

**MEASURING SOIL NITROUS OXIDE EMISSIONS BY USING A NOVEL
OPEN PATH SCANNING TECHNIQUE**

by

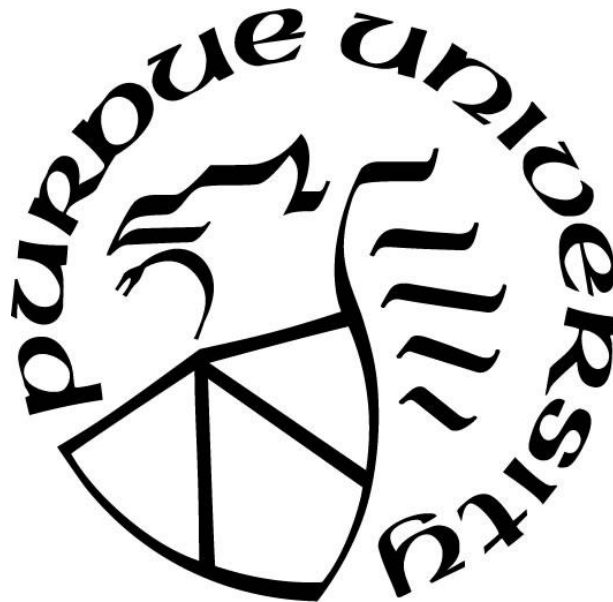
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A Dissertation

Submitted to the Faculty of Purdue University

In Partial Fulfillment of the Requirements for the degree of

Doctor of Philosophy



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West Lafayette, Indiana

August 2019

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To my family and friends for encouragement, support, and love

ACKNOWLEDGMENTS

I would like to thank my advisors, Drs. Cliff Johnston and Richard Grant for inviting me to join their research group. I cannot become a better scientist with a diverse set of skills without their guidance, encouragement, and support. Especially thanks to their incredible patience and mentorship, I was able to concentration on my research and completed my degree. I cannot express my sincere gratitude enough to my advisors.

I would also like to express my appreciation to my advisory committee members, Drs. Tony Vyn, Ronald Turco, and Timothy Filley for their valuable advice to expand my perspectives on the worlds of nitrogen and carbon cycles in the agroecosystem. Specifically, I would like to thank Dr. Tony Vyn for the clear suggestion, input, and the knowledge of maize cropping management, Dr. Ronald Turco for the inspiration and the soil microbiological input in my dissertation, and Dr. Timothy Filley for helping me improve my critical thinking skills and the knowledge of biogeochemistry.

I would also like to express my thanks to Dr. John Graveel, Dr. Michael Mashtare, and Sherry Fulk-Bringman for being supportive and offering me teaching opportunities and experiences that help me improve my teaching and communication skills, Dr. Albert Heber for providing me with the lab-FTIR equipment and productive discussions, my laboratory manager, Dr. Gnanasiri Premachandra, for all of your assistance and experiences when I was working in the lab. Thanks to Jim Beaty, Terry West, Jason Adams, and all of the Purdue ACRE staff, for assisting me with field works and suggestions, and my colleagues, Dr. Rex Omonode and Austin Pearson, for working together in fields and your assistance.

I would like to thank the multiple sources of funding provided by the United States Department of Agriculture National Institute for Food and Agriculture, USDA-NIFA, (grant No. 13-68002-20421) and the Indiana Corn Marketing Council (grant No. 12076053) for this study, and the Purdue Agronomy, Purdue University Climate Change Research Center, and the Ag Spectrum Company for additional funding support, and Purdue University Libraries for the open access publishing fund.

To my officemates, labmates, and close friends, Minerva Dorantes, Shams Rahmani, Mercy Ngunjiri, Heather Pasley, Keru Chen, Andy Park, Min Xu, Yu Shang, Jiaying Hu, Gan Rui, Josh Minai, and Joe Martin, I cannot thank you enough for filling my life with laughter, joy, and all help in Purdue. I cannot imagine what my Purdue life would be without you all. To Purdue Agronomy Department and all Agronomy staff, Connie Foster, Karen Clymer, Mary Wise, Patti Oliver, Cheryl E Long, Jenny Kelly, Suzanne Cunningham, thanks for all of your support, patience, and assistance.

Finally, to my lovely family, my wife, Ya-Yu, and my son, Oliver, for your unconditional love, support, and trust. I am lucky and very grateful to be born in this family.

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LIST OF ABBREVIATIONS

Abbreviation Definition

AA	Anhydrous ammonia
ABS	Absorbance
ACRE	Agronomy Center for Research and Education
bLS	Backward Lagrangian Stochastic model
C _{bg}	Modeled background concentration
ChP	Chisel plow
CLS	Classical least squares
CO ₂ eq	Carbon dioxide equivalent
DFG	Difference frequency generation
FRAC _{air}	Fraction of air parcels
GC	Gas chromatography
GHG	Greenhouse gas
GSS	Gas sampling system
HITRAN	<u>H</u> igh-resolution <u>t</u> ransmission molecular
IFG	Interferogram
LS	Line-sampling
MDL	Minimum detection limit
MOST	Monin-Obukhov similarity theory
N	Nitrogen
N ₂ O	Nitrous oxide
NDIR	Non-dispersive infrared
Nr	Reactive Nitrogen
NRE	Nitrogen recovery efficiency
NT	No-till
NUE	Nitrogen use efficiency
QA/QC	Quality assurance and quality control
OP	Open path
OP-FTIR	Open path Fourier transform spectroscopy
PLS	Partial least squares
ppm	Part per million
ppb	Part per billion
PS	Point-sampling
SB	Single beam
SN	Surplus nitrogen
S-OPS	Synthetic open path gas sampling system
Syn-bkg	Synthetic single beam background
TDF	Touchdown fraction
Zap-bkg	Zapped single beam background

ABSTRACT

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Institution: Purdue University

Degree Received: August 2019

Title: Measuring Soil Nitrous Oxide Emissions by Using a Novel Open Path Scanning Technique

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A better way to improve understanding and quantification of nitrous oxide (N₂O) emitted from intensive maize cropping systems is to develop an advanced emissions measurement method. This study developed an open path (OP) method to measure N₂O emissions from four adjacent maize plots managed by tillage practices of no-till (NT) and chisel plow (ChP), and different nitrogen (N) treatments from 2014 to 2016. Anhydrous ammonia (220 kg NH₃-N ha⁻¹) was applied in once or equally split (full vs. split rate) and applied in different timing (Fall vs. Spring). The spring N application occurred either before planting (pre-plant) or in season (side-dress). Emissions measurements were conducted by using the OP method (the scanning OP Fourier transform infrared spectrometry (OP-FTIR) + the gas point-sampling system + a backward Lagrangian stochastic (bLS) dispersion model) and static closed chamber methods. The performance and feasibility of the OP measurements were assessed by a sensitivity analysis, starting with errors associated with the OP-FTIR for calculating N₂O concentrations, and then errors associated with the bLS model for estimating N₂O emissions. The quantification of N₂O concentrations using the OP-FTIR spectrum was influenced by ambient humidity, temperature, and the path length between a spectrometer and a retro-reflector. The optimal quantitative method mitigated these ambient interference effects on N₂O quantification. The averaged bias of the calculated N₂O concentrations from the spectra acquired from wide ranges of humidity (0.5 – 2.0 % water vapor content), temperature (10 – 35 °C), and path length (100 – 135 meters) was 1.4 %. The precision of the OP-FTIR N₂O concentrations was 5.4 part per billion (3σ) in a stationary flow condition for a 30-minute averaging period. The emissions measurement from multiple sources showed that the field of interest was likely interfered by adjacent fields. Fields with low emission rates were more sensitive to the adjacent fields with high emissions, resulting in substantial biases and uncertainties. The minimum detection limit of the N₂O emission rates was 1.2 μg m⁻² s⁻¹ (MDL; 3σ). The OP measurements showed that the NT practice potentially

reduced N₂O emission compared with ChP. Under the long-term NT treatments, the split-N rate application (110 kg NH₃-N ha⁻¹ in the fall and spring) resulted in lower N₂O emissions than the full application (220 kg NH₃-N ha⁻¹ in the fall). The management of NT coupled with split-N rate application minimized N₂O emissions among treatments in this study, resulting in N₂O-N losses of 3.8, 13.2, and 6.6 N kg ha⁻¹ over 9-, 35-, and 20-days after the spring NH₃ application in 2014, 2015, and 2016, respectively. The spring pre-plant N application in 2015 also resulted in higher N₂O emissions than the spring side-dress application in 2016, and the increased N₂O-N loss was corresponding to lower N recovery efficiency in 2015 measurements. A comparison of chamber and OP measurements showed that soil N₂O emissions were likely underestimated by 10x without considering the wind-induced effect on gas transport at the ground-atmospheric interface. This study showed that the OP method provides a great opportunity to study agricultural N₂O emissions as well as management optimization for the sustainability of the agroecosystems.

CHAPTER 1. INTRODUCTION

1.1 Background and Research Needs

The awareness of agricultural contribution to the global greenhouse gas (GHG) burden in the atmosphere has been increasing in the past decade (e.g., 54% of non-CO₂ emissions from agriculture in 2005) (IPCC, 2007; Smith et al., 2008; US-EPA, 2012; Reay et al., 2012; Davidson and Kanter, 2014). In 2010, agricultural activities contributed between 5.2 and 5.8 GtCO₂eq yr⁻¹ ($n \times 10^9$ tons of CO₂ equivalent per year) non-CO₂ emissions, accounting for 10-12% global anthropogenic emissions (IPCC, 2014). Approximately 2.0 GtCO₂eq (i.e., 34% of non-CO₂ emissions) are N₂O emitted from agricultural soils predominantly because of nitrogen (N) fertilizer uses and field management practices. This value was projected to increase to 2.5 GtCO₂eq yr⁻¹ by 2030 (Davidson, 2009; US-EPA, 2012). The atmospheric N₂O concentration has significantly increased from 270 (pre-industrial era) to 329 (NOAA) part per billion (ppb) and likely increases to 350 ppb by 2050 (Davidson, 2012) due to a growing human population and activities (IPCC, 2007). Soil N cascades result in a great negative impact on the environment. For instance, N₂O is a strong ozone-depleting substance and a potent GHG that is a highly effective trap of infrared radiation (i.e., a global warming potential value of 310 on a 100-year timescale) (Mosier, 2004; Ravishankara et al., 2009). From an economic standpoint, N losses via the fertilizer-induced N₂O and NH₃ emissions from soils during growing seasons indicate inefficient uses of N fertilizers for cereal production (Raun and Johnson, 1999; USDA-ERS, 2018). Fulfilling the growing demands of food for feeding the expanding world populations will increase N fertilizer uses (FAO, 2017) as well as soil N₂O and NH₃ emissions. Therefore, efficiently using N fertilizers to benefit the agroecosystem needs for action (Akiyama, 2010; Linquist et al., 2012; Decock, 2014). Different field (e.g., reduced tillage) and N (e.g., appropriate N source, rate, timing, placement, and uses of nitrification inhibitors) management practices have been proposed to reduce soil N₂O emissions (Snyder et al., 2009; Venterea et al., 2011; Decock, 2014; Lam et al., 2017).

Soil N₂O emissions are mainly a result of microbial transformation (i.e., nitrification and denitrification) of reactive nitrogen (Nr) from biological-fixed N, the decomposed agricultural

residues, and N fertilizers (Mosier et al., 1996). Dynamic changes in the environment (e.g., climate or soil properties) make N₂O emissions highly variable and complex (Mosier et al., 1998; Butterbach-Bahl and Dannenmann, 2011; Venterea et al., 2012; Butterbach-Bahl et al., 2013). Closed chamber methods are the most common approach to measure soil N₂O fluxes for establishing the ecologically friendly practices (e.g., zero tillage) or land-uses to mitigate N₂O emissions mostly due to their simple concept and operation (Hutchinson and Mosier, 1981; Eichner, 1990; IPCC, 2006; Smith et al., 1995; Denmead, 2008). The inherent limitations of chamber methods (e.g., footprint < 1 m²; daily-to-weekly sampling intervals) could lead to biases in N₂O estimations because of the temporal and spatial heterogeneity of soil N₂O emissions (Laville et al., 1999; Rochette and Eriksen-Hamel, 2008; Denmead, 2008; Venterea et al., 2009; Butterbach-Bahl et al., 2013). The low sampling frequency, for instance, resulted in a temporal gap of missing data between two sampled periods. Simply using mathematical functions (e.g., linear) to interpolate these missing data likely caused the unknown bias in flux estimations (Smith and Dobbie, 2001; Parkin, 2008; Decock, 2014). As a result of chambers' small footprints, the selected locations for gas samplings need to represent the area of interest (Ambus and Christensen, 1994; Bouwman et al., 2002; Parkin and Rodney, 2010). To effectively investigate the impact of the land-uses or agronomic practices on N₂O emissions, these unknown biases led by chambers' limitations became an obstacle for side-by-side comparisons.

Gas emissions from the terrestrial biosphere can be estimated by the 'bottom-up' method, estimating the regional-scale emissions by compiling the statistical information of the local sources, or 'top-down' method, inferring the global-scale emissions based on gas accumulations in the atmosphere (Crutzen et al., 2008; IPCC, 2007; Nisbet and Weiss, 2010; Griggs et al., 2013). The most common 'bottom-up' method is the use of chamber measurements which have been used to create inventories of agricultural and forestry N₂O emissions (IPCC, 2006); however, many studies, mostly based on 'top-down' measurements, show that N₂O emissions from agricultural soils are underestimated by chamber measurements (Del Grosso et al., 2008; Griggs et al., 2013; Turner et al., 2015; Chen et al., 2016). The wind (or turbulence) might play a critical role in influencing gas exchanges between the soil-atmosphere interface. For instance, chamber methods measure the accumulation rate of gas diffused from soils in the chamber headspace. The wind-induced emissions tended to be larger than the emissions only via molecular diffusion

(Chapter 3 Gas Diffusion in Soil, 1985; Nazaroff, 1992; Denmead and Reicosky, 2003; Redeker et al., 2015; Pourbakhitar, 2017). The wind-induced emissions is also a function of the atmospheric stability (stable, neutral, and unstable) which affects air mixing and gas transport. Unfortunately, most of the chamber measurements have not considered these meteorological factors (e.g., wind, turbulence, and thermal stability) in flux estimations (Denmead, 2008; Monson and Baldocchi, 2014).

Measuring soil gas emissions in the open system using micrometeorological methods (e.g., mass balance, eddy covariance, flux gradients, dispersion models, etc.) offers numerous advantages for flux estimations: 1) inclusion of ambient environmental conditions on emission rates, 2) provision of better spatial representatives, and 3) near-continuous measurements (Baldocchi et al., 1988; Denmead, 2008). The most significant advantage of the open system measurements over chamber measurements is to continuously acquire gas samples with a high frequency and a large footprint. The large footprint (e.g., > 6 ha), however, makes flux comparisons among treatments more challenging. The interferences of adjacent sources via advection even raise the difficulties in field comparisons (Smith et al., 1994; Christensen et al., 1996; Molodovskaya et al., 2011; Mukherjee et al., 2015). The backward Lagrangian stochastic (bLS) dispersion technique was developed to measure gas fluxes from field-scale areas (e.g., 1-3 ha) (Flesch et al., 1995 and 2004). This method has been often applied in measuring trace gases (e.g., NH₃, CH₄, VOCs) from livestock facilities, animal waste lagoons, and increasingly used to measure gas emissions from the fertilized soils (Bjorneberg et al., 2009; Grant and Boehm, 2015; Bai et al., 2014). The methodology of using the bLS technique to measure gas fluxes from a single source area has been well described and documented (e.g., criteria for quality assurance and control, QA/QC) (Flesch et al., 2004 and 2005). Implementing this technique in a multiple source condition, however, becomes more complicated, and is still an on-going research question (Crenna et al., 2008; Flesch et al., 2009; Hrad et al., 2014; Huo et al., 2014; VanderZaag et al., 2014; Mukherjee et al., 2015).

In corn (*Zea mays L.*) cropping systems, gas emissions from multisource areas are very common due to implementing different agricultural management practices. For instance, N fertilizer applications, tillage farming systems, crop rotations, or irrigation systems substantially influence

the magnitude of soil N_2O emissions (Decock, 2014; Venterea et al., 2011; Omonode et al., 2017). Because of the dynamics of N_2O emissions, there is an urgent need to develop a technique that can measure N_2O -N loss from multiple field management scenarios continuously and simultaneously. The bLS technique is capable of measuring gas fluxes from multiple sources as long as a sufficient amount of concentration sensors are provided (e.g., number of sensors $\geq$ number of sources) (Crenna et al., 2008; Gao et al., 2008; Flesch et al., 2009; Hrad et al., 2014; Huo et al., 2014). For treatment comparisons, gas concentration sensors require high sensitivity and precision to detect the concentration differences among the sampled points (e.g., heights, sampled timing, or treatments) (Denmead, 2008). Lab-based gas chromatography (GC), for instance, can precisely analyze gas concentrations of the extractive sample collected from chambers. Mid-IR laser-based analyzers (e.g., a Difference Frequency Generation absorption or Cavity Ring-Down Spectroscopy) were designed to continuously measure gas concentrations from an air stream with high precision. For both analyzers, gas samples need to be collected and delivered into instruments (e.g., a gas column or cell) to measure gas concentrations. Most gas samples are point-sampled, meaning that selecting appropriate positions for gas samples is still an issue for minimizing the spatial variability in gas emissions.

Open path (OP) Fourier transform infrared spectroscopy (OP-FTIR) is capable of measuring concentrations of multiple atmospheric gas components (e.g., N_2O , CO_2 , CH_4 , and NH_3) simultaneously without collecting physical gas samples (Russwurm et al., 1991; Childers et al., 2001; Loh et al., 2008; Barrancos et al., 2013; Bia et al., 2014 and 2018; Ni et al., 2015). The OP-FTIR measures the path-averaged concentrations with high temporal resolution (seconds to minutes), showing better spatial and temporal representatives than the extractive concentration sensors (ASTM, 2013). The accuracy and precision of gas concentrations derived from the mid-infrared absorption spectra were substantially influenced by spectral qualities as well as the absorption features (Griffiths and de Haseth, 2007). Each gas species has unique mid-IR absorption characteristics and these features have different sensitivities to concentration, optical path distance, humidity, and air temperature (Lacome et al., 1984; Russwurm and Childers, 1999; Muller et al., 1999; Horrocks et al., 2001; Briz et al., 2007; Smith et al., 2011). For N_2O , its rotation-vibrational absorption features are even more complicated and sensitive to environmental variables than other gases (e.g., CO_2 , CH_4 , and NH_3). Changes in the absorption

feature led to biases and a variable precision in N₂O concentration measurements (Russwurm and Childers, 1999; Griffiths and de Haseth, 2007). These uncertainties in N₂O concentrations, fortunately, can be minimized by optimizing the methodology of processing FTIR spectra (Hart et al., 1999 and 2000; Jiang et al., 2002; Briz et al., 2007; Shao et al., 2010; Smith et al., 2011; Lin et al., 2019). Since the bLS technique needs concentration measurements from fields of interest and the atmospheric background to estimate gas fluxes, introducing the concentrations with a certain confidence interval is critical to assess the uncertainties in the bLS-estimated fluxes. For multiple emission measurements, adequate gas sensors are required to measure gas concentrations from different sources. An OP-FTIR sensor joining to a horizontally rotating scanner can measure concentrations from numerous sources sequentially, likely reducing economic costs for measurements. We integrated a scanning OP-FTIR spectrometer, gas sampling systems, and bLS technique to continuously measure multiple N₂O fluxes, which was called the scanning OP measurements.

Both chamber and micrometeorological methods provide their unique strengths for gas flux measurements (Denmead, 2008). In a way, the strengths of chamber methods are complementary to the weaknesses of micrometeorological measurements, and vice versa. For instance, chamber approaches can be responsible for measuring nighttime emissions which are technically difficult for micrometeorological approaches in low wind conditions (Flesch et al., 2004; Grant and Omonode, 2018). Also, chamber methods are able to minimize flux interferences from adjacent sources, which often exists in the open systems, and can be used to compare the effects of different field treatments on soil N₂O emissions from small-scale areas as long as the sampled position was appropriately selected to represent the entire field (Rochette and Eriksen-Hamel, 2008). In this study, both the static chamber and the scanning OP methods were integrated to measure N₂O emissions from soils. Many management strategies were proposed to mitigate N₂O-N loss as well as improve nitrogen use efficiency; however, the effectiveness of these “single-factor” practices (e.g., crop rotation, N applications, and tillage system) is not universal because of environment changes (Decock, 2014). Tillage practices (e.g., zero-, reduced, and conventional tillage), for instance, showed different benefits to N₂O mitigation in terms of the field- and yield-scale emissions (Venterea et al., 2011). These conflicting results were partially due to the sensitivity of measurement methods, and even more substantially influenced by the

environmental conditions (e.g., climate). Based on the matrix of genotype-environment-management (i.e., $G \times E \times M$), these individual practices need to be integrated and optimized to mitigate N_2O -N loss while adapting to changing environments (Hatfield et al., 2015 and 2018).

1.2 Research Hypothesis and Objectives

The general goal of this dissertation is to establish the methodology of using the scanning OP method to measure N_2O emissions from multiple treatments, mainly focusing on the quality assurance and control, and the effectiveness of this method to measure multiple emissions simultaneously. To investigate the optimal management for mitigating N_2O -N loss from corn cropping systems, we focus on integrating the commonly used practices in the US Midwest, including tillage systems of NT and chisel plow, and timing for anhydrous ammonia (NH_3) applications. A total N rate can be applied in once or equally split and applied separately (full vs. split rate). The application timing can be in the prior fall and current spring. For spring N application, N fertilizer can be applied before planting or in-season (pre-plant vs. side-dress). The general hypothesis for optimal management is that integration of NT, split N, and the spring side-dress N application is the most effective management to efficiently use NH_3 -N fertilizers in terms of mitigating the N fertilizer-induced N_2O emissions and increasing plant N recovery (Decock, 2014; Omonode and Vyn, 2019; Tenuta et al., 2016).

The objectives of this study were: (i) to develop a methodology (including spectra collections, processes, and chemometrics methods) to quantify N_2O concentrations accurately and precisely using an OP-FTIR spectrometer (Chapter 2), (ii) to investigate sources of error of OP-FTIR-derived N_2O concentrations (Chapter 3), (iii) to evaluate the feasibility and effectiveness of applying OP-FTIR and bLS technique to measure N_2O emissions (Chapter 4), (iv) to integrate the chamber and the OP measurements to examine management effects on the relationship between N_2O -N losses and N use efficiency (Chapter 5).

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CHAPTER 2. APPLICATION OF OPEN PATH FOURIER TRANSFORM INFRARED SPECTROSCOPY (OP-FTIR) TO MEASURE GREENHOUSE GAS CONCENTRATIONS FROM AGRICULTURAL FIELDS

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Citation: Lin, C. H., Grant, R. H., Heber, A. J., and Johnston, C. T. (2019). Application of open-path Fourier transform infrared spectroscopy (OP-FTIR) to measure greenhouse gas concentrations from agricultural fields, *Atmos. Meas. Tech.*, 12, 3403-3415, doi:10.5194/amt-12-3403-2019.

2.1 Abstract

Open-path Fourier transform infrared spectroscopy (OP-FTIR) has often been used to measure hazardous or trace gases from ‘hot’ point sources (e.g., volcano, industrial or agricultural facilities) but seldom used to measure greenhouse gases (GHGs) from field-scale sources (e.g., agricultural soils). Closed-path mid-IR laser-based N₂O, nondispersive-IR CO₂ analyzers, and OP-FTIR were used to measure concentrations of N₂O and CO₂ at a maize cropping system during 09-19 Jun. 2014. To measure N₂O/CO₂ concentrations accurately, we developed a quantitative method of N₂O/CO₂ analysis that minimized interferences from diurnal changes of humidity and temperature. Two chemometric multivariate models: classical least squares (CLS) and partial least squares (PLS), were developed. This study evaluated various methods to generate the single beam background spectra and different spectral regions for determining N₂O/CO₂ concentrations from OP-FTIR spectra. A standard extractive method was used to measure the ‘actual’ path-averaged concentrations along an OP-FTIR optical path in situ, as a benchmark to assess the feasibilities of these quantitative methods. Within an absolute humidity range of 5,000-20,000 ppmv and a temperature range of 10-35 °C, we found that the CLS model underestimated N₂O concentrations (bias = -4.9 ± 3.1 %) calculated from OP-FTIR spectra, and the PLS model improved the accuracy of calculated N₂O concentrations (bias = 1.4 ± 2.3 %). The bias of calculated CO₂ concentrations was -1.0 ± 2.8 % using the CLS model. These methods suggested that environmental variables potentially lead to biases in N₂O/CO₂ estimations from OP-FTIR spectra and may help OP-FTIR users avoid dependency on extractive methods of calibrations.

2.2 Introduction

Agriculture contributes a substantial amount of greenhouse gas (GHG) emissions (N_2O , CO_2 , and CH_4) to the global GHG budget (IPCC, 2007; Cole et al., 1997; Smith et al., 2008). Among these gases, N_2O is mainly emitted from agricultural soils, accounting for 38% of the global anthropogenic non- CO_2 GHG emissions from agricultural activities (US-EPA, 2006; Smith et al., 2007). Nitrous oxide is produced from biological reactions that transform available N in soils via microbial nitrification and denitrification (Mosier et al., 2004). Considering that the global warming potential value of N_2O is 310, it is estimated that overall GHG emission from soils (based on CO_2 equivalents) is approximately $2500 \text{ MtCO}_2\text{-eq yr}^{-1}$. A significant fraction of soil N_2O emissions results from the use of nitrogen (N) fertilizers in agricultural soils. In addition to contributing to the overall GHG burden of the atmosphere, N_2O emissions also represent a direct loss of N applied to the field, contributing to the decreased nitrogen use efficiency (NUE) (Eichner, 1990; Ryden and Lund, 1980; Bremner et al., 1981; Omonode et al., 2017). Also, soils play the role of a sink or a source for atmospheric CO_2 (Paustian et al., 1997; Smith et al., 2008). Changing land use of crop production, especially agriculture-related uses such as tile drainage and tillage management, and agricultural lime application (e.g., CaCO_3 and $\text{MgCa}(\text{CO}_3)_2$) potentially become a large source of CO_2 released to the atmosphere via microbial decomposition of soil organic carbon (Smith, 2004; IPCC, 2007; Cole et al., 1997, West et al., 2005).

The flux chamber measurement has been the most common method to measure GHG emissions from soils (Denmead, 2008; Rochette and Eriksen-Hamel, 2008). Chamber measurements, however, are subject to significant limitations that lead to uncertainties and biases in estimated GHG emissions. For instance, because chambers have a small footprint ($\sim 0.5 \text{ m}^2$) and generally wide sampling intervals (usually once to twice a week), they are poorly suited for evaluating spatial and temporal variabilities of GHGs from agricultural soils (Laville et al., 1999; Rowlings et al., 2012; Schelde et al., 2012). Also, wind turbulence is known to substantially induce more gas transportation from soils to the atmosphere. Chamber methods do not take this wind-induced effect into account, and this likely results in underestimations of gas emissions (Denmead and Reicosky, 2003; Poulsen et al., 2017; Pourbakhtiar et al., 2017). It is worth mentioning that the eddy covariance flux measurement method, one of the most common micro-meteorological

techniques used to investigate gas exchanges in the agroecosystem, is capable of measuring gas fluxes frequently with an increased footprint (Baldocchi, 2003). A large-scale flux measurement (hundred meters to several kilometers) using this method, however, make comparisons among field-scale treatments (1-5 ha) more difficult than chamber methods (Schmid, 1994; Denmead, 2008).

Open-path Fourier transform infrared spectroscopy (OP-FTIR) is a non-intrusive sensing approach and capable of detecting multiple components simultaneously, acquiring real-time data at a relatively high temporal resolution (seconds to minutes), and providing path-averaged gas concentrations (Russwurm and Childers, 1996). OP-FTIR has been applied to measuring atmospheric gases since the 1970s (e.g., hazardous air pollutants, fugitive volatile organic compounds (VOCs), and trace gases) (Herget and Brasher, 1980; Gosz et al., 1988; Russwurm et al., 1991; Bacsik et al., 2006; Briz et al., 2007; Lin et al., 2008). More recently, OP-FTIR has been increasingly used to measure GHGs or other trace gases in agriculture, mostly in animal facilities (e.g., N_2O , CO_2 , CH_4 , and NH_3 from swine or dairy production) (Childers et al., 2001a; Loh et al., 2008; Bjorneberg et al., 2009; Barrancos et al., 2013; Naylor et al., 2016). Only a few studies, however, implemented OP-FTIR to measure gas emissions from vegetable production fields or fertilized soils (Bai et al., 2014 and 2018; Ni et al., 2015). Integrating OP-FTIR with micrometeorological techniques (e.g., flux gradient or backward Lagrangian stochastic dispersion methods) can measure gas fluxes from the field-scale source of interest with high temporal and spatial representations that are less prone to artefacts induced by point-based sampling (Flesch et al., 2004 and 2016; Bai et al., 2014 and 2018; Ni et al., 2015). Moreover, the OP-FTIR combined with a scanning system can potentially be applied to horizontally or vertically survey numerous fields of interest and measure their gas emissions simultaneously (Flesch et al., 2016).

Despite these advantages, OP-FTIR also faces a number of challenges. In order to resolve the spectral features of GHGs, high spectral resolution ($< 0.5 \text{ cm}^{-1}$) is required to resolve the rotation-vibrational absorption bands of the GHGs of interest (Griffiths and de Haseth, 2007). Calculating concentrations from FTIR spectra requires both a ‘sample’ single beam spectrum and a reference/background spectrum that does not contain spectral contributions from GHGs of

interest, which is not possible at the field scale (e.g., evacuation of the field); thus, mathematical methods have been developed which strip the spectral bands from a ‘sample’ single beam spectrum. This challenge requires the use of instrumental- or spectral-processing methods to create a background spectrum, and these methods are subject to biases in determining GHG concentrations (Griffiths and de Haseth, 2007; Russwurm and Childers, 1996). Furthermore, the atmosphere contains a high concentration of water vapor that interferes with the detection and quantification of GHGs of interest (Russwurm and Childers, 1996; Horrocks et al., 2001; Briz et al., 2007; Smith et al., 2011). These challenges of data processing and the interferences from water vapor likely introduce biases and uncertainties in GHG quantification. Using error-prone concentrations in flux prediction models (micrometeorological techniques) possibly leads to unknown uncertainties in estimated gas fluxes. Thus, it is essential to develop a comprehensive quantitative method to improve and assure the quality of gas quantification using OP-FTIR.

Testing the feasibility of quantitative methods and qualities (accuracy and precision) of OP-FTIR is challenging because a reliable reference is required to validate FTIR-derived concentrations. One of the most common approaches was to position a gas cell filled with known gas concentrations of interest in the optical path and test their quantitative methods (Russwurm et al., 1991; Horrocks et al., 2001; Smith et al., 2011). This approach, however, somewhat controlled the environment and neglected the effect of ambient interferences, such as water vapor, on the quality of gas quantification. The alternative approach is to compare the derived concentrations with ambient concentrations. The ambient concentration of a gas of interest can be determined by averaging the global background concentrations (e.g. N_2O ~310 ppbv or CO_2 ~400 ppmv) or measured from the gas samples that were collected along the OP-FTIR path and analyzing their concentrations using laboratory-based gas chromatography (GC) (ASTM, 2013; Childers et al., 1995; Kelliher et al., 2002; Bai et al., 2014). The experimental designs of these assessment approaches, either the point sampling setup or low sampling frequency or both, became the major problem for cross-validating their OP-FTIR quantitative methods. Since the ambient concentrations likely fluctuate from place to place (e.g., different land uses) and at different times (e.g., diurnal or seasonal variation), the spatial and temporal variations of the ambient concentration were potentially misconceived as ‘bias’ in gas quantification. Up to now, only three studies continuously measured real-time ambient concentration to logically cross-validate

quantitative methods and data qualities under fluctuating environmental factors (e.g., the dynamic water vapor), but none of the prior studies actually assessed their methodologies for quantifying N₂O concentrations (Briz et al., 2007; Reiche et al., 2014; Frey et al., 2015).

Therefore, the objectives of this study were to 1) develop a long-path gas sampling system that can continuously collect numerous gas samples simultaneously along an optical path of OP-FTIR and measure path-averaged concentrations to evaluate quantitative qualities of N₂O/CO₂ concentrations derived from OP-FTIR spectra, and 2) optimize the quantitative method, including post-data processing, analytical window selections, and chemometric multivariate algorithms, that is less sensitive to interferences of ambient humidity and temperature, and capable of determining N₂O and CO₂ concentrations accurately.

2.3 Materials and Methods

2.3.1 Site description

This study was conducted at the Purdue University Agronomy Center for Research and Education near West Lafayette, Indiana, in the United States (86°56′ W, 40°49′ N, elevation 215 m). The experimental site was located between two fields (~3.5 ha per field) with a continuous corn system since 2013. Gas measurements began just after an anhydrous ammonia application with total N rate of 220 kg NH₃-N ha⁻¹ on 09 Jun. and ended on 19 Jun. 2014. The soils were classified as Drummer silty clay loam (fine-silty, mixed, mesic Typic Endoaquoll) with a bulk density of 1.6 g·m⁻³, organic matter of 3.4 %, soil pH of 6.0, and cation exchange capacity of 23 cmol_c·kg⁻¹ (0-20 cm). During 09-19 Jun., the cumulative precipitation was 57 mm, and the average soil temperature and moisture from the depth of 0-10 cm were 23±3 °C and 0.32±0.06 cm³·cm⁻³, respectively, which were determined by the on-site weather station.

2.3.2 Instrumentation setup

The spectrometer was a monostatic open path FTIR air monitoring system (Model2501-C, MIDAC Corporation, Irvine, CA). This instrument included the IR source, interferometer, transmitting/receiving telescope, mercury cadmium telluride (MCT) detector and ZnSe optics. A mid-IR beam in the spectrometer passed through the atmosphere along an optical path and returned to the telescope after reflection from a retro-reflector to collect spectra that included

information about the gas of interest. A cube-corner retroreflector with 26 cubes was mounted on a retractable tripod with 150 m physical path length from the telescope, corresponding to an optical path length of 300 m (Figure 2.1).

Ambient concentrations of N_2O and CO_2 were also determined independently to assess the bias and precision. A difference frequency generation (DFG) mid-IR laser-based $\text{N}_2\text{O}/\text{H}_2\text{O}$ analyzer (IRIS 4600, Thermo Fisher Scientific Inc., Waltham, MA) and the non-dispersive infrared (NDIR) spectrometer $\text{CO}_2/\text{H}_2\text{O}$ gas analyzer (LI-840, LI-COR Inc., Lincoln, NE) were used to measure N_2O and CO_2 concentrations of the sampled gases from a synthetic open path gas sampling system (S-OPS) (Figure 2.1). The DFG laser-based N_2O analyzer determined N_2O concentrations in the mid-infrared wavelength with high precision of < 0.15 ppbv (1σ , 3 min averaging). An NDIR CO_2 analyzer exhibited high accuracy (< 1.5 % of reading) and low noise (< 1.0 ppmv) to determine CO_2 concentrations using a single path, dual-wavelength, and infrared detections system.

