The Effects of Nitrogen-Enriched Biochar on Maize (*Zea mays*) Productivity and Soil Organic Carbon

by

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AUTHOR'S DECLARATION

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

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Abstract

Loss of soil organic carbon (SOC) resulting from intensive agriculture practices has impacts on both climate change, through emissions of greenhouse gases, as well as food security because of declines in soil fertility. A possible solution for rapidly restoring and stabilizing SOC is through additions of biochar to soil. Biochar is a carbon-rich material formed by pyrolysis (heating) of biomass in an oxygen-limited environment. A biofuel company, ABRI-Tech, has proposed an economically feasible method of using biochar in Canadian agriculture that involves enriching biochar with urea ammonium nitrate (UAN) fertilizer and applying small amounts (~1 t/ha) of biochar annually.

The main objectives of this study were to evaluate the ability of biochar-UAN (Char+) to increase agricultural productivity and SOC in temperate regions. This study presents the results of a growth chamber experiment, two field trials and Century Soil Organic Matter modeling. In the growth chamber experiment, Char+ significantly increased the shoot dry mass (DM) of maize (*Zea mays*) by 310% in sandy textured soil, 112% in medium soil and no significant difference was observed in fine soil. However, in all soil textures, as well as the Char+ field trial, the maize DM resulting from 1 t/ha Char+ was not significantly different from UAN treatments. The biochar field trials demonstrated that if 1 t/ha of Char+ was applied annually the maize biomass production would not be affected after 6-12 years (6.2-12.4 t biochar/ha), and there may be slight improvement in yields of about 25% after 25 years (24.8 t biochar/ha).

Although no significant differences in SOC were found in the field trial, there was a trend of increasing SOC as biochar application rates increased. The Century model predicted that annual addition of 1 or 2 t Char+/ha will increase SOC more than other management practices, including crop rotation, no-till and manure, over a 150 year period. The model predicted that applying 1 t Char+/ha per year to a sandy soil will increase SOC by 10% after 10 years and 17% after 20 years. This research is significant because it shows how an economically feasible method of using biochar can improve the sustainability of agroecosystems and increase terrestrial carbon sequestration in temperate regions.

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List of Abbreviations

C - Carbon

CO_2 - Carbon dioxide

CEC - Cation exchange capacity

Char+ - Biochar pre-soaked in urea ammonium nitrate

DM - Dry mass

g - Gram

GHG - Greenhouse gas

GWP - Global warming potential

ha - Hectare

K - Potassium

kg - Kilogram

m – Meter

LSD - Least significant differences (post-hoc test)

N- Nitrogen

NUE - Nitrogen use efficiency

NH_4^+ - Ammonium

NO_3^- - Nitrate

P - Phosphorous

SOC - Soil organic carbon

SOM - Soil organic matter

t - Tonne

TN - Total nitrogen

UAN - Urea ammonium nitrate

Chapter 1
General Introduction

Society currently faces a number of interconnected global environmental challenges which demand innovative, interdisciplinary and complex solutions. Two key issues which will be addressed in this thesis are food security and climate change. The Food and Agriculture Organization of the United Nations defines food security as a condition "when all people, at all times, have physical, social and economic access to sufficient, safe and nutritious food that meets their dietary needs and food preferences for an active and healthy life" (FAO, 2010). Food security is not only a matter of agricultural production; it is a holistic concept encompassing four dimensions: availability, stability, access, and utilization (FAO, 2010). While food security is affected by a number of socio-economic and global market factors, it is ultimately dependent on agroecosystems, which can be defined as: "a biological and natural resource system managed by humans for the primary purpose of producing food as well as other socially valuable non-food goods and environmental services" (Wood et al., 2000). Humans rely on agroecosystems to deliver a number of vital goods and services including food, feed, fiber, bio-energy, water services, biodiversity, and carbon storage. An important component of agroecosystems is the soil, a highly complex and dynamic layer of minerals, air, water, plant nutrients, macro and micro-fauna, and decaying organic matter.

The sustainability of agroecosystems is currently being threatened by intensive agricultural practices and global climate change. Modern agricultural practices including tillage, mono-cropping, and application of inorganic fertilizers and pesticides have negative impacts on soil fertility and the surrounding environment (Wood et al., 2000). Climate change, which is primarily being caused by greenhouse gas (GHG) emissions resulting from human activities (IPCC, 2007a), will also have a negative impact on agroecosystems. It is predicted that the positive effects of climate change on agriculture, including increases in plant growth caused by warming of temperate regions and atmospheric carbon dioxide (CO_2) enrichment, will be outweighed by the negative effects (IPCC, 2007b). Higher temperatures in the tropics, increased frequency of droughts and extreme weather events are predicted to cause a 30% reduction in global grain yields by 2080 (IPCC, 2007b).

Sustainable land management practices have the dual benefit of strengthening food security, through improvements in soil fertility, as well as mitigating climate change, by reducing GHG emissions or sequestering atmospheric carbon (C) in terrestrial systems (Lal, 2004a). Lal (2004) estimated that by applying practices such as conservation tillage, agroforestry, diverse cropping systems and integrated nutrient management the resulting soil C sequestration could offset 5-15% of fossil fuel emissions. A strategy for soil C sequestration that has been recently gaining attention is the application of biochar to agricultural soils (Lehmann, 2007a). Biochar is a C-rich material formed by pyrolysis (heating) of biomass in an oxygen-limited environment (Lehmann, 2007b).

Research has demonstrated that biochar has the potential to increase agricultural yields and long-term (hundreds to thousands of years) C storage in soils (Lehmann, 2007a). However, the agricultural benefits vary depending on a number of factors including biochar production methods and application rates, soil type, and crop species (Jha et al., 2010). Much of the research has focused on tropical regions and uses high biochar application rates that are not economically feasible at present (Atkinson et al., 2010). Further research is needed to evaluate the use of low biochar application rates in Canadian and other temperate agricultural systems, as well as, techniques for enriching biochar with nitrogen (N). This research is critically important for the economic viability of the Canadian biofuel/biochar industry and for scaling up biochar use to meet global soil C sequestration goals.

General Research Goals and Objectives

The general research question of this study is:

Can biochar be used successfully in Canadian agriculture to benefit crop productivity and soil C sequestration?

The general objectives of this study were as follows:

1. Evaluate the use of nitrogen-enriched biochar in temperate agricultural systems as a strategy for:
    - i. Improving agricultural productivity
    - ii. Increasing soil C sequestration
2. Determine the effectiveness of pre-soaking biochar in urea ammonium nitrate as a method of biochar N enrichment.

Specific objectives and hypotheses will be provided at the beginning of Chapter 4.

Chapter 2
Literature Review

2.1 The Green Revolution

In the past half-century the development of modern agriculture has supported a doubling of the global population and a dramatic decrease in the proportion of people living in food insecurity (Tilman et al., 2002). The proportion of undernourished people has declined from roughly one-third in 1970 to 16% in 2010 (FAO, 2010). During the period between the 1940's to 1970's, known as the "Green Revolution", high-yielding varieties of rice, maize and wheat were introduced and supported by high inputs of chemical fertilizers, pesticides and irrigation (Tilman et al., 2002). These new agricultural techniques increased crop yields per unit area and allowed food production to increase without significant expansion of cultivated area (Cassman et al., 2003). Globally, the area of land used for cereal production has remained relatively constant from 1960-2000 while the cereal production has doubled (Cassman et al., 2003). However, the successes of agricultural intensification have been achieved with high environmental costs and the long-term sustainability of our food supply system is a concern (Foley et al., 2005).

2.2 Environmental Impacts of Agriculture

In an undisturbed ecosystem, multiple species interact and there is a balanced cycling of carbon (C), nitrogen (N) and other nutrients between biotic and abiotic components. In contrast, an industrial agriculture operation typically involves one species (mono-cropping), removal of biomass and nutrients (harvesting), regular disturbance of the soil (tillage), and high inputs of inorganic fertilizers, pesticides and irrigation. Intensive agricultural practices cause a number of negative environmental impacts, both locally and in the surrounding ecosystem. Firstly, conversion of forest and native grassland to cropland and pasture causes loss of habitat and biodiversity; around 40% of the earth's land surface is occupied by cropland and pasture (Foley et al., 2005). Secondly, application of fertilizers leads to contamination of water sources and eutrophication (hypoxia) of coastal zones (Woods el al., 2000). Application of N fertilizers has increased more than ten-fold in the past 50 years, from ∼10 Tg (1 Tg = 1 million tonnes) N/year in the late 1950s to ∼100 Tg N/year in 2008 (Robertson and Vitousek, 2009). Thirdly, the area of irrigated cropland has increased by 70% in the past 40 years; crop irrigation can deplete sources of water used by humans and other organisms, and cause salinization of soil (Foley et al., 2005). Fourthly, agriculture currently accounts for about 10-12% of anthropogenic GHG emissions, which cause global climate change (IPCC, 2007a). Finally, soil tillage, lack of organic matter inputs, excessive mineral fertilization and other intensive agricultural practices lead to erosion and degradation of soil quality (Khan et al., 2007; Lal, 2004). A current assessment of global soil degradation is not available; however, a 1991 survey concluded that about 40% of global croplands are experiencing some degree of soil degradation (Oldman et al., 1991).

2.3 The Future of Agriculture

The world population is projected to plateau at around 9 billion by 2050, and this deceleration in population growth is strongly correlated with economic growth (Godfray et al., 2010). A wealthier population will demand more resource intensive products such as processed foods, meat, dairy and fish. Between 1967-97 annual consumption of meat in developing countries rose from 11 to 24 kg per capita (IPCC, 2007c). Higher demand for meat and dairy products will have a significant impact on the demand for cereal crops because 3 kg grain are needed to produce 1 kg of meat (Cassman et al., 2003). Besides meeting the demands of a wealthier population, the food supply system must also expand to meet the needs of the 825 million people currently suffering from food insecurity (Lobell et al., 2008). It is estimated that agricultural production will have to increase by 70% in the next 40 years in order to meet the growing demand (FAO, 2009). The goal for agricultural systems in the future is to sustainably increase food production while reducing impacts on the environment, contributing to renewable energy sources, and adapting to the negative effects of climate change.

2.4 Global Climate Change

The Earth's climate is determined by incoming solar radiation and the properties of the atmosphere and Earth's surface, which reflect and absorb this energy. Trapping of outgoing infrared radiation from the earth's surface by gases in the atmosphere is known as the "greenhouse effect". Greenhouse gases (GHGs) such as water vapour, carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) occur naturally in the atmosphere and without them the Earth's mean surface temperature would be about -18 °C, instead of the current 15 °C (Rastogi et al., 2002). However, in the past 250 years, anthropogenic (human caused) emissions of GHGs have strengthened the greenhouse effect and are causing global climate change. The Intergovernmental Panel on Climate Change (IPCC) has concluded with 95% certainty that increases in anthropogenic emissions of GHGs is the main driver of climate change (IPCC, 2007a).

The three main anthropogenic GHGs that are causing the radiative forcing of the climate are CO_2, CH_4 and N_2O; the radiative forcing associated with increases in CO_2 concentrations is $+1.66 \pm 0.17$ W (Watts)/m^2, while CH_4 contributes $+0.48 \pm 0.05$ W/m^2 and N_2O contributes $+0.16 \pm 0.02$ W/m^2 (IPCC, 2007a). Although CH_4 and N_2O have a smaller contribution to radiative forcing than CO_2, this is because they are present at much lower concentrations, and in fact, the global warming potentials (GWP) of CH_4 and N_2O are 23 and 296 times, respectively, greater than that of CO_2 (IPCC, 2007a). The concentration of atmospheric CO_2 has increased from about 280 ppm in 1750 to about 379 ppm in 2005 and climate models predict that if CO_2 concentrations surpass 500 ppm by 2100 there will be an average warming of 1.5-5.8 °C (IPCC, 2007a). Scientists are warning that if current emission trends continue there will be serious consequences from climate change, including increased frequency of drought, extreme weather events and rising sea levels (IPCC, 2007b).

