The Differing Influences of Soil Moisture and Antecedent Soil Moisture on the Timing and Magnitude of N_2O Production

by

Jennifer Owens

A thesis
presented to the University of Waterloo
in fulfillment of the
thesis requirement for the degree of
Master of Science
in
Geography

Waterloo, Ontario, Canada, 2012

AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

Riparian soils are thought to be potential hotspots for nitrous oxide (N_2O) fluxes from incomplete denitrification, with soil moisture cited as a primary controller, however, because there are multiple potential pathways for N_2O production in soils, each with their own environmental regulators, the timing and magnitude of N_2O fluxes in difficult to predict. Often empirical observations have failed to yield consistent relationships between environmental factors in lab and field scenarios.

This thesis characterizes the hydrological controls (soil moisture, water table depth, and precipitation) on N_2O fluxes from different positions on the riparian landscape (dry, loamy upland, and wet, organic lowland) in the field during the growing season. Nitrous oxide and carbon dioxide (CO_2) fluxes in the field, as well as environmental and climatic variables, were measured in the field. Over the three year study period N_2O fluxes were consistently correlated with soil temperature during the growing season, but not with any hydrological factors. However, direct relationship between soil hydrology and N_2O fluxes was more evident on an "episodic" time scales.

Lab experiments were used to assess the influence of AHC on N_2O production under controlled conditions. Experiment 1 employed intact soil cores collected from the upland and lowland positions of the riparian landscape and the cores were subjected to one of two contrasting moisture regimes (wet-dry-wet or dry-wet-dry). Experiment 2 used homogenized soils from the upland and lowland positions on the landscape to create a multi-factorial experiment that simultaneously altered soil moisture and soil substrate concentrations (nitrate, ammonium, organic carbon). The lab results showed that different AHC resulted in differences to the timing and magnitude of N_2O fluxes, and that these patterns differed with soil type. Nitrous oxide production was often correlated with soil moisture in the lowland soils regardless of AHC. The results from Experiment 2 suggested that the upland soils were C limited, which resulted in an unpredictable relationship between soil moisture and N_2O production during different AHC. The lowland soils were less affected by AHC as they were not N or C limited like the upland soils.

It can be concluded from this research that the relationship between soil moisture and N_2O fluxes is influenced by AHC through the influence of AHC on soil N and C dynamics. Given the differences in C and N dynamics between soils types, and the influence of AHC on soil C and N, it can be concluded that a derived relationship between soil moisture and N_2O fluxes may not be directly transferable between soil types unless C and N are considered.

Acknowledgements

I would first like to acknowledge my advisor, Dr. Merrin Macrae for her advice and encouragement throughout the duration of this seemingly never-ending project. I would like to extend a great deal of thanks to Dr. Rick Bourbonniere of the Canada Centre for Inland Waters (CCIW), Burlington, for taking time out of his exceptionally busy schedule to provide practical advice and invaluable insights though the process of my thesis. I would also like to acknowledge Karen Edmondson, also of CCIW, for taking the time to run my gas samples. I would also like to thank Dr. Bourbonniere and Ms. Edmondson for collecting the three years' worth of field data used in this thesis. It was greatly appreciated and really added value to the work! I would like to thank my other committee members Dr. Petrone and Dr. Schiff for their willingness to make time to help make direct my project to make it a product of which I am proud.

I would also like to thank my lab mates Jamee DeSimone, Jenn Parrot, Jon Goetz, and Miranda Lewis for their help in the field and the lab. Thanks Erich Mulhall for his all-around likability and for calling in sick to work to help with my project with me. Special props go out to my "grad school" friends Sarah DeSilva and Matthew Lee for being awesome. Remember that time we worked late in the lab? I know this isn't an Oscar speech but I have to send out a giant thank you to my friends who were willing to do such kind acts as lend me their expensive things, let me make a mess at their house (for science), and who would pick me up from school at ungodly hours to drive me home.

Yippee! I'm done. Good job Jen!

Table of Contents

List of Figures

List of Tables

Chapter 1 Introduction and Objectives

1.1 Introduction and Rationale for Research

Understanding greenhouse gas (GHG) dynamics is important because of their role in global climate change. Carbon dioxide (CO_2) has experienced the greatest increase in atmospheric concentrations by volume of emissions, however, other GHG's such as nitrous oxide (N_2O) and methane (CH_4) also make significant contributions to climate change (IPCC, 2001). Atmospheric concentrations of N_2O have increased since the industrial revolution from around280 ppbv to current concentrations of about 350 ppbv, and this increase is attributed mainly to anthropogenic activities (Pathak, 1999).

With a Global Warming Potential (GWP) that is 290 times the amount of radiative forcing power of CO_2 over 100 years, N_2O is a potent GHG (Shine et al., 2005). Concentrations of atmospheric N_2O are increasing at a rate of 0.25% year (Pihlate et al., 2004), and this is a concern because N_2O is responsible for an estimated 6% of all global warming (Machefert et al., 2004).

It is thought that soils are the source of 65% of the total global N_2O emissions (Pathek, 1999). Soil N_2O fluxes are known to be highly episodic in nature which makes predicting and modeling terrestrial N_2O dynamics difficult (Li, 1992; Fierer and Schimel, 2002). Soil moisture is often cited as one of the primary controls of N_2O fluxes (Machefert et al., 2004; Du, 2006). However, research has failed to yield consistent empirical relationships between soil moisture and N_2O fluxes (i.e. Dobbie et al., 1999), likely because of the confounding influence of other factors. For example, the "Hole-in-the-Pipe (HIP) model" conceptualized by Firestone and Davidson (1989) suggests that the amount of N_2O production from soils via nitrification and denitrification is regulated by soil moisture, soil N and C dynamics, and soil properties. Thus, the combined influences of these factors on N_2O fluxes would benefit from further evaluation.

Agricultural riparian wetlands, which interface between agricultural fields and aquatic ecosystems or wetlands, can help to reduce the amount of nitrate (NO_3^-) in agricultural runoff (Cey et al., 1999). These landscapes are dynamic over small spatial scales and are credited for their positive influence on water quality (Bradley et al., 2011). Denitrification is often cited as the primary mechanism responsible for removing NO_3^- in riparian zones, but it is also a process that can produce N_2O emissions from soils under some environmental conditions (Bernal et al., 2007). The highly dynamics natural of N_2O fluxes also makes it difficult to characterize the relationships between N_2O fluxes and environmental variables (Davidson et al., 2000). To better understand N_2O dynamics in riparian soils, this research explores some of the uncertainty with regard to the environmental

mechanisms that drive N_2O fluxes, with a focus on the control of soil moisture on the timing and magnitude of N_2O fluxes.

The following section reviews N cycling in riparian soils, discusses biological production of N_2O, describes environmental factors governing biological N_2O, how carbon (C) and nitrogen (N) are linked in soils and to N_2O fluxes, and reviews what is known about the influence of antecedent hydrological conditions (AHC) on the timing and magnitudes of N_2O fluxes.

1.2 Literature Review

1.2.1 Nitrogen Cycling in Riparian Soils

Riparian zones function in agricultural areas as nutrient buffers for runoff between water sources and agricultural developments (Morris, 1991; Entry and Emmingham, 1996). Nitrate is a water soluble form of N (Galloway, 1998) which it contributes to eutrophication (McCarty and Bremner, 1993). If ingested, NO_3^- can cause methemoglobinemia in humans and animals, a condition that affects the ability of the blood to carry oxygen (O_2) (Martin et al., 1999). Thus, riparian areas provide a valuable ecosystem service by reducing NO_3^- concentrations from agricultural runoff before it enters surrounding aquatic systems. However, incomplete denitrification can lead to emissions of N_2O from soils. Nitrous oxide not only contributes to the greenhouse effect, but atmospheric N_2O reacts with molecular O_2 to produce nitric oxide (NO). This in turn degrades the stratospheric ozone (O_3) which is responsible for blocking harmful UV-B (Davidson, 1991). It is thought that the aforementioned environmental-soil conditions make riparian areas potential "hotspots" for N_2O production (Machefert et al., 2004), which means that the removal of NO_3^- from soils may be offset by production of N_2O and this brings into question the net environmental effects of these landscapes.

Riparian areas are characterized by sharp environmental gradients. Variability in environmental factors can foster numerous processes over a relatively small area (Gregory et al., 1999). Biogeochemical processes are known to be highly variable in both space and time, and soil C and N dynamics in soils are prone to "hot moments", which are instances of disproportionately high reaction rates relative to the surrounding soil (McClain et al., 2003). Nitrous oxide emissions are known to be especially episodic in nature (Machefert et al., 2004) and McClain et al. (2003) report that terrestrial-aquatic interfaces, such as those found in riparian areas, are known to enhance instances of hot moments in soils. It may be that while denitrification in riparian areas serves to remediate NO_3^- from soil water, these landscapes may also be contributing to climate change. There is

also considerable evidence to support that nitrification, and potentially nitrifier denitrification can also be implicated in N_2O production from riparian soils (Mosier, 1998), suggesting that more studies would benefit our understanding of the environmental conditions under which N_2O emissions occur from these riparian landscapes.

1.2.2 Biological Production of Nitrous Oxide from Soils

The contribution of soils to climate change is significant and they are thought to be responsible for 65% of anthropogenic N_2O emission (Pathek, 1999). The nitrogen cycle is complex; as the element has seven oxidation states, a variety of conversion mechanisms between N species and can experience various methods of transport and storage (Galloway et al., 2004) (Figure 1). Some portions of the N budget cannot be accounted for, which can make closing the N cycle difficult (Mosier et al., 1998).

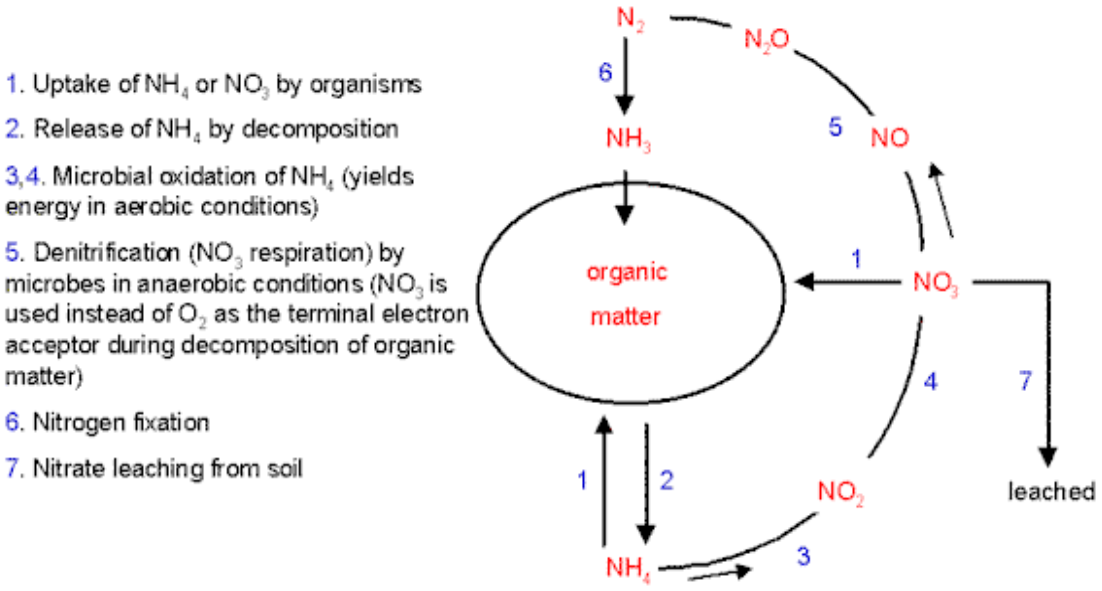

Figure 1 A simplified representation of the Nitrogen Cycle by Deacon, 2007

The number of biological pathways from which N_2O production is possible contributes to high levels of spatial and temporal variability of N_2O fluxes (Figure 2). Nitrous oxide production can be a byproduct of a number of microbial pathways (denitrification, nitrification, and nitrifier-denitrification), each with differing environmental conditions required to facilitate N_2O production (Table 1).

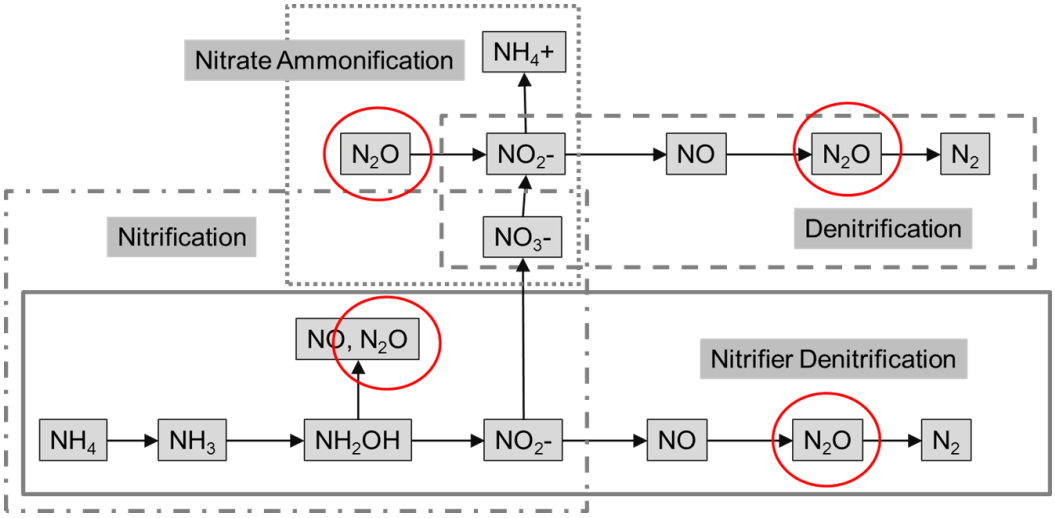

Figure 2 Potential pathways of biological production of N_2O, adapted from Baggs, 2008

Denitrification is the reduction of nitrogen oxides (NO_3^- and NO_2^-) to gaseous oxides (NO or N_2O) which are subsequently reduced to N_2 upon completion of the process (Baggs, 2008). This represents a closing of the N cycle, as N_2 is a natural and abundant constituent of the atmosphere (Mosier et al., 1998; Martin et al., 1999; Hefting et al., 2006). The ability to denitrify has been found in a range of microbes. Many denitrifiers have been identified as heterotrophic, facultative anaerobes (Knowles, 1982; Hill, 1996). It was once thought that O_2 was preferred over NO_3^- as a terminal electron acceptor for denitrifiers, but more recent research has found the occurrence of aerobic denitrification under alternating oxic-anoxic conditions and under fully aerated conditions, which suggest that there may be simultaneous respiration of O_2 and NO_3^- by different genre of denitrifying bacteria (Morley et al., 2008).

Table 1 Environmental regulators of biological denitrification, nitrification, and nitrifier-denitrification, processes that are capable of producing N_2O, and the regulators of N_2O production from these processes

Denitrification favored when:	**Source**	**N_2O production from denitrification favored when:**	**Source**
- High availability of labile C (energy source) [1] - High availability of NO_3^- (as electron acceptor) [1] - Poorly aerated soils (low O_2) - High temperature (between 20 ºC and 35 ºC) [1] - Slightly alkaline soils (pH 7.0-8.0) [2] - High soil moisture (+60% WFPS) [3]	[1] Barnard et al., 2005 [2] Simek and Cooper, 2002 [3] Davidson, 1991	- High availability of NO_3^- as electron acceptor (inhibits reduction of N_2O to N_2) [1] - Temperature below 4 ºC [1] - Slightly acidic soils (pH 4.5-6.0) [1,2] - Reducing conditions (redox potential of 0) [2] - Between 60-80% WFPS [3]	[1] Hefting et al., 2006 [2] Simek and Cooper, 2002 [3] Davidson, 1991
Nitrification favored when:	**Source**	**N_2O production from nitrification favored when:**	**Source:**
- High NH_4^+ [1] - Moderate pH [1] - Well aerated soils (30%-70% WFPS), declining as soils dry [1,2] - High temperature (between 20 ºC and 35 ºC) [1]	[1] Barnard et al., 2005 [2] Davidson, 1991	- Acidic conditions (N_2O from autotrophic and heterotrophic nitrifiers) [2]	[2] Simek and Cooper, 2002
Nitrifier-denitrification favored:	**Source**	**N_2O production from Nitrifier-dentirifiction favored:**	**Source**
- O_2 depleted environments [1]	[1] Bouwman, 1996	- High NO_2^- [1] - between 50 and 70% WFPS [2]	[1] Wrage et al., 2001 [2] Kool et al., 2011

Nitrification converts ammonium (NH_4^+) or ammonia (NH_3) to NO_3^- (Sahrawat, 2008). This process also encompasses ammonia oxidation, which is the oxidation of NH_3 into NO_2^- (Baggs, 2008), as well nitrifier denitrification, which is the reduction of NO_2^- by nitrifiers with N_2O-reductase (Wrage et al., 2001). Together with denitrification, nitrification from soils is thought to be the primary process responsible for anthropogenic N_2O emissions (Baggs, 2008). A group of obligate autotrophic soil bacteria collectively known as *nitrobacteria* are responsible for most of the biological oxidation that occurs during nitrification (Sahrawat, 2008). *Nitosomonas*, a subgroup of *nitrobacteria*, oxidizes NH_3 or NH_4^+ to NO_2^-, and a second subgroup of *nitrobacteria* called *nitrobacter* are responsible for the conversion of NO_2^- to NO_3^- (Sahrawat, 2008). There is evidence to suggest that strains of *nitrobacter* can produce N_2O via anaerobic reduction of NO_3^- but there is very little known about this pathway (Freitag et al., 1987; Wrage et al., 2001).

Nitrifier-denitrification is carried out by a group of autotrophic NH_3-oxidizers (Wrage et al., 2001), and this process contributes to gaseous losses of N from soils by converting NH_4^+ to NO or N_2O (Poth and Focht, 1985). Laboratory results from Kool et al. (2011) found that N_2O production from both denitrification and nitrifier-denitrification decreased with decreasing soil moisture, however, denitrification decreased more so relative to nitrifier-denitrification suggesting rates of nitrifier-denitrification are less influenced by soil moisture. The same study found that the relative contribution of nitrifier-denitrification as a percent of NH_4^+ derived N_2O did not strongly differ with soil moisture, and that the relative contribution of N_2O from nitrifier-denitrification under experimental conditions contributed more N_2O than denitrification of NO_3^- at intermediate to high soil moistures (50 and 70% WFPS) suggesting that at some soil moistures and under certain soil conditions, nitrifier-denitrification may be just as important as pathways as nitrification and denitrification for N_2O production.

Some nitrifiers denitrify during anaerobiosis, but in the presence of relatively higher O_2 will denitrify aerobically, and to further complicate things, the behavior of such microbes may be partially controlled by substrate availability, with different behaviors observed in the presence of NH_4^+, both NH_4^+ and NO_3^-, and NO_2^- (Kuenen and Robertson, 1994). Both autotrophic and heterotrophic nitrifiers have been found to carry out denitrification, though this process is complex and not well understood (Kuenen and Robertson, 1994). Many heterotrophic nitrifiers are also denitrifiers, and are able to reduce nitrification products like NO_2^- and NO_3^- via denitrification, as experiments have confirmed that N_2O can be produced from NH_4^+ (Kuenen and Robertson, 1994). Short-term O_2 stress can result in aerobic, autotrophic microbes switching from nitrification to denitrification, which results in an output of N_2O instead of NO_3^- (Kuenen and Robertson, 1994).

Coupled nitrification-denitrification has also been implicated in N_2O emissions from soils. Rather than being a process carried out by one group of microbes like nitrifier-denitrification, coupled nitrification-denitrification describes instances where both processes happen simultaneously (Wrage et al., 2001; Pihlate et al., 2004). The coupling of these processes tends to occur in microsites or aerobic-anaerobic interfaces (Baldwin and Mitchell, 2000) and N_2O production from coupled nitrification-denitrification is highest when conditions are sub-optimal for either process (Wrage et al., 2001). The congruency of nitrification and denitrification has been attributed to part of the difficultly in consistently modeling and predicting N_2O fluxes from soil because their simultaneous occurrence is dependent upon having conditions in soils that can support both processes, and these conditions are associated with a high degree of spatial and temporal variability in N_2O emissions (Kuenen and Robertson, 1994; Hergoualc'h et al. 2007). Usually, evolution of N_2O is thought to be the result of nitrification in aerobic soils and denitrification under more anaerobic conditions (Barnard at al., 2005). Pihlate et al. (2004) suggest that 60% WFPS is the threshold that determines whether nitrification or denitrification will occur; with nitrification predominating below the threshold and denitrification predominating above the threshold. Simultaneous nitrification-denitrification is expected to be most prevalent between 30% and 70% WFPS (Pihlate et al., 2004) (Figure 3).

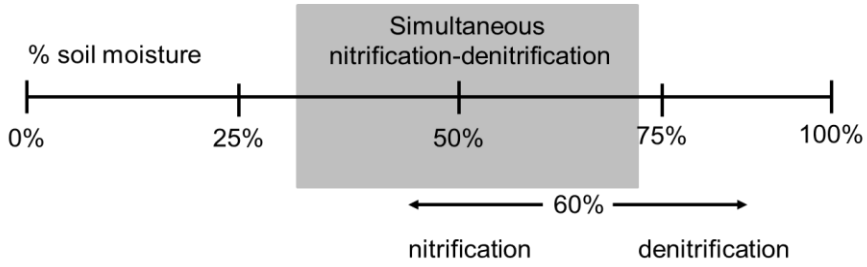

Figure 3 Theoretical soil moisture conditions for simultaneous nitrification-denitrification, adapted from Pihlate et al., 2004

Since there are many possible pathways for biological N_2O production, and the possibility of coupling of the processes, as well as the fact that each of these processes have their own environmental controls for N_2O production, it is difficult to predict the timing and magnitude of N_2O fluxes from soils in the natural environment.

1.2.2.1 Controls on Dynamics of Gaseous End Products of Nitrogen

The existence of multiple pathways for N_2O production contributes to the complexity of N_2O soil fluxes, as does the possibility of gaseous-end products other than N_2O from these pathways. Current and past environmental soil conditions may be influential to the fraction of N_2O produced. Though

soil moisture is often cited as one of the primary variables controlling denitrification and nitrification (Davidson, 1992), these biological processes can have numerous gaseous end-products, which are partially regulated by O_2 availability (Dendooven et al., 1996) and soil moisture (%WFPS) is thought to be a suitable proxy for soil O_2 content (Linn and Doran, 1984) (Figure 4).

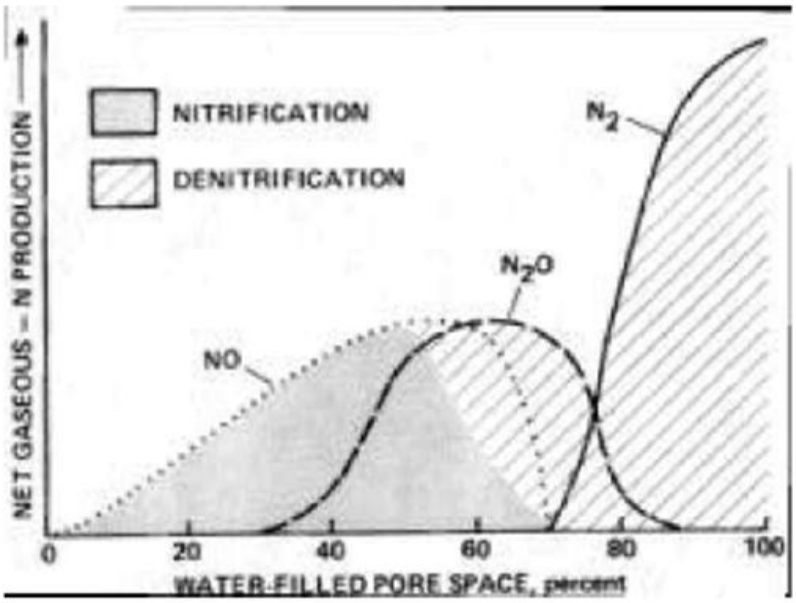

Figure 4 Showing the fractional end products from nitrification and denitrification as a function of %WFPS, as suggested by Davidson (1991)

Dinitrogen production from denitrification is commonly associated with saturated soils, whereas N_2O production is more typical in soils that are highly moist but unsaturated (Linn and Doran, 1984). Studies have found that N_2O fluxes are higher when soil moisture was greater than field capacity, while soil moistures below field capacity seems to favor NO production (Davidson, 1992; Hutchinson et al., 1993; Paul et al., 1993; Skiba et al., 1993). In support of this, the ratio of N_2O/NO has been found to increase with increasing soil water content (Ballmann and Conrad 1998; Skiba et al., 1993).

Studies that compare amounts of the relative fluxes of N_2O and N_2 are commonly studied in laboratory experiments since it is difficult to measure N_2 in the field due to the high ambient atmospheric N_2 concentrations (Skiba et al., 1993). On a cellular level, the enzymes responsible for denitrification (denitrifying enzymes) and their response to changes in soil moisture may influence the N_2O mole faction [N_2O:(N_2O+N_2)] (Bergsma et al., 2002). Denitrification enzymes are quick to trigger, activating within a few hours of when soil conditions become favorable for denitrification

(i.e. anaerobiosis), and denitrification reductases are inactivated within a few minutes or hours when conditions become unfavorable (Knowles, 1982; Simek and Cooper, 2002) suggesting small lags between changes in soil conditions and dynamics of gas production should be expected. Research suggests that though actual rates of denitrification are fastest in slightly alkaline (higher pH) soils, denitrification from acidic soils actually favors N_2O over N_2 production (Simek and Cooper, 2002). Similarly, higher NO_3^- concentrations support higher N_2O production relative to N_2 during denitrification because NO_3^- inhibits N_2O reduction (Morris, 1991; Hefting et al., 2006). The ratio of $[N_2O:(N_2O+N_2)]$ has been found to be higher in soils where the supply of O_2 and NO_3^- is sufficient to meet the demands for terminal electron acceptors (Allsion et al., 1960; Vor et al., 2003). In support of this, a dramatic increase of denitrifying activity and the N_2O release by denitrification has been observed at O_2 partial pressure lower than 0.5% O_2 (Parkin and Tiedje, 1984).

Biological production of N_2O is complex, and that not only are there multiple biological pathways capable of production, each of these pathways has its own environmental constraints, and we do not necessarily have a solid understanding of when and where to expect N_2O production from soils. Methodological constraints as well as the high cost of advanced monitoring techniques make it difficult to accumulate large, high resolution datasets that match biological parameters and environmental conditions with N_2O production in the field. Despite the complexity of N_2O production from soils, some success has been noted in understanding N_2O flux dynamics using just environmental parameters. This topic is reviewed below.

