EFFECT OF NITROGEN FERTILIZER ON NITROUS OXIDE EMISSIONS FROM THE SOIL FOR TWO POTENTIAL ENERGY CROPS AND THE RELATIVE GREENHOUSE GAS EMISSIONS

by

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Submitted in partial fulfilment of the requirements
for the degree of Master of Science

at

Dalhousie University
Halifax, Nova Scotia

in co-operation with

Nova Scotia Agricultural College
Truro, Nova Scotia

August 2010

DALHOUSIE UNIVERSITY

NOVA SCOTIA AGRICULTURAL COLLEGE

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Dated: August 10, 2010

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DALHOUSIE UNIVERSITY

AND

NOVA SCOTIA AGRICULTURAL COLLEGE

DATE: August 10th, 2010

AUTHOR: Adam N. Wile

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DEPARTMENT OR SCHOOL: Department of Environmental Science

DEGREE: M.Sc. CONVOCATION: October YEAR: 2010

Signature of Author

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Acknowledgements

Many people have been involved in helping me prepare this thesis from data collection to writing. David Burton has been an inspiration both academically and personally and I have to thank him for his guidance, patience and good humor for the past two years and more. My committee members Drs. Gordon Price and Derek Lynch have been very helpful in providing suggestions and have helped me to broaden my thesis while keeping me focused on the objectives. Michael Main was also a big part of getting this research off the ground and without his dedication I would not have had a field on which to collect data.

I also would like to thank the lab and field crews, Drucie Janes and Laura Jollymore, for their role in my data collection and analysis as well as the summer students who patiently waited for me to get my field set up for sampling in hot sun, rain and snow. I would also like to acknowledge the help of Matt Crouse during harvest and his work in collecting and weighing yield samples. Without these people my work would have been overwhelming.

I would like to acknowledge my financial support through the Graduate Research Training Initiative (GRTI) scholarship for without this I would not have been able to afford the opportunity to complete this project.

Finally, I need to thank my family, especially Adele, for sticking behind me and providing guidance and support when I thought I didn’t need any. Knowing I have this support gives me the chance to fearlessly pursue my dreams and, for this, I am grateful.

List of Abbreviations Used

AI – Ammonium Intensity

Ar – Argon

BNF – Biological Nitrogen Fixation

CH_4 – Methane

Cl – Chlorine

cm – centimeter

CO_2 – Carbon Dioxide

CO_2e – Carbon Dioxide Equivalent

ECD – Electron Capture Detector

FID – Flame Ionization Detector

g – Gram

GHG – Greenhouse Gas

GJ – Giga Joule

GWC – Gravimetric Water Content

GWP – Global Warming Potential

ha – Hectare

IPCC – Intergovernmental Panel on Climate Change

K – Potassium

K_2SO_4 – Potassium Sulfate

L – Liter

LCA – Life Cycle Assessment

m – meter

MJ – Mega Joule

mL – milliliter

MNI – Mineral Nitrogen Intensity

N – Nitrogen

N_2 – Nitrogen Gas

NH_4^+ – Ammonium

NI – Nitrate Intensity

NO_3^- – Nitrate

NO_2– Nitrogen Dioxide
N_2O – Nitrous Oxide
O_2 – Oxygen
PVC – Polyvinyl Chloride
Si – Silicon
TCD – Thermal conductivity detector
TEA – Terminal Electron Acceptor
μg – Microgram
yr – Year

Abstract

The benefits from energy crops are debated. This two-year study was designed to investigate nitrous oxide (N_2O) emissions, yield and ash content from fertilized bioenergy crops switchgrass and reed canary grass with and without inter-seeded red clover. Overall, N_2O emissions were less than 1kg N_2O-N ha^{-1} in the first year and around 100g N_2O-N ha^{-1} in the second year with a N fertilizer effect in the first year. Plots inter-seeded with red clover received half the N fertilizer of pure grass stands but showed no difference in N_2O emissions compared to the pure stands and also had higher ash content. Cumulative soil mineral N responded to N fertilizer addition but no effect of crop type was evident in 2008 and 2009. Yields for both crops were unresponsive to N fertilizer addition while pure switchgrass yielded higher than inter-seeded switchgrass in 2008 and switchgrass had lower ash content.

CHAPTER 1: INTRODUCTION

Energy is a necessity of modern life and has traditionally been supplied exclusively by fossil fuel products such as coal and oil. A growing concern within the scientific community about climate change and a shortage of fossil fuel resources by society has spurred the initiative to explore alternative sources of energy. There are many alternative energy sources and our energy stream in the future will likely be a more diverse one. This project focuses on one of those alternative sources, perennial grass crops. This biofuel can be pelletized for heat or electricity generation. The two objectives of the project were to assess potential N_2O emissions from the soil from fertilizer application and crop type (Chapter 2) and potential differences in energy yields, global warming potential (GWP) and greenhouse gas offsets (Chapter 3).

Quantifying the nitrous oxide (N_2O) emissions associated with the production of bioenergy crops is an important step is assessing their overall benefits as alternative energy sources and helps in assessing choices of crop type, production system, conversion and combustion processes to minimize the environmental footprint of this energy source. Understanding the environmental attributes of biomass crops is important to maximize environmental gains and avoid making large investments in inefficient products, both from an environmental and a heat/electricity generating point of view. Crop type is also an important consideration when developing a bioenergy industry because ethical arguments, economic feasibility and environmental benefits are different for every crop.

Bioenergy crops have endured controversy, being praised in times of high oil prices while being shunned in times of food shortages. The fact remains, however, that bioenergy crops in the form of a solid feedstock have been the source of energy for work and heat since the beginning of time. It has only been recently, with the extensive use of fossil fuels and the recognition of their rising costs and environmental damage that governments have taken steps to re-instate biofuels into the energy mix. Biofuels come in different forms but the predominant ones are liquid, such as ethanol (biofuel) produced from corn or sugar beets, or a solid, such as wood (forest biomass) or grass biomass (bioenergy crops or non-forest biomass), used for heating or electricity generation. Both forms have their merits as well as their demerits and it is beneficial to discuss the history of the development of solid biomass feedstocks and how we came to favor the crops we do.

The research credited with having catalyzed future developments in bioenergy crop development was done by the 'Bioenergy Feedstock Development Program' at the Oakridge National Laboratory in Tennessee (McLaughlin and Kszos, 2005; Write and Turhollow 2010). In 1978 crop evaluation trials were run to determine those crops that contained the desirable characteristics of a solid feedstock for heat and electricity generation. Early efforts focused on short rotation wood (McLaughlin and Kszos, 2005). Studies in the 1980's identified herbaceous grass crops as good candidates based on their yields and growth habits (Write, 1994). The Oakridge National Laboratory screened more than 30 grass crops and found switchgrass (*Panicum virgatum)* to provide the highest and most consistent yields with the least amount of inputs and greatest compatibility with the objectives of a good quality energy crop. Studies on the chemical composition, yields and suitability of switchgrass and other crops followed in the 1990s and into the 2000's at institutions across the U.S. (e.g.: Adler et al. 2006; Jenkins et al. 1998; Monti et al. 2008; Sanderson et al. 1996).

Switchgrass, a native prairie grass, has quickly become the favorite crop for many researchers in the mid-western states as the grass grows well there. As interest grew from industry and government, research began to expand to other countries and continued in the fields of agronomy, energy and greenhouse gas reduction. The study of greenhouse gas emissions and the ability of bioenergy crops to mitigate carbon emissions increased in the 2000's as life cycle assessments (LCA) became the predominant form of evaluating environmental benefits of a product. Many LCA studies were completed, however these studies focused on broad areas such as energy conversion and transportation of the product (E.G.: Adler et al., 2007; Benetto et al., 2004; Hellebrand et al., 2003; Kaltschmitt et al., 1996; Kim and Dale, 2005). Only the Hellebrand study focused on greenhouse gas emissions from growing a crop but they did not include switchgrass in their study. Furthermore, in the Eastern Canadian climate cool season grasses are often of interest as they may be as competitive, with respect to yields, as warm season grasses. There have been no comparisons of the direct N_2O emissions from producing a warm and cool season grass together at the same time under Easter Canadian growing conditions.

‘Cave in Rock’ Switchgrass and ‘Venture’ Reed Canary Grass (*Phallaris arundinacea)* can be grown on marginal lands thereby not competing with food production, they are high yielding and, other than drying and pelleting, require little in the way of processing once they are harvested (Varvel et al., 2008). These attributes make them ethically and economically attractive and, because they are perennials, they do not require annual seeding or soil tillage, allowing for permanent crop cover making the impacts of fertilization the primary environmental concern (Sampson et al., 2000). Both crops produce a high quality pellet for heating or electricity generating sources and both have good conversion efficiencies however there are issues of fouling and slagging during combustion (McLaughlin et al., 1996). Comparing N_2O emissions, soil mineral N and yield between these two crops is an important step in determining which one of the two crops has the smaller ecological footprint as a biomass crop.

At a time when Nova Scotia is looking to alternative sources of energy to increase the diversity of its energy mix this type of research is important and, until now, has not been completed. The objectives of this project were to determine whether the magnitude of N_2O emissions is larger from the production of switchgrass or reed canary grass and whether these emissions are a function of inorganic nitrogen fertilizer application. To determine this the relative magnitude of biomass yield (and heat equivalent) in response to inorganic nitrogen fertilizer application in relation to GHG emissions was measured. A second objective was to determine if the use of inter-seeded legumes as a nitrogen source would result in lower N_2O emissions with equivalent or better biomass yield and/or quality.

CHAPTER 2: THE EFFECT OF INORGANIC NITROGEN FERTILIZER APPLIED TO SWITCHGRASS, REED CANARY GRASS AND INTER-SEEDED RED CLOVER ON N_2O EMISSIONS.

2.1 Introduction

The anthropogenic production of CO_2, CH_4 and N_2O are believed to be the number one drivers of climate change (Hansen and Sato, 2004; IPCC, 2001; Ledley et al., 1999). Agriculture accounts for ~70% of all anthropogenic N_2O emissions, much of which comes from nitrogen fertilizer. Recently agriculture has been identified as a sector able to be a net carbon sink by enhanced carbon sequestration associated with land management (reduced tillage, permanent cover) and the production of energy crops to offset CO_2 emissions from fossil fuel use (Cole et al., 1997; Crutzen et al., 2007; McCarl and Schneider, 2003). These factors make agriculture a dynamic player in both the reduction of global warming and the production of alternative, sustainable energy sources. The production of energy crops also result in GHG emissions and the production of N_2O is of particular concern as it is a very potent GHG with a GWP 296 times that of CO_2 (Sylvia et al., 2005). Through the biological processes of nitrification and denitrification, N_2O is produced in soil and emitted to the atmosphere. Studies have shown highest fluxes of N_2O to occur immediately after N fertilizer application or after large rainfall events (Burton et al., 2008; Davidson, 1992). On cropped soils in Atlantic Canada, fertilizer is often applied in May and June which tend to have large rainfall events (Environment Canada, 2009) leading to high N_2O emissions (Burton et al., 2008; Zebarth et al., 2008).

The influence of nitrogen fertilization on the biological process of N_2O production and emission from agricultural soils, forest soils and ocean sediment is well-studied (Silva et al., 2008; Verchot at al., 2008). Despite this body of work, few studies have examined energy crops in general, and even fewer on switchgrass and reed canary grass specifically. Those studies that have attempted to quantify GHG emissions from energy crops have been conducted in Europe under climate and farm management conditions different than Atlantic Canada (e.g.: Kavdir et al., 2008). The studies examining the agronomics of switchgrass and other warm season perennial grass production in Ontario and Quebec have not measured GHG emissions or the impact of fertilization on GHG emissions. This is an important unanswered question and a necessary input into a Life Cycle Assessment (LCA) of the carbon footprint of these crops as biofuel sources.

Nitrification and denitrification act together to produce a cumulative flux of N_2O so, while their individual effects vary under specific field conditions, the combined contributions from both nitrification and denitrification are important to understanding the GHG balances of bioenergy crops. Factors affecting nitrification and denitrification include the soil oxygen (O_2) content (as influenced by soil water content), carbon quality and content, presence of NH_4^+ and NO_3^-, the number of nitrifiers and denitrifiers in the soil, soil temperature, and pH (Sylvia et al., 2005).

Ultimately, O_2 content of the soil dictates whether N_2O is produced. Nitrification is predominantly an aerobic process but as O_2 decreases more N_2O is produced as nitrifiers convert NO_2^- to NO_3^- (Poth and Focht, 1985.). Denitrification is the conversion of NO_3^- to N_2 gas and is done by facultative anaerobes using N as a terminal electron acceptor (TEA) instead of O_2. An intermediate of this process is N_2O and, because it is more energetically favorable for microorganisms to use NO_3^- as a TEA than N_2O, there is an accumulation of N_2O in the soil environment when NO_3^- is present (Gillam et al., 2008). The oxygen content is primarily a function of soil water content. Reduced oxygen contents occur as a greater percentage of the pores are filled with water impeding the diffusion of oxygen. Denitrification is commonly observed to occur in soils that have greater than 60% water-filled pore space (Linn and Doran, 1984).