The fundamental cause of climate change is that humans have interfered with the global biogeochemical C cycle by altering the flux rates between the various pools. There are five main global C pools: oceanic (38000 Gt), geologic (4130 Gt), pedologic (2500 Gt), atmospheric (760 Gt) and biotic (560 Gt) (Lal et al., 2007). Since the Industrial Revolution in the early 1700's, the combustion of fossil fuels has dramatically accelerated the flux of C from the geologic pool (oil, natural gas and coal) into the atmospheric pool. Combustion of fossil fuels accounts for about two-thirds of human induced C emissions (IPCC, 2007a). The other one-third of emissions are the result of land-use change. This includes activities such as deforestation, biomass burning and soil cultivation, which accelerate the C flux from the biotic and pedologic pools into the atmospheric pool (IPCC, 2007a).

2.5 The Relationship between Agriculture and Climate Change

Three main connections between agriculture and climate change are: agriculture is a significant source of GHG emissions, agricultural soils have the potential to be an important C sink, and climate change will have regionally specific positive and negative impacts on agriculture that will require adaptation strategies (IPCC, 2007b).

Between 1850 and 2000 intensive agricultural practices have resulted in a release of 78±12 Gt of carbon (C) from soil, and in comparison, fossil fuel combustion has emitted 270±30 Gt C (Lal, 2009). Much of this C is lost through mineralization of soil organic C to CO_2, which is accelerated when soil is tilled and exposed. As a result of converting natural ecosystems to agriculture, the SOC pool has been depleted by up to 60% in temperate regions and 75% or more in in the tropics (Lal, 2004a). Agriculture is also responsible for a large portion of other types of GHGs. Of the total anthropogenic emissions, agriculture accounts for about 47% of CH_4 emissions and 58% of N_2O emissions (IPCC, 2007b). Although the volumes of CH_4 and N_2O emitted are far less than CO_2, their impact is significant because these gases have much higher GWPs. Sources of agriculture-related emissions of CH_4 include biomass burning, rice paddies and livestock, which contribute 6, 13 and 25%, respectively, of total anthropogenic CH_4 emissions (Woods el at, 2000). The principle source of N_2O emissions is nitrification ($NH_4^+ \rightarrow NO_3$), and in turn, denitrification ($NO_3^- \rightarrow N_2O$ and N_2). These processes are driven by soil moisture and occur naturally in soils; however, they are greatly enhanced by excessive use of N fertilizers and excreta from grazing livestock (Taghizadeh-Toosi et al. 2011).

2.6 Climate Change Mitigation

It is important to place biochar and agriculture into the global context of GHG emission reduction and climate change mitigation. The Copenhagen Accord produced at the 2009 United Nations Climate Change Conference does not contain any legally binding agreements. However, it does recognize the goal of limiting global warming to 2 °C above pre-industrial levels to avoid dangerous climate change and it includes emission reduction plans or pledges from Annex I Parties (industrialized countries) and non-Annex I Parties (developing countries) (UNFCC, 2009). Over 100 nations have adopted the 2 °C warming limit goal as a guiding principle for policy on climate change mitigation (Meinshausen et al., 2009). To achieve this temperature goal, the Group of Eight (G8) and other international bodies have agreed to work towards a 50% reduction in global GHG emissions relative to 1990 levels by 2050 (G8, 2010). However, the targets for GHG emission reductions are both challenging and possibly insufficient. A recent paper estimated that, even if the G8's goal is achieved, there is still a 12-45% chance of exceeding the 2 °C warming limit (Meinshausen et al., 2009). Furthermore, another paper estimated that, if the Copenhagen Accord emission reduction plans are fully implemented, global emissions would be 48.6-49.7 $GtCO_2eq$ by 2020 (den Elzen et al., 2011). The recommended emission level required to maintain a ‘‘medium’’ chance (50–66%) of meeting the 2 °C warming limit target is 42-46; this leaves an emission reduction gap of 2.6–7.7 $GtCO_2eq$ (den Elzen et al., 2011).

The concept of “stabilization wedges” has been proposed as a strategy for stabilizing atmospheric CO_2 levels at 500 ppm, or less than a doubling of pre-industrial levels of 280 ppm (Pacala and Socolow, 2004). Each of the seven wedges in the stabilization triangle represents a technology or strategy which achieves a 1 Gt/year reduction in CO_2 emissions by the year 2054. The seven wedges identified are categorized into: “Efficiency and Conservation”, “Decarbonization of Electricity and Fuels”, and “Natural Sinks”. The authors claim that society should not wait for revolutionary technology. Instead, the technology required to carry out each of the seven wedges is already available and it is only a matter of scaling up to meet the targets.

2.7 Soil and the Global Carbon Cycle

The world’s soil C pool is about 2500 Gt and consists of about 40% inorganic and 60% organic C (Lal, 2004a). The inorganic fraction consists of carbonate minerals like calcite, dolomite, and gypsum. The organic C is contained within soil organic matter (SOM), which is formed when roots or above-ground residues of living material are decomposed by micro-organisms (Wood et al., 2000). Soil organic matter ranges from recently introduced intact and labile plant or animal material to highly degraded and recalcitrant material. The range in stages of decomposition can be categorized into the active fraction (10-40%), which includes soil nutrient cycling micro-organisms, and the more stable fraction known as humus (40-60%), which is rich in nutrients vital for plant growth (FAO, 2005). Soil organic matter contains approximately 58% soil organic C (SOC) and 45% other essential elements (Berg and Laskowski, 2006).

The loss of SOC due to intensive agriculture impacts both climate change, through greenhouse gas emissions, as well as food security because of declines in soil fertility, structure and water holding capacity (Lal, 2004a). Loss of SOC occurs when the natural balance between the input and output of the soil C pool is disrupted by cultivation or other intensive agricultural practices (Lal, 2007). The C input to soil is decreased because there is typically less biomass production in cultivated systems compared with natural systems and because harvesting of crops results in less biomass returning to the soil. Simultaneously, the C losses increase due to tillage and reduced soil cover. These two factors lower soil moisture, and increase soil temperatures and exposure to oxygen, which leads to rapid microbial decomposition of SOM (Lal, 2007).

Sustainable agricultural practices should aim to increase the long-term fertility of soils by increasing the SOC input and decreasing the SOC output. Methods for sustainable agriculture include: returning crop residues to the soil, applying organic fertilizers like manure or compost, maintaining soil cover, minimum or no tillage and using complex agroecosystems like intercropping (FAO, 2005). However, consistent use of these methods for 25-50 years will be required in order to restore agricultural soils to historic SOC levels (Lal, 2004b). A promising solution for rapidly restoring SOC is through additions of charcoal or biochar to soil. Biochar is a C-rich material formed by pyrolysis (heating) of biomass in an oxygen-limited environment (Lehmann, 2007a). By increasing SOC of cultivated soils, biochar may be able to simultaneously achieve the dual benefits of mitigating climate change and improving agricultural productivity.

2.8 The Nitrogen Cycle and Agriculture

Nitrogen is a component of nucleic acids and proteins and is, therefore, an essential element in natural systems (Robertson and Vitousek, 2009). The structure and function of ecosystems is dependent on the presence of biologically available N and it is often the main limiting nutrient for plant life. The ability of modern agriculture to keep pace with human demands is due in large part to high application rates of N fertilizers. However, as discussed earlier, these increased yields have come at an environmental cost; less than half of the applied N is taken up by plants and the remainder is released into the surrounding environment (Robertson and Vitousek, 2009). In order to find ways of sustainably increasing food production without damaging natural systems, it is important to understand the complexities of the N cycle.

The largest store of N is in the atmosphere (primarily N_2 gas), which is composed of about 79% N (Robertson and Vitousek, 2009). This N is biologically unavailable and must enter the biosphere through one of two main pathways: (1) N-fixation of N_2 to ammonia (NH_3) by microbes symbiotically associated with plant, free-living microbes or lightening; (2) anthropogenic N-fixation of N_2 to form inorganic N fertilizers which are applied to soil (Robertson and Vitousek, 2009). Organic N in the microbial pool is converted via mineralization to the biologically available ammonium ion (NH_4^+), which can either be taken up by crops or, more commonly, it is first transformed into nitrate (NO_3^-) via nitrification prior to plant uptake. Nitrogen incorporated into crops can be returned to the agricultural soil through two main pathways: (1) decomposition of crop residue or root material by bacteria or fungi to release NH_4^+ or (2) plant material is consumed by livestock and organic N is applied to soil as manure (Robertson and Vitousek, 2009). Soil N is returned to the atmosphere through emissions of N_2O or N_2 following denitrification of soil NO_3^- by bacteria (Robertson and Vitousek, 2009).

2.9 The Benefits of Biochar

Charcoal or biomass-derived black carbon (BC) produced from forest or grass fires is present in many natural ecosystems and forms a significant portion of the soil C pool. Globally, about 0.05 - 0.27 Gt of BC are produced per year (Forbes et al., 2006), which is relatively small compared with the terrestrial net primary productivity of about 60 Gt/yr (IPCC, 2007a). However, research has found that BC makes up around one-third of SOC in the majority of soils worldwide (Major et al., 2010b). Because BC is primarily composed of recalcitrant aromatic C ring structures, it cycles at a much slower rate than the labile fraction of SOC and has the potential to form an important terrestrial sink for atmospheric CO_2 (Lehmann, 2007a).

Biochar is chemically the same as charcoal and is only distinguished by its intended use as a soil amendment and method of terrestrial C sequestration (Lehmann and Joseph, 2009). The term “biochar” first appeared in the peer-reviewed literature in 1999 and was originally used to differentiate activated carbon produced from biomass and coal (Bapat et al., 1999; Woolf et al., 2010b). In 2005, Lehmann et al. (2005) began to associate the term “biochar” with soil C sequestration and climate change mitigation (Woolf et al., 2010b). There are four principal areas that benefit from biochar and its production through pyrolysis: agriculture, renewable energy production, waste management and climate change mitigation (Lehmann and Joseph, 2009). These benefits stem from the chemical and physical properties of biochar and pyrolysis biofuel systems. The following sections will review three of the main areas of investigation identified in the biochar literature.

2.9.1 The Benefits of Biochar: Agriculture

Interest in the application of biochar to soils for agricultural purposes was sparked by the discovery of the "*Terra Preta*" soils in Central Amazônia (Sombroek et al., 2003). These soils contain high amounts of charcoal which is believed to have been produced by pre-Columbian farmers 500 to 2500 years ago (Lehmann et al., 2003). Whether the charcoal additions were purposeful or not is debatable, but the important point is that the soil is still highly fertile today.

Scientific research has demonstrated the ability of biochar to increase agricultural productivity and decrease mineral fertilizer demands in tropical soils that are prone to nutrient leaching (Glaser et al., 2002; Steiner et al., 2008). Although the majority of studies have shown a positive plant response to biochar application, the results are variable and depend on the biochar feedstock, biochar application rate, crop species, soil properties, and additional fertilizer use (Jha et al., 2010). The effects of biochar on plant productivity can be categorized into physical, chemical and biological and there are five main mechanisms identified in the literature: effects on water holding capacity (Glaser et al., 2002), effects on soil pH (Major et al., 2010a), direct supply of plant nutrients (Chan et al., 2008), indirect supply of plant nutrients (Chan et al., 2007), and interactions with soil microfauna (Lehmann et al., 2010).

2.9.1.1 Effects on soil water holding capacity

Biochar is predicted to increase the water holding capacity (WHC) of soil because of increases in particle surface area and storage of water within its porous structure (Lehmann et al., 2003). Water holding capacity will also likely be increased due to storage in mycorrhizal fungi and other microbial biomass. However, at present the evidence and details of this mechanism have not been adequately researched. Busscher et al. (2010) found that pecan shell biochar did not significantly affect the amount of water needed to maintain 10% water content of an Orthic Luvisol. However, when the soil was leached with water, the biochar treatments yielded significantly less leachate (~10% decrease in mass). The authors emphasized that effects of biochar on WHC are probably dependent on the feedstock and pyrolysis conditions used to produce the biochar. In research using lysimeters, Lehmann et al. (2003) found that, although biochar treatments led to reduced water percolation, this effect was due to increased biomass production and not increased WHC. The authors identified an emerging hypothesis that biochar can increase WHC in sandy soils, but has less of an effect in clay soils.