1.2.3 Regulation of N_2O Fluxes

Soil moisture, presence of O_2, availability of C and N, soil pH, and temperature have been cited as regulators of N_2O production from soils (Patten et al. 1980; Groffman and Tiejde, 1988; Rudaz et al. 1991; Martin et al. 1999; Pathak, 1999). However, N_2O fluxes from soils are known to be highly episodic in nature, and there appears to be some inconsistency in the literature with regards to how these environmental variables interact to govern N_2O emissions, and when these factors are significant (Firestone and Davidson, 1989; Baldwin and Mitchell, 2000; Machefert et al., 2004). As a result, empirical observations of N_2O fluxes from soils do not always fit with theoretical expectations (Hefting et al., 2006).

The Hole-in-the-Pipe model (the "HIP" model, also referred to as the leaky pipe model) is a simple yet comprehensive, conceptual model linking together the influence of multiple environmental factors and their influence on N_2O emissions from soils (Firestone and Davidson, 1989). It describes

two levels of regulation; the first is regulation of the rates biological production of gases, which are controlled by the rate at which N is moved through the pipes; and the second is the environmental factors that influence the amounts of type of gaseous end-products, which conceptually refers to size of the hole in the pipes through which the gases "leak". This schema describes controls on N_2O and NO fluxes using two pipes that represent nitrification and denitrification. Nitrogen cycling is represented by the flow of N through the pipe, and soil water content and other soil properties, such as soil pH, affect the ratio of N_2O:NO emissions, symbolized by the relative sizes of the holes through which NO and N_2O escapes (Firestone and Davidson, 1989) (Figure 5). Researchers have used this model to help interpret observations of N_2O (and NO) soil emissions from various environments (Davidson et al., 2000). It demonstrates that though soil moisture is acknowledged as an important physical control on N_2O emissions from soils through its control on O_2, other factors such as soil type and inorganic N are also significant. Soil field capacity (often assumed to be about 60% WFPS (Davidson et al., 2000)) is of significance because it is thought that this is the boundary where both oxidative and reductive processes are both active in soils (Davidson et al., 2000).

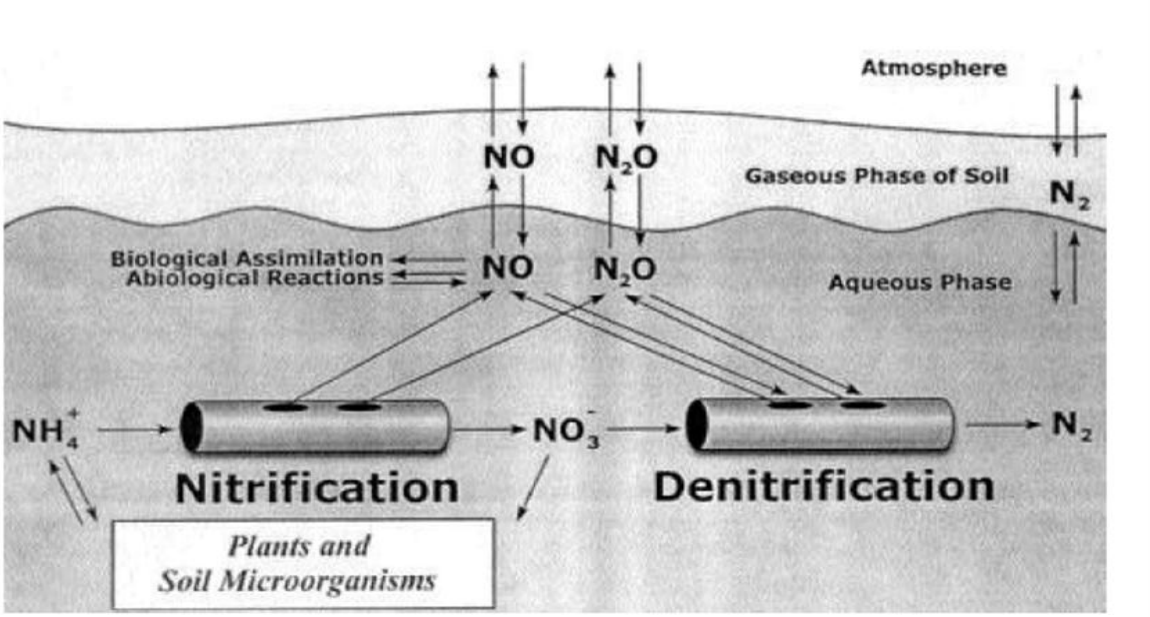

Figure 5 The Hole-in-the-Pipe model, created by Firestone and Davidson (1989), adapted from Davidson et al., 2000

1.2.4 Linking Carbon and Nitrogen Dynamics

Substrates are important microbial nitrification and denitrification. Inorganic forms of N are particularly important to the aforementioned processes because NH_4^+ and NO_3^- are the starting

ingredients of the processes (Austin et al., 2004; Pihlate et al., 2004). It is mineralization that converts organic forms of N to these inorganic forms which can be used by N_2O producing microbes (Sleutel et al., 2008).

Carbon and N dynamics are tightly linked in soils (Mosier et al., 1998; Fontaine et al., 2003) and microbial activity is a dominant factor controlling CO_2 or C respiration. Nitrogen mineralization and immobilization are strongly related to the decomposition of organic C in soils since N in organic matter (OM) and plant debris is often bound to C. Decomposers derive their energy from C compounds found in soil OM (Reddy and DeLaune, 2008). Nitrogen mineralization is limited by the chemical (i.e. lability) and physical (location of OM) bio-availability of organic substrates (Ahn et al., 2009). Carbon respiration (CO_2 production) can use O_2 supplies in soils, and if this occurs at rates that exceed O_2 replenishment into the soils, it can result in anaerobic conditions in the absence of saturated moisture conditions (Luxmoore et al., 1970). However, surface soils are often the focus of attention with regards to mineralization because rates have been found to be highest in the upper soil horizons (Rovira and Vallejo, 1997), and N receives more attention than C with regards to this process because N is often found to be limiting for primary production in agricultural and forest ecosystems (Fontaine et al., 2003).

The microbial activity associated with mineralization is positively related to soil temperature. With respect to soil moisture, mineralization is low in dry soils due to biological limitations that accompany limited water resources, highest at intermediate soil moistures, and relatively lower at saturation because of the limited availability of O_2 (Reddy and Delaune, 2008).

Nitrate is utilized by decomposing microbes, and concentrations of NO_3^- can be temporarily decreased in the soil during decomposition as NO_3^- is immobilized and assimilated by microbes (Reddy and Delaune, 2008). This is likely to occur in soils with greater C:N ratios because microbes need the additional N to meet their biological N requirements in order to use the available C in the OM. Organic soils that are high in N tend to favor ammonification whereas those that are N limited tend to favor immobilization, which results in a temporary decrease in available N (i.e. extractable soil NO_3^- concentrations) (Reddy and Delaune, 2008).

Not only is the soil C:N ratio important to mineralization and ammonification rates, but the quality of the detritus is also significant. Different organic substrates decompose at different rates. In increasing order of lability: proteins, carbohydrates, cellulose and hemicelluloses, lignin can be found in soils (Tan, 2000). Though it is known that not all organic material is equally labile, measuring this quality from substrates is highly intensive (Reddy and Delaune, 2008).

Soil characteristics also influence rates of mineralization. Greater rates of mineralization have been detected in coarse textured, low clay content soils (Reddy and Delaune, 2008). Likewise, finely textured soils high in clay content have more micropores which can serve to physically protect much of the soil matrix from mineralization (Reddy and Delaune, 2008), suggesting soil structure, change in soil structure, and soil composition are all influential to the spatial and temporal variability of N dynamics in soils. The biological pathways of N_2O production are highly dependent on N and C substrates to fuel these processes so linking these processes may be important to our understanding of the timing and magnitude of N_2O fluxes.

1.2.5 The Influence of Wet-Dry Cycles on Soil N_2O Flux Dynamics

Antecedent hydrological conditions (AHC), or soil moisture history, and wet-dry-cycles (WDC) influence the rate and magnitude mineralization, denitrification, and nitrification in soils (Groffman, and Tiedje, 1988; Fierer and Schimel, 2002) but the degree to which moisture variability dictates these processes is difficult to quantify. Past research suggests that AHC can influence variables aspects of the soil environment, including the population and structure of microbial communities and C dynamics, as well as influence the structural integrity of soils (Fierer and Schimel, 2002), suggesting the influence of AHC on soil N_2O emissions from soils may benefit from additional research..

The historical soil moisture conditions may also be influential to "current" N_2O producing processes from soils. For example, results from previous research has found that N2O evolution is minimal from continuously wet or continuously dry soils, while relatively higher N_2O emissions have been observed from soils subjected to alternating WDC (Smith and Patrick, 1983) with high rates of denitrification have been observed from continuously wet soils that were dried and rewet (Groffman and Tiedje, 1988). This appears to be a case for different soil types, as results from Duxbury et al. (1982) and Goodroad and Keeny (1984) demonstrated that N_2O fluxes from both mineral and organic soils were lower during an extended dry period compared to measurements following rainfall event. These higher magnitudes of N_2O fluxes during change soil moisture may be the result of higher rates of biological processes. Wet-dry cycles appear to enhance rates of nitrification and denitrification in soils (Fierer and Schimel, 2002).

Dynamic moisture regimes are thought to stimulate microbial activity and mineralization of soil OM. This has been attributed to death of microbial biomass upon rewetting of dry soils which can result in the lysing of microbial cellular contents into soils. The former contents of the cells can then

be used as substrate for surviving microbes (Bottner, 1985; Van Gestel et al., 1992). It is also thought that WDC facilitate the break-up of aggregates and expose organic matter that was previously protected within the soil matrix (Fierer and Schimel, 2002; Mikha et al., 2005).

The complexities of N_2O production from various pathways and their associated environmental parameters is important to understanding spatial and temporal dynamics, and warrants further research. This research aims to better understand how hydrological variability and AHC influence N_2O dynamics from an agriculturally impacted riparian zone.

1.3 Objectives and Hypotheses

The highly dynamic nature of N_2O makes quantification of fluxes from landscapes difficult without continuous measurements, which are often unrealistic. A more thorough understanding of N_2O production from riparian landscapes can help improve N_2O monitoring protocols and optimize field sampling strategies, improve data interpretation and N_2O modeling efforts, and enhance riparian management strategies.

This research explores the lack of consistency with regards to the timing and magnitude of N_2O emissions from soils and the associated environmental conditions.

Using three years of field data, the primary objectives of this thesis are:

1.1. Characterize temporal dynamics and controls on the magnitude of N_2O fluxes from the field at different positions on the riparian landscapes (upland vs. lowland), and

1.2. Investigate how hydrological variables including soil moisture, water table, and precipitation work together to explain N_2O flux timing and magnitude from two positions on the riparian landscape (upland vs. lowland).

Secondly, this thesis compares the effects of contrasting AHC on N_2O fluxes from two soil types from the riparian landscape (upland mineral soils and lowland organic soils) in a controlled laboratory setting. The objectives of this are to:

2.1 Determine if antecedent soil moisture conditions (wet-dry-wet *versus* dry-wet-dry) influence the timing and magnitude of N_2O fluxes, and determine if this influence differs between upland and lowland soil types, and

2.2 Determine if the combined influence of soil moisture and soil N significantly influences the relationship between soil moisture and N_2O fluxes, and does this differ between the upland and lowland soil types.

It is expected that the results from the field will show that there are differences in the magnitudes of N_2O fluxes from the upland and the lowland field data, since the hydrological regimes and soil properties between the landscape positions differ. It is hypothesized that:

1.1 Temperature and soil moisture will be the primary drivers of N_2O fluxes from both landscapes, but the relative relationships between soil moisture and N_2O fluxes will differ between the upland (dry) and lowland (wet) because of the different hydrological conditions, and

1.2 The combined effect of soil moisture and other hydrological variables (water table and precipitation) will impact the relationship between soil moisture and N_2O fluxes, but this will differ by landscape position. Due to the differences in proximity to Spencer Creek, it is expected that the wetter lowland will be less influenced by precipitation. Water table variability is expected to be important to both landscape positions, given the expected coupling between hydrological variables (soil moisture, water table, and precipitation).

Using the experimental lab results to address Objective 2, it is hypothesized that:

2.1 AHC will influence the timing and magnitude of N_2O fluxes from both landscape positions, and that the timing of N_2O fluxes will be largely related to soil moisture, with a positive relationship observed between fluxes and soil moisture up to 80% WFPS; and

2.2 Nitrogen concentrations will positively influence the relationship between soil moisture and N_2O production, and positively contribute to the magnitude of N_2O emissions.

1.4 Research Approach

To address the objectives of this thesis, field data from two different positions on a riparian landscape were assessed. The field edge (upland) soils are loamy and relatively fine in texture, and the soils at the soil-stream interface (lowland) are characterized as a peaty, organic wetland-type soil. Field data from three climatically contrasting years was compiled to assess the relationship between hydrology and N_2O fluxes in the field, and to determine if the relationship differed based on differences in precipitation, soil moisture, and water table.

This research also employed a series laboratory experiments. Experiment 1 explored the influence of different AHC on the timing and magnitude N_2O production from the upland and lowland soils. In the lab, contrasting soil moisture regimes were created and the soil N, CO_2 production, and N_2O production were monitored from intact soil cores. Soil moisture regimes created during Experiment 1 was cycles of "wet-dry-wet" (WDW) and "dry-wet-dry" (DWD). Experiment 2

was a multi-factorial experiment that helped isolate the relative degrees of influence of soil moisture, and soil C and N, on the magnitude of N_2O production from the two different soil types. This experiment used batched soil to remove the influence of soil structure and decrease the variability associated with soil heterogeneity, to examine under controlled conditions how the N_2O production differed with respect to different levels of soil N and C and soil moisture in the different soil types.

Chapter 2 Site Description and Methods

2.1 Site Description

John Mount Research Farm is located in Flamborough, Ontario, Canada (43°22'55.80" N, 80°07'29.97" W), south-east of the Valens Reservoir. The reservoir is dammed upstream of the site and the dam is the dominant hydrologic control through much of the region (Heagy and McHattie, 1995). The research station is located at the southern end of an agricultural field. The field interfaces with Spencer Creek which flows through Beverly Swamp, a large, undisturbed wetland. The elevation of the site varies between approximately 264-269 meters above sea level (masl).

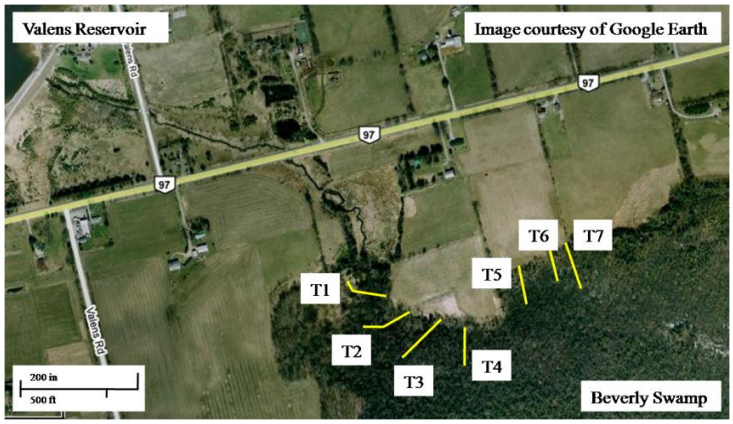

Figure 6 John Mount Farm is situated north of Beverley Swamp, and south-east of the Valens Reservoir

The site is equipped with eight transects. This research was situated on transect 5 (T5) (Figure 6), which is 24m long and has a topographic gradient of about 7% (Figure 7) (DeSimone et al., 2010). The adjacent agricultural fields grow a rotation of corn, barley, and soybeans.

2.1.1 Transect Properties

For this research, the riparian zone at T5 is divided into two sections; the upland position, which is located approximately 2m from the field edge of the adjacent agricultural field, and the lowland position which is located 24m from the agricultural field edge. The upland soils experience longer periods of relative dryness with short periods of rewetting during precipitation events due to the elevated topographic position. The upland is characterized by the clay-loam soils, and is consistently loamy through the first 10 cm of soil depth with no noticeable organic top layer. It receives nutrient

inputs via shallow groundwater flow from the adjacent agricultural fields. The lowland position, is at the northern edge of Beverly Swamp, is characterized by highly organic, peaty soils. The soils are highly reducing in nature since they are susceptible to periods of prolonged inundation due to overbank flooding from Spencer Creek and the presence of a marl layer in the swamp that impedes drainage (DeSimone et al., 2010). A summary of soil properties is found in Table 2.

Table 2 Soil properties for the upland and lowland soils for the surface soil

Characteristic	Upland	Lowland
Field capacity (g/cm^{-3})	0.54	0.65
Field capacity (%WFPS)	80	84
Porosity (%)	40.27	65.17
Bulk density (g/cm^{-3})	0.82	0.16
Organic content (%)	6.9	54.6

The upland and lowland soils have different C:N ratios. Previous research conducted by DeSimone et al. (2010) at this site reported the mean the C:N ratio at the T5 position to be 9.6 in the upland and 18 in the lowland (Figure 7).

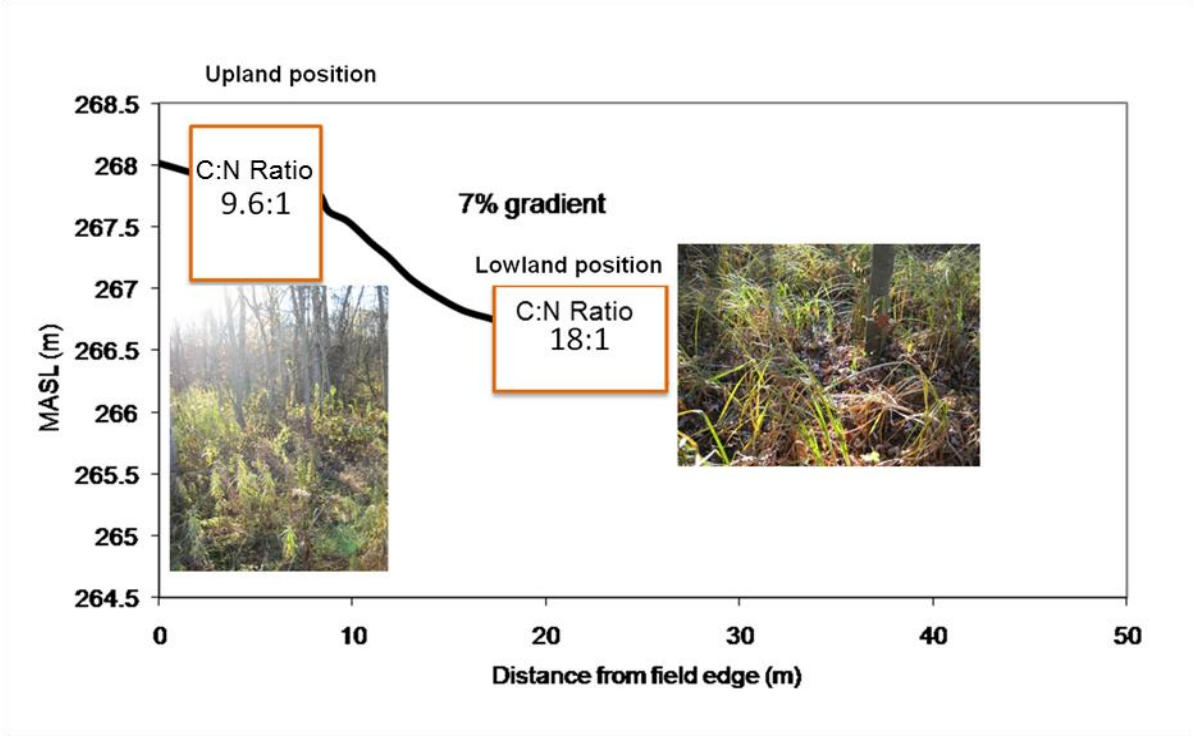

Figure 7 Topographic profile of transect 5, and pictures depicting the vegetation types at the upland and lowland landscape positions

2.1.2 Vegetation

Broadleaf deciduous trees are dominant at the site, with a mean canopy basal area of 17 m^2/ha. The canopy is primary composed of large Silver Maple (*Acer saccharinum* L.), which is 96% of the total, but also included Black Ash (*Fraxinus nigra* Marsh.), White Elm (*Ulmus americana* L.), Eastern White Cedar (*Thuja occidentalis* L.), and Speckled Alder (*Alnus incana*). The area is also sporadically scattered with Red Ash (*Fraxinus pennsylvanica* Marsh.), Trembling Aspen (*Populus tremuloides* Michx.), and Ironwood (*Ostrya virginiana*).

The subcanopy is composed of small trees and shrubs Choke Cherry (*Prunus virginiana* L.), Elderberry (*Sambucus canadensis* L.), Sweet Viburnum (*Viburnum lentago* L.), and Common Buckthorn (*Rhamnus cathartica* L.).

In the upland position, the understory vegetation is dominated by grasses and herbaceous flora including Goldenrod (*Solidago* spp.) and Aster (*Aster* spp.), and in places, there is dense cover of Ostrich Fern (*Matteuccia struthiopteris*).

In the lowland swamp, the understory consists primarily of Jewelweed (*Impatiens capensis*), Tall Meadow Rue (*halictrum polygamum*), Virginia Creeper (*Parthenocissus quinquefolia*), Marsh Marigold (*Caltha palustris*), Dewberry (*Rubus flagellaris*), nettles (e.g. *Laportea Canadensis* and various *Urtica* spp.), violets (*viola* spp.), ferns (predominantly *Onoclea sensibilis*, and *Dryopteris* spp.), sedges (*Carex* spp., especially *Carex comosa*) and some Reedcanary Grass (*Phalaris arundinacea*). An array of aquatic grasses (e.g. *Scirpus* spp.), Smartweeds (*Polygonum* spp.), and native loosestrifes (e.g. *Lysimachia ciliate* and *Lysimachia thyrsiflora*) are also found thriving within 1 m from the stream edge (Cymbaly and Bourbonniere, unpublished data).

2.1.3 Climate and Hydrology

Warren et al. (2001) classify the climate at Beverly Swamp as humid continental. Data from two nearby Environment Canada meteorological stations were used to show the climatic averages for each of the field years compared to a 30 year average (Figure 8). The 30 year average data was from the Hamilton RBG station (Latitude: 43°17'00.000" N, Longitude: 79°53'00.000" W) and the 2007, 2008 and 2009 climatic data are from the Roseland station (Latitude: 43°21'13.026" N, Longitude: 80°28'25.056" W) (Table 3).

Table 3 Comparing the annual average air temperature and the annual total precipitation from the field years to a 30 year record

Year	Average Annual Temperature (°C)	Total Annual Precipitation (mm)
2007	8.4	744.3
2008	7.8	1137.2
2009	6.7	865.2
30 year average	8.5	892.6

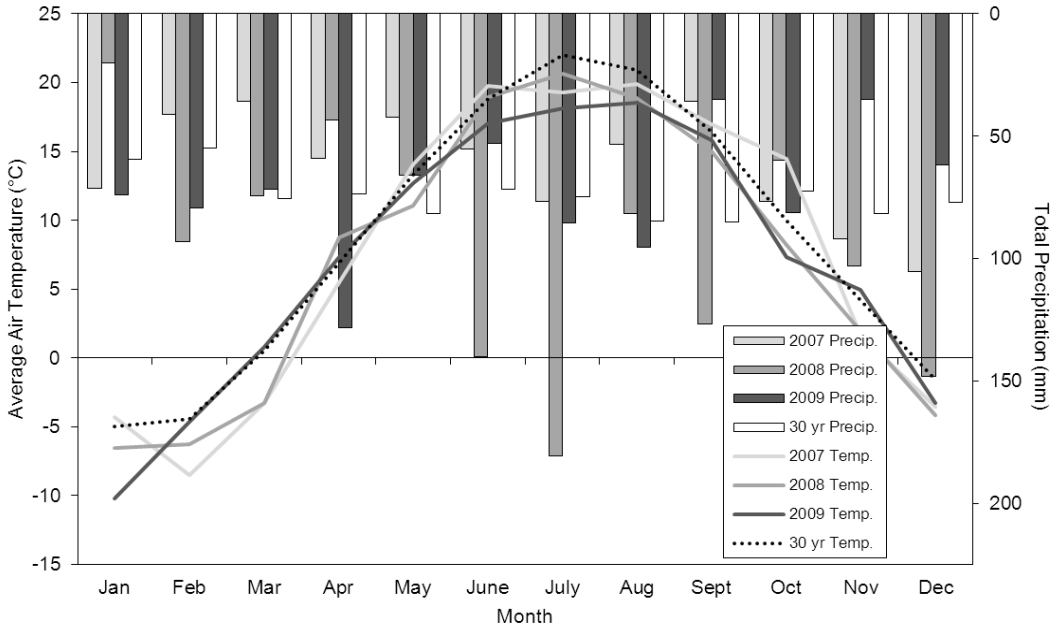

Figure 8 Average mean monthly air temperature and total monthly precipitation for 2007, 2008, 2009 and a 30 year average.

Compared to the 30 year average, 2007 had the lowest annual precipitation, 2008 was wetter than average, and total annual precipitation during 2009 was comparable to the 30 year average (Table 3). As expected, the general annual trend for air temperature was similar in every year (Figure 8). The air temperature in 2007 was cooler in the spring and peaked early (mid-May), resulting in generally warmer year compared to the other field years and to the 30 year average. During 2008, the air temperature was comparable to the long-term average but peaked early resulting in a relatively cooler summer. In 2009, the minimum temperature recorded during the period of interest (May to November) was higher than the other years, reflecting the relatively warmer spring that occurred during that year. Autumn air temperature in 2008 and 2009 were both cooler than the 30 year average (Table 3).

The distribution of annual precipitation varied among the years. 2007 was relatively dry from June onward compared to the other years. 2008 is largely consistent with the 30 year average for most of the year but it was wetter during March and July, which contributed to the greater than average total annual precipitation. The distribution of precipitation throughout 2009 differed slightly from the long term average, with 2009 being wetter in the summer relative to the 30 year average (Figure 8).

2.2 Field Data Collection

Field data for this study was collected from T5 between 2007 and 2009 during the growing season for each year (May to November, inclusive).