While the presence of nitrifiers and denitrifiers in the soil is critical to the process of nitrification and denitrification, seldom do their numbers limit these processes in agricultural soils. Nitrifying bacteria are less common in the soil than denitrifying bacteria, however there are usually sufficient levels of nitrifying and denitrifying bacteria in the soil so as not to pose a constraint to the processes (Sylvia et al., 2005). More significant limiting factors in the processes are the presence of organic carbon, NH_4^+ and NO_3^- in the soil (Bouwman, 1996). Organic carbon and NH_4^+ are the substrates used by the denitrifying and nitrifying bacteria respectively, so without these there is nothing to drive the reaction. Nitrate is a terminal electron acceptor in the denitrification process. Carbon is often an important constraint to biological activity in soil systems and has been shown to limit denitrification (Miller et al, 2008). Agricultural soils usually have large pools of both NH_4^+ and NO_3^-, especially those fertilized with manure and synthetic fertilizers, so potential rates of nitrification and denitrification are high, particularly after fertilization (Dandie et al., 2008).

Environmental factors such as temperature, water content, carbon content, and pH vary over micro-sites and are the cause for the incredibly high spatial and temporal variability of N_2O flux from soils (Burton and Beauchamp, 1985). Generally microbial activity increases as temperature increases, increasing the rate of nitrification and denitrification reactions resulting in higher N_2O production. Studies looking at the effect of freezing and thawing on grassland soils found that during freezing there was an accumulation of NH_4^+ and NO_3^- with a corresponding flush of N_2O during the thawing period (Burton and Beauchamp, 1994; Muller et al., 2002). Water content also impacts N_2O emissions through its influence on soil O_2 content as well as facilitating the movement of nutrients in soil (Pathak, 1999). Organic carbon compounds are the substrates (electron donors) driving denitrification and as a result organic carbon availability is an important rate limiting factor (Miller et al., 2008). Soil carbon content is influenced by additions of manures, barn waste, leaf litter, post harvest residual waste left over after harvest and root exudates. Microbially available carbon content of the soil varies throughout the growing season as plant roots grow and decay. Soil pH also plays a role in controlling the activity of nitrifiers and denitrifiers with an optimal pH of 6.0.

Since high variability exists in N_2O flux because of the unpredictable and variable environmental factors it is important to use methods of data collection that are the most tested and established. Two main methods of collecting plot scale N_2O emissions exist. Chamber methods are best suited to quantifying treatment effects on small plots as they allow precise placement and are cheap and easy to sample so numerous sample points can be examined which addresses spatial variability (Patty et al., 2007; Rochette and Eriksen-

Hamel, 2007). Chambers are very useful for comparing N_2O flux between treatments of fertilizer rates or crop type. Another common method is to estimate fluxes based on hypothesized values for the environmental conditions such as in LCA studies. LCAs contain calculations for GHG emissions that are imprecise because of the many variables involved in the production of GHGs and lack of input data (Adler et al., 2007; Del Grosso et al., 2005; Kim et al., 2005; Patty et al., 2007). While estimation is practical on a global scale from a cost and time perspective they leave out important details that a plot scale study will pick up.

Studies measuring N_2O flux response to nitrogen fertilizer generally focus on crops with relatively high rates of N-fertilizer application such as corn and potatoes which, especially if fertilized above required rates for maximum yields, can result in disproportionately high N_2O emissions (Grant et al., 2006; Zebarth et al., 2008). These crops are also managed differently than switchgrass or reed canary grass in that they are generally part of an intensive row crop management system (Ruser et al., 2001). The large fibrous root systems of grasses like switch grass and reed canary grass are generally good at N uptake and seldom do large amounts of inorganic N accumulate in soils growing these crops (Schimel, 1986). Del Grosso et al. (2005) highlight that regional climate conditions, soil types, crop type and fertilizer rates result in $\pm$50% margin of error for N_2O estimates. There is also discrepancy in the literature about whether N_2O emissions respond linearly to N application or if there is only a response once N exceeds crop demands (Snyder et al., 2009). This underscores the need to measure N_2O emissions from these crops to gain accurate and insightful data and to date there is a lack of N_2O emissions data from perennial grass crops and from switchgrass and reed canary grass specifically.

It is also largely unknown whether the inclusion of inter-cropped legumes can be an effective N source to grasses and whether this might result in lower N_2O emissions. Plots inter-seeded with clover will result in biological nitrogen fixation (BNF). Mycorrhizal hyphea may link the clover roots to grass roots and transfer fixed N decreasing the amount of applied N required to obtain similar yields as pure grass stands and potentially reducing N_2O emissions (He et al., 2003). IPCC guidelines suggest that 1.25% of applied N is returned to the atmosphere as N_2O but this may be different for biological N_2 fixation which occurs over the entire growing season and in synchronicity with growth (Carter and Ambus, 2006). The study by Carter and Ambus determined that clover-grass plots resulted in higher N_2O emissions than unfertilized grass plots but there was no comparison with fertilized grass plots.

Also of interest in this study is the correlation between nitrate intensity (NI), ammonium (NH_4^+) intensity (AI) and mineral N intensity (MNI) with N_2O emissions. NI, AI and MNI are measurements of nitrate, ammonium and mineral N availability for nitrification and denitrification measured as a summation of nitrate, ammonium and mineral N concentration in the soil over all sampling dates (Burton et al., 2008; Zebarth et al., 2008). Nitrate intensity integrates the concentrations of nitrate available to plants in the soil over space and time. If there is a correlation between NI in the soil and N_2O emissions it may be a way to estimate N_2O production based on soil samples which would be a cheaper and easier alternative to gas sampling on a plot level and can also help determine optimal rates of nitrogen application. This type of analysis is relatively new and is used as a measure of nitrate availability by Burton et al. (2008) and Zebarth et al. (2008).

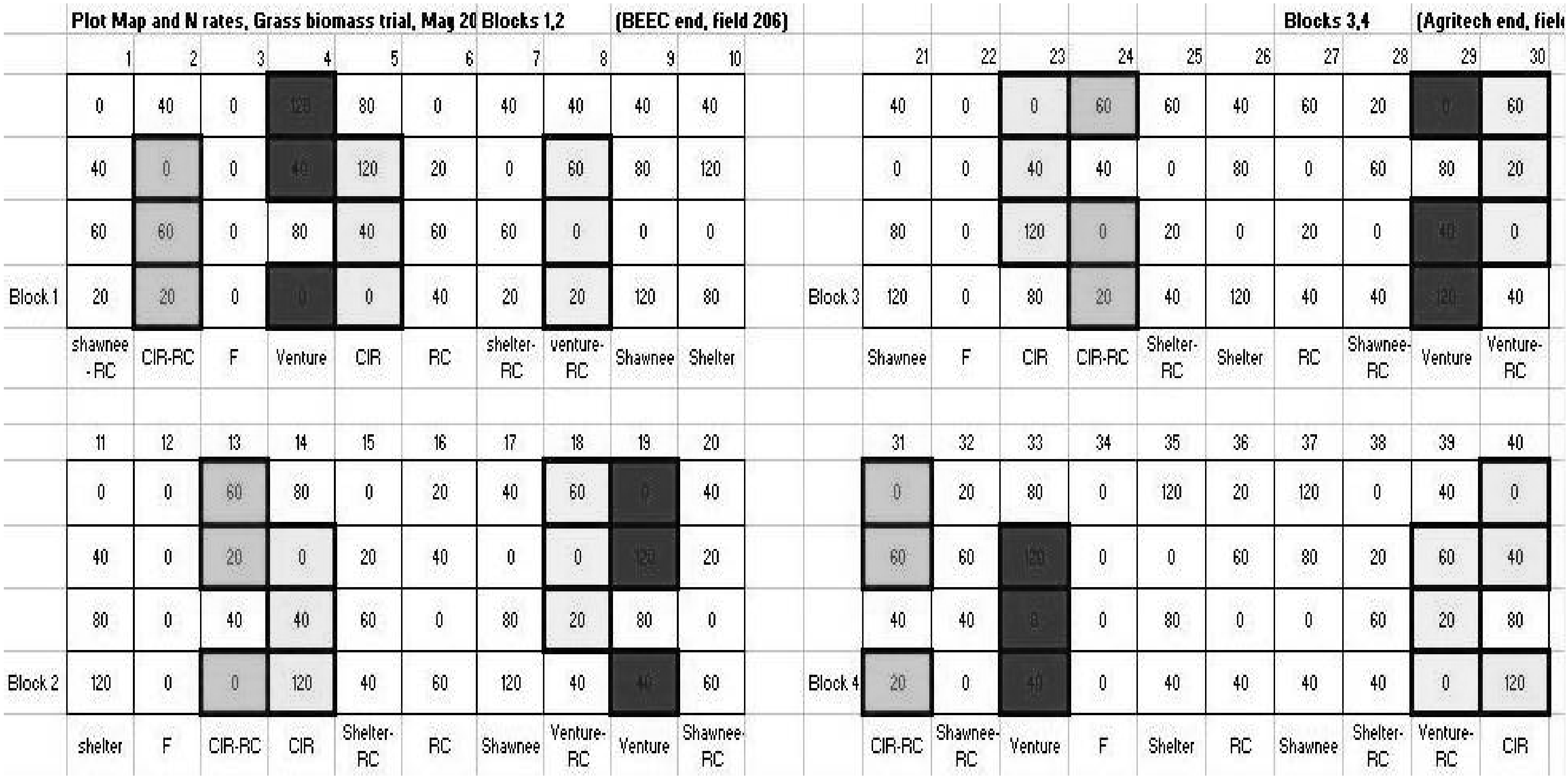
The perennial nature of switchgrass and reed canary grass coupled with the large root systems makes these plants good candidates for large amounts of carbon sequestration. Quantifying carbon sequestration gives us further insight into the environmental benefits of perennial grasses and allows us to further compare the environmental qualities between the switchgrass and reed canary grass. However, due to the two-year duration of this project and the large variability in soil carbon content, it is unlikely that detectable differences in carbon storage will be apparent over the course of this study and as a result measurements of soil carbon storage will not be undertaken.

The objectives of this study are to determine if N_2O emissions are a function of inorganic nitrogen fertilizer application for switchgrass and Reed Canary Grass and if the species of perennial biomass grass crop grown influences N_20 emissions from the soil. Determine if inter-seeded legumes result in lower N_2O emissions with equivalent or better biomass quality. The final objective of this study is to determine the correlation between nitrate soil intensity and N_2O emissions in a low input perennial grass system.

2.2 Materials and Methods

2.21 Field Design and Fertilizer Application

The field location was at the Bio-Environmental Engineering Center located in central Nova Scotia at approximately 45°23'10" N and 63°14'21"W. The site was established in 2006 on land that was previously seeded to alfalfa. The experimental design was a randomized two factor split plot design where fertilizer rate consisted of three levels and was nested within crop type which consisted of four levels (Fig. 1). Whole plots (crop type) were seeded with either pure grass seed or a clover/grass mix in 2006. The whole plots were split into three sub-plots (N fertilizer) 3m wide by 4m long in which different N fertilizer rates were applied. In this study plots contained pure switchgrass and reed canary grass stands received ammonium nitrate fertilizer rates of 0, 40 and 120kg-N ha^{-1} and red clover/switchgrass and red clover/reed canary grass mixes received 0, 20 and 60kg-N ha^{-1}. Fertilizer was applied once in the spring of each growing season. All plots with clover and reed canary grass were fertilized near the beginning of May while the pure switchgrass stands were fertilized near the beginning of June due to the later emergence. Fertilizer was applied by drop application using a calibrated push applicator. In the spring of 2008 the plots received the herbicide roundup "weathermax" in a wicked on format to control for weeds so as to not kill the target species. No herbicide was applied in 2009. Table 1 provides details of all plot management from 2006-2009.



Plot Map and N rates, Grass biomass trial, May 20 Blocks 1,2 **(BEEC end, field 206)**

	1	2	3	4	5	6	7	8	9	10
	0	40	0	120	80	0	40	40	40	40
	40	0	0	40	120	20	0	60	80	120
	60	60	0	80	40	60	60	0	0	0
Block 1	20	20	0	0	0	40	20	20	120	80
	shawnee -RC	CIR-RC	F	Venture	CIR	RC	shelter-RC	venture-RC	Shawnee	Shelter

Blocks 3,4 **(Agritech end, fiel**

	21	22	23	24	25	26	27	28	29	30
	40	0	0	60	60	40	60	20	0	60
	0	0	40	40	0	80	0	60	80	20
	80	0	120	0	20	0	20	0	40	0
Block 3	120	0	80	20	40	120	40	40	120	40
	Shawnee	F	CIR	CIR-RC	Shelter-RC	Shelter	RC	Shawnee-RC	Venture	Venture-RC

	11	12	13	14	15	16	17	18	19	20
	0	0	60	80	0	20	40	60	0	40
	40	0	20	0	20	40	0	0	120	20
	80	0	40	40	60	0	80	20	80	0
Block 2	120	0	0	120	40	60	120	40	40	60
	shelter	F	CIR-RC	CIR	Shelter-RC	RC	Shawnee	Venture-RC	Venture	Shawnee-RC

	31	32	33	34	35	36	37	38	39	40
	0	20	80	0	120	20	120	0	40	0
	60	60	120	0	0	60	80	20	60	40
	40	40	0	0	80	0	0	60	20	80
Block 4	20	0	40	0	40	40	40	40	0	120
	CIR-RC	Shawnee-RC	Venture	F	Shelter	RC	Shawnee	Shelter-RC	Venture-RC	CIR

Figure 1: Experimental layout for both years 2008 and 2009 with the plots selected for this experiment highlighted. CIR-RC = Switchgrass/Red Clover. Venture = Reed Canary Grass. CIR = Switchgrass. Venture-RC = Reed Canary Grass/Red Clover

Table 1: Schedule of all plot management from 2006 until 2009.