2.9.1.2 Effects on soil pH

Acidic soils can pose a problem for agriculturalists because of decreases in P availability (Haynes, 1982) and microbial activity (Aciego-Pietri and Brookes, 2008). Biochar is typically an alkaline material and has been shown to increase the pH of acidic soils to levels optimal for crop growth (pH of 6-7). Van Zwieten et al. (2010) tested two biochars produced from papermill waste with pH values 8-9 and a liming value around 30% that of calcium carbonate ($CaCO_3$). When 10 t/ha of these biochars was added to a Ferralsol soil in a greenhouse experiment, the pH rose from 4.2 to 5.9. Many studies have associated increases in plant growth with biochar's effects on soil pH or pH-related improvements in nutrient availability (Major et al., 2010a; Van Zwieten et al., 2010; Yamato et al., 2006).

2.9.1.3 Direct supply of plant nutrients

A limited number of studies have attributed positive plant responses to nutrients supplied by the biochar itself (Chan and Xu, 2009). The nutrient content of biochar has a large variation and is dependent on the feedstock and production conditions used (Table 2.1). Biochar produced from animal sources (e.g. sewage sludge or poultry manure) tend to have lower C/N ratios than those produced from plant feedstock (e.g. greenwaste or wood). Therefore, biochar produced from animal sources is more likely to enhance plant productivity through direct fertilization effects than biochar produced from plant sources (Chan and Xu, 2009). Higher pyrolysis temperatures (~700 °C) also tend to lower the N content of biochars (Chan and Xu, 2009).

Because biochar is highly stable and resistant to decay, the total nutrient content is not a useful indicator of its fertilizer value. Instead, measurement of the amount of nutrients *available* for plant uptake is a better indicator (Chan and Xu, 2009). Most biochar is typically low in mineral N (NH_4 and NO_3), which is the form used by plants. Chan et al. (2007) found that the mineral N content of green waste biochar was around 2 mg N/kg. In comparison, non-pyrolyzed green waste compost typically has a mineral N content of over 200 mg N/kg (Chan et al., 2007). However, two plant nutrients that are often supplied directly by the biochar are potassium (K) and phosphorus (P). In a potting experiment, Lehmann et al. (2003) concluded that the increased biomass production of rice and cowpea was due to increased availability P and K supplied by wood biochar.

Table 2.1 - Nutrient content of biochars produced from different feedstocks.

Feedstock	C (g/kg)	N (g/kg)	C/N	P (g/kg)	K (g/kg)	P avail. (mg/kg)	N avail. (mg/kg)	Reference
Hardwood	617	2.4	257	0.24	1.71	-	-	This Study
Wood	708	10.9	65	6.8	0.89	-	-	Lehmann et al., 2003
Green waste	680	1.7	400	0.2	1.0	15	<2	Chan et al., 2007
Poultry litter	380	20	19	25	22.1	11600	2	Chan et al., 2008
Sewage sludge	470	64	7	56	-	-	-	Bridle and Pritchard, 2004
Bark of *Acacia*	398	10.4	38	-	-	31	-	Yamato et al., 2006
Pine chip	770	1.7	453	0.58	2.82	-	-	Gaskin et al., 2010
Corn cob	811	6.4	127	0.92	0.43	47	22	Nelson et al., 2011

2.9.1.4 Indirect supply of plant nutrients

Increased plant growth in response to biochar is often attributed to its indirect nutrient value (Chan and Xu, 2009). The biochar itself does not supply significant plant nutrients, instead it increases their retention in soil and availability to plants by binding with positively charged ions in the soil including ammonium (NH_4^+), potassium (K^+), and magnesium (Mg^{2+}) (Chan and Xu, 2009). This ability to bind cation nutrients is known as cation exchange capacity (CEC) and is caused by the negative charge on the surface of biochar particles (Chan and Xu, 2009). In a greenhouse study, Van Zwieten et al. (2010) found that biochar increased the CEC of a Ferralsol soil from 4 cmol (+)/kg to 10.5 cmol (+)/kg. Binding with cation nutrients prevents losses through leaching or volatilization and increases their availability to plants (DeLuca et al., 2009). Binding of NH_4 is of particular importance because this prevents N loss from volatilization ($NH_4^+ \rightarrow NH_3$), nitrification ($NH_4^+ \rightarrow NO_3$), and in turn, denitrification ($NO_3^- \rightarrow N_2O$ and N_2) (DeLuca et al., 2009). Research has shown that aged biochar (five months after production) has a higher CEC than fresh biochar because of increasing surface oxidation over time (Cheng, 2009).

Chan et al. (2007) found evidence of indirect nutrient supply effects in a greenhouse potting experiment that compared the biomass production of radish (*Raphanus sativus*) grown with different amount of greenwaste biochar (0, 10, 50, 100 t/ha) with or without addition of N fertilizer (0 or 100 kg/ha). The soil used in the experiment was a Red Alfisol from New South Wales, Australia, which was acidic, hard-setting and low in SOM. In the absence of N-fertilizer, biochar application did not result in significant increases in biomass production. However, when biochar and N-fertilizer were applied in combination biomass production was greater than with only N-fertilizer. This positive interaction between biochar and inorganic fertilizers has been referred to as a “synergistic effect” (Steiner et al., 2007).

Lehmann et al. (2003) used lysimeters (10 cm deep columns with collection container at bottom) filled with a clay soil and planted with rice (*Oryza sativa*) to determine the effects of biochar on leaching of applied mineral N fertilizer. Chemical analysis of the leachate revealed that leaching of applied N fertilizer was significantly reduced in charcoal treatments. Steiner et al. (2008) corroborated these finding in a field study using sorghum (*Sorghum bicolor*) and ^{15}N isotope labelled NH_4 fertilizer. After the second harvest, the ^{15}N recovery in plant and soil samples was significantly higher in the charcoal amended plots than in plots receiving only mineral fertilizer; the authors concluded that this was due to increased NH_4 fertilizer retention in soil and uptake by plant biomass. Besides benefits to plant growth, the ability of biochar to stabilize fertilizers reduces run-off into surrounding water sources, which prevents eutrophication and contamination of drinking water (Lehmann, 2007b).

2.9.1.5 Combining biochar and mineral N fertilizers

There are a number of possible methods for enriching biochar with mineral N. An industrial method has been theorized for combining biochar, ammonia and CO_2 to create solidified ammonium bicarbonate (NH_4HCO_3) within the mirco-porous structure of biochar (Day et al., 2005). However, there are concerns about the utility of ammonium bicarbonate-biochar. Ammonium bicarbonate is a relatively unattractive fertilizer because it has a low N content per unit mass (14-19%), it attracts water (hygroscopic) to the soil surface leading to increased evaporation, and at temperatures above 35°C it volatizes releasing irritant fumes (Gowariker, 2009). Studies estimate that only 30% of the N applied as ammonium bicarbonate is utilized by plants (Gowariker, 2009). It may also be difficult to market an ammonium bicarbonate product to North American farmers because it is not a commonly used fertilizer.

An alternative method of N-enrichment is to soak biochar in urea ammonium nitrate (UAN; J. Piskorz, personal communication 2010). This liquid N fertilizer is commonly used in North American agriculture and has a high N content (28-32% by weight). Urea ammonium nitrate solution is made by dissolving urea and ammonium nitrate in water, resulting in a solution composed of three forms of N: nitrate (NO_3), ammonium (NH_4^+) and urea ($(NH_2)_2CO$) in a 1:1:2 ratio by weight, respectively. When UAN enters the soil environment, these three N-forms undergo different transformations (Dorn, 2001; Fig. 4.1). The urea is rapidly converted by the enzyme urease to ammonia (NH_3) gas, which is then hydrolyzed to form NH_4^+ in the presence of water. If there is not enough soil moisture the NH_3 is vulnerable to volatilization; it is predicted that 11 Tg NH_3-N/year are lost from N fertilized fields (Beusen et al., 2008). Ammonia is considered an atmospheric pollutant because it forms ammonium particulates, which have been linked to health problems such as asthma, and ammonium aerosols, which contribute to global climate change (Miles, 2009). The NH_4^+ can either be taken up by plants, bound to negatively charged clay particles or converted to NO_3^- by nitrifying bacteria. The NO_3^- is readily taken up by plants; however, because of its negative charge it does not bind with clay particles and is, therefore, highly mobile and vulnerable to losses via leaching or denitrification (transformation into N_2O, NO, or N_2 gases).

It is predicted that the combination of biochar and UAN will improve N use efficiency by limiting losses of N (Fig. 2.1). Since biochar has a high CEC it will bind with positively charged NH_4^+, thereby, limiting nitrification to NO_3^- (Ding et al., 2010). However, Bruun (2011) proposed that fast pyrolysis biochar may increase NH_4^+ leaching because small clay-sized biochar particles will bind with the NH_4^+ and then be transported downward out of the topsoil by water movement. There is evidence that acid functional groups on the surface of biochar contribute to adsorption of ammonia (Asada et al., 2002; Iyobe et al. 2004) and that biochar-adsorbed NH_3 is bioavailable for plant uptake following application to soil (Taghizadeh-Toosi et al., 2011). A study by Knowles et al. (2011) found evidence that biochar will prevent the leaching of NO_3^-. Although the mechanism for this is unclear, the authors suggested that biochar may be inhibiting the growth of nitrifying soil flora by releasing toxic chemicals or providing refugia for microorganisms that compete with nitrifiers. Other studies have reported that aging biochar increases adsorption of NH_4^+, but does not affect nitrification or nitrate leaching (Singh et al., 2010). It is also possible that biochar will prevent N losses because the UAN solution will be absorbed in the microporous structure. No information currently exists on techniques for combining biochar and UAN or the efficacy of biochar-UAN to enhance soil fertility and increase crop productivity.

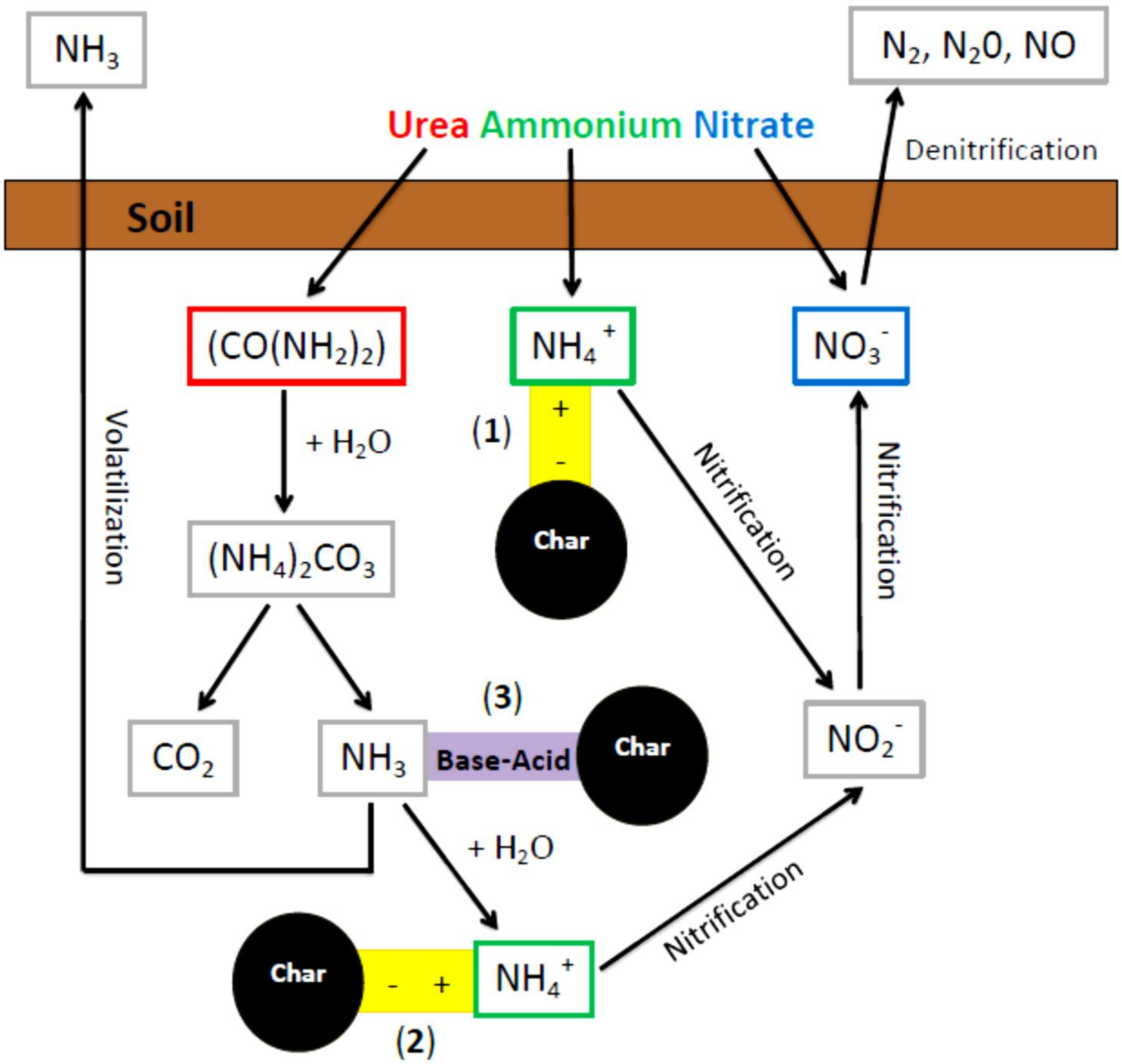


Figure 2.1 - Transformations of urea ammonium nitrate (UAN) fertilizer in soil and proposed interactions with biochar. Following application to soil, biochar prevents fertilizer N loss through denitrification and volatilization by: (1) forming cation exchange bonds directly with NH_4^+ or (2) indirectly with NH_4^+ formed following the breakdown of urea or (3) adsorbing NH_3 through reactions with acid functional groups on biochar surfaces. Diagram independently produced by thesis author.

