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NITROUS OXIDE EMISSIONS IN A LANDSCAPE TRANSITIONING TO THE ENERGY
CROPS MISCANTHUS AND SWITCHGRASS

A Dissertation in
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by

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ABSTRACT

Nitrous oxide (N\textsubscript{2}O) emissions from soils are an important component of the greenhouse gas (GHG) balance of agricultural systems. These emissions are particularly relevant when considering the transition of land under the Conservation Reserve Program (CRP) grassland to energy crop, like switchgrass and Miscanthus. The N\textsubscript{2}O fluxes are in general spatially and temporally variable, which makes field monitoring of this flux challenging. Using the infrequent chamber-based method requires knowledge of spatial and temporal inequality of N\textsubscript{2}O flux distribution. This dissertation focuses on estimating N\textsubscript{2}O flux from energy crops aforementioned in a landscape typical of Ridge and Valley region with soil and hydrologic heterogeneity.

In chapter 2, I used simulation models and statistical methods to assess the uncertainties of cumulative N\textsubscript{2}O flux estimates obtained by different temporal sampling frequencies. As a corollary of this work, a robust rule-based sampling framework was designed that provides better estimates of this flux with a lower number of sampling events than the typical fixed-interval sampling methods. The daily soil N\textsubscript{2}O flux was simulated for Ames, IA; College Station, TX; Fort Collins, CO, and Pullman, WA. A regular sampling of 4- and 8-day interval is required at College Station and Ames, respectively, to yield ±20% accuracy in the flux estimate, while a 12-day interval renders the same accuracy at Fort Collins and Pullman. The uncertainty of the annual N\textsubscript{2}O flux estimation increased with increasing interval in the fixed interval method, higher in sites with greater flux variability. The rule-based method provided the same accuracy as that
of fixed interval with 60% reduction in sampling numbers. The efficiency is higher in sites with greater flux variability.

In chapter 3, I examined the effect of land conversion from CRP to energy crops on N₂O emissions and how biogeochemical and hydrological factors control the spatial and temporal inequality of N₂O flux distribution. The experiment was located in typical Ridge and Valley landscape near the town of Leck Kill, PA. Soil N₂O flux, soil mineral nitrogen availability, and profile soil moisture were monitored in shoulder, backslope, and footslope positions under each plot during the growing season of 2013, the second year after land transition. The cumulative N₂O flux was significantly ($P = 0.009$) influenced by vegetation-by-landscape position interaction. Landscape position, nitrate nitrogen, and subsoil soil aeration ($\theta_A$) were the most important variables to influence soil N₂O emissions. The regression tree identified highest N₂O emissions occur when $\theta_A$ at 20-40 cm depth is $< 0.03 \text{ m}^3 \text{ m}^{-3}$, and when there is nitrate in the soil layer. The footslope positions under energy crops were the hot spots of N₂O emissions due to prolonged soil saturation and mineral nitrogen availability. The peak emission was triggered by a 100-mm rain event in early June, and contributed 26% of the cumulative flux. Nitrogen fertilization in switchgrass and chisel plowing during Miscanthus establishment caused 48 and 78% higher cumulative flux than the CRP, respectively. The results suggest that land transition only caused significant increase in N₂O emissions from the footslope, while the major part of the watershed is at lesser risk of large emissions.

The knowledge of hot spots and hot moments of N₂O emissions in the landscape is important for its accurate spatial and temporal monitoring, quantification of the emissions, and to minimize the adverse environmental effects of landscape management.
A novel application of the concept of inequality (Lorenz curve and Gini coefficients, G) was used to quantify the heterogeneous distribution of N\textsubscript{2}O in space and time. The G was better correlated ($R^2 = 0.71, P < 0.001, n = 16$) with daily N\textsubscript{2}O emissions than the coefficient of variation and skewness. The hot moment by 100 mm rain event caused highly heterogeneous distribution ($G = 0.70$) of N\textsubscript{2}O fluxes in the landscape; however, had little influence on inequality of soil CO\textsubscript{2} ($G = 0.39$) flux distribution among the vegetation types and landscape positions. Overall inequality of N\textsubscript{2}O flux distribution followed the trend: footslope ($G = 0.75$) > backslope ($G = 0.67$) > shoulder ($G = 0.43$).

Event-based evolution of N\textsubscript{2}O flux inequality was in accordance with the hydrologic inequality, given the biogeochemical equality prevails in the landscape. The Lorenz curve and G in association with spatial maps are useful tools to guide landscape-scale management strategies to reduce N\textsubscript{2}O emissions, as well as spatial and temporal monitoring of N\textsubscript{2}O emissions.

Based on the critical threshold of $\theta_A < 0.03 \text{ m}^3 \text{ m}^{-3}$ for N\textsubscript{2}O emissions, I did a detailed study on three dimensional depletion of $\theta_A$ during a saturating rain event in early June of 2013. This information would surrogater the movement of N\textsubscript{2}O emission front in the landscape when other conditions for emissions are satisfied. Faster $\theta_A$ depletion on June 10 was observed in fine textured soils with higher antecedent water content in the western part of the watershed, especially in the subsurface layers. The $\theta_A$ depleted faster in the subsurface layers than the surface layer. Rocky and porous southern slope shoulder and backslope positions drained fast. The drainage was faster from the surface soil layer on June 11, while it was gradual in the subsurface layers. Due to this, $\approx 50\%$ of the watershed area located mostly in the footslope and backslope positions, where a
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The findings of this dissertation improves the characterization of the variability of N$_2$O emission, the strategies to manage these fluxes using the discrete chamber-based measurement method, and provides guidance to manage the establishment of energy crops in CRP land in a typical Ridge and Valley landscape of northeastern United States and beyond.
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Chapter 1

INTRODUCTION

1.1. Background

Energy crops are a potential source of biomass for the production of renewable energy with a low carbon footprint (Tilman et al., 2006). Energy from biomass either for direct burning or a feedstock source for liquid fuel production can replace an important fraction of the energy currently coming from fossil fuels. In the United States (US), ethanol from corn (*Zea mays* L.) is the main source of liquid fuels from biomass. Because corn is used in the food production stream and is normally planted in lands with high agricultural value, there is a strong interest in shifting the production of energy from grain towards cellulosic energy crops. These cellulosic energy crops can be grown in both valuable agricultural soils and soils that are marginal for agriculture due to soil or topographic limitations (Gelfand et al., 2013). Among the crops with potential for energy production are the grasses *Miscanthus* (*Miscanthus x giganteus*) and switchgrass (*Panicum virgatum* L.). These crops can be grown in a large portion of the US, and seem particularly suitable for agricultural landscapes of the northeastern US, which comprises soils with limitations for agriculture. A large fraction (~9% of total US cropland) of these soils are currently enrolled in the Conservation Reserve Program (CRP), a program that sets aside land from agriculture and that targets environmentally sensitive areas, usually prone to erosion (Farm Service Agency, 2012). These lands seem ideal for the production
of perennial energy crops like *Miscanthus* and switchgrass. However, as explained below, the agricultural production of fuels with a low greenhouse gas footprint depends in part on the ability to minimize and quantify the soil emission of the powerful greenhouse gas, nitrous oxide (N\textsubscript{2}O).

Nitrous oxide is the third strongest long-lived greenhouse gas after carbon dioxide (CO\textsubscript{2}) and methane (CH\textsubscript{4}) (Myhre et al., 2013). The N\textsubscript{2}O global warming potential is 296 times higher than that of CO\textsubscript{2} over a 100-year time period (Forster et al., 2007). The atmospheric concentration of N\textsubscript{2}O is growing steadily, with a reported concentration in 2014 of 326.9 ± 0.1 ppb, and an increase rate of ~1 ppb yr\textsuperscript{-1} since 2010, a figure 25\% higher than the average over the previous decade (Blunden and Arndt, 2015). Increasing atmospheric concentration of N\textsubscript{2}O is responsible not only for enhanced greenhouse effect but also stratospheric ozone depletion (Ravishankara et al., 2009). Anthropogenic interferences in the nitrogen (N) cycle are mainly responsible for the increase in atmospheric N\textsubscript{2}O concentration. Globally, 40\% of the anthropogenic N\textsubscript{2}O emissions originates from agricultural soils (Denman et al., 2007), whereas in the US, it accounts for 74\% of total N\textsubscript{2}O emissions (EPA, 2010).

The emission of N\textsubscript{2}O from soils originates from several processes: denitrification, nitrification, fermentative reduction of nitrite (Firestone and Davidson, 1989; Paul and Beauchamp, 1989), and chemo-denitrification (Stevens and Laughlin, 1998). Denitrification and nitrification are the major contributors to N\textsubscript{2}O emissions (Bremner, 1997). Nitrification derived N\textsubscript{2}O emissions under aerobic conditions are considered to be <1\% of the total N involved in nitrification (e.g. Cochran et al., 1981). Accordingly,
emission factors (i.e. the proportion of a given addition of N to the soil that is lost as N₂O) from urea applications, mostly from nitrification, range from 0.2% to 0.9% depending on urea application rate and placement (Engel et al., 2009). In contrast, N₂O losses by denitrification are triggered by transient anoxic conditions in the topsoil (Rolston et al., 1978), conditions that inhibit nitrification. During denitrification, dinitrogen (N₂) losses exceed N₂O losses by a factor of 5 to 40 (Panek et al., 2000). Typically, N₂O emissions by denitrification are event-driven with emission peaks that last three to five days (Mosier et al., 1986; Castellano et al., 2010) after which, if anoxic conditions continue, N losses are mainly as N₂. Greater availability of nitrate (NO₃) under anoxic conditions tilts the emission towards N₂O instead of N₂ (Hefting et al., 2006; Gillam et al., 2008). Thus, soil moisture conditions and the availability of ammonium (NH₄) and NO₃ determine if N₂O emissions are predominantly from denitrification or nitrification. In addition, other soil and environmental factors, such as presence of degradable organic matter to promote microbial activity, soil temperature, pH, and microbial diversity and abundance have also been reported to influence N₂O emissions (e.g. Smith and Dobbie, 2001; Parkin and Kasper, 2006; Regan et al., 2011). However, these variables are not always strongly correlated with N₂O fluxes due to non-linear nature of N₂O emissions. The complex interactions between multiple factors cause high temporal and spatial dependence of soil N₂O emissions. Thus, when and where the critical ingredients converge are critical (McClain et al., 2003).

In agricultural soils, peak N₂O emissions are associated with thawing, irrigation, and rain event-based soil saturation, tillage, fertilizer-N, and manure application (Clayton
et al., 1997; Wagner-Riddle and Thurtell, 1998). These short duration discrete events or ‘hot moments’, dominate the annual flux (Parkin and Kasper, 2006). While an accurate estimation of the annual cumulative flux is critical to assess the global warming footprint of a given system (Jawson et al., 2005), the episodic nature of soil N$_2$O fluxes makes an accurate quantification challenging.

Soil N$_2$O flux is commonly measured manually by a non-steady state static chamber methods (Hutchinson and Mosier, 1981), with a sampling frequency that varies from weekly to monthly. Given the non-linearity of temporal N$_2$O flux, the accuracy of cumulative flux estimation by a temporally discontinuous infrequent sampling strategy is largely unknown. A frequent sampling of every 4-day interval estimated a cumulative flux that is ±20% of the expected flux at Ames, Iowa (Parkin, 2008). However, in designing N$_2$O sampling strategy, extrapolating this finding to a different location may have limited accuracy due to high sensitivity of temporal emission patterns to diverse soil, climate, and management practices. While optimizing sampling frequency to achieve desired estimation accuracy is critical, the lack of availability of intensively measured N$_2$O flux data makes it difficult to assess the uncertainty associated with different sampling frequencies. Simulation models that accurately predict temporal variation of N$_2$O emissions could be a useful tool to design a sampling strategy that would balance the accuracy of estimation and number of sampling events required.

Soil N$_2$O emissions also exhibit high spatial dependence with a coefficient of variation that often exceeds 100% (van Kessel et al., 1993). The spatially variable N$_2$O emissions can be characterized by ‘hot spots’, where high active spatial zones/units
disproportionately contribute to the total flux. Topographic influence on soil N$_2$O emissions has been emphasized by several authors, where wetter footslope positions were the hot spots for N$_2$O emissions (Pennock et al., 1992; Vilain et al., 2010).

This reinforces the potential risks of N$_2$O emissions during land transition from Conservation Reserve Program (CRP) grasslands to energy crops. The conversion of CRP to the perennial warm-season grass energy crops, such as switchgrass and Miscanthus, requires transitioning land use. Switchgrass and Miscanthus are low-input perennial grasses and have potential to grow in poor quality lands that are not suitable for row-crops, while providing the benefits of riparian buffer to reduce nutrient and sediment load to the stream water (Smith et al., 2014). Greater biomass production potential and deep rooting systems of these grasses have been observed to enhance soil C sequestration even after commercial harvest of the above-ground part (Follett et al., 2012), and can produce fuel with a low C footprint (Adler et al., 2007; Gelfand et al., 2013). However, if the N$_2$O emission hot spots and hot moments express strongly during the transition from CRP to energy crops, it could minimize or negate the putative greenhouse gas benefits of producing energy from these biomass sources. The risks of N$_2$O emissions could be severe during land use conversion due to biogeochemical alterations and accelerated carbon (C) and N cycling (Gelfand et al., 2011; Ruan and Robertson, 2013). To produce 1 MJ of biofuel energy, conversion from CRP to grain-based biofuel emitted seven times more greenhouse gas equivalents during the transition year alone than the emissions from fossil fuels to produce equivalent amount of energy (Gelfand et al., 2013).
In the Ridge and Valley physiography of northeastern US, the existing CRP lands are located in the complex landscape positions that are considered marginal due to seasonal wetness, steep, and rocky soils (Ciolkosz et al., 1995). The footslope soils have been reported to have slow permeable fragic layers with shallow, temporary water table, and extended periods of soil saturation are a common phenomenon during snow melt and rain storm events (Ciolkosz et al., 1995; Buda et al., 2009). Formation of biogeochemical hot spots for denitrification, especially for increased N$_2$O emissions in the footslope positions, has been reported earlier (Pennock et al., 1992; Vilain et al., 2010), but has not been studied in the Ridge and Valley region. Biogeochemical perturbation during land transition and N fertilization may accelerate soil C, N cycling and increase N$_2$O emissions, with the magnitude of these emissions potentially varying in different landscape positions due to hydrologic heterogeneity. Thus assessing the risk of N$_2$O emissions on placing energy crops in these landscapes is critical to quantify the greenhouse gas footprint of energy produced from these crops.

This dissertation addresses knowledge gaps related specifically to the N$_2$O footprint of biomass produced in former CRP land transitioning to Miscanthus and switchgrass as energy crops in the Ridge and Valley region. The dissertation focuses on four aspects of the science of quantifying and managing N$_2$O emissions: (1) frequency and strategy of measuring the fluxes of N$_2$O emissions in different systems with unique temporal variability of the N$_2$O depending on soil, climate, and management practices; (2) quantification of the N$_2$O emission in a landscape transitioning from CRP to either switchgrass or Miscanthus; (3) characterization of both the temporal and spatial
variability of the \( \text{N}_2\text{O} \) emission, and (4) characterization of the hydrological conditions that influence this temporal and spatial variability. The chapters of this dissertation address these four aspects, as summarized below.

1.2. Dissertation Structure and Research Questions

This dissertation consists of four main chapters. Chapter 2, titled “Designing efficient nitrous oxide sampling strategies in agroecosystems using simulation models”, blends simulation modeling and statistical tools to define a \( \text{N}_2\text{O} \) flux sampling strategy that yields better cumulative flux estimates, while minimizing uncertainty and sampling cost in a given location. I hypothesized that increasing sampling interval will increase the error of cumulative flux estimation; however, the magnitude of uncertainty would depend on the underlying temporal variability of soil \( \text{N}_2\text{O} \) emissions from a particular site. Thus, a given fixed-time interval sampling frequency may produce varying degrees of error in flux estimation under diverse soil, climate, and management scenarios. My second hypothesis was that a suite of daily time-step simulation model and statistical approaches would lead to construct a decision support tool to predict \( \text{N}_2\text{O} \) sampling events. This framework would produce more accurate estimation with relatively lower number of sampling events than that of the fixed-time interval sampling to achieve the same level of precision. To test these hypotheses, I used the simulation model Cycles to predict \( \text{N}_2\text{O} \) emissions, along with other biogeochemical fluxes, from contrasting agro-ecoregions in the United States. I applied two sampling strategies to the daily simulated fluxes: a fixed-time interval sampling and rule-based sampling as conditioned by the Random Forest and
regression tree-based analytical tools. The performance of these sampling strategies was assessed in terms of estimation accuracy and number of sampling events required. My research questions are: 1) How do different sampling frequencies affect the uncertainty in estimating cumulative N\textsubscript{2}O flux estimates? 2) Does the relative error of a given sampling frequency vary across soil, climate and management scenarios? 3) Is it possible to use the simulation models to build a rule-based sampling strategy for N\textsubscript{2}O sampling that is less costly than the fixed time interval sampling?

Chapter 3, “Nitrous oxide emissions during the transition from conservation reserve program to perennial grasses for bioenergy”, focuses on measuring N\textsubscript{2}O emissions during land transition from CRP grassland to the perennial energy crops switchgrass and Miscanthus. My hypothesis was that water along with mineral N from upper landscapes is transported to the lower slopes by surface runoff and subsurface water transport. This may differentially influence N\textsubscript{2}O emissions in different landscape positions. In particular, I hypothesized that prolonged water saturation in the footslope positions would potentially create biogeochemical hot spots for N\textsubscript{2}O emissions following a precipitation event. The magnitude of emissions could be severe during the transition from CRP to energy crops due to disturbance. To test this hypothesis, I measured growing season (May-September) soil N\textsubscript{2}O emissions, mineral N (NH\textsubscript{4} and NO\textsubscript{3}) availability, and sensor-based profile soil moisture dynamics in CRP and energy crops under different landscape positions during the second year (2013) of land conversion. My research questions are: 1) What is the effect of converting CRP lands to switchgrass and Miscanthus on soil N\textsubscript{2}O emissions? 2) What is the effect of N fertilization in energy
crops on N\textsubscript{2}O emissions? 3) How does landscape heterogeneity and land conversion interact to control N\textsubscript{2}O emissions?

Chapter 4 “Characterization of hot spots and hot moments of nitrous oxide emissions in a transitional bioenergy landscape” is a novel attempt to statistical characterization of spatial and temporal inequality of soil N\textsubscript{2}O emissions. This chapter is a nexus between the spatio-temporal heterogeneity of N\textsubscript{2}O flux distribution and ‘size hierarchy’ concept based on the Lorenz curve and Gini index, widely used in the field of economics and population biology. My hypothesis was that, unlike skewness as a popular measure of asymmetry, the Lorenz curve and associated Gini index would be a better analytical tool for statistical characterization and assessing the real significance of hot spot and hot moments of N\textsubscript{2}O emissions. Systems with greater inequality of N\textsubscript{2}O flux distribution in space and time will have major risks of hot spots and hot moments on overall N\textsubscript{2}O emissions from that system. Simultaneous use of Lorenz curve, Gini index, and spatial map would help us in identifying, assessing severity, and managing the hot spots and hot moments of N\textsubscript{2}O emissions. The application of the inequality concept on N\textsubscript{2}O emissions would greatly help in landscape-scale chamber-based monitoring of N\textsubscript{2}O emissions. To test these hypotheses, I applied the Lorenz curve on the spatial and temporal measured growing season N\textsubscript{2}O fluxes and estimated the Gini index to quantify the distribution inequality. The specific objectives are to: 1) provide a statistical framework for characterizing inequality of N\textsubscript{2}O emissions in response to hot spots and hot moments and 2) provide an insight on the application of the observed inequality of N\textsubscript{2}O emissions on landscape scale monitoring and management of N\textsubscript{2}O emissions
Chapter 5 discusses the depletion of soil air in the profile during a saturating rain event and its potential influence on the spatial variability of soil $\text{N}_2\text{O}$ emissions.

Chapter 6 gives an overall summary and the conclusions of my research and projects the needed future research.
References


denitrification and the partitioning of gaseous losses as affected by nitrate and

Hefting, M.M., R. Bobbink, and M.P. Janssens. 2006. Spatial variation in denitrification
and N₂O emissions in reaction to nitrate removal efficiency in an N-stressed


GRACEnet: Greenhouse gas reduction through agricultural carbon enhancement

Biogeochemical Hot spots and hot moments at the interface of terrestrial and
aquatic ecosystems. Ecosys. 6:301–312.

J. 50:344-348.

Change 2013: The Physical Science Basis, T. F. Stocker et al., Eds., Cambridge


Chapter 2

DESIGNING EFFICIENT NITROUS OXIDE SAMPLING STRATEGIES IN AGROECOSYSTEMS USING SIMULATION MODELS

ABSTRACT

Discrete chamber-based estimations of the cumulative nitrous oxide (N\textsubscript{2}O) fluxes have an unknown uncertainty. This study used the model Cycles to assess the uncertainty of cumulative flux estimates obtained with different sampling frequencies and to design sampling strategies that yield accurate N\textsubscript{2}O flux estimates with a known uncertainty level. Daily soil N\textsubscript{2}O flux was simulated for Ames, IA (corn-soybean rotation, anhydrous ammonia fertilizer injected in fall), College Station, TX (corn-vetch rotation, corn fertilized twice), Fort Collins, CO (irrigated corn, fertilized), and Pullman, WA (winter wheat, fertilized in fall and spring). These fluxes were used as surrogates of daily measurements. The flux data was sampled using either a fixed interval (ranged from 1 to 32 days) or a rule-based (decision tree-based) sampling method. Two types of rule-based regression trees were constructed using high-input (HI, including soil inorganic nitrogen) and low-input (LI, without soil inorganic nitrogen) predictor variables for N\textsubscript{2}O flux as identified by Random Forest, and were used to predict sampling events. The uncertainty of the annual N\textsubscript{2}O flux estimation increases with increasing interval in the fixed interval method. A 4- and 8-day interval sampling is required at College Station and Ames,
respectively, to yield $\pm 20\%$ accuracy in the flux estimate, while a 12-day interval renders the same accuracy at Fort Collins and Pullman. The rule-based method provided the same accuracy as that of fixed interval with 60% reduction in sampling numbers. The efficiency is higher in sites with greater flux variability. Both HI and LI rule-based methods performed identically.

2.1. INTRODUCTION

Nitrous oxide ($\text{N}_2\text{O}$), a potent greenhouse gas (GHG), is mostly emitted from agricultural soils (IPCC, 2007). This gas is produced through microbe-mediated processes, chiefly nitrification and denitrification (Firestone and Davidson, 1989). The temporal patterns of N$_2$O emission from agricultural soils are highly variable due to the episodic and transient nature of the N$_2$O emission peaks (Jacinthe and Dick, 1997; Parkin, 2008). These peak events may occur in response to rainfall, irrigation, thawing, tillage, nitrogen (N) fertilization, and organic matter addition (Clayton et al., 1997; Wagner-Riddle and Thurtell, 1998). These emission peaks can contribute about half of the growing season cumulative N$_2$O flux (Scanlon and Kiely, 2003; Parkin and Kasper, 2006; Kroon et al., 2007). The high temporal variability in N$_2$O emissions makes the estimation of cumulative flux uncertain if measurements are not frequent or continuous (Parkin, 2008). However, assessing the impact of different management practices on N$_2$O emissions requires an accurate estimation of the flux at different temporal scales.

In addition to the temporal variation, N$_2$O emissions vary spatially. Both time and space variation are regulated by a complex interaction of biophysical and biogeochemical
factors such as composition and architecture of the soil matrix, soil oxygen concentration (Smith and Dobbie, 2001), soil temperature (Parkin and Kasper, 2006), carbon and mineral-N availability (Gillam et al., 2008), and microbial community composition and abundance (Regan et al., 2011). Yearly weather can affect the variability of N₂O flux from the same soil and management practices (Dobbie et al., 1999; Burchill et al., 2014), mostly by regulating nitrate (NO₃) movement and degree of soil saturation. Since we have a limited ability to predict how biotic and abiotic factors will interact and drive the temporal and spatial variation of N₂O emissions, and most methods to measure N₂O emission monitoring provide discrete fluxes (1-h in a given day), monitoring N₂O emissions is challenging.

Soil N₂O flux is commonly measured by the inexpensive, non-steady state closed chamber method (Hutchinson and Mosier, 1981). In this method, a vented chamber is closed for half an hour to one hour and the linear increase in N₂O concentration in the headspace air is used to calculate the soil N₂O flux rate. This method is temporally discontinuous and usually applied on fixed intervals that vary from weekly to monthly sampling (Dobbie and Smith, 2003). Low frequency sampling can miss a short-lived peak in between sampling events. The underestimation of the cumulative flux can be significant if the transient peak appeared during an event like snow melt or rainstorm after N-fertilization (Butterbach-Bahl et al., 2013). Thus, sampling at regular weekly or bi-weekly intervals does not ensure an accurate estimation of cumulative N₂O flux. It also wastes samplings in periods with little N₂O emission. Furthermore, since the temporal variability of N₂O emissions is influenced by soil, climate, and agricultural management
practices (Corre et al., 1996; Venterea et al., 2012), the same fixed interval sampling may produce a varying degree of error in cumulative flux estimates in different locations or in the same location in different years, a variation that is as yet unknown.

An alternative to the low frequency chamber-based method are automated chambers (Brumme and Beese, 1992; Ambus and Robertson, 1998; Smith and Dobbie, 2001) and micrometeorological measurements-based techniques (Wagner-Riddle and Thurtell, 1998) with high temporal resolution. However, these are expensive, and have low spatial resolution which limits its use in plot-scale replicated studies or remote areas.

What is the best way to define an N₂O flux sampling strategy that minimizes uncertainty and cost in a given location? In this study I propose the use of agroecological simulation models as tools to determine the error of different sampling frequencies in estimating cumulative N₂O flux in a given location and set of management practices. Simulation models of agroecosystems typically operate on a daily or sub-daily time step, providing detailed outputs of the simulated water and N balance components in the soil-plant system for many years. As long as agroecological models satisfactorily represent the N₂O emission patterns along with other biophysical and biogeochemical processes, the results can be conceived as surrogates of high resolution daily chamber-based flux measurements. The simulation outputs can be “sampled” with different strategies and determine which ones render the lowest uncertainty and cost at a given location and management system.