Date	Field Management
May 2006	Plow down of 40-50% alfalfa stand
May 2006	Plot Preparation
May 31, 2006	Seeding
July 2, 2006	Wicked on Roundup “weathermax” Herbicide 18% mix
May 25, 2007	Fertilized Reed Canary Grass and inter-seeded plots
June 15, 2007	Fertilized pure Switchgrass plots
Sept 14, 2007	Harvest of Reed Canary Grass and inter-seeded plots
October 22, 2007	Harvested Switchgrass
May 7, 2008	Wicked on 0.7% solution of roundup on switchgrass plots
May 8, 2008	Fertilized Reed Canary Grass and inter-seeded plots
June 1, 2008	Fertilized Switchgrass plots
October 28, 2008	Reed Canary Grass and inter-seeded plots harvested
November 7, 2008	Switchgrass plots harvested
May 5, 2009	Fertilized Reed Canary Grass and inter-seeded plots
June 4, 2009	Fertilized Switchgrass Plots
September 9, 2009	Reed Canary Grass and inter-seeded plots harvested
November 29, 2009	Switchgrass harvested

2.22 Greenhouse Gas Flux Measurements

Non-steady state vented chamber (referred hereafter as chambers) were used to measure GHG emissions (Fig. 2). The system has two parts, a permanently placed 10cm tall, 20cm diameter piece of PVC tapered at one end (collar). The chamber consists of a 15cm tall piece of the same diameter PVC with a top (1cm thick PVC sheet) glued to the top of the chamber and fitted with a vent hole and a sampling port fitted with a suba seal (Fisher Scientific Cat. # FB57876). A closed-cell foam gasket was glued to the bottom of the chamber to form a tight seal with the collar and at the time of sampling a brick was placed on the chamber to help form a tight seal. To keep the chamber from heating up during the sampling period and altering the GHG flux foil covered bubble wrap (water heater blanket) was glued to the outside of the chamber. One collar was inserted into the soil in each plot for the duration of the experiment and emissions were measured on a weekly basis from May to August, once every two weeks from August to September and once in October or after harvest. Additional sampling took place approximately one and three days after fertilization. As vegetation grew inside the collar it was clipped at collar height so an unbroken seal between the collar and the chamber could be maintained. On each sampling date the chamber was placed on the collar for a 30 minute period. During the 30 minute deployment four 20mL gas samples were collected from each chamber at 0, 10, 20 and 30 minutes to assess the rate of gas accumulation in the chamber. Gas samples were stored at room temperature in 12mL exetainers and analyzed using a Varian 3800 gas chromatograph (GC) to determine the relative GHG concentrations of CO_2, N_2O and CH_4 between each treatment. Cumulative N_2O emissions for each plot were calculated by linear interpolation between each sampling date. Also measured were air temperature and relative humidity for use in correcting gas volume in samples and the chamber headspace.

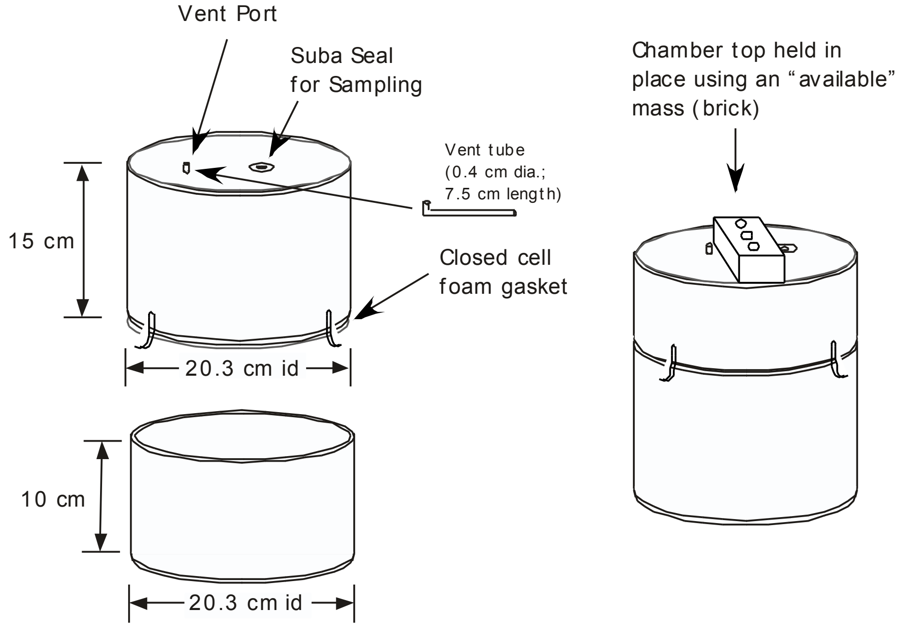


Figure 2. Closed non-steady state vented chamber

2.23 Soil sampling and Physical Characteristics

Three cores 2.5cm wide to a depth of 15cm were collected from each plot on the same day as gas sampling. Cores were composited placed in plastic bag and stored, frozen, until analysis. At the same time as flux measurements were being taken in each plot, soil temperature was measured to a 10cm depth using an Oakton thermometer (Oakton, Vernon Hills, IL) and volumetric moisture content was measured in the top 12cm of soil using a Hydrosense Soil Water probe (Campbell Scientific, Logan, Utah).

2.24 Gas Analysis

Gas samples were analyzed using a Varian 3800 gas chromatograph (Varian, Walnut Creek, California). Samples (2.5mL) were injected with a COMBI PAL auto sampler (Varian, Walnut Creek, California). The autosampler removes a 2.5mL volume from the sample tube and injects this into a sample valve that delivers 0.1mL to an electron capture detector (ECD), and 0.1mL to a flame ionization detector (FID) and thermal conductivity detector (TCD) in series which were used to detect N_2O, CH_4 and CO_2 respectively. The ECD was operated at 300 ^{o}C, 90%Ar, 10%CH_4 carrier gas at 10mL min^{-1}, Haysep N 80/100 pre-column (0.32cm diameter x 50cm length) and Haysep D 80/100 mesh analytical columns (0.32cm diameter x 200cm length) in a column oven operated at 70^{o}C. Pre-column was used in combination with a valve to remove water from the sample. The sample contained in the second sample loop (FID/TCD) passed through a Haysep N 80/100 mesh (0.32cm diameter x 50cm length) pre-column followed by a Porapak QS 80/100 mesh (0.32cm diameter x 200cm length) with a pre-purified helium carrier gas at 20psi maintained at 70 ^{o}C. The TCD was operated at 130^{o}C and the FID was operated at 250^{o}C. Operational conditions and data handling was performed with Varian Star^{TM} software. In each analytical run of 150 samples a five replicates of three concentrations of standard gas mixtures were run between each tray of 50 samples for quality assurance/quality control purposes. Gas samples were converted from uL L^{-1} to g ha^{-1} d^{-1} using equation 1.

Nitrous Oxide Flux

$$\frac{1uL\,N_2O}{L\bullet hr}x\frac{323.7cm^2\bullet(15+h)cm}{0.0324m^2}x\frac{1L}{1000cm^3}=9.99\bullet(15+h)cm\frac{uLN_2O}{m^2\bullet hr}$$

$$9.99\bullet h(cm)\frac{uLN_2O}{m^2\bullet hr}x\frac{1umoleN_2O}{0.0821\bullet T(K)uLN_2O}x\frac{44ugN_2O}{1umoleN_2O}=5{,}353\frac{(15+h)cm}{T(K)}\frac{ugN_2O}{m^2\bullet h}$$

$$5{,}353\frac{(15+h)cm}{T(K)}\frac{ugN_2O}{m^2\bullet h}x\frac{10^3\,ngN_2O}{1ugN_2O}x\frac{1h}{60\min}x\frac{1\min}{60\sec}=1487\frac{(15+h)cm}{T(K)}\frac{ngN_2O}{m^2\bullet\sec}$$

$$5{,}353\frac{(15+h)cm}{T(K)}\frac{ugN_2O}{m^2\bullet h}x\frac{1gN_2O}{10^6\,ugN_2O}x\frac{28gN}{44gN_2O}x\frac{10^4\,m^2}{1ha}x\frac{24h}{1d}=817.6\frac{(15+h)cm}{T(K)}\frac{gN_2O-N}{ha\bullet d}$$

Carbon Dioxide Flux

$$\frac{1uL\,CO_2}{L\bullet hr}x\frac{323.7(cm^2)\bullet(15+h)cm}{0.0324m^2}x\frac{1L}{1000cm^3}=9.99\bullet(15+h)cm\frac{uLCO_2}{m^2\bullet hr}$$

$$9.99\bullet(15+h)cm\frac{uLCO_2}{m^2\bullet hr}x\frac{1umoleCO_2}{0.0821\bullet T(K)uLCO_2}x\frac{44ugCO_2}{1umoleCO_2}=5{,}353\frac{(15+h)cm}{T(K)}\frac{ugCO_2}{m^2\bullet h}$$

$$5{,}353\frac{(15+h)cm}{T(K)}\frac{ugCO_2}{m^2\bullet h}x\frac{1h}{60\min}x\frac{1\min}{60\sec}=1.487\frac{(15+h)cm}{T(K)}\frac{ugCO_2}{m^2\bullet\sec}$$

$$5{,}353\frac{(15+h)cm}{T(K)}\frac{ugCO_2}{m^2\bullet h}x\frac{1kgCO_2}{10^9\,ugCO_2}x\frac{12kgC}{44kgCO_2}x\frac{10^4\,m^2}{1ha}x\frac{24h}{1d}=0.3504\frac{(15+h)cm}{T(K)}\frac{kgCO_2-C}{ha\bullet d}$$

Methane Flux

$$\frac{1uL\,CH_4}{L\bullet hr}x\frac{323.7(cm^2)\bullet(15+h)cm}{0.0324m^2}x\frac{1L}{1000cm^3}=9.99\bullet(15+h)cm\frac{uLCH_4}{m^2\bullet hr}$$

$$9.99\bullet(15+h)cm\frac{uLCH_4}{m^2\bullet hr}x\frac{1umoleCH_4}{0.0821\bullet T(K)uLCH_4}x\frac{16ugCH_4}{1umoleCH_4}=1{,}947\frac{(15+h)cm}{T(K)}\frac{CH_4}{m^2\bullet h}$$

$$1{,}947\frac{(15+h)cm}{T(K)}\frac{ugCH_4}{m^2\bullet h}x\frac{10^3\,ngCH_4}{1ugCH_4}x\frac{1h}{60\min}x\frac{1\min}{60\sec}=540.8\frac{(15+h)cm}{T(K)}\frac{ngCH_4}{m^2\bullet\sec}$$

$$1{,}947\frac{(15+h)cm}{T(K)}\frac{ugCH_4}{m^2\bullet h}x\frac{1gCH_4}{10^6\,ugCH_4}x\frac{12gC}{16gCH_4}x\frac{10^4\,m^2}{1ha}x\frac{24h}{1d}=350.5\frac{(15+h)cm}{T(K)}\frac{gCH_4-C}{ha\bullet d}$$

(1) GHG sample conversion

2.25 Soil Extractions

Stored soil samples were thawed at room temperature before being weighed into 125ml French square bottles. 25g of moist soil was put in a bottle and 50mL of 0.5 M K_2SO_4 was added, the sample was shaken for one hour and allowed to settle for one hour before being filtered through Watman 42 filter paper. The extracts were then stored frozen until analysis. Gravimetric water content was measured by weighing ~ 10g soil into a dish and oven drying the soil for 24 hours at 105^0C and re-weighing the soil. The difference in the weight between the wet and dry sample is the amount of water in the sample. Extracts were thawed for 12-18 hours and analyzed using a refurbished Technicon auto analyzer II (AA; Pulse Instruments, Saskatoon, SK). Ammonium was measured using the Berthelot method (Industrial Method #90-70W) producing a green end-product. The sum of nitrate (NO_3^-) and nitrite (NO_2^-) was measured using the cadmium reduction method (Technicon Method #100-70W/B) which produces a pink end-product. Concentrations were expressed as in mg N L^{-1}. The detection limits were less than 0.03mg N L^{-1} (NH_4^+) and 0.01mg N L^{-1} (NO_3^- + NO_2^-).

The sum of NO_3^-, NO_2^- and NH_4^+ is reported as nitrate, ammonium and mineral N intensity in this study. The mass, in mg N kg^{-1} soil, of NO_3^- , NO_2^- and NH_4^+ was calculated by converting the concentration in the soil extract (mg N L^{-1}) determined using the auto-analyzer in Eq. 2.

$$NO_3^-{}_s = \frac{\left(NO_3^-{}_e - Blank\right)*\left(\quad + \left(M_{ws}*\left(GWC\right)\right)\right)}{\left(\frac{M_{ws}}{GWC}\right)} \qquad \text{(2) Nitrate Concentration}$$

Where: $NO_3^-{}_s$ is the concentration of nitrate in the soil (mg N kg^{-1} dry soil); $NO_3^-{}_e$ is the contenctration of NO_3^- in the soil extract (mg N L^{-1}); Ve is the volume of the soil extract (L); M_{ws} is the mass of wet soil (g); GWC is the gravimetric water content expressed as a decimal (g/g).

Once the concentration of nitrate was known for each sampling date the concentrations where summed using linear interpolation over the number of days in the sampling season (Eq. 3) and divided by the number of days over the sampling period.

$$NI = \frac{\left(\sum_{i=1} [NO_3^{-}{}_s]_i * \left(\frac{d_{i+1} - d_{i-1}}{2} \right) \right)}{d_n - d_1} \qquad \text{(3) Nitrate Intensity}$$

where: $[NO_3^{-}{}_s]_i$ is the concentration of NO_3^- (mg N kg^{-1} soil) measured on day i in the 0-15 cm layer. NI has the units of concentration (e.g., mg N kg^{-1}).

