CHARACTERIZATION OF BIOCHAR FROM DIFFERENT FEEDSTOCKS UNDER LOW AND HIGH TEMPERATURE AND THEIR EFFECTS ON GREENHOUSE GAS EMISSION AND AMMONIA VOLATILAZATION FROM SOIL INCUBATION

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The Supervisory Committee certifies that this ***disquisition*** complies with North Dakota State University's regulations and meets the accepted standards for the degree of

MASTER OF SCIENCE

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ABSTRACT

Biochar is a potential soil amendment that likely to reduce GHG emissions from land application to soil, but their properties depend on biomass types and pyrolysis temperature. In this study, biochars were produced from different biomasses (wet distiller grains (WDG), dry distiller grains (DDG), and corn stover (CS)) at two temperatures (low & high). Biochars were analyzed for pH, electrical conductivity, proximate and ultimate analysis, elemental analysis, and morphological structure. Also, biochar's efficacy on GHGs and ammonia (NH_3) emission were measured from soil and manure incubated at 25℃ for 76 days. DDG and CS derived biochar properties outperformed other biochars. Manure treated with high-temperature DDG biochar emitted the lowest amount of N_2O (0.09 mg N_2O-N kg^{-1}), and CH_4 (0.04 mg CH_4-C kg^{-1}). Biochar application also reduced CO_2 emission from 11 to 59%, but resulted in higher cumulative NH_3 volatilization. Overall, biochars reduced GHG emissions when applied with N treatments.

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DEDICATION

This thesis is dedicated to my parents, my brother, and my wife.

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LIST OF ABBREVIATIONS

BET	The Brunauer-Emmet-Teller
CS	Corn Stover
DDG	Dry Distiller Grain
GHG	Greenhouse Gases
GWP	Global Warming Potential
NUE	Nitrogen Use Efficiency
SSA	Specific Surface Area
US EPA	United States Environmental Protection Agency
WDG	Wet Distiller Grain
WHC	Water Holding Capacity

1. INTRODUCTION

The use of biochar has drawn much attention because of two major global issues: climate change and the realization of the need for more sustainable soil management (Chan et al., 2008). Globally biochar is evaluated as a soil amendment to improve soil properties (such as soil water holding capacity, nutrient retention, and microbial activity) and to mitigate climate change by sequestering carbon (C) from the atmosphere into the soil (Borhan et al., 2018; Jeffery et al., 2011; Lehmann et al., 2011). Biochar is a carbon-rich product obtained by heating the biomass, inside a closed container, under no or limited air supply (Lehman and Joseph, 2009; Ok et al., 2015). Incorporation of biochar into the soil is the strategy for enhancing soil fertility and crop productivity, increasing crop yield, reducing irrigation need, and reducing fertilizer demands, improving the efficiency of N fertilizer, and mitigating greenhouse gas (Ahmad et al., 2014; Lehman and Joseph, 2009; Li et al., 2017; Liu et al., 2018; Speratti et al., 2018). Previous studies reported that biochar applied with mineral fertilizers increases nitrogen use efficiency (NUE) by approximately 21, 44 and 74% in wheat, maize, and rice, respectively, compared to the NUE observed when N fertilizers is used without biochar (Joseph et al., 2013; Zheng et al., 2017; He et al., 2018; Puga et al., 2020). Studies assumed that the NUE values might be increased due to the gradual release of sorbed nutrients in biochar that reduced N leaching (Borchard et al., 2012; Clough et al., 2013, Mandal et al., 2016; Puga et al., 2020). Also, the combination of biochar with fertilizer and carbon storage function in soils would activate the microbial community, which may lead to nutrient release and fertilization causing an increase of the soil productivity (Steinbeiss et al., 2009). Therefore, along with fertilizer, biochar can be applied to soil to improve the quality of soil for crop production.

Similarly, emission of greenhouse gases (GHG) such as nitrous oxide (N_2O), carbon dioxide (CO_2), methane (CH_4), chlorofluorocarbons (CFCs), hydrofluorocarbons (HFC), etc. are a major concern due to their contribution to global climate change (Maurer & Koziel., 2019). Especially, N_2O, CO_2, and CH_4 are the main three GHGs linked with agriculture, where CH_4 and N_2O have 25 and 298 times higher global warming potentials (GWP), respectively, than CO_2 (Niraula et al., 2018; US EPA, 2020b). Recent studies estimated that soil derived GHGs from agricultural inputs contribute more than 13% of global anthropogenic GHG emission and 9.3% of total USA greenhouse gas emissions (Lal 2004; Zhao et al. 2016; Niraula et al., 2018; US EPA, 2020b). The input of nitrogen (N) from manure or synthetic fertilizer (e.g., Urea) applications increases gaseous emissions from soils (Niraula et al., 2018). Along with GHG emissions, N is also lost through ammonia (NH_3) volatilization loss from the soil after the land application of fertilizer. Release of NH_3 to the environment contributes to acidification and eutrophication of the ecosystems due to its deposition of the surface and water body, which leads to an adverse effect on the aquatic system and human health (Aneja et al. 2008; Niraula et al., 2018). To meet the global food and fiber demand, agricultural production needs to increase without unduly opening new agricultural areas that are based on plant breeding, the use of pesticides, and the application of mainly nitrogen-based fertilizers (Smil, 2011, Zhang et al., 2015; Puga et al., 2020). Increasing demand for food production leading to use more N fertilizer that may result in more GHG emissions and NH_3 volatilization. Therefore, sustainable agricultural production is required that will ensure less emission of GHG and NH_3. Biochar can play an important role in mitigating some of these concerns. However, biochar properties vary significantly based on biomass types and pyrolysis temperatures, which needs to be quantified.

The physical and chemical properties of biochar depend on the feedstock and pyrolysis conditions (e.g. residence time, temperature, heating rate, and reactor type) (Cheng et al., 2018). According to Feng et al. (2017), the effect of biochar on GHG emissions and NH_3 volatilization depends on the interactions of several properties, including adsorb ability, pH, and the impact on nitrification that are associated with the physical and chemical properties of biochar. Other researcher finds that biochar effects on GHG emission and NH_3 volatilization also depend on biochar quality and application rate (Pal., 2015). Studies reported that biochar amendment to soil with high pH and rich carbon content is an effective management strategy to counteract soil acidification for sustainable agriculture while reducing soil GHG emissions (Wang et al., 2020). Biochar plays an important role in soil nitrification, denitrification, and organic matter mineralization that affects soil C and N cycling (Van Zwieten et al., 2010). Also, biochar can help to retain nutrients (NH_3, NH_4^+, NO_3^-, etc.), absorb pollutants (heavy metals and agrochemical products), improve soil quality, and crop yield because of its stable quality, and excellent adsorption capacity. Thus, biochar likely to play a significant role in mitigating the environmental consequences caused by intensive agricultural production (Kookana et al., 2011; Cao et al., 2009; Sha et al., 2019). However, limited studies are focused on the efficacy of biochar on GHG and NH_3 volatilization.

The effect of biochar addition on soil GHG emission and NH_3 volatilization are inconsistent (Wang et al., 2020; Zhu et al., 2020). Previous studies showed that in acidic soil, N_2O emissions could be reduced significantly with biochar addition (Yanai et al., 2007; Wang et al., 2011; Cayuela et al., 2014; Nelissen et al., 2014). On the contrary, Zimmerman et al. (2011), Fungo et al. (2014) Maucieri et al. (2017), and Oo et al. (2018) observed that the biochar amendment soil increased CO_2 and CH_4 emissions. In terms of NH_3 volatilization, Mandal et al.

(2016) observed a significant reduction of NH_3 volatilization when added 5% biochar in non-saline soil. In contrast, Feng et al. (2017) found that in non-saline paddy soils, NH_3 volatilization did not significantly increase at low biochar treatment (0.5 wt%), while higher biochar treatment (3 wt%) significantly increased NH_3 volatilization. Furthermore, in coastal saline soil, Sun et al. (2017) found that higher rates (>2%) of biochar application aggravated NH_3 volatilization. Thus, there is limited information on the biochar impact on GHG emission and NH_3 volatilization from the soil and need to be further investigated.

Agriculture is a vital economic force in North Dakota, USA. In 2017, North Dakota produced 0.45 billion bushels of corn and produced approximately 1.5 million tons of dried distiller grains with solubles (DDGS) as a coproduct from corn-based ethanol industries which are widely used as an animal feed that supplies both energy and protein (Schroeder, 2003; Garcia and Taylor, 2006; Borhan et al., 2018). In recent years, wet distiller's grains (WDG) are also included for animal feed, which can also be converted to biochar. Similarly, biomass residue as a stover (the non-grain portion of the corn plant) is produced in significant amounts from corn harvest. According to a recent study, North Dakota utilizes only 10-20% of the residue of corn (Schmer et al., 2017). Corn stover is rich in carbohydrates but low in nutrients. In most cases, agricultural wastes are used as feedstock for biochar production, which helps to reduce the number of agricultural wastes (Lehman and Joseph, 2009; Speratti et al., 2018). Corn stover and DDGS/WDG can be used as carbon conserving soil amendments by converting them to biochar that may ensure sustainable corn production in North Dakota (Borhan et al., 2018). Therefore, the main purpose of this study was undertaken to investigate the quality of biochar produced from corn stover and distiller grain and their effects on GHG and ammonia emission with following the objectives:

i) to produce biochars from two forms of distiller grains (e.g., dry and wet) and corn stover in low temperature (386°C) and high temperatures (500°C)

ii) to characterize their physical, chemical, and surface characteristics, and

iii) to quantify the effects of biochars on GHG and NH_3 emission volatilization from soil incubation with manure and Urea.

2. LITERATURE REVIEW

2.1. History of Biochar

The history of biochar started from the Amazonian rain forests of Brazil (Pleasant, 2000). In the pre-Columbian era, the Amerindian communities first made dark earth soils using slash and char (Lehmann & Joseph, 2012) called terra preta (terra preta de Indio). The study of Pleasant (2000)found that Amazonian dark earth holds plant nutrients, including nitrogen (N), phosphorous (P), calcium (Ca), and magnesium (Mg), much more efficiently than unimproved soil. High carbon (C) content (150 g C/kg soil) of these soils are the main characteristics compared to the surrounding soil (20-30 g/ C/kg soil) (Glaser et al., 2002). It becomes hundreds of years of giving up those soils, but this increased carbon content is still found. That is the proof of the persistence of the organic matter in the terra preta soils. Therefore, the carbon persistence, soil fertility, and sustainability of biochars have drawn the attention of the researchers (Rajapaksha et al., 2016). Glaser et al. (2000) identified black carbon in terra preta soils that are a probable cause of sustainability and fertility of these soils. Besides, the organic matter in terra preta soil has a similar structure of biochar. That explains the reason for the high carbon content and fertility of terra preta (Glaser et al., 2000).

In recent years, several works have been done to explore the knowledge about biochar. The objectives of those studies were mainly to know biochar properties, its effect on soil and mitigation of environmental pollution by using them. Lehmann et al. (2011) examined the influence of biochar on soil microorganisms, fauna and plant roots after the addition to soil. Shaaban et al. (2018) evaluated the strategic application of biochar to the soil that their effect on the soil properties and economic benefits. Ahmad et al. (2014), discussed the properties and key parameters (pyrolysis temperature, heating rate, feedstock type, etc.) of biochar to summarize the current use of biochar as a sorbent for contaminant management in soil and water. El-Naggar et al. (2018) investigated the effect of biochars of different properties on the carbon mineralization and improvement of the quality of different textures soils. Oliveira et al. (2017) explained the production and properties of biochar and the mechanisms involved in the removal of different types of organic and inorganic pollutants from the aqueous and gaseous phase. Aller et al. (2017) conducted an experiment to know more about the impact of fresh and aged biochar on plant available water and water use efficiency. In that study, fresh biochar increased plant available water. Li et al. (2017) conducted a study to explore the effects of apple branch biochar on the dynamic transformation of soil C, N, and P under different application rates and N conditions. Kammann et al. (2017) discussed the mechanisms and formation of two major greenhouse gases (N_2O and CH_4) in soil. That study explored the use of biochar to mitigate greenhouse gas emissions from agricultural land. Feng et al. (2018) investigated the effect of biochar on N_2O emission from dry land at different moisture content. Martin et al. (2015) quantified the effect of biochar application on N_2O emission within soil amended with anaerobic digestates from different feedstock.

2.2. Biochar Production and Characteristics

Biochar is the carbon-rich product obtained by heating the biomass, such as wood, manure, or leaves in a closed container under no or limited air supply. It is basically a soil amendment, which distinguishes it from charcoal (Lehmann & Joseph, 2012). Globally biochar is evaluated as a soil amendment to improve soil properties and to mitigate climate change by sequestering C (Jeffery et al., 2011; Lehmann et al., 2011). The potential biochar applications include carbon sequestration, soil fertility improvement, pollution remediation, and agricultural by-product/waste recycling (Ahmad et al., 2014). An increasing interest in the beneficial application of biochar has opened up multidisciplinary areas for science and engineering. (Ahmad et al., 2014). Yet, very little is known about the mechanisms through which biochar affects the microbial abundance and community composition of the soil (Lehmann et al., 2011).

2.2.1. Production of Biochar

All three forms of carbonaceous materials (biochar, char, and charcoal) Biochar is typically produced by the pyrolysis process. In this process, Carbon bearing solid materials like agricultural and other waste is heated under oxygen-starved condition (Figure 1). Biochar is specifically produced for application to the soil for agronomic and/or environmental management and that makes it different from char and charcoal (Brown et al., 2015). The process of biochar production is not new; it has been used as an energy source for thousands of years for domestic and agricultural use. Anyone can easily understand the concept of biochar production. Thus, farmers can produce biochars on their farm by slow pyrolysis (1-20° C min-1) of agricultural wastes (Ok et al., 2015).

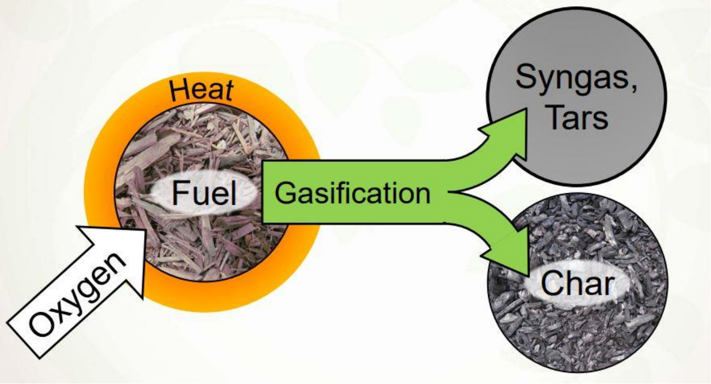


Figure 1. Biochar production process

2.2.2. Factors Affecting Quality of Biochar

Types of feedstock and pyrolysis conditions affect biochar stability and production parameters differently. Pyrolysis temperature is the dominant parameter that determines biochar stability (Leng & Huang, 2018). Higher temperature (>550°C) produces stable and highly aromatic biochars which have a large surface area. Lower temperature (<550°C) pyrolysis produces less condensed biochar structure that is expected to be more biodegradable and is less expensive (Ok et al., 2015). In addition, lower temperature pyrolysis has the environmental advantage that it emits fewer pollutants than the high temperature (Boyle, 2004). To enhance biochar stability at a lower temperature, long reaction residence time, slow heating rate, high pressure, co-pyrolysis with beneficial minerals, biomass feedstock of high-lignin content and large particle size are preferable (Leng & Huang, 2018).

