ABSTRACT

NAHAS, ALBERTH CHRISTIAN. Characterization of Reactive Nitrogen Emissions from Turfgrass Systems: Emission, Emission Factor, and Modeling (Under the direction of Dr. Viney P. Aneja and Dr. John T. Walker).

Turfgrass management is characterized by intensive use of fertilizers, irrigation, and pesticides that contributes to reactive nitrogen (Nr) emissions to the atmosphere. This work aimed to estimate ammonia (NH_3), nitric oxide (NO), and nitrous oxide (N_2O) emissions from turfgrass systems by combining measurements from field experiments and simulations from a biogeochemical model. Field experiments were conducted seasonally using a dynamic flux chamber on a 50 ft by 50 ft experimental plot of tall fescue at Lake Wheeler Turfgrass Field Laboratory, Raleigh, NC. Measurements indicate a wide range of emissions for NH_3 (3.5-117.5 ng NH_3-N m^{-2} s^{-1}), NO (1.9-80.1 ng NO-N m^{-2} s^{-1}), (and N_2O (7.2-24.3 ng N_2O-N m^{-2} s^{-1}). Both NH_3 and NO emissions were higher during summer and fall, suggesting that the emissions are influenced by temperature-regulated soil processes (e.g., NH_3 volatilization and microbially-driven denitrification). N_2O emissions do not show an apparent linear relationship with temperature, but are influenced by the N-fertilizer application. Meanwhile, Nr emission factor was determined to quantify how much Nr is being loss from the system. Emission factors for NH_3, NO, and N_2O vary depending on the amount of N-fertilization application (NH_3: 0.126-0.179; NO: 0.066-0.086; and N_2O: 0.018-0.027).

The biogeochemical modeling simulations were performed using the Environmental Policy Integrated Climate (EPIC) model. The model utilized customized input files such as site information, daily weather data, soil physical and chemical characteristics, fertilizer types, and the site management options. Trace gas fluxes predicted by EPIC showed moderate to good correlation with measured fluxes (0.5-0.8) but tended to be biased low. This underestimation can

be attributed to smaller NH_4^+ and NO_3^- concentrations in soils that are simulated by EPIC. Development of different simulation scenarios is an example of how to use EPIC in addressing different management practices, which can provide a better comprehension of how Nr emissions differ under varying conditions.

Characterization of Reactive Nitrogen Emissions from Turfgrass Systems: Emission, Emission Factor, and Modeling

by
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A dissertation submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

Marine, Earth and Atmospheric Sciences

Raleigh, North Carolina
2021

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Dr. Viney P. Aneja Committee Co-chair	Dr. John T. Walker Committee Co-chair
Dr. Satya P. Arya	Dr. Fred H. Yelverton

DEDICATION

To Father and Mother.

And in living memory of D.
You will sorely be missed.

BIOGRAPHY

Alberth Nahas is a researcher at the Global Atmosphere Watch Observatory in West Sumatra, as part of the Indonesian Agency for Meteorology, Climatology and Geophysics (BMKG). He earned a master's degree in climate science from the Australian National University, Canberra, Australia, in 2014. After completing his master's degree, he returned to Indonesia and worked with BMKG for 18 months. His desire to take another break from work helped him to reach a decision to apply for Fulbright scholarship to study in the U.S. as a PhD student. In 2017, he joined Air Quality Research Group at North Carolina State University under the academic supervision of Dr. Viney P. Aneja, where he started honing his teaching and research skills both on and off campus.

His research interests include atmospheric chemistry, air quality, and climate.

ACKNOWLEDGMENTS

I thank the Center of Turfgrass Environmental Research and Education (CENTERE) at North Carolina State University for funding this project. I am also thankful to Emily Erickson, Marty Parish, and the Lake Wheeler Turfgrass Field Laboratory staff for the logistical support given during the field intensives. I acknowledge Ryan Daly, Kim Hutchinson, Chris Niewoehner, and Mark Barnes for helping me with sample collection and analysis. I am grateful to be introduced to Dr. Limei Ran, who has been tremendously helpful in providing EPIC along with the tutorials. I would like to acknowledge my committee members: Dr. Viney P. Aneja, Dr. John T. Walker, Dr. Satya P. Arya, and Dr. Fred Yelverton, the Air Quality Research Group for the support provided.

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Chapter 1: Introduction

Reactive nitrogen (Nr) is defined as biologically, chemically, and radiatively active nitrogen (N) species, and includes gaseous (e.g., ammonia (NH_3), nitric oxide (NO), nitrous oxide (N_2O)), ionic (e.g., ammonium (NH_4^+), nitrate (NO_3^-)), organic species, amines, proteins, and nucleic acids (James N Galloway et al., 2002). These species are produced as products or byproducts of five main processes in the nitrogen cycle: mineralization (ammonification and nitrification), immobilization or assimilation (NO_3^- to organic N), volatilization (NH_3), denitrification (NO, N_2O, and N_2), and N_2 fixation (Coyne & Frye, 2004). Most of these species are essential to plant growth. However, if emitted in excessive amount, Nr species may have an adverse impact to the environment. NH_3 is a precursor of ammonium aerosol ($PM_{2.5}$) and a component of reactive N deposition (Kwok et al., 2013; Y. Y. Li et al., 2016). NO is a precursor of tropospheric O_3, NO_2, and nitrate aerosol ($PM_{2.5}$) (Seinfeld & Pandis, 2016), while N_2O is a greenhouse gas and contributes to the destruction of stratospheric ozone (Ravishankara et al., 2009). Additionally, Nr species in the atmosphere can impact the climate in various ways. Both NH_3 and NO contribute to climate change indirectly by altering the net balance of atmospheric constituents (Forster et al., 2007; Myhre et al., 2013). A study by Pinder et al. (2012) on climate change impacts on the U.S. reactive nitrogen estimates indicated that it is essential to recognize the importance of Nr emissions into the atmosphere in order to effectively formulate climate change mitigation actions.

Turfgrass industry is an important part of the United States economy in general, and southeast U.S. in particular (Christians et al., 2017; Haydu et al., 2006). Although turfgrass only covers 1.9 % of land in the continental U.S. (Milesi, Running, et al., 2005), this industry is projected to grow rapidly due to strong demand for sports, residential, and commercial property development, rising affluence, and the environmental and aesthetic benefits of turfgrass in the urban landscape (Y. Qian & Follett, 2002). Turfgrass management practices also influence carbon and nitrogen sequestration in the soil (Law & Patton, 2017; Shi, Muruganandam, et al., 2006). However, maintaining the quality of turfgrass might lead to detrimental effects to the environment, particularly through several pathways of nitrogen losses to soil, water, and the atmosphere.

Turfgrass managers use nitrogen-based fertilizers intensively to enhance grass growth, color, quality, and health (Kerek et al., 2003). This practice will contribute to the release of Nr species into the atmosphere. For example, a study by Kaye et al. (2004) conducted in Fort Collins, CO, USA, showed that turfgrass accounted for up to 30 % of N_2O emissions, even though it only covers an area of 6.4%. Elsewhere, Knight et al. (2007) investigate the impacts of fertilizer as nitrogen source on NH_3 volatilization from turfgrass in Auburn, AL, USA. They found that different fertilizer treatments (i.e., type and amount) contribute to different amount of volatilized NH_3. Meanwhile, Maggiotto et al. (2000) examined at the seasonality of N_2O and NO_x emissions from turfgrass in Guelph, ON, Canada, receiving different types of nitrogen-based fertilizer. They concluded that the rates of N loss as N_2O and NO are dependent upon the weather conditions and soil water-filled pore space (WFPS) at the time of fertilizer application.

The utilization of chamber technique on determining Nr emission from turfgrass system is found to be limited, as this technique is more common to be used for other agricultural crops and soils (e.g., Aneja et al., 2006; Lam et al., 2015; Miola et al., 2015; Roelle et al., 1999). In addition, studies that utilized the chamber measurement on turfgrass systems mostly interested in quantifying N_2O emissions. Bijoor et al. (2008) studied N_2O seasonal emissions from turfgrass in Irvine, CA, USA, influenced by different temperature and fertilization treatments using a static polyvinyl chloride (PVC) chamber. A similar method was implemented by (Spence et al., 2015) in Cary, NC, USA, who examined N_2O losses from residential lawns under different management practices. Meanwhile, (Gillette et al., 2016) also conducted N_2O flux chamber measurement from a golf course fairway and rough in Fort Collins, CO, USA, applying different nitrogen fertilizers.

The primary management activities for turfgrass are fertilizer application, mowing, and irrigation. As turfgrass systems mature, adequate productivity can often be maintained with fewer inputs of N fertilizer. For instance, Qian et al. (2003) used the CENTURY biogeochemical model to show that returning grass clippings during mowing to the turfgrass system can reduce N fertilizer requirements by 25 % from 1 to 10 years after turfgrass establishment, 33 % 11 to 25 years after establishment, 50 % 25 to 50 years after establishment, and by 60 % thereafter. Kopp & Guillard (2002) showed that, for systems with clippings returned, N fertilizer rates could be reduced by 75 % or more without impacting turfgrass productivity. While these studies illustrate that reductions in N fertilizer use may be a turfgrass management option, with associated savings in cost and environmental impact to soil and water, no studies have quantitatively assessed potential emissions of NH_3, NO, and N_2O to the atmosphere, and thus their emission factors relative to activities.

Moreover, there are currently no studies in which reactive nitrogen emissions are fully speciated to concurrently examine the individual and total fluxes of NH_3, NO, and N_2O; their emissions are rather presented as total N emitted from turfgrass systems (e.g., Hamido et al., 2016; Lu et al., 2015), or as total N recovered from the removed clippings and above ground cover (e.g., Barraclough et al., 1985; Bowman et al., 2002; Bristow et al., 1987; Fagerness et al., 2004; Miltner et al., 1996; Starr & DeRoo, 2010; Wesely et al., 1987). In addition, previous studies concerning Nr emission from turfgrass were focused only on one or two species (e.g., Gu et al., 2015; Spence et al., 2015; Tidåker et al., 2017). A more comprehensive study that is looking at the emissions of both reduced and oxidized Nr species from turfgrass system has yet to be undertaken.

One of the end goals of this study is to utilize both the field experiments and modeling to examine Nr emissions from turfgrass systems. Results from the field experiment will be used as an input to the Environmental Policy Integrated Climate (EPIC), a process-based biogeochemical modeling framework that has been widely used for terrestrial ecosystem model (J. R. Williams et al., 2008), and coupled with air quality models. The improvement of the model performance, particularly for N species, are much needed to better characterize Nr emissions from turfgrass in the air quality modeling framework, which has not been attempted before.

The focus of this study is to characterize NH_3, NO, and N_2O emissions from turfgrass systems by conducting seasonal field intensives. The intensives are designed to capture the seasonality of both meteorological and soil conditions that may influence Nr emissions to the atmosphere. The N fertilizer treatments applied in this study are carried out to examine the effects of different N input to the soil, and whether this difference will contribute to Nr emission variations. In addition, the development of Nr emission factors from turfgrass system is expected from this study. This is an important output partly because currently such emission factors are unavailable, and thus the Nr emission from turfgrass systems is unaccounted for the total N budget. Another important aspect of developing Nr emission factors is to provide an input for the modeling framework of this study. The EPIC model will be utilized to spatially and temporally assess Nr emissions from turfgrass. The results could offer insights into the potential role of turfgrass on Nr emissions and help optimize the use of fertilizer for minimizing the environmental impact of emitted Nr species from turfgrass system.

1.1 The nitrogen cycle

Nitrogen (N) is one of the essential elements for all forms of life. Its triple-bonded form, N_2, is the most abundant element in the troposphere, accounting for about 79 % of the total tropospheric mass (Seinfeld & Pandis, 2016). Ironically, most of the primary producers (i.e., green plants) cannot directly use N_2 for their metabolic functions; N_2 has to be converted to other forms that are useable for the green plants and other organisms, creating a cycling process of N that flows from one Earth's reservoir to another.

Several studies have focused on the regional and global N cycle from various Earth's compartments (Galloway et al., 2004, 2008; Vitousek et al., 1997). A simplified N cycle involving the major processes in the cycle is illustrated by (Warneck, 1999) in Fig. 1.1. In principle, there are five main processes in the N cycle that determine the fate of N in the environment. These processes are mineralization (constitutes of ammonification and nitrification), immobilization or assimilation (transforms NO_3^- to organic N), volatilization (emission of NH_3 into the air), denitrification (reduces NO_3^- to NO, N_2O, and N_2), and N_2 fixation (performs by N-fixing bacteria in soils or in symbiotic link with plants (Coyne & Frye, 2004; Paul, 2014; Schlesinger & Bernhardt, 2013; Warneck, 1999).

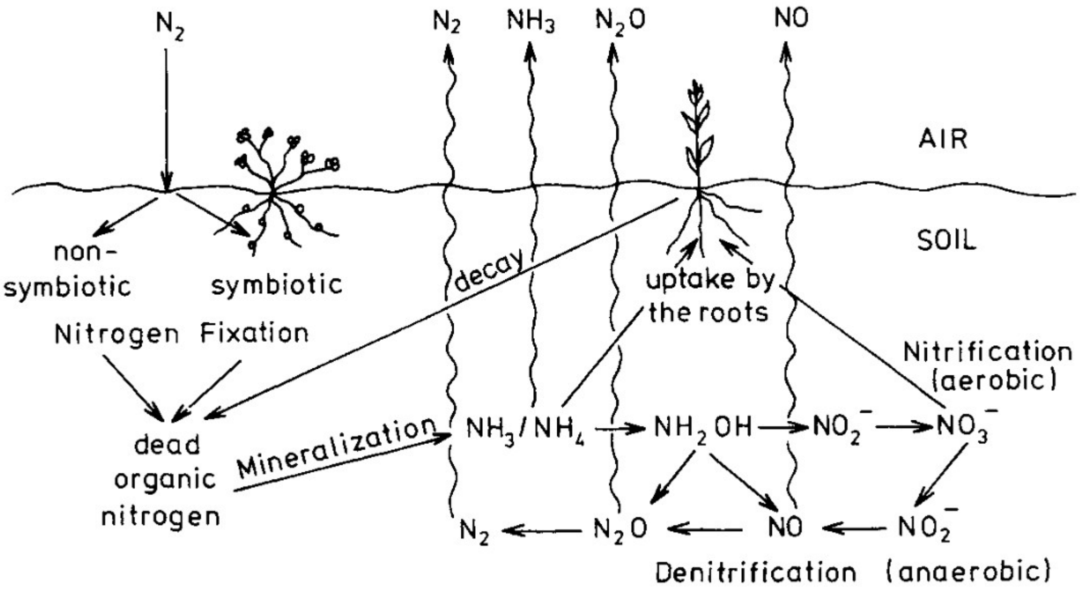

Figure 1.1: A simplified N cycle and the major processes involved in the cycle. The arrows indicate the transformation of N species following the respective processes (Warneck, 1999).

Nitrogen can be accumulated in soils from both natural and anthropogenic sources. The natural processes include N fixation through lightning (thermal fixation) and microorganisms (biological fixation), wet deposition via precipitation, and plant/animal decomposition. The anthropogenic sources come from fossil fuel combustion and organic or inorganic N amendments. As a scarce, yet essential element for organisms, it is critical for plants to uptake adequate amount of N from soils. Therefore, N amendment through fertilization is a common practice to ensure the availability of usable N for plants. As a result, large amount of N required for agricultural activities has become the main driver of N cycle (Bodirsky et al., 2012; James N. Galloway et al., 2008; J. Liu et al., 2010).

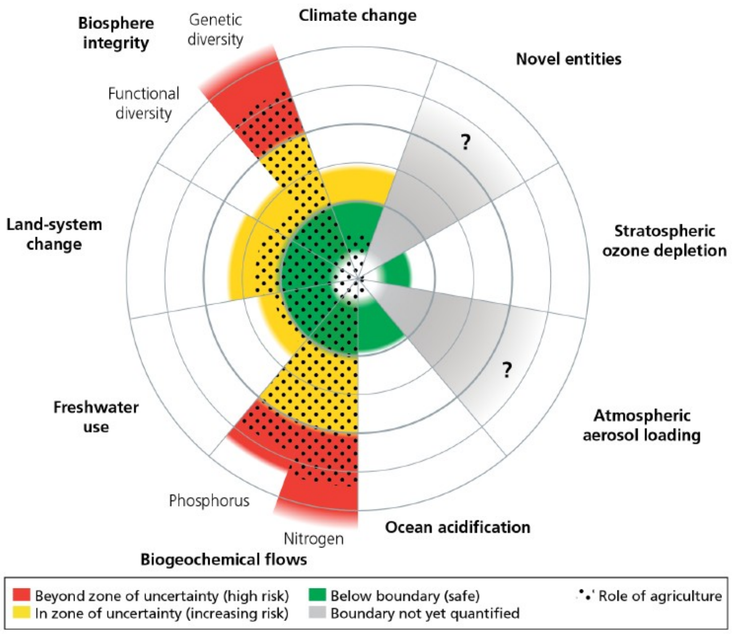

Figure 1.2: The status of nine Planetary Boundaries (PBs) as conceptualized by Rockström et al. (2009) and revised by Steffen et al. (2015). This figure is taken from Campbell et al., (2017) who introduced the contribution from agriculture on the quantification of PBs (indicated by black dots on the sectors). Nitrogen, as one of the two major biogeochemical flows is under high risk of exceeding the uncertainty zone, posing a threat to humans and environments.

Anthropogenic influences on the N cycle have been intensively studied. Swaney et al. (2012) investigated how much human-induced N inputs to watersheds and coastal areas. de Vries et al. (2013) highlighted large contributions from industrial and biological N fixation that need to be reduced in order to avoid eutrophication of aquatic environments. Battye et al. (2017) elaborated three main anthropogenic main inputs: cultivation of N fixing crops, fertilizer run-off, and air pollution deposition, which are all responsible for altering the N cycle balance. Fig. 1.2 above visualizes nine sectors of Planetary Boundaries (PBs), which if passed beyond the critical point could generate major environmental changes and may be harmful to human beings (Campbell et al., 2017). From this figure, it is perceived that the excessive amount of N is at the level where it has become a burden to environment, and agriculture is the main contributor of this condition. This may lead to profound impacts on other sectors such as atmospheric aerosol loading (i.e., formation of $PM_{2.5}$), stratospheric ozone depletion (i.e., intrusion of N_2O to the stratosphere), freshwater use (i.e., contamination of surface and ground water), and climate change.

1.2 Reactive nitrogen species

As previously defined, reactive nitrogen (Nr) species is biologically, chemically, and radiatively active nitrogen species (Galloway et al., 2002). Nr is produced through both natural and human interventions. Under natural conditions, the breaking of N_2 triple bond (i.e., N_2 fixation) requires either lightning or microbial activity. On land, the microbes are bacteria commonly residing in a symbiotic relationship with certain legumes. In the oceans, N_2 fixation is performed by cyanobacteria (Erisman et al., 2011; Galloway et al., 2002). Until the early decades of the 20th century, human interventions on the production of Nr were mainly from fossil fuel combustion and the cultivation of legumes. However, the creation of Haber-Bosch process, an NH_3 synthesis method directly from hydrogen and ammonia, amplified anthropogenic Nr contributions to the environment. In addition, increasing demands of fertilizer for agriculture to meet the food production requirement further multiplies the presence of Nr in the environment (William Battye et al., 2017)

For convenience, all N forms that are fundamental to the environment's chemical and radiative properties are collectively grouped into Nr species (Reis et al., 2009). Arguably, the most important Nr species are ammonia (NH_3), nitric oxide (NO, commonly lumped with its oxidized form NO_2 as NO_x), and nitrous oxide (N_2O). Ammonia is an important component of the global N cycle (Fowler et al., 2013), as well as a large anthropogenic source of Nr, and its emission is primarily from agricultural sources (Viney P. Aneja et al., 2009). A large loss of Nr as NH_3 is a major problem in agricultural systems, which are mainly from the use of animal manure and synthetic fertilizer (van Vuuren et al., 2011). Ammonia reacts with other atmospheric compounds and serves as a precursor of fine particulate matters ($PM_{2.5}$), which is listed as one of the six criteria pollutants by the U.S. Environmental Protection Agency. Exposed to high $PM_{2.5}$ concentration can lead to adverse health effect, even premature death (Kwok et al., 2013; Paulot et al., 2014). It can also reduce the visibility and lead to regional haze (Zhuang et al., 2014). Additionally, NH_3 can deposits on terrestrial, aquatic and marine ecosystems, and then cause ecosystem degradation (Bobbink et al., 2010). Through chemical reactions, NH_3 emission also contribute to the elevated level of N_2O emission by increasing the rate of N cycling in the natural environment (Eric A. Davidson, 2009).

