Ginting et al. (2003) expanded that approach to three general cases for the computation of GHG fluxes from soil surfaces. In this approach, three gas samples from the SFC headspace are needed; those concentrations are called C_0, C_{15}, and C_{30} for each gas at sampling times of 0, 15, and 30 min, respectively. The general equation may be written as:

$$F = k\, d\, \left(\frac{273}{T}\right)\left(\frac{V}{A}\right)\left(\frac{\Delta C}{\Delta t}\right) \tag{2.2}$$

where F is the gas emission rate (mass ha^{-1} d^{-1}), k is a unit conversion factor, d is gas density (g cm^{-3}) at 273 K, T is air temperature within the chamber (K), V is volume of air within the chamber (cm^3), A is area of soil within the chamber (cm^2), ΔC is gas concentration difference (ppm), and Δt is sampling interval (15 min). Equation 2.2 contains the conversion from volume-based to mass-based concentration. The only difference between eq. 2.2 and 2.1 is the way in which the concentration gradient with time $\left(\frac{\Delta C}{\Delta t}\right)$ is calculated. It is based on the following three general cases:

1. Case 1: $[\Delta C_1/\Delta C_2] > 1$ and $C_0 < C_{15} < C_{30}$ (steadily increasing concentrations) or $C_0 > C_{15} > C_{30}$ (steadily decreasing concentrations):

$$\left(\frac{\Delta C}{\Delta t}\right) = \left[\frac{(\Delta C_1)^2}{\Delta t\,(2C_1 - C_2 - C_0)}\, ln\left(\frac{\Delta C_1}{\Delta C_2}\right)\right] \tag{2.3}$$

2. Case 2: $[\Delta C_1/\Delta C_2] \leq 1$ and $C_0 < C_{15} < C_{30}$ (steadily increasing concentrations) or $C_0 > C_{15} > C_{30}$ (steadily decreasing concentrations):

$\left(\frac{\Delta C}{\Delta t}\right)$ is the average rate of change of concentration between ΔC_1 and ΔC_2.

3. Case 3: $[\Delta C_1/\Delta C_2] \leq 1$ and $C_0 < C_{15} > C_{30}$ or $C_0 > C_{15} < C_{30}$ (fluctuating concentrations with sampling time):

$\left(\frac{\Delta C}{\Delta t}\right)$ is the average rate of change of concentration between ΔC_1 and ΔC_3.

In these equations $\Delta C_1 = (C_{15} - C_0)$, $\Delta C_2 = (C_{30} - C_{15})$, and $\Delta C_3 = (C_{30} - C_0)$. Case 1 is based on the diffusion model, considering chamber gas equilibrium with time. Case 2 is based on the average of the two slopes between concentrations when there is no gas equilibrium (linear model). Case 3 is a particular case wherein concentrations fluctuate with time, indicating that the gas flux trend is inconsistent within the selected sampling time (Ginting et al., 2003). This case is based on the average of the slopes between the first and second and between the first and third gas concentrations, respectively.

2.3. Greenhouse Gas Emission from Soils and Animal Feeding Operations

2.3.1. Soils fertilized with animal manure

According to Rochette et al. (2008), agricultural soils amended with manure are known to increase N_2O emissions because of the enhanced nitrification and denitrification processes. However, they also stated that several studies have reported losses of N_2O as much as 20% lower from manure application in agricultural soils than from synthetic fertilizer N application. Fertilization of a silage maize crop with dairy cattle manure and with synthetic fertilizer resulted in similar N_2O emissions; although, short periods of increased emissions following manure application indicated that the enhanced N_2O emissions supported by the manure-derived C and N substrates are often of short duration (Rochette et al., 2008). In a study of N_2O emission fluxes from manure-amended soil under maize, Lessard et al. (1996) reported N_2O fluxes of 0.494 mg m^{-2} h^{-1} compared to 0.070 mg m^{-2} h^{-1} for the same soil without manure application. From a review of 846 N_2O measurements in agricultural fields, Bouwman et al. (2002) reported that organic soils had much higher N_2O emissions than mineral soils. Therefore, there is no clear consensus regarding the net effect on N_2O emission flux in agricultural soils amended with animal manure. Although synthetic fertilizers and animal manures might be important sources of GHGs, their application into the cropping soils is required to provide the N inputs needed for food production (Mosier et al., 1998).

Among factors affecting N_2O emissions from manure-amended soils, Bouwman et al. (2002) indicated that soil organic C content, pH, texture, and drainage have significant influence. Because soil water content and temperature greatly affect the decomposition rate of soil organic matter, these factors also affect the N_2O emission flux (Lee et al., 2008). Results from Hofstra and Bouwman (2005) suggested that agricultural fields with high N inputs and poor soil drainage

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show higher denitrification values because the condition of that soil is commonly anaerobic, with high organic C content. Ellert and Janzen (2008) reported that soil N_2O emissions were remarkably variable among treatment replicates and even among duplicate chambers which were placed only few meters from each other within the same plots. Emission fluxes of N_2O are reported as episodic, without seasonal patterns (Ellert and Janzen, 2008; Lessard et al., 1996; Scheer et al., 2011), and no significant relationship was found among N_2O flux and soil water content and temperature in the top 5-cm layer (Ellert and Janzen, 2008).

In a study of GHG emissions from irrigated cropping soils as influenced by manure and synthetic fertilizer applications, emissions of CO_2 increased after manure application while emissions of CH_4 were negligible (Ellert and Janzen, 2008). In contrast, Li (2007) indicated that when anaerobic conditions are sustained for several days, the major oxidants will be depleted by the microorganisms; methanogens will be activated to use H_2 as an electron acceptor, which will result in CH_4 production. Four years after manure and compost application, Ginting et al. (2003) reported that the soil receiving manure or compost had similar residual CO_2 emissions as the synthetic fertilized soil. They also reported that CH_4 fluxes were not significantly different from zero under manure and synthetic fertilized soils. Emission fluxes of CO_2 varied seasonally, with higher rates during the growing season and lower rates during fall and winter (Ellert and Janzen, 2008; Ginting et al., 2003).

2.3.2. Animal feeding operations

Whereas N_2O emissions from agricultural soils have been extensively studied for several years (Parkin and Kaspar, 2006), scientific studies on GHGs from AFOs, including beef cattle feedlots, are limited. Mosier et al. (1998) reported that there are three potential sources of N_2O in AFOs, i.e., animals, dung and urine deposited on the soil surface by grazing animals, and waste from confined animals. They also indicated that the total amount of N_2O released by cattle themselves is likely very small, because the gut is highly anoxic, and those emissions are lower than 10 g N_2O per kg of N excreted or taken up by the animal.

In contrast, CH_4 emissions from the ruminant digestive tract have been documented as a major contributor to atmospheric CH_4 (Boadi et al., 2004). Grazing-derived N_2O emissions ranged from 2 to 98 g N_2O per kg of N excreted; the lower values are for well-drained unfertilized grassland soils; the larger values are for intensively used and fertilized grasslands

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(Mosier et al., 1998). Flessa et al. (1996) reported an annual N excretion of 40 kg per head of cattle in pasture lands. They also reported that dung and urine patches produced by grazing cattle are active emission hot spots for CH_4 and N_2O, with maximum N_2O emissions of 1.3 and 25.7 mg N_2O m^{-2} h^{-1}, respectively 10 days after excretion. However, even though fresh dung patches showed a maximum CH_4 emission of 30 mg m^{-2} h^{-1}, this flux rapidly decreased to a net emission of approximately zero when patches dried out because aerobic decomposition prevailed (Flessa et al., 1996).

Manure management is considered a key source of anthropogenic N_2O. Meat and milk, among other animal products, generally contain 5 to 20% of the total N present in the animal diet; the remainder is excreted as manure and urine (Mosier et al., 1998), which is deposited on the pen surface and available for microbial decomposition resulting in the emission of N_2O. In AFOs, including cattle feedlots, in which animal intake of N is high, more than half of the intake N is excreted as urine (Mosier et al., 1998). In a laboratory experiment, urine application on soil samples significantly increased N_2O emission rates up to 14 days after application (Klein and Logtestijn, 1994).

Woodbury et al. (2001), in a study of denitrifying enzyme activity in cattle feedlots, reported that the pen surface layer is well aerated due to animal traffic, is highly organic, and receives large inputs of organic and inorganic N from animal wastes; therefore, pen surfaces are favorable for mineralization and nitrification. They also indicated that underneath the pen surface, the soil/manure is a compacted anaerobic zone with likely conditions for the denitrification of leached NO_2^- and NO_3^-. Within the pen surface, denitrifying enzyme activity showed large seasonal and spatial variation, with high values within a pen, even during the winter season, suggesting that there might be large emissions of N as a consequence of local enhanced denitrification. Woodbury et al. (2006) reported that emissions of NH_3, VOCs, and CO_2 were highly variable at small distances within pens in a cattle feedlot. Boadi et al. (2004), in a study of the diet effect on enteric and manure pack GHG emissions from a feedlot during winter season in Canada, reported mean emission rates in manure pack for a high forage:grain ratio diet as 0.127, 1.08, and 2170 mg m^{-2} h^{-1} for N_2O, CH_4, and CO_2, respectively.

2.4. Measures to Minimize GHG Emissions

2.4.1. Nitrification inhibitors

Several compounds have been intended as nitrification and urease inhibitors to control N_2O emissions and NH_3, respectively, from agricultural soils and grassland (Malla et al., 2005; Menéndez et al., 2006; Weiske et al., 2001a, 2001b). Once the nitrification process is inhibited, the result is a decreased amount of NO_3^- in the soil, which will limit denitrification with a net effect of reduced N_2O emissions. Shi et al. (2001) studied several chemical amendments (i.e., alum, calcium chloride, brown humate, black humate, and thiophosphoric triamide-NBPT) to reduce NH_3 emissions from cattle feedlots. Reduced emissions of NH_3 from feedlots by as much as 98% were reported. NO_3^- concentrations were reduced about 50% by alum and 95% by calcium chloride amendments.

Most of the N present in cattle urine is in the form of urea, which is commonly hydrolyzed to NH_4^+ (Taghizadeh-Toosi et al., 2011). That NH_4^+ might be later converted into either NH_3 gas by the enzyme urease, which is produced by soil and fecal microorganisms (Shi et al., 2001) or NO_3^- by nitrification. The NO_3^- fraction likely will result in a net emission of N_2O, as a consequence of denitrification (Mosier et al., 1998; NRC, 1993b; Taghizadeh-Toosi et al., 2011). The reduction of NO_3^- reported by Shi et al. (2001) suggests that such amendments might also reduce N_2O emissions from feedlots; however, the costs might be prohibitive (Shi et al., 2001).

2.4.2. Anaerobic digestion

An alternative to reduce N losses may be manure management strategies such as pen cleaning, which may provide less exposure of manure N to surrounding air and subsequent losses (Adams et al., 2004; Monteny et al., 2006). Anaerobic digestion and aerobic composting of animal manure have been reported by many researchers (Amon et al., 2006; Novak and Fiorelli, 2010; Pattey et al., 2005b) as manure management strategies to minimize emission of GHGs from AFOs. Anaerobic digestion includes several major steps in the process: (1) manure harvesting and transportation from the AFOs to the anaerobic digesters, (2) fermentation process, (3) storage of digested slurries, and (4) field application of the digested slurries. If all the manure produced in an AFO is collected daily or weekly and placed into anaerobic digesters, these steps must be considered and evaluated as potential GHG emission sources:

1. Manure harvesting and transportation. When manure is scraped, the top layer is collected. This operation exposes the underneath and compacted layer to the air. Considering that the top layer is a highly compacted surface, which avoids the oxygen diffusion from the air to the subsurface; it is expected that the underneath moist soil/manure pack is anaerobic. Therefore, amounts of trapped CH_4 and even N_2O will be instantaneously released to the air for several hours until that exposed surface gets enough oxygen diffusion to become aerobic, limiting the production of CH_4 as well as the denitrification process, switching then to nitrification if the soil conditions are adequate. However, if the manure is frequently collected (daily or weekly) and the underneath layer is not perturbed, the GHG emissions will be mainly the amount of CH_4 released from fresh manure.

2. Fermentation. During fermentation, organic dry matter content, NH_3 concentration, pH, and viscosity undergo changes that may affect GHG emissions during storage and after field application of residues. CH_4 emission after fermentation may be reduced because most of the degradable organic C is turned into biogas (Clemens et al., 2006). However, it is important to prevent uncontrolled losses of CH_4 from biogas plants (Clemens et al., 2006).

3. Storage of digested slurries. Novak and Fiorelli (2010) indicated that studies on N_2O emission during storage of digested slurries are inconsistent; while some studies reported higher N_2O emissions, others reported negligible N_2O emissions. In addition, most studies reported that CH_4 emissions in storage are highest from untreated slurries than from the digested slurries (Clemens et al., 2006; Monteny et al., 2006; Novak and Fiorelli, 2010).

4. Field application of the digested slurries. In anaerobic digestion, the readily available carbon is incorporated into microbial biomass or lost as CO_2 or CH_4. There is less available carbon in the slurry to trigger denitrification when the slurry is stored or applied to land, which results in a reduction of N_2O emissions (Amon et al., 2006; Monteny et al., 2006). Clemens et al. (2006) reported substantial CH_4 emissions for a short time after application of digested slurry in the field; they also reported that after field application, there were no significant differences in GHG emissions between untreated and digested cattle slurries.

In terms of net total GHG emissions as CO_2 equivalent from anaerobic digestion, Amon et al. (2006) reported that the net total GHG emissions from untreated dairy cattle slurry amounted to 92.4 kg CO_2 eq. m^{-3}; while net total GHG emissions from anaerobically digested dairy cattle slurry amounted to 37.9 kg CO_2 eq. m^{-3}. This represents a net reduction of 59%. More than 90% of these net total GHG emissions originated from CH_4 emissions during digested slurry storage (Amon et al., 2006). Clemens et al. (2006) also reported that during summer storage, total GHG emissions from untreated slurry were nearly twice as high as from digested slurry.

In summary, GHG emissions from anaerobic digestion of cattle manure slurry are mainly caused by CH_4 emissions during storage and by N_2O emissions during and after field application of the digested slurries. Anaerobic digestion is a very efficient way to reduce the GHG emissions and potentially a 'win–win' management of animal manure slurry, since CH_4 emitted as biogas might be used to produce renewable energy, while N_2O emissions following the spreading of the digested slurry are also reduced (Clemens et al., 2006; Monteny et al., 2006).

2.4.3. Biochar as surface amendment

Biochar is a carbon-rich by-product from pyrolysis of biomass during bioenergy production (Amonette et al., 2010; Sohi et al., 2010; Taghizadeh-Toosi et al., 2011). It is recognized for its potential role in C sequestration, ability to reduce GHG emissions, renewable energy capability, waste mitigation, and as soil fertilizer amendment (Kookana et al., 2011). Several researchers have documented the ability of biochar as soil amendment in controlling N_2O emissions from soils. Among the studies, in a 60-day incubation experiment, Cayuela et al. (2010a) reported that out of 10 bioenergy by-products evaluated, biochars obtained from green waste and poultry manure were the most stable residues, with net reduction of N_2O emissions with respect to the control and also the highest C sequestration potential. Van Zwieten et al. (2010) reported that biochars obtained from pyrolysis of green-waste, poultry litter, paper-mill waste, and bio-solids showed reductions on N_2O emissions from acidic ferrosol soil. Taghizadeh-Toosi et al. (2011) incorporated biochar into grazing land to evaluate its effectiveness in controlling N_2O emissions from cattle-urine patches. After the application of 30 t ha^{-1} of biochar, N_2O emissions from urine patches were reduced by as much as 70%. Scheer et al. (2011) assessed the effect of biochar on GHG emissions from an intensive subtropical pasture in

Australia; 30 months after incorporation of feedlot manure biochar into the soil as fertilizer, they did not find significant differences in the net flux of N_2O, CH_4, and CO_2, between the biochar-treated soil and the control treatment.

2.5. Summary and Research Needs

Microorganisms play an important role in the production or consumption of N_2O, CH_4, and CO_2. The soil microbiological processes responsible for these GHGs are nitrification, denitrification, methanogenesis, and respiration. Those processes are regulated by interactions among soil redox potential, pH, C content, temperature, water content, and oxidants. When the O_2 concentration within the soil decreases, the activity of aerobic microorganisms is depressed, but a special group of microorganisms, capable of using NO_3^- as an electron acceptor, can be activated. Further reductions of NO_3^- might result in a net emission of N_2O. If conditions within the soil become anaerobic for several days, methanogen cells are activated to use H_2 as an electron acceptor, which will result in CH_4 generation.

Several methods can be used to quantify gas fluxes from soils: mass balance, reverse dispersion modeling, micrometeorological techniques, and flux chambers. Static flux chamber is the technique that has contributed the most to the current knowledge of trace gas exchange rates between soil surfaces, lagoons, and vegetation. Additional advantages over other methods are the ability to conduct process-level tests of the factors that control emissions and the significantly less complex infrastructure required compared with micrometeorological methods.

Nitrification and urease inhibitors have been used to control emissions of N_2O and NH_3, respectively, from agricultural soils; however, they might not be applicable for cattle feedlots. An alternative to reduce N losses from AFOs may be manure management strategies such as pen cleaning, anaerobic digestion, and aerobic composting of animal manure. These alternatives may provide less exposure of manure N to surrounding air and subsequent losses. Biochar is being recognized for its potential role in C sequestration, ability to reduce GHG flux levels, renewable energy capability, waste mitigation, and as a soil fertilizer amendment.

The following are key research needs on GHG emissions from AFOs, particularly open beef cattle feedlots:

1. Quantify and characterize GHG emission fluxes from various locations in beef cattle feedlots (i.e., pen surfaces, alleys and waterways, runoff collection ponds, manure storage piles).

2. Develop an understanding of the mechanisms of GHG formation and emission from cattle feedlots.

3. Identify and evaluate measures to minimize GHG emissions from feedlot manure (i.e., nitrification inhibition, anaerobic digestion, manure gasification, pen surface amendment).

4. Determine the effects of water application (i.e., rainfall and water sprinkling) on GHG emissions from pen surfaces.

5. Develop and evaluate approaches to monitor GHG emission fluxes from pen surfaces and/or whole feedlots.

6. Develop and evaluate modeling tools for predicting GHG emissions from cattle feedlots.

2.6. References

Adams, J. R., T. B. Farran, G. E. Erickson, T. J. Klopfestein, and C. N. Macken. 2004. Effect of organic matter addition to the pen surface and pen cleaning frequency on nitrogen mass balance in open feedlots. *Journal of Animal Science* 82: 2153–2163.

Amon, B., V. Kryvoruchko, T. Amon, and S. Zechmeister-Boltenstern. 2006. Methane, nitrous oxide and ammonia emissions during storage and after application of dairy cattle slurry and influence of slurry treatment. *Agriculture, Ecosystems & Environment* 112: 153–162.

Amonette, J. E., M. Camps-Arbestain, C. H. Chia, A. Cowie, N. Foidl, and J. Hook. 2010. An investigation into the reactions of biochar in soil. *Australian Journal of Soil Research* 48: 6–7.

Anthony, W.H., G.L. Hutchinson, and G.P. Livingston. 1995. Chamber measurement of soil-atmosphere gas exchange: linear vs diffusion-based flux models. *Soil Science Society of America Journal* 59(5):1308–1310.

Boadi, D. A., K. M. Wittenberg, S. L. Scott, D. Burton, K. Buckley, J. A. Small, and K. H. Ominski. 2004. Effect of low and high forage diet on enteric and manure pack greenhouse gas emissions from a feedlot. *Canadian Journal of Animal Science* 84: 445–453.

Boreal Laser. 2012. Product catalog. Available at: http://www.boreal-laser.com/products. Accessed 2 November 2012.

Bouwman, A. F., L. J. M. Boumans, and N. H. Batjes. 2002. Emissions of N_2O and NO from fertilized fields: Summary of available measurement data. *Global Biogeochemical Cycles* 16 (4): 1–13.

Bremer, D. J. 2006. Nitrous oxide fluxes in turfgrass: Effects of nitrogen fertilization rates and types. *Journal of Environmental Quality* 35:1678–1685.

Cayuela, M. L., G. L. Velthof, C. Mondini, T. Sinicco, and J. W. van Groenigen. 2010a. Nitrous oxide and carbon dioxide emissions during initial decomposition of animal by-products applied as fertilizers to soils. *Geoderma* 157: 235–42.

Cayuela, M. L., O. Oenema, P. J. Kuikman, R. R. Bakker, and J. W. van Groenigen. 2010b. Bioenergy by-products as soil amendments? Implications for carbon sequestration and greenhouse gas emissions. *Global Change Biology Bioenergy* 2: 201–213.

Clemens, J., M. Trimborn, P. Weiland, and B. Amon. 2006. Mitigation of greenhouse gas emissions by anaerobic digestion of cattle slurry. *Agriculture, Ecosystems & Environment* 112: 171–177.

Davidson, E. A. 1992. Sources of nitric-oxide and nitrous-oxide following wetting of dry soil. *Soil Science Society of America Journal* 56 (1): 95–102.

DeLaune, R. D., and K. R. Reddy. 2005. Redox potential. Gainesville, FL: University of Florida.

Delft University of Technology. 2010. Emissions of greenhouse gases methane and nitrous oxide underestimated, research suggests. *Science Daily*. Available at: www.sciencedaily.com /releases/2010/07/100701090330.htm. Accessed 19 January 2012.

Ellert, B. H., and H. H. Janzen. 2008. Nitrous oxide, carbon dioxide and methane emissions from irrigated cropping systems as influenced by legumes, manure and fertilizer. *Canadian Journal of Soil Science* 88: 207–217.

Farran, T. B., G. E. Erickson, T. J. Klopfenstein, C. N. Macken, and R. U. Lindquist. 2006. Wet corn gluten feed and alfalfa hay levels in dry-rolled corn finishing diets: Effects on finishing performance and feedlot nitrogen mass balance. *Journal of Animal Science* 84(5): 1205–1214.

Flessa, H., P. Dorsch, F. Beese, H. Konig, and A. Bouwman. 1996. Influence of cattle wastes on nitrous oxide and methane fluxes in pasture land. *Journal of Environmental Quality* 25(6): 1366–1370.

Ginting, D., A. Kessavalou, B. Eghball, and J.W. Doran, 2003. Greenhouse gas emissions and soil indicators four years after manure and compost applications. *Journal of Environmental Quality* 32:23–32.

Groffman, P. M., C. W. Rice, and J. M. Tiedje. 1993. Denitrification in a tallgrass prairie landscape. *Ecology* 74 (3): 855–862.

Hofstra, N., and A. F. Bouwman. 2005. Denitrification in agricultural soils: Summarizing published data and estimating global annual rates. *Nutrient Cycling in Agroecosystems* 72 (3): 267–78.

Hossler, K., and V. Bouchard. 2008. The joint estimation of soil trace gas fluxes. *Soil Science Society of America Journal* 72:1382–1393.

Hou, A. X., G. X. Chen, Z. P. Wang, O. Van Cleemput, and W. H. Patrick, Jr. 2000. Methane and nitrous oxide emissions from a rice field in relation to soil redox and microbiological processes. *Soil Science Society of America Journal* 64: 2180–2186.

Hutchinson, G. L., and A. R. Mosier. 1981. Improved soil cover method for field measurement of nitrous oxide fluxes. *Soil Science Society of America Journal* 45: 311–316.

Hutchinson, G. L., and G. P. Livingston. 2001. Vents and seals in non-steady-state chambers used for measuring gas exchange between soil and the atmosphere. *European Journal of Soil Science* 52: 675–682.

Johnson-Beebout, S. E., O. R. Angeles, M. C. Alberto, and R. J. Buresh. 2008. Simultaneous minimization of nitrous oxide and methane emission from rice paddy soils is improbable due to redox potential changes with depth in a greenhouse experiment without plants. *Geoderma* 149: 45–53.

Kanako, K., H. U. Ronggui, T. Sawamoto, and R. Hatano. 2008. Comparison of the closed-chamber and gas concentration gradient methods for measurement of CO_2 and N_2O fluxes in two upland field soils. *Soil Science and Plant Nutrition* 54: 777–785.

Kanako, K., H.U. Ronggui, T. Sawamoto, and R. Hatano. 2006. Three years of nitrous oxide and nitric oxide emissions from silandic andosoils cultivated with maize in Hokkaido, Japan. *Soil Science and Plant Nutrition* 52: 103–113.

Kanako, K., T. Sawamoto, and R. Hatano. 2002. Nitrous oxide emissions for 6 years from a gray lowland soil cultivated with onions in Hokkaido, Japan. *Nutrient Cycling in Agro-ecosystems* 63: 239–247.

Kienbusch, M.R. 1986. Measurement of gaseous emission rates from land surfaces using an emission isolation flux chamber: user's guide. EPA, Contract No. 68-02-3889 Work Assignment 18.

Klein, C. A. M., and R. S. P. Logtestijn. 1994. Denitrification and N_2O emission from urine-affected grassland soil. *Plant and Soil* 163(2): 235–241.

Kookana, R. S., A. K. Sarmah, L. Van Zwieten, E. Krull, and B. Singh. 2011. Biochar application to soil: Agronomic and environmental benefits and unintended consequences. *Advances in Agronomy* 112: 103–43.

Lee, J., J. W. Hopmans, C. van Kessel, A. P. King, K. J. Evatt, D. Louie, D. E. Rolston, and J. Six. 2008. Tillage and seasonal emissions of CO_2, N_2O, and NO across a seed bed and at

the field scale in a Mediterranean climate. *Agriculture, Ecosystems & Environment* 129: 378–390.

Lessard, R., P. Rochette, E. G. Gregorich, E. Pattey, and R. L. Desjardins. 1996. Nitrous oxide fluxes from manure-amended soil under maize. *Journal of Environmental Quality* 25(6): 1371–1377.

Li, C. 2007. Quantifying greenhouse gas emissions from soils: Scientific basis and modeling approach. *Soil Science and Plant Nutrition* 53(4): 344–352.

Li, C., W. Salas, R. Zhang, C. Krauter, A. Rotz, and F. Mitloehner. 2012. Manure-DNDC: a biogeochemical process model for quantifying greenhouse gas and ammonia emissions from livestock manure systems. *Nutrient Cycling in Agroecosystems* 93(2): 163–200.

Livingston, G. P., G. L. Hutchinson, and K. Spartalian. 2006. Trace gas emission in chambers: a non-steady-state diffusion model. *Soil Science Society of America Journal* 70: 1459–1469.

LumaSense Technologies Inc. 2012. Photoacoustic spectroscopy. Available at: http://lumasenseinc.com/EN/solutions/techoverview/pas/. Accessed 20 January2012.

Malla, G., A. Bhatia, H. Pathak, S. Prasad, N. Jain, and J. Singh. 2005. Mitigating nitrous oxide and methane emissions from soils in rice-wheat systems of the Indo-Gangetic Plain with nitrificat. *Chemosphere* 58(2): 141–147.

Marinho, E. V. A., R. D. Delaune, and C. W. Lindau. 2004. Nitrous oxide flux from soybeans grown on Mississippi alluvial soil. *Communications in Soil Science and Plant Analysis* 35(1): 1–8.

McGinn, S. M., and K. A. Beauchemin. 2012. Dairy farm methane emissions using a dispersion model. *Journal of Environmental Quality* 41: 73–79.

McGinn, S. M., K. A. Beauchemin, T. K. Flesch, and T. Coates. 2009. Performance of a dispersion model to estimate methane loss from cattle in pens. *Journal of Environmental Quality* 38: 1796–1802.

McGinn, S. M., T. K. Flesch, B. P. Crenna, K. A. Beauchernin, and T. Coates. 2007. Quantifying ammonia emissions from a cattle feedlot using a dispersion model. *Journal of Environmental Quality* 36(6): 1585–1590.

Menéndez, S., P. Merino, M. Pinto, C. Gonzalez-Murua, and J. M. Estavillo. 2006. 3,4-Dimethylpyrazol phosphate effect on nitrous oxide, nitric oxide, ammonia, and carbon dioxide emissions from grasslands. *Journal of Environmental Quality* 35: 973–981.

Mikha, M. M., C. W. Rice, and G. A. Milliken. 2005. Carbon and nitrogen mineralization as affected by drying and wetting cycles. *Soil Biology & Biochemistry* 37: 339–347.

Monteny, G. J, A. Bannink, and D. Chadwick. 2006. Greenhouse gas abatement strategies for animal husbandry. *Agriculture, Ecosystems & Environment* 112: 163–170.

Mosier, A., C. Kroeze, C. Nevison, O. Oenema, S. Seitzinger, and O. van Cleemput. 1998. Closing the global N_2O budget: nitrous oxide emissions through the agricultural nitrogen cycle. *Nutrient Cycling in Agro-ecosystems* 52: 225–248.

National Research Council (NRC). 1993a. *In Situ Bioremediation-When Does It Work?* Washington, DC: The National Academies Press.

National Research Council (NRC). 1993b. S*oil and Water Quality: An Agenda for Agriculture*. Washington, DC: The National Academies Press.

National Research Council (NRC). 2003. *Air Emissions from Animal Feeding Operations: Current Knowledge, Future Needs*. Washington, DC: The National Academies Press.

Novak, S. M., and J. L. Fiorelli. 2010. Greenhouse gases and ammonia emissions from organic mixed crop-dairy systems: A critical review of mitigation options. *Agronomy for Sustainable Development* 30(2): 215–236.

Osada, T., and Y. Fukumoto. 2001. Development of a new dynamic chamber system for measuring harmful gas emissions from composting livestock waste. *Water Science and Technology* 44(9): 79–86.

Parkin, T. B., and T. C. Kaspar. 2006. Nitrous oxide emissions from corn-soybean systems in the Midwest. *Journal of Environmental Quality* 35: 1496–1506.

Pattey, E., I. B. Strachan, R. L. Desjardins, G. C. Edwards, D. Dow, and J. I. MacPherson. 2005a. Application of tunable diode laser to the measurement of CH_4 and N_2O fluxes from field to landscape scale using several micrometeorological techniques. *Science Direct* 136: 222–236.

Pattey, E., M. K. Trzcinski, and R. L. Desjardins. 2005b. Quantifying the reduction of greenhouse gas emissions as a result of composting dairy and beef cattle manure. *Nutrient Cycling in Agroecosystems* 72(2): 173–187.

Paul, E.A. 2007. Soil microbiology, ecology, and biochemistry. 3rd ed. Burlington, MA: Academic Press.

Predotova, M., J. Gebauer, R. V. C. Diogo, E. Schlecht, and A. Buerkert. 2010. Emissions of ammonia, nitrous oxide and carbon dioxide from urban gardens in Niamey, Niger. *Field Crops Research* 115(1): 1–8.

Predotova, M., R. Kretschmann, J. Gebauer, and A. Buerkert. 2011. Effects of cuvette surface material on ammonia-, nitrous oxide-, carbon dioxide-, and methane-concentration measurements. *Journal of Plant Nutrition and Soil Science* 174(3): 347–349.

Ro, K. P., G. Hunt, M. H. Johnson, A. A. Szogi, and M. B. Vanotti. 2007. Path integrated optical remote sensing technique to estimate ammonia and methane emissions from CAFOs. *Proceedings of the International Symposium on Air Quality and Waste Management for Agriculture*. 16-19 September 2007. ASABE publication number 701P0907cd.

Rochette, P., A. D. Angers, M. H. Chantigny, B. Gagnon, and N. Bertrand. 2008. N_2O fluxes in soils of contrasting textures fertilized with liquid and solid dairy cattle manures. *Canadian Journal of Soil Science* 88(2): 175–187.

Rochette, P., and N. S. Eriksen-Hamel. 2008. Chamber measurements of soil nitrous oxide flux: Are absolute values reliable? *Soil Science Society of America Journal* 72: 331–342.

Saggar, S., R. M. Andrew, K. R. Tate, C. B. Hedley, N. J. Rodda, and J. A. Townsend. 2004. Modelling nitrous oxide emissions from dairy-grazed pastures. *Nutrient Cycling in Agroecosystems* 68: 243–255.

Scheer, C., P. R. Grace, D. W. Rowlings, S. Kimber, and L. Van Zwieten. 2011. Effect of biochar amendment on the soil-atmosphere exchange of greenhouse gases from an intensive subtropical pasture in northern New South Wales, Australia. *Plant and Soil* 345: 47–58.

Scholes, M. C., R. Martin, R. J. Scholes, D. Parsons, and E. Winstead. 1997. NO and N_2O emissions from savanna soils following the first simulated rains of the season. *Nutrient Cycling in Agroecosystems* 48 (1-2): 115–122.

Segers, R. 1998. Methane production and methane consumption: A review of processes underlying wetland methane fluxes. *Biogeochemistry* 41: 23–51.

Shi, Y., D. B. Parker, N. A. Cole, B. W. Auvermann, and J. E. Mehlhorn. 2001. Surface amendments to minimize ammonia emissions from beef cattle feedlots. *Transactions of the ASAE* 44(3): 677–682.

Sohi, S. P., E. Krull, E. Lopez-Capel, and R. Bol. 2010. A review of biochar and its use and function in soil. *Advances in Agronomy* 105: 47–82.

Stelmaszczyk, K., M. Fechner, P. Rohwetter, M. Queißer, A. Czyzewski, T. Stacewicz, and L. Wöste. 2009. Towards supercontinuum cavity ring-down spectroscopy. *Applied Physics B: Lasers and Optics* 94:369–373.

Taghizadeh-Toosi, A., T. J. Clough, L. M. Condron, R. R. Sherlock, C. R. Anderson, and R. A. Craigie. 2011. Biochar incorporation into pasture soil suppresses in situ nitrous oxide emissions from ruminant urine patches. *Journal of Environmental Quality* 40: 468–476.

Thoma, E., R.C. Shores, E.L. Thompson, D.B. Harris, and S.A. Thorneloe. 2005. Open-path tunable diode laser absorption spectroscopy for acquisition of fugitive emission flux data. *Journal of Air & Waste Management Association* 55:658–668.

Van Zwieten, L., S. Kimber, S. Morris, A. Downie, E. Berger, J. Rust, and C. Scheer. 2010. Influence of biochars on flux of N_2O and CO_2 from ferrosol. *Australian Journal of Soil Research* 48: 555–568.

Weiske, A., G. Benckiser, and J. C. G. Ottow. 2001a. Effect of the new nitrification inhibitor DMPP in comparison to DCD on nitrous oxide (N_2O) emissions and methane (CH_4) oxidation during 3years of repeated applications in field experiments. *Nutrient Cycling in Agroecosystems* 60: 57–64.

Weiske, A., G. Benckiser, T. Herbert, and J. C. G. Ottow. 2001b. Influence of the nitrification inhibitor 3,4-dimethylpyrazole phosphate (DMPP) in comparison to dicyandiamide (DCD) on nitrous oxide emissions, carbon dioxide fluxes and methane oxidation during 3 years of repeated application in field experiments. *Biology and Fertility of Soils Journal* 34: 109–117.

Wheeler, M.D., S.M. Newman, A.J. Orr-Ewing, and M.N.R. Ashfold. 1998. Cavity ring-down spectroscopy. *Journal of the Chemical Society, Faraday Transactions* 94: 337–351.

Woodbury, B. L., D. N. Miller, J. A. Nienaber, and R. A. Eigenberg. 2001. Seasonal and spatial variations of denitrifying enzyme activity in feedlot soil. *Transactions of the ASAE* 44(6): 1635–1642.

Woodbury, B. L., D. N. Miller, R. A. Eigenberg, and J. A. Nienaber. 2006. An inexpensive laboratory and field chamber for manure volatile gas flux analysis. *Transactions of the ASABE* 49(3): 767–772.

Chapter 3 - Nitrous Oxide Emissions from a Commercial Beef Cattle Feedlot in Kansas

3.1. 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 the N_2O emission rate from pen surfaces in a commercial open-lot beef cattle feedlot in Kansas. Static flux chambers with a diameter of 30 cm were used to determine the N_2O emission flux from several pens as affected by pen surface conditions (i.e., moist/muddy, dry and loose, dry and compacted, and flooded) from July 2010 through September 2011. Gas samples were collected from the chambers' headspace at 0, 15, and 30 min using syringes and analyzed with a gas chromatograph. From the measured N_2O concentrations, N_2O emission fluxes were calculated. For each pen surface condition, N_2O emission flux varied considerably with sampling day. Emission flux also varied with pen surface condition, with the moist/muddy surface having the largest median emission flux (2.03 mg m^{-2} h^{-1}). The dry and compacted, dry and loose, and flooded surfaces had median emission fluxes of 0.16, 0.13, and 0.10 mg m^{-2} h^{-1}, respectively. Further work is needed to investigate techniques to reduce greenhouse gas emissions from beef cattle feedlots.

3.2. Introduction

Emission of greenhouse gases (GHGs) such as carbon dioxide (CO_2), nitrous oxide (N_2O), and methane (CH_4) are contributing to global warming (Kanako et al., 2002). The 100-year linear trend (1906 through 2005) of the earth's climate system shows an increase of $0.74°C$ in air temperature (IPCC, 2007; US EPA, 2010). The combined radiative forcing due to increased atmospheric concentrations of CO_2, CH_4, and N_2O is $+ 2.30$ W m^{-2} (IPCC 2007). N_2O has a global warming potential (GWP) 296 times greater than that of CO_2 and an atmospheric lifetime of approximately 120 years (IPCC, 2001), yet it is often one of the least known GHGs in terms of source material. Animal agriculture and N-enriched soils from fertilization are the leading biogenic sources of N_2O emissions (Mosier et al., 1998). Total nitrogen (N) retained by the animal and animal products (i.e., 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 (Mosier et al., 1998). Total N excreted in urine alone is estimated to be over 50% of intake N from animal diets (Mosier et al., 1998).

The total inventory of cattle and calves in the United States totaled 100 million head in 2011 (USDA, 2011), with approximately 34% of those animals concentrated in large open feedlots (USDA, 2009). In open beef cattle feedlots, urine deposited on the pen surface undergoes both nitrification and subsequent denitrification processes, both of which are microbial related and result in N_2O emissions (Bremer, 2006; Lee et al., 2008; Saggar et al., 2004). Urine applied to soil surfaces has been shown to increase N_2O emission significantly up to 14 days after application; however, activation of these processes is highly variable in time and space, because they depend on soil water content, temperature, nitrate (NO_3^-) content, ammonium (NH_4^+) content, organic matter content, and microbial community (Bremer, 2006; Kanako et al., 2006; Lee et al., 2008).

Although knowledge on the effects of soil N_2O emissions from tillage operations is extensive (Parkin and Kaspar, 2006), and although ruminant digestive systems have been documented to some extent (Boadi et al., 2004), little information is available on the levels of N_2O emission from commercial feedlots (Woodbury et al., 2001). This research is expected to contribute to the limited data on GHG emissions from beef cattle feedlots. The main purpose of this study was to examine emission rates of N_2O from commercial beef cattle feedlots surfaces as affected by pen surface characteristics and environmental conditions. Feedlot surfaces were characterized for temperature, moisture content, total carbon (C), total N, NO_3^-, NH_4^+, and pH; static flux chambers (SFCs) were used to sample feedlot pens for N_2O gas concentrations. Concentrations of N_2O were determined using evacuated vials with GC analysis.