A 50-m long S-OPS combined with a gas sampling system (GSS) was used to collect gas samples along an optical path of OP-FTIR. An S-OPS consisted of 9.5-mm diameter Teflon[®] tubes and ten inlets fitted with 1.0- μm Teflon[®] filters. The inlet flow rates were adjusted by critical orifices to $0.70 \text{ L} \cdot \text{min}^{-1}$ (± 10 %). Gas samples were drawn through an S-OPS line by a sampling pump in the GSS at approximately $7 \text{ L} \cdot \text{min}^{-1}$ and collected into a Teflon[®] ambient pressure chamber. Then, N_2O and CO_2 analyzers drew air samples from the ambient pressure chamber to measure the ‘actual’ path-averaged concentrations of N_2O and CO_2 along the OP-FTIR path (Heber et al., 2006). The measured $\text{N}_2\text{O}/\text{CO}_2$ concentrations were used to benchmark concentrations calculated from the OP-FTIR spectrum. Temperature, relative humidity, and pressure in the ambient pressure chamber were also recorded every 30 s to monitor the performance of the GSS.

Meteorological measurements of air temperature and relative humidity were measured using an HMP45C probe (Vaisala Oyj, Helsinki, Finland) at 1.5-m above ground level (a.g.l.). The meteorological data were collected by a data logger (Model CR1000, Campbell Scientific, Logan, Utah) and averaged every 30 min. Wind speed and direction were acquired from a 3D sonic

anemometer (Model 81000, RM Young Inc., Traverse City, MI) mounted at 2.5-m height on the meteorological mast and recorded at 16 Hz. The recorded data were telemetered to the on-site instrumentation trailer.

2.3.3 Overview of ambient temperature and concentrations of N₂O/CO₂/water vapor

The 30-min averages of ambient N₂O and CO₂ concentrations were determined by the S-OPS, and water vapor content and air temperature were measured at the meteorological station (Figure 2.2). During the test, 793 valid OP-FTIR spectra with known concentrations of N₂O, CO₂, water vapor, and air temperature were collected. Ninety spectra containing 338±0.3 ppbv N₂O and ninety-three spectra containing 400±3.0 ppmv CO₂ were selected from these valid spectra to calculate concentrations of N₂O and CO₂, respectively, using different quantitative methods. These groups of spectra with consistent N₂O/CO₂ concentrations but covered by broad ranges of water vapor content and air temperature were used to examine the effect of water vapor and temperature on concentration calculations.

2.3.4 OP-FTIR data acquisition and QA/QC procedure

A spectral range of 500.0-4000.0 cm⁻¹ and a resolution of 0.5 cm⁻¹ were selected for spectra acquisition. Each sampled spectrum was acquired by co-adding 64 single-sided interferograms (IFGs) using the AutoQuant Pro4.0 software package (MIDAC Corporation, Irvine, CA). The IFGs were converted to single beam (SB) spectra using a zero-filling factor of 1, triangular apodization, and Mertz phase correction. A stray light SB spectrum was also acquired by daily pointing the transmitting/receiving telescope away from the retroreflector at the beginning of the experiment using the same parameters (Russwurm and Childers, 1996). Each sampled SB spectrum was stray-light corrected by subtracting the stray-light SB spectrum from the sampled SB spectrum before converting to the absorbance spectrum.

The IFGs and corresponding SB spectra were influenced by ambient factors that included wind-derived vibrations, scintillation induced by air mixing, water vapor content, dust accumulation and condensation on the retro-reflector. Criteria of quality assurance were based on the inspection of the IFG and SB spectra, following the standard guideline in the MIDAC instrumentation manual and the FTIR open-path monitoring guidance documents (Russwurm and

Childers, 1996) with the supplement criteria published by Childers et al. (2001b) and Shao et al. (2007) to acquire high-quality spectra. The maximum and minimum of the IFG centerburst were controlled between approximately 0.61 and 1.14 VDC based on the physical path length of 150-m. Any IFG centerburst signals > 2.25 VDC were rejected to avoid a non-linear response of the MCT detector.

2.3.5 Spectral analysis

2.3.5.1 Absorbance spectra

To calculate a concentration for a given solute, a stray-light corrected SB spectrum is ratioed against an SB background spectrum (GHGs-free) to produce an absorbance spectrum from which the gas concentration is determined using the Beer-Lambert law. As discussed earlier, OP-FTIR measurements do not permit the collection of a background spectrum that is ‘free’ of GHGs. Two different approaches were used in this study to overcome this constraint. Both methods required a ‘normal’ SB spectrum corresponding to the path length of interest that was then mathematically manipulated to produce a background spectrum. A representative field SB spectrum and the regions of interest for each GHG are shown in Figure 2.3(a). For the ‘zapped’ background method, a background (zap-bkg) was obtained by drawing a straight line between two selected points which removed, or ‘zapped,’ any spectral contributions below the line using OMINC Macro Basic 8.0 commercial software (Thermo Fisher Scientific, Inc.). This is illustrated for the N_2O region of interest in Figure 2.3(b), with the two points and the line labeled as ‘zapped’ background. For the zap-bkg method, one quality SB spectrum was selected to create a zap-bkg each day, and all of the sampled SB spectra collected from one day were converted to absorbance spectra using this zap-bkg. Another method, referred to as the ‘synthetic’ background method, was generated from this same original SB spectrum using IMACC software (Industrial Monitoring and Control Corp., Round Rock, TX). In this case, numerous points in the ‘non-absorbing’ region of the SB spectrum were selected as ‘base points,’ and a high-order fitting function was used to construct a background spectrum. An example in the $\text{N}_2\text{O}/\text{CO}_2$ regions is illustrated in Figure 2.3(b) and labeled ‘synthetic’ background (syn-bkg). Six points within $2050.0\text{--}2500.0\text{ cm}^{-1}$ were selected to fit the curvature of the SB spectrum using a polynomial function to create a syn-bkg SB spectrum (Figure 2.3b). The mathematically manipulated SB spectra were used as background files to convert the sampled SB spectra into absorbance spectra

(Figure 2.3 c and d). For the syn-bkg method, all data points were stored as one data file, and this file was applied to each sampled SB spectrum to create its syn-bkg. Since the selected points determined the curvature of the syn-bkg SB spectrum, it is critical to choose the data points that do not introduce any distortion (e.g., artificial dips and peaks) into the syn-bkg. In general, we avoided selecting data points within the absorption feature of interest (e.g., 2170.0-2224.0 cm^{-1} for N_2O analysis), and the number of data points used to fit the curvature of the SB spectrum was considered adequate if it produced a smooth function (Russwurm and Childers, 1996). Adding too many data points may lead to artificial distortion in a syn-bkg. Because the syn-bkg is one of the recommended methods for spectral analysis (ASTM, 2013), it was used to assess the feasibility of the zap-bkg method.

2.3.5.2 Gas quantifications: Multivariate models and spectral window selections

Based on the Beer-Lambert law, we used reference spectra to predict gas concentrations from field absorbance spectra. In this study, classical least squares (CLS) and partial least squares (PLS) regressions were used to calculate N_2O and CO_2 concentrations. The details of these two methods are described as follows:

CLS prediction model: Each of the reference spectra used in the CLS model contained only one gas component (e.g., N_2O , CO_2 , or water vapor), and these reference spectra were generated from the high-resolution transmission molecular absorption (HITRAN) database (Rothman et al., 2005). The CLS model (AutoQuant Pro4.0) predicted gas concentrations from the field absorbance spectra converted using the zap-bkg method. In addition, CLS spectra were also calculated using the IMACC software to predict gas concentrations from the spectra converted by the syn-bkg method. The non-linear function between the actual and predicted gas concentrations of the reference spectra was selected in the CLS model in both quantitative packages.

PLS prediction model: Each of the reference spectra used in the PLS model consisted of multiple gas components (e.g., an $\text{N}_2\text{O}/\text{H}_2\text{O}$ mixing spectrum). Gas samples were delivered to a multi-pass gas cell (White cell) with an optical path length of 33-m (Model MARS-8L/40L, Gemini

Scientific Instruments, CA). Spectra were collected by a laboratory-based FTIR spectrometer (Nexus 670, Thermo Electron Corporation, Palatine, IL), which included a global IR source, a KBr beam splitter, and a mercury cadmium telluride High D* (MCT-High D*) detector. The FTIR spectrometer was purged with dry air ($-20\text{ }^{\circ}\text{C}$ dew point) produced by a zero air generator (Model 701H, Teledyne, Thousand Oaks, CA). Certified N_2O was diluted with ultra-pure N_2 gas using a diluter (Series 4040, Environics Inc, Tolland, CT), and the water vapor content was controlled by a Nafion tube (Perma Pure, Lakewood, NJ) contained within a sealed container of saturated water vapor. Temperature and humidity were monitored using a humidity and temperature transmitter (Model HMT330, Vaisala Oyj, Helsinki, Finland). The N_2O concentrations were diluted from 30 ppmv to 0.30, 0.40, 0.50, 0.60 and 0.70 ppmv and mixed with water vapor to the relative humidity of 20, 40, 60, and 80 % at 303 K. Spectra were acquired at 0.5 cm^{-1} resolution and averaged from 64 sample scans with triangular apodization. A total of 60 spectra of $\text{N}_2\text{O}/\text{H}_2\text{O}$ mixtures were used to build the PLS model using quantitative spectral processing software (Thermo Fisher Scientific TQ Analyst Version 8.0). In order to avoid over-fitting the models, the optimum set of factors used in PLS models were determined by cross-validation and justified by the prediction of residual error sum of squares (PRESS) function. The correlation between known and PLS-predicted concentrations was used to quantify N_2O from the field absorbance spectrum converted by syn-bkg within given spectral windows.

Spectral window selections: The window selection (Figure 2.4) was critical because of interferences of water vapor. While a broader window contained more information of the gas of interest and potentially improved the spectral fit between the modeled and sampled spectra and the quantitative accuracy, it also included more features of water vapor and led to biases in gas quantifications. On the other hand, a narrow window can minimize the interfering effect of the uninteresting gases but may reduce the spectral information of the targeted gas which leads to biases in gas calculations (e.g., underestimation of gas quantification). The window used for N_2O quantifications was $2130.0\text{ to }2224.0\text{ cm}^{-1}$ that mainly includes the absorbance features of N_2O (P-branch) and water vapor, and other regions ($W_{\text{N}1-4}$ shown in Figure 2.4a) were also selected for calculating N_2O concentrations. For CO_2 , the spectral windows of $2070.0\text{--}2085.0\text{ cm}^{-1}$ and $722.0\text{--}800.0\text{ cm}^{-1}$ (not shown) contain features of CO_2 and water vapor (Rothman et al., 2005).

Multiple windows (W_C1-3 shown in Figure 2.4c) were selected to calculate CO_2 concentrations and assess the effect of water vapor on gas predictions.

2.3.6 The accuracy of the FTIR-calculated concentration and statistical analysis

Bias, the relative error between the S-OPS and OP-FTIR measured N_2O/CO_2 , indicated the accuracy of the calculated N_2O and CO_2 concentrations using different spectral analyses (i.e., background types, multivariate models, and spectral windows) and can be calculated with Eq. (1):

$$Bias = \frac{(x_i - x_t)}{x_t} \times 100\% \quad [1]$$

, where x_i is the N_2O or CO_2 concentration calculated from the OP-FTIR spectrum, and x_t is the known N_2O or CO_2 concentration measured from the S-OPS. The calculated biases were statistically analyzed by ANOVA procedures and protected least significant difference (LSD) was used for multiple comparisons among population mean biases ($\alpha=0.05$) (SAS 9.3; SAS Institute Inc., 2012).

2.4 Results and Discussion

2.4.1 Quantitative methods (SB backgrounds, spectral windows, and multivariate models)

Both SB background methods (zap- and syn-bkg) were used to convert the sampled SB spectra to absorbance spectra for gas quantifications. Different windows (W_N1-4 for N_2O and W_C1-3 for CO_2) were used to calculate N_2O/CO_2 concentrations from absorbance spectra using CLS and PLS models. A series of the OP-FTIR spectra acquired from broad ranges of humidity (i.e., 5,000-20,000 ppmv water vapor) and temperature (10-35 °C) were used to calculate N_2O and CO_2 concentrations. Within these ranges, the mean bias (%) indicated the accuracy of N_2O or CO_2 quantification and the standard deviation (SD) referred to the sensitivity of quantitative methods to water vapor content and air temperature.

2.4.2 Nitrous oxide (338 ppbv)

Spectral windows that were less interfered by water vapor absorption features generally improved the accuracy of N_2O quantification. In the CLS model, N_2O concentrations calculated from the absorbance spectra converted by zap-bkg were underestimated by 10.7 ± 2.3 % using the broadest window (W_N1 : 2170.0-2223.7 cm^{-1} shown in Figure 2.4a). This bias was reduced using

W_{N2} (2188.5-2223.7 cm^{-1}) (i.e. bias = -9.1 ± 2.5 % shown in Figure 2.5a). Likewise, N_2O concentrations derived from the absorbance spectra converted by syn-bkg were underestimated by 8.2 ± 2.6 % using the W_{N1} . This bias was reduced using W_{N3} (2215.8-2223.7 + 2188.5-2204.1 cm^{-1}) (i.e., bias = -5.6 ± 2.6 % shown in Figure 2.5b). Although interferences of water vapor can be mitigated by narrowing down spectral windows, the narrowest window (W_{N4} : 2188.5-2204.1 cm^{-1}) used in the CLS model resulted in greater biases than the W_{N3} in both zap- and syn-bkg procedures (Figure 2.5 a and b). The narrowed window also lost N_2O absorption features and presumably increased biases if the analytical window was over confined. The P-branch feature of N_2O extended from 2130.0 to 2223.7 cm^{-1} , and this region was also used to calculate N_2O concentrations. In the CLS model, the window of 2130.0-2223.7 cm^{-1} showed the minimum mean bias of -0.4 % of the calculated N_2O concentrations using syn-bkg (data not shown); however, this window was sensitive to interfering water vapor and led to the highest variability in N_2O estimations (i.e., -0.4 ± 5.3 %).

As previously mentioned, it was important to generate a reasonable background for the spectral analysis. In the CLS model, the bias of N_2O quantification using the syn-bkg was significantly lower than the zap-bkg based on the same spectral window (W_{N1-3} ; $p < 0.05$) (Figure 2.5 a and b). The syn-bkg method coupled with the integrated window of 2215.8-2223.7 cm^{-1} and 2188.7-2204.1 cm^{-1} (W_{N3}) were considered as the optimal combination for N_2O quantifications using CLS models (i.e., lowest bias = -5.6 ± 2.6 % in CLS shown in Figure 2.5b). This optimal combination was also used in the PLS model to predict N_2O concentrations. The mean bias of the calculated N_2O was reduced from -5.6 % (CLS model) to -0.3 % (PLS model) (Figure 2.5 b and c). As compared with the CLS model, the PLS model significantly improved the accuracy of N_2O quantification ($p < 0.05$) presumably because the PLS algorithm can extract useful latent factors from the $\text{N}_2\text{O}/\text{H}_2\text{O}$ mixing spectra (e.g., the contribution of water vapor to N_2O).

2.4.3 Carbon dioxide (400 ppmv)

For CO_2 estimations, three spectral windows were used in the 2070.0-2084.0 cm^{-1} range (Figure 2.4c). The accuracy of CO_2 quantification was also improved by narrowing down spectral windows (Figure 2.6). In the CLS model, CO_2 concentrations calculated from the absorbance spectra converted by zap-bkg were underestimated by 6.4 ± 4.1 % using the broadest window

(W_{C1} : 2070.0-2084.0 cm^{-1}). This bias was reduced by the narrowed window of W_{C2} (2075.5-2084.0 cm^{-1}) (i.e., bias = -0.1 ± 4.2 % shown in Figure 2.6a). The bias of the calculated CO_2 concentrations was -4.7 ± 2.5 % using W_{C1} coupled with syn-bkg and reduced to -0.3 ± 2.4 % using W_{C2} (Figure 2.6b). The most confined window (W_{C3} : 2075.5-2080.5 cm^{-1}) resulted in greater biases than W_{C2} , and particularly in conjunction with zap-bkg (i.e. bias = 3.2 ± 3.4 % shown in Figure 2.6a). Thus, the range from 2075.5 to 2084.0 cm^{-1} (W_{C2}) was the optimal window for CO_2 quantification using the CLS model (Figure 2.4c).

The zap-bkg led to a greater underestimate in N_2O (bias = -10 ± 2.3 % shown in Figure 2.5a) than CO_2 calculations (bias = -0.1 ± 4.2 % shown in Figure 2.6a) based on the optimal window (W_{N3} and W_{C2}) used in CLS models. Since the absorbance feature of CO_2 at 2076.9 cm^{-1} (the band center) was less complicated than the P-branch of N_2O from 2170.0 to 2223.7 cm^{-1} , the CO_2 absorbance converted by zap-bkg was similar to syn-bkg (Figure 2.3 c and d). Therefore, the calculated bias showed that there was no significant difference between zap- and syn-bkg methods for CO_2 concentration calculations using the W_{C2} (Figure 2.6). Zap-bkg, however, led to the higher variability in the calculated CO_2 , indicating that simply removing the CO_2 feature by the linear function potentially resulted in biases for CO_2 quantification.

The other potential region for CO_2 quantification was within 722.0-800.0 cm^{-1} (the R-branch of CO_2 ν_2 band shown in Figure 2.3a). Different windows were examined for calculating CO_2 concentrations using the CLS model in this region, and the CO_2 concentrations were underestimated by 40-70 % no matter which window was used in conjunction with zap-bkg. The mean bias was minimized (bias = -9.0 ± 2.9 %) by using two windows of 723.0-727.7 cm^{-1} and 732.0-738.5 cm^{-1} in conjunction with syn-bkg (data not shown). As compared with the results from the 2070.0-2084.0 cm^{-1} range (Figure 2.4c), the 722.0-800.0 cm^{-1} window resulted in a significant underestimation of CO_2 concentration because 1) more water vapor features interfered with the R-branch of CO_2 features in the 722.0-800.0 cm^{-1} range than CO_2 in the 2070.0-2084.0 cm^{-1} range, and 2) it was difficult to simulate the appropriate background at the low wavenumber region in the SB spectrum.

2.4.4 Diurnal N₂O/CO₂ estimations

The quantitative approach leading to the minimum bias in N₂O estimations was to use syn-bkg with the W_{N3} window in the PLS model (Figure 2.5c). For CO₂, only the CLS model was used for calculating concentrations because of missing CO₂/H₂O mixing spectra for PLS models. The approach leading to the minimum bias in CO₂ estimations in this study was to use syn-bkg with the W_{C2} window in the CLS model (Figure 2.6b). These procedures were used to estimate N₂O and CO₂ concentrations from the OP-FTIR spectra collected from 09 to 19 Jun. 2014 (Figure 2.7). The diurnal fluctuations in N₂O and CO₂ concentrations corresponded to diurnal changes of wind speed and air temperature. The higher N₂O/CO₂ concentrations were usually measured during the night because of N₂O and CO₂ accumulations. The accumulation of N₂O/CO₂ occurred near the ground when turbulent mixing was low, resulting from decreasing buoyancy from the ground surface (i.e., a stable atmosphere). The greater density of air parcels due to decreasing temperature also led to gas accumulation. The diurnal variation in CO₂ was greater than N₂O (Figure 2.7b), and we hypothesized it was due to multiple sources of CO₂. While N₂O was mostly produced from soils via microbial nitrification and denitrification, CO₂ was emitted via soil respiration (including microbes and corn root) as well as respiration from grass and corn leaves.

Mixing of the surface layer of air tended to result in greater homogeneity along the optical path. Under low wind speed, the presumably poorly-mixed air increased the variability of the path-averaged N₂O/CO₂ concentrations along the optical path, resulting in the difference between the 50-m S-OPS and the 150-m OP-FTIR. The calculated biases of N₂O and CO₂ were 1.3 ± 2.6 % (n=363) and -0.7 ± 5.8 % (n=327), respectively, while the mean wind velocity ranged from 0.1 to 8.4 m·s⁻¹ (Figure 2.7). The variability of the calculated biases of N₂O and CO₂ were reduced when the data that were collected in low wind speeds (< 1.7 m·s⁻¹) were excluded, i.e. $bias_{N_2O} = 1.4 \pm 2.3$ % (n=298) and $bias_{CO_2} = -1.0 \pm 2.8$ % (n=272).

2.5 Conclusion

We have developed and evaluated different methods for quantifying concentrations of nitrous oxide and carbon dioxide using open-path FTIR based on combinations of single beam

backgrounds (zap-bkg and syn-bkg), analytical windows (W_N1-4 and W_C1-3), and chemometric multivariate calibration models (CLS and PLS). It is challenging to generate the P-branch N_2O absorbance within $2170.0-2223.7\text{ cm}^{-1}$ to predict N_2O accurately but feasible to generate absorbance within $2075.5-2084.0\text{ cm}^{-1}$ for CO_2 prediction using the zap-bkg method. The principle for selecting spectral windows is that using the region with less water vapor features, while over confining the analytical region may lead to biases in gas predictions. The CLS model, the most common approach used for gas retrievals in OP-FTIR commercial packages, underestimates N_2O concentrations but predicts CO_2 accurately within an absolute humidity range of 5,000-20,000 ppmv and a temperature range of 10-35 °C. In this study, the method resulting in the minimum bias for N_2O quantification is to use the combination of syn-bkg, a two bands window ($2188.7-2204.1 + 2215.8-2223.7\text{ cm}^{-1}$), and the PLS model (N_2O bias = $1.4 \pm 2.3\%$). The method leading to the minimum bias in CO_2 quantification is to use the combination of syn-bkg, the $2075.5-2084.0\text{ cm}^{-1}$ window, and the CLS model (CO_2 bias = $-1.0 \pm 2.8\%$). We describe comprehensive methods of N_2O/CO_2 analyses for the increasing number of OP-FTIR users who are interested in greenhouse gas emissions from agricultural fields.

2.6 References

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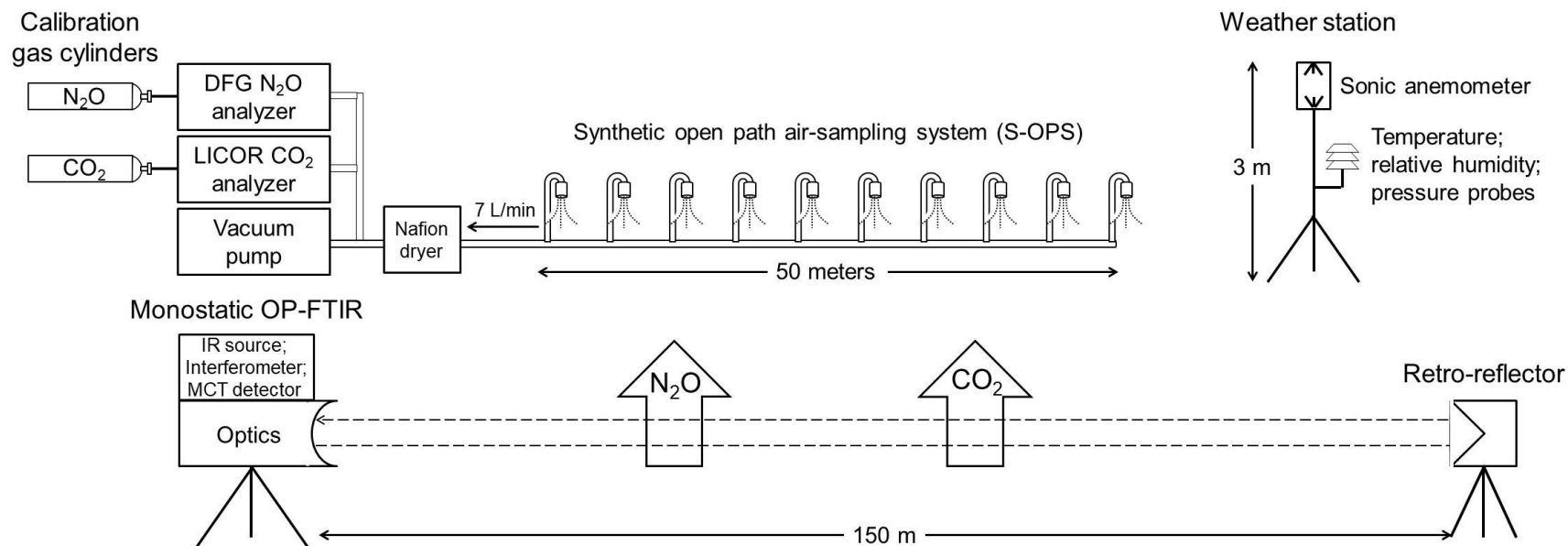


Figure 2.1 Schematic of the instrumentation used to assess the accuracy of N₂O and CO₂ concentration determined by OP-FTIR in this study. DFG N₂O and LI-840 CO₂ analyzers combined with the synthetic open path air-sampling system (S-OPS) were used to measure the ‘actual’ path-averaged N₂O/CO₂ concentrations and benchmark the N₂O and CO₂ concentrations calculated from OP-FTIR spectral analyses. The humidity, air temperature, and wind information were measured from the weather station.

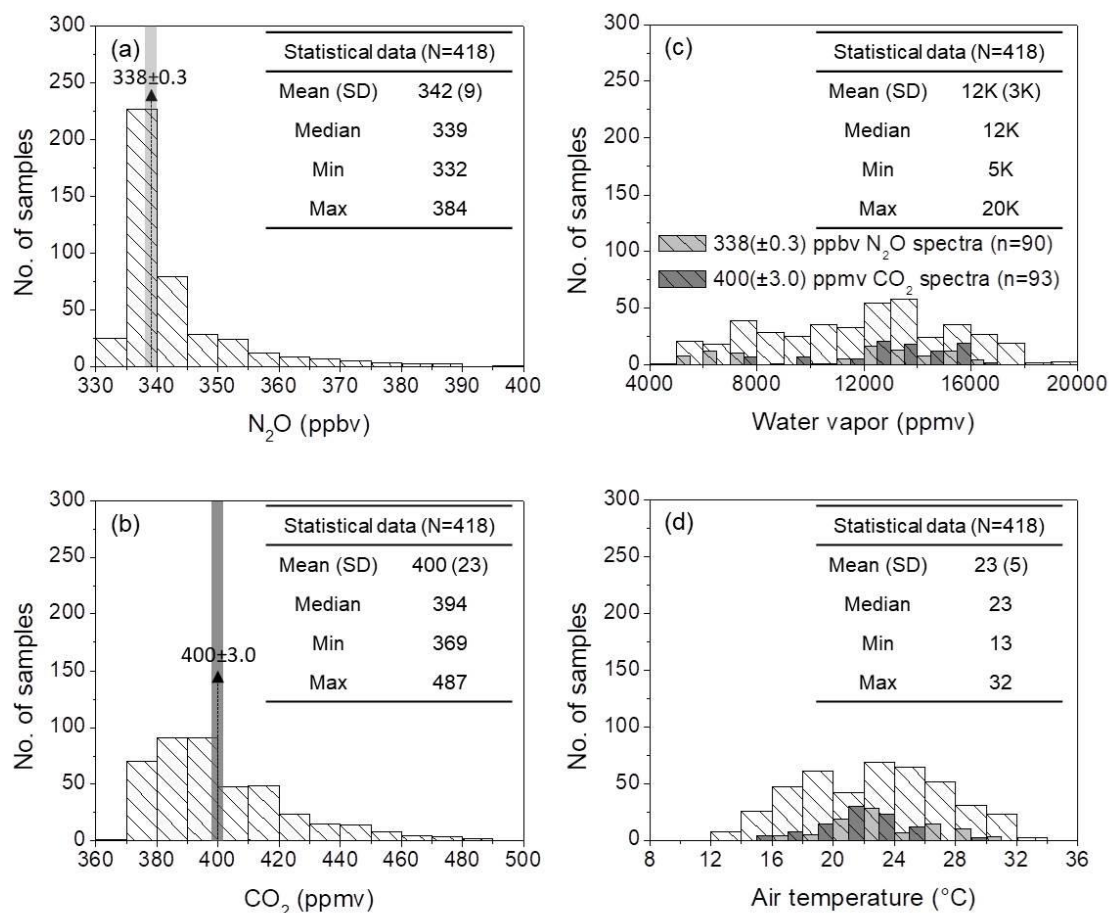


Figure 2.2 The 30-min averaged concentrations of (a) N_2O and (b) CO_2 were measured using N_2O and CO_2 analyzers by sampling the air from S-OPS, and the 30-min averages of (c) water vapor content and (d) air temperature were also measured from the on-site weather station during 09-19 Jun. 2014. The concentrations of N_2O , CO_2 , and water vapor shown in these figures were measured while the air was well-mixed ($U > 1.5 \text{ m}\cdot\text{s}^{-1}$). The light gray bars mean the OP-FTIR spectra contained 338 ± 0.3 ppbv N_2O and the dark gray bars mean the OP-FTIR spectra contained 400 ± 3.0 ppmv CO_2 . Both selected spectra (N_2O 338 ppbv, $n=90$; CO_2 400 ppmv, $n=93$) covered the broad ranges of water vapor and air temperature and were used to assess the sensitivity of the OP-FTIR quantitative methods to dynamic ambient variables.

(a) Single beam (SB) field spectrum

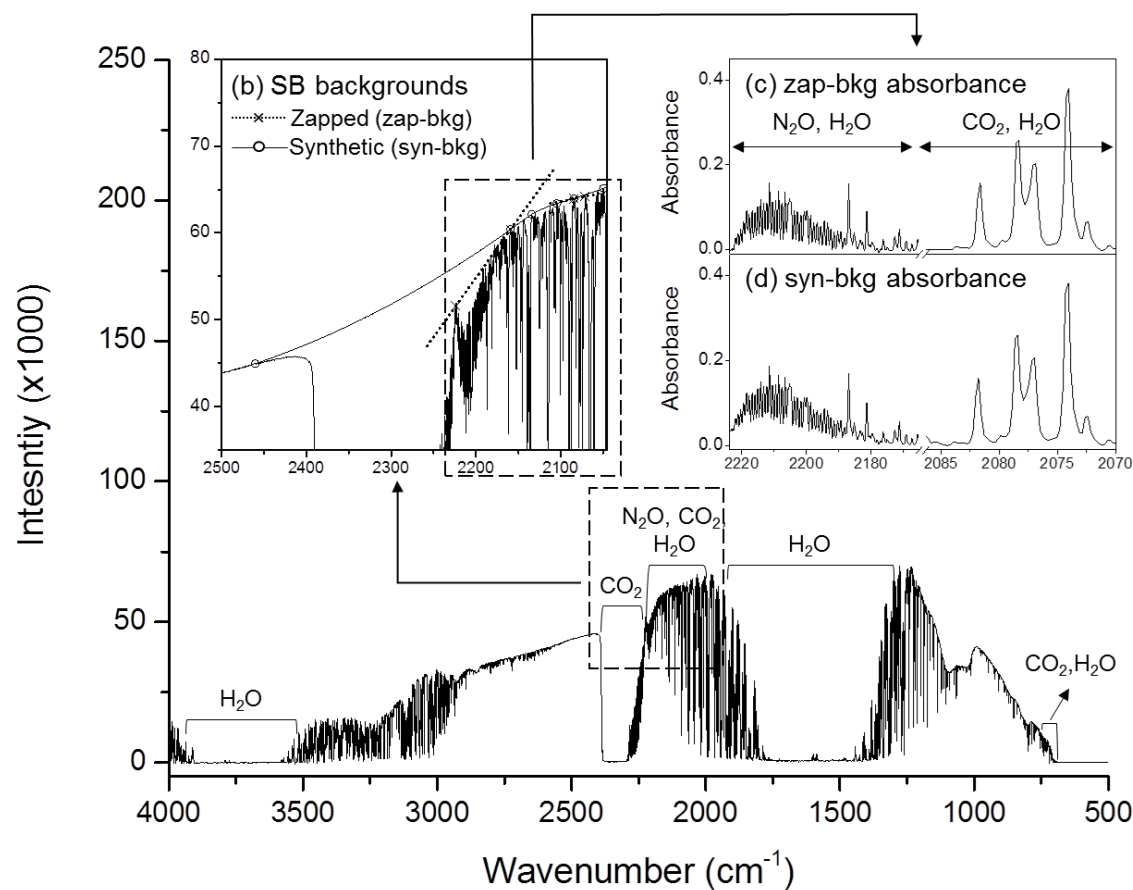


Figure 2.3 The illustrations of (a) a field single beam (SB) OP-FTIR spectrum containing the regions of N_2O , CO_2 , and water vapor was collected through an optical path length of 300 m; (b) zapped and synthetic SB backgrounds (zap-bkg and syn-bkg) were generated from this field SB spectrum and used to convert the sampled SB spectrum to (c) the absorbance spectra that allow us to calculate $\text{N}_2\text{O}/\text{CO}_2$ concentrations using the Beer-Lambert law.

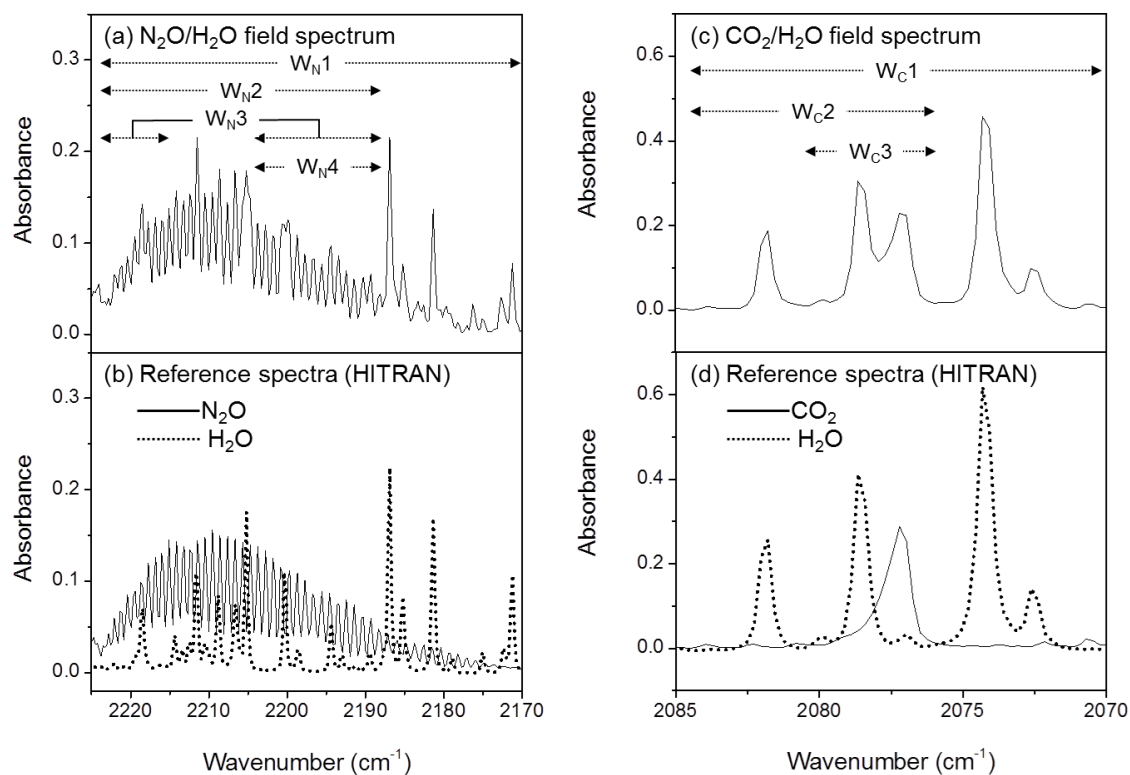


Figure 2.4 Field and HITRAN reference absorbance spectra: (a) field spectrum containing the features of N_2O and water vapor, (b) reference spectra of N_2O and water vapor at $2170.0 - 2224.0 \text{ cm}^{-1}$, (c) field spectrum containing the features of CO_2 and water vapor, and (d) reference spectra of CO_2 and water vapor at $2070.0 - 2084.0 \text{ cm}^{-1}$. $W_N(1-4)$ and $W_C(1-3)$ denote the spectral windows used to calculate N_2O and CO_2 concentrations from field spectra.