Besides temperature, biochar properties also depend on heating rates, types of biomass, and vapor residence times (Ronsse et al., 2013). For agricultural use, slow pyrolysis is the most feasible production process to produce high-quality biochar (Song et al., 2012). In slow pyrolysis, the biomass is burned in an oxygen-limited condition with typical heating rates between 1 and 30 °C min−1 (Lua et al., 2004). In the process, organic materials are heated by an external energy source at atmospheric pressure condition. Then organic material thermally decomposes and produces a solid residue and a vapor phase, and that solid residue is called biochar. (Laird et al., 2009).

2.2.3. Characterization of Biochar

The physical and chemical composition of biochar depends on the type of feedstock and pyrolysis conditions (e.g., residence time, temperature, heating rate, and reactor type); thus, not all biochars are the same and it is difficult to define the exact chemical composition of biochar. Biochars are mainly composed of carbon. The organic portion of biochar has a high carbon content and the inorganic portion mainly contains minerals such as Ca, Mg, K, and inorganic carbonates depending on its feedstock type (Rajapaksha et al., 2016).

Biochar composition can be crudely divided into relatively recalcitrant C, labile or leachable C and ash. The biochar organic carbon is often classified as recalcitrant C. When discussing biochar carbon, it is important to differentiate between total carbon and organic carbon. Studies of biochar used total carbon as a measure for carbon content. However, the use of organic carbon has been argued as a better measure of biochar C because upon pyrolysis some biochar has high carbonate content due to high ash content. The organic carbon of biochar is directly related to both the feedstock and the pyrolysis or gasification condition (Mukome et al., 2015). The greater the proportion of aromatic C, the greater the chemical difference between biochar and other organic matter. The nature of these C structures is the main reason for the high stability of biochars; however, the precise mechanisms of the stability of the aromatic C structures in the soil is less clear (Lehmann et al., 2011).

The mineral ash content reflects the inorganic content of the original feedstock. Common inorganic components include P, S, K, Ca, Mg, sodium (Na), iron (Fe) and zinc (Zn) which varies between the biochars due to the type of feedstocks. Ash content closely related to biochar pH., electrical conductivity (EC) and mineral composition. Knowledge of biochar ash content is important for several agronomic considerations (Mukome et al., 2015).

One of the biochar properties with key agronomic considerations is pH. It is the measure of acidity or alkalinity. Most biochars are alkaline with a pH>7 and their use often raises the pH of acidic soil (liming effect) and affects the mobility of cations in the soil. Biochar pH depends on feedstock type, pyrolysis temperature, and production process. The influence of feedstock type is more than the pyrolysis temperature (Mukome et al., 2015). For example, even if biochar is produced at the same temperature, the non-wood feedstocks (manure, corn-Stover, and algae) derived biochar generally have higher pH than wood feedstocks (Enders et al., 2012; Mukome et al., 2013).

Cation exchange capacity (CEC) is a measure of exchangeable cations (e.g. Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}) and it is an important measure of soil quality and productivity. CEC also depends on biomass feedstock and pyrolysis conditions. Manure based biochar has a higher CEC than plant-based biochar. In addition, fast pyrolysis biochar shows higher CEC than a slow pyrolysis process. On the other hand, greater pyrolysis temperatures cause a decrease in CEC. It has also shown that biochar CEC increases with ages or weathers and with storage conditions (mc, temperature). Addition of biochar to soil increases soil CEC (Mukome et al., 2015)

Electrical conductivity (EC) is a measure of the ability of a material to conduct an electrical current. It is commonly used as a proxy for the salinity in aqueous extracts and soil. Non-manure biochars typically have lower ash content and lower EC values than manure-derived biochars. The high EC values are associated with high amounts of soluble salts. A higher amount of soluble salt affects soil microorganisms that influence some important soil processes, such as nitrification and denitrification, organic matter decomposition and respiration. It can also affect soil structure through flocculation and can cause inhibited plant growth from ion toxicity and ion imbalance (Mukome et al., 2015).

The specific surface area (SSA) of biochar is determined by The Brunauer-Emmet-Teller (BET) analysis and is called area per gram of sample (Mukome and Parikh, 2015). It is measured by exposing biochar surface to a defined gas atmosphere (N_2 gas and CO_2) at the temperature of liquid nitrogen (77k) and then the amount of absorbed gas is measured (F. N. Mukome and Parikh, 2015; Weber and Quicker, 2018). The measurement of the SSA depends on different protocol parameters (e.g., sorption gas, degassing temperature and time (Keiluweit et al., 2010;

Kookana et al., 2011; Mukome and Parikh, 2015). Due to those parameters, the appropriate gas for the biochar SSA measurement has not been fixed yet (McLaughlin et al., 2012; Mukome and Parikh, 2015). However, some studies suggested that CO_2 gas is more accurate for the SSA measurement (McLaughlin et al., 2012; Mukome and Parikh, 2015). Biochar has a high surface area compared to soil (Mukome and Parikh, 2015). There are positive relations between the surface area and the pyrolysis temperature. However, some feedstock does not show the same relation (Keiluweit et al., 2010; Kookana et al., 2011; Mukome and Parikh, 2015). Sometimes the specific surface area is connected to some factors such as cation exchange capacity and/or water holding capacity (Mukome and Parikh, 2015; Weber and Quicker, 2018). During the carbonization process, the volatile gases escape from the biomass and that changes the porosity and the total surface area of the biomass (Weber and Quicker, 2018). The ability of biochar to provide microbial habitats, soil-aggregating nuclei, retaining water and added nutrients to soil depends on surface area (Mukome and Parikh, 2015). In addition, biochar's role as a contaminant removal also depends on SSA. However, the mechanisms of biochar in soil have not been understood yet (Mukherjee and Lal, 2014; F. N. Mukome and Parikh, 2015).

The bulk measure of size, shape, and structure of biochar is called morphology (Mukome and Parikh, 2015). Morphological characteristics of biochar obtained from the image of the biochar surface where numerous macro and micropores can be seen (Lee et al., 2010; Mukome et al., 2013; Mukome and Parikh, 2015). Usually, the surface image of the biochar is taken by the scanning electron microscopy (SEM). The surface images of biochars are different depending on the feedstock type and temperature (Lee et al., 2010; Mukome et al., 2013; Mukome and Parikh, 2015; Özçimen and Ersoy-Meriçboyu, 2010). Mukome and Parikh, 2015, observed that biochar derived from pinewood at 900°C has large pores than the biochar obtained at 300°C.

2.3. Biochar Application to Soil

Carbon sequestration in soil is essential for the enrichment of soil quality (Bruun et al., 2015; Zhang et al., 2017). Thus, a carbon-rich amendment is necessary to improve the quality of the soil. Biochar is a carbon-rich, cost-effective amendment that is used mainly for soil management (Park et al., 2016). There is no need for extensive biomass material preparation or costly product isolation procedures for biochar production (Steinbeiss et al., 2009). For this reason, it has received massive interest in recent years (Rizwan et al., 2016). Researchers suggested that the incorporation of biochar into the soil is the strategy for enhancing soil fertility and crop productivity (Li et al., 2017). Biochar is applied to the soil to improve soil quality, increase crop yield, reduce irrigation and fertilizer application and mitigate greenhouse gas (Liu et al., 2018b). The combination of biochar with fertilizer and carbon storage function in soils would activate the microbial community, which may lead to nutrient release and fertilization causing an increase of the soil productivity (Steinbeiss et al., 2009). Though agricultural productivity often increases with biochar application, it depends on various factors, including types of feedstock, production conditions, type of soil application rates and the use of additional fertilizer (Blackwell et al., 2009; Sui et al., 2016). Therefore, it is difficult to predict the yield responses (Blackwell et al., 2009).

2.3.1. Effects of Biochar as Soil Amendment

The effects of biochar on soil biota have received much less attention than its effects on soil chemical properties (Lehmann et al., 2011). Sorption phenomena, pH, and physical properties of biochars such as pore structure, surface area, and mineral content play important roles in determining how different biochars affect soil biota (Lehmann et al., 2011).

2.3.1.1. Effects of Biochar on Soil Moisture and Soil Nutrients

Soil fertility is the ability of soil to provide sufficient nutrients and water to plants in favorable environmental conditions (Havlin et al., 2005). Steinbeiss et al. (2009), has observed several studies that the addition of biochar to soils improved soil fertility and thus increased crop yield. Additionally, the huge surface area of the biochars increased water retention and cation exchange capacity of the soils that support fertility. In addition, biochar brings additional photosynthetic fixed carbon into the soil, which provides the opportunities to store carbon (C) in the soil for a longer period of time compared to other soil amendments (Sheng & Zhu, 2018; Steinbeiss et al., 2009). Thus, it mitigates CO_2 emission from agricultural lands (Steinbeiss et al., 2009).

The application of biochar may change several soil properties like electrical conductivity (EC), pH, CEC, nutrient levels, porosity, bulk density, and microbial community structures. These changes in soil properties can alter soil fertility and crop productivity in various ways by improving nutrient levels and decreasing nitrogen (N) leaching in soils. Biochar also likely influences the microbial populations in a soil that makes the nutrients available for the plant (Shaaban et al., 2018).

2.3.1.2. Management of Pollutant in Soil

Soil is an essential resource for sustainable agriculture and food production; however, the risk of rapid soil degradation is rising globally (Symeonakis et al., 2016). To improve the soil quality and crop yield, farmers use fertilizers and pesticides. Most of the time, farmers do not know about the application rate, and they apply an excess amount of fertilizer and pesticides in the field. Extreme and inefficient use of pesticides imposes severe toxic effects on living organisms that result in serious soil and water contamination. Using environment-friendly amendments for Soil remediation could be a suitable approach to solve this problem (Liu et al., 2018a). Biochar is a cost-effective amendment for the management and rehabilitation of infertile and contaminates soils; it has received intensive interest in the last decade (Park et al., 2016; Rizwan et al., 2016).

2.3.1.3. Biochar Effects on Greenhouse Gases

Greenhouse gases are gases in the atmosphere that capture solar radiation and warm the surface of the earth (Massey & McClure, 2014). Carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), perfluorocarbons (PFCs), hydrofluorocarbons (HFCs), and Sulphur hexafluoride (SF_6) are the major greenhouse gases (GHGs) that produce as a result of human activities such as energy production, agriculture, forestry, and land-use etc. (Victor D. G et al., 2014). GHG maintains the temperature on the earth and makes it habitable (Ok et al., 2015). An average temperature of the earth is about 59 °F and without GHGs contribution, the earth temperature would be about -2°F (Massey & McClure, 2014). However, due to human activities, GHG emissions are increasing that resulting in increased earth temperature. That leads to adverse effects in the earth’s environment like sea-level rise, floods, droughts, adverse seasonal variations and melting of polar ice caps etc. (Ok et al., 2015).

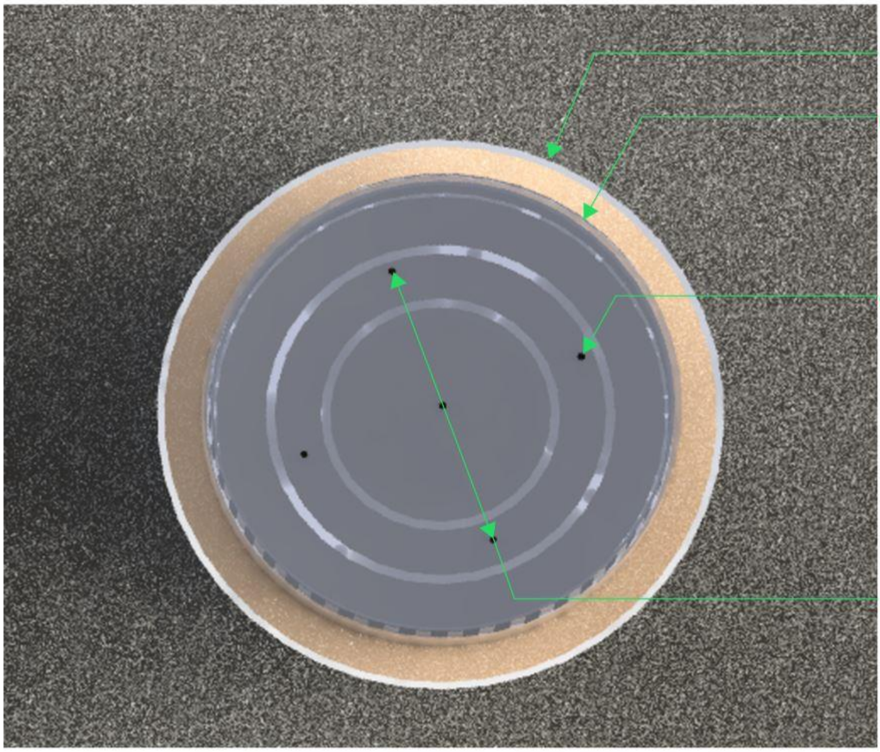
At present, CO_2 contributes 76%; CH_4 about 16%, N_2O about 6%, and the combined Fluorinated gases (F-gases) are contributing about 2% of the total GHG emission (Victor D. G et al., 2014). However, CH_4 and N_2O capture more heat in the atmosphere than CO_2 (Massey & McClure, 2014). GHG emissions from agricultural activities happened through a variety of processes such as enteric fermentation in domestic livestock, livestock manure management, rice cultivation, agricultural soil management, liming, urea fertilization, and field burning of agricultural residues (US EPA, 2020c).In 2018, agricultural activities were responsible for emissions of 9.3 percent of total U.S. greenhouse gas emissions (US EPA, 2020b). The major GHG emitted by agricultural activities are CH_4, N_2O, and CO_2 (US EPA, 2020b). Agriculture is the main source of anthropogenic emissions of CH_4 and N_2O and agricultural activities particularly manure and slurry application to fields, contribute up to 60% of the global annual anthropogenic emissions (Martin et al., 2015). Application of biochar is a potential remedy for carbon sequestration (Feng et al., 2018) and decreasing N_2O emission is reported to be one of the co-benefits of biochar when it is applied to soil (Martin et al., 2015). Feng et al. (2018), found that biochar made from rice straw at the temperature of 300°C decrease N_2O emission at the moisture content of 27% and 30%. The study of Yanai et al. (2007) showed, applying 10% (wt basis) charcoal decrease 89% N_2O emission from loam to clay loam soil when 73% and 78% of the soil pore space was filled by water. Rondon et al. (2006) conducted a glasshouse pot experiment where they applied charcoal at the soil and planted Soybeans and a tropical grass (B. humidicola). The N_2O emission from soybean and the grass pots were reduced by 50% and 80%, respectively. The degree of the reduction of N_2O emission depends on the feedstock used to produce biochar, type of soil, biochar application rate and soil moisture conditions (Martin et al., 2015). Incorporating biochars to soil increases CH_4 uptake from the soil that contributes to mitigating GHG emissions (Van Zwieten et al., 2009). Rondon et al. (2005) and (2006), showed that wood-derived biochar decreases CH_4 emission from soil. Recent literature suggests that biochar may significantly reduce N_2O and CH_4 emissions when applied as a soil ammendment (Kammann et al., 2017). However, limited understanding of the mechanisms through which biochar decreases CH_4 and N_2O emission (Van Zwieten et al., 2009). Thus, there is a need to study the effects of biochar on GHG emissions under different conditions.

