Evaluating the potential of biochar in mitigating greenhouse gases emission and nitrogen retention in dairy manure based silage corn cropping systems

By

Waqar Ashiq

A thesis submitted to the School of Graduate Studies

In partial fulfillment of the requirements for the degree of

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Abstract

Greenhouse gas (GHGs) emissions from the agriculture sector have been accelerating global warming potential (GWP) and greenhouse gas intensities (GHGI). About 8 % of GHG emissions in Canada are contributed by the agriculture sector mainly through methane (CH_4) and nitrous oxide (N_2O). Out of these emissions, 50 % is contributed by manure and fertilizer application to land. Biochar (BC), a stable carbon-rich product has been observed to reduce GHG emissions from soil, increase soil pH, improve soil moisture, enhance nutrient retention in soil and increase biomass production in many crop plants. However, these effects are not constant across all soil types, environmental and climatic conditions, and cropping systems. This study aimed to evaluate the effect of BC on GHGs emissions, soil nitrate and ammonium retention, soil pH, plant nitrogen concentration and dry matter production in dairy manure (DM) based silage corn cropping system in western Newfoundland, Canada. Two sources of dairy manure (DM_1, DM_2), inorganic N (IN), their combination with BC (DM_1+B, DM_2+B, and IN+B), and control (N_0) were used as experimental treatments. Results showed that BC application to DM_1, DM_2 and IN reduced cumulative CO_2 emission by 16, 25.5 and 26.5 %, CH_4 emission 184, 200 and 293 %, and N_2O emission by 95, 86 and 93 %, respectively. BC treatments exhibited significantly higher soil moisture (SM) contents at all sampling points than non-BC treatments. It also reduced the GWP by 24.9, 34.5, and 37 %, and GHGI by 30, 37.5, 43.4 %, respectively. Furthermore, BC enhanced the NO_3^- and NH_4^+ retention in topsoil (decreased their leaching to deep soil) which improved plant N concentration and dry matter yield of silage corn crop. Conclusively, BC application to

soil exhibited to be a promising tool for the mitigation of GHGs emissions, GWP, GHGI and to enhance soil fertility and crop dry matter yield simultaneously.

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List of Abbreviations

BC – Biochar

CEC – Cation exchange capacity

CFIA – Canadian food inspection agency

CH_4 – Methane

CO_2 – Carbon dioxide

DAMA – Days after manure application

DM – Dairy manure

DMY – Dry matter yield

DM_1 – Dairy manure with high nitrogen

DM1+B – Dairy manure with high nitrogen + biochar

DM_2 – Dairy manure with low nitrogen

DM_2+B – Dairy manure with low nitrogen + biochar

DOC – Dissolved organic carbon

DON – Dissolved organic nitrogen

EC – Electrical conductivity

ECD – Electrical conductivity detector

FID – Flame ionization detector

GHG – Greenhouse gas

GHGI – greenhouse gas intensity

GWP – Global warming potential

IN – Inorganic nitrogen

IN+B – Inorganic nitrogen + biochar

IPCC – Intergovernmental panel on climate change

KCL – Potassium chloride

MOP – Murate of potash

N_2O – Nitrous oxide

NH_4^+ - Ammonium

$(NH_2)_2 CO$ – Urea

$(NH_4)_2SO_4$ – Ammonium sulfate

NH_4NO_3 – Ammonium nitrate

NO – Nitric oxide

NO_2^- – Nitrite

NO_3^- – Nitrate

N_2O – Nitrous oxide

N_2 – Dinitrogen

Pg – Petagram (10^{15})

PVC – Polyvinyl chloride

RCBD – Randomized complete block design

SM – Soil moisture

SOC – Soil organic carbon

SOM – Soil organic matter

SRF – Slow release fertilizer

ST – Soil temperature

TCD – Thermal conductivity detector

TSP – Triple superphosphate

Chapter 1

1. General introduction and Overview

1.1. Introduction

1.1.1. Overall scenario of greenhouse gas emissions

The emission of greenhouse gases (GHGs) into the atmosphere is the greatest environmental issue of the current time. The unprecedented increase in GHG emissions lead to significant changes on the face of world climate. The main GHGs of consternation include carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). These gases gather in the atmosphere and cause greenhouse effect which leads to global warming. The global warming effect of GHGs can be reported using a global warming potential (GWP) value which quantifies the warming effect of GHGs relative to CO_2 over a set time period (20 years, 100 years or 500 years). The GWP of CH_4 and N_2O over a time horizon of 100 years (GWP_{100}) is 25 and 298 times greater than CO_2 respectively (IPCC, 2007). The total annual anthropogenic GHGs emissions had reached to 49±4.5 (90 % confidence interval) gigatons of carbon dioxide equivalent ($GtCO_2eq$) in 2010. Industrialized countries emit 2.5 times more GHGs than developing countries. Different economic sectors contribute towards global GHGs emissions. Energy supply sector contributed 35 % (17 $GtCO_2eq$), agriculture, forestry and other land use contributed 24 % (12 $GtCO_2eq$), 21 % (10 GtCO2eq) by industry, transport 14 % (7 $GtCO_2eq$), and construction sector 6.4 % (3.2 $GtCO_2eq$) towards a total of 49 $GtCO_2eq$ GHGs emission in 2010 (IPCC, 2014a). The main controlling forces of GHGs emissions include financial structure, the flow of income, choices of investment, policies, people behavior, consumption patterns, energy resources and land use change (IPCC, 2014a).

1.1.2. Agricultural greenhouse gas emissions

The agriculture industry is the largest contributor to the global anthropogenic non-CO_2 GHGs emission, accounting for 54 % of the global non-CO_2 emissions in 2005 (U.S. EPA, 2011). Individual GHGs from the agriculture sector out of total anthropogenic emissions from all sources constitute CO_2 (15 %), CH_4 (50 %) and N_2O (66 %). Between 1990-2010, non-CO_2 emissions from the agriculture sector grew by 0.9 % per year, totaled to be 5.2-5.8 $GtCO_2eq$ per year and comprised about 10-12 % of total anthropogenic emissions (IPCC, 2014a; Tubiello et al., 2013). Agricultural N_2O emissions are anticipated to increase by 35–60 % by 2030 due to increase in the use of N fertilizers and manures (FAO, 2003). Agricultural activities and practices that emit GHGs include enteric fermentation, dairy manure (DM) storages, and inorganic fertilizer application to soil, rice cultivation, manure management, crop residues and biomass burning. The emissions from enteric fermentation and soils represent about 70 %, paddy rice 9-11 %, biomass burning 6-12 % and manure management accounts for 7-8 % of total agricultural emissions. Global emissions from manure management grew by 1.1 % per year between 1961-2010 from 0.57 to 0.99 $GtCO_2eq$ per year (Herrero et al., 2013) and by 3.9 % per year from inorganic fertilizers (0.07 to 0.68 $GtCO_2$ eq per year) (Tubiello et al., 2013). Following this trend the inorganic fertilizers will become the single largest source of non-CO_2 GHGs after enteric fermentation in less than 10 years (IPCC, 2014a).

1.1.3. Nitrogen loss through nitrate leaching and N_2O

The atmosphere consists of 70 % of inert nitrogen (N_2) by volume although there is an enormous amount of N in the atmosphere; it is the most absorbed and most limiting nutrient in the soil. Nitrogen (N) is essential plant nutrient and inevitable for plant growth and development as it is the constituent of all proteins, chlorophyll, coenzymes and nucleic acids. Therefore, appropriate C:N ratio is vital for successful crop production. The use of inorganic nitrogen (IN) is one of the major contributors towards the increased agricultural production in past decades. The total amount of N fertilizers applied to cropland increased from 11.3 Tg N per year in 1961 to 107.6 Tg N per year in 2013 (Lu and Tian, 2017). The N applied to crops or mineralized N from organic sources in soil is taken up by plants, lost in gaseous form or leached in the form of nitrates (NO_3^-). Soil ammonium (NH_4^+) concentration is usually low as most of the NH_4^+ is readily converted to NO_3^- which is not retained in the soil due to the negative charge on soil clay particles (Di and Cameron, 2002). Excessive use of IN and DM application enhance the risk of NO_3^- leaching and consequently increase cost of production, pollute water bodies and pose a serious threat to human health (Fan et al., 2017; Forge et al., 2016; Jokela et al., 2014; Long and Sun, 2012; Masaka et al., 2015). The NO_3^- leaching losses of 55-59 kg per hectare per year with DM application, 30-35 kg per hectare per year from compost application and 25-33 kg per hectare per year from IN application has been reported in a six-year maize-alfalfa crop rotation (Basso and Ritchie, 2005). The annual estimated loss of NO_3^--N from a cornfield in Manitoba was 160 kg per hectare per year (Hargrave and Shaykewich, 1997), whereas, 39-55 kg per hectare per year NO_3^- load has been reported in wheat-maize cropping system in Southern Turkey (Ibrikci et al., 2015). IN and DM applications in agricultural fields increase the concentration of NH_4^+ and NO_3^- which cause a temporary surplus of these ions in the soil. These ions then undergo nitrification and denitrification processes in soil and release N_2O as a byproduct (Chapuis-lardy et al., 2007; Inselsbacher et al., 2011). During nitrification, NH_4^+ is oxidized to NO_3^- via nitrite (NO_2^-) releasing N_2O as a byproduct (Wrage et al., 2001). This is a two-step autotrophic process. The first step is mostly carried out by ammonia oxidizing bacteria (AOB) and ammonia-oxidizing archaea (AOA) whereas, the second step is facilitated by *Nitrobacter sp.,* and *Nitrospira sp.,* under aerobic conditions (Clough et al., 2001). Nitrification process explained by Hossini et al. (2015) in the Equations (1.1) and (1.2).

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+ \quad (1.1)$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \quad (1.2)$$

During denitrification, NO_3^- is reduced to dinitrogen (N_2) via N_2O. This heterotrophic process takes place under oxygen deficit conditions (Flechard et al., 2007; Toyoda et al., 2011). The denitrification process is shown in the Equations (1.3), (1.4), and (1.5) as described by (Hossini et al., 2015).

$$2NO_3^- + 2H_2O \rightarrow 2NO_2^- + 2H_2O \quad (1.3)$$

$$2NO_2^- + 2H_2 \rightarrow N_2O^- + H_2O + 2OH^- \tag{1.4}$$

$$N_2O + H_2 \rightarrow N_2 \uparrow + H_2O \tag{1.5}$$

An important factor which explains the dominance of nitrification and denitrification in the soil is "soil compaction". Soil compaction reduces the soil porosity which leads to increased water-filled pore spaces and reduced oxygen diffusion resulting in the anaerobic conditions which favor denitrification and N_2O production in the soil (Bessou et al., 2010). Increase in soil temperature results in the development of anaerobic microsites in the soil causing denitrification and N_2O emissions (Smith et al., 2003). Generally, soils are source of N_2O, but under certain conditions like high soil moisture (SM) or low N availability, the soil may act as sink of N_2O either caused by the consumption of N_2O by nitrifier during nitrifier denitrification or reduction of N_2O to N_2 during denitrification (Chapuis-lardy et al., 2007). Nitrogen is applied frequently to crops and is one of the priciest inputs in corn production. The N application averages 12-15 % of the variable costs in a corn - silage corn and 18-21 % in corn - corn cropping systems (Plastina, 2018). In spite of that, its cost–benefit ratio generally surpasses that of other fertilizer inputs, but farmers must use N efficiently to maximize its value. At the same time, farmers must ensure that adequate supply of N is available to crop and its yield is not limited by the shortfall of N throughout the growing season. This means minimizing N loss through the application of the right amount of N at right time and developing strategies which decrease N losses. There are different strategies adopted to reduce GHGs emissions and NO_3^- leaching losses including nitrification inhibitors (NI), adaptation of fertilizer management practices to increase efficiency and reducing excess N application to the soil (Burney et al., 2010), Sustainable agriculture intensification (Garnett et al., 2013; Thomson et al., 2012), land drainage and biological N fixation (Rees et al., 2013).

1.1.4. Mitigation options

Different nutrient management strategies and crop management practices have been reported to reduce GHGs emissions and N losses. Carbon (C) sequestration has great potential to reduce global warming and climate change. Decreasing the atmospheric C by 3.5-4 Gt per year could limit the temperature increase to 2 °C by 2050 (Meinshausen et al., 2009; Minasny et al., 2017), a threshold level beyond which climate change would have a significant impact (IPCC, 2014b). This annual reduction in atmospheric CO_2 concentration could be enhanced by increasing soil C sequestration in agricultural soils globally by 0.4 % per year, producing a C sink of 1.2 petagrams (Pg) per year (Paustian et al., 2016). The soils of agroecosystems have a technical potential of 1.2-3.1 billion ton C sequestration per year (Lal, 2011). Different crop management practices can improve soil C sequestration including crop residues incorporation (Coppens et al., 2006), burial of crop residues and crop rotation (Hirel et al., 2007), addition of perennial crops in rotation, no-tillage (West and Post, 2002), legume-based cropping systems (Drinkwater et al., 1998), cover cropping (Mazzoncini et al., 2011), organic amendments like manure (Maillard and Angers, 2014) and biochar (Bera et al., 2016). Nutrient management strategies have also been practiced to reduce N losses and improve N use efficiency (NUE) that includes the use of slow-release fertilizers (Ye et al., 2013), judicious fertilizer application (Francis, 1992), variable rate technologies (VRT) (Gatti et al., 2018), use of nitrification inhibitors (NI) (Zhang et al., 2015), and plant trait selection (Ju et al., 2015). However, the integration of these practices is complicated to get dual benefits of GHGs reduction and mitigation of NO_3^- losses.

1.1.5. Role of biochar role in mitigating gaseous and N losses

Biochar (BC), is a recalcitrant black C material produced by the baking of organic matter under low oxygen conditions and relatively low temperature (<700 ^{o}C) (Dong et al., 2017; Lehmann and Joseph, 2009; Shackley et al., 2010). It has multifaceted benefits including reduction of GHGs emissions (Woolf et al. 2010) and soil compaction, improvement of soil pH, aggregate stability (Wang et al., 2017), soil, permeability, porosity, water holding capacity (WHC), (Basso et al., 2013; Ulyett et al., 2014; Randolph et al., 2017), soil nutrients retention (Uzoma et al., 2011), nutrient availability (Subedi et al., 2016), carbon sequestration (Atkinson et al., 2010; Khare and Goyal, 2013; Laird, 2008; Matovic, 2011), soil organic matter (SOM), cation exchange capacity (CEC), microbial growth and shelter, microbial activity and pollutant degradation (Amendola et al., 2017; Reed et al., 2017; Tan et al., 2017; Upadhyay et al., 2014; Wang et al., 2014). Organic C is mainly stored in the form of stable aromatic compounds in BC and is not decomposed easily even in suitable environmental conditions (Sohi et al., 2010). It has the ability to sequester C for thousands of years due to its recalcitrant chemical composition (Fowles, 2007). The application of BC has historic importance in some parts of the world in order to sequester C. The Terra Preta soils in the Amazon Basin have a large amount of sequestered C as a consequence of the application of BC by American

Indian people thousands of years ago (Lehmann et al., 2006). It also possesses the nutrient holding ability and improves soil physiochemical and biological life thus improves soil structure, aeration, WHC and provides microsites that act as shelter for soil microbes (Johnson et al., 2007; Lehmann et al., 2006) resulting in increased soil fertility (Koide et al., 2011). It improves the plants nutrient use efficiency which reduces nutrients leaching to watercourses thereby reduces environmental pollution (International Biochar Initiative, 2012). In addition to C sequestration, recently it has shown a great potential to mitigate GHGs emissions from agricultural soils, enhance NO_3^- retention, improve nutrient use efficiency and increase plant yield (Felber et al., 2014; Liu et al., 2012a; Taghizadeh-Toosi et al., 2011; Zhang et al., 2011). The nitrate (NO_3^-) and ammonium (NH_4^+) retention in BC amended soils is linked with the reduction of N_2O emission. The BC has high CEC due to the negative charge on its surface which allows it to retain cations such as NH_4^+ (Cheng et al., 2006; Yao et al., 2012). The NO_3^- and NH_4^+ retention in BC amended soils can decrease leaching of these nutrients from these soils (Winning, 2014). A significant decrease in NH_4^+ loss was observed by Lehmann et al. (2002) and Angst et al. (2013). Few studies have reported no effect or increase in NO_3^- leaching after BC application which could be due to weak adsorption and subsequent desorption of NO_3^- by BC due to its low anion exchange capacity (Kameyama et al., 2012; Singh et al., 2010).

1.2. Purpose of the thesis

The principal aim of this thesis was to investigate the potential role of BC in mitigating GHG losses, global warming potential (GWP), greenhouse gas intensity (GHGI), soil

NO_3^- and NH_4^+ retention, soil pH, N uptake, and dry matter yield of silage corn following DM and inorganic N fertilizer application. Studies were carried out with the following specific objectives:

- i- To assess the GHGs emissions from organic and inorganic sources of nitrogen application in silage corn cropping systems
- ii- To determine the role of BC application in the reduction of GHG emission in silage corn cropping systems in western Newfoundland
- iii- To estimate GWP and GHGI of silage corn cropping systems
- iv- To determine the role of BC application on soil NO_3^- and NH_4^+ retention in silage corn amended with DM and IN fertilizer application
- v- To compare the effects of dairy manure and IN alone and co-application of BC on soil pH, N uptake and biomass production of silage corn.