2.9.1.6 Effects of biochar on soil microfauna

While the effects of biochar on soil chemical and physical properties have been reasonably well researched, understanding of the effects on soil biota is in its infancy (Lehmann et al., 2011). Recent results have shown that biochar may increase soil microbial biomass through the provision of an ideal habitat within the micro-porous structure of biochar particles and by increasing nutrient availability (Thies and Rillig, 2009). However, biochar may not be beneficial for all types of soil microbes; a recent study found that biochar induced taxa-specific changes in the abundance and diversity of soil microbial populations (Khodadad et al., 2011). Biochar-induced increases in soil microbial biomass can be beneficial for agriculture for three main reasons (Thies and Rillig, 2009). Firstly, soil microbes are responsible for the process of nutrient cycling, whereby, SOM is consumed and transformed (mineralization) into compounds that are available for plant uptake. Secondly, the decay of soil microbial biomass contributes to the SOC pool, which is important for soil fertility. Thirdly, some soil microfauna, such as mycorrhizal fungi, engage in symbiotic relationships with plants by forming either intracellular (arbuscular mycorrhizal fungi) or extracellular (ectomycorrhizal fungi) connections with plant roots. Mycorrhizal fungi transfer soil nutrients to the plant while the plant provides carbohydrates in return. Mycorrhizal fungi also allow plants to absorb nutrients, such as P, which would otherwise remain in an unavailable form and limit plant growth (Thomas et al., 2009). However, Warnock et al. (2010) found that biochar produced from pine wood had neutral to negative effects on the abundance of arbuscular mycorrhizal fungi, depending on the biochar application rate. The authors suggest that biochar increased soil pH and P availability, which meant that plants had reduced need for mycorrhizal symbionts (Warnock et al., 2010).

2.9.2 The Benefits of Biochar: Renewable Energy

Modern pyrolysis technology has been developed which efficiently converts biomass into biochar, as well as, two other co-products: synthetic gas (or syngas) and bio-oil (McCarl et al., 2009). Syngas is primarily composed of carbon monoxide (CO) and hydrogen (H_2), as well as small amounts of CO_2, CH_4, and water vapour (Laird et al., 2009). Although syngas has a relatively low heating value (~6 MJ/kg), it can be used to fuel the pyrolysis or feedstock drying processes (Laird et al., 2009). The composition of bio-oil varies depending on the feedstock and pyrolysis process, however, it is typically a mixture of water (~20%) and oxygenated organic compounds, including organic acids, aldehydes, alcohols, phenols, carbohydrates, and lignin-derived oligomers (Laird et al., 2009). There are challenges to using bio-oil as fossil fuel substitute because it is highly acidic (pH ~2) and can become a gel if left unmixed for extended periods of time (Laird et al., 2009). However, bio-oil can be burned in some industrial boilers and upgrading/refining techniques are currently being developed (Laird et al., 2009).

There are two general categories of pyrolysis techniques: fast and slow. While both methods typically operate at around 500 °C, the difference is in the rate of heating: fast pyrolysis heats up biomass at around 300 °C/min. and slow pyrolysis at 5-7 °C/min. This heating rate alters the proportions of bio-oil, biochar and syngas produced. Fast pyrolysis favours production of bio-oil (75% of yield), while slow pyrolysis favours production of biochar (35% of yield).

Two Canadian companies that are involved in the biochar industry are Dynamotive Energy Systems Inc. and ABRI-Tech Inc. Dynamotive is a Vancouver-based company with office in the US and Argentina that uses a fluidized-bed fast pyrolysis reactor and focuses on the production of bio-oil, with biochar as a secondary bi-product. They have one plant capable of processing 130 dry tonnes of biomass per day (DTPD) in West Lorne, as well as a 200 DTPD facility in Guelph, Ontario. These plants are incredibly efficient because the syngas captured is re-circulated to supply approximately 75% of the energy needed (Dynamotive, 2010). In July of 2011 a partnership was announced between Virgin Australia and Dynamotive to develop sustainable aviation fuel from eucalyptus tree feedstock using pyrolysis technology (Virgin Australia, 2011). The other company, ABRI-Tech Inc, is based out of Ottawa, Ontario, and is a currently operating under a joint venture with Forespect Inc., a forest products company from Namur, Quebec (P. Fransham, personal communication 2011). ABRI-Tech has developed mobile pyrolysis units (1 and 50 DTPD) and specializes in farm-scale pyrolysis of agricultural or forestry waste products such as sawmill waste, poultry litter and crop residue into bio-oil, syngas and biochar.

Pyrolysis biofuels are part of a sustainable energy system because they do not require the food portion of crops, and biochar can be returned to the soil to maintain its productivity. Biochar may be the missing link between agriculture and energy systems, which would reduce the food versus fuel conflict created by biofuels (Fig. 2.2). First generation biofuels, which are produced by converting corn (food portion) or sugar cane into ethanol and biodiesel, have received much criticism because farmers are producing crops for energy instead of food, which leads to decreased food supplies, and in turn, increased food prices (Pimentel et al., 2002). Most ethanol and biodiesel fuels are not sustainable because the fossil energy required for production exceeds the amount of renewable energy produced (Pimentel et al., 2002). Furthermore, there is a risk that biofuel production will lead to a net positive effect on GHG emissions because of indirect land-use change (Searchinger et al., 2008). The threefold increase in biofuel production between 2000 and 2008 was largely due to huge subsidies paid to farmers (Koplow, 2006). It is estimated that in 2006 a total of US$ 5.1-6.8 billion was spent on supporting the US biofuel industry (Koplow, 2006). Part of the reason pyrolysis biofuel systems involving biochar are more sustainable is that they can utilize the non-food portion of crops (residue). The other reason is that biochar can be fed back into agricultural systems to produce the biomass needed for biofuel production and increase food production, creating a closed-loop cycle.

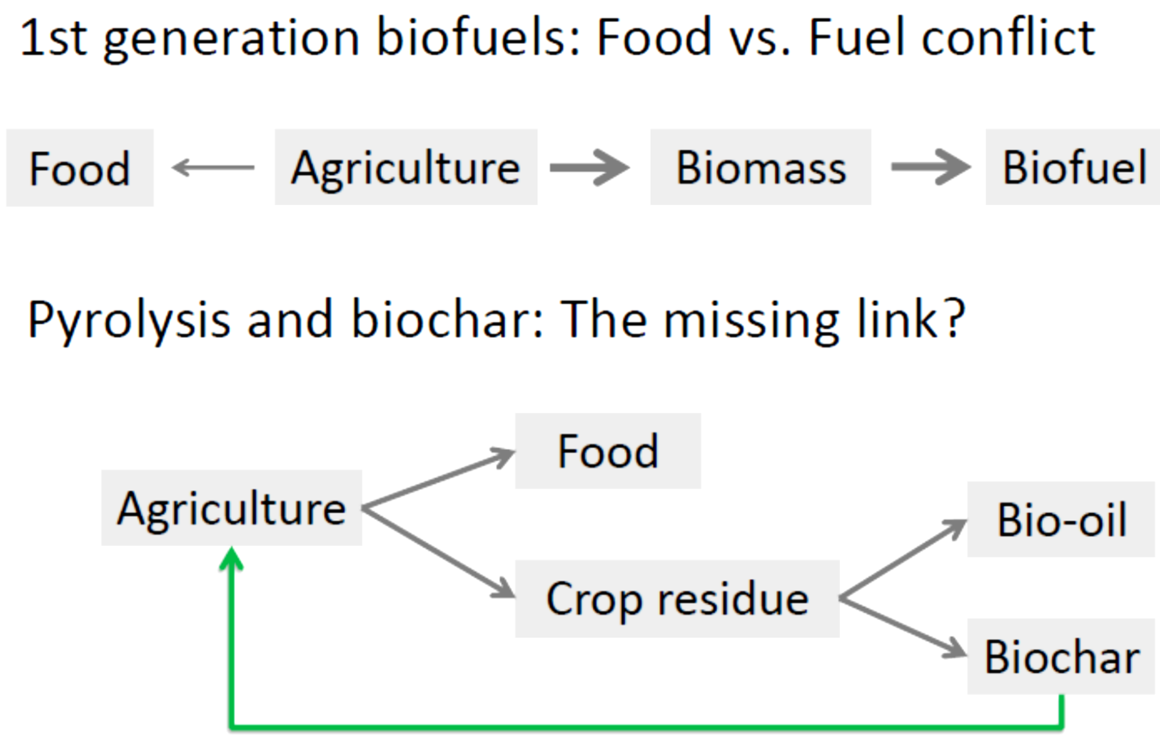


Figure 2.2 - Biochar connects food and energy systems to improve sustainability of biofuel production (lower). First generation biofuel production encourages a food versus fuel conflict (upper). Diagram independently produced by thesis author.

2.9.3 The Benefits of Biochar: Climate Change

Renewable energy technologies such as wind and solar are important for reducing GHG emissions However, if atmospheric GHG levels pass a threshold level that leads to dangerous effects of climate change, C *negative* strategies will become critical for actively removing CO_2 from the atmosphere (Woolf et al. 2010a). In agriculture systems C sinks can be enhanced by returning crop residues to soil, applying organic fertilizers (manure or compost), increasing soil cover and decreasing tillage (Lal, 2004a). However, with these traditional methods there is a limit to the amount of C that can naturally be stored and significant increases in SOC occur on a decadal time scale (Oelbermann and Voroney, 2007). Application of crop residues or manure is a slow method of increasing soil C because much of the organic material decomposes, releasing the C back into the atmosphere.

Producing biochar through pyrolysis of biomass and incorporating it into soil alters biogeochemical pathways to result in net C withdrawal from the atmosphere (Woolf et al., 2010a). Because biochar is resistant to microbial and physical decay, it can be used to sequester large amounts of C for over 1000 years (Major et al., 2010b). It is estimated that if 10% of global net primary production was converted to biochar the C sequestration and avoided fossil fuel emissions would be 4.8 GtC/yr, which is 20% greater than the annual increase in anthropogenic C emissions (Matovic, 2011). Another recent study estimated that sustainable biochar production could offset 12% of global anthropogenic CO_2-C equivalent emissions (1.8 Gt C) and reduce net emissions by 130 Gt C over a 100 year period without negatively impacting food security, habitat or soil conservation (Woolf et al., 2010a). The total GHG reductions actually go beyond the C stored in biochar because of a number of co-benefits. Firstly, studies have shown that soils with biochar have lower emissions of CH_4 and N_2O, two GHGs with higher GWPs than CO_2 (Spokas et al., 2009). Singh et al. (2010) mixed four types of biochar with two soil types and conducted a column leaching experiment with three wetting-drying cycles over a five month period. Although, one biochar type increased N_2O emissions in the first cycle, by the third cycle (four months later) all biochar types significantly lowered emissions by 14 to 73%. Secondly, biochar provides habitat for soil microorganisms including vast underground fungal networks which are composed of C (Warnock et al., 2007). Thirdly, if the co-products of biochar production (bio-oil and syngas) are captured and used for energy, this will replace use of fossil fuels (McCarl et al., 2009).