3. MATERIALS AND METHOD

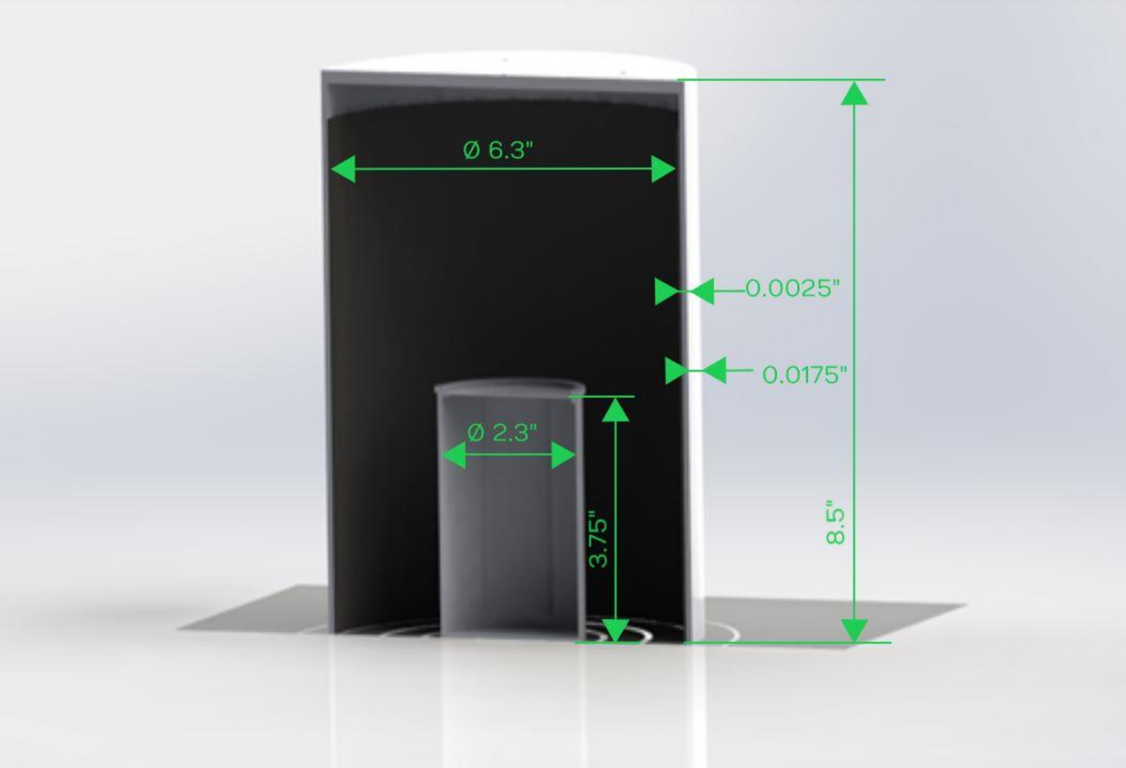
3.1. Feedstock Collection and Charring Biochar

In this study, two types of distiller grains: wet distiller grains (WDG) and dry distiller grains (DDG) were collected in 2018 from the Tharaldson Ethanol, Fargo, ND, USA. The corn stover (CS) was collected from Carrington Research and Extension Center of North Dakota State University (NDSU). Wet distiller grains were dried at ambient temperature to prevent any spoilage before charring. All distiller grains were ground on a milling machine (W6H Schutte Buffalo Hammer Mill, Buffalo, NY) to reduce its size 3-4 mm.

Biochars were produced at two different temperatures such as low temperature (about 386°C) and high temperature (at 500°C) for 45 minutes. In this study, a smaller diameter paint container was used as a retort and a larger paint container used as a pyrolysis chamber to provide uniform heat for charring (Figure 2). To release headspace gas during the charring process, five small openings (0.25 mm) were made at the top of each container. Additionally, four holes were made at the bottom side of the large container. A conventional heater was used to provide heat for burning. Two-third of the small container filled with feedstock and then the top of the container was sealed and placed on the heater. The larger container covered the smaller one to provide uniform heating. Also, inside of the larger container was paired with plaster-of-Paris to provide some insulation to prevent heat loss during the charring process.

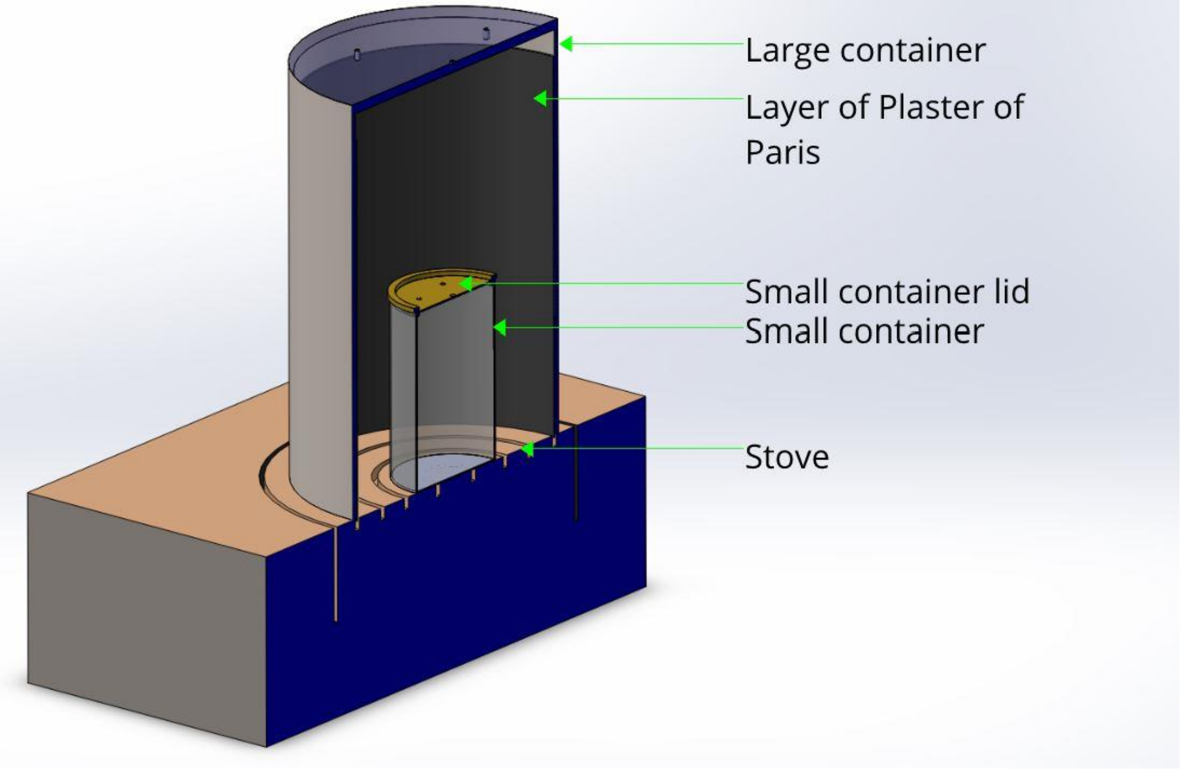


Top view of the pyrolysis chamber

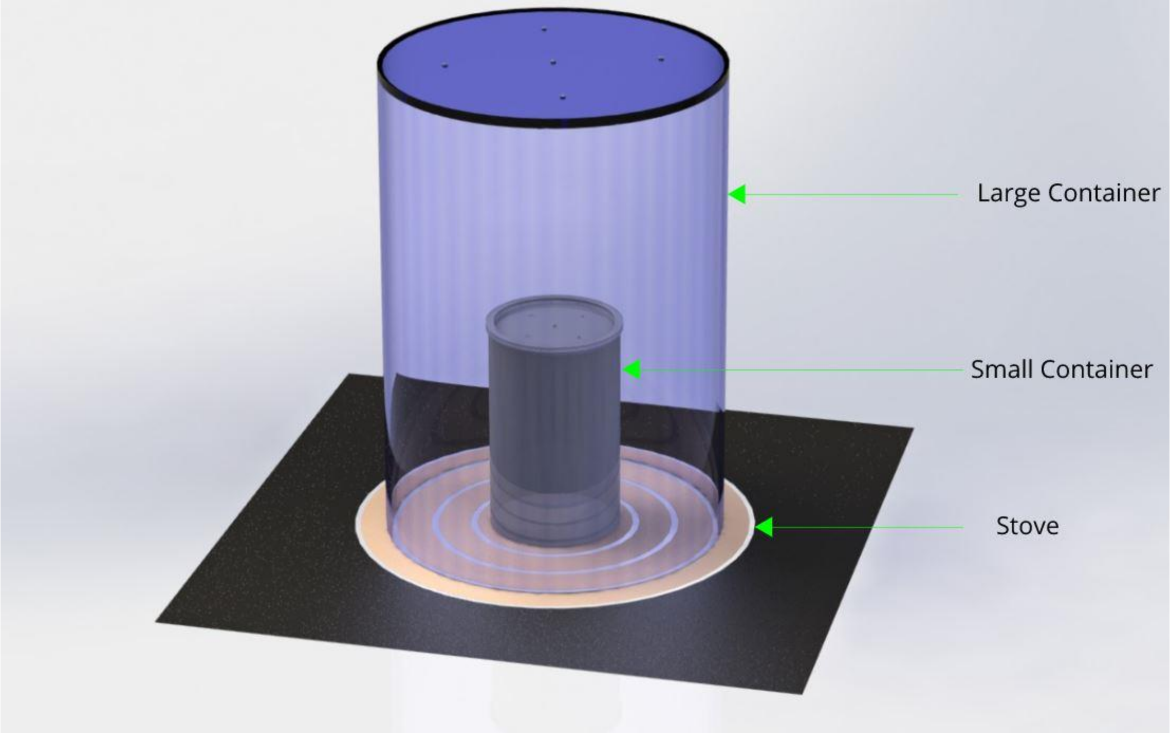


Section view of the pyrolysis chamber

Figure 2. 3-D diagram of the pyrolysis process used in this study



Sectional view of the whole experimental unit



A transparent 3-D view of the pyrolysis chamber showing the arrangement of containers of the experimental unit

Figure 2. 3-D diagram of the pyrolysis process used in this study (Continued)

On the other hand, for the high temperature (500 °C), a temperature-controlled benchtop muffle furnace (Thermolyne FB141M, Thermo Fisher Scientific, Waltham, Mass.) was used. An identical container similar to the low-temperature charring process was filled with ¾ full of biomass and placed on a muffle furnace. The furnace was closed, and the biomass was heated at 500°C for 45 minutes. In both processes, the container was allowed to cool down and biochar was removed from the container and kept them at room temperature. After that, subsamples were collected and stored for analysis.

3.2. Analysis of Biochar Properties

In this study, different properties of biochar were measured. The pH and EC were determined following procedures described previously (Ahmedna et al., 1997; Mary et al., 2016; Borhan et al., 2018). Briefly, a 1% (w/w) suspension of biochar in deionized water was prepared and heated at 90°C for 20 min while continuously stirring. When the suspension was cooled to room temperature, the pH and EC (µS cm^{-1}) were measured using a benchtop pH/MV/ISE/EC meter (HI4522, Hanna Instruments, Ann Arbor, Mich.).

Biochar's ultimate (e.g., total moisture, volatile matter, ash, fixed carbon, total carbon, hydrogen, nitrogen, total sulfur, and oxygen) and proximate analysis (e.g., total moisture, ash, carbon, hydrogen, nitrogen, total sulfur, and oxygen by difference) were done in Minnesota Valley Testing Laboratories, Inc., Bismarck, ND, USA, following EPA 6010D test method (U.S EPA, 2018). The chemical components (Ca, Mg, Na, K, Al, Cu, Fe, Mn, and Zn) of the biochars were also determined in Minnesota Valley Testing Laboratories, Inc., Bismarck, N.D following the EPA 3051A method (U.S. EPA, 2007).

The surface morphological properties, such as changes in texture and structure, of the three-feedstock and 6-biochar samples after pyrolysis were quantified using scanning electron microscopy (JSM-6490LV SEM, JEOL USA, Inc., Peabody, Mass.) paired with energy dispersive x-ray spectroscopy (EDXS). Initially, three levels of magnifications (500x, 750x, and 1500x) were tried to achieve better-quality images for visual evaluation of biochar surfaces and textures. A magnification level of 1500x was chosen for better clarity of the micrographs. EDXS was performed on each image by randomly selecting three locations.

3.3. Soil Assortment and Laboratory Incubation Preparation

Soils for the laboratory incubation study were collected from the North Dakota State University (NDSU) research field in Fargo, ND. The soil was dark-grey very fine sandy loam (75% sand, 13% silt, and 12% clay) soil. A composite sample of soil core (0-0.15 m) were collected from at least three different locations on the same field from a previously cultivated surface. After collecting, the soil was then air-dried for three days, thoroughly mixed, and finely ground down to ~2 mm size using an oscillating stainless-steel sieve in a Wiley mill mechanical grinder (Thomas Scientific, Swedesboro, NJ). The water holding capacity (WHC) of the sieved soil was determined by saturating 10 g of soil with deionized water inside a funnel. Then, the soil was drained for 4 h and WHC was determined gravimetrically by drying soil at 105°C to a constant weight (Bowden et al., 1998; Niraula et al., 2018). Soil bulk density was determined by soil core collection and gravimetric method (Blake and Hartge, 1986). The pH and EC of the soil were determined by following the procedures described by (Thomas, 1996) and (Rhoades, 1996) respectively. The main properties of air-dried soil and manure are presented in Table 1 and 2 respectively.

Table 1. Physical and chemical properties of soil and manure used in the study.