1.3. Thesis organization

This thesis is divided into four chapters with the relevant literature reviewed at the start of each chapter.

Chapter one: Provides a brief overview of global GHG emissions, N losses in the form of NO_3^- and N_2O into the atmosphere, different mitigation strategies to lessen GHGs emissions and NO_3^- leaching and the potential role of BC as a mitigation strategy.

Chapter two: This chapter describes a comparative study about the effect of different organic and inorganic N sources (DM_1, DM_2, IN and BC) on GHGs emissions, GWP, and GHGI of silage corn grown under field conditions in western Newfoundland, Canada.

Chapter three: It covers the potential role of BC on the NO_3^- and NH_4^+ retention, soil pH, plant N concentration and dry matter production of different silage corn genotypes.

Chapter four: This chapter comprised of general discussion, conclusion and recommendations of the study.

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1.5. Co-authorship statement

Manuscripts based on the chapter 2, entitled "*Biochar amendment reduces greenhouse gases emission in silage corn cropping system following dairy manure and inorganic nitrogen application*" and chapter 3 "*Biomass production, and nitrogen dynamics of silage corn as influenced by organic and inorganic nitrogen sources and biochar amendment*" will be submitted to Agriculture, Ecosystems and Environment (Ashiq, W., Nadeem, M., Ali, W., Zaeem, M., Wu, J., Galagedara, L., Kavanagh, V., Cheema, M. 2018). Waqar Ashiq, the thesis author will be the primary author and Dr. Cheema (supervisor), will be the corresponding and the last author. Dr. Wu (co-supervisor) and Dr. Galagedara (committee member) will be sixth and seventh authors, respectively. Dr. Kavanagh, research collaborator, Department of Fisheries and Land Resources will be the eighth author. For the work in Chapter 2 and chapter 3, Dr. Cheema wrote the research grants, developed the layout of this research field trial and helped in results interpretation. Mr. Waqar was responsible for the data collection, analysis, and writing of the manuscript. Dr. Nadeem, Mr. Ali, Mr. Zaeem, contributed in all steps of field and lab work. Dr. Wu provided specific guidance on GHG sample analysis and Dr. Kavanagh helped in experimental layout and seeding of the experiment. Drs. Galagedara, and Nadeem helped in statistical analyses and manuscript editing.

Chapter 2

2. Biochar amendment reduces greenhouse gases emission in silage corn cropping system following dairy manure and inorganic nitrogen application

2.1. Abstract

Biochar (BC) is considered as a mitigation tool for agricultural greenhouse gas (GHG) emissions. To access the effect of biochar application on the GHG emissions from organic and inorganic nitrogen sources applied to silage corn field, a two-year field experiment was conducted in Newfoundland, Canada. The treatments comprised of 1) dairy manure with high N (DM_1:0.37 % N), 2) dairy manure with low N (DM_2:0.13 % N), 3) Inorganic nitrogen (IN), 4) DM_1 + BC, 5) DM_2 + BC, 6) IN + BC, and 7) Control (N_0). Overall, BC application to DM_1, DM_2 and IN reduced cumulative CO_2 emission by 16, 25.5 and 26.5 %, lessened cumulative CH_4 emission by 184, 200 and 293 %, lowered cumulative N_2O emission by 95, 86 and 93 % respectively. It also enhanced the silage corn dry matter yield by 6.8, 4.8, and 11 %, decreased global warming potential (GWP) by 25, 34.6 and 37 %, and contracted greenhouse gas intensity (GHGI) by 29.8, 37.6, and 43 % respectively. In conclusion, BC application demonstrated a great potential to decrease GHG emissions an increase crop yield simultaneously.

Keywords: greenhouse gas emissions, global warming potential, greenhouse gas intensity, silage corn, dairy manure, biochar

2.2. Introduction

Greenhouse gases (GHGs) emitted from different sources gather into the atmosphere and cause higher atmospheric temperature leading to climate change. Anthropogenic greenhouse gas (GHG) emissions have a major contribution towards global warming and climate change and have reached to 49.5 Gt CO_2 equivalent per year in 2010 (IPCC, 2014a). According to Intergovernmental Panel on Climate Change (IPCC, 2014a) "global GHGs emissions have increased to unprecedented levels and must be pulled down by 40-70 % compared to 2010 values by mid-century and near to zero by the end of the century to limit the increase in global mean temperature to 2 °C". Agriculture sector contributes 11-14 % towards global anthropogenic GHG emissions (Conway, 2012; Smith et al., 2007; Tubiello et al., 2015) and these agricultural emissions are increasing at around 1 % per year (Lamb et al., 2016). In 2011, about 8 % of the total GHG emissions in Canada were contributed by the agriculture sector largely through methane CH_4) and nitrous oxide (N_2O) (Agriculture and Agri-Food Canada). From 1981-2011, N_2O emissions had increased by 31 % and CH_4 emission by 2 % from agricultural soils in Canada which were attributed to increased use of nitrogen fertilizers and dairy industry (Agriculture and Agri-Food Canada). Livestock sector produces approximately seven billion tons ($7x10^9$ Mg) of animal manure per year worldwide (Thangarajan et al., 2013). Canadian dairy and livestock sector produces about half a million tons of manure daily which equals to 180 million tons per year (Statistics Canada, 2006). Animal manure is historically known as a rich source of macro and micronutrients, when applied to agricultural soil it improves nutrient availability, soil organic matter (SOM) contents, soil organic carbon (SOC), cation exchange capacity (CEC), and water holding capacity (WHC) etc. (Bolan et al., 2004; Diacono and Montemurro, 2010; Maillard and Angers, 2014). Dairy manure (DM) application to maize increased C sequestration, soil N, P, K concentrations, N, and K uptake, maize biomass and harvest index (Khan et al., 2007). DM application to maize crop improved soil water use, increased SOM, N, P, K, Cu, Zn, Mn, improved biomass allocation into shoot and grains, increased water productivity by 3-5 % and maize yield by 5-10 % (Matsi et al., 2015; X. Wang et al., 2017). However, application of DM and IN to agricultural soils cause emission of a significant amount of GHGs including CO_2, CH_4 and N_2O (Amon et al., 2006; HUANG et al., 2017). Whereas, DM application to soil emits 32.7 % more GHGs than IN alone and these emissions may offset the benefits of improving SOC by DM application (Barneze et al., 2014; M. Zhou et al., 2017). Short-chain volatile fatty acids in the DM are easily available to methanogenic archaea and cause CH_4 outburst into the atmosphere immediately after application (Hrapovic and Rowe, 2002; Sherlock et al., 2002). The total amount of IN applied to agricultural soils is 107.6 Tg N per year worldwide (Lu and Tian, 2017), of which 17 Tg nitrogen is lost every year in the form of N_2O into the atmosphere and the loss is expected to increase four times by 2100 due to increased application of IN (Galloway et al., 2008; Schlesinger, 2009). Reduction of GHG emission and C sequestration has great potential to reduce global warming and climate change. Decreasing the atmospheric carbon by 3.5-4 Gt per year would limit the temperature increase to 2 °C by 2050 (Meinshausen et al., 2009; Minasny et al., 2017), a threshold level beyond which climate change would have a momentous impact (IPCC, 2014b). This annual reduction in atmospheric C concentration could be enhanced by increasing soil C sequestration in agricultural soils globally by 0.4

% per year, producing a C sink of 1.2 petagrams (Pg) per year (Paustian et al., 2016). The soils of agroecosystems have a technical potential of 1.2-3.1 billion ton C sequestration per year (Lal, 2011). A variety of management practices promote soil C sequestration including crop residues incorporation (Coppens et al., 2006), addition of perennial crops in rotation, no-tillage (West and Post, 2002), cover cropping (Mazzoncini et al., 2011), organic amendments like manure (Maillard and Angers, 2014) and biochar (Bera et al., 2016). Some of these practices may be disadvantageous as they increase GHG emissions into the atmosphere like manure application and crop residues incorporation increase N_2O emission (Li et al., 2005; M. Zhou et al., 2017). However, it has been reported that BC application to soil increase C sequestration (Bruun et al., 2012; Hernandez-Soriano et al., 2016; D. A. Laird et al., 2010; D. Wang et al., 2017), increase soil microbial biomass (H. Zhou et al., 2017), enhance WHC and water use efficiency (Ippolito et al., 2016), improve nutrient holding capacity (Hagemann et al., 2017; Laird et al., 2010; Laird et al., 2010), increase crop yield (Liu et al., 2017; Usman et al., 2016; Zhang et al., 2011) and decrease GHGs emission (Ahmed et al., 2016; Cayuela et al., 2013; Chang et al., 2016; Jia et al., 2012; Lan et al., 2017; Liu et al., 2012b; Sun et al., 2014; Wang et al., 2013). Integration of BC in agricultural systems has been proposed as an effective management option to mitigate GHG emissions from soils (Hawthorne et al., 2017; Lehmann, 2007; Thomazini et al., 2015; Van Zwieten et al., 2010a). However, before using BC as a C sequestration tool, it must be verified that its addition does not create adverse effects, e.g. increased GHG emission (Schimmelpfennig et al., 2014). In a two-year field experiment, application of BC increased SOC, pH, total N, and crop productivity however there was no effect on the GWP and GHGI during the first year, but during the second year it decreased GWP and GHGI by 7-18 % and 12-38 %, respectively, in rice cropping system (Zhang et al., 2012). Wheat straw derived BC application at the rate of 24 ton per hectare and 48 ton per hectare decreased GWP by 30.7 and 35.6 %, respectively in double rice cropping system in China (Liu et al., 2014). BC application in intensive vegetable cropping systems with four consecutive vegetable crops had no influence on CH_4 emission while decreased N_2O emission by 1.7-25.4 %, net GWP by 89-700 % and GHGI by 89-644 %, respectively (Li et al., 2015). BC application to soil can reduce GHG emission, GWP and GHGI of maize crop along with improving soil physiochemical and biological properties (Sun et al., 2017; Tan et al., 2017; Yang et al., 2017). It modifies the nutrient transformations in the soil and reduces the emission of GHGs (Castaldi et al., 2011; Liu et al., 2012; Laufer and Tomlinson, 2012; Liu et al., 2017a). BC application to soil amended with slurry reduced the cumulative N_2O and CO_2 emission by 63, and 84 %, respectively while had no effect on CH_4 emissions during first 15 days of slurry application (Brennan et al., 2015). Application of BC to maize crop under field conditions could reduce N_2O emissions by 41.8-52 % (Hüppi et al., 2015; Zhang et al., 2011). In a meta-analysis it was found that BC has the potential to reduce N_2O emissions by 49±5 % and this reduction depends on the degree of polymerization and aromaticity of biochar i.e. biochar with low H : C_{org} ratio reduces N_2O emission more than BC having high H : C_{org} ratio (Cayuela et al., 2015). Soil aeration is significantly increased after BC application which decreases denitrification and reduces N_2O emission (Case et al., 2012; Suddick and Six, 2013). Biochar surface absorbs soil NO_3^- and reduces the substrate for nitrification thus help to reduce N_2O emissions (Mizuta et al., 2004; Taghizadeh-Toosi et al., 2011). Biochar application to soil could also reduce CH_4 emission resulting from manure application. After a series of laboratory and field studies it was found that slurry application increased N_2O and CH_4 emissions from the soil while BC application with slurry increased plant biomass, increased C sequestration, decreased N_2O and CO_2 emission and increased CH_4 oxidation (Schimmelpfennig et al., 2014). Application of bamboo char and straw char reduced CH_4 emissions from waterlogged paddy soil by 51 % and 91 % respectively, which was attributed to inhibition of methanogenic activity and increased CH_4 oxidation (Liu et al., 2011).

There have been numerous studies documenting the GHGs emissions from agricultural soils in tropical areas; however, there is a lack of information concerning the GHG emissions under field conditions in the cool climatic region of Newfoundland. To address this issue and deficit in information, the current study was designed with the following objectives:

i. To assess the GHGs emission from organic and inorganic sources of nitrogen application in silage corn cropping systems.
ii. To determine the role of BC application in enhancing biomass production and reduction in GHG emission in silage corn cropping systems in NL.
iii. To estimate GWP and GHGI of silage corn cropping systems under different dairy manure and biochar treatments

2.3. Materials and Methods

2.3.1. Study site

A field experiment was carried out at Pynn's Brook Research Station, Pasadena (49°04'21.9"N, 57°33'37.4"W) in Newfoundland, Canada, during 2016 and 2017 growing seasons. The soil of this area is classified as rapidly drained, Orthic Humo-Ferric Podzol with reddish brown to brown color. The soil has developed on gravely sandy fluvial deposit of mixed lithology. Due to high coarse fragments and rapid drainage it has a limited agricultural use. The best-suited crops for this soil are hey and forage crops (Kirby, 1988). Basic physio-chemical properties of soil can be seen in Table 2.1.

Table 2.1: Basic soil properties of the experimental site at Pynn's Brook Research Station

Site characteristics	**Description**
Soil class	Orthic Humo-Ferric Podzol
Soil texture (10-15 cm depth)	Gravelly loamy sand: sand (82±3.4 %), silt (11.6±2.4 %), clay (6.4±1.2 %)
Soil parental material	Channery, gravely sandy stratified fluvial deposit
Elevation	45 m
Soil drainage class	Well to rapidly drained
Soil pH	6.3 (2016), 6.8 (2017)
Average bulk density	1.31±0.07 g cm^{-3}
Average porosity	51±0.03 %
Gravel	20 % in top 5 cm layer
Average soil organic matter	3.10 %
CEC	12 cmol/kg
Previous Crop (2015)	Silage corn

2.3.2. Experimental setup and treatments

The experiment comprised of three nitrogen sources amended with BC. Treatments included were; 1) DM with high N conc. (0.37 %) designated as DM_1, 2) DM with low N conc. (0.13 %), designated as DM_2, 3) Inorganic nitrogen (IN), 4) DM_1+Biochar, 5) DM_2+Biochar, 6) IN + Biochar, and 7) control (N_0). DM was collected from two dairy farms (Larch Grove and Rideout Junior) located in Cormack area near Deer Lake, Newfoundland and Labrador (NL). Soil and DM samples were sent for detailed nutrient analyses to Soil, Plant and Feed Laboratory, Department of Fisheries and Land Resources, St. John's, NL. DM from Larch Grove farm (designated as DM_1) exhibited high concentration of N, P, K, Ca, Mg, Fe, Mn, Zn, B whereas, DM sourced from Rideout Junior farm (designated as DM_2) had a low concentration of N, P, K, Ca, Mg, Fe, Mn, Zn, B (Table 2.2). DM was applied before seeding in respective plots according to local farmers practice i.e. 30,000 liters per hectare. Fertilizers were applied to fulfill the required nutrients based on DM and soil analyses reports and regional recommendations of the crop. Ammonium nitrate (AN), triple superphosphate (TSP) and murate of potash (MOP) were used as nitrogen (N), phosphorus (P), and potash (K) sources, respectively and were applied @ 215,110, 225 kg per hectare. DM_1, DM_2 and the entire IN were applied before crop seeding during 2016 while in 2017 DM_1 and DM_2 were applied to all respective treatments (DM_1, DM_2, DM_1+B, DM_2+B) before seeding but the IN fertilizer was applied in two splits (first dose: 6 leaf stage, second dose: 12 leaf stage). The experimental design was a randomized complete block (RCBD) with three replications and net plot size was 4.8 meters x 1.5 meters.

Table 2.2: Chemical analysis of dairy manures used in the study

Characteristic (as received basis)	Larch Grove farm (DM_1) 2016	2017	Rideout Junior farm (DM_2) 2016	2017
Dry matter (%)	9.33	10.9	3.57	1.70
pH	6.80	6.80	7.00	7.10
Total Nitrogen (%)	0.37	0.44	0.14	0.12
Total Phosphorus (%)	0.06	0.08	0.02	0.01
Total Potassium (%)	0.38	0.37	0.12	0.12
Total Calcium (%)	0.16	0.19	0.059	0.04
Total Magnesium (%)	0.07	0.07	0.02	0.01
Total Iron (ppm)	49.0	68	19.0	7.00
Total Manganese (ppm)	23.0	21.0	9.00	5.00
Total Copper (ppm)	4.70	4.50	33.0	20.0
Total Zinc (ppm)	17.0	21.0	8.00	5.00
Total Boron (ppm)	3.00	3.40	1.00	0.50
Total Sodium (ppm)	911	904	275	241

2.3.3. Crop husbandry

DM and BC were applied one day before seeding and mixed in the soil to 15 cm depth. Seeding of silage corn hybrid (Yukon R) was done with the SAMCO 2200 system (SAMCO Agricultural Manufacturing Ltd) on May 24 and May 23 during 2016 and 2017, respectively. This system has an advantage that it can cover the seed rows with degradable polythene sheet while seeding, which allows accumulating maximum heat during the cold season for seed germination (Figure 2.1). This sheet had several pin holes which allow the trapped air under the sheet to escape and keep it tight to the soil. These pin holes weaken the sheet allowing the plants easy access through the sheet while maintaining soil temperature. Seeding rate for the crop was 90,900 seeds per hectare. Weeds were controlled with the spray of Roundup WeatherMax on July 09, 2016 and July 08, 2017 at the rate of 2 L per hectare. BC used in the study was purchased from AirTerra Inc. located in Calgary, Alberta, and is a registered BC product with the Canadian Food Inspection Agency (CFIA), which is the first in Canada. It was produced from yellow pine wood pyrolyzed at 500 ^{o}C for 30 min in oxygen-limited conditions. BC was applied @ 20 tons ha^{-1} (Liu et al., 2012b). The detailed BC analyses report conducted by Gabilan laboratory, Salinas, California, USA can be seen in Table 2.3.