2.26 Statistical Analysis

Data was analyzed using JMP 8.0 software (SAS, Cary, NC) as a randomized two factor split plot design where fertilizer rate consisted of three levels and was nested within crop type which consisted of four levels. Analysis was conducted as described by Jones and Nachtsheim (2009). All data was checked for normality using the Shapiro-Wilk W test and the data was accepted as normal if the p>W was greater than 0.05. Constant variance was checked using a residuals by predicted plot and checking for horizontal banding of the data points. If either of these were violated the data was transformed until both normality and constant variance was achieved. If a significant treatment effect was observed the significant differences between treatments were determined with the Tukey HSD test and a p-value of 0.05. Data was then back-transformed when reported in the results section.

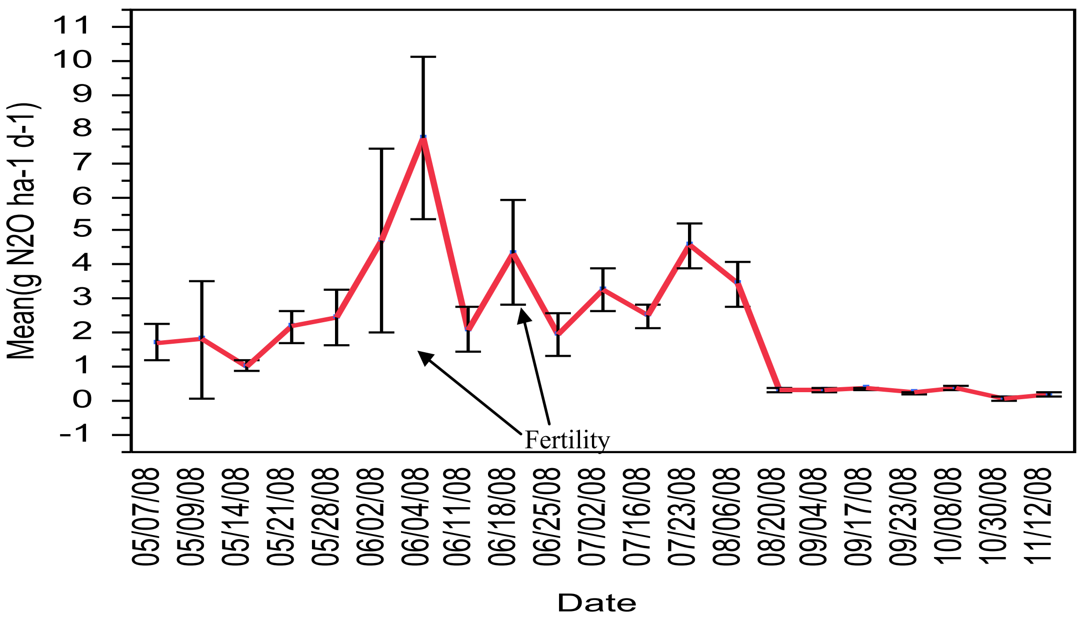
2.3 Results

2.31 N_2O Flux

2.312 Seasonal Trend

Seasonal trends from both 2008 and 2009 field seasons show spikes in N_2O flux shortly after fertilizer application in the spring for the two fertilizer dates followed by a drop to almost zero emissions by late summer (Figure 3). These graphs serve to highlight the fact that the majority of N_2O emissions occur immediately after fertilizer application and proper timing of fertilizer application can help decrease emissions.

Average N2O emissions across all treatments for 2008



Average N2O emissions across all treatments for 2009

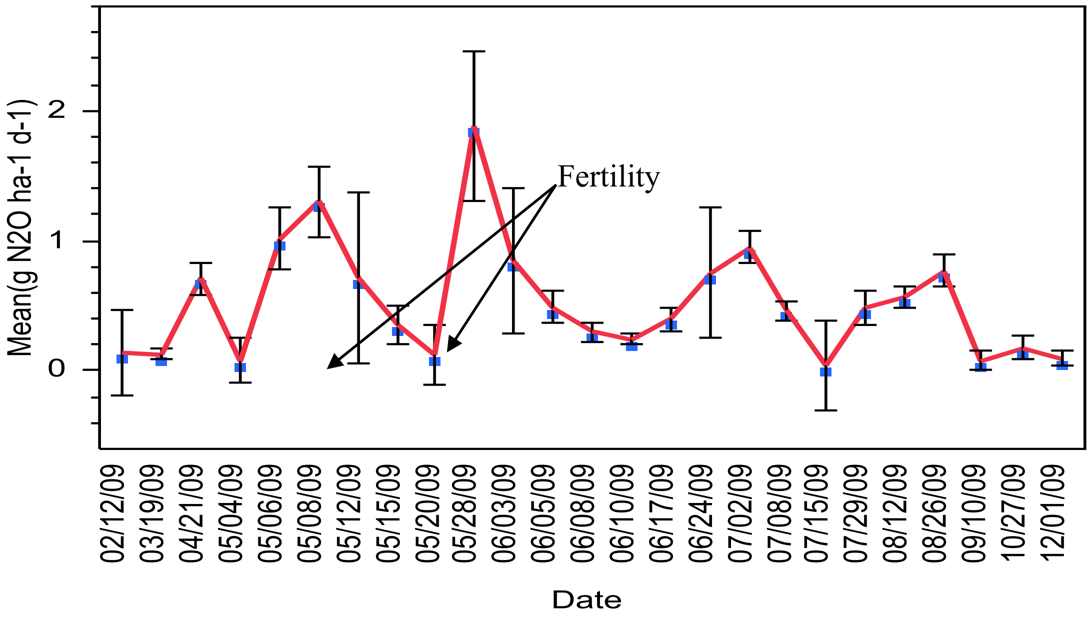


Figure 3: seasonal trend of nitrous oxide emissions

2.313 Cumulative flux

N_2O emissions for both years were low at less than 1kg N ha^{-1}. ANOVA results in 2008 indicate significant effects for crop type and fertility treatments on cumulative N_2O emissions and of all treatments switchgrass fertilized with 120kg N ha^{-1} of ammonium nitrate produced the greatest cumulative N_2O emissions. The switchgrass plots with no fertilizer also showed higher rates of N_2O flux while reed canary grass had the lowest rates of flux. Pure switchgrass had higher emissions than reed canary grass independent of fertility. The high level of fertility also showed significantly higher N_2O emissions than the two lower fertility rates across all cropping systems. ANOVA results for 2009 only shows no significant effect of treatments or interactions and cumulative N_2O emissions in 2009 were lower than in 2008 (Table 2).

Table 2: Cumulative N2O (g N ha-1) as influenced by crop type and rate of N fertilizer application.

Treatment	2008 g N_2O-N $ha^{-1}.yr^{-1}$	2009 g N_2O-N $ha^{-1}.yr^{-1}$
Switchgrass 0	463 ab	175
Switchgrass 40	345 abc	119
Switchgrass 120	933 a	173
Switchgrass and Red Clover 0	223 bc	28
Switchgrass and Red Clover 20	174 bcd	86
Switchgrass and Red Clover 60	308 abc	80
Reed-Canary-Grass 0	46 d	29
Reed-Canary-Grass 40	106 cd	12
Reed-Canary-Grass 120	252 abc	199
Reed-Canary-Grass and Red Clover 0	225 bc	125
Reed-Canary-Grass and Red Clover 20	279 abc	103
Reed-Canary-Grass and Red Clover 60	313 abc	107
Crop Type		
Switchgrass	530 a	
Switchgrass and Red Clover	228 ab	
Reed-Canary-Grass	107 b	
Reed-Canary-Grass and Red Clover	270 ab	
Rate of Fertilizer		
L	181 b	
M	205 b	
H	388 a	
ANOVA		
Crop Type	*	ns
Rate of N fertilizer	*	ns
CT * N	ns	ns

Treatments with the same letter in the same column are not significantly different at the α0.05 level. §ns = no significant difference, * = significant at α=0.05

2.32 Methane Flux

2.321 Cumulative flux

Effects on methane flux due to crop type and the crop type*fertility interaction were significant in 2008. In 2008 intercropped plots absorbed more CH_4 than non-intercropped plots and intercropped switchgrass absorbed more CH_4 than intercropped reed canary grass however there was no difference between pure grass stands. In 2009 there were no significant effects between the treatments (Table 3). The interaction in 2008 was between inter-seeded switchgrass plots with the low fertility rate and pure reed canary grass plots at the medium and high fertility rates. The intercropped plot had more methane absorption into the soil than a pure grass stand with the medium and high rates of fertility.

Table 3: Cumulative CH4 (g N ha-1 yr-1) as influenced by crop type and rate of N fertilizer application.

Treatment	2008 g CH_4-C $ha^{-1}.yr^{-1}$	2009 g CH_4-C $ha^{-1}.yr^{-1}$
Switchgrass 0	-597 ab	363
Switchgrass 40	-249 a	-603
Switchgrass 120	-345 ab	-367
Switchgrass and Red Clover 0	-1074 b	-441
Switchgrass and Red Clover 20	-605 ab	-455
Switchgrass and Red Clover 60	-568 ab	-395
Reed-Canary-Grass 0	-164 a	-381
Reed-Canary-Grass 40	-310 a	-490
Reed-Canary-Grass 120	-125 a	179
Reed-Canary-Grass and Red Clover 0	-25 a	-454
Reed-Canary-Grass and Red Clover 20	-310 a	-525
Reed-Canary-Grass and Red Clover 60	-556 ab	-469
ANOVA		
Crop Type	*	ns
Rate of N fertilizer	ns	ns
CT * N	*	ns

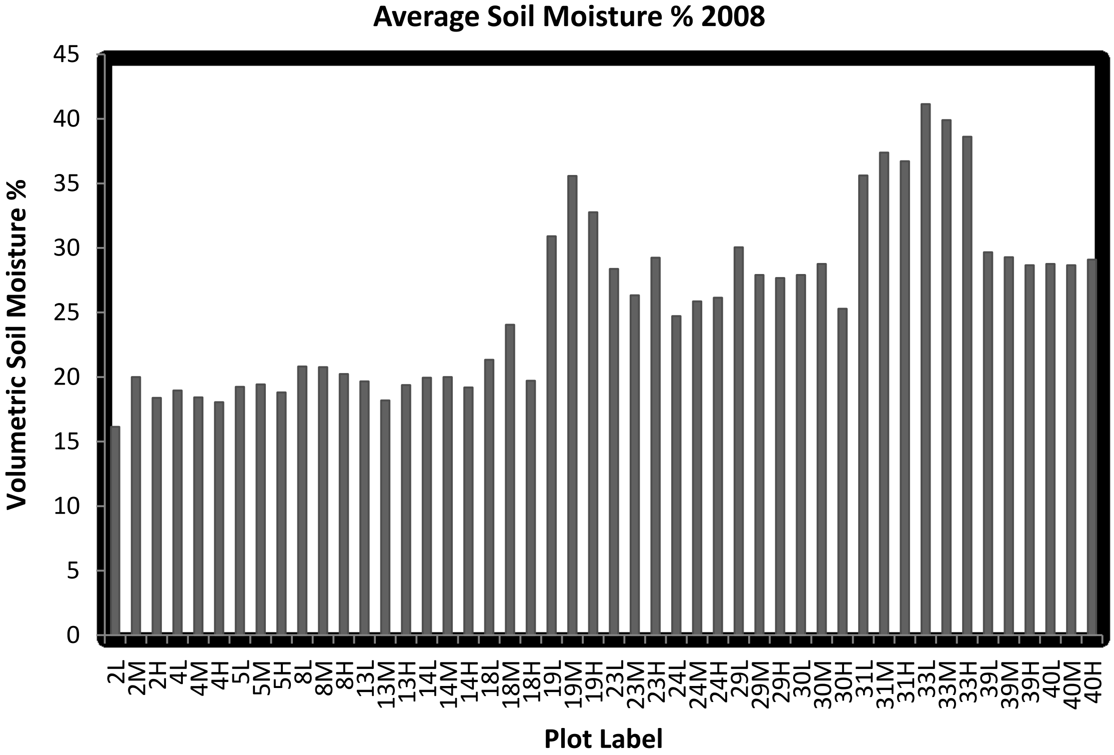
Treatments with the same letter in the same column are not significantly different at the α0.05 level. §ns = no significant difference, * = significant at α=0.05

2.33 Soil

2.331 Moisture Content

2008

Soil moisture was slightly variable between plots and the seasonal trend of soil moisture in 2008 starts relatively high for the year and drops in the mid summer. However due to high precipitation in August and late fall the soil moisture rises and falls accordingly (figure 4a and b).