Research on the stability and movement of biochar in soil is important for understanding potential climate change benefits. A number of methods have been applied to assess the mean residence time (MRT) of biochar in soil including: the analysis of archaeological charcoal deposits, laboratory based simulation of aging, and the application of stable isotope techniques. The MRT of charcoal in *Terra Preta* soils has been estimated to be 4,035 years (Major et al., 2010b). Laboratory degradation studies simulating a mean annual temperature of 10 °C, have estimated that the MRT of biochar is 1,335 years (Cheng et al. 2009). Part of the reason for this discrepancy is that incubation studies are conducted over a short period of time and biochar is composed of labile and recalcitrant fractions, which have been estimated to have half-lives of 20 and 300 years, respectively (Woolf et al., 2010b). Major et al. (2010b) used measurements of $\delta^{13}C$ values and soil profile sampling to determine the MRT and trace the downward migration of applied biochar in a Colombian field study with uncultivated sandy clay loam soil. Biochar produced from wood using primitive kilns was applied at three application rates: 11.6, 23.2 and

116.1 t/ha, which corresponds to a 50%, doubling and fivefold increase in soil C in the top 0.1 m, respectively. After two years, only 2.2% of biochar applied at the 23.2 t/ha rate was lost through respiration, which the authors ascribed to rapid mineralization of the labile biochar fraction. The rate of downward vertical migration of biochar from a depth of 0–0.1m to 0.15–0.3m was estimated at 51.8±18.5 kg C/ha per year for the 23.2 t/ha application rate. As biochar moves downward in the soil profile the MRT likely increases because of decreases in physical and microbial decay (Major et al., 2010b).

Chapter 3
Study Sites

3.1 Soil collection sites in Ontario

The selection of three different soil collection sites in Southern Ontario was based on two criteria: the soils needed to have contrasting soil textures (coarse, medium and fine textures), and soils from agricultural research stations were ideal because of a history of well-documented agroecosystem management practices. Approximately 120 kg of each soil was collected from the upper 10 cm horizon in April, 2010. A description of the chemical and physical properties of the three soils collected is presented in Table 3.1.

The coarse textured soil was collected from Agriculture and Agri-Food Canada's Southern Crop Protection and Food Research Centre in Delhi, ON (42°51′N, 80°29′W). Prior to collection, the plot had been under continuous corn management with conventional tillage and fertilization. However, at the time of collection it had not been fertilized since the previous season. The soils have been classified as Brunisolic Grey Brown Luvisols and are members of the Fox series (Wanniarachchi et al., 1999).

The medium textured soil was collected from the University of Guelph’s Elora Research Station in Elora, ON (43°52′N, 80°21′W). The grey coloured soil has been classified as a Gleyed Melanic Brunisol and belongs to the Woolwich series (Wanniarachchi et al., 1999). The plots had previously been used for corn and corn-soybean rotation trials. In the season prior to collection they were not fertilized and had a clover cover crop.

The fine textured soil was collected from the University of Guelph's Grape Research Station in Vineland, ON (43°10′N, 79°24′W). The soil is a reddish coloured silty clay loam with poor drainage; it is classified as an Eluviated Humic Gleysol and belongs to the Morely series (Staff et al., 1997). The research station has primarily been used for long-term trials of different wine grape varieties. However, the particular area used for the soil collection had mixed grasses, which had been recently tilled and had not received mineral fertilizer since the previous growing season (Fig. 3.1).

Table 3.1- Soil properties of upper 20 cm at the three soil collection sites used for the growth chamber experiment. Data for Delhi and Elora soils were adapted from Wanniarachchi et al. (1999), and data for Vineland soil was adapted from Kingston and Presant (1989).

Property	Coarse texture (Delhi)	Medium texture (Elora)	Fine texture (Vineland)
Sand %	85	21	13
Silt %	11	55	42
Clay %	4	24	45
Organic Matter %	1.2	3.3	4.5
pH	6.9	7.1	6.7
SOC (g/kg)	6.5	18.4	16.4*
Total N (g/kg)	0.4	1.7	1.4*

* Values not available in Kingston and Presant (1989), and therefore, values shown are from control treatments of present study (see Chapter 4).

Figure 3.1 - Soil collection site at the University of Guelph's Grape Research Station in Vineland, ON.

3.2 Field Trial site in Quebec

The field trial was conducted in Namur, Quebec (Fig. 3.2; 45º53' 12" N, 74º54' 45" W, elevation 730 m), which is located 100 km North East of Ottawa, Ontario (Fig. 3.2). The climate is classified in the Koppen system as "Humid Continental, cool summer, no dry season (Dfb)" (NRCAN, 1957) and the average annual precipitation is 1100 mm (Environment Canada, 2000; for monthly climate data see Table 3.2). The soil belongs to the Saint Gabriel sub-group and is a Podzolic sandy loam with some presence of gravels (Foisy, 2010 personal communication). The soil has excessive drainage, poor fertility with low N (35 kg/ha), P (6.2 kg/ha) and K (24 kg/ha), and is weakly acidic (pH 6). Prior to the present study the site had mixed grasses and was used for cattle grazing.

Table 3.2 - Climate data for the Namur, QC field trial based on 30 year average from Cheneville, QC weather station (Environment Canada, 2000).

	Temperature (°C)			Precipitation (mm)
Month	**Minimum**	**Maximum**	**Average**	
January	-18.5	-7.3	-12.9	83.4
February	-17.2	-4.8	-11	73.1
March	-10.5	1.4	-4.6	82
April	-2.1	9.6	3.8	78.5
May	4.3	9.4	11.1	87.6
June	9.4	22.7	16	100.3
July	12	25.1	18.6	102.7
August	11	23.6	17.3	108.6
September	6.4	17.9	12.1	99
October	1.1	10.9	6	102
November	-4.6	3.2	-0.7	98.6
December	-13.5	-4.1	-8.8	89.4

Figure 3.2 - Map of the Namur, Quebec field trial conducted by ABRI-Tech.

Chapter 4

The Effects of Nitrogen-Enrched Biochar on Maize (*Zea mays)* Biomass Production and Soil Organic Carbon

4.1 Introduction

The application of biochar to soils has been proposed as a strategy to sustainably increase crop yields and mitigate global climate change through increased soil carbon (C) sequestration (Lehmann et al., 2006). However, research has revealed that the effects of biochar on plant growth vary depending on the type of biochar feedstock, soil properties and crop species (Van Zweiten et al., 2010). Most of the research reporting agricultural benefits from biochar has been conducted in tropical regions (Major et al. 2010a; Steiner et al., 2007; Yamato et al., 2006) and Atkinson et al. (2010) identified the need for more research in temperate regions. The higher temperatures and precipitation of tropical agroecosystems cause faster organic matter decomposition, lower levels soil organic C (SOC) and greater vulnerability to nutrient leaching than in temperate regions (Six et al. 2002). Therefore, the agricultural productivity and C storage in temperate soils may not be significantly improved by additions of biochar. However, biochar may be useful in specific areas of temperate regions where soil is sandy, infertile or low in organic matter, and some studies have demonstrated the potential benefits of biochar in temperate regions (Downie et al., 2011; Vaccari et al. 2011; Husk and Major, 2011).

In an area of Australia that has a temperate climate, Downie et al. (2011) investigated the human-modified soils, or Anthrosols, on Aboriginal oven mounds and found properties similar to that of the *Terra preta* soils in the Amazon Basin. The authors named the soil "*Terra preta* *australis"* and found that it has charcoal deposits that are 650-1600 years old, as well as significantly greater C, nitrogen (N), phosphorus (P), potassium (K), and cation exchange capacity (CEC) and pH than adjacent soils. In Italy, a two year field trial conducted with durum wheat (*Triticum durum*) found that application of 30 or 60 t/ha of biochar resulted in ~30% increase in yields in the first year, and this increase was sustained in the second year without further biochar applications (Vaccari et al. 2011). The first commercial scale biochar field trials in Canada were conducted in Quebec from 2008-2010 (Husk and Major, 2010; Husk and Major, 2011). These trials did not use a replicated experimental design and, therefore, are intended to be for exploratory or preliminary research. Biochar was applied to a 1000 m^2 plot at a rate of 3.9 tonnes (t) per hectare (ha) and biomass production was compared to a control plot over a 3 year period. In the first year the yield of soybean increased by 20% in the biochar amended plot (Husk and Major, 2010), and in the second and third years fresh biomass of mixed forage species increased by 17% and 4%, respectively (Husk and Major, 2011).

The biochar application rates of more than 10 t/ha that are commonly used in studies are not economically feasible in Canada at present. The problem with using high biochar application rates is that biochar may be more valuable as a fuel for industrial applications, including the pyrolysis process, or as a coal substitute for power generation (P. Fransham, 2010 personal communication). If biochar is combusted it has a heating value of 28-29 gigajoules (GJ) per ton, which is greater than most grades of coal (Dynamotive, 2009); therefore, the value of biochar is about CDN $150/t (P. Fransham, 2010 personal communication). Assuming this $150/t price of biochar and an average farm size in Ontario of about 100 ha (Stat. Canada, 2009), the cost to apply 10 or 20 t/ha of biochar would be $150,000 or $300,000, respectively. In comparison, applying urea, a popular N fertilizer in North America, on a 100 ha grain corn farm would cost about $10,000 (Grain Farmers of Ontario, 1997). This ten-fold cost discrepancy, combined with uncertainty in the yield benefits of biochar, makes it highly unlikely that commercial farms will apply 10-20 t biochar/ha.

The purpose of this research is to contribute to the development of an economically feasible alternative method for using biochar in Canadian agriculture. An Ontario biofuel company, ABRI-Tech, has proposed using low application rates of N-enriched biochar. Most biochars are low in plant-available N and their agronomic benefits are typically dependent on high soil N or addition of fertilizers (Chan et al., 2007). To increase the N content of biochar it can be pre-soaked in liquid urea ammonium nitrate (UAN) fertilizer to create a value-added product. The biochar-UAN (Char+) could be applied at rates of 0.5-1 t/ha and, if fertilization effects persist over multiple years, farmers may only need to repeat applications every 2-3 years. No information currently exists on techniques for effectively combining biochar and UAN or the efficacy of Char+ to enhance soil fertility and increase crop productivity. Combining biochar and N fertilizer may also help to improve N use efficiency (NUE) (Steiner et al., 2008), which has two main definitions: agronomic and N-based (Robertson and Vitousek, 2009). The agronomic definition is a measure of gains in crop yield or per unit of N applied and has important economic implications. The N-based definition is a measure of N recovered by the crop per unit of N applied; this definition is of particular importance to the understanding of N cycling in agroecosystem studies.

Research is needed to evaluate the potential crop yield and C storage benefits of Char+ in different soil textures. A greenhouse experiment in Ghana found that the combination of biochar and N fertilizer improved maize (*Zea mays*) biomass production and N uptake in a sandy texture soil, but not in a finer texture soil (Yeboah et al., 2009). It is predicted that Char+ will have more of an impact on biomass production in sandy soil than finer texture soils because, firstly, the improved N availability resulting from Char+ will have more of an effect in the nutrient-poor sandy soil than in the nutrient-rich fine texture soil, and secondly, the addition of biochar with Char+ will prevent nutrient leaching, which will be more of a concern in the sandy soil.

This chapter is organized into two main sections: field and growth chamber experiments. Field trials were conducted by ABRI-Tech at the Namur, Quebec study site (for description see Chapter 3). **The field data collected is not my own; however, ABRI-Tech has granted permission to use their raw data and I independently completed the statistical analysis and interpretation.** To build on the findings of the field trials, a growth chamber experiment was conducted at the University of Waterloo to compare the effects of Char+, N-fertilizer and biochar in different soil textures.