I further propose that non-parametric statistical methods such as Classification and Regression Trees (CART, Breiman et al., 1984) and Random Forests (RF) (Liaw and
Wiener, 2002) could be applied to the daily simulation output to identify the important predictor variables of soil N$_2$O flux from certain soil, climate, and management practices. These variables can be used to cluster the N$_2$O fluxes (for example, the daily fluxes) into groups that can be identified by specific properties. These properties can be inverted to become rules for sampling, leading to a decision support tool for field N$_2$O sampling. This strategy is hereafter referred to as rule-based sampling.

The goal is to combine the output of simulation models with statistical methods and design a robust framework for N$_2$O sampling that is less expensive than regular fixed interval sampling. The research questions are: 1) How do different fixed interval sampling frequencies affect the uncertainty in estimating cumulative N$_2$O flux? 2) Does the relative error of a given sampling frequency vary across soil, climate and management scenarios? 3) Is it possible to use simulation models to build a decision tree based N$_2$O sampling strategy that is cost effective and accurate? To answer these questions, I simulated N$_2$O emission in four sites in the continental United States (US) with diverse soil, climate, management practices, and temporally distinct N$_2$O emission patterns, and applied the analytical framework briefly described above. The simulation model used is Cycles, an evolution of C-Farm (Kemanian and Stöckle, 2010) and CropSyst (Stöckle, 2008). The simulated N$_2$O emissions serve as surrogates of measured gas flux data.
2.2. MATERIALS AND METHODS

2.2.1. Overview of the Model Cycles

I used the Cycles agroecosystems model to simulate N\textsubscript{2}O emissions along with other hydrological and biogeochemical processes. Cycles is a process-based, multi-year, multi-crop and multi-soil layer simulation model that runs at a daily time step (with hydrology simulated with an adaptive sub-daily time step). It produces daily outputs of N\textsubscript{2}O flux along with other C, N, and H\textsubscript{2}O fluxes. Cycles has modules for crop growth based on radiation and transpiration use efficiency (Stöckle et al., 2008), modules for coupled C and N cycling (White et al., 2014), soil water infiltration and redistribution, and to calculate the effect of management practices on profile soil C and N turnover along with other processes. The inputs required to run Cycles are: i) location longitude, latitude, elevation and long-term daily weather data, ii) layer-by-layer initial soil profile (texture, organic matter, layer depth), iii) description of crop and rotation sequence, and iv) other management practices (fertilization, irrigation, residue addition, tillage, harvest). Cycles has been evaluated for wheat systems in Pendleton OR and the United Kingdom (Kemanian and Stöckle, 2010) and used in production systems sustainability assessments (Schipanski et al., 2014). Earlier validations of CropSyst (Stöckle et al., 2008) are applicable to Cycles as they share several modules.

Cycles simulates N\textsubscript{2}O flux from two biogeochemical processes: nitrification and denitrification. The amount of N\textsubscript{2}O derived from nitrification is a function of the amount of N nitrified, and the N\textsubscript{2}O fraction depends on the absolute air filled porosity. The N\textsubscript{2}O
derived from denitrification is a function of the amount of N denitrified, air filled porosity, and respiration. The total N\textsubscript{2}O flux is the sum of the N\textsubscript{2}O derived from nitrification and denitrification.

**2.2.2. Simulated Site Descriptions**

I selected four sites in the US agricultural landscape: Ames, Iowa (Midwest corn-belt); College Station, Texas (east central Texas plains); Fort Collins, Colorado (irrigated high plains), and Pullman, Washington (rainfed wheat production on the Columbia Plateau). The reasons for selecting these sites were to represent diverse soil, climate and management scenarios and for two of the sites, Ames (Parkin, 2008) and Fort Collins (Halvorson and Del Grosso, 2013), there are published records of N\textsubscript{2}O fluxes along with soil N, water, and management practices. The latter allows validating the simulated results. For College Station and Pullman, information on management and flux measurements were not available and common management practices were followed. Weather data for each location was obtained from different sources. Temperature and precipitation was downloaded from NOAA stations at each location. The dew point temperature was estimated from the minimum temperature. Solar radiation and wind speed was obtained from NASA’s Prediction of Worldwide Energy Resources (NASA/POWER; power.larc.nasa.gov). Ames has a humid continental climate with cold winter; College Station is subtropical, with mild winter and warm and hot summer with highly variable and intense rainfall events; Fort Collins is semi-arid with lower precipitation, mostly in the summer; and Pullman is semi-arid with Mediterranean
precipitation pattern (wet fall, winter and spring, and dry summer). Average weather in
the past 10 years at each location is summarized in Table 2-1. An initial soil profile
database was obtained from the National Cooperative Soil Survey, National Cooperative
Soil Characterization Database (http://ncsslabdatamart.sc.egov.usda.gov). Major soil
types and associated soil series according to USDA classification system were Canisteo
clay loam (Typic Endoaquolls) at Ames, Burleson silty clay loam (Typic Endoaquolls) at
College Station, Fort Collins clay loam (Aridic Haplustalf) at Fort Collins, and Palouse
silt loam (Ultic Haploxerolls) at Pullman. The simulated sites varied in soil organic
matter (range 20 to 45 g kg$^{-1}$) and clay content (range 170 to 400 g kg$^{-1}$) in the top 15 cm
soil layer (Table 2-2). At Ames, chisel plowed and band-fertilized, rainfed corn (Zea
mays L.) was rotated with soybean (Glycine max L.). At College Station, corn was
followed by a winter cover crop. The agroecosystem at Fort Collins was conventionally
tilled, fertilized, and irrigated continuous corn. At Pullman, the system was rainfed,
fertilized, continuous winter wheat (Triticum aestivum L.). A detailed description of soil,
climate, and management practices are given in Table 2-2.

2.2.3. Approach Overview

At each location, the model simulated the daily soil to atmosphere N$_2$O emission
rate for 16 years: 15 years of the data set (training data) were used to develop the
regression tree of N$_2$O emissions and one year of simulation data (testing data) was set
apart for validation. The regression tree was based on variables that are plausible to
monitor on a continuous basis or that can be generated with a model for a given location
and management system. These variables are temperature, precipitation, soil moisture, and mineral nitrogen content. The terminal nodes (or leaves) of the tree show the number of members and average emission rate for each group. Based on these groups, we defined ruled based sampling strategies and compared the results of “sampling” (virtual sampling) with that obtained using unsupervised, fixed interval sampling. For that purpose, we used the simulation year that was not used to develop the regression tree. Details of the methodology are as follow.

2.2.4. Fixed Interval Sampling Strategy

The fixed interval sampling strategy was based on virtually sampling daily model output of soil N₂O flux for a year at regular time intervals, ranging from 1 to 32 days. The total number of samples depends on the sampling interval. For example, an 8-day interval results in 46 samplings per year. Linear interpolation between consecutive samples and integration provided an estimated annual N₂O flux for each sampling interval. The estimate was then compared with the simulated ‘actual’ cumulative flux, obtained by sampling every day, to calculate the deviation of the estimate from the expected value. For Ames and Fort Collins, we applied the fixed interval sampling strategy on the years with published N₂O flux measurements.
2.2.5. Rule-Based Sampling Strategy

The objective of rule based sampling was to distribute the sampling events in a way that most likely captures and balances peak and background emissions. The cumulative flux estimate with this method should be closer to the ‘actual’ cumulative flux than that obtained with the fixed interval sampling, while reducing sampling frequency. Since the N$_2$O emission from soil is highly non-linear and has complex relationships with its controlling variables, I used RF, an ensemble method analyzing a multitude of decision trees, on the simulated data to identify the important variables for N$_2$O emissions at each location. These variables were used to construct a regression tree which becomes the blueprint of the rule-based sampling strategy. The trees were independently developed for each location. The steps are as follow.

2.2.5.1. Selection of Variables Important for N$_2$O Emissions

The randomForest function from the package randomForest in R statistical software (Liaw and Wiener, 2001) was used to determine the variable importance scores. The control parameters for RF were seed = 500 (set random number), ntree = 500 (number of trees), and mtry = n$^{0.5}$ (number of variables used at each split; n is the number of explanatory variables) (Strobl et al., 2009).

I applied RF on 15 years of training data set to select important variables for N$_2$O emissions at each site. To make it useful in practice, I selected variables that are plausible to be measured or generated with an automated algorithm in N$_2$O emission studies. These
variables are: Calendar day (DOY), average air temperature ($T_{avg}, \degree C$), cumulative rainfall (and irrigation) on the sampling day or the 2, 3, 4, 5, 6 or 7 preceding days ($R_1, R_2 \ldots R_7, \text{mm}$), net water inflow or the difference between precipitation and evapotranspiration for the sampling day or the 2-7 preceding days ($I_1, I_2 \ldots I_7, \text{mm}$; it assumes no runoff for simplicity), soil NO$_3$-N content in the 0-15 and 15-30 cm layer ($\text{NO}_3_{15}$ and $\text{NO}_3_{30}; \text{kg ha}^{-1}$), soil NH$_4$-N content in the 0-15 and 15-30 cm layer ($\text{NH}_4_{15}$ and $\text{NH}_4_{30}; \text{kg ha}^{-1}$), total soil inorganic N in 0-15, 15-30, and 0-30 cm layer ($\text{SIN}_{15}$, $\text{SIN}_{30}$, and $\text{SIN}_T; \text{kg ha}^{-1}$), fractional volumetric soil water content in 0-15 and 15-30 cm layer ($\theta_{15}$ and $\theta_{30}; \text{m}^3 \text{m}^{-3}$), and soil temperature in 0-15 and 15-30 cm layer ($T_{15}$ and $T_{30}; \degree C$).

Form a practical viewpoint, the soil NO$_3$ and NH$_4$ content are not always available, and there is no system deployed to remotely monitor them. To account for this reality, I used two types of rule-based sampling strategies. First, a high input rule-based (HI) sampling including the soil mineral N related variables in the decision making process, assuming that future technological advances would make soil N data readily available. Second, a low input rule-based (LI) sampling that assumes unavailability of soil mineral N data. Other than inclusion or exclusion of soil mineral N related variables, the analyses and tree building processes are the same for both HI and LI rule-based sampling. The performance of the two rule-based strategies was then compared to assess the benefits of including soil N variables in the tree on accuracy of estimation and cost effectiveness over the fixed interval sampling.
2.2.5.2. Construction of Regression Tree to Predict N\textsubscript{2}O Flux

I used \textit{rpart} package in R (\textit{seed} = 500) to build the regression tree. The algorithm performs successive binary divisions ("rules") that generate the terminal nodes, each having an average N\textsubscript{2}O flux ($\bar{x}$) and number of members ($n$). The higher the number of terminal nodes ($N$) the more complex the tree is. The total N\textsubscript{2}O flux from each terminal node ($F_i$) is calculated as:

$$F_i = n_i \times \bar{x}_i$$

where, $i$ identifies the terminal node (from 1 to $N$). The total N\textsubscript{2}O flux ($F$) from $N$ terminal nodes is calculated as:

$$F_T = \sum_{i=1}^{N} F_i$$

The proportion of flux contributed by each terminal node ($P_i$) to the $F$ is calculated as:

$$P_i = \frac{F_i}{F_T}$$

2.2.5.3. Application of the Regression Tree to Decide Sampling Events

The above constructed regression tree can be used to decide the rule-based temporal sampling strategy for a test year i.e. the year that was excluded during construction of the tree, since all the information for a given day is known (weather information and model outputs). The tree represents a set of rules or conditions imposed by different variables that influence N\textsubscript{2}O flux and these conditions might be true at
different times in the growing season. For this study, I assumed that we have resources to support 20-sampling events in a year. This is of course an arbitrary decision, but the generic question is: how do we temporally distribute any number of sampling events in a year? Using the decision tree I allocated a number of sampling events to $i^{th}$ terminal node $(T_i)$ based on its fractional contribution to the total flux $(P_i)$:

$$T_i = P_i \times 20$$ (iv)

Each day of the test year was then checked and automatically assigned to a terminal node. The number of days in a terminal node usually exceeds the number of possible samples in that node. Therefore, each day is also assigned to sampling or no sampling days based on a random process. The randomly selected days represent the days to measure N$_2$O flux in the field. The total flux under each node was calculated by multiplying the average flux of the randomly selected days and the frequency $(n)$ of that terminal node in the test year. The sum of the total fluxes by all the terminal nodes that had occurred in the test year gives the overall rule-based cumulative estimate.

It is not necessary that each terminal node in the decision tree happens in the test year. Thus, even though we had 20 sampling events available, the test year may end up using $\leq 20$ sampling events because conditions for certain terminal nodes may not have happened in the test year and the respective sampling events were not used in the estimation. This random process was iterated multiple times for the test year to obtain the N$_2$O emission estimation bias. The performance of fixed interval and rule-based sampling
was assessed based on the estimation accuracy and the required number of samples by the two methods to achieve the same estimation bias.

2.3. RESULTS

2.3.1. Cumulative Soil N₂O Emissions in the Test Years

The simulated cumulative N₂O flux differed greatly among agricultural systems in four ecoregions in the test years (Table 2-3). It was highest at Ames (3.2 kg N ha⁻¹) followed by College Station (2.9 kg N ha⁻¹), Fort Collins (1.0 kg N ha⁻¹), and Pullman (0.4 kg N ha⁻¹) in the respective test years. These values, obtained by summing the daily simulated fluxes, are considered the ‘actual’ cumulative flux at each site.

Since at Ames and Fort Collins we selected as test years these for which there were reported N₂O fluxes, I can compare our simulated estimates with measurements and judge in more depth the adequacy of the model Cycles for this task. The predicted cumulative flux at Ames in 2006 was lower than the reported 4.3 kg N ha⁻¹ but was within the 95% confidence interval of the measured cumulative flux at that location (Jerecky et al., 2008). The model accurately predicted the temporal variability of N₂O emissions at Ames until DOY 223 of 2006 (Fig. 2-1a). The width of the predicted N₂O peaks on DOY 150 and 194 in response to precipitation events were similar to that observed by Jerecky et al. (2008) and Parkin (2008). However, the model did not predict any emissions peak after DOY 210 even though three were a few large precipitation events and peak emissions were reported (Fig. 2-1a). Lack of N₂O emissions after DOY
210 was due to the exhaustion of mineral-N availability in the model due to crop uptake and earlier N losses. The corn N uptake predicted by the model on DOY 210 is in line with that reported for the Midwest (≈200 kg N ha\(^{-1}\)) (Al-Kaisi and Kwaw-Mensah, 2007). Nonetheless, there were substantial observed N\(_2\)O peaks after DOY 210 (Parkin, 2008). This occurred even though there was little mineral-N availability in the top 15-cm layer (Jerecky et al., 2008), a curious result that further emphasize the difficulty in understanding N\(_2\)O fluxes even in systems with large inputs of reactive N. Thus, while the model does not match the measurement exactly, and the measurements are not easy to explain, it does an excellent job before DOY 210.

At Fort Collins, the predicted simulated cumulative flux of 1.0 kg N\(_2\)O-N ha\(^{-1}\) in 2010 was similar to the measured cumulative flux and its temporal progression by Halvorson and Del Grosso (2013); however, the emissions were slightly underestimated immediately after fertilization (Fig. 2-1b).

There were no published data on year-round N\(_2\)O flux measurements for College Station and Pullman. Availability of high frequency measured N\(_2\)O flux along with soil and weather data would be useful in the future to validate the efficiency of the proposed rule-based sampling strategy. The temporal pattern, magnitude, and duration of peak emission events were different among the sites, and are described below.

### 2.3.2. Temporal Patterns of N\(_2\)O Emissions in the Test Years

Ames had a comparatively larger magnitude and time window of N\(_2\)O emissions with multiple peaks. Even though anhydrous-NH\(_3\) was applied in fall of 2005, the first
emission peak (25 g N ha\(^{-1}\) d\(^{-1}\)) did not express until before corn planting on DOY 100 of 2006 (Fig. 2-2a). The next emission peak emerged on DOY 150 in response to precipitation events and was larger in magnitude (111 g N ha\(^{-1}\) d\(^{-1}\)) and duration. A large precipitation event (~55 mm) on DOY 192 initiated the largest emission window (DOY 192 to 202). The emission peak occurred on DOY 194 (256 g N ha\(^{-1}\) d\(^{-1}\)). Although there were many large precipitation events after DOY 202, they were followed by two relatively small emission peaks on DOY 208 and 223 (43 g N ha\(^{-1}\) d\(^{-1}\) and 15 g N ha\(^{-1}\) d\(^{-1}\)).

At College Station, the background emission rate increased after the first N-fertilization on DOY 60 of 2010 and a few precipitation events following fertilization (Fig. 2-2b). Several small peaks (< 20 g N ha\(^{-1}\) d\(^{-1}\)) were simulated after the second N-fertilizer application on DOY 105, but the largest peak (220 g N ha\(^{-1}\) d\(^{-1}\)) appeared on DOY 136 in response to 46-mm of precipitation on DOY 135. There were multiple emission peaks from DOY 154 to 165.

At Fort Collins, emissions were triggered by N-fertilizer application on DOY 145 of 2010 and subsequent irrigation and precipitation events (Fig. 2-2c). Shortly after fertilization and a 20-mm of irrigation event on DOY 148, the largest peak emissions (41 g N ha\(^{-1}\) d\(^{-1}\)) occurred on DOY 147 and 148. The N\(_2\)O emission gradually decreased with crop growth and N-uptake. However, several small peaks (≈10 g N ha\(^{-1}\) d\(^{-1}\)) appeared between DOY 169 to 193 in response to precipitation and/or irrigation events but these peaks were never as large as the ones after N-fertilization.

With the lowest cumulative N\(_2\)O flux (Table 2-3), emissions at Pullman were low throughout the test year 2013 and never exceeded 10 g N ha\(^{-1}\) d\(^{-1}\) (Fig. 2-2d).
2.3.3. Estimation of Cumulative Flux by Fixed Interval Sampling

The cumulative N\textsubscript{2}O flux estimation based on the fixed interval sampling is shown in Figure 2-3. Increasing the interval between two sampling events increases the percent deviation from ‘actual’ cumulative flux. However, the relative deviation associated with different sampling intervals differed among the sites. At Ames, relatively frequent sampling of once every 4 days yielded a fairly accurate (±10%) cumulative flux estimate (Fig. 2-3a). It is necessary to employ an 8-day interval sampling strategy to keep the estimate within -16 to +26% of the expected flux. Further decrease in sampling frequency quickly increased the expected deviation. Similarly, at College Station, relatively high frequency sampling (i.e. 3-4 day intervals) was needed to yield an estimate within 20% of the ‘actual’ cumulative flux (Fig. 2-3b). At sampling intervals greater than 12 days, the deviation in N\textsubscript{2}O flux estimates exceeded ±100% of the expected flux. In contrast, at Fort Collins and Pullman a sampling frequency of once every 12 days can produce an estimate of cumulative flux that is ±20% of the ‘actual’ one (Fig. 2-3c and 2-3d). At these locations, decreasing the sampling intensity up to a 20 day interval yielded an estimate that is still well below ±50% of the expected value. The estimation was least sensitive to sampling frequency at Pullman (Fig. 2-3d).

As expected, the absolute bias of cumulative flux estimation increased with increasing sampling interval; however, the increasing pattern was remarkably different among sites (Fig. 2-4). The increase in the bias with increasing sampling interval was greatest at College Station and Ames followed by Fort Collins and Pullman. Although Ames and College Station yielded overall a similar pattern of bias at different sampling
intervals, College Station produced relatively greater bias than Ames at lower sampling intervals (2 to 8 days). The absolute bias at Fort Collins and Pullman remained relatively constant for sampling intervals of 2 to 4 days; however, it gradually increased at sampling intervals greater than 8 days. At Pullman, even a monthly sampling interval gave a practically insignificant absolute bias of 0.12 kg N ha\(^{-1}\), suggesting little effect of the sampling frequency on the accuracy of cumulative flux estimation (Fig. 2-4).

### 2.3.4. Estimation of Cumulative Flux by Rule-based Sampling

#### 2.3.4.1. Variables Important for N\(_2\)O Emissions

The important variables that explained the variation in N\(_2\)O flux were location specific. At Ames, RF for HI rule-based identified soil NO\(_3\)\(_{15}\), NO\(_3\)\(_{30}\), and \(\theta\)\(_{15}\) as the most important variables driving N\(_2\)O emission (Fig. 2-5a), explaining 83% of its variation. For LI rule-based method, RF identified DOY and \(\theta\) as important, explaining 71% of variability (Fig. 2-5b). At College Station, \(\theta\) and precipitation before sampling were important for HI rule-based sampling, with soil mineral N variables being of secondary importance (Fig. 2-5c). Here as well, the RF for HI rule-based model explained 83% variation in N\(_2\)O flux. The LI rule-based RF also identified the importance of \(\theta\) at College Station; however, the explanatory power of the model noticeably decreased to 55%. It was interesting that DOY, which was the least important in HI-RF, became the second most important variable in LI-RF (Fig. 2-5d). Unlike Ames and College Station, top soil layer \(\theta\) was not as important as mineral N availability for N\(_2\)O emissions as identified by
the RF for HI rule-based analysis at Fort Collins and Pullman (Fig. 2-5e and 2-5g). The RF for HI rule-based explained 99% of the variation in N₂O flux at both Fort Collins and Pullman, and NH₄₁₅, air, and soil temperature were the most important variables explaining N₂O emissions. Removing soil mineral N related variables from the model (as in LI rule-based) increased the importance of the variable DOY for all the sites, a variable that represents the time since fertilization as an important emission driver.

2.3.4.2. Regression Tree for N₂O Emissions

The complexity of the regression tree varied among sites. At Ames, the regression tree for HI rule-based sampling has 13 terminal nodes. The primary node split was NO₃₁₅ (threshold 9 kg ha⁻¹, Fig. 2-6a). Total inorganic N (SIN) and θ were also relevant variables. The highest, but less frequent mean daily N₂O flux is predicted in terminal node 13 as 189 g N ha⁻¹d⁻¹, which results from > 23% and 20% of θ₁₅ and θ₃₀, respectively, R₇ of > 29 mm, and high NO₃₁₅ ( > 36 kg ha⁻¹, Fig. 2-6a). In short, higher N₂O emissions occur in a soil that is moist, has nitrate, and receives enough water input to near saturate or saturate the top soil. On the contrary, the tree for LI rule-based sampling at Ames was even more complex (16 terminal nodes) and had a primary split between observations with T₃₀ less than or more than 13 °C (Fig. 2-6b). Consistent with the LI-RF, the significance of DOY was preserved in the LI rule-based tree as it was the split variable four times in the tree.

The HI rule-based regression tree for College Station was similar to the HI rule-based tree at Ames with a primary node split based on NO₃₁₅ content (13 kg ha⁻¹) and θ
was the next important splitting variable (Fig. 2-6c). This means higher soil N and θ_{15} < 45% are associated with higher emissions. The LI rule-based tree had primary split between days less than or more than T_{15} of 13 °C followed by secondary and tertiary splits on θ_{15} (Fig. 2-6d). Other nodes preceding increased N₂O emissions include R₂, DOY, and T_{15}.

Fort Collins had a relatively simple HI rule-based tree with 7 terminal nodes (6-splits) based on NH₄₁₅, DOY, and T_{avg} (Fig. 2-6e). The primary node showing a split between observations with NH₄₁₅ less than and those more than 47 kg ha⁻¹ indicates relatively higher N₂O emissions in the right branch nodes associated with N-fertilization (Fig. 2-6e). The primary node of LI rule-based tree showed a split based on T_{15} less than or more than 12 °C (Fig. 2-6f). The highest emission was predicted in between DOY 150 to 154, shortly after fertilization, given T_{15} > 12 °C and T_{avg} > 15 °C.

Both HI and LI rule-based trees for Pullman are similar to those at Fort Collins showing primary split on soil N and soil temperature, respectively (Fig. 2-6g and 2-6h). Unlike Ames and College Station, the θ was not the major driver of N₂O emissions at Fort Collins or Pullman.

### 2.3.4.3. Prediction of Sampling Days by Rule-based Strategy

The regression trees based on HI and LI rule-based sampling were used to predict the sampling days in the test year at each site and the results are shown in Figure 2-2. The temporal distribution of the sampling days predicted by HI and LI rule-based sampling differs among sites. Both HI and LI sampling events at Ames were distributed over
almost the same temporal window (Fig. 2-2a). The sampling events were responsive to the precipitation-induced peak N\textsubscript{2}O emission from DOY 104 to 215, after which the N\textsubscript{2}O emissions as well as HI sampling events were not responsive to the precipitation events. However, one sampling on DOY 242 was predicted by LI rule-based in response to a 53 mm of precipitation event. Intensive gas sampling was predicted to start on DOY 196 after receiving almost 70 mm of precipitation in the preceding four days and continued until DOY 215. A 44 mm of precipitation event on DOY 207 resulted in consecutive HI samplings in the next three days, but none by LI method (Fig. 2-2a).

At College Station, the HI sampling events started after the first split application of N-fertilizer followed by a 14 mm of precipitation on DOY 60, whereas intensive LI samplings started after DOY 90 with a temporal spread wider than HI samplings (Fig. 2-2b). Sampling became frequent from DOY 135 to 157 which included major precipitation and peak N\textsubscript{2}O emission events during the corn growing period. In contrast, at Fort Collins, the sampling events were concentrated around the N-fertilization event in corn on DOY 145 (Fig. 2-2c). However, LI sampling events were more evenly spaced than HI events. The predicted sampling was frequent from DOY 145 to 163. At Pullman, both HI and LI rule-based sampling events were more evenly and widely distributed through the growing season (Fig. 2-2d). The split application of N on DOY 90 was associated with frequent sampling events.
2.3.5. Comparison of Rule-based and Fixed Interval Sampling Strategies

Both HI and LI rule-based strategies of sampling yielded reasonable estimates of cumulative N$_2$O flux with a substantially lower number of sampling events than fixed interval strategy (Table 2-3). The HI rule-based estimate at Ames (3.1 kg N$_2$O-N ha$^{-1}$) in 2006 was within ±5% of the simulated ‘actual’ cumulative flux (3.2 kg N$_2$O-N ha$^{-1}$) with only 16 sampling events, whereas fixed interval sampling could reach the same average bias as the HI sampling (0.2 kg N$_2$O-N ha$^{-1}$) with 91 sampling events (Table 2-3 and Fig. 2-4). The LI rule-based also yielded an estimate within ±5% of the expected (3.3 kg N$_2$O-N ha$^{-1}$), but with a bias three times higher than that of HI rule-based method. The rule-based method was even more efficient at College Station with only 14 sampling events to yield a cumulative estimate of 3.0 kg N$_2$O-N ha$^{-1}$ by HI strategy in 2010. The estimate was within ±5% accuracy of the ‘actual’ cumulative flux (2.9 kg N$_2$O-N ha$^{-1}$), while fixed interval strategy needed highly frequent sampling (2 day interval) to achieve the same bias as the HI sampling (0.2 kg N$_2$O-N ha$^{-1}$, Fig. 2-4). At College Station, the LI strategy provided a reasonable estimate (2.7 kg N$_2$O-N ha$^{-1}$) with relatively higher bias and 5 more sampling events than that in HI rule-based. Similarly, the rule-based method at Fort Collins reduced the total sampling events from 37 to 19 events, to yield an estimate of 1.1 kg N$_2$O-N ha$^{-1}$ with an absolute bias of 0.1 kg N$_2$O-N ha$^{-1}$ (Table 2-3). This estimate was within ±10% accuracy of the ‘actual’ cumulative flux (1.0 kg N$_2$O-N ha$^{-1}$). In contrast to other sites, at Pullman, both fixed interval and rule-based sampling performed closely in terms of required number of sampling events to achieve same bias (Table 2-3). The rule-based sampling used 18 sampling events, whereas fixed interval sampling suggested 16
days interval sampling (total 23 fixed interval sampling events). However, the real significance of the absolute error of cumulative flux estimation is negligible at Pullman and a less frequent sampling strategy could be adopted with minor effects on the cumulative estimate. Average N$_2$O emissions are relatively low at that location, and the spatial variation is likely more relevant than the temporal variation due to a strong landscape control of soil humidity in the Palouse hills.