Properties	Soil
pH	8.1±0.06[a]
EC (dSm^{-1})	1.21±0.09[b]
CEC (meq/100g)	22.71±0.23
Bulk density (g/cm^3)	1.1
NO_3-N (%)	0.002±0.0[c]
NH_4-N (%)	0.002±0.0[c]
Sand (%)	75 [d]
Silt (%)	13 [d]
Clay (%)	12 [d]
P (%)	0.001±0.0[c]
K (%)	0.004±0.0[c]
Total N (%)	0.14±0.01[c]
Total C (%)	3.12±0.07[c]
OM (%)	2.1±0.0

[a] soil pH determined in 1:2 soil/water extraction (Thomas, 1996)

[b] Soil EC determined in 1:1 soil/water extraction (Rhoades, 1996)

[c] CEC, P, K, Total C, Total N, and Dry matter content obtained from NDSU Soil Testing Lab., Fargo, North Dakota.

[d] Sand, silt, clay obtained by mechanical Analysis by Hydrometer Method from NDSU Soil Testing Lab., Fargo, North Dakota.

Table 2. Physical and chemical properties of manure used in the study

Properties	Manure
pH	7.65±0.02[a]
EC (dSm^{-1})	3.71±0.31[b]
NO_3-N (%)	0.01±0.0 [c]
NH_4-N (%)	0.42±0.03[c]
P (%)	0.5±0.02[c]
K (%)	1.2±0.13[c]
Total N (%)	2.2±0.03[c]
Total C (%)	30.44±0.51

[a] Manure pH determined in 1:2 water extraction (Wolf and Peters, 2003)

[b] Manure EC determined in 1:2 water extraction (Wolf, 2003)

[c] P, K, Total C, Total N, NO_3-N, NH_4-N, and Dry matter content obtained from NDSU Soil Testing Lab., Fargo, North Dakota.

3.4. Manure Collection and Preparation

Wheat straw-bedded solid beef manure (M) were collected from the manure stockpile outside the NDSU Beef Cattle Research Complex, Fargo, ND, USA, following the procedure of

(Niraula et al., 2018). The average temperature and the wind speed at the time of manure sample assortment was 28°C and 6.35 ms^{-1}. The manure stockpile remained uncovered and exposed to atmospheric conditions before sample collection. Six subsamples from different depth (avoiding surface crust) and locations of a pile was collected in a 10-gallon bucket and mixed thoroughly. Then, manure sample was air-dried, finely ground all the way down to ~2 mm, and mixed thoroughly before use. The EC and pH of the manure were measured at 1:2 manure to water suspension using Accumet AB pH meter (Fisher Scientific, Hampton, NH) (Wolf and Peters, 2003; Wolf, 2003). Some of the properties of the air-dried manure was conferred in table 3.1.

3.5. Soil Incubation Experimental Set-up

Laboratory incubation study was conducted in 1-L clear glass mason jar of 0.00466 m^2 (area=46.6 cm^2) and each jar was filled with 150 g of sieved soil following the procedure presented by Mukome et al., (2013) and Niraula et al., (2018). Soil inside mason jars was compacted to the height of 30 mm to achieve a bulk density similar to field bulk density (1.1 g cm^{-3}).

A completely randomized factorial (5 × 3 × 3) experiment with five treatments including manure (M), Nitrogen (Urea), Manure-Biochar, Nitrogen-Biochar and no Treatment (control) and subplot of three biochars (DDG, WDG and CS) were used. Three replications were used for each treatment. Thus, a total of 45 jars were used.

The N application rates within the incubation jar was established by supporting the typical N application rate (215 kg N ha-1) for corn (Zea mays L.) as recommended for the Eastern North Dakota. For each jar, nitrogen, manure, and biochar application rates were at 204 mg, 11 g, and 8 g per 150 g soil (equivalent to 215 kg N ha-1, 7.5 ton acre-1, 10.5 ton acre-1, respectively), respectively. After mixing soil in a jar, deionized water (60 mL) was added evenly over the surface with a pipette to bring the soil moisture content to 40% WHC to ensure WHC similar to a field. Every jar was weighed soon after the setup and the water lost through evaporation was replaced by adding deionized water during sampling days. Jars were sealed with airtight lids, fitted with gas sampling ports (butyl rubber septum), and incubated at 25 ± 1 °C for 73 days.

3.5.1. Measurement and Analysis of Greenhouse Gases

Headspace air samples (20 mL) were collected from the mason jars on days 0, 10, 40, 59, and 76 days after incubation, following the procedure described by (Awale & Chatterjee, 2015; Mukome et al., 2013 Niraula et al., 2018). Headspace gas sampling was done by inserting a gas-tight luer lock syringe into the jar. Once sampling, jars were left open for an hour for aeration. Immediately after collecting, air samples were analyzed for CH_4, CO_2, and N_2O using a greenhouse gas chromatograph (GC) (Model No. 8610C, SRI Instruments, 20720 Earl St., Torrance, CA 90502) equipped with a flame ionization detector (FID) and an electron captured detector (ECD) following the procedure described by Rahman et al. (2012). A gas sample of 10 mL from the syringe was injected into the GC for the GHG measurements. Before injecting any sample into the GC, the FID and ECD detector temperature was raised to 110°C. The system was operated on a nitrogen carrier at 20 PSI for the ECD, whereas hydrogen and air were supplied to the FID/methanizer using a built-in air compressor at 20 PSI. During this system, the ECD detector detects N_2O, whereas the FID/methanizer detector detects both CH_4 and CO_2. Gas chromatographs were recorded and analyzed with the Peak Simple Chromatography Data System Software (Version 3.72, SRI Instruments, 20720 Earl St., Torrance, CA 90502). Before and after sample analysis, calibration gases were used to ensure that the GC was functioning properly. Blank samples were also run between samples using the same procedure to check any contamination from the previous analysis. To generate calibration equations, three points calibration were conducted for CH_4 (5, 10, and 20 ppm), CO_2 (1000, 1500, and 2500 ppm), and N_2O (5, 10, and 100 ppm) gases.

The N_2O, CO_2, and CH_4 concentrations were converted into mass units assuming ideal gas relations and expressed as micrograms N_2O-N, milligrams CO_2-C, and micrograms CH_4-C produced between sampling dates per kilogram of soil, respectively. The headspace concentration of gas samples measured between the sampling dates were divided by the elapsed time to obtain daily N_2O (mg N_2O-N kg^{-1} moist soil d^{-1}), CH_4-C (mg CH_4-C kg^{-1} moist soil d^{-1}), and CO_2 fluxes (mg CO_2–C kg^{-1} moist soil d^{-1}) using the following equation described by (Niraula et al., 2018):

$$Flux = \frac{\mathrm{P} \times \mathrm{Ct}\,(\mathrm{Vh} + \mathrm{Vw}) \times \mathrm{M}}{\mathrm{R} \times \mathrm{T} \times \mathrm{W} \times \mathrm{t}}$$

Where, C_t is the gas concentration in the gas phase (μL gas L^{-1}), Vh is the volume of the headspace (mL), Vw is the volume of water in the soil (mL); M is the atomic weight of C or N (g mol^{-1}), P is the standard atmospheric pressure (101.325 kPa), R is the universal gas constant (8.31451 L kPa mol^{-1} K^{-1}), T is the temperature in Kelvin (295.15°K), W is the oven dry mass of soil (g), and t is the time between the 1st and 2nd sample collection. Cumulative mg N_2O-N, mg CO_2-C, or mg CH_4-C emission per kg-1 soil during the incubation period was calculated by summing the gas emissions during each sampling period. Emissions were calculated as N_2O-N, CO_2-C, and CH_4-C, however, for simplicity flux is herein referred to as N_2O, CO_2, and CH_4, respectively.

3.5.2. Measurement and Analysis of Soil Inorganic N

At the end of the incubation, 6.5 g of soil samples from each treatment (total of 45 soil samples) were collected and extracted with 25 mL of 2 M potassium chloride (KCl) solution (1:5 soil/extractant ratio), after shaking for 30 min in a reciprocal shaker (Maynard et al., 2007;

Niraula et al., 2018). The soil suspension was then centrifuged for 5 min and filtered through a Whatman no. 2 filter paper. The KCl extracts were analyzed for soil inorganic N (NH_4^+ + NO_3^-) using the Timberline TL2800 Ammonia Analyzer (Timberline Instruments, Boulder, CO).

3.5.3. Measurement and Analysis of NH_3 Volatilization

Ammonia (NH_3) volatilization losses from each experimental jar were measured using the phosphoric acid (H_3PO_4) traps placed inside the headspace of the screw-top mason jar (Khan et al., 2001; Niraula et al., 2018). In order to facilitate the capture of NH_3, 15 mL of 0.5 M H_3PO_4 was placed inside a 50 mL cup and hung above the soil surface using a metal wire from the lid. Following gas sampling, acid traps were collected and replaced with freshly prepared 15 mL H_3PO_4 solution to facilitate NH_3 trapping until the next sampling day. The traps were extracted with 25 mL of 2M KCl, sealed and frozen at -18°C in polypropylene vials, until analysis within 2 d using the automated timberline TL2800 ammonia analyzer (Timberline Instruments, Boulder, CO). Daily NH_3 volatilization loss (mg NH_3–N kg $^{-1}$ soil d^{-1}) was calculated by dividing the NH_3-N emitted between the sampling dates by the elapsed time. In addition, NH_3 volatilization losses during each sampling period were summed to obtain the cumulative NH_3-N losses (mg NH_3–N kg^{-1}) of the entire incubation period. The final ammonia volatilization loss between sampling dates was estimated using the mean loss from the replicated jars. Cumulative NH_3 volatilization loss (mg NH_3–N kg^{-1}) over the entire sampling period was calculated by summing the amount of NH_3 volatilized during each sampling event.

3.6. Overview of the Study

The overall work presented in this study can be divided into a couple of segments. Therefore, for better understanding, the overall study is shown in figure 3.

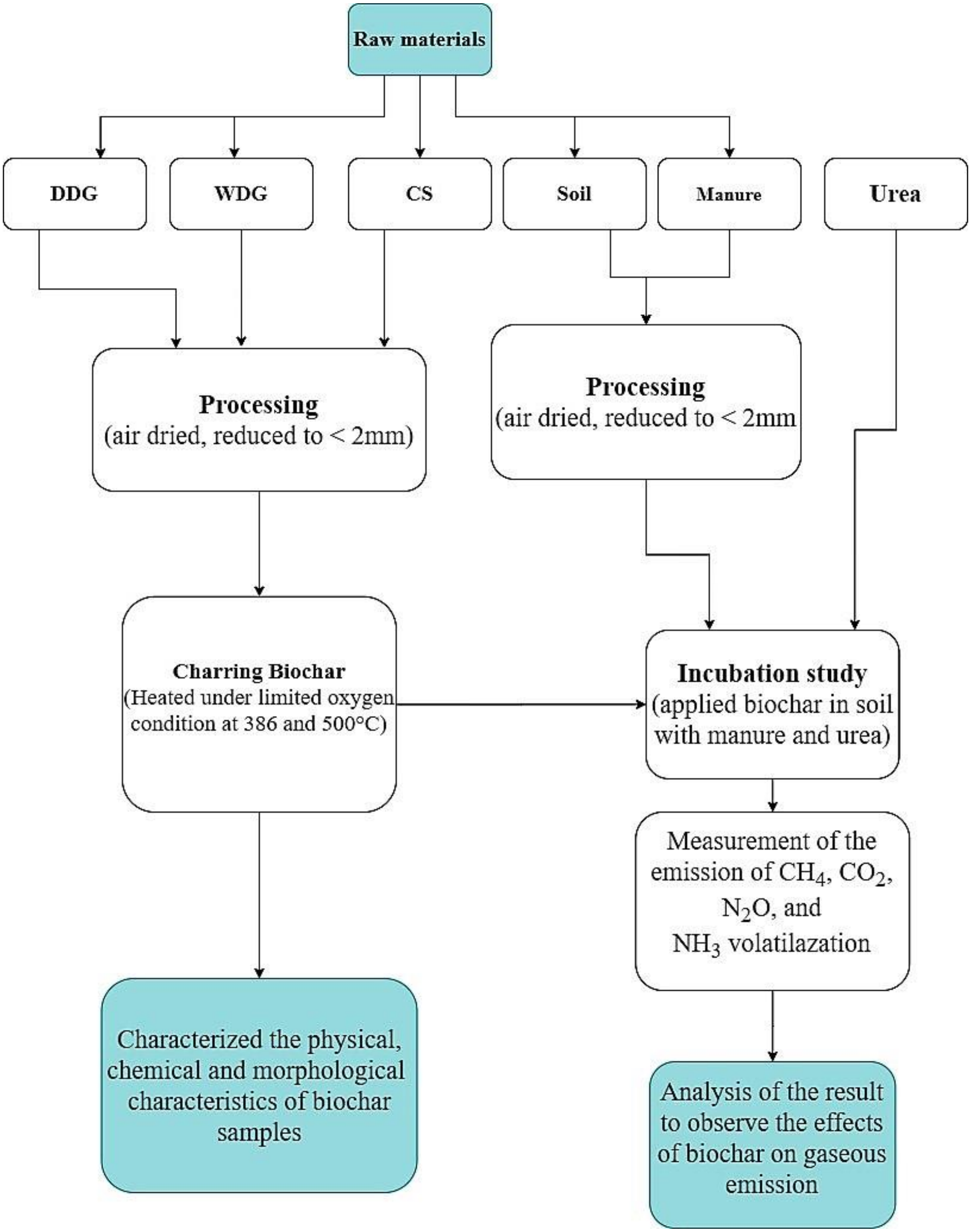


Figure 3. Overview of the study

3.7. Statistical Analysis

Duplicate samples were used for all measurements, except pH and EC analysis, where three replicates were used. The averages of each treatment were compared using the PROC ANOVA procedure in SAS 9.3 software (SAS Institute Inc., Cary, NC, USA). The null hypothesis was treatments had no effects on biochar characteristics, pH and EC at 95% ($P = 0.05$) significance level. Then, variables were separated using Duncan’s Multiple Range Test if the main effect (temperature) using F-test was significant at $P = 0.05$.

Three replications were used for the measurements of the effect of N fertilizers on GHG emissions (N_2O, CO_2, and CH_4), NH_3 volatilization, and soil inorganic N. The Residuals of daily GHG emissions and NH_3 volatilization were evaluated for homogeneity of variance and normality using the UNIVARIATE procedure of SAS 9.3 software SAS Institute Inc., Cary, NC, USA). The effects of N-fertilizers on cumulative GHG emissions, NH_3 volatilization, and soil inorganic N were analyzed using the PROC ANOVA procedure in SAS 9.3 software (SAS Institute Inc., Cary, NC, USA) to test the relative significance of different treatments through calculation of their mean differences. Significant differences among means were determined by Duncan's multiple range test at $P<0.05$ level.