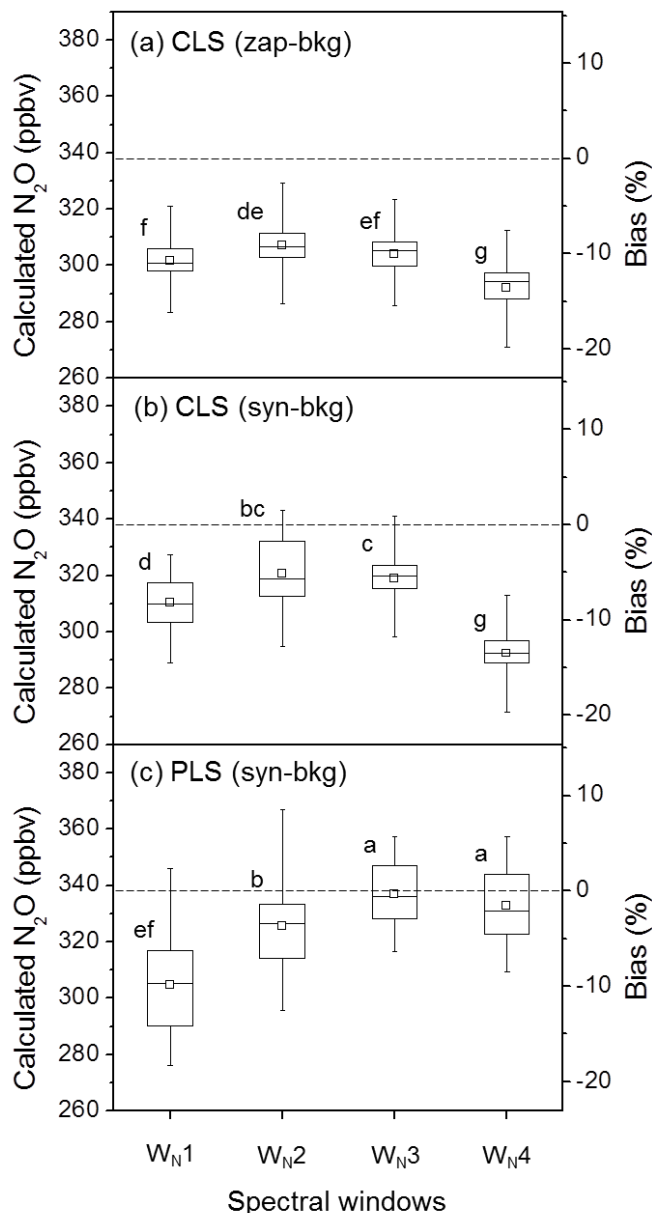


Figure 2.5 The box plots of the calculated N_2O concentrations and the corresponding biases from a series of OP-FTIR spectra ($n=90$) that contain 338 ± 0.3 ppbv N_2O with varying humidity and air temperature using different SB background-processing methods (zap-bkg and syn-bkg), and four spectral windows (W_{N1} -4) in the CLS and PLS models: (a) zap-bkg + CLS model, (b) syn-bkg + CLS model, and (c) syn-bkg + PLS model. The plot displays the mean ($\square$), median (—), interquartile ranges (box), and extreme values (whiskers). Different letters indicate significant differences ($p < 0.05$) among the means calculated by different quantitative methods by the least significant difference (LSD).

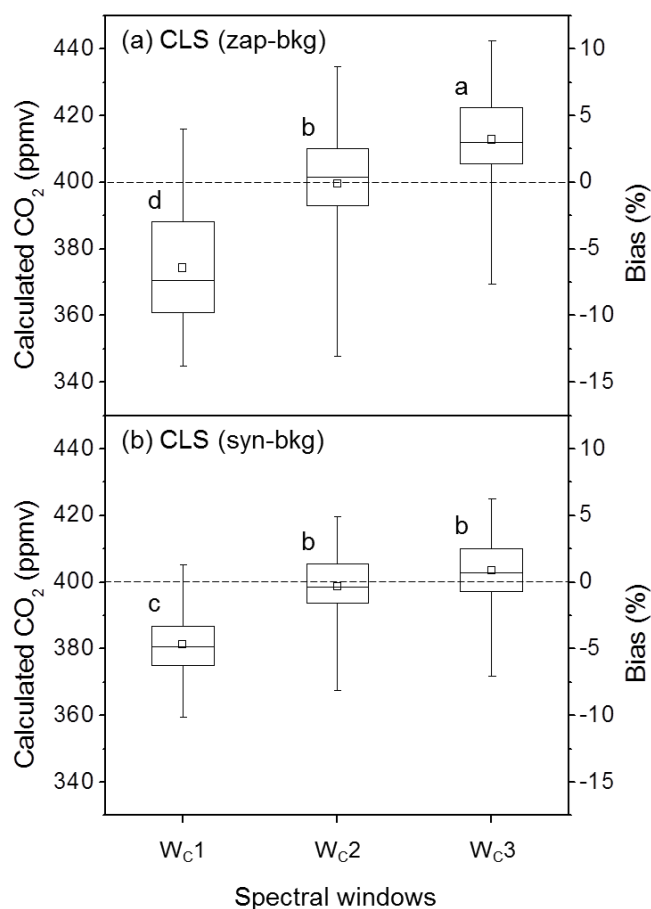


Figure 2.6 The box plots of the calculated CO₂ concentrations and the corresponding biases from a series of OP-FTIR spectra ($n=93$) that contain 400 ± 3.0 ppmv CO₂ with varying humidity and air temperature using different SB background-processing methods (zap-bkg and syn-bkg), and three spectral windows (W_c1-3) in the CLS model: (a) zap-bkg, and (b) syn-bkg. The plot displays the mean ($\square$), median ($-$), interquartile ranges (box), and extreme values (whiskers). Different letters indicate significant differences ($p < 0.05$) among the means calculated by different quantitative methods by the least significant difference (LSD).

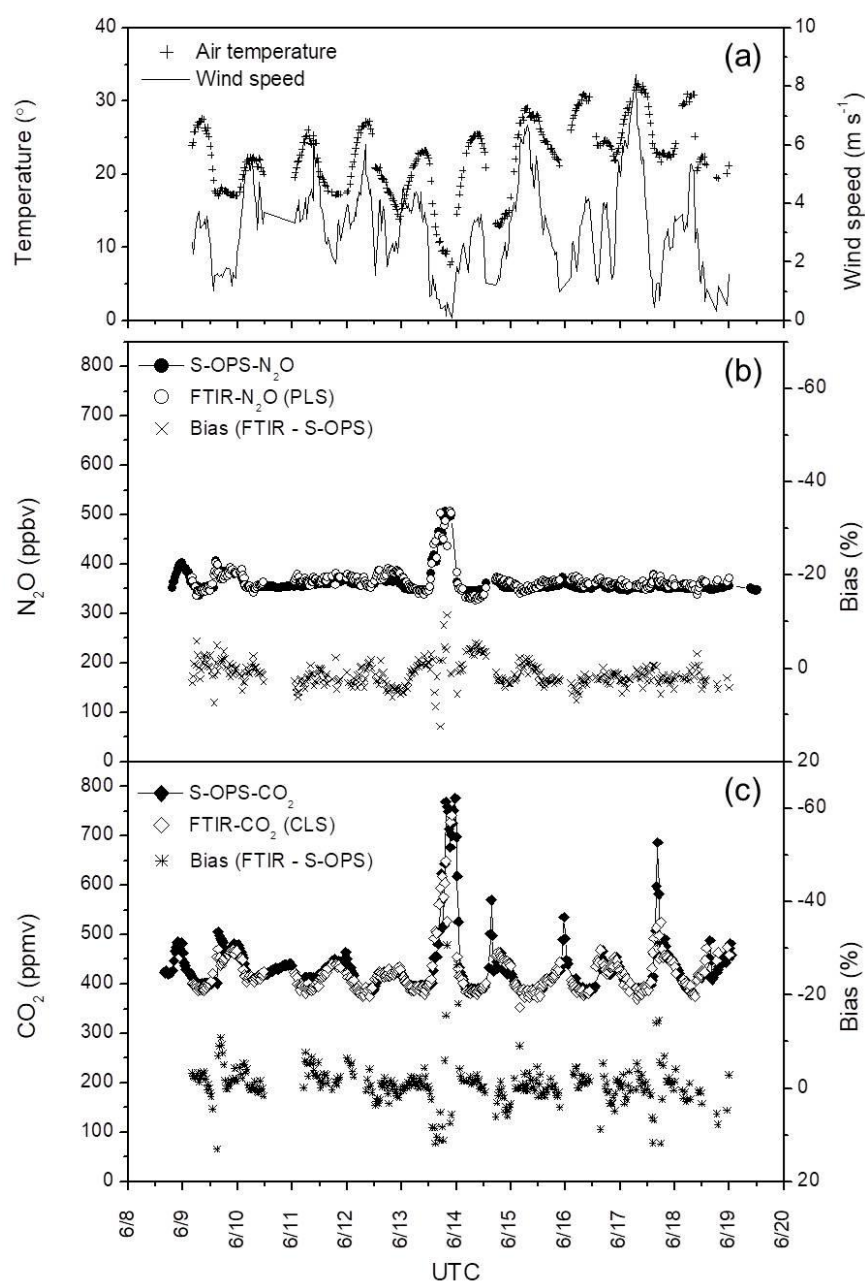


Figure 2.7 Measurements of air temperature, wind speed, N₂O and CO₂ concentrations from 09-19 Jun. 2014. The 30-min averages of (a) air temperature and wind speed, (b) N₂O concentrations measured from S-OPS using the DFG N₂O analyzer and calculated from OP-FTIR using the method of (syn-bkg + W_{N3} + PLS), and the corresponding biases, and (c) CO₂ concentrations measured from S-OPS using LI-840 CO₂ analyzer and calculated from OP-FTIR using the method of (syn-bkg + W_{C2} + CLS), and the corresponding biases.

CHAPTER 3. SOURCES OF ERROR IN OPEN PATH FTIR MEASUREMENTS OF N₂O AND CO₂ EMITTED FROM AGRICULTURAL FIELDS

A version of this chapter has been submitted for review to the open-access journal of Atmospheric Measurement Techniques.

3.1 Abstract

Open-path Fourier transform infrared spectroscopy (OP-FTIR) is susceptible to environmental variables which can become sources of errors for gas quantification. In this study, we assessed the effects of water vapor, temperature, path length, and wind speed on the uncertainty of nitrous oxide (N₂O) and carbon dioxide (CO₂) concentrations derived from OP-FTIR spectra. The presence of water vapor resulted in underestimating N₂O in both lab (−3 %) and field (−12 %) experiments at 30 °C using a classical least squares (CLS) model. Differences in temperature between the sample and reference spectra also underestimated N₂O concentrations due to temperature broadening and the increased interferences of water vapor in spectra of wet samples. Changes in path length resulted in a non-linear response of spectra and bias (e.g., N₂O and CO₂ concentrations were underestimated by 30 % and 7.5 %, respectively, at the optical path of 100-m using CLS models). For N₂O quantification, partial least squares (PLS) models were less sensitive than CLS to the influence of water vapor, temperature, and path length, and provided more accurate estimations. Uncertainties in the path-averaged concentrations increased in low wind conditions (< 2 m s^{−1}). This study identified the most common interferences that affect OP-FTIR measurements of N₂O and CO₂. The quantified errors can be used as references for current or future OP-FTIR users.

3.2 Introduction

Agriculture substantially contributes greenhouse gases (GHGs), mostly N₂O and CH₄, to the atmosphere (IPCC, 2007). In 2010, emissions led by agricultural activities (e.g., crop production and livestock management) were estimated between 5.2 and 5.8 Gt of CO₂ equivalent per year, accounting for 10-12 % global anthropogenic emissions (IPCC, 2014). Estimations of gas fluxes over an extended period (e.g., growing seasons) is complicated due to the dynamic and episodic

nature of gas emissions and measurement complexities. The integrated uses of fast-response gas concentration sensors and micrometeorological techniques were developed to measure long-term gas fluxes continuously (Baldocchi, 2003; Denmead, 2008; Flesch et al., 2016). Open-path Fourier transform spectroscopy (OP-FTIR) is capable of measuring concentrations of multiple gases simultaneously with high temporal and spatial resolution through real-time measurements and path-averaged concentrations (Russwurm and Childers, 2002). OP-FTIR has been applied to measure GHGs, and other trace gases (e.g., NH_3) emitted from agricultural fields (Childers et al., 2001a and 2001b; Bjorneberg et al., 2009; Flesch et al., 2016; Lam et al., 2017). Using OP-FTIR to quantify gas concentrations, however, is a complicated process. Each step in data collection and spectral analyses influences the accuracy and precision of gas quantifications, including spectral resolution, apodization function, choice of background (e.g., zero-path or synthetic backgrounds), and chemometric models (Russwurm and Childers, 1999; Griffiths and de Haseth, 2007; Hart and Griffiths, 2000; Hart et al., 2000). Also, OP-FTIR spectra are sensitive to ambient environmental conditions (e.g., humidity, air temperature, optical distance, and wind speed), which interferes with spectral analyses and quantification of gas concentrations (Griffiths and de Haseth, 2007; Muller et al., 1999; Shao et al., 2007 and 2010).

Water vapor is a major interference in FTIR-derived trace gas quantification due to its strong absorption features within the mid-infrared region ($400\text{-}4000\text{ cm}^{-1}$) (Russwurm and Childers, 1999; ASTM, 2013). For the interference-free spectra, a single absorption line can be easily isolated to calculate gas concentrations (i.e., univariate methods). Using this method, however, is challenging to adequately isolate the absorption feature of the gas of interest from water vapor (Muller et al., 1999; Briz et al., 2007). Multivariate methods have been proposed to improve gas quantification from spectral interferences including water vapor by selecting broad spectral windows of gases of interest (Haaland and Easterling, 1980; Haaland and Thomas, 1988; Hart and Griffiths, 1998 and 2000; Hart et al., 1999 and 2000; Muller et al., 1999). The most common method in commercial quantification packages is the classical least squares (CLS) quantitative model (Griffiths and de Haseth, 2007). Studies showed that the interference of water vapor was mitigated by either considering reference spectra of water vapor or through selection of appropriate spectral windows in CLS models (ASTM, 2013; Haaland and Easterling, 1980; Hart and Griffiths, 2000; Horrocks et al., 2001; Jiang et al., 2002; Du et al., 2004; Briz et al., 2007;

Lin et al., 2019). Other studies, however, found that CLS models resulted in substantial quantification errors of the targeted gas under the interference of the non-targeted gases (mostly water vapor) even if the reference spectra of all gas species and the optimal spectral window were considered (Hart et al., 1999; Briz et al., 2007; Shao et al., 2010; Lin et al., 2019). As a result, the partial least squares (PLS) algorithm was proposed to improve the accuracy of gas quantification (Haaland and Thomas, 1988; Hart et al., 2000; Shao et al., 2010; Lin et al., 2019).

The features of gas rotation-vibrational absorption bands are temperature dependent (Lacome et al., 1984; Rothman et al., 2005). Ideally, sample and reference spectra should be collected at the same temperature to avoid temperature-related bias (Russwurm and Childers, 1999; ASTM, 2013). Training spectra for building quantitative models, such as CLS, were generally collected at the same temperature. The non-linear responses of spectral absorbance to significant diurnal variations in temperature will lead to errors in gas quantification (Russwurm and Phillips, 1999; de Castro et al., 2007; Smith et al., 2011). For continuous field measurements, it is time-consuming to create piecewise models to cover the entire ranges of 1) the path-integrated concentrations of gases of interest and interferences, and 2) temperature. A PLS model was developed to cover the wide ranges of environmental variables, including concentrations, path lengths, humidity, and temperature (Bjorneberg et al., 2009; Griffiths et al., 2009; Shao et al., 2010 and 2011).

Besides changes in water vapor content and temperature, the experimental configuration and optical parameters also influence OP-FTIR spectra. Compared with extractive methods, one of the advantages of OP-FTIR is the ability to use different path lengths to measure gases from multiple sources (Russwurm and Childers, 1999; Bacsik et al., 2006). OP-FTIR measurements require electronic gain to fill the analogue-to-digital converter of the instrument. Consequently, short optical path lengths can over saturate the detector that introduces error in gas quantification (Bartoli et al., 1974; Chase, 1984; Griffiths and de Haseth, 2007). A long path length increases the sensitivity for gas quantification, but the increased length reduces the intensity of the incident signal and decreases the signal-to-noise ratio (Griffith and Jamie, 2006; Nelson et al., 1996; Kosterev et al., 2008). Spectral resolution and apodization also affect the spectral linearity (Griffiths, 1994; Zhu and Griffiths, 1994; Russwurm and Phillips, 1999; Childers et al., 2002).

Lower resolution spectra are incapable of resolving absorption features. Even though the apodized interferogram (IFG) can reduce noises (or spurious oscillations) of a single-beam (SB) spectrum converted by Fourier transformation, different apodization functions affect spectrum linearity differently. The non-linear relationship between absorbance and concentrations disobeys Beer-Lambert Law and leads to biases in gas quantification (Russwurm and Phillips, 1999; Childers et al., 2001a).

For OP-FTIR measurements, many studies minimized environmental interferences (e.g., water vapor or wind speed) by developing methods for spectral analyses and gas quantification (Hong and Cho, 2003; Hart et al., 1999 and 2000; Muller et al., 1999; Childers et al., 2002; Briz et al., 2007; Shao et al., 2007; Griffiths et al., 2009; Shao et al., 2010; Lin et al., 2019). Briz et al. (2007) examined the difference in water vapor content (0.5 % vs. 2.5 %) on trace gas quantification but their study did not include N_2O . Shao et al. (2007) investigated the effect of wind on spectrometer vibrations and spectra qualities but did not address its influence on gas quantification. The influences of temperature on trace gas absorption intensity and bandwidth have been established for some simple systems (e.g., single gas component shown in the high-resolution transmission molecular absorption (HITRAN) database published by Rothman et al., 2005); however, only limited studies assessed temperature effect on gas quantification using OP-FTIR. Horrocks et al. (2001) and Smith et al. (2011) used OP-FTIR spectrometer and a gas cell purged with dry samples to measure the temperature-related error in SO_2 , CO , CO_2 , and CH_4 quantification, but not for N_2O .

To the best of our knowledge, there has never been a study of exploring the influence of changing temperature and path length on N_2O quantification under interferences of water vapor in spectra. It is challenging to test the quality of OP-FTIR methods for multiple gas quantification due to interferences and the lack of proper measurement benchmarks. Also, the influence of water vapor is confounded by temperature and path length effects. In this study, the influence of water vapor, temperature, path length, and wind speed on N_2O and CO_2 quantification are examined using lab and field-based (OP-FTIR) methods.

3.3 Materials and Methods

3.3.1 Lab FTIR experiment

The lab FTIR experiment was used to assess the effects of water vapor and air temperature on N₂O quantification from spectra. An FTIR spectrometer equipped with a variable-path length gas cell was used to acquire reference spectra of N₂O, water vapor, and N₂O plus water vapor mixtures (i.e., wet N₂O) as shown in Figure 3.1a.

3.3.1.1 Instrumentation setup

The lab FTIR spectrometer (Nexus 670, Thermo Electron Corporation, Madison, WI) was equipped with a KBr beam splitter, and a high-D* MCT detector was used to analyze gas samples using a multi-pass gas cell (White cell) (model MARS-8L/40L, Gemini Scientific Instruments, CA) with an optical path length of 33-m. Spectra range of 700.0-4000.0 cm⁻¹, optical velocity of 0.6 cm s⁻¹, and a resolution of 0.5 cm⁻¹ were selected for spectra acquisition. Each spectrum was acquired by co-adding 64 IFGs using the OMNIC software package (Thermo Fisher Scientific, Inc.) A triangular function was applied to apodize an IFG for converting an SB spectrum using the Fourier transform. A sampled SB spectrum contained the visible information of gases of interest and interferences. A background SB spectrum was collected from pure N₂ and used to convert a sampled SB spectrum to an absorbance spectrum. The temperature of the gas cell was controlled and monitored (model 689-0005, Barnant Co., Barrington, IL). The spectrometer was purged with dry air (-20 °C dew point) from a zero air generator (model 701H, Teledyne, Thousand Oaks, CA). Gas samples were produced using a diluter (series 4040, Environics Inc, Tolland, CT). The mixing ratio (or concentration, ppbv) of N₂O was diluted with ultra-pure N₂ gas. Water vapor concentrations (ppmv) were controlled by a Nafion tube (Perma Pure, Lakewood, NJ) enclosed within a sealed container containing saturated water vapor. The concentration of saturated water vapor in the container was adjusted by controlling temperature of the water bath. Wet N₂O gas samples were produced by passing dry N₂O from the diluter through Nafion tube with a constant flow rate (4 L·min⁻¹). Gas samples were continuously introduced into the white cell. Humidity and temperature probes (model HMT330, Vaisala Oyj, Helsinki, Finland) were used to monitor the humidity and temperature of the introduced gas samples. In this study, N₂O (dry and wet) was diluted from 30.0 ppmv (N₂O in N₂) to 310.0,

400.0, 500.0, 600.0 and 700.0 ppbv with various water vapor contents (a relative humidity of 20 %, 40 %, 60 %, and 80 % at 30 °C).

3.3.1.2 Data collections and gas quantification

Spectra were collected when the N₂O and water vapor concentrations and temperature of the introduced samples were steady. Concentrations of N₂O and water vapor were calculated from the mixed-gas (wet N₂O) absorbance spectra by CLS and PLS models using TQ Analyst software Version 8.0 (Thermo Fisher Scientific, Inc.) A total of 9 single-gas spectra of dry N₂O (310.0-700.0 ppbv) and water vapor (7000-28000 ppmv) were used to build CLS models. A total of 60 mixed-gas spectra were used to build PLS models. Spectral windows (Table 3.1) and linear baseline correction were applied in CLS and PLS models to calculate N₂O. Two windows reported by Lin et al. (2019) were used for N₂O quantification (W_{N1}: 2170.0-2223.7 cm⁻¹ and W_{N3}: 2188.7-2204.1 + 2215.8-2223.7 cm⁻¹). In PLS models, optimum factors were determined by cross validation and justified by the prediction of residual error sum of squares (PRESS) function to avoid over-fitting issues (see Table S2 in the Supplement published by Lin et al., 2019). The influence of air temperature on N₂O quantification using CLS and PLS was examined by collecting spectra at 30, 35, and 40 °C.

3.3.2 Open-path FTIR experiment

The OP-FTIR experiment was used to assess the effects of water vapor, air temperature, path lengths, and wind speed on the quantification of N₂O and CO₂ from field spectra. The field instrumentation and configuration were shown in Figure 3.1b.

3.3.2.1 Site description and instrumentation setup

The field study was conducted at Purdue University Agronomy Center for Research and Education of West Lafayette, Indiana, the United States (86°56' W, 40°49' N). The predominant soil series at the study site was a Drummer silty clay loam (fine-silty, mixed, mesic Typic Endoaquoll). The bulk density of topsoil (0-10 cm) and organic matter (0-20 cm) was measured 1.6 g·cm⁻³ and 3.8 %, respectively. The experimental site (Purdue Field Trace Gas Flux Facility) was between two maize cropping fields (~10-m apart) with anhydrous ammonia applications. A monostatic OP-FTIR (IR source, interferometer, transmitting and receiving telescope, and detector combined in one instrument) spectrometer (model 2501-C, MIDAC Corporation, Irvine,

CA) was used to collect field-IR spectra. A retroreflector with 26 corner-cubes (cube-length of 76-mm) was mounted on a tripod 150-m from the spectrometer corresponding to an optical path of 300-m. The experiment of varying path lengths was conducted using optical path lengths of 100-, 200- and 300-m.

3.3.2.2 Data collection and gas quantification

The same sample collection parameters were used to collect both OP-FTIR and lab-FTIR spectra. OP-FTIR spectra were collected using the AutoQuant Pro4.0 software package (MIDAC Corporation, Irvine, CA). Each field spectrum was collected by co-adding 64 IFGs and a resolution of 0.5 cm^{-1} . A zero-filling factor of one, triangular apodization, and Mertz phase correction were applied to convert an IFG into an SB spectrum. A stray-light SB spectrum was collected by pointing the spectrometer telescope away from the retroreflector and subtracted from sampled SB spectra for stray-light correction. Quality control and assurance procedures (Russwurm, 1999; ASTM, 2013; Russwurm and Childers, 1999; Childers et al., 2001b; Shao et al., 2007) were used to evaluate spectra qualities and the influence of wind-induced vibrations. The corrected field SB spectra were converted to absorbance spectra using the synthetic SB background spectra shown by Lin et al. (2019).

Gas concentrations derived from the OP-FTIR absorbance spectra were also calculated by CLS and PLS models. Single-gas reference spectra were generated from the HITRAN database (Rothman et al., 2005) and used to create CLS models using the IMACC software (Industrial Monitoring and Control Corp., Round Rock, TX). Identical parameters, including resolution, apodization, zero-filling factor, were used to acquire both reference and field spectra. The HITRAN reference spectra, including N_2O , CO_2 , and water vapor, were generated at 30°C to calculate N_2O and CO_2 concentrations from field spectra using optimum windows ($W_{\text{N}3}$ for N_2O and $W_{\text{C}2}$ for CO_2 shown in Table 3.1) published by Lin et al. (2019). Non-linear least square regressions between absorbance and the path-integrated concentrations of reference spectra were used to create CLS models. PLS models were built using lab-FTIR measurements and only used for estimating N_2O concentrations.

Ambient temperature and relative humidity in the field were measured using an HMP45C probe (Vaisala Oyj, Helsinki, Finland) at 1.5-m above ground level (a.g.l.). The mean wind speed was measured by a 3-D sonic anemometer (model 81000, RM Young Inc., Traverse City, MI) mounted at 2.5-m a.g.l. and recorded at 16 Hz. A 50-m synthetic open path gas sampling system (S-OPS) (Heber et al., 2006) was used to collect gas samples along the OP-FTIR optical path to analyze the path-averaged concentrations of N₂O and CO₂ using a difference frequency generation mid-IR (DFG-IR) laser-based N₂O gas analyzer (IRIS 4600, Thermo Fisher Scientific Inc., Waltham, MA) and a non-dispersive IR (ND-IR) CO₂ gas analyzer (LI-840, LI-COR Inc., Lincoln, NE), respectively. The N₂O and CO₂ analyzers provided a high precision for N₂O (< 0.15 ppbv, 1 σ) and CO₂ (< 1.0 ppmv, 1 σ) measurements, so the path-averaged concentrations measured from the S-OPS were used as benchmarks to examine the accuracy and the sensitivity of OP-FTIR on gas quantification.

3.3.2.3 Path lengths experiment

A variable path length between an OP-FTIR spectrometer and a retroreflector resulted in different path-integrated concentrations and the depth of gas absorbance in SB spectra. The complexities of N₂O absorption features within the 2170.0-2224.0 cm⁻¹ range required high spectral resolution (Figure 3.3). For N₂O, the increased absorbance, resulting from a longer path length, likely improves its quantitative sensitivity and accuracy. Spectra were collected from physical lengths of 50-, 100-, and 150-m (Figure 3.1b) using the same parameters. During the measurement (14:30-18:30, local time (LT) on 6 May 2016), background concentrations of N₂O (349.0 $\pm$ 0.5 ppbv) and CO₂ (400.0 $\pm$ 4.4 ppmv), ambient temperature and humidity (the relative humidity of 35.0 % at 25 °C) remained nearly constant. The spectra acquired from different path lengths were analyzed by CLS models for N₂O and CO₂ concentrations and by PLS models only for N₂O.

3.3.3 Quantification accuracy

Quantitative accuracy/bias was determined by the relative error of the path-averaged concentrations between FTIR (x_i) and the true gas concentrations (x_t) of either the introduced gas (Lab) or the S-OPS measurements (Field), following Eq. (1):

$$Bias = [(x_i - x_t)/x_t] \times 100\% \quad [1]$$

3.4 Results and Discussion

Quantification of target gas concentrations from either lab- or field-based FTIR spectra requires knowledge of the optimum spectral window (the spectral region used for quantification). In general, broadening the spectral windows will contain more spectral features that can be used for quantification. At the same time, however, broader windows will also contain more contributions from interfering constituents (e.g., water vapor). The optimum window would have clean spectral features of the target species with minimal spectral interference from other gases. For N₂O quantification, our previous work showed that the optimum window was to integrate two intervals of 2215.8-2223.7 and 2188.5-2204.1 cm⁻¹ (W_{N3} shown in Lin et al., 2019). In this paper, two windows (W_{N1} and W_{N3}) and models (CLS and PLS) from the previous study were used to predict N₂O concentrations.

3.4.1 Lab FTIR experiment

3.4.1.1 Water vapor effect

Water vapor interfered with spectral windows and resulted in underestimations of N₂O concentrations using CLS models; increased water vapor increased the bias (Figure 3.2). The PLS model provided more accurate predictions for N₂O than the CLS. The CLS accurately predicted gas concentrations only when the water vapor was absent or limited in spectra (Hong and Cho, 2003; Esler et al., 2000; Shao et al., 2010; Smith et al., 2011). In open-path measurements, CLS was often observed to underestimate gas concentrations, as reported by Childers et al. (2002), Briz et al. (2007), Shao et al. (2010), and Lin et al. (2019). Absorbance spectra of dry and wet N₂O (Figure 3.3) showed that the interference of water vapor compromised the intensity of N₂O absorbance (P branch). The reduced N₂O absorbance in wet samples resulted in underestimations of N₂O concentrations using CLS models created based on references of dry N₂O samples and water vapor. PLS models, created by wet N₂O references, showed improved accuracy in wet samples but overestimated N₂O in dry samples (Figure 3.2). It is still unclear how water vapor interfered with gas quantification. The N₂O underestimation (based on the CLS model predictions) resulting from the attenuated absorbance was hypothesized due to the inadequate spectral resolution. High resolution is required to resolve rotation-vibrational gas spectral features (e.g., full-width at half height ~ 0.2 cm⁻¹) to avoid spectral nonlinearity to concentrations (ASTM, 2013; Griffiths and de Haseth, 2007; Russwurm

and Phillip, 1999; Muller et al., 1999). Absorption features of N₂O were strongly overlapped by water vapor within 2170.0-2224.0 cm⁻¹. In order to resolve absorbance spectra of multiple gases and spectral overlaps, spectral resolution higher than 0.2 cm⁻¹ would be suggested.

3.4.1.2 Temperature effect

The temperature-sensitivity of gas-phase FTIR spectra results in non-linearity of absorbance to temperature. Bias will be introduced if there is a temperature difference between reference and sample spectra (Russwurm and Phillip, 1999; Smith et al., 2011). The effect of this delta temperature on N₂O quantification is shown in Figure 3.4a. Spectra of wet N₂O (310 ppbv N₂O blending with 21000 ppmv water vapor) were collected at 30 °C, 35 °C, and 40 °C. Reference spectra of dry N₂O, water vapor, and wet N₂O were acquired at 30 °C and used to calculate N₂O concentrations from spectra collected at temperatures of 35 °C and 40 °C. The difference in temperature led to biases in N₂O calculations (Figure 3.4a). Smith et al. (2011) calculated concentrations of CO₂, CH₄, and CO using the Multi-Atmospheric Layer Transmission (MALT) (Griffith, 1996) and showed that temperature-related error was approximately 3.0 % when the delta temperature was within 10 °C. The interference of water vapor, however, was not considered in their study. As mentioned, water vapor present in spectra resulted in underestimations of N₂O by CLS models (Figure 3.2), and this bias further increased with increasing the delta temperature. For instance, the bias increased from -3.0 to -5.0 % with increasing temperature from 30 to 40 °C using CLS models (Figure 3.4a). Sources to this bias appeared to include 1) temperature-broadening of N₂O and 2) temperature-induced interference of water vapor (i.e., greater interference at increased temperature). The increased strength of water vapor led to more interference in spectral analyses and great biases (Figure 3.4b). PLS methods showed less sensitivity to temperature (Figure 3.4a).

3.4.2 Open-path FTIR experiment

3.4.2.1 Water vapor effect

In fields, water vapor ranged from 5000 to 20000 ppmv during 9-19 June 2014, and the increased water vapor increased N₂O biases using CLS (Figure 3.5a). In the lab experiment, the increased water vapor from 5000 to 20000 ppmv at 30 °C only showed consistent underestimations of N₂O by approximately 3.0 % using CLS (Figure 3.2). Since water vapor and air temperature are

confounding variables, it is difficult to isolate their contributions to quantitative errors in the field. The negligible correlation ($R^2 = 0.20$ shown in Figure 3.5a) between water vapor content and the N_2O bias was because water vapor was confounded by temperature (i.e., temperature ranged from 10 °C to 35 °C in fields) and became insignificant when the calculated biases were categorized by temperature (i.e., $R^2 = 0.01$ at the interval of 25-30 °C, data not shown). CO_2 measured by CLS was less sensitive to changing water vapor content ($R^2 = 0.05$) than N_2O (Figure 3.5b) in field measurements, presumably due to the less water vapor absorption features in 2075.5-2084.0 cm^{-1} than 2170.0-2224.0 cm^{-1} (Lin et al., 2019). For PLS calculations, N_2O biases became consistent but slightly increased with increasing water vapor (Figure 3.5c).

3.4.2.2 Temperature effect

Increased air temperature increased both N_2O and CO_2 bias estimations from CLS models (Figure 3.5d and 3.5e). Since the temperature-dependent absorbance varied with species and wavelengths, gas quantification reacts differently to a changing environmental temperature (Smith et al., 2011). The strong correlation of air temperature to N_2O biases ($R^2 = 0.86$) showed the N_2O quantification was more sensitive to temperature effects than CO_2 ($R^2 = 0.39$). The lab experiment (Figure 3.4) showed that CLS underestimated N_2O by 3.0 % in wet air for samples with a low delta-temperature. N_2O calculations from OP-FTIR spectra, however, were underestimated by 12.0 % (approximately 36 ppbv less than the true value) even if the HITRAN reference and sample spectra were collected at the same temperature (i.e., 30 °C). The excess bias (12.0 % minus 3.0 %) presumably resulted from interferences from CO and CO_2 in 2170.0-2224.0 cm^{-1} and inherent uncertainties in line intensities and bandwidths of gas absorbance from HITRAN database (Rothman et al., 2005). CLS-calculated CO_2 values were less influenced by temperature ($R^2 = 0.39$) than N_2O (Figure 3.5e), attributed to the reduced complexity of CO_2 absorption features in the 2075.0-2085.0 cm^{-1} region, and less interference of water vapor within this region (Lin et al., 2019). The PLS models were less influenced by temperature for N_2O quantification ($R^2 = 0.05$) and provided better accuracy for N_2O estimations (Figure 3.5f).

3.4.2.3 Path length effect

OP-FTIR spectra containing N_2O concentrations of 349.0 ± 0.5 ppbv and CO_2 concentrations of 400.0 ± 4.4 ppmv were collected from optical lengths of 100-, 200-, and 300-m. As path lengths

decreased, both N₂O and CO₂ concentrations were underestimated (Figure 3.6a and 3.6b). For N₂O, CLS-derived concentrations were more sensitive to changing path lengths than PLS (Figure 3.6a). The Beer-Lambert law should show a linear response of absorbance to the path-integrated concentration. Nevertheless, the path-averaged absorbance of N₂O and CO₂ (i.e., $\frac{\text{Absorbance}}{\text{Path length(m)}}$) did not conform to the Beer-Lambert law even though background concentrations of N₂O and CO₂ were consistent (Figure 3.6c and 3.6d), showing that there was a non-linear response of OP-FTIR spectra to the path-integrated concentrations. Several reasons may have caused non-linearity issues, such as detector saturation, spectral resolution, and apodization (ASTM, 2013; Russwurm and Childers, 1999; Griffiths and de Haseth, 2007). Detector saturation at short distances was avoided by examinations of the IFG centre burst and SB spectra (i.e., the elevated baseline below the detector cut-off, usually 600.0 cm⁻¹) in this study (ASTM, 2013).