3.3. Materials and Methods

3.3.1. Feedlot description

This study was conducted in an open beef cattle feedlot in Kansas from June 2010 through September 2011. 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 land. Each pen was scraped two to three times per year, and manure was removed at least once per year. During the measurement period, total

rainfall in the feedlot area was 352 mm, with the largest total seasonal rainfall of 134 mm in summer 2010 and the smallest rainfall amount of 20 mm in the winter 2011. The prevailing wind direction in the feedlot was from the south/southwest. Air temperature, total rainfall amount, and wind direction were measured with a meteorological station deployed in the field.

3.3.2. Sampling and measurement

Emission fluxes of N_2O from the pen surface were measured using SFCs following the procedure that has been used for soils (Boadi et al., 2004; Hutchinson and Livingston, 2001; Hutchinson and Mosier, 1981; Livingston et al., 2006; Rochette and Eriksen-Hamel, 2008; Whalen, 2000). Each SFC had the following components (Fig. 3-1): cylindrical body, metal ring, cap, and peripheral accessories (i.e., 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 (Bremer, 2006; Hutchinson and Mosier, 1981). The sampling port was fitted with 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), following the recommendations by Hutchinson and Mosier (1981). A small blower, a single-phase, 6-pole brushless direct-current motor with dimensions of 30x30x3 mm (Newark Company, Chicago, IL) with a rated volumetric flow rate of 7.5 L min^{-1} was used for internal forced air circulation. This small flow rate was designed to prevent internal pen surface disturbance and the subsequent effect on emission flux measurement. Soil/manure temperature and air temperature sensors were HOBO TMC6-HD sensors (-40 to 100 °C ± 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_2O concentrations using a GC (model GC14A, Shimadzu, Kyoto, Japan). It 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_4 (95:5 ratio). The column (oven), injector, and ECD were set up at 85, 100, and 320°C respectively.
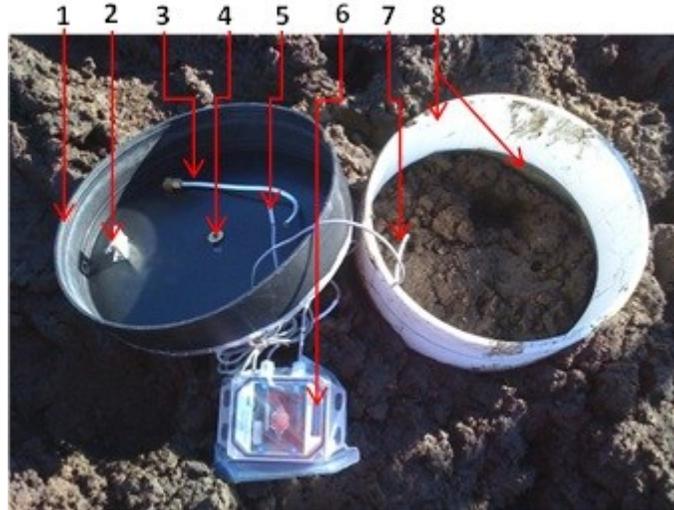
Figure 3-1 Photograph of the static flux chamber showing the major components: (1) chamber cap, (2) small blower, (3) pressure equalizer, (4) sampling port, (5) air temperature sensor, (6) data logger, (7) soil/manure temperature sensor, and (8) body with the stainless steel ring.

Soil/manure temperature through the first 10 cm below the surface and air temperature in the SFC headspace were measured every 60 s during the sampling time. Volumetric soil/manure water content (5 cm, 0.3 L measurement volume) was averaged from four measurements before capping the chamber. During each field sampling campaign, after 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 soil/manure cores were used to determine the soil/manure bulk density and gravimetric water content. The cores were also analyzed at the Kansas State University Soil Testing Laboratory (Manhattan, KS) for pH (soil:water 1:1 method), NH_4^+ and NO_3^- (KCl extraction method), total N (dry combustion method), and total C (salicylic-sulfuric acid digestion method).

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 transport in the vertical direction (Hutchinson et al., 2000; Livingston et al., 2006). Rochette and Eriksen-Hamel (2008) stated that "leakage or contamination can occur by lateral diffusion of N_2O beneath the base in response to deformation of the vertical N_2O concentration gradient in the soil." Previous studies inserted the chambers 2 to 7.5 cm deep into the soil (Kanako et al., 2002; Ginting et al.,

2003; Parkin, and Kaspar, 2006; Marinho et al., 2004; Whalen, 2000; Lee et al., 2008; Boadi et al., 2004). Based on the procedure suggested for Rochette and Eriksen-Hamel (2008), SFCs in this research were inserted 6 cm deep for 30-min deployment time.

In general, the N_2O concentration inside the SFC would increase with time until steady-state condition was reached. To calculate the emission flux, the change in concentration with time ($\Delta C/\Delta t$) was determined, and gas samples taken as quickly as possible (Rochette and Eriksen-Hamel, 2008). Preliminary tests were performed with a deployment time of 60 min, collecting chamber headspace sample each 5 min; results showed relatively constant concentration gradient during the first 30 min. As such, for this study, the sampling protocol involved sampling at 0, 15, and 30 min after the cap has been put in place. This protocol was similar to those developed for soil surfaces. Gas samples were collected with 20-mL disposable plastic monoject syringes with detachable 25GX 1 ½-in. needles and injected into previously flushed and evacuated 12-mL glass vial. Overpressure was intended to prevent sample contamination with atmospheric gases (Marinho et al., 2004) and to have a sample sufficient for multiple analyses in the GC. In addition, as a reference of the ambient N_2O concentration (background), one gas sample was collected at 1-m height just before and after the sampling period in each pen.

From preliminary work, four main pen surface conditions were identified (Fig. 3-2): I - moist/muddy, II - dry and loose, III - dry and highly compacted, and IV - flooded. Their respective average dry bulk densities were 0.86, 1.06, 1.03, and 0.82 g cm^{-3}. The presence and locations of the surface conditions changed rapidly with time. During two sampling days in March 2011, the relative sizes of the surface conditions were estimated. Mean areas (and standard deviations) as percent of total pen area were 14 (10), 47 (27), 24 (2), and 15 (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), there were 10 field sampling campaigns with a total of 23 sampling days. Three pens were randomly selected. In July 2010, paired SFCs were installed covering different surface conditions in a pen. Gas samples were taken from the chamber headspaces four times a day, twice in the morning and twice in the afternoon. From September through November 2010, and based on presence of the different pen surface conditions, SFCs were deployed in three pens, with each available surface

condition covered by one SFC. Gas samples were collected twice a day, during the morning and afternoon. Analysis of those data indicated that the N_2O fluxes were not significantly different between the morning and afternoon sampling periods; as such, in succeeding sampling campaigns (i.e., February through September 2011), two to four SFCs were deployed in each pen and sampled only once a day.
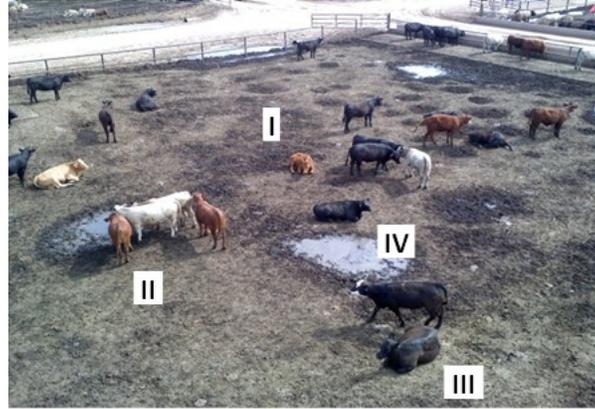
Figure 3-2 Photograph of a pen showing the different pen surface conditions (I- moist/muddy, II- dry and loose, III- dry and compacted, and IV- flooded).

3.3.3. Calculation of N_2O emission fluxes

Emission fluxes were computed from the change in N_2O concentration with time, as described by Anthony et al. (1995), Ginting et al. (2003), and Hutchinson and Mosier (1981):

$$F = \left[\left(\frac{V}{A} \right) \left(\frac{\Delta C}{\Delta t} \right) \right] \tag{3.1}$$

where F is the gas emission rate in ($\mu g\ m^{-2}\ h^{-1}$), V is volume of air within the chamber (m^3), A is the surface area of soil/manure within the chamber (m^2), ΔC is N_2O concentration difference (ppm), and Δt is sampling interval (h). The gas concentration must be converted from volume-based (ppm) to mass-based concentration ($\mu g\ m^{-3}$) using (Cooper and Alley, 2002):

$$C_m = 1000\ Cppm\ MW\ \frac{P}{RT} \tag{3.2}$$

where C_m is mass concentration ($\mu g\ m^{-3}$), C_{ppm} is volume concentration (ppm), MW is the molar mass of the gas (g $gmol^{-1}$), P is atmospheric pressure (mm Hg), T is temperature (K) within the enclosed space, and R is the ideal gas constant (62.36 mm Hg L $gmol^{-1}$ K^{-1}). The concentration gradient with time, $\Delta C/\Delta t$, was calculated based on three general cases (Ginting et al., 2003):

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

$$\frac{\Delta C}{\Delta t} = \left[\frac{(\Delta C_1)^2}{\Delta t\,(2C_{15} - C_{30} - C_0)} ln\left(\frac{\Delta C_1}{\Delta C_2}\right)\right] \tag{3.3}$$

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

$$\frac{\Delta C}{\Delta t} = \left[\frac{\Delta C_1 + \Delta C_2}{2\Delta t}\right] \tag{3.4}$$

- 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)

$$\frac{\Delta C}{\Delta t} = \left[\frac{\Delta C_1}{2\Delta t} + \frac{\Delta C_3}{4\Delta t}\right] \tag{3.5}$$

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 N_2O concentrations (ppm) within the SFC at 0, 15, and 30 min, respectively; and $\Delta t = 0.25$ h. Case 1 is based on the diffusion approach considering SFC N_2O saturation with time (Ginting et al., 2003; Anthony et al., 1995; Hutchinson and Mosier, 1981). Case 2 is based on the average of the two slopes between concentrations when there is no N_2O saturation; that is, the gas concentration gradient is linear over time (Hossler and Bouchard, 2008; Ginting et al., 2003). Case 3 is based on the average of the slopes between the first and second and between the first and third N_2O concentrations, respectively (Ginting et al., 2003).

3.3.4. Statistical analysis

Emission flux data and soil/manure chemical and physical characteristics were first analyzed for normality using the univariate procedure in SAS (Peng, 2004). Normality for each individual factor was analyzed based on the complete dataset, then classified by pen, season, and pen surface condition. In general, soil/manure characteristics, including water content, temperature, pH, total N content, total C content, and chamber air temperature were normally distributed. Nitrous oxide emission fluxes, soil/manure NH_4^+ content, and NO_3^- content, on the other hand, were not normally distributed at the 5% level. The N_2O emission flux data showed positively skewed distribution; as such, log transformation was performed (Bland and Altman, 1996a, 1996b). The log-transformed data were normally distributed and were then analyzed for unequal variances using the MIXED procedure in SAS (SAS, 2008). P-values and confidence intervals were adjusted for Bonferroni (Milliken and Johnson, 2009). In addition, the median of

the N_2O emission fluxes and the confidence interval for the median were reported rather than the mean and standard deviation (Bland and Altman, 1996a). Regression analyses between N_2O 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 multicolinearity based on the variance inflation factor (Kutner et al., 2005).

3.4. Results and Discussion

3.4.1. Nitrous oxide emission rates

Measured concentrations of N_2O inside the SFCs at sampling times of 0, 15, and 30 min and in background air are summarized in Table 3-1. In general, N_2O concentrations inside the SFCs increased steadily; i.e., $C_0<C_{15}<C_{30}$. Based on the concentration gradients, 41% out of 176 samples followed case 1 (i.e., $\Delta C_1>\Delta C_2$ and $C_0<C_{15}<C_{30}$), 40% followed case 2 (i.e., $\Delta C_1\leq\Delta C_2$ and $C_0<C_{15}<C_{30}$), and the remaining 19% followed case 3 (i.e., $\Delta C_1\leq\Delta C_2$ and $C_0<C_{15}>C_{30}$ or $C_0>C_{15}<C_{30}$).

Table 3-1 Measured N_2O concentrations inside the static flux chambers and in background air.

Surface condition	Sampling time (min)	Number of data points	N_2O concentration (ppm)			
			Average	Standard deviation	Minimum	Maximum
I- Moist/muddy	0	39	0.53	0.31	0.29	1.89
	15	39	4.49	8.94	0.40	42.9
	30	39	7.75	17.06	0.41	78.3
II- Dry and loose	0	54	0.42	0.13	0.31	0.94
	15	54	0.60	0.28	0.33	1.71
	30	54	0.75	0.45	0.32	2.46
III- Dry and compacted	0	51	0.38	0.07	0.26	0.70
	15	51	0.55	0.28	0.32	1.78
	30	51	0.64	0.32	0.34	1.69
IV- Flooded	0	32	0.47	0.17	0.32	1.07
	15	32	0.59	0.22	0.37	1.26
	30	32	0.70	0.34	0.41	1.93
Background air	--	136	0.42	0.11	0.32	0.87

Emission fluxes of N_2O for each pen surface condition and season during the study period are shown in Figure 3-3a. 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 and soil/manure average temperature during the study period were the largest. In one of the pens, the highest fluxes (15 to 28 mg m^{-2} h^{-1}) were observed in July 2010, three days after a heavy rainfall event. During that period, air temperatures were greater than 40°C, resulting in some areas in the pen that were partially dried on the surface and wet 5 to 10 cm deeper underneath. Those areas, identified as moist/muddy (surface condition I), accounted for those largest fluxes during three different sampling days in that pen.

In contrast, the total rainfall during summer 2011 was less than half the amount during summer 2010, which corresponds with the lower N$_2$O fluxes observed during summer 2011. The increased emission rate after rainfall events was consistent with general observations for soils (Parkin and Kaspar, 2006). Kanako et al. (2006) also reported that N$_2$O emission fluxes after heavy rainfall in agricultural soils ranged from 1.73 to 6.42 mg m^{-2} h^{-1}. Increased N$_2$O emission rates following rainfall events have been reported in both agricultural (Marinho et al., 2004) and turfgrass soils (Bremer, 2006); the level of activity also has been associated with seasonality and NO$_3^-$ availability (Groffman et al., 1993). These findings confirm that emissions from cattle feedlots are episodic and related to rainfall events and warm temperatures, as noted by Von Essen and Auvermann (2005).

During fall 2010 sampling, N$_2$O fluxes were large in the second studied pen (39 to 42 mg m^{-2} h^{-1}) in October. The pen included an area that was flooded most of the time, but after two dry summer months with a total combined precipitation of only 14 mm, the flooded area became moist/muddy (surface condition I), resulting in large N$_2$O emission fluxes. In the same pen, high N$_2$O emission fluxes were observed again during the summer 2011 sampling campaign, with peak flux of 22 mg m^{-2} h^{-1} in July 2011.
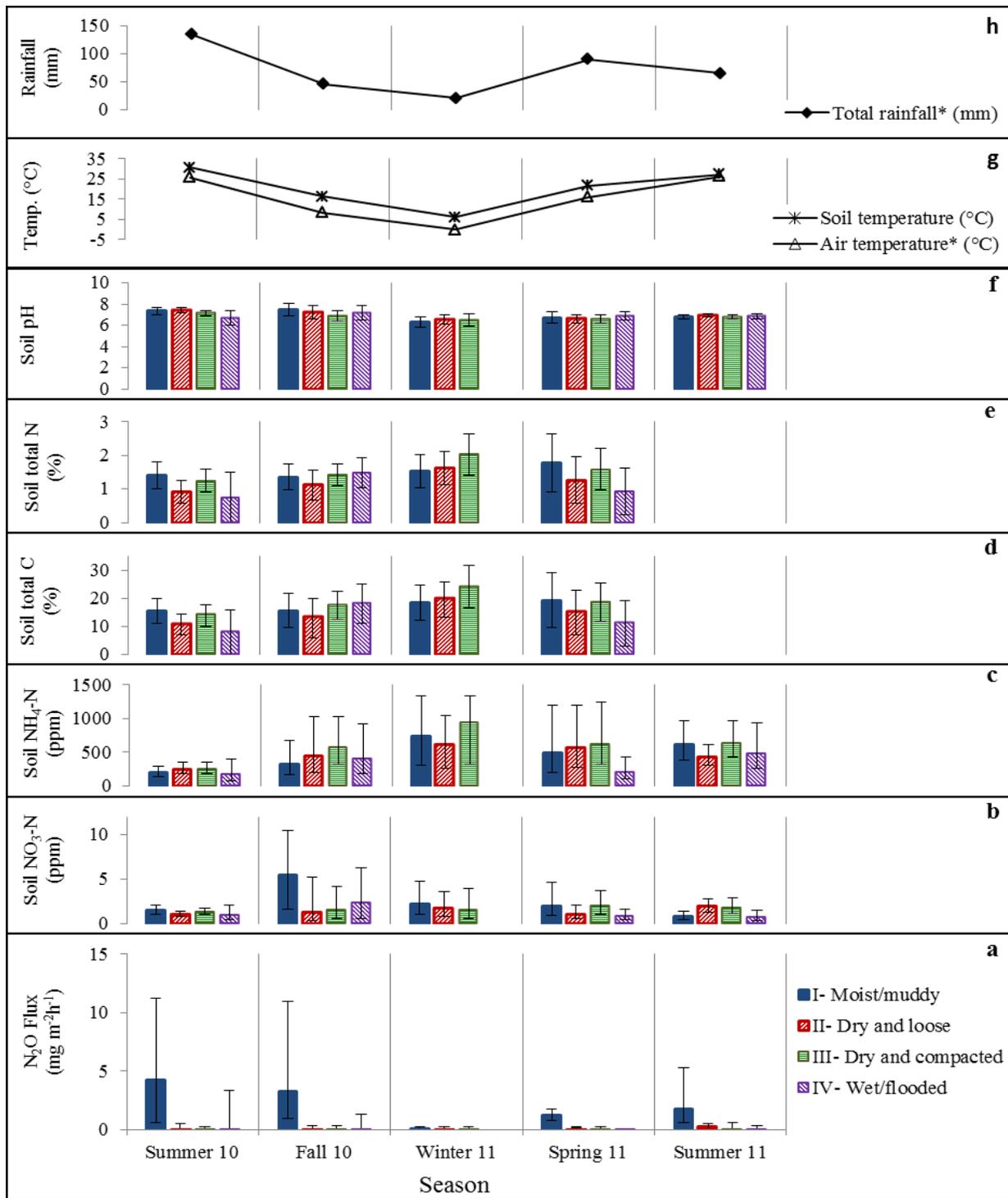
Figure 3-3 N$_2$O emission fluxes and related factors as affected by pen surface conditions and season: (a) median N$_2$O flux, (b) median nitrate content, (c) median ammonium content, (d) median total carbon content, (e) median total nitrogen content, (f) median pH, (g) median soil/manure temperature and air temperature by season, and (h) median rainfall amount by season. Error bars represent 95% CI. *Rainfall and air temperature were measured continuously; all other measurements were at selected times.

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Median N_2O emission fluxes, soil/manure temperature, air temperature, and soil/manure water content for the different pen surface conditions are summarized in Table 3-2. 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. Surface conditions II (dry and loose), III (dry and compacted), and IV (flooded) did not differ significantly in median emission flux. Emission fluxes for surface conditions II, III, and IV were comparable to those of Boadi et al. (2004), who reported mean N_2O emission rate in manure pack of 0.134 mg-N_2O m^{-2} h^{-1}.

Surface condition I (moist/muddy) could be considered "hot spots" (Woodbury et al., 2001), which are localized micro-sites with physical and chemical conditions favoring intense microbial activity. Surface condition II (dry and loose) was dry on the surface and below it, and had lower N_2O emission fluxes. In the same way, surface condition III (dry and compacted), which represented the pen mound, also produced small N_2O 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_2O emission flux.

The large variability among pen surface conditions was consistent with observations for agricultural soils. Parkin and Kaspar (2006) reported high emission fluxes related to positional differences in chamber placement in the field. The reported spatial variability also may be explained by the activation of nitrification and denitrification processes, which are dominant factors in soil N_2O emission (Bremer, 2006; Lee et al., 2008; Woodbury et al., 2001). The activation of these processes varies in time and space due to factors such as temperature, NO_3^-, NH_4^+, water, and organic matter content (Bremer, 2006; Kanako et al., 2008, 2006). Woodbury et al. (2006) reported that emissions of NH_3, VOC, and CO_2 were highly variable at small distances within pens in a cattle feedlot.

Table 3-2 Data summary for the experimental period.

Parameter	Surface condition			
	I Moist/muddy	II Dry and loose	III Dry and	IV Flooded
N_2O emission flux (mg m^{-2} h^{-1})				
Median	2.03 [a]	0.16 [b]	0.13 [b]	0.10 [b]
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 ± standard deviation	26.6±9.2 [a]	29.3±7.8 [a]	28.5±8.6 [a]	26.0±8.6 [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 ± standard deviation	20.9±8.6 [a]	24.9±8.2 [b]	25.0±9.0 [b]	19.5±6.4 [c]
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^3 cm^{-3})				
Mean ± standard deviation	0.52±0.06 [a]	0.26±0.09 [b]	0.19±0.10 [c]	0.60±0.0 [d]
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 NO_3^- content (ppm)				
Median	1.9 [a]	1.3 [a]	1.6 [a]	1.1 [a]
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 NH_4^+ content (ppm)				
Median	359.9 [a]	416.7 [a]	505.4 [a]	275.6 [a]
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 deviation	16.7±4.2 [a]	13.6±6.1 [a]	17.1±5.3 [a]	13.6±7.1 [a]
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 (%)				
Mean ± standard deviation	1.5±0.4 [a]	1.2±0.5 [a]	1.5±0.4 [a]	1.1±0.6 [a]
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 deviation	7.0±0.5 [a]	7.0±0.5 [a]	6.8±0.4 [a]	6.9±0.6 [a]
Minimum/maximum	6.1/7.7	6.0/8.1	6.1/7.7	6.2/8.1
Sample size	21	26	27	13

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

3.4.2. Effects of soil/manure properties

Pen surface conditions differed significantly in water content and temperature (Table 3-2). Mean values of volumetric water content during the experimental period were 0.52, 0.26, 0.19, and 0.60 $cm^3 cm^{-3}$ for surface conditions I, II, III, and IV, respectively. Mean soil/manure temperatures were 20.9, 24.9, 25.0, and 19.5^{o}C for surface conditions I, II, III, and IV, respectively. Figures 3-4a and b show mean values of soil water content and temperature by season and surface condition. In general, soil/manure temperature significantly decreased as soil/manure water content increased (p=0.0025) with R^2= 0.15 (Fig. 3-4c). For surface conditions II and III, soil/manure temperature and water content were significantly correlated (p=0.0002) with R^2=0.13. Because of their large water content, surface conditions I and IV did not show significant correlation between soil/manure temperature and water content. Surface conditions I and IV observed large changes in soil/manure temperature with small to constant changes in soil/manure water content, respectively.

The largest difference in soil/manure temperature within a pen during the same sampling period was 9.6°C; it was observed in the 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 the winter 2011, among surface conditions I (2.2°C) and III (8.5°C). Surface condition I, due to its higher soil water content (0.53 $cm^3 cm^{-3}$), remained colder than the drier surface condition III (0.30 $cm^3 cm^{-3}$). 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. During the experimental period, differences in soil/manure temperature such as 2 to 5°C were commonly observed within the same pen in different surface conditions.
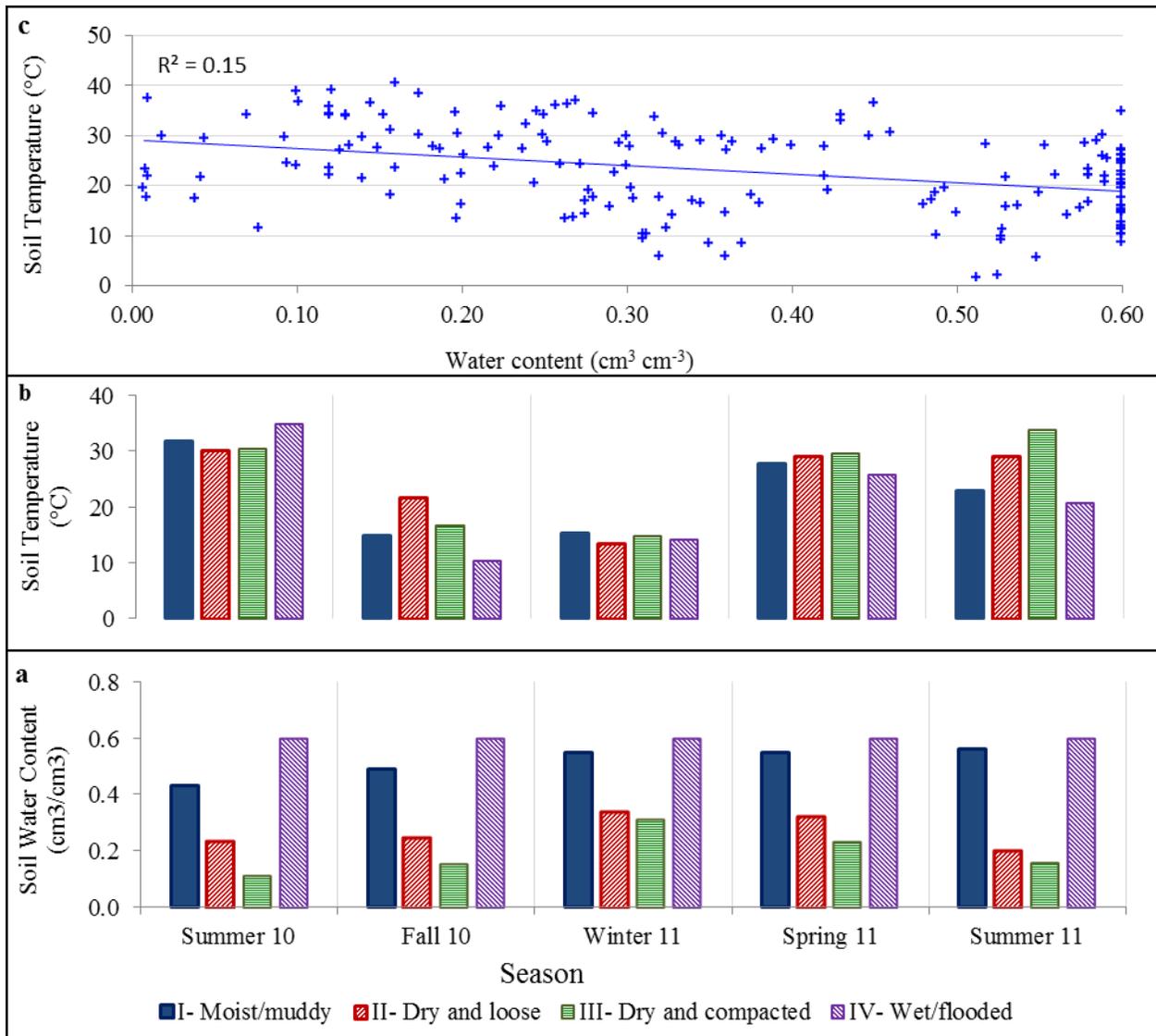
Figure 3-4 (a) Soil/manure water content, (b) soil/manure temperature by season and surface condition, and (c) soil/manure temperature vs. soil/manure water content.

Kanako et al. (2002) reported that dry soil conditions combined with high soil temperatures resulted in low N_2O emission fluxes; hence, low soil/manure water content combined with soil/manure temperatures greater than 35°C (Lee et al., 2008) may explain in part the consistently lower N_2O emission fluxes observed for surface conditions II and III. Surface condition IV had the lowest soil/manure temperature, and because of its flooded condition, its redox potential must have been reduced considerably. Hou et al. (2000) reported that redox potential less than -200 mV in flooded fields fertilized with organic manure had significant reduction in N_2O emission fluxes; this holds true for other soils with low soil redox potential

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(Johnson-Beebout et al., 2008). Therefore, reduced redox potential may explain in part the lowest N_2O emission in surface condition IV. In addition, because of its flooded condition, gas diffusion through the soil would be lower, corresponding to low N_2O emission flux.

For surface condition I, the higher N_2O emission rate is most likely due to the higher soil/manure water content and high NO_3^- concentrations in that surface condition compared with the other surface conditions, because rates of denitrification are correlated with high water content and NO_3^- content (Groffman et al., 1993). In contrast, the lower water content and higher soil/manure temperature of surface conditions II and III compared with surface condition I (Table 3-2) may explain in part their lower N_2O emission fluxes, similar to what has been seen in soils as they dry (Beare et al., 2009; Maia et al., 2012). 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 be present in the deeper layers, as suggested by the strong darker coloration (Mayer and Conrad, 1989; Woodbury et al., 2001) and smooth/homogeneous texture observed in the subsurface (Fig. 3-5). Therefore, reduced redox potential in the subsurface also 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 also may be limited, consequently decreasing the N_2O emission flux.

Figure 3-5 Darker coloration underneath surface condition III (dry and compacted).

The effects of soil/manure water content and soil/manure temperature on N_2O emission flux were analyzed. No significant relationship was observed between N_2O emission flux and soil/manure water content and temperature (Fig. 3-6). 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. Nitrous oxide emission flux from surface condition I (moist/muddy) decreased as soil/manure water content increased and increased with increments of soil/manure temperature, as shown in Figures 3-6a and b. In surface condition I, as water content increased over 0.50 cm^3cm^{-3}, the soil/manure became closer to saturation, decreasing the soil air-filled porosity, which may reduce gas diffusion through the soil. Lee et al. (2008) reported limited N_2O emission flux in extremely wet soil conditions. In surface conditions II (dry and loose) and III (dry and compacted), N_2O emission flux tends to decrease as soil/manure temperature increases. This may be explained by their drier conditions wherein increased soil temperatures combined with low water content becomes a limiting factor for denitrification activity. Lee et al. (2008) also reported limited N_2O emission flux in soil with temperatures higher than 35°C. Because of the saturated condition of surface IV (flooded), N_2O emission flux did not show any relationship with soil/manure water content and temperature.
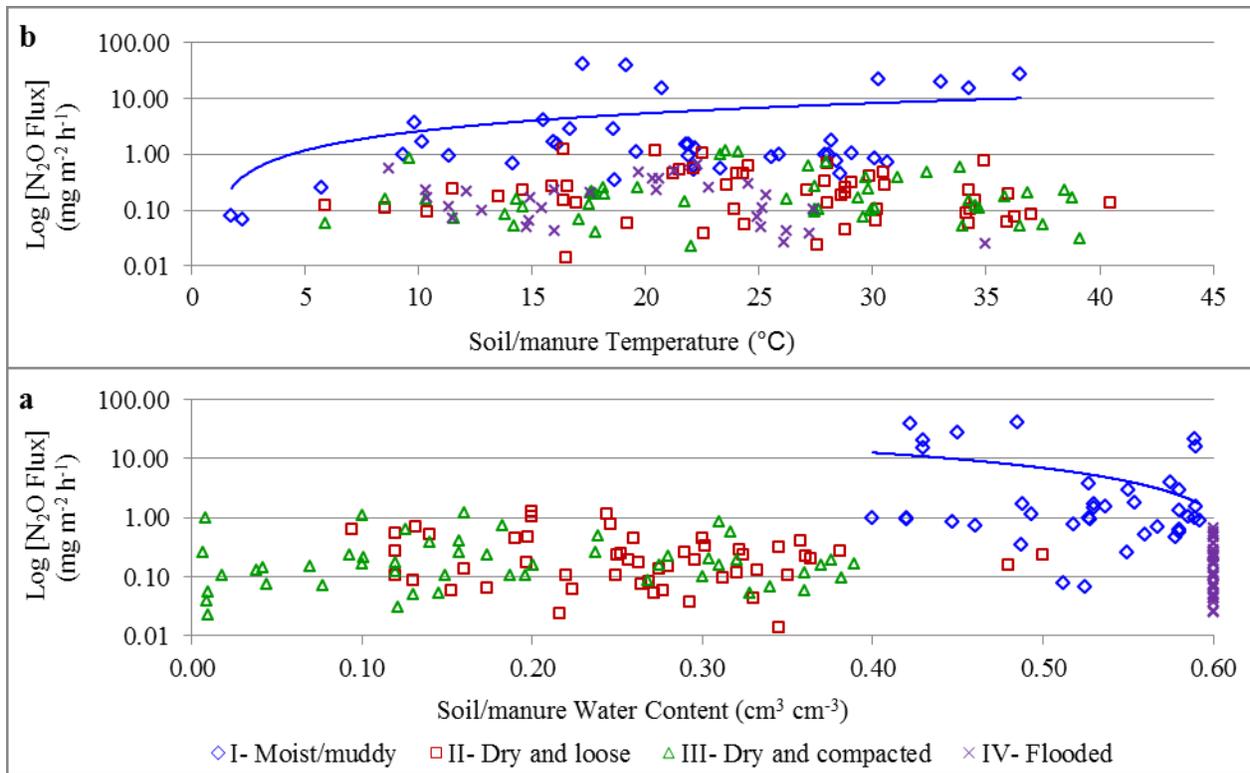
Figure 3-6 Nitrous oxide emission flux vs (a) soil/manure water content and (b) soil/manure temperature.

3.4.3. Relationship between N₂O emission flux and soil/manure properties

Analyses on the effects of soil/manure properties such as NO_3^-, NH_4^+, pH, total C, and total N contents on N₂O emission flux were performed for each pen surface condition. Figures 3-3b and c show that NO_3^- and NH_4^+ contents for all surface conditions were inversely related, as might be expected in agricultural soils; however, in this case, those inverse relationships were not significant at the 5% level. Unlike agricultural soils, fresh manure and urine are constantly added on 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, and total N were significantly larger in the top layer. This result is explained by the fact that the deeper the soil/manure layer, the less the availability of O_2, which is a limiting factor in nitrification. In

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addition, O_2 limitation is another factor that promotes denitrification, reducing even more the NO_3^- as well as the total C and N contents in the deeper soil/manure layers.

Figures 3-3a, b, and c show that the lowest NO_3^- and NH_4^+ content corresponds to seasons with the largest N_2O fluxes. As the soil/manure conditions (i.e., water content and temperature) become favorable for microorganism activity, the rate of denitrification increases (Groffman et al., 1993; Kanako et al., 2006; Kanako et al., 2002; Lee et al., 2008). 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 NO_3^- and NH_4^+ contents and increase in N_2O emission flux. Hofstra and Bouwman (2005) reported that organic soils have high denitrification rates due to their generally anaerobic condition and their high soil organic C content. Additionally, the decrease in NH_4^+ content in the summer also might be explained by the high surface temperatures, which favor the losses of NH_4^+ to the air in the form of NH_3, as suggested by the observed inverse relationship between surface temperature and NH_4^+ content. From the analysis of the soil/manure chemical conditions, none of the factors (i.e. NO_3^-, NH_4^+, total C, total N, and pH) were significantly different between surface conditions within each weather season.

Because of the large temporal and spatial variability in N_2O emission fluxes among the different surface conditions, further analysis of fluxes was performed for each pen surface condition. Multiple linear regression was performed at 10% level of significance. For surface condition I, the log (N_2O flux) was directly related to soil/manure water content (sw) and inversely related to the log (NH_4^+), with R^2=0.52:

$$\log(N_2O \text{ flux}) = 9.433 + 1.615 \, (sw) - 2.674 \log(NH_4^+) \tag{3.6}$$

For surface condition II, the log (N_2O flux) was directly related to log (NO_3^-) and inversely related to log (NH_4^+) and soil/manure pH, with R^2=0.44:

$$\log(N_2O \text{ flux}) = 12.730 + 1.679 \log(NO_3^-) - 1.872 \log(NH_4^+) - 0.839 \, (pH) \tag{3.7}$$

For surface condition III, log (N_2O flux) was directly related to water content and log (NO_3^-) but inversely related to soil/manure total C content (tc), with R^2=0.56:

$$\log(N_2O \text{ flux}) = 2.584 + 0.372 \log(NO_3^-) + 1.803 * (sw) - 0.048 \, (tc) \tag{3.8}$$

For surface condition IV, log (N_2O flux) was significantly inversely related to soil temperature (st), with R^2=0.42:

$$\log(N_2O \text{ flux}) = 2.661 - 0.033 \, (st) \tag{3.9}$$

Table 3-3 compares the measured and predicted median N_2O fluxes obtained from Equations 3.6 through 3.9. Nitrous oxide fluxes shown in this table represent median N_2O fluxes per surface condition based on those field-measured fluxes, which included their respective soil/manure chemical properties at the sampling time. Because of this, fluxes reported in Table 3-3 are different from the corresponding fluxes reported in this study. Using Equation 3.6 overestimated the lower fluxes and underestimated the peaks for surface condition I, with a mean prediction error of 69%. Equation 3.7 (surface condition II) also overestimated the individual fluxes, with a mean prediction error of 10%. Equations 3.8 and 3.9 resulted in an overall underestimation of N_2O fluxes, with mean prediction errors of 7 and 19% for the surface conditions III and IV, respectively.

Equations 3.6 through 3.9 should be used only for prediction within the range of the experimental data. As previously indicated, those errors of the predicted N_2O fluxes are for the individual computed fluxes per each chamber deployed on the field; however, when the complete dataset was analyzed and the median of predicted fluxes per surface condition were computed, the actual N_2O median fluxes were not significantly different from the predicted N_2O median fluxes at $\alpha=0.05$. Moreover, predicted median fluxes kept the same data distribution and significant differences among surface conditions as the actual N_2O median fluxes. Therefore, based on the complete dataset, there were no significant differences between the actual and predicted median N_2O emission fluxes for each surface condition, as shown in Table 3-3.

Table 3-3 Comparison of actual and predicted N$_2$O fluxes for each surface condition.

	N$_2$O median flux (mg m^{-2} h^{-1})	
	Actual	Predicted
I - Moist/muddy		
Median	1.51 [a]	1.93 [a]
95% CI	0.73 – 3.1	0.9 – 4.0
Sample size	20	20
II- Dry and loose		
Median	0.15 [b]	0.15 [b]
95% CI	0.09 – 0.24	0.09 – 0.24
Sample size	26	26
III- Dry and compacted		
Median	0.17 [b]	0.14 [b]
95% CI	0.12 – 0.23	0.1 – 0.21
Sample size	19	19
IV- Flooded		
Median	0.12 [b]	0.12 [b]
95% CI	0.07 – 0.19	0.07 – 0.19
Sample size	12	12

Medians followed by the same letter are not significantly different at 5% level.

3.5. Summary and Conclusions

This study used static flux chambers and gas chromatograph to measure N$_2$O 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^{-2} h^{-1}), 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^{-2}h^{-1}, 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, total C, pH, NO$_3^-$, and NH$_4^+$.

3.6. References

Anthony, W.H., G.L. Hutchinson, and G.P. Livingston. 1995. Chamber measurement of soil-atmosphere gas exchange: linear vs diffusion-based flux models. *Soil Science Society of America Journal* 59(5):1308–1310.

Beare, M., E. Gregorich, and P. St. Georges. 2009. Compaction effects on CO$_2$ and N$_2$O production during drying and rewetting of soil. *Soil Biology Biochemistry* 41:611–621.

Bland, J.M. and D.G. Altman. 1996a. Statistics notes: Transformations, means, and confidence intervals. *British Medical Journal* 312(7038):1079.