Nitric oxide (NO) is one of the most important precursors of tropospheric ozone (O_3) formation. NO_2 reacts in the presence of air and sunlight to produce NO. Tropospheric ozone pollution is the one of the most significant air pollution problems in the United States, as well as in other countries (Pinder et al., 2012; Seinfeld & Pandis, 2016). It is harmful to both human health and environment. In rural environments, the reaction of NO with biogenic volatile organic compounds (VOCs) can be a predominant source of O_3. Both NO and NO_2 in troposphere can be captured by moisture in the form of nitric acid (HNO_3) to form acid rain, which directly accelerating acidification and eutrophication processes in the regional ecosystems (Fowler et al., 2013; Schlesinger & Hartley, 1992).

The largest human influence on climate since the end of the 20th century is the emission of greenhouse gases to the atmosphere. In addition to carbon dioxide (CO_2), N_2O is one of the most important greenhouse gases that has a global warming potential (GWP) of ~300 for a 100-year timescale (Myhre et al., 2013). N_2O also contributes to the destruction of O_3 in the stratosphere (Ravishankara et al., 2009). The lifetime of N_2O in the atmosphere is ~114 years, indicating its long-term influence on a planetary scale (Forster et al., 2007). Since 1978, global N_2O concentrations in the atmosphere has increased by 18%, from ~270 ppb to the present value of ~332 ppb (NOAA, 2020). This increase is primarily due to intensive human activities, particularly related to agriculture (Schlesinger & Bernhardt, 2013; Tubiello et al., 2013).

1.3 Nitrogen and turfgrass

Nitrogen is required by turfgrass for establishment, reproduction, and amino acid formation (Christians et al., 2017) . The N requirement for turfgrasses varies from one cultivar to another (Bauer et al., 2012; Bijoor et al., 2008; Carrow, 1997; H. Liu & Hull, 2006; Petrovic, 1990; Starr & DeRoo, 2010). Turfgrass management is largely controlled by the rate of N fertilizer application (Carrow, 1997; Landschoot & Waddington, 1987). In addition, N fertilizer plays an important role in maintaining shoot growth, color, quality, and health (Kerek et al., 2003). Turfgrass N uptake efficiency from soils varies from 5 % to 74 % (Petrovic, 1990). Lawn mowing is considered as a major N loss from the clipping removal. Kopp & Guillard (2002) conducted a study to evaluate clipping return to the lawn and found that returned clippings increased dry matter yield from 30% to 72 %, simultaneously improved N uptake by 28 % and increased N use efficiency by 19 %. Several factors govern the fate of N applied to turfgrass. These factors are N release rate, N source, N rate, species, cultivar, clipping management, soil texture, and irrigation (Petrovic, 1990).

Mineralization is one of the main processes involved in the N cycling in the soils (Warneck, 1999). Organic N is mineralized to NH_3 then protonated chemically to form ammonium ion (NH_4^+). Ammonium is a stable form of N in the soil, and its loss as leachate is often negligible (Behera et al., 2013; Marshall et al., 1998; Mazur & White, 2010; Paul, 2014). Ammonification in the first step of mineralization (see Fig. 1.1), and NH_3 is easily loss to the atmosphere through volatilization (Freney et al., 1983). Ammonia volatilization has been shown to be variable and is drastically reduced by watering immediately after N fertilizer application (Petrovic, 1990; Torello et al., 1983).

Ammonium can be converted into nitrate (NO_3^-) during the nitrification processes. Nitrate is highly mobile in soils and can be leached out, denitrified, and/or absorbed by the plant roots (Civeira & Lavado, 2008; Johnson et al., 2006). Nitrate may be controlled through management practices. A study by Erickson et al. (2001) found that NO_3^- leaching can be reduced by planting St. Augustine (*Stenotaphrum secumdatum*) on lawns. Guillard & Kopp (2004) investigated the potential of organic N sources on cool season turfgrasses by using three different N fertilizer types. They found that the use of Suståne®, a slow release N fertilizer, was able to minimize NO_3 leaching to near 0 %.

Nitrate can undergo denitrification through microbial processes that convert NO_3^- to N_2, with subsequent release to the atmosphere (Firestone & Davidson, 1989; Schlesinger & Bernhardt, 2013). Denitrification rate may be influenced by irrigation system (Herrmann & Cadenasso, 2017), rate of N inputs (Petrovic, 1990; Raciti, Groffman, et al., 2011), addition of organic matter (Li et al., 2013), soil moisture (Firestone & Davidson, 1989; Petrovic, 1990), and soil temperature (Bijoor et al., 2008). Nitrate may also be immobilized via microbial processes and becomes unavailable for the roots in soils. Organic matter, C:N ratio, and soil microbial biomass contribute to this process (Petrovic, 1990; Shi, et al., 2006).

1.4 The Environmental Policy Integrated Climate (EPIC) model

The EPIC model was developed in the 1980's to estimate soil erosion by water under different crop and land management practices, and was originally known as the Erosion

Productivity Impact Calculator model (Gerik et al., 2013; Williams et al., 1984). Over the years, the model has been updated and expanded to accommodate other important processes in agricultural management (Sharpley & Williams, 1990). EPIC is a process-based computational model that simulates the physicochemical processes in soils and water under agricultural management, and is designed to simulate a field, farm or small watershed that is homogenous with respect to climate, soil, landuse, and topography (Gerik et al., 2013). The model can be subdivided into nine separate components: weather, hydrology, erosion, nutrients, soil temperature, plant growth, plant environmental control, tillage, and economic budgets (J. R. Williams, 1990). The model requires knowledge or model estimates of physical properties of the ambient soil profile, weather, and crop management actions such as tillage and, if available, fertilizer application timing and amount (Cooter et al., 2010).

A number of studies have utilized the EPIC model for assessing gaseous emissions to the atmosphere by combining the model with another more sophisticated computer model (e.g., Community Multiscale Air Quality (CMAQ) model). Cooter et al. (2010) integrated the outputs from EPIC with the existing resistance-based flux model to estimate ammonium and hydrogen ion concentrations in the soil required for determining soil NH_3 flux. A study by (Cooter et al. (2012) looked at the implementation of EPIC to simulate plant demand-driven fertilizer applications to commercial croplands throughout the continental U.S. Bash et al. (2013) coupled EPIC with a regional air quality model and evaluated the bi-directional NH_3 exchange from the simulation results. Meanwhile, Rasool et al. (2016) incorporated daily year-specific fertilizer data from EPIC to replace the default annual data on CMAQ version 5.0.2 to enhance the representation of soil NO emissions. (Izaurralde et al., 2017) used EPIC to simulate the microbial denitrification process and compared the results with data from a 2-year field experiment in southwest Michigan, MI, USA, on N fertilizer rate applied to maize fields.

The utilization of EPIC for estimating Nr emissions from turfgrass has not been undertaken before. In fact, no process-based biogeochemical modeling framework has ever been used to investigate gaseous emissions from turfgrass. Given its capability to simulate the soil processes, as well as its modularity to be coupled with another, more complex computational model, EPIC could serve as a tool to complement the field experiment. Furthermore, the EPIC application for simulating Nr emissions from turfgrass is of importance to overcome the limitations of field measurements. For example, EPIC can be used to estimate the optimum fertilizer application on turfgrass by taking into account the various soil profile, meteorological parameters, and turfgrass management practices. Additionally, the outputs from EPIC will provide a spatially and temporally resolved estimate of Nr emissions to generate continental-scale Nr emissions from turfgrass systems.

1.5 Research objectives

A common practice in turfgrass management is the use of N fertilizer intensively to maintain its aesthetic values. As a consequence, accumulated N in soils may be released into the atmosphere as Nr species. In order to quantitatively determine Nr emissions from turfgrass systems, this study combines two approaches. First, this study attempts to examine Nr emissions by conducting seasonal field experiments to characterize NH_3, NO, and N_2O emissions from turfgrass systems. Results from these experiments will be used as a foundation for the second approach using a modeling framework assessing Nr emissions as the response of turfgrass receiving different management practices and under various meteorological and soil conditions.

The main research questions of this study are as follows:

1. *How much are Nr species being emitted from turfgrass systems seasonally and how much is the contribution of each Nr species to the total emission?*
2. *Does the N fertilizer have any influence on the Nr emission and is there any observable trend from these emissions with respect to the amount of N fertilizer applied?*
3. *Are there any identifiable relationships between Nr emissions and soil conditions?*
4. *What are the estimated Nr emission factors from turfgrass determined using controlled conditions?*
5. *How will Nr emissions from turfgrass change with different management practices and under various weather and soil conditions?*

Questions 1-3 were addressed by the seasonal intensives conducted in the field. The N fertilizer treatments chosen in this study followed the typical management practice at the site, and a gradual N fertilizer amount reduction was implemented to examine the response of turfgrass with respect to the change in the N input. Meteorological and soil parameters were measured during the intensives to analyze the interactions between these parameters and observed Nr emissions. Meanwhile, Question 4 was partly developed from the seasonal intensives and will be used in the modeling framework. Question 5 was exercised by running EPIC simulations with inputs from the seasonal intensives and different parameterizations within the model.

Chapter 2: Emission of reactive nitrogen from turfgrass systems using a dynamic chamber technique

2.1 Introduction

Reactive nitrogen (Nr) is defined as biologically, chemically, and radiatively active nitrogen compounds, and includes gaseous (e.g., ammonia (NH_3), nitric oxide (NO), nitrous oxide (N_2O)), ionic (e.g., ammonium (NH_4^+), nitrate (NO_3^-)), organic species, amines, proteins, and nucleic acids (Galloway et al., 2002). These compounds are produced as products or byproducts of five main processes in the nitrogen cycle: mineralization (ammonification and nitrification), immobilization or assimilation (NO_3^- to organic N), volatilization (NH_3), denitrification (NO, N_2O, and N_2), and N_2 fixation (Coyne & Frye, 2004). Most of these compounds are essential to plant growth. However, if emitted in excessive amount, Nr species may have an adverse impact to the environment. NH_3 is a precursor of ammonium aerosol ($PM_{2.5}$) and a component of reactive nitrogen deposition (Kwok et al., 2013; Li et al., 2016). NO is a precursor of tropospheric O_3, NO_2, and nitrate aerosol ($PM_{2.5}$) (Seinfeld & Pandis, 2016), while N_2O is a greenhouse gas and contributes to the destruction of stratospheric ozone (Ravishankara et al., 2009), Additionally, Nr species in the atmosphere can impact the climate in various ways. Both NH_3 and NO contribute to climate change indirectly by altering the net balance of atmospheric constituent (Forster et al., 2007; Myhre et al., 2013). A study by Pinder et al. (2012) on climate change impacts on the U.S. reactive nitrogen estimates indicated that it is essential to recognize the importance of Nr emissions into the atmosphere in order to effectively formulate climate change mitigation actions.

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Turfgrass managers use nitrogen-based fertilizers intensively to enhance grass growth, color, quality, and health (Kerek et al., 2003). This practice will contribute to the release of Nr compounds into the atmosphere. For example, a study by Kaye et al. (2004) conducted in Fort Collins, CO, USA, showed that turfgrass accounted for up to 30 % of N_2O emissions, even though it only covers an area of 6.4%. Elsewhere, Knight et al. (2007) investigate the impacts of fertilizer as nitrogen source on NH_3 volatilization from turfgrass in Auburn, AL, USA. They found that different fertilizer treatments (i.e., type and amount) contribute to different amount of volatilized NH_3. Meanwhile, Maggiotto et al. (2000) examined at the seasonality of N_2O and NO_x emissions from turfgrass in Guelph, ON, Canada, receiving different types of nitrogen-based fertilizer. They concluded that the rates of nitrogen loss as N_2O and NO are dependent upon the weather conditions and soil water-filled pore space (WFPS) at the time of fertilizer application.

The utilization of chamber technique on determining Nr emission from turfgrass system is found to be limited, as this technique is more common to be used for other agricultural crops and soils (e.g., Aneja et al., 2006; Lam et al., 2015; Miola et al., 2015; Roelle et al., 1999). In addition, studies that utilized the chamber measurement on turfgrass systems mostly interested in quantifying N_2O emissions. Bijoor et al. (2008) studied N_2O seasonal emissions from turfgrass in

Irvine, CA, USA, influenced by different temperature and fertilization treatments using a static polyvinyl chloride (PVC) chamber. A similar method was implemented by Spence et al. (2015) in Cary, NC, USA, who examined N_2O losses from residential lawns under different management practices. Meanwhile, Gillette et al. (2016) also conducted N_2O flux chamber measurement from a golf course fairway and rough in Fort Collins, CO, USA, applying different nitrogen fertilizers.

The primary management activities for turfgrass are fertilizer application, mowing, and irrigation. As turfgrass systems mature, adequate productivity can often be maintained with fewer inputs of nitrogen fertilizer. For instance, Qian et al. (2003) used the CENTURY biogeochemical model to show that returning grass clippings during mowing to the turfgrass system can reduce N fertilizer requirements by 25 % from 1 to 10 years after turfgrass establishment, 33 % 11 to 25 years after establishment, 50 % 25 to 50 years after establishment, and by 60 % thereafter. Kopp & Guillard (2002) showed that, for systems with clippings returned, N fertilizer rates could be reduced by 75 % or more without impacting turfgrass productivity. While these studies illustrate that reductions in fertilizer use may be a turfgrass management option, with associated savings in cost and environmental impact to soil and water, no studies have quantitatively assessed potential emissions of NH_3, NO, and N_2O to the atmosphere, and thus their emission factors relative to activities.

Moreover, there are currently no studies in which reactive nitrogen emissions are fully speciated to concurrently examine the individual and total fluxes of NH_3, NO, and N_2O; their emissions are rather presented as total nitrogen emitted from the turfgrass system (e.g., Hamido et al., 2016; Lu et al., 2015), or as total N recovered from the removed clippings and above ground cover (e.g., Barraclough et al., 1985; Bowman et al., 2002; Bristow et al., 1987;

Fagerness et al., 2004; Miltner et al., 1996; Starr & DeRoo, 2010; Wesely et al., 1987). In addition, previous studies concerning Nr emission from turfgrass were focused only on one or two species (Gu et al., 2015; Spence et al., 2015; Tidåker et al., 2017). A more comprehensive study that is looking at the emissions of both reduced and oxidized Nr species from turfgrass system has yet to be undertaken.

The objectives of this study were to: (i) quantify emissions of NH_3, NO, N_2O as seasonal flux from turfgrass systems; (ii) characterize relationships between flux and fertilizer application; (iii) identify interactions between emissions and the primary soil conditions that influence soil trace gas production at the biological level (e.g., soil temperature and moisture); and (iv) determine the emission factor of each reactive nitrogen species. The results can provide insights into the potential role of turfgrass on Nr emissions and help optimize the use of fertilizer for minimizing the environmental impact of emitted Nr species from turfgrass system.

2.2 Materials and Methods

2.2.1 Sampling site and periods

The sampling intensives were conducted at the Lake Wheeler Turfgrass Field Laboratory, Raleigh, NC, USA (Fig. 2.1a), utilizing a dynamic chamber system interfaced to an environmentally controlled mobile laboratory (Aneja et al., 2000). The mobile laboratory (Fig. 2.1b) houses spectroscopic analytical instruments and calibration gases. The sampling site was a 50 ft by 50 ft tall fescue (*Festuca arundinacea*) field, divided into 30 plots following a randomized complete block design. Each plot covers an area of 2.25 m^2 with a 60 cm unfertilized margin between each plot and ~3 m wide alley in the middle of the site to accommodate movement of the mobile laboratory. Within each plot, a permanent soil PVC collar was randomly inserted into the soil to a depth of ~15 cm.


(a) (b)

Figure 2.1: (a) The view from one of the fields at Lake Wheeler Turfgrass Field Laboratory; (b) Mobile laboratory (modified Ford Aerostar minivan) was parked in the middle of the sampling field. The mobile laboratory was about 100 ft away from the office, from where the electricity to power the instruments and air conditioner was supplied.

The field intensives took place during the period between February 2018 and February 2019 to capture a comprehensive seasonal analysis. Each of the intensives was conducted between 12 days and 19 days, depending on weather conditions during which the intensive was undertaken. The seasonal field intensives covering periods are as follows: (i) Spring, February 28 - March 18, 2018; (ii) Summer, May 26 - June 6, 2018; (iii) Fall, October 1 - 14, 2018; and (iv) Winter, February 3 - 13, 2019.

The plots received three different fertilizer application treatments: 0 kg N ha^{-1} (hereinafter: treatment A), 36.5 kg N ha^{-1} (treatment B), and 73 kg N ha^{-1} (treatment C). A 25 % (w/w) N fertilizer (2.3 % ammoniacal N, 22.7 % urea, polyon fertilizer, Harrell's) was used for these treatments. During the intensives, the plots were only fertilized at the beginning of Spring and Fall intensives. Fertilizer was not applied during Summer and Winter. Treatment A may be referred to as the management goal, which is no N fertilizer input to the turfgrass system, minimizing Nr emissions while maintaining the growth (Petrovic, 1990; Qian et al., 2003).

Treatment B is considered as the gradual N fertilizer reduction to examine the effects of fertilizer application at a lesser amount to the turfgrass system. Treatment C reflects the fertilizer application for this site (i.e., 1.5 lbs N per 1000 ft^2), which follows the typical fertilizer application practiced by the caretaker of the site. The plots were not irrigated when the intensives were conducted. The experimental design of the field site is shown in Fig. 2.2.

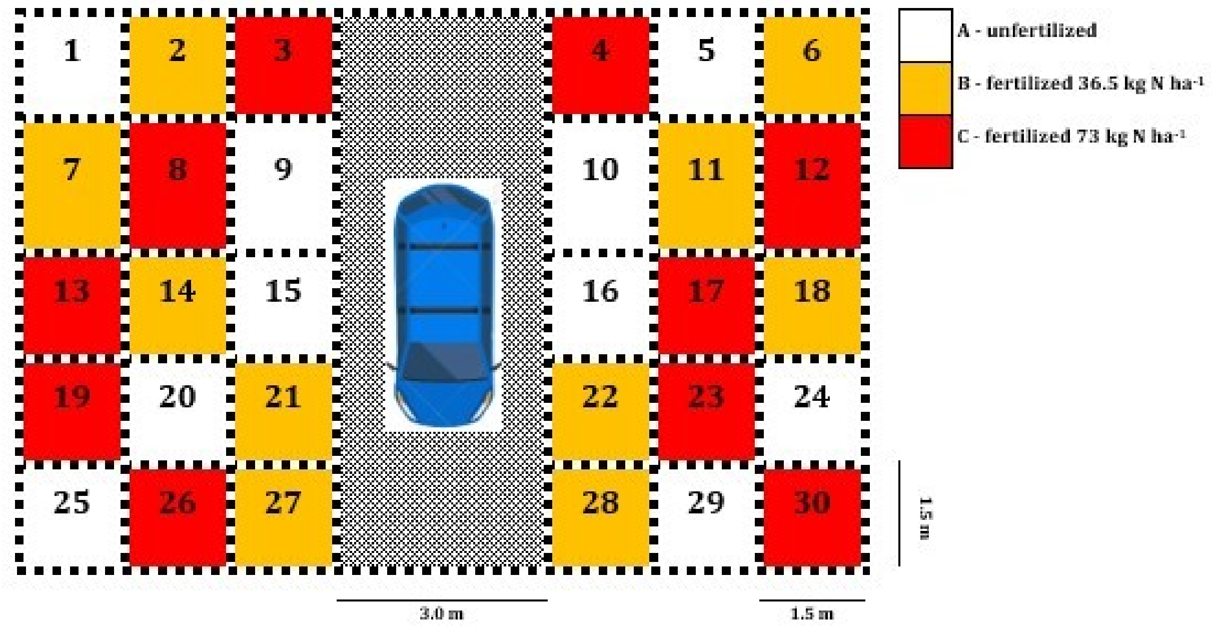


Figure 2.2: Field design showing individual plots (numbered 1-30) with their respective, color-coded fertilization treatments.