4. RESULTS AND DISCUSSIONS

4.1. Characterization of Biochar

4.1.1. pH and EC of Biochars

Figure 4 shows the variations of pH among the three-biochar produced at two different pyrolysis temperatures. Bars with the same letter indicate they are not significantly different at $p<0.05$. All biochars were alkaline (pH ranged between 7.76 and 10.63) in nature and pH values in this study were similar to biochars produced from beef feedlot manure (9.81 to 10.10), dairy manure (10.45 to 10.76), DDG (8.11 to 8.72), CS (9.65 to 10.15) wheat straw (pH 8.2 to 9.2), peanut shells (pH 9.3 to 9.9), and corn straw (pH 10.2 to 10.4) that reported similar pH ranges (Gai et al., 2014; Gaskin et al., 2008; Spokas et al., 2012; Borhan, et al., 2018).

The pH value of all biochars, however, decreased with the increase in temperature. According to the previous report, biochars are persistent soil additives that carry out the benefit of carbon sequestration, which influences the soil pH (Chintala et al., 2014; Lehmann, 2007; Xu et al., 2006). Alkaline biochars, when applied to acidic soil, may decrease the soil's acidity and increase its nutrient sorption capacity, thus establishing a more conducive environment for many plants and microbes (Sohi et al., 2010; Borhan et al., 2018). In addition, major GHG such as N_2O is a byproduct during nitrification and that process depends on the soil pH (7 to 8), aeration, temperature (25-35°C) water filled pore space etc. (Pal. 2015). Biochar can alter the soil aeration, gas diffusivity and moisture content and reduce N_2O emissions via denitrification. Nitrification produces H^+ ions that results in a decrease in the soil pH. Biochar with higher pH can promote the last step of denitrification to produce N_2 rather than N_2O resulting the reduction of N_2O

production (Cayuela et al., 2013 & Pal. 2015). In addition, by enhancing soil O_2 diffusion, biochar can hinder CH_4 production. (Spokas et al., 2009 & Pal. 2015).

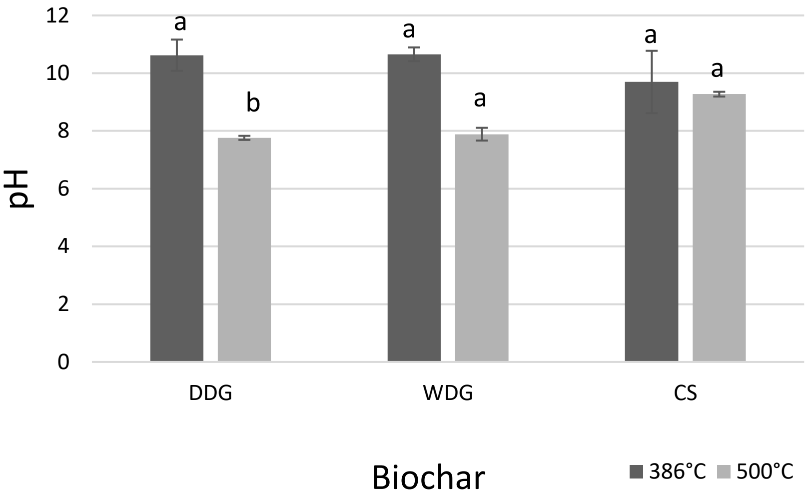


Figure 4. pH of biochars samples pyrolyzed at 386°C and 500°C
Note: DDG= Dry Distiller Grain; WDG= Wet Distiller Grain; CS=Corn Stover
Vertical bars are standard deviation (n=3).

Similarly, the variations of EC among the three-biochar produced at two different temperatures (Figure 5). The EC of biochar produced from CS at both temperatures varied significantly than the biochar produced from the DDG and WDG. The EC of biochar samples except CS increased with the increase of pyrolysis temperature. The EC of the biochar determines the exchange of ions and reflects the total amount of dissolved salts or the total amount of dissolved ions in the sample. This study supports the previous reports (except CS) that EC generally increases with higher pyrolysis temperature (Gai et al., 2014, Borhan et al., 2018**)**. In both pyrolysis temperature (high and low) WDG has the highest EC and the values were 1242.67 μS cm^{-1} and 995.1 μS cm^{-1} for the high and low temperature, respectively. The CS showed the lowest EC for both temperatures. For low temperature, the value was 538.87 μS cm^{-1} and it decreased to 208 μS cm^{-1} with the increase of temperature. The EC for CS-derived biochar (327 μS cm^{-1}) is comparable with a recent study (Borhan et al., 2018). Except for CS, the EC increased with increasing pyrolysis temperature that supports previous reports (Cantrell et al., 2012; Rajkovich et al., 2012, Borhan et al., 2018).

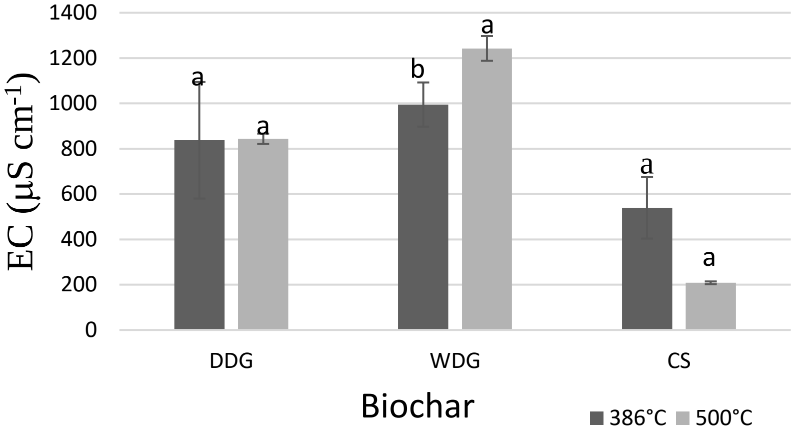


Figure 5. Electrical conductivity (EC) of biochars samples pyrolyzed at 386°C and 500°C.
Note: DDG= Dry Distiller Grain; WDG= Wet Distiller Grain; CS=Corn Stover.
Vertical bars are standard deviation (n=3).

4.1.2. Proximate and Ultimate Analysis

The overall biochar ash content varied from 16.12 to 28.06%. Among all the biochars, the highest ash content was found in the CS (19.54 to 28.06%), followed by DDG (17.85 to 23.17) and WDG (16.12 to 22.69%) (Table 3). The results are in contrast with Borhan et al., (2018), where the ash content for CS was about 10.6%, 12.6%, and 10.8% for 1, 2, and 3 h, respectively, at 400°C. Increasing the charring temperature from 386 °C to 500°C causes a substantial decrease in ash content. The low ash content of WDG biochar was due to the low mineral content in the feedstock and high ash content in CS and DDG derived biochar is due to the build-up of different inorganic components (Wang et al., 2013; Borhan et al., 2018; Pariyar et., al 2020). Like ash, total moisture, fixed carbon (FC), and carbon (C) content reduced due to the increase in pyrolysis temperature. Unlike ash content, the highest FC resulted in WDG (~57%), followed by DDG (~56%), and CS (~52%) biochars (table 4.1). The higher FC in the WDG, DDG, and CS biochars was likely due to the lignin content as reported by Borhan et al. (2018) in a similar study. However, lignin content was not measured in this study. The higher fixed carbon (FC) content results in higher biochar yield and better carbon sequestration (Borhan et al., 2018). Rajkovich et al., (2012) observed lower FC value (42%) for CS derived biochar under a similar charring condition in a commercial pyrolizer and he found that FC decreased with the increase in temperatures. The heat release and volatile matter (VM) of the biochars increased with an increase of temperature. DDG released the highest amount of heat that is ranged from 9892 to 10676 BTU/lb. on the other hand, WDG showed highest amount VM i.e. 45.35 wt. %.

Table 3. Mean and standard deviation of proximate analysis (n = 2).

Feedstock	Treatments	TM (wt. %)	Ash	VM (wt. %)	FC (wt. %)	BTU/lb
DDG	L	2.11±0.1^{a*}	23.17±0.41^{a}	20.77±1.89^{b}	56.08±1.48^{a}	9892 ± 136^{a}
	H	1.68±0.02^{b}	17.85±0.1^{b}	39.34± 0.34^{a}	42.82± 0.44^{b}	10676±132^{a}
WDG	L	3.18±0.06^{a}	22.69±0.53^{a}	19.94±1.51^{b}	57.39±0.99^{a}	10082 ± 58^{a}
	H	1.48±0.27^{b}	16.12±0.7^{b}	45.35± 3^{a}	38.54±2.3^{b}	10667±104^{a}
CS	L	2.07±0.03^{a}	28.06±1.71^{a}	19.5 ± 0.82^{a}	52.45±2.53^{a}	9023 ± 363^{a}
	H	1.11±0.01^{b}	19.54±0.07^{a}	37.08±0.48^{a}	43.39±0.55^{a}	10518± 49^{a}

Note: L=Low pyrolysis temperature (386°C); H=High pyrolysis temperature (500°C); DDG= Dry Distiller Grain, WDG= Wet Distiller Grain; CS=Corn Stover; TM = Total moisture; FC =Fixed carbon; VM = Volatile matter; BTU/lb= British thermal unit per pound.

*= Means in the same column with the same alphabet(s) are not significantly different at P= 0.05.

4.1.3. Ultimate Analysis

Table 4 shows the result of the ultimate analysis of the biochars obtained from different feedstock in different temperatures. Like FC content, the highest C was obtained with WDG, followed by CS, and DDG biochars (table 4.1) and C content of biochars decreased with increased temperature. The C contents of CS, DDG and WDG obtained at 386°C temperature were 0.09%, 2.08% and 4.42% higher, respectively, than the values obtained at the temperature 500°C. The C content of CS in this study was similar to Rajkovich et al., (2012) observed (68.7%) under a similar pyrolysis condition. The presence of Nitrogen (N), total Sulphur (TS), Hydrogen (H), and oxygen (O) increased with the pyrolysis temperature. The highest concentration of TS obtained with WDG (1.15% to 1.58%), followed by DDG (0.74% to 1.17%) and CS (0.37% to 0.44%) biochars (Table 4.2). Similarly, DDG showed the highest nitrogen (N) content, followed by CS, and WDG biochars. The average N contents of DDG, WDG, and CS biochars ranged approximately from 6.78% to 7.55%, from 6.75% to 7.41%, and from 6.22% to 7.47%, respectively (Table 4.2). Nitrogen is the most sensitive to heating (Shenbagavalli and Mahimairaja, 2012; Tryon, 1948); thus, biomass type, heating time, and temperature have profound impacts on N content (Borhan et al., 2018). On the other hand, C/N ratio varied between 8.3-10.1 (Table 4.2), and CS had the highest C/N ratio, followed by the DDGS, and CS biochars. The optimum C/N ratio for soil microorganisms is 24:1 (USDA, 2011). However, C/N ratio of biochars in this study is lower indicates higher N content. A higher or lower C/N ratio indicates a nitrogen deficit or excess nitrogen in the biochar, respectively. Thus, when applying biochar to soil, attention must be given to the soil N content (Borhan et al., 2018). The highest hydrogen concentration was obtained with WDG (1.84% to 4.25%), followed by DDG (1.97% to 3.89%), and CS (1.54% to 3.87%), biochars. Overall, hydrogen showed an increasing trend with increased temperature for all six biochars (table 4.1). The oxygen contents were comparable among the biochars and WDG showed the highest O content (7.8%) (table-4.1). In this study, the oxygen content of the biochar was determined by the difference method. However, according to Borhan et al., (2018), oxygen content determined by the difference method is more prone to measurement error. Previous studies mainly focused on the feedstock types and the pyrolysis conditions (temperature and duration) that reported that C/N ratio of feedstock has a positive relationship with the reduction of N_2O production from soil (Cayuela et al., 2014). Pal. (2015) suggested that biochar feedstock has C/N ratio ≥30 can reduce GHG emission by C and N immobilization.

Table 4. Mean and standard deviation of ultimate analysis (n = 2).

Feedstock	Treatments	TS (wt. %)	C (wt. %)	H (wt. %)	N (wt. %)	O (wt. %) (by difference)	C/N (calculated)
DDG	L	0.74±0.07^{b*}	65.67±0.27^{a}	1.97±0.15^{b}	6.78±0.12^{b}	1.69±0.35^{b}	9.68±0.17
	H	1.17±0.03^{a}	63.59±0.01^{b}	3.89±0.01^{a}	7.55±0.02^{a}	5.96±0.03^{a}	8.35±0.09
WDG	L	1.15±0.02^{b}	67.29±0.05^{a}	1.835±0.12^{b}	6.75±0.17^{a}	0.3±0.22^{b}	9.46±0.75
	H	1.58±0.03^{a}	62.87±0.34^{b}	4.25±0.38^{a}	7.41±0.21^{a}	7.79±0.22^{b}	8.50±0.28
CS	L	0.37±0.03^{a}	61.17±2.29^{a}	1.54±0.05^{b}	6.22±0.11^{a}	2.66±0.61^{b}	10.1±0.42
	H	0.44±0.01^{a}	61.26±0.23^{a}	3.87±0.01^{a}	7.47±0.06^{a}	7.43±0.36^{a}	8.47±0.37

Note: H=High pyrolysis temperature (500°C)**,** L=Low pyrolysis temperature (386°C)**,** DDG= Dry Distiller Grain**,** WDG= Wet Distiller Grain**,** CS=Corn Stover TS = Total sulpher**,** C = Carbon**,** H = Hydrogen N = Nitrogen**,** O = Oxygen**,** C/N = Carbon Nitrogen ratio.

*= Means in the same column with the same alphabet(s) are not significantly different at P≤ 0.05.

4.1.4. Chemical Properties of Biochar

The results of the chemical properties of biochars are listed in Table 5. Calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), aluminum (Al), copper (Cu), iron (Fe), manganese (Mn), and zinc (Zn) concentration decreased with the increases of pyrolysis temperature except for DDG. CS showed the highest concentration of Ca (41950 to 60350 µg/g) and biochar from all feedstocks from the two temperatures are significantly different ($p<0.05$)

from each other. Similar to Ca content, CS also showed maximum concentration for Mg, Al, Fe, Mn, and B that is ranged from 17250 to 22750 µg/g, 376 to 753 µg/g, 617 to 1630 µg/g, 165.5 to 202.5 µg/g, and 49 to 56.45 µg/g, respectively. Except for Mg and B, six biochar derived from CS, DDG, and WDG at two temperatures were significantly different ($p<0.05$) from each other. Unlike CS, WDG contained the highest concentration of Na, K, Cu, Mo, and Zn *i.e* 14350 to 19400 µg/g, 13.35 to 15.5 µg/g, 6.09 to 7.35 µg/g, and 152.5 to 198.5 µg/g, respectively. In DDGs and CS, the concentration of Mo increased with the increase of pyrolysis temperature. In both pyrolysis conditions, CS derived biochar has the highest concentration of Ca and Mg but has the lowest concentration of Na. Previous studies reported that oxygen containing organic functional groups, mineral deposits such as Calcium carbonate , and ample quantities of soluble base cations in biochar can be released rapidly into the soil and increase soil pH that results into the completion of denitrification process and finally causes the reduction of N_2O production (Cayuela et al., 2013 & Pal. 2015). However, the relation of the chemical properties of biochars to the GHG gases is not known yet.