In brief, the rule based strategy provided the same accuracy of estimation as fixed interval with a remarkably lower number of sampling events. Comparing the two rule-based strategies, the HI rule-based sampling yielded the same estimation accuracy as in LI with less bias at Ames and College Station, while they worked identically at Fort Collins and Pullman.

2.4. DISCUSSION

While the importance of accurately estimating N$_2$O emissions from agricultural systems is widely recognized (Parkin and Kaspar, 2006), the dependence on the chamber-based method casts uncertainty on the reliability, practicality, and cost of this technique. This study proposed that a suite of simulation modeling and non-parametric statistical approaches can help improve the timing of N$_2$O sampling, leading to a less costly and more accurate estimate of the annual cumulative N$_2$O flux. However, using models to predict sampling events requires certain level of reliability on the model’s prediction accuracy of N$_2$O emissions in response to soil, climate and management variables. Overall, the model reasonably predicted the temporal variability of N$_2$O emission at
Ames and Fort Collins (Fig. 2-1) along with N balance, crop growth, and N uptake under different soil, climate and management practices (Table 2-4) and gave us the confidence to use the simulation results for further analysis to predict sampling events.

When comparing Ames and College Station, it is instructive to consider how soil properties such as organic matter and clay content interact with nitrogen management and climate (Table 2-1 and 2-2, Fig. 2-2). At both locations, the soil is likely to enter early spring with moisture in the soil. At Ames, the subsequent warming coupled with a soil with a high load of mineral N in a band opens a wide window of time in which \( \text{N}_2\text{O} \) emissions can be sustained as long as leaching or the crop uptake do not remove mineral N and the soil remains moist enough so that timely precipitation events trigger \( \text{N}_2\text{O} \) emissions. This mechanism underlies the relevance of mineral N and soil moisture in the variable importance plots and regression trees for these two sites (Fig. 2-5a and c, Fig. 2-6a and c). The episodic nature of \( \text{N}_2\text{O} \) emissions is exacerbated at College Station because the soil dries faster due to the warmer climate, but convective storms and hurricanes can bring substantial precipitation quickly. When coupled with a clay soil that impedes drainage and causes soil saturation, the drying and wetting can cause sudden denitrification events. Accordingly, Asgedom et al. (2014) observed increased \( \text{N}_2\text{O} \) flux from clay soil after rainfall following N-fertilization. Sampling or not sampling one of these peaks can bias the estimation of the cumulative \( \text{N}_2\text{O} \) flux. This seems to be the situation where a rule-based sampling can be most useful. Otherwise, frequent sampling at time intervals (2 to 8 days interval) would be needed at College Station and Ames to
yield an estimate within ± 20% of accuracy (Fig. 2-3a and b). These results obtained with
a simulation model are remarkably similar to those of Parkin (2008) at Ames.

In contrast, Fort Collins had predictable N₂O emission peaks following N-
fertilization and subsequent irrigation events (Fig. 2-2c). Peak emissions occur in
response to precipitation and irrigation events soon after N-fertilization, a phenomenon
observed in other studies (Clayton et al., 1997; Dobbie et al., 1999; Baggs et al., 2003).
The importance of the top layer NH₄-N content on N₂O emissions as well as the primary
split on the same variable (Fig. 2-5e and Fig. 2-6e) suggests that nitrification of applied
urea is the main component of the N₂O emission at this location, as observed in relatively
dry locations in Montana by Engel et al. (2010). Thus, reasonable cumulative estimates of
N₂O emission (within 20% of the actual flux) can be obtained with a relatively low
intensity fixed interval sampling of once every two weeks (Fig. 2-3c). At Pullman,
conditions are not prone for large emissions, and the relatively dry summer and cold
winter probably caused lower N₂O emissions from winter wheat. In addition to relatively
low precipitation, good soil drainage limits large emissions. However, there can be
spatial hotspots of emissions since the Palouse is a landscape of rolling hills, where
swales are wetter than ridgetops (Mulla et al., 1992) and accumulated runoff and
subsurface flow may favor N₂O emissions. Frequent occurrences of air and soil
temperature in the regression tree indicate the strong control of temperature on
nitrification induced N₂O emissions (Fig. 2-6g and h). The lower temporal variability
(Fig. 2-2d) allows an infrequent sampling (16 days interval) to achieve ± 20% accuracy
in the estimate (Fig. 2-3d). Furthermore, a ± 20% error at Pullman is likely to be very
small as compared to ± 20% error at Ames or College Station. The relatively low peak N₂O emissions at Fort Collins and Pullman suppressed the consequences of sampling or not sampling one of these peak events on the cumulative flux estimation. Hence, a weekly fixed interval sampling at two contrasting sites may produce different errors of cumulative flux estimates, both in relative and absolute terms. This is due to different temporal patterns and the magnitude of N₂O emissions at different sites given the variation in soil, climate, and management practices (Flechard et al., 2007), which results in variations of accuracy in estimation for same sampling frequency. This study contributes to the interpretation and translation of these differences into a specific set of rules to sample N₂O fluxes.

The rule-based method performed better than the fixed interval strategy in estimating cumulative flux with minimum number of sampling events at the four sites. The peak N₂O emission events are ephemeral ‘hot moments’, and usually comprise < 5% of the total temporal window, thus the bias associated with infrequent fixed interval sampling could be large (Liengaard et al., 2014). It is therefore important to anticipate the occurrences of ‘hot moments’, which is what the rule based sampling accomplishes. This method does both, allocates a greater proportion of the sampling events to the peak emission periods and fewer to the low, background emissions, to yield an overall estimate closer to the ‘actual’ cumulative flux, and provides a mean to weight the importance of each sampling event.

In general, soil moisture, water input through precipitation, availability of mineral-N, and temperature were the critical factors for N₂O emissions. The importance
of these variables for N₂O emission has also been observed in other studies (Dobbie et al., 1999; Davidson et al., 2000; Ma et al., 2010). The contribution of this paper is that the specific thresholds for these variables at a given location and for a management system can be quantified. The differences in the temporal distribution of predicted sampling events among the sites were due to distinct temporal variability of N₂O emissions at each site. The sampling events as predicted by the rule-based method were in accordance with the probability of hot moment occurrences (Fig. 2-2). This enables the rule-based method to yield a more accurate estimation by using substantially lower number of sampling events than the fixed interval method, particularly in the locations with large variability and amplitude of temporal N₂O emissions (Table 2-3). When the variability is low, a low frequency fixed interval sampling can be adopted, which returns a reliable cumulative flux estimate. Excluding the soil N related variables from the rule-based method (as in LI rule-based) did not have a substantial trade-off in accuracy of estimation or increase in sampling numbers, and important results that makes this approach inexpensive and user friendly (does not need information of soil N content). This could be due to the importance of DOY, which surrogated the role of soil N level on N₂O emissions in the LI rule-based method (Fig. 2-5). However, this came at a cost of a wider temporal spread of the predicted sampling events in the LI rule-based method, which implies a loss of accuracy in predicting ‘hot moments’ of N₂O emissions when N information is missing. Thus, the sites with higher amplitude in temporal variability of N₂O emissions may be associated with higher bias of estimation by LI than that in HI rule-based sampling method. Nonetheless, the LI rule based method still performed better than the fixed
interval method, with better accuracy, time use, and cost savings on gas sampling and analysis.

2.5. CONCLUSIONS

The results showed that a simulation model that satisfactorily simulates variations in N₂O emissions regarding both peak amplitude and duration could be a useful tool to assess the accuracy of sampling frequency in estimating cumulative flux. Increasing the sampling interval in a uniform sampling scheme increases the error of the cumulative flux estimation, but the magnitude of the error depends on the underlying temporal variability of N₂O emissions. When using a low frequency sampling, sites with greater temporal flux variability are at higher risk of large errors in the N₂O flux estimation. The rule-based method quantifies the specific thresholds for site-specific variables that are important for N₂O emissions and proved to be more efficient in predicting sampling events. Estimation of cumulative N₂O flux by the rule-based sampling, with or without including the variables related to mineral N availability in soil, returns the best balance between total sample number and accuracy. This rule-based method can be a powerful tool to define cost effective and efficient estimations of cumulative N₂O fluxes, especially under soil, climate, and management practices associated with greater variability and amplitude of N₂O fluxes.
References


understand the processes and their controls? Phil. Trans. R. Soc. B. 368:20130122.


Firestone, M.K., and E.A. Davidson. 1989. Microbiological basis of NO and N₂O production and consumption in soil. In: M.O. Andreae and D.S. Schimel, editors,


### Table 2-1. Past 10-years of average seasonal weather at the simulated sites

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<th>Jan - Mar</th>
<th>Apr - Jun</th>
<th>Jul - Sept</th>
<th>Oct - Dec</th>
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<th>Apr - Jun</th>
<th>Jul - Sept</th>
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<td>Burleson Silty clay loam</td>
<td>Fort Collins clay loam</td>
<td>Palouse silt loam</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>USDA Classification</td>
<td>Typic Endoaquolls</td>
<td>Typic Endoaquolls</td>
<td>Aridic Haplustalf</td>
<td>Ultic Haploxerolls</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clay (g/kg)*</td>
<td>230</td>
<td>400</td>
<td>340</td>
<td>170</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sand (g/kg)</td>
<td>370</td>
<td>130</td>
<td>400</td>
<td>190</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silt (g/kg)</td>
<td>400</td>
<td>470</td>
<td>260</td>
<td>640</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Org. matter (g/kg)</td>
<td>45</td>
<td>24</td>
<td>20</td>
<td>32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Management practices</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cropping system</td>
<td>Corn-soybean</td>
<td>Corn-\textit{Vicia} (cover crop)</td>
<td>Continuous Corn</td>
<td>Winter wheat</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tillage</td>
<td>Chiesel-plow</td>
<td>Conventional-till</td>
<td>Conventional-till</td>
<td>Conventional-till</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-fertilization</td>
<td>Anhydrous NH$_3$ @ 168 kg-N ha$^{-1}$ in Nov.</td>
<td>UAN @ 64 and 56 kg-N ha$^{-1}$ in March and April</td>
<td>Urea @ 202 kg-N ha$^{-1}$ in May and 23 kg NO$_3$N from irrigation water</td>
<td>Urea @ 92 kg-N ha$^{-1}$ in April and 92 kg N ha$^{-1}$ as UAN in Oct.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Application mode</td>
<td>Banding at 20-cm depth</td>
<td>Incorporation</td>
<td>Broadcasting</td>
<td>1$^{\text{st}}$ split broadcast 2$^{\text{nd}}$ split Incorporation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irrigation</td>
<td>NA</td>
<td>NA</td>
<td>Scheduled sprinkler irrigation (460 mm in corn)</td>
<td>NA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Soil properties for top 15 cm layer.
Table 2-3. Actual cumulative flux, estimation by rule-based method and associated absolute bias of estimation and required number of sampling events by rule-based and fixed-time interval method under the four simulated sites in their respective test years.

<table>
<thead>
<tr>
<th>Site</th>
<th>Test year</th>
<th>Simulated actual flux (kg N/ha/yr)</th>
<th>Rule based sampling estimation</th>
<th>No. of sampling events</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cumulative flux (kg N/ha/yr)</td>
<td>Absolute bias (kg N/ha/yr)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>HI*</td>
<td>LI</td>
</tr>
<tr>
<td>Ames</td>
<td>2006</td>
<td>3.2</td>
<td>3.1</td>
<td>3.3</td>
</tr>
<tr>
<td>College Station</td>
<td>2010</td>
<td>2.9</td>
<td>3.0</td>
<td>2.7</td>
</tr>
<tr>
<td>Fort Collins</td>
<td>2010</td>
<td>1.0</td>
<td>1.1</td>
<td>0.9</td>
</tr>
<tr>
<td>Pullman</td>
<td>2013</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
</tbody>
</table>

* HI, High input rule-based; LI, Low input rule-based.

† The number of sampling events for fixed interval sampling was estimated from Fig. 2-4 based on the required sampling interval to achieve the absolute bias of HI rule-based sampling for the respective sites.
Table 2-4. Simulated biomass yield, crop N uptake and grain yield at the simulated sites.

<table>
<thead>
<tr>
<th>Site</th>
<th>Test year</th>
<th>Crop</th>
<th>Above-ground biomass (Mg/ha)</th>
<th>Crop N uptake (kg/ha)</th>
<th>Grain yield (Mg/ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ames</td>
<td>2006</td>
<td>Corn</td>
<td>18</td>
<td>169</td>
<td>10</td>
</tr>
<tr>
<td>College Station</td>
<td>2010</td>
<td>Corn</td>
<td>15</td>
<td>201</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Vicia</em></td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fort Collins</td>
<td>2010</td>
<td>Corn</td>
<td>23</td>
<td>188</td>
<td>12</td>
</tr>
<tr>
<td>Pullman</td>
<td>2013</td>
<td>Winter wheat</td>
<td>14</td>
<td>157</td>
<td>5</td>
</tr>
</tbody>
</table>

*Cover crop
**Figure 2-1.** Comparison of predicted and measured temporal N$_2$O emissions at (a) Ames and (b) Fort Collins in 2006 and 2010, respectively. The measured N$_2$O fluxes were adopted from Jereky et al. (2008) for Ames and Halvorson and Del Grosso (2013) for Fort Collins.
Simulated daily N\textsubscript{2}O flux

HI rule-based samplings

LI rule-based samplings
Figure 2.2. Simulated daily N$_2$O flux and gas sampled days as predicted by high input and low-input rule-based sampling at (a) Ames (2006), (b) College Station (2010), (c) Fort Collins (2010), and (d) Pullman (2013). The inverted graph on top of each panel shows daily precipitation (P) and irrigation (I, in case of irrigated system). The arrow indicates the day of N-fertilization. The gray, hatched, and dotted region in each panel represent corn, cover crop (Vicia), and winter wheat growing seasons, respectively.
Figure 2-3. Effect of fixed-time interval sampling on relative deviation of estimated cumulative N$_2$O flux at (a) Ames (2006), (b) College Station (2010), (c) Fort Collins (2010), and (d) Pullman (2013).
Figure 2-4. Average absolute bias of cumulative flux estimation at different sampling frequencies by fixed-time interval sampling.
Figure 2-5. Variable importance plot from random forest for predictor variables for high input (HI) and low input (LI) rule-based sampling at Ames (a, b), College Station (c, d), Fort Collins (e, f), and Pullman (g, h). Higher values of percent increase in MSE indicates variables that are important for N$_2$O emissions.

* The top of each panel represents the percent variability explained by random forest.
(a) Ames - HI rule-based

(b) Ames - LI rule-based
(c) College Station - HI rule-based

(d) College Station – LI rule-based
(e) Fort Collins – HI rule-based

(f) Fort Collins – LI rule-based
Figure 2-6. High input (HI) and low input (LI) rule-based trees for Ames (a, b), College Station (c, d), Fort Collins (e, f), and Pullman (g, h). Upon satisfaction of the splitting conditions, the tree progresses to the left. Each terminal node contains average $N_2O$ flux ($g \, N \, ha^{-1} \, d^{-1}$) for that group and number of observations (n).
Chapter 3

NITROUS OXIDE EMISSIONS DURING THE TRANSITION FROM
CONSERVATION RESERVE PROGRAM TO PERENNIAL GRASSES FOR
BIOENERGY

ABSTRACT

Converting seasonally wet marginal lands currently under Conservation Reserve Program (CRP) to energy crop may increase nitrous oxide (N\textsubscript{2}O) emissions, thus limiting the carbon benefits of energy crops. The transition period is the critical when elevated N\textsubscript{2}O emissions due to soil disturbance can be expected from energy crops, spatially variable within the landscape. I measured N\textsubscript{2}O emissions and influencing environmental drivers during the transition of CRP grassland to switchgrass (*Panicum virgatum* L.) and *Miscanthus* × *giganteus* in a typical Ridge and Valley landscape of northeastern USA. Replicated treatments including CRP (unconverted), unfertilized switchgrass (switchgrass), N-fertilized switchgrass (switchgrass-N), and *Miscanthus*, were randomized in four blocks within a 5-ha watershed. Plots were established along the slope and segmented into shoulder, backslope, and footslope positions based on moisture gradient. Soil N\textsubscript{2}O flux was measured by non-steady state chamber method and soil mineral nitrogen availability was monitored during the growing season of 2013, the second year after land transition. Autonomous sensor network continuously monitored soil moisture dynamics in the landscape. Growing season N\textsubscript{2}O flux shows a significant ($P$
vegetation-by-landscape position interaction. The switchgrass-N and *Miscanthus* had 48 and 78% higher cumulative flux than the CRP, while the difference was not significant with unfertilized switchgrass. The peak N$_2$O emission event, contributing 26% of the cumulative flux, occurred after a 100-mm rain event during early June. Prolonged soil saturation coinciding with high mineral N concentration expressed hot spots of N$_2$O emissions in the footslopes under energy crops. The non-parametric statistical analysis identified the importance of landscape positions, mineral nitrogen, and subsoil aeration on N$_2$O emissions. The results suggest that land transition only caused significant increase in N$_2$O emissions from the footslope, while the major part of the watershed is at lesser risk. These findings have significant implications on transitional landscape management strategies to reduce N$_2$O emissions.

### 3.1. INTRODUCTION

Renewable fuels are an increasing portion of the liquid fuels portfolio of the United States. It is envisaged that to fulfill federal mandates, the nation should produce approximately 80 billion liters of ethanol from cellulosic sources by 2022 (Kim et al., 2009). This will require that up to 21 million ha will have to be planted with cellulosic crops (McLaughlin et al., 2002) like switchgrass (*Panicum virgatum*) and *Miscanthus* (*M. × giganteus*). In the United States (US) land seemingly suitable for energy crops is that currently enrolled in the Conservation Reserve Program (CRP), which amounts to ~12 million hectares (Farm Service Agency, 2012) of agriculturally marginal and environmentally sensitive land.
Energy crops like switchgrass and *Miscanthus* can provide crucial ecosystem services when placed in environmentally sensitive lands across the landscape. When planted in floodplains or in lower landscape positions within watersheds, these grasses can serve as riparian buffers to reduce nutrient and sediment load to surface water and groundwater (Pérez-Suárez et al., 2014; Smith et al., 2014). Furthermore, due to the low soil disturbance and perennial rooting systems, even with a substantial fraction of the biomass harvested, they still can store carbon (C) in the system due to below-ground C allocation (Lemus and Lal, 2005; Follett et al., 2012).

Nonetheless, a key component of the societal benefit of energy crops is that they produce fuel with a low C footprint (Tilman et al., 2006; Adler et al., 2007; Gelfand et al., 2013). The United States Environmental protection Agency’s (USEPA) revision to the National Renewable Fuel Standard requires that to qualify as renewable, advanced biofuels lifecycle GHG emissions must be 50% of those from fossil fuel (USEPA, 2010). To achieve this goal it is critical that at the feedstock production level emissions of nitrous oxide ($\text{N}_2\text{O}$) remain low, because it is a potent greenhouse gas (GHG) whose emissions are typically associated with agriculture. There are arguments positing that converting historically managed CRP lands to energy crops may increase $\text{N}_2\text{O}$ emissions (Ruan and Robertson, 2013).

In the Ridge and Valley province across the Allegheny Plateau in the northeastern (NE) US, many lands are considered marginal due to being seasonally wet. These landscapes have characteristically shallow, coarse, and rocky ridge top soils as well as fractured subsoils that drain water to the back and footslope positions. The footslope soils
are derived from mixed colluvial sandstone and shale often with fragic properties at shallow depth that limit drainage (Ciolkosz et al., 1995). Restricted drainage may cause a shallow, temporary water table and extended periods of soil water content above field capacity or near saturation during spring snowmelt and rainstorm events (Buda et al., 2009). The steep slopes with a semi-impermeable subsoil favor nitrate (NO$_3$) transport to stream water (Kleinman et al., 2006; Zhu et al., 2011). The simultaneous occurrence of well drained upper lands and poorly drained footslope positions may create biogeochemical hot spots for denitrification and N$_2$O emissions (Vilain et al., 2010).

The N$_2$O emissions from soil predominantly originate from nitrification and denitrification (Paul and Beauchamp, 1989). Soil oxygen, NO$_3$, ammonium (NH$_4$), and labile organic C concentration determine the contribution of nitrification and denitrification to the total N$_2$O flux (Weier et al., 1993; Gillam et al., 2008). In seasonally wet lands of the NE, the N$_2$O emissions could be severe during the transition from to CRP to energy crops due to accelerated C and nitrogen (N) cycling from above and below-ground residues from the former CRP vegetation, soil disturbance during the land conversion (Nikiema et al., 2012; Ruan and Robertson, 2013), and relatively low crop growth rate and N uptake in the first two years of a stand. Furthermore, if the energy crops are fertilized, co-locating N fertilizer with decomposable organic residues along the terrain water flow paths can cause large N$_2$O emissions. Thus, managing N and N$_2$O emissions in energy crops in this region of the US requires understanding the interaction of landscape, crop growth, biogeochemistry, and hydrology as determinants of N cycling.
In this research, I measured the N\textsubscript{2}O emission during the transition from CRP to the energy crops *Miscanthus* and switchgrass in a watershed in the Ridge and Valley region. The area has been in CRP since 1999. In 2011, it was divided in 16 plots along hydrological flow paths. Four of the 16 plots were retained as CRP (control) and the remaining plots were planted with *Miscanthus* and switchgrass in 2012. Nitrous oxide flux was monitored during the 2013 growing season. In June of 2013, 100 mm downpour from hurricane ‘Andrea’ caused sudden soil saturation across the watershed. This event gave me an excellent opportunity to measure the event-based response of N\textsubscript{2}O emissions during the transition from CRP to energy crops. The research questions were: 1) What is the effect of converting CRP lands to switchgrass and *Miscanthus* on soil N\textsubscript{2}O emissions? 2) What is the effect of N fertilization of energy crops on N\textsubscript{2}O emissions? 3) How does landscape heterogeneity and land conversion interact to control N\textsubscript{2}O emissions?

### 3.2. MATERIALS AND METHODS

#### 3.2.1. Site Description

The experimental watershed, hereafter called Mattern (40°42’ N, 76°36’W), is located near the town of Leck Kill in east-central Pennsylvania (PA), approximately 40 km north of Harrisburg, PA. It is part of a long-term monitoring site of the USDA-Agricultural Research Service (Sharpley et al., 2008). The site has a temperate humid climate with annual mean temperature and precipitation of ~9.2° C and ~100 cm,
respectively. Mattern is a small (11ha) part of a larger (726 ha) watershed (WE-38) that drains to the Mahatango Creek, a tributary of the Susquehanna River (Sharpley et al., 2008). The Susquehanna River is the main fresh water contributor to the Chesapeake Bay, making this research relevant to the larger Chesapeake Bay Basin. The topography and land use of the studied site is representative of the larger Ridge and Valley province.

Mattern has a typical upland mixed land use (57% cropland, 30% forest, 4% pasture, 9% meadow, and < 1% buildings). The upper valley lands have rotations of soybean (*Glycine max* L.), wheat (*Triticum aestivum* L.), and corn (*Zea mays* L.). Slope ranges from 1 to 20%. The elevation above sea level varies from 267 m in the valley floor to 285 m near the summit. The soils formed in shale, siltstone, and sandstone residuum and colluvium materials (Buda et al., 2009). They typically have a silt loam surface grading with 20 to 40% rock volume (Table 3-1) to a loam and/or silty clay loam texture at depth (~1 m), and include the Albright soils in colluvial deposits and residual Berks soil series (Ciolkosz et al., 1995; Needelman et al., 2004). The Albright soils are distributed along the stream and valley floor and have a fragipan and argillic horizon beginning at a depth of 0.5-0.7 m (Needelman et al., 2004). Prolonged soil saturation during spring and after extensive precipitation events are common in the footslope Albright soils. Subsurface lateral water flow above the upper boundary of the fragipan dominates the saturated flow. In contrast, the Berks soils in the shoulder and backslope positions are relatively shallow and well drained.

The plots were established in the lower portion of the watershed, in an area of approximately 5-ha that includes the watershed outlet. Mattern has an ephemeral stream
that is active most of the year except during dry summers. This area along with the upland was, until 1999, under conventionally tilled corn, soybean, wheat, and alfalfa \((Medicago\ sp.)\) rotation with poultry manure applied at rate of 5 Mg ha\(^{-1}\) yr\(^{-1}\), corresponding to 205 kg total N ha\(^{-1}\) yr\(^{-1}\) (Kleinman et al., 2006). These areas were considered marginal for agriculture due to seasonal wetness and the slope, and were brought under CRP in 1999. The CRP vegetation comprises a permanent cover of introduced perennial cool-season grasses such as orchard grass \((Dactylis\ sp.)\), fescue \((Festuca\ sp.)\), timothy \((Phleum\ sp.)\), and legumes like alfalfa and clover \((Trifolium\ sp.)\).

3.2.2. Experimental Design

To conduct this research, the CRP lands were partially converted to warm-season perennial energy crops in 2012. The watershed was divided in four blocks with relatively uniform aspect, each containing four future plots. In the plots converted to energy crops, which comprise 75\% of the area (12 out 16 plots), CRP vegetation was killed with glyphosate in the summer of 2011, and the aboveground biomass baled and removed from the field. The plots were no-till planted with a winter rye cover crop in the fall of 2011, which was in turn killed with glyphosate prior to the planting of the energy crops in the spring of 2012.