Figure 2.1: Silage corn seeding with SAMCO 2200

Table 2.3: Physio-chemical properties of biochar used in the study

Property	Wet basis	Dry weight basis
pH	9	-
ECe (mmhos/cm	0.43	-
Moisture (%)	15.2	
WHC (mL water per 100g dry char)	74.9	74.9
Volatile matter (%)		8.5
Ash (%)		6.7
Fixed carbon (%)		84.5
H (%)		0.68
O (%)		7.84
N (%)		0.22
S (%)		0
H/C		0.1
O/C		0.07
Total ash (%)	6	7.1
Recalcitrant carbon (%)	64.6	76.2
Neutralizing value (% as $CaCO_3$)	4.2	4.9
Carbonate value (% as $CaCO_3$)	0.5	0.6
Butane activity (g/100g dry char)		5.1
Bulk density (Mg/m^3)	0.23	0.19
Particle density (acetone) (g/cc)		1.57
Solid space (% v/v)		12.5
Void space (% v/v)		87.5

2.3.4. Greenhouse gas sampling and analysis

GHG samples were collected weekly in the first month and then fortnightly for the whole growing seasons using static chamber method (Holland et al., 1999). The Polyvinyl chloride (PVC) collars with an inner diameter of 26 cm were inserted permanently to a depth of 10 cm in each plot one week before the start of 1st GHGs sampling to mitigate any placement disturbance. A 50 cm high PVC chamber with 26 cm diameter and covering lid was fixed on the top of each collar during GHGs sampling. Chamber top lid had tubing outlets connected with three-way stopcocks with Luer-lock tip. For each measurement, four gas samples were taken from the chamber using a 30 mL non-sterile syringe fitted with a three-way stopcock (BD Luer-lock tip) at 10 min intervals (0, 10, 20 and 30 min after lid closure) (Wang et al., 2012; Chen et al., 2015). To minimize any effect of diurnal variation in emissions, the samples were taken at the same time of the day (9 am - 3 pm) on each sampling occasion. During each GHG sampling event, soil moisture (SM) content (volume basis) and EC (5 cm depth), and soil temperature (ST) (5 cm and 20 cm depth) were also monitored by SM and temperature probes (EC-TM model, Decagon Devices Inc.) from each treatment (Figure 2.2).

GHG samples were transferred to evacuated clear Labco Exetainer® glass vials (Vial type 3-soda glass, height 101 mm, diameter 15.5 mm, capacity 12 mL) sealed with gas-tight neoprene septum. Quantification of GHGs i.e. CO_2, CH_4 and N_2O was carried out by gas chromatography (SICON GC-456 Bruker) equipped with thermal conductivity detector (TCD), flame ionization detector (FID), and electron capture detector (ECD) (Collier et al., 2014). All the fluxes were adjusted for headspace volume and chamber area as explained by (Holland et al., 1999), and calculated by linear regression using all time points sampled: $F = (dC/dt) \times V/A$ (where, V is volume of the chamber, A is the area covered by chamber, and dC/dt is the rate of concentration change). Cumulative GHG fluxes during the experimental period were calculated by multiplying the mean fluxes of two successive determinations by the length of the period between samplings and adding that amount to the previous cumulative total as described in Equation (2.1) (Cai et al., 2013; Menéndez et al., 2006).

$$\text{Cumulative flux} = \sum_{i=1}^{n} (F_i + F_{i+1}) / 2 \times (t_{i+1} - t_i) \times 24 \tag{2.1}$$

Where F is the GHGs flux (mg m^{-2} h^{-1}), i is the i^{th} measurement, the term of (t_{i+1} - t_i) is the days between two adjacent sampling events, and n is the total number of sampling events.

Figure 2.2: Recording soil temperature, moisture and EC (a), sampling chambers fixed over sampling spots in a crop row (b), GHGs sample collection with (c)

2.3.5. Global warming potential and greenhouse gas intensity calculation

Global warming potential is the relative measure of how much warming is caused by a certain gas as compared to same mass of CO_2. Whereas greenhouse gas intensity is the measurement of the total emissions from a system per unit of the produce. GWP of CO_2, CH_4, and N_2O and GHGI were calculated by Equation (2.2) and (2.3), respectively (Yang et al., 2017; Zhang et al., 2013, 2012; Z. S. Zhang et al., 2014).

$$\text{GWP (kg CO}_{2\text{ eq}}) = \text{CO}_2 + \text{CH}_4 \times 25 + \text{N}_2\text{O} \times 298 \quad (2.2)$$

$$\text{GHGI (kg CO}_{2\text{ eq}} \text{ per kg dry matter yield}) = {}^{\text{GWP}}/_{\text{dry matter yield}} \quad (2.3)$$

2.3.6. Dry matter production

Plants were harvested from a 1 m^2 area at black layer stage from each plot and their fresh weight was recorded. Plants were oven dried at 70 ^oC for 48 h and dry matter yield (DMY) was calculated from each treatment plot using Equations(2.4) and (2.5).

Percent dry matter was calculated by;

$$\text{Percent dry matter (\%)} = \frac{\text{oven dry weight}}{\text{fresh weight}} \times 100 \quad (2.4)$$

DMY was calculated by multiplying dry matter percentage with the fresh weight of plants

$$\text{DMY per hectare} = \text{Percent dry matter} \times \text{fresh weight m}^{-2} \times 10{,}000 \quad (2.5)$$

2.3.7. Statistical analysis

The analysis of variance (ANOVA) was used to determine the effect of different treatments on the emission of CO_2, CH_4 and N_2O, DMY, GWP and GHGI. Where treatment effects were significant, the means were compared with LSD ($\alpha = 0.05$). The data were analyzed using the Statistix 10 software package (Analytical software, FL, USA) and figures were prepared using SigmaPlot 12.0 software program (Systat Software Inc., San Jose, CA).

2.4. Results

2.4.1. CO_2 flux

Data presented in Tables 2.4 and 2.5 show that DM_1, DM_2, and IN alone and in combination with BC had significantly (*$p<0.05$*) affected CO_2 emission during both growing seasons. Cumulative CO_2 emission was maximum (7,834 kg ha^{-1} season^{-1}) in DM_1 treatment and minimum cumulative CO_2 emission (5,576 kg ha^{-1} season^{-1}) was observed in IN+B treatment during the 2016 growing season (Table 2.4). In the 2017 growing season, CO_2 emission pattern in treatments was the same as 2016, but cumulative emission was lower. The DM_1 treatment emitted more cumulative CO_2 (7,078 kg ha^{-1} season^{-1}) while minimum (3,800 kg ha^{-1} season^{-1}) was noted in the IN+B treatment (Table 2.5). BC application to DM_1, DM_2 and IN significantly (*$p<0.05$*) reduced cumulative CO_2 emission by 17, 25 and 26 % in 2016 (Table 1), while it was reduced by 15, 26 and 27 % in 2017, respectively. Significant temporal variation in CO_2 emission was noted in both years. Maximum CO_2 emission (439 mg m^{-2} h^{-1}) was observed 90 days after manure application (DAMA) in DM_2 treatment and minimum emission (77 mg m^{-2} h^{-1}) was noticed in N_0 (control) treatment at 146 DAMA during 2016 (Figure 2.3a). In 2017, CO_2 emission at 60 DAMA was greatest (462 mg m^{-2} h^{-1}) in DM_1 and least emission (44 mg m^{-2} h^{-1}) was recorded in N_0 treatment at 29 DAMA (Figure 2.4a).

Table 2.4: Cumulative greenhouse gas emission/absorption of CO_2, CH_4 and N_2O (Kg ha^{-1} $season^{-1}$), global warming potential (kg CO_2 equivalent), silage corn dry matter yield (kg ha^{-1}), and greenhouse gas intensity (kg CO_2 equivalent per kg dry matter yield), during growing season 2016.

Treatment	**CO_2**	**CH_4**	**N_2O**	**GWP**	**DMY**	**GHGI**
DM1	7834±476^{a}	1.26±0.9^{a}	1.69±0.2^{a}	8372±433^{a}	19797±173^{c}	0.42±0.02^{a}
DM1+B	6430±169^{b}	-1.42±0.1^{b}	-0.15±0.1^{d}	6350±203^{b}	21050±125^{a}	0.30±0.01^{b}
DM2	7652±31^{a}	0.83±0.5^{a}	2.17±0.1^{a}	8319±293^{a}	19567±240^{c}	0.42±0.01^{a}
DM2+B	5666±16^{b}	-1.01±0.4^{b}	0.59±0.1^{bc}	5819±202^{cd}	20433±176^{b}	0.28±0.01^{bc}
IN	7566±37^{a}	0.86±0.5^{a}	1.80±0.3^{a}	8126±332^{a}	18813±135^{d}	0.43±0.02^{a}
IN+B	5576±29^{b}	-1.69±0.6^{b}	0.24±0.1^{bc}	5607±268^{d}	20533±176^{ab}	0.27±0.01^{c}
N0	5961±11^{b}	-0.10±0.2^{ab}	0.89±0.0^{b}	6224±105^{bc}	15300±152^{e}	0.40±0.00^{a}

Means sharing common letters in each column are not significantly different (at 0.05 probability level).

Table 2.5: Cumulative greenhouse gas emission/absorption of CO_2, CH_4 and N_2O (Kg ha^{-1} $season^{-1}$), global warming potential (kg CO_2 equivalent), silage corn dry matter yield (kg ha^{-1}), and greenhouse gas intensity (kg CO_2 equivalent per kg dry matter yield), during growing season 2017

Treatment	**CO_2**	**CH_4**	**N_2O**	**GWP**	**DMY**	**GHGI**
DM1	7078 ± 639^{a}	11.6 ± 3^{a}	1.95 ± 0.27^{a}	7953 ± 660^{a}	15983 ± 258^{bc}	0.49 ± 0.04^{a}
DM1+B	5957 ± 714^{ab}	-6.5 ± 3^{bc}	0.33 ± 0.13^{b}	5894 ± 653^{b}	17160 ± 105^{a}	0.34 ± 0.04^{c}
DM2	5601 ± 806^{abc}	11.5 ± 2^{a}	1.63 ± 0.10^{a}	6377 ± 770^{b}	15667 ± 218^{c}	0.40 ± 0.04^{b}
DM2+B	4100 ± 754^{bc}	-9.1 ± 5^{bc}	-0.01 ± 0.51^{b}	3868 ± 999^{cd}	16483 ± 44^{ab}	0.23 ± 0.06^{d}
IN	5248 ± 740^{abc}	9.9 ± 3^{a}	1.47 ± 0.20^{a}	5936 ± 659^{b}	14580 ± 408^{d}	0.40 ± 0.05^{b}
IN+B	3800 ± 465^{c}	-19 ± 5^{c}	0.19 ± 0.16^{b}	3382 ± 539^{d}	16483 ± 130^{ab}	0.20 ± 0.03^{d}
N0	3997 ± 561^{bc}	-0.28 ± 5^{ab}	0.96 ± 0.56^{ab}	4277 ± 745^{c}	11200 ± 152^{e}	0.38 ± 0.06^{bc}

Means sharing common letters in each column are not significantly different (at 0.05 probability level)

2.4.2. CH_4 flux

Experimental treatments (DM_1, DM_2, and IN alone and in combination with BC) had significantly ($p<0.05$) affected CH_4 emission during 2016 and 2017 growing seasons (Table 2.4 & 2.5). Comparison of treatment's means showed that cumulative CH_4 emission was greatest (1.26 kg ha^{-1} $season^{-1}$) in DM_1 treatment, whereas, IN+B treatment exhibited maximum (1.69 kg ha^{-1} $season^{-1}$) cumulative CH_4 absorption during 2016 growing season (Table 2.4). However, DM_1, DM_2, and IN treatments were statistically non-significant with each other. In the 2017 growing season, cumulative CH_4 emission was higher as compared to 2016 and DM_1 treatment emitted more cumulative CH_4 (11.6 kg ha^{-1} $season^{-1}$), while maximum absorption (19.5 kg ha^{-1} $season^{-1}$) was noted in the IN+B treatment (Table 2.5). BC application to DM_1, DM_2 and IN treatments significantly ($p<0.05$) reduced cumulative CH_4 emission/increased absorption by 213, 221 and 295 % in 2016 (Table 1), while it was 156, 179 and 291 % in the 2017 growing season, respectively. There was a significant temporal variation in CH_4 emission/absorption during both years, which may be attributed to great variation in soil temperature during both growing seasons (Helbig et al., 2017). Maximum CH_4 emission (0.13 mg m^{-2} h^{-1}) was noted in DM_1 treatment after 103 DAMA and maximum absorption (0.17 mg m^{-2} h^{-1}) was observed in IN+B treatment at 20 DAMA during 2016 (Figure 2.3b). In 2017 growing season, DM_2 treatment emitted more CH_4 emission (1.78 mg m^{-2} h^{-1}) at 127 DAMA and IN+B treatment showed the highest absorption (1.2 mg m^{-2} h^{-1}) at 127 DAMA (Figure 2.4b).

2.4.3. N_2O flux

Data presented in Tables 2.4 and 2.5 show that DM_1, DM_2, and IN treatments alone and in combination with BC had significantly (*$p<0.05$*) affected N_2O emission during both growing seasons. Cumulative N_2O emission was maximum (2.17 kg ha^{-1} $season^{-1}$) in DM_2 treatment compared to minimum cumulative N_2O emission (-0.15 kg ha^{-1} $season^{-1}$) that was observed in DM_1+B treatment during 2016 growing season (Table 2.4). Whereas, in 2017 DM1 treatment produced more cumulative N_2O (1.95 kg ha^{-1} $season^{-1}$) while DM_2+B treatment emitted minimum (-0.01 kg ha^{-1} $season^{-1}$) N_2O (Table 2.5). BC application to DM_1, DM_2 and IN significantly (*$p<0.05$*) reduced cumulative N_2O emission by 108, 72 and 86 % in 2016 (Table 2.4), while in 2017 it was reduced by 82, 100 and 86 %, respectively (Table 2.5) Significant temporal variation in N_2O emission was also noted in both years. N_2O emission was greatest (0.25 mg m^{-2} h^{-1}) in DM_2 treatment at 34 DAMA and minimum emission (-0.07 mg m^{-2} h^{-1}) was noted in the DM_1+B treatment at 117 DAMA during 2016 (Figure 2.3c). In 2017, N_2O emission at 127 DAMA was greatest (0.15 mg m^{-2} h^{-1}) in DM_1 and least emission (-0.05 mg m^{-2} h^{-1}) was recorded in the DM_1+B treatment at 46 DAMA (Figure 2.4c).

2.4.4. Global warming potential, dry matter yield and greenhouse gas intensity

GWP and GHGI of all experimental treatments are shown in Table 2.4 for the 2016 growing season and in Table 2.5 for the 2017 growing season. There was a significant ($p<0.05$) effect of treatments on the GWP and GHGI during both years. During 2016, the highest GWP (8,372 kg CO_2 equivalent) and the lowest GWP (5,607 kg CO_2 equivalent) were observed in DM_1 and IN+B, respectively. DMY ranged from 15,300 kg ha^{-1} in the control to 21,050 kg ha^{-1} in DM_1+B. Maximum GHGI (0.43 kg CO_2 equivalent kg^{-1} dry matter) was in IN whereas minimum (0.27 kg CO_2 equivalent kg^{-1} dry matter) was observed in IN+B. BC application to DM_1, DM_2, and IN reduced GWP by 24, 30, and 31 % respectively, increased dry matter production by 6.3, 4.4, and 9 %, and decreased GHGI by 28.9, 33 and 36.8 % respectively. **During 2017,** the maximum GWP (7,954 kg CO_2 equivalent) and the lowest (3,382 kg CO_2 equivalent) were observed in DM_1 and IN+B respectively. DMY ranged from 11,200 kg ha^{-1} in control to 17,160 kg ha^{-1} in DM_1+B. GHGI was highest in DM_1 (0.49 kg CO_2 equivalent kg^{-1} dry matter) whereas minimum (0.20 kg CO_2 equivalent kg^{-1} dry matter) was observed in IN+B. BC application to DM_1, DM_2, and IN reduced GWP by 26, 39, and 43 %, increased DMY by 7, 5, and 13 %, and decreased GHGI by 31, 42 and 50 %, respectively.