4.1.1 Research Questions and Objectives

The main research question of this study is:

> Can Char+ be used as a mineral N fertilizer substitute in Canadian agriculture to sustainably increase maize productivity and terrestrial C storage?

Three sub-questions of this study were:

1. Does the combination of biochar and N fertilizer have a synergistic effect on maize biomass production that is greater than the effect of N fertilizer alone?

2. Can the combination of biochar and N fertilizer improve NUE?

3. Can Char+ provide sustained crop nutrition over multiple growing seasons or act as a “slow-release” fertilizer?

4. How does Char+ affect maize biomass production and SOC in soils with different textures?

4.1.1.1 Field Trial Objectives

The specific objectives of the field trial were as follows:

1. To compare the effects of different Char+ applications rates and N fertilizer on maize biomass production under temperate field conditions.

2. To determine the effects of different Char+ applications rates on maize tissue nutrient concentrations and N uptake under temperate field conditions.

3. To determine the agronomic and N-based NUE of different Char+ applications rates for maize grown in temperate field conditions.

4. To determine the effects of different Char+ applications rates on SOC and soil nutrient concentrations under temperate field conditions.

4.1.1.2 Growth Chamber Experiment Objectives

The specific objectives of the growth chamber experiment were:

1. To compare the effects of Char+, N fertilizer and biochar on maize biomass production in sandy, medium and fine textured soils.

2. To determine effects of Char+ on plant tissue N concentrations and N-uptake of maize grown in sandy, medium and fine textured soils.

3. To determine effects of Char+ on SOC and total N in sandy, medium and fine textured soils.

4. To synthesize the soil and plant tissue results, and propose mechanisms that explain the effects of Char+ on maize biomass production.

4.1.2 Hypotheses

4.1.2.1 Field Trial

The hypotheses and null hypotheses were:

1. That the maize biomass production will increase with increasing biochar application rates when a constant amount of N fertilizer is supplied.

   H_O: There will be no significant differences in maize biomass production between different biochar application rates.

2. When an equal amount of N fertilizer is supplied as Char+ or UAN, the Char+ treatment will result in greater maize biomass production than UAN.

   H_O: There will be no significant differences in maize biomass production between Char+ and UAN treatments.

3. When an equal amount of N fertilizer is supplied as Char+ or UAN, the Char+ treatment will result in greater maize tissue N concentrations and N-uptake than UAN.

   H_O: There will be no significant differences in maize tissue N concentrations and N-uptake between Char+ and UAN treatments.

4. That the SOC and soil nutrient concentrations will increase with increasing biochar application rates and be greater in biochar treatments than UAN treatments.

   H_O: There will be no significant differences in SOC or soil nutrient concentrations between treatments with different biochar application rates and UAN treatments.

4.1.2.2 Growth Chamber Experiment

The hypotheses and null hypotheses were:

1. That the maize biomass production will be significantly greater in the Char+ treatments than in the UAN and biochar treatments.

   H_O: There will be no significant differences in maize biomass production between treatments.

2. That the maize biomass response to Char+ will be greater in the sandy textured soil than the medium soil, which will be greater than the fine soil.

   H_O: There will be no differences in maize biomass response to Char+ between sandy, medium and fine textured soils.

3. That the maize tissue N concentrations and N uptake will be significantly greater in Char+ treatments than in the UAN treatments.

   H_O: There will be no significant differences in maize tissue N concentrations and N uptake between treatments.

4. That the SOC and soil TN will be significantly greater in Char+ treatments than in the UAN treatments.

   H_O: There will be no significant differences in SOC or soil TN between treatments.

4.2 Material and Methods

4.2.1 Field Trial

4.2.1.1 Experimental Design

Two separate field trials with maize were conducted: 1) the "Char+ Trial", which compared different Char+ application rates, and 2) the "Biochar Trial", which compared different biochar (not pre-soaked in UAN) application rates. The Biochar Trial used application rates of 6.2-24.8 t biochar/ha, which may not be economically feasible. However, the purpose of the Biochar Trial is to demonstrate the effects of 6-25 years of annual 1 t Char+/ha additions on maize productivity and SOC. The Biochar Trial also included a treatment with agricultural lime (used to increase soil pH). The lime treatment was included in the analysis, but is not a primary interest of this thesis. The Biochar Trial was initiated in 2009 and repeated in 2010 without further additions of biochar, while the Char+ Trial was initiated in 2010. Results from the Biochar Trial presented in this thesis are based on the 2010 data only because in 2009 much of the crop was lost as a result of birds and cattle eating the seeds/seedlings.

In the **Char+ Trial** there were five treatments with four replications each:

1. No biochar or UAN ("Control")
2. 0.27 t biochar/ha + 50 kg N/ha ("Char+50")
3. 0.54 t biochar/ha + 100 kg N/ha ("Char+100")
4. 0.91 t biochar/ha + 170 kg N/ha ("Char+170")
5. 170 kg N/ha applied as UAN ("UAN")

All treatments in the Char+ Trial, including the control, received 95 and 185 kg/ha of P and K, respectively, which were the rates recommended by soil tests.

In the **Biochar Trial** there were also five treatments with four replications each:

1. Control (with NPK, but no biochar)
2. 6.2 t biochar/ha + NPK
3. 6.2 t biochar/ha + agricultural lime + NPK
4. 12.4 t biochar/ha + NPK
5. 24.8 t biochar/ha + NPK

The amount of P and K fertilizer added to each treatment in the Biochar Trial was adjusted according to the P and K contribution from biochar (Table 4.1). All treatments in the Biochar Trial, including the control, received 135 kg N/ha applied as UAN. In both the Char+ and Biochar Trial, the replicate plot size was 3 m x 6 m and the plots were located 3 m away from adjacent plots to minimize any competitive interaction effects. The Char+ Trial replicates were assigned randomly to plots (Fig. 4.1), and the Biochar Trial replicates were organized in a randomized complete block design (Fig. 4.2).

Table 4.1 Amounts of N, P and K fertilizer added (kg/ha) for each treatment in the Biochar Trial. The amount of P and K added decreases with higher biochar application rates because the contribution from biochar is accounted for.

Biochar (t/ha)	Fertilizer Applied			Biochar Contribution			Total		
	N	P	K	N	P	K	N	P	K
0	135	89	181	0	0	0	135	89	181
6.2	135	86	143	0	2.6	38	135	89	181
12.4	135	84	106	0	5.2	75	135	89	181
24.8	135	79	30	0	10.4	151	135	89	181

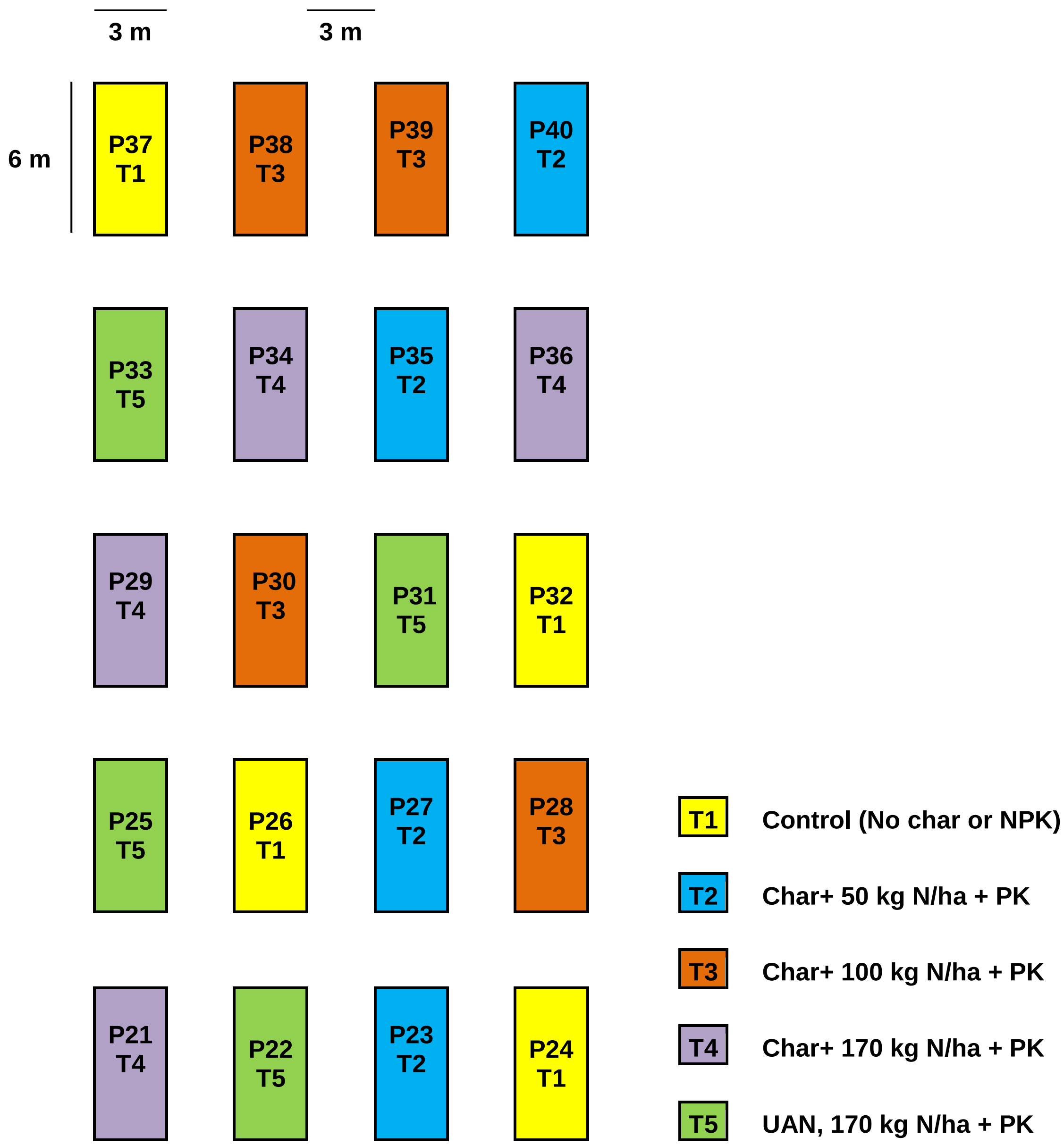


Figure 4.1 - Experimental design including treatments and replicates of the Char+ Field Trial.