2.2.1 Greenhouse Gases

Emissions of greenhouse gases from the soil were determined as non-steady state fluxes using the static chamber method (Hutchinson and Moiser, 1981). Square aluminum collars with an inside length of 47.5 cm (area = 0.2088 m^2), and with a channel on top to provide a water seal were inserted into the soil to a depth between 5 and 10 cm. After leveling and settling for a week or more the depth from the top of the collar to the soil surface was measured at 16 grid points and a reference corner. This collar topography allowed calculation of the air space in the collar, which could be adjusted for each sampling event by measuring the reference. Vegetation in the collars was clipped and the clippings remained in the collar; moss was left intact because clipping it would disturb the soil.

Nitrous oxide fluxes were determined on the same collars using smaller square PVC chambers (l = 50.6 cm, h = 7.9 cm; V = 12.03 L after correcting for 3.2 cm overlap with the collar water channel), painted white on the outside, fitted with a 1-in fan, an expansion vent loop, and a quick-connect fitting with a check valve. Samples of chamber air were collected at 20, 40, and 60 minute intervals using a 30 mL syringe connected to a PVC tube with a quick connect at the end, along with samples of ambient air collected at the beginning and end of the sampling interval to serve as the time zero point. Air samples were stored in evacuated 12 mL Exetainers by over-pressuring with 20 mL injected.

To determine soil respiration (Rs, CO_2) we used large square acrylic chambers (l = 49.5 cm, h = 40 cm; V = 90.2 L after correcting for 3.2 cm overlap with the collar water channel) covered with reflective insulation, fitted with a 3-in fan to promote mixing and an expansion vent loop. An infrared gas analyzer (IRGA, Vaisala Model GMP343) and a temperature and relative humidity probe (Vaisala Model TRH-75) were installed onto the chamber and connected to a logger/controller

(Vaisala Model MI-70). Static flux runs were 5 minutes in duration with a sampling frequency of 15 sec; CO_2 concentrations were determined in ppmv corrected for chamber temperature and ambient barometric pressure.

Every effort was made to use the same collars and chambers at all samplings. On a few occasions when flooding was extensive and the square collars were underwater so deep that the short chambers could not be used for N_2O, or so unstable that the heavier large chambers could not be used for CO_2 by IRGA, cylindrical tethered floating chambers were used to determine all three GHGs at the same collar sites. These PVC chambers (d = 19.9 cm, h = 25 cm; V = 6.843 L after correcting for the 3 cm immersion for which they were designed), were covered with reflective insulation and, like the short square chambers they were fitted with quick connects, sampling tubes with syringes and expansion vent loops, but no fan. They were sampled in the same manner as the short square chambers. Gas flux calculations are detailed in the Field Methods Appendix.

2.2.2 Environmental Variables

Measurements of environmental variables accompanied the GHG data. For each sampling event air and soil temperature (5 and 10 cm) were taken with a digital thermometer, and soil moisture (average of 4 positions around each collar) was determined using a Theta-Probe (Delta-T Systems), which was calibrated to Percent Water-Filled Pore Space (%WFPS) using soils from the site.

A Hobo Weather Station (Onset Computer Inc.) at the site recorded wind speed, wind direction, air temperature, relative humidity, rainfall, total solar radiation, photosynthetically active radiation (PAR) and station pressure logged at 15 minute intervals. These data were used to accompany the field N_2O and CO_2 fluxes to help characterize local climatic variability for the area. Though the site meteorological data was recorded at 15 minute increments, a daily total precipitation was used for the purpose of this analysis, and air temperature was averaged on a daily time step. Daily average water table depth (meters below the surface) was determined from continuously monitored wells equipped with a Hobo Water Level Logger at 15 minute intervals (calibrated with manual measurements). Water table measurements were averaged at a daily time step.

2.1 Laboratory Experiments

2.1.1 Experimental Design: Overview

A suite of laboratory experiments was designed to observe the influence of AHC on spatial and temporal dynamics of N_2O production, and to isolate the combined influence of N and C, and soil

moisture on N_2O production. Experiment 1 used intact soil cores extracted from the upland and lowland positions and subjected each soil type to one of two contrasting soil moisture regimes. Experiment 2 used homogenized soils from the upland and lowland landscape positions to mitigate the influence of soil texture which contributes to variability and to better articulate the influence of soil moisture, soil N and C, and soil type on N_2O production.

2.1.2 Experiment 1: The Influence of Wetting and Drying Cycles on N_2O Flux Timing and Magnitude

In October, 2008, 87 intact soil cores (42 from the upland position and 45 from the lowland position) were collected from T5 at John Mount Farm for Experiment 1 (Figure 9).

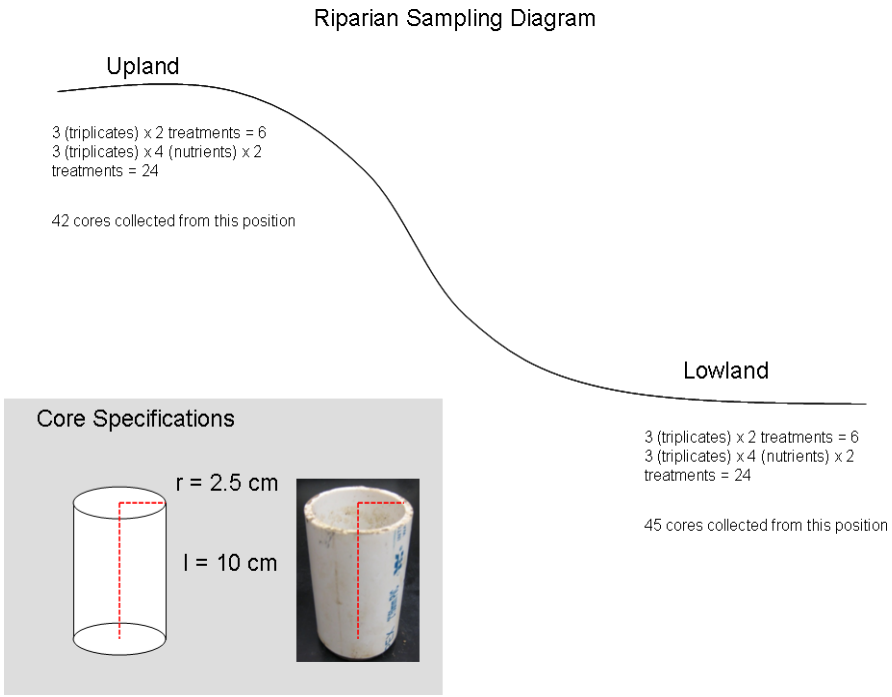

Figure 9 The relative positions from which the soil extraction took place on the riparian zone, as well as specifications for the intact soil cores

The cores were acquired from an area 15 m west of the T5 boardwalk to prevent disturbance to on-going hydrological and gas measurements. Litter (leaves, branches etc.) was cleared from the soil prior to collection of the soil cores. Using a mallet and small wooden board, the cores were randomly placed within a 1 x 1 m plot and hammered evenly into the ground until the top of the PVC tube was flush to the soil surface (Figure 10). The cores were excavated using a small trowel. A bread

knife was used to level the bottom of the soil cores with that of the PVC tube. The cores were wrapped in aluminum foil and stored in ziplock bags.

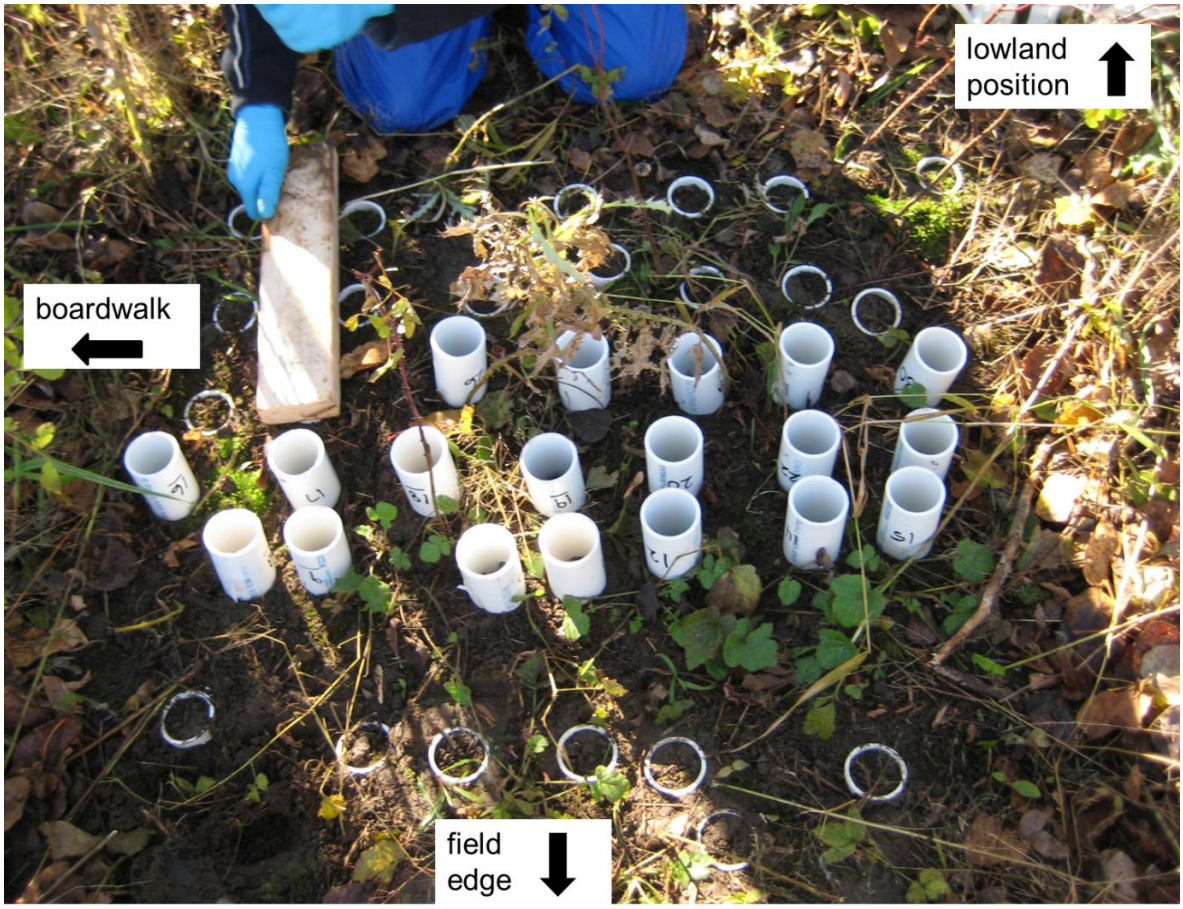

Figure 10 Extraction of the intact soils cores from the upland position

The cores were kept overnight in the lab in a cooler. Nylon window screen was wrapped around the bottom of the samples and secured with electrical tape to prevent loss of loose soil. The samples were placed in aluminum trays and their weights (of the trays, PVC tubes, nylon window screen, tape and soil cores) were recorded (Denver Instrument, 0.0001 g precision). Any excess water that was present in the ziplock bags was added to the samples prior to weighing.

Results from the preliminary experimental work showed that the N_2O fluxes were below detection. It was hypothesized that this was due to the time of year (October) as recent conditions had been wet and cold. Thus, prior to the experiment, all of the cores were subjected to a two month drying period to promote mineralization. The soil cores dried gradually in the lab at 25°C. At the end

of the drying period, the upland soil cores were on average 27.5% WFPS, while the lowland cores were much drier, reaching an average of 6% WFPS.

2.1.2.1 Antecedent Soil Moisture Regimes

All cores were subjected to either a "wet-dry-wet" (WDW) or a "dry-wet-dry" (DWD) soil moisture regime after the two month drying period. Following the initial saturation event, which lasted three days, the first phase of moisture change, also called phase 1, lasted 27 days, and the second phase of soil moisture change, also called phase 2, lasted 28 days. The "moisture pivot" refers to the change in direction of soil moisture at the mid-point of the experiment (Figure 11).

The WDW moisture regime began by saturating the soils and holding at the highest achievable soil moisture during the "initial saturation event". Soils were then dried for 27 days to simulate a dry down period (phase 1 WDW, wet → dry), and subsequently rewet to near saturation gradually over 28 days (phase 2 WDW, dry → wet). The DWD moisture regime began with dry soils that were gradually wet up (phase 1 DWD, dry → wet). Once at the highest achievable soil moisture, the soils were re-dried for 28 days (phase 2 DWD, wet → dry). While soil moisture changed from wet to dry during phase 1 of the WDW moisture regime, the soils were air dried for the first 18 days and then fans were used to assist drying for the remainder of the phase. During phase 2 of the DWD moisture regime, when soils changed from wet to dry, the cores were air dried for 23 days, and fans were used to assist drying for the final week. Fan assisted drying was employed as a way to boost the increasingly slow water loss.

Half the cores from each landscape position were randomly assigned to each of the respective soil moisture treatments. The subsets for the soil moisture regime and landscape position were upland wet-dry-wet (Up_{WDW}), upland dry-wet-dry (Up_{DWD}), lowland wet-dry-wet (Low_{WDW}) and lowland dry-wet-dry (Low_{DWD}). Three cores from each subset were randomly selected to be incubated for GHG measurements. These "flux cores" were used for gas measurements for the entire duration of Experiment 1, and the experimental design assumed that measurements from the flux cores were representative of all of the cores in their associated subset. When not being incubated, treatment and storage of the flux cores was identical to all of the other cores in the subset.

Cores that were subjected to a "wet up" or a "wetting phase" (increase in water content) were stored in a terrarium to minimize evaporation. The terrarium consisted a small elevated rack inside a storage cooler. The soil cores were placed on the rack and below a shallow pool of water was maintained in an attempt to minimize water loss from the soils. The cooler lid was left ajar so as to

not facilitate anoxic conditions while also minimizing evaporation from the soil cores. Cores that were being "dried down" or subjected to a "drying phase" were left out on the counter and placed under a screen to prevent contamination of the soil.

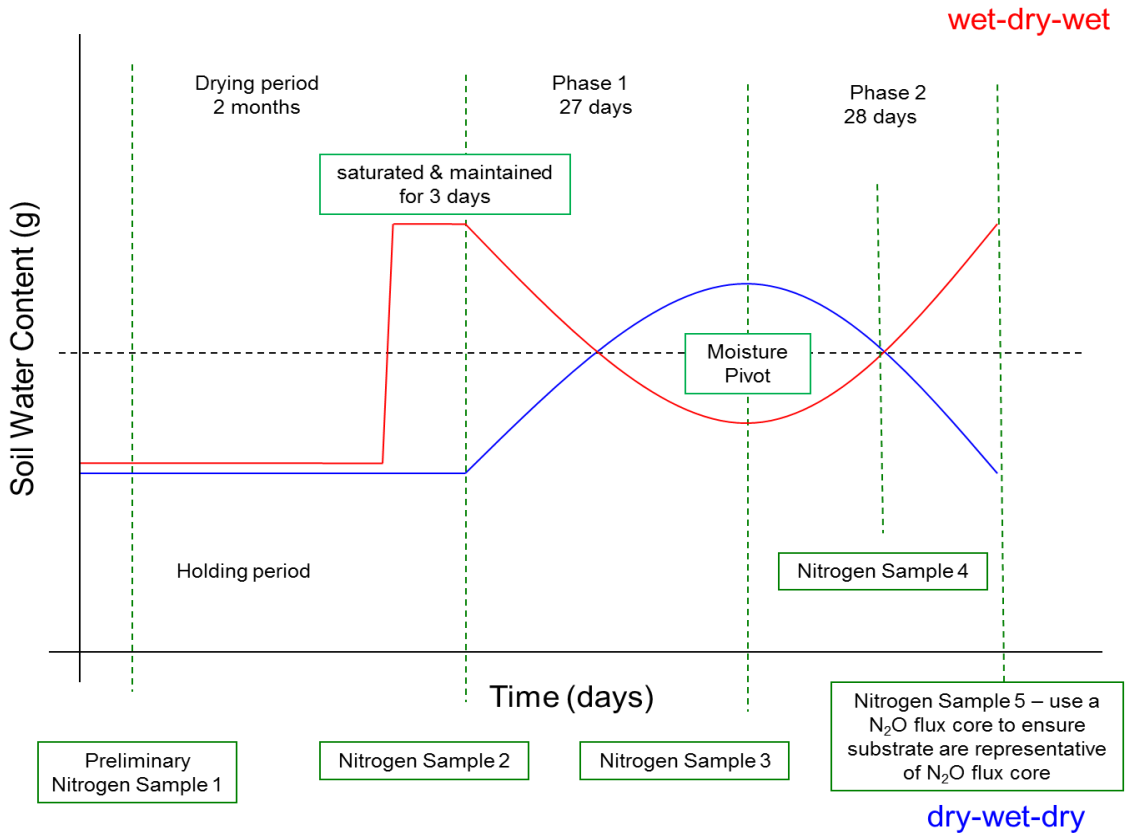

Figure 11 Relative times for the moisture treatments and inorganic N extractions

Following the extended drying period, soil moisture was modified gravimetrically using deionized (DI) water. At a daily time step, masses of the soils cores were measured, and since all other variables were constant, changes in core weights represented a change in the water content. The amount of water lost from the drying cores was added to the cores being wet up to simultaneously reverse the moisture status of the soils from opposing moisture regimes at approximately the same rate. The calculations that were used to determine the daily change in soil moisture are located in the Appendix.

The soil cores were capped at the bottom and remained capped for the entirety of the experiment. Capping allowed for the water content of the soil cores to be easily altered. Without a way to stop and hold the water that was added to the cores, the water would often drain out the

bottom of the cores, especially from the porous peat based lowland cores, and it would have been nearly impossible to achieve high the soil moisture levels during the saturation event, and maintain it for the three day holding period. Water was applied to the top of the soil cores to increase the soil moisture. Thus, N_2O fluxes were considered to be measured only from the soil surface

2.1.2.2 Flux Quantification

Mason jars with a volume of 1.5 L and air-tight screw cap lids equipped with two two-way stop cocks were used as incubation chambers to determine soil gas production during Experiment 1. Extractions of gas measurements from the headspace of the jars were taken at the beginning (T_0) and the end (T_n) of a 120 minute the incubation period. The gas samples were extracted using a plastic syringe secured onto one of the two two-way stopcocks which was attached to the lid of the Mason jar. The syringe was inserted into the stopcock while fully evacuated and pumped five times before the sample was extracted.

Gas samples from both the field and the lab were collected using a 20 mL syringe equipped with a two-way stop cock. Purged syringes were overfilled with gas samples, and a needle tip was then secured on to the syringe. Gas in excess of 20 mL was removed from the syringe to avoid dilution of the gas sample with ambient air from within the needle tip, which helps to ensure the integrity of the sample. The 20 mL samples were stored in an evacuated 12 mL Exetainers containing desiccant (to remove moisture). The Exetainers were sent to Canada Center for Inland Waters (CCIW) in Burlington, Ontario for analysis.

In the laboratory the samples from the Exetainers were analyzed on an SRI Model 8610C Gas Chromatograph (GC) (R. Bourbonniere, Environment Canada) with chromatography optimized to determine CH_4, CO_2 and N_2O. The GC is fitted with two detectors: flame ionization (FID) and electron capture (ECD). Carbon dioxide is detected by the FID after passing through a post column methanizer where CO_2 is converted to CH_4 with a Ni/H_2 catalytic system to increase FID response. Nitrous oxide is detected on the ECD, which contains a sealed Ni-63 source (5 millicuries). Calibration is achieved using a mixture of CH_4, CO_2 and N_2O (balance N_2) obtained as a certified custom mixture from Linde Gases. Chromatograms are controlled and results are integrated using the Peak Simple chromatography software package (SRI Instruments). To ensure quality control, a calibration standard was injected every 12^{th} sample. The detection limit for CO_2 was 0.2 µL/L and for N_2O was 0.004 µL/L in the chamber air sample. The gas production was derived from the linear slope

of the ambient (T_0) and accumulated (T_n) concentration measurements. Greenhouse gas flux values were corrected for ambient temperature and barometric pressure.

2.1.2.3 Inorganic N Extractions

Inorganic N extractions were completed in triplicate and were done five times throughout the experiment (Figure 11). As with the soil cores selected for gas incubations, cores that were sacrificed for inorganic N extractions were subjected to the same treatment as the rest of the soil cores in their associated subset and thus were assumed to be representative of inorganic N conditions in all of the soil cores from that subset.

The initial inorganic N extraction was performed to establish baseline inorganic N concentrations prior to implementation of the moisture regimes. The first four inorganic N extractions were completed by randomly selecting three cores for each subset and sacrificing the cores. The flux cores were sacrificed at the end of the experiment for the final inorganic N extraction.

Each core used for determining inorganic N concentrations was homogenized in a ziplock bag. Ten grams of soil (at current soil moisture) and 8 grams of lowland soils were sub-sampled from the batched soils. In a 120 mL specimen cup, the soil and 50ml of 2 M KCl were combined and the specimen cups were sealed with plastic lids. The samples were placed on a shaking tray for one hour, and each mixture was filtered twice; first through a Whatman no. 42 filter, and a second time through 0.45 µm membrane Schleicher and Schuell filter. The filtered samples were stored in 20 mL scintillation vials at 4°C until analyzed. All NO_3^- and NH_4^+ samples were run with a Bran Luebbe AA3 AutoAnalyzer (M. Macrae, University of Waterloo) using the salicylate method for NH_4^+ (Folio method number: G-102-93) and the hydrazine method for NO_3^- (Folio method number: G-109-94) with a detection limit of 0.001 mg/L.

2.1.3 Experiment 2: The Combined Influence of Soil Moisture and Inorganic N Pools on N_2O Fluxes

2.1.3.1 Experimental Design

Experiment 2 was conducted to isolate how simultaneous changes to soil moisture and inorganic N concentrations influence the magnitude and variability of N_2O production from the upland and lowland soils (Figure 12).

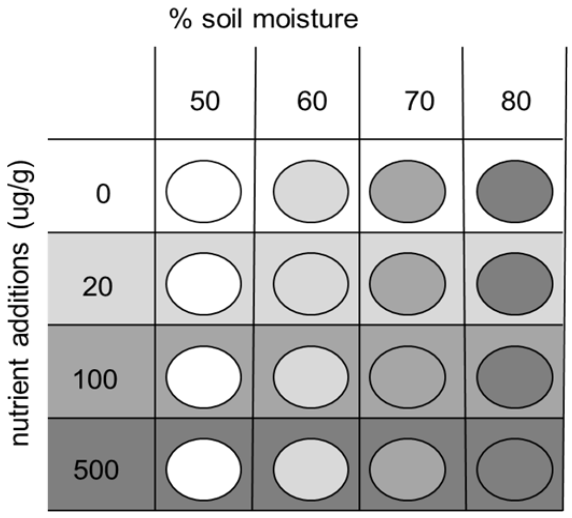

Figure 12 Diagrammatic representation of soil moisture and inorganic N levels employed during experiment 2

The design for this experiment employed four levels of inorganic N concentrations and four levels of soil moisture. Soil was collected from the surface of the upland and the lowland landscape positions during spring 2009. Upland and lowland soils were homogenized and dried with the assistance of fans for four days in the lab to allow for mineralization. The soil was periodically mixed to ensure homogeneous drying of the batch.

2.1.3.2 Altering Moisture and Inorganic N Concentrations

Soil moisture and inorganic N concentrations were altered simultaneously during Experiment 2. Using a subsample from each landscape type, preliminary soil properties had been determined. The soil properties were re-determined from re-packed cores because the soils were homogenized. The current soil moisture of the batched soils was also determined. Using re-packed cores, the water holding capacity (*WHC*) of the soils was calculated and these calculations are detailed in Appendix B**.**

Potassium chloride (KCl) extractions were completed on the upland and lowland batches to determine inorganic N pools prior to the start of the experiment. The initial inorganic N were assumed to be the same for all soils from the same landscape position because they were from the same batch.

Potassium nitrate (KNO_3) was used as a source of NO_3^- substrate, ammonium chloride (NH_4Cl) was used as a source of NH_4^+, and dextrose (anhydrous D-L) was used as a C source.

The inorganic N levels chosen were 20 µg/g, 100 µg/g, 500 µg/g, and blank (no inorganic N additions), and 75µg/g of glucose was added to every sample.

The inorganic N and glucose additions were created in bulk to minimize variability. The inorganic N was weighed and added to a larger solution. The inorganic N additions were mixed with DI water and were used to create a concentrated solution that was then used to simultaneously increase the soil moisture and inorganic N status of the soils. The calculations are detailed in Appendix B

The mixture of water and inorganic N was slurried with the soils in the 250 mL Mason jars. Ten g of soil from the upland and 8 g of soil from the lowland of soil was thinly and evenly smeared onto a Whatman filter. The filter had been wetted slightly so as to not absorb the moisture from the soil. Once the soils of various soil moistures were prepared, the filter was placed on a structure composed of aerated PVC piping and placed into the Mason jars (Figure 13). The screw caps for the jars were the same design as employed in Experiment 1 which consisted of two two-way stop cocks. The samples were incubated for 180 minutes and the incubations were completed using the same equipment (with the exception of smaller Mason jars) as procedures detailed in Experiment 1.

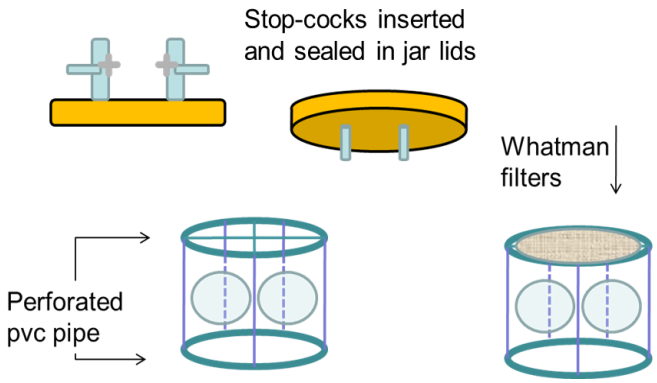

Figure 13 A detailed set up of the modified Mason jar screw caps and silicone tube structure to elevate moisture Whatman filter

2.2 Data Analysis

Statistical analysis was competed using Microsoft Excel 2007 and 2010, R statistics (v 2.1.18), and Sigma Plot v. 11.

The results of a one-sided Kolmogorov Smirnov test for normality for N_2O fluxes from the field for each year, and N_2O production for the lab results from Experiment 1 indicated that statistically, the data was highly skewed and not normally distributed, thus non-parametric statistics were used during data analysis. Spearman rank correlations were completed to assess strength of correlations between gas fluxes and environmental factors.