Bland, J.M. and D.G. Altman. 1996b. Statistics notes: The use of transformation when comparing two means. *British Medical Journal* 312(7039):1153.

Boadi, D. A., K. M. Wittenberg, S. L. Scott, D. Burton, K. Buckley, J. A. Small, and K. H. Ominski. 2004. Effect of low and high forage diet on enteric and manure pack greenhouse gas emissions from a feedlot. *Canadian Journal of Animal Science* 84:445–453.

Bremer D. J. 2006. Nitrous oxide fluxes in turfgrass: effects of nitrogen fertilization rated and types. *Journal of Environmental Quality* 35:1678–1685.

Cooper, D.C., and F.C. Alley. 2002. *Air Pollution Control: A Design Approach*. 3rd ed. Long Grove, IL: Waveland Press Inc.

Ginting, D., A. Kessavalou, B. Eghball, and J.W. Doran, 2003. Greenhouse gas emissions and soil indicators four years after manure and compost applications. *Journal of Environmental Quality* 32:23–32.

Groffman, P. M., C. W. Rice, and J. M. Tiedje. 1993. Denitrification in a tallgrass prairie landscape. *Ecology* 74 (3): 855–862.

Hofstra, N., and A. F. Bouwman. 2005. Denitrification in agricultural soils: Summarizing published data and estimating global annual rates. *Nutrient Cycling in Agroecosystems* 72 (3): 267–78.

Hossler, K., and V. Bouchard. 2008. The joint estimation of soil trace gas fluxes. *Soil Science Society of America Journal* 72:1382–1393.

Hou, A.X., G. X. Chen, Z. P. Wang, O. Van Cleemput, and W. H. Patrick, Jr. 2000. Methane and nitrous oxide emissions from a rice field in relation to soil redox and microbiological processes. *Soil Science Society of America Journal* 64:2180–2186.

Hutchinson G.L., and A.R. Mosier. 1981. Improved soil cover method for field measurement of nitrous oxide fluxes. *Soil Science Society of America Journal* 45:311–316.

Hutchinson, G.L., and G.P. Livingston. 2001. Vents and seals in non-steady-state chambers used for measuring gas exchange between soil and the atmosphere. *European Journal of Soil Science* 52: 675–682.

Hutchinson, G.L., G.P. Livingston, R.W. Healy, and R.G. Striegl. 2000. Chamber measurement of surface-atmosphere traces gas exchange: numerical evaluation of dependence on soil, interfacial layer and source/sink properties. *Journal of Geophysical Research* 105: 8865–8875.

IPCC. 2001. Working Group I Report: The Scientific Basis. IPCC Third Assessment Report - Climate Change 2001 (TAR). Intergovernmental Panel on Climate Change. Available at: www.grida.no/publications/other/ipcc_tar/. Accessed 8 October 2010.

IPCC. 2007. Working Group I Report: The Physical Science Basis. IPCC Fourth Assessment Report - Climate Change 2007. Intergovernmental Panel on Climate Change. Available at: www.ipcc.ch/ipccreports/ar4-wg1.htm. Accessed 20 August 2012.

Johnson-Beebout, S.E., O.R. Angeles, M.C. Alberto, and R.J. Buresh. 2008. Simultaneous minimization of nitrous oxide and methane emission from rice paddy soils is improbable due to redox potential changes with depth in a greenhouse experiment without plants. *Geoderma* 149:45–53.

Kanako, K., H.U. Ronggui, T. Sawamoto, and R. Hatano. 2006. Three years of nitrous oxide and nitric oxide emissions from silandic andosoils cultivated with maize in Hokkaido, Japan. *Soil Science and Plant Nutrition* 52: 103–113.

Kanako, K., H.U. Ronggui, T. Sawamoto, and R. Hatano. 2008. Comparison of the closed-chamber and gas concentration gradient methods for measurement of CO_2 and N_2O fluxes in two upland field soils. *Soil Science and Plant Nutrition* 54: 777–785.

Kanako, K., T. Sawamoto, and R. Hatano. 2002. Nitrous oxide emissions for 6 years from a gray lowland soil cultivated with onions in Hokkaido, Japan. *Nutrient Cycling in Agro-ecosystems* 63: 239–247.

Kutner, M.H., C. Nachtsheim, J. Neter, and W. Li. 2005. *Applied Linear Statistical Models*. 5th ed. New York, NY: McGraw Hill.

Lee, J., J.W. Hopmans, C. van Kessel, A. P. King, K.J. Evatt, D. Louie, D.E. Rolston, and J. Six. 2008. Tillage and seasonal emissions of CO_2, N_2O, and NO across a seed bed and at the field scale in a Mediterranean climate. *Agriculture, Ecosystems & Environment* 129:378-390.

Livingston, G.P., G.L. Hutchinson, and K. Spartalian. 2006. Trace gas emission in chambers: A non-steady-state diffusion model. *Soil Science Society of America Journal* 70:1459–1469.

Maia, G., V. Day, R. Gates, J. Taraba, and M. Coyne. 2012 Moisture effects on greenhouse gases generation in nitrifying gas-phase compost biofilters. *Water Resourses* 46:3023–3031.

Marinho, E.V.A., R.D. Delaune, and C.W. Lindau. 2004. Nitrous oxide flux from soybeans grown on Mississippi alluvial soil. *Communications in Soil Science and Plant Analysis* 35:1, 1–8.

Mayer, H. and R. Conrad. 1990. Factors Influencing the Population of Methanogenic Bacteria and the Initiation of Methane Production upon Flooding of Paddy Soil. *FEMS Microbiology Ecology* 73(2): 103–111.

Milliken, G. A. and D. E. Johnson. 2009. *Analysis of Messy Data Vol. 1: Designed Experiments*. 2nd ed. New York, NY: Taylor & Francis Group.

Mosier, A., C. Kroeze, C. Nevison, O. Oenema, S. Seitzinger, and O. van Cleemput. 1998. Closing the global N_2O budget: nitrous oxide emissions through the agricultural nitrogen cycle. *Nutrient Cycling in Agro-ecosystems* 52: 225–248.

Parkin, T.B., and T.C. Kaspar. 2006. Nitrous oxide emissions from corn-soybean systems in the Midwest. *Journal of Environmental Quality* 35: 1496–1506.

Peng, G. 2004. Testing normality of data using SAS. Indianapolis, IN: Lilly Corporate Center.

Rochette, P., and N.S. Eriksen-Hamel. 2008. Chamber measurements of soil nitrous oxide flux: Are absolute values reliable? *Soil Science Society of America Journal* 72(2): 331–342.

Saggar, S., R.M. Andrew, K.R. Tate, C.B. Hedley, N.J. Rodda, and J.A. Townsend. 2004. Modeling nitrous oxide emissions from dairy-grazed pastures. *Nutrient Cycling in Agroecosystems* 68:243–255.

SAS. 2008. *SAS/STAT 9.2 User's Guide*. Cary, NC: SAS Institute, Inc.

US EPA. 2010. State of knowledge. Climate change – science. U.S. Environmental Protection Agency. Available at: www.epa.gov/climatechange/science/stateofknowledge.html#ref. Accessed 14 December 2010.

USDA. 2009. Census of agriculture 2007, U.S. Summary and State Report, Vol. 1, Chapter 2, Table 11. The Census of Agriculture. USDA National Agricultural Statistics Service. Available at: www.agcensus.usda.gov/. Accessed 9 October 2010.

USDA. 2011. Cattle 2011, Economics, Statistics and Market Information System, Washington, D.C.: USDA National Agricultural Statistics Service. Available at: www.usda01.library.cornell.edu/usda/nass/Catt// 2010s/2011/Catt-07-22-2011.pdf. Accessed 28 December 2011.

Von Essen, S., and B. W. Auvermann. 2005. Health effects from breathing air near to CAFOs for feeder cattle or hogs. *Journal of Agromedicine* 10(4):55–64.

Whalen, S. C. 2000. Nitrous oxide emission from an agricultural soil fertilized with liquid swine waste or constituents. *Soil Science Society of America Journal* 64:781–789.

Woodbury, B. L., D. N. Miller, J. A. Nienaber, and R. A. Eigenberg. 2001. Seasonal and spatial variations of denitrifying enzyme activity in feedlot soil. *Transactions of the ASABE* 44(6): 1635–1642.

Woodbury, B. L., D. N. Miller, R. A. Eigenberg, and J. A. Nienaber. 2006. An inexpensive laboratory and field chamber for manure volatile gas flux analysis. *Transactions of the ASABE* 49(3): 767–772.

Chapter 4 - Laboratory Evaluation of Surface Amendments for Minimizing Greenhouse Gas Emissions from Beef Cattle Feedlots

4.1. Abstract

Pen surface amendments for mitigating emissions of greenhouse gases (GHGs), such as nitrous oxide (N_2O), methane (CH_4), and carbon dioxide (CO_2), from beef cattle feedlots, were evaluated under controlled laboratory conditions. Amendments were organic residues (i.e., sorghum straw, prairie grass, woodchip), biochar from those organic residues and from beef cattle manure, and activated carbon. Manure samples were collected from several randomly selected pens from two beef cattle feedlots in Kansas and used in the experiments, either as dry (0.10 g g^{-1} wet basis water content) or moist (0.35 g g^{-1} wet basis). For each amendment, four different treatment levels (i.e., amounts of material) were placed on top of manure samples in glass containers and analyzed for GHG emission fluxes using a photo-acoustic infrared multi gas analyzer. From measured concentrations, emission rates were determined. For the dry manure conditions, all amendment materials showed significant reduction of N_2O and CO_2 emission fluxes compared to the control (i.e., no amendment). For the moist manure conditions, none of the amendment showed significant effects on GHG emission fluxes during the first 8 days; at days 10 and 15 after application, however, the biochar materials performed significantly better than the control (i.e., no surface amendment) in reducing N_2O and CH_4 emission fluxes. No significant difference was observed in GHG emission fluxes when the amendments were placed on top or mixed within the top surface layer of the manure.

4.2. Introduction

Animal feeding operations (AFOs) emit a variety of air pollutants, including particulate matter (PM), ammonia (NH_3), odor, and volatile organic compounds (VOCs) that have the potential to cause health problems to workers and neighbors. In addition, they are important sources of greenhouse gases (GHGs), including carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) (Mosier et al., 1998), and their contribution to climate change is a growing public concern (Stackhouse et al., 2011). Global increases in anthropogenic CO_2 concentrations are largely due to fossil fuel use and industrial processes. For CH_4, increases have come through both industrial and agricultural activities, whereas, increases in N_2O are primarily from

agricultural activities with soil management as its main source (IPCC, 2007; Raupach and Fraser, 2011). Ruminant livestock operations are a significant contributor to global CH_4 concentration (IPCC, 2007; Raupach and Fraser, 2011) but their contribution to global N_2O concentration is largely unknown since there is little information on the impact of these operations on GHG emissions.

Woodbury et al. (2001) reported that the pen surfaces in cattle feedlots were aerated and highly organic and favorable for both mineralizing and nitrification, while the sub-surfaces were compacted with anaerobic zones making them susceptible to denitrification. This co-existence of both nitrification and denitrification processes in tandem have also been reported to occur with manure composting (Ma et al., 2008; Maeda et al., 2010). However, the process of denitrification and subsequent N_2O emission is highly variable with surface water content controlling surface emission flux rates. This observation is supported by Woodbury et al. (2001) who found that denitrifying enzyme activity was highly variable both seasonally and spatially. In Chapter 3, it was reported that moist/muddy surface conditions (0.52 cm^3 cm^{-3}) had the largest median emission flux of 2.03 mg m^{-2} h^{-1} compared to either dry or flooded conditions with median fluxes ranging from 0.10 to 0.16 mg m^{-2} h^{-1}. The highly variable nature of emissions from feedlot surfaces has also been shown to occur for other compounds such as NH_3, VOCs, and CO_2 associated with feedlot surfaces (Woodbury et al., 2006).

Considering that cattle feedlots could potentially contribute significantly to global N_2O levels, some mitigation strategies must be undertaken to reduce emissions. Nitrification inhibitors have been suggested as a possible mitigation strategy and research has shown the effectiveness of these compounds (Malla et al., 2005; Menéndez et al., 2006; Parkin and Kaspar, 2006; Weiske et al., 2001a, 2001b). Nitrification inhibitors are chemicals used to reduce the rate ammonium converts to nitrate and they have been shown to be effective in reducing N_2O emissions from soils. However, costs and animal safety issues make the use of nitrification inhibitors less attractive for AFOs. Alternatively, Adams et al. (2004) reported that the manipulation of manure carbon:nitrogen (C:N) ratio by direct application of organic matter to the pen surfaces, might be an effective mitigation strategy used to decrease N losses. Consequently, soil amendments that can change the C:N ratio might be cost effective means of reducing GHG emissions from cattle feedlots.

The purpose of this study was to investigate the effectiveness of surface amendments in reducing emission of GHGs from feedlot manure. Amendments included organic residues and biochar. The effects of manure water content (i.e., dry vs. moist) and the means of application (i.e., topical vs. mixed) were also considered.

4.3. Materials and Methods

4.3.1. Experiments

A series of laboratory experiments was conducted to evaluate the effectiveness of pen surface amendments in reducing emissions of N_2O, CH_4, and CO_2 from feedlot manure. Amendments were organic residues (i.e., sorghum straw, prairie grass, woodchip), biochar from those organic residues and from beef cattle manure, and activated carbon. Table 4-1 summarizes the experimental parameters for the different experiments. Approximately 130 kg of manure was collected from several randomly selected pens in two beef cattle feedlots in Kansas. The collected manure was completely mixed and air dried for several days until the average gravimetric water content (wet mass basis) reached approximately 0.10 g g^{-1}. Large clods were removed manually from the dry manure and from the amendment materials. The dry manure and amendment materials were sieved using an ASTM E-II No 4 (4.75 mm) standard testing sieve. For each amendment, four different amounts of material were applied on top of manure samples within glass containers and analyzed for GHG emission fluxes using a photo-acoustic infrared multi gas analyzer.

The elemental composition of each organic residue and biochar was measured (Table 4-2). A sample (30 g) of each material was ground to 0.5 mm using a sample mill (Model 3010-018, Udy Corp., Fort Collins, CO). Then, the elemental content of each ground sample (2 – 3 mg ± 0.001 mg) was measured in an Elemental Analyzer (Model 2400, Series II Perkin Elmer, Norwalk, CT). Each material was tested in duplicate samples.

Table 4-1 Experimental parameters.

Experiment	Manure Conditions (wet basis)		Amendment				
	Water Content (g g^{-1})	Bulk Density (g cm^{-3})	Material †	Wet Bulk Density (g cm^{-3})	Treatment		
					Amount (mm or g)	Equivalent Application Rates Mass/Surface (kg m^{-2})	
1 - Topical application of organic residues and biochar on moist manure +	0.35	1.1	WC	0.360	0, 1, 3, 5 mm	0, 0.36, 1.08, 1.80	
			SS	0.141	0, 1, 3, 5 mm	0, 0.14, 0.42, 0.71	
			PG	0.117	0, 1, 3, 5 mm	0, 0.12, 0.35, 0.58	
			WCB	0.411	0, 1, 3, 5 mm	0, 0.41, 1.23, 2.05	
			SSB	0.159	0, 1, 3, 5 mm	0, 0.16, 0.48, 0.79	
			PGB	0.142	0, 1, 3, 5 mm	0, 0.14, 0.43, 0.71	
2 - Topical application of biochar and activated carbon on moist manure +	0.35	1.1	WCB	0.411	0, 1, 3, 5 mm	0, 0.41, 1.23, 2.05	
			SSB	0.159	0, 1, 3, 5 mm	0, 0.16, 0.48, 0.79	
			PGB	0.142	0, 1, 3, 5 mm	0, 0.14, 0.43, 0.71	
			PMB	1.016	0, 1, 3, 5 mm	0, 1.02, 3.05, 5.08	
			LMB	0.530	0, 1, 3, 5 mm	0, 0.53, 1.59, 2.65	
			EAC	0.619	0, 1, 3, 5 mm	0, 0.62, 1.86, 3.09	
			PAC	0.379	0, 1, 3, 5 mm	0, 0.38, 1.14, 1.89	
3 - Topical application of organic residues and biochar on dry manure ǂ	0.10	0.48	WC	0.360	0, 1, 3, 5 mm	0, 0.36, 1.08, 1.80	
			SS	0.141	0, 1, 3, 5 mm	0, 0.14, 0.42, 0.71	
			PG	0.117	0, 1, 3, 5 mm	0, 0.12, 0.35, 0.58	
			WCB	0.411	0, 1, 3, 5 mm	0, 0.41, 1.23, 2.05	
			SSB	0.159	0, 1, 3, 5 mm	0, 0.16, 0.48, 0.79	
			PGB	0.142	0, 1, 3, 5 mm	0, 0.14, 0.43, 0.71	
4 - GHG emission from the organic residues and biochars ‡	-	-	WC	0.360	0, 10 g	0, 1.5	
			SS	0.141	0, 10 g	0, 1.5	
			PG	0.117	0, 10 g	0, 1.5	
			WCB	0.411	0, 10 g	0, 1.5	
			SSB	0.159	0, 10 g	0, 1.5	
			PGB	0.142	0, 10 g	0, 1.5	
			PMB	1.016	0, 10 g	0, 1.5	
			LMB	0.530	0, 10 g	0, 1.5	
			EAC	0.619	0, 10 g	0, 1.5	
			PAC	0.379	0, 10 g	0, 1.5	
5 – Mixing of organic residues and biochars with manure +	0.35	0.60	LMB	0.530	0, 20 g	0, 3.0	
			EAC	0.619	0, 20 g	0, 3.0	
6- Adsorption as mechanism of GHG mitigation *	-	-	WCB	0.411	0, 25 g	0, 3.8	
			LMB	0.530	0, 60 g	0, 9.0	
			EAC	0.619	0, 50 g	0, 7.5	

† WC=Woodchip; SS=Sorghum straw; PG= Prairie grass; WCB= Woodchip biochar; SSB= Sorghum straw biochar; PGB= Prairie grass biochar; PMB= Pellet manure biochar; LMB= Loose manure biochar; EAC= Extruded (Pellet) activated carbon; PAC= Powder activated carbon.

+ Control was moist manure with no amendment (0.35 g g^{-1} gravimetric water content wet basis and 1.1 g cm^{-3} wet bulk density).

ǂ Control was dry manure with no amendment (0.10 g g^{-1} gravimetric water content wet basis and 0.5 g cm^{-3} wet bulk density).

‡ Two controls and 1 treatment per material. Control 1 was indoor air. Control 2 was moist manure with no amendment (0.35 g g^{-1} gravimetric water content wet basis and 1.1 g cm^{-3} wet bulk density).

* Control was indoor air.

Table 4-2 Elemental composition of the materials used as surface amendments.

Material	Composition (%)				C:N
	Carbon	Hydrogen	Nitrogen	Sulfur	
Woodchip (WC)	46.85	6.13	0.53	1.03	89:1
Sorghum Straw (SS)	43.11	5.93	0.92	1.04	47:1
Prairie Grass (PG)	44.19	6.07	0.90	1.10	49:1
Woodchip Biochar (WCB)	59.82	2.42	0.94	0.40	64:1
Sorghum Straw Biochar (SSB)	58.38	1.63	1.13	0.28	52:1
Prairie Grass Biochar (PGB)	63.32	2.51	1.65	0.43	38:1
Pellet Manure Biochar (PMB)	10.39	0.46	1.05	0.31	10:1
Loose Manure Biochar (LMB)	14.13	0.51	0.92	0.25	15:1
Pellet Activated Carbon (EAC)	83.44	0.43	0.83	0.41	101:1
Powder Activated Carbon (PAC)	86.69	0.53	0.54	0.06	162:1

4.3.1.1. Experiment 1 – Topical application of organic residues and biochar on moist manure

Experiment 1 considered the effects of topical application of organic residues and biochar on moist manure. Samples were prepared by mixing 238.3 g of relatively dry manure (0.10 g g^{-1} water content wet basis) and 91.7 g of water at 22°C in 1-L wide mouth glass containers, which were used as static flux chambers (SFCs). The water content of the moist manure sample was 0.35 g g^{-1} wet basis, which is similar to the average manure water content for pen surfaces observed in the field (Chapter 3). The moist manure was then compacted at 1.1 g cm^{-3}. Containers were kept uncapped in an enclosed space at approximately constant humidity and temperature for stabilization purposes during a period of 12 h before treatment application (Fig. 4-1b). In this experiment, amendments were woodchip, sorghum straw, prairie grass, woodchip biochar, sorghum straw biochar, and prairie grass biochar (Fig. 4-1a). Biochars were obtained from the gasification process of the organic residues in a laboratory updraft reactor.

Figure 4-1 Photographs of the experiment: (a) amendment materials, (b) glass containers with the compacted moist manure, within a plastic container with water at the bottom to maintain constant manure water content, and (c) measurement set up.

The prepared glass containers were randomly selected and fixed amounts (treatments) of the amendment were applied on top of the compacted manure within the containers, as indicated in Table 4-1. The containers with just manure but without any amendment served as the control. The amendment materials showed large differences in wet bulk density (Table 4-1). Therefore, the same mass of those materials would result in large difference in the volumes occupied. Moreover, due to the small volume of the containers (1 L) used in the experiment and due to the required headspace volume for the gas accumulation and sampling, treatments were designed in such a way that each would result in the same headspace gas volume for all amendment materials under analysis. Therefore, for each amendment material, treatments consisted of different thicknesses of the material applied on top of the manure surface within the containers. There were four treatments (i.e., 0 mm or control, 1 mm, 3 mm, and 5 mm), with three replicates each. The amount of amendment corresponding to each layer thickness was computed based on the actual wet bulk density of each amendment. As a consequence of the different wet bulk densities, the same treatment applied to different amendments, required different amounts of mass per surface area (kg m^{-2}). The smallest treatment (i.e., 0.12 kg m^{-2} or 12 t ha^{-1}) was for prairie grass and the largest (5.1 kg m^{-2} or 51 t ha^{-1}), as shown in Table 4-1, was for pellet manure biochar, used in the second experiment.

The initial gas sampling of each container was performed 45 min after treatment application, and before sampling, the headspace of each glass container was flushed with

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ambient air to ensure that GHG concentrations were at ambient levels (Chiyoka et al., 2011). Then, the container being sampled was capped and immediately, air from its headspace was circulated through a photo-acoustic infrared multi-gas analyzer or PIMA (Model 1312, AirTech Instruments, Ballerup, Denmark) (Cayuela et al., 2010a; Predotova et al., 2011) equipped with optical filters for measuring N_2O, CH_4, CO_2, and water vapor. The PIMA was connected by two 0.5 m long Teflon tubes as inflow and outflow to the glass container, as shown in Figure 4-1c. Readings of the headspace concentrations were taken every 50 s from 0 to 10 min. Gas emission fluxes were determined for each container. Sampling was conducted once a day for 3 days within a 5-day period (i.e., days 1, 3, and 5, with the day of treatment application serving as day 1). During this period, containers were kept uncapped in an enclosed space at an approximately constant humidity and temperature (Fig. 4-1b). For each sampling day, the laboratory air temperature and pressure were recorded. Manure gravimetric water content and temperature from each container were also measured during the sampling period. Temperature was measured with liquid-in-glass thermometers. Atmospheric pressure was measured using a barometer (Princo Southampton, Penn.).

4.3.1.2. Experiment 2 – Topical application of biochar and activated carbon on moist manure

Based on results from Experiment 1, Experiment 2 was conducted to further evaluate the effectiveness of biochars in mitigating GHG emission fluxes from moist manure. In this experiment, sample preparation, treatments, and the experimental set up, were similar to those for Experiment 1. However, sampling was conducted once a day for 6 days within a 15-day period (i.e., days 1, 3, 5, 8, 10, and 15). In addition to the biochars in Experiment 1 (i.e., woodchip, sorghum straw, and prairie grass), Experiment 2 also included manure biochar and activated carbon as amendments.

4.3.1.3. Experiment 3 – Topical application of organic residues and biochar on dry manure

Experiment 3 was conducted to evaluate the effectiveness of several amendment materials in mitigating GHG emissions from dry manure. In this experiment, 238.3 g of dry manure (0.10 g g^{-1} water content wet basis and 0.55 g cm^{-3} wet bulk density) were placed into 1-L glass containers; no water was added. Amendments and treatments were the same as those for Experiment 1. Control was dry manure without any amendment. Gas sampling was performed in

the same fashion as for Experiments 1 and 2; however, in this case, sampling was conducted once a day for 3 days within a 5-day period (i.e., days 1, 3, 5).

4.3.1.4. Experiment 4 – GHG emission from the organic residues and biochars

To assess the potential contribution of the amendments to the GHG emission, 10 g of each amendment material were placed in 1-L glass containers. Treatments were the organic residues and biochars. Two controls were considered: (i) empty containers containing indoor air and (ii) containers containing moist manure with a gravimetric water content of 0.35 g g^{-1} wet basis and wet bulk density of 1.1 g cm^{-3}. Each treatment had two replications. All amendment materials used in the previous experiments were assessed (Fig. 4-1a). Gas samples were collected once a day for 3 days within a 5-day period (i.e., days 1, 3, and 5).

4.3.1.5. Experiment 5 – Mixing of biochars with manure

Experiment 5 was conducted to evaluate the effectiveness of biochars in mitigating GHG emissions when mixed within the top manure layer. Amendment materials to mitigate GHG emission fluxes from pen surfaces in beef cattle feedlots are meant to be placed on the pen surfaces; however, with animal activity, some of the amendments are expected to be mixed with the top surface layer of the moist and loose areas of the pen, while others will remain on the top of the harder and drier pen surfaces.

Fixed amounts of manure and water, as described in Experiment 1, were mixed in the 1-L glass containers within 2 min (0.35 g g^{-1} wet gravimetric water content and 0.66 g cm^{-3} wet bulk density). As soon as each manure sample was prepared, the treatment was mixed within the first 5 cm top layer in the container. Treatments included 20 g of manure biochar and 20 g of activated carbon. Control was moist manure without any amendment. There were two replications for each treatment. Gas samples were collected once a day for 4 days within a 10-day period (i.e., days 1, 3, 5, and 10).

4.3.1.6. Experiment 6 – Mechanism of GHG emission reduction

Experiment 6 was conducted to determine if gas adsorption is a possible mechanism in mitigating GHG emission from pen surfaces. In this experiment, 500-cc glass containers were used as sealed chambers, in which, 150 cc of standard N_2O gas (3.5 ppm) were injected into the container to evaluate the adsorption capability of the amendments materials. Amendment

materials (treatments) were woodchip biochar, loose manure biochar, and activated carbon. They were first oven-dried at 125 °C for 12 h to desorb any trace gases. During sampling, 25, 60, and 50 g of woodchip biochar, manure biochar, and activated carbon, respectively, were placed into the containers and capped with a lid prepared for syringe sampling. The control treatment was an empty container with indoor air. There were two replications for each treatment. The amendments' masses were computed to allow a headspace volume of 400 cc. Within 2 min after treatment preparation, 3-cc air samples were collected from the containers and analyzed for N_2O concentration using a GC (model GC-14B, Shimadzu Scientific Instrument, Columbia, MD). The GC had a Porapak-Q (80/100 mesh) stainless steel column (3.175 x 10-3 m dia. by 1 m length), electron-capture detector (ECD), and UHP/zero nitrogen carrier gas. The oven, injector, and detector temperatures were 60, 100, and 300°C respectively, as described by Bremer (2006). The first sample was considered as the base line N_2O concentration for each treatment. As soon as the first sample was collected, 100 cc of air were extracted from the containers and then, 150 cc of N_2O 3.5 ppm standard gas were injected into each container. In this manner, a low positive pressure was always present in the containers even after the final sampling event. Ten min after the N_2O standard gas injection, a second 3-cc headspace air sample was collected from each container and analyzed in the GC for N_2O concentration. Fifty min later, gas sampling was repeated. After the first day, headspace gas sampling was then repeated once a day for 4 more days within a 6-day period (i.e., days 2, 3, 4, and 6).

As soon as the last gas samples were taken, the containers were placed into an oven (model OV-500B-1, Blue M Electric Co., Blue Island, IL) and heated to reach different temperatures (35, 40, 75, and 100°C). Each temperature setting was kept for 2 h and then, 3-cc gas samples were taken from the containers and analyzed in the GC for N_2O gas concentration. Finally, once the final temperature was reached and gas samples collected, the oven was turned off, letting the containers to cool down to room temperature (23°C) for 24 h. A final gas sample was collected from each container and analyzed in the GC.

4.3.2. Computation of gas emission fluxes

In general, the gas concentration within the container headspace increased linearly with time. As such, fluxes were calculated from the slope of the linear regression between gas

concentration and time (Whalen, 2000). From mass balance, the hourly flux (F) from an enclosed soil surface area (A) within a space volume (V) is given by:

$$F = \left(\frac{V}{A}\right)\left(\frac{\Delta C}{\Delta t}\right)$$ (4.1)

where $\Delta C/\Delta t$ is the change in gas concentration with time within the enclosed space. If the relationship between gas concentration and time within the enclosed space is linear, then the slope (S) of the linear regression between gas concentration and time can be used to represent $\Delta C/\Delta t$ (ppm min^{-1}). The gas concentration can be converted from ppm to μg m^{-3} using (Cooper and Alley, 2002):

$$C_m = 1000\ Cppm\ MW\ \frac{P}{RT}$$ (4.2)

where C_m is mass concentration (μg m^{-3}), C_{ppm} is volume concentration (ppm), MW is the molar mass of the gas (g gmol^{-1}), P is atmospheric pressure (mm Hg), T is temperature (K) within the enclosed space, and R is the ideal gas constant (62.36 mm Hg L gmol^{-1} K^{-1}). Combining equations 4.1 and 4.2,

$$F = 9.622\ x\ 10^{-3}\ V\ S\ MW\ \frac{P}{A\ T}$$ (4.3)

where F is the gas emission flux in (mg m^{-2} h^{-1}), V is headspace volume of air (cm^3), A is surface area of manure (cm^2) within the glass container, and S is the slope of the linear regression between gas concentration and time within the container (ppm min^{-1}).

In this study, the linear relationship between gas concentration and time within the containers was confirmed. For experiments involving moist manure (Experiments 1, 2, and 5), the average R^2 values $\pm$ standard deviation were 0.99 ± 0.01, 0.99 ± 0.01, and 0.90 ± 0.20 for N_2O, CO_2, and CH_4, respectively. For experiments involving dry manure and amendment only (Experiments 3and 4), R^2 values for the regression lines were lower possibly due to the small emission fluxes (mostly 0); average R^2 values $\pm$ standard deviation for N_2O, CO_2, and CH_4 fluxes were 0.67 ± 0.28, 0.86 ± 0.22, and 0.34 ± 0.24, respectively.

4.3.3. Statistical analysis

In general, the gas emission fluxes depended on their previous day's emission flux. To account for the correlation between emission flux readings, the Autoregressive One, AR(1), structure was used on the residuals. Data were analyzed using Proc Glimmix of SAS (SAS, 2008) using a 5% level of significance. P-values were adjusted by Tukey (Milliken and Johnson,

2009). When the Type III test of fixed effects indicated no significant (treatment)x(time) interaction, the treatment effects were analyzed and compared to the control. When (treatment)x(time) interaction was significant, analysis was done based on sampling days.

4.4. Results and Discussion

4.4.1. Experiment 1 – Topical application of organic residues and biochar on moist manure

For each treatment and control, emission fluxes of N_2O and CH_4 increased with sampling day; the increase was generally much higher from sampling day 3 to 5 than from sampling day 1 to 3. The emission fluxes of CO_2, on the other hand, did not change much with sampling day. Figure 4-2 shows results of GHG emissions from moist manure amended with woodchip and woodchip biochar. Statistical analysis showed significant (treatment)x(time) interactions, as such, comparison of treatments with control was based on sampling days.

In general, topical application of the organic residues on the manure sample showed some reduction, although not significant, in emission fluxes. However, the biochars at 3 and 5 mm treatments significantly reduced GHG emission fluxes at sampling day 5; CO_2 emissions were also significantly reduced on day 5 even with 1-mm amendment of woodchip biochar (Fig. 4-2). A treatment effect was not commonly observed unless emission of GHG was significantly higher than initial levels. Therefore, it should be noted that both CH_4 and N_2O emission flux did not significantly increase until after three days of treatment.
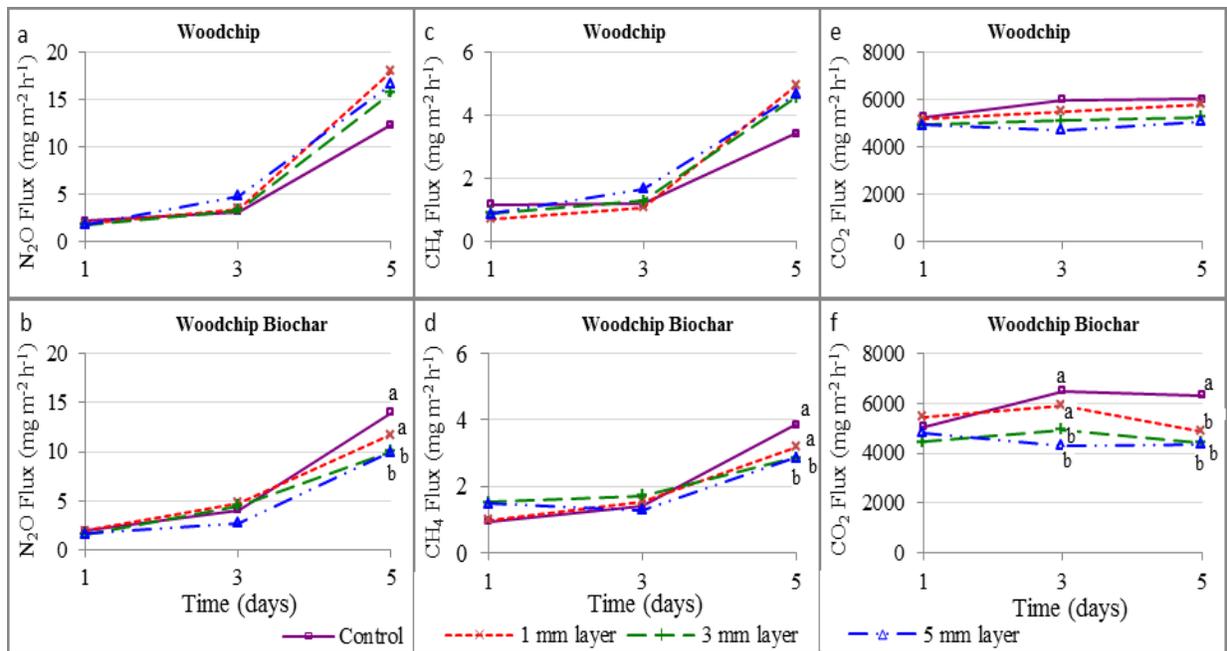
Figure 4-2 Effects of topical application of woodchips and woodchip biochar on greenhouse gas emissions from the moist manure. Within the same day, treatments with the same letter or those with no letters are not significantly different at α=5%.

4.4.2. Experiment 2 – Topical application of biochar and activated carbon on moist manure

Similar to Experiment 1, there were significant (treatment)x(time) interactions. As such, treatment effects were analyzed based on sampling days. Topical application of 3 mm and 5 mm of loose manure biochar (Fig. 4-3b) and pellet manure biochar (Fig. 4-3c) showed similar effects as pellet activated carbon (Fig. 4-3a) in reducing N_2O emissions after day 10. For all sampling days, N_2O emission flux from the control was larger than those from the 3-mm and 5-mm treatments of both manure biochars, as also occurred with the three treatments of pellet activated carbon (Fig. 4-3a). However, in the case of manure biochars, those differences were significant only on day 15, while activated carbon significantly reduced N_2O emissions starting at day 10. Powder activated carbon, as expected, showed the same behavior in GHG reduction as pellet activated carbon. The 3-mm treatment of loose manure biochar and pellet manure biochar, compared to the control, reduced N_2O emission fluxes by 63% and 57%, respectively, on day 15. The reduction was slightly lower than that from the 3-mm treatment of activated carbon, which had a reduction of 73%. Reductions of N_2O emissions by activated carbon and manure biochar

increased with sampling day (Figs. 4-3a, b, and c). Moreover, with the exception of activated carbon, the 1-mm treatment did not result in any significant reduction in N_2O emission flux possible because of poor surface covering.

The 3-mm and 5-mm treatments of woodchip biochar also resulted in significant reduction of N_2O starting at day 10 (Fig. 4-3d). Moreover, 5-mm treatment of prairie grass biochar also reduced N_2O emissions on day 15 (Fig. 4-3f). No treatment of sorghum straw biochar showed any significant effect on N_2O emissions (Fig. 4-3e). Among biochar materials, the 3-mm treatment of loose manure biochar was best in reducing N_2O emissions from the moist manure on day 15 (Fig. 4-3b).

The reduction in N_2O emission with biochar-amended manure is not surprising since previous researches on biochar have reported significant reductions in N_2O emissions from soils (Aguilar-Chávez et al., 2012; Cayuela et al., 2010b). Taghizadeh-Toosi (2011) reported reductions in N_2O fluxes by as much as 70% for pasture soils following the incorporation of 3 kg m^{-2} of biochar into the soil. In addition, others have shown that emissions of N_2O decreased as soil was amended with increased amounts of biochar (Bruun et al., 2011; Rogovska et al., 2011). Even in rice paddy soils amended with biochar, there was a significant reduction (51%) in total N_2O emission, but higher levels of biochar amendments did not necessarily decreased N_2O emission rates (Zhang et al., 2012; Zhang et al., 2010).