Presumably, this short-path-derived bias (Figure 3.6a and 3.6b) resulted from the inadequate spectral resolution. Short path lengths reduced the absorbance depth in an SB spectrum and sensitivity for quantification. Poorly resolved absorbance spectra could lead to a spectral non-linear response with different path-integrated concentrations (Zhu and Griffiths, 1994; Russwurm and Phillips, 1999). Also, N₂O quantification was more sensitive to path lengths than CO₂. With increasing optical path lengths from 100-m to 300-m, the accuracy of N₂O calculated from CLS models increased by approximately 20.0 % (N₂O biases reduced from -30.0 % to -10.0 % shown in Figure 3.6a). For CO₂, the accuracy only increased 2.5 % (CO₂ biases reduced from -7.5 % to -5.0 % shown in Figure 3.6b). The difference in sensitivity between gas quantification and path length was attributed to the complexity of absorbance spectra. N₂O absorption features in 2170.0-2224.0 cm⁻¹ were more complicated than CO₂ in 2075.0-2085.0 cm⁻¹; furthermore, more interfering gases (CO, CO₂, and water vapor in 2170.0-2224.0 cm⁻¹) interfered with N₂O quantification (Lin et al., 2019). A triangular apodization function applied in spectra results in a non-linear response (Russwurm and Phillips, 1999). The poorly-resolved spectra containing multiple gas species likely complicated the magnitude of the non-linearity led by apodization, which, however, was not evaluated by this study. The PLS methods reduced N₂O biases and showed less sensitivity to path length than CLS (Figure 3.6a).

3.4.2.4 Wind speed effect

Nitrous oxide is predominately produced via soil microbial activities (nitrification and denitrification) and CO₂ is from respirations from soil microbes and vegetation (Mosier et al., 1996). As a result of soil and crop heterogeneities, multiple sources, and intermittent fluxes of N₂O and CO₂ from soil and/or canopy result in inhomogeneous gas concentrations under low winds. Since the path length of the S-OPS (50-m) was different from the OP-FTIR (the physical length of 150-m), the gas uniformity across the 150-m influenced their path-averaged concentrations. The difference in the path-averaged N₂O and CO₂ concentrations between the S-OPS and OP-FTIR was used to calculate quantification bias (Figure 3.7). Variabilities of N₂O and CO₂ biases were small but increased when the wind speed was less than 2 m s⁻¹ (Figure 3.7c and Supplementary Table 3.1). This increased variability inferred the poorly-mixed air (< 2 m s⁻¹). Thus, decreasing wind speed and turbulent mixing tended to increase gas concentration differences between the S-OPS and OP-FTIR. During the low wind environment, CO₂ bias showed higher variability than N₂O presumably due to a greater environmental variation in CO₂ concentrations than N₂O (Lin et al., 2019). Low wind conditions likely occurred during the night period. For instance, 22.0 % (57 out of 259) of the collected data (30-min-averaged N₂O) collected from low winds (< 2 m s⁻¹) was from daytime measurements (06:00-20:00, LT), and 36.2 % (47 out of 130) was from nighttime measurements (20:00-06:00, LT) (Figure 3.7a).

3.5 Conclusion

In this study, we have evaluated the effects of water vapor, temperature, path length, and wind speed on open-path FTIR measurements of N₂O and CO₂ quantified by CLS and PLS models. Water vapor in spectra underestimated N₂O concentrations by 3.0 % (lab experiment) and 12.0 % (field experiment) at 30 °C using CLS models. PLS models improved the accuracy of N₂O quantification (lab bias = -0.6±0.4 % and field bias = 2.0±0.8 %). Differences in temperature between reference and sample spectra led to errors in gas quantification. Increased air temperature significantly increased quantification bias using CLS models. For wet N₂O, 10 °C difference introduced 1.9 % (Lab) and 9.1 % (Field) more biases in gas concentrations. PLS models were less sensitive to temperature. Short path lengths reduced the sensitivity and accuracy for gas quantification, and CLS models were more sensitive to changing path lengths

than PLS. These short-path-led biases were presumably due to the inadequate spectral resolution. CO₂ quantification using CLS model was less influenced by environmental variables than N₂O likely due to the less complex absorption features. The wind affected the mixings of gases and the low wind speed ($< 2 \text{ m s}^{-1}$) led uncertainties in the path-averaged concentrations.

The partial least squares model generally provided more accurate measurements than CLS if the gas of interest is strongly interfered by water vapor (or other interferences) (e.g., strong overlap of water vapor absorbance features or broad spectral windows). PLS is also less sensitive to environmental variables than CLS. For OP-FTIR measurements, the CLS-calculated concentrations need to be verified carefully for quality assurance and to avoid substantial underestimations. Path lengths must be adequate, which can be checked by conducting a path length experiment before measurements. For the users interested in multi-source measurements, we suggested avoiding a great difference in path lengths if CLS models are used for gas quantification. High spectral resolution ($< 0.5 \text{ cm}^{-1}$) is recommended to resolve complex spectral features of either gas of interest or interferences. A high resolution also introduces more noises and increasing the scan time is suggested to increase the single-to-noise ratio (Griffiths and de Haseth, 2007).

3.6 References

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Table 3.1 Spectral windows for quantification of N₂O and CO₂.

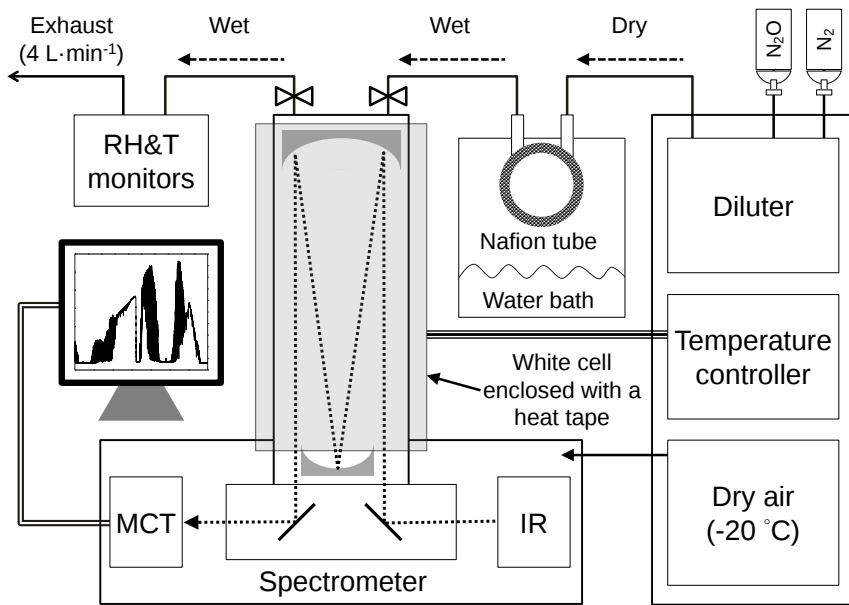
Gas	Windows (cm ⁻¹)	Interferences
N ₂ O	W _N 1: 2170.0-2223.7	H ₂ O, CO, CO ₂
	W _N 3: 2188.7-2204.1 + 2215.8-2223.7	H ₂ O, CO, CO ₂
CO ₂	W _C 2: 2075.5-2084.0	H ₂ O

Supplementary Table 3.1 Quantification biases (%) of N₂O and CO₂ were categorized by wind speed (e.g., 1 m s⁻¹ interval), and statistics of biases were calculated from seven groups. Levene's test was used to compare variances of biases among the group to test the low wind speed threshold. Levene's hypothesis test is defined as: $H_0: \sigma_1^2 = \sigma_2^2 \dots \sigma_n^2 (n \geq 1)$ and $H_a: \text{at least one variance is different.}$

Statistics of quantification bias (%) and Levene's variance test

Groups	1	2	3	4	5	6	7
Wind speed (m s ⁻¹)	0.0-1.0	1.0-2.0	2.0-3.0	3.0-4.0	4.0-5.0	5.0-6.0	6.0-7.0
N ₂ O Bias (%)							
Mean	-0.93	0.33	1.58	1.16	1.31	1.32	0.93
SD	4.92	3.39	2.90	2.63	1.81	1.79	1.87
N	22	82	73	108	53	32	18
Test Groups	(1-7)	(2-7)	(3-7)	(4-7)	(5-7)	(6-7)	
F-value	7.45	6.81	4.67	4.46	0.19	0.35	
P-value	0.000	0.000	0.001	0.005	0.830	0.555	
CO ₂ Bias (%)							
Mean	1.14	-0.26	-0.78	-1.10	-1.50	-1.56	-1.20
SD	10.24	10.84	3.74	2.06	2.29	2.42	2.33
N	21	75	69	98	46	28	17
Test Groups	(1-7)	(2-7)	(3-7)	(4-7)	(5-7)	(6-7)	
F-value	11.10	9.77	2.05	0.36	0.23	0.09	
P-value	0.000	0.000	0.088	0.779	0.796	0.767	

(a) A lab FTIR



(b) A monostatic OP-FTIR

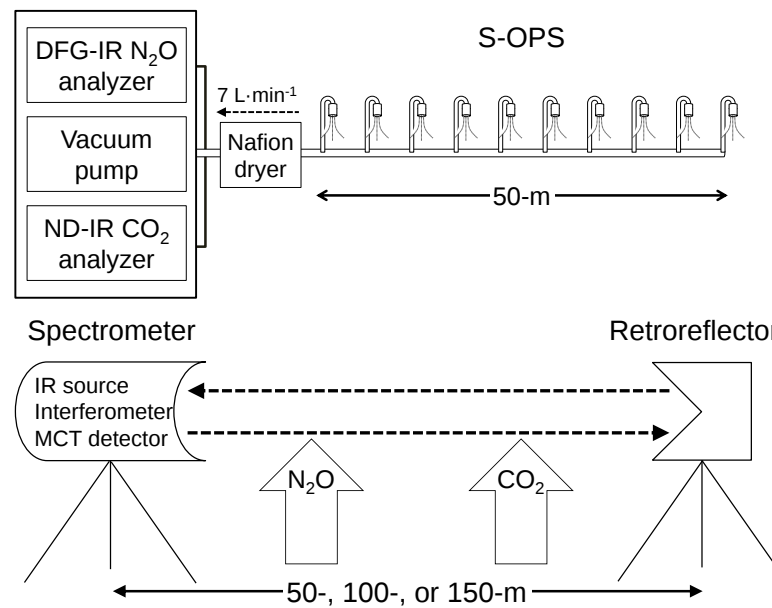


Figure 3.1 Schematic of the instrumentation used to assess the effects of water vapor and temperature on gas quantification: (a) lab-FTIR with a multi-pass gas cell (optical path length of 33-m); (b) DFG-IR N₂O and ND-IR CO₂ analyzers combined with synthetic open path gas sampling system (S-OPS) were used as benchmarks to assess quantification of N₂O and CO₂ from OP-FTIR.

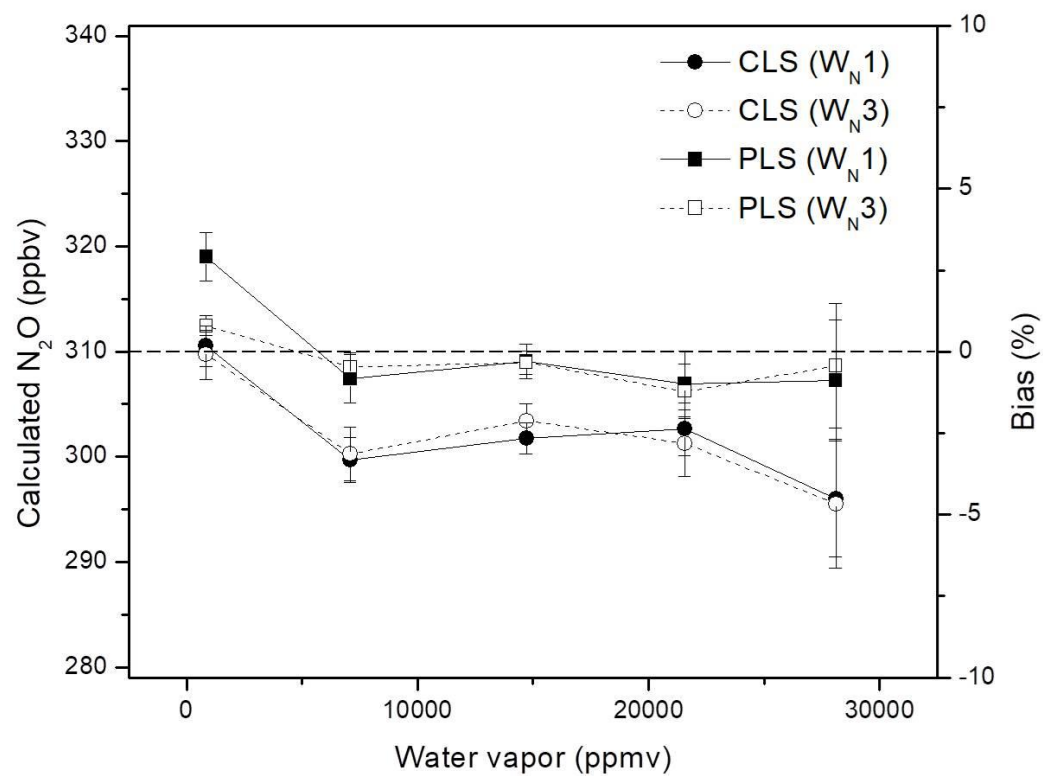


Figure 3.2 Effects of water vapor on N_2O quantification: the lab-FTIR spectra of dry N_2O and N_2O /water vapor mixtures (310 ppbv N_2O at the relative humidity of 20 %, 40 %, 60 %, and 80 % at 30 °C) were used to calculate N_2O concentrations using CLS and PLS models and two spectral windows (W_{N1} and W_{N3}).

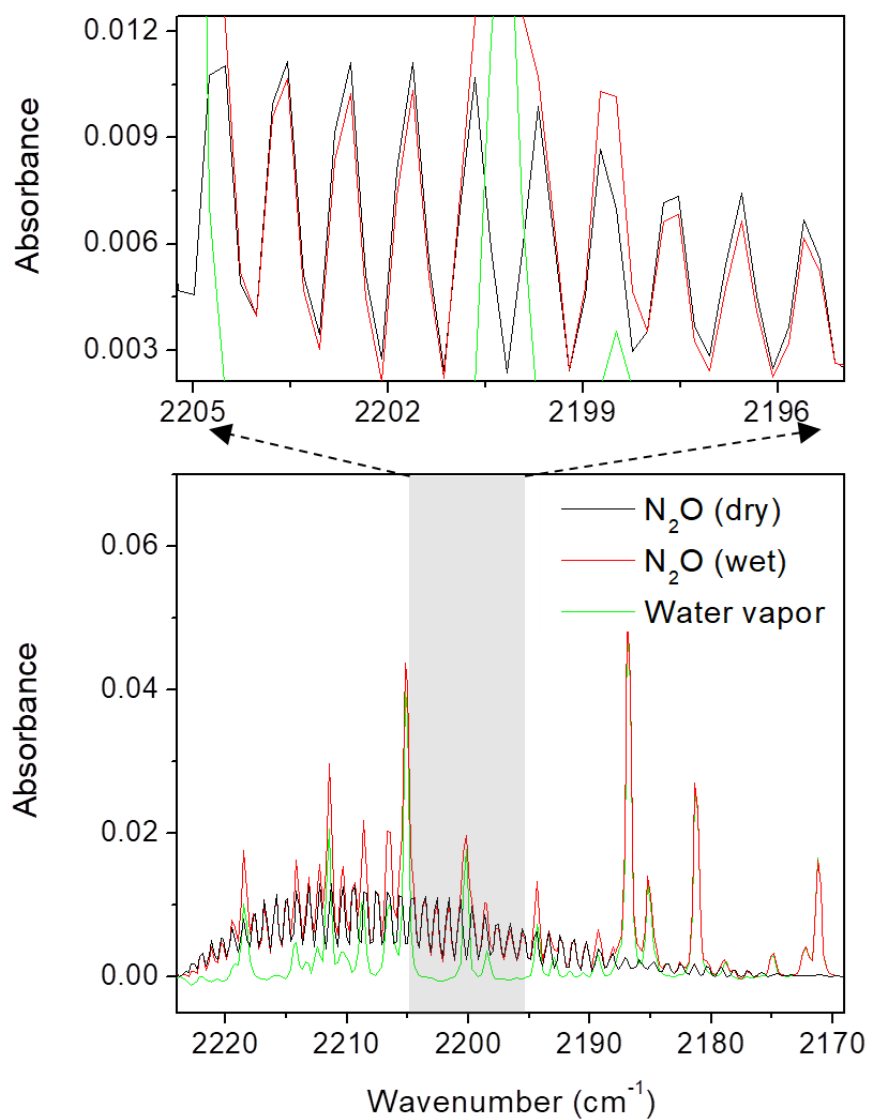


Figure 3.3 The lab-FTIR spectra of dry N_2O (i.e., 310 ppbv), wet N_2O (i.e., 310 ppbv N_2O + 28,000 ppmv water vapor), and water vapor (28,000 ppmv) were acquired at 30 °C.

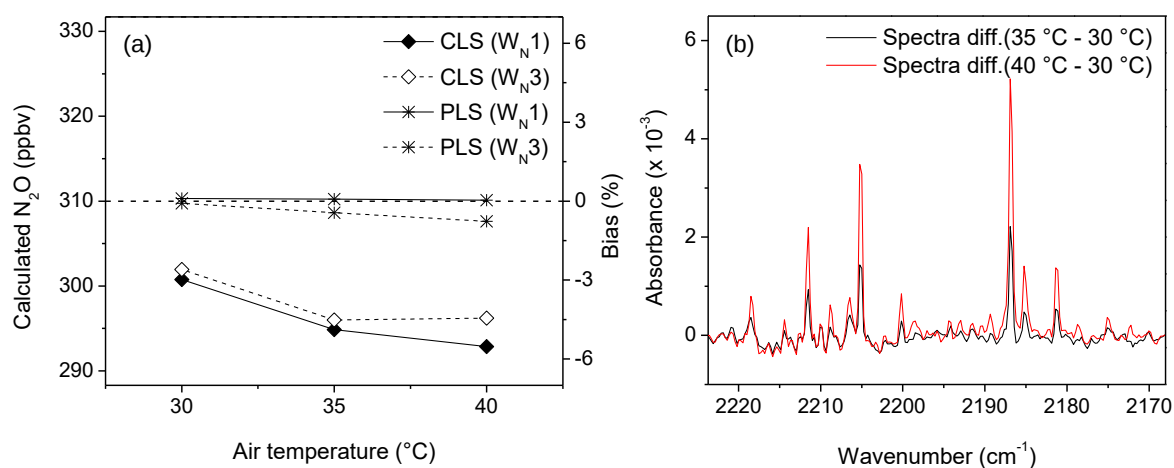


Figure 3.4 Effects of temperature on N_2O quantification: the lab FTIR spectra containing wet N_2O (310 ppbv N_2O plus 21 500 ppmv water vapor) were acquired at 30 $^{\circ}C$, 35 $^{\circ}C$, and 40 $^{\circ}C$. Temperature affected (a) N_2O concentrations calculated by the CLS and PLS models and two spectral windows (W_{N1} and W_{N3}) and (b) spectral differences in wet N_2O absorbance (310 ppbv N_2O plus 21 500 ppmv water vapor) among different temperature.

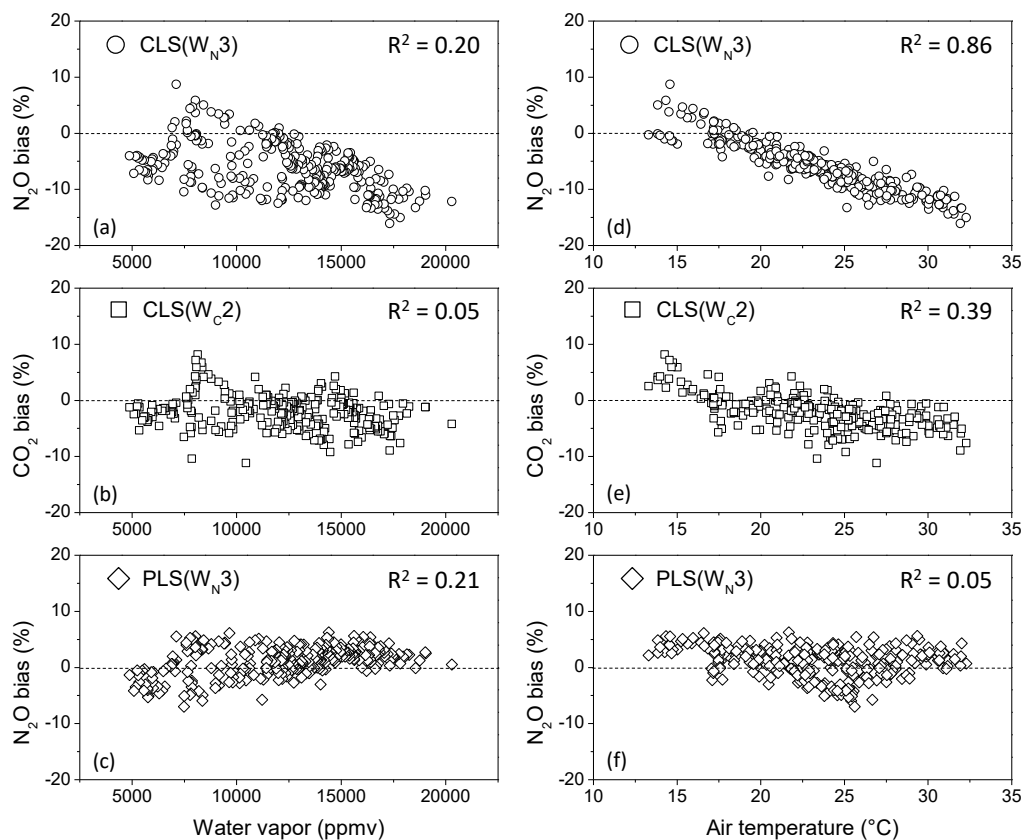


Figure 3.5 Effects of water vapor and temperature on N₂O and CO₂ concentrations from OP-FTIR spectra using CLS and PLS models and the optimal windows (i.e., W_{N3} for N₂O and W_{C2} for CO₂) during 09-19 Jun. 2014. Assumed temperature and bias are a linear relationship.

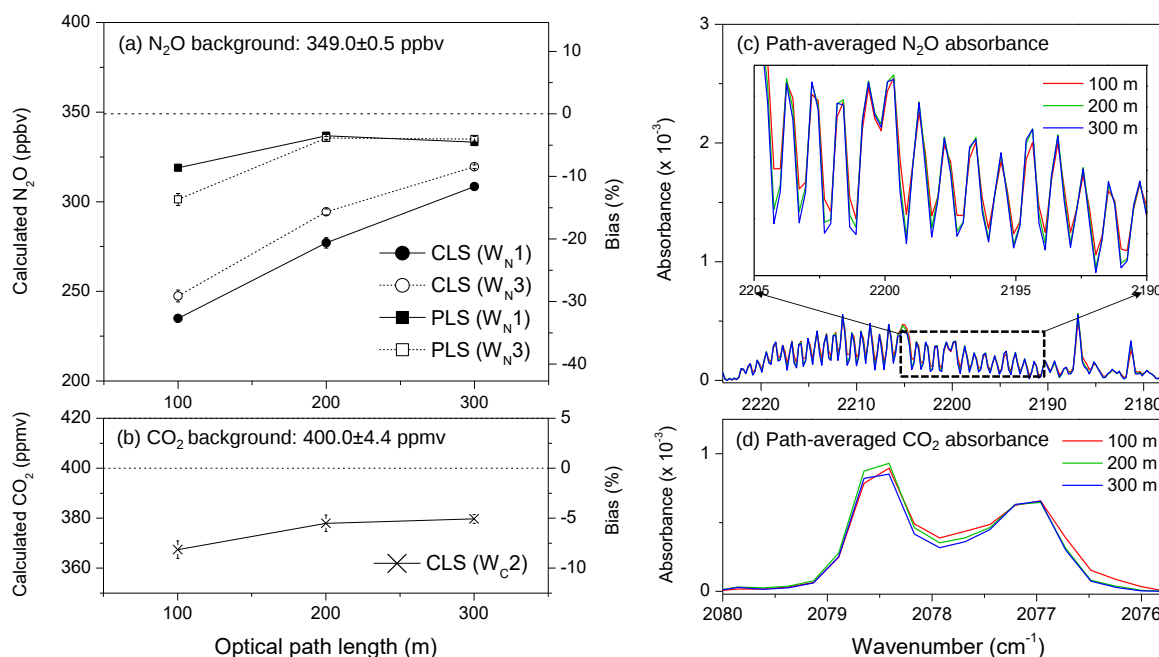


Figure 3.6 Effects of path lengths on N_2O and CO_2 quantification: OP-FTIR spectra were acquired under backgrounds of N_2O (349.0 ± 0.5 ppbv) and CO_2 (400.0 ± 4.4 ppmv), and relative humidity of 35 % at 25 °C from optical path lengths of 100-, 200-, and 300-m for quantification of (a) N_2O using CLS and PLS and windows of W_{N1} and W_{N3} , (b) CO_2 using a CLS model and the window of W_{C2} . The path-averaged absorbance spectra of (c) N_2O and (d) CO_2 showed the inconsistency of absorbance spectra.

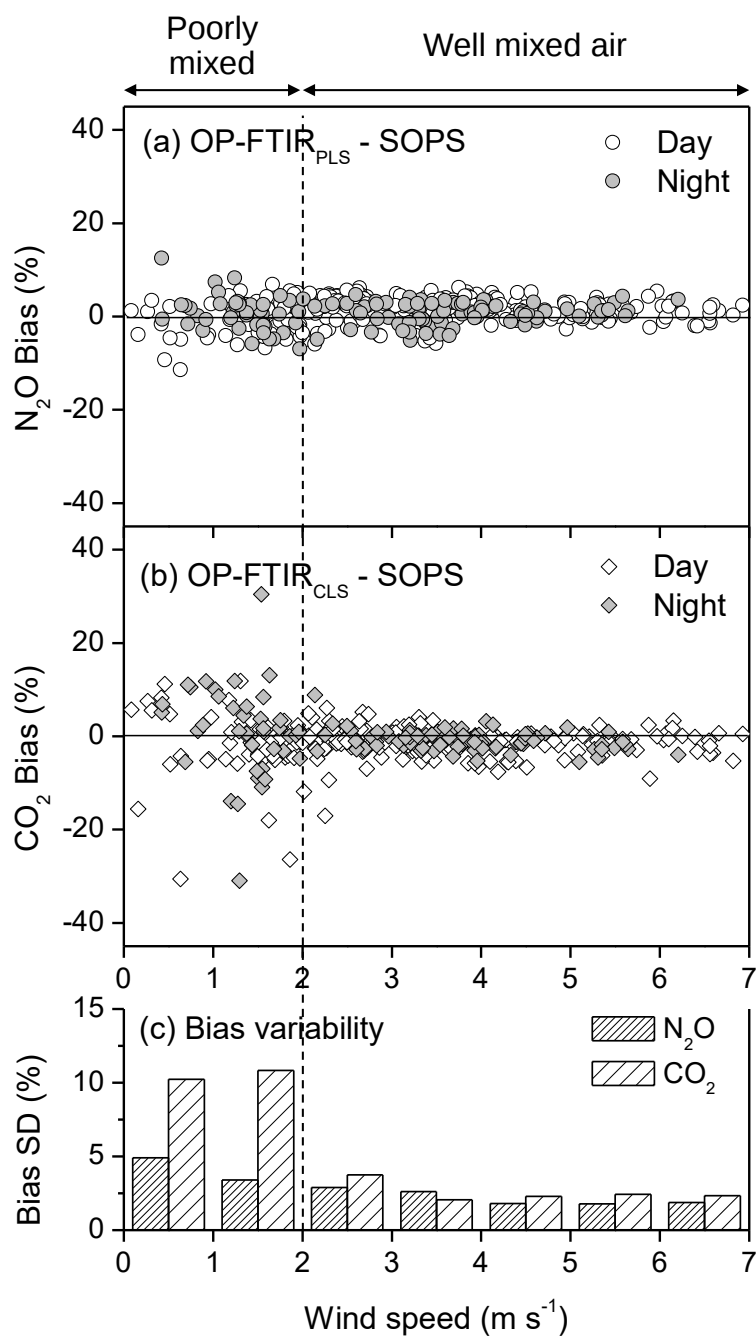


Figure 3.7 Effects of the wind speed on differences in the path-averaged concentrations between the OP-FTIR and S-OPS: (a) N_2O , (b) CO_2 , and (c) variability of biases (Standard deviation, SD).

CHAPTER 4. MEASURING N₂O EMISSIONS FROM MULTIPLE SOURCES USING A BACKWARD LAGRANGIAN STOCHASTIC MODEL

A version of this chapter will be submitted for review to the open-access journal of Atmosphere.

4.1 Abstract

Nitrous oxide (N₂O) emissions from agricultural soil are substantially influenced by nitrogen and field management practices. It is challenging and an ongoing research question to implement a backward Lagrangian stochastic (bLS) technique to measure gas emissions from different treatments (multiple sources) simultaneously. A scanning open-path (OP) Fourier transform infrared spectrometer (OP-FTIR), and a bLS emissions model were integrated to measure N₂O emissions from four adjoining fields with differing management in 2015. The field practices were no-till (NT) and chisel plow (ChP). For nitrogen (N) management, the total rate of 220 kg NH₃-N ha⁻¹ was applied as full-N or split-N rate application in the fall or spring before planting. This method (scanning OP-FTIR + bLS) showed that the minimum detection limit (MDL) for the multi-source N₂O emission measurements was $\pm 1.2 \mu\text{g m}^{-2} \text{s}^{-1}$ (3σ). The averaged emission rates of the treatments ranged from 0.4 to 2.5 $\mu\text{g m}^{-2} \text{s}^{-1}$ over 44 days after spring fertilizer application. This study showed that the management of the full-N rate applied in fall led to higher N₂O emissions than the split-N rates applied in the fall and spring. Based on the same N application (i.e., split-N rates applied in the fall and spring), the ChP practice tended to increase N₂O emissions compared with NT. The uncertainty (1σ) in emissions measurements was $0.5 \pm 0.3 \mu\text{g m}^{-2} \text{s}^{-1}$ if the field of interest received a clean upwind background. Increased advective interferences from the upwind treatments increased uncertainties to $0.6 \pm 0.4 \mu\text{g m}^{-2} \text{s}^{-1}$ (one predominant source), and $1.1 \pm 0.5 \mu\text{g m}^{-2} \text{s}^{-1}$ (three upwind sources).

4.2 Introduction

At present, more than 50% of non-CO₂ greenhouse gas (GHG) emissions (mainly N₂O and CH₄) come from agricultural sources (US-EPA, 2012; IPCC, 2013; Smith et al., 2008; Reay et al., 2012). N₂O emitted from agricultural soils is mainly attributed to the application of nitrogen (N) fertilizers (Bouwman, 1996; Mosier et al., 1998). Nitrogen losses via N₂O emissions not only

give rise to a negative impact on the environment (strong GHG input into the atmosphere) but also reduce N fertilizer use efficiency (NUE) (Decock, 2014; USDA-ERS, 2018). Several N management practices were proposed to mitigate N₂O emissions, such as reducing application rates (right rate) or applying N fertilizers at the timing to meet the crop N demands (right timing) (Akiyama, 2010; Decock, 2014). Conservation field practices (e.g., zero tillage) has been suggested to reduce soil CO₂ emissions, but their effects on N₂O emissions are still unclear (Decock, 2014; Snyder et al., 2009; Venterea et al., 2011).

A backward Lagrangian stochastic (bLS) dispersion technique has been developed to estimate gas emissions from field-scale source areas (e.g., 100-300 m), such as feedlots, animal waste lagoons, and fertilized soils (Flesch et al., 1995 and 2004; Yang et al., 2013; Grant and Boehm, 2015; Huo et al., 2015; Flesch et al., 2016; Lam et al., 2018). A bLS technique can predict trajectories of trace gases (gas particles) from sensors to sources based on Monin-Obukhov similarity theory (MOST). The MOST theory uses friction velocity (u^*), Monin-Obukhov (MO) length (L), and surface roughness (z) to describe statistical properties of the surface wind field. The principle of the MOST theory, as well as the bLS-simulated trajectories, were considered as valid if the MOST-descriptive variables meet the criteria of $u^* > 0.15 \text{ m s}^{-1}$ and $|L| > 5 \text{ m}$ (Flesch et al., 1995 and 2004). During the ‘backward travels’ from the downwind sensor to the upwind source, gas particles intersect with the surface of the source (touchdowns), providing a predictive relationship between gas concentrations and emission rates ($(C/Q)_{sim}$) (Flesch et al., 1995 and 2004). Given the known downwind concentrations, the bLS model estimates emissions (Q) from the source of interest.

The bLS method has been usually used to predict emission rates from a single source. (McBain and Desjardins, 2005; Flesch et al., 2004). Implementing the bLS method to measure multiple source emissions is more complicated than single-source emissions when a gas concentration sensor can simultaneously detect gas concentrations from several sources (Crenna et al., 2008; Gao et al., 2008; Flesch et al., 2009; Hrad et al., 2014; Huo et al., 2014). For multi-source emissions measurements, the minimum requirement in the bLS model is that the number of concentration sensors (n) must be at least equal to emission sources (m) (i.e., $n \geq m$) (Crenna et al., 2008; Flesch et al., 2009). The placement of sensors deployed in sources of interest

substantially influenced the quality of emissions quantification. The ideal sensor-source geometry was that each sensor only detects gas from one source (Crenna et al., 2008; Gao et al., 2008; Flesch et al., 2009; Hrad et al., 2014). Some studies, however, showed that such ‘optimal’ sensor placement did not improve the accuracy of emissions measured from multiple sources (Ro et al., 2011 and 2013).

Most studies of multi-source emissions have focused on optimizing the sensor-source geometry to improve flux calculations (Crenna et al., 2008; Gao et al., 2008; Flesch et al., 2009; Hrad et al., 2014). Few papers have investigated the effect of interferences from adjacent fields on emission estimations via advection (In meteorology, advection refers to the horizontal transport of the atmospheric properties, such as heat or matter) (Ro et al., 2011; Mukherjee et al., 2014; Huo et al., 2014). Also, the criteria used for quality assurance of the single-source estimation cannot be directly applied for multi-source estimations. For instance, the fraction of source region of interest covered by touchdowns (TDF) is used to assure the quality of emissions estimation, and at least 10% of a field needs to be covered by touchdowns ($TDF > 0.1$) for emission estimations (Flesch et al., 2004 and 2005). Higher TDF (0.1 – 0.6) was often used to improve the accuracy of flux measurements (Flesch et al., 2009; Ro et al., 2011 and 2013; VanderZaag et al., 2014).

In order to investigate the effect of these management practices on GHG emissions and optimize the management to mitigate GHG emissions, there is an increasing demand to develop a method to measure multiple-source emissions continuously and simultaneously. Emissions from adjacent treatments create multiple sources in close proximity (e.g., N fertilizer application, tillage practices, or irrigation). In this study, a scanning open-path Fourier transform spectrometer (OP-FTIR), and the bLS technique were integrated to measure N_2O emissions from four adjoining fields with contrasting management (i.e., Fall vs. Spring N application; full- vs. split-N rate application; no-till (NT) vs. chisel plow (ChP)). The objective of this study was to evaluate the feasibility of bLS methods to measure multi-source emissions, including uncertainty analysis of N_2O concentrations and emissions.