Chapter 3 Results

3.1 Characterization of Field N_2O Fluxes

3.1.1 Growing Season N_2O Fluxes

Time series graphs for each year show the temporal and spatial (upland and lowland) trends of N_2O fluxes and environmental factors. The climatic variability between the years resulted in different inter-annual trends. The time series graphs showed that 2007 was comparatively very dry, and both water table depth and soil moisture decreased at both landscape positions (Figure 14). Daily total precipitation was greater during 2008 (Figure 15) and 2009 (Figure 16), and the water table and soil moisture levels were often comparable between those two years. During these latter years, the lowland water table position was consistently at or near the surface, and the instantaneous soil moisture was consistently at or near saturation (100% WFPS). The upland water table and soil moisture measurements demonstrated high degrees of temporal variability.

Nitrous oxide fluxes were greater from the lowland during 2007 compared the upland, and largely comparable between landscapes for the rest of the measurements (Table 4).

Table 4 N_2O fluxes from the upland and lowland, interpolated for days without measurements, and averaged by number of day during the growing season (ranging from 206 to 208 days) during 2007, 2008, and 2009

	Upland	Lowland
Year	**nmol/m^2/sec**	**nmol/m^2/sec**
2007	0.1736	1.8614
2008	0.3233	0.2158
2009	0.3645	0.3868

Variability in N_2O fluxes was greatest during 2007 from the lowland, and followed by the upland during the same year, while it was comparable during the other years from both landscapes. This greater variability in N_2O fluxes during 2007 is associated with greater variability in soil moisture and precipitation that were observed during that year compared to the other field years (Table 5).

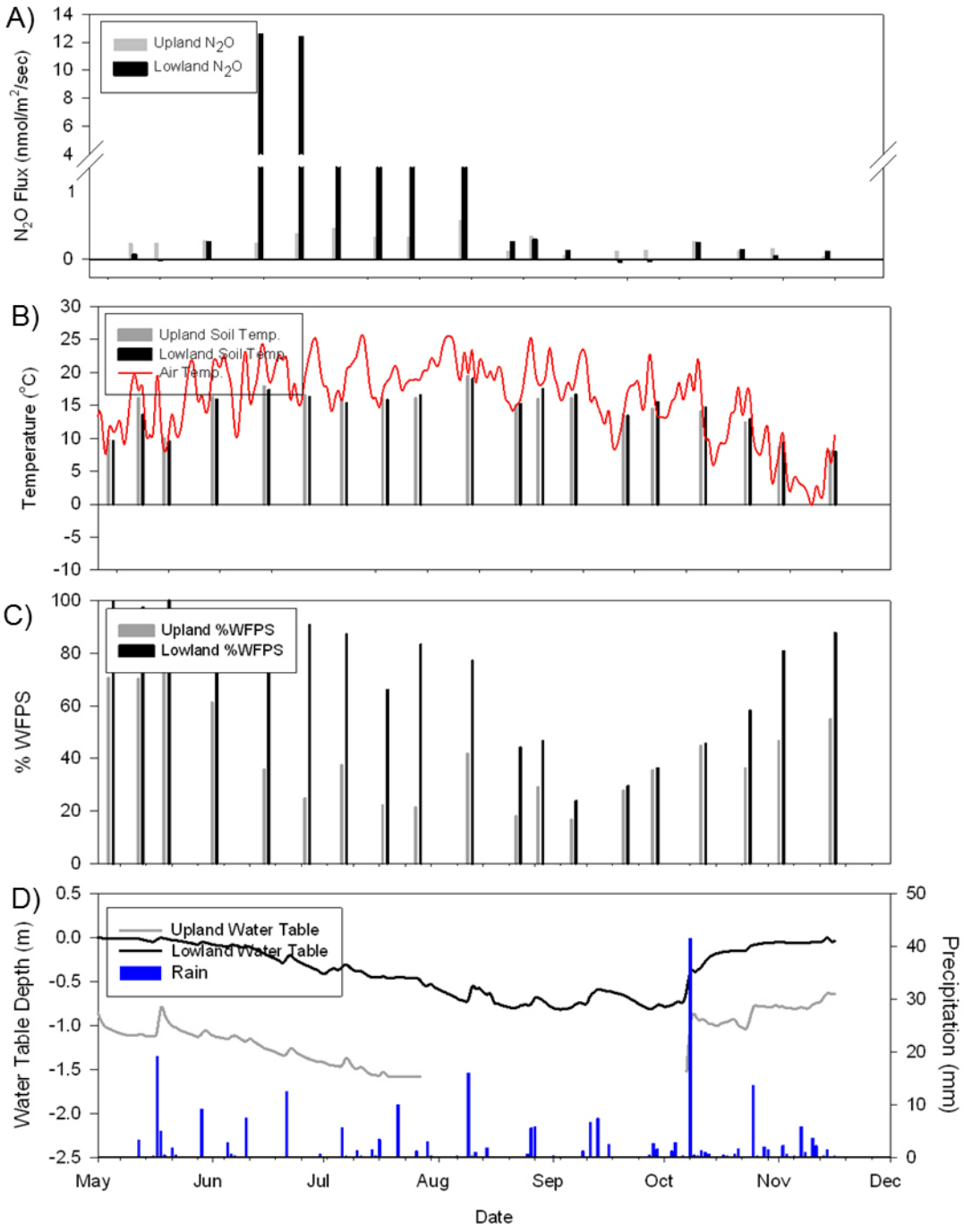

Figure 14 Field data from 2007, showing the N_2O fluxes (A) and environmental factors soil and daily average air temperature (B), soil moisture (C), daily average water table depth, and daily cumulative precipitation (D) by date from both the upland (grey) and lowland (black). Note that the y-axis on graph (A) in 2007 differs from 2008 and 2009.

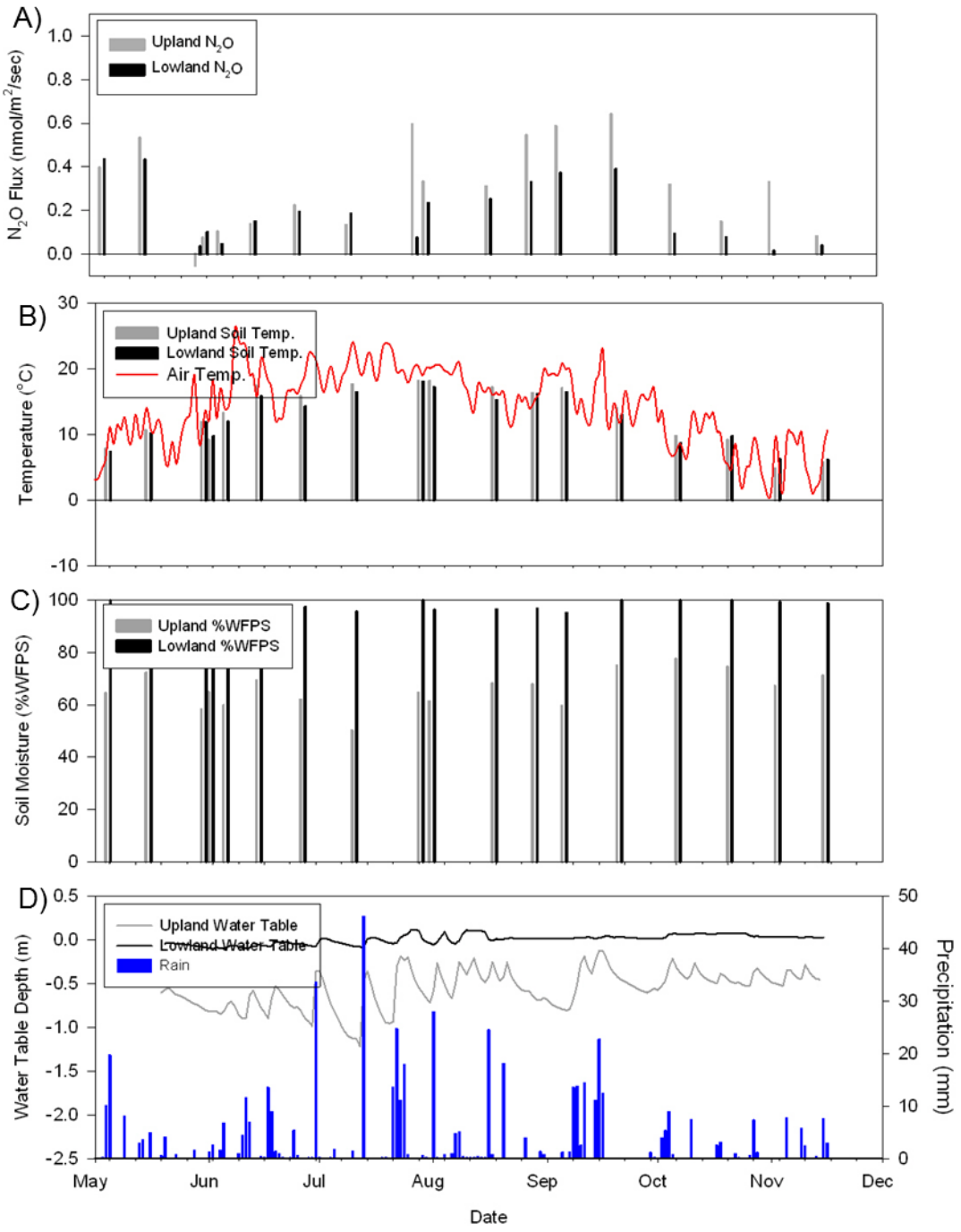

Figure 15 Field data from 2008, showing the N_2O fluxes (A) and environmental factors soil and daily average air temperature (B), soil moisture (C), daily average water table depth, and daily cumulative precipitation (D) by date from both the upland (grey) and lowland (black). Note that the y-axis on graph (A) in 2007 differs from 2008 and 2009.

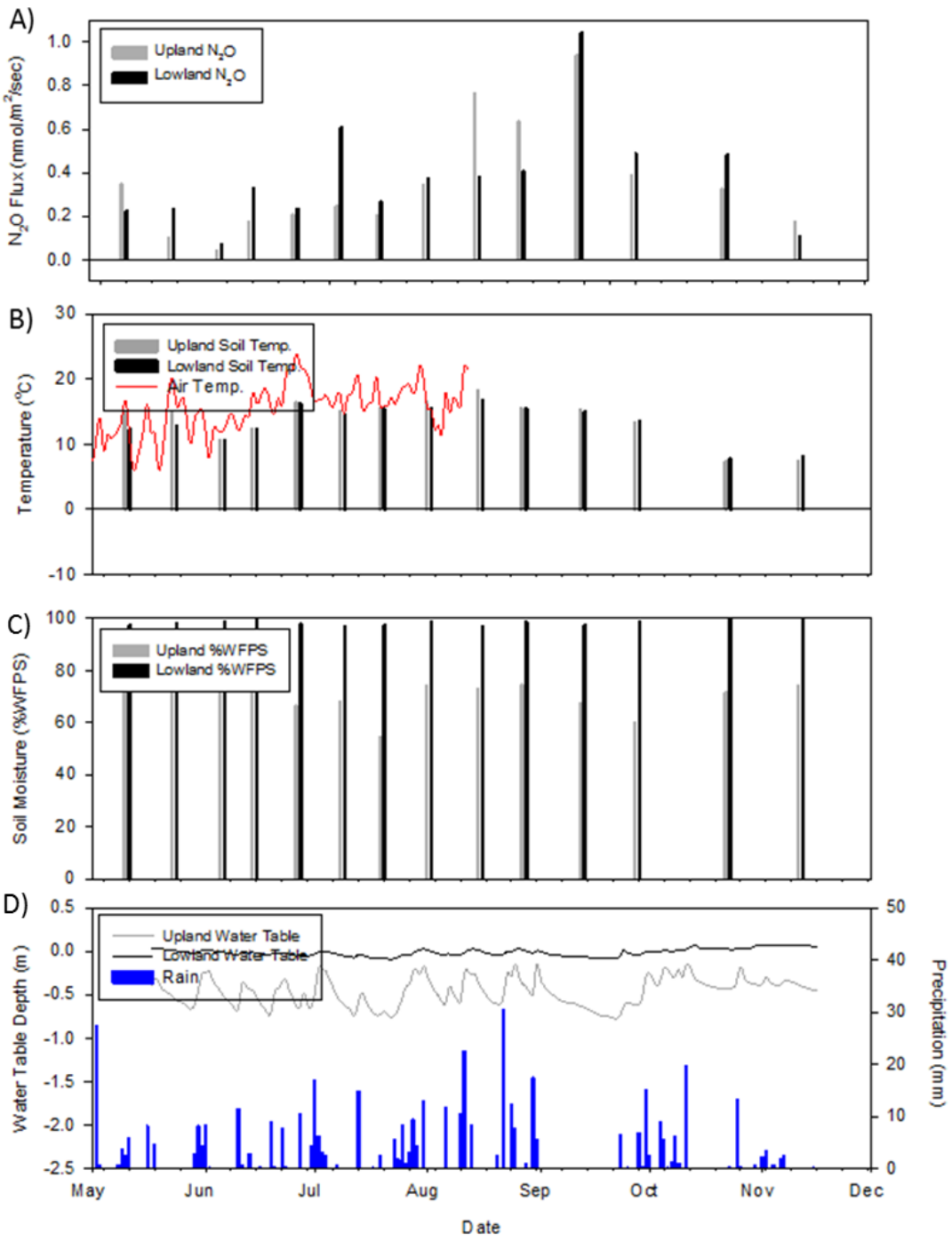

Figure 16 Field data from 2009, showing the N_2O fluxes (A) and environmental factors soil and daily average air temperature (B), soil moisture (C), daily average water table depth, and daily cumulative precipitation (D) by date from both the upland (grey) and lowland (black). Note that the y-axis on graph (A) in 2007 differs from 2008 and 2009.

Table 5 The mean and standard deviation (StDev) for each of the field variables are presented, and the coefficient of variation (CV)

	Factor	Mean	StDev	CV (%)
Upland				
2007	N_2O Flux (nmol/m^2/sec)	0.17	0.18	105
	Soil Temperature (°C)	11.79	5.94	50
	Soil Moisture (%WFPS)	49.61	25.26	51
	Precipitation (mm)	1.26	3.85	306
	Water Table Depth (m)	-1.07	0.28	26
2008	N_2O Flux (nmol/m^2/sec)	27.93	16.15	58
	Soil Temperature (°C)	12.94	4.37	34
	Soil Moisture (%WFPS)	65.96	6.69	10
	Precipitation (mm)	2.48	5.95	240
	Water Table Depth (m)	-0.56	0.22	39
2009	N_2O Flux (nmol/m^2/sec)	0.35	0.26	75
	Soil Temperature (°C)	13.79	3.32	24
	Soil Moisture (%WFPS)	70.30	6.68	9
	Precipitation (mm)	2.39	5.32	222
	Water Table Depth (m)	-0.47	0.16	34
Lowland				
2007	N_2O Flux (nmol/m^2/sec)	1.70	3.72	218
	Soil Temperature (°C)	13.51	3.87	29
	Soil Moisture (%WFPS)	72.57	25.61	35
	Precipitation (mm)	1.26	3.85	306
	Water Table Depth (m)	-0.31	0.30	98
2008	N_2O Flux (nmol/m^2/sec)	0.22	0.14	65
	Soil Temperature (°C)	12.42	3.83	31
	Soil Moisture (%WFPS)	96.57	3.61	4
	Precipitation (mm)	2.48	5.95	240
	Water Table Depth (m)	0.01	0.05	500
2009	N_2O Flux (nmol/m^2/sec)	0.37	0.24	65
	Soil Temperature (°C)	13.32	2.90	22
	Soil Moisture (%WFPS)	98.17	1.07	1
	Precipitation (mm)	2.39	5.32	222
	Water Table Depth (m)	-0.01	0.04	299

Time series data for CO_2 fluxes from the upland and lowland field positions for each field year are presented in Figure 17. The greatest CO_2 fluxes occurred from the lowland during 2007. Similar to the N_2O measurements, CO_2 fluxes from the upland and the lowland showed similar temporal patterns during all years, but magnitudes differed seasonally and by year. Carbon dioxide fluxes were typically greater from the lowland than from the upland during the first half of the year in 2007 and 2008, while the upland exhibited higher magnitudes CO_2 fluxes during the first half of 2009. During the second half of each year, plant senescence became evident in the data and the magnitudes of CO_2 fluxes decreased. During this time, greater magnitudes of CO_2 fluxes were consistently observed from the upland soils relative to the lowland.

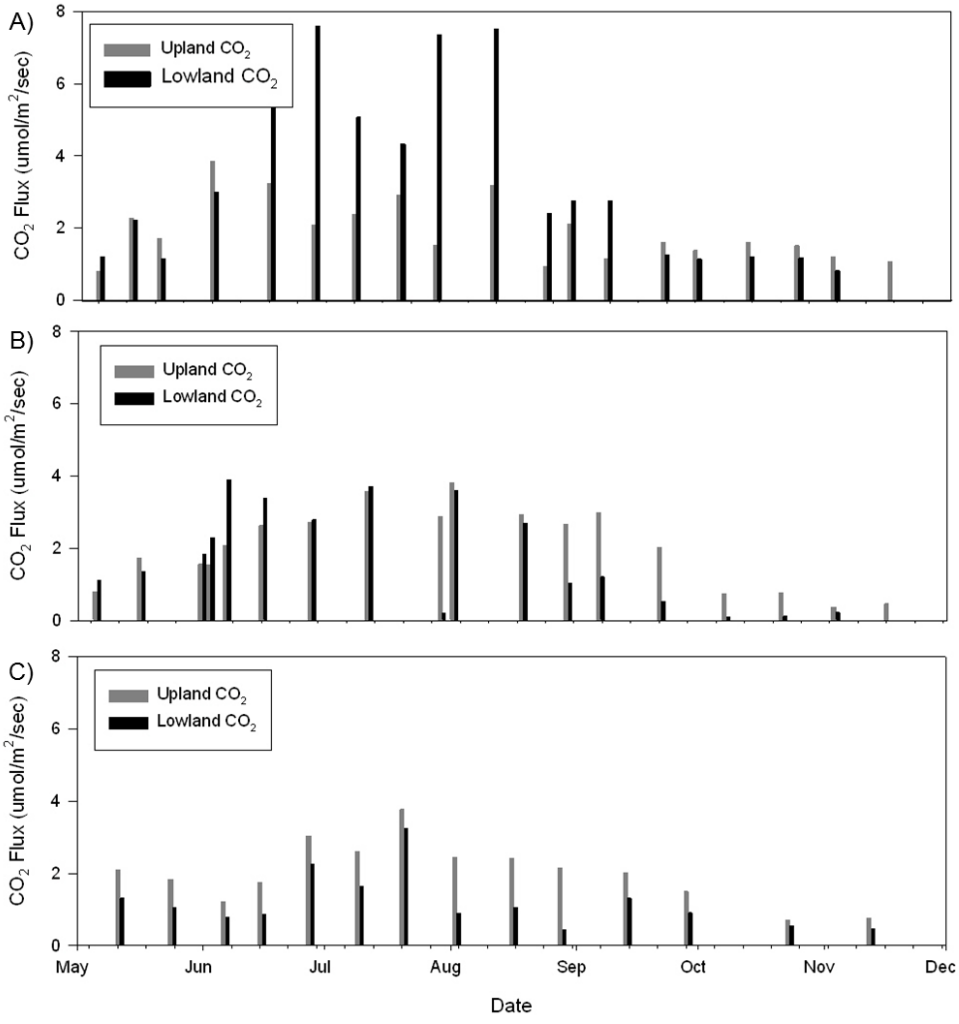

Figure 17 Temporal dynamics of CO_2 fluxes from both the upland (grey) and lowland (black), from 2007 (A), 2008 (B), and 2009 (C)

Significant correlations were determined at a value of $P \leq 0.05$. There was no one environmental soil factor that consistently correlated with N_2O fluxes throughout the growing season, for all years, but soil temperature was most often correlated with N_2O fluxes, demonstrating significant correlations in the upland during 2007 (Spearman Rank Correlation, rho=0.51, n=24) and 2009 (Spearman Rank Correlation, rho=0.86, n=18), as well as from the lowland during 2007 (Spearman Rank Correlation, rho=0.63, n=21) and 2008 (Spearman Rank Correlation, rho=0.57, n=18). There were no significant correlations detected between soil moisture and N_2O fluxes, water table and N_2O fluxes, or precipitation and N_2O fluxes during any of the years, at either landscape

position. Considering all of the years together for each landscape position, soil temperature and N_2O fluxes were significantly correlated ($P \leq 0.05$) in the upland (Spearman Rank Correlation, rho=0.44, n=42) and the lowland (Spearman Rank Correlation, rho=0.51, n=48). However, N_2O fluxes were not significantly correlated with soil moisture, water table, or precipitation from either landscape position.

To assess why environmental controls on N_2O fluxes appear to be lacking, environmental variables (soil moisture, soil temperature, water table depth, and precipitation events greater than 0.25mm) are plotted against field N_2O fluxes. Variability in the environmental factors showed that the dominant factor driving N_2O fluxes appeared to vary, given that relationships between N_2O fluxes and environmental factors were inconsistent (Figure 18). The variability of the environmental factors failed to yield consistent responses from N_2O fluxes. For example, though the relationship between soil temperature and N_2O fluxes was generally positive from both landscapes, both high and low N_2O fluxes were observed at high soil temperatures.

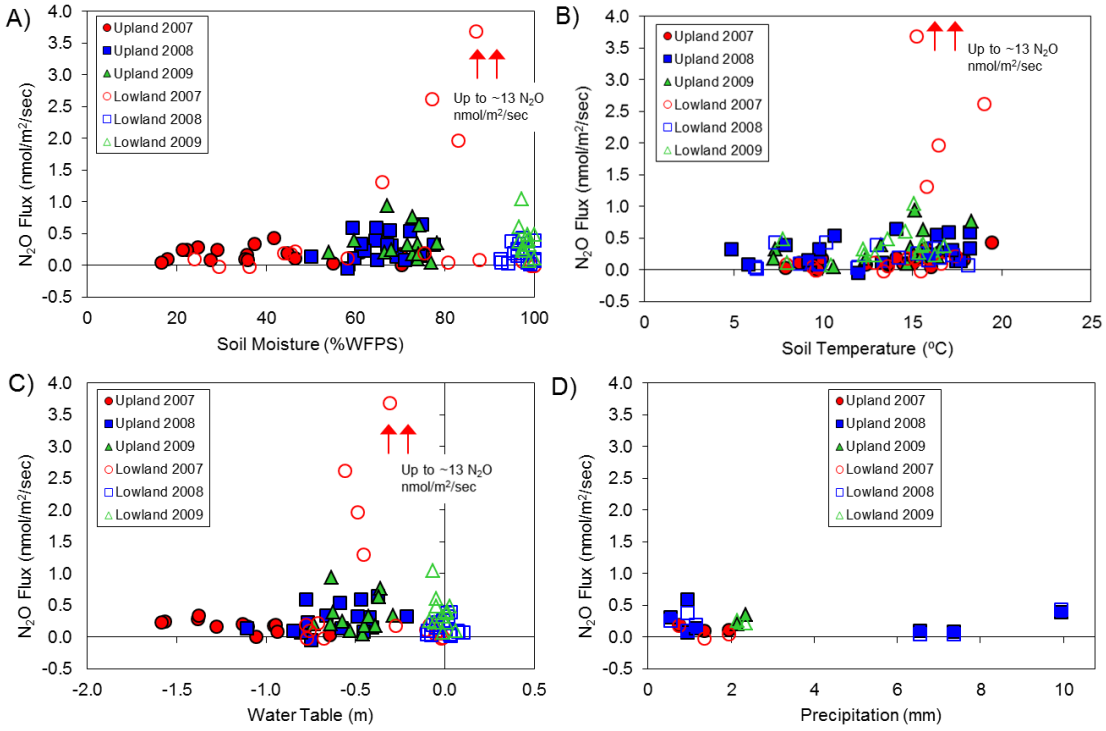

Figure 18 N_2O fluxes for each year and landscape plotted against soil moisture (A), soil temperature (B), water table (C), and precipitation greater than 0.25mm (D). Note the arrows in graphs (A), (B), and (C) show the position of N_2O fluxes that are greater than the span of the y-axis, and reach magnitudes of ~13 nmol/m^2/sec

3.1.2 The Influence of Environmental Factors Coupled with Soil Moisture on N_2O Fluxes

Table 6 summarizes the environmental conditions associated with the highest N_2O fluxes for each year, from both landscape positions, and the results show that there were no consistent environmental conditions that acted as precursors to the highest N_2O fluxes. In fact, there were a number of environmental conditions that appear to have prompted high N_2O fluxes. The highest fluxes total occurred during 2007 from the lowland, when soil temperature was high and the soil was drying, however, the same magnitudes of fluxes were not observed when water table and soil moisture increased following re-wetting of the dried soils.

The influence of environmental factors was coupled with soil moisture as a way to help explain N_2O fluxes in the field (Figure 19). In this analysis, data from all years was used to minimize inter-annual variability and assess potential controls on N_2O fluxes by landscape position. High soil temperature and relatively high soil moisture (70%-80% WFPS) appear to contribute positively to N_2O fluxes in the upland, as do low soil temperature and low soil moisture. Precipitation and water table when coupled with soil moisture appear to have variable influences on N_2O fluxes. Relatively high soil moisture associated with low water table or low precipitation events appear to drive N_2O fluxes. There is a positive relationship observed between soil moisture and N_2O fluxes at low water table depths. Observed precipitation events were low, and there were no precipitation events greater than 7.6mm that occurred on the same day as flux measurements, but the data shows that relatively high precipitation events of +5mm (but still low in absolute values) are associated with N_2O fluxes at intermediate-to-low soil moistures.

The coupled influence of other environmental factors and soil moisture on N_2O fluxes in the lowland appears to differ from observations in the upland (Figure 20). Coupled with soil moisture, precipitation had little apparent influence on N_2O fluxes, while coupled variability of soil moisture and water table depth, and soil moisture and soil temperature, showed that a slight decrease in water table depth and high soil temperature at high soil moisture contributed to the large fluxes (i.e. observed from the lowland during 2007).