Table 5. Chemical properties of biochars (n=3)

Feedstock	Treatment	Ca (μg/g)	Mg (μg/g)	Na (μg/g)	K (μg/g)	Al (μg/g)	Cu (μg/g)	Fe (μg/g)	Mn (μg/g)	Mo (μg/g)	Zn (μg/g)	B (μg/g)
DDG	L	35900±1000^{a*}	16150±450^{a}	11350±450^{a}	37900±700^{a}	487±9 ^{a}	11.14±1.7^{a}	1300±108^{a}	108±2^{a}	6.075±0.6^{a}	145±5^{a}	35.45±1^{a}
	H	18250±150^{b}	12150±250^{b}	12050±150^{a}	33700±500^{b}	103±7 ^{b}	13.25±0.2^{a}	461±8^{b}	55.65±0.1^{b}	6.94±0.4^{a}	134.5±1.5^{a}	39.65±1^{a}
WDG	L	6180±860^{b}	19000±200^{a}	19400±200^{b}	52800±600^{b}	138±1.5^{b}	15.5±0.3^{a}	1120±10^{b}	73.85±0.5^{a}	7.35±0.05^{a}	198.5±3.5^{a}	39.75±1.35^{a}
	H	807.5±10.5^{a}	14350±650^{a}	14850±850^{a}	41700±1800^{a}	24±0.8^{a}	13.35±1.5^{a}	332±8.5^{a}	51.65±3.5^{b}	6.09±0.7^{a}	152.5±9.5^{b}	39.2±0.7^{a}
CS	L	60350±850^{a}	17250±250^{a}	4570±70^{a}	30800±100^{a}	376±16^{a}	12.8±0.3^{a}	617±26.5^{a}	164.5±1.5^{a}	6.94±0.9^{a}	123.5±3.5^{b}	49±0.5^{b}
	H	41950±1050^{b}	22750±850^{b}	6420±40^{b}	41550±1150^{b}	753±18.5^{b}	12.5±1.1^{a}	1630±40^{b}	202.5±1.5^{b}	6.02±0.1^{a}	145.5±1.5^{a}	56.45±1.4^{a}

Note: L=Low pyrolysis temperature (386°C); H=High pyrolysis temperature (500°C); DDG= Dry Distiller Grain; WDG= Wet Distiller Grain; CS=Corn Stover; Ca = Calcium; G= Magnesium; Na = Sodium; K = Potasium; Al = Aluminum; Cu =Copper; Fe = Iron; Mn = Manganese; Mo = Molybdenum; Zn = Zinc; B = Boron.

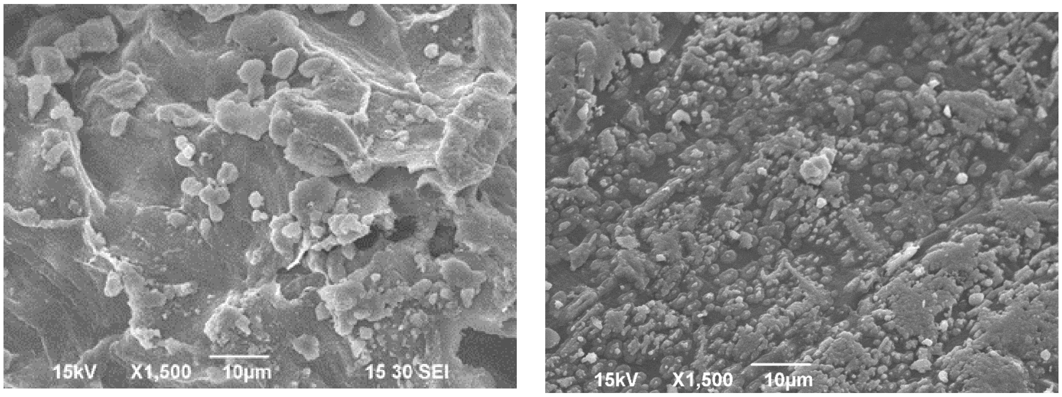
*****= Means in the same column with the same alphabet(s) are not significantly different at P≤ 0.05.

4.1.5. Surface Characteristics of Biochar

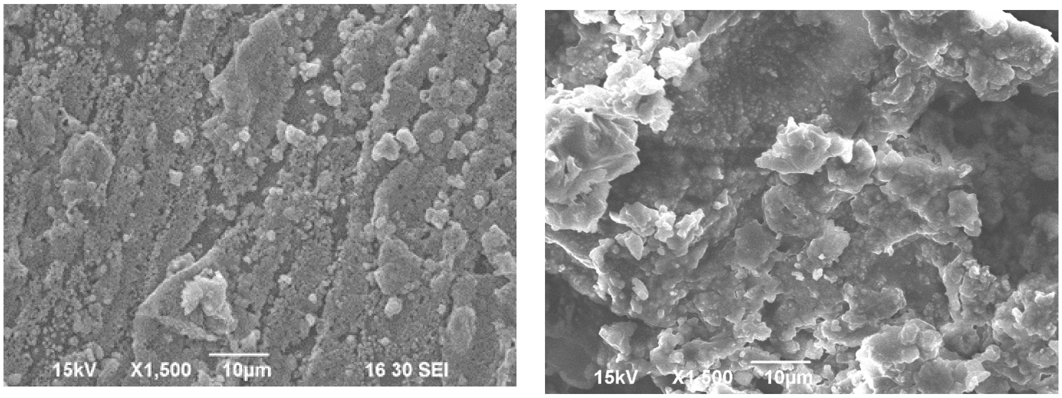
The pore structures, as shown in SEM micrographs showed changes in the biochar particles due to pyrolysis. Figure 4.3 showed the SEM micrographs of different biochar samples pyrolyzed at low (386°C) and high (500°C) for the three-biomass types. Biochar particles from two temperatures for a given biochar were randomly selected to acquire the SEM micrographs.

Overall, the biochars preserved the macrocellular morphology of the original feedstock particles. Pyrolysis produced biochar particles with rough surfaces and multiple tiny pores, thus achieved a larger surface area. Biochars with a larger surface area can be used as sorbent materials (Borhan et al., 2018). The SEM micrographs of the biochars showed that increasing the temperatures from low to high at 45 mins caused significant changes in the surface microporosity and morphological structure of the biomass (Figure 6). The variations of the surface morphology of biochar samples indicated the decrease of moisture and ash content with the increase of pyrolysis temperature. The SEM micrographs of DDG biochar showed that micro particles with a regular folded structures changed into an irregular layer (Figure 6 a & b). The CS biochar showed a soft structure with pores that indicated the presence of high ash content, showed opposite changes of the DDG biochar (e, and f in Figure 6) (Borhan et al., 2018). On the other hand, the WDG biochar contained high moisture at low temperature, and the micrograph showed more pores as the pyrolysis process progressed (Figure 6 c & d). Similar to other studies, with pyrolysis temperature increasing, more pores and cracks were generated (Ma et al., 2016). Generally, these biomass types contained low lignin and high volatile matter contents, which affected the pore formation (Lehmann et al., 2011; Mary et al., 2016, Borhan et al., 2018). In addition, the previous report also said that a well-developed pore structure and pore size distribution in biochar could adsorb ammonium (NH_4^+-N) when NH_4^+-N or NH_3 is a concern

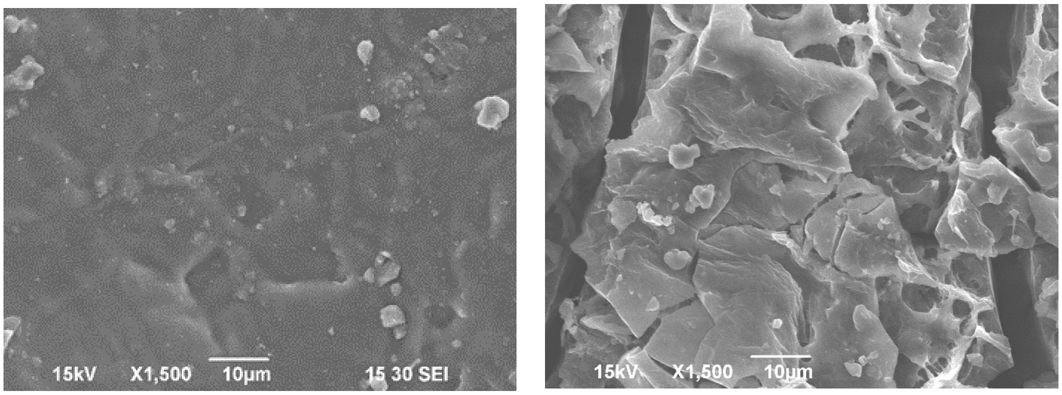
(Gai et al., 2014; Sun et al., 2013, Borhan et al., 2018). In general, the biochars mainly consisted of aggregated microspheres 2 to 10 μm in diameter with aliphatic bromo and aromatic structures and the presence of carboxyl and hydroxyl functional groups (Borhan et al., 2018).



(a) DDG- 386°C (b) DDG-500°C



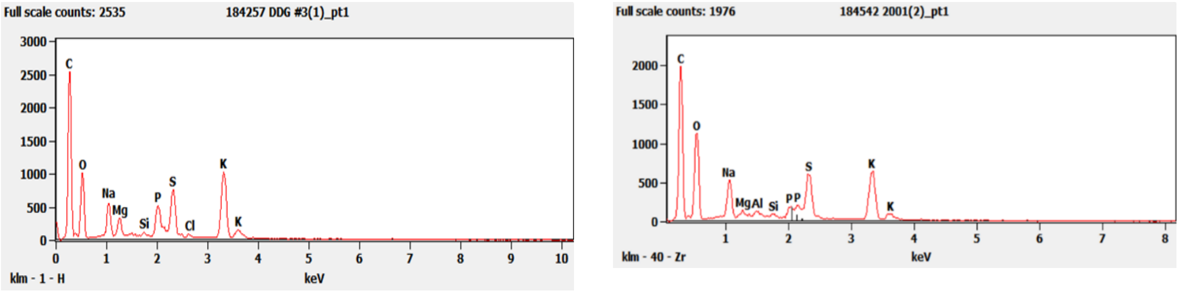
(c) WDG- 386°C (d) WDG- 500°C



(e) CS- 386°C (f) CS- 500°C

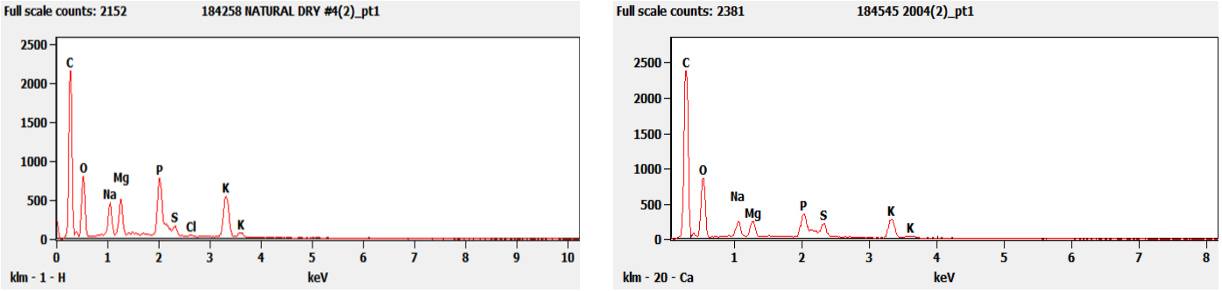
Figure 6. SEM micrographs of different biochar samples pyrolyzed at 386°C and 500°C.
Note: DDG= Dry Distiller Grain; WDG= Wet Distiller Grain; CS=Corn Stover

Analysis of the elemental composition using EDXS revealed that the biochars were composed of a wide range of valuable minerals, including sodium, aluminum, calcium, silicon, phosphorus, potassium, carbon, oxygen, chlorine, sulfur, and magnesium (Figure 7). EDX spectrographs of the six biochars show that CS has the more significant number of minerals (C, O, Na, Al, Si, P, S, Cl, K, Ca, and Mg) followed by DDG (C, O, Na, Al, Si, P, S, Cl, K, and Mg) and WDG (C, O, Na, Mg, P, S, Cl, and K). These mineral agglomerates were close to the values reported previously (Varela Milla et al., 2013; Borhan et al., 2018). However, the carbon content of the biochars was CS > DDG > WDG.



(a): DDG- 386°C

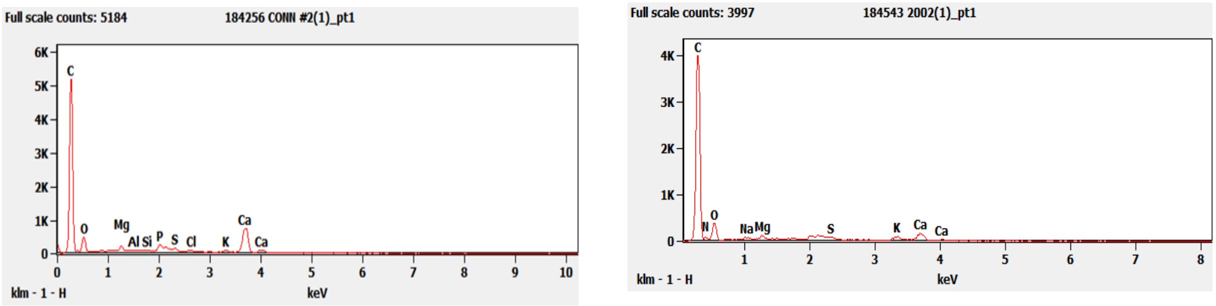
(b): DDG- 500°C



(c): WDG- 386°C

(d): WDG- 500°C

Figure 7. Showing EDX spectrograms elements of different biochar samples pyrolyzed at 386°C and 500°C.



(e): CS- 386°C (f): CS- 500°C

Figure 7. Showing EDX spectrograms elements of different biochar samples pyrolyzed at 386°C and 500°C (continued).

Note: DDG= Dry Distiller Grain; WDG= Wet Distiller Grain; CS=Corn Stover

4.2. Biochar Effects on Greenhouse Gases and Ammonia Volatilizations

4.2.1. Effects of Biochar on N_2O Emission

Until 10 days, N_2O concentrations were very low in all treatments (≤ 0.01 mg N kg^{-1}) (Figure 8), indicating that nitrification rates were high in the soil that supports a previous study (Nelissen et al., 2014). The daily mean of N_2O emissions ranged from 0.01 to 2.12 mg N_2O-N kg^{-1} d^{-1}, with the highest daily emission from Urea amended soil (Figure 8). There was no significant ($p \leq 0.05$) N_2O emission until day 10. After that, a significant ($p \leq 0.05$) amount of N_2O emission occurred from Manure, Urea, and UDDG until 59th day.