2.2.2 Measurements of NH_3, NO, and N_2O

The mobile laboratory was parked at the sampling site to house all instruments, the datalogger (Series CR800, Campbell Scientific, Logan, UT, USA). Two compressed NIST-traceable gas calibration standards (10.04 ppm NO and 10.27 ppm NH_3, both balanced in N_2, Airgas, Raleigh, NC, USA), and two zero-grade air cylinders (Airgas, Raleigh, NC, USA). During the measurement, the dynamic chamber (FEP Teflon-lined, open- bottom white PVC cylinder) was placed on the turfgrass plot and was attached to an air-tight sealed soil collar (Fig.

2.3). Zero air was continuously supplied into the chamber at a constant rate of 1.2 L min^{-1} to flush the ambient air from the chamber and to ensure the instrument only analyzed Nr emissions from turfgrass. The chamber was immediately adjacent to the NH_3 converter to minimize NH_3 loss from the measurement. The air volume inside the chamber was kept constant (~3900 cm^3) to maintain the consistency of measurement. The residence time inside the chamber is ~3.25 minutes. Additionally, the turfgrass inside the chamber was clipped so that its height was at the same level as the soil collar. The clipped turfgrass was removed from the chamber to avoid unintended additional Nr emissions to the chamber (Kopp & Guillard, 2002).

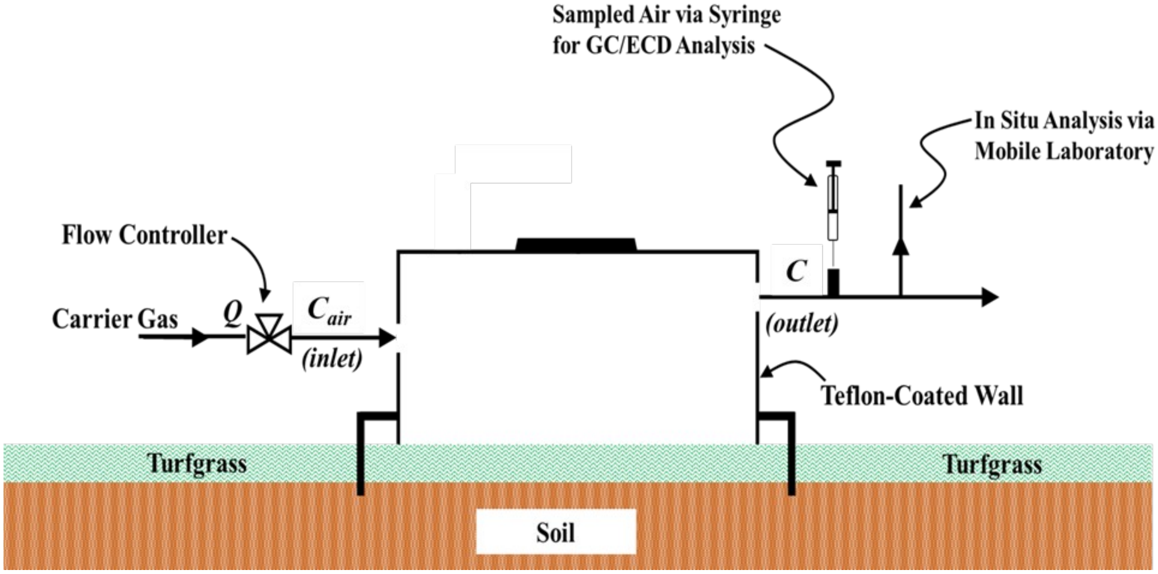


Figure 2.3: Schematic of a dynamic flow through chamber.

The NH_3 and NO concentrations inside the chamber were measured in near real time using a chemiluminescence-based analyzer that converts NH_3 to NO by a heated (up to 825 °C) stainless steel catalyst (Thermo Environmental Instruments Model 17C NH_3, NO, and NO_2 Analyzer, Thermo Fisher Scientific, Waltham, MA, USA). The concentration data analyzed by the analyzer were stored in the datalogger. Concentrations from each plot were measured for approximately 68 minutes. The first eight minutes of the measurement were intended to equilibrate the air inside the chamber, ensuring the ambient air was flushed out by zero air. Thus, the data for this period were omitted and an interval of one hour was used for further analysis.

To ensure the quality of measurements, accuracy and precision tasks were performed to the analyzer. A multi-point calibration against an NO standard gas was conducted at the beginning of each sampling. The acceptance criteria for accuracy and precision from the calibrations were 10 % and 5 %, respectively. Some corrective measures were undertaken following the failure of meeting the criteria. Such measures were examining the flow rate and possible leakage within the analyzer or in the chamber, and cleaning the reaction cell. A similar calibration approach was also used for NH_3. However, due to logistical issue with the calibration procedures, the multipoint calibrations were performed less frequently. During the field intensives, zero and span checks were conducted at the beginning of each daily measurement. A 10 % accuracy criterion was applied for both checks and corrective actions were carried out if this criterion was not fulfilled.

Meanwhile, 20 ml of the chamber outlet air was collected in pre-evacuated glass vials (Labco, Ceredigion, UK) for N_2O analysis in the laboratory at the U.S. EPA (Research Triangle Park, NC, USA). The air samples for N_2O concentrations (and subsequent emission analysis) were collected at 20th, 40th, and 60th minutes during the 1-hour chamber measurement interval. The N_2O concentrations were measured by using a gas chromatography (SRI Model 8610C, Torrance, CA, USA) equipped with an electron capture detector (GC-ECD). The GC-ECD was calibrated following a five-point standard curve method. A gas dilution system (Thermo Environmental Instruments Model 146 Dynamic Gas Calibration Unit, Thermo Fisher Scientific, Waltham, MA, USA) was used to dilute 19.8 ppm N_2O with compressed zero air to a range of 26 to 497 ppb N_2O. Check standards were analyzed after a batch of 10 samples to assess the stability of the calibration curve. An accuracy of 10 % was applied for assessing the curve.

2.2.3 Soil and meteorological parameters

Soil and meteorological parameters are continuously monitored at Lake Wheeler Rd Field Lab, located approx. 0.6 mi from the field site as part of the North Carolina Environment and Climate Observing Network (NC ECONet) maintained by the State Climate Office of North Carolina. The NC ECONet combines sensors from several networks into a single comprehensive database. Parameters include air temperature, humidity, winds, precipitation, pressure, solar radiation, soil temperature, and soil moisture. In addition to the continuous measurements, several parameters were instantaneously measured during the chamber measurement. Air temperature, pressure, wind speed, and wind direction were recorded at the beginning of each sampling using a handheld weather and wind speed meters (Kestrel series 5500, Boothwyn, PA, USA). Meanwhile, soil temperature (Model Acorn Temp 6 RTD probe, Oakton Instruments, Vernon Hills, IL, USA) and soil volumetric water content (Model CS620 probe, Campbell Scientific, Logan, UT, USA) were measured every 30-minute measurement interval by inserting the probes into the soil adjacent to the chamber at a 10-cm depth.

2.2.4 Soil sampling

Soil sampling was conducted twice during the field intensive period. The first soil sampling on July 2, 2018 was intended to collect samples for analyzing the soil chemical properties. A more comprehensive sampling was conducted on March 15, 2019 to provide samples for both chemical and physical analyses of the soil. For the soil chemistry analysis, a total of 18 samples (i.e., six samples from each fertilizer treatment) were collected from the site. Soil samples were collected by using a tubular soil core sampler and covered the depth from 0 cm to 10 cm. Each sample was sectioned into two soil depths, 0-5 cm and 5-10 cm, was stored and labelled into separate bags. The collected soil samples were sieved to remove visible roots and plant residues and were extracted in 1 M KCl solution before further analyzed at the Environmental and Agricultural Testing Service at North Carolina State University (Raleigh, NC, USA). The analyzed parameters for these samples were soil pH, soil moisture content, soil organic matter (SOM), cation exchange capacity (CEC), total extractable N (as NH_4^+ and NO_3^- ions), and total P.

For the soil physical analysis, six soil samples from three randomly selected plots were collected using a soil bulk density sampler. Three samples contained soil collected from surface to 3-in depth, while three others were for soil from 3-in to 6-in depth. After carefully stored and labeled, samples were then sent to the Soil Physical Properties Laboratory at North Carolina State University (Raleigh, NC, USA) for further soil physical analysis. The soil physical analysis included particle density, saturated hydraulic conductivity, bulk density, water retention (low and high pressures), and wilting point.

2.2.5 Emission factors of Nr species

Emission factors (EFs) of Nr species from this study were determined by first calculating the seasonal emission of each species. The seasonal emission took into account the measured Nr flux from the field intensive and was calculated using Eq. (2.1) below:

$$Seasonal\,Nr\,Emission = \frac{ng\,N}{m^2 \cdot s} \times \frac{kg}{10^{12}\,ng} \times \frac{10^4\,m^2}{ha} \times \frac{(60 \times 60 \times 24 \times 90)\,s}{season} \tag{2.1}$$

In Eq. (1) the number of days in each season is assumed to be 90 days and the seasonal emission is expressed as kg N ha^{-1} $season^{-1}$. The total emission for the entire four seasons or the total annual emission of Nr species is mathematically expressed as Eq. (2.2):

$$Annual\,Nr\ emission = Spring\,emission + Summer\ emission + Fall\,emission + Winter\ emission \quad (2.2)$$

EF calculations were based on the ratio between the amount of annual Nr emission and the total annual N fertilizer application (Eq. (2.3)), and are expressed as kg N kg^{-1} N fertilizer.

$$EF = \frac{Annual\,Nr\ emission}{Annual\ N\,fertilizer\ applied} \quad (2.3)$$

Since this study used two different N fertilizer applications (treatment B and treatment C) during the field intensives, EFs of each Nr species were determined separately for both treatments.

2.3 Results and Discussion

2.3.1 Meteorological and soil conditions

2.3.1.1 Air and soil temperatures

The 2-m air temperature daily average from all intensive and their respective 30-year averages (climatology) are depicted in Fig. 2.4a, 2.4c, 2.4e, and 2.4g. The air temperature ranges during each intensive are as follows: Spring, 2.3 °C - 13.7 °C (average: 7.4 °C); Summer, 22.3 °C - 26.8 °C (24.2 °C); Fall, 14.1 °C - 25.6 °C (21.7 °C); and Winter, 2.6 °C - 20.5 °C (10.9 °C). From these temperature ranges, it is shown that the air temperatures during the Spring intensive were lower than those during the Winter intensive. This can be reflective of the fact that the air temperatures during the Spring intensive were lower than the climatology by ~3 °C on average, while in Winter the air temperatures were approximately 5 °C higher than the climatology. Another warmer sampling condition that the climatology also occurred during the Fall intensive, where the air temperatures were about 4 °C higher than the climatology. It was only during the Summer intensive where the air temperatures were close to the climatology.

The 0.1-m depth soil temperature daily average, shown in Fig. 2.4b, 2.4d, 2.4f, and 2.4h, indicates persistent warmer conditions during Summer, Fall, and Winter. During these seasons, soil temperatures were above the climatology. In contrast, the soil temperature trend for Spring was dominated by lower than the climatology conditions. The disparity of these temperature patterns, particularly when most of the intensive conditions were warmer than the typical condition, may influence the N losses from the microbial-driven chemical reactions taken place in soil (i.e., nitrification and denitrification), where soil temperature plays a role in affecting the reaction rates of cells (Bremer, 2006; Maggiotto et al., 2000; Petrovic, 1990; Raciti et al., 2011).

The diurnal trends of 2-m air temperature and 0.1-m soil temperature for each intensive are graphically represented in Fig. 2.5. The minimum and maximum temperatures are typically occurred at 6-7 AM and 2-3 PM, respectively. The dynamic chamber measurements were only performed during daytime, typically from 8 AM to 5 PM. During this time window, the surface heating took place and reached the maximum in the afternoon, followed by the heat loss from the surface in the evening. Concurrently, the air humidity during daytime usually drops between morning and early afternoon, and increases back in the late afternoon and evening.

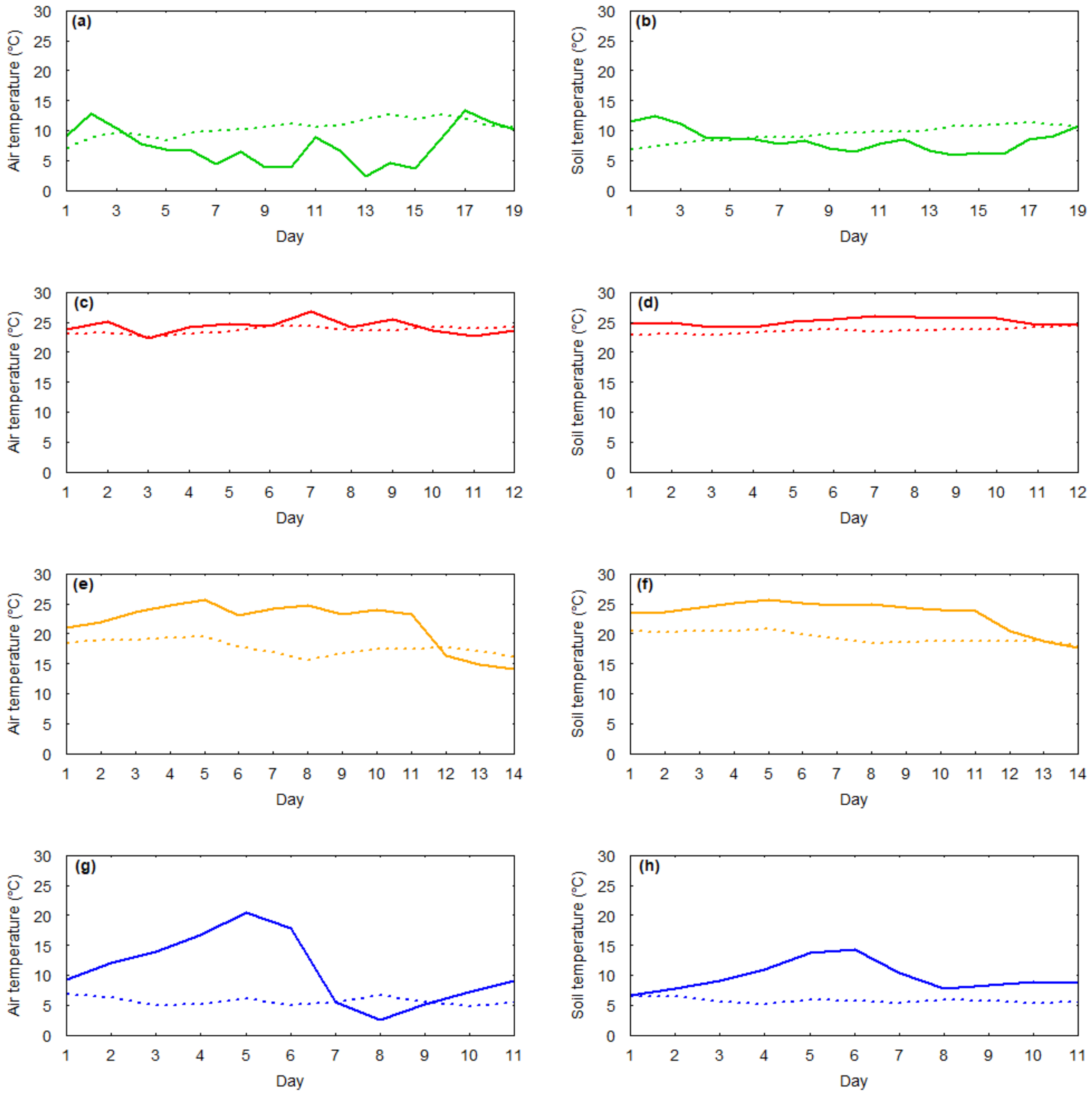


Figure 2.4: Daily average of 2-m air temperature and 0.1-m depth soil temperature for all field intensives. The number of days for each intensive on the x-axes follows the number of days in which the measurement was conducted. The solid lines represent the measured temperatures while the dashed lines indicate the 30-year average of daily average temperature respective to each date at which the field intensive was conducted. The lines are color-coded according to the respective season. Green is for Spring, red for Summer, orange for Fall, and blue for Winter.

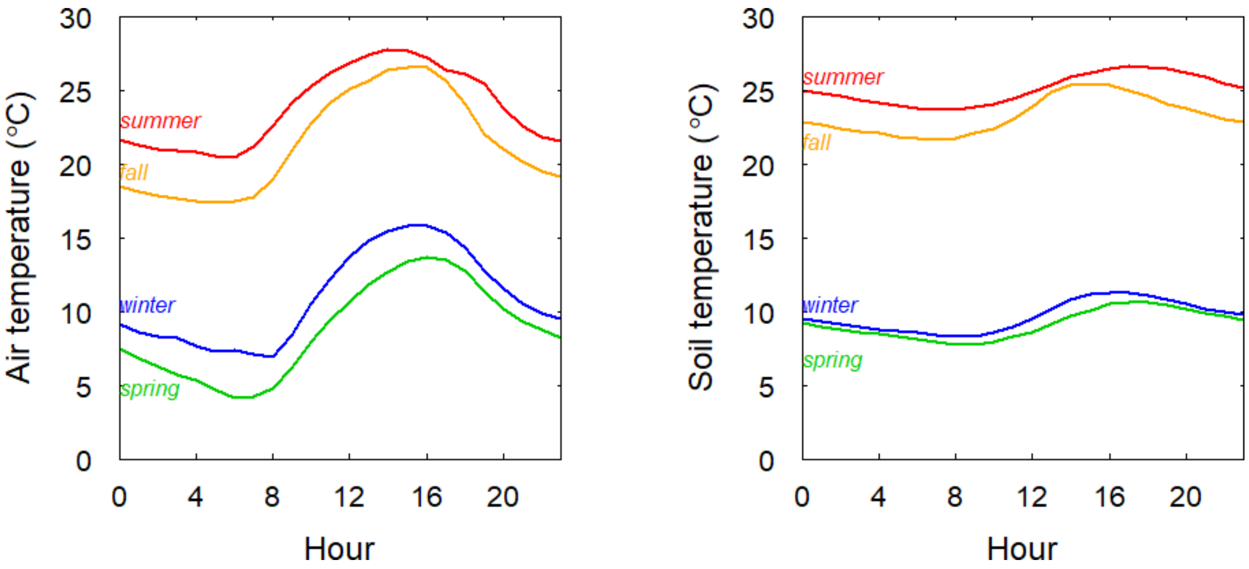


Figure 2.5: Diurnal 2-m air temperature (left) and 0.1-m soil temperature (right) for each intensive. Data are taken from NC ECONet (State Climate Office of NC). The hourly data were averaged for the entire covering period of each intensive.