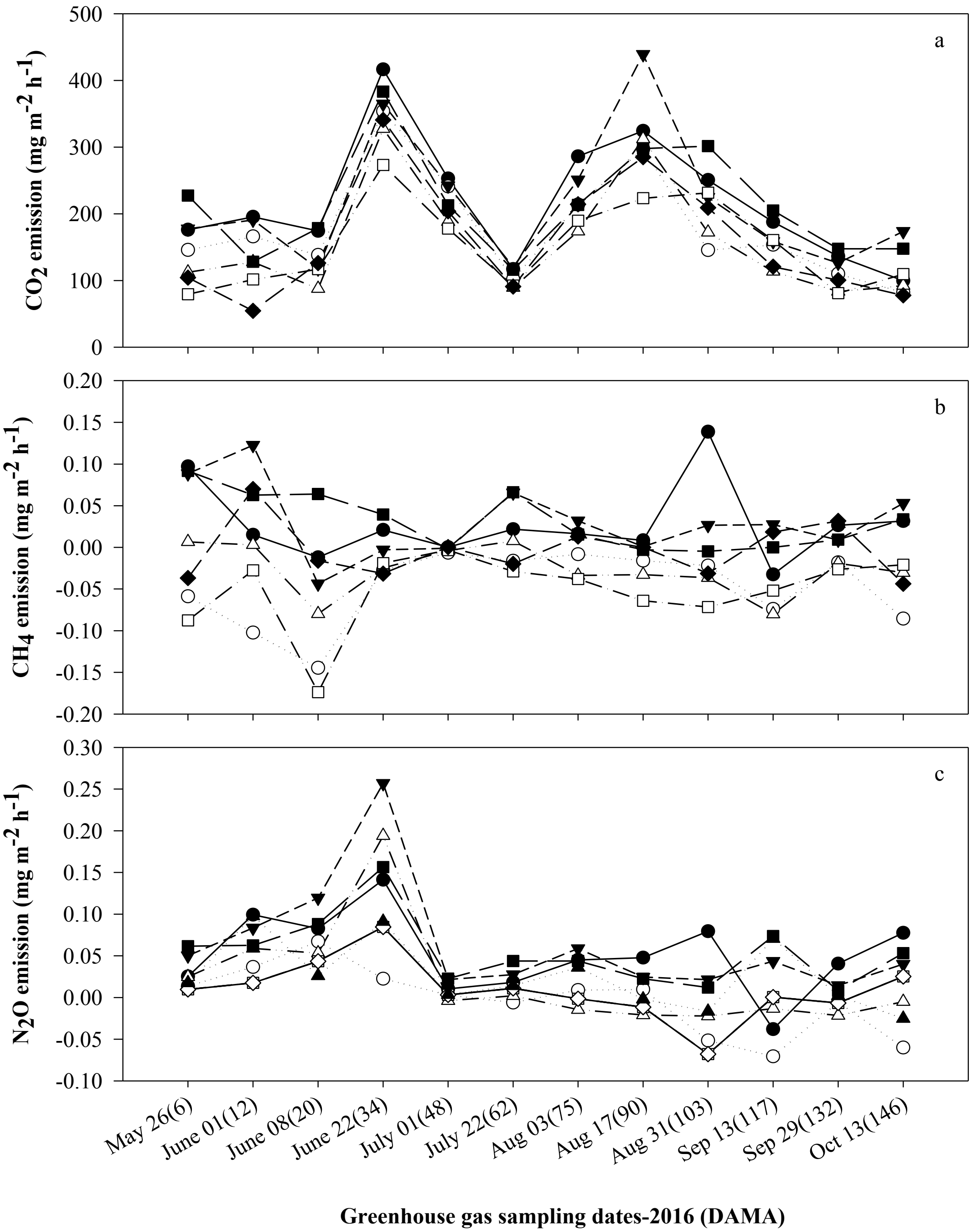

Figure 2.3: Temporal greenhouse gas emission during growing season 2016

(a) CO_2 (b) CH_4 (c) N_2O, Solid circle (DM_1), empty circle (DM_1+B), solid triangle (DM_2), empty triangle (DM_2+B), Solid square (IN), empty square (IN+B), solid diamond (N_0)

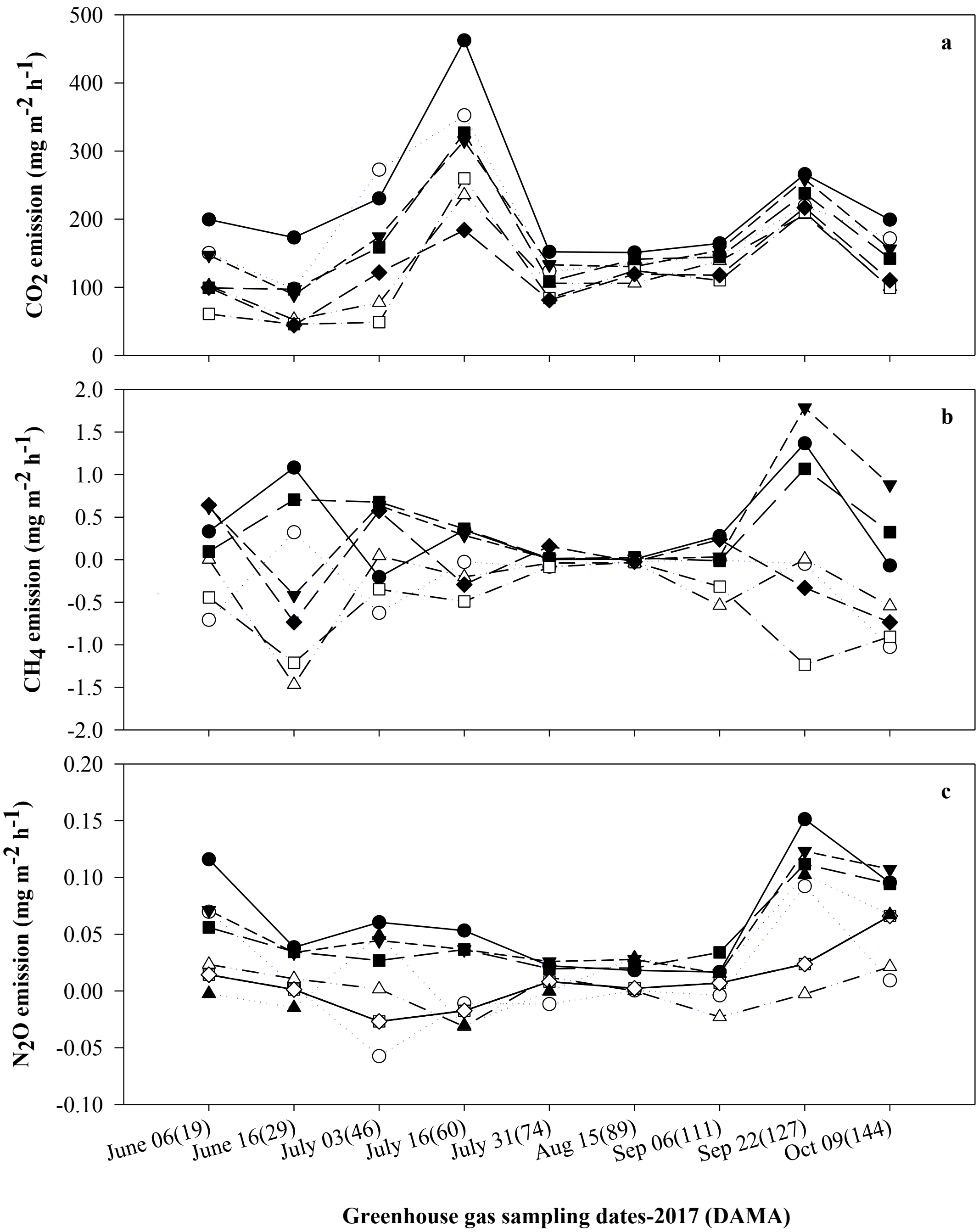

Figure 2.4: Temporal greenhouse gas emission during growing season 2017

(a) CO_2 (b) CH_4 (c) N_2O, Solid circle (DM_1), empty circle (DM_1+B), solid triangle (DM_2), empty triangle (DM_2+B), Solid square (IN), empty square (IN+B), solid diamond (N_0)

2.5. Discussion

2.5.1. Meteorological conditions:

Newfoundland has a unique climate and characterized with relatively short and cool growing period from May to October. Relatively low temperature was recorded during crop seeding (May) and harvesting (October) periods during both study years. However, mean maximum, mean minimum and mean average temperature was slightly lower during 2017 than 2016 with few exemptions. The average seasonal rainfall was significantly lower (30 % less) in 2017 compared to 2016 (Table 2.6). Well distributed rainfall was recorded during 2016 whereas the second growing season was characterized not only by low rainfall but also a completely dry period during June where the crop was at the active growth stage.

Table 2.6: Weather conditions (biweekly average) during silage corn growing season in 2016 and 2017 at Pynn's Brook Research Station

Growth period	Mean max. Temp. (^oC)	Mean min. temp. (^oC)	Average temp. (^oC)	Rain (mm)	Mean Max. Temp. (^oC)	Mean Min. temp. (^oC)	Average temp. (^oC)	Rain (mm)
	2016				2017			
May 01-15	12.06	0.26	6.16	37	12.8	-1.46	5.66	11
May 16-31	16.06	2.68	9.37	47	13.06	0.0	6.53	47
June 01-15	14.86	4.40	9.63	107	15.33	3.53	9.43	35
June 16-30	23.26	7.73	15.5	41	21.46	8.40	14.93	45
July 01-15	21.0	7.93	14.46	42	23.33	8.8	16.06	29
July 16-31	24.81	10.93	17.87	40	24.18	8.31	16.25	12
August 01-15	23.06	10.06	16.56	27	23.8	9.46	16.63	58
August 16-31	21.75	10.0	15.87	112	22.12	6.87	14.5	32
September 01-15	18.4	7.46	12.93	98	19.06	7.53	13.3	80
September 16-30	14.2	3.26	8.73	35	15.33	2.86	9.1	76
October 01-20	14.05	0.4	7.22	118	12.8	2.4	7.6	76
Total				704				501

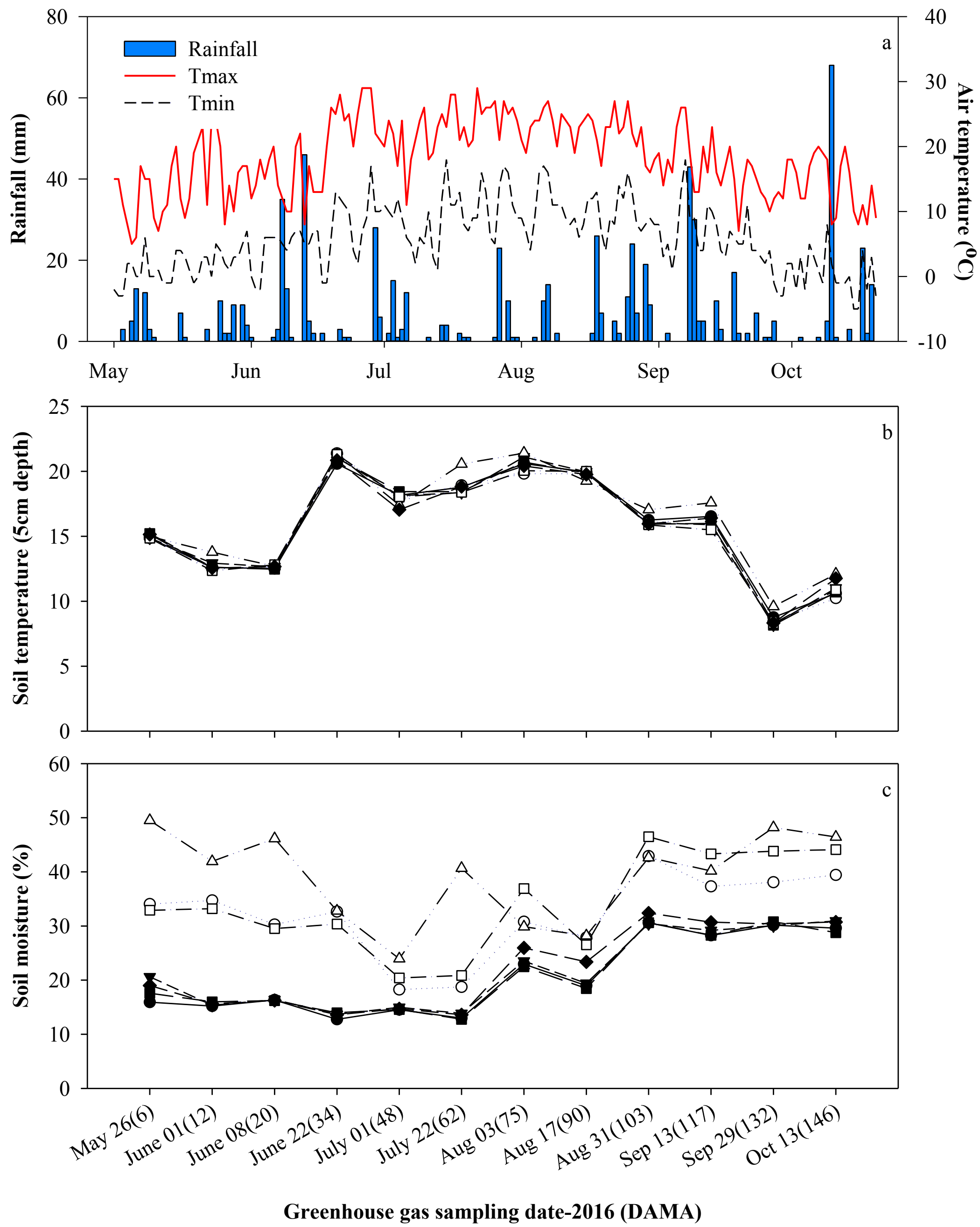

Figure 2.5: (a) Air temperature and rainfall at Pynn's Brook Research Station (b) soil temperature at 5cm depth, and (c) soil moisture at different greenhouse gas sampling dates during growing season 2016.

Solid circle (DM_1), empty circle (DM_1+B), solid triangle (DM_2), empty triangle (DM_2+B), Solid square (IN), empty square (IN+B), solid diamond (N_0)

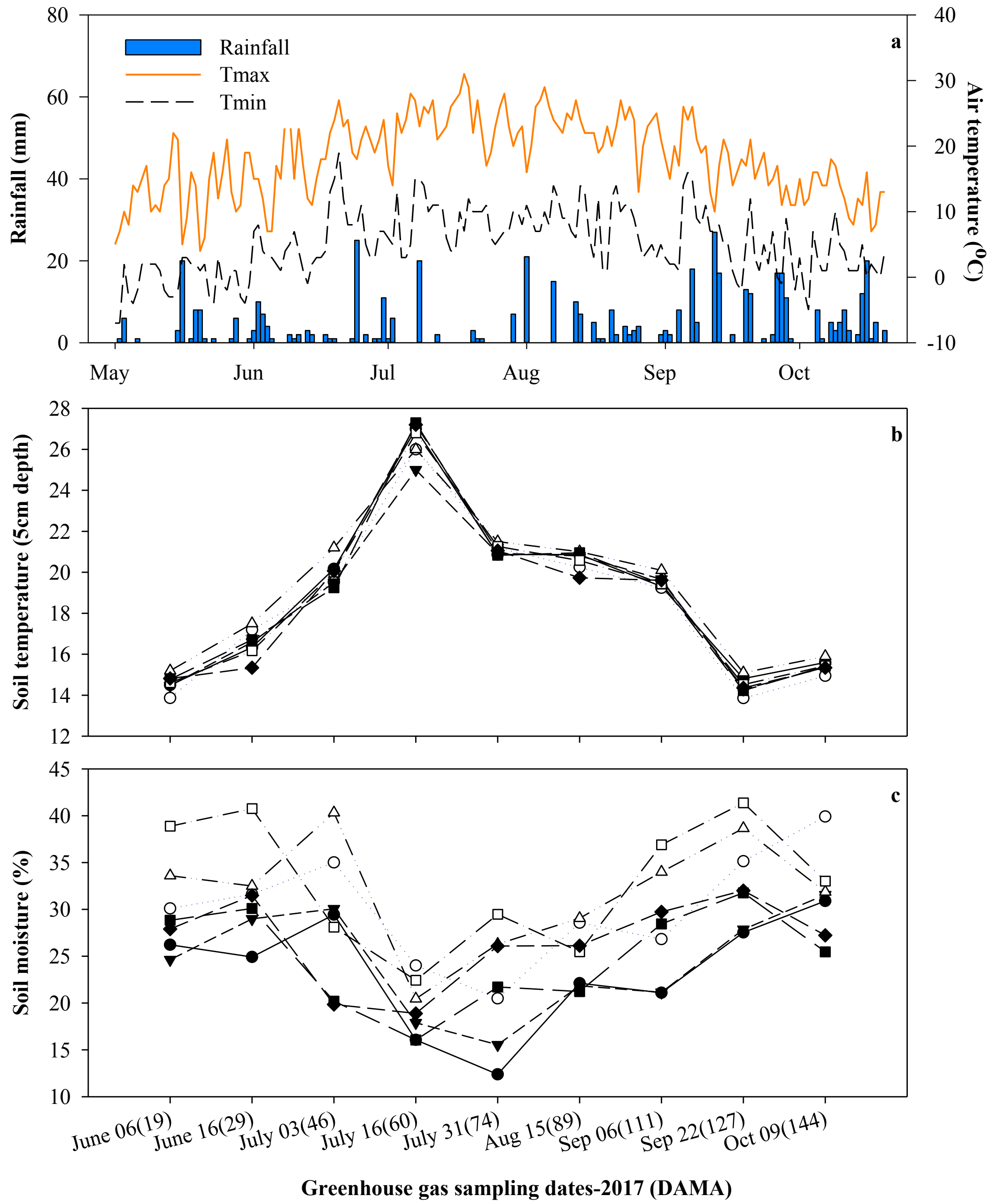

Figure 2.6: (a) Air temperature and rainfall at Pynn's Brook Research Station (b) soil temperature at 5cm depth, and (c) soil moisture at different greenhouse gas sampling dates during growing season 2017.