The four treatments were: 1) intact CRP, 2) N-fertilized switchgrass (switchgrass-N), 3) unfertilized switchgrass (switchgrass), and 4) unfertilized \(Miscanthus\). The plots (~60×30 m each) were arranged in a randomized complete block design for a total of 16 plots (4 treatments × 4 replications). The switchgrass-N plots received 50 kg ha\(^{-1}\) of N as
broadcasted urea on May 29th, 2013 (a year after planting). The switchgrass plots were no-till drilled in rows 20-cm apart. The Miscanthus plots were hand planted in chisel-made furrows to facilitate rhizome planting. Thus, the Miscanthus plots had a higher level of soil disturbance. Throughout 2012, the plots of both species were hand replanted to cover areas where the switchgrass drilling or the Miscanthus planting failed (mostly the challenging wet footslope positions). By 2013, plot establishment was exceptional. In 2012, weeds were controlled with herbicide and due to the good establishment and vigorous growth of both switchgrass and Miscanthus weed pressure was low in 2013.

As stated above, each plot was established along a hydrological flow path. From the upland portion that borders cropland to the drainage that merges into the ephemeral stream, each plot has a moisture gradient in predominantly north and south facing aspect (Fig. 3-1). Based on this increasing soil wetness from top to bottom, each plot was divided into three segments along the toposequence: shoulder, backslope, and footslope (Fig. 3-1). This is customary when studying topographic effects on soil N2O emissions (e.g. Pennock et al., 1992 and Vilain et al., 2010). The combination of four treatments, three landscape positions, and four replications (blocks) yielded a total of 48 monitoring points within the 5-ha lower portion of the Mattern watershed. Biomass samples were taken at harvest from 1-m² areas in each plot. In addition, the plots were machine harvested in the winter, bailed, and the biomass removed from the field.
3.2.3. Measurement of Soil Water Content and Air Filled Soil Volume

We continuously monitored volumetric soil water content ($\theta_V$, m$^3$ m$^{-3}$) with CS-616 soil moisture sensors (Campbell Scientific Inc., Logan, UT). The sensors were installed at three depths (0-20, 20-40, and 40-60 cm) in each of the 48 monitoring points (3 landscape positions × 16 plots), for a total of 144 sensors. Each sensor was connected to one of four dataloggers through a network of buried cables. The $\theta_V$ was used to calculate the volumetric air content in the soil layer ($\theta_A$, m$^3$ m$^{-3}$):

$$\theta_A = \theta_S - \theta_V$$  

where $\theta_S$ is the total porosity of a layer after correcting for rock volume (m$^3$ m$^{-3}$), calculated assuming a mineral particle density of 2.65 Mg m$^{-3}$. The $\theta_A$ is more directly related to the soil aeration condition and is preferred over either $\theta_V$ or the commonly used water filled pore space which is reported to be an inconsistent scaler of trace gas fluxes across different soil texture and structural properties (Schjønning et al., 2003; Castellano et al., 2010).

3.2.4. Measurement of N$_2$O Emissions

We measured N$_2$O emissions during the 2013 growing season (May to September). The sampling frequency varied from weekly to biweekly, increasing after fertilization and precipitation events. The N$_2$O flux from soil to atmosphere was measured by the static, vented, aluminum-foil insulated chamber method (Hutchinson and Mosier, 1981). In 2012, PVC collars of 30 cm diameter were inserted 5 cm in the soil
in each of the 48 monitoring points. The collars support the chamber (10 cm height) placed on top of it. The fitting is sealed with an outer gas-tight rubber seal. The chamber inside was free of any vegetation.

At measurement time, chambers were placed on top of the collars and left there for 45 minutes. Gas samples of 20 ml were drawn from each chamber through a rubber septum connected to a manifold inside the chamber diameter. Samples were taken 15, 30, and 45 minutes after the chamber closure. Soil temperature near the chamber was measured during gas sampling.

The 20-ml gas samples were transferred to 12-ml pre-evacuated Labco extetainer vials that were over pressurized. The N₂O concentration in the gas samples was measured with a Varian CP3800 gas chromatograph (with Compi-Pal autosampler) equipped with a ⁶³Ni electron capture detector that operates at 300 °C to detect N₂O. Helium was used as the carrier gas at a flow rate of 40 ml min⁻¹. The ideal gas law was used to calculate the μg N₂O -N and the flux was calculated from the rate of increase in N₂O concentration in the chamber headspace. Cumulative N₂O flux (May 9th to September 13th) was calculated by interpolation and numerical integration. We refer to this as the growing season flux as it roughly corresponds to the period when the grasses were green and soils were not frozen. The N₂O flux on the days in between two sampling days was estimated as:

\[ F_L = F_o + \frac{(F_f - F_o)}{d_f - d_o} \times (d_i - d_f) \]  

(ii)
where, \( F_L \) is the estimated flux of \( \text{N}_2\text{O} \), \( F_o \) and \( F_f \) are the measured fluxes bracketing the days interpolated, \( d_o \) and \( d_f \) are the days corresponding to \( F_o \) and \( F_f \), and \( d_i \) is the \( i^{th} \) day in between \( d_o \) and \( d_f \).

### 3.2.5. Soil Sampling

Soil samples (0-20 cm) were taken during every other gas flux measurement to determine \( \text{NH}_4 \) and \( \text{NO}_3 \) concentration. Moist soil samples were extracted with 100 ml 2M KCl and the N species determined by colorimetric analysis (Lachat QuickChem 8000). All values were corrected for gravimetric water content measured on a 10 g subsample oven dried at 105 °C for 48h.

A deep soil core, approximately 0.5 to 1.2 m in length, was also collected from each sampling point in spring 2012. The samples were taken with a tractor mounted Giddings probe with plastic tube liner (4.5 cm in diameter) and tip diameter of 3.8-cm. The soil core was used for geomorphic description (color, structure, concretion, depletion), to estimate bulk density (rock-free), particle size distribution (USDA-pipette method; Day, 1965), total soil C and N concentration (Elemental Combustion System auto-analyzer, Costech Analytical Technologies, Inc.), and rock volume (water displacement method).
3.2.6. Statistical Analysis

I used parametric and non-parametric statistical methods for data analysis. All statistical analysis was performed on R statistical software (R Development Core Team, 2012). First, a classical analysis of variance (ANOVA) included block, treatment, and landscape position effect. The residuals of the daily \( \text{N}_2\text{O} \) fluxes were not always normally distributed and were log-transformed for ANOVA, whereas soil variables were untransformed. The residuals of the cumulative \( \text{N}_2\text{O} \) fluxes were not normally distributed and were transformed using the reciprocal square root transformation based on the “ladder of powers” method (Tukey, 1977) to achieve normality (Shapiro-Wilk, \( P = 0.17 \)) and variance homogeneity. Data were back transformed for tabular presentation. Marginal means were compared using Tukey-adjusted \( P \)-values at a 5% significance level. The main effect and the interactions on daily and cumulative \( \text{N}_2\text{O} \) flux were assessed with the following linear model:

\[
Y_{ijk} = \mu + \alpha_i + \gamma_k + (\alpha\gamma)_{ik} + \beta_j + (\alpha\beta)_{ij} + (\beta\gamma)_{jk} + e_{ijk} \tag{iii}
\]

where, \( Y_{ijk} \) represents the response variable \( \text{N}_2\text{O} \) flux; \( \alpha, \beta, \) and \( \gamma \) represent the main effect of vegetation type, landscape position, and block, respectively; and \( i, j, k \) denote the respective levels of the main factors.

Second, I used Random Forest, a non-parametric method, to analyze which variables explain better the observed variation in log\(_{10}\) transformed \( \text{N}_2\text{O} \) flux. The Random Forest was applied to the pooled data including only the days when soil mineral N was measured along with soil \( \text{N}_2\text{O} \) flux, \( \theta_A \), and weather variables. I used the function \text{randomForest} from the package \text{randomForest} in R statistical software (Breiman, 2001).
The control parameters for random forest were $\text{seed} = 500$ (set random number), $\text{ntree} = 500$ (number of trees). The control parameter $\text{mtry}$ indicates the number of variables available for splitting at each node and calculated as square root of total number of variables (Strobl et al., 2009). The variable importance was plotted by using the function `varImpPlot`. The variables used for this analysis are: crop (type of vegetation), landscape position, soil NO$_3$ and NH$_4$ concentration in the top 20 cm layer (NO$_3$-N and NH$_4$-N; mg kg$^{-1}$ dry soil), clay concentration in 0-20, 20-40, and 40-60 cm depth (Clay$_{20}$, Clay$_{40}$, and Clay$_{60}$; %), fraction air content in 0-20, 20-40, and 40-60 cm depth ($\theta_{A20}$, $\theta_{A40}$, and $\theta_{A60}$), and cumulative precipitation in the last two days (R$_2$, mm).

Finally, we constructed a conditional inference tree based on the data having soil mineral N information (i.e. five soil N sampling days) including the above mentioned variables to predict N$_2$O emissions. We used `tree` package in R with seed = 500 to build the regression tree. Each terminal node of the tree has an average N$_2$O flux and frequency (n).

### 3.3. RESULTS

#### 3.3.1. Weather, Soil Properties, and Biomass Yield

The C and N distribution and bulk density in the top 20 cm did not differ along the slope positions; all the treatments started with the same background level of C and N (Table 3-1). Soils had moderate organic C (mean 19.5 g kg$^{-1}$ soil) and N (mean 2.1 g kg$^{-1}$ soil). Soil bulk density (free of rocks) varied from 1.0 to 1.5 Mg m$^{-3}$, with a mean of 1.2
Mg m$^{-3}$. Rocks occupy a substantial soil volume (mean rock fraction 0.32 m$^3$ m$^{-3}$), with a greater rock fraction in the shoulder position (0.35 ± 0.06 m$^3$ m$^{-3}$) and decreasing down the slope. The clay concentration varied from 130 to 290 g kg$^{-1}$, with the highest figures in the footslope position (Table 3-1).

Mean daily air temperature was 19.1° C for the study period from May to September, 2013. Cumulative precipitation was 402 mm with a large, 108-mm rain event during hurricane ‘Andrea’ on June 10th.

The aboveground biomass yield of the energy crops in the fall of the second year (2013) exceeded 10 Mg ha$^{-1}$, and was 2 to 4 times higher than that of the CRP (Fig. 3-2). While the figure for the CRP reflects the harvestable biomass in fall, it does not represent the totality of the aboveground biomass produced because a large part is produced in spring, senesces in early summer and is not harvestable in fall. There was no significant effect of the landscape and N-fertilization on biomass yield.

### 3.3.2. Soil Ammonium and Nitrate Concentration

Soil NH$_4$ concentration during the growing season was relatively high, even in unfertilized plots, and ranged from 0.1 to 77 mg N kg$^{-1}$ soil, with a mean of 10 ± 12 mg N kg$^{-1}$ soil (Table 3-2). The mean NH$_4$ concentration was lowest in Miscanthus (6 ± 5 mg N kg$^{-1}$ soil) whereas the highest mean concentration (14 ± 20 mg N kg$^{-1}$ soil), as expected, was observed in the switchgrass-N treatment. There was a very narrow variation among landscape positions (8.8 to 10.4 mg N kg$^{-1}$ soil). The N-fertilization in switchgrass-N in the end of May increased the mean NH$_4$ concentration from 0.8 ± 0.5 mg N kg$^{-1}$ soil
before the fertilization to 48 ± 22 mg N kg⁻¹ soil on June 7ᵗʰ, a week after fertilization (Fig. 3-3a). However, the effect of fertilization faded away after the hurricane. A substantial increase in NH₄ concentration, higher in CRP, was also observed in unfertilized grasses during summer and tended to decrease over the growing season (Fig. 3-3a). In general, no plot showed N stress, but the N-fertilized plots had a darker green color and the plants lodged in mid-July.

Mean growing season soil NO₃ concentration in the landscape was 19 ± 14 mg N kg⁻¹ soil, and ranged from 0.2 to 85 mg N kg⁻¹ soil (Table 3-2). In contrast to NH₄, mean growing season soil NO₃ concentration was highest in Miscanthus plots (25 ± 17 mg N kg⁻¹ soil); almost 2-times higher than that in CRP (13 ± 13 mg N kg⁻¹ soil). Again, the variation among landscape positions was narrow (footslope 17 and shoulder 20 mg N kg⁻¹ soil, respectively). In the switchgrass-N plots, the N-fertilization had a minor effect on NO₃ dynamics in shoulder and backslope positions, while footslope position showed an increase in soil NO₃ concentration (30 mg N kg⁻¹ soil) during early June. This concentration was five-times higher than that in CRP (6 mg N kg⁻¹ soil) (Fig. 3-3b). On June 7ᵗʰ, just before the hurricane, Miscanthus plots had the highest NO₃ concentration in all landscape positions (mean 43 ± 20 mg N kg⁻¹ soil), while CRP plots had the lowest NO₃ concentration (8 ± 3 mg N kg⁻¹ soil). These differences were not discernible after the hurricane and NO₃ concentration became comparable among treatments.
3.3.3. Soil Air Content

Soil profile air concentration greatly varied spatially and temporally during the growing season in response to precipitation events, and ranged from 0 m$^3$ m$^{-3}$ (soil water saturation) to 0.32 m$^3$ m$^{-3}$ (Fig. 3-4). The greatest variation in $\theta_A$ among the treatments was in the footslope positions. Mean $\theta_A$ in the profile was lowest (0.14 ± 0.03 m$^3$ m$^{-3}$) in 20-40 cm followed by 40-60 cm (0.15 ± 0.04 m$^3$ m$^{-3}$), and 0-20 cm (0.19 ± 0.04 m$^3$ m$^{-3}$) depth (Table 3-2). The start of the N$_2$O flux measurement coincided with a rain event that reduced $\theta_A$ in the soil profile. The $\theta_A$ reduction was more prominent and prolonged in the footslope positions (Fig. 3-4). There was a steady increase in $\theta_A$ from May 9th onwards until the onset of the hurricane in June 10th. The event saturated the soil and decreased $\theta_A$ in the top 20 cm soil layer of footslope (0.02 ± 0.02 m$^3$ m$^{-3}$), which was significantly ($P < 0.05$) lower than that in the backslope (0.08 ± 0.07 m$^3$ m$^{-3}$), and shoulder (0.12 ± 0.06 m$^3$ m$^{-3}$) positions on June 11th. Soil aeration started to increase after June 14th due to drainage and crop water uptake and subsequent precipitation events decreased soil aeration, but never to the extent or length of the hurricane driven storm.

3.3.4. N$_2$O Emissions

The soil N$_2$O flux widely varied among the treatments and landscape positions, ranging on average per treatment from 4 to 305 g N ha$^{-1}$ d$^{-1}$. Averages for the season are presented in Table 3-2. The N$_2$O flux was lowest in the CRP (8 g N ha$^{-1}$ d$^{-1}$) and highest in Miscanthus (16 g N ha$^{-1}$ d$^{-1}$). The footslope positions were the hot spots with greater
variability of N₂O emissions in the landscape, where the mean flux (18 g N ha⁻¹ d⁻¹, range of 60 g N ha⁻¹ d⁻¹) was more than two-times higher than that of the shoulder positions (8 g N ha⁻¹ d⁻¹). Specifically, footslope positions under Miscanthus had highest (26 g N ha⁻¹ d⁻¹) mean growing season emission followed by switchgrass-N (23 g N ha⁻¹ d⁻¹), switchgrass (16 g N ha⁻¹ d⁻¹), and CRP (7 g N ha⁻¹ d⁻¹).

During early May, the emission from the footslope positions (55 g N ha⁻¹ d⁻¹) was significantly (P < 0.05) higher than that from the shoulder positions (19 g N ha⁻¹ d⁻¹); however it was not statistically different in the backslope positions (30 g N ha⁻¹ d⁻¹) (Fig. 3-5). During that period, the average N₂O emission from energy crops (41 g N ha⁻¹ d⁻¹) was 2.6-times higher than that from CRP. The N-fertilization did not have an immediate effect on N₂O flux from switchgrass-N in the shoulder and backslope positions; however, a small peak of 35 g N ha⁻¹ d⁻¹ occurred in the footslope position (Fig. 3-5).

Peak N₂O emissions coincided with the hurricane event on June 10th (Fig. 3-5). The rain saturated the soil and reduced θ_A severely (Fig. 3-4), coinciding with a period of high mineral N concentration in soil (Fig. 3-3). Averaged over all plots, the N₂O flux was 84 g N ha⁻¹ d⁻¹ on June 11th, a day after the large precipitation event. This flux was roughly four-times higher than the pre-hurricane flux of 22 g N ha⁻¹ d⁻¹ on June 7th. This flux, however, was not distributed homogeneously through the landscape. Emissions from the footslope (156 g N ha⁻¹ d⁻¹) and backslope (76 g N ha⁻¹ d⁻¹) positions were significantly (P < 0.05) higher than the shoulder positions (20 g N ha⁻¹ d⁻¹). The hurricane effect on the N₂O emissions from the grasses was in the order of: Miscanthus (130 g N ha⁻¹ d⁻¹) > switchgrass-N (103 g N ha⁻¹ d⁻¹) > switchgrass (69 g N ha⁻¹ d⁻¹) >
CRP (34 g N ha\(^{-1}\) d\(^{-1}\)). Significant interaction between vegetation type and landscape position \((P = 0.03)\) was only observed during this hot moment. The emissions from lower landscape positions of *Miscanthus* (305 g N ha\(^{-1}\) d\(^{-1}\)) and switchgrass-N (233 g N ha\(^{-1}\) d\(^{-1}\)) was significantly \((P < 0.05)\) higher than that in CRP (20 g N ha\(^{-1}\) d\(^{-1}\), \(P < 0.05\)). The flux from switchgrass-N was not significantly different from unfertilized switchgrass \((P > 0.05)\), which is somewhat surprising. The hurricane induced peak N\(_2\)O emission waned to background level after June 18\(^{th}\) as the water drained and oxic conditions prevailed in the landscape (Fig. 3-4).

### 3.3.5. Growing Season Cumulative N\(_2\)O Flux

The ANOVA of cumulative N\(_2\)O flux shows a significant \((P = 0.009)\) vegetation-by-landscape position interaction (Table 3-3). Landscape position had the strongest effect on cumulative N\(_2\)O flux \((P < 0.001)\), with the footslope positions having the highest flux (mean 2.1 kg N ha\(^{-1}\), lower and upper limit of 1.3 and 11.6 kg N ha\(^{-1}\)), significantly \((P < 0.05)\) higher than that of the backslope position (mean 1.4 kg N ha\(^{-1}\), with lower and upper limit of 0.9 and 3.6 kg N ha\(^{-1}\)) and shoulder position (mean 0.9 kg N ha\(^{-1}\), with lower and upper limit of 0.6 and 1.4 kg N ha\(^{-1}\)). Except for unfertilized switchgrass, energy crops had significantly \((P < 0.05)\) higher cumulative flux than the CRP. The mean flux for CRP was 1.0 kg N ha\(^{-1}\) (lower and upper limit of 0.7 and 1.6 kg N ha\(^{-1}\)), while that of *Miscanthus* was 1.8 kg N ha\(^{-1}\) (lower and upper limit of 1.4 and 7.9 kg N ha\(^{-1}\), \(P < 0.05\)). Surprisingly, the fertilization effect was not obvious on cumulative flux as switchgrass-N yielded a cumulative estimate (1.5 kg N ha\(^{-1}\)), statistically similar to other
energy crops, but higher than that of CRP. The differences in cumulative N₂O emissions between the CRP and energy crops were greater in the footslope positions (Table 3-3).

3.3.6. Conditions Leading to N₂O Emissions

The Random Forest analysis identified landscape position, soil NO₃ concentration, and cumulative precipitation in the last two days (R²) as the most important factors influencing N₂O emissions (Fig. 3-6). It is the soil aeration (θₐ) in subsurface layers (20-40 and 40-60 cm) that seem to be related to the gas flux, rather than that in the top layer. The Random Forest model was able to explain only 26% of the variation in N₂O flux. Clearly, there are other controls of the flux that we did not measure and can include microsite properties that are difficult to characterize.

The predictor variables as identified by the Random Forest were used to classify the N₂O fluxes in groups that can be identified by specific conditions. The regression tree contains 7 terminal nodes. The primary node shows a split based on θₐ₄₀ = 0.03 m³ m⁻³, with the highest emission when θₐ₄₀ < 0.03 m³ m⁻³ (Fig. 3-7). The secondary split was on soil mineral N availability. The highest N₂O emissions (146 g N ha⁻¹ d⁻¹, n=5) were observed when θₐ₄₀ < 0.03 m³ m⁻³ and NH₄ < 1 mg N kg⁻¹ soil. When the θₐ₄₀ > 0.03 m³ m⁻³, NO₃ < 10 mg N kg⁻¹ soil, higher emission can be expected from the footslope and backslope positions (terminal node 5). High clay (> 27%) containing subsoil layers restrict water percolation and may have higher N₂O emissions (36 g N ha⁻¹ d⁻¹, n=16), when availability of NO₃ is not limiting (> 10 mg N kg⁻¹ soil, terminal node 7). Since the construction of the regression tree excluded the highest N₂O emission period after the
hurricane event, the potential emissions can be much higher than the values predicted by
the tree. However, the tree was useful in unraveling the risks of high N\textsubscript{2}O emissions,
especially from the footslope positions, under high NO\textsubscript{3} and aeration stressed soil
environment.

3.4. DISCUSSION

Converting CRP lands to energy crops significantly increased N\textsubscript{2}O emissions
during the second year of the transition; the effect was substantially influenced by the
landscape position (Table 3-3). The transition from CRP to switchgrass-N and
\textit{Miscanthus} increased the growing season flux by 48 and 78\%, respectively ($P < 0.05$);
the difference between CRP and unfertilized switchgrass was not statistically significant
($P > 0.05$). For comparison, Gelfand et al. (2011) reported 4.5 times higher cumulative
N\textsubscript{2}O emissions from no-till soybean converted from CRP grassland. Most of the
difference between CRP and the energy crops accrued in the footslope (Table 3-3), where
the cumulative flux from \textit{Miscanthus}, switchgrass-N, and switchgrass was 6.1, 3.3, and
2.4 times higher, respectively, than that of CRP.

The difference among treatments in the footslope built up over three distinctive
periods: during early season growth which coincides with the pre-hurricane period, the
week of the hurricane in mid-June, and the post hurricane period until the end of the
growing season. In the early season, the CRP vegetation starts growing actively to
deplete mineral N. Lower NO\textsubscript{3} concentration during early June was observed in CRP,
significantly ($P < 0.05$) lower than that in \textit{Miscanthus} in the footslopes (Fig. 3-3b). On
the contrary, the energy crops have limited growth and show NO₃ accumulation, with an average NO₃ concentration of 25 mg N kg⁻¹ soil, a situation conducive to N₂O emissions from denitrification. A similar situation was reported by Gauder et al. (2012), who explained higher N₂O emission from Miscanthus compared with shrub willow (Salix spp.) during early summer due to lack of Miscanthus plant cover and in high soil mineral N after fertilization. Ecosystems with low soil disturbance compared to agriculture such as tropical grassland and forests show low nitrification rates (Rice and Pancholy, 1972; Vitousek and Matson, 1984), and it has been hypothesized that phytochemicals inhibit biological nitrification in mature ecosystems (Subbarao et al., 2006a and 2009a). Nikiema et al. (2012) reported 6-fold increase in nitrification potential when long-term undisturbed pasture land was cleared and cultivated for short-rotation poplar (Populus spp.) and shrub willow. Thus, it can be hypothesized that the more than the 10 years of undisturbed soil in the CRP might have a comparatively limited nitrification potential compared to the recently disturbed soils in energy crops, limiting emissions from CRP.

Over the early season, several factors contributed to relatively high NO₃ accumulation in the energy crops, particularly in Miscanthus. First, since 1999, the CRP soils had accumulated relatively high amount of soil C and N due to manure applications and abundance of legumes. Killing of the CRP vegetation during land conversion accelerated decomposition of dead grass and legume roots and increased C and N availability due to soil organic matter mineralization in the converted lands (Ruan and Robertson, 2013). Second, decomposable surface residues from the previous year and remaining rye cover crop biomass, although low (< 2 Mg ha⁻¹), possibly supplied
additional decomposable C to power N cycling. And third, chisel plowing during rhizome establishment caused greater level of soil disturbance in Miscanthus, which may have accelerated soil decomposition (Grandy and Robertson, 2006a; Alluvione et al., 2009). The N-fertilization in switchgrass also increased mineral N availability (Fig. 3-3a). In short, disturbing C- and N-rich CRP lands can cause high concentration of mineral N, favoring N₂O emissions even under no-till (switchgrass) but more so in tilled soils (Miscanthus) (Table 3-3). But these potentially higher emissions are mostly realized only in the landscape position more vulnerable to soil saturation and anoxia. According to our non-parametric statistical analysis, these potentially higher emissions are mostly realized only when the convergence of high mineral N and soil saturation occur in the landscape, predominantly in the footslope positions (Fig. 3-6, 3-7). Furthermore, the analysis identified greater influence of subsoil aeration, a fact that is often overlooked, on N₂O emissions in these landscapes. Nonetheless, limited drainage through the fragipans and argillic subsoil layers within the colluvial footslopes (Ciolkosz et al., 1995; Needelman et al., 2004) causes extended periods of water saturation, even when the top layer is relatively drained (Fig. 3-4). The juxtaposition of oxic top layer and anoxic subsurface layer could be a hot spot for N₂O production from denitrification, given the NO₃ is not limited (Firestone and Davidson, 1989).

The hot moment and the hot spots for N₂O emissions came together with the arrival of hurricane Andrea (June 10th to 13th): the soils under energy crops have high NO₃, and the soil and landscape were conducive to accumulation of water in the footslopes (Needelman et al., 2004). It is in this one week where the difference among
treatments in the footslope builds up significantly, mostly in the footslopes (Fig. 3-5). Given the high level of soil NO$_3$ before the event, denitrification was most likely the dominant contributor of peak N$_2$O emissions under low oxygen tension in the soil profile during the hot moment (Weier et al., 1993; Gillam et al., 2008). The hot moment contributed on average 26% of the growing season cumulative N$_2$O flux in 2013. This is in proportion with Parkin and Kasper (2006), who reported that two 29 days-long peak events accounted for 45% of annual N$_2$O flux from corn in Midwest.