Table 6 Environmental conditions associated with the highest upland and lowland field based fluxes during each field year

Date(s)	(Range of) N_2O Flux Magnitude (nmol/m^2/sec)	Conditions associated with the highest N_2O fluxes
Upland		
August 8, 2007	0.426	- Low soil moisture (41% WFPS) - Highest recorded soil temperature for that year (19.5°C) - Precipitation event of 16 mm
May 13, 2008	0.533	- Increasing air temperature (12.8°C - 17.5°C) - Low but increasing soil temperature (7.9°C - 10°C) - Intermediate soil moisture (64% - 72% WFPS)
July 26-Sept 3, 2008 (6 measurements)	0.312-0.641	- General decline of air and soil temperature - Soil moisture between 60% and 75% WFPS - High rates of CO_2 production
September 10, 2009	0.941	- Intermediate soil moisture (67.1% WFPS) - Temperature and soil moisture was on a downward trend - Lull in water table depth - Absence of precipitation
Lowland		
June 13-August 7, 2007 (6 measurements)	12.579-1.304	- Decrease in soil moisture from 94.7% - 66% WFPS - Decrease in water table depth from -0.085 m to -0.72 m below the surface - Decrease and subsequent increase in soil and air temperature
May 12, 2008	0.433	- Increase in soil and air temperature - Slight decrease in soil moisture (100.9% - 97.4% WFPS)
September 3 - September 18, 2008 (2 measurements)	0.374-0.389	- Air and soil temperature were on a seasonal downward trend - Stable soil moisture near saturation
September 10, 2009	1.044	- Stable average soil and air temperature - High soil moisture (97% WFPS) - High water table level that has experienced a slight decrease (-0.065 m) below the surface

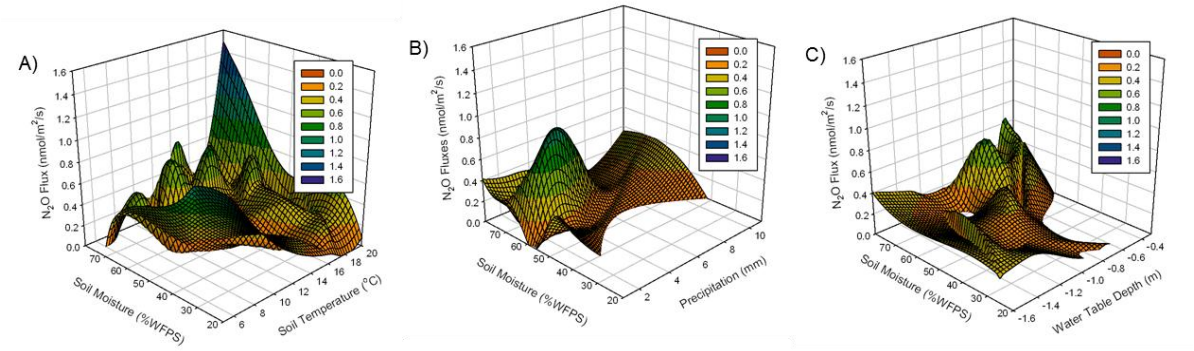

Figure 19 The combined influence of soil moisture and N_2O fluxes with soil temperature (A), precipitation (B), and the water table (C) from the upland. Blanked out areas of the graph represent a lack of data.

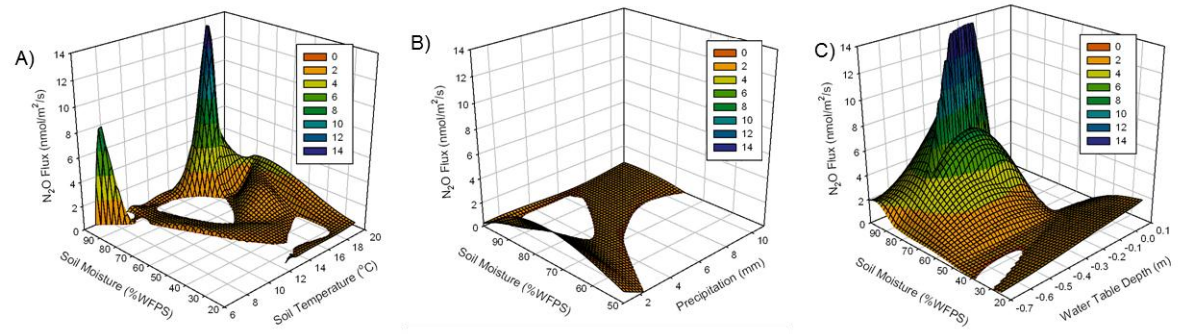

Figure 20 The combined influence of soil moisture and N_2O fluxes with soil temperature (A), precipitation (B), and the water table (C) from the lowland. Blanked out areas of the graph represent a lack of data.

3.1.3 Summary

Soil temperature most strongly and consistently characterizes N_2O fluxes from both landscape positions during the growing season as demonstrated by the correlation results, however, an assessment of the variability in the data suggested that, though not well represented statistically over the course of the growing season, other factors are contributing to driving N_2O fluxes, thus also characterizing N_2O fluxes. How these factors differ between landscape position, and their respective influence on N_2O fluxes, can be assessed by coupling the influence of environmental factors with soil moisture, itself an often cited controller of N_2O dynamics. These results show that the coupled influence of environmental factors in the upland are varied, with a suspected decoupling of soil moisture and water table when water table is low, resulting in a positive relationship between soil moisture and N_2O fluxes at the lowest observed water table depths. Otherwise, the combined influence of water table and soil moisture appears to have a variable effect on N_2O fluxes from the

upland landscape. In the lowland, it appears as though it was primarily water table variability at high soil moistures that drove the large fluxes that were observed during 2007. It is likely that the decrease in water table depth coupled with high soil moisture fostered conditions that were less reducing and thus more favorable for N_2O production rather than N_2 production via denitrification. Recall that N_2O fluxes of comparable magnitudes that were often observed between the landscape positions in the time series graphs (Figure 14, Figure 15, Figure 16) despite the differences in moisture conditions between the landscape positions. These similarities in fluxes are likely driven by coupled variability of multiple environmental factors whose relative importance differed between the upland and lowland. That is, variations in the water table and/or soil moisture in the lowland may result in a small decrease in redox potential and thus N_2O production, which is helped by high soil temperature. The results failed to show that there was a predictable influence of precipitation when coupled with soil moisture on N_2O fluxes in either the upland or lowland. This may be primarily due to a lack of data where gas flux measurements occurred at the same time, or shortly after, a precipitation event. In the lowland, most observed precipitation events were associated with high soil moisture, suggesting that their influence on N_2O fluxes is muted.

3.2 Soil Moisture and N_2O Production Relationships from Differing Antecedent Hydrological Conditions

3.2.1 Antecedent Soil Moisture and the Relationship between Soil Moisture and N_2O Fluxes

The results from Experiment 1 showed that there were differences in the timing and magnitude of N_2O flux from different moisture regimes subjected to the same soil type. Likewise, there were differences in the timing and magnitudes of N_2O flux from different soil types that experienced the same moisture regime. During the experiment, the magnitudes of N_2O flux observed from the lowland soils were approximately an order of magnitude greater than those observed from the upland soils (Figure 21).

Despite these differences, soil moisture and N_2O fluxes were often well correlated in the subsets during Experiment 1. Significant correlations ($P \leq 0.05$) were detected between soil moisture (%WFPS) and N_2O fluxes from the Up_{WDW} moisture regime (Spearman Rank Correlation, rho=0.45, n=48), the Low_{WDW} moisture regime (Spearman Rank Correlation, rho=0.43, n=48) and the Low_{DWD}

moisture regime (Spearman Rank Correlation, rho=0.71, n=47), while no significant correlation between soil moisture and N_2O flux was detected from the Up_{DWD} moisture regime.

The highest N_2O production during Experiment 1 occurred between ~60% and ~80% WFPS. However, relatively high N_2O production was also observed at instances above and below this window. Saturation of the lowland cores failed to exceed greater than ~80% WFPS but the upland cores held water to ~100% WFPS during saturation.

This data demonstrates that N_2O flux timing and magnitude differ with AHC and that the influence of AHC differs between the upland and lowland soil types. This data fails to sufficiently explain why there are differences in the timing and magnitude of N_2O fluxes given the lack of correlations between soil moisture and N_2O fluxes, thus N and C dynamics are explored.

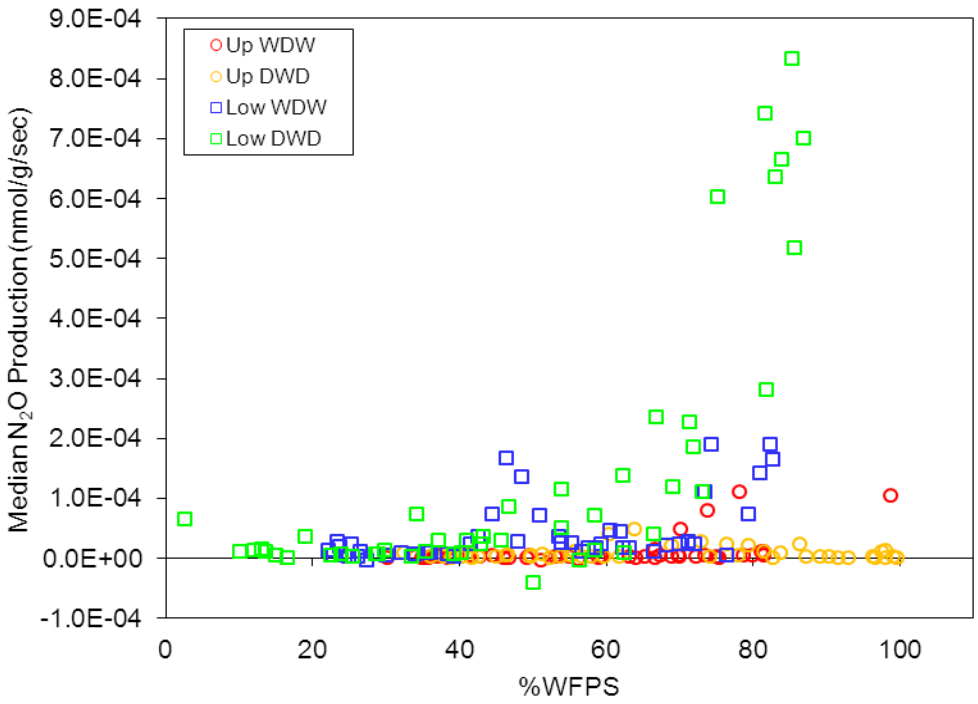

Figure 21 Data from each subset which shows the magnitude of N_2O production by soil moisture.

3.2.2 The Influence of Antecedent Soil Moisture, and Nitrogen and Carbon, on N_2O Production

There were differences between the moisture regimes and soil types with respect to when (at what soil moisture) the greatest N_2O fluxes occurred. Nitrous oxide fluxes from both the upland and

lowland soil types during Experiment 1, from both soil moisture regimes, was always greater during phase 1 than during phase 2 (Figure 22, Figure 23). The exception to this is the Low_{WDW} moisture regime, where maximum N_2O flux magnitudes were comparable during phase 1 and phase 2.

With the exception of phase 1 of the Low_{WDW} moisture regime (which included the saturation event), N_2O flux dynamics mimicked changes to soil moisture, with increasing soil moisture associated with increasing N_2O fluxes. This was not the case with the upland soils, which only showed this kind of direct association between soil moisture dynamics and N_2O fluxes during the saturation event in the Up_{WDW} moisture regime.

Inorganic N concentrations were often lower during phase 1 of the experiment, with the exception the inorganic N extraction coinciding with Low_{WDW}, where concentrations of NH_4^+ were high. Nitrate concentrations increased throughout the experiment for both soil types subjected to the WDW moisture regime. Likewise, both soil types showed that NH_4^+ was highest when soil moisture was highest from the DWD moisture regimes.

Despite the similarities between the soils subjected to the same moisture regimes, there was evidence of differing processes from the soil types, especially during phase 2. For example, both NH_4^+ and NO_3^- increased during the Up_{WDW}, but there were minimal N_2O fluxes observed. However, during phase 2 of the Low_{WDW} moisture regime, there was an increase in NO_3^- accompanied by an increase in N_2O, but no increase in NH_4^+.

The differences in the concentrations of inorganic N and the magnitude of N_2O fluxes suggests fundamental differences in N dynamics between the upland and lowland soils. Notice that the N_2O fluxes observed from the lowland are an order of magnitude higher than those observed from the upland, and that the highest N_2O fluxes observed from the Low_{DWD} moisture regime are double the magnitude of N_2O fluxes observed from the Low_{WDW} moisture regime.

While the temporal dynamics of N_2O production and inorganic N turnover varied by soil type and moisture regime, temporal dynamics of CO_2 production were more predictable. The WDW moisture regime yielded relatively high CO_2 production immediately after the initial saturation event and lower, but stable CO_2 during phase 2. Carbon dioxide production from the DWD moisture regime showed that CO_2 production was high at intermediate soil moisture during phase 1 and gradually decreased during phase 2.

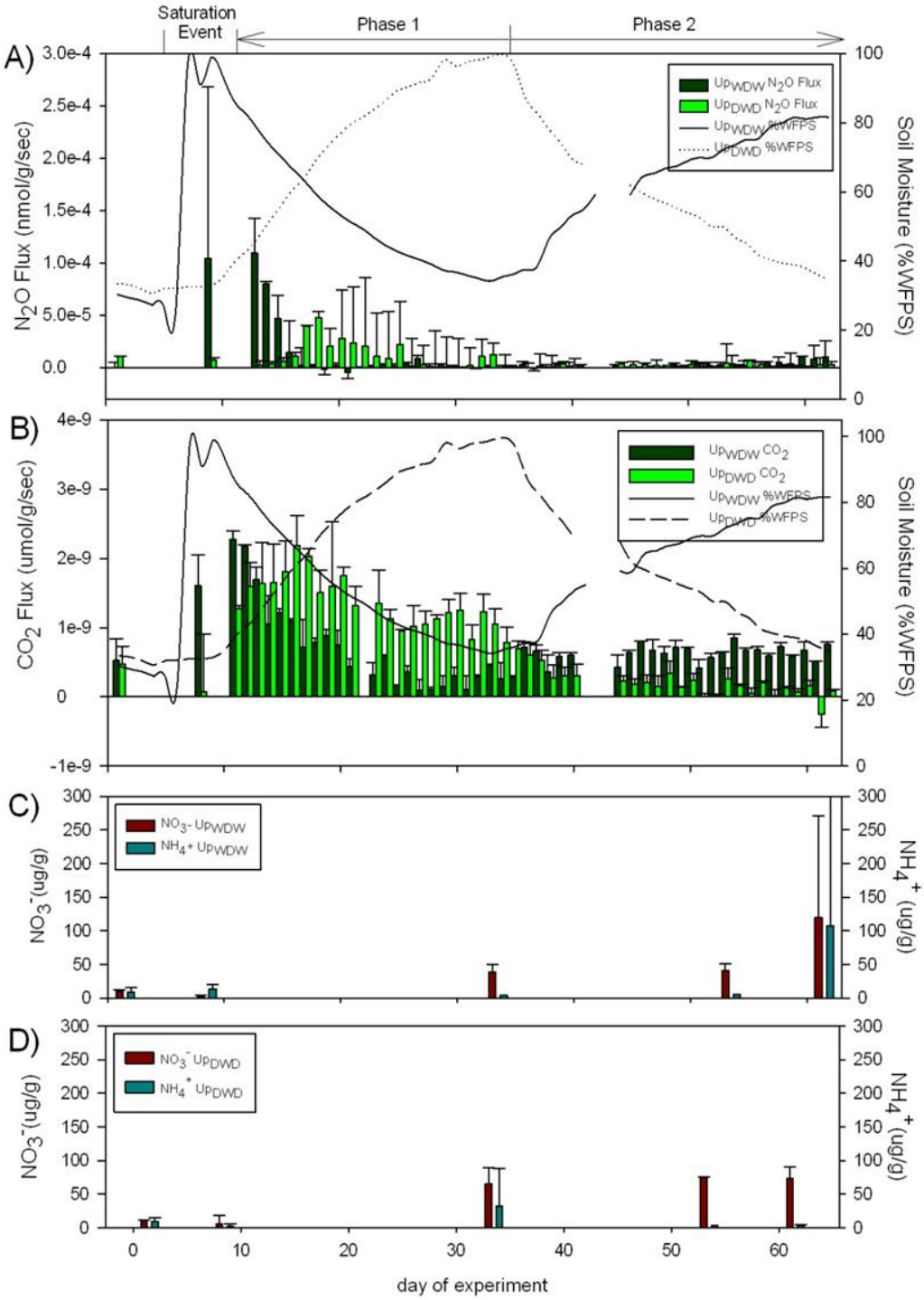

Figure 22 Upland N_2O production (A), CO_2 production, extracted inorganic N from the Up_{WDW} (C) and the Up_{DWD} (D)

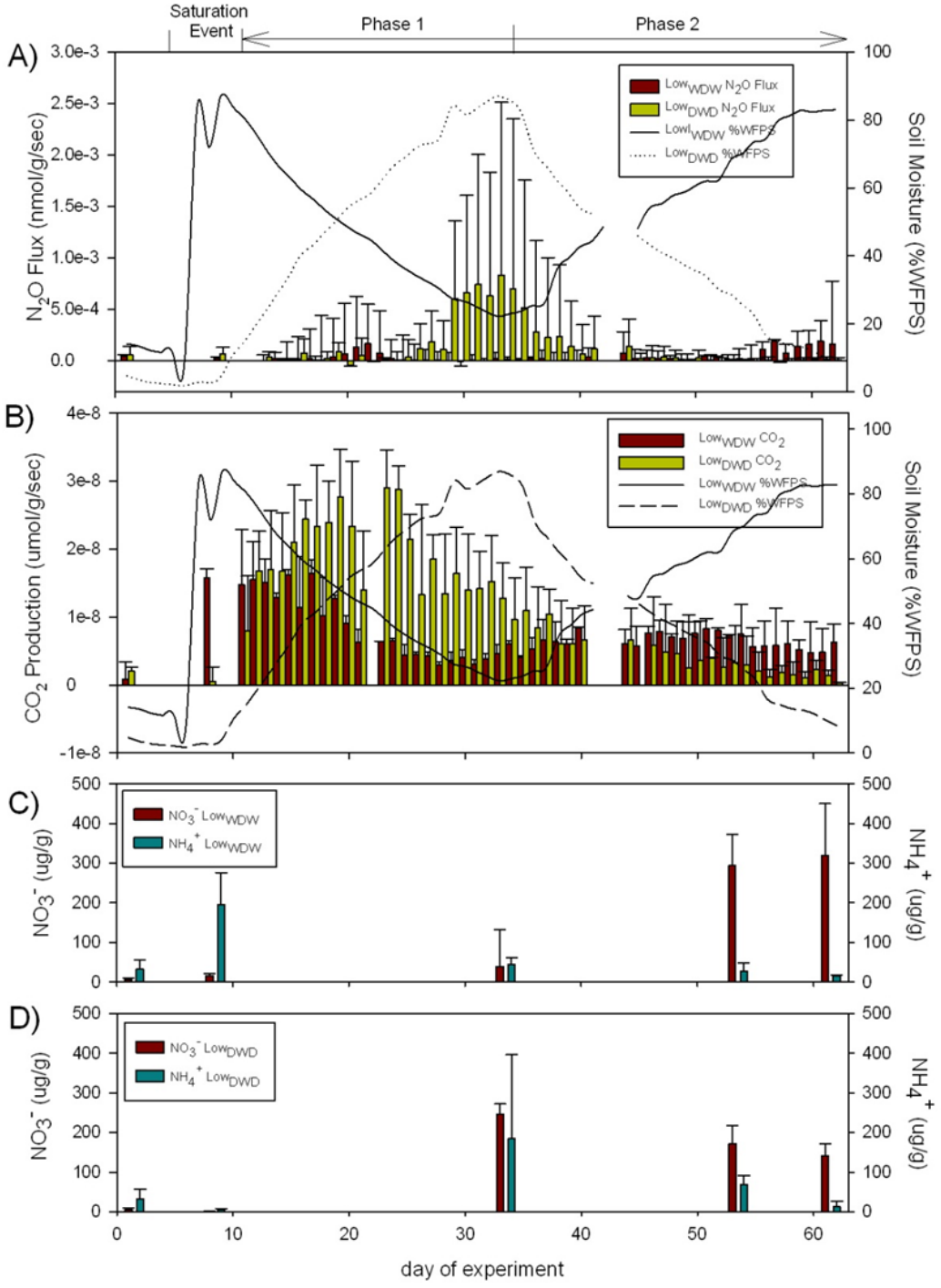

Figure 23 Lowland N_2O production (A), CO_2 production, extracted inorganic N from the Up_{WDW} (C) and the Up_{DWD} (D)

3.2.3 Isolating the Influence of Soil Moisture and Inorganic N on N_2O Production

The relationship between soil moisture and extractable inorganic N was assessed to try to better understand the influence of AHC on soil N dynamics. This analysis was completed using data from Experiment 1, using linear regressions to assess the direct strength of the influence of soil moisture on inorganic N. The results from Experiment 2 are also presented to better isolate the simultaneous influence of inorganic N concentrations and soil moisture on N_2O magnitudes.

Extractable inorganic N is plotted against soil moisture at the time of extraction from the upland subsets (A) and the lowland subset (B) from Experiment 1 (Figure 24). The results show that there were generally strong positive relationships between soil moisture and inorganic N from the lowland but not the upland. There were a few notable exceptions to this. In the lowland, the weaker linear relationships between soil moisture and inorganic N were all associated with inorganic N extractions that occurred at the time of the saturation event. The Low_{WDW} moisture regime showed generally weaker relationships between soil moisture and inorganic N than was observed from the Low_{DWD} moisture regime. During the Low_{WDW} moisture regime, there was no relationship observed between soil moisture and NH_4^+, with all data points being low except the point associated the saturation event. Likewise, there was a weak linear relationship between soil moisture and NO_3^- during the Low_{WDW} moisture regime, which was weakened by the one low data point at high soil moisture, which was associated with the saturation event. Contrasting the rest of the upland results, there was a strong positive relationship noted between soil moisture and NH_4^+ during the Up_{DWD} moisture regime.

Though the highest extracted inorganic N occurred when soil moisture was high (~80% WFPS) from both soil types, but there were instances from both soil types where relatively high soil moisture did not equate to high inorganic N, and vice versa.

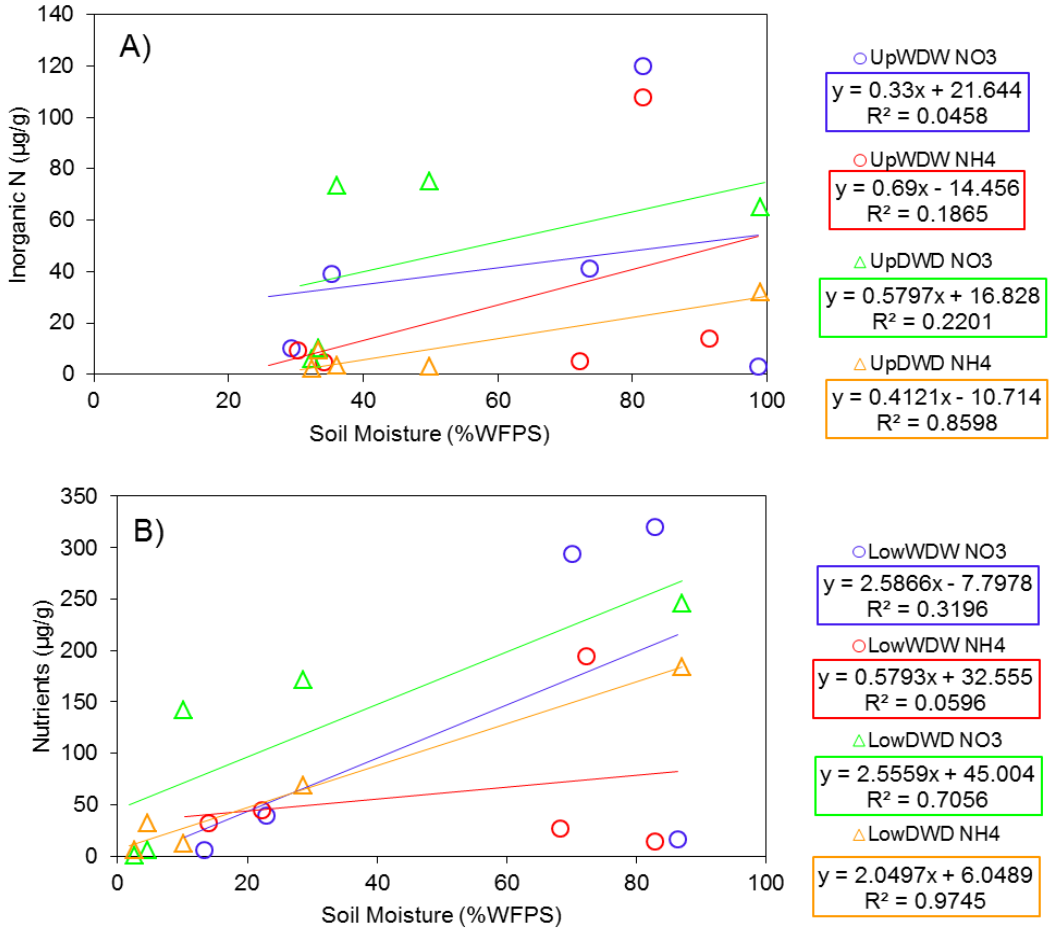

Figure 24 The extractable inorganic N (NO_3^-, NH_4^+) from the upland subsets (A) and lowland subsets (B) against soil moisture at the time of extraction. The colored boxes show the linear regression equation and R^2 value. Note the differences in y-axis scale between figures A and B.

Experiment 2 was conducted in triplicate and the results are presented as median N_2O production with the error bars representing the range of observed N_2O production (Figure 25). Nitrous oxide production was plotted against the soil moisture by level of inorganic N concentration.

Contrasting the results from Experiment 1, N_2O production from the upland soils was greater in magnitude than those observed from the lowland soils. Also, there was no observable pattern between N_2O production, soil moisture, and inorganic N from the lowland, however, there was a positive relationship observed between the variables in the upland. The greatest overall magnitudes of N_2O production were associated with NO_3^- additions at 80% soil moisture from the upland soils. Carbon dioxide was similar in temporal dynamics and magnitude of production between soil types and demonstrated a positive relationship with soil moisture in both the upland and the lowland, with

the highest CO_2 production reaching a maximum at 70% WFPS from the upland and at 80% WFPS from the lowland.