The cumulative N_2O emission from N treatments with biochar followed the decreasing order of UDDG > Urea > UCS > UWDG > UHDDG > UHCS > Control > UHWDG > Manure > MHWDG > MHCS > MCS > MDDG > MWDG > MHDDG, indicating that biochar conditions favor lower N_2O emission when applied with manure (Table 6). UDDG showed significantly higher N_2O concentration than other treatments. Biochar suppressed the N_2O emission while comparing the application with manure and Urea. Biochar pyrolyzed at 500° significantly reduced cumulative N_2O (UHWDG 70%, and UHCS 51%, UHDDG 41%) emission than the Urea. Application of high-temperature biochar with Urea produced from DDG, WDG, and CS resulted in reducing N_2O by 44, 62, and 38%, respectively, than biochar obtained at low temperature. This is in agreement with a previous study where reductions of N_2O emission was significantly higher at high temperatures (≥550°C) compared to low pyrolysis temperatures (<550°C) (Nelissen et al., 2014).

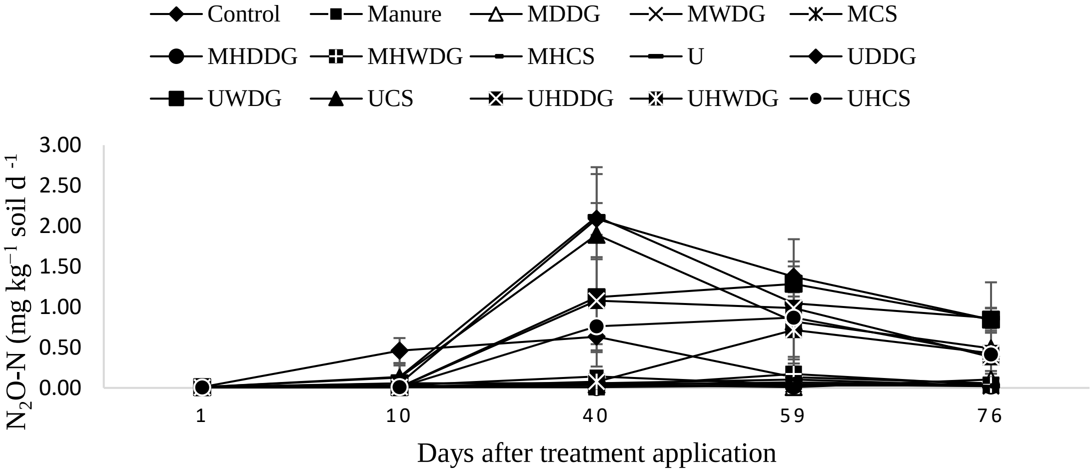


Figure 8. Daily soil N_2O emission after N fertilizers over 76 days of incubation.
Note: MDDG = Manure with low temperature Dry Distiller Grain biochar; MWDG = Manure with low temperature Wet Distiller Grain biochar; MCS = Manure with low temperature Corn Stover biochar; MHDDG = Manure with High temperature Dry Distiller Grain biochar; MHWDG = Manure with High temperature Wet Distiller Grain biochar; MHCS = Manure with High temperature Corn Stover biochar; Urea = Soil with Urea; UDDG = Urea with low temperature Dry Distiller Grain biochar; UWDG = Urea with low temperature Wet Distiller Grain biochar; UCS = Urea with low temperature Corn Stover biochar; UHDDG = Urea with High temperature Dry Distiller Grain biochar; UHWDG = Urea with low temperature Wet Distiller Grain biochar; UHCS = Urea with low temperature Corn Stover biochar.

Also cumulatively, Urea treated soil showed significantly higher N_2O−N concentrations (on average 4.17 mg N_2O-N kg^{-1}) compared to the manure (0.26 mg N_2O-N kg^{-1}) and control treatment (1.29 mg N_2O-N kg^{-1}) (Table 6). In general, when biochar is applied with manure, irrespective of biochar types, N_2O emission decreased between 82 to 93% as compared to control. Overall, the application of biochar decreased N_2O emission 9 to 66% and 20 to 70% compared to the manure and urea treatments, respectively.

Table 6. Cumulative N_2O emission and residual inorganic N presents from N fertilizers over 76 days of incubation (n=3).

Treatments	N_2O emission (mg N_2O-N kg^{-1})	Soil residual inorganic N (mg kg^{-1} soil)
Control	1.29 ± 0.06^{def}	2.2 ± 0.3^{cd}
M	0.26 ± 0.14^{ef}	3.5 ± 0.5^{bcd}
MDDG	0.17 ± 0.15^{ef}	7.2 ± 5.5^{bcd}
MWDG	0.17 ± 0.07^{ef}	7.5 ± 5.9^{bcd}
MCS	0.19 ± 0.10^{ef}	3.4 ± 0.2^{bcd}
MHDDG	0.09 ± 0.04^{f}	3.3 ± 1.2^{bcd}
MHWDG	0.24 ± 0.23^{ef}	3.9 ± 1.1^{bcd}
MHCS	0.21 ± 0.10^{ef}	3.2 ± 0.3^{bcd}
Urea	4.17 ± 0.92^{ab}	16.0 ± 0.1^{a}
UDDG	4.37 ± 0.51^{a}	1.8 ± 0.2^{d}
UWDG	3.27 ± 1.37^{abc}	9.9 ± 4.2^{abc}
UCS	3.34 ± 1.73^{abc}	2.2 ± 0.2^{cd}
UHDDG	2.47 ± 1.67^{bcd}	6.5 ± 6.6^{bcd}
UHWDG	1.24 ± 0.64^{def}	7.5 ± 3.2^{bcd}
UHCS	2.06 ± 0.84^{cde}	10.3 ± 4.1^{ab}

Note: Control = Soil; M = Manure with soil; MDDG = Manure with low temperature Dry Distiller Grain biochar; MWDG = Manure with low temperature Wet Distiller Grain biochar; MCS = Manure with low temperature Corn Stover biochar; MHDDG = Manure with High temperature Dry Distiller Grain biochar; MHWDG = Manure with High temperature Wet Distiller Grain biochar; MHCS = Manure with High temperature Corn Stover biochar; Urea = Soil with Urea; UDDG = Urea with low temperature Dry Distiller Grain biochar; UWDG = Urea with low temperature Wet Distiller Grain biochar; UCS = Urea with low temperature Corn Stover biochar; UHDDG = Urea with High temperature Dry Distiller Grain biochar; UHWDG = Urea with low temperature Wet Distiller Grain biochar; UHCS = Urea with low temperature Corn Stover biochar.

[*] Means in the same column with the same alphabet(s) are not significantly different at $P \leq 0.05$.

4.2.2. Effects of Biochar on CH_4 Emission

The daily mean CH_4 emission from all treatments ranged from 0 to 0.91 mg CH_4-C kg^{-1} d^{-1}, whereas at day 40 every treatment except UWDG showed the highest peak of CH_4

production (0.91 mg CH_4-C kg^{-1} d^{-1}) from Urea amended soil (Figure 9). Daily CH_4 emission trend is somewhat similar to N_2O emission and there was no significant ($p \leq 0.05$) emission measured until day 10th when Control treatment resulted in significant emission. However, on day 40th, a significant CH_4 emission was observed from Manure, Urea, and UDDG treatments compare to control. After that, CH_4 emission reduced with some treatments.

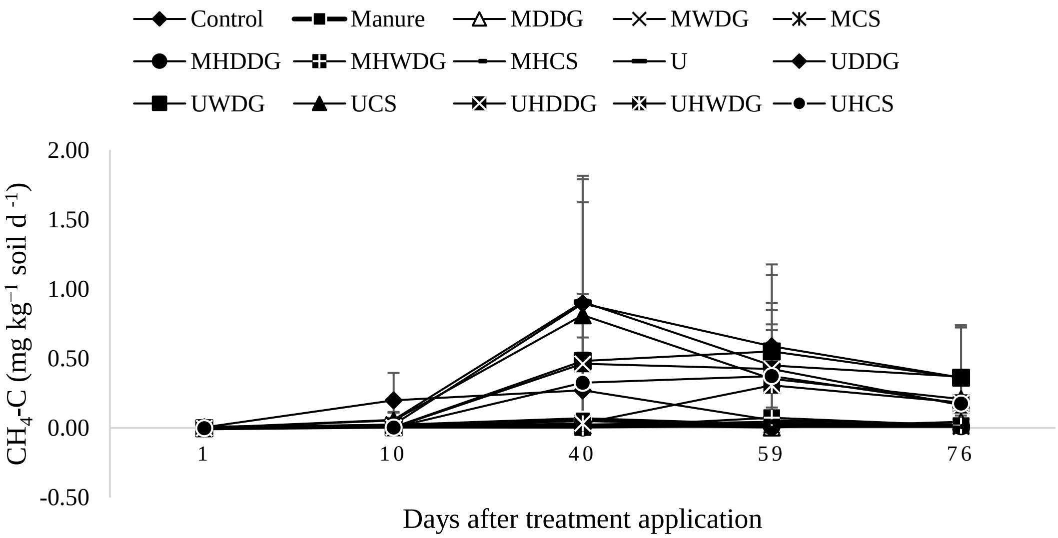


Figure 9. Daily soil CH_4 emission after N fertilizers over 76 days of incubation.
Note: Control = Soil; Manure = Manure with soil; MDDG = Manure with low temperature Dry Distiller Grain biochar; MWDG = Manure with low temperature Wet Distiller Grain biochar; MCS = Manure with low temperature Corn Stover biochar; MHDDG = Manure with High temperature Dry Distiller Grain biochar; MHWDG = Manure with High temperature Wet Distiller Grain biochar; MHCS = Manure with High temperature Corn Stover biochar; Urea = Soil with Urea; UDDG = Urea with low temperature Dry Distiller Grain biochar; UWDG = Urea with low temperature Wet Distiller Grain biochar; UCS = Urea with low temperature Corn Stover biochar; UHDDG = Urea with High temperature Dry Distiller Grain biochar; UHWDG = Urea with low temperature Wet Distiller Grain biochar; UHCS = Urea with low temperature Corn Stover biochar.

The cumulative CH_4 emission ranged between 0.04 mg CH_4-C kg^{-1} from MHDDG and 1.87 mg CH_4C kg^{-1} from UDDG (Table 7), indicating that soil amended with N treatments were the net emitter of the CH_4 gas that confirms a previous study (Niraula et al., 2018). When soil amended with manure and biochar, CH_4 emission decreased by 82% to 93%, whereas MHDDG treatment resulted in the highest reduction of CH_4 emission (93%) than the control. Although, soil amended with Urea and biochar resulted in a higher amount of CH_4 emissions than control and manure treatments, UHWDG treated soil decreased CH_4 emission by 4% compared to control. It is likely that soils can be a source or sink of CH_4 emission (Bowden et al., 1998; Hutsch, 2001; Van den Pol-van Dasselaar et al., 1998; Whalen and Reeburgh, 1996). In anaerobic conditions, methanogens degrade hydrocarbons in soil organic matter to produce CH_4 and CO_2 and that reflects on our results that on the 40th day the highest amount of CH_4 emitted from the soils due to anaerobic conditions (figure 9). On the other hand, soil consumes CH_4 under aerobic conditions, where CH_4 is oxidized to CO_2 by methanotrophs (Topp and Pattey, 1997). Previous reports suggested that methanotrops can survive under extreme acidic and saline conditions but their optimum activity ranged from a pH of 5-7.5. HDDG and HWDG showed the highest suppression of CH_4 emission (both had the pH of 7.8) following the studies reflecting that methanotrops was active well due to that pH range (Dalal et al., 2008). In addition, according to previous studies, biochar application may cause enhanced soil aeration by affecting soil macro and micro porosities that decrease CH_4 production. Overall, biochars with manure and Urea reduce CH_4 emission comparing with manure and urea treatment only that support a previous study where CH_4 emission reduced 51% when a paddy soil amended with biochars obtained from bamboo and rice straw pyrolyzed at 600°C (Liu et al. 2011).

Table 7. Cumulative CH_4, CO_2 emission from N fertilizers over 76 days of incubation (n=3).

Treatments	CH_4 emission (mg CH_4-C kg^{-1})	CO_2 emission (mg CO_2-C kg^{-1})
Control	$0.55 \pm 0.02^{def*}$	133.40 ± 13.71^{a}
M	0.11 ± 0.06^{ef}	122.71 ± 2.64^{ab}
MDDG	0.07 ± 0.07^{ef}	118.93 ± 14.37^{abc}
MWDG	0.07 ± 0.03^{ef}	117.63 ± 9.70^{abc}
MCS	0.08 ± 0.04^{ef}	133.42 ± 3.21^{a}
MHDDG	0.04 ± 0.02^{f}	107.47 ± 12.47^{abc}
MHWDG	0.10 ± 0.10^{ef}	118.99 ± 10.88^{abc}
MHCS	0.09 ± 0.04^{ef}	105.46 ± 15.32^{abc}
Urea	1.79 ± 0.39^{ab}	94.06 ± 20.84^{bc}
UDDG	1.87 ± 0.22^{a}	80.67 ± 5.87^{cd}
UWDG	1.40 ± 0.59^{abc}	81.03 ± 33.97^{cd}
UCS	1.43 ± 0.74^{abc}	82.80 ± 13.30^{cd}
UHDDG	1.06 ± 0.71^{bcd}	85.90 ± 23.60^{bcd}
UHWDG	0.53 ± 0.28^{def}	87.66 ± 7.51^{bcd}
UHCS	0.88 ± 0.36^{cde}	54.32 ± 23.37^{a}

Note: Control = Soil; M = Manure with soil; MDDG = Manure with low temperature Dry Distiller Grain biochar; MWDG = Manure with low temperature Wet Distiller Grain biochar; MCS = Manure with low temperature Corn Stover biochar; MHDDG = Manure with High temperature Dry Distiller Grain biochar; MHWDG = Manure with High temperature Wet Distiller Grain biochar; MHCS = Manure with High temperature Corn Stover biochar; Urea = Soil with Urea; UDDG = Urea with low temperature Dry Distiller Grain biochar; UWDG = Urea with low temperature Wet Distiller Grain biochar; UCS = Urea with low temperature Corn Stover biochar; UHDDG = Urea with High temperature Dry Distiller Grain biochar; UHWDG = Urea with low temperature Wet Distiller Grain biochar; UHCS = Urea with low temperature Corn Stover biochar.

[*]Means in the same column with the same alphabet(s) are not significantly different at $P \leq 0.05$.

4.2.3. Effects of Biochar on CO_2 Emission

Carbon dioxide (CO_2) emission generally followed about a mixture of W and M-shaped patterns and the trend was unstable unlike the N_2O and CH_4. The daily mean CO_2 emission ranged from 5.5 to 36.03 mg CO_2-C kg^{-1} d^{-1} (Figure 10), and MCS amended soil had the highest cumulative CO_2 emission (Table 4.4). The daily average CO_2 emission showed that some biochars daily emitted more CO_2 than the control and showed unstable trends. The unstable trend may support a previous study where the author reported that biochar applications to soil produce an initial pulse of CO_2 due to enhanced microbial respiration and decomposition of liable C fraction (Pal, 2015). However, no significant differences in CO_2 emission were observed in this study.