The comparison of unfertilized and N-fertilized switchgrass in this period also reflects the concurrence of hot spots and hot moments. The response of N$_2$O flux to N fertilization was not very prominent or immediate because the soil was dry for more than a week after N-fertilization (May 29$^{th}$ to June 9$^{th}$) (Fig. 3-4), limiting N transformations (Bateman and Baggs, 2005; Davidson et al., 2008; Gauder et al., 2012). However, there was a small peak from the footslope positions which may be attributed to favorable soil water content for nitrification. A similar lag period between fertilization and peak emission due to a dry period has been reported by Baggs et al. (2003). During the hurricane, however, both Miscanthus and switchgrass-N are the two treatments with more responsive N$_2$O emission in the footslope (Fig. 3-5).

The hurricane rinsed the soil mineral N and equalized all treatments for this variable (Fig. 3-3). In addition, shortly after the hurricane, depletion of mineral N due to crop growth and soil drying due to increased evapotranspiration during peak vegetative growth decreased the chances of high nitrate and anoxia co-occurrences, which decreased N$_2$O emissions later in the growing season.
Previous studies on landscape scale N$_2$O emissions also identified the footslope positions as the hot spots for N$_2$O emissions (van Kessel et al., 1993; Castellano et al., 2010; Vilain et al., 2010). The same processes seem to operate in this watershed, with localized zones of water accumulation causing spatially variable N$_2$O emissions. Remarkably, fast drainage and redistribution of water in the shoulder positions never caused severe aeration limitation as to favor denitrification, even after receiving a 100 mm of rainfall by the hurricane. In fact, the critical 0.03 m$^3$ m$^{-3}$ threshold identified through the regression tree analysis is rarely, if ever, reached in the backslope and shoulder positions. It is not clear from this data, however, if the sources of N for N$_2$O emission in the footslope are in upslope processes. Thus, in the Ridge and Valley region, while footslopes are at risk of high N$_2$O emissions, backslope and ridges posit a much lesser risk of emissions, even in the transitional years and in N-rich soils.

Given the results, one concern could be the interannual variability of N$_2$O emissions as reported by many studies (Burchill et al., 2014; Oates et al., 2015), and representability of the studied period. It is important to reinforce that the studied year had a wet early summer (Fig. 3-5a) coinciding with high mineral N availability in the energy crop plots (Fig. 3-3), a perfect co-occurrence and the adverse situation for a transitional system, when N$_2$O emissions are the concern. Thus, our results represent the potential risks of transitional N$_2$O emissions, which could be a significant component of the C-footprint of energy crop production in the Ridge and Valley landscapes.
3.5. CONCLUDING REMARKS

Management strategies to control C and N cycling during the first and second year of the energy crops following CRP seem critical to reduce transitional N\textsubscript{2}O flux, which may significantly affect the C-footprint of renewable feedstock production. The major insight of this research is that the high risk of N\textsubscript{2}O emission is concentrated not on the entire watershed but mostly on the footslope positions. As shown in Figures 3-3 and 3-5, once the mineral N concentrations drops due to crop uptake (and N losses), N\textsubscript{2}O emissions are very low.

A clear outline of N management emerges from this research. First, to minimize N\textsubscript{2}O fluxes in N-rich environments, soil disturbance needs to be minimized to prevent an increase in organic matter mineralization (compare unfertilized, no-till switchgrass with Miscanthus). With equal yield between the two species as obtained in this experiment, this makes Miscanthus a riskier crop in this regard than no-till switchgrass. Higher yield from Miscanthus (Arundale et al., 2014) may compensate for such inherent weakness if no or minimum N fertilizer is applied (Drewer et al., 2012). It is not customary to fertilize Miscanthus or switchgrass in the first year of planting due to slow growth during the establishment phase, but later, monitoring soil mineral N in spring seems critical to avoid over fertilization. It was not expected that the soil at Mattern, which is rocky and marginal for agriculture, would mineralize such substantial amounts of N on land conversion (Fig. 3-3). Although the original concern was the need to manage N supply through fertilization, it is clear that CRP land transitioning to energy crops has a strong potential for reactive N releases due to previous manure application or due to the
abundance of legumes. Second, the major risks are in the footslope positions. While well drained landscape positions can be fertilized with lesser risks of enhancing emissions, NO$_3$ can be transported to high emission areas, and it is unknown exactly how much of the N$_2$O emission in the footslope positions originated from the N transported from upslope areas. Third, a multi-phased land transition strategy could be recommended in these areas, where when practical, the shoulder and backslope positions should be converted first, and the lower portion planted two years later, when the energy crops are competent enough to minimize downslope water and nutrient transport.
References


### Table 3-1. Basic physical and chemical soil properties in the top 20 cm soil layer.

<table>
<thead>
<tr>
<th>Treatments and landscape position</th>
<th>Total C … g kg(^{-1}) soil …</th>
<th>Total N</th>
<th>Bulk density g cm(^{-3})</th>
<th>Rock fraction</th>
<th>Clay %</th>
<th>Silt %</th>
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<td><strong>CRP</strong></td>
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<tr>
<td>Shoulder</td>
<td>21±3*</td>
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<td>1.12±0.04</td>
<td>0.37±0.03</td>
<td>17±2</td>
<td>47±3</td>
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*Mean ± standard deviation (n=4)
Table 3-2. Mean growing season soil N<sub>2</sub>O fluxes, soil mineral N (top 20 cm layer), and soil aeration in different landscape positions under CRP and energy crops

<table>
<thead>
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<th>Treatments and landscape position</th>
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<td></td>
<td>g N ha&lt;sup&gt;-1&lt;/sup&gt; d&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>... mg N kg&lt;sup&gt;-1&lt;/sup&gt; soil ...</td>
<td>... m&lt;sup&gt;3&lt;/sup&gt; m&lt;sup&gt;-3&lt;/sup&gt; ...</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>CRP</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shoulder</td>
<td>7†</td>
<td>15±13*</td>
<td>12±10</td>
<td>0.17±0.03</td>
<td>0.12±0.03</td>
<td>0.19±0.02</td>
</tr>
<tr>
<td>Backslope</td>
<td>11</td>
<td>14±14</td>
<td>11±10</td>
<td>0.20±0.04</td>
<td>0.17±0.03</td>
<td>0.18±0.03</td>
</tr>
<tr>
<td>Footslope</td>
<td>7</td>
<td>11±10</td>
<td>10± 9</td>
<td>0.21±0.07</td>
<td>0.14±0.05</td>
<td>0.14±0.06</td>
</tr>
<tr>
<td><strong>Switchgrass</strong></td>
<td></td>
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</tr>
<tr>
<td>Shoulder</td>
<td>7</td>
<td>15±11</td>
<td>7±6</td>
<td>0.16±0.03</td>
<td>0.11±0.02</td>
<td>0.14±0.03</td>
</tr>
<tr>
<td>Backslope</td>
<td>13</td>
<td>19±17</td>
<td>7±6</td>
<td>0.16±0.03</td>
<td>0.11±0.03</td>
<td>0.13±0.03</td>
</tr>
<tr>
<td>Footslope</td>
<td>16</td>
<td>18±12</td>
<td>6±5</td>
<td>0.17±0.04</td>
<td>0.10±0.06</td>
<td>0.08±0.05</td>
</tr>
<tr>
<td><strong>Switchgrass-N</strong></td>
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</tr>
<tr>
<td>Shoulder</td>
<td>8</td>
<td>22±10</td>
<td>16±23</td>
<td>0.18±0.03</td>
<td>0.13±0.02</td>
<td>0.12±0.03</td>
</tr>
<tr>
<td>Backslope</td>
<td>13</td>
<td>17±13</td>
<td>14±20</td>
<td>0.20±0.03</td>
<td>0.20±0.03</td>
<td>0.19±0.03</td>
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<tr>
<td>Footslope</td>
<td>23</td>
<td>17±11</td>
<td>13±19</td>
<td>0.28±0.04</td>
<td>0.21±0.03</td>
<td>0.25±0.06</td>
</tr>
<tr>
<td><strong>Miscanthus</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Shoulder</td>
<td>9</td>
<td>26±20</td>
<td>6±5</td>
<td>0.18±0.03</td>
<td>0.13±0.03</td>
<td>0.10±0.03</td>
</tr>
<tr>
<td>Backslope</td>
<td>12</td>
<td>27±16</td>
<td>6±5</td>
<td>0.19±0.04</td>
<td>0.14±0.04</td>
<td>0.12±0.04</td>
</tr>
<tr>
<td>Footslope</td>
<td>26</td>
<td>21±14</td>
<td>6±6</td>
<td>0.18±0.05</td>
<td>0.13±0.04</td>
<td>0.14±0.04</td>
</tr>
</tbody>
</table>

†Daily N<sub>2</sub>O fluxes were log10 transformed and then presented as back-transformed means of growing season flux with comparable dimensions

*Mean ± standard deviation (n=4)
Table 3-3. Analysis of variance for significance of differences in N₂O flux and growing season cumulative N₂O (kg N ha⁻¹) emission in different landscape positions under CRP and energy crops

<table>
<thead>
<tr>
<th>Sources of variance</th>
<th>Df</th>
<th>Mean square</th>
<th>F value</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vegetation (V)</td>
<td>3</td>
<td>0.14</td>
<td>6.25</td>
<td>0.004**</td>
</tr>
<tr>
<td>Block (B)</td>
<td>3</td>
<td>0.02</td>
<td>1.21</td>
<td>0.333</td>
</tr>
<tr>
<td>Landscape position (LP)</td>
<td>2</td>
<td>0.59</td>
<td>26.92</td>
<td>0.000***</td>
</tr>
<tr>
<td>V × LP</td>
<td>6</td>
<td>0.09</td>
<td>4.10</td>
<td>0.009**</td>
</tr>
<tr>
<td>B × LP</td>
<td>6</td>
<td>0.02</td>
<td>0.90</td>
<td>0.514</td>
</tr>
<tr>
<td>V × B</td>
<td>9</td>
<td>0.04</td>
<td>1.96</td>
<td>0.106</td>
</tr>
<tr>
<td>Error</td>
<td>18</td>
<td>0.02</td>
<td></td>
<td></td>
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</tbody>
</table>

Growing season cumulative N₂O flux

<table>
<thead>
<tr>
<th>Landscape position</th>
<th>CRP</th>
<th>Switchgrass</th>
<th>Switchgrass-N</th>
<th>Miscanthus</th>
<th>Mean†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shoulder†</td>
<td>0.81⁺</td>
<td>0.75</td>
<td>0.92</td>
<td>1.05</td>
<td>0.88c</td>
</tr>
<tr>
<td>Backslope</td>
<td>1.39</td>
<td>1.60</td>
<td>1.40</td>
<td>1.37</td>
<td>1.44b</td>
</tr>
<tr>
<td>Footslope</td>
<td>0.89</td>
<td>2.15</td>
<td>2.94</td>
<td>5.48</td>
<td>2.11a</td>
</tr>
<tr>
<td>Mean†</td>
<td>0.99b</td>
<td>1.31ab</td>
<td>1.48a</td>
<td>1.77a</td>
<td></td>
</tr>
</tbody>
</table>

†Similar letters associated with N₂O flux between the landscape positions and among the treatments are not significantly different at p = 0.05

⁺The cumulative N₂O flux was reciprocal square root transformed before performing ANOVA to follow the assumption of normality for parametric test, and then presented as back-transformed means with comparable dimensions
**FIGURES**

**Figure 3-1.** Map showing the location of the Mattern watershed (Upper left, black point) within the Susquehanna River basin (grey shaded) and Ridge and Valley physiographic province (dotted region). The upper right panel is a Google Earth aerial view of the Mattern watershed. The lower map panel represents the detailed experimental set up at Mattern including treatment plots and measurement location at three landscape positions within each plot.
Figure 3-2. Dry biomass yield of CRP and perennial warm season grasses under different landscape positions in 2013. Data are mean ± standard error (n=4).
Figure 3.3. Dynamics of soil NH\textsubscript{4}-N (Panel a) and NO\textsubscript{3}-N (Panel b) concentration in the top 20 cm soil layer under CRP and bioenergy grasses at different landscape positions during the growing season of 2013. Each point is a mean of four replicates for each treatment. Error bars represent ± standard error of mean. The solid and broken arrows indicate N-fertilization in switchgrass-N treatment and hurricane ‘Andrea’, respectively.
Figure 3-4. Temporal and spatial variation of air content in 0-20, 20-40, and 40-60 cm soil depth under CRP and energy crops.
Figure 3-5. Daily precipitation, air temperature (a) and log$_{10}$ transformed daily N$_2$O fluxes from CRP and bioenergy grasses under (b) shoulder, (c) footslope, and (d) backslope position. Each point is a mean of four replicates for each treatment. Error bars represent ± standard error of mean. The arrow indicates N fertilization in switchgrass-N treatment.
Figure 3-6. Random Forest based variable importance plot for N₂O flux (log₁₀ transformed). The % increase in the mean square error represents the accrued error when a variable is not included in the analysis. Higher values of percent increase in MSE indicates variables that are important for N₂O emissions. It therefore allows ranking the variables by interest of importance in controlling the gas flux. (Type of random forest: regression; number of trees: 1000; no. of variables tried at each split: 3; mean of squared residuals: 0.041; variation explained: 26%). R², cumulative precipitation in preceding two days; θ_{A20}, θ_{A40}, and θ_{A60}, volumetric soil air content (m³ m⁻³) in 0-20, 20-40, and 40-60 cm depth, respectively; Clay₂₀, Clay₄₀, and Clay₆₀, clay concentration (%) in in 0-20, 20-40, and 40-60 cm depth, respectively.
Figure 3-7. Regression tree to predict N\textsubscript{2}O emissions from a marginal landscape during its transition from CRP to energy crops. Each terminal node represents mean N\textsubscript{2}O flux for that bin and number of observations (n). Upon satisfaction of the condition, the tree is routed to the left. The average node properties characterize the soil conditions under each node. The values in parenthesis beside each landscape position represent the number of observations out of total number of observations (n) belong to each landscape position.
CHARACTERIZATION OF HOT SPOTS AND HOT MOMENTS OF NITROUS OXIDE EMISSIONS IN A TRANSITIONAL BIOENERGY LANDSCAPE

ABSTRACT

Reduced greenhouse gas (GHG) emissions are among the primary goals of promoting energy crops to replace fossil fuels. To ensure enough fertile lands for food security, one option is to convert marginal lands currently under Conservation Reserve Program (CRP) to bioenergy production. Converting these environmentally sensitive landscapes may increase the emission of a potent GHG gas, nitrous oxide (N$_2$O), thus limiting the putative GHG abatement of bioenergy crops. Soil N$_2$O emission is associated with high spatial temporal variability as characterized by hot spots and hot moments nature. The knowledge of hot spots and hot moments of N$_2$O emissions in the landscape is important for its accurate spatial and temporal monitoring, quantification of the emissions, and to minimize the adverse environmental effects of converting CRP lands to energy crops. In 2013, a field measurement of N$_2$O was conducted in a typical Ridge and Valley landscape of northeastern USA during the transition of CRP grassland to perennial energy crops (switchgrass and Miscanthus) for bioenergy production. Static-vented chambers and soil moisture sensors were installed at shoulder, backslope, and footslope positions of each plot to measure N$_2$O flux and soil water dynamics, respectively. A novel application of the concept of inequality (Lorenz curve and Gini coefficients, G) was employed to quantify the heterogeneous distribution of N$_2$O in space and time. The G was better correlated ($R^2 = 0.71$, $P <$
with daily N₂O emissions than the coefficient of variation and skewness. The hot moment of N₂O emission occurred after a 100-mm rain event by hurricane Andrea during June 8-10th that caused sudden soil saturation- the exact conditions that triggers bursts of N₂O emission. As a result, the average watershed N₂O flux increased from 16 g N₂O-N ha⁻¹ da⁻¹ on June 7th to 124 g N₂O-N ha⁻¹ da⁻¹ on June 11th. The hot moment caused highly heterogeneous distribution (G = 0.70) of N₂O fluxes in the landscape. The storm event had little influence on inequality of soil CO₂ flux distributions among the vegetation types and landscape positions. Relatively wetter lower landscape positions were the hot spots for N₂O emissions, with a high inequality of N₂O flux distribution (G = 0.75). In contrast, upper landscape positions were the cold spots with comparatively equal distribution (G = 0.43) of low N₂O fluxes. The relative inequality of N₂O fluxes and its biogeochemical drives were always greater than 1 during the growing season. Event-based evolution of N₂O flux inequality was in accordance with the hydrologic inequality, given the biogeochemical equality prevails in the landscape. The Lorenz curve and G in association with spatial maps clearly represented the expression of hot spots and hot moments on the inequality of N₂O emissions. This information will guide landscape-scale management strategies to reduce N₂O emissions, as well as spatial and temporal monitoring of N₂O emissions.

4.1. INTRODUCTION

Emissions of the greenhouse gas nitrous oxide (N₂O) from soils often exhibit high spatial and temporal variability (Pennock et al., 1992; van Kessel et al., 1993; Izaurralde et al., 2004; Vilain et al., 2010). This variability stems from the collective forcing by hydrologic and
biogeochemical factors that control soil nitrogen (N) transformations, which are in turn spatially and temporally variable.

Two microbial processes are the main sources of the N$_2$O emitted from the soil: nitrification and denitrification (Firestone and Davidson, 1989). These processes are controlled by a dynamic interaction among soil nitrate (NO$_3$), ammonium (NH$_4$), decomposable organic matter (Weier et al., 1993; Gillam et al., 2008), soil oxygen (O$_2$) concentration (Dobbie et al., 1999), temperature, and pH (Mehmood et al., 1998). When the soil has high concentration of O$_2$ and NH$_4$, high nitrification rates are the main contributor of N$_2$O emissions. In contrast, when anoxic conditions coincide with high availability of NO$_3$, denitrification is the main contributor to this flux. Because the processes controlling the concentration of these compounds are highly dynamic and spatially variable, it is difficult to predict the N$_2$O emission rates for different soil, climate, and management practices. However, these emissions occur in spatially and temporally localized “spots”, which are accordingly described as biogeochemical ‘hot spots’ and ‘hot moments’ (McClain et al., 2003, Liengaard et al., 2014).

The hot spots of N$_2$O emissions are isolated zones/patches with disproportionately high flux relative to the neighboring patches. Hot moments are brief temporal windows with several fold higher emission rates above the threshold background level emissions (McClain et al., 2003; Groffman et al., 2009; Molodovskaya et al., 2012). The hot moments have been observed in response to management disturbances and climatic events like N-fertilization, organic matter addition, tillage, rainfall, and freeze thaw cycles (Clayton et al., 1997; Wagner-Riddle and Thurtell, 1998; Parkin and Kasper, 2006). Large spatial variability of N$_2$O flux with a coefficient of variation (CV) exceeding 100% is common (van Kessel et al., 1993; Yates et al., 2006). Spatially variable N$_2$O emissions have been observed from agricultural landscapes with varied
topography, land cover, soil, and management practices (Corre et al., 1996; Gu et al., 2011). Topography interacts with landscape hydrology to influence pedological processes and C, N biogeochemical cycling which in turn forms hot spots of N₂O emissions in the lower landscape positions due to high moisture and therefore low air content in the soil that favors N₂O production from denitrification (Pennock et al., 1992; Izaurralde et al., 2004; Vilain et al., 2010). The “pulse” nature of the N₂O fluxes can contribute approximately half of the annual N₂O flux (Parkin and Kasper, 2006). Hot spots and hot moments may not coincide, but when they do, they magnify the N₂O flux (Vilain et al., 2010). Hot spots and hot moments are the drivers of the spatial and temporal variability of N₂O emissions.

A given population of N₂O fluxes has the following attributes: i) large variation in individual N₂O fluxes, ii) a few individuals with larger N₂O fluxes and many with small fluxes, iii) the individuals with large flux greatly contribute to the total N₂O flux of the population. Most of the studies addressing N₂O emissions characterize the distribution of the emissions with indicators like the skewness and CV as the measures of hierarchy of spatial and temporal N₂O flux distribution (Pennock et al., 1992; Yates et al., 2006); however, these measures only describe satisfactorily the second of the three attributes listed above. The skewness does not respond to the degree of variation in N₂O flux among the individuals. The CV describes the average degree of variation, but does not describe the distribution of this variation.

In this paper, I use both a graphical and a quantitative indicator of inequality, the Lorenz inequality curve and associated Gini (G) index (Lorenz, 1905), to represent the inequality of N₂O emissions. The Lorenz curve gives a graphical representation of qualitative distribution inequality, while G provides a measure of the inequality magnitude. These indicators link the distribution of fluxes with the “size hierarchy” concept (Weiner and Solbrig, 1984). These
indicators have been used on a limited basis in agronomic studies (e.g. Sadras and Bongiovanni, 2004), and only recently in hydrology and sediment transport studies (e.g. Jawitz and Mitchell, 2011; Gall et al., 2013; Shi et al., 2013). The application of this concept can be readily understood through the following example. A hypothetical population with twenty individuals with N$_2$O flux of two units and two individuals with N$_2$O flux of four units, has less variation in individual N$_2$O flux relative to the mean flux than that a population with twenty individuals with N$_2$O flux of two units and two individuals with N$_2$O flux of forty units. The later has greater inequality (and hence greater risk of hot spots or hot moments’ contribution to the cumulative N$_2$O flux), yet they have the same skewness. In fact, this limitation to describe variability of N$_2$O fluxes has been observed by van Kessel et al. (1993).

In Chapter 3 of this dissertation, I show that in the second year of transition from CRP to energy crops, a year broadly representative of the transition from CRP to a mature energy landscape, a large fraction of the N$_2$O emissions occur in hot spots and hot moments. This variability stems from: i) hydrological and biogeochemical heterogeneity of the landscape, ii) legacy effect of the prior CRP, iii) soil disturbance during land conversion and crop establishment, and iv) N-fertilization of energy crops. The specific objective is to apply the Lorenz curve and G index to the characterization of N$_2$O emissions in hot spots and hot moments.
4.2. MATERIALS AND METHODS

4.2.1. Site Description

The study area is located near the town of Leck Kill in east-central Pennsylvania (PA). It occupies 5 ha at the bottom of a small 11-ha watershed (hereafter called Mattern) that belongs to the larger Mahantango Creek watershed. The latter is a tributary of the Susquehanna River (Sharpley et al., 2008). The site represents the topography of the Ridge and Valley province. The weather variables were measured by a nearby local USDA-ARS weather station. The climate is temperate humid climate with past 10 years mean annual temperature ~9.2° C and precipitation ~100 cm.

Mattern has a typical upland mixed land use with 57% cropland (corn-soybean-wheat), 30% forest, 4% pasture, 9% meadow, and <1% buildings. Slopes range from 1 to 20%, while the elevation ranges from 267 (valley floor) to 285 m (summit position) above mean sea level. Mattern soil is typically a silt loam surface grading to a loam and/or silty clay loam texture at depth (~1 m), and include the Albrights soils in colluvial deposits and residual Berks soil series (Buda et al., 2009). The Albrights soils near the stream and valley floor have a fragipan and argillic horizon beginning at a depth of 0.5-0.7 m (Needelman et al., 2004), causes prolonged soil saturation during spring and after extensive precipitation events. Shallow and well drained residual Berks soils are predominant in the shoulder and backslope positions. Due to seasonal wetness and limited trafficability during spring, the lower ~5-ha of Mattern was converted to CRP in 1999.
4.2.2. Plot Establishment

In 2011, the CRP vegetation in the area to be planted with energy crops was killed with glyphosate, baled, and planted with a winter rye cover crop. The warm-season grasses *Miscanthus* and switchgrass were planted in 2012. The treatments were: N-fertilized switchgrass (switchgrass-N), unfertilized switchgrass (switchgrass), unfertilized *Miscanthus*, and the unconverted CRP. The switchgrass was planted by no-till drilling in rows 20 cm apart, whereas *Miscanthus* was hand-planted through rhizome in chisel-made rows. The fertilized switchgrass plots received 50 kg N ha\(^{-1}\) as broadcasted urea on May 29, 2013. Each plot was divided into three segments along the toposequence, shoulder, backslope, and footslope positions (see chapter 3). The treatment plots (~60 m × 30 m each) were randomized in four blocks with a total of 16 plots (4 treatments × 4 replications).

4.2.3. Monitoring Soil N\(_2\)O and CO\(_2\) Emissions

The N\(_2\)O and CO\(_2\) emission were monitored during the 2013 growing season (May to September) with weekly to biweekly sampling frequency. On each sampling event, 48 sampling points (16 plots × 3 landscape positions) were monitored for N\(_2\)O and CO\(_2\) fluxes with the static chamber method (Hutchinson and Mosier, 1981). For sampling, the chamber was closed and headspace gas samples of 20 ml were drawn at 15, 30, and 45 minutes after chamber closure. The gas samples were transferred to 12 ml pre-evacuated Labco exetainer vials. The gas samples were analyzed for N\(_2\)O and CO\(_2\) concentration in a Varian CP3800 gas chromatograph with autosampler.
4.2.4. Soil Water and Inorganic N Monitoring

Soil water was monitored at 30 min intervals with three CS-616 soil moisture sensors (Campbell Sc. Inc.) installed at 0-20, 20-40, and 40-60 cm depth in each of the 48 monitoring points, for a total of 144 sensors (3 landscape positions × 3 depths × 16 plots). Each sensor was connected to one of four data loggers.

Soil inorganic N was measured five times during the growing season of 2013 and concomitant with five of the gas sampling events. The soil cores from 20 cm depth were collected by auger from each gas sampling point, close to the gas chamber. The samples were extracted with 100 ml 2M KCl and analyzed for soil ammonium (NH$_4$) and nitrate-N (NO$_3$) concentration by colorimetric analysis in a Lachat QuickChem 8000.

4.2.5. Lorenz Curve and Gini Coefficient

The Lorenz curve (Lorenz, 1905) is constructed as follows. The observed N$_2$O and CO$_2$ fluxes are sorted from minimum to maximum and the “total” flux calculated as the sum of all measurements for a given day. The proportion contributed by each observation is thereafter calculated. The Lorenz curve is a plot of the cumulative fraction of total N$_2$O flux versus the cumulative fraction of the observations. This relationship is presented as a curve with a concave slope (Fig. 4-1). The upper limit of the Lorenz curve is y = x, or the line of perfect equality. This line represents a hypothetical population in which all individuals contribute equally to the total N$_2$O flux; the greater the gap between the Lorenz Curve and the line of perfect equality the greater the distribution inequality. The curve is convex to the y-axis and never rises above the
line of perfect equality. The degree of the curvature of Lorenz curve gives a visual characterization of the N\textsubscript{2}O flux distribution inequality.