4.3 Materials and Methods

4.3.1 Field description and management

The field experiment was located and operated in the field of Agronomy Center for Research and Education (ACRE) of Purdue University (86°59'41.09"W, 40°29'44.46"N). The soil type was mainly categorized as Drummer silty clay loam (fine-silty, mixed, mesic Typic Endoaquoll). Drainage type was classified from somewhat poorly to poorly drained (Soil survey, USDA). The bulk density (0-10 cm) and organic matter (0-20 cm) was measured 1.4-1.6 g cm⁻³ and 3.5-4.5 %, respectively. The cropping system was continuous corn fields grouped into four treatments based on the different field (NT vs. ChP) and N (Fall vs. Spring N application; full vs. split N rate) management practices since 2013 shown in Figure 4.1. All fields used NT with the exception of T3 that used ChP. In 2015, anhydrous ammonia (AA) was used as an N source, and the total N rate was 220 kg NH₃-N ha⁻¹ applied as a full or split application at the different timing (Fall vs. Spring). For instance, the full-N rate was applied in T1 after harvest in the prior fall and T4 before planting in the spring of 2015. The split-N application, 110 kg NH₃-N ha⁻¹ in the previous fall and the present spring, was applied in T2 and T3 (Table 4.1).

4.3.2 Experimental configuration

N₂O concentrations were measured using an open path line-sampling (LS) and point-sampling (PS) concentration sensors (Figure 4.1). The open path LS sensor was a monostatic OP-FTIR spectrometer (MIDAC Model2501-C, MIDAC Corporation, Irvine, CA) bounded by a cube-corner retroreflector (i.e., 26 cubes). The LS length was between 100- and 150-m, and at a measurement height of approximately 1.5-m above ground level (a.g.l). An OP-FTIR was mounted on a scanner with horizontal and vertical rotaries (YUASA computer numerical control, CNC) to scan seven retroreflectors deployed in or on borders of four fields to create seven open path sampling lines (LS-1 – LS-7) and it took nearly thirty minutes to complete one cycle of the scanning (i.e., from LS-1 to LS-7). The scanner and OP-FTIR were not synchronized. A dwell time of each path was approximately three minutes to collect two-to-three FTIR spectra per retroreflector (one spectrum per minute). The LS sensors were placed in emission sources to increase the sensitivity of concentration measurements (e.g., relatively high concentrations from an emission source) (Flesch et al., 2007). Each spectrum was acquired by co-adding 64 interferograms (IFG) at a resolution of 0.5 cm⁻¹, and a co-added IFG was apodized using a

triangular function and converted to a single beam (SB) spectrum by Fourier transform using AutoQuant Pro4.0 software package (MIDAC Corporation, Irvine, CA). Details of acquiring OP-FTIR spectra were described in Lin et al. (2019).

A difference frequency generation (DFG) mid-IR laser-based N₂O/ H₂O analyzer (IRIS 4600, Thermo Fisher Scientific Inc., Waltham, MA) was conjoined with a gas sampling system (GSS) to measure N₂O concentrations from multiple air streams. The DFG N₂O analyzer was capable of measuring N₂O concentration precisely (i.e., $\sigma < 0.15$ ppbv for three-minute average) with calibration checked with a standard N₂O concentration of 520 ppbv every four hours. The GSS system included a sampling pump and four DC power solenoids connected to four sampling lines to collect gas samples by drawing the air through lines. Each sampling line consisted of a 9.5-mm diameter Teflon® tube and fitted with 1.0- μ m Teflon® filter (Heber et al., 2006). Then, lines were located on a border of the field (N, W, E) (Figure 4.1). In addition to three PS lines, a 50-m synthetic open path sampling system (SOPS) was made up ten tubes (i.e., ten inlets) and deployed along one of the OP-FTIR paths (LS-4 between T2 and T3) to measure the path-averaged N₂O concentration and benchmark N₂O concentrations measured by OP-FTIR (Chapter 2). Thus, four sampling lines included three PS lines on the edges of the field and one SOPS line between the T2 and T3 treatments (i.e., NT and ChP). Each line was used to collect gas samples at approximately 7 L min⁻¹, and the sampling interval was five minutes which was controlled by electrifying solenoids.

Wind information (i.e., direction, velocity, and turbulence statistics) was measured using a 3D sonic anemometer (Model 81000, RM Young Inc., Traverse City, MI) which was installed at 2.5-m height on the meteorological mast and recorded at 16Hz. Ambient temperature, humidity, and barometric pressure were measured using a temperature-humidity sensor (Model HMP45C, Vaisala Oyj, Helsinki, Finland) and a pressure sensor (278, Setra, Inc., Boxborough, MA) which were installed at 1.5-m a.g.l. mast. These meteorological data were averaged every five minutes by a data logger (Model CR1000, Campbell Scientific, Logan, Utah).

4.3.3 Open-path FTIR

Calculations: A synthetic SB background was generated using IMACC software (Industrial Monitoring and Control Corp., Round Rock, TX) to convert sample SB spectra to absorbance spectra. N₂O concentrations were quantified by partial least square (PLS) algorithms based on the Beer's law quantitative spectral processing software (Thermo Fisher Scientific TQ Analyst Version 8.0). Sixty spectra of mixed-gas standards (water vapor + N₂O) were generated using a laboratory FTIR spectrometry joined with a multi-pass gas cell (i.e., optical path = 33-m) and used to build PLS quantitative models. The analytical region for N₂O calculations was used the combination window of 2188.7-2204.1 cm⁻¹ and 2215.8-2223.7 cm⁻¹. Details of the quantitative method of calculating N₂O concentrations from OP-FTIR spectra was shown in Chapter 2.

Calibrations: Fluctuations of ambient humidity, temperature, and path length substantially influenced the accuracy and precision of N₂O calculations. The bias of the N₂O concentrations derived from the OP-FTIR was calibrated by the path-averaged N₂O concentration measured from the SOPS. The relative error between the FTIR- and SOPS-measured N₂O concentrations (i.e., $bias = [(x_{FTIR}/x_{SOPS}) - 1] \times 100\%$) was calculated to infer the accuracy of N₂O concentrations determined by OP-FTIR. The variations in ambient humidity and temperature are regarded as leading error sources for OP-FTIR quantification (Chapter 3). We assumed that ambient humidity and temperature were relatively constant within thirty minutes; as a result, the offset of the path-averaged concentration between the SOPS and OP-FTIR (LS-4) was considered as a constant within each 30-min interval and applied to calibrate other OP-FTIR paths (LS-1 to LS-7).

Uncertainty: N₂O background concentrations (i.e., 349±0.5 ppbv) (measured by the SOPS), ambient temperature (i.e., 23.6±0.8 °C), and humidity (i.e., RH = 29.4±2.9%) remained nearly constant between 14:30-18:30, local time (LT) on 6 May 2016. It was assumed that ambient humidity, temperature, and N₂O concentrations remained stationary in a well-mixed surface layer within thirty-minute intervals. For each path length (i.e., optical path = 100-, 200-, and 300-m), ten OP-FTIR spectra were acquired in the 30-min interval and calculated for N₂O concentrations. A standard deviation of N₂O concentration from ten spectra represented the

uncertainty in N₂O concentrations measured by the OP-FTIR using a PLS algorithm in specific path lengths.

4.3.4 Emission measurements

4.3.4.1 A backward Lagrangian Stochastic (bLS) model

Emission rates (Q) of N₂O were estimated by bLS model (Windtrax2.0: Thunder Beach Scientific, <http://www.thunderbeachscientific.com>). Given the measured turbulence statistics of a wind field in a surface layer (i.e., u^* , L , z , β), the bLS model can simulate the ratio of gas concentration (C) to the surface emission rate (Q) by ‘backward’ tracing trajectories of gas particles from sensors (downwind) to source (upwind). Emission rates can be inferred based on the deviation of concentration between the downwind fields and background (C_{bg}) (i.e., $\Delta C_{downwind-C_{bg}}$), which is described as:

$$Q = \frac{\Delta C_{(downwind-C_{bg})}}{(C/Q)_{sim}} \quad [1]$$

, where $(C/Q)_{sim}$ is the bLS-simulated ratio of concentration to emission rate, Q is the inferred surface emissions from the source of interest, ΔC and is the deviation of gas concentrations.

Both point-sampled, measured by the PS sensor, and path-averaged, measured by the LS sensor, concentrations were used in this study. For the PS sensors, the simulated ratio can be calculated as the following equation:

$$(C/Q)_{sim} = \frac{1}{N} \sum \left| \frac{z}{w_0} \right| \quad [2]$$

, where N is the number of the released particles from a sensor, and w_0 is the vertical velocity of ‘touchdowns’ which is the function of u^* , L , Z_0 , and β . For LS sensors (i.e., LS-1 to LS-7), thirty equidistant points were defined within the path, and the same number of particles (N) is released from each point. The equation can be described as:

$$(C/Q)_{sim} = \frac{1}{30} \sum_{j=1}^{30} \left(\frac{1}{N} \sum \left| \frac{z}{w_0} \right| \right) \quad [3]$$

For a single-source area, one sensor would be needed to estimate emissions by solving Eq.1 if the C_{bg} is known. For a multi-source area, the number of sensors (n) needs to be at least equal to

the number of sources (m) (i.e., $n \geq m$) to estimate the unknown emissions (Crenna et al., 2008; Flesch et al., 2009). Then, the concentration can be expressed as:

$$a_{ij}Q_j + C_{bg} = C_i \quad [4]$$

, where a_{ij} represents the ratio of concentrations to emission rates simulated $((C/Q)_{sim})$, from the contribution of the j^{th} source ($j = 1, 2, \dots, m$) to the i^{th} sensor ($i = 1, 2, \dots, n$). Thus, the entire system of equations can be expressed as an algebraic formula:

$$\begin{bmatrix} a_{11} & \dots & a_{1m} \\ \vdots & \ddots & \vdots \\ a_{n1} & \dots & a_{nm} \end{bmatrix}_{n \times m} \begin{bmatrix} Q_1 \\ \vdots \\ Q_m \end{bmatrix}_{m \times 1} + C_{bg} \begin{bmatrix} 1 \\ \vdots \\ 1 \end{bmatrix}_{n \times 1} = \begin{bmatrix} C_1 \\ \vdots \\ C_n \end{bmatrix}_{n \times 1} \quad [5]$$

In this study, there were four N_2O sources ($m = 4$) and up to ten gas sensors ($n = 10$), meaning that the source-sensor equations are over-determined (Flesch et al., 2009). Consequently, the four emissions (Q) and single C_{bg} can be calculated by simultaneous solution of ten equations (seven LS + three PS sensors) using a standard singular value decomposition (SVD) algorithm.

4.3.4.2 A forward Lagrangian Stochastic (fLS) model

Given the measured turbulence statistics, the Lagrangian stochastic model can simulate the $(C/Q)_{sim}$. This ratio can be used to estimate either emission rates of sources of interest or gas concentrations detected by sensors of interest. The downwind gas concentrations can be predicted based on the measured emission rates of the upwind source using a fLS model.

4.3.4.3 Emissions quality assurance

Numerous filtering criteria have been published for quality assurance of the bLS-estimated emissions. Thresholds of low wind conditions (i.e., $u^* < 0.15 \text{ m s}^{-1}$), and exclusion of extremely stable and unstable atmosphere (i.e., $|L| \leq 5 \text{ m}$) are likely universal criteria for using the bLS model. Other published criteria vary with different experimental configurations. For instance, a $TDF > 0.1$ was the most commonly used threshold in the literature. Since the threshold for TDF has not been standardized (e.g., varied from 0.1 to 0.7) (Flesch et al., 2004; Ro et al., 2011 and 2013; VanderZaag et al., 2014), this study investigated the effect of TDF on emissions estimations from multiple sources. Also, the sensitivity of N_2O concentrations determined by OP-FTIR (i.e., σ ppbv) was used to provide additional criteria for checking the model

performance. Ideally, the minimum concentration of the measured N_2O among sensors (i.e., 7 LSs + 3 PSs) should be the same with the modeled background (C_{bg}) (Eq. 5). The C_{bg} was compared with the lowest N_2O concentration within all of the gas sensors (including SOPS), and data were considered abnormal and excluded if the deviation between C_{bg} and the lowest concentrations was out of the range of $\pm 3\sigma$ ppbv ($|\text{N}_2\text{O}_{\text{min}} - C_{\text{bg}}| > 3\sigma$ ppbv).

4.3.4.4 Assumptions for field measurements

Assumptions required for this experiment included: (1) Stationary variables: the averaged quantities of variables were invariant within thirty minutes. (2) Homogeneous variables: the 30-min averaged quantities of variables are invariant under a spatial translation. (3) Identical N sources: N source for N_2O production was predominately from the applied NH_3 within sixty days after applications. The atmospheric N deposition (i.e., NH_3), (a)biotic N fixation, and (in)organic N residues (i.e., soil organic matter, or 2:1 clay minerals) were neglected. Gas measurements began just after NH_3 application from 29 Apr. to 12 Jun. 2015. There were 691 emission data (30-min averages) were measured, but only 357 passed QA criteria.

4.3.4.5 Wind-induced interferences

In a multi-source configuration, air parcels advected from adjacent fields can be detected by sensors deployed in a field of interest and interfere with bLS gas emission estimations. The output TDF and the known areas of emission fields (T1-T4) were used to evaluate the magnitude of air parcels from adjacent fields. For instance, T2 was interfered by T1, T3, and T4 when the wind came from NW (Figure 4.1). In order to evaluate the magnitude of interferences from T1, T3, and T4, only the LS sensors of LS-2 - LS-4 deployed in the T2 treatment were used to calculate TDFs. First of all, the T1-T4 treatments were assumed to have the same emission rates. Based on the same turbulent statistics, the TDFs were calculated by changing the sizes of areas (i.e., T2 only, T2+T1, T2+T3, and T2+T4). Given the known TDF and area, the released particles from LS-2, LS-3, and LS-4 sensors covered 0.36, 0.76, 0.93, and 1.12 hectares of the areas of T2 (1.5 ha), T2+T1 (2.7 ha), T2+T3 (2.9 ha), and T2+T4 (2.6 ha), respectively (Table 4.2). The individual field (ha) covered by touchdowns was calculated and fractionized to represent the fraction of air parcels (FRAC_{air} , %) from either the field of interest (i.e., T2) or adjacent fields (i.e., T1, T3, and T4). These fractions (%) of T1, T3, and T4 were inferred as

adjacent interferences to the T2 treatment. In this case, more interferences came from the T4 (36% of $FRAC_{air}$) than the T1 (19% of $FRAC_{air}$) treatment for the T2 treatment at NW wind.

4.3.4.6 Emissions uncertainty analysis

According to *Eq.1*, the uncertainty in gas concentrations influences emission estimations. In this scanning system, the uncertainty in N_2O concentrations was introduced in the bLS emissions model to estimate the uncertainty in emission measurements. The procedure for estimating the uncertainty in emission rates is shown in Figure 4.2.

First of all, the known emission rates of the T1-4 treatments were used to ‘forward’ calculate N_2O concentrations of seven LS and three PS sensors using the measured turbulence statistic. The background (C_{bg}) of N_2O was assumed 350 ppbv, and 50,000 particles (N) were considered in the bLS model (step-1). Secondly, the uncertainty in N_2O concentrations (σ ppbv) was introduced into the forward-calculated concentrations to infer emission rates using the bLS model. It was assumed that the uncertainties in N_2O measured from three PS sensors were negligible. Only the uncertainty from seven LS sensors was considered in the model. As a result of two possibilities ($N_2O \pm \sigma$ ppbv) for each LS sensor, there were 128 possible permutations (2^7) of N_2O concentrations of LS-1 – LS-7 (step 2). Lastly, 128 combinations of N_2O concentrations of LS-1 – LS-7 were used to ‘backward’ calculate 128 possible emissions for each treatment at each 30-min interval. The standard deviation of the 128 emissions represented the uncertainty in N_2O emissions. Different turbulence statistics were used to examine the effect of wind conditions ($n=357$) on emission uncertainties (step 3).

4.4 Results and Discussion

Emissions measurements from multiple sources were influenced by the sensitivity of gas sensors (i.e., OP-FTIR) (*Eq.1*) and advection from adjacent fields. Uncertainties in N_2O concentrations were determined by the path length experiment. The $FRAC_{air}$ (%), an index described the proportion of air parcels coming from the field of interest or adjacent fields, was used to estimate the magnitude of advective interferences from adjacent fields. The OP-FTIR sensitivity analysis showed uncertainty in N_2O concentrations was ± 1.8 ppbv (Figure 4.3). A $FRAC_{air}$ of adjacent fields of less than 20% indicated minimum advective interferences (Figure 4.4). Under these

conditions, the emission estimations had high TDFs (> 0.9) of fields of interest (Figure 4.4) and low uncertainties (i.e., $0.5 \pm 0.3 \mu\text{g m}^{-2} \text{s}^{-1}$ shown in Figure 4.6). Higher FRAC_{air} from adjacent fields reduced TDFs (< 0.9) of fields of interest and led to higher uncertainties in emission measurements. The mean uncertainties were measured $1.1 \pm 0.5 \mu\text{g m}^{-2} \text{s}^{-1}$ when TDFs were less than 0.5. The minimum detection limit (MDL) of this scanning OP method for N_2O emission measurements was $\pm 1.2 \mu\text{g m}^{-2} \text{s}^{-1}$ (3σ) (grey bars shown in Figure 4.5).

4.4.1 OP-FTIR sensitivity

Both the precision and accuracy of N_2O concentrations increased with increasing path lengths. Uncertainties in N_2O concentrations (standard deviation) reduced from ± 3.3 to ± 1.4 ppbv by increasing optical path lengths from 100-m to 300-m (Figure 4.3). N_2O concentrations were underestimated by 14%, relative to the background concentration of 349 ppbv, at the optical path length of 100-m. By increasing path lengths to 300 m, the quantification bias was reduced from -14% to -4%. The chapter-3 reported that increased path length increased the path-integrated concentrations (i.e., concentration $\times$ path length) as well as improved gas quantification. Since the OP lengths were between 200- (i.e., LS-2 and LS-6) and 300-m (i.e., LS-1, -3, -4, -5, and LS-7) in this scanning system, the uncertainties determined from the OP paths of 200-m (± 2.3 ppbv) and 300-m (± 1.4 ppbv) were averaged to calculate the overall uncertainty in N_2O concentration of each OP sensor (i.e., ± 1.8 ppbv). Concentration biases ($\sim -4\%$) were calibrated by the S-OPS before flux calculations. The uncertainty in N_2O concentrations (± 1.8 ppbv) was used to calculate the uncertainty in N_2O emission rates using the perturbation experiment (Figure 4.2).

4.4.2 Emission measurements

In bLS models for one source, the minimum requirement of TDF is generally 0.1 (10% of the sensor-released gas particles covered the field of interest). Some studies used higher TDFs to improve the accuracy of flux estimations in multi-source conditions (Balde et al., 2016; VanderZaag et al., 2014; Ro et al., 2011 and 2013). None of these studies interpreted how the ‘higher’ TDFs improved flux measurements and the effect of interferences from adjacent fields on flux measurements. We investigated the relationship between advective interferences (denoted by FRAC_{air}) and TDFs (Figure 4.4). Also, the measured emissions were sorted into

three categories based on high (> 0.9), median ($0.9 > \text{TDF} > 0.5$), and low ($0.5 > \text{TDF} > 0.1$) TDFs to examine the relationships between emissions and TDFs (Figure 4.5).

4.4.2.1 High TDFs (> 0.9)

In the high TDF (> 0.9) category, the averaged FRAC_{air} of the T1 – T4 treatments were 89 ± 12 %, 87 ± 14 %, 84 ± 16 %, and 80 ± 19 %, respectively (Figure 4.4). A targeted field received a ‘clean’ upwind background and resulted in high TDFs (~ 1.0) when $\text{FRAC}_{\text{air}} \sim 100\%$. For instance, T1 received a clean background when the wind came from SW ($202.5\text{--}247.5^\circ$) as well as high TDFs (1.0) (Figure 4.4). Likewise, the wind direction of SE ($112.5\text{--}157.5^\circ$), NE ($22.5\text{--}67.5^\circ$), and NW ($292.5\text{--}337.5^\circ$) led the TDFs of 1.0 to T2, T3, and T4 treatments, respectively. Increased interference ($0\text{--}20\%$ of the FRAC_{air} of the adjacent upwind field) reduced TDFs from 1.0 to 0.9 . For instance, T1 was interfered by T2 (~ 12 % of FRAC_{air} from T2) at wind directions of $180\text{--}202.5^\circ$, and interfered by T4 ($\sim 6\%$ of FRAC_{air} from T4) at the direction of $247.5\text{--}292.5^\circ$ (Figure 4.4a). The averaged emissions of the T1-T4 treatments from this category were 3.9 ± 3.2 , 0.8 ± 1.1 , 1.5 ± 1.1 , and $1.5 \pm 2.1 \mu\text{g m}^{-2} \text{s}^{-1}$, respectively (Figure 4.5). The corresponding averaged uncertainties of the T1-T4 were 0.6 ± 0.2 , 0.3 ± 0.1 , 0.1 ± 0.1 , and $0.5 \pm 0.3 \mu\text{g m}^{-2} \text{s}^{-1}$, respectively (Figure 4.6). The emission rates measured from this category implied that the integration of NT and full N rates applied in the fall (T1) resulted in higher N_2O losses than other treatments.

Negative emissions implied a ‘sink.’ Soil uptake of N_2O , however, was unlikely when the soil enriched with available N-substrates after NH_3 application. One of the assumptions of the bLS model required a substantial difference in emission rates between the source (hotspot) and background to make the ‘delta concentration’ (*Eq.1*) detectable. Negative emissions measured from a clean background and minimum interferences (Figure 4.5) were attributed to emissions lower than the detection limit. The standard deviation of the ‘negative’ emissions of T1-4 (TDF > 0.9) was $0.4 \mu\text{g m}^{-2} \text{s}^{-1}$, so the MDL of the OP method was calculated as $\pm 1.2 \mu\text{g m}^{-2} \text{s}^{-1}$ (3σ) (Figure 4.5).

4.4.2.2 Median TDFs ($0.9 > \text{TDF} > 0.5$)

In the median TDF ($0.9 > \text{TDF} > 0.5$) category, the averaged FRAC_{air} of the T1 – T4 treatments were 52 ± 20 %, 65 ± 19 %, 43 ± 15 %, and 40 ± 11 %, respectively (Figure 4.4). The averaged

emission rates of the T1-T4 treatments were 1.1 ± 1.9 , -0.3 ± 1.6 , 1.0 ± 2.2 , and $-1.2 \pm 1.4 \mu\text{g m}^{-2} \text{s}^{-1}$, respectively (Figure 4.5). The averaged uncertainties in emissions were 0.8 ± 0.5 , 0.4 ± 0.3 , 0.3 ± 0.3 , and $0.5 \pm 0.4 \mu\text{g m}^{-2} \text{s}^{-1}$, respectively (Figure 4.6). For TDF between 0.5 and 0.9, fields of interest were interfered by one predominant upwind field. For instance, the T2 treatment predominately interfered with the T1 treatment at the direction of $90 - 225^\circ$ (Figure 4.4a). Increased T2 interferences (i.e., the FRAC_{air} of T2 increased from approximately 20 to 80%) reduced the TDFs of T1 from 0.9 to 0.5.

Adjacent field interferences not only led to increased uncertainties but also increased biases in flux measurements. The bias became substantial if the upwind treatment emitted higher rates than the downwind field. For instance, high N_2O emissions were measured from T1 at the S wind ($180-225^\circ$) (Figure 4.5a). During the S wind, the T1 plot substantially interfered with the T4 measurements (FRAC_{air} of T1 = 60 % in Figure 4.4d), and great ‘negative’ emissions (lower than the MDL of $\pm 1.2 \mu\text{g m}^{-2} \text{s}^{-1}$) were measured from the T4 treatments (Figure 4.5d). Since the T1 (upwind) treatment emitted more N_2O than T4 (downwind), the air parcels from T1 treatment carried higher N_2O concentrations over the surroundings of T4 plot (i.e., Field-to-field carryover) and introduced substantial biases in the downwind flux measurements. Emissions lower than the MDL ($< -1.2 \mu\text{g m}^{-2} \text{s}^{-1}$) were considered as ‘false’ estimations and excluded.

4.4.2.3 Low TDFs ($0.5 > \text{TDF} > 0.1$)

In the low TDF ($0.5 > \text{TDF} > 0.1$) category, the averaged FRAC_{air} of the T1 – T4 treatments were only 20 ± 5 %, 16 ± 6 %, 19 ± 6 %, and 22 ± 5 %, respectively (Figure 4.4), showing that substantial interferences from adjacent fields. The averaged emission rates of the T1-T4 treatments were 0.2 ± 1.9 , -1.2 ± 2.1 , 3.0 ± 3.3 , and $-1.1 \pm 1.4 \mu\text{g m}^{-2} \text{s}^{-1}$, respectively (Figure 4.5). The averaged uncertainties were 1.0 ± 0.4 , 1.2 ± 0.4 , 0.5 ± 0.5 , and $1.0 \pm 0.6 \mu\text{g m}^{-2} \text{s}^{-1}$, respectively (Figure 4.6). The previous categories (high and median TDFs) showed that the field of interest was interfered by one predominant upwind field (e.g., T4 was predominately interfered by T1 at the S wind). In this low TDFs category, the increased FRAC_{air} (%) of adjacent fields showed that more than two adjacent fields interfered with fields of interest (Figure 4.4). For example, the T1 treatment was interfered by T2, T3, and T4 treatments at the direction of $0-90^\circ$ (Figure 4.4a). Likewise, T2, T3, and T4 fields were interfered by their neighbors when the wind came from the

directions of 270-360°, 180-270°, and 90-180°, respective (Figure 4.4). These ‘two-source’ interferences resulted in low TDFs (< 0.5) as well as high flux uncertainties (Figure 4.6).

The interference-led biases in emission measurements substantially influenced the field with low emission rates. For instance, emissions lower than MDL ($< -1.2 \mu\text{g m}^{-2} \text{s}^{-1}$) were measured in T4 measurements at the S wind because of the interferences from the T1 treatment (Figure 4.4 and Figure 4.5). The T3 treatment was subjected to interferences from T1, T2, and T4 at the wind direction of 180-270° (prevailing SW wind in 2015 measurements). In contrast to the T4 treatment, most of the emissions from the T3 treatment were still measurable and greater than the MDL ($\pm 1.2 \mu\text{g m}^{-2} \text{s}^{-1}$) (Figure 4.5c) even under the interferences of T1, T2, and T4 plots. Emissions less than $-1.2 \mu\text{g m}^{-2} \text{s}^{-1}$ (MDL) resulting from the advective interferences were excluded in this study. Then, the averaged emissions of the T1 – T4 treatments were 2.5 ± 3.0 ($n = 347$), 0.4 ± 1.1 ($n = 291$), 2.5 ± 2.8 ($n = 339$), and 0.4 ± 1.6 ($n = 255$) $\mu\text{g m}^{-2} \text{s}^{-1}$, respectively, over 44 days (Figure 4.5).

4.4.3 Influence of sensor placement

Uncertainties in emissions measurements were affected by the placement of sensors and estimated by the permutation experiment (Figure 4.2). Good sensor placement, adequate upwind and downwind sensors to ‘see’ the source of interest and adjacent fields, was important for multi-source emissions measurements (Crenna et al., 2008; Flesch et al., 2009). The averages of the T1 – T4 emissions (2.5, 0.4, 2.5, and 0.4 $\mu\text{g m}^{-2} \text{s}^{-1}$, respectively) and the uncertainty of N_2O concentration (± 1.8 ppbv) were used to estimate the uncertainty in emissions using the procedure shown in Figure 4.2.

Lack of upwind or downwind sensors resulted in errors in flux estimations. An LS sensor between T1 and T4 and a PS sensor at the S of the field were absent in this study. An extra LS (i.e., LS-8 between T1 and T4) and PS (i.e., at the S of the field) sensors were added in the bLS model, and concentrations of the LS-1 – LS-8 were permuted (i.e., 2^8) to investigate the effect of the sensor placement on emission uncertainties. Uncertainties were estimated from the two types of sensor placement (i.e., 7 LS + 3 PS sensors and 8 LS + 4 PS sensors), shown in Figure 4.6. The T1 treatment ideally received a clean upwind background and resulted in low uncertainties

(< 0.4 $\mu\text{g m}^{-2} \text{s}^{-1}$) for emission measurements under S (160-180°) winds. The placement of seven LS joined with three PS sensors, however, showed irregularly high uncertainties (up to 2.0 $\mu\text{g m}^{-2} \text{s}^{-1}$) in emission measurements under S winds (Figure 4.6a). These uncertainties were reduced by order of two by adding the LS-8 sensor between T1 and T4 plots and the PS sensor at the S of the field (Figure 4.6a). Likewise, high uncertainties ($\sim 1.8 \mu\text{g m}^{-2} \text{s}^{-1}$) occurred in the T4 measurement under N (360°) winds and were reduced by adding LS-8 sensors. Uncertainties in the T3 measurement were not affected by these additional sensors (Figure 4.6c) because the upwind and downwind sensors were well deployed in T3 plot (LS-4 – LS-6 and two PS sensors at the N and E of the field shown in Figure 4.1). For T2, the decreased uncertainties occurred from wind direction of 0-90° due to adding the south PS sensor, and LS-8 sensor also created the additional downwind sensor for T4 from wind direction of 270-360° (Figure 4.6b and 4.6d). Although the uncertainty led by advective interferences was inevitable, the deployment of the sensors is critical to avoid the irregularly high uncertainties. A good sensor-source deployment is to create a well-mapped upwind and downwind sensor for each source (Flesch et al., 2009).

4.4.4 Treatment comparisons

Soil N_2O emissions were substantially influenced by N and field management practices (Decock, 2014; Robertson and Vitousek, 2009; Venterea et al., 2011; van Kessel et al., 2013). In multiple source emissions measurements, fields with low emissions were more sensitive to interferences from the upwind field with high emissions. For the T2 (NT+F110/S100) and T4 (NT+F0/S220) treatments, up to 18% and 29% of the emissions ($n = 357$) were less than the MDL ($-1.2 \mu\text{g m}^{-2} \text{s}^{-1}$) and excluded. For T1 (NT+F220/S0) and T3 (ChP+F110/S100) treatments, only 3% and 5% of the qualified emissions were excluded. The averaged emissions of the T1-T4 treatments (2.5, 0.4, 2.5, and 0.4 $\mu\text{g m}^{-2} \text{s}^{-1}$, respectively) showed that the split-N rate application resulted in lower N_2O emissions than the full-N rate application in the NT field. The ChP practices led to higher N_2O emissions compared with the NT treatment under the same N management. The split-N rate application was consistently reported to result in lower N_2O emissions than the full-N rate application (e.g., T1 vs. T2) (Decock, 2014; Robertson and Vitousek, 2009; Burton et al., 2008). For tillage system, however, many studies showed that inconsistent results of the NT effect on N_2O emissions (e.g., reduced tillage practice either increased or decreased N_2O emissions) (Decock, 2014; Venterea et al., 2011; van Kessel et al., 2013). In this experiment site

(Purdue ACRE), the NT practices were continuously reported to reduce N fertilizer-induced N₂O emissions (e.g., T2 vs. T3) (Omonode et al., 2011, 2015, and 2019).

4.4.5 Combined influences of wind speed and direction

Both wind direction and velocity influenced advective interferences and measurement qualities (i.e., biases and uncertainties). Increased wind speed resulted in great ‘biased’ measurements (i.e., emissions < MDL) (Figure 4.7a) and increased measurement uncertainties (Figure 4.7b). For instance, increased wind speed amplified the interferences from T1 and emission biases for the T4 measurements at the S wind (Figure 4.7a). Wind speed affected the horizontal transport of air parcels (an air parcel refers to a body of air which thermodynamic properties were approximately uniform) and field-to-field carryover via advection. Advective interferences and the corresponding uncertainties in emissions were highly wind-dependent. For instance, the wind of 0-90 resulted in high TDFs (> 0.9) and low uncertainties ($0.1 \pm 0.1 \mu\text{g m}^{-2} \text{s}^{-1}$) for T3 measurements. Interferences and emission uncertainties ($0.5 \pm 0.5 \mu\text{g m}^{-2} \text{s}^{-1}$) increased at the wind from 180-270° for T3 measurements. These uncertainties increased with increasing the wind velocity (e.g., $R^2 = 0.20$ from 0-90°; $R^2 = 0.68$ from 90-180°; $R^2 = 0.90$ from 180-270°; $R^2 = 0.42$ from 270-360°), shown in Figure 4.7b.

4.5 Conclusion

This study shows that wind direction and speeds significantly influence the modeled footprint, interferences from adjacent fields, emission estimations for multi-source measurements. The universal threshold of touchdown criteria (i.e., $\text{TDF} > 0.1$) are unlikely applicable to a multi-source situation. In this study, the fraction of touchdowns (TDF) greater than 0.9 indicated that a field of interest received a clean upwind background and resulted in low emission uncertainties ($0.5 \pm 0.3 \mu\text{g m}^{-2} \text{s}^{-1}$). Reduced TDF (< 0.9) resulted from the increased interference from the upwind fields. The TDFs ranging from 0.5 and 0.9 showed that one predominant upwind source interfered with the downwind field of interest and increased emission uncertainties (i.e., $0.6 \pm 0.4 \mu\text{g m}^{-2} \text{s}^{-1}$). The 0.1-0.5 TDFs indicated three upwind interferences and resulted in high emission uncertainties (i.e., $1.1 \pm 0.5 \mu\text{g m}^{-2} \text{s}^{-1}$). High emission rates from the upwind field ‘contaminate’ the downwind field emission estimations resulting in large biases. Emissions less than the minimum detection limit (MDL) of $-1.2 \mu\text{g m}^{-2} \text{s}^{-1}$ were removed. Although advective

interferences were inevitable, proper deployment of upwind and downwind gas sensors can avoid the irregularly high uncertainty in emission measurements. Implementing the bLS method in a multi-source area is still ongoing research and becoming interesting to many users. This study provides the current or future users with the approaches to identify the issues, potential solutions, and uncertainty analyses in a multi-source situation.

4.6 References

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Table 4.1 Four treatments (T1-4) were conducted to represent four N₂O sources. Field practices were no-till (NT) and chisel plow (ChP). With the total N rate of 220 kg NH₃-N ha⁻¹, NH₃ was applied as a full (220 kg N ha⁻¹ in the fall or spring) or a split (total N rate was equally split and applied in the fall and spring) application at two timings of the fall (F) in 2014 and the spring (S) before planting in 2015. The management of each field was: (T1) NT + full application in the Fall and zero N input in the Spring (F220/S0); (T2) NT + split application in the Fall and Spring (F110/S110); (T3) ChP + F110/S110; (T4) NT + F0/S220.

N and Field Management

Treatment (ha)	Tillage	Anhydrous ammonia (Total = 220 NH ₃ -N kg ha ⁻¹)	
		2014 Fall	2015 Spring
T1 (1.2)	No-till	220	0
T2 (1.1)	No-till	110	110
T3 (1.1)	Chisel plow	110	110
T4 (1.2)	No-till	0	220

Table 4.2 An example of determining the fraction of air parcel ($FRAC_{air}$) that traveled from adjacent fields (i.e., T1, T3, and T4) to the field of interest (i.e., T2), representing the magnitude of interferences, under a particular wind condition.