Solid circle (DM_1), empty circle (DM_1+B), solid triangle (DM_2), empty triangle (DM_2+B), Solid square (IN), empty square (IN+B), solid diamond (N_0)

2.5.2. CO_2 emission

Maximum CO_2 emission reached the peak of 439 mg m^{-2} h^{-1} at 90 DAMA in the 2016 growing season. This peak could be directly related to highest ST and lowest SM, during the period between 79-90 DAMA (Figure 2.5b). In 2017, the maximum CO_2 emission peak occurred at 60 DAMA when ST was the highest (25 ^{o}C) and SM was the lowest of the whole growing season (Figure 2.6). Similarly, the minimum CO_2 emission events in both growing seasons were related to ST and SM. During 2016, minimum CO_2 emission was observed at 146 DAMA when ST was the lowest (9.8 ^{o}C) and SM was the maximum (35.7 %) (Figure 2.5), while in 2017, minimum emission was recorded at 29 DAMA when ST was relatively low (16.5 ^{o}C) and SM was relatively high (31 %). There was a significant reduction in CO_2 emission in BC treatments (DM_1+B, DM_2+B, IN+B) as compared to non-BC treatments (DM_1, DM_2, IN) (Figure 2.6). DM incorporation to soil increased cumulative CO_2 emission over the season. DM application increases the soil CO_2 emission directly from C compounds in the DM and also by inducing a priming effect on native soil C (Bol et al., 2003). It had been reported in several studies that BC application reduces CO_2 emission. BC application to DM amended soil reduced cumulative CO_2 emission by 84 % most probably due to sorption of CO_2 on BC surface or a reduction in the availability of labile C (Brennan et al., 2015). Both positive and negative response of BC have been reported on CO_2 emission, for example, (Spokas and Reicosky, 2009)of the sixteen BC types evaluated, three have reduced, five have increased and eight have no impact on CO_2 emissions from agricultural soils (Spokas and Reicosky, 2009). Manure treatments (DM_1, DM_2) have high CO_2 emission rates than IN and BC treatments, which can also be supported with previous studies (Agegnehu et al., 2016; Lentz et al., 2014; Schimmelpfennig et al., 2014). The decline in dissolved organic carbon (DOC) from native SOC after BC addition reduced the decomposition of organic C which reduced CO_2 emission from the soil by 64-68 % (Lu et al., 2014). BC induced negative priming effect and slowed the breakdown of SOM by different mechanisms including; (1) sorption of enzymes responsible for SOM breakdown, (2) shift in microbial metabolism, (3) enhanced stability of soil aggregates and microbial community shift towards low C turnover bacteria taxa (Zheng et al., 2018), and (4) decreased bioavailability of SOC via adsorption on BC large surface area (Sheng and Zhu, 2018).

2.5.3. CH_4 flux

The studied site acted both as a source and a sink of CH_4. During the 2016 growing season, the highest CH_4 emission (0.13 mg m^{-2} h^{-1}) occurred at 103 DAMA when the SM was the highest (36.5 %) (Figure 2.5), whereas in 2017, the highest emission (1.78 mg m^{-2} h^{-1}) was recorded at 127 DAMA when the SM was the highest (40 %) (Figure 2.6). Minimum CH_4 emission of -0.17 mg m^{-2} h^{-1} (from IN+B in 2016 and -1.2 mg m^{-2} h^{-1} (from IN+B) in 2017 was not related to SM or ST. Increase in CH_4 production after DM application as in this experiment has been reported in previous studies. Short-chain fatty acids present in DM become available to methanogenic archaea after application to land and cause CH_4 outbursts (Hrapovic and Rowe, 2002; Sherlock et al., 2002). Significant reduction in CH_4 emission was observed in BC treatments (DM_1+B, DM_2+B, IN+B) as compared to non-BC treatments (DM_1, DM_2, IN). The decrease in CH_4 emission after BC application might be due to the stimulation of methanotrophic activity or the increased abundance of the methanotrophic proteobacterial community (Feng et al., 2012; Liu et al., 2011). Kim et al (2017) studied the effect of BC and slow release fertilizer (SRF) on rice yield and CH_4 emission and concluded that BC suppressed methanogenesis by increasing the oxygen supply in the soil through increased aeration.

2.5.4. N_2O flux

The experimental site was a source as well as a sink of N_2O. The highest N_2O emission peak (0.25 mg m^{-2} h^{-1} from DM_2) at 34 DAMA was correlated to the highest ST (19.9 ^oC) during 2016 (Figure 2.5). Whereas, the high emission peak (0.15 mg m^{-2} h^{-1} from DM_1) at 127 DAMA in 2017 growing season was related to the highest SM (33.5 %) at that day (Figure 2.6). BC amendment suppressed N_2O emissions from DM_1, DM_2 and IN during both years. The decrease in N_2O emissions with BC incorporation was observed by several researchers previously (Augustenborg et al., 2012; Singh et al., 2010; Spokas and Reicosky, 2009; Taghizadeh-Toosi et al., 2011; Van Zwieten et al., 2010b; Yanai et al., 2007). There are several mechanisms by which BC could reduce N_2O emissions. Application of BC improves soil aeration by reducing the soil bulk density resulting in a decrease in the activity of denitrifiers in paddy fields (Zhang et al., 2010). Reduction of N_2O emissions after BC amendment had been explained due to different mechanisms including modification of SM, increased aeration, inhibition of nitrifier and denitrifier communities (Laird et al., 2009; Yanai et al., 2007). BC application to soil accelerates; (1) the growth of soil microbes (e.g. Bradyrhizobiaceae and Hyphomicrobiaceae families) that can decrease N_2O emission by supporting denitrification of NO_3^- to N_2, (2) the mycobacterial reduction of NO_3^- to NH_4^+, and (3) adsorption of NH_4^+ on BC surface decreasing the abundance of microorganisms involved in nitrification of NH_4^+ to nitrite (NO_2^-) (Anderson et al., 2011). BC particles adsorb NH_4^+ on their surface and, reduce its availability for nitrification, as a result, N_2O emission is declined (Berglund et al., 2004; Lehmann et al., 2006).

2.6. Conclusion

BC application reduced the cumulative GHG emission during both growing seasons from silage corn cropping system in western Newfoundland. Overall, BC application to DM_1, DM_2 and IN decreased cumulative CO_2 emission by 16, 25.5 and 26.5 %, cumulative CH_4 emission by 184, 200 and 293 %, and cumulative N_2O emission by 95, 86 and 93 %, respectively. BC treatments exhibited significantly higher SM contents at all sampling points than non-BC treatments. BC incorporation also reduced the GWP by 24.9, 34.5, and 37 %, and GHGI by 30, 37.5, and 43.4 % in DM_1, DM_2 and IN treatment, respectively. Based on the results of this study, it is concluded that BC application to soil with DM and IN fertilizer have a great potential to reduce GHGs emissions, global warming and climate change without compromising the dry matter yield of silage corn crop in western Newfoundland.

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Chapter 3

3. Biomass production, and nitrogen dynamics of silage corn as influenced by organic and inorganic nitrogen sources and biochar amendment

3.1. Abstract

Most of the nitrogen (N) applied to crops is leached down in the form of nitrates (NO_3^-) resulting in reduced N use efficiency. To assess the potential of biochar (BC) application for the mitigation of NO_3^- leaching and retention of NO_3^- and ammonium (NH_4^+) , a two year field study was conducted with two dairy manure sources (DM_1, DM_2), inorganic N (IN), their combination with BC and a control (no N). Three silage corn genotypes (A4177G3RIB, DKC26-28 RIB, Yukon R) were used. BC application significantly reduced the NO_3^- and NH_4^+ movement to deep soil and it enhanced their retention in topsoil, increased soil pH, enhanced N concentration in plant tissues and increased dry matter yield in all silage corn genotypes. On average, BC addition to DM_1, DM_2, and IN enhanced N uptake by 13.5, 11.5 and 17.3 % and dry matter yield by 6, 5.5, and 8.75 %, respectively. Conclusively, BC application to soil could improve soil pH, reduce NO_3^- and NH_4^+ loses by increasing their residence time in soil, hence N concentration and dry matter production in silage corn cropping systems in western Newfoundland.

Keywords: nitrate/ammonium retention, silage corn, dairy manure, biochar

3.2. Introduction

Dairy manure (DM) and inorganic nitrogen (IN) fertilizers are the major sources of plant nutrients and are being applied to crops worldwide to boost the agricultural productivity (Jokela et al. 2014; Wang et al. 201 7c; Parker et al. 2018). DM application improves physiochemical properties of soil and agronomic performance of plants e.g. soil organic carbon (SOC), bulk density, soil aggregation, nutrient status and uptake, crop growth and yield (Forge et al., 2016; Martínez et al., 2017). However, excessive IN fertilizers and DM application enhance the risk of NO_3^- leaching in different cropping systems and consequently increase cost of production, pollute water bodies and pose a serious threat to human health (Fan et al., 2017; Forge et al., 2016; Jokela et al., 2014; Long and Sun, 2012; Masaka et al., 2015). It has been reported that 34-92 % of the N is leached from manure application to soil was in the form of NO_3^- and 14-57 % in dissolved organic nitrogen (DON) form (Fan et al., 2017). However, soil NO_3^- concentration and leaching is site-specific and is mainly driven by rainfall, management practices (cover crop, fertilizer sources, crop rotation), and soil texture (Gaines and Gaines, 1994; Jabloun et al., 2015; Jean et al., 2000). For instance, NO_3^- leaching losses of 55-59 kg per hectare per year with DM application, 30-35 kg per hectare per year from compost application and 25-33 kg per hectare per year from IN application has been reported in a six-year corn - alfalfa crop rotation (Basso and Ritchie, 2005). Significant variation in NO_3^- losses has been observed in different cropping systems, but corn-based cropping systems have been found to have the highest NO_3^- leaching (Hargrave and Shaykewich, 1997; Hernandez-Ramirez et al., 2011; van Es et al., 2006). The annual estimated loss of NO_3^- from cornfield amended with Ammonium nitrate (NH_4NO_3) in Manitoba was 160 kg per hectare per year (Hargrave and Shaykewich, 1997), whereas, in Southern Turkey, the annual NO_3^- load was 39-55 kg per hectare per year in wheat-corn cropping system when a mixture of NH_4NO_3, ammonium sulfate $(NH_4)_2\ SO_4$, urea $(NH_2)_2\ CO$, and compound fertilizer was applied (Ibrikci et al., 2015). These N losses indicate ineffectiveness in the current nutrient management strategies or management practices that result not only in environmental pollution but also an economic loss to the farmers (Güereña et al., 2013). Different nutrient management strategies and crop management practices have been practiced to reduce N losses and improve N use efficiency (NUE). These include, slow-release fertilizers (Ye et al., 2013), burial of crop residues and crop rotation (Hirel et al., 2007), judicious use of fertilizers (Francis, 1992), legume-based cropping systems (Drinkwater et al., 1998), variable rate technologies (VRT) (Gatti et al., 2018), use of nitrification inhibitors (NI) (Zhang et al., 2015), and plant trait selection (Ju et al., 2015).

Biochar (BC) is a form of black carbon (C) created by thermal degradation of organic material (e.g., wood, manure, leaves, etc.) in zero or low oxygen environments (Lehmann and Joseph, 2009). BC is recalcitrant in nature (Spokas, 2010) and its reactive surfaces are capable of sorbing and exchanging nutrients and native organic matter (Liang et al., 2006); therefore, there is a great potential and interest in utilizing BC as a soil amendment to sequester C and improve soil fertility in agricultural soils. Additionally, BC application could be one of the best approaches to improve N retention in topsoil, reduce NO_3^- leaching and improve soil fertility in agricultural systems (Haider et al., 2015; Knowles et al., 2011; Laird et al., 2010; Lehmann, 2007). BC application decreases soil bulk density, increases porosity, pH, nutrient use efficiency, N_2-fixation, soil saturation, water holding capacity (WHC) (Busch et al., 2012; Busscher et al., 2010; Harter et al., 2014; Hussain et al., 2017; Jervin et al., 2017; Kammann et al., 2012; Karhu et al., 2011), enhances Ammonium (NH_4^+) retention and availability, increases urease activity preventing ammonia losses, and eventually reduces NO_3^- leaching loses (Amendola et al., 2017; Cao et al., 2017; Huang et al., 2017; Sun et al., 2017). BC amendment increased hydraulic conductivity, soil water availability and infiltration (Asai et al., 2009; Baronti et al., 2014; Buss et al., 2012; Ippolito et al., 2012), and improved soil aeration (Case et al., 2012; Cayuela et al., 2013) and nutrient retention (Clough et al., 2013; Ventura et al., 2012; L. Wang et al., 2017). BC can also increase soil microbial activities, alter microbial community structure and extracellular enzymatic activities (Foster et al., 2016; Gul et al., 2015; Lu et al., 2015). There is a significant effect of feedstock source and pyrolysis process on characteristics of BC that consequently affect the physiochemical and biological properties of soil (Borchard et al., 2014; Gul et al., 2015; Lentz and Ippolito, 2012; Schmidt et al., 2014; Spokas and Reicosky, 2009; Vitkova et al., 2017). Application of BC produced at 550 $^{\circ}C$ increased soil NO_3^- concentration, nutrient uptake, and corn dry matter yield (Haider et al., 2015; Smider and Singh, 2014). Pinewood BC amendment at the rate of 0.5, 2.5 and 10 % w/w in sandy soil reduced NO_3^- leaching by 26, 42 and 96 %, respectively (Sika and Hardie, 2014). BC amendment to soil may increase NO_3^- residence time in soil possibly due to unconventional H-bonding in micro and nano-pores (Kammann et al., 2015), or development of functional groups and organo-mineral complexes on BC surface (Joseph et al., 2013; Lin et al., 2013; Prost et al., 2013), acting as slow-release fertilizer which allows plants to absorb more NO_3^- from the soil

(Hagemann et al., 2017; Kameyama et al., 2012; Uzoma et al., 2011). A significant increase in inorganic N pool (NH_4^+-N, NO_3^--N), leaf N concentration, photosynthesis rate, and pod yield have been recorded with BC application (Xu et al., 2015). Incorporation of rice straw BC to acidic soil accelerated nitrification but decreased NO_3^- leaching and improved N adsorption (Zhao et al., 2014). BC amendment to a degraded Chernozem soil at 5 % (w/w) application rate significantly improved spinach growth, increased uptake of K in plant tissues, free amino acid contents, and proline content but limited Ca, Mg and Na concentrations (Zemanová et al., 2017). Contrary to reported above (Tammeorg et al., 2014) observed that BC application did not improve N uptake and grain yield of wheat, faba bean and turnip rape in a three-year field experiment. In Newfoundland, most of the cultivated soils are acidic and sandy and the growing season is short with frequent rainfall events. The average precipitation received in this area is 1113 mm per year with less than 410 mm as snow during last 30 years (1986-2016) recorded from the nearest weather station in Deer Lake by Environment Canada (Badewa, 2017). This is a most favorable condition for N leaching. Most of the N applied to sandy soils is lost and is not available to crops (Gaines and Gaines, 1994; Jabloun et al., 2015; Jean et al., 2000), which results in low crop productivity and economic loss. Therefore, I hypothesized that BC amendment would reduce nitrate leaching; enhance soil pH and biomass production of silage corn in the podzolic soil. This research project was planned with the following specific objectives;

i- To investigate the role of BC amendment on soil's NO_3^- and NH_4^+ dynamics after dairy manure and IN fertilizer application in silage corn cropping systems.

ii- To compare the effects of DM, IN alone and co-application of BC on soil pH, N concentration and biomass production of silage corn.

3.3. Material and Methods:

3.3.1. Study site

A field experiment was conducted at Pynn's Brook Research Station, Pasadena (49°04'21.9"N, 57°33'37.4"W), Newfoundland and Labrador (NL), Canada, during 2016 and 2017 growing seasons. The soil was classified as rapidly drained, Orthic Humo-Ferric Podzol with reddish brown to brown color, and developed on gravely sandy fluvial deposit of mixed lithology (Kirby, 1988). Moreover, this soil has limited agricultural use because of its high coarse fragment contents and rapid drainage (Kirby, 1988). Basic physio-chemical properties of the soil are described in Table 2.1.