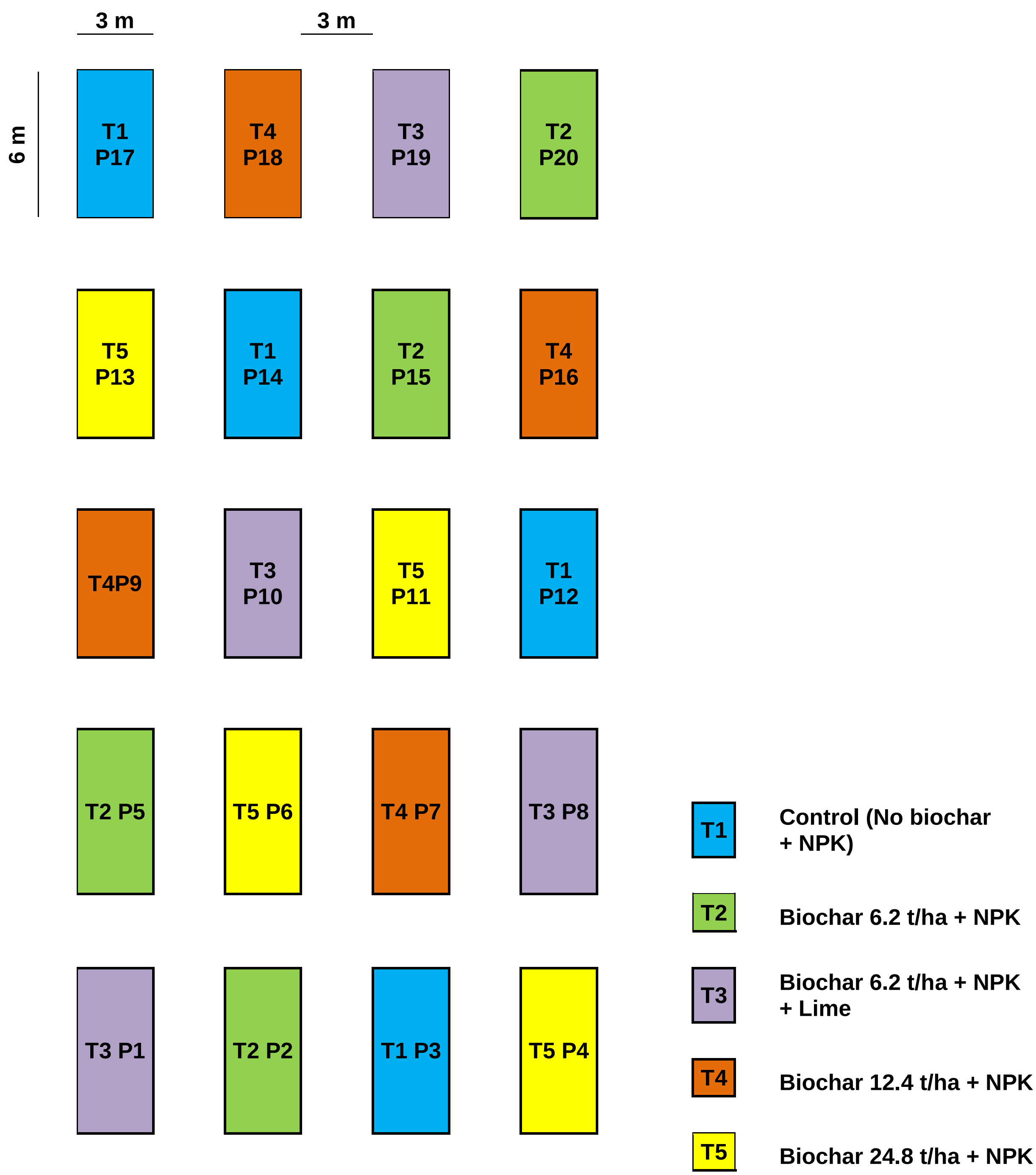


Figure 4.2- Experimental design including treatments and replicates of the Biochar Field Trial.

4.2.1.2 Biochar, Char+ and UAN Preparation

The biochar produced by ABRI-Tech Inc. was made from a mix of hardwood (maple, oak and birch) and was fast pyrolyzed at 450 °C. The chemical properties of the biochar were assessed by the *Institut de Recherche et de Developpement en Agro-environnement* (IRDA) in Quebec and results are presented in Table 2.1. Based on absorbency tests conducted by ABRI-Tech, the optimal ratio of UAN:biochar was determined to be 2:3 (by weight). Char+ was prepared by thoroughly mixing the amount of biochar and UAN fertilizer required for each treatment replication (18 m^2 plot) in plastic buckets (Table 4.2). The mixtures were transferred into plastic bags and sealed for approximately 24 hours, allowing the biochar to fully combine with the UAN. For the UAN treatment, the fertilizer was first diluted by mixing two parts de-ionized water with one part UAN in accordance with product information.

Table 4.2 - Quantity of biochar and fertilizer applied to replication plots (18 m^2) for each treatment and equivalent field application rates of biochar (t/ha) and UAN (kg/ha)

Treatment	Biochar (g/plot)	UAN (g/plot)	Biochar (t/ha)	UAN (kg/ha)
Control	0	0	0	0
Char+50	500	320	0.27	50
Char+100	1000	640	0.54	100
Char+170	1600	1090	0.91	170
UAN	0	1090	0	170

4.2.1.3 Planting and Post-harvest measurements

For both the Biochar and Char+ trials, the site was prepared by treating the plots with glyphosate herbicide and roto-tilling. The amount of Biochar or Char+ was weighed separately for each plot, spread evenly over the plot by hand, and then thoroughly incorporated within the upper 10 cm using rakes/shovels (Fig. 4.3). Maize (*Zea mays*) was planted in May 2010 at a seed density of 140,350 plant/ha, which was later thinned by half when seedlings were 10 cm tall (final density of 70,175 plants/ha). The maize seed used for both trials was a silage corn hybrid (Helite variety G4066, UTM 2400) with an anti-pest/fungal coating.

In September 2010 both trials were harvested by collecting the above-ground portion of plants in the middle row of each replicate's plot. Fresh plant samples were weighed and dried at 60 °C until constant weight to determine dry mass. One 20 g soil sample per replicate was collected from the 0-10 cm horizon and air-dried. A full chemical analysis of plant, soil and biochar samples was conducted by the *Institut de Recherche et de Developpement en Agro-environnement* (IRDA) in Quebec using standard methodology. Due to budgetary constraints the soil samples from the Char+ Trial were not analyzed.

4.2.1.4 Nitrogen Use Efficiency

Nitrogen use efficiency was determined for the Char+ field trial, but could not be calculated for the biochar field trial because an unfertilized control plot was not included in the experimental design and this is required for the equations. The following equations are used to calculate agronomic and N-based NUE:

$$\textbf{Agronomic NUE} = ((Y_f - Y_o)/N_{app}) * 100\%$$

$$\textbf{N-based NUE} = ((N_f - N_o)/N_{app}) * 100\%$$

where Y_f and Y_o are the yields of fertilized and unfertilized plots, respectively, and N_f and N_o is the N uptake of fertilized and unfertilized plots, respectively, and N_{app} is the N fertilizer application rate (kg/ha) (Robertson and Vitousek, 2009; Yeboah et al., 2009).

(A) 

(B) 

Figure 4.3 – Char+ and Biochar field trials in Namur, Quebec. (A) Method of applying biochar to test plots; note the sandy texture of the soil. (B) Experimental plot layout and weeding conducted at seedling stage. Photos courtesy of P. Fransham.

4.2.2 Growth Chamber Experiment

4.2.2.1 Soil Collection

In the spring of 2010, about 120 kg of each soil type from the University of Guelph's Grape Research Station (Vineland, ON), the University of Guelph's Research Station (Elora, ON), and the Agriculture and Agri-Food Canada's Southern Crop Protection and Food Research Centre (Delhi, ON) were taken from the upper 10 cm of unplanted and recently tilled fields. Soils were stored in unsealed buckets at room temperature until the beginning of the experiment (about one week).

4.2.2.2 Experimental Design

The growth chamber experiment was designed to evaluate the performance of the N-enriched biochar or "Char+". The effects that Char+ may have on plant growth can be divided into three aspects: biochar, N fertilizer, and interactive combination of both the fertilizer and biochar. There are numerous treatment possibilities within these three categories depending on the application rates of biochar (t/ha) and fertilizer (kg N/ha), and the ratio of biochar to fertilizer in Char+. However, due to time and space limitations the study concentrated on four treatments:

1. No UAN or biochar ("Control")
2. 1 t/ha biochar ("Biochar")
3. 187 kg N/ha UAN ("UAN")
4. 1 t/ha biochar pre-soaked in 187 kg N/ha ("Char+")

Each of these four treatments were combined with the three soil textures (sandy, medium, fine), and with five replicates for a total of 60 pots. Twenty pots could be grown in each of the two chambers; therefore, one chamber was used twice (two time slots). Although the growth chambers can be programmed to have the same climatic conditions, there is the possibility of slight differences between chambers. Placement of the pots within the chamber is also a possible source of variation: pots in the corners may receive less light and air flow. To minimize the contribution of between-chamber variation, the 60 pots were randomly assigned to one of the three chamber-time blocks, and to minimize within-chamber effects each pot's initial position within the chamber was randomized using a random number generator (MS Excel) with a new arrangement created weekly.

4.2.2.3 Preparation of Biochar, Char+ and UAN Treatments

The biochar provided by ABRI-Tech Inc. was made from a mix of hardwood (maple, oak and birch) and was fast pyrolyzed at 450 °C. The chemical properties of the biochar were assessed by the *Institut de Recherche et de Developpement en Agro-environnement* (IRDA) in Quebec (Table 2.1). Based on absorbency tests conducted by ABRI-Tech, the optimal ratio of UAN:biochar was determined to be 2:3 (by weight). Char+ was prepared by thoroughly mixing 25 g of biochar with 16.6 g of UAN fertilizer in aluminum containers. The containers were sealed with tin foil and stored for approximately 24 hours, allowing the biochar to fully combine with the UAN. For the UAN treatment, the fertilizer was first diluted by mixing two parts de-ionized water with one part UAN in accordance with product information. Each treatment (including the control) received equal amounts of phosphorous (P) and potassium (K) fertilizer;

the equivalent of 95 kg/ha of P and 185 kg/ha of K was applied as P_2O_5 and KCl, respectively. These rates were chosen based on the fertilizer additions used in the Namur, QC field trials.

The logic used to convert field application rates (t/ha) to pot application rates (g/pot) was based on the idea of collecting soil from a hypothetical field trial where the treatments had been applied. The following assumptions were made:

1. Biochar was incorporated in the field within the top 10 cm of soil
2. Bulk density of the field soil was 1.3 g/cm^3.

The amount of biochar, Char+ or UAN to be added to the pots was calculated by working backwards from the soil weight in the pot (5 kg). The soil weight was converted to dry weight based on the % moisture, then divided by the bulk density (1.3 g/cm^3) to find the soil volume. The soil volume was divided by the depth of incorporation (10 cm) to calculate the area which would be occupied by 5 kg of soil in the field. This area was then multiplied by the field application rate (t/ha or kg/ha) of biochar, Char+ or UAN and converted to grams. The amounts of biochar, Char+ and UAN added to the pots are summarized in Table 4.3. For the biochar and Char+ treatments the concentration of biochar in the soil was 0.074 % by weight.

Table 4.3 - Summary of treatment preparations and equivalent field application rates. For the Char+ treatment biochar and UAN were combined prior to mixing with soil. For the UAN treatment, UAN was diluted 2:1 with de-ionized water.

Treatment	Biochar (g/pot)	UAN (g/pot)	Biochar (t/ha)	N (kg/ha)
Control	0	0	0	0
Biochar	3.7	0	1	0
Char+	3.7	2.5	1	187
UAN	0	2.5	0	187

Each replicate was prepared separately by mixing 5 kg of soil with their respective amounts of biochar, Char+ or UAN, and P and K in a large plastic bucket with a gardening shovel. The soil was mixed for one minute and then placed into pots, which contained a lining of burlap material (used to prevent soil loss). Soil for the control pots was also mixed for one minute. A shallow depression was dug on the soil surface to concentrate water towards the plant roots and prevent seepage down the sides of the pot.

4.2.2.4 Plant Growth Conditions

The temperature, light, and humidity settings for the growth chamber (Conviro, PGR15, Manitoba, Canada) were chosen based on a balance between simulating a realistic Ontario climate and optimizing plant growth (Table 4.4).

Table 4.4 - Values of light, temperature and humidity conditions in the growth chambers over a 24 hour cycle.

Variable	5:00 - 7:00	7:00 - 19:00	19:00 - 21:00	21:00 - 5:00
Light (μmol/m^2 * sec.)	300	450	300	0
Humidity (%)	60	50	60	70
Temperature (°C)	20	25	20	18

Photoperiod - 16 hour day, 8 hour night
CO_2 - Set to 380 ppm. However, due to lack of air circulation in the room and people breathing the levels were typically 400-600 ppm.

The maize (*Zea mays*) used for the experiment was "Silage corn hybrid: Helite (HTE) variety G4066" (provided by ABRI-Tech). In commercial operations, silage corn is harvested by removing the above ground portion of the plants, which is then used as cattle feed. Because this study measured shoot biomass (as opposed to grain yield), silage corn is an appropriate test species. Prior to planting, the seeds were primed by soaking in a shallow tray of water for 24 hours and replacing the water every 6 hours. Four seeds were planted in each pot and after one week the seedlings were thinned and only the tallest seedling remained in each pot. Plants were watered with 500 mL of purified water every two days. The rate of watering was chosen to optimize plant growth (Lynn Hoyle, personal communication 2010)

4.2.2.5 Plant Biomass and Elemental Analysis

Six weeks after planting the maize plants were cut at the soil surface to remove the above-ground portion (shoots). The shoots were weighed, dried in a drying oven at 60 °C until constant weight (about 48 hrs), and then weighed again to determine dry mass. At the same time, a 200 g sample of soil from the middle of each pot was collected and air-dried.