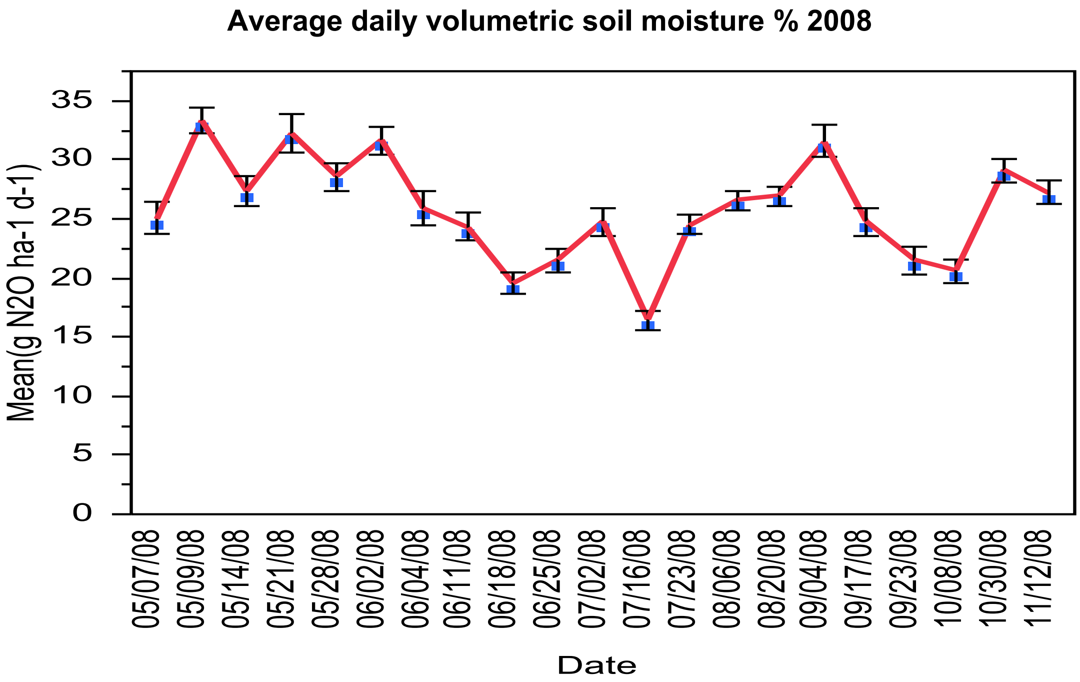


Figure 4a and b: Soil Moisture data 2008

2009

In 2009 the differences in soil moisture between the plots were noticeable however, a more typical soil moisture trend over the season was evident with a decline as the soils dried out through the summer. A spike at the very end was a result of a sampling date very late in the year in the midst of an early season rain/snow storm (figure 5a and b).

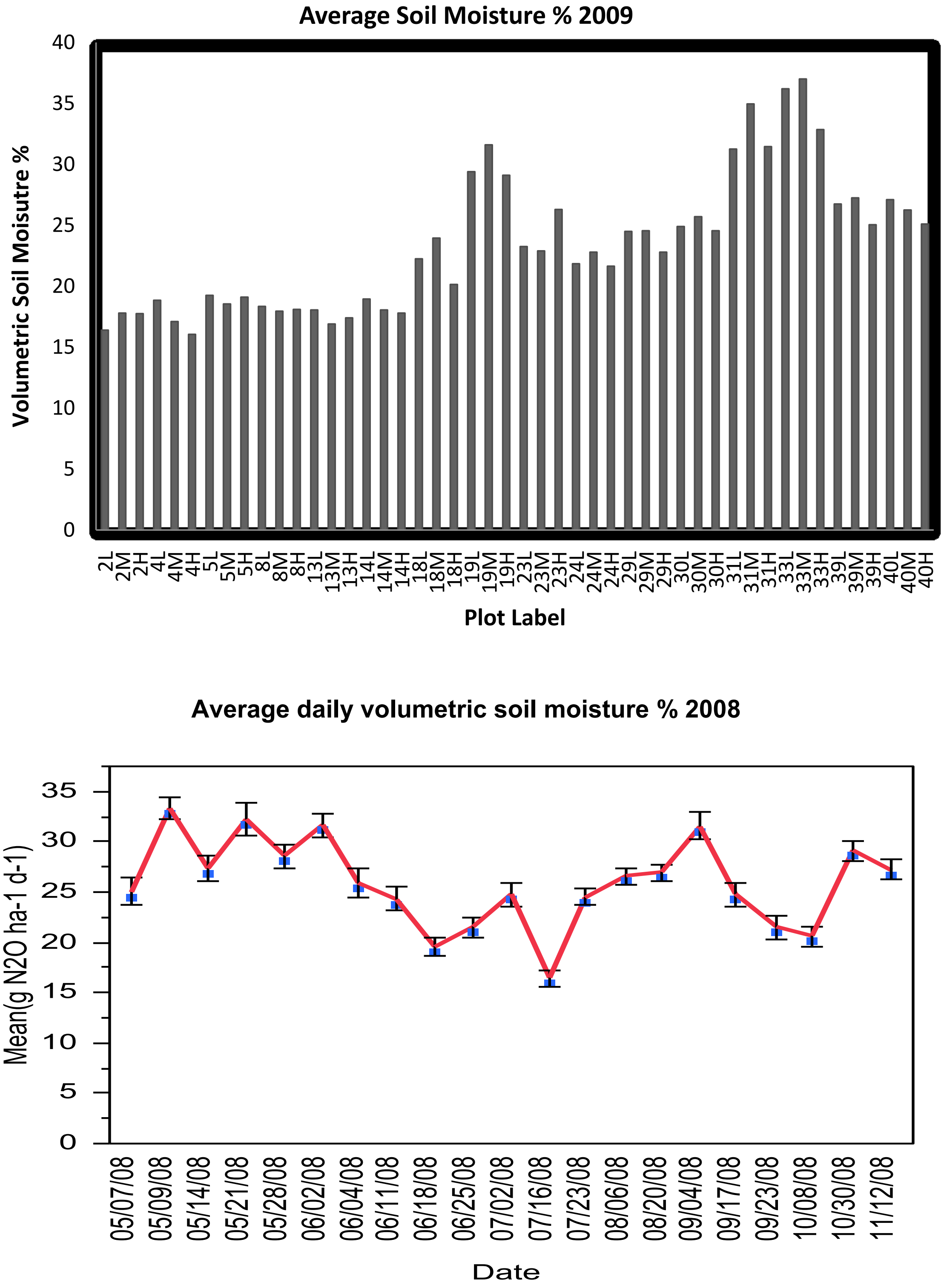
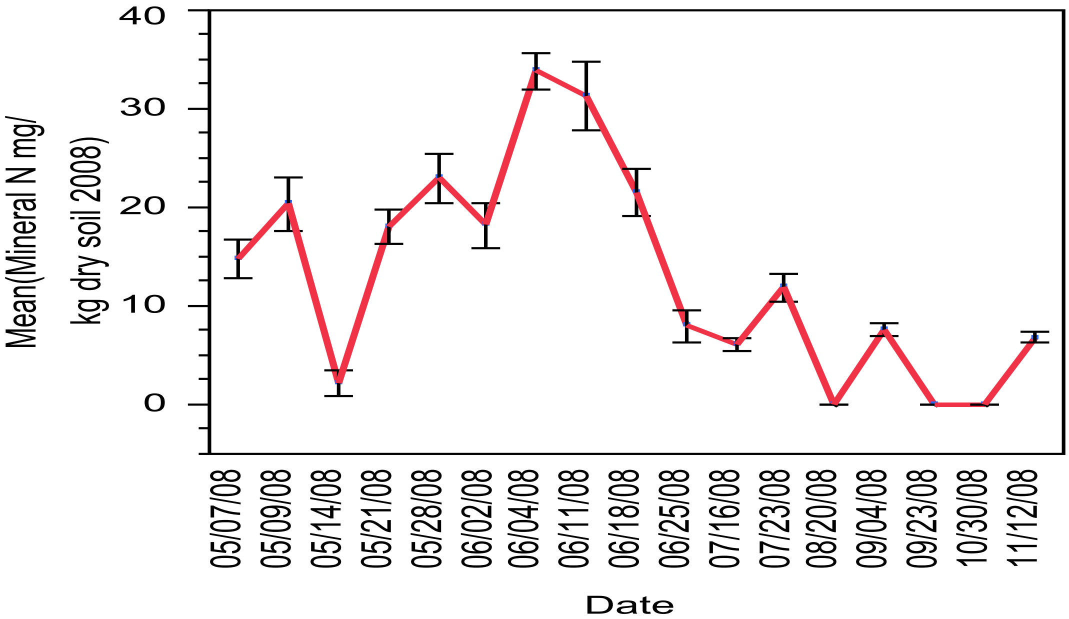


Figure 5a and b: Soil Moisture data 2009

2.332 Seasonal trends in mineral N concentrations

In both years the seasonal trend for mineral N concentration increased after both fertilization dates in May and June and a rapid decline in concentration near the end of the growing season (Fig. 6a and 6b). The sharp drop in mineral N concentrations after fertilization, as seen in Fig. 6a and 6b is evidence of these crops ability to quickly take up nitrogen when it is applied in the spring, leaving small amounts of residual ammonium or nitrate to drive N_2O production. A typical season was observed in 2008 where the soils were wet, warming and full of substrate for N2O production so higher rates were observed. Rainfall was minimal right after fertilization occurred so leaching was not an issue.

Average daily mineral N mg kg^{-1} dry soil 2008



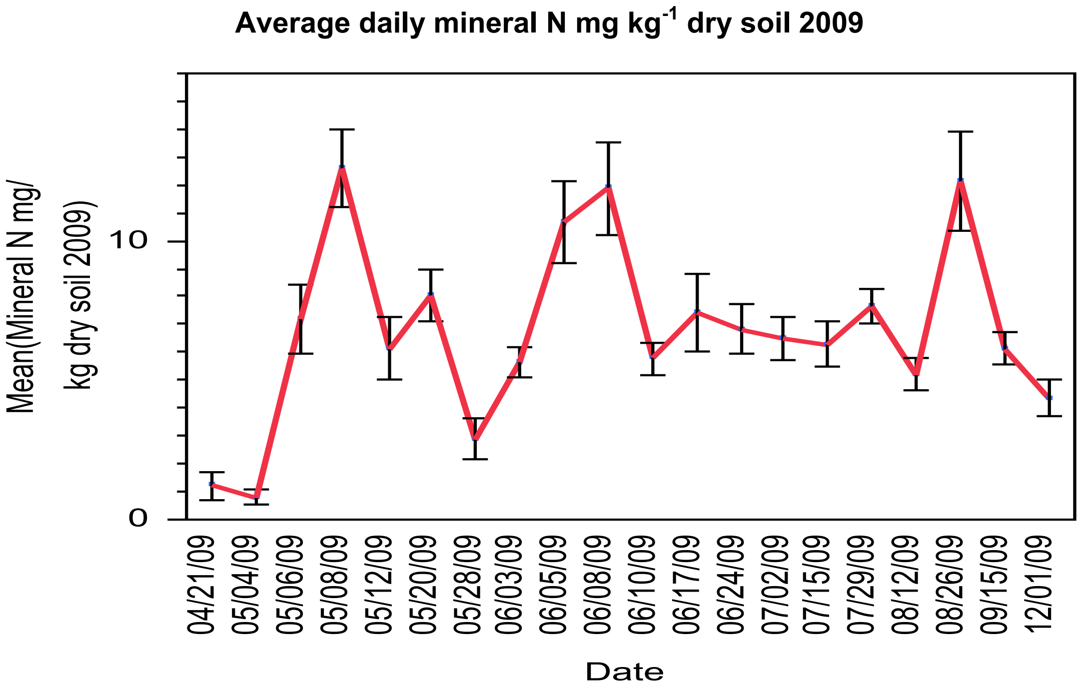


Figure 6a and b: Seasonal trends for mineral concentrations in the soil.

2.333 N Intensity

There was correlation between N_2O flux and nitrate and mineral N intensity in 2008 and no significant correlation between N_2O and ammonium. The nitrate intensity correlation had a reasonably high r-squared value and was very significant. In 2009 there was a correlation between N_2O and ammonium intensity (Figure 7). Results in 2008 show fertility effects on nitrate and mineral N intensity with the high rate of fertility having significantly higher N intensity than the two other fertility treatments. Results in 2009 again showed fertility effects for nitrate intensity where the low fertility rate was significantly different than the two higher fertility rates as well as a fertility effect for ammonium intensity with the high fertility treatment significantly different from the other two fertility treatments. Fertility treatments for mineral N were all significantly different from one another with the high treatment having the highest intensity and the low treatment having the lowest intensity (Tables 4-6).