3.3.2. Experimental setup

The experiment comprised of seven treatments with organic and inorganic N sources and BC. Treatments included were; 1) DM with high N conc. (0.37 %) designated as DM_1, 2) DM with low N conc. (0.13 %), designated as DM_2, 3) IN, 4) DM_1 + BC, 5) DM_2 + BC, 6) IN + BC, and 7) control (N_0). The experimental design was a randomized complete block (RCBD) in a factorial setting with three replications. Plots were 1.5 m wide and 4.8 m long. DM procured from Larch Grove and Rideout's dairy operations located at Cormack area near Deer Lake, NL was used. DM samples were collected from these two dairy operations and were sent to Soil, Plant and Feed Laboratory, Department of

Fisheries and Land Resources, St. John's, NL for detailed analysis. Larch Grove's DM had a high concentration of macro and micronutrients and was designated as DM_1 while DM from Rideout's dairy had a low concentration of macro and micronutrients and was titled as DM_2 (Table 2.2). Representative soil sample collected from the experimental site was also sent to the same laboratory for physiochemical analyses. DM was applied each year before seeding in corresponding plots @ 30,000 liters per hectare (local farmers practice). Inorganic fertilizers were applied to fulfill the required NPK nutrients based on DM and soil analyses reports. Ammonium nitrate (NH_4NO_3), triple superphosphate (TSP) and murate of potash (MOP) were used as nitrogen (N), phosphorus (P), and potash (K) sources, and were applied at the rate of 215,110, 225 kg ha^{-1}, respectively. DM_1, DM_2 and the entire IN were applied before crop seeding during 2016 while in 2017 DM_1 and DM_2 were applied to all respective treatments (DM_1, DM_2, DM_1+B, DM_2+B) before seeding but the IN fertilizer was applied in two splits (first dose: 6 leaf stage, second dose: 12 leaf stage). BC was applied only once in 2016 and incorporated to top 15 cm of the soil before DM application. BC is produced at AirTerra Inc. located in Calgary, Alberta, and is a registered BC product with the Canadian Food Inspection Agency (CFIA). This BC was produced from yellow pine wood pyrolyzed at 500 ^{o}C for 30 min by slow pyrolysis in oxygen-limited conditions. BC was applied @ 20 tons ha^{-1} as reported by (Liu et al., 2012b). The detailed BC analyses report conducted by Gabilan laboratory, Salinas, California, USA can be seen in (Table 2.3).

3.3.3. Crop husbandry

Three silage corn genotypes, Yukon R, A4177G3 RIB, and DKC26-28 RIB were selected and used as test hybrids in this experiment. Selection of these hybrids was made on the basis of high biomass production performance in a previous field trial conducted during 2015 and low heating unit requirements. Detailed information about hybrids can be seen in Table 3.1. Seeding was done on May 24, 2016 and May 23, 2017 with the SAMCO 2200 system (SAMCO Agricultural Manufacturing Ltd.). SAMCO 3 in 1 machine which sows seed, sprays the soil with pre-emergence herbicide, and lays a thin layer of biodegradable plastic film over the seedbed. This operation protects the young plants from late frost, increases the soil temperature and thereby maximizes silage corn yield per hectare. Biodegradable plastic provides additional heat units which enhance seed germination during cold and frost days (Figure 2.1). Seeding rate for the crop was 90,900 seeds per hectare. Weeds were controlled with the spray of Roundup WeatherMax on July 09, 2016 and July 08, 2017 at the rate of 2 L per hectare.

Table 3.1: Silage corn genotypes used in the experiment.

Number	**Genotype name**	**CHU**	**Company**	**Trait**
1	Yukon R	2150	Brett Young	RR2
2	A4177G3 RIB	2175	Pride	VT3/RR
3	DKC26-28 RIB	2150	DEKLAB	GENVT2P

CHU = corn heat units, RIB= Refuge is in the bag, RR = Roundup Ready, VT3= VT TriplePro insect protection, RR2 = resistance gene to Roundup® and Factor 540®

3.3.4. Soil sampling and analysis

Soil sampling for NO_3^- and NH_4^+ determination was done from 20 cm and 40 cm depths at four stages (seedling emergence, 6 leaves, 12 leaf and black layer stage) during 2016 and (6 leaves, 12 leaves, tasseling and black layer stage) in 2017. Samples were collected with augur and sealed in marked plastic bags and transferred to the laboratory within six hours of collection, where they were stored at -20 $^{\circ}$C until further analysis. Soil samples were sieved through a 2 mm sieve to remove stones and other residues. Sieved soil (5 g) was weighed in a pre-weighed aluminum dish, and dried overnight in an oven at 105 $^{\circ}$C and final dry weight was recorded. Moisture factor was calculated by weight difference. Sieved soil sample (5 g) was taken into a 125 mL Erlenmeyer flask and 50 mL, 2 molars KCl (potassium chloride) solution was added (1:10 soil to solution ratio) and shaken for 30 min on a reciprocating shaker (Cao et al., 2017; Carter et al., 2008; Heman et al., 2016; Sika and Hardie, 2014), and filtered into sterile 50 mL plastic tubes. The filtrate was stored at -20 $^{\circ}$C until further analysis. NO_3^- and Ammonium NH_4^+ concentrations in the soil extract were determined using AutoAnalyzer (Seal analytical continuous flow analyzer (AA3 HR) (Cao et al., 2017; Heman et al., 2016). NO_3^- is reduced to nitrite (NO_2^-) by a cadmium-copper reduction column at a pH of 8, NO_2^- ion then reacts with sulfanilamide to form a diazo compound. This compound then reacts with N-1-naphthylethylenediamine dihydrochloride to form a reddish-purple azo dye. NH_4^+ was determined using the salicylate chemistry and the results obtained were calculated using the formulas in Equations (3.1), (3.2), and (3.3).

Moisture factor was calculated by dividing weight of moist soil by dried soil weight

$$\text{Moisture factor (MF)} = \frac{\text{Moist soil weight (g)}}{\text{Oven dry weight (g)}} \tag{3.1}$$

Soil NO_3^- and NH_4^+ in moist soil was calculated by;

$$NO_3^- \text{ or } NH_4^+ \text{ in moist soil (mg g}^{-1} \text{ of wet soil)} \tag{3.2}$$

$$= NO_3^- \text{ or } NH_4^+ \text{ in soil extract (mg L}^{-1}) \times 10$$

Nitrate and ammonium quantity was multiplied with 10 as the soil-to-solution ratio was 1:10 in extract.

Soil NO_3^- and NH_4^+ in dry soil was calculated by;

$$NO_3^- \text{ or } NH_4^+ \text{ in dry soil (mg g}^{-1} \text{ of dry soil)} = NO_3^- \text{ or } NH_4^+ \text{ in moist soil} \times \text{MF} \tag{3.3}$$

3.3.5. Soil pH determination

Soil pH was determined from the samples collected for NO_3^- and NH_4^+ determination at three crop growth stages during 2016 and two stages in 2017. Air-dried soil samples (10 g) were taken in long plastic tubes and 20 mL, 0.01 M $CaCl_2$ (calcium chloride) was added to each tube. It was stirred for 30 minutes and let it stand for one hour (Carter et al., 2008). The pH was measured using benchtop pH meter (Oakton Instruments) (Zhang et al., 2014).

3.3.6. Dry matter production

Plants were harvested from a 1 m^2 area at black layer stage from each plot and their fresh weight was recorded. Plants were oven dried at 70 ^oC for 48 h and dry matter yield was calculated from each treatment plot using the formula given in Equation (2.4) and (2.5).

3.3.7. Plant tissue nitrogen concentration

Three dried plants from each treatment were grounded using Wiley Mill (Arthur H. Thomas) and then with CryoMill (Retsch, Germany) to a fine powder. Ground plant samples (4.5±0.5 mg) were weighed in tin capsules and analyzed with PerkinElmer CHN 2400 Series II for total nitrogen contents.

3.3.8. Statistical analysis

The analysis of variance (ANOVA) was used to determine the effect of different treatments on soil NO_3^- and NH_4^+, soil pH, plant N concentration and biomass production. Where treatment effects were significant, the means were compared with LSD ($\alpha = 0.05$). The data were analyzed using the Statistix 10 software package (Analytical software, FL, USA) and figures were prepared using SigmaPlot 12.0 software program (Systat Software Inc., San Jose, CA).

3.4. Results

3.4.1. Nitrate and ammonium dynamics

Soil NO_3^- and NH_4^+ concentration in DM, IN alone and BC amended treatments varied significantly ($p<0.05$) during both growing seasons from IN, manure treatments (DM_1, DM_2, IN) and control (N0).

Nitrate and ammonium during 2016

DM_1, DM_2 and the entire IN were applied before crop seeding. The NO_3^- concentration in all treatments ranged from 7.3-55 (mg g^{-1} dry soil) in top 20 cm soil layer at seedling emergence stage of the crop. Soil NO_3^- concentration in all treatments and stages at 20 cm depth is shown in the Figure 3.1a and 40 cm depth in Figure 3.1b. BC treatments (DM_1+B, DM_2+B, and IN+B) have high soil NO_3^- concentration, but it was not significantly different from their non-BC treatments (DM_1, DM_2 and IN) (Figure 3.1a) as N was applied at the same rate in all plots (DM treatments received some IN as well to balance the N requirement of the crop). Soil NO_3^- concentration in deep soil (40 cm) ranged from 4.3-35.3 (mg g^{-1} dry soil) in all treatments. BC treatments have relatively low NO_3^- concentration in deep soil layer as compared to non-BC treatments which indicate less NO_3^- movement to the deep soil at seedling emergence stage of the crop (Figure 3.1b). Soil NO_3^- increased after seedling establishment and it reached to 78-120 (mg g^{-1} dry soil) in all treatments (except control where it was 6.5 mg g^{-1} dry soil) in topsoil layer at 6 leaf stage of the crop. Here BC treatments have significantly higher NO_3^- concentration ($p<0.05$) than non-BC treatments and the control (Figure 3.1a) which was due to the retention of NO_3^- in BC amended soil as more NO_3^- moved to deep soil layer in non-BC treatments (Figure 3.1b). At 12 leaf stage there was a significant effect of BC treatments on NO_3^- concentration ($p<0.05$) in the topsoil as most of the NO_3^- in DM_1, DM_2, and IN leached to deep soil but BC treatments have more NO_3^- retained in the topsoil layer. At black layer stage there was very little NO_3^- amount left in soil ranging from 1.13 (mg g^{-1} dry soil) in control to 4.9 (mg g^{-1} dry soil) in DM_1+B in topsoil and 1.40 (mg g^{-1} dry soil) in control to 2.5 (mg g^{-1} dry soil) in DM_1 treatments in deep soil layer. Soil NH_4^+ concentration in all treatments and stages at 20 cm depth is shown in the Figure 3.1c and 40 cm depth in Figure 3.1d. There was significantly higher NH_4^+ concentration present in the topsoil layer at seedling emergence stage as compared to other stages and dropped to near zero at black layer stage. The NH_4^+ concentration ranged from 3.2 (mg g^{-1} dry soil) in the control treatment to 80.1 (mg g^{-1} dry soil) in DM_1+B at seedling emergence stage. There was significantly higher NH_4^+ concentration in BC treatments as compared to non-BC treatments and control in 20 cm soil depth (Figure 3.1c). No significant difference between BC and non-BC treatments with respect to the NH_4^+ concentration at 40 cm soil depth was observed whereas control treatment had the lowest NH_4^+ at seedling emergence stage. At 6 leaf stage NH_4^+ in the topsoil layer decreased as compared to seedling emergence stage, and BC treatments had significantly high NH_4^+ than non-BC treatments and control. Whereas in deep soil layer NH_4^+ increased as compared to the seedling stage with significantly lower NH_4^+ in BC treatments than non-BC treatments as most of the NH_4^+ retained in BC in topsoil. At 12 leaf stage NH_4^+ concentration further decreased and it ranged from 1.2 (mg (g^{-1} dry soil) in control to 25.4 (mg (g^{-1} dry soil) in DM_1+B at 20 cm depth whereas, in deep soil NH_4^+ ranged from 1.4 (mg (g^{-1} dry soil) in control to 20 (mg (g^{-1} dry soil) in DM_1+B. At black layer stage NH_4^+ dropped to near zero. Maximum NH_4^+ i.e. 1.1 (mg (g^{-1} dry soil) was found in DM_1+B whereas 0 (mg (g^{-1} dry soil) in control treatment.

Nitrate and ammonium during 2017

DM_1 and DM_2 were applied to all respective treatments (DM_1, DM_2, DM_1+B, DM_2+B) before seeding but the IN fertilizer was applied in two splits (first dose: two days after 6 leaf stage sampling, second dose: one day before 12 leaf stage sampling). Soil NO_3^- and NH_4^+ concentrations were measured at four crop growth stages (6 leaves, 12 leaves, tasseling and black layer stage). Soil NO_3^- concentration was low at 6 leaf stage as compared to 12 leaves and tasseling stage. Manure treatments (DM_1, DM_2, DM_1+B, DM_2+B) have high NO_3^- concentration in soil than IN, and IN+B as fertilizer was not applied to any treatment before seeding. DM_1+B, and DM_2+B had low NO_3^- concentration at 40 cm soil depth as most of the NO_3^- retained in topsoil in biochar (Figure 3.2a). At 12 leaf stage, NO_3^- concentration increased in DM+BC treatments and BC helped to reduce NO_3^- movement to the deep soil (Figure 3.2b). At the tasseling stage, as there was fertilizer (NH_4NO_3) application one day before sampling so there was high NO_3^- observed in all treatments except control. There was more NO_3^- in BC treatments at 20 cm depth and in DM_1, DM_2, and IN at 40 cm depth (Figure 3.2c). At black layer stage, soil NO_3^- deceased in all treatments with significantly high NO_3^- concentration in BC treatments than DM_1, DM_2, IN and control (Figure 3.2d). Soil NH_4^+ concentrations were lowest at both soil depths at 6 leaves stage of the crop. But after that an increase in NH_4^+ was observed in DM_1, DM_1+B, DM_2, DM_2+B at 12 leaves the stage with the highest NH_4^+ as 41.2 (mg g^{-1} dry soil) in DM_1+B at 20 cm soil layer. At tasseling stage as sampling was done one day after fertilizer application there was an increase in NH_4^+

concentration and it reached a maximum of 46.3 (mg g^{-1} dry soil) in IN+B. At black layer stage the NH_4^+ was significantly higher in DM_1+B, DM_2+B, and IN+B than DM_1, DM_2, IN and control (Figure 3.2c).

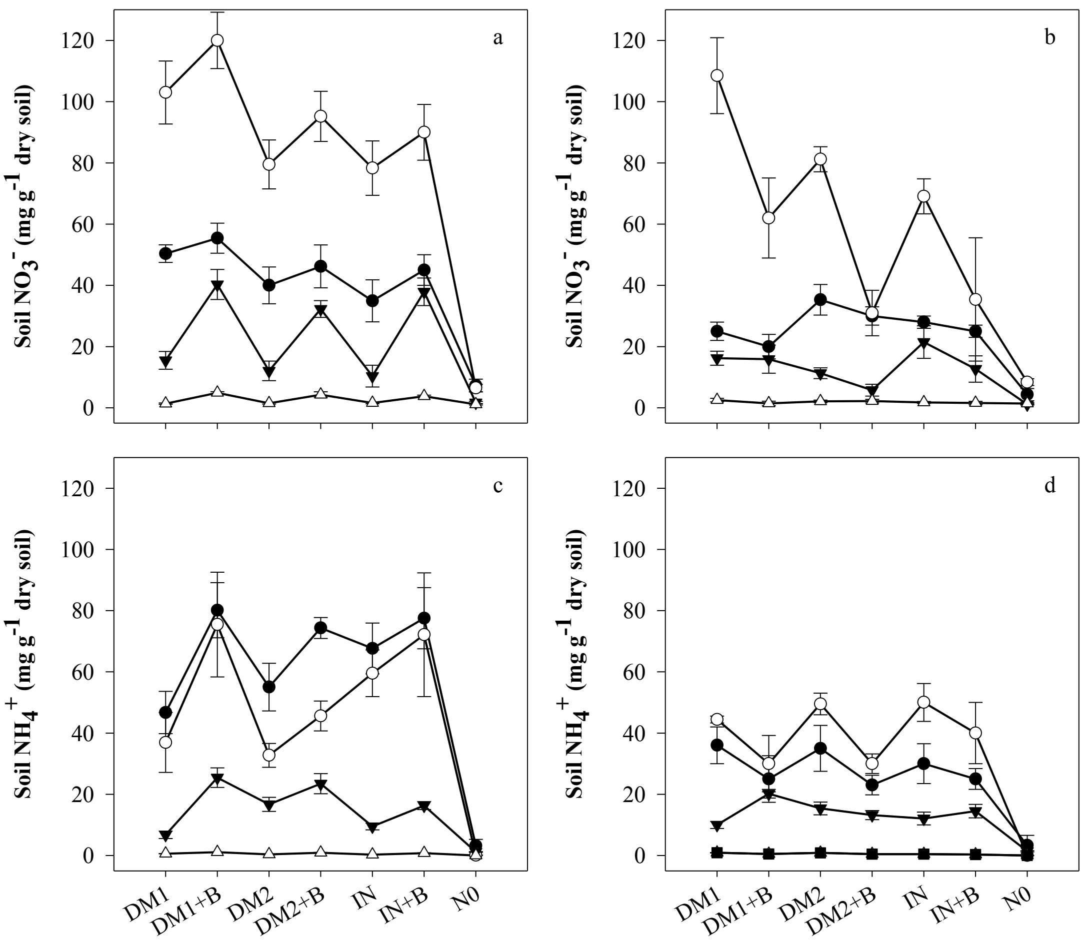

Figure 3.1: Soil nitrate (NO_3^-) and ammonium (NH_4^+) concentrations (mg g^{-1} dry soil) in experimental treatments at four crop growth stages during 2016