2.3.1.2 Precipitation

Figure 2.6 shows the accumulation of precipitation during each of the intensives, measured in mm. With the exception of Fall, all seasonal intensives observed a lesser amount of precipitation when compared with the climatology. The reduction of precipitation during these periods are between 10 % and 45 % less than the 30-year average. On the contrary, total precipitation in Fall was more than three times higher than the climatology. Such a large addition of precipitation came from Hurricane Michael that crossed over the field as a tropical storm on October 11, 2018. The one-day precipitation during this extreme weather event accounted for 91 % of total precipitation measured over the entire Fall intensive.

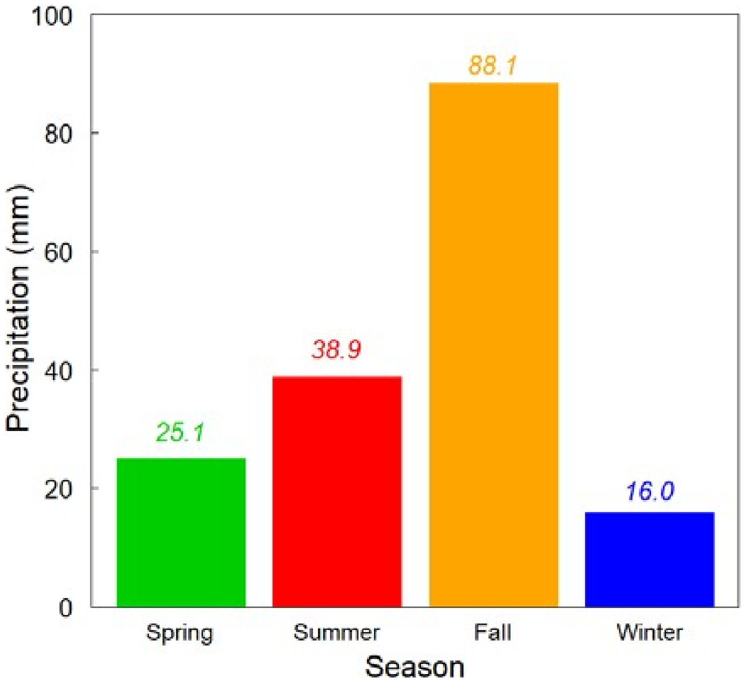


Figure 2.6: Total precipitation during each of the intensive measured in mm. The 30-year averages of each season are as follows: Spring, 46.2 mm; Summer, 43.7 mm; Fall, 25.8 mm; and Winter, 22.9 mm. During the course of conducted field intensives, only precipitation in Fall that exceeded the 30-year average.

2.3.1.3 Soil physics and chemistry

The summary of soil physical characteristics is presented in Table 2.1. Under the USDA soil texture classification, the soil is categorized as sandy loam. The average bulk densities of the soil are 1.12 g cm^{-3} for the 0-3 in layer and 1.59 g cm^{-3} for the 3-6 in layer. The later soil depth is denser due to higher clay composition in the soil. The saturated hydraulic conductivity, water retention, and wilting point are typically higher in the 0-3 in layer than those in the 3-6 in layer, all indicating less dense soils near the surface.

Meanwhile, Table 2.2 shows the chemical properties of the soil from where the Nr emissions from turfgrass were measured. From the chemical analysis, the differences between the two soil layers are apparent. For instance, the 0-5 cm soil layer is slightly less acidic than the layer below. Meanwhile soil water content, soil organic matter, NH_4^+, and NO_3^- measured in the first 5 cm are higher than the next 5 cm. These high chemical compositions can be attributed to high root biomass concentration in the near surface soil, though tall fescue has the potential of deep root systems (Fu et al., 2007; Raciti et al., 2011).

Table 2.1: Analysis of soil physical property taken from two soil depths. Numbers in the bracket indicate the average value of each soil property.

Soil physical property	Soil depth	
	0-3 in	3-6 in
Sand (%)	71.1-71.8 (71.4)	69.4-71.9 (70.8)
Silt (%)	18.7-21.1 (20.1)	16.2-21.4 (18.4)
Clay (%)	7.8-9.5 (8.5)	9.2-11.8 (10.8)
K_{sat} (cm h^{-1})	2.65-38.49 (22.90)	1.22-6.00 (2.83)
Bulk density (g cm^{-3})	1.09-1.15 (1.13)	1.53-1.68 (1.59)
Volumetric water content		
0.10 bar	0.366-0.434 (0.405)	0.244-0.295 (0.263)
0.33 bar	0.320-0.391 (0.363)	0.204-0.252 (0.222)
Gravimetric water content (g g^{-1} soil)		
15 bars	0.084-0.127 (0.105)	0.055-0.065 (0.059)

Table 2.2: Analysis of soil chemical property taken from two soil depths with three N-fertilizer treatments A, B, and C on July 2, 2018 (Soil Sampling I) and on March 15, 2019 (Soil Sampling II). Numbers in brackets indicate the average value of each soil property. Ammonium (NH_4^+) and nitrate (NO_3^-) ions are expressed in their respective soil dry weights.

Soil chemical property	Soil depth 0-5 cm			Soil depth 5-10 cm		
	A	B	C	A	B	C
			Soil Sampling I (Summer 2018)			
pH						
H_2O	5.62-6.34 (6.02)	5.31-6.04 (5.80)	5.19-6.06 (5.75)	5.50-6.01 (5.79)	5.27-5.98 (5.68)	5.12-5.98 (5.63)
$CaCl_2$	4.79-5.46 (5.09)	4.60-5.21 (4.98)	4.49-5.52 (5.00)	4.57-5.19 (4.93)	4.60-5.07 (4.86)	4.39-5.08 (4.81)
Soil moisture content (%)	19.7-32.5 (27.0)	18.7-62.2 (30.6)	14.8-37.5 (27.4)	8.2-13.5 (10.5)	7.8-14.3 (10.4)	6.6-15.9 (10.9)
Soil organic matter (%)	7.6-12.0 (9.4)	7.1-11.9 (9.4)	6.2-11.3 (9.5)	3.4-4.8 (4.2)	3.5-5.6 (4.4)	3.7-5.2 (4.4)
NH_4^+ (mg N kg^{-1} soil)	4.9-17.8 (12.0)	4.5-14.2 (11.0)	5.8-20.4 (13.0)	2.2-4.5 (3.1)	1.5-4.7 (3.2)	2.7-5.3 (3.7)
NO_3^- (mg N kg^{-1} soil)	3.2-9.8 (7.1)	4.5-16.5 (7.9)	3.8-35.8 (11.6)	0.9-1.9 (1.4)	0.9-12.1 (3.1)	1.0-27.5 (5.9)
			Soil Sampling II (Spring 2019)			
pH						
H_2O	4.85-5.80 (5.10)	4.44-5.73 (5.00)	4.67-5.47 (5.02)	5.16-6.12 (5.71)	4.94-5.75 (5.44)	5.07-5.95 (5.55)
$CaCl_2$	4.29-5.10 (4.63)	3.87-4.48 (4.24)	4.06-4.80 (4.34)	4.43-5.02 (4.77)	4.12-4.83 (4.53)	4.23-4.91 (4.57)
Soil moisture content (%)	34.3-36.5 (35.5)	24.1-37.5 (32.9)	29.9-37.9 (32.4)	14.2-21.2 (17.0)	14.1-20.3 (17.2)	14.7-20.0 (17.0)
Soil organic matter (%)	6.8-8.0 (7.5)	5.3-8.1 (7.4)	6.7-8.9 (7.8)	2.7-3.8 (3.5)	3.1-4.3 (3.8)	3.3-4.6 (3.8)
NH_4^+ (mg N kg^{-1} soil)	23.7-44.5 (33.7)	19.3-32.9 (25.9)	23.2-39.2 (30.8)	5.4-9.9 (7.2)	4.0-8.5 (6.4)	4.0-9.7 (7.3)
NO_3^- (mg N kg^{-1} soil)	8.0-20.6 (11.0)	2.9-19.3 (7.7)	3.2-12.8 (7.0)	1.3-3.5 (2.2)	0.8-3.3 (2.1)	1.1-3.2 (2.4)
P (mg kg^{-1} soil)	431-556 (472)	372-554 (488)	423-559 (487)	212-439 (301)	272-371 (319)	257-377 (310)
CEC (meq $100g^{-1}$ soil)	Soil depth: 0-3 in		14.3-19.9 (16.7)	Soil depth: 3-6 in		9.71-11.9 (10.7)

2.3.1.4 Soil moisture and volumetric water contents

Soil moisture is an important variable that determines the emissions of Nr from turfgrass. Knight et al. (2007) have investigated the relationship between soil moisture and NH_3 volatilization on different types of fertilized warm-season sod and found out that the amount of irrigation received would affect the NH_3 volatilization process. Another study by Braun & Bremer (2018) indicated that the right level of soil moisture, in combination with a controlled-release fertilizer may reduce N_2O emissions by ~20 %. Figure 2.7 depicts continuous measurements of 0.1-m depth soil moisture from the ECONet overlaid with the instantaneous volumetric water content (VWC) records during the field intensives.

The soil moisture averages from the long-term measurement for each season are as follows: Spring, 0.313 m^3 m^{-3} soil; Summer, 0.282 m^3 m^{-3} soil; Fall, 0.292 m^3 m^{-3} soil; and Winter, 0.313 m^3 m^{-3} soil. Meanwhile, the seasonal averages of VWC are 0.183 m^3 m^{-3} soil (Spring), 0.100 m^3 m^{-3} soil (Summer), 0.351 m^3 m^{-3} soil (Fall), and 0.209 m^3 m^{-3} soil (Winter). The soil moisture profile shown in Fig.6 shows a discrepancy between the continuous measurements and the instantaneous readings; the continuous measurements measured soil moisture higher than the instantaneous readings., with Fall being the only exception. The difference between the two measurements may lie in the fact that the soil conditions from which the soil moisture measurements were taken are different. Also, the probe used for the continuous measurement was permanently placed into the same location whereas the probe for the instantaneous measurement was only inserted for a short period of time and was moved from one plot to another. Despite the difference, there is a common pattern observable from both datasets that soil moisture during Summer is at the lowest. This suggests that the prevalent soil condition during this period is warm and dry. Contrastingly, soil moisture in Spring and Winter is generally higher than in Summer, indicating a cool and wetter soil condition in this period.

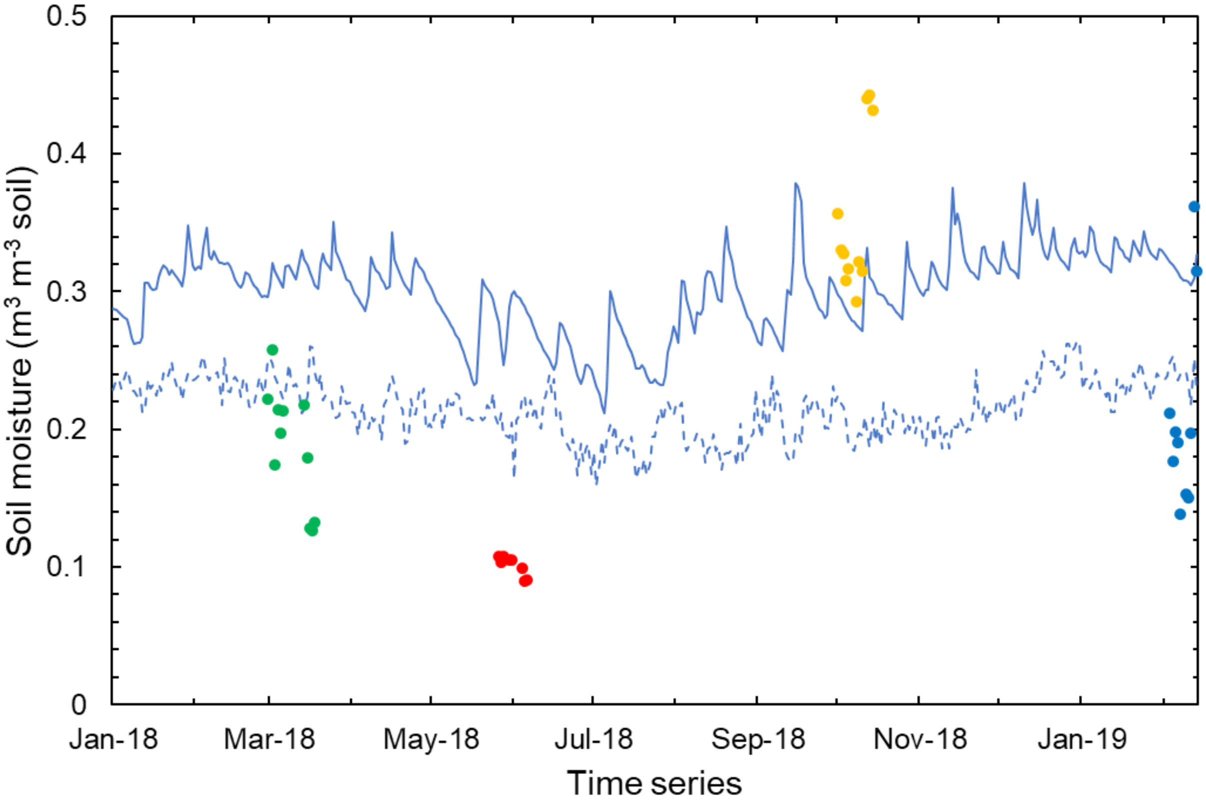


Figure 2.7: Daily average of 0.1-m depth soil moisture for all field intensives. The solid lines represent the measured temperatures while the dashed lines indicate the 30-year average of daily average temperature respective to each date at which the field intensive was conducted. The colored points reflect the instantaneous reading from the probe inserted into the soil adjacent to the chamber for each seasonal intensive. Green points are for Spring, red for Summer, orange for Fall, and blue for Winter.

2.3.2 Characteristics of Nr emissions from turfgrass field intensives

2.3.2.1 Ammonia (NH_3)

Ammonia emissions are expected to be the highest among the three species. This is due to the fact that the fertilizer used in this study is NH_3-based. Table 2.3 summarizes the statistics of NH_3 seasonal emissions from three N fertilizer treatments. Overall, NH_3 emissions accounts for about 62 % of the total Nr emissions measured in this study. Although there was no fertilizer applied during the Summer intensive, the highest emissions were observed during this period.

The next highest NH_3 emissions was during the Fall intensive, followed by Winter and Spring intensives.

Ammonia loss to the atmosphere through volatilization (Schlesinger & Bernhardt, 2013), and this process is more prevalent in alkaline soils and warmer climates (Clay et al., 1990; Ferguson & Kissel, 1986). On average, NH_3 emission flux in Summer (93.4 ± 19.6 ng N m^{-2} s^{-1}) and Fall (72.1 ± 20.3 ng N m^{-2} s^{-1}), or the periods when the soil temperatures were warmer, were substantially higher than those in Spring and Winter. Additionally, the inter-quartile range (IQR) at which NH_3 is emitted was much wider in the warmer periods, suggesting the emissions during these intensives varied from one plot to another. Such variations were not observed in Spring and Winter, as indicative from low IQR values.

The effect of N fertilizer treatments on NH_3 emissions is presented as boxplots in Fig. 2.8a, 2.8b, and 2.8c. In agreement with Table 3, NH_3 emission in Summer was the highest across all N fertilizer treatments. Although no N fertilizer being applied during this period, NH_3 was still emitted to the atmosphere. This is due to the fact that the N fertilizer used in this study was a controlled-release N fertilizer that provided a delayed N supply to the soils. Meanwhile, the fertilizer applications at the beginning of Spring and Fall intensives show that more NH_3 was being emitted within the first days of the measurement. As shown in Fig. 2.9, the rates of NH_3 emission in the first week after the application were consistently higher than those in the second week. This is a typical NH_3 emission profile receiving fertilizer as previous research has demonstrated a similar finding (Petrovic, 1990). However, there is an approximately ten orders of magnitude difference with regard to NH_3 flux between the Spring and Fall intensives, which may be influenced by some differences on the soil conditions during the respective seasons.

Nemitz et al. (2001) introduced a modeling approach based on the apoplastic ratio (Γ_s =

$[NH_4^+]$/pH) to account for bi-directional NH_3 soil-air exchange, and calculated the compensation point (χ_s) that determines whether NH_3 is being deposited or emitted. By taking this approach to estimate the NH_3 emission potential from the soil to the atmosphere, it is found that Γ_s values for Spring and Fall intensives are 1685 and 2786, respectively, while χ_s values for those seasons are 2.2 μg m^{-3} and 16.7 μg m^{-3}, respectively. These values suggest that the NH_3 is more prevalently being emitted in Fall than in Spring. The bi-directional NH_3 soil-air exchange from Nemitz et al. (2001) is driven by soil properties, such as $[NH_4^+]$, $[H^+]$, water content, and soil temperature. While increasing $[NH_4^+]$ in the soil, additional N from the fertilizer application may exhibit a different NH_3 volatilization process, which in turns shows soil condition dependent NH_3 emissions. The soil condition during the Spring intensives was cooler, drier, and slightly more acidic than that during the Fall intensives. Warmer, wetter and more alkaline soils, conditions that could be attributed to the Fall intensives, have found to potentially emit more NH_3 into the atmosphere (Clay et al., 1990; Ferguson & Kissel, 1986).

Soil temperature and moisture are the two soil properties in this study that were directly measured during the sampling. Myrold (2005) has identified that, among other variables, these variables are affecting the N transformation through microbial activity and chemical reaction in soil. Fig. 2.10a and 2.10d show the linear correlation between NH_3 emissions in logarithmic form and soil properties (Aneja et al., 2000). From these figures, there is a positive and statistically significant correlation ($R^2 = 0.51$, P-value < 0.001) between emissions and soil temperature; within a certain temperature range, higher soil temperatures correspond to larger NH_3 emissions. This correlation is in support with the fact that high NH_3 emissions were observed during the warmer seasonal intensives. However, the figure indicates that NH_3 emissions and VWC have a low and statistically insignificant correlation ($R^2 = 0.01$, P-value = 0.12).

Table 2.3: Summary statistics for NH_3 emissions measured during the seasonal intensives. Ammonia emissions are expressed in ng NH_3-N m^2 s^{-1}.