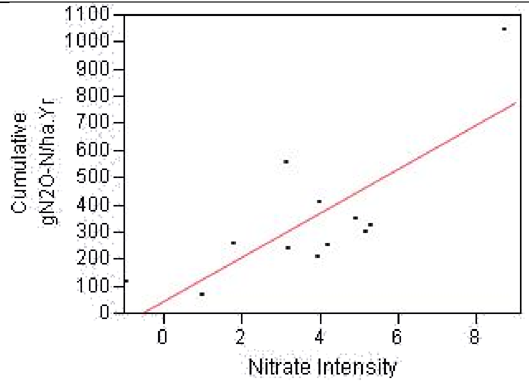
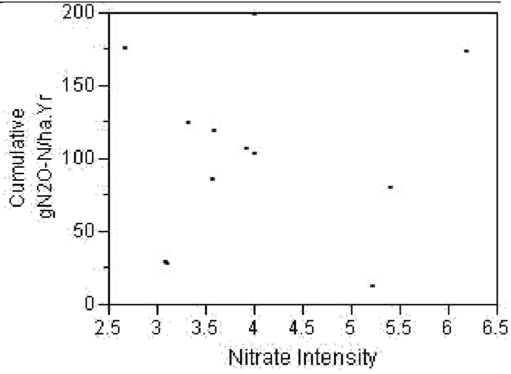
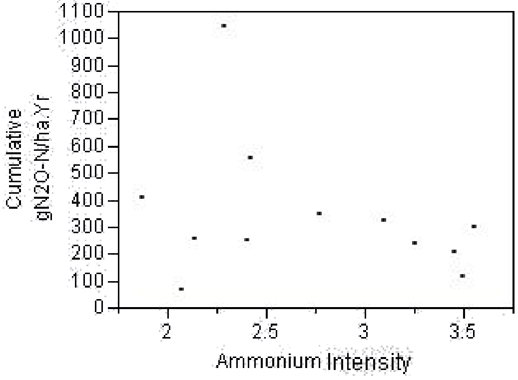
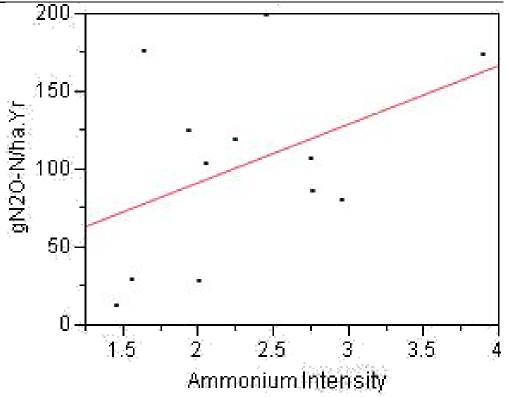
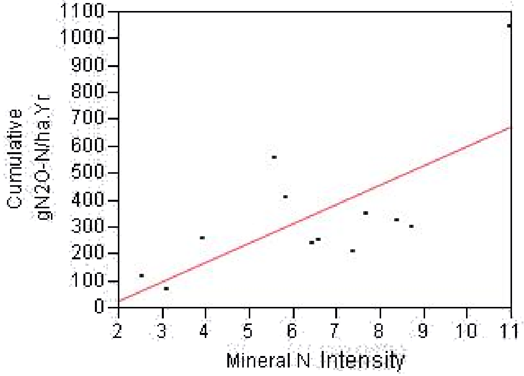
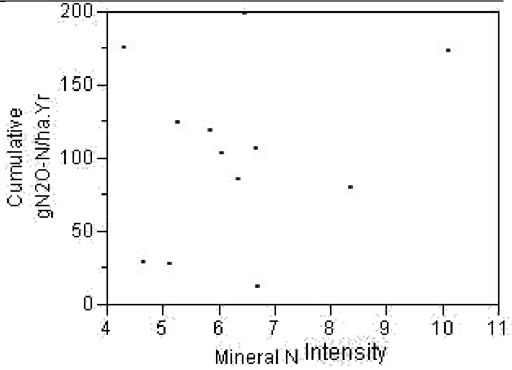
	2008	**2009**
N_2O vs. Nitrate Intensity	 Cumulative gN_2O-N/ha.= 42.133089 + 81.574174*Nitrate Intensity mg N/kg soil R-Square: 0.59 Prob > F: 0.0032*	 Cumulative gN_2O-N/ha. = 92.479949 + 2.6433177*Nitrate Intensity mg N/kg soil R-Square: 0.00 Prob > F: 0.88
N_2O vs. Ammonium Intensity	 Cumulative gN_2O-N/ha.= 704.03204 - 132.20368*Ammonium Intensity mg N/kg soil R-Square: 0.09 Prob > F: 0.32	 Cumulative gN_2O-N/ha.= 16.56675 + 37.440849*Ammonium Intensity mg N/kg soil R-Square: 0.18 Prob > F: 0.15
N_2O vs. Mineral N Intensity	 Cumulative gN_2O-N/ha.Yr = -116.1757 + 71.542174*Mineral N Intensity mg N/kg soil R-Square: 0.47 Prob > F: 0.01*	 Cumulative gN_2O-N/ha.Yr = 50.575638 + 8.314398*Mineral N Intensity mg N/kg soil R-Square: 0.05 Prob > F: 0.49

Figure 7. N_2O vs. NI, AI and MNI 2008 and 2009

Table 4: Nitrate intensity g N kg-1 dry soil 0-15cm as influenced by crop type and rate of N fertilizer application.

Treatment	2008 Mean	2009 Mean
Switchgrass 0	3.1 bc	2.6 b
Switchgrass 40	4.0 abc	3.5 ab
Switchgrass 120	8.7 a	5.8 a
Switchgrass and Red Clover 0	4.2 ab	3.0 ab
Switchgrass and Red Clover 20	3.9 abc	3.5 ab
Switchgrass and Red Clover 60	4.9 ab	5.1 ab
Reed-Canary-Grass 0	1.0 bc	3.0 ab
Reed-Canary-Grass 40	0 c	5.1 ab
Reed-Canary-Grass 120	1.8 bc	4.0 ab
Reed-Canary-Grass and Red Clover 0	3.2 bc	3.3 ab
Reed-Canary-Grass and Red Clover 20	5.2 ab	3.8 ab
Reed-Canary-Grass and Red Clover 60	5.3 ab	3.8 ab
Rate of N fertilizer		
L	2.8 b	3.0 b
M	3.0 b	4.1 ab
H	5.2 a	4.9 a
ANOVA		
Crop Type	ns	ns
Rate of N fertilizer	*	*
CT * N	ns	ns

Treatments with the same letter in the same column are not significantly different at the α0.05 level. §ns = no significant difference, * = significant at α=0.05

Table 5: Ammonium intensity g N kg^{-1} dry soil 0-15cm as influenced by crop type and rate of N fertilizer application.

Treatment	2008 Mean	2009 Mean
Switchgrass 0	2.4	1.6 bc
Switchgrass 40	1.9	2.2 bc
Switchgrass 120	2.3	3.9 a
Switchgrass and Red Clover 0	2.4	2.0 bc
Switchgrass and Red Clover 20	3.4	2.8 abc
Switchgrass and Red Clover 60	2.8	3.0 ab
Reed-Canary-Grass 0	2.1	1.6 bc
Reed-Canary-Grass 40	3.5	1.5 c
Reed-Canary-Grass 120	2.1	2.5 abc
Reed-Canary-Grass and Red Clover 0	3.2	1.9 bc
Reed-Canary-Grass and Red Clover 20	3.5	2.1 bc
Reed-Canary-Grass and Red Clover 60	3.1	2.8 abc
Rate of N fertilizer		
L		1.8 b
M		2.1 b
H		3.0 a
ANOVA		
Crop Type	ns	ns
Rate of N fertilizer	ns	*
CT * N	ns	ns

Treatments with the same letter in the same column are not significantly different at the α0.05 level. §ns = no significant difference, * = significant at α=0.05

Table 6: Mineral N intensity g N kg^{-1} dry soil 0-15cm as influenced by crop type and rate of N fertilizer application.

Treatment	2008Mean	2009 Mean
Switchgrass 0	5.5 bc	4.2 c
Switchgrass 40	5.8 abc	5.7 bc
Switchgrass 120	11.0 a	9.5 a
Switchgrass and Red Clover 0	6.6 abc	5.0 bc
Switchgrass and Red Clover 20	7.4 abc	6.2 abc
Switchgrass and Red Clover 60	7.7 abc	7.9 ab
Reed-Canary-Grass 0	3.1 c	4.6 bc
Reed-Canary-Grass 40	2.5 c	6.6 abc
Reed-Canary-Grass 120	3.9 bc	6.4 abc
Reed-Canary-Grass and Red Clover 0	6.4 abc	5.1 bc
Reed-Canary-Grass and Red Clover 20	8.7 ab	5.7 bc
Reed-Canary-Grass and Red Clover 60	8.4 ab	6.5 abc
Rate of N fertilizer		
L	5.4 b	4.8 b
M	6.1 b	6.2 b
H	7.7 a	7.9 a
ANOVA		
Crop Type	ns	ns
Rate of N fertilizer	*	*
CT * N	ns	ns

Treatments with the same letter in the same column are not significantly different at the α0.05 level. §ns = no significant difference, * = significant at α=0.05

2.4 Discussion

Nitrous oxide emissions and soil mineral N increased in the spring after fertilization followed by a sharp decrease once the plants began actively growing and taking up nitrogen. This seasonal pattern of N_2O emissions is consistent with results from Burton et al. (2008) and Zebarth et al. (2008). The drop in mineral N post fertilizer supports the theory that both grasses are good at absorbing nitrogen early in the spring and that there may have been some leaching of nitrate from the soil as the spring season in Nova Scotia is, generally, wet. Other possibilities for decreases or low mineral N are complete denitrification or immobilization of N. The mineral N concentrations found in the soil in this study are in line with other studies. Highly tilled soils with high rates of N fertilizer generally produce mineral N concentrations between 40-100 mg N kg^{-1} dry soil while unfertilized grasslands generally have concentrations of <1 mg N kg^{-1} dry soil (Kavdir et al. 2008; Mosier et al. 1991; Muller et al. 2002). The results in this study show that mineral N concentrations fall between unfertilized grasslands and tilled, highly fertilized soils. One might expect that due to the high water content of these soils in the spring and the timing of nitrogen fertilizer application, that N_2O emissions would be high however in both years overall the N_2O fluxes are low (~0.4kg ha^{-1}) relative to other crops in the region (Burton et al., 2008; Zebarth et al., 2008). The N_2O emissions are also lower than those for two other bioenergy crops, hemp and miscanthus, which both emitted more than 1kg N_2O-N ha^{-1} (Hanegraaf et al., 1998; Jorgensen et al., 1997). The N_2O emissions measured in this study are also much lower than the 1.25% allotted by the IPCC which suggests that Eastern Canada may be subject to different parameters, based on soil and climate characteristics as they relate to N_2O emissions, than other parts of the World or that these perennial grass crops are particularly good at mitigating the soil N_2O emissions associated with N fertilizer. This may be due to nutrient leaching from the soil which might explain why we only see N_2O emissions when nitrogen fertilizer is applied in great excess of crop demand. After considering both field seasons together reed canary grass presented an advantage as far as N_2O emissions go in 2008 however 2009 showed relatively low N_2O emissions, even compared to 2008, and no difference between crops. The lack of difference in N_2O emissions between the crops is not entirely surprising as Epstein et al. (1998) have suggested that differences depend on site-specific conditions. Higher fertility did result in higher N_2O emissions in 2008 however grass crops are good at absorbing nitrogen from the soil into above and below ground plant tissue. Much of the applied nitrogen, which was a low rate to begin with, may have been fully denitrified to N_2 which resulted in the low N_2O emissions from the soil. Full denitrification would require a water filled pore space of between 70% and 90% which only occurred on some days immediately post fertilizer application. Other causes of low N_2O emissions could be leaching or immobilization. Likely a combination of factors was the cause of low N_2O.

The soil moisture content in 2009 also decreased over the season (until the late fall when sampling was stopped) more than in 2008, which would have lead to a more aerobic environment in which less N_2O would have been produced.

Across crop type and fertilizer rate, the intercropped plots did not have a significantly different N_2O flux than pure grass stands. It was hypothesized that supplying some of the N to the crop via an intercropped legume might reduce total N_2O emissions compared with using only ammonium nitrate fertilizer on pure grass stands. This study found no difference in N_2O emissions from pure grass plots fertilized with twice the rate of fertilizer as intercropped plots so it is suggested that clover, due to BNF, is resulting in similar levels of N_2O emissions. This is in contrast to the Carter and Ambus (2006) study which found that N_2O emissions, while being higher for clover-grass plots than unfertilized plots, were a small part of the total N_2O budget of growing the crop. More research needs to be completed in this area to support and clarify these results.

In general, soil was a net sink for CH_4, with average fluxes being negative. In 2008 inter-seeded plots had greater CH_4 consumption than pure stands and inter-seeded reed canary grass had less CH_4 absorption than inter-cropped switchgrass. There were no differences in CH_4 emissions due to fertilizer application suggesting that CH_4 consumption was occurring naturally in the soil. Methane consumption was a small component of the overall GHG balance of the crop in 2008 but that changed in 2009, when averaged across all plots and expressed as CO_2e, average methane consumption (-12kg CO_2e ha^{-1}) was only 7.5% of average N_2O emissions (160kg CO_2e ha^{-1}) in 2008 and average methane consumption (-10kg CO_2e ha^{-1}) was 21% of average N_2O emissions (48kg CO_2e ha^{-1}) in 2009. In 2009, because of the low N_2O emissions methane absorption was a greater proportion of the GHG balance and significantly impacted the GWP between treatments (Ch.3). The ratio between CH_4 uptake and N_2O emissions found in this study are in the range that Mosier et al. (1991) found for fertilized pasture land in their study.

Generally, a good correlation exists between N_2O and NI, AI and MNI however my system shows such a relationship only in 2008 (Burton et al., 2008; Zebarth et al., 2008).

Zebarth reported a similar difference between years where one year had a good correlation while the other year did not. Low rates of fertility and a flush of N from the soil in 2009 corresponding to plant uptake and leaching caused no correlation with N_2O. Crop type was not a significant effect in this study indicating that neither crop has an advantage over the other as far as absorbing nutrients to minimize environmental damage. The only effect was fertility where, in almost all cases, the high fertility rate caused higher N intensity in the soil.

2.5 Conclusions

High variability in N_2O flux rates makes determining the effect of fertilizer on N_2O emissions difficult however there are statistically significant effects due to intercropping and fertility in some cases. N_2O emissions were low and may not be a significant contributor to the overall GHG emissions of producing a bioenergy crop if all other GHG production is considered. Other production factors such as transportation of the final product and manufacturing of fertilizer would be much higher proportions of the total GHG budget. This study was not designed to determine this definitively and so to strengthen this conclusion further work would need to be done. This research does highlight that the IPCC co-efficient for N_2O emissions of 1.25% of applied N overestimates the actual emissions of 0.1-0.5% of applied N for these crops in this region which is an important consideration when developing policy to support renewable energy technologies. Methane is an important contributor to global warming but within the context of bioenergy crops is an insignificant contributor. Within the agricultural industry there is much more methane pollution from livestock and efforts focused on methane reduction would be best used there.