The G index quantifies the inequality magnitude by comparing the area between the line of perfect equality and that corresponding to the Lorenz curve (A) and the area under the line of equality i.e. between the line of equality and the x-axis (Fig. 4-1):

$$G = \frac{A}{A + B}$$

(i)

The G index ranges from 0 to 1, with G = 0 meaning that all units contribute equally to the total N\textsubscript{2}O flux, and G = 1 meaning that all units, but one, have 0 contributions (Weiner and Solbrig, 1984). The calculated G index was multiplied by \(n / (n - 1)\) to give an unbiased index estimator (Weiner and Solbrig, 1984; Pan et al., 2003).

4.2.6. Relative Inequality

Temporal inequality of N\textsubscript{2}O fluxes and its biogeochemical drivers was assessed by the relative inequality \(\Phi\), which is the ratio of the G index of the response to that of a driver variable:

$$\Phi_{R/D} = \frac{G_R}{G_D}$$

(ii)

where \(G_R\) and \(G_D\) are the Gini indices for the response (N\textsubscript{2}O flux) and driving variables (NO\textsubscript{3}-N, NH\textsubscript{4}-N, and soil C). When \(\Phi_{R/D} = 1\), the relationship is described as chemostatic (Gall et al., 2013). The \(\Phi_{R/D} < 1\) represents accretion, when inequality of N\textsubscript{2}O emissions is greater than that of its biogeochemical drivers, whereas \(\Phi_{R/D} > 1\) indicates lower inequality of N\textsubscript{2}O emissions than that of its biogeochemical drivers.
4.2.7. Temporal Stability of Soil N\textsubscript{2}O Emissions and Soil Moisture

The temporal stability of the N\textsubscript{2}O flux or top 20 cm layer volumetric soil moisture (\(\theta_V\)) was evaluated using the relative difference between individual measurement at location \(i\) at time \(j\) (\(x_{ij}\)) and the watershed mean at time \(j\) (\(\bar{x}_j\)) (Vachaud et al., 1985). The relative difference (\(\alpha_{ij}\)) can be expressed as follows:

\[
\alpha_{ij} = x_{ij} - \bar{x}_j \quad \text{(iii)}
\]

\[
\bar{x}_j = \frac{1}{N} \sum_{i=1}^{N} x_{ij}
\]

where \(N\) is the number of measurement points (here 48). A temporal mean relative deviation (\(\bar{\alpha}_i\)) for each location was used to determine the temporal stability of N\textsubscript{2}O emissions and soil wetness, and expressed as:

\[
\bar{\alpha}_i = \frac{1}{m} \sum_{j=1}^{m} \alpha_{ij} \quad \text{(iv)}
\]

where \(m\) represents the number of measurement days. The \(\bar{\alpha}_i > 0\) indicates that the \(\theta_V\) or N\textsubscript{2}O emission at location \(i\) is greater than the watershed average \(\theta_V\) or N\textsubscript{2}O flux.

4.2.8. Statistical and Spatial Analysis

Treatment (vegetation) and landscape effects on hot moment’s contribution to the cumulative flux were analyzed using Analysis of Variance (ANOVA) including block, treatment, and landscape position as main effects (see chapter 3). Means were compared using Tukey-
adjusted p-values at a 5% significance level. When comparing energy crops (e.g. Miscanthus vs switchgrass), I simply used the raw measured data for each crop. To characterize the sole effect of landscape on the inequality of N₂O and CO₂ emissions, I eliminated the effect of CRP vegetation and categorized switchgrass, switchgrass-N, and Miscanthus as energy crop to represent a landscape under a uniform cover of energy crop. For each sampling day, the statistical model (described in chapter 3) predicted a flux for each measurement point, along with an intercept and estimates for each component (sources of variation) of the model. For each plot, the flux was estimated additively from the block, landscape, and energy crop effects predicted by the linear model plus the residual corresponding to this plot.

To depict the spatial patterns of top 20 cm layer soil moisture in the landscape, data from 48 monitoring points were interpolated by ordinary kriging in ArcGIS environment using Geostatistical Analyst (Johnston et al., 2001).

4.3. RESULTS

4.3.1. Inequality of N₂O Emissions

Mean daily N₂O flux was highest in the footslope positions under Miscanthus and lowest in the shoulder positions in CRP lands (mean of 100 vs. 7 g N ha⁻¹ d⁻¹, Table 4-1). The N₂O flux distribution was highly asymmetrical among the treatments and landscape positions, and CV and skewness ranging from 64 to 333% and 0.7 to 6.5, respectively. The greatest variability in temporal N₂O flux distribution was observed in the energy crop plots, especially in the footslope positions, whereas the shoulder positions showed the lowest variability. The difference between mean and median flux was greater in the footslope position. The skewness did not always vary in
proportion to the degree of variation in N$_2$O flux, whereas the inequality metrics G index was in accordance with the degree of variability or flux hierarchy (Table 4-1). For example, the mean N$_2$O flux in Miscanthus footslope position was 82 g N ha$^{-1}$ d$^{-1}$ higher than the median, with observations varying considerably (range 1 to 2247 g N ha$^{-1}$ d$^{-1}$) relative to the population mean (100 g N ha$^{-1}$ d$^{-1}$). However, the skewness of 5.7 in Miscanthus footslope is lower than that in switchgrass backslope position (skewness = 6.5), but with a degree of variation relative to the mean flux that was comparatively lower in the latter (mean 32 g N ha$^{-1}$ d$^{-1}$, range -4 to 758 g N ha$^{-1}$ d$^{-1}$). In contrast to the skewness, the G index suggests greater inequality in temporal N$_2$O emissions from Miscanthus footslope positions than from switchgrass backslope positions (G = 0.82 and 0.75, respectively); the inequality is high in both cases.

The G index showed a significant positive correlation with average N$_2$O emissions ($r^2 = 0.71$, $P < 0.001$, n = 16, Fig. 4-2). The exponential increase in N$_2$O flux with increase in G index indicates that the increase in inequality due to hot spots and hot moments increases the overall risks of N$_2$O emissions. The CV and skewness correlated poorly with average flux (Fig. 4-2).

4.3.2. Temporal Inequality of N$_2$O Emissions

The G index of N$_2$O emissions greatly varied during the growing season and was substantially higher than that of soil CO$_2$ flux or soil respiration (Fig. 4-3a). The G index increased remarkably after a storm event by a tropical hurricane during early June, which caused more than 100 mm of rain in one day. The rain event initiated the hot moment of N$_2$O emissions, which was visible as a hump that extended from June 10 to June 18 (Fig. 4-3b). However, different treatments and landscape elements responded differently to the hot moment in terms of its contribution to the cumulative N$_2$O flux (Fig. 4-3b, Table 4-2). Landscape position exerts
significant influence on the hot moment’s contribution to the cumulative flux \((P < 0.05, \text{ Table 4-2})\). The footslope positions had significantly \((P < 0.05)\) higher contribution (33\%) by the single hot moment than that in the shoulder position (14\%); however, the effect differed among the grasses and was highly variable. The contribution of the hot moment to the total growing season flux was greater in *Miscanthus* (32\%), yet it was not statistically different from other grasses. Both, the inequalities for N\(_2\)O and CO\(_2\) diminished over time (Fig. 4-3a).

### 4.3.3. Spatial Inequality of N\(_2\)O Emissions

Lorenz curves and frequency distributions of overall growing season N\(_2\)O and CO\(_2\) flux in different landscape positions are shown in Fig. 4-4. The inequality of N\(_2\)O emissions were ordered as follows: footslope \((G = 0.75) >\) backslope \((G = 0.67) >\) shoulder \((G = 0.43)\) positions (Fig. 4-4a). In the shoulder position, N\(_2\)O fluxes were concentrated in a range between -3 to 60 g N ha\(^{-1}\) d\(^{-1}\), with more than 60\% of the population in a narrow range between 0 to 10 g N ha\(^{-1}\) d\(^{-1}\) (Fig. 4-4b). This was also exhibited by the Lorenz curve for the shoulder position, which is relatively closer to the line of equality (Fig. 4-4a). In contrast, the backslope and footslope positions had a wider range of flux with an L-shaped frequency distribution (Fig. 4-4b). In the footslope positions, 97\% of the observations were within a range of 0 to 200 g N ha\(^{-1}\) d\(^{-1}\) and 75\% of the total N\(_2\)O flux is contributed by only 10\% of the observations, as represented by an inflection point at \(x \sim 0.9\) in the Lorenz curve (Fig. 4-4a). This was reflected in greater inequality of N\(_2\)O emissions from the footslope positions.

Unlike N\(_2\)O flux, the spatial inequality of CO\(_2\) flux did not differ among the landscape positions and was substantially lower than that of N\(_2\)O emissions (Fig. 4-4c). The magnitude of difference between inequality of N\(_2\)O and CO\(_2\) fluxes is greater in the footslope positions. The
frequency distribution of CO$_2$ fluxes is close to symmetrical in the shoulder and backslope position; however, the footslope had an L-shaped distribution (Fig. 4-4d), which resulted in a slightly higher inequality (G = 0.34).

4.3.4. Event-based Evolution of Inequality of N$_2$O and CO$_2$ Fluxes

Since the G index for N$_2$O flux sharply increased following a storm event (Fig. 4-3a), it was considered relevant to investigate drivers of the spatial and temporal N$_2$O and CO$_2$ fluxes in terms of inequality as well. Before the storm event (June 7), the distribution of N$_2$O fluxes was relatively homogeneous, low (mean and median 16 g N ha$^{-1}$ d$^{-1}$), and concentrated in a range between 0 and 61 g N ha$^{-1}$ d$^{-1}$. This was reflected in a Lorenz curve close to the 1:1 line associated with a low inequality index (G = 0.32) on June 7 (Fig. 4-5a, b). The distribution of soil water content was also uniform in the landscape (Fig. 4-5b), and mostly in the drier range (< 20% $\theta_v$). A similar pattern were observed for CO$_2$ flux (Fig. 4-5c, d), which had low inequality (G = 0.18). Shortly after the storm, the inequality of N$_2$O emissions roughly doubled (G = 0.70) on June 11 and the Lorenz curve greatly deviated from the line of equality, with 75% of the population only contributed 24% of the total N$_2$O flux (Fig. 4-5e). The spatial distribution of N$_2$O fluxes become relatively heterogeneous, with fluxes ranging from 1 to 1000 g N ha$^{-1}$ d$^{-1}$ and a higher mean flux (125 g N ha$^{-1}$ d$^{-1}$), which was 3.3 times higher than the median flux (38 g N ha$^{-1}$ d$^{-1}$). The inequality of CO$_2$ emissions also increased after the storm, albeit to a lesser extent than that of the N$_2$O emissions (Fig. 4-5g).

The spatial enhancement (as in N$_2$O) or suppression (as in CO$_2$) of fluxes followed the pattern of storm induced soil wetness in the landscape (Fig. 4-5f, h). The inequality of N$_2$O emissions further increased on June 14 (G = 0.82), when 90% of the population contributed 20%
of the total watershed N\textsubscript{2}O flux, whereas a few hot spots (only 10\% of the population) remained active and contributed the 80\% of the N\textsubscript{2}O flux (Fig. 4-5i, j). In contrast, the inequality in spatial distribution of CO\textsubscript{2} fluxes started to decrease on June 14 (G = 0.33) (Fig. 4-5k, l).

With respect to landscape position, the storm event caused the greatest inequality of N\textsubscript{2}O fluxes in the footslope positions (G = 0.78), whereas for vegetation type, the increase in inequality was highest (44\%) in Miscanthus (G = 0.79). The inequality of N\textsubscript{2}O fluxes in the shoulder positions remained insensitive to the effect of storm (Table 4-3). The inequality of CO\textsubscript{2} fluxes was least sensitive to the storm event, irrespective of landscape position and vegetation type.

### 4.3.5. Drivers of Inequality

The relative inequality of N\textsubscript{2}O fluxes and its related biogeochemical variables were mostly greater than 1 during the growing season, indicating greater inequality of N\textsubscript{2}O emissions than that of its controlling biogeochemical variables (Fig. 4-6a). However, relative inequality of N\textsubscript{2}O with NH\textsubscript{4} (Φ\textsubscript{N\textsubscript{2}O/NH\textsubscript{4}}) and NO\textsubscript{3} (Φ\textsubscript{N\textsubscript{2}O/NO\textsubscript{3}}) tended to approach unity during early June, after N fertilization in switchgrass-N. As shown earlier, greater inequality of N\textsubscript{2}O than that of CO\textsubscript{2} fluxes, resulted in a relative inequality of Φ\textsubscript{N\textsubscript{2}O/C0\textsubscript{2}}, that is always greater than 1. In contrast, the relative inequality of CO\textsubscript{2} fluxes and its related biogeochemical variables were much lower than that for N\textsubscript{2}O (Fig. 4-6b). The inequality of CO\textsubscript{2} fluxes was modified more by the distribution of soil inorganic N content. The soil C content had little role in shaping the distribution of the gas fluxes, even for CO\textsubscript{2} fluxes.

Due to the custom way the Lorenz curve and G are usually calculated, we were not able to calculate the inequality of soil water distribution. However, event-based inequality of N\textsubscript{2}O
emissions was related to the landscape heterogeneity of soil hydrology (Fig. 4-5). Pre-event uniform distribution of low soil moisture significantly controlled the inequality of N₂O emissions, which was low (G = 0.32) on June 7 (Fig. 4-5a). Greater wetness in the backslope and footslope positions was associated with larger N₂O fluxes, and increased the overall G index for N₂O after the storm. Similarly, suppression of CO₂ fluxes were also related with the spatial inequality of soil water distribution, homogenously distributed low fluxes in the wetter backslope and footslope positions (Fig. 4-5g, h). These findings support the hypothesis that during the period of biogeochemical homogeneity, the hydrological inequality was the most important factor influencing short-term inequality of N₂O emissions.

Although event-based inequality of soil N₂O emissions were in accordance with soil moisture heterogeneity, our analysis of temporal stability of growing season N₂O emissions and soil moisture content does not always follow the same pattern (Fig. 4-7). The hot spots, where the average temporal N₂O emissions are greater than the average landscape scale temporal emissions, were generally associated with temporal surface layer soil moisture content greater than or equal to the temporal watershed average. However, the cold spots for N₂O emissions (\( \bar{\alpha}_i \) for N₂O < 0) also exist in areas that had average temporal soil moisture content greater than the average watershed moisture content (\( \bar{\alpha}_i \) for \( \theta_V > 0 \)). The shoulder positions, where \( \bar{\alpha}_i \) for \( \theta_V \) was < 0, were always a cold spot for N₂O emissions (Fig. 4-7).
4.4. DISCUSSION

4.4.1. Lorenz Curve and Gini Coefficient in Assessing Inequality of N₂O Emissions

In this study, high inequality was associated with large average N₂O fluxes (Fig. 4-2). The often observed high spatial and temporal variation in soil N₂O emissions from the same treatment or management practice (Corre et al., 1996; Vilain et al., 2010) can be clearly represented with the G index and the Lorenz curve. These indicate that highly active times and locations contribute disproportionately to the total N₂O flux, as shown earlier (Parkin and Kaspar, 2006). This is analogous to the hydrological importance of stream flow intermittency in determining the inequality of river flow and solute loads (Jawitz and Mitchell, 2011).

In comparison, the skewness and CV provide limited information to characterize this spatial and temporal variation in N₂O emissions. For example, van Kessel et al. (1993) observed extremely high CV (339%) and skewness (5.4) for soil N₂O flux on a day with low N₂O fluxes concentrated within a narrow range (mean < 0.2 and range 0 to 5 g N ha⁻¹ d⁻¹), and comparably high CV and skewness (303% and 4.6, respectively) on a day with high emissions with greater dispersion (mean 11 and ranged from 0 to 199 g N ha⁻¹ d⁻¹). The latter case has much higher contribution from the few high emitting observations. The high degree of dispersion in the lower emission day is of little practical importance for management or monitoring purposes. This is because skewness does not address the variation in individual flux size relative to the mean flux. In a population where the difference in N₂O flux size between the largest and smallest individuals is greater, the population would have a greater hierarchy as compared to a population where the that difference is smaller. However, they both can have the same skewness. Thus, the skewness and the CV provide at best ambiguous information.
The G index and associated Lorenz curve avoid this ambiguity. The increase in the G index was only associated with the hot moments and hot spots of N₂O emissions that contributed substantially to the total flux, and therefore there is also positive relationship between G and N₂O fluxes (Table 4-2; Fig. 4-2). A positive relationship between flow and load inequality was observed by Jawitz and Mitchell (2011) while studying catchment-scale hydrologic influence on solute transport. This high inequality - high flux relationship is a characteristic of these processes, and not a generic property of the G index. For instance, the G index was inversely related with grain yield in the study by Sadras and Bongiovanni (2004). This is because all points where grain yield is measured will tend to respond to improvements in the growing conditions, and because grain yield has in relative terms a sharply defined “ceiling”. Once the yields start increasing they can only do so up to the ceiling yield. The inequality in these studies were caused by the low-yielding crops and attributed to the intraspecific competition, which facilitated more vegetative than reproductive growth for resource allocation and reduced the harvest index under stress condition (Weiner and Solbrig, 1985; Zhang et al., 1999; Pan et al., 2003).

4.4.2. Sources of Inequality: Land Conversion and Landscape Heterogeneity

Greater inequality of N₂O flux distribution in energy crops, especially in the footslope positions, can be explained by land conversion, topography and soil controlled variable hydrology, and non-linear response of N₂O emissions to hot spots and hot moments.

The higher N₂O emissions from the energy crops were attributed to increases in mineral N availability due to increased mineralization of soil organic matter following disturbance, especially in Miscanthus (see Chapter 3). Mineral N and labile C are the key ingredients for N₂O production from nitrification and denitrification (Gillam et al., 2008). Slow growth during the
spring, particularly from an initially sparse Miscanthus canopy, favors mineral N accumulation greatly increasing the risk of liquid and gaseous losses; this is in sharp contrast with the CRP (see Chapter 3). The risk is greater in seasonally wet footslope positions, where the expression of hot moment by the tropical storm during early June was greatest due to activation of the hot spots of N₂O emissions, mostly in the energy crops (Table 4-3).

This phenomenon became more prominent when the CRP and individual energy crop effect were eliminated in favor of a generic energy crop flux to represent the sole landscape effect on spatial inequality of N₂O flux distribution under a uniform cover of energy crop (Fig. 4-4a). The temporal population of N₂O fluxes from the footslope positions exhibited greater inequality due to disproportionate response of the footslope positions, acting as hot spots (Fig. 4-4a and Fig. 4-5a, d, h). The average N₂O emissions from pre to post-storm event only increased from 10 to 16 g N ha⁻¹ d⁻¹ in the shoulder positions, whereas it was 21 to 238 g N ha⁻¹ d⁻¹ in the footslope positions. The footslope positions are the sites where the hot moment facilitates the convergence of two crucial reactants for biogeochemical production of N₂O: soil saturation to limit O₂ availability in presence of available N (especially NO₃⁻), resulting in conditions that favor N₂O emissions from denitrification (Weier et al., 1993; Gillam et al., 2008). Additive effects of hot moment and hot spot on cumulative N₂O emissions from the footslope positions have been observed by Vilain et al. (2010). Furthermore, the life time of the hot moment was not evenly distributed in all the footslope positions. Few spots remained active for extended period of time and further added to the inequality (Fig. 4-5h).

In contrast, the well-drained shoulder positions were never oxygen limited (see chapter 3), a critical trigger for N₂O emissions from denitrification, other than mineral N availability
(Weier et al., 1993). The low fluxes (mean 9 g N ha\(^{-1}\) d\(^{-1}\)) were concentrated within a relatively narrow range, and resulted in lower inequality (Fig. 4-4a, b).

In contrast to N\(_2\)O fluxes, the distribution of CO\(_2\) fluxes showed greater equality due to little variation among the vegetation types and landscape positions. The storm event had little influence on the heterogeneity of CO\(_2\) flux distribution (Fig. 4-5, Table 4-3). Lower inequality is proportional to the lower degree of hierarchy in CO\(_2\) efflux, implying that the variation in individual CO\(_2\) fluxes relative to the mean flux was less than that in N\(_2\)O fluxes. It indicates that the elevation or suppression of CO\(_2\) fluxes is relatively more uniform in the landscape.

Soil respiration has been found to be positively correlated with the size of the soil C and N pools (Wan et al., 2007; Chen et al., 2010). Thus, we can expect that the spatial variation in soil CO\(_2\) flux is regulated by the spatial distribution of soil C and N (Davidson et al., 1998; Buchmann, 2000; Saiz et al., 2006). The inequality in spatial C distribution was less (\(G = 0.13\), data not shown) in the current study and most likely explains the equality in CO\(_2\) emissions.

4.4.3. Biogeochemical and Hydrological Drivers of Inequality

Greater relative inequality for N\(_2\)O emission and its biogeochemical drivers (NO\(_3\)-N, NH\(_4\)-N, soil moisture, and C content), compared with soil CO\(_2\) fluxes, indicates that soil wetness beyond a threshold triggers highly localized N\(_2\)O emissions. The variability of N\(_2\)O emissions on May 9, after a rain event, and June 18, a week after the storm, was controlled by hydrological rather than biogeochemical variability as reflected by the \(\Phi_{N_2O/NH_4}\), \(\Phi_{N_2O/NO_3}\), and \(\Phi_{N_2O/C} \gg 1\) (Fig. 4-6a). The predominance of hydrologic discontinuity was conspicuous in controlling the spatial distribution of N\(_2\)O fluxes after the storm event (Fig. 4-5e). A dry period from May 23 to June 7 brought a chemostatic behavior or a decoupling between N\(_2\)O emissions and soil mineral N.
distribution and represented by $\Phi_{N_2O/\text{NH}_3}$ and $\Phi_{N_2O/\text{NO}_3}$ approaches unity on May 28 and June 7 (Fig. 4-6a).

In contrast, hydrologic variability had little influence on relatively uniform low CO$_2$ flux distribution after the storm (Fig. 4-5g). Greater soil moisture content has been observed to suppress soil CO$_2$ efflux due to reduced O$_2$ availability for heterotrophic and autotrophic respiration (Linn and Doran, 1984; Davidson et al., 1998; Wan et al., 2007). While post-saturation pulses of CO$_2$ flux have been observed by Castellano et al. (2011), our sampling frequency was not frequent enough to capture this short-term variability (hours). The CO$_2$ emissions were in a chemostatic relationship ($\Phi \sim 1$) with soil mineral N availability throughout the growing season (Fig. 4-6b), which has also been observed by Kosugi et al. (2008). The greater relative inequality for $\Phi_{N_2O/C}$ and $\Phi_{CO_2/C}$ indicates additional influence of soil hydrology and mineral N availability on $N_2O$ and CO$_2$ flux distributions, respectively (Weier et al., 1993).

This study reinforces the crucial role of the landscape in controlling $N_2O$ flux distribution. If water and the substrates required for large $N_2O$ emission are in convergent spatial and temporal patterns, a large inequality of $N_2O$ emissions may occur. If this convergence weakens or decouples, the fluxes decrease and equality increases. This is illustrated in Fig. 4-7, where a poor relationship between the growing season temporal stability of $N_2O$ emissions and $\theta_V$ reinforces that at extended temporal-scales, the effect of the rain events on inequality of $N_2O$ emissions is attenuated by other biogeochemical and environmental factors.
4.4.4. Advantages, Limitations, and Implication of Inequality for Landscape Management and Monitoring of N$_2$O Emissions

The G index and the Lorenz curve represent with clarity the expression of hot spots and hot moments on the inequality of N$_2$O emissions. It allows comparing the inequality of two populations with different means and can be used to characterize the temporal inequality of N$_2$O fluxes with increasing, decreasing, or fluctuating trends. Similarly, the dimensionless nature of the Lorenz curve gives a visual of the fluxes distribution.

However, there are limitations of these two expressions of inequality. The G index is non-spatial and anonymous (Pringle et al., 2003; Sadras and Bongiovanni, 2004), meaning that it does not provide information about the spatial emission pattern of the individuals responsible for the large fluxes; in fact, if the individuals interchange their N$_2$O fluxes, the G index remains the same. This can be addressed by adding spatial maps of both fluxes and drivers to aid the interpretation.

Despite these limitations, the G index and Lorenz curve pair are aid to characterize the spatial and temporal inequality of N$_2$O emissions from a landscape with soil, vegetation, and hydrological heterogeneity, with multiple applications. For instance, the Lorenz curve for spatial N$_2$O flux distribution on June 14 (Fig. 4-5i) shows that 90% of the population contributes only 20% of the total flux, while the rest is contributed by the high emitting sites, representing 10% of the total population only, and can be identified from the complementary spatial map (Fig. 4-3j). It is also expected that climate change will increase the frequency of soil saturation events due to intense wetting-drying cycles (Kunkel et al., 2008). This information is important to communicate the need for landscape or site specific management that suppresses inequality, because reducing inequality of N$_2$O emissions is associated with reducing total emissions. These
management practices may include avoiding soil disturbance, site specific fertilization, and phased planting of energy crops as discussed in Chapter 3.

Another application is for designing landscape scale spatio-temporal monitoring of N$_2$O emissions with reduced number of sampling events or locations. An intensive sampling frequency is required in hot moments (storm events) and hot spots (lower landscape positions), and while it is not warranted that large fluxes will be captured, resources will not be wasted measuring locations that have low emissions and high spatial and temporal equality.

4.5. CONCLUSIONS

It has been shown that the Lorenz curve and G, focused on the variation of individual flux relative to the mean flux, can be an efficient tool for assessing the real significance of spatial and temporal heterogeneity of N$_2$O emissions. Increase in G by the hot moments and hot spots, increases the risk of N$_2$O emissions. Conversion from CRP to energy crops increased the inequality of N$_2$O emissions, especially in the wetter footslope positions, where the hot moment became hotter. The event-based short-term inequality of N$_2$O emissions was primarily driven by hydrologic heterogeneity in the landscape, given that other biogeochemical drivers, especially mineral N availability, were not limiting. However, the biogeochemical inequality drives the inequality of N$_2$O emissions under soil moisture limitation. The sites and temporal windows with greater flux inequality need to be monitored frequently, whereas infrequent sampling can be adopted when and where lower inequality exists. The joint use of the Lorenz curve, G index, and spatial maps are useful to assess the severity and the sources of inequality, which can be translated to site-specific management strategies to reduce inequality and N$_2$O emissions. This
approach may also serve in defining watershed-scale spatial and temporal monitoring of N\textsubscript{2}O emissions.
References


Table 4-1. Descriptive statistics and inequality of growing season N\textsubscript{2}O flux from CRP and energy crops under different landscape positions.