Effects of application of biochar on CH_4 emission fluxes were generally similar to those of N_2O emission fluxes. Application of 3 mm and 5 mm of manure biochars showed significant reductions of CH_4 emission fluxes compared to the control on day 15 (Figs. 4-3h and i). All three treatments of activated carbon (Fig. 4-3g) and prairie grass biochar (Fig. 4-3l) resulted in significant reduction of CH_4 emission on day 15. The 1-mm and 3-mm treatments of sorghum straw biochar (Fig. 4-3k) also showed significant reduction of CH_4 emission on day 15. The 3-mm treatment of activated carbon showed significant reduction of CH_4 emission on day 15 at 72% compared to the control treatment, while pellet manure biochar, loose manure biochar, sorghum straw biochar, and prairie grass biochar had significant reductions of 73%, 63%, 39%, and 47%, respectively, on day 15. There was no significant reduction in CH_4 emission treated with woodchip biochar. Aguilar-Chávez et al. (2012) also did not find any significant effect on CH_4 emissions due to application of biochar to agricultural soils.
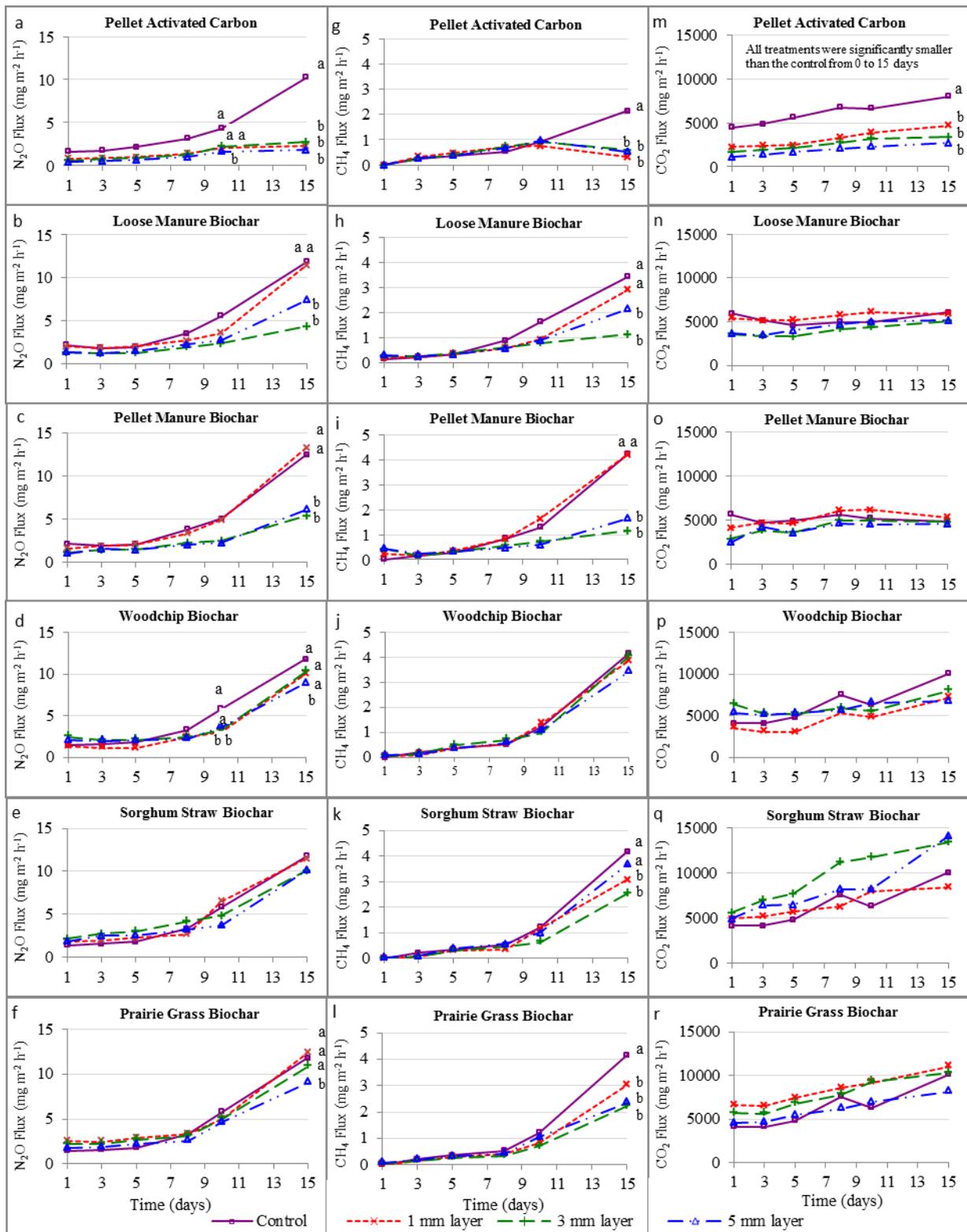
Figure 4-3 Effects of topical application of biochar and activated carbon on GHG emissions from moist manure. Within a same day, treatments with the same letter or those with no letters are not significantly different at α=5%.

In the case of CO_2, the three treatments of activated carbon (Fig. 4-3m) resulted in significant reduction of CO_2 emissions during the whole experimental period, with the larger reduction obtained from the largest amount of activated carbon placed on the moist manure surface, i.e., 5-mm treatment (3.09 kg m^{-2}). The 5-mm treatment of woodchip biochar (Fig. 4-3p) also significantly reduced CO_2 emissions but only at day 15. No other material/treatment combination significantly influenced CO_2 emissions from moist manure.

Differences in CO_2 emissions from soil amended with several biochars have been reported as a result of the differences in the biochars used (Aguilar-Chávez et al. (2012). Cayuela et al. (2010b) reported that biochar, used as soil amendment, was the most stable residue with the lowest CO_2 loss with respect to the total C added. Rogovska et al. (2011) reported that biochar sequestered large amounts of highly stable C, but either increased or decreased CO_2 emissions from the soils, depending on soil characteristics. Scheer et al. (2011) reported no significant differences in net fluxes of GHGs between biochar-amended pastures and control plots. In that study, the biochar from cattle feedlot manure was applied at a rate of 1 kg m^{-2} to a depth of 10 cm and the GHG emission was measured 28 months later.

In summary, during the first 8 days after biochar application on moist manure, there was no significant difference in GHG emissions between treatments and control. From day 10, however, the amended manure performed significantly better than the untreated moist manure (control). Thus, using a biochar as surface amendment appeared to be at least as good and over time, better at controlling GHGs than the untreated manure.

4.4.3. Experiment 3 – Topical application of organic residues and biochar on dry manure

Figure 4-4 summarizes the emission fluxes from the dry manure samples as affected by application of biochars. As expected, emission fluxes from the dry manure samples were considerably lower than those from the moist manure samples (Figs. 4-2 and 4-3). Even though emission fluxes were small, all amendment materials showed significant reduction in N_2O and CO_2 emissions. The three treatments of prairie grass and sorghum straw significantly reduced N_2O emissions. For the woodchip biochars, only the 3-mm and 5-mm treatments showed significant effect in reducing N_2O emissions. This might be a consequence of the poor surface area coverage by the 1-mm treatment of woodchip biochar.

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In the case of CH_4, only the three treatments of prairie grass and sorghum straw biochars significantly affected CH_4 emissions but only during the first day of the experiment. This result was possibly a consequence of the low emission flux of CH_4 from the substrate due to its low water content. It should also be noted that for Experiment 3, the manure samples were not compacted due to their dry condition. Therefore, manure conditions within the glass containers were likely aerobic, which may significantly reduce denitrification or methanogenesis, the main mechanisms of N_2O and CH_4 formation in the soil, respectively (Hofstra and Bouwman, 2005; Li, 2007).

In the case of CO_2, the three treatments of all amendments, with the exception of the 1-mm treatment of woodchip biochar, significantly reduced CO_2 emission flux (Figs. 4-4g, h, and i). Under aerobic conditions, most soil microorganism use O_2 as an electron acceptor, releasing CO_2 into the atmosphere (Li, 2007).
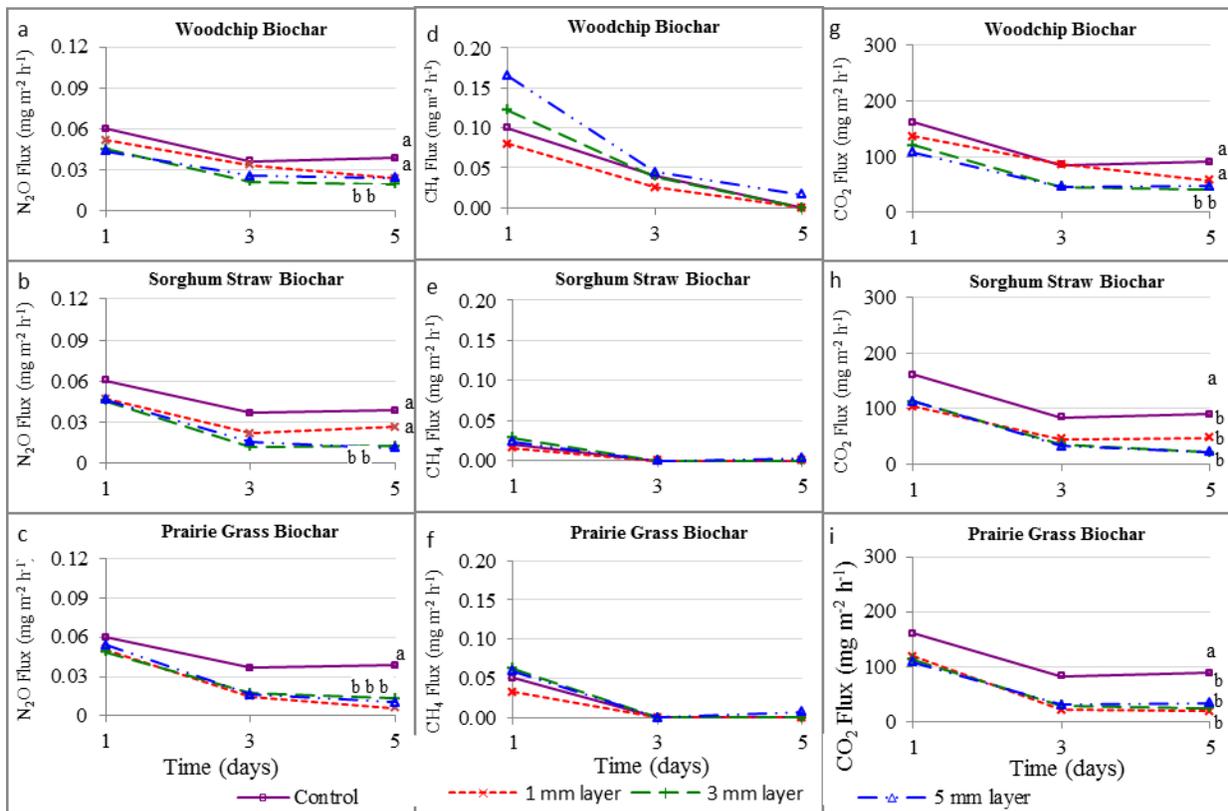
Figure 4-4 Effects of topical application of biochars on greenhouse gas emissions from dry manure. Within the same day, treatments with the same letter and those with no letters are not significantly different at α=5%.

4.4.4. Experiment 4 – GHG emission from the organic residues and biochars

Table 4-3 and Figure 4-5 summarize the GHG emission fluxes from the amendment materials, tested without manure, and the control. Emission fluxes from the organic residues and biochars were not significantly different from those for control 1 (indoor air). Also, emission fluxes of all three GHGs from the amendment materials were significantly lower than those from control 2 (moist manure). As such, there was no significant contribution of GHGs from the organic materials and biochars when used as soil amendment.

Table 4-3 Mean emission fluxes of greenhouse gases from the amendment materials.

Treatment	Flux (mg m^{-2} h^{-1})		
	N$_2$O	CH$_4$	CO$_2$
Control-1 (indoor air)	0.01 a	0.00 a	0.7 a
Control-2 (moist manure)	6.00 b	2.01 b	5782 b
Loose manure biochar	0.01 a	0.00 a	11.7 a
Pellet activated carbon	0.03 a	0.00 a	70.3 a
Pellet manure biochar	0.01 a	0.00 a	2.8 a
Powder activated carbon	0.03 a	0.00 a	46.8 a
Prairie grass	0.02 a	0.00 a	9.0 a
Prairie grass biochar	0.03 a	0.00 a	43.0 a
Sorghum straw	0.04 a	0.00 a	69.5 a
Sorghum straw biochar	0.04 a	0.00 a	82.0 a
Woodchip	0.02 a	0.00 a	13.8 a
Woodchip biochar	0.02 a	0.03 a	21.5 a

Values are mean fluxes for the 5-day experimental period. Mean values followed by the same letter within a specific GHG are not significantly different at α=5%.
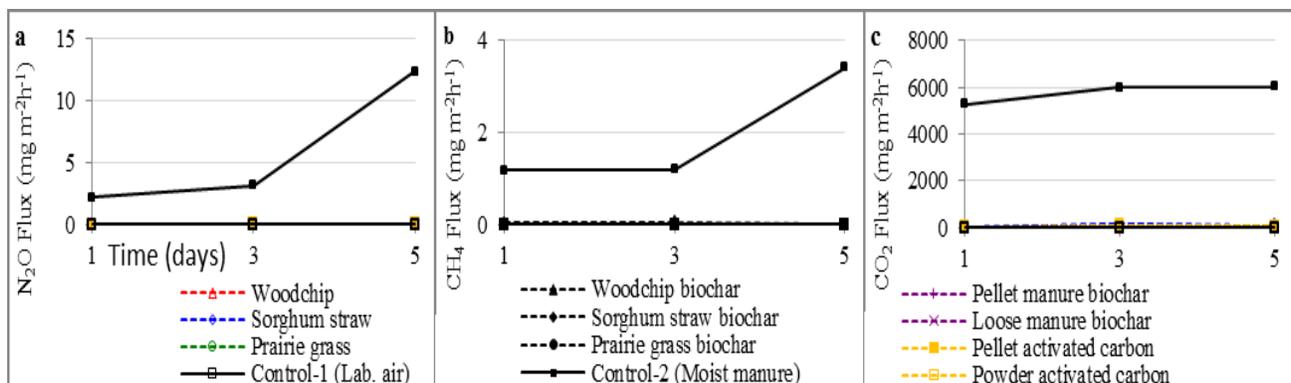
Figure 4-5 Emissions from the amendment materials (no manure) and manure (no amendment): (a) nitrous oxide, (b) methane, and (c) carbon dioxide.

4.4.5. Experiment 5 – Mixing of biochars with manure

Table 4-4 summarizes the GHG emission fluxes from the control and from the manure biochar and activated carbon treatments. Both manure biochar and activated carbon significantly reduced emission fluxes of N_2O (Fig. 4-6a) and CO_2 (Fig. 4-6c) compared with the control. There was no significant reduction of CH_4 emission flux; nevertheless, as in Experiment 2, at day10 there was significant reduction in CH_4 emission flux for both moist manure treatments compared with the control (Fig. 4-6b). The manure biochar showed similar effect as pellet activated carbon in reducing N_2O emissions (Table 4-4) and their mitigating effect became increasingly larger with time (Fig. 4-6a). These results suggest that mixing the biochar with the top loose and moist surface layers in the pens would be at least as good as or better than the topical application of the amendments in controlling GHGs from pen surfaces. In this experiment, the manure samples were not compacted, which could help explain the larger fluxes compared with those from Experiments 1 and 2.

Table 4-4 Mean emission fluxes of GHGs under mixed moist manure/amendment condition.

Treatment	Flux (mg m^{-2} h^{-1})		
	N_2O	CH_4	CO_2
Control (no amendment)	12.05 a	2.05 a	12051 a
Loose manure biochar mixed with moist manure	8.71 b	1.52 a	9151 b
Activated carbon mixed with moist manure	8.11 b	1.58 a	6735 c

Values are mean fluxes for the 10-day experimental period; column means followed by the same letter are not significantly different at α=5%.
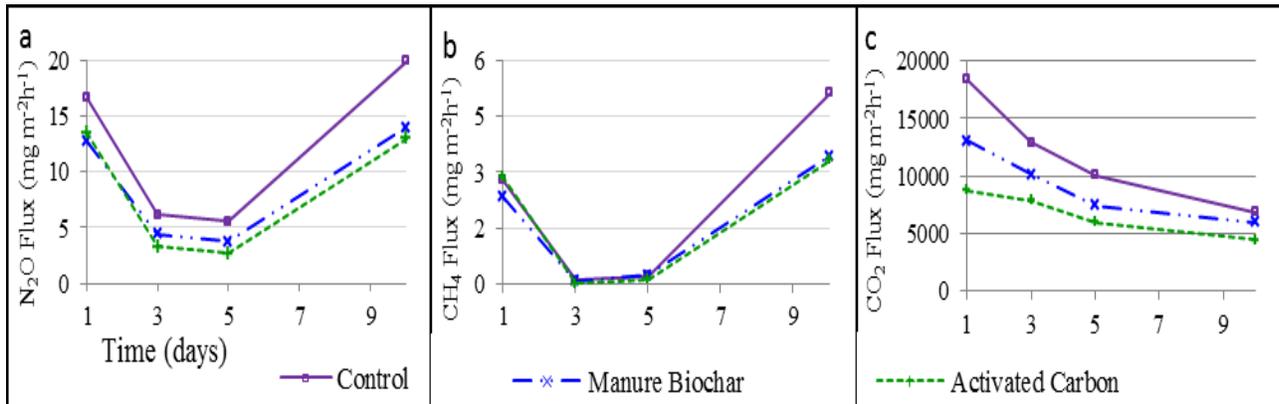
Figure 4-6 Effect of mixed manure/amendment on GHG emissions: (a) nitrous oxide, (b) methane, and (c) carbon dioxide.

4.4.6. Experiment 6 – Mechanism of GHG emission reduction

Figure 4-7 plots the headspace concentration of N_2O in the different containers without (control) and with amendments. A known amount of N_2O (i.e., 150 cc) was injected into the containers at 0.17 h. As soon as the N_2O was injected, measured concentration of N_2O for the control (indoor air without any amendment) increased from 0.48 ppm to 1.65 ppm. For containers with treatments (i.e., woodchip biochar, manure biochar, and activated carbon), the increase in concentrations after injection of the same standard N_2O gas was significantly lower. No further significant changes in N_2O concentrations were observed after the first hour of the experiment and no more N_2O standard gas was added into the glass containers (Fig. 4-7). The significant difference in N_2O concentration might be consequence of several mechanisms, including adsorption. When biochar materials are added to the soil, they are able to adsorb organic molecules through several mechanisms (Joseph et al., 2010). Peng et al. (2009) reported activated carbon with high pore volume as a good N_2O adsorbent.
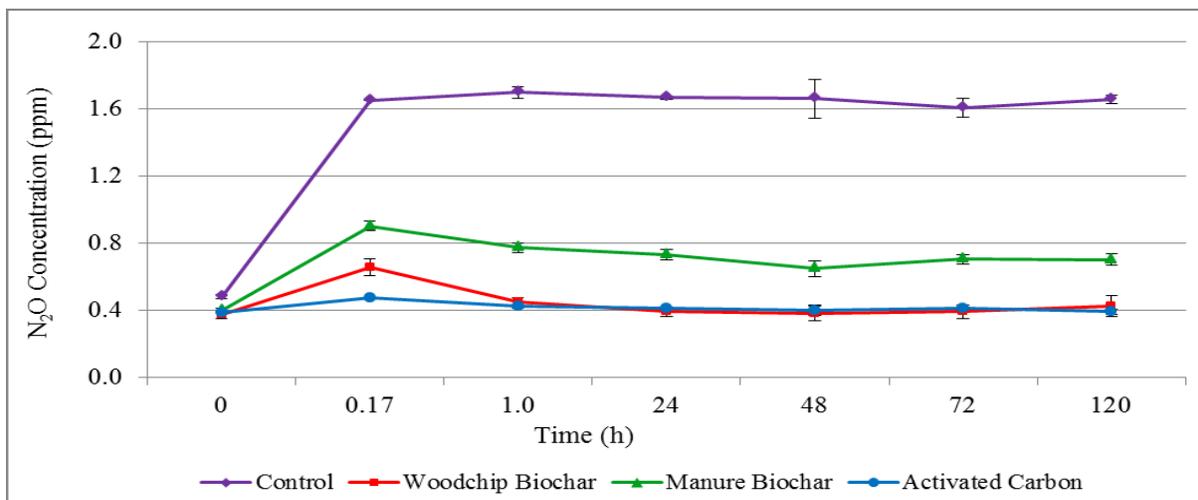
Figure 4-7 Nitrous oxide concentrations at the headspace of the containers without (control) and with amendments. A known amount of N_2O was injected into each container at 0.17 h.

To confirm if adsorption was a possible mechanism of N_2O concentration reduction within the containers, once the 120-h period of gas sampling at room temperature (23°C) was completed, each container still capped was heated to 35°C, 40°C, 75°C, and 100°C. Then, gas samples were drawn from the container headspace at each temperature and immediately analyzed for N_2O concentration in a GC. Results indicated that at temperatures higher than room

temperature (23°C), the N_2O gas concentration within the containers increased but remained relatively constant at constant temperatures (Fig. 4-8). Apparently, the adsorbed N_2O at room temperature was released at higher temperature, but once that temperature stabilized, there was no any additional desorption.
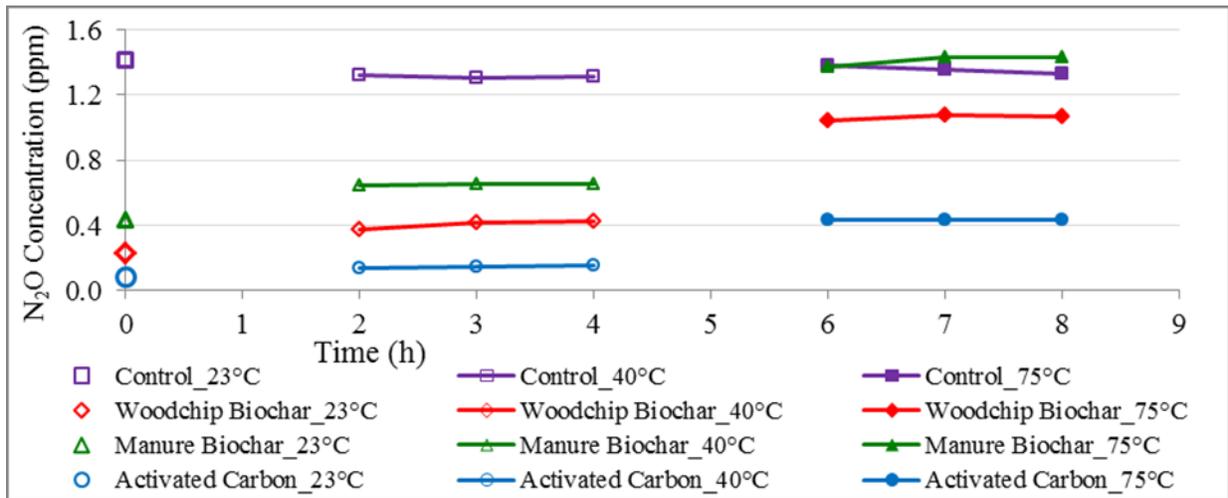
Figure 4-8 Effect of temperature on N_2O concentrations inside the containers with various amendment materials.

Figure 4-9a shows the concentrations of N_2O inside the containers with biochar materials when heated. For each material and control, there was no significant change in N_2O concentrations when samples were heated from 23°C to 40°C. From 40°C to 100°C, however, all materials showed a significant N_2O desorption. Moreover, N_2O concentrations for the control treatment did not change much with increasing temperatures. These results confirm that there was no chemical reaction between the biochar and the N_2O injected into the containers, suggesting that the main mechanism responsible for the increase in N_2O concentration within the containers when heated is desorption. Therefore, adsorption is a possible mechanism responsible for the reduction of N_2O gas emission from the manure treated with biochar and/or activated carbon in the previous experiments. Once the containers were cooled to room temperature, the final N_2O concentrations decreased to levels comparable to those for the 23°C to 40°C range.
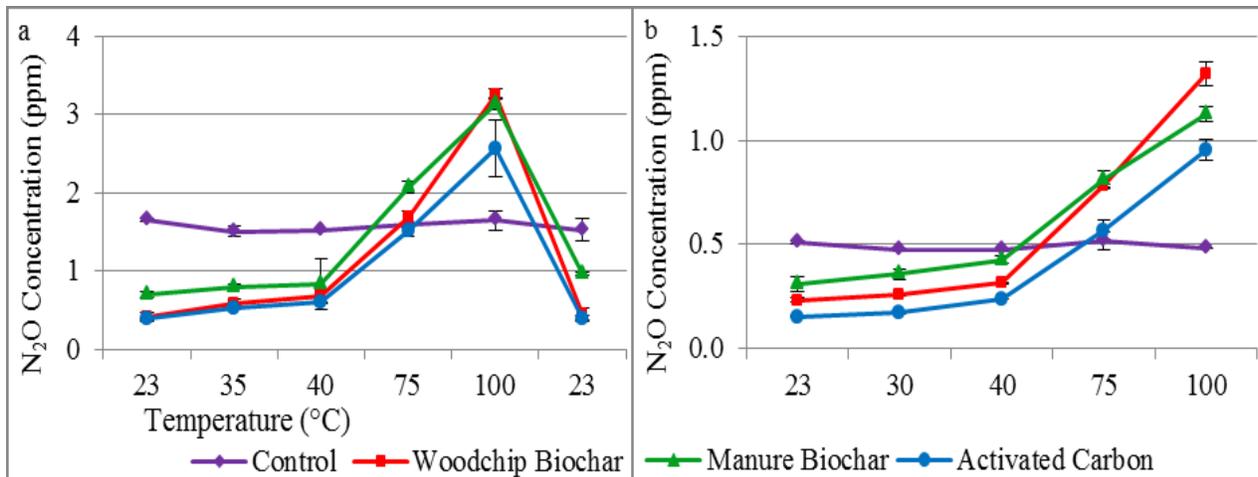
Figure 4-9 Nitrous oxide concentrations inside the containers with amendment materials: (a) effect of temperature on desorption of N_2O after injection of 150 cc of 3.5 ppm N_2O standard gas and (b) effect of temperature on desorption of N_2O from the amendment materials without the injection of N_2O standard gas.

From the field study presented in Chapter 3, the higher manure temperature in pen surfaces in a beef cattle feedlot in Kansas during 15 consecutively months was 40.5°C. The lack of significant change in N_2O gas concentration within the containers when temperature rose from 23°C to 40°C is useful because this suggests that the GHGs adsorbed on the amendment materials in the feedlot surfaces would not be desorbed even during the higher summer temperatures. Moreover, the fact that there was a significant difference in N_2O gas concentration within the containers between the treatments (materials) and the control (Figs. 4-7 and 4-9a) supports the hypothesis that the biochar materials can be used as surface amendments to reduce GHG emissions from pen surfaces of beef cattle feedlots, even though significant effect in GHG reduction was observed only from days 10 and 15 after biochar application (Fig. 4-3).

As expected, significant N_2O desorption was observed when substrates were heated (Fig. 4-9a); however, the desorbed gas was as much as twice the expected amount. In the interval from 40°C to 75°C all materials reached the N_2O concentration of the control. This suggests that at 75°C both biochar and activated carbon have at least released 100% of the N_2O previously adsorbed. Moreover, when the temperature exceeded 75°C and reached 100°C, the desorbed N_2O largely exceeded the previously adsorbed gas, suggesting that a mechanism of gas generation from the amendment materials is activated at temperatures far larger than field manure temperatures.

Figure 4-9b represents the N_2O gas desorption from the amendment materials themselves without any external addition of N_2O gas standard into the containers. At 23°C, the N_2O concentration in all containers with the three amendment materials was significantly lower than the one in the control at the same temperature. This finding suggests that the amendment materials adsorbed part of the N_2O concentration present in the indoor air within the containers. As expected, from 23°C to 40°C there was no significant gas desorption from the materials. Once the temperature exceeded 40°C, a large amount of N_2O was released from the materials themselves. That extra amount of N_2O released from the materials cannot be explained from the adsorbed N_2O at room temperature. In addition, because the amendment materials were oven-dried at 125 °C for 12 h before the experiment, the possibility that previously adsorbed N_2O which might be bound to the material and released after 40°C might be also discarded. Therefore, because the materials did not react at temperatures between 23°C to 40°C, no gas desorption is expected from the biochars in the field since temperature did not commonly reach 40°C (Chapter 3). This fact makes the biochars good candidates as surface amendment materials to reduce GHG emissions from pen surfaces in open-lot beef cattle feedlots.

To verify if the adsorption mechanism was able to account for the N_2O mitigation from feedlot manure observed in this study, the adsorption capacities of selected amendment materials were estimated. From Figure 4-7, N_2O concentrations within the containers remained relatively constant over time, indicating that the adsorption capacity of the amendment materials might have been reached. Based on the average gas concentration, the adsorption capacity of each material was computed with respect to the control. The adsorption capacities (< 0.1 µg N_2O/g of material) were orders of magnitude lower than the reduction in N_2O emission observed from Experiment 2 (Figs. 4-3a, b, and d). As such, adsorption was not the main mitigation mechanism and other mechanisms were likely present.

In addition to N_2O adsorption, other possible mitigation mechanisms include NH_4^+ immobilization, NO_3^- adsorption, and NH_4^+ adsorption (Fig. 4-10). Paul (2007) described these mechanisms for soils. The first mechanism, NH_4^+ immobilization, is related to the C:N ratios of biochars. Table 4-2 shows that with the exception of manure biochar, all other amendments have a C:N ratio greater than 20:1, which represents low N content (Barbarick, 2012). When the biochars were mixed with the top manure surface layer, the microorganisms' activity will increase due to the addition of extra C although they might not obtain enough extra N from the

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amendments to synthesize their increasing protein needs and other cellular components (Barbarick, 2012; Robertson and Groffman, 2007). The microorganisms will likely immobilize part of the available inorganic N (NH_4^+) in the manure surface. Once the NH_4^+ is used to supply the microorganisms' need, it will not be plentiful and readily available for nitrification, which consequently, will also decrease the subsequent process of denitrification, with a final net effect of reduced emissions of N_2O (Robertson and Groffman, 2007) from manure surfaces. Adams et al. (2004) reported lower N losses in feedlot pens under increased surface manure C:N ratio as result of the application of sawdust on pen surfaces during winter/spring months. Other researchers reported a linear relationship between the organic matter content and the amount of N preserved in the manure (Erickson and Klopfenstein, 2001). Therefore, as manure C content increases, it is expected that less N will be volatilized from the manure surfaces.
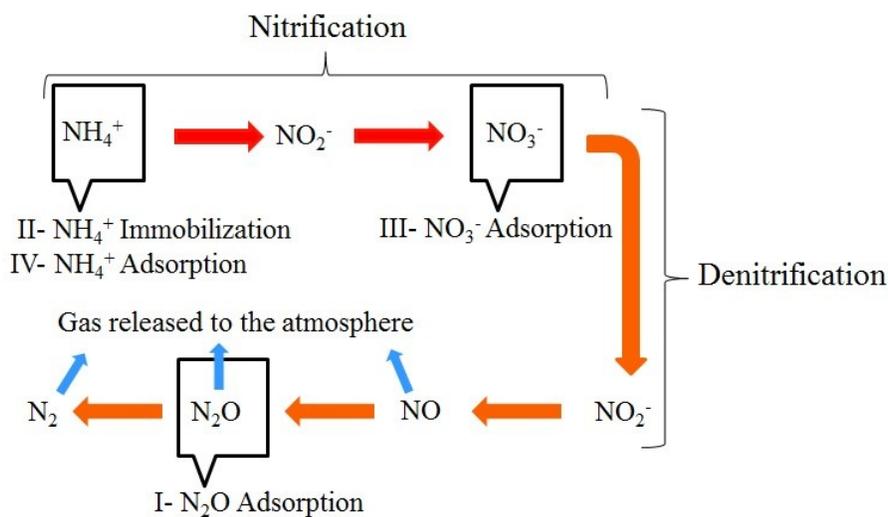
Figure 4-10 Possible mechanisms for the mitigation of N_2O emission from feedlot manure by biochar or activated carbon.

The second possible mechanism is NO_3^- adsorption by the biochar (Fig. 4-10). Several studies have reported NO_3^- adsorption from soil, drinking water, and wastewater, using biochar and activated carbon as adsorbents. Kameyama et al. (2012), in a study on the effect of biochar (from sugar cane bagasse) on NO_3^- leaching in soil, reported significant NO_3^- adsorption on biochar obtained at temperatures greater than 700°C. They also reported that basic functional groups present in the biochar surface contributed more to NO_3^- adsorption than physical adsorption mechanisms. Yao et al. (2012), in an evaluation of 13 biochar materials on sorption

effectiveness of soil nutrients, reported that four biochars obtained at high temperature (600°C) significantly adsorbed NO_3^-, with removal rates up to 3.7%. Nunell et al. (2012), in a study of NO_3^- removal from wastewater using activated carbon, reported high NO_3^- adsorption on wood saw dust activated with potassium hydroxide. They reported that a combined effect of carbon surface chemistry (high basic functional groups and low acidic groups) and carbon porous characteristics were responsible for the NO_3^- adsorption, with surface chemistry playing a prevalent role. Mizuta et al. (2004), in a study of NO_3^- removal from drinking water using bamboo powder charcoal and commercial activated carbon, reported that the bamboo charcoal was 15% more effective in adsorbing NO_3^- than the commercial activated carbon.

The third possible mechanism is nitrification inhibition through the adsorption of NH_4^+. Yao et al. (2012) reported that nine biochars out of 13 significantly adsorbed NH_4^+, with removal rates up to 15.7%.

Based on results from those studies, biochar and activated carbon can adsorb N_2O, NO_3^-, and NH_4^+. If the adsorbed NH_4^+ from manure is not available for microbial activity, nitrification inhibition might result, with a reduction of NO_3^- generation. If NO_3^- is also directly adsorbed onto the biochar and not available for microbial activity, a net denitrification reduction is expected. The net result would be a reduction on N_2O emission rates.

4.5. Summary and Conclusions

This research evaluated, under controlled laboratory conditions, the effectiveness of application of organic residues, biochar, and activated carbon in controlling emissions of N_2O, CH_4, and CO_2 from beef cattle feedlot manure. The following conclusions were drawn:

1. Topical application of organic residues and biochar on dry manure showed significant reduction of N_2O and CO_2 emission fluxes but did not affect CH_4 emission flux.

2. Topical application of organic residues (i.e. prairie grass, sorghum straw, and woodchip) on moist manure did not significantly affect GHG emission fluxes. Topical application of biochar also did not show significant reduction of GHG emissions for the first 8 days. From day 10 and 15, application of biochar materials significantly reduced N_2O and CH_4 emissions compared with the control. Only activated carbon and woodchip biochar showed significant effect in reducing CO_2 emissions.

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3. The method of application of biochar (i.e., topical vs. mixed) did not significantly influence the effectiveness of the material in reducing GHG emissions.

4. Adsorption on biochar or activated carbon appeared to be a mechanism for reducing N_2O emission from feedlot manure; however, other mechanisms (e.g., NH_4^+ immobilization, NO_3^- adsorption, and NH_4^+ adsorption) might be more important.

4.6. References

Adams, J.R., T.B. Farran, G.E. Erickson, T.J. Klopfenstein, C.N. Macken, and C. B. Wilson. 2004. Effect of organic matter addition to the pen surface and pen cleaning frequency on nitrogen mass balance in open feedlots. *Journal of Animal Science* 82(7): 2153–63.

Aguilar-Chávez, A., M. Díaz-Rojas, M. Cárdenas-Aquino, L. Dendooven, and M. Luna-Guido. 2012. Greenhouse gas emissions from a wastewater sludge-amended soil cultivated with wheat (*triticum* spp. L.) as affected by different application rates of charcoal. *Soil Biology and Biochemistry* 52(9): 90–95.

Barbarick, K. A. 2006. Organic materials as nitrogen fertilizers. Fact Sheet No. 0.546. Colorado State University. Available at: www.ext.colostate.edu/PUBS/CROPS/00546.pdf. Accessed 25 July 2012.

Bremer, D. J. 2006. Nitrous oxide fluxes in turfgrass: Effects of nitrogen fertilization rates and types. *Journal of Environmental Quality* 35:1678–1685.

Bruun, E. W., D. Muller-Stover, P. Ambus, and H. Hauggaard-Nielsen. 2011. Application of biochar to soil and N_2O emissions: Potential effects of blending fast-pyrolysis biochar with anaerobically digested slurry. *European Journal of Soil Science* 62(4): 581–589.

Cayuela, M. L., G. L. Velthof, C. Mondini, T. Sinicco, and J. W. van Groenigen. 2010a. Nitrous oxide and carbon dioxide emissions during initial decomposition of animal by-products applied as fertilizers to soils. *Geoderma* 157: 235–42.

Cayuela, M. L., O. Oenema, P. J. Kuikman, R. R. Bakker, and J. W. van Groenigen. 2010b. Bioenergy by-products as soil amendments? Implications for carbon sequestration and greenhouse gas emissions. *Global Change Biology Bioenergy* 2: 201–213.

Chiyoka, W. L., X. Hao, F. Zvomuya, and X. Li. 2011. Nitrous oxide emissions from chernozemic soils amended with anaerobically digested beef cattle feedlot manure: A laboratory study. *Animal Feed Science and Technology* 166: 492–502.

Cooper, D.C., and F.C. Alley. 2002. *Air Pollution Control: A Design Approach*. 3rd ed. Long Grove, IL: Waveland Press Inc.

Erickson, G.E., and T.J. Klopfenstein. 2001. Managing N inputs and the effect on N losses following excretion in open-dirt feedlots in Nebraska. *The Scientific World Journal* 1: 830–835.

Hofstra, N., and A. F. Bouwman. 2005. Denitrification in agricultural soils: Summarizing published data and estimating global annual rates. *Nutrient Cycling in Agroecosystems* 72 (3): 267–78

IPCC. 2007. Working Group II Report: Impacts, Adaption and Vulnerability. IPCC Fourth Assessment Report: Climate Change 2007. Intergovernmental Panel on Climate Change. Available at: www.ipcc.ch/publications_and_data/ar4/wg2/en/contents.html. Accessed 7 October 2010.

Joseph, S.D., M. Camps-Arbestain, Y. Lin, P. Munroe, C.H. Chia, J. Hook, L. van Zwieten, S. Kimber, A. Cowie, B.P. Singh, J. Lehmann, N. Foidl, R.J. Smernik, and J.E. Amonette. 2010. An investigation into the reactions of biochar in soil. *Australian Journal of Soil Research* 48: 501–515.

Kameyama, K., T. Miyamoto, T. Shiono, and Y. Shinogi. 2012. Influence of sugarcane bagasse-derived biochar application on nitrate leaching in Calcaric dark red soil. *Journal of Environmental Quality* 41(4): 1131-1137.

Li, C. 2007. Quantifying greenhouse gas emissions from soils: Scientific basis and modeling approach. *Soil Science and Plant Nutrition* 53(4): 344–352.

Ma, W. K., R. E. Farrel, and S. D. Siciliano. 2008. Soil formate regulates the fungal nitrous oxide emission pathway. *Applied and Environmental Microbiology* 74(21): 6690–6696.

Maeda, K., S. Toyoda, R. Shimojima, T. Osada, D. Hanajima, R. Morioka, and N. Yoshida. 2010. Source of nitrous oxide emissions during the cow manure composting process as revealed by isotopomer analysis of and amoA abundance in betaproteobacterial ammonia-oxidizing bacteria. *Applied and Environmental Microbiology* 76(5): 1555–1562.

Malla, G., A. Bhatia, H. Pathak, S. Prasad, N. Jain, and J. Singh. 2005. Mitigating nitrous oxide and methane emissions from soil in rice–wheat system of the Indo-Gangetic plain with nitrification and urease inhibitors. *Chemosphere* 58(2): 141–147.

Menéndez, S., P. Merino, M. Pinto, C. Gonzalez-Murua, and J. M. Estavillo. 2006. 3,4-Dimethylpyrazol phosphate effect on nitrous oxide, nitric oxide, ammonia, and carbon dioxide emissions from grasslands. *Journal of Environmental Quality* 35: 973–981.

Milliken, G. A., and D. E. Johnson. 2009. *Analysis of Messy Data Vol. 1: Designed Experiments.* 2nd ed. New York, NY: Taylor & Francis Group.

Mizuta, K., T. Matsumoto, Y. Hatate, K. Nishihara, and T. Nakanishi. 2004. Removal of nitrate-nitrogen from drinking water using bamboo powder charcoal. *Bioresource technology* 95(3): 255-257.

Mosier, A., C. Kroeze, C. Nevison, O. Oenema, S. Seitzinger, and O. van Cleemput. 1998. Closing the global N_2O budget: nitrous oxide emissions through the agricultural nitrogen cycle. *Nutrient Cycling in Agro-ecosystems* 52: 225–248.