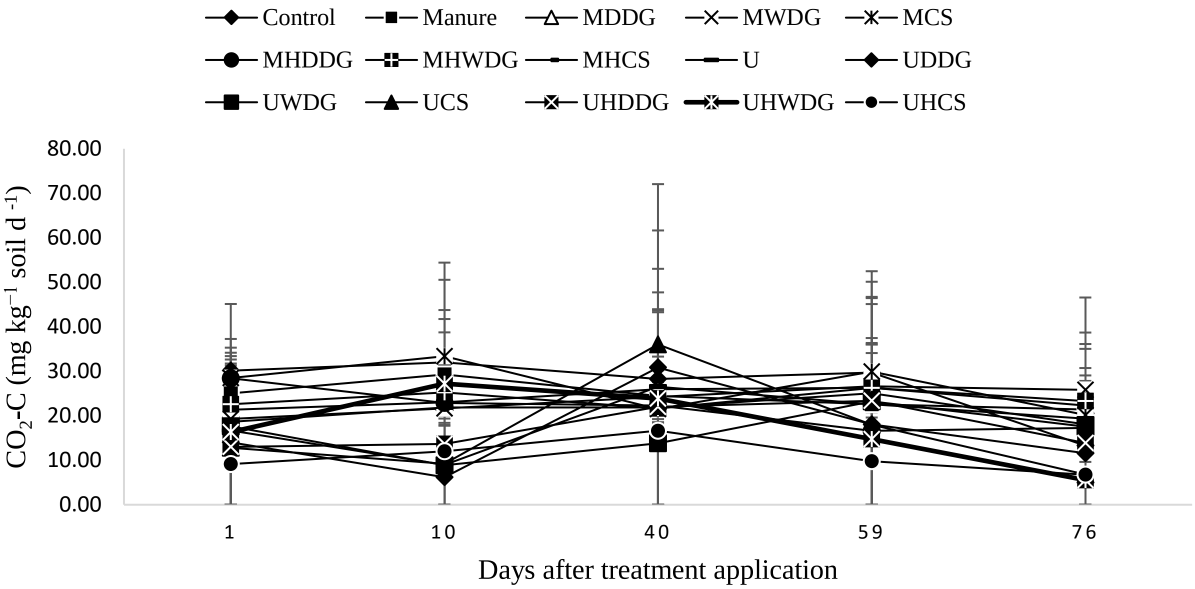


Figure 10. Daily soil CO_2 emission after N fertilizers over 76 days of incubation.
Note: Control = Soil; Manure = Manure with soil; MDDG = Manure with low temperature Dry Distiller Grain biochar; MWDG = Manure with low temperature Wet Distiller Grain biochar; MCS = Manure with low temperature Corn Stover biochar; MHDDG = Manure with High temperature Dry Distiller Grain biochar; MHWDG = Manure with High temperature Wet Distiller Grain biochar; MHCS = Manure with High temperature Corn Stover biochar; Urea = Soil with Urea; UDDG = Urea with low temperature Dry Distiller Grain biochar; UWDG = Urea with low temperature Wet Distiller Grain biochar; UCS = Urea with low temperature Corn Stover biochar; UHDDG = Urea with High temperature Dry Distiller Grain biochar; UHWDG = Urea with low temperature Wet Distiller Grain biochar; UHCS = Urea with low temperature Corn Stover biochar.

Cumulative CO_2 emission followed an order as MCS > Control > Manure > MHWDG > MDDG >MWDG > MHDDG > MHCS > Urea > UHWDG > UHDDG > UCS > UWDG > UDDG > UHCS (Table 7). That order indicates that biochars did not favor CO_2 emission. In this study, the cumulative CO_2 emission (except MCS) decreased 11 to 59% than control while we added biochar. In addition, Urea emitted 29% less CO_2 than control that indicates that urea-biochar-amended soils emitted more CO_2 than Urea amended soil. Therefore, some biochar-amended soil emitted more CO_2 than manure and Urea that supports some previous studies. According to those studies, biochar may stimulate soil microorganisms due to the priming effect to decompose the organic matter and provide a readily available substrate for denitrifying microorganisms (Bünemann et al. 2006; Blagodatskaya and Kuzyakov 2008; Smith et al. 2010; Nelissen et al. 2012; Ameloot et al. 2013; Sun et al. 2014). Then that mineralizes the labile biochar C fraction by biotic or abiotic ways in soil that increase CO_2 emissions (Kolb et al. 2009; Zimmerman et al. 2011). However, others also observed that in the long term biochar is expected to sequester C and principally emit negligible quantities of CO_2 (Pal. 2015). For example, Kuzyakov et al. (2014) found that only 6% of initially added biochar mineralized to CO_2 during eight and half years.

4.2.4. Effects of Biochar on NH_3 Volatilization

The daily mean NH_3 volatilization loss ranged from 0.07 to 8.36 mg NH_3-N kg^{-1} soil (Figure 11). The cumulative soil NH_3 volatilization loss ranged from 0.75 to 24.7 mg NH_3-N kg^{-1} soil, with the highest loss from UHWDG amended soils, and the lowest from Control (Table 8). NH_3 volatilization fluxes sharply increased, peaked on the 10th day except for UHWDG and UHCS, and then most treatments decreased rapidly. On day one, control, UDDG, UHWDG, and UHCS treatment lost a significant amount of NH_3 compared to other treatments and continued until day 10. After that, ammonia emission reduced for all treatments except UHDDG until day 59. In the present study, soil receiving N amendments had significantly higher NH_3 volatilization compared to control ($P \leq 0.05$), which is most likely due to the addition of NH_4^+

containing substrate that increased the soil pH during hydrolysis as observed by Niraula et al. (2018).

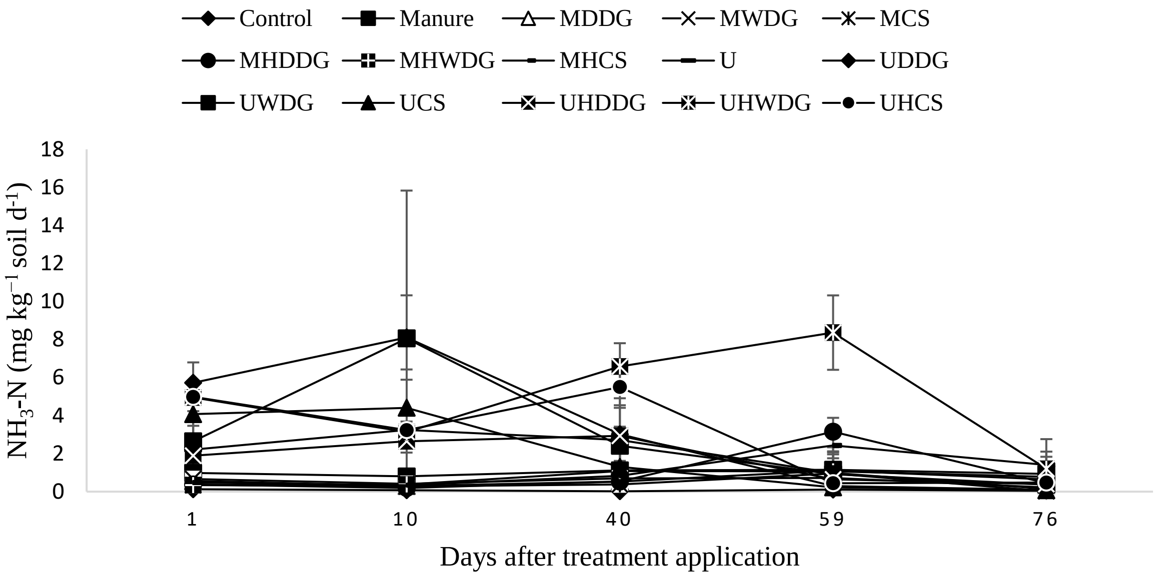


Figure 11. Daily soil NH_3 volatilization after N fertilizers over 76 days of incubation.
Note: Control = Soil; SM = Solid Manure; MDDG = Manure with low temperature Dry Distiller Grain biochar; MWDG = Manure with low temperature Wet Distiller Grain biochar; MCS = Manure with low temperature Corn Stover biochar; MHDDG = Manure with High temperature Dry Distiller Grain biochar; MHWDG = Manure with High temperature Wet Distiller Grain biochar; MHCS = Manure with High temperature Corn Stover biochar; Urea = Soil with Urea; UDDG = Urea with low temperature Dry Distiller Grain biochar; UWDG = Urea with low temperature Wet Distiller Grain biochar; UCS = Urea with low temperature Corn Stover biochar; UHDDG = Urea with High temperature Dry Distiller Grain biochar; UHWDG = Urea with low temperature Wet Distiller Grain biochar; UHCS = Urea with low temperature Corn Stover biochar.

The soil used in this study had an initial pH of 8.1. When NH_4^+ containing fertilizers were added, the $NH_4 + \rightleftarrows NH_3$ equilibrium during hydrolysis reaction may have shifted to the right due to consumption of H^+ , thus favoring more NH_3 volatilization from N amended soils (Overrein & Moe, 1967; Al-Kanani et al., 1991; Rochette et al., 2009; Niraula et al., 2018). In this study, biochar amendment influences the NH_3 volatilization rate when fertilized with N that followed the previous study that reported that biochar application did not change NH_3 volatilization fluxes pattern after N fertilization (Feng et al,. 2016). Overall, biochar treatments showed relatively higher cumulative NH_3 volatilization than that of control, which may be due to pH of soil and biochar.

Table 8. Cumulative NH_3 volatilization loss from N fertilizers over 76 days of incubation (n=3).

Treatments	NH_3 volatilization (mg NH_3-N kg^{-1})
Control	0.37 ± 0.04^{e}
SM	5.00 ± 1.48^{de}
MDDG	3.15 ± 1.13^{de}
MWDG	2.71 ± 0.25^{de}
MCS	1.97 ± 1.36^{de}
MHDDG	4.70 ± 0.04^{de}
MHWDG	3.65 ± 1.52^{de}
MHCS	5.48 ± 2.39^{de}
Urea	9.31 ± 1.47^{bcd}
UDDG	17.24 ± 1.33^{ab}
UWDG	14.40 ± 9.79^{bc}
UCS	10.09 ± 5.81^{bcd}
UHDDG	8.50 ± 4.37^{cde}
UHWDG	24.22 ± 4.20^{a}
UHCS	14.64 ± 0.88^{bc}

Note: Control = Soil; SM = Solid Manure; MDDG = Manure with low temperature Dry Distiller Grain biochar; MWDG = Manure with low temperature Wet Distiller Grain biochar; MCS = Manure with low temperature Corn Stover biochar; MHDDG = Manure with High temperature Dry Distiller Grain biochar; MHWDG = Manure with High temperature Wet Distiller Grain biochar; MHCS = Manure with High temperature Corn Stover biochar; Urea = Soil with Urea; UDDG = Urea with low temperature Dry Distiller Grain biochar; UWDG = Urea with low temperature Wet Distiller Grain biochar; UCS = Urea with low temperature Corn Stover biochar; UHDDG = Urea with High temperature Dry Distiller Grain biochar; UHWDG = Urea with low temperature Wet Distiller Grain biochar; UHCS = Urea with low temperature Corn Stover biochar.

[*] Means in the same column with the same alphabet(s) are not significantly different at P≤ 0.05.

5. CONCLUSION AND FUTURE STUDY

5.1. Conclusion

Biochar properties depend on the feedstock types and pyrolysis temperatures. Biochars were alkaline (pH ranged 10.65 to 7.89) in both temperatures. Biochar from DDG and CS had a high concentration of calcium (Ca), magnesium (Mg) and potassium (K) ranged between 60350 to 35900 µg/g compared to WDG (6180 µg/g) at 386°C and decreased dramatically with the increase of temperature. The SEM analysis of biochar showed that the porous structure of biochars also changed significantly and different from each other. Corn stover biochar contained the highest number of minerals and the highest concentration of (C, O, C, Na, Mg, Al, Si, P, S, Cl, K, Ca, and Mg) on the surface than the other. Biochars pH, total moisture, ash, FC, C, Ca, Mg, Na, K, Al, Cu, Fe, Mn, and Zn decreased with the increase of pyrolysis temperature.

The concentration of GHG emissions were related to N treatments. For example, the emission of N_2O from soil mixed with Urea and urea-biochar treatments were always higher than the emission from manure and manure-biochar treatments. The cumulative N_2O emissions were reduced significantly as compared to manure and Urea. In addition, CH_4 emission from manure treated with biochar resulted in 7 to 18% less emission than the control treatment, but urea-biochar amended soil emitted 38 to 71% more CH_4 than urea treatment. However, UHWDG treatment emitted 4% less CH_4 than control. Considering, CO_2 emission, all treatments except MCS emitted less CO_2 than control. Comparing manure and urea treatmnents, urea-biochar treatments produced 20 to 48% less CO_2 than manure-biochar treatment. In addition, urea-biochar amended soils emitted 7 to 42% less CO_2 than Urea amended soil. Therefore, the CO_2 emission reduced while biochar was applied. However, the trend of daily emission was not stable. So, a long run of study may be needed to understand the trend of CO_2 emission. Ammonia

(NH_3) volatilization from biochar amended soil were more than control, which is likely due to the pH of soil and biochar. Overall, the effects of biochar on gaseous emission influenced by the biochar types and their characteristics. Therefore, further study is needed at a different application rate of biochar to understand what combination of treatment is influencing more on the reduction of gaseous emission. Also, the microbial analysis will generate further knowledge to address some of the gaps. Overall, biochars reduced major GHG emissions when compared with the N treatments. Thus, the application of biochar may have environmental benefits.

5.2. Future Study

- The study provided information about biochar properties based on feedstock types and at two temperatures. In the future, charing can be done at both temperatures for a longer duration to quantify the variation of the same properties.
- In addition, biochar properties can also be compared using a mixture of biomasses as feedstock. Additionally, different pyrolysis chambers could be made and calculate the efficiencies of the designs and yield of biochar.
- Moreover, a study can be conducted to observe the effects of biochars on the properties of soil.
- This study also revealed that biochar could be used as an amendment for reducing N_2O, CH_4, and CO_2 from fertilizer application to soil. Further study can be done with different soils and application rates of biochar to establish a relationship between the effects of biochar on GHG emission with soil properties.
- A study can be done with different N treatments to observe their influence on the effect of biochar on soil.

- A long term study could be done to observe the effects of biochar on CO_2 emission to understand the mechanism of it.
- Since no field studies were done in this study, to support the incubation study a field study is needed to ensure sustainable agricultural production without harming our environment.

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