<table>
<thead>
<tr>
<th>Vegetation</th>
<th>Landscape position</th>
<th>Mean</th>
<th>Median</th>
<th>Min.</th>
<th>Max.</th>
<th>CV\textsuperscript{*}</th>
<th>Skewness</th>
<th>Gini</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRP</td>
<td>Shoulder</td>
<td>7\textdagger</td>
<td>7</td>
<td>-1</td>
<td>24</td>
<td>64</td>
<td>1.0</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>Backslope</td>
<td>15</td>
<td>10</td>
<td>0</td>
<td>150</td>
<td>150</td>
<td>4.9</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>Footslope</td>
<td>10</td>
<td>8</td>
<td>-9</td>
<td>44</td>
<td>98</td>
<td>1.3</td>
<td>0.54</td>
</tr>
<tr>
<td>Switchgrass</td>
<td>Shoulder</td>
<td>9</td>
<td>7</td>
<td>-3</td>
<td>60</td>
<td>112</td>
<td>3.3</td>
<td>0.58</td>
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<tr>
<td></td>
<td>Backslope</td>
<td>32</td>
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<td>-4</td>
<td>758</td>
<td>333</td>
<td>6.5</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>Footslope</td>
<td>33</td>
<td>14</td>
<td>0.3</td>
<td>639</td>
<td>273</td>
<td>6.3</td>
<td>0.66</td>
</tr>
<tr>
<td>Switchgrass-N</td>
<td>Shoulder</td>
<td>10</td>
<td>8</td>
<td>0.3</td>
<td>28</td>
<td>73</td>
<td>1.0</td>
<td>0.48</td>
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<td>Backslope</td>
<td>16</td>
<td>12</td>
<td>0</td>
<td>148</td>
<td>131</td>
<td>4.8</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>Footslope</td>
<td>53</td>
<td>17</td>
<td>1</td>
<td>1000</td>
<td>264</td>
<td>6.1</td>
<td>0.71</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>Shoulder</td>
<td>11</td>
<td>8</td>
<td>0.4</td>
<td>27</td>
<td>65</td>
<td>0.7</td>
<td>0.40</td>
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<tr>
<td></td>
<td>Backslope</td>
<td>18</td>
<td>9</td>
<td>0</td>
<td>147</td>
<td>167</td>
<td>3.6</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>Footslope</td>
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<td>18</td>
<td>1</td>
<td>2247</td>
<td>333</td>
<td>5.7</td>
<td>0.82</td>
</tr>
</tbody>
</table>

\textdagger The basic statistical characteristics of N\textsubscript{2}O fluxes were based on observed and untransformed data.

\textsuperscript{*}CV, Coefficient of variation
Table 4-2. Analysis of variance for significance of differences in hot moment’s contribution on the cumulative N₂O flux in different landscape positions under CRP and energy crops.

<table>
<thead>
<tr>
<th>Sources of variance</th>
<th>Df</th>
<th>MS</th>
<th>F value</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vegetation (V)</td>
<td>3</td>
<td>497.3</td>
<td>1.996</td>
<td>0.151</td>
</tr>
<tr>
<td>Block (B)</td>
<td>3</td>
<td>302.0</td>
<td>1.212</td>
<td>0.334</td>
</tr>
<tr>
<td>Landscape position (LP)</td>
<td>2</td>
<td>1708.9</td>
<td>6.86</td>
<td>0.006*</td>
</tr>
<tr>
<td>V*LP</td>
<td>6</td>
<td>399.9</td>
<td>1.605</td>
<td>0.203</td>
</tr>
<tr>
<td>B*LP</td>
<td>6</td>
<td>332.1</td>
<td>1.333</td>
<td>0.294</td>
</tr>
<tr>
<td>V*B</td>
<td>9</td>
<td>199.1</td>
<td>0.799</td>
<td>0.062</td>
</tr>
<tr>
<td>Error</td>
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<td>248.1</td>
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<td></td>
</tr>
</tbody>
</table>

% hot moment’s contribution to the cumulative N₂O flux

<table>
<thead>
<tr>
<th>Landscape position</th>
<th>CRP</th>
<th>Switchgrass</th>
<th>Switchgrass-N</th>
<th>Miscanthus</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shoulder</td>
<td>11 ± 3**</td>
<td>16 ± 10</td>
<td>17 ± 8</td>
<td>12 ± 4</td>
<td>14**</td>
</tr>
<tr>
<td>Backslope</td>
<td>26 ± 13</td>
<td>35 ± 20</td>
<td>25 ± 14</td>
<td>36 ± 11</td>
<td>31a</td>
</tr>
<tr>
<td>Footslope</td>
<td>16 ± 11</td>
<td>22 ± 34</td>
<td>46 ± 18</td>
<td>49 ± 34</td>
<td>33a</td>
</tr>
<tr>
<td>Mean</td>
<td>18a</td>
<td>24a</td>
<td>29a</td>
<td>32a</td>
<td></td>
</tr>
</tbody>
</table>

*Significant effect at P=0.05
**Mean % hot moment’s contribution ± standard deviation (n=4)
†Similar letters associated with % hot moment’s contribution by the landscape positions and treatments are not significantly different at P=0.05
Table 4-3. Decomposition in growing season inequality of soil N\textsubscript{2}O and CO\textsubscript{2} fluxes from CRP and energy crops under different landscape positions as influenced by including or not including the storm event in the analysis.

<table>
<thead>
<tr>
<th>Storm in June included</th>
<th>Overall G</th>
<th>Landscape position</th>
<th>CRP</th>
<th>Switchgrass</th>
<th>Switchgrass-N</th>
<th>Miscanthus</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrous oxide</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No*</td>
<td>0.55</td>
<td>Shoulder</td>
<td>0.38</td>
<td>0.45</td>
<td>0.41</td>
<td>0.38</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Backslope</td>
<td>0.36</td>
<td>0.55</td>
<td>0.37</td>
<td>0.40</td>
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<tr>
<td></td>
<td></td>
<td>Footslope</td>
<td>0.44</td>
<td>0.70</td>
<td>0.57</td>
<td>0.62</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Mean</td>
<td>0.40</td>
<td>0.63</td>
<td>0.51</td>
<td>0.55</td>
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<tr>
<td>Yes</td>
<td>0.72</td>
<td>Shoulder</td>
<td>0.41</td>
<td>0.58</td>
<td>0.48</td>
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<td></td>
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<td>Backslope</td>
<td>0.52</td>
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<td>0.49</td>
<td>0.58</td>
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<tr>
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<td>Footslope</td>
<td>0.54</td>
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<td>0.71</td>
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<td>0.78</td>
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<td></td>
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<td>Mean</td>
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<td>0.72</td>
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<tr>
<td>Carbon dioxide</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>No</td>
<td>0.31</td>
<td>Shoulder</td>
<td>0.27</td>
<td>0.29</td>
<td>0.26</td>
<td>0.36</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Backslope</td>
<td>0.23</td>
<td>0.27</td>
<td>0.24</td>
<td>0.41</td>
<td>0.30</td>
</tr>
<tr>
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<td>Footslope</td>
<td>0.25</td>
<td>0.25</td>
<td>0.33</td>
<td>0.38</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mean</td>
<td>0.24</td>
<td>0.27</td>
<td>0.28</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
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<td>0.32</td>
<td>Shoulder</td>
<td>0.27</td>
<td>0.28</td>
<td>0.26</td>
<td>0.34</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Backslope</td>
<td>0.23</td>
<td>0.28</td>
<td>0.25</td>
<td>0.42</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Footslope</td>
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<td>0.29</td>
<td>0.35</td>
<td>0.42</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Mean</td>
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<td>0.29</td>
<td>0.29</td>
<td>0.40</td>
<td></td>
</tr>
</tbody>
</table>

*In order to assess the effect of not including the storm event on flux inequality, I removed the consecutive two events after the storm from the analysis, June 11 and 14.
**FIGURE 4-1.** Lorenz diagram, defined as the cumulative proportion of the total N$_2$O flux plotted against the cumulative proportion of the population. The Gini coefficient, $G$, is the ratio of the area (A) between the line of equality ($y = x$) and the Lorenz curve to the total area under the line of equality ($A + B$).
Figure 4-2. Relationship between N\textsubscript{2}O emissions and scalers of inequality (Gini index) and dispersion (CV and skewness). For each N\textsubscript{2}O flux measurement day, the CRP effect was eliminated to represent the sole landscape effect under a uniform cover of an averaged energy crop (average of the three energy crops; switchgrass, switchgrass-N, and Miscanthus). Thereafter, the Gini index, coefficient of variation, and skewness were calculated for each day based on the estimated data.
Figure 4-3. Temporal inequality of (a) soil N$_2$O and CO$_2$ fluxes and (b) growing season cumulative precipitation and cumulative N$_2$O emission from CRP and energy crops under different landscape positions. The daily inequality of N$_2$O and CO$_2$ fluxes (panel a) were calculated based on the estimated data after the CRP effect was eliminated to represent the sole landscape effect under a uniform cover of an averaged energy crop.
Figure 4-4. Inequality and frequency distribution of soil N$_2$O (a, b) and CO$_2$ (c, d) flux in different landscape positions. The CRP effect was eliminated to represent the sole landscape effect under a uniform cover of an averaged energy crop (average of the three energy crops).
June 7th (Before storm)  
\( G_{\text{N}_2\text{O}} = 0.32 \)
- Mean = 16
- Min = 0.4
- Max = 61

June 11th (After storm)  
\( G_{\text{N}_2\text{O}} = 0.70 \)
- Mean = 124
- Min = 2
- Max = 1000

June 14th (After storm)  
\( G_{\text{N}_2\text{O}} = 0.82 \)
- Mean = 75
- Min = 0.3
- Max = 2246

\( G_{\text{CO}_2} = 0.18 \)
- Mean = 27
- Min = 5
- Max = 53

\( G_{\text{CO}_2} = 0.39 \)
- Mean = 26
- Min = -2
- Max = 101

\( G_{\text{CO}_2} = 0.33 \)
- Mean = 34
- Min = 5
- Max = 129

Figure 4-5. Storm event-based evolution of spatial and temporal inequality in soil \( \text{N}_2\text{O} \) and \( \text{CO}_2 \) flux in the landscape. The Lorenz curve and Gini for each day were calculated after the CRP effect was eliminated to represent the sole landscape effect under a uniform cover of an average energy crop.
Figure 4-6. Relative inequality measures for (a) N$_2$O and (b) CO$_2$ fluxes with their biogeochemical drivers. The dotted line represents unity relative inequality that occurs when the inequality of response signal is equal to inequality of driver signals.
Figure 4-7. Spatial distribution of the mean relative deviation of volumetric soil moisture content and N$_2$O emissions for each monitoring point, indicating the temporal stability of a given monitoring location relative to the overall watershed mean. Size of N$_2$O flux circle indicates the magnitude of $\bar{\alpha}_i$, with the smaller circle indicating temporally average emission from that location is closer to the average watershed flux. The grey circles represent negative $\bar{\alpha}_i$ (lower emission than the overall watershed mean, the cold spots). The red circles indicate positive $\bar{\alpha}_i$ (greater emission than the overall watershed mean, the hot spots). Likewise, towards dark brown color represents negative $\bar{\alpha}_i$ (sites drier than overall watershed mean soil moisture content in the top 20 cm layer), and towards blue color suggests positive $\bar{\alpha}_i$ (sites wetter than overall watershed mean soil moisture content).
Chapter 5

THREE DIMENSIONAL RESPONSE OF SOIL AIR CONTENT TO A SATURATING STORM TRIGGERING NITROUS OXIDE EMISSIONS IN A WATERSHED IN THE RIDGE AND VALLEY REGION

ABSTRACT

Understanding spatially variable soil wetting pattern is a prerequisite for accurate quantification of spatial variability of nitrous oxide ($\text{N}_2\text{O}$) fluxes during a hot moment like a saturating rain event, a critical trigger for $\text{N}_2\text{O}$ emissions. Soil and topographic variability within a landscape predominantly drive the soil wetting pattern, both horizontally and vertically through the soil profile, and directly influence soil aeration ($\theta_A$). Based on the statistical analysis in chapter 3, peak emissions occur when $\theta_A < 0.03$ m$^3$ m$^{-3}$ in presence available soil nitrate. This study was conducted in a typical Ridge and Valley landscape, partially converted from Conservation Reserve Program (CRP) to perennial energy crops, to determine the landscape-scale pattern of $\theta_A$ depletion during a hurricane rain event in early June of 2013. In presence of high soil nitrogen availability during early summer, the spatial pattern of $\theta_A$ depletion in the soil profile can help to understand the progression, dissipation, and persistence of the $\text{N}_2\text{O}$ emission front in the landscape. Infrequent chamber-based $\text{N}_2\text{O}$ flux monitoring and daily time-step simulation models often fail to capture these transient phenomena. Sensor-based soil moisture was monitored every half an hour in 0-20, 20-40, and 40-60 cm soil depths at each monitoring point, a total 48 monitoring points in the 5-ha watershed. The volumetric soil moisture was
converted to $\theta_A$ from soil porosity. Profile soil cores were collected from each monitoring point to characterize the soils in the landscape. Soil bulk density and volumetric rock fraction was lower in the footslope positions than the shoulder and backslope positions, while clay concentration was greater in the footslopes. The southern slope soils are rocky and coarse textured, causing faster soil drainage. Higher antecedent soil moisture content in fine textured soils in the western part of the watershed caused faster depletion of $\theta_A$, especially in the subsurface layers, which reached the critical level of $\theta_A (< 0.03 \text{ m}^3\text{ m}^{-3})$ on June 10. The progression of the $\theta_A$ depletion front was faster in the subsurface layers than the surface layer, suggesting preferential macro-pore flow. On June 11, drainage was sharp from the top 20 cm layer of shoulder and backslope positions, especially in the southern slope, while it was more gradual in the subsurface layers. As a result, ~50% of the watershed area located mostly in the footslope and backslope positions, where a coexistence of an aerobic layer on top of anoxic ($\theta_A < 0.03 \text{ m}^3\text{ m}^{-3}$) subsurface layer occurred: a critical combination for N$_2$O emissions. The measured N$_2$O fluxes on June 11 were in greater association with the spatial extent of $\theta_A < 0.03 \text{ m}^3\text{ m}^{-3}$ in the subsurface layers of footslope and backslope positions than the surface layer. Annual frequency of $\theta_A < 0.03 \text{ m}^3\text{ m}^{-3}$ also followed the same pattern as the hurricane-induced profile $\theta_A$ depletion in the landscape. These findings are important for assessing the spatial distribution and risks of high N$_2$O emissions in the landscape, and strongly suggest that land use should be landscape-driven to reduce watershed-scale N$_2$O emissions.

5.1. INTRODUCTION

Soil moisture is a critical driver of nitrous oxide (N$_2$O) emissions as it regulates the oxygen (O$_2$) supply for two major N$_2$O producing microbial processes: nitrification and
denitrification (Linn and Doran, 1984; Davidson, 1992). Nitrification dominates under aerobic soil conditions with N₂O losses considered < 1% of the total nitrogen (N) nitrified (Cochran et al., 1981). Denitrification predominates over nitrification under strictly anaerobic conditions, with losses of N₂ exceeding N₂O by a factor of 5 to 20 (Panek et al., 2000). The greater risk of N₂O emissions is associated with anoxic conditions during soil wetting triggered by rainfall or irrigation events (Mosier et al., 1986; Parkin and Kasper, 2006; Castellano et al., 2010; Halvorson and Del Grosso, 2013). Since, water infiltration, redistribution, and drainage are major drivers of diffusivity of gases and O₂ concentration in the soil atmosphere, understanding the tridimensional progression of the “water front” during events that trigger denitrification can help to manage and model N₂O emissions and other processes related to nitrogen (N) cycling.

During rain events supplying water to the soil surface, it is typically assumed that water penetrates downward in soils due to the gradient in water potential between the wet soil at the infiltration boundary and the dry interface, with water storage as the wetting front advances downward. However, the complexity of the soil pore arrangements can cause strong departures from such pattern, in particular due to the existence of preferential pathways for water flow through soil macropores. This macropore flow may cause a pattern of wetting with saturated macropores that isolates micropores and favor suboxic conditions rather than complete O₂ limitation. This is important because in suboxic environments, a small amount of O₂ can inhibit further reduction of N₂O to N₂ and as a result N₂O is emitted as the dominant product of denitrification (Cavigelli and Robertson, 2001).

In addition to the complexity of vertical water redistribution, soil and topography influence landscape-scale hydrologic processes. In the Ridge and Valley province across the Allegheny plateau in the northeastern United States, the ridge-top soils are shallow, coarse, and
rocky, and drain fast to the backslope and footslope positions via lateral subsurface flow, overland flow, and/or flow along the soil-bedrock interface (Ciolkosz et al., 1995; Lin, 2006). The footslope soils are derived from mixed colluvial sandstone and shale often associated with fragipans at shallow depth that restrict drainage (Ciolkosz et al., 1995). Restricted drainage as well as infiltration excess surface runoff and subsurface lateral flow from upslope contributing areas may cause a shallow, temporary water table in the footslope positions during rainstorm events (Buda et al., 2009).

At a landscape scale, the concept of the “wetting front”, if valid, has vertical as well as horizontal components, which can be conceptualized as a tridimensional wetting front. Spatial progression and persistence of the wetting front, both horizontally across the landscape and vertically within the soil profile, may differentially regulate the non-linear spatial behavior of N\textsubscript{2}O emissions in response to precipitation events, given the other conditions for emissions are not limiting. The zone of transition between well-drained upland and imperfectly drained near stream floodplains, as well as vertical coexistence of aerobic and anaerobic soil layers, increase the probability of hot spots formation for N\textsubscript{2}O emissions (Groffman et al., 2009). The landscape-scale studies (Pennock et al., 1992; Vilain et al., 2010), as well as earlier chapters (chapter 3 and 4) have shown that the footslope positions dominate the total emission from an area planted with energy crops. Fast wetting and draining suggest that the areas in the landscape prone to N\textsubscript{2}O emissions arrange in seemingly concentric bands centered along the watershed drainage or lower portion. These areas are like an aeration depletion front that moves upward from the footslope towards the backslope during wetting and downward towards the stream during drainage. However, apart from differences in soil hydraulic conductivity across the landscape, other controls during wetting can modify these patterns for: (1) macropore connectivity may facilitate
preferential flow towards the subsoil and can favor macropore saturation and rapid evacuation preventing the development of a clean vertical wetting front (Beven and Germann, 1982); and (2) infiltration excess runoff can move water downhill (Buda et al., 2009), but subsurface preferential flow on top of restrictive subsoil layers can also change the wetting patterns (Ciolkosz et al., 1995; Day et al., 1998).

It is well known that landscape position causes distinct spatial patterns of denitrification and N\textsubscript{2}O emissions (Pennock et al., 1992; van Kessel et al., 1993; Vilain et al., 2010). However, landscape-scale monitoring of N\textsubscript{2}O emissions are often spatially and temporally infrequent to accommodate the logistic challenge of measuring large and inhospitable areas or sampling times. Understanding the spatial and temporal behavior of soil moisture would help to approximate the spatial locations and periods of elevated risks of emissions in the landscape when other conditions are suitable.

Accordingly, my objective is to analyze the landscape-scale wetting pattern during a hurricane driven storm that saturated the lower part of a small watershed, partially converted to energy crops. As shown in previous chapters, this event triggered the largest peak of N\textsubscript{2}O emission and therefore it is important to understand the hydrologic conditions leading to that emission.

5.2. MATERIAL AND METHODS

5.2.1. Site Description

The experimental watershed, hereafter called Mattern (40°42’ N, 76°36’W), represents a topography and land use typical of the larger Ridge and Valley physiography. The watershed is
located near the town of Leck Kill in east-central Pennsylvania (PA), approximately 40 km north of Harrisburg, PA. The site has a temperate humid climate with annual mean temperature and precipitation of ~9.2° C and ~100 cm, respectively. Mattern is a small (11ha) part of a larger (726 ha) watershed (WE-38) that drains to the Mahatango Creek, a tributary of the Susquehanna River (Sharpley et al., 2008). It is part of a long-term monitoring site of the USDA-Agricultural Research Service (Sharpley et al., 2008).

The upper valley lands have rotations of soybean (*Glycine max* L.), wheat (*Triticum aestivum* L.), and corn (*Zea mays* L.). Slope ranges from 1 to 20%. The elevation above sea level varies from 267 m in the valley floor to 285 m near the summit. The soils formed in shale, siltstone, and sandstone residuum and colluvium materials and include the Albright soils in colluvial deposits and residual Berks soil series (Buda et al., 2009). The Albrights soils are distributed along the stream and valley floor and have a fragipan and argillic horizon beginning at a depth of 0.5-0.7 m (Needelman et al., 2004). Prolonged soil saturation during spring and after extensive precipitation events are common in the footslope Albright soils. Subsurface lateral water flow above the upper boundary of the fragipan dominates the saturated flow (Day et al., 1998). In contrast, the Berks soils in the shoulder and backslope positions are relatively shallow and well drained.

Due to seasonal wetness and steep slope, the lower part of Mattern (~5 ha), including its ephemeral stream in the bottom land, was retired from cropping and brought under Conservation Reserve Program (CRP) in 1999. For the purpose of this research, the CRP lands were partially converted to warm-season perennial energy crops in 2012 and 16 treatment plots, including unconverted CRP plots as controls. The four treatments were: 1) intact CRP, 2) N-fertilized switchgrass (switchgrass-N), 3) unfertilized switchgrass (switchgrass), and 4) unfertilized
Miscanthus, arranged in a randomized complete block design for a total of 16 plots (4 treatments × 4 replications). A detailed description of plot establishment and crop management has been provided in chapter 3.

5.2.2. Landscape Segmentation and Measurement of Soil Water and Aeration

Based on the increasing soil wetness from top to bottom, each plot was divided into three segments along the toposequence: shoulder, backslope, and footslope (see chapter 3). This is customary when studying topographic effects on soil N₂O emissions (e.g. Pennock et al., 1992 and Vilain et al., 2010).

Soil moisture along the hydrological flow paths was monitored every 30-min with CS-616 soil moisture sensors (Campbell Scientific Inc., Logan, UT). Within each monitoring point, we measured soil moisture at three depths: 0-20, 20-40, and 40 to 60 cm. The combination of four treatments, three landscape positions, three depths, and four replications (blocks) yielded a total of 144 soil moisture monitoring points within the 5-ha lower portion of the Mattern watershed. The sensor signals in microseconds was converted to volumetric soil water content (θᵥ, m³ m⁻³) using company provided polynomial calibration curve (Campbell Scientific Inc., Logan, UT).

The θᵥ was used to calculate the volumetric air content (θₐ) in the 0-20, 20-40 and 40-60 cm soil layers (θₐ₂₀, θₐ₄₀, and θₐ₆₀, m³ m⁻³):

\[
θₐ = θₛ - θᵥ
\]  

where, θₛ is the total porosity of a layer after correcting for rock volume (m³ m⁻³), calculated assuming a mineral particle density of 2.65 Mg m⁻³. The θₐ is more directly related to the soil aeration condition and is preferred over either θᵥ or the commonly used water filled
pored space (WFPS). The relationship between N$_2$O emissions and WFPS weakens under soil with different physical properties (texture and structural differences) (Conen et al., 2000; Castellano et al., 2010).

To install and wire the sensors to the datalogger in spring 2012, a network of ~70-cm deep trenches was made, connecting each measurement point to a datalogger. The cables from the sensor to the datalogger were installed inside PVC tubes of 10-cm in diameter that were buried in the trenches. Each datalogger controlled 4 plots, two in north and two in south slope, hence recorded measurements from 36 sensors. The clocks were synchronized with a portable computer so they measure soil moisture simultaneously. The soil moisture was measured throughout all of year 2013; however, I will focus this chapter on the event-based soil saturation by a tropical hurricane during early June.

5.2.3. Soil Sampling

A deep soil core, approximately 0.5 to 1.2 m in length, was also collected from each sampling point in spring 2012. The samples were taken with a tractor mounted Giddings probe with plastic tube liner (4.5 cm in diameter) and tip diameter of 3.8-cm. Each soil core was used for geomorphic description, to estimate bulk density, particle size distribution (USDA-pipette method; Day, 1965), and rock volume (water displacement method).

5.2.4. Data Analysis

It has been shown in chapter 3 that a regression tree predicts high risk of N$_2$O emissions when $\theta_A < 0.03$ m$^3$ m$^{-3}$, given the soil NO$_3$ availability is not a limiting factor. In this chapter, I
assumed $\theta_A$ of 0.03 m$^3$ m$^{-3}$ as a threshold below which the risk of emission increases. Half-hourly $\theta_A$ data from each sensor was checked for the frequency when $\theta_A$ was < 0.03 m$^3$ m$^{-3}$ and summed for the year 2013. The cumulative frequency (i.e. counts) of $\theta_A$ < 0.03 m$^3$ m$^{-3}$ was natural log transformed before spatial interpolation.

To depict the spatial patterns of $\theta_A$ in the landscape during wetting-drying and other soil variables, data from 48 monitoring points were interpolated by ordinary kriging in the ArcGIS environment using Geostatistical Analyst (Johnston et al., 2001). Topographic wetness index (TWI) for each monitoring point was calculated as:

$$TWI = \ln \frac{A}{\tan B}$$ (i)

where, A is the upslope contributing area (m$^2$) and B is the slope in radians.

To analyze the effect of soil texture and antecedent soil water and air content on event-based soil aeration depletion, I used the relative difference between individual measurement at location $i$ at time $j$ ($x_{ij}$) and the watershed mean at time $j$ ($\bar{x}_j$) (Vachaud et al., 1985). The relative difference ($\alpha_{ij}$) can be expressed as follows:

$$\alpha_{ij} = x_{ij} - \bar{x}_j$$ (ii)

$$\bar{x}_j = \frac{1}{N} \sum_{i=1}^{N} x_{ij}$$

where, N is the number of measurement points (here 48 for each depth). When $\alpha_{ij} > 0$, it indicates that the location $i$ has greater soil moisture/air content than the average watershed moisture/air content for that layer at time $j$. 
5.3. RESULTS

5.3.1. Spatial Distribution of Bulk Density, Volumetric Rock Fraction, and Soil Texture

Average soil bulk density was 1.18 ± 0.11, 1.46 ± 0.21, and 1.63 ± 0.23 Mg m\(^{-3}\) for the 0-20, 20-40, and 40-60 cm soil depth (Table 5-1). The northern slope had higher average bulk density than in the southern slope at all soil depths. The southeastern portion of the watershed is dominated by highly porous and rocky soils as reflected by the low bulk density in all measured depths in that part of the landscape (Fig. 5-1a, b, c). The footslope positions had lower bulk density than the backslope and shoulder positions, and the differences were more prominent in the deeper soil layers (Table 5-1). At 20-40 cm soil depth, the bulk density increased substantially in the shoulder landscape positions of the southwestern and to some extent in the northeastern landscape portions. The bulk density increased in all shoulder landscape positions at 40-60 cm layer (Fig. 5-1c).