(a) NO_3^- at 20 cm depth (b) NO_3^- at 40 cm depth (c) NH_4^+ at 20 cm depth (d) NH_4^+ at 40 cm depth, filled circle (seedling emergence), empty circle (6 leaves stage), filled triangle (12 leaves stage), empty triangle (Black layer stage)

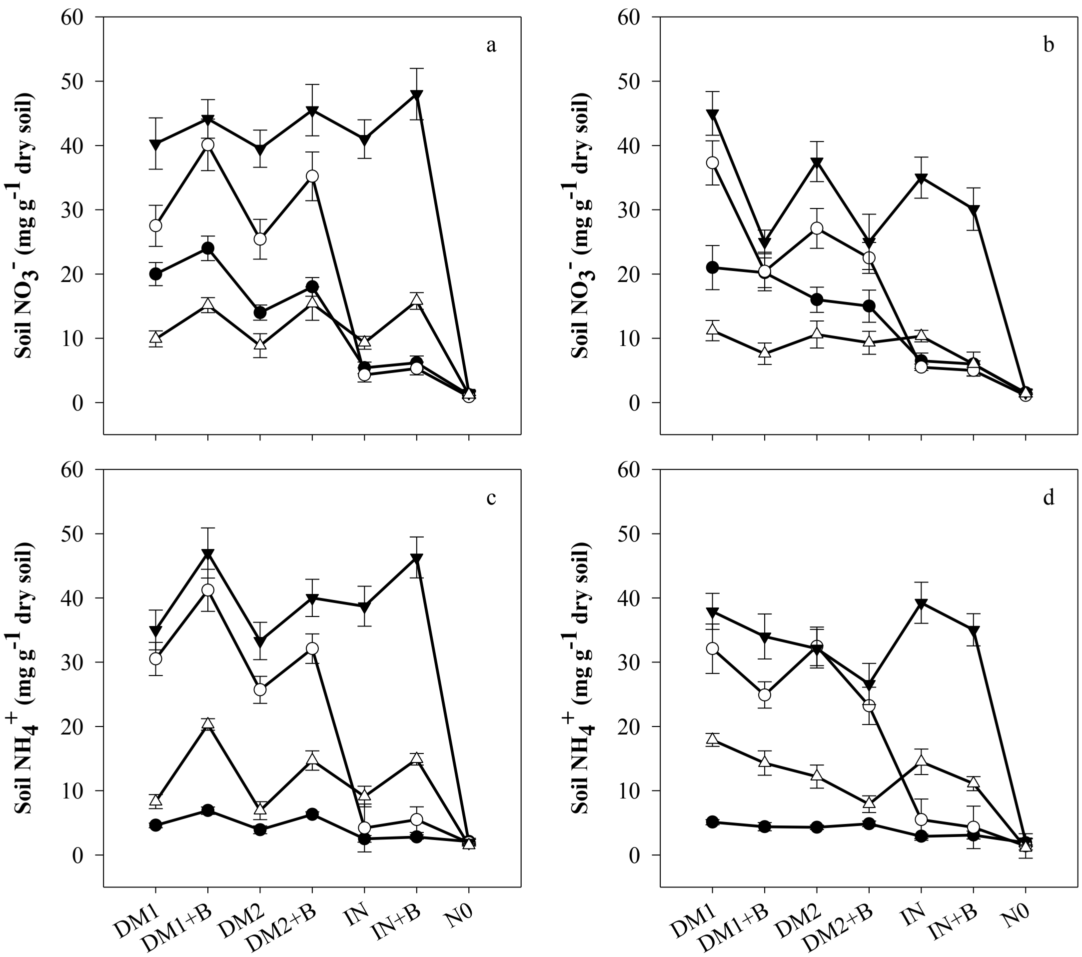

Figure 3.2: Soil nitrate (NO_3^-) and ammonium (NH_4^+) concentrations (mg g^{-1} dry soil) in experimental treatments at four crop growth stages during 2017

(a) NO_3^- at 20 cm depth (b) NO_3^- at 40 cm depth (c) NH_4^+ at 20 cm depth (d) NH_4^+ at 40 cm depth, filled circle (seedling emergence), empty circle (6 leaves stage), filled triangle (12 leaves stage), empty triangle (Black layer stage)

3.4.2. Soil pH

Soil pH in experimental treatments was measured at three crop growth stages in 2016 and at two stages during 2017. There was a significant temporal variation in soil pH in all treatments measured at different crop growth stages in both seasons (Figure 3.3). BC treatments have high soil pH at each sampling event than non-BC treatments. Generally, soil pH increased with DM application; however, a significant increase was noticed with BC amendment and declined as the season proceeded. For example, DM_1, DM_2, and IN treatments exhibited pH values of 6.23, 6.17 and 6.02 at the seedling stage during 2016. BC addition to these treatments significantly increased pH to 6.46, 6.34, and 6.21 respectively (Fig. 8). There was a reduction in soil pH in all treatments except IN, IN+B, and the control at 12 leaf stage compared to seedling stage. The mean values of soil pH at 12 leaf stage in all treatments were 6.20, 6.31, 6.15, 5.20, 6.15, 6.23, and 6.0 in DM_1, DM_1+B, DM_2, DM_2+B, IN, IN+B, and the Control. At black layer stage, soil pH further decreased in all treatments with relatively high pH in BC amended treatments. At the end of the growing season of 2016 (black layer stage), the BC amended treatments have high soil pH by 0.18, 0.10, and 0.06 units than non-BC amended treatments. At six-leaf stage during 2017, soil pH was stable, however again decreased at black layer stage in 2017 but BC treatments have relatively high pH. The mean values of soil pH at black layer stage (2017) in all treatments were 5.87, 6.05, 5.50, 5.70, 5.68, 5.73, and 5.50 in DM_1, DM_1+B, DM_2, DM_2+B, IN, IN+B, and control treatment with an overall increase by 0.14 unit in BC than non-BC amended treatments.

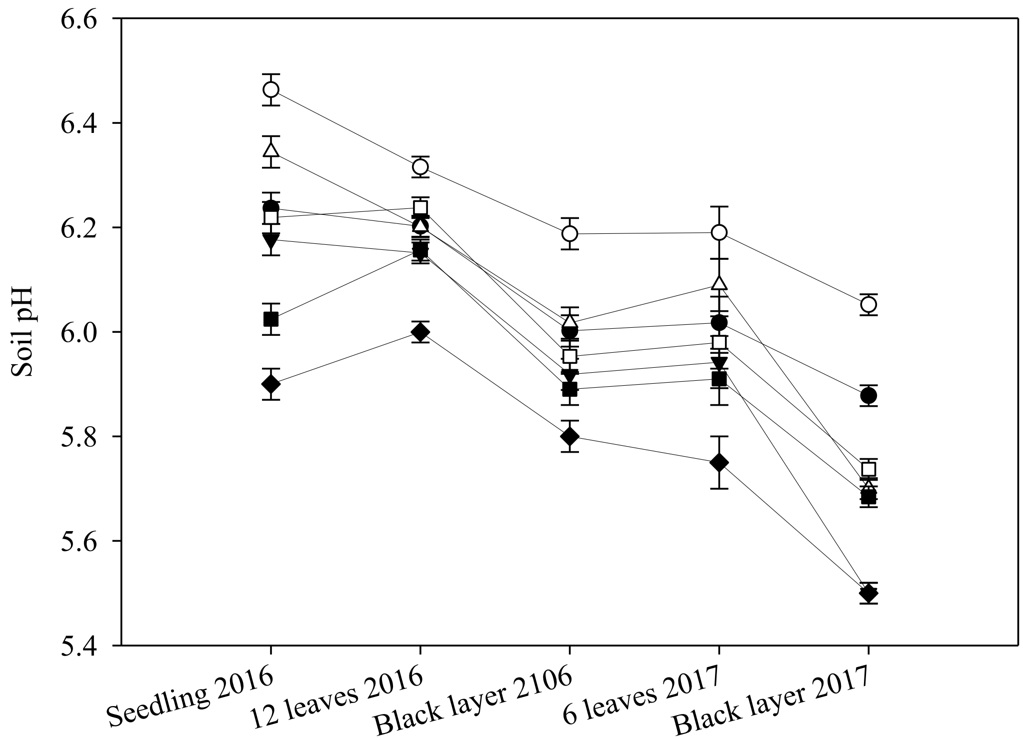

Figure 3.3: Soil pH at 20 cm depth at different crop growth stages during 2016 and 2017

Solid circle (DM_1), empty circle (DM_1+B), solid triangle (DM_2), empty triangle (DM_2+B), Solid square (IN), empty square (IN+B), solid diamond (N_0)

3.4.3. Plant tissue N concentration

DM and IN alone and co-application with BC significantly (*$p<0.05$*) influenced the N concentration in silage corn genotypes. BC amended treatments enhanced the N concentration in silage corn tissues, however, maximum N concentration was noted in IN+B treatment, compared to the minimum concentration in the control treatment. Among the genotypes, A4177G3 RIB exhibited higher N concentration compared to DKC26-28 RIB and Yukon R during 2016 (Table 3.2). Overall, maximum mean N concentration was noted in IN+BC treatment compared to control treatment. BC addition to DM_1, DM_2, and IN enhanced N concentration by 10, 13 and 27 % respectively. In 2017, A4177G3 RIB exhibited the highest tissue N concentration in IN+BC treatment, whereas lowest was noted in DKC26-28 RIB in control treatment. Overall, BC addition to DM_1, DM_2, and IN enhanced N concentration by 17, 8 and 7.6 % respectively. N concentration was maximum in DM_1+BC treatment compared to control treatment whereas, A4177G3 RIB genotype was the most efficient in N uptake followed by Yukon R and DKC26-28 RIB.

Table 3.2: Plant tissues nitrogen concentration (%) in silage corn genotypes under different experimental treatments during growing season 2016

Treatments	A4177G3 RIB	DKC26-28 RIB	Yukon R	Mean
DM1	$1.25{\pm}0.15^{abcd}$	$1.03{\pm}0.03^{defg}$	$1.07{\pm}0.17^{cdefg}$	$1.11{\pm}0.07^{BC}$
DM1+B	$1.28{\pm}0.01^{abc}$	$1.07{\pm}0.13^{cdefg}$	$1.32{\pm}0.05^{ab}$	$1.22{\pm}0.05^{AB}$
DM2	$1.09{\pm}0.06^{bcdefg}$	$1.17{\pm}0.12^{bcdef}$	$0.99{\pm}0.12^{efg}$	$1.08{\pm}0.06^{BC}$
DM2+B	$1.45{\pm}0.05^{a}$	$1.08{\pm}0.04^{bcdefg}$	$1.14{\pm}0.05b^{cdefg}$	$1.23{\pm}0.06^{AB}$
IN	$1.18{\pm}0.03^{bcde}$	$0.93{\pm}0.06^{fg}$	$0.96{\pm}0.04^{efg}$	$1.02{\pm}0.03^{C}$
IN+B	**$1.47{\pm}0.02^{a}$**	$1.16{\pm}0.11^{bcdefg}$	$1.28{\pm}0.04^{abc}$	$1.30{\pm}0.05^{A}$
N0	$1.11{\pm}0.01^{bcdefg}$	$0.93{\pm}0.02^{fg}$	**$0.92{\pm}0.09^{g}$**	$0.99{\pm}0.05^{C}$
	$1.26{\pm}0.03^{A}$	$1.05{\pm}0.03^{B}$	$1.10{\pm}0.04^{B}$	

Means sharing common letters are not significantly different at 0.05 probability level**.**

Table 3.3: Plant tissues nitrogen concentration (%) in silage corn genotypes under different experimental treatments during growing season 2017

Treatments	A4177G3 RIB	DKC26-28 RIB	Yukon R	Mean
DM1	$1.40{\pm}0.03^{abcd}$	$1.08{\pm}0.00^{fg}$	$1.24{\pm}0.05^{def}$	$1.24{\pm}0.05^{C}$
DM1+B	$1.41{\pm}0.01^{abcd}$	$1.45{\pm}0.03^{abc}$	$1.50{\pm}0.06^{ab}$	**$1.45{\pm}0.02^{A}$**
DM2	$1.40{\pm}0.03^{abcd}$	$1.10{\pm}0.06^{fg}$	$1.22{\pm}0.04^{defg}$	$1.24{\pm}0.05^{C}$
DM2+B	$1.45{\pm}0.08^{abc}$	$1.26{\pm}0.07^{cdef}$	$1.31{\pm}0.02b^{bcde}$	$1.34{\pm}0.04^{ABC}$
IN	$1.47{\pm}0.03^{ab}$	$1.10{\pm}0.16^{fg}$	$1.32{\pm}0.01^{bcde}$	$1.30{\pm}0.07^{BC}$
IN+B	**$1.54{\pm}0.07^{a}$**	$1.31{\pm}0.03^{bcde}$	$1.33{\pm}0.01^{bcde}$	$1.39{\pm}0.04^{AB}$
N0	$1.14{\pm}0.03^{efg}$	**$1.03{\pm}0.16^{g}$**	$1.09{\pm}0.13^{fg}$	**$1.08{\pm}0.06^{D}$**
	$1.40{\pm}0.03^{A}$	$1.19{\pm}0.04^{C}$	$1.29{\pm}0.03^{B}$	

Means sharing common letters are not significantly different at 0.05 probability level**.**

3.4.4. Dry matter yield

The application of DM_1, DM_2 and IN alone or in combination with BC had significantly *($p<0.05$)* affected dry matter yield (DMY) of silage corn. BC amended treatments (DM_1+B, DM_2+B, and IN+B) yielded significantly *($p<0.05$)* higher biomass than without BC and the control treatment. Genotype × N source interaction ($p<0.05$) had significantly influenced dry matter yield during both years. Yukon R produced the maximum dry matter yield of 21 Mg ha^{-1} in DM_1+BC treatment, compared to minimum dry matter production (14 Mg ha^{-1}) by A4177G3 RIB in the control treatment (Table 3.4). N sources had a significant effect on dry matter production in all genotypes. BC addition to IN, DM_1, and DM_2 increased dry matter yield by 5, 3, and 4.5 % in A4177G3 RIB, 3.6, 7.5 and 8 % in DKC26-28 RIB, 6, 4, and 8 % in Yukon R, respectively. Overall, BC application to IN, DM_1 and DM_2 increased the dry matter production by 5, 5, and 7 % respectively during 2016. Similarly, in 2017 growing season, the highest dry matter yield of 17.1 Mg ha^{-1} was observed in Yukon R while minimum 10.1 Mg ha^{-1} in A4177G3 RIB in the control treatment (Table 3.5). BC addition to IN, DM_1, and DM_2 increased dry matter yield by 6.8, 3, and 7 % in A4177G3 RIB and 7.6, 9 and 12.5 % in DKC26-28 RIB and 6.8, 5, and 11.5 % in Yukon R, respectively. Overall BC application to IN, DM_1 and DM_2 increased the dry matter production by 7, 6, and 10.5 %, respectively.