WD = NW (317°), $U = 3.7 \text{ m s}^{-1}$, $u^* = 0.32 \text{ m s}^{-1}$, $L = -37 \text{ m}$

Fields	Area (ha)	TDF	TD area (ha)	Fields	Each TD area (ha)	$FRAC_{air}$ (%)
T2	1.5	0.24	0.36	T2	0.36	17
T2+T1	2.7	0.28	0.76	T1	0.40	19
T2+T3	2.9	0.32	0.93	T3	0.57	27
T2+T4	2.6	0.43	1.12	T4	0.76	36

WD, wind direction; U, mean wind velocity; u^* , friction velocity; L, Monin-Obkov length

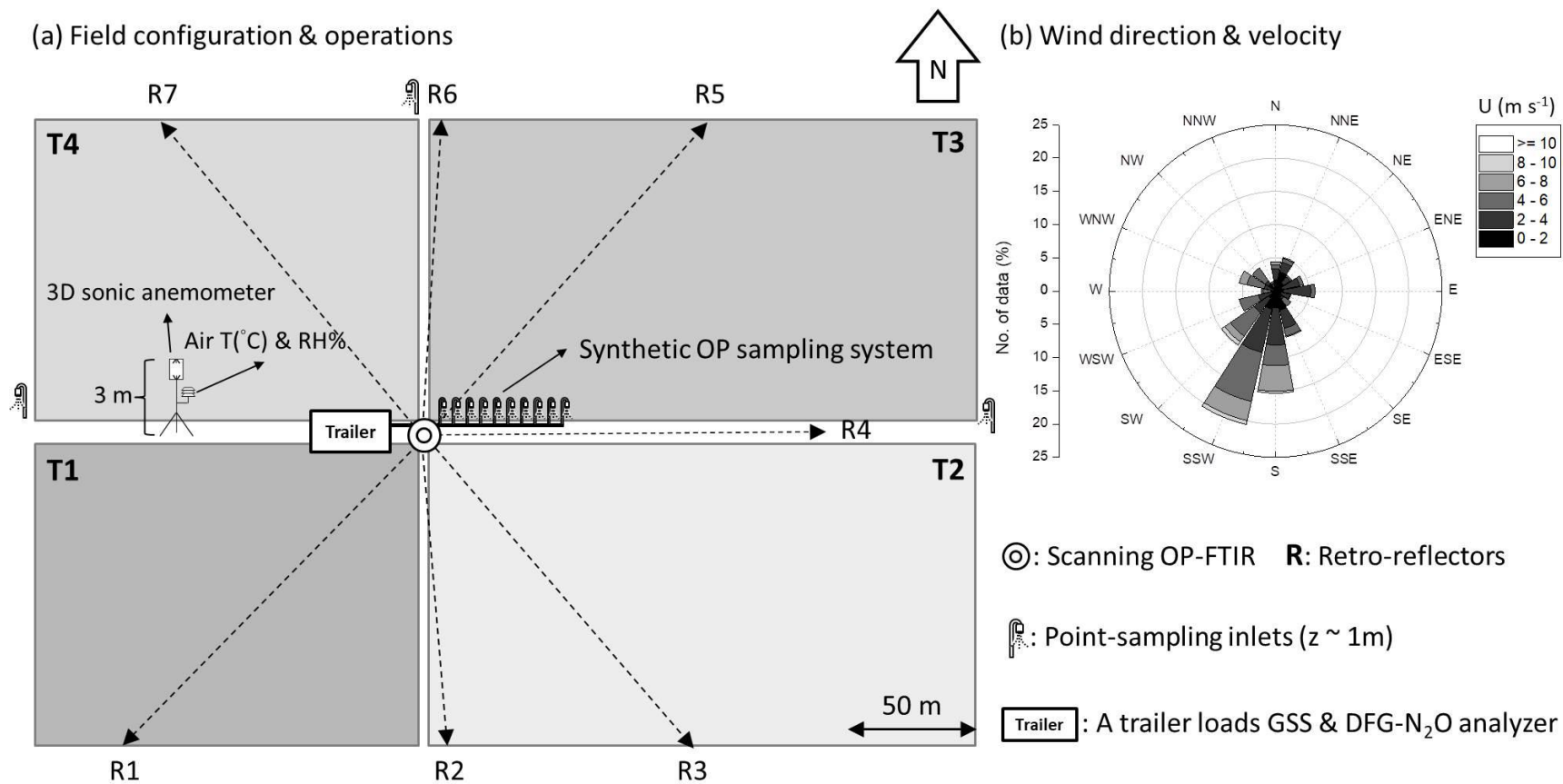


Figure 4.1 The experimental site was at the Purdue Agronomy Center for Research and Education (ACRE). The field experiment was operated by (a) a scanning OP-FTIR and seven retroreflectors created seven line-sampling (LS) concentration sensors (LS-1 – LS-7) concentrations sensors to ‘scan’ four treatments (T1-T4) managed by contrasting field and N practices shown in Table 4.1. Three point-sampling (PS) inlets were deployed at the edges of fields (W, N, and E) to measure the background N_2O concentrations or provided additional downwind sensors for fields of interest. (b) the prevailing wind came from the SSW and the mean wind velocity was $3.6 \pm 1.8 \text{ m s}^{-1}$.

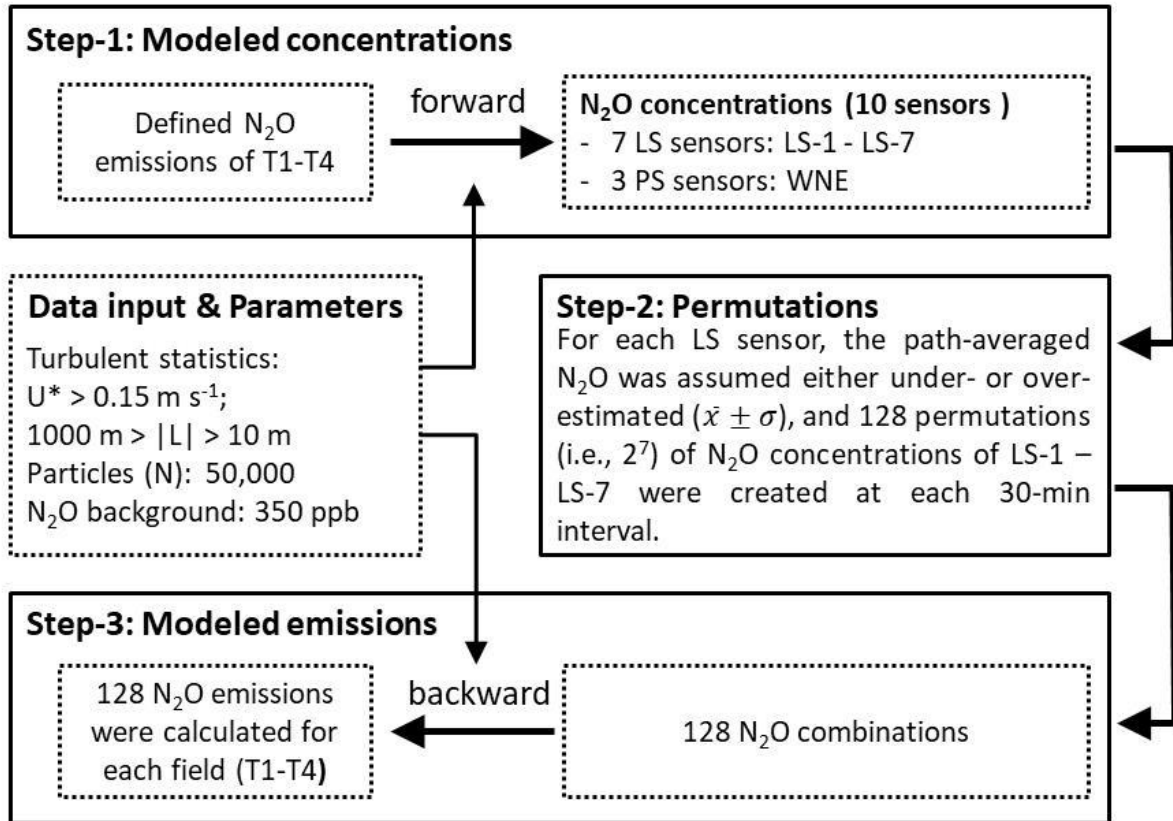


Figure 4.2 The procedure used to estimate uncertainties in emission rates measured by the bLS model. Step1: N₂O concentrations of the seven line-sampling (LS) and three point-sampling (PS) sensors were ‘forward’ calculated based on the known emission rates of the T1-T4 treatments. Step2: the ‘biased’ concentrations ($N_2O \pm \sigma$) of the LS-1 – LS-7 sensors were permuted. Step3: 128 N₂O emissions were ‘backward’ calculated, and their standard deviation represented emission uncertainties at every 30-min interval.

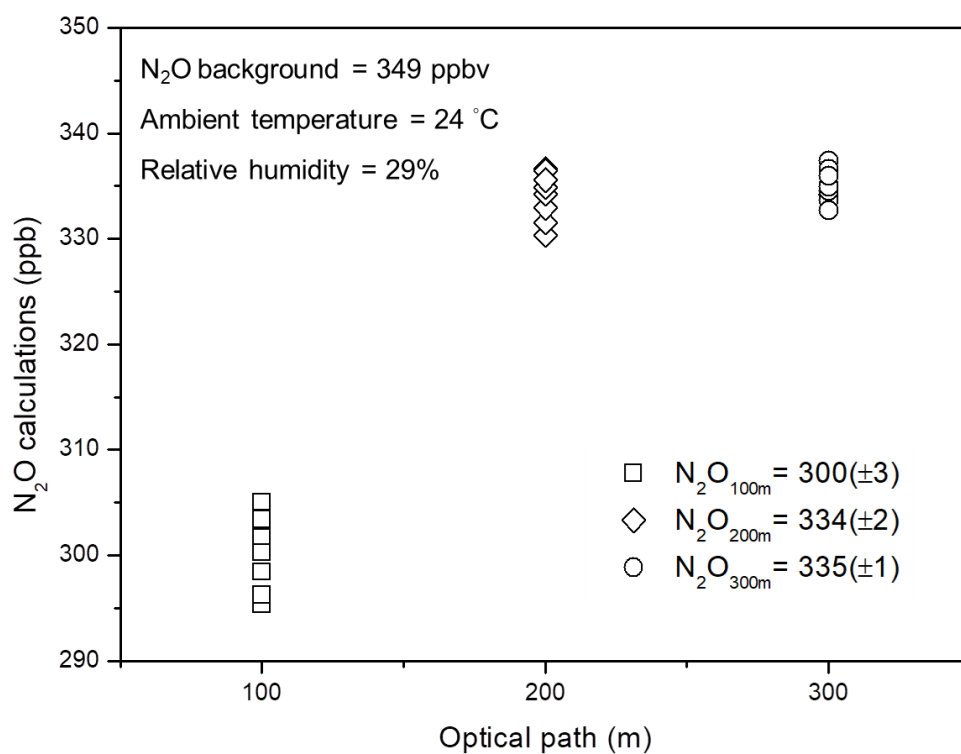


Figure 4.3 Open path FTIR spectra were acquired from optical paths of 100-, 200-, and 300-m and calculated for N_2O concentrations using a partial least square (PLS) algorithm. The mean concentration ($\bar{x}$) and standard deviation (σ) represented the accuracy and uncertainties in the PLS-calculated concentrations.

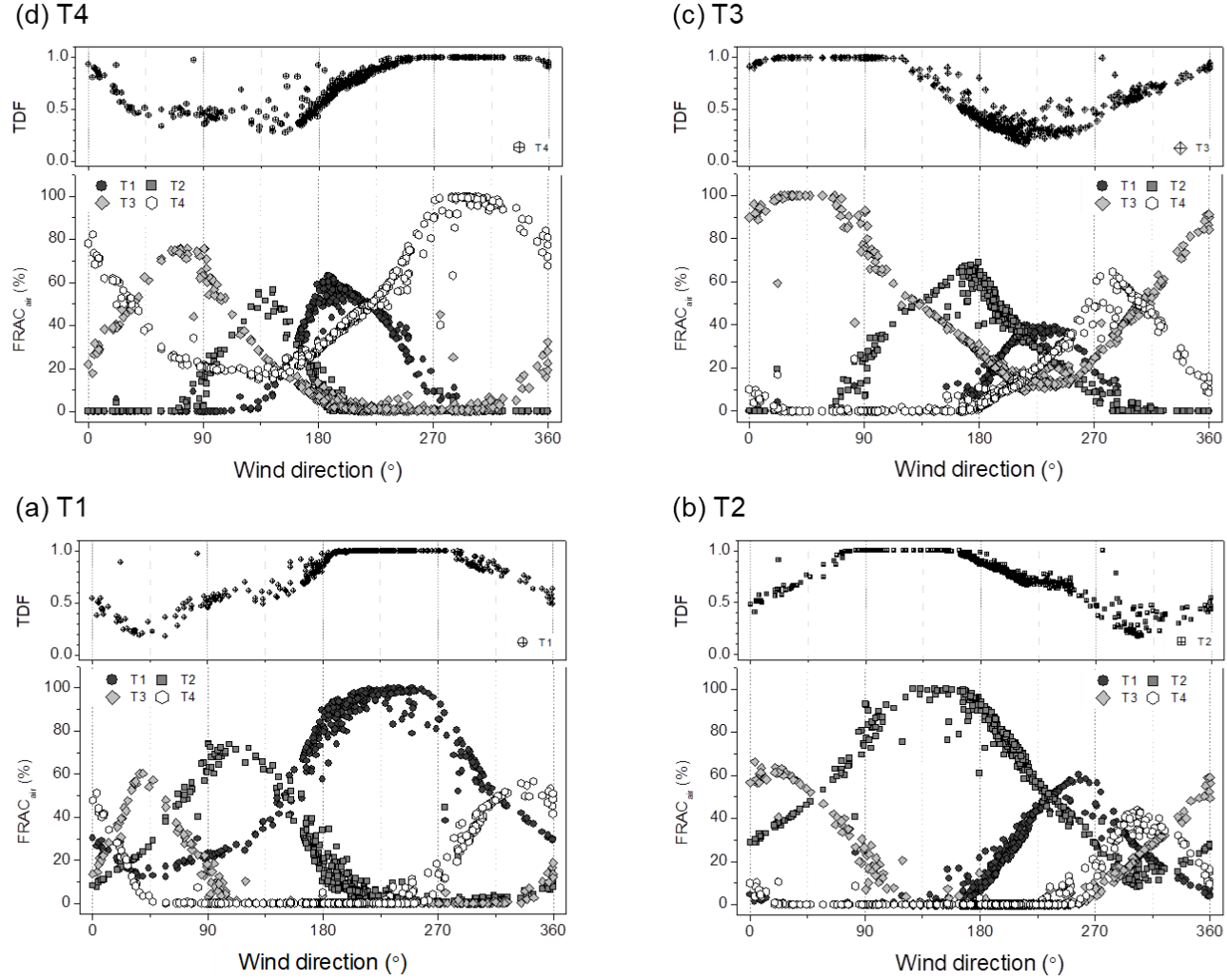


Figure 4.4 The relationship between the ‘touchdowns’ fraction (TDFs) of fields of interest and the interferences from the adjacent fields. For the field of interest, the fraction of air parcels (FRAC_{air}) traveling from adjacent fields was used to represent the magnitude of the upwind interferences.

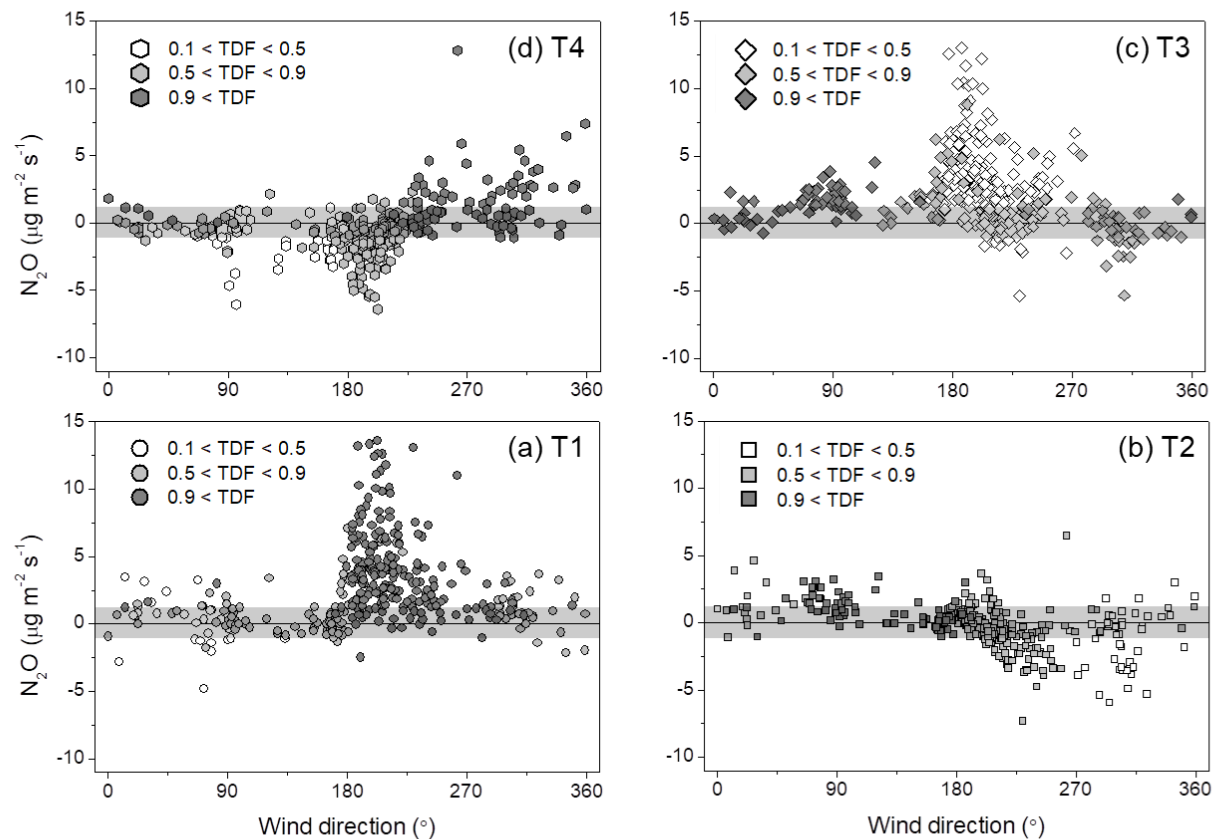


Figure 4.5 The relationship between the estimated emissions and the touchdowns fraction (TDFs) of fields of interest, (a) T1 (circle), (b) T2 (square), (c) T3 (diamond), and (d) T4 (hexagon). Emissions were classified into three categories of TDF > 0.9 (grey), $0.9 > TDF > 0.5$ (light grey), and $0.5 > TDF > 0.1$ (white).

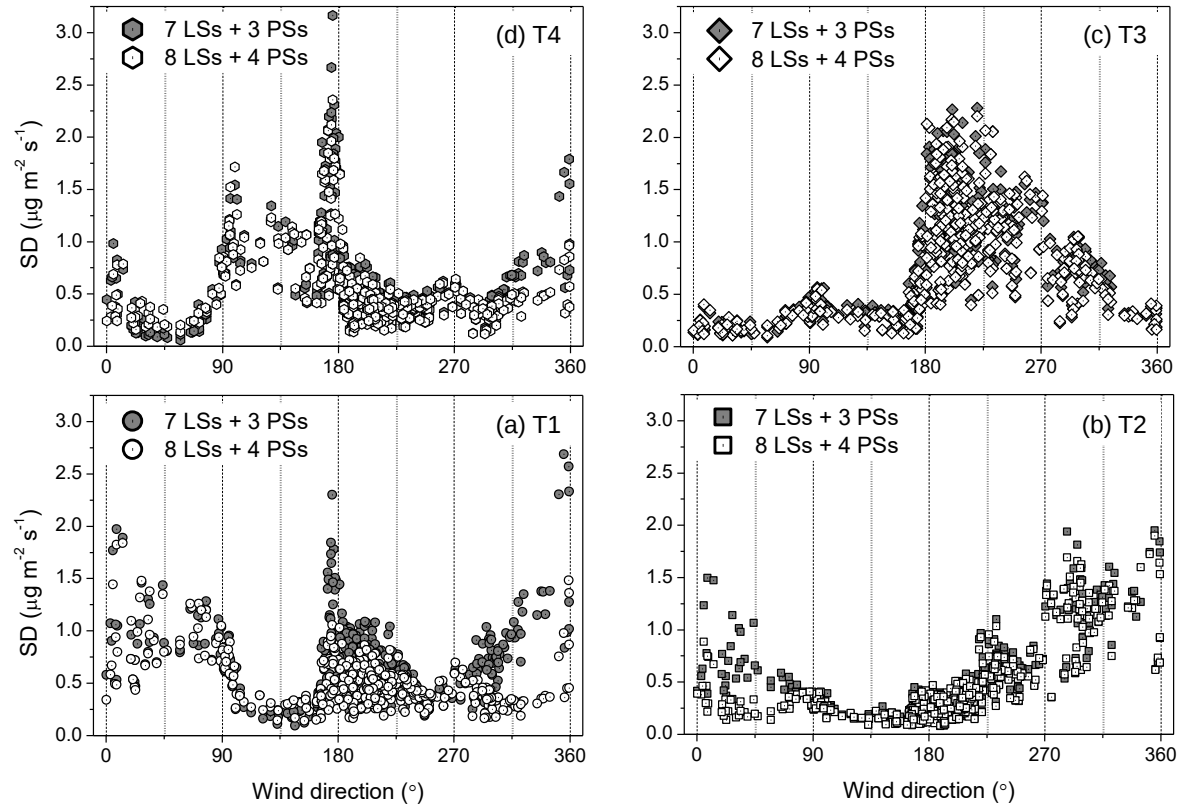


Figure 4.6 The effect of the sensor placement on the estimated uncertainties in emission measurements. Uncertainties were estimated by two types of the sensor placement, (1) seven LS and three PS sensors used in this study (grey) and (2) eight LS and four PS sensors considered as ideal sensor placement (white). The eighth LS (LS-8) was added between the T1 and T4 treatments, and the fourth PS sensor was added at the S of the field. All symbols were with a dot in the center to differentiate from Figure 4.5.

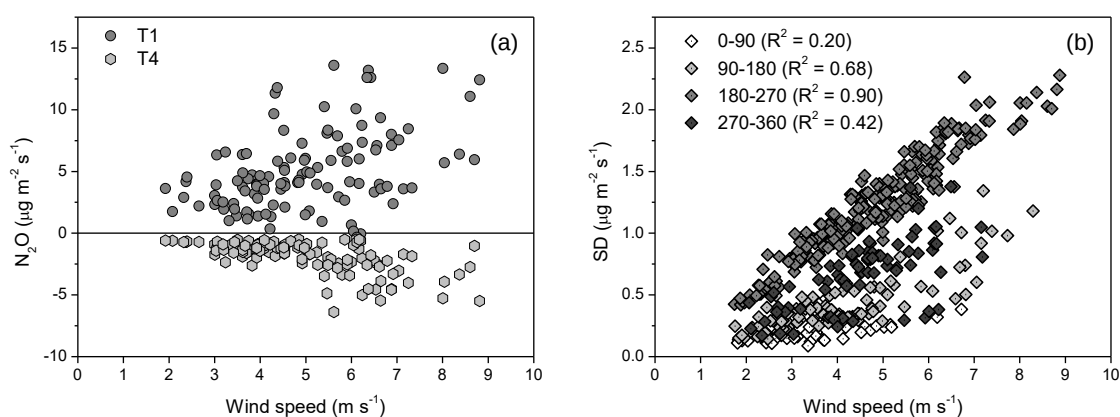


Figure 4.7 The effect of the mean wind speed on interferences from the upwind fields: (a) the T1 treatment interfered with the T4 treatment at the S wind and these interferences increased with increasing the wind speed. The increased wind speed led great biases (emissions < MDL of $-1.2 \mu\text{g m}^{-2} \text{s}^{-1}$) in the T4 measurements; (b) the increased wind speed increased uncertainties in the T3 measurements.

CHAPTER 5. DETERMINE DIRECT N₂O EMISSIONS FROM MAIZE CROPPING SYSTEM BY INTEGRATING THE CHAMBER AND OPEN PATH METHODS

A version of this chapter will be submitted for review to the Journal of Environmental Quality.

5.1 Summary of Chapter 5

Toward a better understanding and quantification of nitrous oxide (N₂O) emissions from fertilizer-intensive corn cropping systems needed to integrate different emissions measurement methods. An open path (OP) method (a scanning OP Fourier transform infrared spectrometer + the backward Lagrangian stochastic model) and vented static closed chamber method were used to continuously measure N₂O emissions from a continuous corn system after the spring nitrogen (N) application (220 kg NH₃-N ha⁻¹) for 11-, 44-, and 21-day in 2014, 2015, and 2016, respectively. The effect of different N application timing and a long-term no-till (NT) practices on N₂O emissions and N recovery efficiency (NRE) were assessed in this study. This study showed that N₂O emissions increased with increasing wind speed (> 4 m s⁻¹) and the static chamber measurements could underestimate soil N₂O emissions by 10x without considering the wind-induced emissions. In NT farming systems, the split-N rate application (split-N: a total of 220 N kg ha⁻¹ was equally split and applied in prior fall and current spring) resulted in lower N₂O emissions (0.42, 0.38, and 0.33 N₂O-N kg ha⁻¹ day⁻¹ in 2014, 2015, and 2016, respectively) than the full-N rate (a total N was applied in once) applied in fall (0.78, 1.13, and 0.47 N₂O-N kg ha⁻¹ day⁻¹ in 2014, 2015, and 2016, respectively). Based on the same N application (split-N), the chisel plow (ChP) practice showed higher N₂O emissions (0.79, 1.08, and 0.46 N₂O-N kg ha⁻¹ day⁻¹ in 2014, 2015, and 2016, respectively) than NT. The spring N application before planting (pre-plant) resulted in lower NRE than the application in season (side-dress) presumably due to more N loss before plant N uptake. Reduced NRE was also corresponding to higher N₂O emissions.

5.2 Introduction

Soil N₂O is produced from a series of microbial transformation of reactive nitrogen (Nr) (e.g., N fertilizers, biological-fixed N, and N mineralized from soil organic matter and crop residues) via

nitrification and denitrification (Bouwman, 1996; Mosier et al., 1998; Butterbach-Bahl et al., 2013). Microbial communities and activities are substantially influenced by the environment, including soil conditions, textures, topography, field practices, and climate (Bailey, 1976; Bremner and Blackmer, 1978; Parkin, 1985; Smith, 1990; Bouwman, 1996; Maag, 1996; Schaufler et al., 2010; Kong et al., 2013; Signor and Cerri, 2013). For instance, the concave and convex topography of fields influences soil physical and chemical properties (e.g., moisture, organic matter content, cation exchange capacity, pH, redox, etc.). Changed properties result in different spatial distributions of soil microbes across a field (Ambus and Christensen, 1994; Schelde et al., 2012; Li et al., 2013). The dynamic changes in environmental variables (e.g., diurnal or seasonal fluctuations in solar radiation, soil temperature, and moisture) led to highly temporal variations in microbial activities as well as N_2O productions (Smith et al., 1998; Xu et al., 2017). Since winds influence gas exchange between the soil and atmosphere, increased wind speeds potentially increase N_2O emissions (Maier et al., 2012; Poulsen et al., 2017; Pourbakhtiar et al., 2017).

Emissions of N_2O from soils are complex biogeochemical processes (i.e., continuous, dynamic, and episodic emissions) (Mosier et al., 1998; Butterbach-Bahl and Dannenmann, 2011; Butterbach-Bahl et al., 2013). Field management effects (e.g., N and tillage practices) on soil conditions increase the complexity of N_2O emission processes (Six et al., 2004; Venterea et al., 2012; Lenka and Lal, 2013; Kong et al., 2013). For instance, N_2O emitted from cereal cropping systems during growing seasons mainly resulted from N fertilizer (Bouwman, 1996). Different N fertilizer management (e.g., N source, application rate, timing, and placement) substantially influences the amount of the applied-N taken up by crops. The extra N-substrates potentially became sources of N_2O (Decock, 2014; Shcherbak et al., 2014; Abalos et al., 2016; Venterea et al., 2016). For N management, the strategies proposed to mitigate N_2O emissions (e.g., reduced N rate or changing application timing close to actual crop N demands) (Decock, 2014; Omonode et al., 2017). The effect of tillage practices on N_2O emissions, however, is highly variable and has been reported to conflicting results (Rochette et al., 2008; Venterea et al., 2011; van Kessel et al., 2013). For instance, reduced (RT) or no-tillage (NT) practices were reported to mitigate N_2O emissions (Omonode and Vyn, 2019). Other studies reported higher N_2O emissions (Ball et al., 1999) or no difference between RT/NT and conventional tillage (Decock, 2014). These

inconsistent conclusions of tillage effects on N₂O emissions were not only attributed to changing environments (Six et al., 2004; van Kessel et al., 2013) but presumably the uncertainties led by the emissions measurement method.

Chamber techniques have been used to measure gas emission rates for almost 100 years and remain the most common method for direct/indirect N₂O emission measurements from soils (Lundegårdh, 1927; Rochette and Eriksen-Hamel, 2008). Many field practices proposed to mitigate soil N₂O-N loss were based on chamber measurements because of their simple implementation and widespread use (Eichner, 1990; Denmead, 2008; IPCC, 2006; Decock, 2014). Chamber measurements, however, have a small footprint (i.e., < 1.0 m²) and low sampling frequencies (i.e., usually 1-2 samples a week). Because of spatial variability, sampling location must be selected to represent the entire field (Röver et al., 1999; Yanai et al., 2003). Low sampling frequency not only results in a temporal gap of missing data between two sampled periods but may not capture the N ‘loss events’ (e.g., intermittent rainfall or spring thawing) (Mosier et al., 1996; Parkin, 2008; Schelde et al., 2012; Decock, 2014). These limitations led uncertainties in long term flux measurements (e.g., cumulative N₂O-N loss during growing seasons) due to the spatial and temporal heterogeneity of soil N₂O emissions (Laville et al., 1999; Denmead, 2008; Rochette and Eriksen-Hamel, 2008; Venterea et al., 2009; Butterbach-Bahl et al., 2013). Alternative approaches with higher sampling frequency and larger footprints, such as open chamber systems or micrometeorological techniques (e.g., mass balance, or eddy covariance methods), can be used to measure gas emissions for missing data gaps (Baldocchi et al., 1988; Laville et al., 1999; Denmead, 2008; Jones et al., 2011).

‘Optimal’ management ideally meets the requirement of increasing N uptake and use efficiency and mitigating the environmental impacts (N losses via gas emissions and leaching) simultaneously. Simply investigating the relationship of management practices to a single outcome (e.g., area-scale emissions) likely resulted in a questionable conclusion for optimizing management (Venterea et al., 2011 and 2012). It is important to investigate management effects on the relationship between N₂O emissions, and crop yield, or other N uptake-derived parameters, including N uptake and use efficiency, and N balance in soils. For instance, the N recovery efficiency (NRE: total aboveground N uptake (TNU) in fertilized treatments minus TNU in control treatment relative to applied N-fertilizer rate) is one of the useful parameters to

recommend suitable management for achieving both efficiency and environmental purposes. The common hypothesis is that increased NRE likely reduces N₂O emissions (Snyder et al., 2014; Venterea et al., 2016; Omonode et al., 2017). In this study, a scanning open path Fourier transform spectrometer (OP-FTIR) coupled with a backward Lagrangian stochastic (bLS) dispersion technique (an open path (OP) method) was integrated to measure gas emission from multiple sources at high spatial and temporal resolution (Chapter 1-3). This method, however, was limited to measure emissions in low wind conditions, mostly during the night. The missed ‘nighttime emissions’ can be compensated by chamber measurements (Grant and Omonode, 2018). Thus, the objectives of this chapter were 1) to integrate an OP and chamber methods to measure N₂O emissions from four treatments with contrasting management by integrating different tillage system and N application timings; 2) to investigate management effects on the relationship between corn N uptake and use efficiency and N₂O emissions.

5.3 Materials and Methods

5.3.1 Site description and management

This study was conducted at the field of Agronomy Center for Research and Education (ACRE) of Purdue University near West Lafayette, IN (86°59'41.09"W, 40°29'44.46"N, elevation 215 m). The soil type was mainly classified as Drummer silty clay loam (fine-silty, mixed, mesic Typic Endoaquoll). Drainage type was classified from somewhat poorly to dominantly poorly drained (Soil survey, USDA). The organic matter (OM), pH, and cation exchange capacity (CEC) of the soil of 0-20 cm were analyzed by a commercial laboratory (Midwest Laboratories, Inc.) in 2017. The soil OM was determined by the loss-on-ignition (LOI) method (Nelson and Sommers, 1996). The soil pH was measured by the ratio of soil to water of 1:1. The ranges of the OM, pH, and CEC over treatments were 3.3 - 3.9 %, 6 - 6.9, and 21 - 25 cmol_c kg⁻¹, respectively. The Illinois soil nitrogen test (ISNT) was used to estimate the potential soil nitrogen (N) supply for crop use during the growing season (Khan et al., 2007). The increased ISNT value inferred that the increased amount of the ‘readily used’ soil organic N (e.g., amino sugar). More details were shown in Supplementary Table 5.1.

The cropping system was continuous corn (*Zea mays* L.) from 2013 to 2016 and managed by different tillage and N practices (Table 5.1). Tillage practices were no-till (NT) and chisel plow (ChP) which was performed in the fall to the depth of 0-20 cm and followed by spring secondary tillage. The corn was planted with a population of approximate 85,000 seeds ha⁻¹ with N added as a result of 143 L ha⁻¹ of 10-34-0 starter in a 50 x 50 mm² band placement. For N management, anhydrous ammonia (NH₃) was used as N sources with a total N rate of 220 kg NH₃-N ha⁻¹, which was applied either one time (full application: 220 kg N ha⁻¹) or separately (split application: a total N rate was equally split) (Table 5.1). NH₃ was applied by coulter injection (~ 10 cm deep into the soil) after harvest during the fall or the following spring. The fall N application occurred when the soil temperature was below 10 °C; the spring N application was conducted either before planting (pre-plant) or in-season when the corn stage was between V5 and V6 (side-dress). The experimental field was grouped into four treatment based on different management. The placement of each treatment (T1 – T4) was shown in Figure 5.1, and the land area was approximately 1.0 hectare for each treatment. The tillage of the T1 and T2 plots was consistently NT practice, and the T3 was ChP each year. The T4 plot was converted from ChP in 2013 to NT in the fall of 2014 (Table 5.1). NH₃ treatments were identical in 2014-2016. A full N rate application (220 kg NH₃-N ha⁻¹) was performed at T1 in the fall and T4 in the spring, and a split N rate application (110 kg-N ha⁻¹ in the prior fall and the following spring) was completed at T2 and T3. For the spring N application, NH₃ was applied as a side-dress application in 2014 and 2016, and as a pre-plant application in 2015.