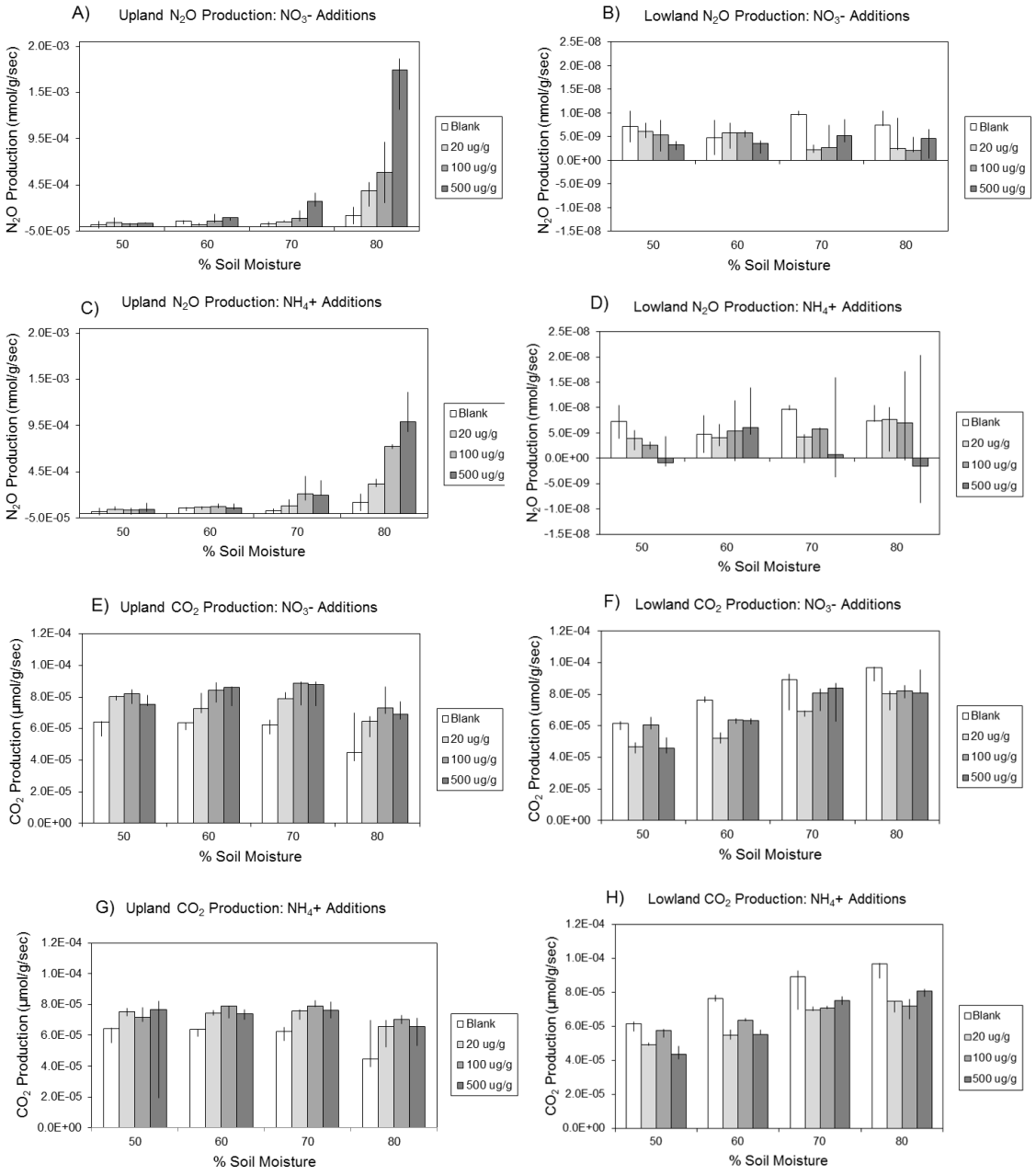

Figure 25 The upland N_2O production (A) and CO_2 production (B) for NO_3^- additions, upland N_2O production (C) and CO_2 production (D) for NH_4^+ additions, lowland N_2O production (E) and CO_2 production (F) for NO_3^- production, and lowland N_2O production (G) and CO_2 production (H) for NH_4^+ additions.

3.2.4 Summary

There are differences in N_2O dynamics from soils subjected to different AHC, as demonstrated by the results from Experiment 1. It was originally hypothesized that differences in soil N dynamics would help explain the observed differences in N_2O fluxes between moisture regimes and soil type. Though the results of Experiment 1 appear to show that inorganic N concentrations are largely dictated by moisture regime, and that concentrations of inorganic N differ between soil types, the results also suggest that the processes related to the saturation event differ from the processes during the rest of Experiment 1, when soil moisture change was gradual. The accompanying extractable inorganic N results from Experiment 1 failed to consistently support the original hypothesis that inorganic N concentrations would positively influence the relationship between soil moisture and N_2O fluxes in the upland soils, but appear to support this hypothesis in the lowland soils. Contrasting the results from Experiment 1, Experiment 2 appears to demonstrate that there is a positive relationship between soil moisture, inorganic N concentrations, and N_2O fluxes in the upland, suggesting there was high spatial variability amount the upland soil cores during Experiment 1. However, the lowland results from Experiment 2 fail to support the evidence of a positive relationship between soil moisture, inorganic N, and N_2O fluxes that was apparent in Experiment 1, suggesting added inorganic N was immobilized during the experiment by soil microbes rather than being nitrified or denitrified. The CO_2 flux data suggests that there are differences in C dynamics between the soil types, with the upland having lower organic C (and thus lower CO_2 fluxes) than the lowland, which may have been partially responsible for the differences in N_2O dynamics between the upland and lowland, especially during Experiment 1. During Experiment 2, when both soil types received the same amount of a highly labile form of organic C (glucose), magnitudes of CO_2 production were comparable, suggesting that the lowland soils may have contained more labile forms of organic C compared to the upland soils during Experiment 1.

Chapter 4 Discussion

4.1 Characterization of Field N_2O Fluxes

4.1.1 Growing Season N_2O Fluxes

The magnitude N_2O fluxes observed in this study are often comparable to those observed from other studies. In general, fluxes measured in the field fell between -0.085 and ~1.0 (mg N-N_2O/m^2/day) in this study with a slight greater spread observed in the lab data, with the exception of high fluxes observed in the field from the lowlands during 2007 which coincided with a drought when fluxes of up to 15.22 (mg N-N_2O/m^2/day) were observed. Similarly high fluxes have been observed by others, for example, van den Heuvel et al., (2009) observed instances of high fluxes in a riparian area, and Morse et al., (2012) observed high instances of fluxes from wetlands (Table 7).

Soil temperature was found to characterize growing season fluxes in this study, with it being most strongly and consistently correlated with N_2O fluxes from both landscape positions. Temperature is often cited for its positive influence on N_2O fluxes as a control on biological processes (Firestone and Davidson, 1989; Martin et al., 1999), and this is in line with what other have reported with respect to seasonal or annual scale relationships between temperature and N_2O fluxes. Alves et al. (2012) reported significant correlations between soil N_2O fluxes and 10 cm depth soil temperature and air temperatures, while Kusa et al. (2002) detected a significant correlation between N_2O fluxes and soil temperature on a seasonal scale.

The influence of hydrological variability on N_2O fluxes in the field is often difficult to characterize because of the complexity of the interactions between soil moisture and the factors it influences like O_2, and the various N_2O production pathways. Sometimes field studies find that precipitation can be a prevalent controlling factor on N_2O flux dynamics rather than soil moisture. Skiba et al. (1996) observed that daily and seasonal changes in moisture were not well correlated with N_2O fluxes, but that there was a strong correlation between annual precipitation and annual N_2O fluxes. Liu et al. (2010) identified high inter-annual variability of field N_2O observations from native and grazed semi-arid steppes in Inner Mongolia, China, and found that seasonal variability was regulated by rainfall distribution during the growing season. In agreement, the results from Du et al. (2006), who used a five year dataset from a native semi-arid grassland soils of inner Mongolia, found rainfall distribution to be a significant regulator of N_2O fluxes.

Table 7 The observed N_2O fluxes from various landscapes, with the results from this study from the field and lab (manipulated)

Location	Ecosystem	Range N_2O Flux (mg N-$N_2O/m^2/day$)	Average N_2O Flux (mg N-$N_2O/m^2/day$)	Source
Southern Ontario (this study)	Forested Riparian Zone	-0.085 – 15.22	0.967	Owens et al., 2012
Southern Ontario (this study)	Forested Riparian Zone (manipulated)	-2.99 – 20.33	0.829	Owens et al., 2012
Netherlands	Riparian buffer zone (summer) - High nutrient removal - Low nutrient removal	n/a	8.2 4.44 13.6	Hefting et al., 2006
Netherlands	Riparian buffer	47.7 (maximum)	1.44	van den Heuvel et al., 2009
Belgium	Riparian buffer zone	-0.6 – 2.5	0.4	Dhondt et al., 2004
Ohio	Created riparian marshes - high marsh - edge plots - open water - low marsh	n/a	 0.528 ± 0.06 0.312 ± 0.046 0.238 ± 0.050 0.168 ± 0.113	Hernandez and Mitsch, 2006
China	Maize	-0.28 – 13.44	2.928	Chen et al., 1997
China	Soybean	-0.48 – 5.28	1.02	Chen et al., 1997
China	Temperate meadow grassland	0.11 – 6.19	0.986	Huang et al., 2003
China	Temperate meadow grassland	0.04 – 0.44	0.19	Huang et al., 2003
Japan	Cultivated (onion) field	0.00 – 44.64	3.84	Kusa et al., 2002
Europe	Forest - Deciduous - Coniferous	0.007 – 0.49	 0.264 0.168	Pilegaard et al., 2006
Finland	Estuary	-1.19 – 1.42	0.043	Liikanen et al., 2009
North Carolina	Restored wetland	-4.36 – 8.81	0.53	Morse et al., 2012

There are apparent differences in the hydrological drivers of N_2O fluxes between the drier upland and the wetter lowland landscape positions on a growing season scale, though both positions are correlated with soil temperature, the differences in hydrological regimes suggest differences in processes. Despite the differences in soil moisture and water table depth, N_2O flux magnitudes were often comparable between landscape positions, suggesting that AHC influenced how environmental factors worked to regulate biological N dynamics. There is evidence in the literature to suggest that moisture history has an important influence on the dynamics of nitrification and denitrification. For example, soil moisture conditions, along with denitrifying enzymes, can change quickly, and if soil moisture conditions are different between soils, it can be assumed that this will influence the relative rates of biological processes and end product ratios (NO vs. N_2O vs. N_2) (Bergsma et al., 2002).

Since biological processes were not measured during this study, and soil nutrients were not measured in the soil, we cannot say for certain how different AHC and soil moisture influence the rates of N_2O producing processes differently between the upland and lowland. However, there are a few other ways in which the differing AHC between the upland and lowland may have influenced the soil conditions. The first is redox potential. Yu et al. (2001) identified redox potentials of between +400 to +700 mV in well oxidized soils, whereas flooded soils had redox potentials of -300 mV, suggesting drastically different environments in terms of O_2 availability, creating different constraints of the rates of biological processes in the drier upland versus the wetter lowland. The second is the differences in selection of microbial communities, as different hydrological conditions are expected to select for communities with different characteristics. Flooded soils, for example, like those from the lowland, have been found to have higher activity facultative and obligate anaerobic microbes (Yu et al., 2001).

Firestone and Davidson's "Hole-in-the-Pipe" (HIP) model (1989) suggests that because there are a range of environmental variables that contribute to or limit N_2O fluxes, which makes the prediction of N_2O fluxes from soils difficult. While other studies have found that a range of environmental factors can correlate with N_2O fluxes over similar time horizons, there were no correlations detected between N_2O fluxes and hydrological factors, and that there were low amounts of variability in soil moisture during 2008 and 2009 from both landscape positions, especially compared to the observations from 2007. Davidson et al. (2000) noted that sometimes relationships between environmental factors and N_2O fluxes are not observed in data because the spread of observations is not sufficient to statistically identify relationships. The lack of growing season scale relationships between hydrological factors and N_2O fluxes may also be due to the confounding

influence of temperature. It has been noted that environmental factors such as temperature can exert strong controls on N gas fluxes, and because temperature is highly dynamic, varying on both daily and seasonal scales, it can mask the effects of other variables known to be important to the processes, like soil moisture (Gödde and Conrad, 2000). It is also likely that the field data is biased based on the time of day it was collected. There has been little success simulating daily N_2O fluxes owing to the complex nature N_2O producing processes (Stolk et al., 2011) despite the evidence that rates of N_2O production are strongly influenced by temperature (Parkin, 1998). There is research to suggest that other microbial processes like soil respiration (CO_2 fluxes) exhibit a daily hysteric effect as well as a lag in response to temperature which can bias data interpretation (Phillips et al., 2010), suggesting that a similar diel relationship between temperature and N_2O production may exist and occurs in both landscape positions, but it is not visible with this data and may be partially the reason why N_2O fluxes on a growing season scale appear to be only correlated with soil temperature. These considerations may have affected the ability to derive relationships from the field data over the growing season.

4.1.2 The Influence of Environmental Factors Coupled with Soil Moisture on N_2O Fluxes

Coupling of environmental factors with soil moisture provides a context within which to discuss how environmental factors interact to regulate N_2O fluxes and how it differs between the upland and lowland landscape positions. The response of N_2O fluxes to the combined consideration of variability in environmental factors differed between the lowland and the upland. With soil moisture as a familiar gauge against which to assess N_2O fluxes, the results suggested that though soil moisture in the lowland was often high (near saturation), and thus are likely highly reducing, coupled soil moisture and water table showed that when the water table dropped slightly below the surface, it is likely that less reducing conditions were created, despite the high soil moisture, and these conditions resulted in high N_2O fluxes.

This decrease in water table in the lowland during 2007 which was associated with high soil moisture resulted in a “hot moment” or disproportionally high rates N_2O fluxes (McClain et al., 2003). Similarly others have referred to “moisture thresholds”, with similar observations. A range of moisture thresholds for N_2O fluxes have been identified in other studies, most commonly from agricultural and forest soils and these other thresholds compare favorably with the observations from this study. Moisture thresholds resulted in abrupt increases in N_2O magnitudes by 6 to 9 times, as reported by Dobbie et al. (1999) and Flessa et al. (2002), while Ruser et al. (2006) observed that N_2O

production increased by a factor of 40-2000 above the threshold. A range of moisture values have been identified with respect to soil moisture-N_2O thresholds; 60% WFPS (Flessa et al., 2002), >60% WFPS (Ruser et al., 2006), soil gravimetric water content of about 60-70% (Mogge et al., 1998), and between 75%-85% WFPS (Dobbie at al., 1999).

The reason for the existence of soil moisture thresholds is not well understood. Ruser et al. (2006) reported that nitrification was the primary source of N_2O below their identified threshold of approximately 60% WFPS, while denitrification dominated above the threshold. This may be the key to understanding thresholds; the processes producing N_2O fluxes may differ on either side of the moisture threshold. Given that the environmental constraints for N_2O production are different for nitrification, denitrification, and nitrifier-denitrification it stands to reason that if below the threshold nitrification is the main source of N_2O, and above the threshold denitrification is the main source of N_2O, as Ruser et al. found. The same relationships between N_2O fluxes and environmental factors should not be expected on either side of the threshold. This complicates finding relationship between environmental variables and N_2O fluxes.

Recall that soil field capacity is sometimes used as the soil moisture threshold differentiating between nitrification and denitrification (Davidson et al., 2000, Pilhate et al., 2004), because it is thought be the boundary between oxic and anoxic conditions in soils. The field capacity in this study was calculated to be 80% WFPS for the upland and 84% WFPS for the lowland. This supports the idea of a moisture threshold between 80% and 100% WFPS in the lowland, suggesting that the high magnitude N_2O fluxes may have been driven by high rates of denitrification, whereas the "threshold" or soil field capacity may not have been passed in the upland and consequently "hot moment" fluxes were not observed.

Accompanying CO_2 flux data associated with the lowland drop in water table and soil moisture in 2007, showed that CO_2 fluxes also increased in magnitude during this change in soil moisture. This suggests conditions were not C limiting. The higher CO_2 production support the idea that conditions were less reducing with decreased soil moisture. However, when soil moisture and water table increased following rewetting, the absence of high N_2O and CO_2 fluxes suggested the processes were limited. Conditions that promote heterotrophic denitrification include NO_3^-, labile OM and low O_2, and it is often assumed that this process occurs in the surface horizon of riparian soils in association with wet periods when the water table is close to the surface (Bernal et al., 2007). Similar to the field observations from this study, there is evidence from other studies that shows that CO_2 fluxes are higher from wet soils that experience a drying because the most labile forms of C are

rapidly utilized when wet soils are dried (Baldwin and Mitchell, 2000). Rates of C mineralization are highly sensitive to O_2 availability (Torsten et al., 2003) and the lowering of water table has been found to also increase CO_2 effluxes in peatlands via increasing respiration and depression of photosynthesis (Aurela et al., 2001). These decreases in water table depth leads to an increase in the aerobic zone depth, higher O_2 availability, and greater rates of organic matter decomposition (Bubier et al., 2003). Availability of C is importance to denitrification, and O_2 (aerobic status) is important because it is a primary factor in regulating the N_2O production via nitrification and denitrification (Weier et al., 1993; Bollmann and Conrad, 1998). More directly related to the results from this study, other studies have also found that lowering of the water table in peatlands can result in pulses of N_2O emissions by affecting the rates of denitrification (Martikainen et al., 1993) and increasing rates of N mineralization (Updegraff et al., 1995).

Likewise, the relatively lower water table levels (further from the surface) from the upland soils may be partially responsible for the lack of "hot moment" N_2O pulses from this landscape position, as it is known that fluctuations in water table depth have important influences on soil redox potential and chemistry (Hill, 1996). Similar to the results from this study, when comparing the upland and lowland, Machefert et al. (2004) also observed the highest N_2O fluxes at the down slope positions of riparian zone, where the water table resided closest to the surface or was flooded.

The results suggest that though precipitation events are often cited as a factor that promote N_2O fluxes because they can increase available C and N by suddenly changing osmotic pressure in the soil causing microbial cells to lysis, and increase soil moisture creating conditions that are more biological favorable for N_2O production, precipitation was found to have little direct influence of N_2O fluxes in either landscape position in the field. This is likely because soil moisture in the lowland was often already saturated, muting any effects of a precipitation event, upland soil moisture often ranged between 60%-80% WFPS, which are moisture conditions which are already thought to be optimal for fostering N_2O production from denitrification, and there were no large (greater than 10mm) rain events that occurred in association with N_2O flux measurements in the field.

The results from this research suggest that though precipitation failed to strongly correlate with growing season N_2O fluxes, and failed to be a strong driver of N_2O fluxes when coupled with soil moisture, the combined influence of soil moisture conditions and precipitation can be important consideration because precipitation events on dry soils are expected to have a different effect on the soil C and N than the same magnitude of precipitation event on moist soil. This study fails to demonstrate these points because of the lack of large rain events associated with N_2O flux

measurements, and more importantly, the lack of precipitation data associated with N_2O fluxes. In the upland, small amounts of precipitation had minimal influence on N_2O dynamics when the soil moisture was already high. Though it is more likely that associated N_2O fluxes are related to optimal soil moisture for N_2O production given that N_2O fluxes from denitrification are expected between 60% and 80% WFPS. Precipitation events are often thought to promote high N_2O fluxes by increasing rates of denitrification (Mosier et al., 1988; Ashby et al., 1998). Magnitudes of N_2O fluxes associated with precipitation events on relatively drier soils are thought to be significant because N_2O flux processes are not N-limited immediately after precipitation events (Austin et al., 2004). Pulses of N_2O and N mineralization following wetting of relatively dry soil, however, are thought to be due to the availability of readily decomposable organic matter. These substrates are released from non-living organic matter and from the death of microorganisms due to rapid changes in water potential (Kieft et al., 1987; Groffman and Tiedje, 1988; Burke, 1989). These sudden increases in soil moisture and their associated effects are greater on dry soils (Austin et al., 2004) and both the upland and lowland soils were rarely dry (with the upland often between 60%-80% WFPS, and the lowland often between 90%-100% WFPS). The influence of precipitation on N_2O fluxes from wetter soils is muted, which was expected in the saturated lowland soil. Holtgrieve et al. (2006) found that mean annual precipitation and soil N_2O flux rates failed to correlate in soils after the soils reached saturation (greater than 75% volumetric moisture content).

In this study, the coefficient of variation (CV) of soil moisture from both the upland and lowland landscape positions was greater during 2007 compared to the other years, when the CV of precipitation was also greatest. The greatest variability in N_2O fluxes was observed from the lowland during 2007 (218% CV), and others have observed similarly high CV for N_2O fluxes (van den Pol-van Dasselaar et al., 1998). Moisture variability, specifically wet-dry cycles, have been identified as important factors for soil C and N dynamics. Fierer and Schimel (2002) showed that frequent changes to soil moisture could increase N losses from soils and enhance nitrification rates, though, the mechanisms and processes influenced by moisture variability in the field, and their respective influence on N_2O fluxes in this analysis. The results from this study differ from many of those mentioned earlier because it failed to characterize precipitation as a significant driver of N_2O fluxes, but greater variability in precipitation during the growing season did coincide with greater moisture variability (Table 5). The importance of precipitation events on soil moisture variability and subsequently N2O fluxes has been previously noted. Mummey et al. (1997) have estimated that N_2O fluxes occurring within 48 hours after warm season precipitation events can account for 20% of the

total annual N_2O flux. Mogge et al. (1998, 1999) have similarly concluded that precipitation events that result in increased soil moistures contribute to increases in N_2O fluxes.

Soil moisture as a controller of N_2O fluxes is complex in the field because it is influenced by factors like precipitation and water table, and is important to both levels of regulation of N_2O fluxes from the HIP model. Recall that the first level of regulation refers to the rates of N_2O producing processes (i.e. denitrification, nitrification, and nitrifier-denitrification), and the second level of regulation refers to the relative proportion of gaseous end products "leaking" from the holes in the pipe, which are largely dictated by soil properties. Soil moisture is thought to largely influence the rates of N_2O producing processes through its control on O_2 (Firestone and Davidson, 1989). Soil moisture, and other environmental factors like temperature, directly limits rates of biological N_2O producing processes. While this study was unable to detect correlations between hydrological variables and N_2O fluxes in the field data, others have successfully found relationships between soil moisture and N_2O fluxes when associated with N_2O producing processes. For example, Linn and Doran (1984) found a positive relationship between soil moisture and N_2O fluxes from nitrification up to 60% WFPS, while an exponential relationship between N_2O fluxes and soil moisture from denitrification has been noted (Ashby et al., 1998; Machefert et al., 2004). Without a reliable indication of the process of origin, deriving simple relationships between soil moisture and N_2O fluxes is difficult, especially in field data because of the confounding influence of other environmental factors.

Antecedent hydrological conditions and wet-dry cycles influence C availability, which is an important regulator of rates of denitrification, and is indirectly a controller on O_2 through C respiration, with O_2 levels in soils being important for biological regulation of denitrification, and nitrification. The field results largely support the original hypothesis that N_2O fluxes are characterized by temperature and moisture, and the growing season N_2O flux magnitudes are similar between the upland and lowland. However, we know from deviations from the "normal" (i.e. 2007) that an unmeasured regulator of N_2O fluxes differs between landscape positions. The upland and lowland landscape positions had different AHC and soil moistures in the field while N_2O flux measurements were comparable. These differing hydrological conditions likely influenced other factors like N availability. The influence of soil moisture on N_2O fluxes is not only a regulator of biological processes responsible for N_2O fluxes, but also of soil C and N dynamic, which are also important to N_2O fluxes via biological production because these act as substrates for microbes. By suggesting that AHC (rapid vs. gradual soil moisture changes, direction of moisture change from wet to dry vs. dry to

wet) are important to the influence of soil moisture because they influence soil C and N, and further, that AHC are influential to C and N dynamics through their influence of soil integrity, microbial communities, and their influence the proportion gases end-products. The results from the lab are discussed below to aid in understanding these interactions.

4.2 Soil Moisture and N_2O Flux Relationships from Differing Antecedent Hydrological Conditions

4.2.1 Antecedent Soil Moisture and the Relationship between Soil Moisture and N_2O Fluxes

The results from Experiment 1 suggest that AHC is influential to N_2O soil dynamics by influencing the relationship between N_2O fluxes and soil moisture, and this is largely supported by the results from other studies. There was a particularly convincing study recently published by Bergstremann et al. (2011) where they performed an experiment using repacked soil cores. The experiment held the cores at either "pre-dry" conditions of 20% WFPS, or "pre-wet" conditions of 75% WFPS for four weeks. Then soil moisture content was increased to 90% WFPS, and the soils were amended with glucose and potassium nitrate, and incubated for 10 days. They reported that more N as N_2 compared to N_2O was emitted when soils were pre-wet, and more N as N_2O compared to N_2 was emitted when soils were pre-dry. They also reported that on a whole, more N was lost from the soils from pre-dry conditions than pre-wet conditions. They hypothesized that this was because the pre-dry cores had more available C, and suggested that the pre-dry conditions may have facilitated the selection of a stronger community of facultative anaerobic denitrifiers in the soils. Under the latter assumption, this would result in more denitrifiers under the pre-dry scenario at the start of the experiment. All of the soil cores during Experiment 1 were subjected to drying prior to the experiment which should have minimized the variability that pre-experimental conditions would have had on the gaseous N mole fractions. However, the lowland soils were notably drier than the upland soils at the start of Experiment 1, which impairs direct comparability of the upland and lowland soil cores. The hypothesis made by Bergstermann et al. with respect to the influence of drier conditions on the dynamics of microbial communities suggests that the structure of the communities may have differed between the relatively wetter upland and the drier lowland soil cores at the start of Experiment 1, which may have influenced the N_2O dynamics throughout the experiment. Under this assumption, the lowland soils, which had lower pre-experimental soil moisture conditions, would have selected for

more vigorous and robust facultative anaerobic denitrifiers, which may have contributed to the stronger relationship between N_2O dynamics and environmental factors during Experiment 1. There was a stark contrast between the upland and lowland soils during Experiment 1 with respect to N_2O dynamics following the saturation event. Observations from the Low_{WDW} saturation event, showed that the initial N_2O flux measurements were low following saturation, unlike the upland. These differences between the upland and lowland responses may be related to differences in the soil moisture at which they dried to, with the lowland soils being drier compared to the upland soils, as mentioned earlier. Sometimes the assumption is made that microbes require time to "wake up" following rewetting of dry soils (Davidson, 1992), and it can take between a few hours and a few days for the enzymatic functions of denitrifiers to resume following a drying period (Simek and Cooper, 2002). Gödde and Conrad (2000) reported in their study that analyzed nitrification and denitrification rates at constant temperature and soil moisture from bulked soil, that 5 days was enough to re-establish nitrifying microbes to pre-experimental conditions, suggesting that the 3 day saturation period employed in Experiment 1 may not have been long enough to re-establish microbial communities to pre-experimental conditions. Patter et al. (1980) suggest the influence of AHC on denitrification is related to the influence of AHC on soil N, and that wetting dry soils can result in an increase in the amount of N denitrified. The extractable inorganic N and CO_2 flux data provides some insight into the role of these factors on N_2O dynamics from the differing AHC and differing soil types during Experiment 1, and this is discussed below.