Table 3.4: Dry matter yield (Mg ha^{-1}) of three silage corn genotypes during growing season 2016

Treatment/Genotype	A4177G3 RIB	DKC26-28 RIB	Yukon R	Mean
DM_1	18.0 ± 0.14^{ij}	19.3 ± 0.28^{de}	19.7 ± 0.17^{b}	19.0 ± 0.28^{C}
DM_1+B	19.0 ± 0.12^{ef}	$20.0\pm0.12b^{c}$	**21.0 ± 0.12^{a}**	20.0 ± 0.29^{A}
DM_2	18.0 ± 0.18^{ij}	18.3 ± 0.11^{hi}	19.5 ± 0.24^{d}	18.6 ± 0.25^{D}
DM_2+B	18.6 ± 0.15^{fgh}	19.8 ± 0.17^{cd}	20.4 ± 0.17^{b}	19.6 ± 0.28^{B}
IN	17.6 ± 0.18^{j}	17.9 ± 0.16^{ij}	18.8 ± 0.13^{ef}	18.1 ± 0.19^{E}
IN+B	18.4 ± 0.29^{ghi}	19.5 ± 0.16^{cde}	20.5 ± 0.17^{c}	19.5 ± 0.32^{B}
N0	**14.0 ± 0.15^{l}**	14.3 ± 0.15^{l}	15.3 ± 0.15^{i}	14.5 ± 0.21^{F}
	17.6 ± 0.35^{C}	18.4 ± 0.41^{B}	**19.3 ± 0.40^{A}**	

Means sharing common letters are not significantly different at 0.05 probability level

Table 3.5: Dry matter yield (Mg ha^{-1}) of three silage corn genotypes during growing season 2017

Treatment/Genotype	A4177G3 RIB	DKC26-28 RIB	Yukon R	Mean
DM1	14.1 ± 0.13^{hijk}	14.9 ± 0.19^{fg}	15.9 ± 0.25^{bcd}	15.0 ± 0.22^{C}
DM1+B	15.1 ± 0.23^{ef}	16.1 ± 0.09^{bc}	**17.1 ± 0.10^{a}**	16.1 ± 0.25^{A}
DM2	$14.0\pm0.08i^{jk}$	14.1 ± 0.16^{hij}	15.6 ± 0.21^{cde}	14.6 ± 0.23^{D}
DM2+B	14.5 ± 0.06^{ghi}	15.6 ± 0.04^{de}	16.4 ± 0.04^{b}	15.5 ± 0.24^{B}
IN	13.6 ± 0.18^{k}	13.7 ± 0.39^{jk}	14.5 ± 0.40^{gh}	13.9 ± 0.18^{E}
IN+B	14.6 ± 0.11^{fg}	15.7 ± 0.11^{cd}	$16.4\ \pm0.13^{b}$	15.6 ± 0.24^{B}
N0	**10.1 ± 0.15^{m}**	10.3 ± 0.03^{m}	11.2 ± 0.15^{l}	10.5 ± 0.14^{F}
	13.7 ± 0.35^{C}	14.3 ± 0.41^{B}	15.3 ± 0.42^{A}	

Means sharing common letters are not significantly different at 0.05 probability level

3.5. Discussion

Soil NO_3^- retention after BC addition had been reported in various studies. In this study, NO_3^- and NH_4^+ concentration increased in BC amended treatments in the top 20 cm soil layer where BC prevented the downward movement of NO_3^- and NH_4^+ to a deep soil layer. Manure and inorganic nitrogen fertilizer application increased NO_3^- and NH_4^+ in all manure and BC amended treatments compared to the control. For example, increased soil NO_3^- was observed after swine slurry application (Bertora et al., 2008). BC amended treatments further increased NO_3^- and NH_4^+ concentration than manure and IN treatments alone which could be attributed to the adsorption of these ions on BC surfaces which decreased their downward movement. Acid functional groups present on BC surface i.e. carboxylic, hydroxyl, lactone, lactol, phenol and carbonyls which have a negative charge and attract NH_4^+ ions (Amonette and Joseph, 2009; Brennan et al., 2001; Montes-Morán et al., 2004; Zheng et al., 2010). Other functional groups i.e. chromenes, ketones and pyrones etc. also exist on BC surface which facilitate NO_3^- adsorption to its surface (Amonette and Joseph, 2009; Montes-Morán et al., 2004). Another possible mechanism could be unconventional H-bonding between NO_3^- and BC surface, which might increase the NO_3^- adsorption on BC surface (Kammann et al., 2015; Lawrinenko, 2014; Mukherjee et al., 2011). Over the time, the adsorbed N could be desorbed and become available in soil (Kameyama et al., 2012; Taghizadeh-Toosi et al., 2012), depending on BC adsorption capacity, amount of BC applied, soil cation and anion exchange capacity, soil microbial community and crop N demand (Clough et al., 2013). Application of BC to soil increased soil N mineralization, enhanced nitrification ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$) by 34 %, suppressed denitrification ($NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$) by 37 %, and reduced cumulative N_2O emission by 91 % in a sandy loam soil (Case et al., 2015). BC induced reduction in denitrification can be explained by changes in soil aeration brought by low soil bulk density and high WHC which lower the denitrifier activity (Karhu et al. 2011; Basso et al. 2013). Most of the biochars decrease soil acidity due to their high pH buffering capacity and alkaline nature (pH > 7) at least 1.5 units higher than acid soils (pH < 5.5). BC used in this study was alkaline (pH = 9), and at each sampling point, BC amended treatments exhibited high soil pH compared to non-BC amended treatments and the control. The carbonates and oxides formed during pyrolysis from the cations (Ca, Mg, K, Na etc.) in feedstock react with H^+ and monomeric aluminum species in acidic soils and increased soil pH (Brewer et al., 2012; Enders et al., 2012; Novak et al., 2009). In addition to the carbonates and oxides, $–COO^−$ ($–COOH$) and $–O^−$ ($–OH$) also play important role in BC alkalinity (Yuan et al., 2011).

BC increased NH_4^+ retention in the soil and improved N uptake (Sun et al., 2017), enhanced lettuce yield and nutrient concentrations in plant tissues (Upadhyay et al., 2014; Woldetsadik et al., 2017), increased soil pH, CEC, Ca, total C, N uptake and biomass production of wheat up to 250 % (Van Zwieten et al., 2010a). It diminished the nutrient losses due to winter freeze-thaw cycle and increased N uptake in the subsequent crop (Zhou et al., 2017). Gunes et al. (2014) reported that BC application increased uptake of N, P, K and reduced Fe, Cu, Zn, and Mn in lettuce grown in alkaline soils. DM application to soil decreased the soil pH while BC amendment increased soil pH along with increasing *Lolium perenne* biomass by 29 % in a growth experiment (Schimmelpfennig et al., 2014). There was significantly low dry matter recorded during

2017 because 30 % less rain was received in this season especially during the crop active growth period (July-August). However, BC increased dry matter yield during both years. Maximum DMY was observed in Yukon R while maximum N concentration was observed in A4177G3 RIB. The N concentration of corn hybrids is influenced by their genetic characters and environment (Gautam et al., 2011). The increase in plant N concentration and DMY could be attributed to improvement in soil fertility, soil physical properties and nutrient retention after BC application. Contrasting effects of BC application on N uptake and plant yield had been reported in the literature depending upon BC feedstock, pyrolysis conditions, soil type etc. (Agegnehu et al., 2016; Borchard et al., 2014; Griffin et al., 2017; Lentz et al., 2014; Lentz and Ippolito, 2012; Schmidt et al., 2014; Tammeorg et al., 2014; Upadhyay et al., 2014; Vitkova et al., 2017; Wang et al., 2016; Woldetsadik et al., 2017).

3.6. Conclusion

Application of BC to DM_1, DM_2, and IN increased the soil NO_3^-, NH_4^+ retention, soil pH, plant N concentration, and DMY. BC application to these treatments decreased leaching which improved plant N concentration and DMY of silage corn crop. BC application also decreased soil acidity. At each sampling interval, high soil pH was observed in BC treatments than non-BC treatments. On an average, BC addition to DM_1, DM_2, and IN enhanced N concentration by 13.5, 11.5 and 17.3 %, respectively. Overall BC application to IN, DM_1 and DM_2 increased the dry matter production by 6, 5.5, and 8.75 %, respectively.

3.7. References

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Chapter 4

4. General discussion and conclusion

The specific objectives of this thesis were:

i- To assess the GHGs emissions from organic and inorganic sources of nitrogen application in silage corn cropping systems

ii- To determine the role of BC application in the reduction of GHG emission in silage corn cropping systems in western Newfoundland

iii- To estimate GWP and GHGI of silage corn cropping systems

iv- To determine the role of BC application on soil NO_3^- and NH_4^+ retention in silage corn amended with DM and IN fertilizer application

v- To compare the effects of dairy manure and IN alone and co-application of BC on soil pH, N uptake and biomass production of silage corn.

This thesis sought to achieve these objectives through two main experimental works as described in chapters 2 and 3. Estimation of GHG emission, GWP and GHGI under DM, and IN application and the potential role of BC in mitigating GHG emissions, GWP and GHGI have been described in chapter 2. Whereas, NO_3^- and NH_4^+ retention/losses in the soil with DM, and IN application alone and combined application of BC, plant N uptake, soil pH and dry matter yield of silage corn genotypes are presented in chapter 3.

4.1. Effect of biochar application on GHGs emission, GWP and GHGI

About 8 % of the total GHGs emissions in Canada are contributed by the agriculture sector largely through methane (CH_4) and nitrous oxide (N_2O) (Kebreab et al., 2006). N_2O emissions from agricultural soils represent 3 % of anthropogenic sources in Canada (Environment and Climate Change Canada, 2017). DM and inorganic fertilizers application to agricultural soils emit significant amount of GHGs including CO_2, CH_4 and N_2O (Amon et al., 2006; Burton et al., 2008; Kebreab et al., 2006), and emissions were more pronounced with DM application than chemical fertilizers (Barneze et al., 2014; M. Zhou et al., 2017). The C compounds in the DM increase the soil CO_2 emission by inducing a priming effect on native soil C (Bol et al., 2003). However, application of BC decreases the decomposition of soil organic matter (SOM) present in the soil so, it remains in the soil for a longer period (Cui et al., 2017) and reduces the cumulative CO_2 emission either by the sorption of CO_2 on its surface or by reducing the availability of labile C (Brennan et al., 2015). In the present study DM_1 (low N dairy manure) and DM_2 (high N dairy manure) treatment produced significantly higher CO_2 emission than IN and BC amended treatments, which is in accordance with some previous studies (Agegnehu et al., 2016; Lentz et al., 2014; Schimmelpfennig et al., 2014). BC application induces negative priming effect and decelerates the breakdown of SOM by the sorption of enzymes responsible for SOM breakdown, shifting the microbial metabolism, by increasing the stability of soil aggregates (Zheng et al., 2018) and by reducing the bioavailability of soil organic carbon (SOC) via adsorption on BC large surface area (Sheng and Zhu, 2018). It decreases the dissolved organic carbon (DOC) from native SOC and reduces the decomposition of SOC after IN addition which reduces CO_2 emission from the soil (Lu et al., 2014). High CH_4 emission after DM application as observed in our experiment had been reported in other studies (Troy et al., 2013). Short-chain fatty acids present in manure are readily available to methanogenic archaea and cause CH_4 emissions after application to the soil (Hrapovic and Rowe, 2002; Sherlock et al., 2002). Significant reduction in CH_4 emission was observed in BC amended treatments (DM_1+B, DM_2+B, IN+B) as compared to non-BC treatments (DM_1, DM_2, IN). The decrease in CH_4 emission after BC application may be due to the stimulation of methanotrophic activity or the increased abundance of methanotrophic proteobacterial community abundance (Feng et al., 2012; Liu et al., 2011). The BC suppresses methanogenesis by increasing the oxygen supply in the soil through increased aeration (Kim et al., 2017). There are several mechanisms by which BC could reduce N_2O emissions. It improves soil aeration by reducing the soil bulk density which decreases the activity of denitrifiers in the soil (Zhang et al., 2010). The reduction in N_2O emissions after BC application may be due to modification of SM, increased aeration, inhibition of nitrifier and denitrifier communities (Laird et al., 2009; Yanai et al., 2007). Application of BC (1) may accelerate the growth of soil microbes which reduce N_2O emission by supporting denitrification of NO_3^- to N_2 (2) facilitates the mycobacterial reduction of NO_3^- to NH_4^+ (3) adsorbs NH_4^+ on its surface (4) decrease the abundance of microorganisms involved in nitrification of NH_4^+ to nitrite (NO_2^-) (Anderson et al., 2011) (5) act as "electron shuttle" facilitating electron transfer to soil denitrifying microbes (Cayuela et al. 2013). BC adsorb NH_4^+ on its surface and reduces its availability for nitrification as a result, N_2O emission is declined (Berglund et al., 2004; Lehmann et al., 2006). Application of BC to soil increased soil N mineralization, suppressed denitrification and reduced cumulative N_2O emission by 91 % in a sandy loam soil (Case et al., 2015). Application of pine wood chips BC produced at 550 ^{o}C to kurosol soil (pH = 5) increased the NO_3^- concentration in the soil and decreased the abundance of *nar*G (a gene involved in NO_3^- reduction to NO_2^-) (Bai et al., 2015). It also increased the abundance of *nosZ* (a gene involved in N_2O reduction to N_2) by providing suitable conditions for nosZ including increased soil pH and microbial respiration (Van Zwieten et al., 2014). Similarly, some other studies also confirmed that BC increased the abundance of *nos*Z, *nir*K, and *nir*S (both NO_2^- reductase genes) and favored the last step of denitrification (converted N_2O to N_2) which ultimately decreased N_2O emission (Cayuela et al., 2013; Ducey et al., 2013; Harter et al., 2014; Van Zwieten et al., 2010b). Molar H:C ratio of BC also affects N_2O emission. BCs with high H: C_{org} ratio is more effective in reducing N_2O emission. For example, BC having a molar H: C_{org} ratio less than 0.3 (have high degree of aromaticity) decreased N_2O emission by 73 % whereas, BCs with a molar H: C_{org} ratio more than 0.5 decreased N2O emission by 40 % (Cayuela et al., 2015). BC with high H:C ratio reduces the bioavailability of C for the growth of denitrifying communities (Van Zwieten et al., 2014). It has been reported in several studies that BC application improves soil aeration and increase oxygen supply, these conditions decrease the rate of denitrification in the soil. In the present study, more NO_3^- and NH_4^+ was observed to be retained in BC amended soils as described in chapter 3. So that, the reduction in N_2O emissions was most probably due to the reduction in denitrification or due to complete denitrification (reduction of N_2O to N_2) after BC application (Cayuela et al. 2013, 2014, 2015).

4.2. Biochar effects NO_3^- and NH_4^+ retention, soil pH, plant N concentration and dry matter production

In this study, DM and IN application to soil increased NO_3^- and NH_4^+ retention (concentration) in 20 cm soil in all treatments compared to the control treatment. The BC application reduced the movement of NO_3^- and NH_4^+ to 40 cm deep soil layer which could be attributed due to the adsorption of these ions to BC surface area. Similar results have been reported in a 4-year long field experiment where BC increased the NO_3^- concentration in topsoil and decreased its movement to deep soil layer (Haider et al., 2017). Acid functional groups present at BC surface i.e. carboxylic, hydroxyl, lactone, lactol, phenol and carbonyls attract NH_4^+ ions (Amonette and Joseph, 2009; Brennan et al., 2001; Montes-Morán et al., 2004; Zheng et al., 2010). Some other functional groups i.e. chromenes, ketones and pyrones also exist on BC surface which facilitates NO_3^- adsorption to its surface (Amonette and Joseph, 2009; Montes-Morán et al., 2004). Unconventional H-bonding between NO_3^- and BC surface possibly increased the NO_3^- adsorption on BC surface (Kammann et al., 2015; Lawrinenko, 2014; Mukherjee et al., 2011). Over the time, the adsorbed N could be desorbed and become available in soil (Kameyama et al., 2012; Taghizadeh-Toosi et al., 2012). Application of BC to soil augmented soil N mineralization, boosted nitrification and inhibited denitrification (Case et al., 2015). Most of the biochars increase soil acidity due to their high pH buffering capacity and alkaline nature. In the present study, BC amended treatments exhibited high soil pH as compared to non-BC and the control treatments at each sampling point. The carbonates and oxides formed during pyrolysis from the cations (Ca, Mg, K, Na etc.) in feedstock react with H^+ and monomeric aluminum species in acidic soils and increase soil pH (Brewer et al., 2012; Enders et al., 2012; Novak et al., 2009). The BC increased NH_4^+ retention in the soil and improved N uptake (Z. Sun et al., 2017), enhanced lettuce yield and nutrient concentrations in plant tissues (Upadhyay et al., 2014; Woldetsadik et al., 2017), increased soil pH, CEC, Ca, total C, N uptake and biomass production of wheat up to 250 % (Van Zwieten et al., 2010a). The increase in plant N concentration and dry matter yield (DMY) could be attributed to improvement in soil fertility, soil physical properties and nutrient retention after BC application (Mukherjee et al., 2014; Randolph et al., 2017).

4.3. Conclusion and Recommendations

BC application to DM_1, DM_2 and IN significantly reduced GHG emissions, decreased GWP and lowered GHGI of silage corn cropping system tested in western Newfoundland. It also improved soil pH, increased soil NO_3^- and NH_4^+ retention, enhanced N concentration in plant tissues, and DMY of silage corn during the two-year field experiment. BC amended treatments reduced CO_2 emission by 22 %, CH_4 emission by 225 %, N_2O emission by 91 %, GWP by 32 %, and GHGI by 37 % compared to the control treatment. Additionally, BC amended treatments also improved Plant N concentration by 16 %, dry matter yield by 6.7 % of silage corn during two consecutive growing seasons. This study was conducted in a cool climate system. The soil of the study site was rapidly drained, Orthic Humo-Ferric Podzol which have loamy sand texture with pH of 6.3. Based on the results of this two-year field study it was concluded that:

i- Different sources of N have a significant impact on GHGs emissions, IN (NH_4^+ and NO_3^-) concentrations in soil, soil pH, plant N concentration and DMY of silage corn in cool climate cropping system.

ii- Pinewood BC could be used to mitigate GHG emissions, decrease GWP and GHGI with great success, and to increase soil pH, decrease NH_4^+ and NO_3^- losses to the deep soil, increase plant N concentration and DMY.

iii- BC maintains high soil moisture which favors crop growth during a dry spell.

Further studies exploring the role of soil bulk density, porosity, SOC contents on GHGs emissions are required as BC amendment to soil modifies soil physical properties. It also affects soil biota which affects the emission of GHGs (methanogenic, methanotrophic communities, soil nitrifying and denitrifying microbe's population) which can provide more insights into the mechanism underlying the BC role in GHGs emission reduction.

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