Switchgrass and reed canary grass crops appear to be very good bioenergy crops, require little in the way of fertility, provide minimal negative impact to the environment and could likely be considered good candidates for wet areas, marginal lands, and riparian zones or for farm operations that have excess manure for their land base or in areas where municipal solid waste or other composts are applied. Development of an industry in Eastern Canada should focus on seedbed preparation, the most economic rate of nitrogen given the yields and fertility rates presented in this research as well as the establishment of a market for the product and a cooperative equipment sharing program. These areas all present good opportunities for further research as this experiment was only a piece of the much larger puzzle.

CHAPTER 3: EFFECT OF INORGANIC NITROGEN FERTILIZER APPLICATION AND CROP TYPE ON BIOMASS YIELD RESPONSE AND RELATIVE GHG OFFSETS.

3.1 Introduction

To assess the ability of a biofuel crop to reduce net carbon emissions consideration must be paid to the GHG emissions associated with crop production and, further, the sustainability of the biofuel production system should consider changes to soil quality. Improvements in soil quality, measured as increases in organic carbon, result from converting from annual crops, such as corn, to a perennial grass crop. The sequestration of carbon in agricultural soils has a positive net benefit of reducing the GHG emissions of these systems and in many cases can result in negative net emissions. The cropping of switchgrass has shown a very good ability to increase soil organic carbon (Lee et al., 2007; Tolbert et al., 2002). McLaughlin and Walsh (1998) selected switchgrass as the best herbaceous energy crop out of 34 other species based on its low nutrient and pesticide requirements and perennial growth habit combined with high yields and good combustion properties. They noted that switchgrass requires about half the amount of fertilizer required by corn and, usually, only requires herbicides in the first year of a 10 year growth cycle which results in significantly less input costs and a lower potential for environmental damage. A switchgrass fertility trial conducted in Italy in 1998 concluded that switchgrass can be grown with minimal inputs and could be viable as a bioenergy feedstock (Piscioneri et al., 2001).

Bioenergy crops have potential to offset GHG emissions from fossil fuel use however, through their production, also emit GHGs. Variations in N_2O emissions have been documented from traditional food crops like corn and potatoes however there is a lack of studies examining the N_2O emissions from the soil as influenced by perennial grass crop type and it is expected that perennial grass crops will be different from annually cropped species (IFA/FAO, 2001; Ruser et al., 2001; Zebarth et al., 2008). Correct timing of fertilizer can play an important role in decreasing N_2O emissions from some crops but not in others (Burton et al., 2008; Zebarth et al., 2008). Delaying N fertilization to the time of maximum plant N demand has been shown to decrease the risk of N_2O emissions (Burton et al., 2008; Snyder et al., 2009). A study conducted by Epstein et al. (1998) on differences in trace gas exchange between C_3 and C_4 grasses determined that differences depend on site-specific conditions and on their site which contained a sandy-clay loam soil they noticed that CH_4 uptake and NO emissions were greater for C_4 plots. There is uncertainty surrounding the magnitude of N_2O emissions emitted from different cropping systems with different fertilizer regimes.

The agronomic characteristics and quality of the biofuel crop produced is also an important consideration in assessing its potential to offset petroleum use and/or reduce net GHG emissions. A comparison of the non-GHG attributes of switchgrass and reed canary grass indicate that reed canary grass has more ether-extractable lipids and ash while switchgrass has lower protein and organic acid concentrations and a higher level of total carbohydrates (Dien et al., 2006). Higher levels of carbohydrates are desirable when the conversion to energy process involves fermentation and lower ash content decreases fouling and slagging in furnaces when the pellets are combusted directly for heat.

Agronomically, switchgrass (C3) and reed canary grass (C4) represent different growth physiologies. Switchgrass is also slightly cheaper to establish and maintain per unit of output on a yearly basis than reed canary grass (Hallam et al., 2001). Reed canary grass, however, is a cooler-season grass that is responsive to nitrogen making it a desirable crop when a large amount of manure is available for utilization (Dien et al. 2006 from Martin et al., 1979). The cool season preference of reed canary grass and the high biomass quality of switchgrass make comparing these two crops important in Nova Scotia.

There are many potential bioenergy crops and several ways of converting them to energy, each with an associated environmental impact. Many of the discrepancies between the benefits of energy crops relate to how the benefits are calculated and reported. Life Cycle Analysis (LCA) is a common method of comparing environmental (and often economic) aspects of different bioenergy crops. LCAs are a ‘cradle-to-grave’ assessment of all components of producing a product and they can focus on energy balances or environmental balances and are generally large projects encompassing both direct and indirect production inputs (Adler et al., 2007; Benetto et al., 2004; Gagnon et al., 2002; Heller et al., 2004). Each LCA sets boundaries for indirect inputs after which it does not count their energy or environmental requirements. This subjectivity can lead to conflicting outcomes between LCAs done on the same product. LCAs on biofuels energy and environmental requirements often include manufacture of fertilizers, transportation, conversion to fuels, tractor and fuel use but often leave out or assume many of the biological processes associated with growing the crop that incur environmental implications. Two commonly assumed environmental implications are carbon sequestration and nitrous oxide emissions. Both of these can be estimated with fairly good accuracy however there is high variability associated with N_2O emissions that is caused by soil type, climate and the crop being grown. LCAs are effective for generalizing about potential energy crops however for specific recommendations to be made on a regional basis it is important to compare all components of growing the crops. This data also fits into the more general, and larger, LCA and helps to verify or counter the accepted conclusion that N_2O emissions play an insignificant role in the overall GHG balance of energy crops.

This project assumes all non-fertility inputs for the switchgrass and reed canary grass are the same and the best recommendations for the greatest environmental benefits can be made based on the differences in yield, N_2O emissions and energy density of the two crops. The availability of relevant data, particularly environmental data, is a common shortcoming of LCA. Often in large studies, boundaries have to be set which may be arbitrary and assumptions are generally made about certain biological processes with environmental impacts. In 1998 an LCA looked at ecological impacts of growing silage corn, hemp and miscanthus “Giganteus” and converting the biomass to energy using several different conversion technologies. They found that these crops produced high energy yields, regardless of conversion technology, at an average (across conversion technologies) of 208GJ of fossil energy ha^{-1}, 173GJ of fossil energy ha^{-1}, and 128GJ of fossil energy ha^{-1} for silage corn, hemp and miscanthus respectively (Hanegraaf et al., 1998). However, silage corn, hemp and miscanthus produced 14.7, 12.7 and 9.6t CO_2 ha^{-1}

and 6.3, 1.9 and 1.1kg N_2O ha^{-1} respectively, which was high compared to the other crops they studied (Hanegraaf et al., 1998).

Jorgensen et al. (1997) grew miscanthus, a similar perennial grass to switchgrass, in experimental plots in Denmark in 1997 with two rates of nitrogen fertilizer of 0 and 75kg ha^{-1}. They used a modified version of the chamber method to collect N_2O samples and results showed an average N_2O flux from April to November (207 days) of 1.09kg N_2O-N ha^{-1} from the plots with the high rate of fertilizer. This is on the low end of the range presented in the LCA studies, suggesting that LCAs may overestimate the amount of N_2O emissions and highlights the importance of taking real measurements. Switchgrass was not included in the Jorgensen study however miscanthus is a similar crop to switchgrass in that they are both perennial C_4 plants and prefer warm soil to begin growth but miscanthus over-winters poorly, is expensive to establish and its ash has a low melting temperature. These are two deterrents for its use as a biofuel in N.S. (Lewandowski et al., 2003; Monti et al., 2008).

Greater complications in choosing the most environmentally efficient crop arise when energy to produce the crop is taken into account. For example, in data compiled by Shapouri et al. 1995, Tyson et al., 1994 and McLaughlin and Walsh (1998) make the claim that, once the crop is at the ethanol plant, it takes approximately the same amount of energy, in GJ ha^{-1} yr^{-1}, to produce ethanol from switchgrass as it does to produce ethanol from corn. However, switchgrass ethanol yields ha^{-1} are much greater which results in a net energy gain of 343% for switchgrass compared to just 21% for corn and the energy requirements to grow switchgrass are less. The efficiency can be even higher for switchgrass if pellets are used directly as a heat source or co-fired to generate electricity. The high levels of energy efficiency over traditional energy crops like corn plus the ability of perennial grasses to be grown with low inputs on marginal soils make them a good prospect for energy production. It is with these criteria that I chose to study reed canary grass and switchgrass.

The objectives of this experiment are to measure biomass yield response on a per hectare to inorganic nitrogen fertilizer application and relative GHG emissions and compare levels of ash content between the two crops grown in the same soils at the same time.

3.2 Materials and Methods

Refer to Ch. 2 for materials and methods of field and fertilizer, GHG flux measurements, gas analysis, and statistical analysis.

3.21 Harvesting

Yields were harvested at two different times in the fall. Reed canary grass and intercropped plots were harvested first while switchgrass, with a later date of maturity, was harvested later in the season. Entire plots were harvested using a Haldrup mechanical harvester and grab samples from each plot were collected, weighed wet, dried for at least 72h at 50°C and weighed dry. Dry mass of the entire plot was calculated, scaled up and reported in t ha^{-1}. Yield is calculated using the following formula (Eq. 4):

$$\text{Dry Weight t/ha} = (((W_P \text{ in tonnes} * (1 / \text{plot size in ha})) * (1 - M_C))$$

(4) Dry Weight

Where W_P is the weight harvested from the plot, and M_C is the moisture content of the harvested mass.

3.22 GWP and GHG offsets

I converted cumulative N_2O and CH_4 emissions to global warming potential in CO_2 equivalents and combined them to determine the overall direct GHG production from nitrogen fertilizer application for each treatment. Eq. 4 describes this calculation. Eq. 5 describes the conversion to CO_2-e offsets.

$$((((\text{Cumulative } gN_2O\text{-N } ha\text{-}^1 * (44/28)) * 296) / 1000) + (((\text{Cumulative } gCH_4\text{-C } ha\text{-}^1 * (16 / 12)) * 23) / 1000))$$

(4) GWP

$$((((\text{MJ ha}^{-1} / \text{MJ kg}^{-1}\text{ oil}) * \text{Density of oil kg L}^{-1}) * \text{kg CO}_2\text{-e L}^{-1}) + \text{CO}_2\text{-e from plot})$$

(5) CO_2-e offsets

3.3 Results

3.31 Yield

There was no yield response to N fertilizer however there was a response to crop type in 2008 (table 7). Pure switchgrass yield averaged across all fertility rates was higher than inter-seeded switchgrass averaged across fertility rates. There were no significant treatment effects in 2009.

Pure switchgrass stands had lower concentrations of ash than the inter-seeded switchgrass and pure reed canary grass plots but there was no difference as a result of fertility rate (table 8). At this time no ash data is available for 2009.

Table 7: Average Yield dry t ha^{-1} as influenced by crop type and rate of N fertilizer application.

Treatment	2008 Mean yield dry t ha^{-1}	2009 Mean yield dry t ha^{-1}
Switchgrass 0	7.1 a	5.1
Switchgrass 40	6.6 a	4.4
Switchgrass 120	7.0 a	3.8
Switchgrass and Red Clover 0	4.1 b	4.1
Switchgrass and Red Clover 20	4.7 b	4.6
Switchgrass and Red Clover 60	4.6 b	5.2
Reed-Canary-Grass 0	3.8 ab	4.2
Reed-Canary-Grass 40	4.4 ab	3.9
Reed-Canary-Grass 120	5.6 ab	5.4
Reed-Canary-Grass and Red Clover 0	5.9 ab	5.2
Reed-Canary-Grass and Red Clover 20	5.9 ab	5.0
Reed-Canary-Grass and Red Clover 60	6.0 ab	5.1
Crop Type		
Switchgrass	7.0 a	
Switchgrass and Red Clover	4.5 b	
Reed-Canary-Grass	4.6 ab	
Reed-Canary-Grass and Red Clover	6.0 ab	
ANOVA		
Crop Type	*	ns
Rate of N fertilizer	ns	ns
CT * N	ns	ns

Treatments with the same letter in the same column are not significantly different at the α0.05 level. §ns = no significant difference, * = significant at α=0.05

Table 8: Average crop Percent Ash content as influenced by crop type and rate of N fertilizer application.

Treatment	2008 Mean % Ash
Switchgrass 0	3.9bcd
Switchgrass 40	3.4 d
Switchgrass 120	3.6 cd
Switchgrass and Red Clover 0	5.2 abc
Switchgrass and Red Clover 20	5.6 a
Switchgrass and Red Clover 60	5.2 abc
Reed-Canary-Grass 0	5.6 ab
Reed-Canary-Grass 40	4.8 abcd
Reed-Canary-Grass 120	4.4 abcd
Reed-Canary-Grass and Red Clover 0	4.6 abcd
Reed-Canary-Grass and Red Clover 20	4.8 abcd
Reed-Canary-Grass and Red Clover 60	4.5 abcd
Crop Type	
Switchgrass	3.7 b
Switchgrass and Red Clover	5.4 a
Reed-Canary-Grass	5.0 a
Reed-Canary-Grass and Red Clover	4.7 ab
ANOVA	
Crop Type	*
Rate of N fertilizer	ns
CT * N	ns

Treatments with the same letter in the same column are not significantly different at the α0.05 level. §ns = no significant difference, * = significant at α=0.05

3.32 Combined GHG Emissions

In 2008 switchgrass had the highest CO_2e and was significantly different from the switchgrass/clover mix and pure reed canary grass (Table 9). The high rate of fertility also showed significantly higher GWP than the medium and low fertility rates. 2009 showed no significant difference between treatments.

Table 9: Combined N_2O and CH_4 emissions as influenced by crop type and rate of N fertilizer application expressed as CO_2-e.