4.2.2 The Influence of Antecedent Soil Moisture, Nitrogen and Carbon, on N_2O Production

The laboratory results suggest that influence of AHC on N_2O fluxes appears to be largely driven by the influence of AHC on N and C dynamics in soils. The results support the idea that soil moisture is considered a control on biological processes through its control on O_2 availability, and AHC, through its influence on soil C and N dynamics, provides a second level of regulation. Experiment 1 provides evidence that AHC, both the pre-experimental conditions and the dynamics of moisture change (sudden changes to moisture vs. gradual changes to moisture), are important factors to consider and the combined results from Experiment 1 and Experiment 2 to support the idea that greater concentrations of soil N and C will positively influence N_2O flux magnitude.

The differences between the upland and lowland soils in N_2O dynamics and extractable inorganic N following the saturation event suggest differences in the pre-experimental conditions and

the level of saturation achieved may have influenced the timing and magnitude of N_2O fluxes during Experiment 1. It may also be that the upland and lowland soils respond differently to re-wetting of dry soils. It is hypothesized that different processes were associated with the saturation event (a rapid change to soil moisture) than the gradual changes in soil moisture during Experiment 1, inferring that the rate of moisture change, as a factor of AHC, is an important consideration to the influence of AHC on soil N and C, and thus N_2O fluxes. Rapid changes soil to moisture from dry to wet conditions can cause microbial cells to lysis (Bottner, 1985; Van Gestel et al., 1992), resulting in a temporary increase in highly labile, low C:N ratio substrate (Fontaine et al., 2003) that can be readily mineralized by surviving microbes (Birch, 1959; Kieft et al, 1987). Gradual changes to soil moisture are not expected to have the same influence on microbial communities given that the changes to osmotic pressure are not expected to be sudden when associated with gradual changes to soil moisture.

The differences in starting soil moistures from Experiment 1 may have influenced the results, as the lowland soils were desiccated and the upland soils were not. The actual drying of the soils during the pre-experimental conditions may have been influential to the N_2O dynamics during the saturation event. Desiccation of soils that are usually inundated, like the lowland soils, can result in a rapid loss of bioavailable C (i.e. CO_2) as soils dry because aerobic heterotrophs are more efficient than anaerobic microbes at using organic substrates like lignin (Baldwin and Mitchell, 2000). The pulse of N_2O fluxes associated with the saturation event, as was observed from the Up_{WDW} moisture regime, was expected and is thought to be associated with the stimulation of C and N mineralization, and microbial stress or lysising of microbes (Davidson, 1992; Fierer and Schimel, 2003), or the alteration of soil properties which expose previously protected organic matter (Goebel et al., 2005). However, the absence of a pulse of N_2O fluxes following the Low_{WDW} saturation event may have been reflective of the loss of highly labile C following the extended drying, or the lower moisture level achieved during the pre-experiment drying.

Recall that during phase 2 of Experiment 1, there were limited N_2O fluxes observed from both of the upland moisture regimes. However, NO_3^- did not appear to be limiting during this phase from either moisture regime. Accumulation of NO_3^- for most of phase 2 for the upland soils and the lack of accumulation of NH_4^+ (with the exception of the final extraction during the Up_{WDW} moisture regime), suggests that nitrification was the dominant process in the upland soils during the second half of the experiment. This is further supported by the fact that during that phase soil moisture was between 40 and 60% WFPS when soil extractions were completed. Nitrous oxide production from

nitrification would not necessarily be expected unless soil was slightly acidic, or NO_2^- had accumulated in the soil (Firestone and Davidson, 1989) hence the limited N_2O fluxes. Recall that nitrifier-denitrification can produce N_2O when O_2 is high (Table 1), but the conditions during this phase fail to support that nitrifier-denitrification was occurring because of the lack of N_2O production.

Antecedent hydrological conditions appeared to influence the temporal dynamics of extractable inorganic N differently from the upland and lowland soils with greater concentrations of N being observed from the lowland. It was difficult to predict how the extractable inorganic N dynamics should respond to differing AHC based on past studies. Fierer and Schimel (2002) who performed a series of wet-dry cycles with 2 day drying intervals on soils from under a perennial oak (loam) and annual grassland (clay loam), found that extractable NO_3^- did not change 1 or 7 days following the stress treatment (wet-dry cycle) but instead they observed a lag of 6 weeks post moisture changes for a decrease in to NO_3^- concentrations to occur. The same study reported that the stress treatments did not affect extractable NH_4^+ (Fierer and Schimel, 2002), which is similar to the Up_{WDW} during Experiment 1, which saw little change to NH_4^+ until the end of the experiment (62 days).

After the fourth extraction from the Up_{WDW} moisture regime, the soil moisture range was relatively higher (60-80% WFPS) suggesting N_2O production from denitrification may be expected if no factors were limiting. However, N_2O fluxes were minimal, despite the presence of NO_3^-. Typically when denitrification is not limiting, high concentrations NO_3^- are thought to inhibit N_2O reduction to N_2 as NO_3^- will out-compete N_2O as an electron acceptor (Bergstermann et al., 2011) resulting in even grater fluxes of N_2O. The Experiment 1 results from the upland point to C limitation of denitrification because of the persistently low CO_2 fluxes during phase 2. The importance of C turnover in association with N_2O production should not be overlooked because of the partial control of C availability has on denitrification (McClain et al., 2003; Hefting et al., 2006), but this study lacked direct measurements to assess how the amount of organic C changed over the course of Experiment 1, and lacked measurements to indicate the lability of C in the soils.

Carbon dioxide fluxes during Experiment 1 and 2 provided some insight into the C dynamics in the soils and how they differed between the different soil types. Recall that during Experiment 1, CO_2 fluxes were about an order of magnitude lower from the upland than from the lowland, but they were comparable between the soil types during Experiment 2, when soils were amended. These results suggest that there were differences in the C dynamics between the soils, which is further supported by the differences in C:N ratio between the soil types, and the differences in the pre-

experimental conditions (extended drying period) during Experiment 1 which likely influenced C dynamics between the upland and lowland (i.e. how dry the soils became). Recall that comparable magnitudes of CO_2 production were observed between the upland and lowland soil types during Experiment 2. The comparability between CO_2 fluxes from the different soil types during experiment 2 can likely be attributed to the addition of a standard amount of a highly labile C source to all of the soils, which was easily respired by the microbes in both the upland and lowland soil types. Together, the experimental results suggest that amount of labile C was generally greater in the lowland than the upland, as noted during Experiment 1. Moreover, the greater levels of both CO_2 and N_2O fluxes from the Low_{DWD} moisture regime compared to the Low_{WDW} moisture regime, despite the often similar inorganic N concentrations during extractions, suggests C was a driver of N_2O flux magnitudes in the lowland soils

These results suggest that denitrification was primarily responsible for the high N_2O fluxes from the lowland during Experiment 1. Others have identified C as an important component in understanding soil N_2O flux dynamics. Groffman and Teidje (1988), who related soil moisture to rates of denitrificaiton, similarly found that both C and N mineralization were stimulated by the wet-dry cycle with denitrification rates being limited by C and/or NO_3^-. Linn and Doran (1984) identified a high correlation between water soluble C levels and N_2O production, but not between N_2O production and NO_3^- levels. The results from Fierer and Schimel (2002) demonstrated that a higher frequency of rewetting events resulted in decreased CO_2 magnitudes following rewetting. Recall that a decrease in CO_2 fluxes was observed during phase 2 of Experiment 1 from both the upland and lowland in both moisture regimes, however, CO_2 fluxes in the lowland soils during Experiment 1 was an order of magnitude greater than from the upland, as were N_2O fluxes. This suggests that C supplies were depleted early from the both soils types during the experiment, but more so from the upland relative to the lowland. The results from Fierer and Schimel did not conclude the mechanism controlling the depletion of C during wet-dry cycles, but suggested it was either related to a decrease in OM exposure from aggregate breakup, or adjustments of the microbial communities to changes in water potential, thus less instances of cellular lysis, and ultimately less C substrate.

4.2.3 Isolating the Influence of Soil Moisture and soil N on N_2O Production

The results from Experiment 2 when both soil moisture and nutrient concentrations were modified suggest that increased inorganic N and soil moisture (between 50% and 80% WFPS) results in greater magnitudes of N_2O production from the upland soils, but the relationship between soil moisture,

inorganic N, and N_2O fluxes in the upland was less well defined from the results in Experiment 1. Recall that the opposite results were observed from the lowland soils, with the results from Experiment 1 suggesting that increased concentrations of inorganic N and soil moisture, under conditions that were not C limited, showed high magnitudes of N_2O fluxes, while the lowland results from Experiment 2 did not show any relationship between soil moisture, inorganic N, and N_2O fluxes.

Others have noted the importance of inorganic N concentrations and soil moisture to N_2O flux magnitudes and N_2O flux relationships with other environmental factors. Dobbie et al. (1999) demonstrated that a stronger relationship existed between soil moisture and N_2O fluxes when inorganic N was not limited. They showed that low NO_3^- (less than 5 mg NO_3^--N kg^{-1}) weakened the relationship between soil moisture and N_2O fluxes, and further showed that when NO_3^- concentrations were low, N_2O fluxes were also low, despite high soil moisture. By removing data that was limited by low inorganic N concentrations, a relatively strong exponential relationship was found between soil moisture and N_2O fluxes from grassland and arable lands in that study. The reason for the lack of observed relationship between soil moisture, inorganic N, and N_2O fluxes during Experiment 2 from the lowland may have been because the N was immobilized. Recall that N rather than C mineralization is often a limiting factor in soil systems, and that the soil C:N ratio is important to mineralization dynamics. In soils with relatively higher C:N ratios, like the lowland soils, immobilization is more likely to occur because the microbes require more N to meet their biological requirements, thus levels of NO_3^- can temporarily decrease in soils (Reddy and Delaune, 2008). Without NO_3^-, denitrification can be inhibited. (Nitrification and nitrifier-denitrification have not been found to have strong, direct relationships to NO_3^-, Table 1) Reactions in soils are known to occur quickly following amendments. Williams et al. (1999) demonstrated that N_2O effluxes from grassland soils amended with bovine urine occurred almost instantaneously (<4 hours), therefore, if immobilization did occur in the lowlands, a longer time interval between the addition of the N and C to the soil and the incubation, or repeated incubations over a longer time horizon, may have yielded different results. Typically, additions of NH_4^+ are thought to increase rates of nitrification, and the additions of NO_3^- should increase denitrification but studies have shown a variable response to N additions (Barnard et al., 2005). Both NO_3^- and NH_4^+ additions yielded increases in N_2O fluxes during Experiment 2 from the upland soils but because N_2O producing processes were not measured, it is not clear what process(es) were responsible for production of N_2O. Similar to the upland results from this study, Murray et al. (2004) who amended loam soils with NO_3^- and a C source (including glucose) found that N_2O production increased in the short term (between 0 and 42 hours) at 70% WFPS. It is

apparent from the results from Experiment 2 that high concentrations of inorganic N can result in high magnitudes of N_2O production. However, the results from the upland soils during Experiment 2 and the lowland soils during Experiment 1 suggest that this high magnitudes of N_2O production is driven primarily by dentirification, because when C is otherwise limiting (i.e. in the upland soil during Experiment 1, and during the Low_{WDW} moisture regime during Experiment 1 when CO_2 production was lower compared to the Low_{DWD} moisture regime), magnitudes of N_2O fluxes are relatively lower.

4.3 Summary

Soil moisture is often cited as a strong controller of N_2O production both through its influence on O_2, which dictates the biological processes that are responsible for N_2O production. Soil moisture is also a known controller of C and N turnover rates in soils, which influences the availability of substrates to fuel N_2O producing processes. The experimental work in this study suggests that soil C and N help regulate the magnitude of N_2O fluxes. Soil moisture's influence on these variables, and on N_2O fluxes is complex, as the influence of soil moisture includes both instantaneous soil moisture (a regulator of soil O_2) and AHC (largely a driver of soil C and N dynamics), with the influence of AHC being important not only with respect to whether soil is wetting up or drying down, but with respect to the rate of moisture change as well as the level of wetness or dryness when the soil moisture does change, relative to the level of wetness of dryness that the soil achieves by the end of the moisture change.

The complexities of the influence of soil moisture and AHC on N_2O fluxes can be empirically observed in the lab to some extent, when environmental are controlled. However, in the field, these influences are confounded by natural spatial and temporal variability inherent in the natural environment and are further confounded by the influence of other environmental factors that are either controlled for or not existent in the lab environment. Most prevalent in this study was the influence of soil temperature and the combined influence of water table and soil moisture, which, when coupled, appeared to be highly influential to N_2O dynamics from both landscape positions in the field.

The Hole in Pipe (HIP) model by Firestone and Davidson (1989) details two levels of regulation of N_2O fluxes. The first level of regulation describes controls on factors that regulate the overall rates of biological processes (nitrification, denitrification, and nitrifier-denitrification), and the second level of regulation controls the partitioning of the reacting N species to NO, N_2O, and N_2, and this is controlled the size of the holes through which N gases are "leaked from the pipe", which is

largely dictated by soil properties. The results from Experiment 1 and 2 re-enforce the concepts articulated by the HIP model and show that the levels of N_2O production are positively related to the concentrations of N and C. These results also suggest that soil type is important to N_2O dynamics, which is in line with the second level of regulations of the HIP model, which suggests that soil properties (i.e. pH) influence biological N_2O fluxes. The lab results are largely consistent with the original hypothesis that soil moisture, inorganic N and organic C, and N_2O production would be positively related, and the influence of AHC on these relationships re-enforces the complexity of scenarios under which N_2O fluxes from different soils moisture conditions will occur.

Recent research suggests that AHC is influential to the end-product of N gases from biological production, which describes the second level of regulation of the HIP model. Though this study only measured N_2O fluxes, the results from Experiment 1 showed that differing moisture regimes applied to the same soil types resulted in different N_2O flux dynamics, and that is the likely due to the influence of AHC on soil C and N dynamics, which has direct consequences for the second level of regulations in the HIP model. With numerous biological pathways for N_2O production, each with their own limiting factors, and multiple environmental factors acting to influence variables of significance like N and C, it is difficult to predict the timing and magnitude of N_2O fluxes from soils (Figure 26).

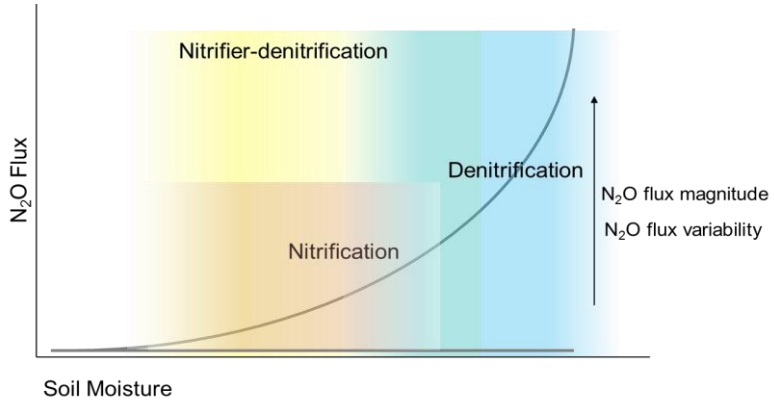

Figure 26 A conceptual diagram showing where on a soil moisture spectrum N_2O fluxes from nitrifier-denitrification (yellow) and nitrification (red) are generally expected at lower soil moistures than denitrification (blue), but with plenty of overlap, and increasing magnitudes and variability of N_2O fluxes also often expect.

The field data lacked associated soil inorganic N measurements, so we are unable to estimate from this data how AHC and soil moisture influenced N concentrations dynamics in the soils, like was done in the lab data. However, the field data shows that the hydrological controls on the N_2O fluxes in the field are highly complex, with interactions between temperature, soil moisture, water

table, and precipitation showing varying degrees of influence on the timing and magnitude of N_2O fluxes. The field data shows that soil moisture as a control on N_2O fluxes is complicated by the confounding influence of other hydrological factors, and the combination of these factors likely influences redox and soil N and C dynamics, which are all influential to the biological pathways of N_2O production (Figure 27).

Conceptually, the combination of the lab and field data largely supports the concepts put forth by the Firestone and Davidsons HIP model (1989) by demonstrating the complexity of the relationships between N_2O fluxes and environmental factors, especially hydrology. This study adds to the concepts proposed by the HIP by suggesting that AHC are influential to both levels of N_2O regulation (process of biological production and determination of gaseous end-product) through its influence on soil C and N dynamics, while supporting the HIP concepts that fundamental controls of the leaks in the pipes are largely related to soil properties, meaning relationships derived in one soil type not necessarily directly transferrable to other soil types, as demonstrated in the differences observed between the upland and lowland soil types.

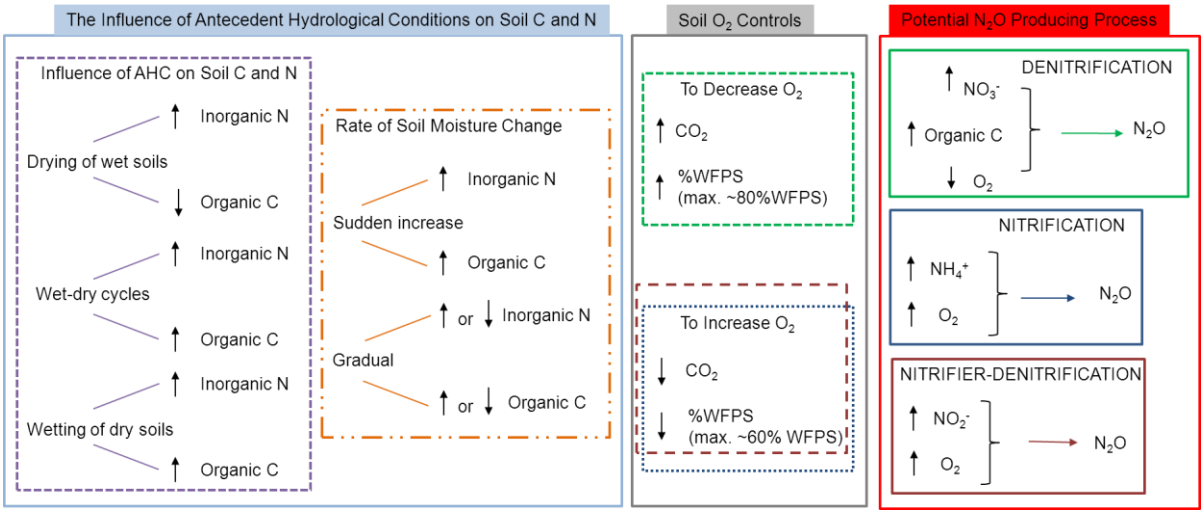

Figure 27 A simple, conceptual diagram showing how AHC (purple) and rates of moisture change (orange) influence soil N and C, along with controls of soil O_2, and the N, C (if any) and O_2 requirements for N_2O production from denitrification (green), nitrification (blue) and nitrifier-denitrification (red)

Chapter 5 Conclusions and Suggestions for Future Research

This thesis sought to better understand the influence of soil moisture and AHC on the timing and magnitude of N_2O fluxes from a riparian zone. To do this, N_2O fluxes along with environmental factors were monitored in the field for three years from upland and lowland positions on a riparian landscape. These positions differed hydrologically, with the upland consisting of relatively drier conditions and the lowland consisting of relatively wetter conditions. The results found that N_2O fluxes were most strongly correlated with soil temperature, and often failed to yield the expected relationship between soil moisture and N_2O fluxes. Further analysis of the interactions of hydrological factors suggested that the reason for the lack of the expected theoretical relationship between soil moisture and N_2O fluxes was because this relationship was also influenced by the other hydrological factors (precipitation, water table). It is suspected that these hydrological interactions influence soil redox conditions, which is imperative to N_2O production. These inter-relationships between hydrological factors differed between the upland and lowland, suggesting that these hydrological interactions and their control on N_2O fluxes is influenced by AHC, with N_2O fluxes from the drier upland being more strongly influenced by a combination of soil moisture and precipitation, while the wetter lowland was influenced by a combination of soil moisture and water table.

To better isolate the influence of AHC on the relationship between soil moisture and N_2O production from soils, lab experiments were conducted. The results from Experiment 1 showed that AHC influenced the timing and magnitude of N_2O fluxes, and that this influence differed between the upland and lowland. In the upland, N_2O production was not consistently correlated with soil moisture throughout the experiment, while N_2O production from the lowland soil, however, was often correlated with soil moisture. However, the timing and magnitudes of N_2O fluxes differed when different moisture regimes were applied to the same soil type.

Accompanying inorganic N extractions and CO_2 production data from that experiment suggested that AHC influenced the soil inorganic N dynamics differently in the upland and lowland soils. The upland soils were inorganic N and carbon limited, which limited the influence of soil moisture on N_2O fluxes. Further complicating the results, high amounts of spatial variability in the upland was inferred from the high degrees of variability observed in the N_2O production and the inorganic N extractions. The inorganic N limited status of the upland soils was confirmed by

Experiment 2 results, which showed that simultaneous increases in soil moisture and inorganic N resulted in greater N_2O production from the upland soils. The lowland soils were not inorganic N limited, hence the stronger relationship between soil moisture and N_2O production during Experiment 1.

The results suggest that there is a positive relationship between the concentrations of C and N, and the magnitude of N_2O fluxes/production in soils. When N and C are not limiting, there is a positive relationship between soil moisture and N_2O fluxes. In this sense, soil moisture can both thought of as the driver of temporal N_2O dynamics and soil C and N can be thought of as the drivers N_2O magnitudes. The results suggest that antecedent hydrological conditions influence the timing and magnitude of N_2O fluxes primarily through its influence on factors like availability of N and C, which influence flux magnitudes; microbial dynamics, which influence temporal dynamics; and perhaps O_2 diffusion dynamics, which influences soil redox status.

This research makes it clear that the influence of AHC, and hydrology in general, on N_2O fluxes are complex, and there are still many unanswered questions that require further research. Inorganic N data to accompany future field data would be beneficial in tying the role of inorganic N to the inter-related hydrological dynamics between soil moisture, water table, and precipitation. Likewise, soil oxygen data from the field would be beneficial to understanding the inter-play between hydrological dynamics and redox.

Further exploration of AHC in the lab would aid in understanding of N_2O dynamics from different AHC. Conducting the experiment again with different pre-experimental conditions (wet, at field capacity, dry) for different durations (1 week, 1 month, etc.) would help to understand how these pre-experiment conditions influence the results with respect to the relationship between soil moisture and N_2O fluxes, and may provide insight into how far back antecedent conditions should be considered. Moreover, it would be interesting to re-run Experiment 1 with different combinations of moisture regimes. For example, instead of moving between very dry to very wet, creating moisture regimes that moved between field capacity and saturation, or from dry to field capacity, and this would help to better relate the lab results to the field scenarios.

Bibliography

Ahn, J., Sungpyo, K., Hongkeun, P., Dimitrios, K., Krishna, P., & Kartik, C. (2009). Spatial and temporal variability in N2O generation and emission from wastewater treatment facilities. *Water Environment Federation, 9*, 401-409.

Allison, F. E., Cartner, J. N., & Sterling, L. D. (1960). The effect of partial pressures of oxygen on denitrification. *Soil Science Society of America Proceedings, 24*, 283-285.

Alves, Bruno J.R., Smith, Keith A., Flores, Rilner A., Cardoso, Abmael S. & Oliveira, William R.D. (2012). Selection of the most suitable sampling time for static chambers for the estimation of daily mean N2O flux from soils. *Soil Biology and Biochemistry, 46,* 12-19.

Ashby, J. A., Bowden, W. B., & Murdock, P. S. (1998). Controls on denitrification in riparian soils in headwater catchments of a hardwood forest in the catskill mountains, U.S.A. *Soil Biology and Biochemistry*, 853-864.

Aurela, M., Laurila, T., & Tuovinen, J. (2001). Seasonal CO2 balances of a subarctic mire. *Journal of Geophysical Research, 106*, 1623-1637.

Austin , A. T., Yahdjian, L., John, S. M., Belnap, J., Porporto, A., Norton, U., et al. (2004). Water pulses and biogeochemical cycles in arid and semiarid ecosystems. *Oecologica. 141*, 221-235.

Baggs, E. M. (2008). A review of stable isotope techniques for N2O sources partitioning is soils: recent progress, remaining challenges and future considerations. *Rapid Communication in Mass Spectrometry*, (22), 1664-1672.

Baldwin, D. S., & Mitchell, A. M. (2000). The effects of drying and re-flooding on the sediment and soil nutrient dynamics of lowland river–floodplain systems: a synthesis. *Regulated Rivers: Research & Management, 16*(5), 457-467.

Barnard, R., Leadley, P. W., & Hun, B. A. (2005). Global change, nitrification, and denitrification: A review. *Global Biogeochemical Cycles, 19*, 1-13.

Bergsma, T. T., Robertson, G. P., & Ostrom, N. E. (2002). Atmospheric Pollutants and Trace Gases: Influence of soil moisture and land use history on denitrification end-products. *Journal of Environmental Quality, 31*, 711-717.

Bergstermann, A., Cardenas, L., Bol, R. et al. (2011) Effect of antecedent soil moisture conditions on emissions and isotopologue distribution of N2O during denitrification. *Soil Biology & Biochemistry, 43,* 240–250.

Bernal, S., Francesc , S., Butturin, A., Nin, E., & Sabater, S. (2007). Factors limiting denitrification in a Mediterranean riparian forest. *Soil Biology and Biochemistry, 39*, 2685-2688.

Birch, H. (1959). Further observations on humus decomposition and nitrification. *Plant and Soil, 3*(11), 262-286.

Bollmann, A., & Conrad., R. (1998). Influence of O2 availability on NO and N2O release by nitrification and denitrification in soils. *Global Change in Biology, 4*, 387-396.

Bottner, P. (1985). Response of microbial biomass to alternate moist and dry conditions in a soil incubated with 14C- and 15N-labelled plant material. *Soil Biology and Biochemistry, 17*, 329-337.