Volumetric fraction of rock widely ranged from 0.19 to 0.62 m\(^{3}\) m\(^{-3}\). The rock volume increases with increase in soil depth (Table 5-1). The spatial distribution of rock content clearly indicates the differences in soil matrix architecture between the northern and southern slopes, as well as footslope, backslope, and shoulder positions; the latter is dominated by greater macro-pore connectivity (Fig. 5-1d, e, f).

Clay concentration ranged from 11 to 33%, and was greater in the footslope positions (Table 5-1). Higher clay concentration, in the range of 20-25%, was observed in the surface soils of northwestern, southwestern, and the footslope and backslope positions in the eastern corner (Fig. 5-1g). At 40-60 cm depth, all the footslope positions have higher clay concentration (20-25%); however, the spatial extent of this high clay band towards the upslope was greater in the
northern slope. Sand concentration ranged from 17 to 58% and followed the similar trend as in volumetric rock fraction, higher concentration in the southern shoulder positions and lower in the footslope positions (Fig. 5-1j, k, l).

5.3.2. Profile Air Dynamics during Soil Wetting and Drying

The antecedent $\theta_{A20}$ ranged from 0.09 to 0.38 m$^3$ m$^{-3}$ and more than 50% of the watershed area was in the drier range ($\theta_{A20} > 0.20$ m$^3$ m$^{-3}$, Fig. 5-2). While, the subsurface soils were typically wetter than the surface soils, the pre-event dry condition was conspicuous in the steep and rocky soils of southwestern corner. The storm event on June 10 caused abrupt changes in $\theta_A$. Variable landscape wetting in conjunction with the landscape and vertical profile soil variability differentially regulated the depletion of $\theta_A$ in space and time. The $\theta_A$ in all soil depths first reached the threshold depletion ($< 0.03$ m$^3$ m$^{-3}$) in the extreme western part of the watershed, with greater clay (Fig. 5-1g) and relatively lower antecedent $\theta_A$ (Fig. 5-2). Increasing rainfall led to the progression of the critical range of $\theta_A$ ($< 0.03$ m$^3$ m$^{-3}$) within the watershed. However, it is important to notice that the “speed of encroachment” of $\theta_A$ depletion was faster in the subsurface soil layers, especially in the 20-40 cm soil layer, indicating significant contribution of lateral flow in controlling soil aeration in this landscape. For example, during the wetting process on June 10 at 9 pm, only 39% of the watershed area was at $\theta_A < 0.03$ m$^3$ m$^{-3}$, in the top 20 cm soil layer (mean $\theta_{A20} = 0.05$ m$^3$ m$^{-3}$), whereas it was approximately 60 and 50% for 20-40 (mean $\theta_{A40} = 0.03$ m$^3$ m$^{-3}$) and 40-60 cm (mean $\theta_{A60} = 0.04$ m$^3$ m$^{-3}$) layers. On June 11, the top 20 cm soil layer produced a distinct band of $\theta_A < 0.03$ m$^3$ m$^{-3}$ concentrated along the drainage channel, mostly comprising the footslope and backslope positions, while more than 80% of the watershed area was at $\theta_A < 0.03$ m$^3$ m$^{-3}$ in the 20-40 cm layer (Fig. 5-2). The spatial pattern of $\theta_{A60}$ was in
accordance with the clay concentration at 40-60 cm depth (Fig. 5-1i). The southern slope of the watershed was at the lowest exposure to the $\theta_A < 0.03 \text{ m}^3 \text{ m}^{-3}$ during the wetting process, specifically in the top 20 cm layer where it never reached to that level of aeration limitation (Fig. 5-2).

The drainage after the cessation of rainfall was fast from the top 20 cm layer of shoulder and backslope positions, especially in the southern slopes (Fig. 5-2). On June 11 at 12 pm, twelve hours after the rainfall ceased, the average $\theta_{A20}$ reached to 0.07 m$^3$ m$^{-3}$, above the $\theta_A$ that is prone to N$_2$O emissions. The change of $\theta_A$ from anoxic to aerobic conditions was more gradual in the subsurface layers under the footslope positions. This emphasizes that even though the top 20 cm layer quickly approaches aerobic conditions after cessation of rainfall, slow subsurface drainage may cause persistent coexistence of two soil layers with distinct aeration status: an aerobic layer on top of an anoxic.

**5.3.3. Effects of the Wetting Event on Soil N$_2$O Emissions in the Landscape**

The frequency of chamber-based N$_2$O flux measurement was not as high as soil aeration measurement as shown in Figure 5-2. However, available measurements of soil N$_2$O fluxes on June 11, after cessation of rainfall, have been presented in Figure 5-3, superimposed on $\theta_A$ in three soil layers. The N$_2$O fluxes on June 11 ranged from -4 to 1000 g N ha$^{-1}$ d$^{-1}$, and larger fluxes were mostly concentrated in the footslope and backslope positions. However, the spatial extent of $\theta_A$ depletion $< 0.03 \text{ m}^3 \text{ m}^{-3}$ in the top 20 cm layer was not always associated with high N$_2$O emitting locations in the landscape (Fig. 5-3a). In contrast, $\theta_A$ in the subsurface layers (20-40 and 40-60 cm) was mostly $< 0.03 \text{ m}^3 \text{ m}^{-3}$ in the high emitting landscape positions (Fig. 5-3b,
c). This finding is in accordance with the Random Forest and regression tree analysis in chapter 3, showing greater influence of subsurface $\theta_A$ on soil $N_2O$ flux.

5.4. DISCUSSION

The observed event-based $\theta_A$ depletion front in the landscape does not follow the expected pattern: that the anoxic (low $\theta_A$) front extends from the footslope to the backslope during wetting and reverses as drainage progresses. It was not expected that the progression of the $\theta_A$ depletion font would occur from the western and northern aspects of the terrain. Moreover, the faster movement of the wetting front in the subsurface layer than that in the surface layer results in a non-uniform three dimensional soil profile of $\theta_A$, a strong evidence of lateral movement of soil water in this landscape. The soil variability modifies the redistribution of water during and after the rainfall in this landscape. A linear positive relationship was observed between antecedent soil moisture, clay concentration, and relative deviation of profile soil moisture during the wetting event (Fig. 5-4a, b, c). However, this relationship was weak between antecedent $\theta_A$, clay concentration, and relative deviation of profile $\theta_A$ (Fig. 5-4d, e, f). In general, greater antecedent water content (Fig. 5-2) in association with higher clay concentration (Fig. 5-1g, h, i) in the northwestern and western part of the landscape drove the early saturation, with soil moisture content greater than the watershed mean soil moisture content, and accelerated the $\theta_A$ depletion front. In addition, relatively greater wetness index in this part of the landscape accumulates water from a larger contributing area (Fig. 5-1m). This pattern was more obvious in the subsurface layers, where more homogeneous distribution of higher antecedent soil moisture guided the aeration depletion at a faster rate than that in the surface soils. This also explains the fact that the coarse and rocky soils in the steep southeastern slopes with lower wetness index had
lower antecedent water content and took longer time to limit soil aeration. However, the near saturating conditions lasted for a few hours, if at all, probably due to faster drainage.

Assuming a rock-free homogeneous soil with 50% of porosity, a 60 cm soil profile would require 108 mm of rainfall to saturate one pore volume. However, the actual amount would be lower and variable in the landscape due to wider variability (0.19-0.62 m$^3$ m$^{-3}$) of volumetric rock fraction in these soils. As a matter of chance, the cumulative rainfall was 108 mm on June 10. Thus, there was a good chance that this rain volume sufficed to saturate 60 cm of soil profile.

Threshold for lateral flow is reached when water input exceeds field capacity of shallow soils in sloping terrain (McNamara et al., 2005; Williams, 2005). The lateral flow and interflow from the shoulder and backslope positions intersects vertically infiltrating water in the footslope positions. The convergence of these two flow paths may develop a variable subsurface source area responsible for extended periods of aeration limitation in the lower landscape positions.

The temporal extent of exposure to N$_2$O emissions (if threshold $\theta_A$ is assumed to be 0.03 m$^3$ m$^{-3}$) varies across the landscape and within the vertical soil profile. The shoulder positions in the western and northwestern part of the landscape may be active for a short time period during wetting; however, this flux is difficult to measure with the infrequent chamber-based method or to model with daily time-step simulation models. In contrast, the southeastern aspect of the landscape has always been a risk free zone of N$_2$O emissions, even after a saturating rain event.

Once the redistribution of water reaches equilibrium following an event, soil drying is dominated by evapotranspiration, predominantly from the surface layer. Thus the surface soils become aerobic first, while the anoxic condition still prevails in the subsurface layers. Persistent wet conditions in the subsurface footslope positions could be attributed to the soil properties (finer particles in the colluvial soils) that promote water retention and extended continuity of
lateral flow routing to the lower slopes (Grayson et al., 1997; Williams et al., 2009). For example, on June 11 at 12 pm, < 10% area of the watershed was at threshold \( \theta_A < 0.03 \text{ m}^3 \text{ m}^{-3} \) in the top 20 cm layer, while > 60% of the watershed area was still at the emission prone range of \( \theta_A \) in the 20-40 cm soil layer (Fig. 5-2). Thus, approximately 50% of the watershed area was featured by two overlapping soil layers with \( \theta_A > 0.03 \text{ m}^3 \text{ m}^{-3} \) on top of anoxic (\( \theta_A < 0.03 \text{ m}^3 \text{ m}^{-3} \)) subsurface layer. The risk of N\(_2\)O emissions is lower when two vertical soil layers are saturated, restricted diffusion is most likely to further reduce N\(_2\)O to N\(_2\) (Gillam et al., 2008). In contrast, the interface of unsaturated and saturated zone often been observed to develop ecological hot spots for carbon and nitrogen cycling (Mcclain et al., 2003). The increased diffusion of O\(_2\) from the top aerobic layer to the interface of underlying anoxic layer inhibits the reduction of N\(_2\)O to N\(_2\), and N\(_2\)O is easily released through the aerobic top layer to the atmosphere. The most probable occurrence of this phenomenon can be seen as high N\(_2\)O fluxes from the footslope and backslope positions on June 11 (Fig. 5-3), when \( \theta_{A20} \) was > 0.03 m\(^3\) m\(^{-3}\), but the subsurface layers were otherwise aeration limited to promote emissions. However, due to lack of measurements on profile contribution to the total surface N\(_2\)O flux, it remains uncertain if those high fluxes were mainly contributed by the subsurface layers, but based on the observed statistical relationships between N\(_2\)O emissions and its controlling variables (see chapter 3), this is certainly a strong possibility.

The seasonal risk of variable emission prone zone was the reflection of event based pattern of aeration depletion in the landscape, and suggests similar patterns of three dimensional wetting and subsequent drying by all rainfall events (Fig. 5-5). Cumulative risks of emissions were low in the surface layer (Fig. 5-5a). Two emission prone patches in top 20 cm layer reflect the soil wetting pattern on June 11 (Fig. 5-2). The continuity of the emissions prone zone
increases with depth and usually aligned with the footslope positions; however, it can extend to the backslope and shoulder positions in the northwestern corners (Fig. 5-5b, c). This can be attributed to the conjunctive effect of greater wetness index and higher clay concentration in this part of the landscape (Fig. 5-1). It is worth noting that the extent of the emission prone zone, especially in the subsurface layers, is greater in the northern than southern slope. In addition to higher clay concentration (Fig. 5-1), greater spatial extent of Albright soils containing fragipan in the northern slope (Fig. 5-1n) might have caused greater aeration limitations than that in the well-drained southern slope. Due to the same reason, greater volume of saturation excess runoff was observed by Buda et al. (2009) in the northern footslope of the same study site. Higher cumulative frequency of $\theta_A < 0.03$ m$^3$ m$^{-3}$ in the subsurface than the surface soil layers is attributed to lateral flow and drainage limitations, resulting in prolonged risks of $\text{N}_2\text{O}$ emissions from the subsurface layers, especially in the footslope positions. Formation of perched water table in the fragipan containing footslope colluvial soils has been observed in this landscape by Buda et al. (2009) and Needelman et al. (2004) due to the convergence of infiltration water and upslope contributed lateral flow.

The data suggests that extended period of soil saturation in the subsurface layers probably caused greater risk of event-driven $\text{N}_2\text{O}$ emissions from the footslope and backslope positions, even after the top layer drains. Depletion of subsurface water by crop water uptake may help to reduce the emission risks mostly by augmenting the volume needed to saturate the soil due to earlier consumptive water use. The CRP, dominated by the cool-season grasses, can dry the soil in the early growing season (Fig. 5-6). In the summer, the opposite happens; the growth of warm-season grasses can deplete the soil of water, and delay the onset of saturation, so warm
season energy crops are not, by default, favoring N\textsubscript{2}O emission, but can do so early in the season, especially during the establishment.

5.5. CONCLUSIONS

In contrast to my expectations, the spatial pattern of soil air depletion due to wetting seems to show a macropore-controlled pattern with fast wetting in deep layers due to both infiltration, but in particular lateral flow. Porous, rocky southern slope not only drains quickly, but can contribute water to the footslope position. Convergence of vertical infiltrating water and lateral flow contributed by the upslope positions can further slow drainage of the fine textured and less rocky footslope soils frequently associated with restrictive layers in the subsoils. The data suggests that prolonged anoxia in the subsurface, rather than surface layer, has greater influence in shaping the N\textsubscript{2}O emission front, as strongly suggested by the analysis in chapter 3. It is difficult, if possible at all, to predict these patterns without prior knowledge of the soil properties across the landscape. The southeastern aspect of the landscape poses negligible risks of N\textsubscript{2}O emissions even after a saturating rain event; however, poor water retention may limit crop productivity. Furthermore, mineral N from fertilizer or mineralization of organic matter and manures can move quickly to footslope positions during fast drainage events. The implications for management are the northern slope, and not only the footslope, is more prone to N\textsubscript{2}O emission peaks. To control soil moisture and \( \theta_A \) in these landscapes, a combination of C4 and C3 species (e.g. shrub willow Salix spp. or cool season grasses), may minimize the risk of water accumulation and reduced aeration, and therefore minimize the fraction of the area prone to N\textsubscript{2}O emissions. Once again, landscape design emerges as one management option that can help
minimize the risk of N₂O emissions from the complex landscapes of the Ridge and Valley region.

References


Biogeochemical Hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. Ecosys. 6:301–312.


**TABLES**

**Table 5-1.** Soil properties under different landscape positions and soil depths in northern and southern slopes of Mattern. Each value is the mean of four replicates (n=4).

<table>
<thead>
<tr>
<th>Attributes</th>
<th>Landscape position</th>
<th>Northern slope</th>
<th>Southern slope</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0-20 cm</td>
<td>20-40 cm</td>
</tr>
<tr>
<td>Bulk density (Mg m$^{-3}$)</td>
<td>Shoulder</td>
<td>1.21</td>
<td>1.57</td>
</tr>
<tr>
<td></td>
<td>Backslope</td>
<td>1.24</td>
<td>1.51</td>
</tr>
<tr>
<td></td>
<td>Footslope</td>
<td>1.22</td>
<td>1.46</td>
</tr>
<tr>
<td>Vol. fraction rock (m$^3$ m$^{-3}$)</td>
<td>Shoulder</td>
<td>0.31</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>Backslope</td>
<td>0.28</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>Footslope</td>
<td>0.25</td>
<td>0.29</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>Shoulder</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>Backslope</td>
<td>19</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Footslope</td>
<td>21</td>
<td>22</td>
</tr>
<tr>
<td>Sand (%)</td>
<td>Shoulder</td>
<td>37</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>Backslope</td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>Footslope</td>
<td>29</td>
<td>30</td>
</tr>
</tbody>
</table>
FIGURES

0-20 cm depth

20-40 cm depth

40-60 cm depth

(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)

(i)
Figure 5-1. Spatial distribution of bulk density (a, b, c), volumetric rock fraction (d, e, f), clay (g, h, i), sand concentration (j, k, l) in 0-20, 20-40, and 40-60 cm soil layer and wetness index (m) and presence of fragic soil layer (Btx horizon) in the soil profile (n).
Figure 5-2. Landscape dynamics of soil air depletion at 0-20 cm (upper horizontal panel), 20-40 cm (middle panel), and 40-60 cm (lower panel) soil layer during an event-based wetting.
Figure 5-3. Soil $N_2O$ fluxes and soil aeration ($\theta_A$) in (a) 0-20, (b) 20-40, and (c) 40-60 cm soil depths on June 11, after the wetting event.
Figure 5-4. Relationship between clay concentration, antecedent soil moisture content (top panel)/antecedent $\theta_A$ (bottom panel), and relative deviation of soil moisture (top panel)/$\theta_A$ (bottom panel) during wetting at (a, c) 0-20, (b, d) 20-40, and (c, e) 40-60 cm soil depths under different landscape positions. Positive relative deviation indicates soil moisture/$\theta_A$ content greater than the mean watershed values.
Figure 5-5. Seasonal cumulative frequency (log-transformed) of soil air content $< 0.03 \text{ m}^3 \text{ m}^{-3}$ in (a) 0-20 cm, (b) 20-40 cm, and (c) 40-60 cm soil layer.
Figure 5-6. Seasonal dynamics volumetric soil water under CRP and energy crops. Lower amount of soil water under CRP during early season represents the early growth habit of cool-season grasses.
Chapter 6

CONCLUSIONS

6.1. Implications of Temporal and Spatial Variability of N\textsubscript{2}O Emissions

Despite the importance of nitrous oxide (N\textsubscript{2}O) emissions in determining the carbon footprint of agricultural management practices, which requires a certain level of confidence on reported annual fluxes, the magnitude of the error from a given sampling strategy is often unknown. In general and using a regular sampling scheme, increasing the sampling interval increases the estimation error. However, the increase in the error and its importance (i.e. in low or high flux environments) are greater in sites with greater temporal variability of N\textsubscript{2}O emissions. In this research these are exemplified by Ames in Iowa, and College Station in Texas (chapter 2). The practical significance of this finding is that the extrapolation of a given frequency of uniform N\textsubscript{2}O sampling may produce varying degree of accuracy in flux estimation at different locations due to soil, climate, and management driven differences in temporal flux variability. An effective sampling design should assure that the peak emission moments are sampled intensively, while allowing a lower sampling frequency in “cold moments”. However, it is difficult to predict when the peak emissions will occur.

I showed in this research that the combination of simulation model outputs and a regression tree-based statistical approach can help in designing a temporal N\textsubscript{2}O flux measurement strategy that is efficient in capturing the hot moments of emissions and provides estimates of annual fluxes of N\textsubscript{2}O with high accuracy and with a low number of samplings (chapter 2). The temporal allocation of the sampling events as predicted by this strategy
reemphasized the need to use a sampling strategy tailored to the production system; no simple strategy with a limited number of samples per year works well everywhere. The proposed sampling strategy is more beneficial in terms of both real significance of accuracy and greater saving of sampling events under sites with greater emission variability. Nonetheless, an infrequent uniform sampling can yield a reasonable estimate in sites with low temporal variability. The findings in this research have practical significance in the area of chamber-based temporal N₂O monitoring to assess the accuracy of different sampling frequency and helping in designing an efficient sampling strategy. However, validation of the accuracy of this proposed strategy requires high frequency measured chamber-based fluxes, preferably by automated chambers.

Spatial variability of N₂O emissions becomes significant under landscape-scale studies with topography, soil, and hydrological variability. Accurate estimation of N₂O flux from each spatial unit is important to achieve representative landscape-scale flux. Some spatial units, such as well-drained shoulder landscape positions in this study (chapter 3 and 4), have homogeneously distributed low fluxes even during hot moments in other landscape positions. Thus, it is not worth sampling all of the shoulder locations as it adds little to the estimation accuracy. This is analogous to investing a lot of effort when sampling cold moments. It has been shown in chapter 4 that Lorenz curve and associated Gini index can be a useful statistical tool to assess the spatial distribution inequality of N₂O fluxes and has an application on spatial and temporal flux monitoring. Both the Lorenz curve and Gini index focus on the variation in the flux size of individuals relative to the mean size of an individual and provides advantages over other indices of spatial and temporal heterogeneity such as skewness. Greater inequality in temporal N₂O fluxes from a spatial unit indicates a non-linear increase of flux during a hot
moment and emphasizes frequent sampling from that particular unit during a hot moment. Spatial inequality of N$_2$O emissions emerges when landscape redistributes water and other essential reactants such as nitrate, creating a non-uniform spatial pattern of emissions. Applications of simulation models that ignore these spatial mosaics may give biased estimation of N$_2$O flux from the landscape.

Although the dissertation presented a simulation model based approach for temporal N$_2$O sampling strategy, application of Gini index can also provide qualitative information on temporal sampling intensity required for a given scenario. For example, it has been shown in chapter 2 that the site at Pullman has little temporal flux variation. Given the custom way in which the simulation-based method works, it gives an outsized weight to relatively minor increases in emissions from the background level, suggesting intensification in the sampling frequency. However, it does not account for the relative significance of the peak’s contribution to the total flux. In contrast, it is most likely that the temporal inequality would be very small for Pullman as each temporal unit has almost similar contribution to the annual flux. Thus, only few sampling events, even fewer than that predicted by the simulation-based strategy, may produce the same level of accuracy.

6.2. CRP Transitioning to Energy Crops: Implications for Landscape Management

The land conversion of historic CRP to energy crops in marginal landscapes, as those in the northeast, requires a prudent and strategic transition to abate initial N$_2$O emissions, while assuring proper plant establishment. Chapter 3 demonstrated a large potential of former CRP lands to release reactive nitrogen following land conversion to energy crops, and to a greater extent when the land is tilled like under Miscanthus. Although not certain, a precondition for this
to occur is that the landscape was previously manured or that the CRP has a sizeable contribution of legumes. Under such conditions, the removal of the CRP vegetation and tillage cause an increase in the supply of mineral nitrogen. This fuels N₂O emissions, especially in the footslope positions where hydrologic convergence creates anoxic conditions for extended period of time. In contrast, the footslopes under CRP maintained lower emissions than that under energy crops even during a hot moment, when the conditions were otherwise suitable for emissions. These high transitional fluxes can negate carbon benefits of the energy crops and negatively impact the feedstock’s life cycle assessment and sustainability of energy crop production in these landscapes.

The present research findings have several potential implications on landscape placement of energy crops during transition to reduce N₂O emissions. Since the lower landscape positions were the hot spots of N₂O emissions from energy crops, one straightforward option is to avoid land conversion in these positions, and keep it under CRP. The drawback of this strategy is that land with high production potential, particularly in dry years, is removed from production. The well-drained shoulder and backslope positions may face greater risk of water stress during a dry year, whereas relatively wet footslope positions can maintain the productivity. Thus, higher biomass production from the footslope positions would provide greater fossil fuel offset benefits and may compensate the higher N₂O emissions from footslopes. However, biomass yields were not different in different landscape positions in the studied year, which was a wet year. To decide on the better strategy for land conversion, I suggest assessing the cost/benefit in terms of the global emission per unit of biomass production for the total area and for a short term period of 10 years (i.e. an estimated rotational cycle). To make this assessment, it is important to consider hybrid options, such as a multi-phased land transition where the shoulder and backslope
positions can be converted first, with minimum risks of increased N$_2$O emissions. After two years, when the upslope well-established energy crops can control the downhill movement of water and nitrogen, the footslope positions can be planted with energy crops. However, it can be argued that it is not known how much of the N$_2$O fluxes from the footslope positions originated from mineral nitrogen translocated from the upslope positions. Strip tilling and establishing energy crops within existing CRP can also be an option to reduce soil disturbance. In general, options that reduce nitrogen availability in excess of initial low plant demand and minimize subsequent losses require further investigation and include the use of cover crops during the establishment year.

A clear N management strategy that emerges from this research is that during the establishment years, the energy crops need to be grown without nitrogen fertilizer, and perhaps a minor level of stress might be permissible. The greater storage of soil carbon and nitrogen in the former CRP soils can mineralize enough nitrogen following disturbances, exceeding the nitrogen demand of slow growing energy crops. Furthermore, wider spacing in Miscanthus plots leaves large proportions of bare ground with abundant mineral nitrogen exposed to greater risks of N$_2$O emissions when other conditions are suitable. Thus, minimizing tillage intensity is essential; however, to date there are no available technologies for rhizome planting other than chisel plowing. One alternative of this could be mixed planting of Miscanthus with winter cover crop rye or Setaria that can cover the exposed ground and sequester soil nitrogen within plant biomass, which will be released gradually during decomposition after killing the nursing crop. Once Miscanthus is well-established, the intercrops can be herbicide killed. However, this strategy needs to be tested experimentally.
The analysis in Chapter 3 suggested that the soil aeration in the subsurface soil layers is in greater association with N₂O emissions than with the aeration of surface layers. Following up on this subject, I show in Chapter 5 that faster wetting in the subsurface than the surface layer, as well as extended periods of anoxia in the subsoil even when the top layer drains. These findings indicate preferential lateral movement of water, fueling the N₂O emissions in these landscape positions. The risk is greater in the northern than the southern slope due to differences in soils. Porous and rocky southeastern aspects of the landscape also cast risks of downhill nitrogen movement from fertilizer, manure, or organic matter mineralization through subsurface lateral flow and fuel emissions in the footslope positions. Depletion of subsurface soil water by crop uptake could help to increase soil aeration, especially early in the season when energy crops are not yet started growing, and minimize N₂O emissions. Thus, instead of a continuous cover of energy crops, a spatially variable mosaic of C3 and C4 species combination can help reduce water accumulation and minimize the N₂O emission prone area, which may ultimately help in reducing average landscape flux.

The insights from this dissertation provide foundational knowledge on the characterization of the variability of N₂O emission from energy crops and practical knowledge to manage N₂O emission in a typical Ridge and Valley landscape. This knowledge can be used to define management strategies and to set new directions for research in the controls of the landscape of both, the rate of N₂O emissions as well as the rate of emission per unit of biomass produced across the landscape. Site and time specific management of energy crops in the landscape, including different combinations of crops along slopes, aspects, and soil, emerge as a power tool to abate and perhaps eliminate the risk of N₂O emissions during the transition from CRP to energy crops in the Ridge and Valley Region and beyond.
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