Treatment	2008 kg CO_2 ha.yr^{-1}	2009 kg CO_2 ha.yr^{-1}
Switchgrass 0	206 ab	93
Switchgrass 40	157 ab	37
Switchgrass 120	435 a	69
Switchgrass and Red Clover 0	54 b	-1
Switchgrass and Red Clover 20	69 b	26
Switchgrass and Red Clover 60	128 ab	25
Reed-Canary-Grass 0	46 b	2
Reed-Canary-Grass 40	35b	-9
Reed-Canary-Grass 120	114ab	98
Reed-Canary-Grass and Red Clover 0	105 ab	44
Reed-Canary-Grass and Red Clover 20	122 ab	32
Reed-Canary-Grass and Red Clover 60	159 ab	36
Crop Type		
Switchgrass	247 a	
Switchgrass and Red Clover	72 b	
Reed-Canary-Grass	59 b	
Reed-Canary-Grass and Red Clover	127 ab	
Rate of N Fertilizer		
L	83 b	
M	86 b	
H	184 a	
ANOVA		
Crop Type	*	ns
Rate of N fertilizer	*	ns
CT * N	ns	ns

Treatments with the same letter in the same column are not significantly different at the α0.05 level. §ns = no significant difference, * = significant at α=0.05

3.33 Relative GHG emissions offset

In 2008 Switchgrass had higher GHG fluxes of than reed canary grass however switchgrass has an energy density of 18.4 MJ/kg (McLaughlin et al. 1996) while reed canary grass has an energy density of 17.2 MJ/kg (Strasil et al., 2005). Table 10 shows the rank of GHG offsets for treatments containing pure grass crops with the three rates of fertilizer. The emissions from each treatment were compared with the amount of GHGs that could be offset from decreased use of heating oil. 2008 and 2009 had no significant differences between treatments at the α0.05 level.

Table 10: Average CO_2e offsets as influenced by crop type and rate of N fertilizer application.

Treatment	2008 Mean T CO_2-e offset/ha	2009 Mean T CO_2-e offset/ha
Switchgrass 0	7.5	5.1
Switchgrass 40	7.0	4.3
Switchgrass 120	6.7	3.8
Reed Canary Grass 0	3.9	4.0
Reed Canary Grass 40	4.5	3.7
Reed Canary Grass 120	4.8	5.2
ANOVA		
Crop Type	ns	ns
Rate of N fertilizer	ns	ns
CT * N	ns	ns

Treatments with the same letter in the same column are not significantly different at the α0.05 level. §ns = no significant difference, * = significant at α=0.05

3.4 Discussion

Research projects across North America suggest that switchgrass should yield more than reed canary grass and have less of a response to nitrogen fertilizer however the crops were not grown in the same soil at the same time (Lewandowski et al., 2003). Higher yielding switchgrass proved not to be the case in the Nova Scotia climate as differences between switchgrass and reed canary grass were not present. Inter-seeded plots had lower yields because the clover choked out the switchgrass early in the season and prevented good establishment of the higher yielding grasses. Yields were also lower in 2009 than 2008 which may have been a result of the relatively cool season and that both crops were harvested later than in 2008. Some biomass is lost due to leaf drop and there was a large windstorm in the fall of 2009 prior to harvest that knocked over some stands. While the harvester picked up most of the stalks that were knocked over there would have been some biomass lost. Despite these setbacks the yields are still considered good for this climate. A longer-term study might be required to determine if one crop has a greater advantage over time. Switchgrass is believed to have a very long stand life and may actually maintain higher yields than reed canary grass after 10 years or more. A long-term study may also show a greater response to fertilizer once the lower fertilizer treatments deplete the base level of nutrients in the soil.

There was no significant yield response to fertilizer which corresponds with other studies who report switchgrass yields in the range of 6 to 8t ha^{-1} and reed canary grass yields in the range of 2 to 6t ha^{-1} and 7 to 9t ha^{-1} (Adler et al., 2006; Christian et al., 2006; Landstrom et al., 1996). In the eastern Canada climate switchgrass yields are expected to be slightly lower compared to warmer climates and this appears true although they are still respectable and farmers, if they received a reasonable price for the crop (~$150/tonne), should be able to grow switchgrass or reed canary grass with minimal inputs on marginal land profitably. This profit could be used as a sole income or to support the rest of the farm in the, currently, less profitable food production area.

Switchgrass proved to have a lower ash content than inter-seeded plots and reed canary grass indicating that switchgrass would be an easier fuel to combust. Adler et al. (2006) determined ash content to be approximately 3.5% for switchgrass while Burvall (1997) determined ash content to be 6.4% for fall harvested reed canary grass and the ash content found in this study confirms that. Inter-seeded mixes had higher ash content which would be harder to burn and garner a lower price for the product. Since yields were lower in some cases for the inter-seeded mix and ash contents higher it does not seem advisable to recommend inter-seeding. Overall ash content is between 3% and 5% which is on the upper end of the acceptable scale for the given combustion technology commercially available today. However technology is improving and should soon be able to handle feedstock’s with this ash content. Time and money would be better spent on advancing the technology to burn these high ash feed-stocks than spending many years breeding perennial grass crops with even lower ash content. This is not to say that specialized breeding programs should be ignored but rather the best short-term solution is to focus on technology. Both of the perennial grasses grown in this experiment provide fairly equal rates of CO_2e offsets within the growing system and therefore crop selection should consider more heavily invasiveness, ease of harvest and establishment as opposed to GHG emissions. Other considerations for combustion would be to separate leaf and stem material and analyze each component for better combustion properties.

Combining GHG emissions is a step involved in calculating the relative GHG offsets for each treatment however it is useful to report the GWP for each treatment without taking into account yield as well. 2008 and 2009 GWP data followed the same trend as the N_2O data presented in CH. 2. When methane and nitrous oxide were combined the lower two rates of fertility had the lowest GWP. Overall the total emissions are very low and are not believed to be a significant contribution to the overall GHG budget. There are much greater emissions, and potential for reduction, from using cleaner burning fuels for transportation and farm equipment, fine-tuning the conversion process to obtain the greatest energy returns and developing a regional network for bioenergy production and use so crops can be used locally to where they are grown. The emissions calculated in this study are also only from the growing process and do not include the emissions from the manufacture of nitrogen fertilizer which contributes approximately 1kg CO_2 for every 1kg N. This would make the higher fertilizer rates less attractive that the lower rates considering there is little to no yield response to fertilizer. Combined GHG emissions of ~100 to 200kg CO_2-e ha^{-1} yr^{-1} from growing the crop are small compared to the GHG mitigation potential of 4t CO2-e ha^{-1} yr^{-1} even when the crop is gasified for electricity generation (Adler et al., 2007). An important point to highlight is the fact that these crops are yielding their highest levels with very small amounts of nitrogen input and show almost no response to fertilizer. With the manufacturing, transporting and physical application of nitrogen fertilizer being one of the biggest contributors to the negative aspect of growing energy crops these perennial grass crops have a huge advantage over first generation or more traditional energy crops such as corn or sugar beets.

3.5 Conclusions

Overall emissions of N_2O were small at less than 1kg ha^{-1} yr^{-1} for even the highest flux. Yields were lower in the inter-seeded mixes because clover tended to choke out the switchgrass early in the spring and it could not establish properly. The ash content for inter-seeded mixes was also higher than pure switchgrass plots resulting in a lower quality product as well. It appears that the clover established too early in the spring and out competed switchgrass resulting in lower yields and lower quality biomass. It is not recommended to inter-seed clover with switchgrass however tilling in alfalfa or clover prior to planting switchgrass may be a good idea because of the base of biologically fixed nitrogen that will be incorporated into the soil. If inter-seeding is desired it would be best to match the N-fixing crop to the growth physiologies of the grass such as inter-seeding a southerly adapted legume to switchgrass however, combustions properties would likely still not be as good as pure switchgrass.

The results of this experiment provide an often ignored or assumed piece of information in N_2O emissions which is important to policy decisions as well as providing information to farmers and extension workers about expected yields of two potential perennial grass energy crops in the Eastern Canadian climate. We have proven that it is possible to grow these crops with minimal inputs and, if the rest of the pieces of the puzzle fall into place, there can be a profitable industry in Nova Scotia providing a grass feedstock for heating or electricity generation. This research has particular relevance to Nova Scotia as a renewable energy industry is in its budding stages and it is my hope that this type of work can continue in the future and examine long-term effects of fertility on yields as well as carbon sequestration in the soil.

CHAPTER 4: CONCLUSIONS

Seasonal and temporal effects appear to be the biggest influence on the cumulative N_2O emissions from the soil, which is not contrary to other research, however between treatments is appears that crop type is the biggest influence on N_2O emissions. This study also shows low N_2O emissions which indicate that N_2O emissions may be a small component of the overall GHG budget of bioenergy crops. The results of this experiment provide an often ignored or assumed piece of information in N_2O emissions which is important to policy decisions as well as providing information to farmers and extension workers about expected yields of two potential perennial grass energy crops in the Eastern Canadian climate. Switchgrass and reed canary grass crops appear to be very good bioenergy crops from both a GHG and combustion point of view which are benefits to development of policy and industry. Some agronomic considerations, such as seedbed preparation, inter-seeding of nitrogen fixing crops and timing of fertilizer, must be made before a successful industry can be developed.

Appendix: ANOVA Tables

2008 N_2O

Source	DF	Sum of Squares	Mean Square	F-Ratio
Model	23	29.9404093	1.30175693	4.79861103
Error	24	6.51066861	0.27127786	Prob > F
C. Total	47	36.4510779	.	0.00015141

2008 CH_4

Source	DF	Sum of Squares	Mean Square	F-Ratio
Model	23	0.11308544	0.00491676	2.28763911
Error	24	0.05158252	0.00214927	Prob > F
C. Total	47	0.16466796	.	0.02467201

2009 N_2O

Source	DF	Sum of Squares	Mean Square	F-Ratio
Model	23	233921.265	10170.4898	1.39119237
Error	24	175455.069	7310.62789	Prob > F
C. Total	47	409376.334	.	0.21368365

2009 CH_4

Source	DF	Sum of Squares	Mean Square	F-Ratio
Model	23	5129543.42	223023.627	1.54903586
Error	24	3455418.43	143975.768	Prob > F
C. Total	47	8584961.85	.	0.14691915

2008 Nitrate Intensity

Source	DF	Sum of	Mean	F-Ratio

		Squares	Square	
Model	23	466.616114	20.2876571	5.1946299
Error	24	93.7321388	3.90550578	Prob > F
C. Total	47	560.348252	.	7.8404e-5

2008 Ammonium Intensity

Source	DF	Sum of Squares	Mean Square	F-Ratio
Model	23	25.3157285	1.10068385	1.35260215
Error	24	19.5300683	0.81375285	Prob > F
C. Total	47	44.8457968	.	0.2337597

2008 Mineral N Intensity

Source	DF	Sum of Squares	Mean Square	F-Ratio
Model	23	522.834142	22.7319192	5.51874219
Error	24	98.8569573	4.11903989	Prob > F
C. Total	47	621.6911	.	4.68576e-5

2009 Nitrate Intensity

Source	DF	Sum of Squares	Mean Square	F-Ratio
Model	23	6.29042165	0.27349659	3.84485274
Error	24	1.70719627	0.07113318	Prob > F
C. Total	47	7.99761792	.	0.00085702

2009 Ammonium Intensity

Source	DF	Sum of Squares	Mean Square	F-Ratio
Model	23	64.7285829	2.81428621	8.35472173
Error	24	8.08439482	0.33684978	Prob > F
C. Total	47	72.8129777	.	1.06497e-6

2009 Mineral N Intensity

Source	DF	Sum of	Mean	F-Ratio

		Squares	Square	
Model	23	11.340362	0.49305922	7.04126471
Error	24	1.68058179	0.07002424	Prob > F
C. Total	47	13.0209438	.	5.33594e-6

Yield 2008

Source	DF	Sum of Squares	Mean Square	F-Ratio
Model	23	3.35338949	0.14579954	2.32858749
Error	24	1.50270885	0.06261287	Prob > F
C. Total	47	4.85609835	.	0.0223937

Yield 2009 *

Source	DF	Sum of Squares	Mean Square	F-Ratio
Model	23	2.18016219	0.09478966	2.5515503
Error	24	0.89159592	0.03714983	Prob > F
C. Total	47	3.07175812	.	0.0133083

Percent Ash 2008

Source	DF	Sum of Squares	Mean Square	F-Ratio
Model	23	33.6132479	1.46144556	3.43463785
Error	24	10.21205	0.42550208	Prob > F
C. Total	47	43.8252979	.	0.00194215

2008 Combined GHG emissions

Source	DF	Sum of Squares	Mean Square	F-Ratio
Model	23	20.3692191	0.88561822	2.74351922
Error	23	7.42448567	0.32280372	Prob > F
C. Total	46	27.7937048	.	0.00947858

2009 Combined GHG emissions

Source	DF	Sum of	Mean	F-Ratio

		Squares	Square	
Model	23	65614.1458	2852.78895	1.45054504
Error	24	47200.8333	1966.70139	Prob > F
C. Total	47	112814.979	.	0.18583133

2008 Average CO_2 offsets

Source	DF	Sum of Squares	Mean Square	F-Ratio
Model	11	0.00163779	0.00014889	1.08155367
Error	12	0.00165195	0.00013766	Prob > F
C. Total	23	0.00328974	.	0.44485846

2009 Average CO_2 offsets

Source	DF	Sum of Squares	Mean Square	F-Ratio
Model	11	26.0716667	2.37015152	1.40095977
Error	12	20.3016667	1.69180556	Prob > F
C. Total	23	46.3733333	.	0.28516148

*Shows significant p-value however it was not due to any treatment effects.

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