	NH_3 flux (ng NH_3-N m^{-2} s^{-1})[a]			
	Spring	**Summer**	**Fall**	**Winter**
		Treatment A		
Mean[b]	3.5 ± 1.0	72.5 ± 32.2	47.2 ± 21.6	6.2 ± 2.1
Median	2.9	50.5	32.4	4.9
Std. deviation	2.3	73.5	46.8	4.7
IQR[c]	3.2	85.0	66.9	4.3
N	20	20	18[d]	20
		Treatment B		
Mean[b]	5.3 ± 1.6	90.0 ± 32.4	65.4 ± 25.3	7.2 ± 3.3
Median	5.1	88.7	60.0	4.4
Std. deviation	3.6	73.9	54.8	7.6
IQR[c]	6.3	111.3	73.6	6.2
N	20	20	18[d]	20
		Treatment C		
Mean[b]	8.5 ± 3.4	117.5 ± 35.7	103.7 ± 48.7	7.1 ± 2.7
Median	7.4	102.0	54.3	5.2
Std. deviation	7.8	81.5	105.5	6.0
IQR[c]	12.1	123.0	128.8	5.8
N	20	20	18[d]	20

[a] 1 ng = 10^{-9} g

[b] Used a 95% confidence interval

[c] Inter-quartile range (i.e., the difference between third quartile and first quartile)

[d] Data from one day after Hurricane Michael were omitted from the statistics

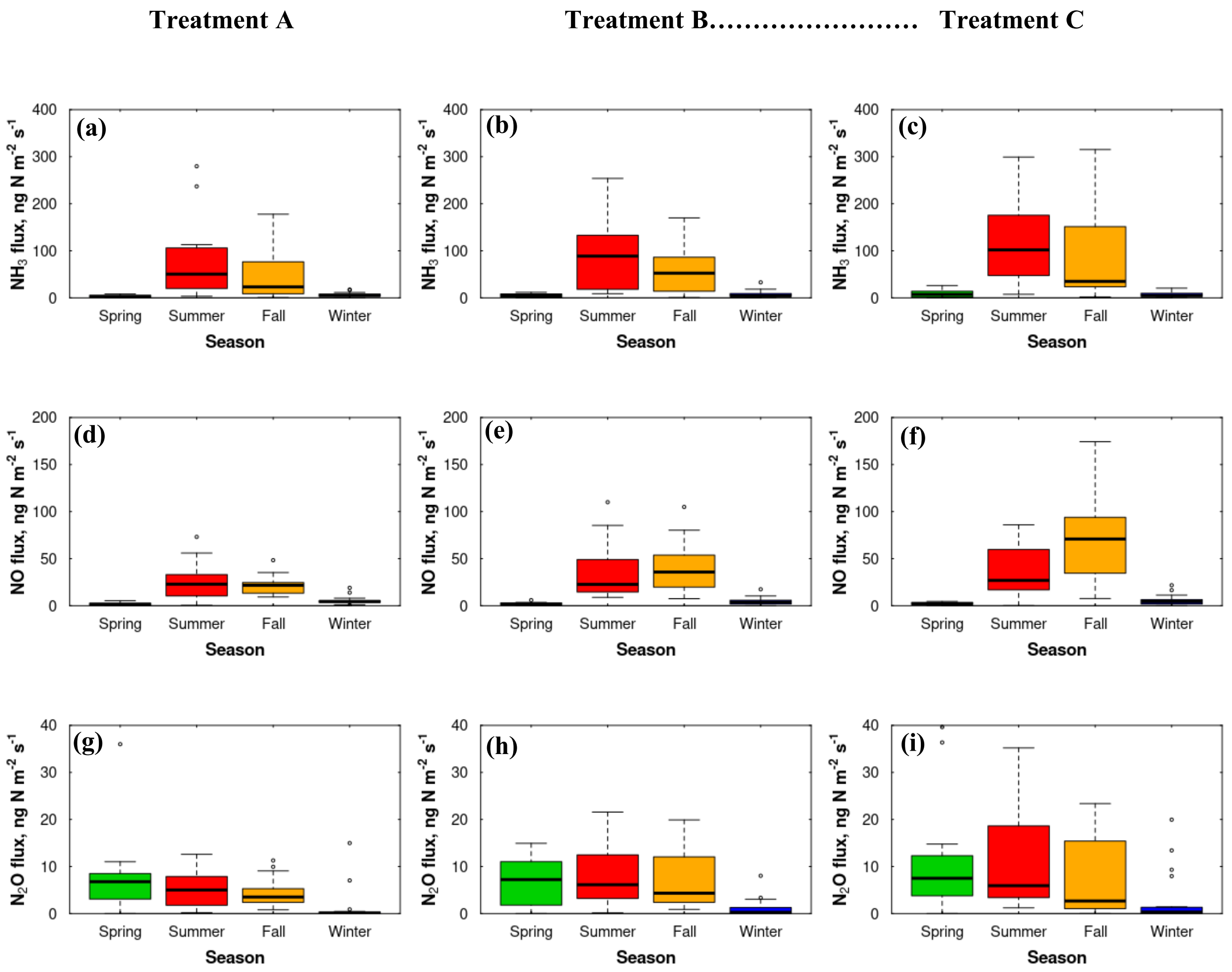


Figure 2.8: Seasonal variation of NH_3 emissions (a-c), NO (d-f), and N_2O (g-i) observed from three N fertilizer treatments. Emission fluxes are expressed as ng N m^{-2} s^{-1}.

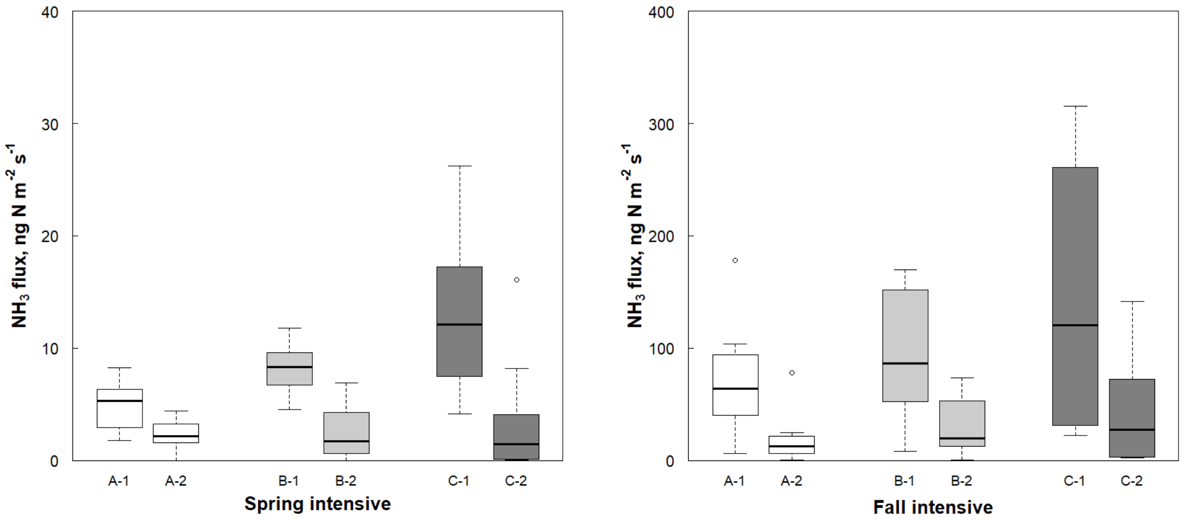
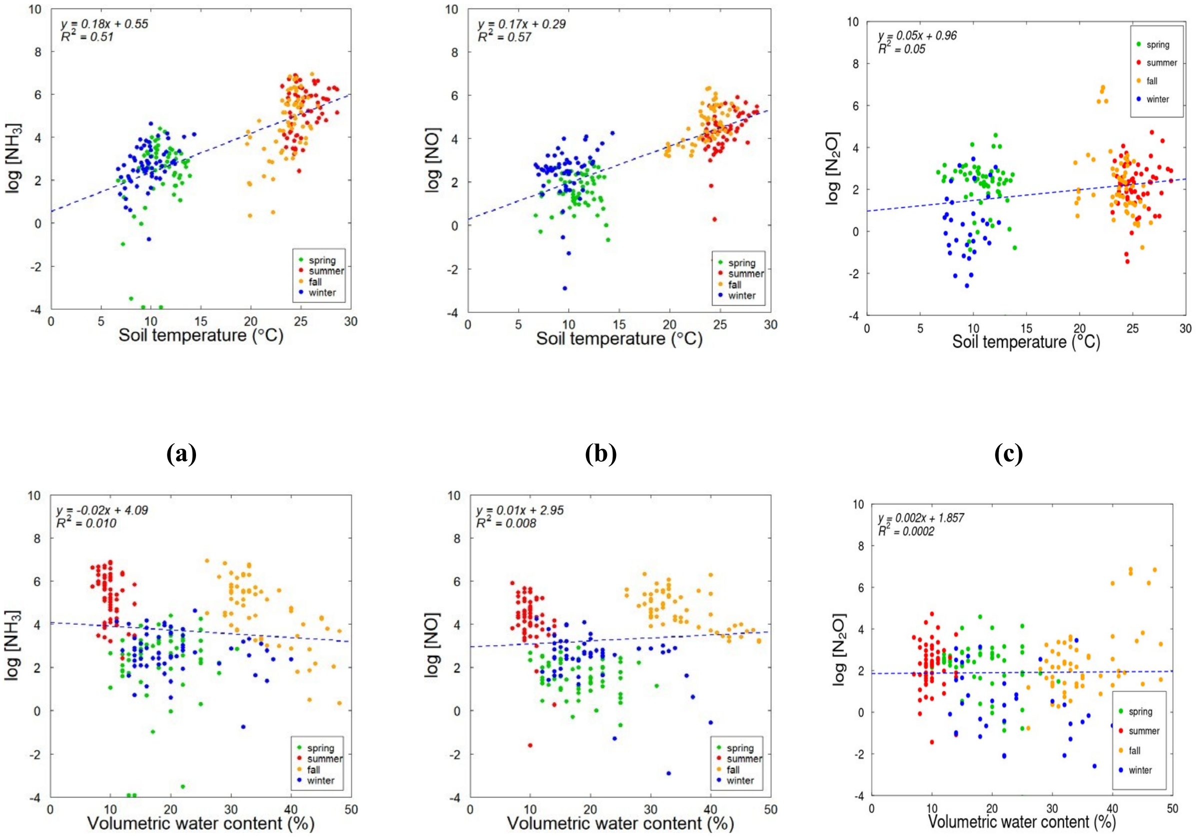


Figure 2.9: Weekly variations of NH_3 flux during the Spring intensive (left) and Fall intensive (right). The letters A, B, and C indicate the N fertilizer treatment. The numbers 1 and 2 reflect the first and second week of measurement. Fertilizer was being applied at the beginning of both intensives.



(a) **(b)** **(c)**

(d) **(e)** **(f)**

Figure 2.10: Relationship between log [Nr] and soil properties. The plot on the left shows a correlation with soil temperature, while figure on the right is with volumetric water content as a surrogate of soil moisture. The log [Nr] is color-coded according to the seasonal intensive (green = spring; red = summer; orange = fall; blue = winter).

2.3.2.2 Nitric oxide (NO)

Nitric oxide is primarily produced from the nitrification process in the soil (Firestone & Davidson, 1989; Paul, 2014; Schlesinger & Bernhardt, 2013). Table 2.4 summarizes the statistics for the seasonal emissions of NO. The NO emissions from this study was between NH_3 and N_2O, which accounted for 29 % of the total Nr measured emissions. The highest NO emissions occurred during the Fall intensive, followed by Summer, Winter, and Spring intensives. Similar to NH_3 emissions, the warmer periods of measurement show much higher NO emissions than in the cooler periods. However, for NO the emissions in Fall were higher than in Summer, suggesting the influence of N-fertilizer applied in the beginning of the Fall intensive on the emitted NO. When comparing the emission variations, the IQR for NO emissions was much wider in the warmer periods, which is similar with NH_3.

The effect of applied N-fertilizer on NO emissions is shown as boxplots in Fig. 2.8d, 2.8e, and 2.8f. Overall, NO emissions increased following the increase of applied fertilizer as the emissions grew larger from treatment A to treatment C. However, the highest emission in treatment A, where there was no fertilizer being applied, observed in Summer, whereas for two other treatments, where fertilizer was added to turfgrass, the emission was at the highest in Fall. This pattern suggests that NO emissions are sensitive to the fertilizer in a warmer condition. Such a pattern was not apparent for NH_3.

The linear correlation between NO emissions in a logarithmic form and soil properties is depicted in Fig. 2.10b and 2.10e. Similar to NH_3, NO emissions and soil temperature exhibit a good and statistically significant correlation ($R^2 = 0.57$, P-value < 0.001). This result corroborates with the previous study by Aneja et al. (1997) that found that NO emissions from soils increase exponentially with increased soil temperature. Meanwhile, the emissions and

VWC result in a low and statistically insignificant correlation ($R^2 = 0.01$, P-value = 0.17), indicating there is no observable trend between the NO emission and soil water content.

Table 2.4: Summary statistics for NO emissions measured during the seasonal intensives. Nitric oxide emissions are expressed in ng NO-N m^2 s^{-1}.

	NO flux (ng NO-N m^{-2} s^{-1})[a]			
	Spring	**Summer**	**Fall**	**Winter**
		Treatment A		
Mean[b]	1.9 ± 0.7	25.0 ± 8.1	22.7 ± 4.5	5.1 ± 2.0
Median	1.4	22.9	22.8	4.6
Std. deviation	1.5	18.5	9.8	4.5
IQR[c]	1.8	21.5	9.3	1.7
N	20	20	18[d]	20
		Treatment B		
Mean[b]	2.0 ± 0.6	33.1 ± 12.0	40.8 ± 12.0	4.6 ± 1.8
Median	1.5	22.7	39.7	3.8
Std. deviation	1.3	27.3	26.0	4.1
IQR[c]	1.8	32.0	35.0	3.8
N	20	20	18[d]	20
		Treatment C		
Mean[b]	2.2 ± 0.6	36.4 ± 11.6	80.1 ± 20.9	5.8 ± 2.4
Median	2.1	26.9	75.6	4.4
Std. deviation	1.4	26.4	45.3	5.4
IQR[c]	2.4	36.70	33.3	4.3
N	20	20	18[d]	20

[a] 1 ng = 10^{-9} g
[b] Used a 95% confidence interval
[c] Inter-quartile range (i.e., the difference between third quartile and first quartile)
[d] Data from one day after Hurricane Michael were omitted from the statistics

2.3.2.3 Nitrous oxide (N_2O)

Together with NO, N_2O is a byproduct of denitrification process in the soil (Firestone & Davidson, 1989; Schlesinger & Bernhardt, 2013). From this study, N_2O emissions contributed 9 % of the total Nr emissions, which is the lowest of all measured Nr in terms of the emission rate. Table 2.5 summarizes the statistics for the seasonal emissions of N_2O, while Fig. 2.8g, 2.8h, and 2.8i shows the influence of N-fertilizer on the emissions. Overall, the highest N_2O emission observed during the Summer intensive, whereas the lowest occurred in Winter. From this study, air and soil temperatures play an important role in the amount of N_2O emitted, though it is not always necessary the case. Emissions during the Spring intensive show that during a colder condition N_2O is relatively high. Here the application of N-fertilizer might contribute to emitted N_2O in Spring, which is not observed for NH_3 and NO. When comparing the N-fertilizer application periods, N_2O emissions in Spring are about 30% higher than those in Fall. This finding suggests that N_2O is more sensitive to added N-fertilizer during a cold condition then

Both soil temperature and VWC show a positive linear correlation with N_2O emissions (Fig. 2.10c and 2.10f). However, the relationship between N_2O emissions and soil temperature indicates a weaker correlation ($R^2 = 0.05$, P-value < 0.001) than those shown for the other two species. This is indicative of what has observed from the seasonal emissions depicted in Fig. 2.8g-2.8i where N_2O flux measured during the Spring, Summer, and Fall were similar. As for the relationship between N_2O emissions and VWC, the correlation ($R^2 = 0.002$, P-value = 0.84) indicates that correlation coefficient does not provide indication on an observable influence of soil water content on the emitted N_2O.

Table 2.5: Summary statistics for N_2O emissions measured during the seasonal intensives. Nitrous oxide emissions are expressed in ng N_2O-N m^2 s^{-1}.

	N_2O flux (ng N_2O-N m^{-2} s^{-1})[a]			
	Spring	**Summer**	**Fall**	**Winter**
Treatment A				
Mean[b]	7.1 ± 3.4	5.2 ± 1.6	4.6 ± 1.4	1.2 ± 1.6
Median	6.8	5.0	3.5	0.0
Std. deviation	7.7	3.6	2.1	3.6
IQR[c]	4.8	5.8	2.9	0.3
N	20	20	18[d]	20
Treatment B				
Mean[b]	9.5 ± 5.7	8.1 ± 2.7	6.9 ± 2.8	1.1 ± 0.9
Median	7.2	6.1	4.3	0.3
Std. deviation	13.1	6.2	6.1	1.9
IQR[c]	8.8	8.5	8.4	1.2
N	20	20	18[d]	20
Treatment C				
Mean[b]	10.1 ± 4.6	14.0 ± 7.6	7.3 ± 3.8	2.8 ± 2.4
Median	7.5	5.9	2.7	0.3
Std. deviation	10.5	17.3	8.2	5.5
IQR[c]	7.8	13.5	12.4	1.3
N	20	20	18[d]	20

[a] 1 ng = 10^{-9} g

[b] Used a 95% confidence interval

[c] Inter-quartile range (i.e., the difference between third quartile and first quartile)

[d] Data from one day after Hurricane Michael were omitted from the statistics

2.3.3 Effects of soil conditions on Nr emissions

Soil conditions affect Nr emissions through their effects on regulating N cycling processes, particularly processes that involve microbial activity (Bauer et al., 2012; Dell et al., 2010; Izaurralde et al., 2017; Shi et al., 2006; Shi et al., 2006). However, these conditions can be considerably different from one turfgrass system to another (Lu et al., 2015; Shi et al., 2006; Yao & Shi, 2010), resulting in large variations on the observed Nr emissions. This study attempted to quantify seasonal Nr emissions by interpreting their relationship with soil temperature and soil moisture. Since there was no direct measurement on soil microbial activity during the field intensives, soil temperature was used as a surrogate, as chemical reactions in the soils driven by soil microbes are temperature dependent (Bijoor et al., 2008; Firestone & Davidson, 1989; Schlesinger & Bernhardt, 2013).

Results suggest that the emissions of all Nr species considered in this study are positively correlated with the soil temperature. Of the three species, however, the correlation between N_2O emission and soil temperature is the weakest ($R^2 = 0.05$; $R^2 > 0.5$ for both NH_3 and NO), indicating N_2O emissions are less sensitive to the change of soil temperature. Indeed, from this study high N_2O emissions occurred in Spring, while NH_3 and NO emissions were peaked in Summer and in Fall, respectively. Although N_2O emissions in Summer was higher in Treatment C, the emission pattern in Spring is uncharacteristically different from those of the other two species.

One possible reasoning that can be attributed to this pattern is the seasonal variation of soil moisture content over the course of field intensives. The measured 0.1-m soil moisture in Spring averaged higher than that in both Summer and Fall. A higher soil moisture leads to an increase in denitrification potential, as more water in the soil limits oxygen (O_2) availability to create an anoxic environment (Firestone & Davidson, 1989; Groffman et al., 2009). In addition, the soil was fertilized at the beginning of the Spring intensive, providing more NH_4^+ (and NO_3^- after conversion) to the systems. This may be the reason why N_2O emissions in Winter were low, even though the soil moisture level was similar to that in Spring.

Meanwhile, the partitioning of soil into to two layers indicates that the layer near the surface has higher moisture content, organic matter, and total extractable N than the layer below. Enriched soil organic matter is often related to a higher microbial biomass in the soil (Paul, 2014), which results in most microbial activity relevant to the production of Nr species being held near the soil surface. In addition, nitrification and denitrification rely on the amount of available NH_4^+ and NO_3^- in soil. The availability of both ions in the near surface layer is found to be higher than the layer below. This condition is consistent in both soil samplings, with a wider discrepancy of ionic concentrations between the two layers observed in the second soil sampling in Spring. Although this study does not attempt to distinguish the sources from which Nr species was emitted, this finding suggests that both nitrification and denitrification at the near surface layer may contribute to larger Nr emissions, signifying the importance of N transformation near the turfgrass surface.