Bouwman, A. F. (1996). Direct emission of nitrous oxide from agricultural soils. *Nutrient Cycling in Agroecosystems, 46*, 53-70.

Buiber , J., Moore, T., & Roulet, N. (1993). Methane emissions from wetlands in the midboreal region of northern Ontario, Canada. *Ecology, 74*, 2240-2254.

Burke, I. (1989). Control of nitrogen mineralization in a sagebrush steppe landscape. *Ecology, 70*(4), 1115-1126.

Cates, R., & Keeney, D. (1987). Nitrous oxide emissions from native and reestablished prairies in Southern Wisconsin. *American Midland Naturalist, 117*(1), 35-42.

Cey , E. E., Rudolph, D. L., Aravena, R., & Parkin, G. (1999). Role of the riparian zone in controlling the distribution and fate of agricultural nitrogen near a small stream in southern Ontario. *Journal of Contaminant Hydrology, 39,* 45–67.

Chen, G.X., Huang, G.H., Yu, K.W. & Xu, H. (1997). Nitrous oxide and methane emissions from soil-plant systems. *Nutrient Cycling in Agroecosystems, 49,* 41-45.

Davidson, E.A., M. Keller, H.E. Erickson, L.V. Verchot, and E. Veldkamp. (2000). Testing a conceptual model of soil emissions of nitrous and nitric oxides. *BioScience. 50*(8), 667-680.

Davidson, , E. A. (1992). Pulses of Nitric Oxide and Nitrous Oxide Flux following Wetting of Dry Soil: An Assessment of Probable Sources and Importance Relative to Annual Fluxes. *Ecological Bulletins, 42,* 149-155.

Davidson, E. A. (1991). Fluxes of nitrous oxide and nitric oxide from terrestrial ecosystems. In J. E. Rogers, & W. B. Whitman, Microbial Production and Consumption of GreenhouseGases:

Methane, Nitrogen Oxides and Halomethanes. Athens, Georgia, USA: American Society for Microbiology. pp. 219-235

Deacon, J. (2007). *Institute of Cell and Molecular Biology*. (The University of Edinburgh.) Retrieved August 9, 2011, from The Microbial World: The nitrogen cycle and nitrogen fixation: http://www.biology.ed.ac.uk/research/groups/jdeacon/microbes/nitrogen.htm

DeSimone, J., Macrae, M.L., Bourbonniere, R.A. (2010). Spatial variability in surface N2O fluxes across a riparian zone and relationships with soil environmental conditions and nutrient supply. *Agriculture, Ecosystems and Environment, 138,* 1–9.

Dendooven, L., Duchateau, l., & Anderson, J. M. (1996). Gaseous products of denitrification process as affected by the antecedent water regime of the soils. *Soil Biology and Biogeochemistry, 28*, 239-245.

Dhondt, K., Boechx, P., Hofman , G., & Van Cleemput, O. (2004). Temporal and spatial patterns of denitrification enzyme activity and nitrous oxide fluxes in three adjacent vegetated riparian buffer zones. *Biology and Fertility of Soils 40*, 243–251.

Dobbie, K., McTaggart, I., & Smith, K. (1999). Nitrous oxide emissions from intensive agricultural systems: variations between crops and seasons, key driving variables, and mean emission factors. *Journal of Geophysical Research,104*, 26891–26899.

Du, R., Lu, D., & Wang, G. (2006). Diurnal, seasonal, and inter-annual variations of N2O fluxes from native semi-arid grassland soils of inner Mongolia. *Soil Biology and Biochemistry. 38*(12), 3474–3482.

Duxbury, J. M., Bouldin, D. R., Terry, R. E., & Tate, R. L. (1982). Emissions of nitrous oxide from soils. *Nature, 298*, 462-464.

Entry, J. A., & Emmingham , W. H. (1996). Nutrient content and extractability in riparian soils supporting forest and grassland. *Applied Soil Ecology, 4*, 119-124.

Fierer, N., & Schimel., J. P. (2002). Effects of drying-rewetting frequency on soil carbon and nitrogen transformations. *Soil Biology and Biochemistry, 34*, 777-787.

Firestone, M.K., Davidson, E.A. (1989). Microbiological basis of NO and N2O production and consumption in soil. Andreae MO, Schimel DS (eds). Exchange of Trace Gases between Terres trial Ecosystems and the Atmosphere. New York: John Wiley & Sons. pp. 7–21

Flessa, H., Ruser, R., Dorsch, P., Kamp, T., Jimenez, M., Munch, J., et al. (2002). Integrated evaluation of greenhouse gas emissions (CO2, CH4, N2O) from two farming systems in southern Germany. *Agriculture, Ecosystems & Environment, 91*(1-3), 175-189.

Fontaine, S., Mariotti, A., & Abbadie , L. (2003). The priming effect of organic matter: a question of microbial competition? *Soil Biology and Biochemistry, 35*(6), 837–843.

Freitag, A., Rudert, M., & Bock, E. (1987). Growth of Nitrobacter by dissimilatoric nitrate reduction. *FEMS Microbiological Letters, 48*, 105-109.

Galloway , J. N. (1998). The global nitrogen cycle: changes and consequences. *Environmental Pollution, 102*, 15-24.

Galloway, J. N., Dentener, F. J., Capone, D. G., Boyer, R. W., Howarth, R. W., Seitzinger, S. P., et al. (2004). Nitrogen Cycles: Past, Present, and Future. *Biochemistry, 70*, 153-226.

Gödde, M., & Conrad, R. (2000). Influence of soil properties on the turnover of nitric oxide and nitrous oxide by nitrification and denitrification at constant temperature and moisture. *Biology and fertility of soils, 32*(2), 120-128.

Goebel, M.O., Bachmann, J., Woche, S.K., & Fischer, W.R. (2005). Soil wettability, aggregate stability, and the decomposition of soil organic matter. *Geoderma, 128*, 80–93.

Goodroad, L. L., & Keeney, D. (1984). Nitrous oxide production in aerobic soils under varying pH, temperature and water content. *Soil Biology and Biochemistry, 16*, 39-43.

Gregory, S. V., Swanson, F. J., McKee, W. A., & Cummins, K. W. (1991). An Ecosystem Perspective of Riparian Zones: Focus on links between land and water. *BioScience, 41*(8), 540-551.

Groffman, P. M., & Tiedje, J. M. (1988). Denitrification Hysteresis during Wetting and Drying Cycles in Soil. *Soil Science Society of America Journal, 52*, 1626-1629.

Hefting, M. M., Bobbink, R., & Janssens, M. P. (2006). Spatial variation in denitrification and N2O emissions in reaction to nitrate removal efficiency in an N-stressed riparian buffer zone. *Ecosystems, 9*, 550-563.

Hergoualc'h, K., Shiba, U., Harmand, J. M., & Oliver, R. (2007). Processes responsible for the nitrous oxide emission from a Costa Rican Andosol under a coffee agroforestry plantation. *Biology of Fertile Soils, 43*, 787-795.

Hernandez, M.E. & Mitsch, W.J. (2006). Influence of hydrologic pulses, flooding frequency, and vegetation on nitrous oxide emissions from created riparian marshes. *Wetlands, 26*, 862-877.

Hill, A. R. (1996). Nitrate removal in stream riparian zones. *Journal of Environmental Quality, 25*, 743-755.

Holtgrieve, G., Jewett, P., & Matson, P. (2006). Variations in soil N cycling and trace gas emissions in wet tropical forests. *Oecologia, 146*(4), 584-594.

Huang, B., Chen, G., Huang, G., & Hauro, T. 2003. Nitrous oxide emission from temperate grassland and emission estimation for temperate grassland in China. *Nutrient Cycling in Agroecosystems. 67,* 31–36.

Hutchinson , G. L., Guenzi , W. D., & Livingston , G. P. (1993). Soil water controls on aerobic soil emissions of gaseous nitrogen oxides. *Soil Biology and Biogeochemistry, 25*, 1-9.

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

Intergovernmental Panel on Climate Change. (2001). *Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessement Report of the Intergovernmental Panel on Climate Change*. [Houghton, J.T.,Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden, X. Dai, K. Maskell, and C.A. Johnson (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, pp. 881.

Kieft, T. L., Soroker, E., & Firestone, M. K. (1987). Microbial biomass response to a rapid increase in water potential when dry soil is wetted. *Soil Biology and Biochemistry, 19*(2), 119-126.

Knowles, R. (1982). Denitrification. *Microbiological Review, 46*(1), 43-70.

Kool, D. M., Dolfing, J., Wrage, N., & Van Groenigen, J. W. (2011). Nitrifier denitrification as a distinct and significant source of nitrous oxide from soil. *Soil Biology and Biochemistry, 43*(1), 174-178.

Kuenen, G. J., & Robertson., L. A. (1994). Combined nitrification-denitrification processes. *Microbiological Review, 15*, 109-117.

Kusa, K., Sawamoto, T., & Hatano, R. (2002). Nitrous oxide emissions for six years from a gray lowland soil cultivated with onions in Hokkaido, Japan. *Nutrient Cycling in Agroecosystems, 63*(2-3), 239-247.

Li, C., Frolking, S., & Frolking, T. A. (1992). A Model of Nitrous Oxide Evolution From Soil Driven by Rainfall Events: 1. Model Structure and Sensitivity. *Journal of Geophysical Research, 97*(D9), 9759-9776.

Liikanen, A., Silvennoinen, H., Karvo, A. Rantakokko, P., & Martikainen, P. J. 2009. Methane and nitrous oxide fluxes in two coastal wetlands in the northeastern Gulf of Bothnia, Baltic Sea. *Boreal Environment Research, 14*, 351-368.

Linn, D. M. & Doran, J. W. (1984). Effect of water-filled pore space on carbon dioxide and nitrous oxide production in tilled and nontilled soils. *Soil Science Society of America Journal, 48*(6), 1267-1272.

Liu, B., Mørkved, P., Frostegård, Å., & Bakken, L. (2010). Denitrification gene pools, transcription and kinetics of NO, N2O and N2 production as affected by soil pH. *FEMS Microbiology Ecology, 72*(3), 407-417.

Luxmoore, R., Stolzy, L., & Letey, J. (1970). Oxygen Diffusion in the Soil-Plant System I. A Model. *Agronomy Journal, 62*(3), 317-322.

Machefert, S. E., Dise, N. B., Goulding, K. W., & Whitehead, P. G. (2004). Nitrous oxide emissions from two riparian ecosystems: Key controlling variables. *Water, Air and Soil Pollution: Focus, 4*, 427-436.

Martikainen, P., Nykänen , H., Alm , J., & Silvola , J. (1993). Effect of water table on nitrous oxide from northern peatlands. *Nature, 366*, 51-53.

Martin, T. L., Kaushik, N. K., Trevors, J. T., & Whiteley, H. R. (1999). Review: Denitrification in temperature climate riparian zones. *Water, Air and Soil Pollution, 111*, 171-186.

McCarty, G. W., & Bremner, J. M. (1993). Factors affecting the availability of organic carbon for denitrification of nitrate in subsoils. *Biology and Fertility of Soils, 15*(2), 132-136.

McClain, M. E., Boyer, E. W., Dent, C. L., Gergel, S. E., Grimm, N. B., Groffman, P. M., et al. (2003). Biogeochemical Hot Spots and Hot Moments at the Interface of Terriestal and Aquatic Ecosystems. *Ecosystems, 6*, 301-312.

Mikha, M., Rice, C., & Milliken, G. (2005). Carbon and nitrogen mineralization as affected by drying and wetting of soil. *Soil Biology & Biochemistry, 37*, 339-347.

Mogge, B., Kaiser, E., & Munch, J. (1998). Nitrous oxide emissions and denitrification N-losses from forest soils in the Bornhöved Lake region (Northern Germany). *Soil Biology & Biochemistry, 30*, 703-710.

Mogge, B., Kaiser, E. A., & Munch, J. C. (1999). Nitrous oxide emissions and denitrification N-losses from agricultural soils in the Bornhöved Lake region: influence of organic fertilizers and land-use. *Soil Biology and Biochemistry, 31*(9), 1245–1252.

Morley, N., Baggs, E. M., Dorsch, P., & Bakken, L. (2008). Production of NO, N2O and N2 by extracted soil bacteria, regulation by NO2− and O2 concentrations. *FEMS Microbiology Ecology, 65*(1), 102-112.

Morris, J. T. (1991). Effects of Nitrogen Loading on Wetland Ecosystems with Particular Reference to Atmospheric Deposition. *Annual Reviews of Ecological Systems, 22*, 257-279.

Morse, Jennifer L., Ardón, Marcelo, & Bernhardt. Emily S. (2012). Greenhouse gas fluxes in southeastern U.S. coastal plain wetlands under contrasting land uses. *Ecological Applications 22*, 264-280.

Mosier, A., Kroeze, C., Nevison, C., Oenema, O., Seitzinger, S., & van Cleemput., O. (1998). Closing the global N2O budget: nitrous oxide emission through the agricultural nitrogen cycle. *Nutrient Cycling in Agroecosystems, 52*, 225-248.

Mummey, D. L., Smile , J. L., & Bolton Jr., H. (1994). N2O fluxes from a shrub-steppe ecosystem: sources and regulations. *Soil Biology & Biochemistry, 26*(2), 279-286.

Mummey, D. L., Smith, J. L., & Bolton Jr., H. (1997). Small-scale spatial and temporal variability of N2O flux from a shrub-steppe ecosystem. *Soil Biology and Biochemistry, 29*(11-12), 1699-1706.

Murray, P. J., Hatch, D. J., Dixon, E. R., Stevens, R. J., Laughlin, R. J., & Jarvis., S. C. (2004). Denitrification potential in a grassland subsoil: effect of carbon substrates. *Soil Biology and Biochemistry, 36*, 545-547.

Parkin, T. B., & Tiedje , J. M. (1984). Application of a soil core method to investigate the effect of oxygen concentration on denitrification. *Soil Biology and Biochemistry, 16*(1), 331–334.

Parkin, T. B. (1998). Effect of sampling frequency on estimates of cumulative nitrous oxide emissions. *Journal of Environmental Quality. 37*(4), 1390-1395

Pathak, H. (1999). Review Article: Emissions of nitrous oxide from soil. *Current Science, 77*(3), 359-369.

Patten, D., Bremner, J., & Blackmer, A. (1980). Effects of drying and air-dry storage of soils on their capacity for denitrification of nitrate. *Soil Science Society of America Journal, 44*, 67-70.

Paul, J. W., Beauchamp, E. G., & Zhang , X. (1993). Nitrous and nitric oxide emissions during nitrification and denitrification from manure-amended soil in the laboratory. *Canadian Journal of Soil Science, 73*, 539-553.

Phillips, C.L., Nickerson, N., Risk, D., and Bond, B.J. (2010). Interpreting diel hysteresis between soil respiration and temperature. *Global Change Biology. 17*, 515–527.

Pihlate, M., Syvasal, E., Esala, M., Simojoki, A., & Regina, K. (2004). Contribution of nitrification and denitrification to N2O production in peat, clay and loamy soils under different soil moisture conditions. *Nutrient Cycling in Agroecosystems. 70*, 135-141.

Pilegaard, K., Skiba, U., Ambus, P., Beier, C., Brüggemann, N., Butterbach-Bahl, K. et al. (2006). Factors controlling regional differences in forest soil emission of nitrogen oxides (NO and N_2O). *Biogeosciences, 3*, 651-661

Poth, M., & Focht , D. D. (1985). 15N Kinetic Analysis of N2O Production by Nitrosomonas europaea: An Examination of Nitrifier Denitrification. *Applied Environmental Microbiology, 49*(5), 1134-1141.

Reddy, K. R., & DeLaune, R. D. 2008. Biogeochemistry of Wetlands: Science and Applications. Flordia: Taylor Francis Group. pp 115, 257-258

Rovira, P., & Vallejo, V. R. (1997). Organic carbon and nitrogen mineralization under Mediterranean climatic conditions:the effects of incubation depth. *Soil Biology and Biochemsitry, 29*, 1509-1520.

Rudaz, A. O., Davidson, E. A., & Firestone, M. K. (1991). Sources of nitrous oxide production following wetting of dry soil. *FEMS Microbial Ecology, 85*, 117-124.

Ruser , R., Flessa, H., Russow, R., Schmidt, G., Buegger, F., & Munch, J. C. (2006). Emissions of N2O, N2, and CO2 from soil fertilized with nitrate: effect of compaction, soil moisture and rewetting. *Soil Biology and Biochemistry, 38*, 263-274.

Sahrawat, K. L. (2008). Factors affecting nitrification in soils. *Communication in Soil Science and Plant Analysis, 39*, 1436-1446.

Seitzinger, S. (1994). Linkages between organic matter mineralization and denitrification in eight riparian wetlands. *Biogeochemistry, 25*, 19-39.

Shine , K. P., Fuglestvedt, J. S., Hailemariam, K., & Stuber , N. (2005). Alternatives to the global warming potential for comparing climate impacts of emissions of greenhouse gases. *Climatic Change, 68*, 281-302.

Simek , M., & Cooper, J. E. (2002). The influence of soil pH on denitrification: progress towards the understanding of this interaction over the last 50 years. *European Journal of Soil Science., 53*, 345-354.

Skiba , U., Smith, K. A., & Fowler , D. (1993). Nitrification and denitrification as sources of nitric oxide and nitrous oxide in a sandy loam soil. *Soil Biology and Biochemistry, 25*, 1527-1536.

Skiba, U., Sheppard, L., Pitcairn, C., & Fowler, D. (1996). Nitrous oxide emission and methane oxidation in woodland soil downwind of a poultry farm. *Transactions of the 9th Nitrogen Workshop, Braunschweig*, 561-564.

Sleutel, S., Moeskops, , B., Huybrechts , W., Vandenbossche, A., Joost , S., De Bolle, S., et al. (2008). Modeling soil moisture effects on net mineralization in loamy wetland soils. *Wetlands, 28*(3), 724-734.

Smith, C.J., Patrick Jr., W.H. (1983). Nitrous oxide emission as affected by alternate anaerobic and aerobic conditions from soil suspensions enriched with ammonium sulfate. *Soil Biology and Biochemistry. 15,* 693-697.

Stolk, P. C., Hendriks, R. F. A., Jacobs, C. M. J., Moors, E. J., & Kabat, P. (2011). The effect of aggregates on N2O emission from denitrification in an agricultural peat soil. *Biogeosciences Discussions, 8,* 3253–3287,

Tan, K. H. (2000). Environmental Siol Science Second Edition, Revised and Expanded (2nd ed.). New York, New York, USA: Marcel Derkker, Inc. pp. 109.

Torsten , V., Dyckmans, J., Loftfield, N., Beese, F., & Flessa, H. (2003). Aeration effects on CO2, N2O and CH4 emission and leachate composition of a forest soil. *Journal of Plant Nutrition and Soil Science, 166,* 39-46.

Updegraff, K., Bridgham, S. D., Pastor, J., & Johnston, C. A. (1995). Environmental and substrate controls over carbon and nitrogen mineralization in northern wetlands. *Ecological Applications, 5,* 151-163.

van den Pol-van Dasselaar, A., Corré, W. J., Priemé, A., Klemedtsson, Å. K., et al. (1998). Spatial Variability of Methane, Nitrous Oxide, and Carbon Dioxide Emissions from Drained Grasslands. Soil Science Society of America. Journal. 62, 810–817

Van Gestel, M., Ladd, J., & Amato, M. (1992). Microbial biomass responses to seasonal change and imposed drying regimes at increasing depths of undisturbed topsoil profiles. *Soil Biology and Biochemistry, 24*(2), 103-111.

Vor, T., Dyckmans, J., Loftfield, N., Beese, F., & Flessa , H. (2003). Aeration effects on CO2, N2O, and CH4 emission and leachate composition of a forest soil. *Journal of Plant Nutrition and Soil Science, 166*(1), 39-45.

Wagner-Riddle, C., Rapai, J., Warland, J., & Furon, A. (2010). Nitrous oxide fluxes related to soil freeze and thaw periods identified using heat pulse probes. *Canadian Journal of Soil Science, 90*(3), 409-418.

Weier, K., Doran, J., Power, J., & Walters, D. (1993). Denitrification and the dinitrogen nitrous oxide ratio as affected by soil water, available carbon and nitrate. *Joural of Soil Science Society of America, 57*, 66-72.

Williams, D., Ineson, P., & Coward, P. (1999). Temporal variations in nitrous oxide fluxes from urine-affected grassland. *Soil Biology and Biochemistry*, *31*(5), 779-788.

Wrage, N., Velthof, G. L., van Beusichem, M. L., & Oenema. , O. (2001). Role of nitrifier denitrification in the production of nitrous oxide. *Soil Biology and Biochemistry, 33*, 1723-1732.

Yu , K. W., Wang , Z. P., Vermoesen, A., Patrick Jr, W. H., & Van Cleemput., O. (2001). Nitrous oxide and methane emissions from different soil suspensions: effect of soil redox status. *Biology and Fertility of Soils*, *34*, 25-30.

Appendix A Field Methods

Field Based N_2O Flux Calculations

Molar volume temperature and pressure correction:
=22.414*((273.16+Temp in C)/273.16)*(101.32/Pressure kPa)

The slope of the concentrations (1 ambient and 3 from chamber over a time interval of 30 minutes) against time (0-30 minutes) is divided by 60 (seconds /minute), resulting in the Slope N_2O uL/L/sec

The above value is then multiplied by the total volume of the chamber, divided by the molar volume, and all of this is multiple by 1000 (to convert to nmol,):
((Slope of N2O uL/L/sec)*(total volume L)/(Molar Volume)) * 1000
= nmol/m2/sec

Appendix B Lab Methods

Experiment 1: Moisture Alterations

Water was added to cores being "wet up" at the same rate that it was lost from cores that were "drying down". The amount of water evaporated from the cores held in the terrarium was considered. The calculations were as follows:

For the "dry down" cores (cores losing water):

$$W_{LD} \leftarrow Ms_{\ current} - Ms_{\ pervious} \quad (1)$$

W_{LD} represents water loss while soil dries down (g)

$M_{s\ current}$ represents the mass of the soil for the current day (g)

$M_{s\ pervious}$ represents the mass of the soil recorded the previous day (g)

For the "wet up" cores (cores having DI water added):

$$W_{LW} \leftarrow [M_{s\ current}\ day - M_{s\ previous}\ day\ post\ addition\ DI\ water] \quad (2)$$

W_{LW} represents water loss when soils is wetting up (g)

$M_{s\ current}$ represents the mass of the soil for the current day (g)

$M_{s\ pervious}$ represents the mass of the soil recorded the previous day (g)

These values were averaged for all the cores in each of soil type in each soil moisture treatment.

Therefore:

$$W_{LW\ total} \leftarrow Avg(W_{LD}) + Avg(W_{LW}) \quad (3)$$

Where Avg($W_{L\,D}$) represents the water loss while soil dries down (g), and

Avg(W_{LW}) represents the water loss when soils is wetting up (g).

This is the amount of water that was added to cores being "wet up".

Experiment 2: Moisture and Inorganic N Modifications

Water Holding Capacity of Batched Soils

Soil subsamples were dried at 105ºC for 16 hours. The soil moisture percentages (*% SM*) of the batches were calculated by:

$$\%SM \leftarrow \left[\frac{Mws - Md}{Md}\right] \quad (4)$$

Where M_{WS} represents the wet mass of the soil subsample (g), and
M_D represents the dry mass of the soil subsample (g)

Equation 4 was the current soil water content of the batched soils. Subsamples of the batched soils were collected and lightly packed into a small cap of a known volume. The caps were weighed before and after the soils were added to determine the mass of the soil. The soils were then saturated and reweighed and dried in an oven at 105ºC for 16 hours, and reweighed. This allowed for soil properties of the batched soils (Link to Appendix) and water holding capacity of the batched soils (*WHC*) to be determined.

The *WHC* for soil from the upland and lowland was calculated using the following method:

$$WHC \leftarrow \left[\frac{Mwater}{Mss}\right] * 100\% \quad (5)$$

Where *Mwater* is the mass of the water contained in the saturated soil, and
Mss is the mass of the saturated soils.

Simultaneous Changes to Moisture and Inorganic N

The % *WHC* of upland was calculated to be approximately 60% and the % *WHC* of the lowland was calculated to be approximately 43%. Knowing the *WHC* of the soils, the % saturations were adjusted to account for this property. Thus, 50%, 60%, 70% and 80 % soil moisture levels selected for this experiment referred to these percentages as a percentage of the *WHC* for each of the soil types, with the *WHC* representing the maximum (100%) soil moisture. For the upland, this means that 50% saturation of a soil with 60% WHC results in a true % saturation of 30%, and a 50 % saturation of a soil with a % WHC of 43% results in a % soil moisture value of 21.5% need to be 50% saturated. Knowing the current % soil moisture of the batch (for each respective landscape), and the amount of water required to reach the desired % soil moisture level, as well as knowing the amount inorganic N/glucose per g of solution, the inorganic N/glucose were added along with DI water to manipulate the soil moisture. The amount of required inorganic N/glucose per gram of dry weight was multiplied by dry weight of the soil sample.

Table 8 Inorganic N Levels from Experiment 1 and Inorganic N Addition Amounts for Experiment 2

NO_3^- levels from experiment 1	**µg/g dwt**	**NO_3^- levels chosen for experiment 3**	**µg/g**
Minimum	0	Low	20 (* grams in soil)
Maximum	396	Intermediate	100 (* grams in soil)
Average	42	High	500 (* grams in soil)
NH_4^+ levels from experiment 1	**µg/g dwt**	**NH_4^+ levels chosen for experiment 3**	**µg/g**
Minimum	0	Low	20 (x grams of soil)
Maximum	450	Intermediate	100 (x grams of soil)
Average	99	High	500 (x grams of soil)

Experiment 1 and Experiment 2

Flux = ([ΔConc (uL/L)* V (L) / MV (uL/umol)]*1000)/dry weight of sample (g)/(180 minutes*60 seconds)

Flux = umol/g/sec

Final Flux: umol/g/sec *1000/10800

(*1000 to convert umol to nmol)

(/10800 to convert (180) minutes to seconds)

ΔConc=Difference in concentration (T180-T0)

Wdry=Dry weight of soil sample (g)

Corrected volume for headspace (Vcorr)

Vcorr=(Vj –Vc)

Where Vj is the volume of the jar in L, and

Vc is the volume of the core in L

Temperature and Pressure corrected Molar Volume (MV)

22.414 (uL/umol)*((273.16 ˚K +Temp in C)/273.16 ˚K)*(101.32kPa/101.32kPa +Pressure in lab kPa)

An arithmetic average of the three cores is the “average flux”.