5.3.2 Scanning open path (OP) system operations

Nitrous oxide emissions from four treatments were measured by the scanning open path (OP) emissions measurement system. This scanning OP system was integrated by the OP line-sampling (LS) and point-sampling (PS) N₂O concentration sensors, and the bLS emissions measurement technique. The LS sensor was a monostatic OP-FTIR spectrometer (MIDAC Model2501-C, MIDAC Corporation, Irvine, CA) bounded by a distant retro-reflector (between 100 and 135 meters) to measure path-averaged N₂O concentrations. An OP-FTIR was installed on a scanner with vertical and horizontal rotaries (YUASA computer numerical control, CNC) and 6-7 retro-reflectors were mounted in fields or on field edges to create LS sensors to scan four treatments (Figure 5.1). The PS sensor was a difference frequency generation (DFG) mid-IR

laser-based $\text{N}_2\text{O}/\text{H}_2\text{O}$ analyzer (IRIS 4600, Thermo Fisher Scientific Inc., Waltham, MA) coupled with a gas sampling system (GSS) to measure background concentrations of N_2O and upwind or downwind point measurements for the field of interest. Emission measurements began just after the spring N application and stopped until the corn crop canopy was higher than the LS sensors (i.e., the OP-FTIR spectrometer was at approximately 1.5-m height above ground level (a.g.l.)). The measurement periods from 2014-16 were 09 – 20 Jun. 2014, 30 Apr. – 12 Jun. 2015, and 07 – 26 Jun. 2016, respectively.

5.3.2.1 Line-sampling sensors

The process used to quantify gas concentrations from OP-FTIR spectra is described in Chapter 2. Briefly, the emitted IR radiation from a spectrometer traveled through the air and returned to the telescope which included Mercury Cadmium Telluride (MCT) detector after a reflection from a retro-reflector (26 cubes). An interferogram (IFG) was generated approximately every minute and transformed to a single beam (SB) spectrum using Fourier transform algorithms. The SB spectrum was converted to an N_2O absorbance (ABS) spectrum, which was used to calculate N_2O concentration using partial least squares quantitative models based on the Beer-Lambert law. One of the advantages of a monostatic OP-FTIR is high sensitivity for gas quantification because of doubling absorbance path length.

5.3.2.2 Point-sampling sensors

A GSS system, including a sampling pump and four DC-powered solenoids, linked to four 9.5-mm diameter Teflon® tubing to create four sampling lines. Gas samples were drawn through the sampling inlets deployed in fields by a sampling pump in the GSS at approximately $7 \text{ L} \cdot \text{min}^{-1}$ and collected into a Teflon® ambient pressure chamber. Then, $\text{N}_2\text{O}/\text{H}_2\text{O}$ analyzer drew air samples from the ambient pressure chamber to measure N_2O concentrations (Heber et al., 2006). One of the sampling lines was attached to a 50-m line sampling system to benchmark the N_2O concentration calculated from OP-FTIR spectra (described in Chapter 2 and 3), and the other three lines were designed as the PS sensors deployed at the border of fields (Figure 5.1).

5.3.2.3 Sensor layouts

For a configuration with four emission sources, the ideal scanning system required eight LS sensors and four PS sensors to produce adequate upwind and downwind sensors under changing

wind direction shown in Figure 5.1. One of the limitations was the lack of complete upwind concentration measurements. The configuration in 2014 had only six LS sensors (i.e., LS-1 – LS-5, and LS-7) and three PS sensors (i.e., east, south, and west) sensors deployed in the field (Table 5.1). In 2015 and 2016, the LS-6 was installed between T3 and T4 plots to improve the scanning system; however, the LS-8 between T1 and T4 was still absent due to limited rotation of the scanner. The placement of the LS and PS sensors was varied from 2014-16 (Table 5.1). The scanner and OP-FTIR were not synchronized. A dwell time of each path (LS-1 to LS-7) was three minutes to collect two to three N₂O samples (spectra) of each LS. The scan of all LS took nearly thirty minutes to complete one cycle. A 3D sonic anemometer (Model 81000, RM Young Inc., Traverse City, MI) was mounted on a meteorological mast (height $\approx$ 3-m a.g.l.) and measured 16Hz wind information and turbulent statistics. Ambient air temperature, humidity, and pressure were measured every minute using a temperature/humidity sensor (Model HMP45C, Vaisala Oyj, Helsinki, Finland) and a pressure sensor (Model 278, Setra, Inc., Boxborough, MA) at 1.5-m height a.g.l. All data were averaged at the thirty-minute interval for flux calculations using the bLS model.

5.3.3 OP emission measurements and quality assurance

Emission rates of N₂O were estimated using the measured concentrations and turbulent statistics in a bLS model (Windtrax2.0: Thunder Beach Scientific, <http://www.thunderbeachscientific.com>). The bLS technique ‘backward’ models the trajectories of gas particles from sensors to a source of interest using turbulent statistics (i.e., u^* , L , z , β) to simulate the ratio of gas concentration (C) to the surface emission rate (Q) (i.e., $(C/Q)_{sim}$). Given the known downwind and background (C_{bg}) concentrations, the unknown emissions can be estimated from the model-simulated ratio (i.e., $Q_{unknown} = (\Delta C_{downwind - C_{bg}}) / (C/Q)_{sim}$). This technique is flexible to use different types of gas sensors (e.g., LS or PS sensors). For multi-source measurements, the minimum requirement is that the number of gas sensors (n) needs to be equal or greater than the number of emission sources (m) (i.e., $n \geq m$) (Crenna et al., 2008; Flesch et al., 2009). In this study, ten gas sensors (i.e., seven LS + three PS sensors) were used to estimate N₂O emissions from four sources (T1-4). Consequently, the source-sensor equations were over-determined (Flesch et al., 2009). Since the scanning OP-FTIR took thirty minutes (30-min) to complete ‘one scanning cycle’ to measure N₂O concentrations from four treatments, all

of the measured parameters (LS and PS concentrations, turbulent statistics, air temperature and humidity) were averaged at 30-min interval to calculate the 30-min N_2O emissions. Assumptions required for the field measurements included that the averaged quantities of the environmental variables were (1) invariant within thirty minutes (stationary) and (2) invariant under a spatial translation (homogeneous). (3) Sources for N_2O production was predominately from the NH_3 fertilizer over measurement periods after N applications. The N sources from (a)biotic N fixation, (in)organic N residues (i.e., soil organic matter, or 2:1 clay minerals), and the atmospheric N deposition (i.e., NH_3) were neglected.

5.3.3.1 Inherent model errors

The bLS technique is based upon the Monin-Obukhov (MO) similarity theory (MOST). The MOST theory can describe statistical properties of a wind field in a surface layer using friction velocity (u^*), MO length (L), and surface roughness length (z_0). The MOST theory, however, becomes inaccurate in conditions of low winds and extremely unstable or stable atmosphere. The estimated emissions were excluded when $u^* < 0.15 \text{ m s}^{-1}$ and $|L| < 5 \text{ m}$. In bLS model, 10% of the field covered by ‘touchdown’ particles ($\text{TDF} > 0.1$) was the minimum requirement for quality assurance of the inferred emissions. In addition to these criteria, the modeled background concentration (C_{bg}) was also applied to investigate the model performance as well as emission estimations. One of the purposes of PS sensors was to detect the upwind background concentration of N_2O , and the minimum concentration ($\text{N}_2\text{O}_{\text{min}}$) obtained from one of three PS sensors ideally represented the background concentration. The $\text{N}_2\text{O}_{\text{min}}$ occasionally occurred from one of seven LS sensors, meaning that PS sensors detected high N_2O concentrations emitted from the outside sources. Theoretically, the $\text{N}_2\text{O}_{\text{min}}$ equals the C_{bg} inferred by the simultaneous solution of gas concentrations (*Eq. 5* in Chapter 4). Based on the sensitivity of the OP-FTIR measurements of N_2O (i.e., $\sigma = 1.8 \text{ ppbv}$) (Chapter 3), the deviation between the $\text{N}_2\text{O}_{\text{min}}$ and C_{bg} should be within the range of $\pm 5.4 \text{ ppbv}$ (i.e., 3σ). Thus, the bLS model was considered ‘poorly-performed’ if $|\text{N}_2\text{O}_{\text{min}} - C_{\text{bg}}| > 5.4 \text{ ppbv}$, and the modeled emissions were excluded.

5.3.3.2 Advection errors

Implementing the bLS technique to estimate multi-source emissions needs to be aware of interferences from adjacent fields via advection (advection refers to the horizontal transport of the atmospheric properties, such as heat or matter, in meteorology). The advective interference led to both biases and uncertainties in emission estimations. For instance, high emission rates from upwind fields tended to carry air parcels (an air parcel refers to a body of air which thermodynamic properties were approximately uniform) with high concentrations over downwind fields with low emission rates. This mass advection led to substantial biases in emission measurements of downwind fields. The minimum detection limit (MDL) of this scanning OP system for emission measurements was approximately $\pm 1.2 \mu\text{g m}^{-2} \text{s}^{-1}$ (i.e., 3σ) (Chapter 4). Since N_2O sinks were unlikely in N-enriched soils after NH_3 applications, the estimated emission rates less than the MDL of $-1.2 \mu\text{g m}^{-2} \text{s}^{-1}$ were considered as results of the advection-induced biases and excluded (Chapter 4).

Gas sensors in fields not only detect air parcels from a treatment of interest but also from adjacent treatments via advection, resulting in emission uncertainties. These advection-induced uncertainties in emissions were estimated by introducing uncertainties of N_2O concentrations measured by OP-FTIR ($\text{N}_2\text{O} \pm 1.8 \text{ ppbv}$) into the bLS model, shown in Chapter 4. For multiple source measurements, enough sensors are required for upwind and downwind concentration measurements. Lack of gas sensors increased uncertainties in emission estimations (Crenna et al., 2008; Flesch et al., 2009). For instance, eight LS coupled with four PS sensors were considered adequate and as an ideal scanning system in this study. Only seven LS and three PS sensors were used in 2015 and 2016 (and six LS and three PS sensors in 2014 shown in Table 5.1). The ideal scanning system minimized emission uncertainties compared to the real scanning system ($\sigma_{\text{ideal}} \leq \sigma_{\text{real}}$) in the same environment (e.g., the same wind velocity, direction, turbulent statistics, ambient temperature, and pressure). Thus, σ_{ideal} was used as a baseline to examine the real scanning system. The estimated emissions were excluded if σ_{real} is 50% greater than σ_{ideal} (i.e., $\frac{\sigma_{\text{real}} - \sigma_{\text{ideal}}}{\sigma_{\text{ideal}}} > 0.5$).

Also, more fields interfering with the field of interest increased emission uncertainties. For instance, the uncertainty increased by orders of two or more if interferences from three adjacent

fields (TDFs of interest < 0.5) (e.g., Figure 4.6 in Chapter 4). Thus, the estimated emissions were excluded if the uncertainties measured from the real scanning system were greater than 50% of the emission rates ($\frac{\sigma_{real}}{Q} > 0.5$).

5.3.4 Static chamber measurements

Soil N_2O emissions were also measured by the static vented chamber. Daily emissions of N_2O were measured from 06 to 20 Jun. 2014, 08 May to 29 Jun. 2015, and from 06 Jun. to 10 Aug. 2016 for a total of 6, 17, and 13 measurement days, respectively (Supplementary Table 5.2). Each chamber consisted of an aluminum anchor (0.74 m x 0.35 m x 0.12 m) driven into the soil to approximately 0.10 m depth. During sampling, a lid covered an anchor to make up a chamber with an approximate volume of 32.4 L. The anchors were positioned across rows to capture gas emissions from rows and inter-row areas. Three replicate chamber sets were equally deployed along the LS path in each treatment (Figure 5.1) and across the control plots (i.e., NT and ChP practices with zero N input). Gas sample collections were conducted between 11:30 and 14:00 (local time, LT). Gas samples were collected from the chamber headspace through a sampling port consisted of rubber septa using a gas-tight polypropylene syringe (~25 mL) at intervals of 0, 10, 20, and 30 minutes after chamber deployment. The collected gas samples were transferred into the pre-evacuated Labco Exetainer vials (~12 mL). Gas samples were injected into a gas chromatograph (GC, Varian 3800) using an automatic Combi-Pal injection system (Varian Mississauga, Canada). The injected gases were delivered by Argon (95%) carrier gas through a 3.05m-long Porapak Q column. An electron capture detector set at 350 °C was used to determine N_2O concentrations collected from different timing (i.e., 0-30 min). Ideally, multiple standard gases covering the range of N_2O concentrations collected from chambers (e.g., 0 – 2,000 ppbv) are required to build a standard calibration curve. A single standard N_2O gas with the concentration of 1430 ppbv was used to calibrate the GC for determining N_2O concentrations in this study. The standard gas was regularly injected in the GC (once every 12-16 samples) to assure the stability of the instrument. Emission measurements were calculated using the following equation:

$$F_{N_2O} = \frac{\Delta C}{\Delta t} \times \frac{V}{A} \quad [1]$$

, where $\Delta C/\Delta t$ is the gradient of the changed concentration with time, V is the volume of a chamber (~32.4 L), and A is the surface area covered by the chamber (~0.26 m²).

5.3.5 Data transformation and statistical analysis

The simulation of OP- and chamber-measured emission distributions during a given season were evaluated using the Chi-square Goodness-of-fit test, following the equation of:

$$\chi^2 = \sum_{i=1}^k \frac{(o_i - e_i)^2}{e_i} \quad [2]$$

, where o_i is the observed frequencies, e_i is the expected frequencies, and k is the number of class intervals (categories). The calculated χ^2 was compared with $\chi^2_{(\alpha, \nu)}$ table with the desired level ($\alpha = 0.05$) and the degree of freedom ($\nu = k - 1 - p$) for testing the hypothesis (the null hypothesis, H_0 , means that there is no significant difference between o_i and e_i). Two extra degrees of freedom were lost (p) because two parameters from the estimated data set were used to fit the distribution (e.g., mean and standard deviation were used for fitting normal distribution).

A square-root transformation was applied to transform the data to improve the normality of the N_2O emissions estimated from the OP and chamber methods. Since emission rates less than the OP method minimum detection limit ($MDL = 1.2 \mu g m^{-2} s^{-1}$, 3σ) possibly resulted in negative emissions (i.e., $-1.2 \mu g m^{-2} s^{-1}$), the entire data set were shifted by adding extra $1.2 \mu g m^{-2} s^{-1}$ and converted to hourly average (i.e., $\mu g m^{-2} hr^{-1}$) before the square-root transformation. The transformed data were statistically analyzed by ANOVA procedures, and the transformed means were compared using Tukey significant difference test ($\alpha=0.05$) in OriginPro 8 (OriginLab, Massachusetts, USA).

5.3.6 Daily emissions and cumulative N_2O -N loss

For multi-source emissions measurements, a great number of data were filtered using the scanning OP method. The remained data were sporadic. Treatments with high emission rates likely had higher data density than treatments with low emissions (e.g., T1 vs. T2). These episodic data points (30-min averages) resulted in inconsistent intervals of the daily averaged emissions (DAE). Thus, emissions measured from each treatment were averaged to calculate representative daily emissions over the measurement period in order to compare emission rates among treatments.

The mean value usually represented the entire population as a given normal-distributed data set. The measured emissions were transformed to meet the normal-distribution requirement for statistical comparisons among treatments. To ‘back-transform’ these mean emission, however, would not represent the actual populations. The mean value calculated from non-normally distributed data set was likely driven by the skewed tails of the population (e.g., OP-measured emissions followed gamma (γ) distribution). Therefore, the three ‘means’ were investigated to calculate the DAE in this study by averaging emissions measured from 1) the measurement period (Mean_{All}), 2) the interquartile range ($\text{IQR} = 25\% - 75\%$) (Mean_{IQR}), and 3) the mode range of the population ($\text{Mean}_{\text{mode}}$).

The emission rates measured from the OP and chamber methods were integrated to estimate the DAE, so the measurement periods of these two methods were aligned. For instance, emissions measurements were from 30 Apr. – 12 Jun. using the OP method and 08 May – 29 Jun. using the chamber method in 2015. Only the period of 08 May – 11 Jun. was used to calculate the DAE of both methods. Because the OP method is limited to measure emissions in low wind conditions (mostly nighttime), the OP-measured emissions at the interval of 6:00-21:00 (LT) were used to calculate the daytime averaged emissions, and the chamber-measured emissions were used to calculate the nighttime averaged emissions from 21:00-6:00 (LT). The DAE was calculated by integrating daytime and nighttime averaged emissions. Then, the DAE multiplied by the measurement days to estimate the cumulative N_2O -N loss over the measurement period.

5.3.7 Grain yield, nitrogen uptake, and use efficiency

The entire plant aboveground biomass was sampled for yield and N uptake measurements from the field of interest and control plots (zero N application) at physiological maturity. For each treatment, ten plants were sampled from the third or fourth row in the sampled area of approximately 1.2 m^2 , and three areas (replicates) were collected to represent the entire field. Ears were air-dried and shelled, and components (grains, cobs, and stover) further dried at 65°C to a constant weight to obtain dry yields. Subsamples of the plant components were ground for analyzing total N content (%) in a commercial laboratory (A&L Great Lakes Laboratories, Fort Wayne, IN). Dry yield and N content (%) were used to calculate grain N uptake (GNU, kg ha^{-1}) and total plant (grain + cob + stover) N uptake (TNU, kg ha^{-1}). Grain yield (GY, Mg ha^{-1}) was

adjusted from dry yields assuming 155 g kg⁻¹ moisture content. Nitrogen use efficiency (NUE), N recovery efficiency (NRE), and surplus N (SN) were calculated as:

$$NUE(kg\ kg^{-1}) = \frac{GY_{treatment} - GY_{control}}{\Delta N_{applied}} \quad [3]$$

$$NRE(\%) = \frac{TNU_{treatment} - TNU_{control}}{\Delta N_{applied}} \times 100\% \quad [4]$$

$$SN(kg\ kg^{-1}) = N_{rate} - TNU \quad [5]$$

, where $GY_{treatment}$ and $GY_{control}$ (or $TNU_{treatment}$ and $TNU_{control}$) are GY (or TNU) for different treatments (T1-T4) and control plots (zero N input for NT and ChP practices), respectively. $\Delta N_{applied}$ is the difference in NH₃-N applied between treatments and controls, which is 220 kg NH₃-N ha⁻¹; N_{rate} is the applied N rate (kg N ha⁻¹)

5.4 Results and Discussion

5.4.1 Data filtering

The sampling frequency of the OP emissions measurement was 30-min intervals, so a total of forty-eight samples could be collected for each treatment every day. For instance, 2,016 half-hour emission values (48 x 42 days) were ideally acquired for each treatment throughout 01 May – 11 Jun. 2015. The scanning OP-FTIR did not operate during intermittent rain events and field operations (e.g., herbicide spraying). Also, OP-FTIR was incapable of measuring concentrations from low-quality spectra resulting from the out-of-alignment led by strong wind-induced vibration, the dusty wind-blown events, and mostly condensation (often occurred during at night or early morning) on the spectrometer or retro-reflector. As a result, 691 half-hour emission estimations (approximate 34%) were available to assess treatment effects on emissions in 2015 (Table 5.2).

The half-hour estimated emissions were excluded during $u^* < 0.15\ m\ s^{-1}$, $|L| < 5\ m$ (the MOST theory failed), $TDF < 0.1$, and $|N_2O_{min} - C_{bg}| > 5.4\ ppbv$. Nearly 49% of total collected half-hour emissions ($n = 691$) were remained for each treatment (error-1 shown in Table 5.2). Most of the excluded emissions were collected during the nighttime (i.e., 20:00 – 06:00, LT) which was frequently under conditions of low winds ($u^* < 0.15\ m\ s^{-1}$) and stable atmosphere ($L < 5\ m$).

Air parcels carrying high N₂O concentrations can be transported horizontally via advection and lead to biases in emissions estimations of adjacent fields (error-2 shown in Table 5.2). Additional 75 and 118 half-hour periods of estimated emissions were less than MDL ($-1.2 \mu\text{g m}^{-2} \text{s}^{-1}$) and excluded from analysis for the T2 and T4 treatments, respectively (Table 5.2). For the T1 and T3 measurements, only 17 and 24 half-hour emissions were excluded. In 2015, the T1 treatment (upwind) emissions substantially interfered with emission estimations for T4 treatment (downwind) because the prevailing wind was from the SSW (Chapter 4). The T1 emissions also interfered with the T2 emission estimations when the wind drifted from 180° to 270° . Although emissions estimations of the T3 treatment was interfered by emissions from three adjacent fields (T1, T2, T4), most of the emissions from T3 were measurable ($> \text{MDL}$). Emission rates from the T2 and T4 treatments were lower than the T1 and T3 treatments.

Uncertainties in emissions measurements led by advective interferences increased if the number of sensors was inadequate (error-3 shown in Table 5.2). An additional 71 half-hour emissions were excluded from the T1 measurement if uncertainties measured from the ‘real’ scanning system (σ_{real}) were 50% greater than uncertainties from the ‘ideal’ scanning system (σ_{ideal}). Only an extra 16 and 15 half-hour emissions were excluded from the T2 and T4 measurements, respectively (Table 5.2). The 2015 configuration did not have N₂O concentration measurements at the S of the field or between the T1 and T4 plots. Two sensors (LS and PS) were absent for the T1 emission estimations. Only one sensor was missing for estimating emissions from the T2 and T4 (Figure 5.1). For T3 measurements, none of the estimated half-hour emissions were excluded because T3 received good upwind-downwind sensor deployment (LS-4, -5, -6 and PS sensors at the E and N sides).

The advection-induced uncertainties also increased with increasing interferences (error-4 shown in Table 5.2). The range of σ_{real} was from 0.1 to $2.0 \mu\text{g m}^{-2} \text{s}^{-1}$ with changing wind conditions (Figure 4.6 in Chapter 4). A field of interest which received a clean upwind background resulted in low uncertainties in emissions measurements (i.e., $\sigma_{\text{real}} < 0.5 \mu\text{g m}^{-2} \text{s}^{-1}$). For instance, the T1 emission estimations were advantaged by the prevalent (70%) SSW wind during measurements in 2015. An additional 68 half-hour emissions were excluded from the T1 measurements based on the threshold of $(\sigma_{\text{real}}/Q) > 0.5$ (Table 5.2). For T3 measurements, an additional 119 half-

hour emissions were excluded. Fields with lower emission rates were more vulnerable to these uncertainties. An additional 128 and 107 half-hour emissions were excluded from T2 and T4 plots, respectively, because of their relatively low emission rates.

5.4.2 N₂O emissions (OP vs. Chambers)

A general comparison between years showed that the OP-measured N₂O emission rates averaged across treatments were $2.1 \pm 1.9 \mu\text{g m}^{-2} \text{s}^{-1}$ ($n = 431$), $2.7 \pm 2.9 \mu\text{g m}^{-2} \text{s}^{-1}$ ($n = 635$), and $1.5 \pm 1.6 \mu\text{g m}^{-2} \text{s}^{-1}$ ($n = 306$) from 2014, 2015, and 2016 measurements, respectively (Figure 5.2). The higher emission rates in 2015 than 2014 and 2016 were attributed to 1) the timing of the N-fertilizer application (Decock, 2014) and 2) the generally windy conditions (Nazaroff, 1992; Denmead and Reicosky, 2003; Redeker et al., 2015). In 2015, the spring NH₃ was applied before planting (Table 5.1). The spring pre-plant N application enriched soil N-substrates before meeting corn needs for N, and these reactive N supplies likely induced more N₂O emissions via the increased microbial activities (Drury et al., 2012; Roy et al., 2014).

Furthermore, the higher wind speed ($3.6 \pm 1.8 \text{ m s}^{-1}$, $P < 0.05$) during the measurement in 2015 tended to increase N₂O emissions relative to 2014 and 2016 (Figure 5.2). Since chamber methods were limited to consider the ‘wind-induced effect’ into account, the emission rates determined by the OP and chamber methods were ratioed to investigate the impact of the wind velocity on gas emission rates. Within the interval of 11:30-14:00 (LT), one chamber and multiple OP measurements were conducted, and the emission ratio of the OP to chamber methods ($R_{\text{OP/chamber}}$) was against the mean wind velocity (Figure 5.3). The emission ratio ($R_{\text{OP/chamber}}$) exponentially increased ($P < 0.05$) with increasing the wind velocity. The magnitude of the wind-induced emissions became substantial when the wind speed was greater than 4 m s^{-1} , and interestingly, the variances in $R_{\text{OP/chamber}}$ also increased. The increased variances in $R_{\text{OP/chamber}}$ ($> 4 \text{ m s}^{-1}$) were presumably due to different diffusive resistances between soil and the atmosphere (Chapter 3: Gas diffusion in soil, 1985; Monson and Baldocchi, 2014). Under the relatively and consistently high wind speed ($> 4 \text{ m s}^{-1}$), the lower emission rates consistently followed the high emission rate from the previous half an hour. The high wind speed tended to ‘flush out’ N₂O near the surface soils, and the flushed N₂O was slowly refilled because of the lower diffusion rate in soils (or the slow N₂O production rate).

5.4.3 Treatment comparisons

The estimated N₂O fluxes, including the OP and chamber measurements, were shifted and transformed to meet the normally distributed dataset and to statistically examine the effect of management practices on mean N₂O emissions over measurement periods. For the OP measurement, the transformed emissions were averaged either from the interval of 00:00 – 24:00 (00 – 24, LT) or 06:00 – 21:00 (06 – 21, LT) over the measurement period.

5.4.3.1 Full vs. Split nitrogen application

NT practices integrated with the full (220 kg NH₃-N ha⁻¹ in fall) and split (110 kg NH₃-N ha⁻¹ in fall and spring) N application rates were continuously conducted in the fields of T1 and T2, respectively. For the T2 treatment, the averages of the transformed OP emissions at the interval of 00 – 24 (LT) were 82±31, 75±30, and 74±27 (µg m⁻² hr⁻¹)^{0.5} in 2014, 2015, and 2016, respectively (Table 5.3). The OP measurements consistently showed that the split N rate application (T2) significantly reduced N₂O emissions ($P < 0.05$) compared with other treatments (Table 5.3). The split application with ChP also showed less mean N₂O emissions (T3 = 99±33 (µg m⁻² hr⁻¹)^{0.5}) than the full application (T4 = 113±27 (µg m⁻² hr⁻¹)^{0.5}) in 2014. The split application can avoid a considerable amount of available N substrates in soils and ideally meet crop N demands, so N₂O produced by soil microbes is likely mitigated (Burton et al., 2008; Robertson and Vitousek, 2009; Decock, 2014).

5.4.3.2 No-till vs. Chisel plow

The split N rate application under NT and ChP was continuously practiced in the fields of T2 and T3, respectively. The NT practice (T2) showed consistently lower mean N₂O emissions than the ChP practice over the years ($P < 0.05$) (Table 5.3). Chamber measurements also showed a tendency of lower N₂O emissions in the T2 plot (NT + split N rate), but statistical comparisons were weak. The reduced or zero tillage practices were reported to mitigate N₂O emissions (Jacinthe and Dick, 1997; Mosier et al., 2006; Ussiri et al., 2009; Omonode et al., 2011 and 2019). Many studies, however, showed inconsistent results of tillage effects on N₂O emissions (e.g., reduced tillage could either increase or decrease N₂O emissions) (Venterea et al., 2011; van Kessel et al., 2013; Decock, 2014). Tillage effects on N₂O reductions were influenced by different environmental variables (e.g., soil properties, climate regions, and crop management)

and considered as ‘site-preference.’ NT practice with side-dress N application had been continuously reported to reduce fertilizer-derived N_2O emissions in this experimental location (Purdue ACRE) for the entire growing seasons (Omonode et al., 2011, 2015, and 2019). The OP measurements showed that the integrated practice of NT and split N application (T2) consistently resulted in the lowest mean N_2O emissions among four treatments ($P < 0.05$) (Table 5.3).

5.4.3.3 Fall vs. Spring nitrogen application

The full N application with previous fall or current spring was consistently practiced in the fields of T1 (fall) and T4 (spring). For the spring application, the NH_3 was injected either in season (side-dress in 2014 and 2016) or before planting (pre-plant in 2015) in T4 (Table 5.1). In 2015, the OP measurement showed that the T1 plot resulted in higher N_2O emissions than T4 (spring pre-plant) ($P < 0.05$) over the measurement period (Table 5.3). The pre-plant applications (fall and spring) likely led to a higher amount of reactive N in soils and risks of N loss via nitrification and denitrification (e.g., leaching and $\text{N}_2\text{O}/\text{N}_2$ emissions) before plant uptakes (Rochette et al., 2004). In 2014 and 2016, however, T1 and T4 (spring side-dress) showed no difference in the mean transformed N_2O emission, presumably because the applied $\text{NH}_3\text{-N}$ from the previous Fall has been losing over warming soils in early spring (e.g., thawing) before starting the gas measurements on 09 Jun. 2014 and 07 Jun. 2016 (Table 5.1) (Tenuta et al., 2016).

5.4.4 Daily emissions and cumulative N_2O -N loss

The mean emissions from the entire population (Mean_{All}) were consistently higher than Mean_{IQR} over treatments (Table 5.4) because the Mean_{All} were substantially influenced by the occasionally high emissions from the tail (e.g., pulse emissions after rain events). Using Mean_{All} to calculate representative daily emissions possibly overestimated cumulative N_2O emissions from measurement periods. Although the Mean_{IQR} avoided the influence of the skewed tail on mean calculations, Mean_{IQR} somehow neglected the contribution of the low emissions (e.g., MDL of the OP method = $1.2 \mu\text{g m}^{-2} \text{s}^{-1}$, grey bars in Figure 5.2). Likewise, the Mean_{IQR} was likely overestimated without considering the low emission rates. Instead, the mean value from the mode of the population ($\text{Mean}_{\text{mode}}$) was calculated to represent the entire population for both OP (bin range = $2 \mu\text{g m}^{-2} \text{s}^{-1}$) and chamber (bin range = $0.03 \mu\text{g m}^{-2} \text{s}^{-1}$) measurements.

The integrated practice of NT and split N rate (T2) consistently resulted in the lowest cumulative N_2O -N loss among treatments over measurement periods, accounting for 3.81, 13.22, and 6.55 $\text{kg N}_2\text{O-N ha}^{-1}$ over 9, 35, and 20 days in 2014-2016, respectively (Table 5.4). The ChP practice (T3), by contrast, continuously resulted in higher cumulative N_2O -N losses (i.e., 7.07, 37.86, and 9.23 $\text{kg N}_2\text{O-N ha}^{-1}$ over the 9, 35, and 20 measurement days in 2014, 2015, and 2016, respectively, shown in Table 5.4) than NT (T2). The NT and split N practices have been reported to mitigate the fertilizer-induced N_2O -N loss (Burton et al., 2008; Robertson and Vitousek, 2009; Decock, 2014; Omonode et al., 2011, 2015, and 2019).

In 2015, the combination of the full N rate and fall application (T1) resulted in 39.41 $\text{kg N}_2\text{O-N ha}^{-1}$ loss as emissions in 35 days, but only a 6.98 $\text{kg N}_2\text{O-N ha}^{-1}$ loss in 9 days in 2014 and a 9.31 $\text{kg N}_2\text{O-N ha}^{-1}$ loss in 20 days in 2016. The 2014 and 2016 measurements began right after the side-dress NH_3 applications when the crop was approximately at V5-6 stage. The excessive N_2O -N loss from 2015 measurement (i.e., additional 32.43 $\text{kg N}_2\text{O-N ha}^{-1}$ ($39.41 - 6.98$) and 30.10 $\text{kg N}_2\text{O-N ha}^{-1}$ ($39.41 - 9.31$) emissions compared with 2014 and 2016, respectively) showed that a great amount of soil N was potentially lost via N_2O emissions before the high demand for N in maize (V5-6) (the 2015 measurement started before planting, Table 5.1) (Rochette et al., 2004; Drury et al., 2012; Roy et al., 2014). Likewise, the T3 plot in 2015 resulted in additional 30.79 and 28.63 kg ha^{-1} $\text{N}_2\text{O-N}$ losses compared with in 2014 and 2016 measurements, respectively.

5.4.5 Grain yield, nitrogen uptake, and use efficiency

Grain yield (GY), grain and total N uptake (GNU and TNU), surplus N in soils (SN), N use and recovery efficiency (NUE and NRE) among years and treatments were compared using the paired sample t-test ($\alpha = 0.05$) (Table 5.5). The mean values of GNU, TNU, and NRE averaged across treatments (T1-4) were higher in 2016 than 2015 ($P < 0.05$, Table 5.5). Omonode (2019) also reported similar results for this location based on the same N rate (urea ammonium nitrate applied at a rate of 220 kg N ha^{-1}). The increased crop performance was attributed to favorable weather conditions (e.g., the quantity and distribution rainfall in July and August) in 2016 (Omonode et al., 2019). Cumulative precipitation during 01 Apr. – 31 Jul. was greater in 2015 (460 mm) than 2016 (357 mm), likely resulting in N loss and lower GNU, TNU, and NRE.

The spring side-dress N application significantly increased NRE (i.e., 75% NRE averaged from T2, T3, and T4 in 2016) compared with the spring pre-plant application (i.e., 61% NRE averaged from T2, T3, and T4 in 2015) ($P < 0.05$). The averaged NRE values in both years were higher than the average from the North America maize cropping systems (55% NRE for N rates $> 150 \text{ kg N ha}^{-1}$ shown in Omonode et al., 2017). The NRE value of 75% in this study was similar to the value of 70% reported by Omonode (2019) and higher than 59% reported by Burzaco (2014) for this location for the spring N side-dress application. In-season (at V5-6) or late-split (at R1) N application practices were reported to increase NRE, attributed to a better synchrony between N supply and crop N demand than the pre-plant application (Cassman et al., 2002; Shanahan et al., 2008; Burzaco et al., 2014; Mueller et al., 2017). The side-dress practice, however, might not be the only reason for increased NRE which is also significantly influenced by the applied N rate. Omonode (2017) proposed a model showing that NRE progressively increased with reducing N rate at the low rate of $< 100 \text{ kg N ha}^{-1}$ and became leveled ($\sim 60\%$) if N rate exceeded than 150 kg N ha^{-1} . High risks of N loss via leaching or gas emissions from the fall N application could lead to an inconsistent amount of N in soils and affect NRE values.

Statistical comparisons of crop GY and other N uptake-derived parameters among treatments were stronger in 2015 than 2016. In 2015, the T1 plot (full N rate + fall application) showed significant lower GY, GNU, TNU, NUE, and NRE than the T2 plot (split N rate + fall and spring pre-plant application) ($P < 0.05$ shown in Table 5.5). The low NUE and NRE of T1 were attributed to a great loss of fall-applied NH_3 via emissions (e.g., $39.41 \text{ kg N}_2\text{O-N ha}^{-1}$ (T1) vs. $13.22 \text{ kg N}_2\text{O-N ha}^{-1}$ (T2), Table 5.4) and leaching before plant uptakes (Rochette et al., 2004). Comparisons between T1 and T2 did not show any significant difference in 2016. In 2016, the ChP practice (T3) in this study only showed higher GY and NUE than NT (T2) ($P < 0.05$). Conventional tillage (e.g., moldboard plow, strip plow, and chisel plow) have been consistently reported to increase GY relative to NT (Omonode and Vyn, 2019; Omonode et al., 2015; Pittelkow et al., 2015) probably because tilled practices provided better seed beds for early plant establishment (Gentry et al., 2013).

5.4.6 N₂O emissions vs. crop nitrogen use efficiency

Both NRE and SN were used to investigate cropping management effects on N₂O emissions (Grassini and Cassman, 2012; Omonode et al., 2017). The previous section showed that reduced NRE in 2015 possibly resulted from more N loss due to the increased precipitation. Significantly increased SN values in 2015 (averaged either across treatments or controls, Table 5.5) also inferred that more N-substrates potentially became N₂O or NO₃⁻¹ sources in 2015 than 2016. Both reduced NRE and increased SN values corresponded to the increased N₂O emission rates averaged across treatments (2015: 107±46 (μg m⁻² hr⁻¹)^{0.5} vs. 2016: 91±32 (μg m⁻² hr⁻¹)^{0.5}, P < 0.05). As previously mentioned, the spring pre-plant N application resulted in lower NRE (averaged across T2-4) than side-dress application. Reduced NRE was also corresponding to higher N₂O emission rates in 2015 (pre-plant in 2015: 96±45 (μg m⁻² hr⁻¹)^{0.5} (n = 269) vs. side-dress in 2016: 89±32 (μg m⁻² hr⁻¹)^{0.5} (n = 130), P = 0.06).