Nunell, G. V., M. E. Fernandez, P. R. Bonelli, and A. L. Cukierman. 2012. Conversion of biomass from an invasive species into activated carbons for removal of nitrate from wastewater. *Biomass & Bioenergy* 4487-95.

Parkin, T. B., and T. C. Kaspar. 2006. Nitrous oxide emissions from corn-soybean systems in the Midwest. *Journal of Environmental Quality* 35: 1496–1506.

Paul, E.A. 2007. Soil microbiology, ecology, and biochemistry. 3rd ed. Burlington, MA: Academic Press.

Peng, Y., F. Zhang, C. Xu, Q. Xiao, Y. Zhong, and W. Zhu. 2009. Adsorption of nitrous oxide on activated carbons. *Journal of Chemical & Engineering Data* 54: 3079–3081.

Predotova, M., R. Kretschmann, J. Gebauer, and A. Buerkert. 2011. Effects of cuvette surface material on ammonia, nitrous oxide, carbon dioxide, and methane concentration measurements. *Journal of Plant Nutrition and Soil Science* 174(3): 347–349.

Raupach M., and P. Fraser. 2011. Chapter 2: Climate and greenhouse gases. CSIRO Publishing. Available at: http://dx.doi.org/10.1071/CSIRO_CC_Chapter 2. Accessed 29 June 2012.

Robertson, G.P, and P.M. Groffman. 2007. Chapter 13: Nitrogen Transformation. In *Soil Microbiology, Ecology, and Biochemistry*, 341–359. E.A. Paul (ed). 3rd ed. Burlington, MA: Academic Press.

Rogovska, N., D. Laird, R. Cruse, P. Fleming, T. Parkin, and D. Meek. 2011. Impact of biochar on manure carbon stabilization and greenhouse gas emissions. *Soil Science Society of America Journal* 75(3): 871–879.

SAS. 2008. SAS/STAT 9.2 *User's Guide*. Ver. 9.2. Cary, NC: SAS Institute, Inc.

Scheer, C., P.R. Grace, D.W. Rowlings, S. Kimber, and L. van Zwieten. 2011. Effect of biochar amendment on the soil-atmosphere exchange of greenhouse gases from an intensive subtropical pasture in northern New South Wales, Australia. *Plant Soil* 345: 47–58.

Stackhouse, K. R., Y. Pan, Y. Zhao, and F. M. Mitloehner. 2011. Greenhouse gas and alcohol emissions from feedlot steers and calves. *Journal of Environmental Quality* 40(3): 899–906.

Taghizadeh-Toosi, A., T. J. Clough, L. M. Condron, R. R. Sherlock, C. R. Anderson, and R. A. Craigie. 2011. Biochar incorporation into pasture soil suppresses in situ nitrous oxide emissions from ruminant urine patches. *Journal of Environmental Quality* 40: 468–476.

Weiske, A., G. Benckiser, and J. C. G. Ottow. 2001a. Effect of the new nitrification inhibitor DMPP in comparison to DCD on nitrous oxide (N_2O) emissions and methane (CH_4)

oxidation during 3years of repeated applications in field experiments. *Nutrient Cycling in Agroecosystems* 60: 57–64.

Weiske, A., G. Benckiser, T. Herbert, and J. C. G. Ottow. 2001b. Influence of the nitrification inhibitor 3,4-dimethylpyrazole phosphate (DMPP) in comparison to dicyandiamide (DCD) on nitrous oxide emissions, carbon dioxide fluxes and methane oxidation during 3 years of repeated application in field experiments. *Biology and Fertility of Soils Journal* 34: 109–117.

Whalen, S. C. 2000. Nitrous oxide emission from an agricultural soil fertilized with swine waste or constituents. *Soil Science Society of America Journal* 64:781–789.

Woodbury, B. L., D. N. Miller, J. A. Nienaber, and R. A. Eigenberg. 2001. Seasonal and spatial variations of denitrifying enzyme activity in feedlot soil. *Transactions of the ASAE* 44(6): 1635–1642.

Woodbury, B. L., D. N. Miller, R. A. Eigenberg, and J. A. Nienaber. 2006. An inexpensive laboratory and field chamber for manure volatile gas flux analysis. *Transactions of the ASABE* 49(3): 767–772.

Yao, Y., B. Gao, M. Zhang, M. Inyang, and A. R. Zimmerman. 2012. Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil. *Chemosphere* 89(11): 1467-1471.

Zhang, A., B. Rongjun, P. Genxing, C. Liqiang, H. Qaiser, L. Lianqing, Z. Jinwei, Z. Jufeng, Z. Xuhui, H. Xiaojun, and Y. Xinyan. 2012. Effects of biochar amendment on soil quality, crop yield and greenhouse gas emission in a Chinese rice paddy: A field study of 2 consecutive rice growing cycles. *Field Crops Research* 127: 153–160.

Zhang, A., C. Liqiang, P. Genxing, L. Lianqing, H. Qaiser, Z. Xuhui, Z. Jinwei, and D. Crowley. 2010. Effect of biochar amendment on yield and methane and nitrous oxide emissions from a rice paddy from Tai Lake plain, China. *Agriculture, Ecosystems & Environment* 139(4): 469–475.

Chapter 5 - Greenhouse Gas Emissions from Feedlot Pen Surfaces: Effects of Water Application

5.1. Abstract

The effects of water application (e.g., through rainfall or sprinkler system) on emissions of greenhouse gases (GHGs), such as nitrous oxide (N_2O), methane (CH_4), and carbon dioxide (CO_2), from pen surfaces of open-lot beef cattle feedlots was evaluated under controlled laboratory conditions. Manure samples were collected from several randomly selected pens from two beef cattle feedlots in Kansas and were used as simulated pen surfaces. Three treatments (i.e., dry and loose, moist and loose, and moist and compacted pen surface conditions) were considered, simulating surface conditions in the field after a typical rainfall event or water application with a sprinkler system. Manure and water were mixed within glass containers and analyzed for GHG emission using a photo-acoustic infrared multi gas analyzer. From measured concentrations, emission rates were calculated. GHG emissions from the dry manure were low, with mean values of 0.02, 0.00, and 45 mg m^{-2} h^{-1} for N_2O, CH_4, and CO_2, respectively. When water was applied on the dry manure samples, emission fluxes increased rapidly with peak values of 99, 29, and 15,443 mg m^{-2} h^{-1} for ^{1}for N_2O, CH_4, and CO_2, respectively, just 15 min after water application, and then decreased rapidly. A second but lower peak for all three GHGs was observed 120 h after water application, with peak value higher for the moist/compacted than for the moist/loose manure.

5.2. Introduction

Agricultural operations, including rice cultivation, soil management, and animal feeding operations (AFOs), account for large portion of the anthropogenic emissions of CH_4 and N_2O (IPCC, 2007; Raupach and Fraser, 2011). AFOs, in particular, contribute to climate change and have become a public environmental concern (Stackhouse et al., 2011).

In most soil substrates, microorganisms play an important role in the production or consumption of N_2O, CH_4, and CO_2. The microbiological processes that are responsible for emissions of these GHGs (i.e., nitrification, denitrification, methanogenesis, and respiration) are regulated by interactions among soil redox potential, pH, carbon (C) content, temperature, water content, and oxidants (i.e., oxygen (O_2), nitrate (NO_3^-), manganese (Mn^{4+}), iron (Fe^{3+}), sulfate

(SO_4^{2-}), and CO_2) (Hou et al., 2000; Li et al., 2012). To survive, grow, and reproduce, most soil microorganisms need a source of C, as a basic building block for new cells and they obtain energy by catalyzing redox chemical reactions, in which inorganic compounds accept electrons (electron acceptors), allowing the complete oxidation of organic substrates (electron donors) (NRC, 1993a). To accomplish this process, electrons are transferred from the organic C substrate to an electron acceptor. Under aerobic conditions, most soil microbial cells use O_2 as an electron acceptor, releasing CO_2 into the atmosphere (Li, 2007). When oxygen concentration within the soil decreases, e.g., as occurs in highly compacted or high water content substrates, as in feedlot pen surfaces, the activity of aerobic microorganisms is depressed, but a special group of microorganisms, capable of using NO_3^- as an electron acceptor, can be activated. Further reductions of NO_3^- might result in a net emission of N_2O (Hofstra and Bouwman, 2005; Li, 2007). If conditions within the soil become anaerobic for several days, methanogen cells will be activated to use hydrogen as an electron acceptor, resulting in CH_4 production (Li, 2007).

Over the past several decades, agricultural impacts on GHGs emissions have been extensively studied (Healy et al., 1996; Parkin and Kaspar, 2006). As reported by Kanako et al. (2006), peaks of N_2O emissions as much as 22 times larger than normal emission rates were obtained several days after rainfall in agricultural soils. Davidson (1992) and Scholes (1997) also reported increased emissions of N_2O within minutes after adding water to dry agricultural soils. Ellert and Janzen (2008), in a study of GHG emissions from irrigated cropping systems as influenced by manure and synthetic fertilizer, reported fluxes that were 55 times the mean values of the other plots. They also stated that the causes and the extension of those emission hotspots remained unknown and that those hotspots might be responsible for a very large proportion of the N_2O emissions. Mikha et al. (2005) reported increased microbial activity 8 h after watering dry soil. De Klein et al. (1999) also reported N_2O fluxes increasing from 20 g ha^{-1} day^{-1} before irrigation to 740 g ha^{-1} day^{-1} 2 h after irrigation and up to 1050 g ha^{-1} day^{-1} 24 h after the initial irrigation event.

Despite the extensive GHG emission research for soils, scientific information on GHG emissions from cattle feedlots after a rainfall event or water application on pen surfaces is limited. Several control strategies for particulate matter (PM) have been suggested for beef cattle feedlots. Increasing the pen surface water content through water sprinkling is one the best ways to reduce and control dust emissions (Guo et al., 2011; Razote et al., 2006). Because GHGs are

produced from the manure due to microbial activity and because this activity might be triggered by high water content, the potential for GHG emission while controlling dust through water sprinkling must be evaluated. This study evaluated the effects of water application on the emission rates of GHGs from feedlot manure. The major objectives of this study were to assess under controlled laboratory conditions GHG emissions after water application on dry feedlot manure.

5.3. Materials and Methods

Samples of beef cattle feedlot manure (approximately 130 kg) were collected from several randomly selected pens in two beef cattle feedlots in Kansas. The samples were completely mixed and air dried for several days until the average gravimetric water content was approximately 0.10 g g^{-1} wet basis. Large clods were removed by sieving using an ASTM E-II No. 4 (4.75 mm) to achieve a more uniform particle size distribution. These sieved samples were placed in glass containers and used as simulated pen surfaces, as described below.

Two sets of experiments were conducted (Table 5-1). The first set (Experiments 1a and 1b) involved determination of emission fluxes of N_2O, CH_4, and CO_2 from the simulated dry pen surfaces after a rainfall event or water application. The second set (Experiments 2a and 2b) was designed to investigate the factors that influence the emission of those GHGs from the manure after water application.

Table 5-1 Experimental parameters.

Experiments	Treatments (Pen Surface Conditions)	Manure Conditions (wet basis)		Parameters Measured		Sampling Time (h)
		Water Content $(g\ g^{-1})$	Bulk Density $(g\ cm^{-3})$	Gases	Manure	
1a. Effect of water application on GHG emission fluxes	1- Control (Dry/loose) 2- Moist/loose 3- Moist/compacted	0.10 0.40 0.40	0.55 0.69 1.1	N_2O, CH_4, CO_2	Temperature, water content	3.5, 6, 9, 24, 27, 48, 54, 72, 96, 120, 146, 172, 220, 314, 362, 410, 483, 531, 581, 720
1b. Effect of water application on GHG emission fluxes	1- Control (Dry/loose) 2- Moist/loose 3- Moist/compacted	0.10 0.40 0.40	0.55 0.69 1.1	N_2O, CH_4, CO_2	Temperature, water content	0.08, 0.25, 0.50, 0.75, 1, 1.5, 2, 3
2a. Mechanisms of GHG emissions from manure after water application	1- Control (Dry/loose) 2- Moist/loose 3- Moist/compacted	0.10 0.40 0.40	0.55 0.69 1.1	N_2O, CH_4, CO_2	Temperature, water content, NO_3^-, NH_4^+, pH	0, 1, 4, 408, 720 0.17, 0.5, 1, 4, 48, 120, 312, 408, 480, 720 0.17, 1, 4, 48, 120, 312, 408, 480, 720
2b. Mechanisms of GHG emissions from manure after water application	1- Control (Dry/loose) 2- Moist/loose 3- Moist/compacted	0.10 0.40 0.40	0.55 0.69 1.1	--	Temperature	Every 5 min for 45 d

5.3.1. Experiment 1 – Effects of water application on GHG emission fluxes

Experiment 1 had two parts (Table 5-1). The first part (Experiment 1a) assessed the long-term (up to 30 d) trend of emissions of N_2O, CH_4, and CO_2 from simulated pen surfaces after water application. In this experiment, 218.8 g of processed dry manure (0.10 g/g water content wet basis) were placed into 1-L glass containers, which were used as static flux chambers or SFCs (Fig. 5-1a). There were three treatments, including the control, with three replications for each treatment (Fig. 5-1c). For the control (i.e., no water application), three containers with the dry manure were randomly selected. For the moist/loose manure treatment, three other containers were randomly selected and 111.2 g of water at room temperature (22°C) were added and slowly

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mixed with the dry manure. That amount of water represented 16.7 mm of a simulated short-term rainfall or water sprinkling. In the field, during the 2010 spring and summer seasons, rainfall events between 8 mm and 22 mm were common (Chapter 3). Final wet bulk density in the containers (Table 5-1) was within the range measured under field conditions, as described in Chapter 3. For the moist/compacted manure treatment, samples were prepared in the same fashion as the moist/loose manure treatment; immediately after mixing the water and the dry manure, samples were uniformly compacted until a wet bulk density of 1.1 g cm^{-3} was reached to simulate field conditions. Compaction was performed manually using a cylindrical wooden stick and rubber mallet. To standardize the compaction process, samples were compacted until a final volume of 300 cc of moist manure within the containers was reached. That final volume was computed based on /manure physical conditions.
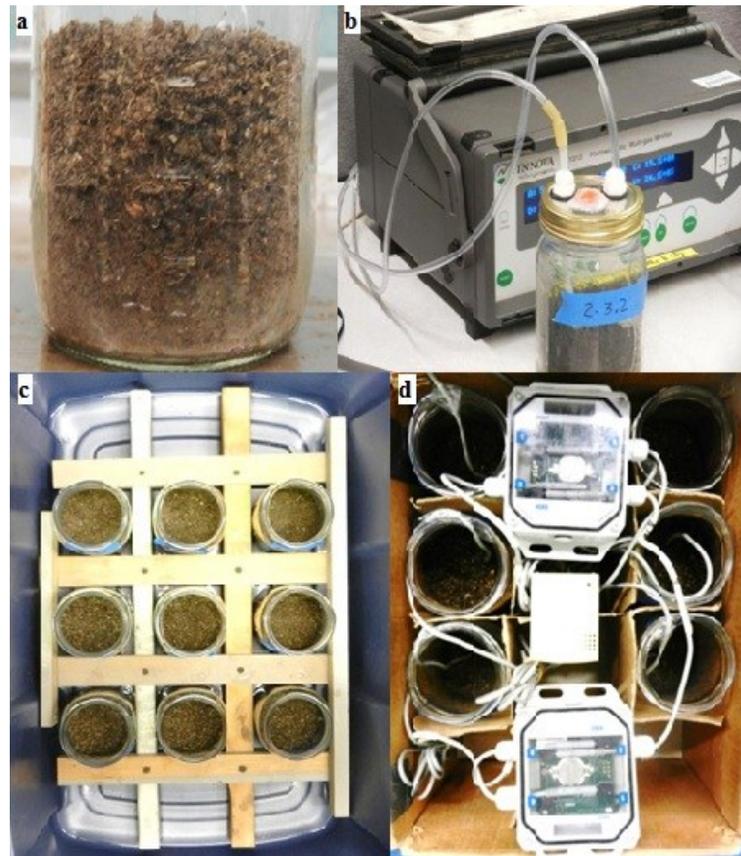
Figure 5-1 Photographs of the experiment: (a) glass container with moist/loose manure several days after water application; (b) sampling set up; (c) treatments with the first horizontal row corresponding to the control (no water application), the second to the moist/loose condition, and the third to the moist/compacted condition; and (d) temperature measurement.

The first gas sampling and measurement for each container was performed 3.5 h after water application. Immediately before sampling, the headspace of each container was flushed with ambient air (Chiyoka et al., 2011) to ensure that GHG concentrations were at ambient levels at the start of measurement. Sampling was performed using a photo-acoustic infrared multigas analyzer, PIMA (Model 1312, Innova AirTech Instruments, Ballerup, Denmark), equipped with optical filters for measuring N_2O, CH_4, and CO_2, and water vapor, as shown in Figure 5-1b. Gas sampling was repeated within a period of 30 d (Table 5-1). During this period, containers were kept uncapped within the laboratory. During sampling, the air temperature and pressure were measured. Manure temperature from each container was also measured using a thermometer (Model 14-983-17A, Fisherbrand, Pittsburgh, PA). Atmospheric pressure was measured using a barometer.

The second part of the experiment (Experiment 1b) assessed the short-term (up to 3 h) effects of water application on GHG emissions. The experimental set up, including sample preparation, treatments and instrumentation, was the same as that for Experiment 1a. Because of the higher sampling frequency in Experiment 1b, there were only two replications for each treatment. Gas sampling and measurement was done at 0.08, 0.25, 0.50, 0.75, 1.0, 1.5, 2.0, and 3.0 h after water application (Table 5-1).

5.3.2. Experiment 2 – Mechanisms of GHG emissions after water application

Similar to Experiment 1, Experiment 2 had two parts. The first part (Experiment 2a) evaluated the mechanisms of GHG formation in the manure after water application. Treatments were the same as in Experiment 1. Twenty four manure samples were prepared following a similar process as described for Experiment 1. Five glass containers were used for the control (dry/loose manure, no water application).

GHG concentrations, manure physical and chemical characteristics (i.e., water content, temperature, pH, ammonium (NH_4^+), and nitrate content (NO_3^-)) were measured over the 30-d experimental period. Each container was sampled once, following the sampling scheme shown in Table 5-1. During sampling, the headspace gas concentration in the container was analyzed for GHGs in the same manner as described for Experiment 1. After gas concentration measurement, a manure core was collected from the sampled container. Those cores were kept frozen and at the end of the 30-d experimental period, they were analyzed at the Kansas State University Soil

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Testing Laboratory for pH, NH_4^+, and NO_3^-, as described in Chapter 3. Each container was discarded after core sampling. Manure temperature in each container was measured immediately before and after gas sampling using glass thermometers. The air temperature and pressure in the laboratory were also measured using the same glass thermometers and the barometer, respectively, as in Experiment 1.

Experiment 2b was conducted in parallel to Experiment 2a. In Experiment 2a, the manure temperature was measured only during gas sampling; in Experiment 2b the manure temperature was measured continuously every 5 min for 45 d, as indicated in Table 5-1. Treatments were the same as described in Experiment 1, with two replicates each (Fig. 5-1d). Two different water applications were performed. The first water application was at time 0 h; the second one was at day 35 after the first water application. Manure temperature was measured using HOBO TMC6-HD sensors (-40 to 100°C ± 0.25°C, resolution 0.03°C), connected to a data logger (HOBO U12-008, Onset Computer Corp., Bourne, MA).

5.3.3. Statistical analysis

The emission flux for each container during sampling was computed using the following equation, as described in Chapter 4:

$$F = 9.622 \; x \; 10^{-3} \; V \; S \; MW \; \frac{P}{A \, T} \tag{5.1}$$

where F is gas emission flux (mg m^{-2} h^{-1}), MW is molar mass of the gas (g gmol^{-1}), V is headspace volume of air (cm^3), A is surface area of manure (cm^2), P is atmospheric pressure (mm Hg), T is air temperature (K), and S is slope of the least squares regression line between measured gas concentration and time (ppm min^{-1}).

The gas emission flux at a given day was generally correlated with the previous day's emission flux. As such, the Autoregressive One, AR(1), structure was used on the residuals. Significant difference between treatments was assessed using Proc Glimmix and paired t-test (SAS, 2008) with a 5% level of significance. At gas emission peaks and when (treatment)x(time) interactions were present, treatment differences were assessed for each sampling. Significant differences between treatments were determined using Tukey p-value adjustments (Milliken and Johnson, 2009). Correlation was assessed by Proc Corr of SAS (SAS, 2008). Analysis of differences in the processes that generated time-series /manure temperature was assessed by White Noise using R Project (R project, 2012).

5.4. Results and Discussion

5.4.1. Experiment 1 - Effects of water application on GHG emission fluxes

Figure 5-2 plots the emission fluxes of N_2O, CH_4, and CO_2 as affected by water application. Emission fluxes from the dry/loose manure (control) were negligible. Application of water on the manure resulted in significantly larger emission fluxes for all three GHGs. This suggests that water application is a trigger factor of GHG emission. Table 5-2 summarizes the mean and peak emission fluxes for Experiments 1a and 1b.

Table 5-2 Effects of water application on mean and peak emission values.

Treatment	N_2O			CH_4			CO_2		
	Mean	Peak	Time†	Mean	Peak	Time†	Mean	Peak	Time†
	$(mg\ m^{-2}\ h^{-1})$		(h)	$(mg\ m^{-2}\ h^{-1})$		(h)	$(mg\ m^{-2}\ h^{-1})$		(h)
	0 to 3 h after water application								
Dry/loose (Control)	0.0	no peak	-	0.0	no peak	-	0.7	no peak	-
Moist/loose	29.3	99.2	0.25	7.4	28.6	0.25	11678	15443	1.0
Moist/compacted	19.3	75.4	0.25	5.1	21.7	0.25	4411	6237	1.5
	3.5 to 720 h after water application								
Dry/loose (Control)	0.02	no peak	-	0.00	no peak	-	45	247	120
Moist/loose	2.60	6.38	120	0.29	1.33	146	3935	6153	120
Moist/compacted	4.33	17.2	410	0.89	4.51	410	3894	5980	220

† Time in which peaks were observed.
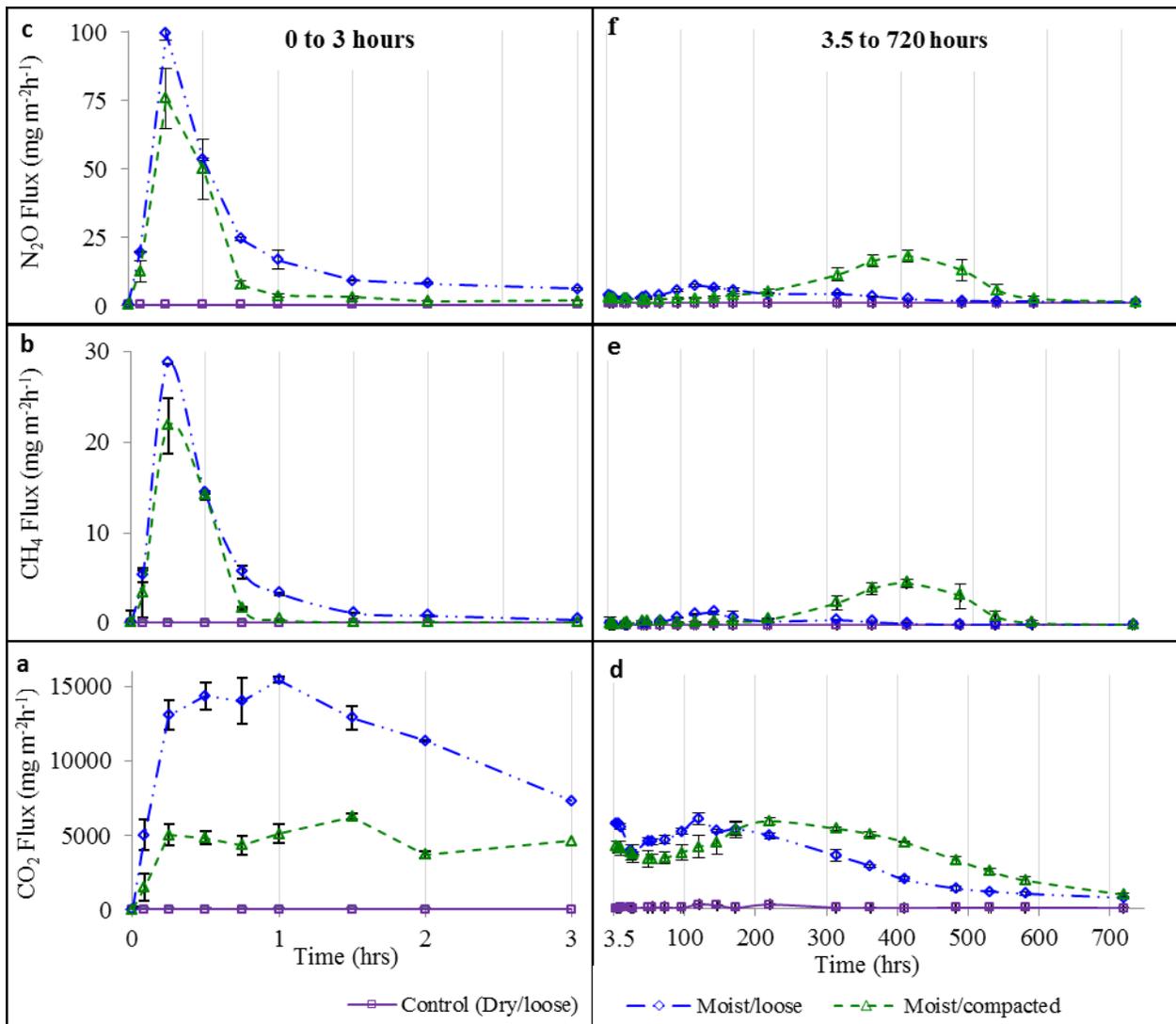
Figure 5-2 Effects of water application on emission fluxes of GHGs: a, b, and c, correspond to CO_2, CH_4, and N_2O fluxes, respectively during the first 3 h after water application (Experiment 1b); d, e, and f represent CO_2, CH_4, and N_2O, respectively, from 3.5 to 720 h after water application (Experiment 1a).

5.4.1.1. Nitrous oxide

Nitrous oxide emission fluxes for the control (dry/loose condition, no water application) were generally low (Figs. 5-2c and f). This is consistent with results from field measurements presented in Chapter 3 and with published research for soils. De Klein et al. (1999) reported very low N_2O fluxes from soils before water application. The N_2O emission fluxes from the moist/loose and moist/compacted manure samples were significantly larger than those for the control. Moreover, N_2O emissions from the moist/loose and moist/compacted manure samples

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were not significantly different; however, they significantly differed in the peak emission values. Figure 5-2c shows that for the dry manure (control), the N_2O flux remained almost zero during the complete experimental period; on the other hand, the N_2O fluxes from the moist/loose and moist/compacted manure increased to 99 and 74 mg $m^{-2}h^{-1}$, respectively, approximately 15 min after water application. The first N_2O peak from the moist/loose manure was significantly larger than that for the moist/compacted manure. The difference in the peak values between moist/compacted and moist/loose manure might be due to the larger wet bulk density of the moist/compacted manure (Table 5-1), which could have delayed gas diffusion from the substrates to their surface/air interface. Therefore, just the top layer of the moist/compacted manure was able to quickly diffuse N_2O to the headspace, which can also explain its quick and large N_2O flux decline during the first hour of the experiment. Previous researchers (Davidson, 1992; Kanako et al., 2008; Kanako et al., 2006; Kanako et al., 2002; Marinho et al., 2004; Scholes, 1997) have reported increased N_2O emission rates after rainfall events or artificial watering processes in agricultural soils. Nitrous oxide emission peaks as much as 22 times larger than normal emission fluxes were obtained at different times after a watering event (Kanako et al., 2006). While several studies have reported large emissions of N_2O several hours or even several days after rainfall events, other studies, including Davidson (1992) for dry grassland soil and Scholes (1997) for dry savanna soil, reported that N_2O emissions markedly increased within minutes after adding water to soil at the end of the dry season. This is comparable to results in this study.

A second N_2O emission peak was observed for both the moist/loose and moist/compacted manure at 120 and 410 h after water application, respectively. The second N_2O peak for the moist/loose manure was observed when the N_2O flux of the moist/compacted manure and the control were not significantly different. The increased N_2O emission rate of the moist/compacted manure may be a consequence of the accumulated water underneath the surface due to manure compaction, which might have resulted in anaerobic conditions within the packed manure, triggering the denitrification process and enhancing N_2O emissions (Kanako et al., 2006).

After air-drying of manure, considerable NO_3^- as result of nitrification is expected to remain within the manure; then, when water is applied under these conditions, denitrification might lead to a large N_2O production (Kanako et al., 2006). Therefore, the remarkably high N_2O emission rate just within 15 min after water application (Fig. 5-2c) likely resulted as a

consequence of a high concentration of NO_3^- in the dry manure which after the addition of water, suddenly triggered the activation of denitrification activity. As suggested by Davidson (1992), nitrifying and denitrifying microorganisms appear to be well adapted to surviving for long periods of time on dry conditions and extreme high and low temperatures simultaneously; they become active within minutes after watering the dry manure. In this experiment, as the moist/loose manure dried, conditions likely became more aerobic, reducing the denitrification activity, which could help explain the sustained reduction of N_2O emission flux one hour after watering (Fig. 5-2c), reaching background levels 24 d later (Fig. 5-2f). As described in NRC (1993b), in a soil normally dominated by air-filled pore space and oxidizing conditions, the soil may become saturated with water during recharge events, and reduced conditions and denitrification may dominate temporarily.

5.4.1.2. Methane

Figures 5-2b and e show that CH_4 emission fluxes followed the same trend as N_2O emission fluxes. Emission fluxes from the control (dry/loose manure) were also negligible. Emission fluxes from the moist /loose and moist/compacted manure were significantly larger than that for the control (dry/loose manure). The first CH_4 emission peak from the moist/loose manure (28.6 mg m^{-2} h^{-1}) was significantly larger than that for the moist/compacted manure (21.7 mg m^{-2} h^{-1}); this might be a consequence of the higher wet bulk density of the moist/compacted manure (Table 5-1). A second CH_4 emission peak was observed for both moist manure treatments at 146 and 410 h after watering, respectively (Fig. 5-2e). The second CH_4 emission peaks were lower than the first. Also, the CH_4 emission peak of the moist/compacted manure (4.5 mg m^{-2} h^{-1}) was significantly larger than that of the moist/loose manure (1.3 mg m^{-2} h^{-1}). Results suggest that at 120 h after watering, the moist/compacted manure, which trapped water underneath the surface, could have become from its partial and temporary anoxic to completely anoxic conditions; the moist/loose manure had recovered its oxidizing conditions at that time. This is confirmed for the almost negligible CH_4 emission flux from the moist/loose manure while the moist/compacted manure showed at the same time, larger CH_4 emission flux, as shown in Figure 5-2e.

As described by Li (2007) and Saggar et al. (2004), during a rainfall or watering event, the top surface layer might become saturated, and therefore the water would block the diffusion of O_2 into the soil profile, depleting the O_2 left in the soil pore space due to microbial

consumption. Because microbial activity in the dry/loose manure is enhanced as manure water content increases, this might quickly result in the formation of anaerobic microsites following watering, which will result in anoxic conditions in the manure (Saggar et al., 2004). Reduced conditions may dominate temporarily in a dry soil after watering (NRC, 1993b); furthermore, in the same manner as those temporary anoxic conditions triggered denitrification, they also enhanced the activity of methanogenic bacteria, which resulted in large peaks of CH_4 fluxes in both moist treatments after watering.

5.4.1.3. Carbon dioxide

Carbon dioxide emission fluxes from all treatments and control were significantly different (Figs. 5-2a and d). The larger CO_2 emission fluxes were observed from the moist/loose manure. Similar to N_2O and CH_4, CO_2 emission fluxes from the dry manure were low throughout the experimental period. Approximately 581 h after water application, emission fluxes for both moist treatments were not significantly different from that for the control.

In the case of the moist/loose manure, as soon as the pore space was filled out with water, conditions could have become temporarily anoxic. Moreover, because of the loose condition, the water was exposed to vaporization and also moved deeper into the manure, which could have allowed O_2 diffusion from the air to the pore spaces, recovering the substrate its aerobic conditions, as suggested by the wider CO_2 peak compared to the narrower N_2O and CH_4 peaks. Therefore, GHG emission fluxes from the moist/loose manure were likely the result of a combination of aerobic and anaerobic conditions present at the same time. Because under aerobic conditions, most soil microbial cells use O_2 as electron acceptor, releasing CO_2 into the atmosphere as its main respiratory product (Li, 2007), as expected, the largest CO_2 emission flux was observed for the moist/loose manure.

Carbon dioxide emissions from the moist/compacted manure were significantly lower than those for the moist/loose manure during the first 3 h after water application (Fig. 5-2a). This might be due to the limited gas diffusion and anaerobic conditions. Its compacted condition, in addition to the decreased gas diffusion through the manure (which limited O_2 diffusion), also kept anoxic conditions for longer time as consequence of the trapped water. That sustained anoxic condition enhanced denitrification and methanogenesis resulting in large emissions of N_2O and CH_4 but lower emissions of CO_2. Figure 5-2d shows the decreasing trend of CO_2 emission flux for the moist/compacted manure 200 h after watering while the emission fluxes of

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CH$_4$ (Fig. 5-2e) and N$_2$O (Fig. 5-2f) increased during the same time period. These results support the possible presence of mostly anoxic conditions in the moist/compacted manure.

5.4.2. Experiment 2 - Mechanisms of GHG emissions after water application

5.4.2.1. Nitrous oxide

The control and moist manure treatments showed significant inverse correlation between manure NO$_3^-$ and NH$_4^+$ content (Fig. 5-3). Field measurements presented in Chapter 3 indicated inverse, but non-significant correlation between manure NO$_3^-$ and NH$_4^+$ contents. The non-significant inverse correlation between NO$_3^-$ and NH$_4^+$ from pen surfaces was expected because of the likely constant manure NH$_4^+$ content with time as consequence of the random and continuous inputs of fresh cattle urine and manure to the pen surfaces. In this study, there was no additional input of nitrogen with time; as such, a sustained decrease of manure NH$_4^+$ content as nitrification increases with time was expected.
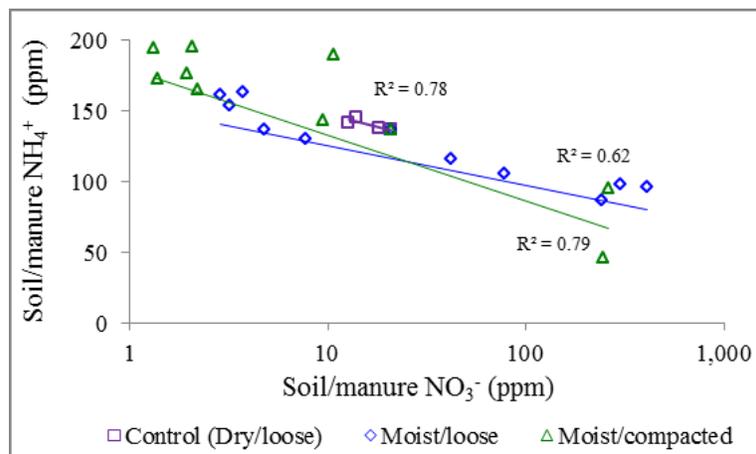
Figure 5-3 Relationship between manure ammonium and nitrate contents.

The N$_2$O emission fluxes in Experiment 2 (Fig. 5-4f) followed the same trend as that in Experiment 1. In this experiment, the control (dry/loose manure) showed a sustained small increase of NH$_4^+$ (Fig. 5-4d) and a sustained but small decrease of NO$_3^-$ (Fig. 5-4e) during the 30-d experimental period. This explains the almost negligible emission of N$_2$O from the control in Experiments 1 and 2 (Figs. 5-2c and 5-4f). These results suggest that even though conditions were aerobic in the control, due to the low water content, there was limited nitrification as nitrifying microorganisms were likely inactive. However, in both moist manure treatments, there

was a sudden, although non-significant, decrease of NO_3^- content after watering (from 0 to 1 h) and thereafter, a significant large production of NO_3^- and significant large decrease of NH_4^+ were observed ($p < 0.05$) (Figs. 5-4e and d). These results suggest that while the manure was dry, both NO_3^- and NH_4^+ were being accumulated because only a small denitrification occurred, but as soon as water was added, both nitrifying and denitrifying microorganisms were activated, as also suggested by the sudden increase of more than 2°C just within 10 min after watering in both moist treatments (Fig. 5-4b). This may have triggered the transformation of NO_3^- into N_2O. Mikha et al. (2005) reported increased microbial activity after watering dry soil; however, unlike this study, that is reported at 8 h after the watering event.

In the moist/loose manure, as suggested for the quick decrease of NO_3^- content after water application (Fig. 5-4e), a sudden denitrification might be responsible for the large but narrow N_2O emission peak within the first 10 min after watering (Figs. 5-2c and 5-4f). That N_2O emission peak lasted for 30 min, after that, it quickly decreased to a minimum level, which was sustained during 120 h after watering. Apparently, up to one hour after watering, the dominant process within the moist/loose manure was denitrification. One hour after watering, nitrification took place surpassing the rate of denitrification, as suggested by the significant decreasing rate of NH_4^+ content (Fig. 5-4d) while NO_3^- content significantly increased at the same time (Fig. 5-4e). At 120 h when the manure water content began to steadily decline (Fig. 5-4a), aerobic conditions dominated in the manure, then, a sudden increase of NO_3^- content (from 42 to 409 ppm) was observed. In that same time period, N_2O emission flux declined from its previous intermediate level (Fig. 5-4f) to the background level. A corresponding decline in the manure temperature was also observed (Fig. 5-4b). These results suggest that 120 h after water application, aerobic conditions and so nitrification, were predominant within the moist/loose manure and responsible for the decreased emission of N_2O at that time.

As shown in Figure 5-4c, the pH in the control was slightly alkaline during the experiment. Moreover, in both moist manure treatments, the pH slightly decreased with respect to the control as soon as water was mixed with the manure. In the moist/loose manure, an hour after watering, the pH increased above that of the control, reaching a maximum of 7.3 at 48 h after watering and then, decreased to the background level. In the moist/compacted manure, unlike the moist/loose manure, an hour after watering the pH quickly decreased reaching a minimum of 6.78 at 48 h and then, increased up to 7.34 at 312 h after watering, staying around

that value until the end of the experiment. The lowest pH was observed for the moist/compacted manure. At the time of this minimum pH, the largest NH_4^+ content and the lowest NO_3^- content were also observed (Figs. 5-4c, d, and e). In general, pH remained around 7, which is favorable for N_2O and CH_4 production (Hou et al., 2000).