2.3.4 Impacts of N-fertilizer treatments on Nr emissions

The impacts of N fertilizer treatments on Nr emissions from turfgrass systems can be viewed from two aspects. The first aspect is the timing of fertilizer application on turfgrass. In this study, N fertilizer was applied at the beginning of Spring and Fall intensives, adopting the usual application practiced by the turfgrass caretaker. After applying fertilizer in Spring, the results indicate that about 49% of Nr emission during this period came in the form of N_2O, representing a bigger portion than either NH_3 (41 %) or NO (10 %). This emission pattern can be associated with the soil condition after fertilizing in Spring that has been discussed earlier. However, a different Nr emission pattern was observed after the N fertilizer application in Fall. Results show that the highest contributor of Nr emissions was NH_3 (54 %), followed by NO (42 %) and N_2O (4 %). During this period, Nr emissions were much higher than they were during the previous N fertilizer application. This observation suggests that the coupling effect of increased soil temperature and N input to the soil was attributable to the higher emission, as soil microbial activity driven processes (i.e., NH_3 volatilization, nitrification, and denitrification) were enhanced (Firestone & Davidson, 1989; Schlesinger & Bernhardt, 2013). As NH_3 and NO were the more dominant Nr species, it is an indication that the soil conditions favored NH_3 volatilization and nitrification more than denitrification. As previously studied elsewhere (Bijoor et al., 2008; Bremer, 2006; Maggiotto et al., 2000), variations of N_2O emissions following N fertilizer was observed to be different from one fertilizer application to another. Much of the variation is reflective to the soil conditions by the time fertilizer was applied.

The second aspect of the impacts of N fertilizer treatment on Nr emissions is related to the amount of applied N fertilizer. The amount of applied fertilizer might be an arbitrary value as previous studies used different amount of N fertilizer, ranging from 0 kg ha^{-1} (usually indicated as the control) to as much as 150 kg ha^{-1} yr^{-1} (e.g, Bijoor et al., 2008; Qian et al., 2003). This study used three N fertilizer treatments (A: 0 kg ha^{-1} yr^{-1}; B: 73 kg ha^{-1} yr^{-1}; C: 146 kg ha^{-1} yr^{-1}) as a set of variables to examine the fertilizer application practice and management goal. One can perceive that adding no fertilizer is the ideal practice by which Nr emissions will be minimized. It was indeed the case for NH_3 and NO, where the emission patterns follow the applied fertilizer amount (treatment C > treatment B > treatment A). A similar observation was made by other studies that saw an agreement between the applied N fertilizer and the emitted Nr rates (Hamido et al., 2016; Knight et al., 2007; Maggiotto et al., 2000). However, a different N_2O emission pattern was noticeable from turfgrass receiving N fertilizer treatments, where all treatments do not show significant median difference. This result indicates that N_2O emissions were insensitive to the amount of fertilizer since adding more N fertilizer does not necessarily correspond to higher Nr emissions. Such a pattern, where N_2O emissions from an unfertilized field were higher than those from fertilized fields, has not been observed from the previous studies. A possible explanation could be related to the age of the site used in this study, which has been established as a field laboratory for more than 20 years. Shi et al. (2006) and Gu et al. (2015) linked N_2O

emissions with the age of the turfgrass field, and found that aged fields became less sensitive to the addition of N fertilizer, leading to an increase in N_2O emissions when fertilizer is applied. Although their studies did not compare the impacts of N fertilizer on N_2O emissions between unfertilized and fertilized fields, an aging turfgrass field may emit more N_2O due to the cumulative N pool in the soil as a result of years of fertilizer application.

2.3.5 Extreme rainfall event and Nr emissions

Hurricane Michael was a Category 5 hurricane making landfall in the U.S. It started to develop as a low-pressure system on October 6, 2018 and dissipated from an extratropical cyclone form on October 16, 2018 (Beven et al., 2019). The occurrence of Hurricane Michael coincided with the Fall intensive, and on October 11, 2018, Michael passed over the site as a tropical storm, bringing heavy rainfall and strong winds. The total one-day precipitation during this extreme weather event was 80.4 mm or equivalent to 91 % of total precipitation during the entire Fall intensive. This massive amount of water was soaked up by the soils and likely changed the dynamics of the processes within the soil.

A series of chamber measurements conducted one day after Hurricane Michael indicates that there was some unusual Nr emissions. After the event, NH_3, NO, and N_2O emission fluxes (95 % confidence interval) were 8.2 ± 6.1 ng N m^{-2} s^{-1}, 14.0 ± 4.8 ng N m^{-2} s^{-1}, and 372.6 ± 153.3 ng N m^{-2} s^{-1}. While NH_3 and NO emission flux recorded much lower values than the Fall intensive averages, the N_2O emission flux was considerably higher than the average. In fact, such high emissions were only observed from this single event and were not measured either before or after the event. The suppressed NH_3 and NO emissions, and immensely enhanced N_2O emissions as a result of heavy rainfall from Michael can be attributed to the amount of water entered the soils. Firestone & Davidson (1989) suggest that excessive water limits in the soil the O_2

availability, supporting soil microbes that thrive in an anoxic condition to carry out denitrification. Consequently, more N_2O was produced and emitted while the soil was filled with water. This condition, however, only lasted for one day as N_2O emissions dropped to near the average on the following days.

2.3.6 Estimation of Nr emission factors from turfgrass systems

Based on the current knowledge, the interests for inventorying Nr emissions are mainly concentrated for crops and agricultural soils (e.g, Battye et al., 2003, 2017; E. A. Davidson & Kanter, 2014; Mosier, 1994; E. J. Williams et al., 2012). Less information is available for turfgrass while this industry is growing to be an important part of the United States economy (Haydu et al., 2006). This study attempted to estimate Nr emission factors from turfgrass after receiving N fertilizer treatments. From the earlier discussions, the amount of fertilizer might not have a one-to-one relationship with the emitted Nr species. Therefore, this study provides two different sets of Nr emission factors (EFs) in conjunction with the two N fertilizer treatments (treatment B and C).

Table 2.6 summarizes the Nr EFs from turfgrass system with respect to the fertilizer treatments. Overall, NH_3 has the highest annual EF from both N fertilizer treatments (EF_{NH3} = 0.13-0.18 kg N kg^{-1} N fertilizer; EF_{NO} = 0.07-0.09 kg N kg^{-1} N fertilizer; EF_{N2O} = 0.02-0.03 kg N kg^{-1} N fertilizer). There is, however, a discrepancy for the second highest emission factor according to the fertilizer application. In treatment B, N_2O has a higher emission factor than NO, whereas in treatment C it is the other way around. Additionally, Nr emission factors in treatment B are higher than those in treatment C. The difference suggests the importance of optimizing the application of N fertilizer in order to reduce Nr emissions without compromising the turfgrass growth.

Table 2.6: Emission factors of NH_3, NO, and N_2O from turfgrass system receiving two N-fertilizer treatments. The separation between the two N fertilizers is to highlight the difference of emissions relative to the amount of N input.

Nr species	Emission factor (kg N-species kg^{-1} N-fertilizer)	
	Treatment B (73 kg N ha^{-1} yr)	Treatment C (146 N ha^{-1} yr^{-1})
NH_3	0.179	0.126
NO	0.086	0.066
N_2O	0.027	0.018

The amount of emitted NH_3 in this study is within the range of previous studies. Knight et al. (2007) reported a 0-40 % NH_3 volatilized during a 10-day period of field experiment on turfgrass in Auburn, AL, USA. Elsewhere in Lidköping, Sweden, Larsson et al(1998) conducted a study on NH_3 emissions from grass with high N-content and found that NH_3 emissions were 39 % from the applied fertilizer. The amount of emitted NH_3 in this study is within the range of these studies. Meanwhile, Aneja et al. (1997) estimated that around 1.2 % NO is loss as biogenic emissions from fertilizer use in Raleigh, NC, USA. This estimate came with an assumption that the only fertilized areas are lawns. By using this assumption, this study calculates an estimate of 2.4 % NO loss from turfgrass. The annual N_2O emission from this study is slightly larger than a previous study by Spence et al. (2015), which estimated that an overall 1 % of N_2O were loss from highly maintained fescue lawn from residential areas. They also added that the emissions are fluctuate from one residential unit to another, reflecting different types of lawn management. Meanwhile, Smit et al. (2020) have estimated N_2O emission factors for intensive pasture-based dairy systems in South Africa. They found that N_2O emission factors vary significantly with the amount of applied N-fertilizer, which can be in the range between 0 % to 7.7 %. The N_2O emission factors in this study is comparable to what they have estimated in their study, where the amount of N-fertilizer applied in this study falls in the lower range of their emission factors estimated from low amount N-fertilizer applications.

2.4 Summary and conclusions

Seasonal emissions of NH_3, NO, and N_2O from turfgrass system were influenced by several factors. This study aimed at quantifying and characterizing these emissions by conducting measurements using the dynamic chamber technique while at the same time recording meteorological and soil parameters. Emission patterns of NH_3 and NO were observed to be attributed to soil temperature and the amount of applied N-fertilizer, as demonstrated by increased emissions in Summer and Spring, and higher emissions following higher amount of applied N-fertilizer. However, the emission pattern of N_2O was proved to be less discernible since the relationships between N_2O emissions and soil temperature, and between N_2O emissions and N-fertilizer are not immediately apparent. The dynamics of soil microbial driven processes is the key for determining the N_2O emission profile in a more elaborative way.

An important outcome from this study is to estimate emission factors of NH_3, NO, and N_2O from turfgrass systems, as these systems currently receive little attention with respect to the Nr emission inventory. Collectively, the results suggest that Nr emission factors vary from one season to another, and are dependent upon N input to the soil, soil conditions, and meteorological parameters. These variables need to be taken into considerations when developing an estimate of Nr emissions from turfgrass system.

As a further direction of this study, several limitations pertaining to logistical challenges in conducting the chamber measurement could be addressed by a modeling study that complements the field intensives. Variables such as cultivars of turfgrass, amount of applied N-fertilizer, timing of fertilizer application timing, and chronosequence look of turfgrass field are among some components that can be assessed by using this type of modeling study. In addition, the spatial and temporal analysis using the model will be useful to examine more extensive aspects of Nr emissions, particularly with regard to environmental pollution and climate change.

Chapter 3: Application of EPIC for simulating ammonia and nitrous oxide emissions from turfgrass systems

3.1 Introduction

Turfgrass industry is an important part of the United States economy in general, and southeast U.S. in particular (Christians et al., 2017; Haydu et al., 2006). Although turfgrass only covers 1.9 % of land in the continental U.S. (Milesi, Elvidge, et al., 2005), this industry is projected to grow rapidly due to strong demand for sports, residential, and commercial property development, rising affluence, and the environmental and aesthetic benefits of turfgrass in the urban landscape (Qian & Follett, 2002) . Turfgrass management practices also influence carbon and nitrogen sequestration in the soil (Law & Patton, 2017; Shi et al., 2006). However, maintaining the quality of turfgrass might lead to detrimental effects to the environment, particularly through several pathways of nitrogen losses to soil, water, and the atmosphere.

Turfgrass managers use nitrogen-based fertilizers intensively to enhance grass growth, color, quality, and health (Kerek et al., 2003). This practice will contribute to the release of Nr compounds into the atmosphere. For example, a study by conducted in Fort Collins, CO, USA, showed that turfgrass accounted for up to 30 % of N_2O emissions, even though it only covers an area of 6.4% (Kaye et al., 2004). In Auburn, AL, USA the impacts of fertilizer as nitrogen source on NH_3 volatilization from turfgrass were analyzed (Knight et al., 2007). It was found that different fertilizer treatments (i.e., type and amount) contribute to different amount of volatilized NH_3. In Ontario, Canada, (Maggiotto et al., 2000) examined at the seasonality of N_2O and NO_x emissions from turfgrass, receiving different types of nitrogen-based fertilizer. They concluded that the rates of nitrogen loss as N_2O and NO are dependent upon the weather conditions and soil water-filled pore space (WFPS) at the time of fertilizer application.

The Environmental Policy Integrated Climate (EPIC) model was developed in the 1980's to estimate soil erosion by water under different crop and land management practices, and was originally known as the Erosion Productivity Impact Calculator model (Gerik et al., 2013; Williams et al., 1984). Over the years, the model has been updated and expanded to accommodate other important processes in agricultural management (Sharpley & Williams, 1990). EPIC is a process-based computational model that simulates the physicochemical processes in soils and water under agricultural management, and is designed to simulate a field, farm or small watershed that is homogeneous with respect to climate, soil, landuse, and topography (Gerik et al., 2013). The model can be subdivided into nine separate components: weather, hydrology, erosion, nutrients, soil temperature, plant growth, plant environmental control, tillage, and economic budgets (Williams, 1990). The model requires knowledge or model estimates of physical properties of the ambient soil profile, weather, and crop management actions such as tillage and, if available, fertilizer application timing and amount (Cooter et al., 2010).

A number of studies have utilized the EPIC model for assessing gaseous emissions to the atmosphere by combining the model with another more sophisticated computer model (e.g., Community Multiscale Air Quality (CMAQ) model). Cooter et al. (2010) integrated the outputs from EPIC with the existing resistance-based flux model to estimate ammonium and hydrogen ion concentrations in the soil required for determining soil NH3 flux. A study by Cooter et al. (2012) looked at the implementation of EPIC to simulate plant demand-driven fertilizer applications to commercial croplands throughout the continental U.S. Bash et al. (2013) coupled EPIC with a regional air quality model and evaluated the bi-directional NH_3 exchange from the simulation results. Meanwhile, Rasool et al. (2016) incorporated daily year-specific fertilizer data from EPIC to replace the default annual data on CMAQ version 5.0.2 to enhance the representation of soil NO emissions. (Izaurralde et al., 2017) utilized EPIC to simulate the microbial denitrification process and compared the results with data from a 2-year field experiment in southwest Michigan, MI, USA, on N fertilizer rate applied to maize fields.

The utilization of EPIC for estimating Nr emissions from turfgrass has not been undertaken before. In fact, no process-based biogeochemical modeling framework has ever been used to investigate gaseous emissions from turfgrass. Given its capability to simulate the soil processes, as well as its modularity to be coupled with another, more complex computational model, EPIC could serve as a tool to complement the field experiment. Furthermore, the EPIC application for simulating Nr emissions from turfgrass is of importance to overcome the limitations of field measurements. For example, EPIC can be used to estimate the optimum fertilizer application on turfgrass by taking into account the various soil profile, meteorological parameters, and turfgrass management practices.

3.2 Materials and Methods

3.2.1 Field experiment dataset for model evaluation

Datasets from seasonal field experiments were utilized in this study for evaluation the performance of EPIC. These data were taken from one-year field experiments conducted at the Lake Wheeler Turfgrass Field Laboratory, Raleigh, NC, USA during the period between February 2018 and March 2019. Each of the seasonal experiments lasted between 12 days and 19 days. The experiments employed a dynamic chamber system interfaced to an environmentally controlled mobile laboratory (Aneja et al., 2000). The sampling site was a 50 ft by 50 ft tall fescue (*Festuca arundinacea*) field, divided into 30 plots. The NH_3 concentrations were measured in near real time using a chemiluminescence-based analyzer that converts NH_3 to NO by a heated (up to 825 °C) stainless steel catalyst. Meanwhile, 20 ml of the chamber outlet air was collected in pre-evacuated glass vials for N_2 O analysis using a gas chromatography equipped with an electron capture detector (GC-ECD) method.

3.2.2 EPIC model

The EPIC model used in this study is a component of the Fertilizer Emission Scenario Tool for CMAQ (FEST-C) v1.4.1 (https://www.cmascenter.org/fest-c/). FEST-C is a Java-based interface system that facilitates the integration of agriculture, atmosphere, and hydrology simulations for larger spatial resolutions(Ran et al., 2019). The EPIC model used in this integrated system is EPIC v0509 that has been modified to meet CMAQ requirements. For the purposes of this study, the input files and routines in EPIC have been adjusted to satisfy the objectives of this study. The adjusted input files include the selected site for simulation, the daily weather database, the soil physical and chemical characteristics, the fertilizer type, and the site management options.

3.2.2.1 Site description

The FEST-C integrated EPIC model in this study produces CMAQ output files with a spatial resolution of 12 km by 12 km grid cells for a region that covers CONUS and parts of Canada and Mexico. Since this study only evaluates the simulation outputs from one field experiment site (35.7341 °N, 78.6561°W), one grid cell (ID 54512) where this site is situated was chosen. The default settings indicate that this grid cell contains around 5.9 % rainfed hay fesuce and 0.4 % irrigated hay fescue fields, which is a reasonable parameterization of the real condition. The default settings of the grid cell was kept as is during the model run.

3.2.2.2 Daily weather database

The daily weather database was modified by incorporating data collected by the North Carolina Environment and Climate Observing Network (NC ECONet) maintained by the State Climate Office of North Carolina. Datasets from a monitoring site at Lake Wheeler Rd Field Lab, located 0.6 mi from the field site, were selected. The weather variables used as the EPIC input files are daily total solar radiation (in MJ day^{-1}), daily maximum and minimum temperatures (°C), daily total precipitation (mm), daily average relative humidity (%), daily average wind speed (m s^{-1}). The dataset covers the period between 2017 and 2019, which corresponds to the period in which the field campaigns were deployed.

3.2.2.3 Soil physics and chemistry

A number of field soil chemical and physical variables were measured during the field experiment. The EPIC soil input files were modified based on these values. Two sets of soil data were used to reflect the soil conditions during the field experiments; these datasets will be referred to as Soil I and Soil II, with the description of each variable in the respective soil condition is given in Table 3.1. The EPIC soil input files itself encompasses other variables that were not measured during the field experiments. These soil variables were kept as default in the model simulations.

3.2.2.4 Fertilizer input

The type of fertilizer is an important component of the EPIC model simulation since it provides additional source of N and affects the dynamics in soil N chemistry. The fertilizer used in the field experiments was a 25% N fertilizer that consists of 2.3 % ammoniacal N and 22.7 % urea. This fertilizer is not available in the original fertilizer database and was added accordingly.

Table 3.1: Soil physical and chemical parameters given as an input files to EPIC. Soil I and Soil II indicate two soil conditions that reflect the measured parameters during the field experiments. A, B, and C are the fertilizer application treatments utilized during the field experiment. Treatment A is for 0 kg N ha^{-1} applied fertilizer, treatment B is 36.5 kg N ha^{-1}, and treatment C is 73 kg N ha^{-1}.

Parameter	Unit	Soil I			Soil II		
		A	B	C	A	B	C
Bulk density	ton m^{-3}	1.13	1.13	1.13	1.13	1.13	1.13
Water content at wilting point (1500 kPa)	m m^{-1}	0.11	0.11	0.11	0.11	0.11	0.11
Water content at field capacity (33 kPa)	m m^{-1}	0.36	0.36	0.36	0.36	0.36	0.36
Sand	%	71.40	71.40	71.40	71.40	71.40	71.40
Silt	%	20.10	20.10	20.10	20.10	20.10	20.10
Soil pH	-	6.02	5.80	5.75	5.10	5.00	5.02
Organic carbon concentration	%	5.45	5.45	5.51	4.35	4.29	4.52
Cation exchange capacity	cmol kg^{-1}	16.70	16.70	16.70	16.70	16.70	16.70
Initial NO_3^- concentration	g ton^{-1}	7.10	7.90	11.60	11.00	7.70	7.00
Initial NH_4^+ concentration	g ton^{-1}	12.00	11.00	13.00	33.70	25.90	30.80
Saturated conductivity	mm h^{-1}	229.00	229.00	229.00	229.00	229.00	229.00

3.2.2.5 Management practices

EPIC allows the users to parameterize management practices as part of the simulation. The management practices include, among other s, fertilizer amount and application, soil preparation, and types of irrigation. In this study, the input file for this feature was modified to reflect the amount and timing of fertilizer application during the field experiments. The amount of fertilizer applied in this study follows the fertilizer treatments implemented in the field experiments. There were three different fertilizer application treatments, which are 0 kg N ha^{-1} (hereinafter: treatment A), 36.5 kg N ha^{-1} (treatment B), and 73 kg N ha^{-1} (treatment C). These treatments were applied twice during the period of field experiments, one at the beginning of Spring field experiments and the other at the beginning of Fall. The amount and timing of fertilizer application were implemented in the field experiments following the recommendation of the site manager.