Omonode (2017) consistently showed a ‘negative’ relationship of NRE or a ‘positive’ relationship of SN to N₂O emissions based on the management focusing on N application rate or rate-by-timing combination. Comparisons among treatments in the same year, however, did not exactly show the negative correlation between NRE and N₂O. For instance, the consistently low emission rates from the management of the NT practice coupled with the split N application (T2) was not corresponding to high NRE (Table 5.3 and Table 5.5). The reduced NRE corresponding to the increased N₂O only occurred in the treatment of NT coupled with the full N rate application in fall (T1) in 2015. This inconsistent relationship between NRE and N₂O was attributed to a single N rate (220 kg N ha⁻¹) used in this study. Both NRE, N₂O and their relationship were substantially influenced by N application rates. Reduced N rate not only improved NRE but also reduced N₂O emissions (Omonode et al., 2017). Low N rates (< 150 kg N ha⁻¹), however, usually reduce grain yield. Since a recommendation range of N rate for the North America states maize systems were from 150 kg N ha⁻¹ (Minnesota) to 220 kg N ha⁻¹ (Indiana) for optimum yield, a reduced N rate practice within the 150-220 kg N ha⁻¹ range can be integrated with different management practices to increase NRE and mitigate N₂O emission simultaneously (Omonode et al., 2017).

5.4.7 Strengths and weaknesses of the open path and chamber methods

Both OP and chamber methods have their strengths and limitations for measuring gas emissions from soils (Table 5.6). In this study, the OP method showed a high potential to measure emission rates with high temporal and spatial resolutions and to compensate for the weaknesses of chamber method (e.g., low sampling frequency and small footprint) for a long-term emissions measurement. The OP method was also able to investigate the ‘wind effect’ on emission rates, measure sticky gases (e.g., NH_3), and operate semi-automatically to reduce labor intensity. This method, however, was limited to measure gas emissions in low wind conditions. For multi-source measurements, the OP method was subject to advective interferences between fields, leading to biases and uncertainties in emissions estimations. Since the OP method measured gas emissions from entire cropping systems, it is difficult to identify gas exchanges within soils, canopies, and the atmosphere.

Although it is challenging to measure dynamical N_2O emissions using static closed chamber methods, chamber measurements provide a simple concept and operation for estimating soil gas emissions. Also, chambers require no power for sample collections and can be operated in most of the weather conditions (e.g., rain events or low winds). One of the powerful advantages of chamber methods is that gas emissions can be measured in multiple plots (> 10 plots) near simultaneously (daily-wise) for treatment comparisons because these methods do not require large experimental areas. Chamber methods also provide a higher sensitivity to distinguish differences in emission rates among treatments than the OP method because the accumulated gases in the headspace provide a large increase in gas concentrations (Denmead, 2008).

Since different methods serve different purposes of studies, the weaknesses of methods could become advantages for measuring gas emissions. Small footprints of chambers, for instance, not only benefit chamber methods to measure gas emissions from multiple sources, but also the small-scale ‘hot spots’ of interest, such as different locations over terrains (e.g., slope profiles). For the small-area emissions measurements, the local information of soil (e.g., soil organic matter, temperature, moisture, N contents, and pH) and gas (isotopic ratios of N and O of N_2O) can be measured to investigate the relationship between these variables and emissions (Rochette, 2011; Yang et al., 2011; Oertel et al., 2016). Therefore, simply using one method to measure gas

emissions likely introduced unknown uncertainties into estimations due to the complexities of soils gas emissions. Emissions estimations can be improved by integrating different method strengths.

5.5 References

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Table 5.1 Nitrogen (N) and field management of 2014-2016. Four treatments (T1-4) were managed by integrating different N applications: anhydrous ammonia (AA: 220 kg NH₃-N ha⁻¹) was applied as full or split rate in different timing (i.e., fall vs. spring) and tillage practices (no-till, NT vs. chisel plow, ChP). The management for each field was: T1) full application in the fall and zero N input in the spring (F220/S0) + NT; T2) split application in the fall and spring (F110/S110) + NT; T3) F110/S110 + ChP; T4) F0/S220 + ChP in 2014 and NT in 2015 and 2016. The spring N application occurred in-season at the corn growing stage of V5-6 (side-dress) in 2014 and 2016, and before planting (pre-plant) in 2015. Numerous line-sampling (LS) sensors (six in 2014 and seven in 2015 and 2016) were used to scan T1-T4, and three point-sampling (PS) sensors were deployed at the edges of fields. The OP emissions measurements began just after AA applications.

N and field management

Treatment (ha)	N (AA) (Total = 220 NH ₃ -N kg ha ⁻¹)	Tillage	Footnotes
T1 (1.2)	F220/S0	NT	AA: Anhydrous ammonia
T2 (1.1)	F110/S110	NT	F: Fall N application
T3 (1.1)	F110/S110	ChP	S: Spring N application
			NT: No-till
			ChP: Chisel plow
T4 (1.2)	F0/S220	ChP --> NT	*Tillage practice of T4 switched from ChP to NT in Fall, 2014*

Application dates and experimental operations in each year

Year	2014	2015	2016
Applications timing			
Fall AA (prior year)	20 Nov. 2013	11 Nov. 2014	11 Nov. 2015
Planting	01 May	03 May	23 May
Spring AA	09 Jun. (side-dress)	30 Apr. (pre-plant)	03 Jun. (side-dress)
Sensor layouts & Operations			
LS sensors	LS-1 – LS-5, LS-7	LS-1 – LS-7	LS-1 – LS-7
PS sensors	E,S,W	N,E,W	N,S,W
Measurement periods (No. of samples)			
OP	9-20 Jun. (354)	30 Apr. – 12 Jun. (691)	7-26 Jun. (537)
Chamber	6-20 Jun. (6)	8 May – 29 Jun. (17)	6 Jun. – 10 Aug. (13)

Table 5.2 Stepwise criteria for data filtering in the open path multiple flux measurements. The total of 691 samples collected from each treatment (T1-T4) in 2015 was used as an example.

2015 Open Path Measurements				
Treatments	T1	T2	T3	T4
Total Samples	691	691	691	691
Criteria	No. of samples remaining			
Er1	339	339	339	339
Er1+Er2	322	264	315	221
Er1+Er2+Er3	251	248	315	206
Er1+Er2+Er3+Er4	183	120	196	99

Er1: Error1 – Inherent model errors

Er2: Error2 – Advection-induced biases

Er3: Error3 – Inadequate-sensors-induced uncertainties

Er4: Error4 – Advection-induced uncertainties

Table 5.3 Effects of N and field management on N₂O emissions in 2014-2016. The estimated fluxes were equally shifted, converted, and transformed to statistically compare the magnitude of N₂O emission rates among treatments. The estimated flux was shifted by adding 1.2 $\mu\text{g m}^{-2} \text{s}^{-1}$ to avoid the negative data. The shifted data were converted to hourly fluxes ($\mu\text{g m}^{-2} \text{hr}^{-1}$). The converted data were transformed by square-root to improve the population normality. For each treatment, the transformed data were analyzed by ANOVA procedures, and the Tukey analysis was used to compare the means of the transformed emission among treatments ($\alpha=0.05$).

Methods		2014 (Jun. 9-19 th)				2015 (Apr. 30 th – Jun. 12 th)				2016 (Jun. 7-27 th)			
		T1	T2	T3	T4	T1	T2	T3	T4	T1	T2	T3	T4
		Square root of the shifted N ₂ O, ($\mu\text{g m}^{-2} \text{hr}^{-1}$) ^{0.5}											
Open Path													
00 – 24, LT	N	148	122	78	83	197	130	204	104	100	48	60	98
	Mean	112(±28)	82(±31)	99(±33)	113(±27)	127(±41)	75(±30)	124(±37)	71(±41)	92(±28)	74(±27)	93(±35)	92(±31)
	Tukey	a	b	c	a	a	b	a	b	a	b	a	a
06 – 21, LT	N	124	106	66	66	172	108	165	92	80	41	53	87
	Mean	115(±28)	86(±31)	102(±33)	117(±28)	129(±42)	75(±30)	126(±38)	69(±38)	93(±31)	74(±27)	96(±35)	93(±30)
	Tukey	a	b	c	a	a	b	a	b	a	b	a	a
Chamber													
	N	12	12	12	12	38	38	39	39	21	20	20	20
	Mean	21(±3)	20(±3)	21(±1)	21(±3)	13(±3)	11(±1)	14(±3)	13(±3)	20(±10)	17(±8)	24(±10)	24(±10)
	Tukey	a	a	a	a	abc	ac	b	c	a	a	a	a

Table 5.4 For 2014-2016 measurements, the collected N₂O emissions at the interval of 6:00-21:00 (LT) were averaged over 1) the entire population (Mean_{All}), 2) the interquartile range of the population (Mean_{IQR}), and 3) the mode of the population (Mean_{Mode}) categorized by the bin range of 2 µg m⁻² s⁻¹ and 0.03 µg m⁻² s⁻¹ for the OP- and chamber-measured emissions, respectively. The OP measurements represented daytime emissions (6:00-21:00, LT) and chamber measurements represented nighttime emissions (21:00-6:00, LT). The daily representative emission rate was calculated by integrating the daytime and nighttime emissions (based on the Mean_{Mode}), and the cumulative N₂O-N loss was calculated by multiplying the daily representative emission and the measurement days.

Mean N₂O emissions during measurement periods

Methods	2014				2015				2016			
	June 10 th – 18 th (9 days)				May 8 th - June 11 th (35 days)				June 7 th – 26 th (20 days)			
	T1	T2	T3	T4	T1	T2	T3	T4	T1	T2	T3	T4
OP (06 – 21, LT)	N ₂ O _{mean} (mg m ⁻² hr ⁻¹)				N ₂ O _{mean} (mg m ⁻² hr ⁻¹)				N ₂ O _{mean} (mg m ⁻² hr ⁻¹)			
All	10.78	4.34	8.80	12.68	13.22	2.90	13.70	2.88	5.98	2.52	6.92	6.06
IQR	9.29	4.12	7.50	11.46	11.58	3.04	10.70	1.82	5.36	2.28	5.26	6.08
Mode	7.40	3.94	7.50	10.94	10.98	3.64	10.52	-2.58	4.50	3.14	4.40	4.42
Chamber												
All	0.46	0.40	0.44	0.44	0.16	0.14	0.20	0.16	0.50	0.34	0.66	0.70
IQR	0.46	0.42	0.42	0.44	0.16	0.14	0.20	0.16	0.32	0.26	0.40	0.48
Mode	0.44	0.44	0.44	0.54	0.16	0.14	0.18	0.14	0.16	0.16	0.26	0.34

Cumulative N₂O-N estimations by integrating the open path (daytime) and chamber (nighttime) methods

N ₂ O-N (kg ha ⁻¹)	6.98	3.81	7.07	10.28	39.41	13.22	37.86	-	9.31	6.55	9.23	9.35
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Table 5.5 Management effects on means of crop variables including grain yield (GY), grain N uptake (GNU), total plant N uptake (TNU), surplus N (SN), N use efficiency (NUE), and N recovery efficiency (%NRE) in 2015 and 2016. For each treatment, the crop data were compared using the paired sample t-test ($\alpha = 0.05$).

Treatments		2015						2016					
		GY	GNU	TNU	SN	NUE	NRE	GY	GNU	TNU	SN	NUE	NRE
		Treatment means											
		Mg ha ⁻¹	——	kg ha ⁻¹	——	kg kg ⁻¹	%	Mg ha ⁻¹	——	kg ha ⁻¹	——	kg kg ⁻¹	%
T1: NT+F220/S0		9.8	87.8	164.3	55.7	26.5	38.1	13.5	135.2	251.3	-31.3	41.7	68.7
T2: NT+F110/S110		12.1	114.8	202.1	17.9	36.9	55.3	12.8	136.0	253.4	-33.4	38.6	69.6
T3: ChP+F110/S110		13.9	142.9	235.7	-15.7	42.0	67.8	15.0	156.9	288.3	-68.3	30.1	72.0
T4: NT+F0/S220		11.8	114.2	211.5	8.5	35.3	59.6	13.3	152.2	286.3	-66.3	40.6	84.6
Mean of T1 – T4		11.9	114.9	203.4	16.6	35.2	55.2	13.7	145.1	269.8	-49.8	37.7	73.7
Control (NT)		4.0	34.0	80.5	-80.5	-	-	4.4	36.5	100.2	-100.2	-	-
Control (ChP)		4.7	39.6	86.5	-86.5	-	-	8.0	62.6	129.9	-129.9	-	-
Comparisons		P value											
T1	T2	0.01	0.05	0.03	0.03	0.01	0.03	0.70	0.97	0.94	0.94	0.70	0.94
T1	T3	0.13	0.07	0.08	0.08	0.17	0.09	0.41	0.43	0.40	0.40	0.21	0.85
T1	T4	0.31	0.26	0.15	0.15	0.31	0.15	0.88	0.50	0.40	0.40	0.88	0.40
T2	T3	0.41	0.29	0.31	0.31	0.59	0.38	0.00	0.11	0.22	0.22	0.01	0.82
T2	T4	0.84	0.98	0.73	0.73	0.84	0.73	0.39	0.22	0.26	0.26	0.39	0.26
T3	T4	0.13	0.00	0.00	0.00	0.23	0.01	0.06	0.34	0.71	0.71	0.04	0.03
Control (NT vs. ChP)		0.60	0.48	0.69	0.69	-	-	0.06	0.10	0.18	0.18	-	-

Table 5.6 Strengths and limitations of the scanning open path (OP-FTIR + bLS) and the vented static closed chamber methods for multi-source N₂O emissions measurements.

Features	Open path	Chamber
Concept and operation	Complex	Simple
Cost	High	Low
Power	Yes	No
Footprint	1-3 ha	< 1 m ²
Sampling frequency	< 30 minutes	1-2 times a week
Wind and turbulence effect	Yes	No
Advective interferences	Yes	No
Measurements in Low winds	No	Yes
Local information (soil and N ₂ O)	No	Yes
Gas fluxes sensitivity	μg m ² s ⁻¹	ng m ² s ⁻¹
Emission sources	Soils and canopies	Soils
Treatment comparisons	Few (< 5)	Many (> 10)
Multiple gases	Yes (including NH ₃)	Yes (no NH ₃)
Labor intensity	Low	High

References: Denmead (2008); Rochette (2008 and 2011); Davidson et al. (2002); Yang et al. (2011)

Supplementary Table 5.1 The basic soil information and the Illinois soil nitrogen test (ISNT) test of four treatments (T1-T4) in the experimental site (Purdue ACRE).

Treatment	OM (%)	pH	CEC (cmol _c kg ⁻¹)	ISNT (ppm)
T1	3.9	6.0	24.4	307.7
T2	3.5	6.3	21.0	261.0
T3	3.5	6.5	21.7	N/A
T4	3.3	6.9	21.8	N/A
Control(NT)	2.2	6.2	13.5	162.9
Control(ChP)	N/A	N/A	N/A	N/A

Soil OM, pH, and CEC analyses

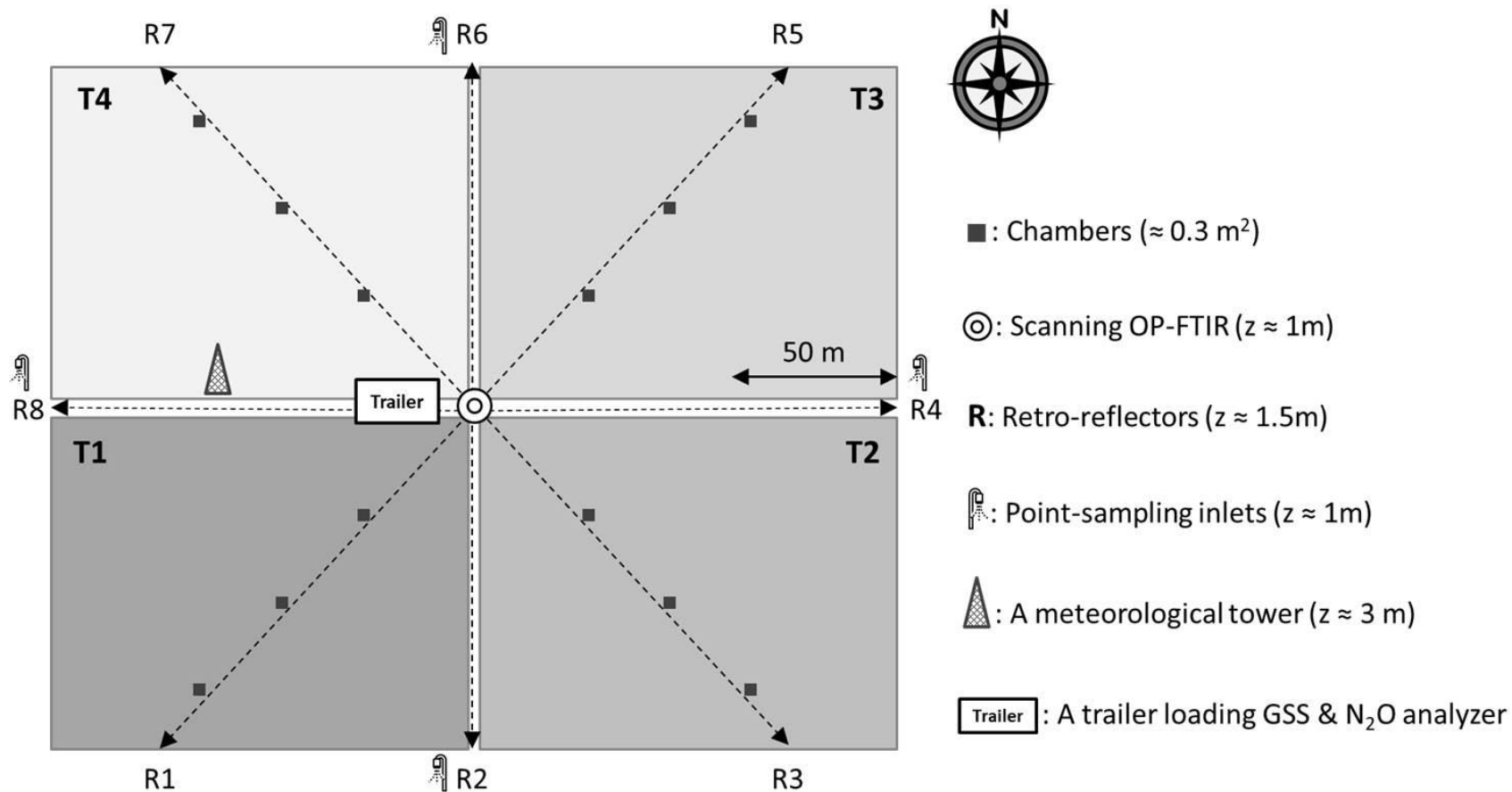
T1-T4: Samples were collected twice in 2017

Control(NT): Samples were collected twice in 2018

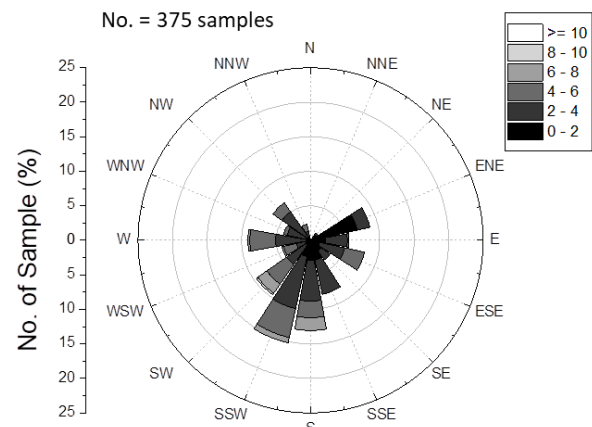
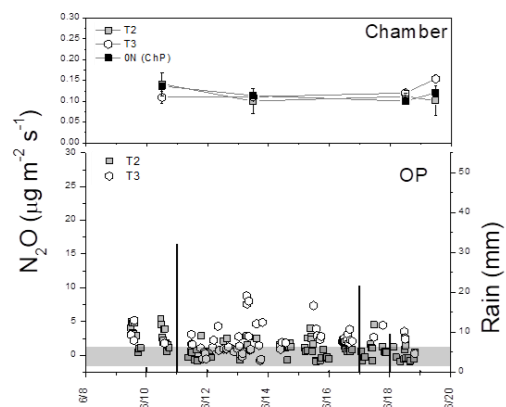
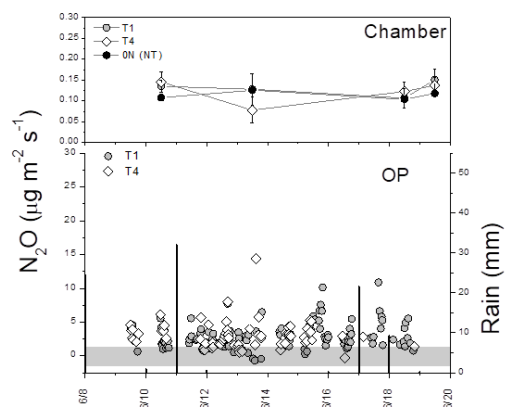
ISNT analysis: Samples were collected twice in 2018

Supplementary Table 5.2 Dates of gas samplings using chamber methods.

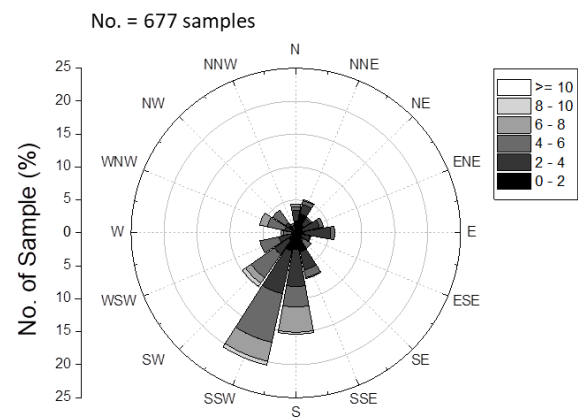
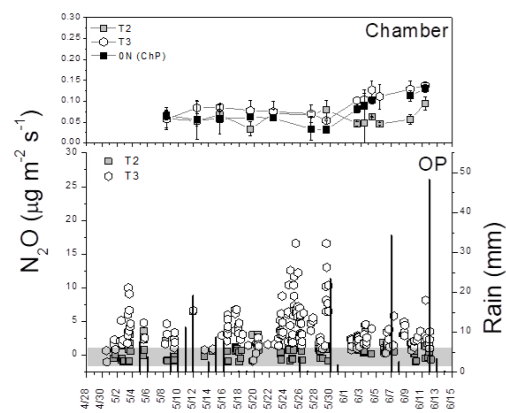
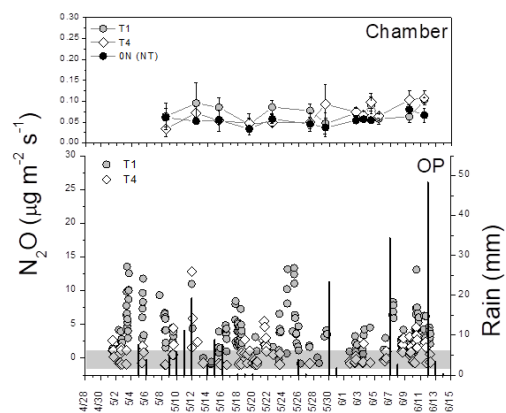
Year	Chamber measurement dates				Sample (No.)
	May	Jun.	Jul.	Aug.	
2014	N/A	6, 10, 13, 18, 19, 20	N/A	N/A	6
2015	8, 12, 15, 19, 22, 27, 29	2, 3, 4, 5, 9, 11, 16, 22, 25, 29	N/A	N/A	17
2016	N/A	6, 10, 14, 17, 20, 24, 28	1, 5, 7, 14, 21	10	13



(a) 2014 measurements



(b) 2015 measurements



(c) 2016 measurements

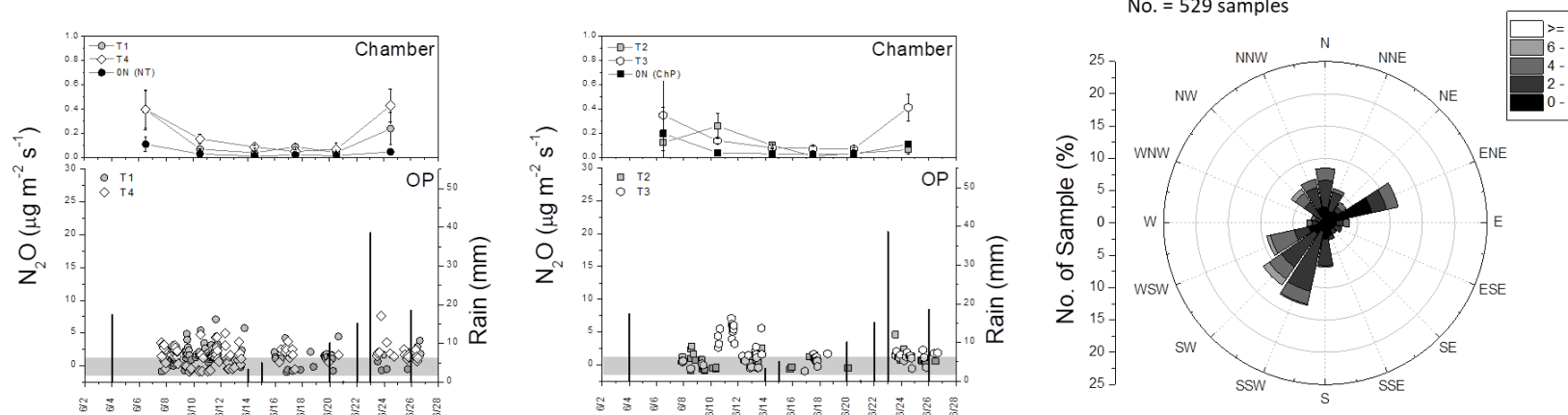


Figure 5.2 Measurements of N_2O emissions estimated by the static chamber and open path (OP) methods, precipitation (mm), and general wind information (direction and velocity) in (a) 2014, (b) 2015, and (c) 2016. The OP N_2O emissions were cleaned by the stepwise criteria of error-1 – error-4.

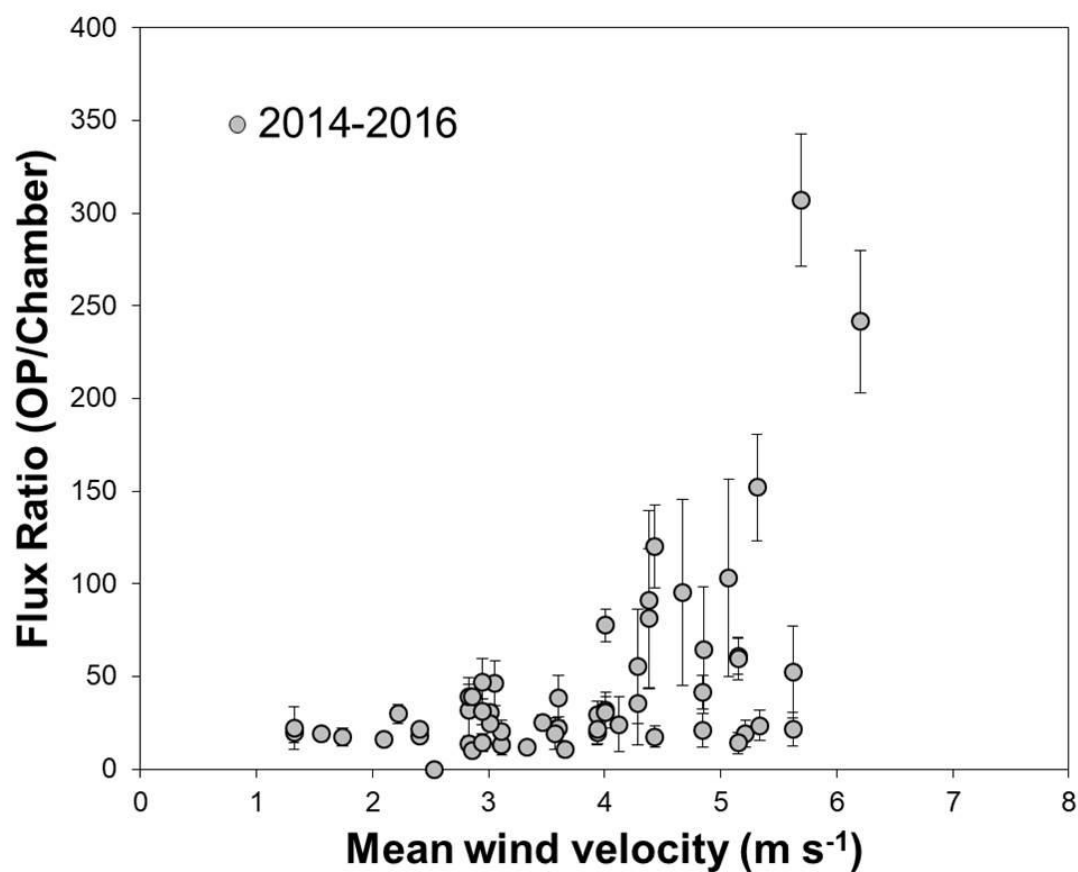


Figure 5.3 The effect of the increased wind speed on N₂O emission rates. N₂O emissions were estimated by the OP and chamber methods within 11:30-14:00 (local time) from 2014-16 measurements. The emission ratios of the OP to chamber measurements ($R_{OP/chamber}$) were against the mean wind velocity.

CHAPTER 6. CONCLUSION

6.1 Summary of Findings

Implementing the scanning open path (OP) Fourier transform infrared spectrometry in the backward Lagrangian stochastic technique to measure N₂O emissions from multiple plots is a complex process. As an open system, the OP measurement is subject to interferences from environmental variables, and its quantitative methodology needs to be optimized to ensure an adequate sensitivity to distinguish N₂O fluxes from fields managed by different tillage and nitrogen (N) practices. Considering the propagation of measurement uncertainties, the process of optimization needs to start with the fundamental measurement of gas concentrations. Because of the complexity of the P-branch N₂O spectral features (2170.0 – 2224.0 cm⁻¹), the quantification of N₂O concentrations are more susceptible to the diurnally fluctuated ambient humidity and temperature than other greenhouse gases (e.g., CO₂). For N₂O quantification, the optimal method by integrating the synthetic single beam background, a two bands window (2188.7-2204.1 + 2215.8-2223.7 cm⁻¹), and the partial least squares regressions (Chapter 1) was capable of minimizing the interferences of ambient variables and optical path lengths. Assuming stationary conditions over 30 min, the minimum detection limit of OP-FTIR N₂O concentrations was 5.4 ppmv (MDL; 3σ). For multisource emissions measurements, gas transport via advection between adjacent fields is inevitable and interfered with emission estimations. Thus, the emissions from adjacent fields lead to substantial biases and uncertainties in flux estimations. The absence of the upwind or downwind gas sensors likely increased uncertainties in flux estimations. Generally summarizing, the MDL of the OP N₂O flux measurements was 1.2 μg m⁻² s⁻¹ (3σ). Only 15-30% of the collected data remained based on the criteria of Error 1-4. Fields with lower N₂O emission rates had a greater risk for advective interference and lost more data.

The pre-plant full-N application during the fall resulted in higher N₂O emissions than the split-N application (fall and spring). Compared with the chisel plow (ChP) tillage, the long-term no-till (NT) practice mitigated N loss via N₂O emissions as consistent with prior literature. Owing to the lack of N₂O emission measurements in the early spring, it is risky to claim that the integration of NT and the split application is the optimal management even though this

combination results in the lowest N_2O -N loss during the measurement period. The timing of N application indicates that the full N rate applied during the spring tended to have a better NRE than the fall application, presumably due to N loss via leaching or gas emissions over the winter or the early spring. The OP and chamber measurements showed the same tendencies of management effects on N_2O emissions. The OP method, however, showed a higher magnitude of emission rates for all treatments than chamber measurements, likely due to wind-induced emissions.

6.2 Future research

6.2.1 Limitations of this study

To estimate the entire amount of the fertilizer-induced N_2O -N losses, the continuous gas measurement needs to cover a longer duration (e.g., an entire growing season or ≥ 60 days) after fertilizer application. In this study, gas measurements were restricted to within 60 days of application (11-, 44-, and 21-day measurements in 2014-2016, respectively) because the fast-growing corn likely blocks the IR traveling between spectrometer and retro-reflector after N application (e.g., side-dress). The scanning FTIR was limited to a full rotation of 0-300, so the path-averaging measurement was always absent between the T1 and T4 plots. In addition, only three point-sampling inlets were used to measure background concentrations of N_2O because one inlet was used for bias corrections of the OP-FTIR, meaning that one of the N, E, S, and W of the fields had no inlet. Emissions measurements during the night were generally limited by the OP method due to mostly low wind conditions. Nocturnal emission measurements were roughly estimated using chamber methods and can be alternated by the mass accumulation method (Grant and Omonode, 2018).

6.2.2 Future improvement and needs

An adjustable height for the spectrometer and retro-reflectors are needed to adapt to the height of the canopy to extend the measurement time. The missed OP sensor can be fixed by adding more synthetic open path gas sampling systems, and adequate point-sampling inlets need to be deployed at the edge of fields to detect the background concentration of N_2O from N, E, S, and W.

To complete the N budget of the applied N fertilizers, a number of questions remain unanswered in this study. The information of N loss via leaching or gas emissions ($\text{NH}_3/\text{N}_2\text{O}/\text{N}_2$) over the winter and early spring is needed for fall applications. The other part is no estimate of N gas losses from June to the plant maturity. Even though the amount of N rate recovered by plants (NRE) and surplus N in soils (SN) roughly offers information on N fertilizer use efficiency, the proportion of the leached and emitted N are still mysteries. The missing N data may be the reason why the process of optimizing field management is difficult and ineffective (i.e., time-, labor-, cost-, and resource-consuming). Different perspectives (e.g., yield production, environmental impact, etc.) lead to different definitions of the ‘optimal’ management. Generally speaking, one of the reasons that makes the ‘optimization’ so complicated and gives rise to a lot of conflicting results regarding optimal management is the lack of efficient measurement methods. Because of the complexity and dynamic changes of N fluxes among phases (i.e., the soil, plants, water, and air), it is essential and demanded to keep developing methods to continuously and frequently measure N fluxes in a long-term period to understand the entire N budget in the agroecosystem. This scanning OP measurement is a cutting-edge method to measure N fluxes at the soil-atmospheric interface (i.e., N_2O and NH_3). The Water Quality Field Station (WQFS) could provide unique opportunities to measure N loss via leaching continuously. Integrating the OP and WQFS measurements would help understand the applied N budget further as well as optimize field and N management practices. Furthermore, integrating isotopic tracing techniques in this system to identify the microbial pathways of the input N among solid, liquid, and gas phases would be a powerful addition study in the dynamic N fluxes.

6.2.3 Implications in Agriculture

Because the scanning OP system is capable of measuring multiple gas species from different sources near simultaneously and continuously in a long-term period, this method is considered as more efficient if users want to extract the same amount of information by chamber measurements. This method also can be easily applied to capture the agricultural emissions of most greenhouse gases (i.e., CO_2 , CH_4 , and N_2O) to study the entire global warming potential contributed by agricultural activities as well as the C and N cycles in the ecosystem. From economic standpoints, this method could provide crop modelers with useful information of the emitted N from the applied fertilizers for improving yield predictions.