The moist/compacted manure behaved in a similar manner as the moist/loose manure as shown in Figure 5-4. Because rates of denitrification are higher with high water content (Groffman et al., 1993) and anoxic conditions, during the first hour after watering, the denitrification process was stronger in this treatment than in the moist/loose manure, as suggested by Figure 5-4e. Moreover, the narrow peak of N_2O emission flux was lower (Fig. 5-4f) likely a result of reduced gas diffusion through the highly compacted surface. In this treatment, anaerobic conditions remained dominant until 408 h after watering. At 120 h, when the compacted manure started drying out, nitrification also took place, as suggested by the large increase of NO_3^- content for moist/compacted manure (Fig. 5-4e). After 120 h, a large N_2O emission flux began, with a large and broader peak at 408 h. That large N_2O emission peak might be the result of N_2O accumulation underneath the surface during the time that manure conditions were anoxic, and then, released once the surface drying process began. The sustained (broader) peak can also be explained by the increase of the manure temperature (Fig. 5-4b), suggesting that completely anoxic conditions were reached and kept deeper in the manure after 120 h. Even though the N_2O peak showed up at 408 h, 120 h after watering, nitrification was the dominant process in the top manure surface with a large conversion of NH_4^+ into NO_3^-, as suggested by Figures 5-4d and f, while anoxic conditions still remained at the bottom.
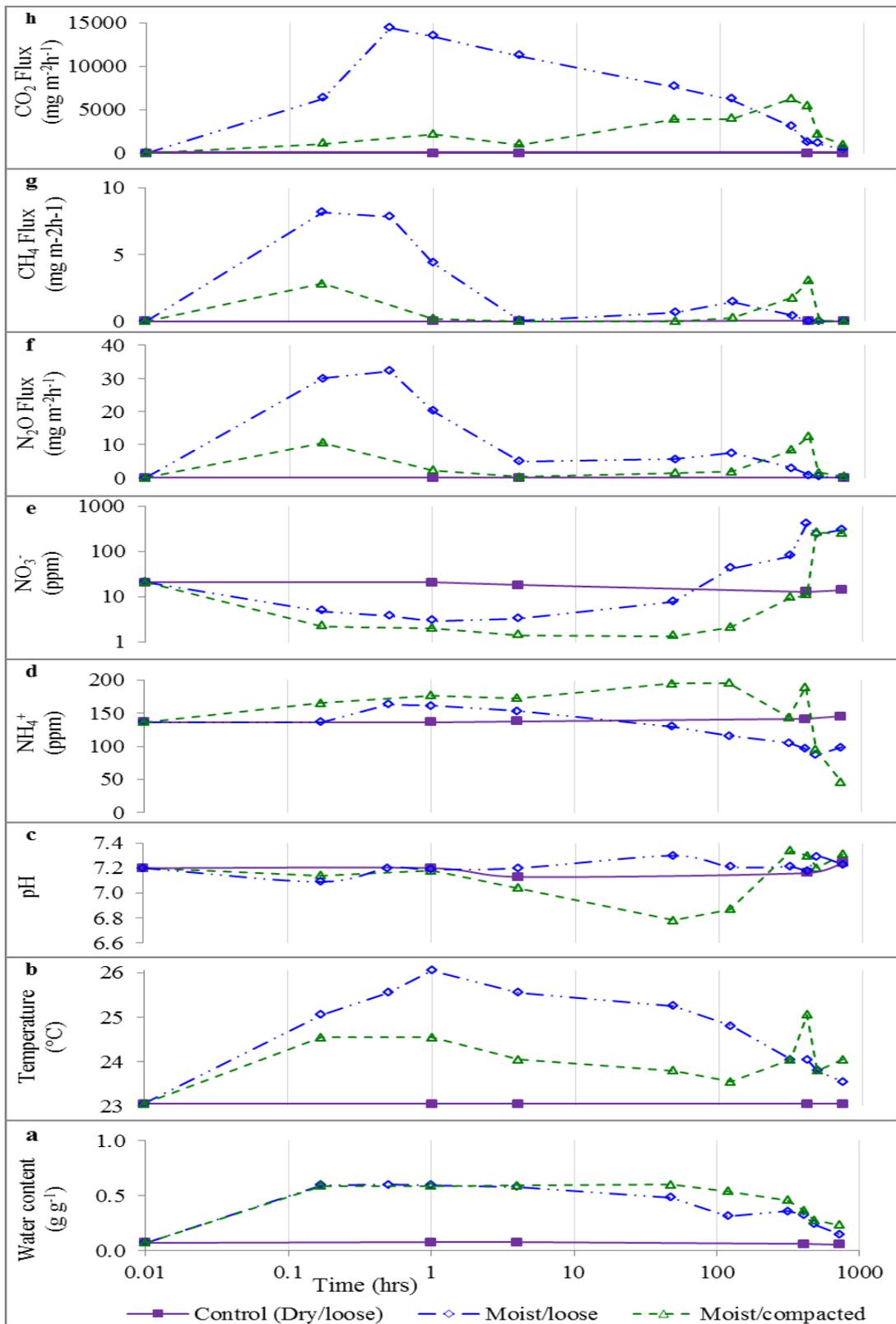
Figure 5-4 Relationship among factors affecting GHG emission fluxes during 30 days after water application.

Several researchers (Klein and Logtestijn, 1994; Lee et al., 2008; Mosier et al., 1998; Woodbury et al., 2001) have reported that N_2O is produced by the activation of both nitrification and denitrification processes. Groffman et al. (1993), Kanako et al. (2006), and Taghizadeh-Toosi et al. (2011) reported that nitrification activity is activated under low water conditions and that it is enhanced by the presence of NH_4^+, which results in the production of NO_3^- in the soil. They also suggested that denitrification is enhanced by the presence of a high amount of NO_3^- and that it is activated under high water content. Davidson (1992) and Saggar et al. (2004) reported that below field water capacity, nitrification accounted for the emission of N_2O and above field capacity denitrification is the dominant process. The formation of anaerobic sites following watering was responsible for N_2O emission rates up to 5 times larger when soil water content was above field capacity compared to rates observed below water field capacity (Saggar et al., 2004). This suggests that well-drained pens in cattle feedlots will emit lower amounts of N_2O compared to poorly drained pens because the main driving agent in the dry pen is nitrification.

In general, as shown in Table 5-3, the N_2O emission flux from the moist/loose manure was positively correlated with manure factors such as water content, temperature, and NH_4^+ content, and inversely correlated with pH and NO_3^- content. Ammonium was directly correlated with manure water content and temperature, but inversely correlated with NO_3^- content. Nitrate content was inversely correlated with manure temperature. In the case of the moist/compacted manure, N_2O emission flux was significantly correlated only with manure temperature. Ammonium was positively correlated with manure water content, but inversely correlated with pH and NO_3^- content. Nitrate content showed significant monotonic relationship with manure water content (inverse) and pH content (direct), as indicated in Table 5-3. Moreover, N_2O, CH_4, and CO_2 emission fluxes were significantly correlated with each other.

Table 5-3 Correlation matrix.

		Moist/compacted Treatment †							
		CH_4	N_2O	CO_2	Soil Water	Soil Temp.	pH	NH_4^+	NO_3^-
‡ M o i s t / l o o s e	CH_4		0.990 (<0.0001)	0.656 * (0.039)	+	0.696 (0.025)	+	+	+
	N_2O	0.990 (<0.0001)		0.552 (0.098)	+	0.734 (0.016)	+	+	+
	CO_2	0.620 (0.042)	0.723 (0.012)		+	+	+	0.576 * (0.082)	+
	Soil Water	0.635 (0.036)	0.711 (0.014)	0.847 (0.001)		+	-0.578 * (0.0804)	0.621 (0.055)	-0.806 * (0.0049)
	Soil Temp.	0.596 (0.053)	0.692 (0.018)	0.931 (<0.0001)	0.955 (<0.0001)		+	+	+
	pH	-0.601 (0.050)	-0.557 (0.075)	+	+	+		-0.566 (0.088)	0.748 * (0.013)
	NH_4^+	0.606 (0.048)	0.681 (0.021)	0.844 (0.001)	0.553 (0.078)	0.694 (0.018)	+		-0.887 (0.0006)
	NO_3^-	-0.688 * (0.019)	-0.523 (0.099)	-0.645 (0.032)	-0.745 * (0.0085)	-0.561 (0.072)	+	-0.788 (0.004)	

† Values above diagonal represent the Pearson Correlation Coefficients and their respective p-values (in parentheses), for the moist/compacted treatment.

‡ Values below diagonal represent the Pearson Correlation Coefficients and their respective p-values (in parentheses), for the moist/loose treatment.

* No linear relationship was present; instead, a monotonic relationship was observed. Therefore, a Spearman Correlation Coefficient and its p-value are given, rather than the Pearson Correlation Coefficients.

+ Empty cells indicate no significant correlation.

5.4.2.2. Methane and carbon dioxide

The CH_4 and CO_2 emission fluxes in Experiment 2 (Figs. 5-4g and h) followed the same trends as those in Experiment 1, with also two different sets of gas emission peaks. Those sudden peaks of CH_4 and CO_2 emission fluxes after watering the dry manure, also coincided with a sudden increase in manure temperature just 10 min after watering (Fig. 5-4b). One hour later, the CH_4 emission peak of both moist manure treatments reached the background level (control), as also occurred in Experiment 1. Temperature in the moist/compacted manure also decreased to the background level, suggesting little microorganism activity at that time.

In the moist/loose manure, after the first CH_4 and CO_2 emission peaks, its temperature steadily decreased and the CH_4 emission flux also declined to the background level. The CO_2 emission flux, on the other hand, although decreasing, was still high 408 h later, when it also reached its background level. These results suggest that conditions in the manure were progressively becoming aerobic as the water content decreased. This trend also matched the large nitrification activity previously suggested in the same period of time.

In the moist/compacted manure, 120 h after watering, the temperature began to steadily increase, reaching a maximum of 25°C at 408 h, 2°C above room temperature (Fig. 5-4b). This

second increase of temperature might have resulted from increasing microorganism activity deeper in the manure after several days of high water content and limited gas diffusion through the manure. At that time, a second and broader CH_4 emission peak was reached. A CO_2 emission peak coinciding with the CH_4 emission peak was also observed. This suggests that in the vertical manure profile of the moist/compacted manure, two different conditions were reached at the same time. At the top surface, there was an increasing aerobic condition as water evaporated; this substrate section might be responsible for the increasing temperature and CO_2 emission peak as well as for the nitrification activity previously reported for this treatment during that time interval. Furthermore, deeper in the manure, conditions became strongly anoxic; this condition might also be responsible for part of the increase in the substrate temperature and for the CH_4 emission peak at that time interval.

As described by Paul (2007) and Segers (1998), microbial production of CH_4 in soils results from the action of methanogenic microorganisms that decompose organic material in the absence of O_2, using CO_2 as an electron acceptor and a reduced organic compound as the donor. The reduction of CO_2 occurs under extended reduced conditions such as in flooded soils or in any soil under severely limited O_2 diffusion (Li, 2007; Paul, 2007). Major factors that influence CH_4 emission flux in soils are soil O_2, soil CH_4 concentrations, and gas transport, which is driven mainly by soil water content and temperature (Segers, 1998). The initiation of CH_4 production is not affected when the dry substrates are stored under dry air, O_2, or N_2 atmospheres but it is affected by storage under moist conditions (Mayer and Conrad, 1990). Therefore, the watering process, in addition to triggering N_2O emission flux, might also have triggered the CH_4 and CO_2 production, as shown in Figures 5-4g and h. Mikha et al. (2005) indicated that after watering dry soil, there was a quick release of readily degradable organic compounds from dead cells, such as amino acids, NH_4^+ compounds, and glycerol, which may be utilized by living microorganisms, resulting in a pulse of CO_2 emission after watering.

Unlike results in this study, previous studies have reported inverse correlation between N_2O and CH_4 (Hou et al., 2000; Johnson-Beebout et al., 2008). Delaune and Reddy (2005) reported that in soil sediments, anaerobic conditions were reached at redox potential below +400 mV, that the approximate range of denitrification activity was between +400 to +300 mV, and that the reduction of CO_2, which yields CH_4 (Paul, 2007; Segers, 1998), is below -200 mV. Hou et al. (2000) in a rice paddy soil and Johnson-Beebout et al. (2008) in a rice paddy greenhouse

experiment, reported that significant N_2O emissions only occurred at approximated redox potentials above +200 mV and significant CH_4 occurred below -200 mV. Based on those results, high emissions of both N_2O and CH_4 did not occur simultaneously.

Unlike those previous studies, this study evaluated the effect on GHGs of water application on dry manure. Mayer and Conrad (1990) demonstrated that unlike forest and arable soils, rice paddy soils contain a large methanogenic biomass even under dry and aerobic soil conditions and that the production and emission of CH_4 is only limited by the establishment of low redox potential as well as to the supply of dissolved organic compounds and oxidants. Moreover, Gattinger et al. (2007) reported increased methanogenic biomass in soils with high rate of manure application. In addition, a soil dominated by air-filled pore space and oxidizing conditions may quickly become saturated with water during recharge events and reduced conditions and denitrification may dominate temporarily (NRC, 1993b). After water application in Experiments 1 and 2, the potential large aerobic biomass present in the dry manure might have quickly consumed the O_2 left in the substrate with a rapid O_2 partial pressure drop (Li, 2007); with the consequent also rapid activation of the likely large population of denitrifiers and methanogens present in the dry manure. This is also supported by the sudden increase in manure temperature after water application (Fig. 5-4b). Therefore, sudden denitrification and methanogenesis could be present simultaneously, as consequence of water saturation of the dry manure, which limited O_2 diffusion and enhanced microorganism activity.

Table 5-3 shows that CH_4 emission flux from the moist/loose manure was significantly directly correlated with water content, temperature, and NH_4^+ content, and inversely correlated with pH. It also showed a significant monotonic relationship with NO_3^- content (Table 5-3). For the moist/compacted manure, on the other hand, CH_4 emission flux was only significantly correlated with manure temperature. For CO_2 emission flux, the moist/loose manure showed significant direct correlation between CO_2 emission flux and manure water content, temperature, and NH_4^+ content, and inverse correlation with NO_3^- content. Furthermore, the moist/compacted manure showed significant monotonic correlation between CO_2 emission flux and NH_4^+ content.

Figure 5-5 shows the temperature trends for the control (dry/loose) and for the moist manure treatments after water application (Experiment 2b). The processes that generated those temperatures were significantly different at 5% level of significance. For both moist manure treatments, there was a quick decrease of 0.5°C as soon as water was mixed within the manure. It

might be a result of direct contact of water with the buried sensors in the manure. After that initial temperature drop, temperature began and kept increasing (Fig. 5-5a).

Within the first hour, the moist/loose manure showed an increment of 3.9°C, which is larger than the 3.0°C observed in Experiment 2a (Fig. 5-4b). Moreover, this treatment had a net temperature increment of 5°C, 3 h after watering, then dropping 3°C at 20h after watering (Fig. 5-5b). After this, it showed a second peak of temperature, with an increment of 1°C. These temperature peaks coincided with the peaks of N_2O and CH_4 emission peaks previously described for the moist/loose manure.

Temperature for the moist/compacted manure exhibited a similar trend as that for the moist/loose manure; however, its maximum increment was 2.75°C and the respective peak times were different, as shown in Figures 5-5a and b. Nevertheless, these temperature peaks also coincided with the GHG emission peaks. Field experiments (Chapter 3) indicated changes in manure temperature, over 9°C between different surface conditions within a pen in a beef cattle feedlot. In general, results shown in Figure 5-5 confirms results from previous experiments, as the temperature trends support the GHG emission peaks reported in this study.

Thirty five days after first watering, a second watering event took place. As shown in Figure 5-5a (840 h), a new set of temperature peaks was observed; however, those peaks did not reach the levels of the previous ones. It might be a consequence of organic substrate and NH_4^+ depletion because, in this experiment, no new urine or manure was added. That NH_4^+ depletion might result in a low nitrification activity in the manure, which will also decrease denitrification; therefore, those small temperature peaks might be a result of substrate limited microbial activity. Unlike these experiments, in an open-lot beef cattle feedlot, the N inputs as urine and manure on a pen surface may be considered inexhaustible; therefore, it might be suggested that large emission peaks of GHGs are emitted after each rainfall event on dry manure surfaces.
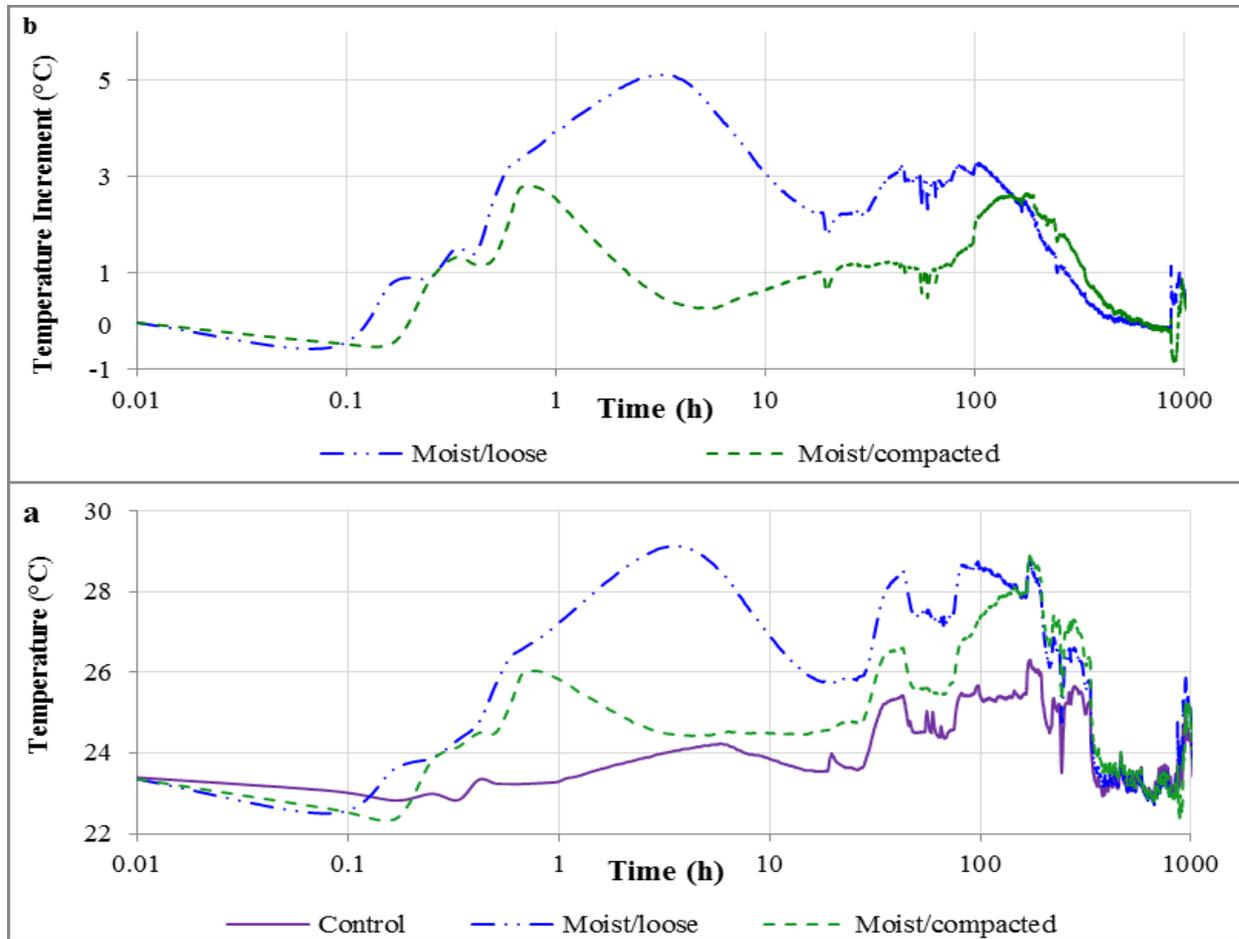
Figure 5-5 Manure temperature measured every 5 min during a 45-day period after two water applications: (a) manure temperature by treatment and (b) net temperature in the moist manure treatments with respect to the control.

5.5. Summary and Conclusions

This study evaluated the effects of water application on greenhouse gas emission fluxes from feedlot manure. The following conclusions can be drawn:

1. Emission fluxes of GHGs from dry/loose manure were significantly lower than those from moist manure. As soon as 10 min after water application on the dry manure, large peaks of emission fluxes were observed. Emission flux peaks for the moist/compacted manure were significantly lower than those for the moist/loose manure. Both the moist/loose and the moist/compacted manure showed a second set of GHG emission peaks, which were lower than the first peaks, a few days after water application.

2. Apparently, a large but short-term denitrification occurred within 10 min after water application on dry manure, this might be responsible for the large GHG emission fluxes.

3. When the manure dried and with no additional inputs of urine, feces, or water, the GHG emission fluxes decreased to the level for dry/loose manure.

4. For the moist/loose manure, direct significant correlation was found among N_2O, CH_4, and CO_2 emission fluxes with water content, temperature, and NH_4^+ content; also significant but inverse correlation was observed between those GHGs and manure pH and NO_3^- content.

5. For the moist/compacted manure, N_2O and CH_4 emission fluxes showed significant direct correlation only with manure temperature.

5.6. References

Chiyoka, W. L., X. Hao, F. Zvomuya, and X. Li. 2011. Nitrous oxide emissions from chernozemic soils amended with anaerobically digested beef cattle feedlot manure: A laboratory study. *Animal Feed Science and Technology* 166: 492–502.

Davidson, E. A. 1992. Sources of nitric-oxide and nitrous-oxide following wetting of dry soil. *Soil Science Society of America Journal* 56 (1): 95–102.

De Klein, C. A., P. McTaggart, K. A. Smith, R. J. Stevens, R. Harrison, and R. J. Laughlin. 1999. Measurement of nitrous oxide emissions from grassland soil using photo-acoustic infra-red spectroscopy, long-path infra-red spectroscopy, gas chromatography, and continuous flow isotope-ratio mass spectrometry. *Communications in Soil Science and Plant Analysis* 30(9-10): 1463–1477.

DeLaune, R. D., and K. R. Reddy. 2005. Redox potential. Gainesville, FL: University of Florida.

Ellert, B. H., and H. H. Janzen. 2008. Nitrous oxide, carbon dioxide and methane emissions from irrigated cropping systems as influenced by legumes, manure and fertilizer. *Canadian Journal of Soil Science* 88: 207–217.

Gattinger, A., M. G. Hoefle, M. Schloter, A. Embacher, F. Bohme, J. C. Munch, and M. Labrenz, 2007. Traditional cattle manure application determines abundance, diversity and activity of methanogenic Archaea in arable European soil. *Environmental Microbiology* 9(3): 612–624.

Groffman, P. M., C. W. Rice, and J. M. Tiedje. 1993. Denitrification in a tallgrass prairie landscape. *Ecology* 74 (3): 855–862.

Guo, L., R. G. Maghirang, E. B. Razote, and B. W. Auvermann. 2011. Laboratory evaluation of dust-control effectiveness of pen surface treatments for cattle feedlots. *Journal of Environmental Quality* 40: 1503–1509.

Healy R.W., R.G. Striegl, T.F. Russel, G.L. Hutchinson, and G.P. Livingston. 1996. Numerical evaluation of static-chamber measurements of soil-atmosphere gas exchange-

identification of physical processes. *Soil Science Society of America Journal* 60: 740–747.

Hofstra, N., and A. F. Bouwman. 2005. Denitrification in agricultural soils: Summarizing published data and estimating global annual rates. *Nutrient Cycling in Agroecosystems* 72 (3): 267–78

Hou, A. X., G. X. Chen, Z. P. Wang, O. Van Cleemput, and W. H. Patrick, Jr. 2000. Methane and nitrous oxide emissions from a rice field in relation to soil redox and microbiological processes. *Soil Science Society of America Journal* 64: 2180–2186.

IPCC. 2007. Working Group II Report: Impacts, Adaption and Vulnerability. IPCC Fourth Assessment Report: Climate Change 2007. Intergovernmental Panel on Climate Change. Available at: www.ipcc.ch/publications_and_data/ar4/wg2/en/contents.html. Accessed 7 October 2010.

Johnson-Beebout, S. E., O. R. Angeles, M. C. Alberto, and R. J. Buresh. 2008. Simultaneous minimization of nitrous oxide and methane emission from rice paddy soils is improbable due to redox potential changes with depth in a greenhouse experiment without plants. *Geoderma* 149: 45–53.

Kanako, K., H.U. Ronggui, T. Sawamoto, and R. Hatano. 2006. Three years of nitrous oxide and nitric oxide emissions from silandic andosoils cultivated with maize in Hokkaido, Japan. *Soil Science and Plant Nutrition* 52: 103–113.

Kanako, K., H.U. Ronggui, T. Sawamoto, and R. Hatano. 2008. Comparison of the closed-chamber and gas concentration gradient methods for measurement of CO_2 and N_2O fluxes in two upland field soils. *Soil Science and Plant Nutrition* 54: 777–785.

Kanako, K., T. Sawamoto, and R. Hatano. 2002. Nitrous oxide emissions for 6 years from a gray lowland soil cultivated with onions in Hokkaido, Japan. *Nutrient Cycling in Agroecosystems* 63: 239–247.

Klein, C. A. M., and R. S. P. Logtestijn. 1994. Denitrification and N_2O emission from urine-affected grassland soil. *Plant and Soil* 163(2): 235–241.

Lee, J., J. W. Hopmans, C. van Kessel, A. P. King, K. J. Evatt, D. Louie, D. E. Rolston, and J. Six. 2008. Tillage and seasonal emissions of CO_2, N_2O, and NO across a seed bed and at the field scale in a Mediterranean climate. *Agriculture, Ecosystems & Environment* 129: 378–390.

Li, C. 2007. Quantifying greenhouse gas emissions from soils: Scientific basis and modeling approach. *Soil Science and Plant Nutrition* 53(4): 344–352.

Li, C., W. Salas, R. Zhang, C. Krauter, A. Rotz, and F. Mitloehner. 2012. Manure-DNDC: a biogeochemical process model for quantifying greenhouse gas and ammonia emissions from livestock manure systems. *Nutrient Cycling in Agroecosystems* 93(2): 163–200.

Marinho, E. V. A., R. D. Delaune, and C. W. Lindau. 2004. Nitrous oxide flux from soybeans grown on Mississippi alluvial soil. *Communications in Soil Science and Plant Analysis* 35(1): 1–8.

Mayer, H.P., and R. Conrad. 1990. Factors influencing the population of methanogenic bacteria and the initiation of methane production upon flooding of paddy soil. *FEMS Microbiology Ecology* 73 (2): 103–11.

Mikha, M. M., C. W. Rice, and G. A. Milliken. 2005. Carbon and nitrogen mineralization as affected by drying and wetting cycles. *Soil Biology & Biochemistry* 37: 339–347.

Milliken, G. A., and D. E. Johnson. 2009. *Analysis of Messy Data Vol. 1: Designed Experiments*. 2nd ed. New York, NY: Taylor & Francis Group.

Mosier, A., C. Kroeze, C. Nevison, O. Oenema, S. Seitzinger, and O. van Cleemput. 1998. Closing the global N_2O budget: nitrous oxide emissions through the agricultural nitrogen cycle. *Nutrient Cycling in Agroecosystems* 52: 225–248.

National Research Council (NRC). 1993a. *In Situ Bioremediation - When Does It Work?* Washington, DC: The National Academies Press.

National Research Council (NRC). 1993b. *Soil and Water Quality: An Agenda for Agriculture*. Washington, DC: The National Academies Press.

Parkin, T. B., and T. C. Kaspar. 2006. Nitrous oxide emissions from corn-soybean systems in the Midwest. *Journal of Environmental Quality* 35: 1496–1506.

Paul, E.A. 2007. *Soil Microbiology, Ecology, and Biochemistry*. 3rd ed. Burlington, MA: Academic Press.

R Project. 2012. *Ver. 2.15.1 (Roasted Marshmallows)*. Nashville, TN: The R Project for Statistical Computing.

Raupach M., and P. Fraser. 2011. Chapter 2: Climate and greenhouse gases. CSIRO Publishing. Available at http://dx.doi.org/10.1071/CSIRO_CC_Chapter 2. Accessed 29 June 2012.

Razote, E.B., R. G. Maghirang, B. Z. Predicala, J. P. Murphy, B. W. Auvermann, J. P. Harner III, and W. L. Hargrove. 2006. Laboratory evaluation of the dust-emission potential of cattle feedlot surfaces. *Transactions of the ASABE* 49(4): 1117–1124.

Saggar, S., R. M. Andrew, K. R. Tate, C. B. Hedley, N. J. Rodda, and J. A. Townsend. 2004. Modeling nitrous oxide emissions from dairy-grazed pastures. *Nutrient Cycling in Agroecosystems* 68: 243–255.

SAS. 2008. *SAS/STAT 9.2 User's Guide.* Cary, NC: SAS Institute, Inc.

Scholes, M. C., R. Martin, R. J. Scholes, D. Parsons, and E. Winstead. 1997. NO and N_2O emissions from savanna soils following the first simulated rains of the season. *Nutrient Cycling in Agroecosystems* 48 (1-2): 115–122.

Segers, R. 1998. Methane production and methane consumption: a review of processes underlying wetland methane fluxes. *Biogeochemistry* 41: 23–51.

Stackhouse, K. R., Y. Pan, Y. Zhao, and F. M. Mitloehner. 2011. Greenhouse gas and alcohol emissions from feedlot steers and calves. *Journal of Environmental Quality* 40(3): 899–906.

Taghizadeh-Toosi, A., T. J. Clough, L. M. Condron, R. R. Sherlock, C. R. Anderson, and R. A. Craigie. 2011. Biochar incorporation into pasture soil suppresses in situ nitrous oxide emissions from ruminant urine patches. *Journal of Environmental Quality* 40: 468–476.

Woodbury, B. L., D. N. Miller, J. A. Nienaber, and R. A. Eigenberg. 2001. Seasonal and spatial variations of denitrifying enzyme activity in feedlot soil. *Transactions of the ASAE* 44(6): 1635–1642.

Chapter 6 - Evaluation of Photo-acoustic Infrared Multi-gas Analyzer in Measuring Concentrations of N_2O and CO_2 Emitted from Feedlot Manure

6.1. Abstract

Measurement of emission fluxes of greenhouse gases (i.e., N_2O, CO_2, and CH_4) at the soil surface with photo-acoustic infrared multi-gas analyzers (PIMAs) is becoming more popular because of cost, portability, and ease of operation. This research evaluated the PIMA, in combination with static flux chambers (SFCs), in measuring the concentrations of N_2O and CO_2 emitted from beef cattle feedlot manure. The concentrations of N_2O and CO_2 emitted from feedlot manure were measured simultaneously using a gas chromatograph (GC) and PIMA. The GC and PIMA were significantly correlated but differed in measured concentrations. The PIMA showed generally lower N_2O concentrations and greater CO_2 concentration than the GC. Linear regression equations were developed between the GC and PIMA and then verified using data from a related experiment.

6.2. Introduction

Non-steady-state chambers or static flux chambers (SFCs) have been the most widely used method in measuring emission fluxes of trace gases from soil surfaces (Conen and Smith, 2000; Hutchinson et al., 2000; Kroon et al., 2008; Venterea, 2010) because of their simplicity, ease of fabrication (De Klein, et al., 1999; Reichman and Rolston, 2002), low cost, and ease of operation (Healy et al., 1996). No other method has contributed more to the current knowledge of the magnitude and temporal and spatial variability of emission fluxes of trace gases, including GHGs, as well as their biochemical and biophysical processes and control (Livingston et al., 2006; Livingston et al., 2005). Static flux chambers were identified as the method of choice for measuring trace gas fluxes at Long-Term Ecological Research (Hutchinson and Livingston, 2001); and it has been well established that chamber technique is the best way to assess spatial variability of surface emissions (Guimbaud et al., 2011).

The SFCs are often used in combination with GC analysis. The technique generally requires field sample collection and transport to a laboratory for GC analysis (Predotova et al., 2011). Consequently, this technique is time-consuming and the results are commonly obtained

several days after field sampling. Another technique that is becoming more common involves use of real-time measuring instruments, including the photo-acoustic infrared multi-gas analyzer (PIMA) (Ambus and Robertson, 1998; Yamulki and Jarvis, 1999; Cayuela et al., 2010a). The PIMA is a portable and accurate gas monitor commonly used to measure concentrations in air and stack emissions of almost any gas that absorbs infrared radiation (California Analytical Instruments, 2012). Using a PIMA in combination with the SFC allows rapid collection of larger data sets of several gases simultaneously and their immediate analysis *in situ* (Predotova et al., 2011). The portability of PIMA, the rapid and ease of measurement, linearity of gas concentrations, and capacity of measuring up to five gases simultaneously are significant advantages over the GC (De Klein et al., 1999; Iqbal et al., 2012).

More researchers rely on the use of PIMA for the measurement of gases both at laboratory and field applications. Most of the research has been conducted on soil surfaces; no published research has compared GCs and PIMAs in beef cattle feedlots. Cayuela et al. (2010a) evaluated the effect of organic animal by-product wastes and a commercial mineral fertilizer as soil amendments on N_2O and CO_2 emissions from agricultural soils. Cayuela et al. (2010b) evaluated the impact of bioenergy by-products as soil amendments on GHG. Predotova et al. (2011) assessed the effect of several materials used for static flux chamber construction, on NH_3^-, CH_4, CO_2, and N_2O concentration readings. Predotova et al. (2010) determined emissions of NH_3, N_2O, and CO_2 from urban gardens. Osada and Fukumoto (2001) assessed emissions of NH_3, CH_4, and N_2O from composting livestock waste; they reported that measured values of those gases obtained from the PIMA technique compared to the respective values obtained from conventional methods (i.e., sulfuric acid trap for NH_3 and GC for CH_4 and N_2O) showed small differences when total emissions from composting swine waste were compared. Ambus and Robertson (1998) also reported that N_2O and CO_2 fluxes based on gas concentrations measured with both methods were not significantly different. Nevertheless, Akdeniz et al. (2009) reported significant differences between N_2O concentrations measured with both methods. Iqbal et al. (2012) tested six PIMAs simultaneously connected to a SFC and compared those results to gas concentrations from GC analysis. They reported that soil gas flux computation based on gas concentrations simultaneously measured with both a SFC/PIMA and a SFC/GC were similar; they also reported that linear regression between the fluxes computed by those two methods had $R^2 > 0.99$.

More research is needed to evaluate the PIMA in measuring GHG concentrations. This research is expected to contribute to the still limited data on the use of PIMA, in combination with SFCs, in measuring the concentrations of GHGs emitted from open beef cattle feedlots. The major objective of this research was to evaluate the PIMA in measuring the concentrations of N_2O and CO_2 emitted from beef cattle feedlot manure, under both field and laboratory conditions. Greenhouse gases analyzed were N_2O and CO_2 and data were obtained from field and laboratory experiments that are described in other chapters of this thesis.

6.3. Materials and Methods

To compare the GC and the PIMA, data from three research studies were analyzed. The first study was a field study to quantify the N_2O emission flux from pen surfaces in a commercial beef cattle feedlot (Chapter 3).The second study was conducted under controlled laboratory conditions to evaluate the effectiveness of surface amendments in mitigating GHG emissions from feedlot manure (Chapter 4). The third study was a controlled laboratory study that was designed to determine the effects of water application on GHG emissions from feedlot manure (Chapter 5). In all three studies, SFCs were used and the concentrations of N_2O and CO_2 were measured using a PIMA. In addition, gas samples were collected from the SFCs and analyzed in the laboratory using a GC. A total of 1708 paired (GC and PIMA) concentration values were collected. Because of GC calibration limitations, samples in which N_2O concentrations were larger than 100 ppm from the GC were not considered. Data were also screened for outliers. A total of 1646 paired data points of gas concentrations of N_2O and 1685 paired data points of CO_2 concentrations were used in this study. Approximately 70% of the data was used for regression analysis and the remaining 30% was set aside for verification of the regression equation.

6.3.1. Studies

The first study involved field measurements in which SFCs were used to sample GHGs from pen surfaces in a beef cattle feedlot. Details of the SFC design, experimental setup, and measurement protocol are presented in Chapter 3. For the GC method, gas samples were collected from the SFC headspace using 20 mL disposable plastic syringes and injected into evacuated 12-cc glass vials. During sampling, six 20-cc samples were drawn from each SFC headspace at time intervals of 0, 5, 10, 15, 20, and 30 min. Gas samples were analyzed for N_2O concentrations using a GC (Model GC-14B, Shimadzu Scientific Instrument, Columbia, MD)

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with a Porapak-Q (80/100 mesh) stainless steel column (0.318-cm dia. by 1 m length) and an electron-capture detector (ECD); carrier gas was UHP/zero nitrogen. The oven, injector, and detector temperatures set up were 60, 100, and 300°C respectively. For CO_2 concentrations, gas samples were analyzed in a GC (Model GC-8A, Shimadzu CR-501Chromatopac) fitted with a thermal conductivity detector (TCD); the carrier gas was UHP/zero Helium. The oven, injector/detector temperatures were set at 65°C and 160°C, respectively.

For the PIMA method, the same SFCs were simultaneously connected by two-1.0 m long Teflon tubes as inflow and outflow to a PIMA (Model 1312, Innova AirTech Instruments, Ballerup, Denmark), as shown in Figure 6-1a. The PIMA was equipped with optical filters for measuring N_2O, CH_4, CO_2, NH_3, and water vapor and set up to compensate for the cross-interference of water vapor with N_2O and CO_2. The PIMA collected concentration data every 50 ± 2 s during the 30-min sampling period for each SFC, for a total of 36 concentration readings for each gas. The first two concentration readings were considered part of the initial flushing of the PIMA sampling lines and therefore discarded. From the remaining 34 gas concentration readings, the concentrations corresponding to times 0, 5, 10, 15, 20, and 30 min were used to compare with those from the GC analysis. At least a 10-min period elapsed between chambers sampling allowing ambient air to purge the PIMA.