3.2.3 Model evaluation

After parameterizing EPIC input files to reflect-specific characteristics of turfgrass, soils, and management practices in the field, the model was run to generate the outputs. The outputs from model simulations were evaluated against the results from the field experiment. The main outputs are NH_3 and N_2O emissions, as well as additional soil physical and chemical parameters. These parameters were selected to make some comparison of different aspects of turfgrass systems that influence turfgrass growth, soil physical and chemical dynamics, and soil nutrient cycling.

Typical statistical evaluations in modeling exercises and model comparisons include analysis of coefficient of determination (R^2), root mean squared error (RMSE), coefficient of determination (R 2), and model bias. These metrics describe the total variation in observed data captured by simulated data (R^2), the error associated with model estimates (RMSE), and whether the model overestimate or underestimate a mean observation in the prediction of observed data. Together, these metrics indicate how well models perform and if their use improves the ability to estimate data relative to observations. EPIC provides two sets of output files that indicate the sources of soil water in the simulation. These sources are rain-fed and irrigated. Among the two, the rain-fed simulations are considered a close representation of the actual condition since there was no designated irrigation application for the field during the field experiments. However, outputs from both types of simulations will be compared and analyzed in this study.

3.2.4 Simulation scenarios

The simulation scenarios used in this study were aimed at understanding the characteristics of NH_3 and N_2O emissions if the field conditions are modified. In this study, two simulation scenarios were employed to analyze NH_3 and N_2O emissions from the point of view of the management practice. The two scenarios are as follows:

1. **Addition of N-fertilization treatments in the simulation**. The rates of applied N-fertilizer affects turfgrass growth, which at the same time influences the amount of emitted reactive nitrogen to the air (Bélanger et al., 1992; Gaillard et al., 2018; Salazar et al., 2012; Wilson et al., 1981). In this modeling study, five different N-fertilizer treatments were introduced to the model: 50 kg N ha^{-1} (hereinafter: F50), 100 kg N ha^{-1} (F100), 200 kg N ha^{-1} (F150), 400 kg N ha^{-1} (F400), and 800 kg N ha^{-1} (F800). For the purposes of focusing the analysis on emission comparison, the simulation was performed under the rain-fed condition for water source and Soil I for soil physics and chemistry.
2. **Modification of N-fertilization application on the soil in the simulation**. Tall fescue is a cool-season turfgrass that grows better when applied with N-fertilizer during the cool period (Oral & Acikgoz, 2001). The best periods for fertilization are in early Spring and late Fall (Gastal & Bélanger, 1993; Gerrish et al., 1994). During the field intensives, N-fertilizer was applied in the last weeks of February and September of 2017. The weather conditions in February 2017 was still winter-like while in September the air and soil temperatures were too warm for a typical season. For this scenario, the period of N-fertilization were modified to March and November to inflict a more suitable temperature for tall fescue.

3.3 Results and Discussion

3.3.1 Soil physical and chemical properties

The soil physical and chemical properties from EPIC simulations are tabulated in Table 3.2 (for the rain-fed simulation) and in Table 3.3 (irrigated). Results for soil physics suggest some differences between Soil I and Soil II for both types of simulation, and between the observation and the model. Soil I is slightly more dense than Soil II, a condition that affects soil water pressure in the system. The water contents from the simulation are lower than that from the measurements, indicating that the actual soil has the more capacity to hold soil water. This can possibly be attributed to soil porosity of the actual soils that has more space. Lower water contents might affect the air and nutrients cycling in the soil that are responsible for the chemical reactions that govern NH_3 volatilization and N_2O from denitrification.

Table 3.2: Soil physical and chemical parameters simulated by EPIC for the rain-fed type simulation. The NO_3^- and NH_4^+ concentrations were converted from kg ha^{-1} to g ton^{-1} to make the results comparable to the initial input values given in Table 3.1. A, B, and C indicate the fertilizer application treatments (see Table 3.1 for definition).

Parameter	Unit	Soil I			Soil II		
		A	B	C	A	B	C
Bulk density	ton m^{-3}	1.60	1.60	1.60	1.52	1.52	1.52
Water content at wilting point (1500 kPa)	m m^{-1}	0.07	0.07	0.07	0.08	0.08	0.08
Water content at field capacity (33 kPa)	m m^{-1}	0.16	0.16	0.16	0.14	0.14	0.14
Soil pH	-	5.69	5.69	5.69	5.42	5.42	5.42
Cation exchange capacity	cmol kg^{-1}	5.20	5.20	5.20	6.50	6.50	6.50
NO_3^-	g ton^{-1}	7.50	8.60	10.40	7.40	5.20	10.50
NH_4^+	g ton^{-1}	9.40	13.10	16.90	9.00	13.10	16.30

The simulated soil pH lies between the measured soil pH given as an initial input. Soil I and Soil II have a closer simulated pH difference than the measured, which might be indicative of how EPIC considers the two soils to be similar. Meanwhile, cation exchange capacity for Soil

II is higher than Soil I, which influences the availability of soil nutrients.

Nitrate concentrations between Soil I and Soil II for both types of water source also shows a pattern, with Soil I has higher values across different fertilizer application treatments. This is consistent with the decreasing soil pH simulated for Soil II, which reduces the nitrification rate to provide NO_3^- in the soil (Gregorich et al., 2015).Furthermore, NO_3^- for the rain-fed simulation is comparable to the measured NO_3^-. This similarity suggests that the potential influence of soil NO_3^- availability as a result of water addition. The addition of water decreases NO_3^- concentrations in soils by limiting soil aeration, hence reducing O_2 supply in the soil (Firestone & Davidson, 1989; Gregorich et al., 2015; Majumdar et al., 2000).In contrast to NO_3^-, the added water to the field tends to have little effect on the NH_4^+ concentration variations in different soil types. Chemical reactions involving NH_4^+ are less sensitive to water stress, which might explain the NH_4^+ profile in both rain-fed and irrigated simulations.

Table 3.3: Soil physical and chemical parameters simulated by EPIC for the irrigated type simulation. The NO_3^- and NH_4^+ concentrations were converted from kg ha^{-1} to g ton^{-1} to make the results comparable to the initial input values given in Table 3.1. A, B, and C indicate the fertilizer application treatments (see Table 3.1 for definition).

Parameter	Unit	Soil I			Soil II		
		A	B	C	A	B	C
Bulk density	ton m^{-3}	1.60	1.60	1.60	1.52	1.52	1.52
Water content at wilting point (1500 kPa)	m m^{-1}	0.07	0.07	0.07	0.08	0.08	0.08
Water content at field capacity (33 kPa)	m m^{-1}	0.16	0.16	0.16	0.14	0.14	0.14
Soil pH	-	5.69	5.69	5.69	5.42	5.42	5.42
Cation exchange capacity	cmol kg^{-1}	6.30	6.30	6.30	6.80	6.80	6.80
NO_3^-	g ton^{-1}	5.20	6.30	8.20	4.20	3.10	10.00
NH_4^+	g ton^{-1}	8.20	12.70	15.30	8.80	13.20	14.90

Overall, soil physical and chemical properties simulated by EPIC varied from field experiment datasets given as input values. Soil parameters such as soil pH, NO_3^-, and $NH_4^{+,}$

affect the soil chemical reactions involved in the NH_3 volatilization and N_2O production from denitrification. However, these parameters are inadequate to explain the complexity of soil N cycling in turgrass. Nevertheless, some similarities and agreement produced from the simulation provide a good prospectus for the use of EPIC in simulating soil properties in turfgrass systems.

3.3.2 Comparing simulated NH_3 and N_2O from EPIC with results from field experiment

The modularity of EPIC gives an advantage for users to use the model in coupling with different models. One of the model couplings is with an air quality model for simulating reactive nitrogen emissions in agricultural soils (Bash et al., 2013; Cooter et al., 2010; Rasool et al., 2016). The application of EPIC in these studies, however, was mainly to be used to produce an input file for further processing in a more complex modeling exercise. In this study, EPIC simulation outputs were directly compared with datasets collected from field experiments. Additionally, the use of gas outputs from EPIC (i.e., volatilized NH_3 and denitrification N_2O) has not been attempted in previous studies.

Table 3.4 and 3.5 summarize the statistics of EPIC evaluation for NH_3 and N_2O. The R^2 values for NH_3 range from 0.39 to 0.63 (coefficient correlation, R = 0.62-0.79), while R^2 values for N_2O are between 0.22 and 0.38 (R = 0.47-0.62). In general, EPIC simulates NH_3 better than N_2O across different fertilizer application treatments, soil types, and water source.

EPIC also underestimates both NH_3 and N_2O in all simulations. The model underestimates NH_3 by 12-19 % for rain-fed and by 14-21 % for irrigated; N_2O by 16-24% for rain-fed and by 18-24%. This underestimation can be attributed to smaller NH_4^+ and NO_3^- concentrations in soils that are simulated by EPIC. A study by Gaillard et al. (2018) found a similar outcome in which EPIC underestimates N_2O. Their study indicates variation in model estimates in respiration, denitrification, NH_4^+, and NO_3^-. They concluded that more types of observational data are needed to better understand how EPIC simulates the N cycling. The same recommendation is applicable for this study, where additional soil parameters can be used to address the variation in the results.

From this finding, it is important to recognize the underestimation produced by the model when analyzing NH_3 and N_2O from EPIC. A careful adjustment should be attempted in order to correctly represent the estimates that are comparable to the measurements. In this case, the average NH_3 and N_2O biases are 14% and 18%, respectively. These biases will be incorporated to other emission outputs from EPIC simulations.

Table 3.4: EPIC model evaluation for simulating NH_3 from turfgrass systems. R^2 (coefficient of determination), RMSE (root mean square error), and bias (difference between observation and model) are the statistical parameters used to evaluate EPIC performance.

Statistical parameter	Soil I			Soil II		
	A	B	C	A	B	C
Rain-fed:						
R^2	0.49	0.58	0.59	0.46	0.60	0.63
RMSE	0.34	0.22	0.23	0.42	0.22	0.17
Bias (%)	-16	-12	-14	-18	-17	-19
Irrigated						
R^2	0.42	0.53	0.56	0.39	0.54	0.52
RMSE	0.62	0.31	0.37	0.81	0.40	0.41
Bias (%)	-17	-14	-14	-21	-17	-17

Table 3.5: EPIC model evaluation for simulating N_2O from turfgrass systems. R^2 (coefficient of determination), RMSE (root mean square error), and bias (difference between observation and model) are the statistical parameters used to evaluate EPIC performance.

Statistical parameter	Soil I			Soil II		
	A	B	C	A	B	C
Rain-fed:						
R^2	0.26	0.33	0.34	0.25	0.38	0.34
RMSE	0.42	0.23	0.34	0.52	0.33	0.38
Bias (%)	-22	-16	-18	-24	-24	-21
Irrigated						
R^2	0.22	0.28	0.27	0.23	0.27	0.29
RMSE	0.55	0.42	0.60	0.51	0.47	0.39
Bias (%)	-22	-23	-19	-18	-24	-21

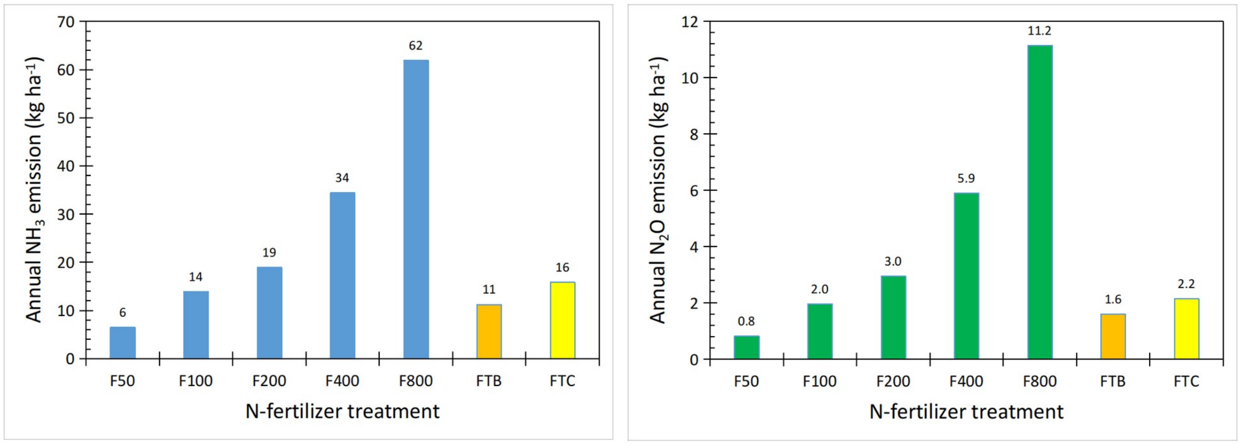
3.3.3 Emissions of NH_3 and N_2O from simulation scenarios

Estimating NH_3 and N_2O emissions from turfgrass by conducting field experiments poses some logistical challenges in determining the experimental design. This is related to, for example, the number of N-fertilizer treatments, the period of fertilizer application, and the type of management practices implemented on the field. These challenges inherit some limitations on the analysis of obtained data. A modeling study using EPIC provides features that may overcome these limitations. The caveat is that the model performance has to be first assessed in order to understand the comparability between the model and the actual measurements.

From the model evaluation it is found that there is emission underestimation produced by EPIC. The underestimation comes as a result of a lower NH_4^+ and NO_3^- simulated by EPIC. The correction that incorporates this underestimation is included when calculating the emissions from the simulation scenarios.

3.3.3.1 Addition of N-fertilization treatments in the simulation

Previous studies have indicated that Nr emissions increase with respect to the increasing amount of N-fertilization (e.g., Knight et al., 2007; Maggiotto et al., 2010; Spence et al., 2015). Indeed, Fig. 3.1 shows that the simulated NH_3 and N_2O emissions increase following the increasing amount of N-fertilizer. The highest NH_3 emission is 63 kg ha^{-1} when 800 kg of N-fertilizer is applied, while the highest N_2O emission at the same amount of N-fertilizer is 11.2 kg ha^{-1}. However, to assess how much actually these species being emitted as a loss from the N-fertilizer is better expressed as emission factors. Here, Eq. 3.1 is used to determine the emission factors of both Nr species for each N-fertilizer amount. The results are presented in Table 3.6.



(a) (b)

Figure 3.1: Annual emissions (in kg ha^{-1}) of (a) NH_3 and (b) N_2O with respect to different N-fertilizer treatments. Numbers on the x-axis represent the amount of N-fertilizer in kg ha^{-1} (e.g., F50 indicates a 50 kg ha^{-1} is applied). FTB and FTC are for the same amounts of N-fertilizer for Treatments B and C in the field experiment.

Table 3.6 indicates that the highest emission factors for NH_3 and N_2O is achieved when 100 kg ha^{-1} of N-fertilizer is applied. In fact, if Treatment B is included on the list the highest emission factor will be at 73 kg ha^{-1} of applied N-fertilizer (0.179 for NH_3 and 0.027 for N_2O). These results suggest that there is a saturation point at which the addition of N source to soil do not contribute to the either NH_3 volatilization or N_2O production from denitrification. These results exhibit some similarities with what have been indicated from the field experiment.

Table 3.6: Emission factors for NH_3 and N_2O calculated from the EPIC simulated emissions. The adjusted emission factors are introduced to account for the underestimation of Nr emissions by EPIC.

N-fertilizer (kg ha^{-1})	NH_3 emission factor (kg kg^{-1} N-fertilizer)		N_2O emission factor (kg kg^{-1} N-fertilizer)	
	Calculated	Adjusted	Calculated	Adjusted
50	0.130	0.151	0.016	0.020
100	**0.139**	**0.162**	**0.020**	**0.024**
200	0.095	0.110	0.015	0.018
400	0.086	0.100	0.015	0.018
800	0.077	0.090	0.014	0.017

Reactive nitrogen such as NH_3 and N_2O are regarded as by-products of the N cycle in the soil. They are counted as the loss of N to the environment, and do not account for the N intake for turfgrass growth. Results from both field experiment and EPIC have shown that when emission factor is taken into consideration, the amount of N-fertilizer that contributes to Nr emissions is not linearly correlated. This means that at a certain level, the emission levels from added N-fertilizer tend to be leveling off or even going slightly downward. The downward trend is more apparent for NH_3, as shown in Table 3.1; the emission factor for NH_3 is seen to be stabilized with increasing amount of N-fertilizer.

3.3.3.2 Modification of N-fertilization application on the soil in the simulation

Another important factor influencing the growth of turfgrass is the timing of N-fertilization. When conducting the field experiment, the time of N-fertilizer application was decided following the recommendation of the field caretaker and the logistical preparation for deploying the instrumentation. Utilizing EPIC provides a freedom of simulating the time of N-fertilization. Here, a modification of both application times was performed. March was selected for the application time in Spring while November was for Fall. The simulation results for NH_3 and N_2O are shown in Figure 3.2 as seasonal emissions.

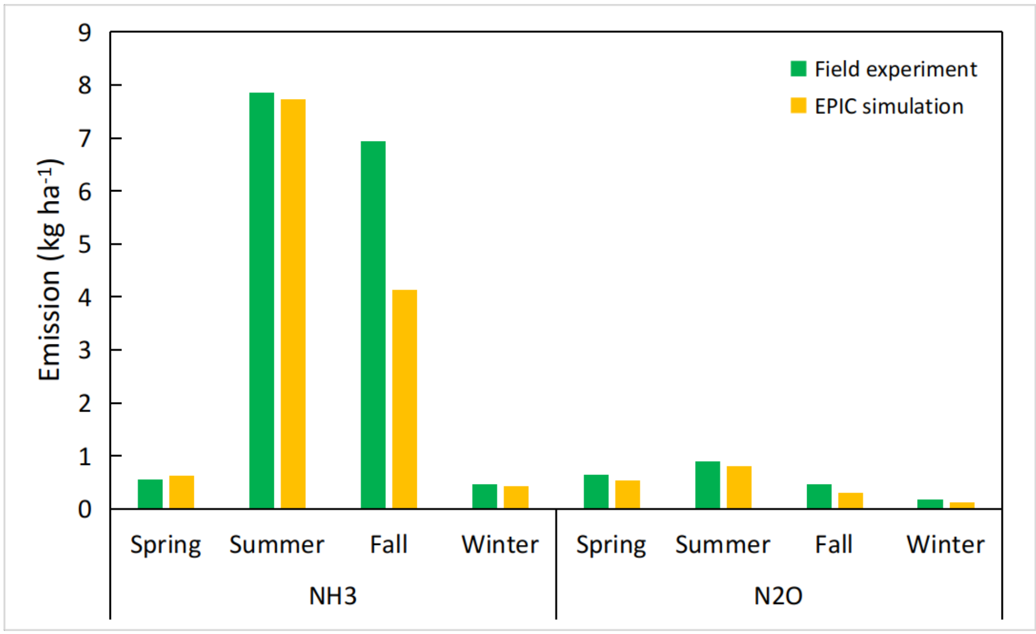


Figure 3.2: Comparison of seasonal emissions of NH_3 and N_2O (in kg ha^{-1}) between field experiment (green) and EPIC simulation (orange).

With the exception of NH_3 emissions in Spring, both NH_3 and N_2O seasonal emissions saw varying degrees of reduction. The largest drops in NH_3 and N_2O emissions both occurs in Fall, where emission reductions of ~40 % and ~35% are observed respectively. The shift of N-fertilization application from September to November seems to affect the soil N cycle processes that contribute to NH_3 and N_2O emissions. Air and soil temperature in November are considerably lower than in September, which may result in slower temperature-driven microbial activities in the soil.The increased NH_3 emissions in Spring indicates that warmer conditions are preferable for more volatilized NH_3 from soil, which is not the case when the application is done in February.