In the second study, three out of the six laboratory experiments described in Chapter 4 were set up to measure GHG concentrations using both methods. Those experiments evaluated the effect of topical application of: (1) organic residues and biochar on moist manure, (2) biochar and activated carbon on moist manure, and (3) organic residues and biochar on dry manure. The third study evaluated the effect of water application on GHG emissions from feedlot manure (Chapter 5). The GHG concentrations were measured with both methods. The experimental set up of the second and third studies are described in Chapters 4 and 5, respectively. Briefly, as shown in Figure 6-1b, 1-L glass containers were used as SFCs and a PIMA was connected by two 0.5-m long Teflon tubes as inflow and outflow to the containers. In order to account for the headspace gas equilibrium due to diffusion of gases from the manure, the gas sampling interval was shortened to 10 min (Predotova et al., 2010). During sampling, the PIMA collected 12 readings of N_2O and CO_2 concentrations. The first gas concentration reading was discarded. Each sampling interval was followed by a 5-min purging period, allowing fresh air to purge the PIMA before continuing the measurement to the next container. Concentrations corresponding to

the syringe sampling times were used to compare with those from the GC analysis. For GC analysis, 15-cc gas samples were collected from the container headspace using 20-mL disposable plastic syringes and placed into evacuated 12-mL glass vials at time intervals of 0, 5, and 10 min. A total of 1388 concentration measurements of N_2O and CO_2 were obtained.
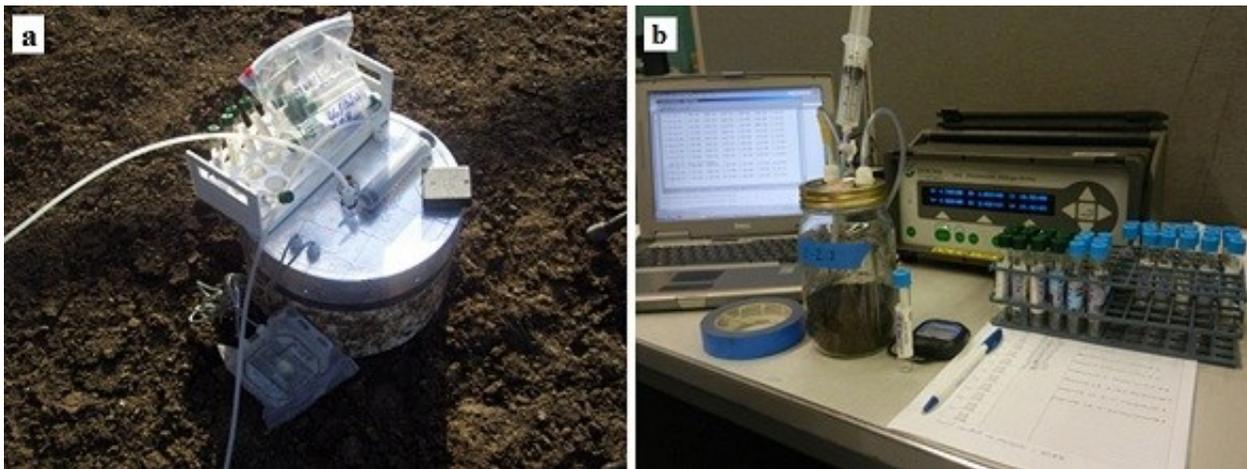
Figure 6-1 Photographs of the experimental set up: (a) field measurement with a static flux chamber and (b) laboratory set up.

6.3.2. PIMA and GC calibration

The PIMA was calibrated in accordance with the manufacturer's recommendations (Luma Sense Technologies, 2009) using standard calibration gases and diluter with dry air. For the water-vapor filter, zero-point calibration using zero-gas (zero air N_2) and span-gas calibration (with a known concentration of water vapor) were performed. Full calibration of each optical filter consisted of zero-point calibration, humidity interference calibration, cross interference calibration, and span-gas calibration. Consequently, each optical filter was corrected for zero, water vapor interference, cross interference compensation among the other gases being measured, and against known concentrations of standard calibration gases on each measured compound.

Calibration curves of the GC for CO_2 analysis were obtained each time a new set of air samples were analyzed or when more than two days elapsed between gas analysis. Fixed volumes (0.2, 0.4, 0.6, 0.8, and 1.0 cc) of standard CO_2 gas (10,000 ppm) were consecutively injected into the GC and analyzed for CO_2 concentration. Linear regression analysis was

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conducted between the peak areas of the chromatograms and their respective CO_2 masses. At least four different sets of CO_2 standard gas were analyzed each time, resulting in a linear calibration curve for each set. An additional set of four 0.5-cc standard gas was analyzed in the GC and the average of those four peak areas was taken for validation of the complete set of calibration curves. The calibration curve that reported the smallest difference in concentration compared to the standard gas was selected for the respective batch of unknown samples being analyzed.

Regression analysis was performed with four N_2O standard gas concentrations (0.035, 3.5, 6, and 60 ppm) and their respective peak areas of the chromatograms. The analysis was performed by a peak area integrator incorporated to the GC. The GC instrumental set up reported directly N_2O concentrations in ppm. This calibration was performed once at the beginning of each measuring season. Every day before gas analysis, a set of four 3.5-cc of 3.5 ppm standard gas was analyzed in the GC for calibration validation purposes. During gas analysis, before and after every batch (6 to 9 unknown gas samples), the calibration of the GC was validated based on injection of at least two 3.5-ppm standard gas. Validation of calibration was considered good if results were within ±5% difference compared to the N_2O standard gas injected. When results were out of the accepted range, the integrator was adjusted based on the current reported peak area for the N_2O standard gas used as validation.

6.3.3. Statistical analysis

From the gas concentration values from the GC and/or PIMA, emission fluxes can be determined following the procedure outlined in Chapters 3 and 4. For example, from the GC measurements in the field study, emission fluxes for each SFC can be calculated using three different sets of gas concentration readings (i.e., 0-5-10 min, 0-10-20 min, and 0-15-30 min). Preliminary analysis of N_2O data, however, showed that the three emission fluxes were significantly different. It appears then the calculated emission flux depends on the flux computation approach; as such, this chapter focused on the gas concentration readings, rather than the computed emission fluxes. Gas concentrations from the two measurement methods were analyzed for correlation, linear regression, and paired comparison by Proc Corr, Proc Reg, and Proc Ttest of SAS (SAS, 2008), respectively. The level of significance was set at $\alpha=5\%$.

6.4. Results and Discussion

Data obtained from Study 1 (field) and from Study 2 - experiment 2 resulted in mostly low N_2O concentrations with respective mean values of 0.76 and 0.84 ppm, measured with the GC method. Data from Study 2 –experiments 2 and 3 resulted in very low N_2O concentrations (means= 0.84 and 0.56 ppm, respectively), while data from Study 3 resulted in mostly high N_2O concentrations (mean= 3.24 ppm). Moreover, data from Study 2 - experiment 1 had a range from low to high N_2O concentrations (mean= 12.54 ppm). Table 6-1 summarizes those results. Data from Study 1, Study 2- experiments 2 and 3, and from Study 3 were used for the regression analysis between the GC and PIMA. Because the Study 2 - experiment 1 had the widest range of N_2O concentrations, which included the N_2O field range (Chapter 3), and the largest experimental data set (n=643 for N_2O and n=647 for CO_2), 75% of the data from this experiment was used for verification of the regression analysis.

Table 6-1 Summary of measured gas concentrations using the GC.

Experiment	N_2O (ppm)				CO_2 (ppm)			
	N	Minimum	Mean	Maximum	N	Minimum	Mean	Maximum
Study 1 – Field	277	0.31	0.76	3.29	306	543	3729	17143
Study 2- Experiment 1	643	0.54	12.54	91.7	647	443	26.31	11059
Study 2- Experiment 2	185	0.56	0.84	4.75	185	426	1936	6393
Study 2- Experiment 3	360	0.33	0.56	1.19	360	426	767	1221
Study 3	181	0.4	3.24	90.34	187	395	2508	8218

Paired t-test indicated that N_2O concentrations measured with PIMA and GC were significantly different ($p \leq 0.001$). Results showed that the GC measurements of N_2O were consistently higher than the PIMA measurements, similar to the observations reported by De Klein et al. (1999). Yamulki and Jarvis (1999) reported N_2O fluxes measured with PIMA were higher by a factor of 1.4. When the gas concentrations measured with PIMA and GC were compared, the overall mean N_2O concentration measured with PIMA was 41.9% lower than that measured with GC (Table 6-2). Iqbal et al. (2012) also reported that absolute differences between the two N_2O measurements methods were larger as N_2O concentrations decreased.

The overall mean CO_2 concentration measured with PIMA was 6.6% larger than that measured with GC. Paired t-test also indicated that the measurement methods were significantly different ($p \leq 0.001$).

Table 6-2 Differences in gas concentrations measured by PIMA and GC methods.

N$_2$O			CO$_2$		
Range of PIMA Measurement (ppm)	Difference (%) †	Sample (n)	Range of PIMA Measurement (ppm)	Difference (%) †	Sample (n)
0 ≤ PIMA ≤ 1	- 28.2	684	0 ≤ PIMA ≤ 1000	-16.3	595
1 < PIMA ≤ 5	9.3	413	1000 < PIMA ≤ 5000	12.0	439
5 < PIMA ≤ 10	- 65.7	37	5000 < PIMA ≤ 10000	10.8	146
10 < PIMA ≤ 40	- 63.6	24	10000 < PIMA ≤ 16000	11.0	13
0 ≤ PIMA ≤ 40	- 41.9	1158	0 ≤ PIMA ≤ 16000	6.6	1193
0 ≤ PIMA ≤ 40	- 12.2 ‡	488	0 ≤ PIMA ≤ 16000	3.1 ‡	492

† Difference between the two methods was computed as the difference between PIMA and GC as a proportion of the GC measurement. Negative difference means that the PIMA concentration was lower than the GC concentration for that gas concentration range.

‡ Computed from validation of the linear regressions obtained from 1158 and 1193 data points of N_2O and CO_2, respectively.

Even though individual paired gas concentrations of N_2O and CO_2 measured with PIMA and GC were significantly different, there was significant correlation between the measurement methods for N_2O and CO_2 concentrations. Table 6-3 summarizes the correlation between PIMA and GC methods on the concentrations of N_2O and CO_2 emitted from feedlot manure. When measured gas concentrations were low (<1.0 ppm for N_2O or <1,000 ppm for CO_2), the Pearson correlation coefficients were lower (<0.40). Nitrous oxide concentrations larger than 10 ppm resulted in Pearson correlation coefficients larger than 0.80. In the case of CO_2, concentrations larger than 5000 ppm resulted in Pearson correlation coefficients larger than 0.90. In general, the Pearson correlation coefficient was lower at low gas measured concentrations than at larger concentrations.

Table 6-3 Pearson pairwise correlation between PIMA and GC GHG measurements.

PIMA Gas Concentration Interval (ppm) †	PIMA/GC Correlation	
	N_2O ‡	CO_2 ‡
$N_2O \leq 1$	0.39 (<0.0001)	
$N_2O \leq 5$	0.60 (<0.0001)	
$N_2O \leq 10$	0.83 (<0.0001)	
$N_2O \leq 100$	0.96 (<0.0001)	
$CO_2 \leq 1000$		0.33 (<0.0001)
$CO_2 \leq 5000$		0.88 (<0.0001)
$CO_2 \leq 10000$		0.91 (<0.0001)
$CO_2 \leq 15000$		0.92 (<0.0001)

Data from the Study 1-Field and from Study 2 (Experiments 2 and 3) and Study 3.
† Interval of the GHG measured with PIMA.
‡ Values represent Pearson Correlation Coefficients and their respective p-values (in parentheses).

Linear regression analysis on data from Study 2 - experiment 1 (moist manure, Figs. 6-2b and d) and from experiment 3 (dry manure, Figs. 6-2a and c) indicated that the drier the manure, the lower the R^2 value of the linear relationship between the GC and PIMA concentrations. Dry manure pen surfaces have small GHG emission fluxes (Chapters 3 and 5). Even though all linear regressions (Fig. 6-2) were significant (α= 5%), when field conditions were dry, with small GHG fluxes and small N_2O and CO_2 concentrations, the PIMA did not agree well with the GC. Nevertheless, gas concentrations from the PIMA, on dry or moist soil conditions, generally showed a smooth increase with time (Fig. 6-3). However, gas concentrations obtained through the GC method did not show that stable increment of concentrations with time, neither on dry nor on moist manure conditions. Both N_2O and CO_2 exhibited linear response, close to unity, for a wide range of concentrations measured with the PIMA, as also described by Ambus and Robertson (1998), Iqbal et al. (2012), and Yamulki and Jarvis (1999).
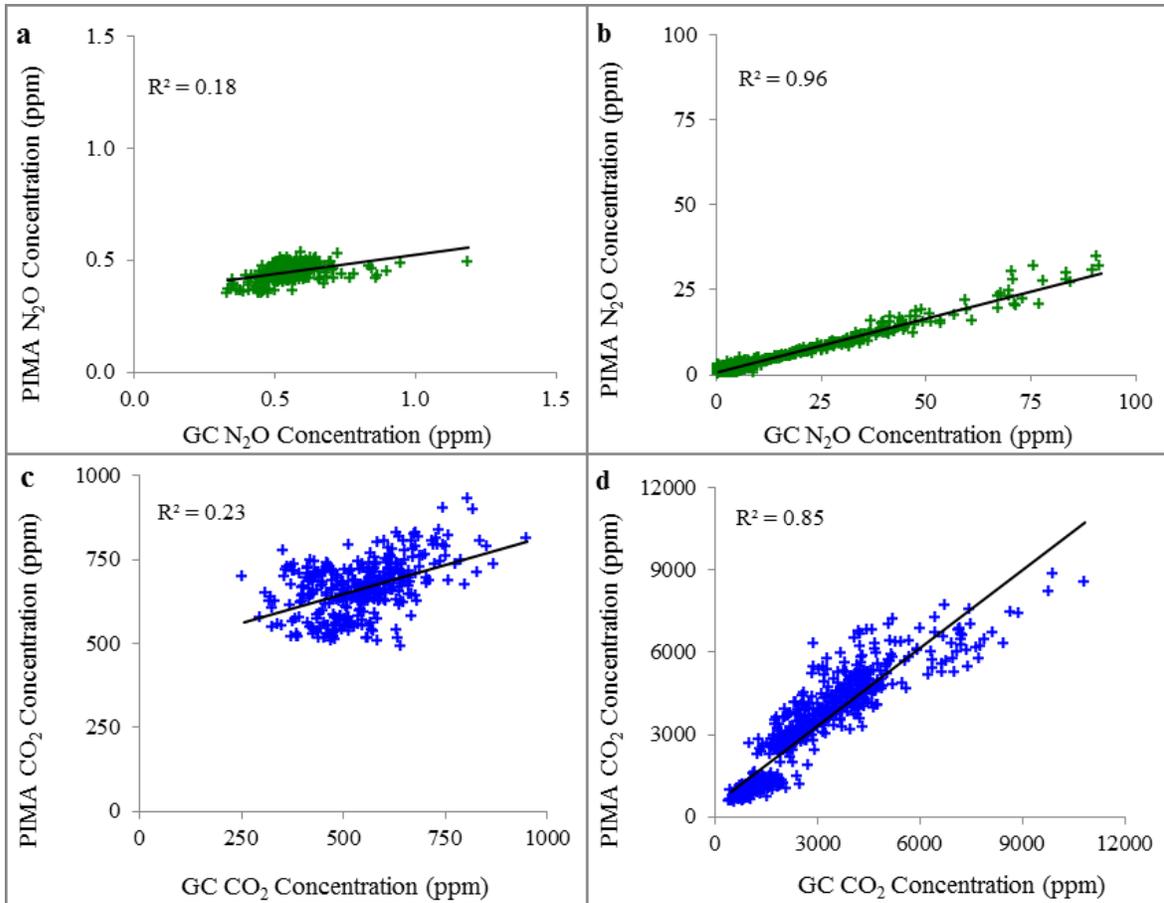
Figure 6-2 Linear regression between GHG concentrations measured by the GC and PIMA in two laboratory experiments: (a) low N_2O concentration measured in dry manure, (b) large N_2O concentration measured in moist manure, (c) low CO_2 concentration measured in dry manure, and (d) large CO_2 concentration measured in moist manure.
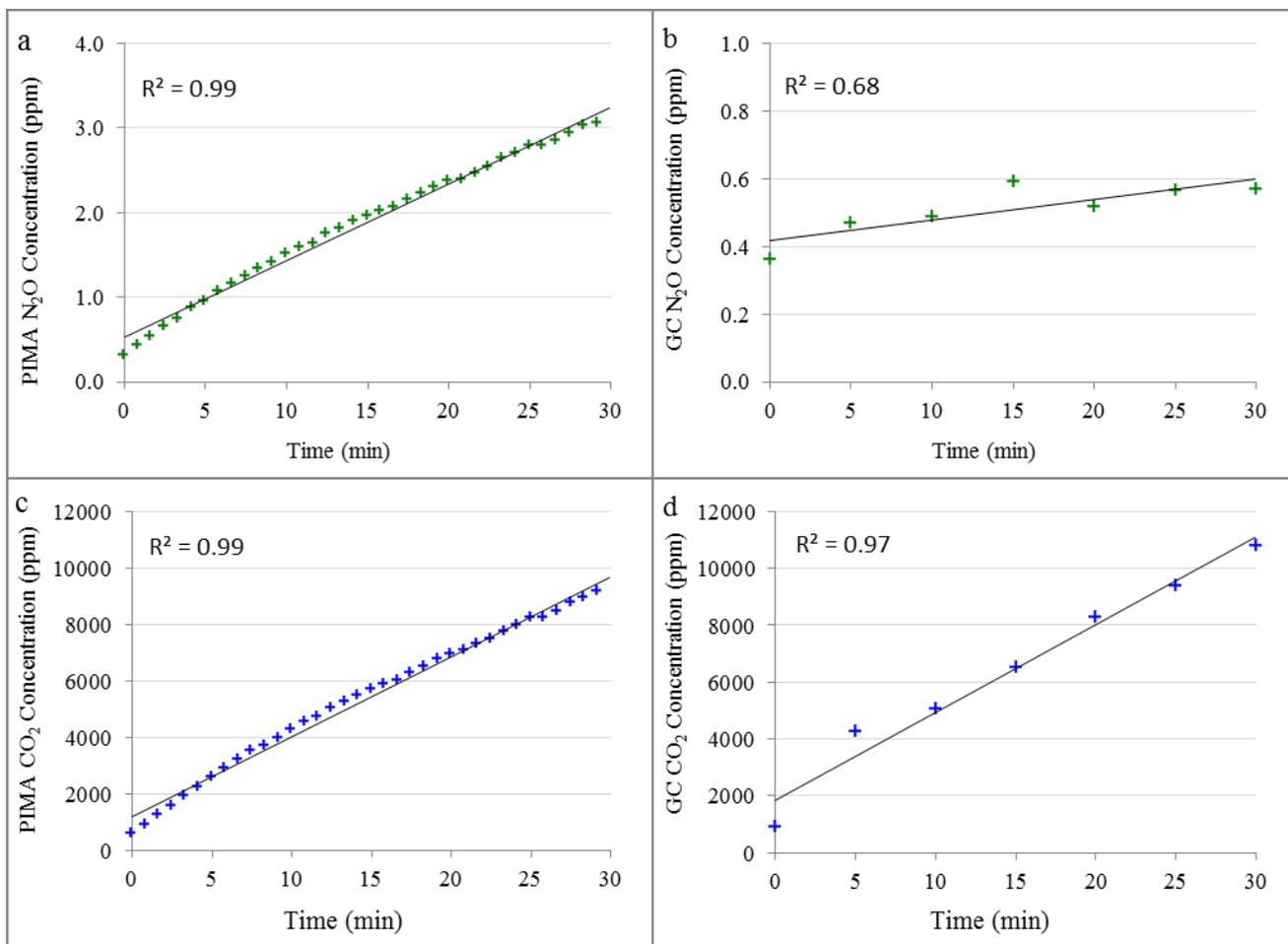
Figure 6-3 Typical regression between GHG concentrations and time in the chamber headspace: (a) N_2O measured with the PIMA, (b) N_2O measured with the GC, (c) CO_2 measured with the PIMA, and (d) CO_2 measured with the GC.

Linear regression was tested using paired data points from GC and PIMA measurements of N_2O and CO_2 gas concentrations (Fig. 6-4). The linear regressions were significant ($p < 0.001$) with R^2 values of 0.93 and 0.85 for N_2O and CO_2, respectively. The relationship between the GC and PIMA in N_2O and CO_2 concentrations can be described by the equations obtained from linear regression as shown in Figure 6-4. The 95% CI for the intercept / slope of N_2O and CO_2 are respectively as follows: (0.62 to 0.73) / (0.34 to 0.35) and (125 to 273) / (0.95 to 1.00).
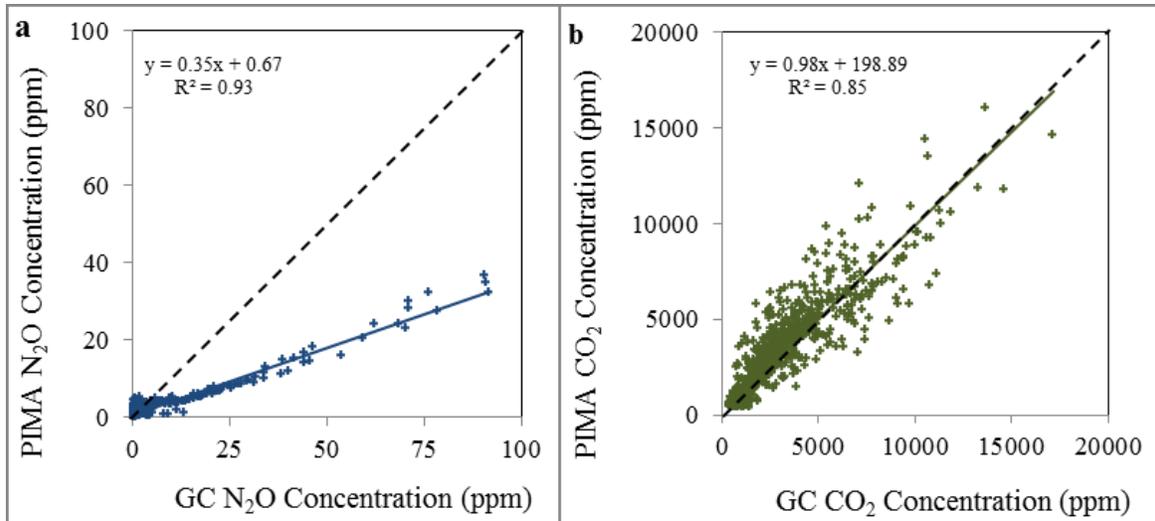
Figure 6-4 Linear regression between GHG concentrations measured by both GC and PIMA: (a) N_2O and (b) CO_2 concentrations. Solid lines represent the least-squares regression lines, while dashed lines represent 1:1 correspondence.

The residual plot in Figure 6-5a shows that for N_2O, the data were more disperse at concentrations lower than 5 ppm and for concentrations greater than 10 ppm. Between 5 and 10 ppm, N_2O concentrations measured with the GC were consistently larger than those measured with the PIMA. For CO_2, on the other hand, the data dispersion increased as CO_2 gas concentrations measured with the PIMA method increased (Fig. 6-5b). When the regression lines are forced to pass through the origin (0), the equations indicated that N_2O concentrations measured with the PIMA were consistently 2.7 times lower than the N_2O measured with the GC. The CO_2 concentrations measured with the PIMA were consistently 1.02 times larger than the CO_2 measured with the GC.
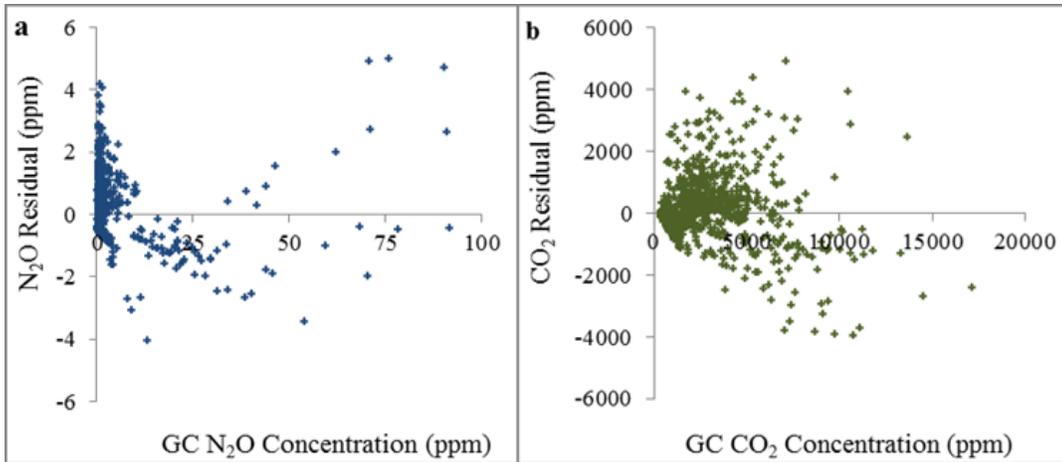
Figure 6-5 Residual plots for (a) N_2O and (b) CO_2 concentrations.

When the linear equations were verified with the validation data set (Fig. 6-6), there was no significant difference between means of measured (PIMA) and predicted N_2O concentrations. Mean of measured CO_2 concentrations with PIMA was also not significantly different from the predicted CO_2 concentrations. Figures 6-6a and c plot the relationships between the two methods for the verification data set both for N_2O and CO_2, respectively; similar trends as in the previous data set can be seen (Figs. 6-4 and 6-6). When the regression equations were applied on the verification data set, there was better agreement between GC and PIMA measurement methods (Fig. 6-6b and d). The overall mean N_2O and CO_2 gas concentrations measured with PIMA were 12.2% lower and 3.1% larger than the average predicted values, respectively.
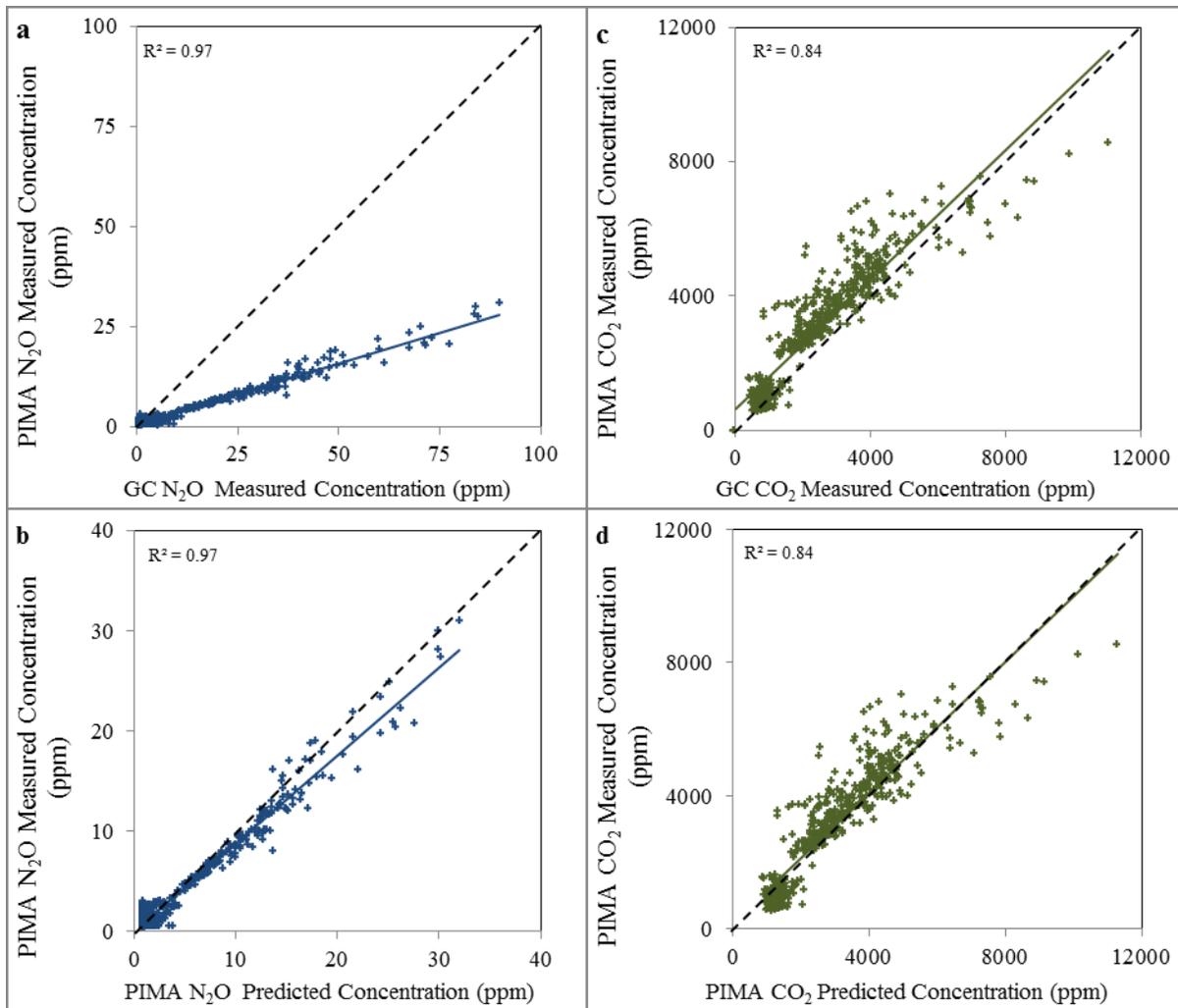
Figure 6-6 Verification of the linear regression equations: (a) actual relationship between GC and PIMA N_2O measurement methods, (b) linear regression between predicted N_2O PIMA and measured N_2O PIMA, (c) actual relationship between GC and PIMA CO_2 measurement methods, and (d) linear regression between predicted CO_2 PIMA and measured CO_2 PIMA. Solid lines represent the least-squares regression lines, while dashed lines represent 1:1 correspondence.

Verification of field data from the commercial open-lot beef cattle feedlot was also intended. In this case, the data were configured such that the complete data set from the laboratory experiments (Study 2 - Experiments 1, 2, 3 and Study 3) were used for the regression analysis, while data from Study 1 - Field were used for verification. Because the range of the laboratory data were from low to very high N_2O concentrations and data from the field, obtained under dry manure conditions, had low N_2O concentrations (Table 6-1), there was no good agreement of N_2O measured by the two methods (Figs. 6-7a and b). However, CO_2

concentrations measured by the two methods showed better agreement (Figs. 6-7c and d). Therefore, a complete data set within the field range, from low to medium (50 ppm) of N_2O concentrations is needed to compute the relationship between both measurement methods. To be able to validate those relationships, a second data set of GHG concentrations obtained directly from the field is desirable.
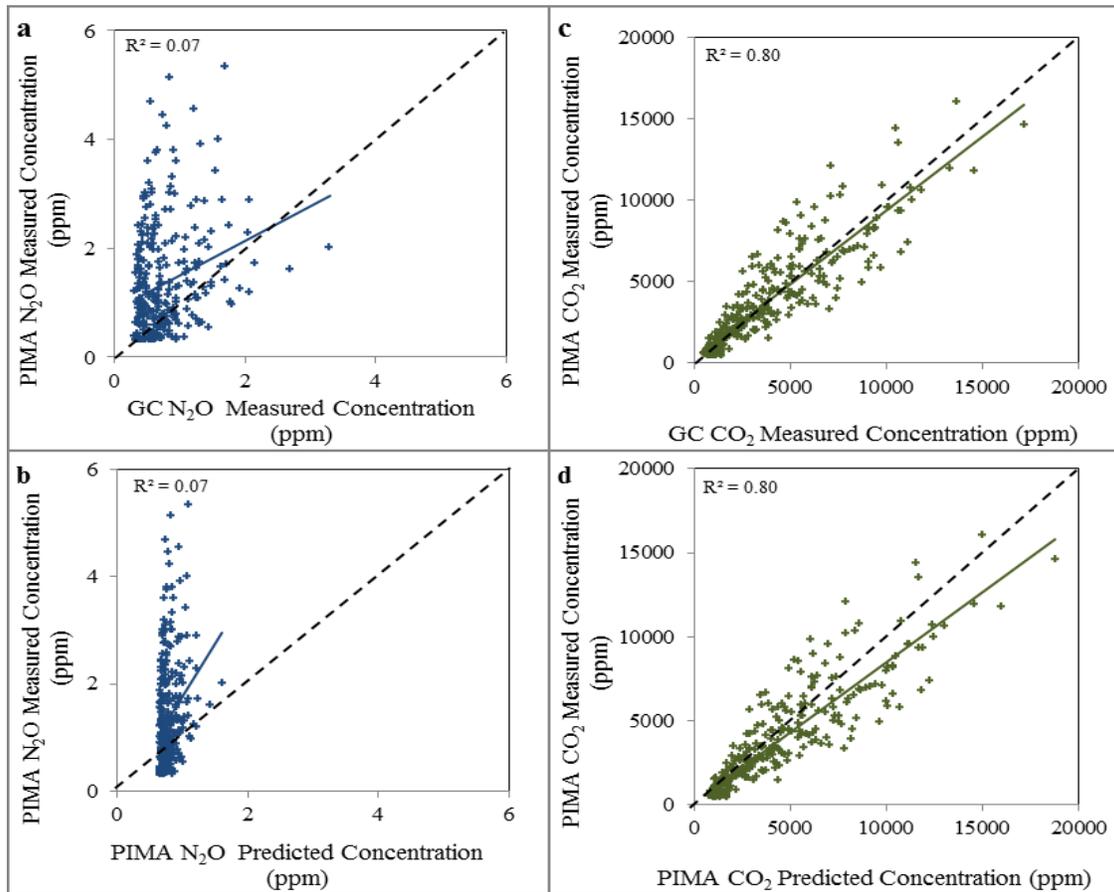
Figure 6-7 Verification of the linear regression equations with a field data set: (a) measured N_2O concentrations - GC vs. PIMA, (b) predicted vs. measured N_2O concentrations - PIMA, (c) measured CO_2 concentrations – GC vs. PIMA, and (d) predicted vs. and measured CO_2 concentration - PIMA. Solid lines represent the least-squares regression lines, while dashed lines represent 1:1 correspondence.

Linear regression between N_2O fluxes computed from N_2O concentrations measured with PIMA and GC has been reported (Ambus and Robertson, 1998; Yamulki and Jarvis, 1999). Both studies reported different linear regression equations. Linear regression has been also reported for CO_2 fluxes computed from PIMA and GC concentration measurements (Ambus and

Robertson, 1998). From the linear regression, Ambus and Robertson (1998) reported a factor of 1.05 to compare both N_2O flux measurement in the range of fluxes typically observed in cropping systems i.e., 0.30, 0.16, 0.133, with peak of 0.67 mg m^{-2} h^{-1}, as reported by Kanako et al, 2006; Kanako et al., 2002; Lee et al., 2008; Saggar et al., 2004, respectively.

In this study, N_2O concentrations were measured on dry and moist manure from beef cattle pen surfaces. Fluxes from moist manure in beef cattle feedlots have been reported as much as 20 times larger than fluxes from cropping soils (Chapter 3). When the GC is used for N_2O analysis, saturation of the ECD at high N_2O concentrations may result in non-linear relationship (Yamulki and Jarvis, 1999). Because this study dealt with high N_2O concentrations, it might be expected to have larger differences between the PIMA and GC.

Individual differences on N_2O gas concentrations measured with PIMA and GC were larger than in previous studies; there was no obvious explanation for this discrepancy, as also reported by De Klein et al. (1999) and Yamulki and Jarvis (1999). In explaining those differences, some researchers have reported that crossed-interferences between CO_2 and water vapor with N_2O negatively affected the N_2O measurement with the PIMA (Akdeniz et al., 2009; Yamulki and Jarvis, 1999). However, other researchers suggested that the differences between methods were a consequence of calibration error rather than CO_2 and water vapor interference with N_2O (Iqbal et al., 2012). Ambus and Robertson (1998) also reported no CO_2 and water vapor cross-interference with N_2O gas measurements through the PIMA method.

In this study, the accuracy of the PIMA calibration stability over time was unknown. Furthermore, regarding GC analysis, the potential error associated with gas standards used for GC calibration (Iqbal et al., 2012) as well as potential contamination of the carrier gas, GC needs of maintenance, GC calibration accuracy, and gas sample manipulation, could yield significant bias in the GC gas analysis. Even though GC technique has been the most common method to measure N_2O and CH_4, and to assess emission fluxes, it is quite difficult to determine which method is closer to the true value, as reported by Iqbal et al. (2012).

6.5. Summary and Conclusions

This research evaluated a photo-acoustic infrared multi-gas analyzer attached to static flux chambers for the measurement of N_2O and CO_2 concentrations from feedlot manure, under

both field and laboratory conditions, in comparison with gas chromatography. The following conclusions are drawn:

1. Paired t-test on the data set indicated that the GC and PIMA measurement methods of N_2O and CO_2 gas concentrations were significantly different. The mean N_2O concentration measured with PIMA was 41.9% lower than that measured with the GC. The mean CO_2 concentration measured with PIMA, on the other hand, was 6.6% larger than that measured with the GC. The PIMA and GC measurement methods for N_2O and CO_2 concentrations were significantly correlated and linearly related (R^2=0.93and 0.85 for N_2O and CO_2, respectively).

2. Verification of the linear regression equations with data set from a related experiment showed good agreement between predicted and measured concentrations of N_2O and CO_2.

6.6. References

Akdeniz, N., L. D. Jacobson, B. P. Hetchler, R. T. Venterrea, and K. A. Spokas. 2009. Measurement of nitrous oxide concentrations from Wisconsin dairy barns. ASABE Paper No. 096595. St. Joseph, MI: ASABE.

Ambus, P., and G. P. Robertson. 1998. Automated near-continuous measurement of carbon dioxide and nitrous oxide fluxes from soil. *Soil Science Society of America Journal* 62(2): 394–400.

California Analytical Instruments, Inc. 2012. Manual Photoacoustic Multigas Analyzer, Model 1312. Worthington, OH: I.E. Monitoring Instruments. Available at: www.ierents.com/ProductInfo.aspx?productid=RCAI1312. Accessed 14 September 2012.

Cayuela, M. L., G. L. Velthof, C. Mondini, T. Sinicco, and J. W. van Groenigen. 2010a. Nitrous oxide and carbon dioxide emissions during initial decomposition of animal by-products applied as fertilizers to soils. *Geoderma* 157: 235–42.

Cayuela, M. L., O. Oenema, P. J. Kuikman, R. R. Bakker, and J. W. van Groenigen. 2010b. Bioenergy by-products as soil amendments? Implications for carbon sequestration and greenhouse gas emissions. *Global Change Biology Bioenergy* 2: 201–213.

Conen, F., and K.A. Smith. 2000. An explanation of linear increases in gas concentration under closed chambers used to measure gas exchange between soil and the atmosphere. *European Journal of Soil Science* 51: 111–117.

De Klein, C. A., P. McTaggart, K. A. Smith, R. J. Stevens, R. Harrison, and R. J. Laughlin. 1999. Measurement of nitrous oxide emissions from grassland soil using photo-acoustic infra-red spectroscopy, long-path infra-red spectroscopy, gas chromatography, and

continuous flow isotope-ratio mass spectrometry. *Communications in Soil Science and Plant Analysis* 30(9-10): 1463–1477.

Guimbaud, C., V. Catoire, S. Gogo, C. Robert, M. Chartier, F. Laggoun-Défarge, A. Grossel, P. Albéric, L. Pomathiod, B. Nicoullaud, and G. Richard. 2011. A portable infrared laser spectrometer for flux measurements of trace gases at the geosphere-atmosphere interface. Measurement Science & Technology 22(7): 1-17. DOI: 10.1088/0957-0233/22/7/075601.

Healy, R.W., R.G. Striegl, T.F. Russel, G.L. Hutchinson, and G.P. Livingston. 1996. Numerical evaluation of static-chamber measurements of soil-atmosphere gas exchange-identification of physical processes. *Soil Science Society of America Journal* 60: 740–747.

Hutchinson, G. L., and G.P. Livingston. 2001. Vents and seals in non-steady-state chambers used for measuring gas exchange between soil and the atmosphere. *European Journal of Soil Science* 52: 675–682.

Hutchinson, G. L., G.P. Livingston, R.W. Healy, and R.G. Striegl. 2000. Chamber measurement of surface-atmosphere traces gas exchange: numerical evaluation of dependence on soil, interfacial layer and source/sink properties. *Journal of Geophysical Research* 105: 8865–8875.

Iqbal, J., M. J. Castellano, and T. B. Parkin. 2012. Evaluation of photoacoustic infrared spectroscopy for simultaneous measurement of N_2O and CO_2 gas concentrations and fluxes at the soil surface. *Global Change Biology* n/a-n/a. doi: 10.1111/gcb. 12021.

Kanako, K., H.U. Ronggui, T. Sawamoto, and R. Hatano. 2006. Three years of nitrous oxide and nitric oxide emissions from silandic andosoils cultivated with maize in Hokkaido, Japan. *Soil Science and Plant Nutrition* 52: 103–113.

Kanako, K., T. Sawamoto, and R. Hatano. 2002. Nitrous oxide emissions for 6 years from a gray lowland soil cultivated with onions in Hokkaido, Japan. *Nutrient Cycling in Agro-ecosystems* 63: 239–247.

Kroon, P. S., A. Hensen, W. C. M. van den Bulk, P. A. C. Jongejan, and A. T. Vermeulen. 2008. The importance of reducing the systematic error due to non-linearity in N_2O flux measurements by static chambers. *Nutrient Cycling in Agro-ecosystems* 82:175–186.

Lee, J., J. W. Hopmans, C. van Kessel, A. P. King, K. J. Evatt, D. Louie, D. E. Rolston, and J. Six. 2008. Tillage and seasonal emissions of CO_2, N_2O, and NO across a seed bed and at the field scale in a Mediterranean climate. *Agriculture, Ecosystems & Environment* 129: 378–390.

Livingston, G. P., G. L. Hutchinson, and K. Spartalian. 2006. Trace gas emission in chambers: a non-steady-state diffusion model. *Soil Science Society of America Journal* 70: 1459–1469.

Livingston, G.P., G.L. Hutchinson, and K. Spartalian. 2005. Diffusion theory improves chamber-based measurements of trace emissions. *Geophysical Research Letters* 32, L24817.

Luma Sense Technologies. 2009. Instruction Manual 1314 Photoacoustic Multi-gas Monitor, 1412 Photoacoustic Field Gas-Monitor BE6011-16. DK-2750 Ballerup, Denmar: LumaSense Technologies A/S.

Osada, T., and Y. Fukumoto. 2001. Development of a new dynamic chamber system for measuring harmful gas emissions from composting livestock waste. *Water Science and Technology* 44(9): 79–86.

Predotova, M., J. Gebauer, R. V. C. Diogo, E. Schlecht, and A. Buerkert. 2010. Emissions of ammonia, nitrous oxide and carbon dioxide from urban gardens in Niamey, Niger. *Field Crops Research* 115(1): 1–8.

Predotova, M., R. Kretschmann, J. Gebauer, and A. Buerkert. 2011. Effects of cuvette surface material on ammonia, nitrous oxide-, carbon dioxide-, and methane-concentration measurements. *Journal of Plant Nutrition and Soil Science* 174(3): 347–349.

Reichman, R., and D. Rolston. 2002. Atmospheric pollutants and trace gases. Design and performance of a dynamic gas flux chamber. *Journal of Environmental Quality* 31:1774–1781.

Saggar, S., R. M. Andrew, K. R. Tate, C. B. Hedley, N. J. Rodda, and J. A. Townsend. 2004. Modeling nitrous oxide emissions from dairy-grazed pastures. *Nutrient Cycling in Agroecosystems* 68: 243–255.

SAS. 2008. *SAS/STAT 9.2 User's Guide*. Cary, NC: SAS Institute, Inc.

Venterea, R.T. 2010. Simplified method for quantifying theoretical underestimation of chamber-based trace gas fluxes. *Journal of Environmental Quality* 39:126–135.

Yamulki, S., and S. C. Jarvis. 1999. Automated chamber technique for gaseous flux measurements: Evaluation of a photoacoustic infrared spectrometer-trace gas analyzer. *Journal of Geophysical Research* 104(d5): 5463–5469.

Chapter 7 - Conclusions and Recommendations

7.1. Conclusions

Emission of greenhouse gases (GHGs), including nitrous oxide (N_2O), methane (CH_4), and carbon dioxide (CO_2), from open beef cattle feedlots is becoming an environmental concern; however, scientific information on emissions and abatement measures for open-lot beef cattle feedlots is limited. This research was conducted to quantify GHG emissions from feedlots and evaluate abatement measures for mitigating emissions. Specific objectives were to: (1) measure the N_2O emission fluxes from pen surfaces in a commercial open-lot beef cattle feedlot, as affected by pen surface characteristics and weather conditions; (2) evaluate the effectiveness of surface amendments in mitigating GHG emissions from feedlot manure; (3) evaluate the effects of water application on GHG emissions from feedlot manure; and (4) compare the photo-acoustic infrared multi-gas analyzer and gas chromatograph in measuring the concentrations of N_2O and CO_2 emitted from feedlot manure.

The following conclusions were drawn from this research:

1. Field measurements at a commercial cattle feedlot showed that emission fluxes of N_2O varied with pen surface condition, with the moist/muddy surface condition having the largest median flux (2.03 mg m^{-2} h^{-1}), 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^{-2}h^{-1}, respectively. Emission fluxes varied seasonally as affected by rainfall events and soil temperature. Depending on the surface condition, emission fluxes were affected by one or more feedlot manure properties, such as water content, temperature, total C, pH, NO_3^-, and NH_4^+.

2. Laboratory experiments on feedlot manure indicated that topical application of organic residues and biochar on dry manure significantly reduced N_2O and CO_2 emission fluxes but did not affect CH_4 emission fluxes. For moist manure (0.35 g g^{-1} wet basis), biochar and activated carbon significantly reduced GHG emissions at days 10 and 15 after application; the other amendments had little effects on GHG emissions. Laboratory experiments suggested that adsorption by biochar or activated carbon is a possible mitigation mechanism for N_2O.

3. Water application significantly influenced GHG emissions from feedlot manure. A few minutes after water application on dry manure, large peaks of N_2O, CH_4, and CO_2 emission fluxes were observed compared to the control (dry manure). Both the moist/loose and the moist/compacted manure showed a second set of GHG emission peaks, although lower than the first peaks, a few days after water application. Emission fluxes of N_2O, CH_4, and CO_2 were positively correlated with water content, temperature, and NH_4^+ content and inversely correlated with manure pH and NO_3^- content.

4. Comparison of the gas chromatography and photo-acoustic infrared multi-gas analyzer showed that they were significantly correlated but differed in measured concentrations of N_2O and CO_2. The photo-acoustic analyzer showed generally lower N_2O concentrations and higher CO_2 concentrations than the gas chromatograph.

7.2. Recommendations for Further Studies

This research used both field and laboratory research to measure emissions of GHGs from feedlot manure and to evaluate the effectiveness of surface amendments in controlling GHG emissions. The following are recommendations for further study:

1. Because field studies require large amounts of resources, this work focused only on two cattle feedlots located in Kansas, i.e., one large commercial open-lot beef cattle feedlot and one research-scale beef cattle feedlot. Additional field sampling campaigns on other feedlots should be conducted. Because GHG emissions largely depend on the physical and chemical characteristics of the feedlot manure and on microorganism activity, and because N_2O emission fluxes in the beef cattle feedlot significantly varied with pen surface conditions, field measurements should include emission fluxes of N_2O and CH_4, as well as the physical, biological, and chemical characteristics of the feedlot pen surfaces. Measurements should also include nitrification/denitrification activities, redox potential, water content, temperature, NO_3^- and NH_4^+ content, and characterization of the microorganism population in the manure under different conditions.

2. Laboratory research indicated the potential of biochar in minimizing GHG emissions from feedlot manure. Field-scale measurements should be conducted to evaluate the effectiveness of biochar and other promising materials. A better understanding of the mechanisms involved in GHG emission mitigation by biochar should be developed.

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3. Laboratory research also indicated the potential increase in GHG emissions from feedlot manure after water application. Field measurements should also be conducted to determine the effects of water sprinkler systems (for dust control) and rainfall events on GHG emissions from pen surfaces. A better understanding of the mechanisms involved in GHG emission associated with water application should also be established.

4. This research considered emissions from pen surfaces. Measurements of the relative size of the different pen surface conditions must be conducted to develop GHG emission factors from pen surfaces. There is also a need to quantify emissions from the whole feedlot. Emissions estimating methodologies should be developed to predict GHG emissions from the whole feedlot or components of a feedlot. The applicability of the DNDC (denitrification-decomposition) model and/or other models in predicting GHG emissions from cattle feedlots should be evaluated.

5. Comparison of the photo-acoustic infrared multi-gas analyzer and gas chromatograph indicated significant differences in measured values. Reasons for those differences should be established and, if necessary, correction factors should be established for the use of the photo-acoustic infrared multi-gas analyzer.

Appendix A - Static Flux Chamber Design

The static flux chamber (SFC) technique for measuring emission of greenhouse gases (GHGs) from soil surfaces offers the most useful approach (Hutchinson and Mosier, 1981). However, it is necessary to implement a good design and follow a protocol to overcome potential errors. Several chambers have been designed and implemented in the field to measure carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O), among other gases from the soil surface. The SFC technique is also applicable to measure emission rates from hazardous waste land treatment and land fill facilities, as well as from contaminated areas with volatile organic compounds due to spills and leaking from underground pipelines and storage tanks and from surface impoundments (Kienbusch, 1986). A summary of the main aspects considered in SFCs design is presented in this appendix.

A.1. Types of Chambers

Flux chambers can be classified as: (1) open soil covers, (2) closed soil covers, and (3) sealed soil covers (Hutchinson and Mosier, 1981; NRC, 2003).

1. Open soil covers are chambers with external forced air flow-through circulation (Hutchinson and Mosier, 1981; NRC, 2003). External clean and dry sweep air is used to continually dilute the emitted gases from the enclosed soil surface as well as for removing the gas mixture from the chamber. The gas mixture passes through a sampling port wherein the concentrations of the gases of interest are measured (Kienbusch, 1986). These chambers continuously replace the internal air-mixture by the sweep air, which maintains gas concentrations inside the chamber in a similar way as in the open soil surface.

2. Closed soil covers, referred to here as SFCs, have two main characteristics: (a) there is no sweep air, so the emitted gas accumulates within the chamber and (b) they include vents through which external pressure fluctuations are transmitted to the internal spaces (Hutchinson and Mosier, 1981). The chambers may or may not include internal forced air circulation (Hutchinson and Mosier, 1981). Internal forced air circulation is provided to achieve uniform gas concentration within the chamber.

3. Sealed soil covers are sealed and do not include external sweep air or vent. The chambers may or may not include internal forced air circulation (Hutchinson and Mosier, 1981).

An SFC could represent an invasive technique because it can influence the microenvironment within the chamber. Because gas concentration gradient in the headspace decreases with time (Hutchinson and Mosier, 1981), the main impact of this technique is observed whenever the chamber is deployed on the surface and utilized to perform gas sampling for several hours from the same enclosed space. To minimize the problem, they should be used for periods less than 40 min continuously (Rochette and Eriksen-Hamel, 2008). In situations requiring continuous gas measurement, open soil covers should be used. For periodic and instantaneous gas sampling, closed soil covers are recommended because lower fluxes can be measured and the presence of the vent maintains equal pressure outside and inside the chamber, thereby reducing potential measurement errors (Hutchinson and Mosier, 1981).

Rochette and Eriksen-Hamel (2008) classified the chambers in two main groups based on deployment method:

1. A push-in chamber is a one-piece body. The complete chamber is inserted into the soil at the time of measurement. This type of chambers has the disadvantage of producing a disturbance in the soil surface at sampling time.

2. A composed chamber is a two-piece body (base and chamber). The base has to be inserted into the surface previously to the sampling process. After base insertion, the chamber is adjusted onto the base at the moment of sampling. The composed chamber is preferred because the previous deployment of the base decreases the potential negative effects in the gas flux at the sampling time.

The basic design of sealed soil covers, suggests that those chambers can negatively affect the microenvironment within them; therefore, they were not considered in this study. A comparative analysis between types of flux chambers is shown in Table A-1.

Table A-1 Advantages and disadvantages of soil covers.

Chamber Type	Advantages	Disadvantages
Open Soil Cover	• Continuous replacement of the enclosed air, maintaining gas concentrations inside the chamber in a similar way as in the open soil surface. • Good for continuous flux monitoring.	• Potential for influx of gases from outside the chamber. • Needs ultrahigh purity air for purging between samples whenever high and low concentrations samples are sequentially analyzed. • Needs sweep air equal or better than commercial ultrahigh purity air grade. • Needs high accurate air flow meter with no internal rubber parts.
Closed Soil Cover	• Lower detection limits. • Simple and economical. • Good for short periods of time for instantaneous flux computation. • Potential for influx of gases from outside the chamber is reduced. • Requires less time to perform a complete cycle of instantaneous gas concentration measurement.	• Air conditions in the enclosure space may vary because the emitted gas accumulates within the headspace whenever it is operated continuously. • Should not be used for continuous sampling for more than 40 minutes.
Sealed Soil Cover	• Simple and economical. • May be used for shorter periods of time for instantaneous flux computation.	• Air pressure and temperature might change quickly within the enclosed space. • Air conditions in the enclosure may vary because the emitted gas accumulates within the headspace. • Must be used for shorter times than the closed covers.

Sources: Hutchinson and Mosier, 1981; NRC, 2003; Rochette and Eriksen-Hamel, 2008.

A.2. Static Flux Chamber Design

Based on data compilation of 356 studies of N_2O emission flux, Rochette and Eriksen-Hamel (2008) reported characteristics listed below and their respective score values as "good" or "very good" that must be considered in order to design an adequate SFC.

1. Type of chamber: Composed base and chamber equipped with vent and insulation; scored as "very good".

2. Ratio of chamber's height to deployment time > 40 cm hr^{-1}. This could be approximated as 8 in. height for a deployment time of 30 min; scored as "very good"; 5 to 6 in. height and 30 min are scored as "good".

3. Ratio of area to perimeter: 6.26 < d/4 < 10 cm. This could be approximated as a diameter equal to 10 to 16 in.; scored as "good". Larger than 16 is scored as "very good".

4. Ratio of chamber base insertion to deployment time ≥ 12 cm/hr. This could be approximated as an insertion of 6 cm for a deployment time of 30 minutes; scored as "very good".

5. Chamber deployment time: ≤ 20 minutes, scored as "very good", or 30 to 40 min, scored as "good".

6. Number of samples during deployment time: More than 3 samples per deployment is scored as "very good"; 3 samples, is scored as "good".

The SFCs for measuring GHG emission fluxes from cattle feedlots were made from PVC pipe 12-in. diameter. The net volume of air after chamber insertion (6 cm) into the soil was approximately 12 L. The pressure equalizer (vent tube) was designed following the recommendations by Hutchinson and Mosier (1981). Table A-2 shows the parameters selected for the SFC design. Figure A-1 shows the chamber design. Figure A-2 shows pictures of the fabrication process. Figure A-3 shows the chamber sampling in the field.

Table A-2 Parameters selected for the static flux chamber design.

Parameter	Design	Graded Score †
Type of chamber	Composed of base and chamber, with insulation and equipped with vent	Very good
Chamber diameter	30 cm	Good
Chamber height	22.7 cm ‡	Very good
Chamber base insertion	6 cm	Very good
Chamber deployment time	29 to 30 min	Very good
Number of gas samples	6	Very good
Vent tube (length x diameter)	15 cm x 8 mm	Very good
Chamber net air volume	12 L	--

† As described by Rochette and Eriksen-Hamel (2008).

‡ Height includes the base (16 cm), metal ring beyond the base (5 cm), and the free cap space above the chamber (1.7 cm).

Plastic PVC pipe -Cap

12-in. PVC pipe base

Base inner lip for adjustment
of the metal ring

Stainless steel ring

1.7 cm

15 cm

5 cm

5 cm

29.9 cm

32.1 cm

1.1 cm
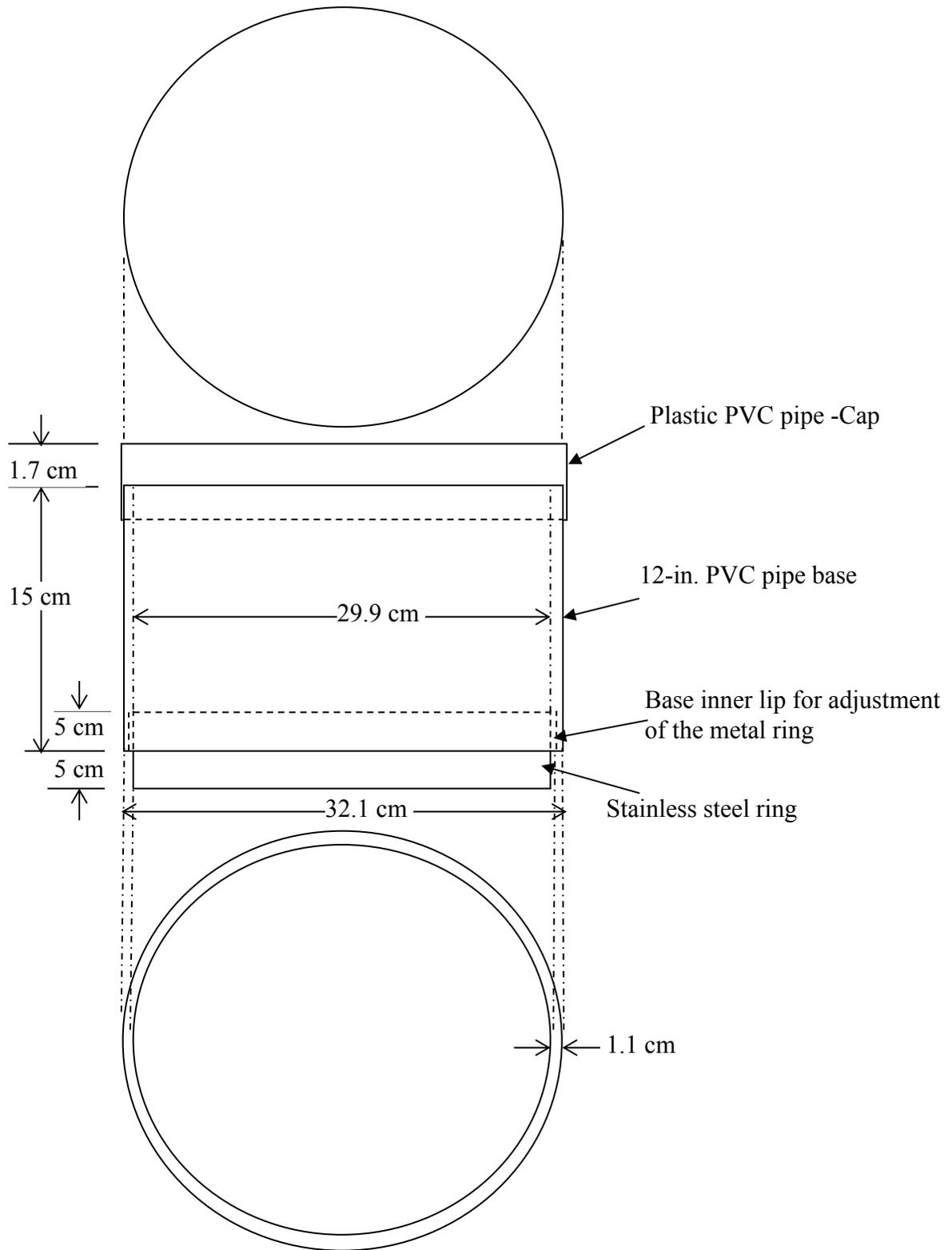
Figure A-1 Schematic diagram of the chamber design.
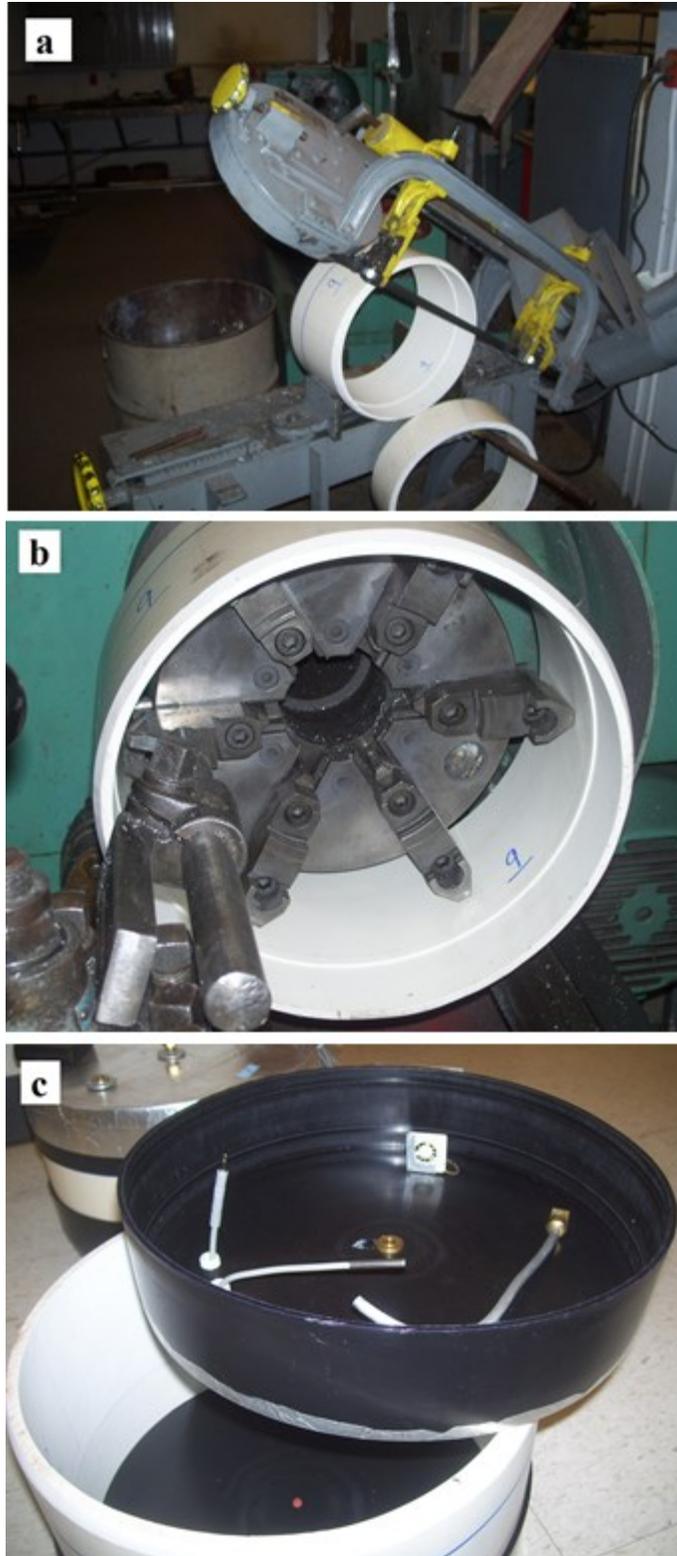
Figure A-2 Chamber construction: (a) 12-in. PVC pipe cutting process, (b) inner lip cutting, and (c) finished chamber.

Figure A-3 Static flux chamber in the field: (a) set up and (b) gas sampling.

A.3. Preliminary Testing

Six SFCs were randomly selected from a set of 10 SFCs for preliminary testing. For this purpose, the stainless steel metal ring (Fig. A-4a) was removed and replaced with a plastic cap, as shown in Figure A-4b. The dimensions of the SFC for computation of the internal volumes are shown in Figure A-5. The dimensions and internal air volumes of the six SFCs are summarized in Table A-3.
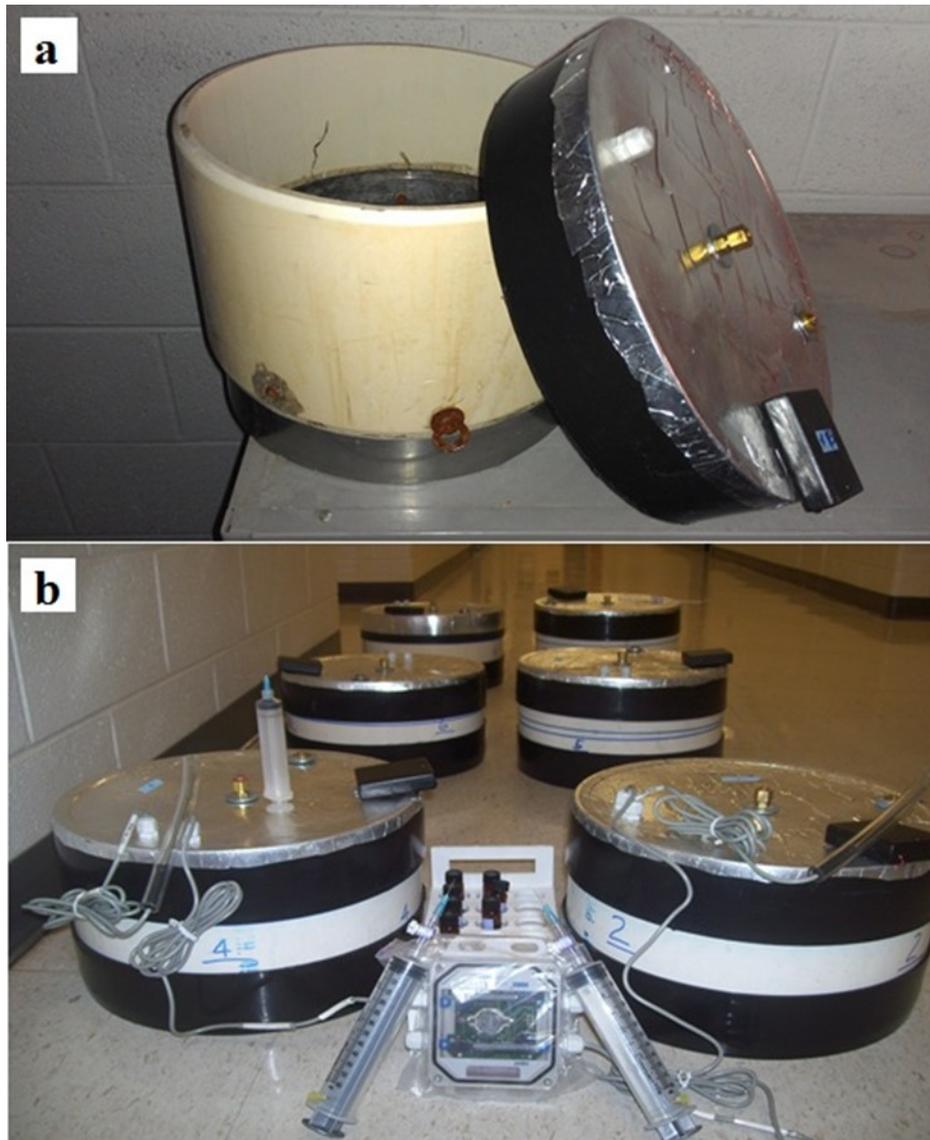
Figure A-4 (a) Static flux chamber showing the stainless steel ring in the base and its cap and (b) experimental set up for preliminary testing.
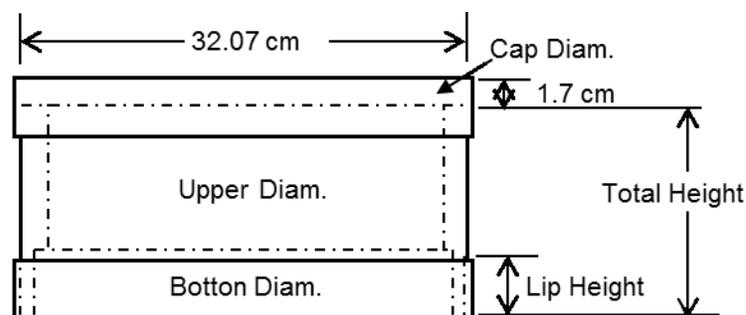
Figure A-5 Internal dimensions of the static flux chamber.

Table A-3 Dimensions and volumes of the static flux chambers.

Chamber	Upper Diameter (cm)	Bottom Diameter (cm)	Total Height (cm)	Lip Height (cm)	Total Gas Volume (L)
1	29.85	30.32	17.25	5.25	13.56
2	29.85	30.32	17.20	4.75	13.52
3	29.53	30.00	15.50	5.20	12.10
4	29.53	30.00	15.30	5.20	11.97
5	29.85	30.32	17.60	5.50	13.81
6	29.53	30.00	17.70	5.00	13.61

The sampling protocol involved sampling at 0, 5, 10, 15, and 30 min. Gas samples (20 cc) were collected with 20-cc disposable plastic syringes with 25GX 1 1/2 in. needle and injected into previously flushed and evacuated 12-mL glass vials. Overpressure was intended to prevent sample contamination with atmospheric gases. As soon as each SFC was capped, within 1 min, the first gas sample (S_0) was drawn from the chamber headspace and 120-cc of 3.5 ppm N_2O standard gas was injected into each of the chambers. A second gas sample was collected (S_5) from each SFC 5 min later and 120-cc of the N_2O standard gas was again injected into the chambers. At time 10 min, a third gas sample was collected (S_{10}) and a third 120-cc of the N_2O standard was injected into the SFC. At time 15 min, the fourth gas sample was collected (S_{15}); no N_2O standard gas was injected. At time 30 min, the fifth gas sample (S_{30}) was collected from the SFCs. Because the vials containing the 30-min gas samples from three chambers lost their internal pressure, the 30-min samples were eliminated from the analysis.

Gas samples were analyzed in the laboratory for N_2O concentrations using a gas chromatograph (GC) (Model GC14A, Shimadzu, Kyoto, Japan). It was fitted with a Porapak-Q

(80/100 mesh) stainless steel column (0.318-cm dia. by 74.5 cm long) and an electron-capture detector (ECD). The GC carrier gas was Ar/CH_4 (95:5 ratio). The column (oven), injector, and detector (ECD) were set up at 85, 100, and 320°C respectively. Air temperature sensors were HOBO TMC6-HD sensors (-40 to 100 °C ± 0.25 °C, resolution 0.03°C) and were connected to a data logger (HOBO U12-008, Onset Computer Corp., Bourne, Mass.).

For each sampling period, the theoretical (calculated) N_2O concentration (ppm) in each SFC was computed based on the initial N_2O concentration (S_0) measured in each chamber with the GC, plus addition of the respective 120-cc of the N_2O standard gas. Table A-4 summarizes the calculated and measured N_2O concentration values. With the calculated value as reference, the average difference between measured and calculated N_2O concentrations from the six SFCs was -2.7% with standard deviation of 6.8%. As sampling time increased, the difference between the calculated and measured N_2O concentration values increased (Table A-4 and Fig. A-6).

Paired t-test indicated no significant differences between the theoretical and measured N_2O concentration values during the first 15-min of sampling. The gas recovery from the SFCs at sampling times 5 and 10 min was 99%, while at sampling time 15 min was 94% (Fig. A-7).

Table A-4 Calculated and measured N_2O concentrations for each static flux chamber (SFC).

Time N$_2$O Injection Sample	SFC #	Internal Volume (L)	Chamber Air Temperature (°C)	Initial N$_2$O Concentration (ppm)	Syringe N$_2$O Volume (cc)	Total Chamber N$_2$O Mass (µg)	Calculated N$_2$O Concentration (ppm)	Measured N$_2$O Concentration (ppm)
	1	13.6	23.4	0.35 †	120	8.50	-	0.35
Time: 0 min	2	13.5	23.4	0.35 †	120	8.47	-	0.35
N$_2$O Injection: 1st	3	11.4	23.5	0.35 †	120	7.15	-	0.35
Sample: S$_0$	4	12.0	23.4	0.35 †	120	7.50	-	0.35
	5	13.8	23.1	0.35 †	120	8.67	-	0.35
	6	13.6	23.1	0.35 †	120	8.53	-	0.35
	1	13.6	23.4	0.35	120	9.77	0.40	0.42
Time: 5 min	2	13.5	23.4	0.35	120	9.74	0.40	0.40
N$_2$O Injection: 2nd	3	11.4	23.4	0.35	120	8.43	0.41	0.37
Sample: S$_5$	4	12.0	23.3	0.35	120	8.77	0.41	0.37
	5	13.8	23.2	0.35	120	9.93	0.40	0.42
	6	13.6	23.1	0.35	120	9.81	0.40	0.40
	1	13.6	23.4	0.40	120	11.04	0.45	0.44
Time: 10 min	2	13.5	23.3	0.40	120	11.02	0.45	0.44
N$_2$O Injection: 3rd	3	11.4	23.4	0.41	120	9.70	0.46	0.49
Sample: S$_{10}$	4	12.0	23.3	0.41	120	10.05	0.46	0.40
	5	13.8	23.3	0.40	120	11.21	0.45	0.45
	6	13.6	23.3	0.40	120	11.08	0.45	0.49
	1	13.6	23.4	0.45	0	12.32	0.50	0.45
Time: 15 min	2	13.5	23.4	0.45	0	12.29	0.50	0.44
N$_2$O Injection: No	3	11.4	23.4	0.47	0	10.97	0.52	0.49
Sample: S$_{15}$	4	12.0	23.4	0.46	0	11.32	0.52	0.47
	5	13.8	23.5	0.45	0	12.48	0.50	0.49
	6	13.6	23.4	0.45	0	12.35	0.50	0.52

† Measured with the gas chromatograph.
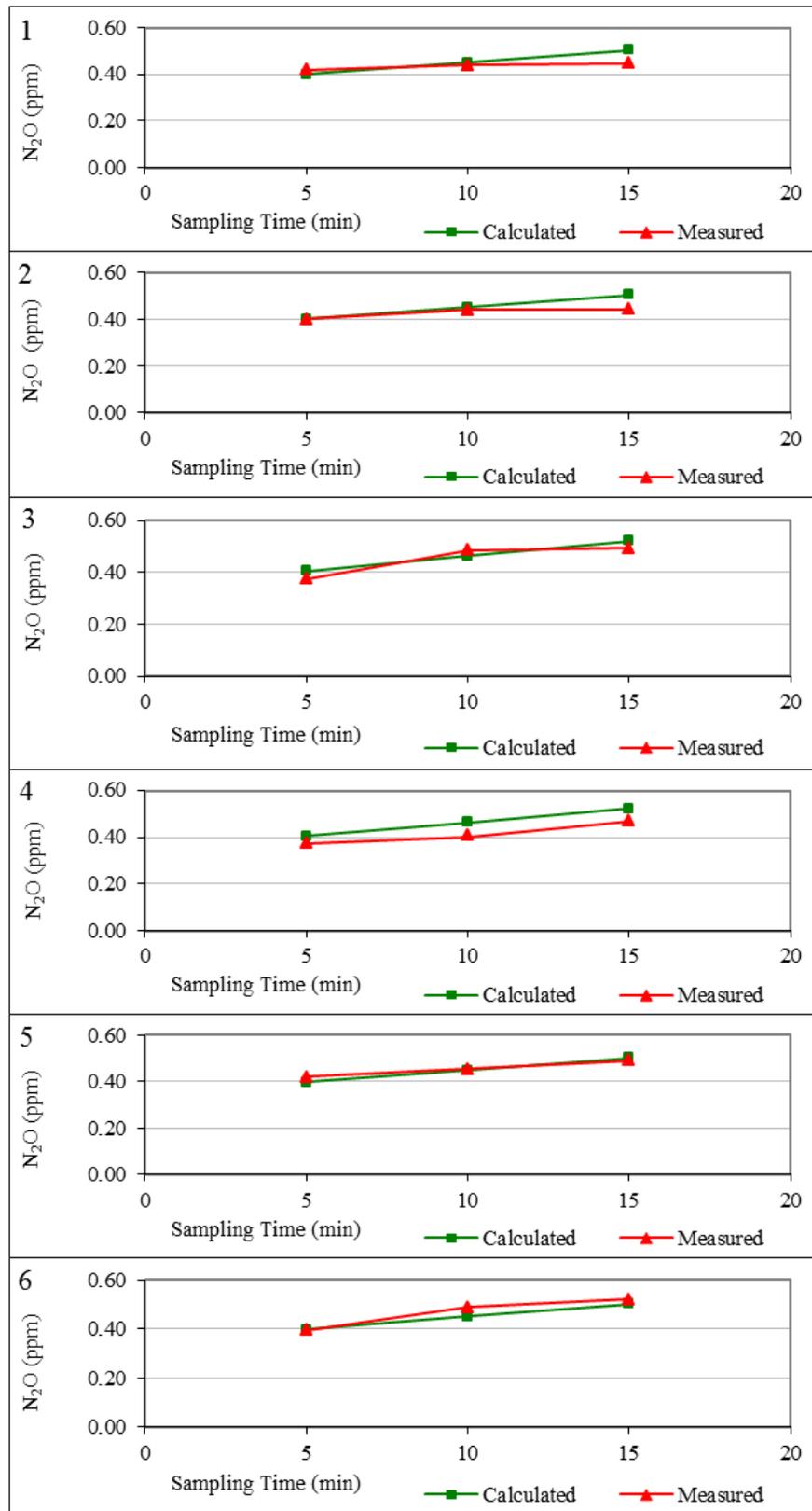
Figure A-6 Calculated and measured N$_2$O concentrations for static flux chambers 1 - 6.
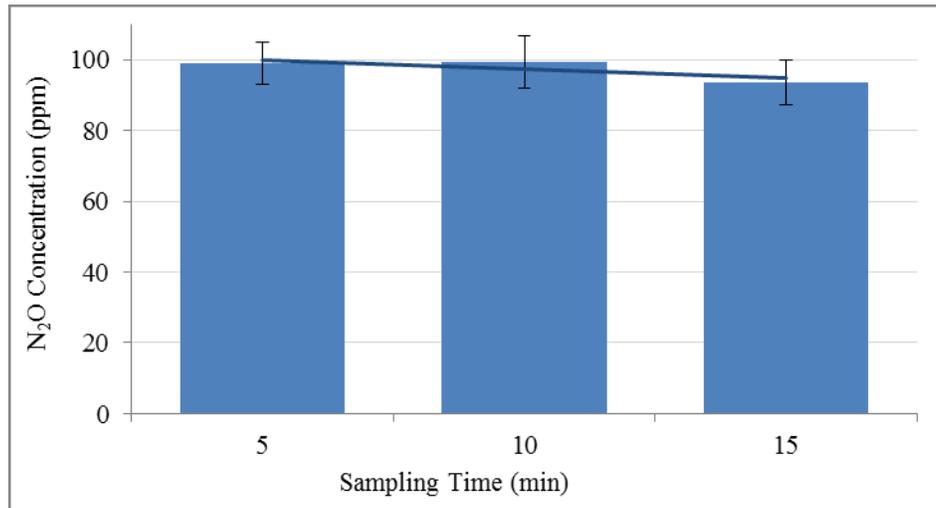
Figure A-7 Nitrous oxide recovery from the static flux chambers.

A.4. References

Hutchinson, G. L., and A. R. Mosier. 1981. Improved soil cover method for field measurement of nitrous oxide fluxes. *Soil Science Society of America Journal* 45: 311–316.

Kienbusch M.R. 1986. Measurement of gaseous emission rates from land surfaces using an emission isolation flux chamber: User's guide. EPA, Contract No. 68-02-3889.

National Research Council (NRC). 2003. *Air Emissions From Animal Feeding Operations: Current Knowledge, Future Needs*. Washington, DC: The National Academies Press.

Rochette, P., and N. S. Eriksen-Hamel. 2008. Chamber measurements of soil nitrous oxide flux: Are absolute values reliable? *Soil Science Society of America Journal* 72: 331–342.