3.4 Summary and conclusions

This study utilized EPIC for simulating NH_3 and N_2O emissions from turfgrass systems. NH_3 simulated from EPIC is the result of how much soil NH_4^+ became volatile and released into the atmosphere, while N_2O is released from denitrification. Results indicate that EPIC is able to simulate soil physical and chemical properties with a reasonable agreement with data from field experiment. However, lower soil NH_4^+ and NO_3^- from EPIC may result in smaller NH_3 and N_2O in the simulation.

Simulation using EPIC allows modification on different components of the model. In this study, two simulation scenarios that are aiming at variations of N-fertilizer amount and application time were conducted in order to better comprehend the characteristics of NH_3 and N_2O from turfgrass. Results suggest that the fraction between emitted Nr relative to the amount of applied N-fertilizer is not linearly correlated. A threshold level at which the maximum emission is reached is present for both species. Meanwhile, time for N-fertilization application indicates how the emission is regulated by temperature-driven process in the soil. This is shown by the changes in NH_3 and N_2O emissions when N-fertilizer is applied on different soil and air temperatures.

Chapter 4: Conclusions

This study attempted to address the research questions posed in the beginning of dissertation. The following are some concluding remarks based on the results and analyses given in the previous chapters.

4.1 Seasonal Nr emissions from turfgrass systems

Nr emissions are characterized by the N cycle processes involved in the production of these species. These processes are driven by soil physical and chemical conditions, as well as meteorological parameters. Air and soil temperatures are the most important factor that determine the seasonality of Nr emissions. This is in particular apparent for NH_3 and NO, where the emissions prefer warmer condition. For N_2O, air and soil temperatures are not the determining factor as its emission can be high during the cold period. In addition to temperatures, soil water content may contribute to the seasonal Nr emissions. However, the results from the intensives indicate that this is not the case for turfgrass in this field. One factor that might influence this outcome is the soil characteristics.

4.2 Influence of N-fertilizer to Nr emissions from turfgrass systems

There are two ways in which N-fertilization application influences Nr emissions from turfgrass systems. Firstly, the timing of N-fertilization affects the availability of soil N. This is the driver of N_2O emission in Spring where the highest proportion of Nr emission comes from this species. In Fall, NO emission is at the highest level when compared against its emission in other seasons. The differences of Nr species in responding to the timing of N-fertilization application may be attributed to the complex interaction between soil and air that affect the processes in the soil.

Secondly, Nr emission is influenced by the amount of N-fertilizer applied. This is observed for NH_3 and NO where more N-fertilizer corresponds to more emissions. For N_2O, the increased emission with respect to N-fertilizer amount is less obvious. Some previous studies have pointed out that the age of the field may cause the difference in N_2O emissions from other Nr species.

4.3 Relationships between Nr emissions and soil conditions

Soil physical and chemical conditions determine the rates of processes in the soil. This is particularly relevant to the processes driven by soil microbial activities. Soil temperature, water content, organic matter, and soil pH are among the identified parameters that affect Nr emissions. Seasonal variations of these parameters regulate the production of Nr in the soil, and in the case of NH_3, how much this species can be emitted to/deposited from air. Also, the difference in soil depth contribute to Nr emissions. This is related to the availability of the nutrient and interaction between soil and air.

4.4 Nr emission factor from turfgrass

Nr emission factor is an important indicator to assess how much Nr is loss from any particular activity. In this study, N-fertilization reflects to the activity from which Nr might be loss from the system. Results from this study indicate that the largest Nr emission from turfgrass systems comes in the form of NH_3, followed by NO and N_2O. The N-fertilizer treatments performed in this study suggest that more Nr is being emitted from a lower N-fertilizer level, promoting a concept of a non linear response of Nr emissions to the N-fertilizer amount.

4.5 Estimation Nr emissions using EPIC model

EPIC is capable of simulating NH_3 and N_2O emission from turfgrass system with proper input files adjustments. A decent correlation between model and observation provides some confident in using the model for simulating processes in soils that contribute to NH_3 and N_2O emissions. However, the fact that EPIC underestimates the emissions suggests that a bias correction is necessary when analyzing the results. Nevertheless, the modularity of EPIC can be offered as a solution to overcome the limitations of experimental design used in a field campaign. Development of different simulation scenarios is an example of how to use EPIC in addressing different situations. In this study, modifications of management practices were used to assess Nr emissions. Other attempts involving varying meteorological and soil conditions, or under a changing climate can be proposed as future studies.

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APPENDICES

Appendix A

Abstract for a poster presentation at the Third Annual Research Symposium, Center for Turfgrass Environmental Research and Education (CENTERE), Raleigh, NC, December 6th, 2018

Characterization of Reactive Nitrogen Emissions from Turfgrass

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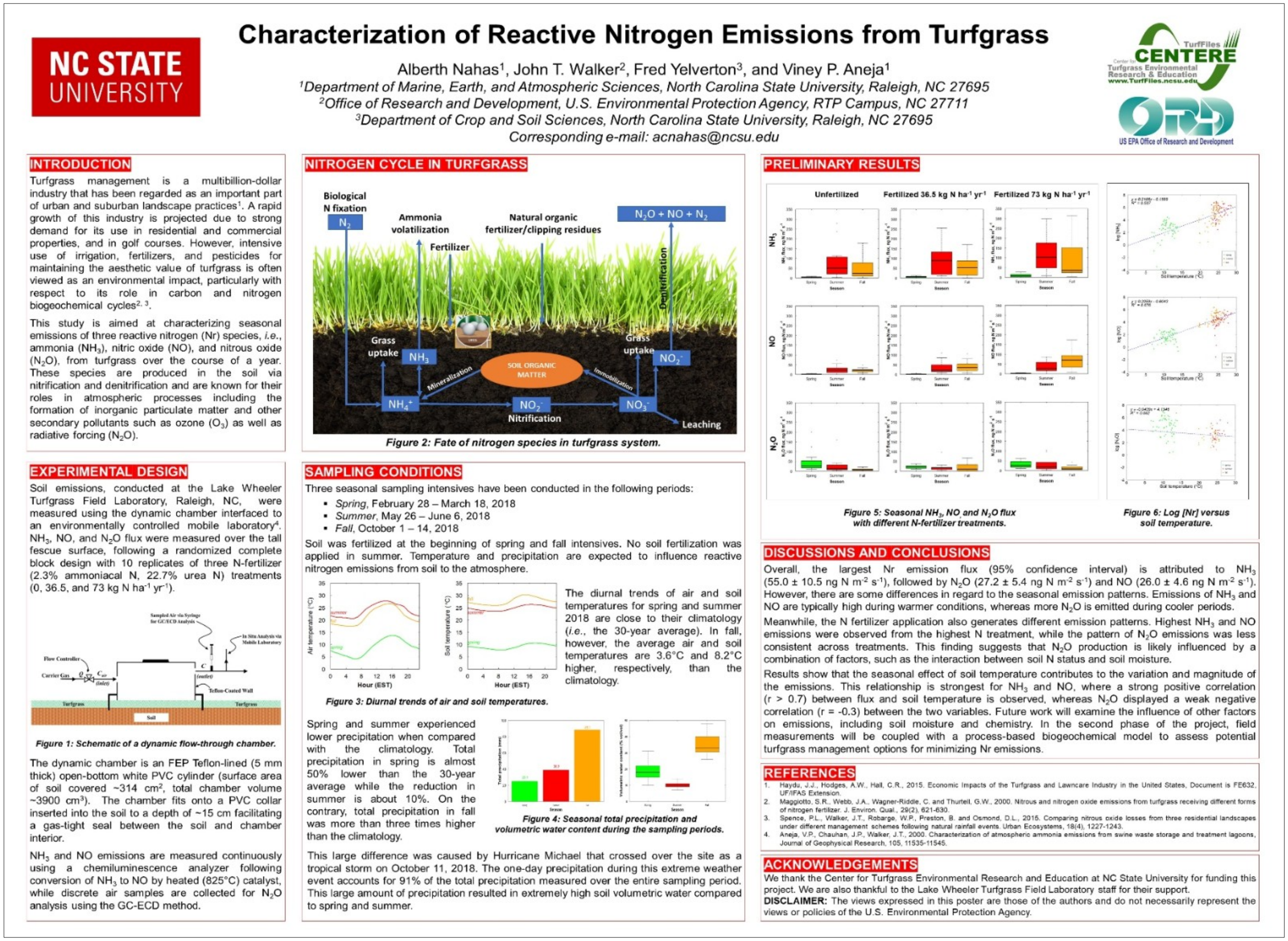
Turfgrass management is a multibillion-dollar industry that has been regarded as an important part of urban and suburban landscape practices. A rapid growth of this industry is projected due to strong demand for its use in residential and commercial properties, and in golf courses. However, intensive use of irrigation, fertilizers, and pesticides for maintaining the aesthetic value of turfgrass is often viewed as an environmental impact, particularly with respect to its role in carbon and nitrogen biogeochemical cycles. This study, conducted at the Lake Wheeler Turfgrass Field Laboratory in Raleigh, NC, is aimed at characterizing seasonal emissions of three reactive nitrogen species, i.e., ammonia (NH_3), nitric oxide (NO), and nitrous oxide (N_2O), from turfgrass over the course of a year. These species are produced in the soil via nitrification and denitrification and are known for their roles in atmospheric processes including the formation of inorganic particulate matter (NH_4^+ and NO_3^-) and other secondary pollutants (e.g., NO_2 and O_3) as well as radiative forcing (N_2O). Soil emissions are measured using the dynamic chamber approach following a randomized complete block design with 10 replicates of three N-fertilizer (2.3% ammoniacal N, 22.7% urea N) levels (0, 36.5, and 73 kg N ha^{-1} yr^{-1}). NH_3 and NO emissions are measured continuously using a chemiluminescence analyzer following conversion of NH_3 to NO by heated (825°C) catalyst, while discrete air samples are collected for N_2O analysis using the GC-ECD method. Emission measurements during 2018 spring and summer intensives indicate a wide range of emissions for NH_3 (21.8-1384.6 ng N m^{-2} s^{-1}); NO (15.5-307.7 ng N m^{-2} s^{-1}); and N_2O (186.5-635.8 ng N m^{-2} s^{-1}). Results show that the seasonal effect of warmer soil temperature contributes to the variation and magnitude of the emissions. Highest NH_3 and NO emissions were observed from the highest N treatment, while the pattern of N_2O emissions was less consistent across treatments. The role of external physicochemical factors, such as local meteorology, soil properties, and microbial activity, will be further analyzed. Field measurements will be coupled with a process-based biogeochemical model to produce a temporal and spatial analysis of reactive nitrogen emissions from turfgrass on a larger scale.

Appendix B

Poster presentation at the 2018 AGU Fall Meeting, Washington, D.C., December 10-14, 2018.



Characterization of Reactive Nitrogen Emissions from Turfgrass

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INTRODUCTION

Turfgrass management is a multibillion-dollar industry that has been regarded as an important part of urban and suburban landscape practices[1]. A rapid growth of this industry is projected due to strong demand for its use in residential and commercial properties, and in golf courses. However, intensive use of irrigation, fertilizers, and pesticides for maintaining the aesthetic value of turfgrass is often viewed as an environmental impact, particularly with respect to its role in carbon and nitrogen biogeochemical cycles[2, 3].

This study is aimed at characterizing seasonal emissions of three reactive nitrogen (Nr) species, *i.e.*, ammonia (NH_3), nitric oxide (NO), and nitrous oxide (N_2O), from turfgrass over the course of a year. These species are produced in the soil via nitrification and denitrification and are known for their roles in atmospheric processes including the formation of inorganic particulate matter and other secondary pollutants such as ozone (O_3) as well as radiative forcing (N_2O).

EXPERIMENTAL DESIGN

Soil emissions, conducted at the Lake Wheeler Turfgrass Field Laboratory, Raleigh, NC, were measured using the dynamic chamber interfaced to an environmentally controlled mobile laboratory[4]. NH_3, NO, and N_2O flux were measured over the tall fescue surface, following a randomized complete block design with 10 replicates of three N-fertilizer (2.3% ammoniacal N, 22.7% urea N) treatments (0, 36.5, and 73 kg N ha^{-1} yr^{-1}).

Figure 1: Schematic of a dynamic flow-through chamber.

The dynamic chamber is an FEP Teflon-lined (5 mm thick) open-bottom white PVC cylinder (surface area of soil covered ~314 cm^2, total chamber volume ~3900 cm^3). The chamber fits onto a PVC collar inserted into the soil to a depth of ~15 cm facilitating a gas-tight seal between the soil and chamber interior.

NH_3 and NO emissions are measured continuously using a chemiluminescence analyzer following conversion of NH_3 to NO by heated (825°C) catalyst, while discrete air samples are collected for N_2O analysis using the GC-ECD method.

NITROGEN CYCLE IN TURFGRASS

Figure 2: Fate of nitrogen species in turfgrass system.

SAMPLING CONDITIONS

Three seasonal sampling intensives have been conducted in the following periods:

- *Spring*, February 28 – March 18, 2018
- *Summer*, May 26 – June 6, 2018
- *Fall*, October 1 – 14, 2018

Soil was fertilized at the beginning of spring and fall intensives. No soil fertilization was applied in summer. Temperature and precipitation are expected to influence reactive nitrogen emissions from soil to the atmosphere.

The diurnal trends of air and soil temperatures for spring and summer 2018 are close to their climatology (*i.e.*, the 30-year average). In fall, however, the average air and soil temperatures are 3.6°C and 8.2°C higher, respectively, than the climatology.

Figure 3: Diurnal trends of air and soil temperatures.

Spring and summer experienced lower precipitation when compared with the climatology. Total precipitation in spring is almost 50% lower than the 30-year average while the reduction in summer is about 10%. On the contrary, total precipitation in fall was more than three times higher than the climatology.

Figure 4: Seasonal total precipitation and volumetric water content during the sampling periods.

This large difference was caused by Hurricane Michael that crossed over the site as a tropical storm on October 11, 2018. The one-day precipitation during this extreme weather event accounts for 91% of the total precipitation measured over the entire sampling period. This large amount of precipitation resulted in extremely high soil volumetric water compared to spring and summer.

PRELIMINARY RESULTS

Figure 5: Seasonal NH_3, NO and N_2O flux with different N-fertilizer treatments.

Figure 6: Log [Nr] versus soil temperature.

DISCUSSIONS AND CONCLUSIONS

Overall, the largest Nr emission flux (95% confidence interval) is attributed to NH_3 (55.0 ± 10.5 ng N m^{-2} s^{-1}), followed by N_2O (27.2 ± 5.4 ng N m^{-2} s^{-1}) and NO (26.0 ± 4.6 ng N m^{-2} s^{-1}). However, there are some differences in regard to the seasonal emission patterns. Emissions of NH_3 and NO are typically high during warmer conditions, whereas more N_2O is emitted during cooler periods.

Meanwhile, the N fertilizer application also generates different emission patterns. Highest NH_3 and NO emissions were observed from the highest N treatment, while the pattern of N_2O emissions was less consistent across treatments. This finding suggests that N_2O production is likely influenced by a combination of factors, such as the interaction between soil N status and soil moisture.

Results show that the seasonal effect of soil temperature contributes to the variation and magnitude of the emissions. This relationship is strongest for NH_3 and NO, where a strong positive correlation ($r > 0.7$) between flux and soil temperature is observed, whereas N_2O displayed a weak negative correlation ($r = -0.3$) between the two variables. Future work will examine the influence of other factors on emissions, including soil moisture and chemistry. In the second phase of the project, field measurements will be coupled with a process-based biogeochemical model to assess potential turfgrass management options for minimizing Nr emissions.

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ACKNOWLEDGEMENTS

We thank the Center for Turfgrass Environmental Research and Education at NC State University for funding this project. We are also thankful to the Lake Wheeler Turfgrass Field Laboratory staff for their support.

DISCLAIMER: The views expressed in this poster are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.

Appendix C

Submitted abstract for a presentation at the 18th Annual Research Symposium, Center for Turfgrass Environmental Research and Education (CENTERE), Raleigh, NC, December 6th, 2018.

Emissions of reactive nitrogen from a turfgrass system using a dynamic chamber technique

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Turfgrass systems, including sports and amenity turfs, are an important part of urban, suburban, and rural landscapes. Intensive use of irrigation, fertilizers, and pesticides for maintaining the aesthetic value of turfgrass is often viewed as an environmental impact, particularly with respect to carbon and nitrogen biogeochemical cycles. However, emission inventories for reactive nitrogen species emitted from turfgrass systems are currently unavailable. This study, conducted at the Lake Wheeler Turfgrass Field Laboratory in Raleigh, NC, is aimed at characterizing seasonal emissions of three reactive nitrogen species, i.e., ammonia (NH_3), nitric oxide (NO), and nitrous oxide (N_2O), from turfgrass over the course of one year. These species are known for their roles in atmospheric processes including the formation of inorganic particulate matter (NH_4^+ and NO_3^-) and other secondary pollutants (e.g., NO_2 and O_3) as well as radiative forcing (N_2O). Soil emissions are measured using the dynamic chamber approach following a randomized complete block design with 10 replicates of three N-fertilizer levels (2.3% ammoniacal N, 22.7% urea N): 0, 36.5, and 73 kg N ha^{-1} yr^{-1}. NH_3 and NO emissions are measured continuously using a chemiluminescence analyzer following conversion of NH_3 to NO by heated (825°C) catalyst, while discrete air samples are collected for N_2O analysis using a gas chromatography equipped with an electron capture detector. Seasonal intensives indicate a wide range of emissions for NH_3 (5.8-93.4 ng N m^{-2} s^{-1}) and NO (2.0-47.9 ng N m^{-2} s^{-1}) and a narrower range for N2O (15.3-35.0 ng N m^{-2} s^{-1}). Highest NH_3 and NO emissions were observed from the highest N-fertilizer treatment, while the relationship between N_2O emissions and fertilizer amount was less consistent. Temperature is an important driver of NO and NH_3 emissions across seasons while N_2O emissions were only elevated after an extreme rainfall event (Hurricane Michael). Emission factors developed from this study highlight the importance of seasonality, as well as N input, in estimating reactive nitrogen emissions from turfgrass systems.

Appendix D

Submitted abstract for an oral presentation at the 2020 NADP Meeting in October 2020 and an oral presentation at the 2020 AGU Fall Meeting in December 2020. Session: Agricultural systems: links between hydrology and biogeochemical cycling.

Estimation of ammonia and nitrous oxide emissions from turfgrass systems using a dynamic chamber method and a biogeochemical modeling framework

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Turfgrass management is characterized by intensive use of fertilizers, irrigation, and pesticides that contributes to reactive nitrogen emissions to the atmosphere. This work aimed to estimate ammonia (NH_3) and nitrous oxide (N_2O) emissions from turfgrass systems by combining measurements from field experiments and simulations from a biogeochemical model. Field experiments were conducted seasonally using a dynamic flux chamber on a 50 ft by 50 ft experimental plot of tall fescue at Lake Wheeler Turfgrass Field Laboratory, Raleigh, NC. Measurements indicate a wide range of emissions for NH_3 (3.5-117.5 ng NH_3-N m^{-2} s^{-1}) and N_2O (7.2-24.3 ng N_2O-N m^{-2} s^{-1}). Both NH_3 and N_2O emissions were higher during spring and summer, suggesting that the emissions are influenced by temperature-regulated soil processes (e.g., NH_3 volatilization and microbially-driven denitrification). Meanwhile, the biogeochemical modeling simulations were performed using the Environmental Policy Integrated Climate (EPIC) model. The model utilized customized input files such as site information, daily weather data, soil physical and chemical characteristics, fertilizer types, and the site management options. Trace gas fluxes predicted by EPIC showed moderate to good correlation with measured fluxes (0.5-0.8) but tended to be biased low. Ongoing work seeks to refine the model configuration to reduce the observed bias. EPIC will then be used to explore optimal fertilization scenarios that balance turfgrass productivity with minimizing trace gas emissions.