A sample of plant material and soil from each pot was analyzed for organic C and total N (TN). To prepare the plant samples for chemical analysis 3-5 g of leaf material was ground: first, with a plant grinder (Kinematica, Switzerland), and then with a Retsch ball mill (MM 200 PA; Haan, Germany) to produce a fine powder. Prior to SOC and TN analysis, a 5 g sample of soil was passed through a 2 mm sieve to remove the coarse mineral fraction and large plant residue fragments, and then ground using a Retsch ball mill. Carbonates (inorganic C) were removed by mixing 2 g of ground soil with 50 mL of 0.5 M hydrochloric acid (HCl) and shaking the mixture for 10 minutes three times over a 24-h period using a laboratory shaker. After the soil settled, the acid-solution was removed by pouring off the top portion and removing the remaining 5-10 mL with a 5 mL pipette. The acid-solution was replaced with 50 mL of de-ionized water once daily for 4 days. The soils were then dried in an oven at 40 ºC for 2 days (Midwood and Boutton, 1998) and ground again using a mortar and pestle. About 5 mg of plant and soil material were loaded into tin capsules and analyzed for SOC and TN concentrations using a Costech Elemental Analyzer (Model 4010; Cernusco, Italy).

4.2.2.6 Statistical Analysis

Data for the field trials and growth chamber experiment were examined for homogeneity of variance using the Levene Test and normal distribution using the Shapiro-Wilk test. A one-way analysis of variance (ANOVA) was run in SPSS (IBM, version 19.0, 2010) and was used to compare differences between treatments. Any significant differences were further analyzed using Fisher's Least Significant Differences (LSD) multiple comparison tests. If data did not meet homogeneity of variance requirements a Welch test was used to evaluate overall treatment effects, followed by Games-Howell post-hoc tests. If data did not meet normal distribution requirements a Kruskal-Wallis was used for overall treatment effects, followed by Mann-Whitney post-hoc tests. For all statistical analyses, the threshold probability level was $P < 0.05$ unless stated otherwise. The LSD test is known to be less conservative than other post-hoc tests, such as Tukey's Honest Significant Difference test. However, because the experimental designs in this study only have 4-5 treatments, the use of the LSD test is appropriate (CFIA, 2008). In the context of developing a national-level strategy for biochar-C sequestration, it may not be necessary to use highly conservative statistical tests. For example, if we can conclude that about 8 out 10 farms in Ontario ($\alpha = 0.2$) will experience an increase in yields as a result of biochar, this would be a positive incentive for implementing a biochar strategy.

4.3 Results

4.3.1 Char+ Field Trial Results

4.3.1.1 Maize Biomass

Maize biomass (dry mass, DM) increased relative to the control with increasing application rates of Char+. However, only the highest application rate (0.91 t biochar + 170 kg N/ha) was significantly different from the control (Table 4.5). The UAN treatment was also significantly different from the control and resulted in the highest biomass production, but it was not significantly different from any of the Char+ treatments, including the lowest Char+ application rate (0.27 t biochar + 50 kg N/ha). Relative to the control, Char+50 and Char+100 both increased mean DM by 27%, while Char+170 and UAN treatments increased mean DM by 55% and 62%, respectively.

4.3.1.2 Maize Leaf Carbon and Nutrient Concentrations

No significant differences in maize leaf C concentrations were found, except for the Char+50 treatment, which was significantly lower than the control (Table 4.5). The maize leaf N concentration of the control was not significantly different from the 50 and 100 kg N/ha Char+ treatments. Char+170 resulted in the highest maize leaf N concentration and was significantly different from the control and UAN treatments (Table 4.5). The UAN treatment had the second highest N concentration and was significantly different from the control, but was not significantly different from the Char+100. The C/N ratio of the maize leaves was lower in the Char+170 and UAN treatments and increased with decreasing N-fertilizer additions in Char+100 and Char+50 treatments (Table 4.5).

No significant differences or trends in maize leaf P concentrations were found among treatments (Table 4.5). The highest concentrations of maize leaf K were found in the Char+50 treatments and this was significantly different from the UAN treatment, which had the lowest concentration of K (Table 4.5). The Char+170 resulted in maize leaf K concentrations that were 1.5 g/kg greater and significantly different than the UAN treatment.

Table 4.5 - Maize leaf C, N, P and K concentrations, C/N ratio and shoot dry mass of maize grown with three Char+ application rates, UAN and a control.

Treatment	C (%)	N (%)	C/N	P (g/kg)	K (g/kg)	Dry Mass (t/ha)
Control	43.07 (0.12) A	0.96 (0.03) A	45.03 (1.53) B	1.57 (0.38) A	10.2 (0.5) AB	15.96 (2.62) A
Char+ 50 kg N/ha	42.80 (0.10) B	0.87 (0.06) A	49.53 (3.25) A	1.48 (0.5) A	11.43 (1.2) B	20.28 (2.91) AB
Char+ 100 kg N/ha	43.05 (0.21) A	1.0 (0.05) AB	43.2 (1.98) B	1.33 (0.08) A	9.94 (0.81) AB	20.3 (1.76) AB
Char+ 170 kg N/ha	43.18 (0.17) A	1.24 (0.12) C	35.0 (3.0) C	1.51 (0.12) A	10.92 (0.76) B	24.67 (7.4) B
UAN 170 kg N/ha	43.15 (0.06) A	1.12 (0.04) B	38.5 (1.29) C	1.5 (0.13) A	9.4 (0.88) A	25.78 (3.8) B

Means followed by different letters are significantly different (LSD, $p < 0.05$) between treatments.

For shoot K and dry mass, the overall treatment effect significance was $p < 0.1$.

4.3.1.3 Maize N Uptake and NUE

The highest mean N uptake was found in the Char+170. However, due to high variation, the Char+ treatment was not significantly different from the control (Table 4.6). The UAN treatment resulted in the second highest mean N uptake and was significantly different from the control. Nitrogen uptake resulting from Char+50 and Char+100 was 23 and 49 kg/ha greater than the control, respectively; however, they were not significantly different than the control.

Even though UAN resulted in slightly higher DM than Char+170, the differences in maize leaf N concentration between treatments translated into greater N-based NUE in the Char+170 compared with UAN; NUE was calculated to be 80% for UAN and 90% for Char+ (Table 4.6). The other two Char+ treatments of 50 and 100 kg N/ha did not significantly increase leaf N concentrations or DM, and this resulted in lower NUE values of 50% and 48% for Char+100 and Char+50, respectively. In terms of agronomic NUE, the best performance was observed in the Char+50 treatment (8.6%) followed by UAN (5.8%), Char+170 (5.1%), and finally Char+100 was had the lowest (4.3%) (Table 4.6).

Table 4.6 - Maize shoot N uptake (leaf N concentration * dry mass), N-based N use efficiency (NUE) and Agronomic NUE of maize grown with three Char+ application rates, UAN and a control.

Treatment	N uptake (kg/ha)	N-based NUE (%)	Agronomic NUE (%)
Control	152.4 (27.3) ^{A}	-	-
Char+ 50 kg N/ha	175.7 (27.3) ^{A}	48	8.6
Char+ 100 kg N/ha	201.5 (7.5) ^{A}	50	4.3
Char+ 170 kg N/ha	305.4 (88.2) ^{AB}	90	5.1
UAN 170 kg N/ha	287.8 (35.0) ^{B}	80	5.8

Means followed by different letters are significantly different (LSD, $p < 0.05$) between treatments.
Due to lack of homogeneity of variance in N uptake results, the Welch test was used for measuring significant treatment effects ($p < .05$) and Games-Howell was used for post-hoc tests.

4.3.2 Biochar Field Trial Results

4.3.2.1 Maize Biomass

There were no significant differences in maize DM between treatments. However, the mean DM of the 24 t biochar/ha treatment was about 2 t/ha (or 25%) greater than the control (Fig. 4.4 and Table 4.7). The variation in DM for the 6.2+Lime and 12.4 t biochar/ha treatments was about double that of the other treatments. At the biochar application rate of 6.2 t/ha the addition of lime did not significantly affect the DM of maize.

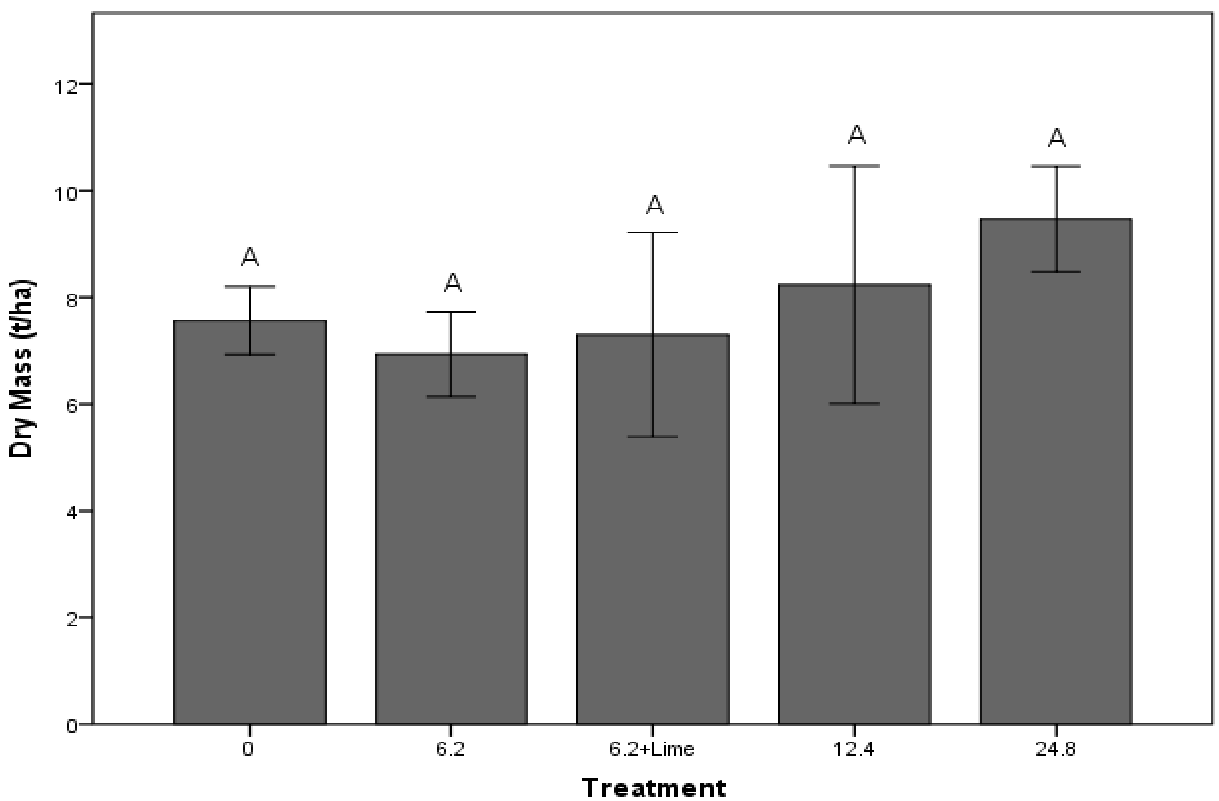


Figure 4.4 – Maize dry mass for three biochar application rates (6.2, 12.4 and 24.8 t/ha) and one treatment with biochar and agricultural lime (6.2 + Lime). Error bars represent +/- one standard error. Means followed by different letters are significantly different (LSD, $p < 0.05$) between treatments

4.3.2.2 Maize Leaf C and Nutrient Concentrations, and N Uptake

Maize leaf C concentrations ranged from 43.5-43.8% and there were no significant differences between treatments (Table 4.7). Relative to the control, the maize leaf N, P and K concentrations were slightly lower in the 6.2 t/ha +lime and 12.4 t/ha biochar treatments. However, no significant differences were found among treatments for leaf N, P or K concentrations (Table 4.7). Besides these primary nutrients, the only other significant difference found in the tissue chemical analysis was for sodium. The 6.2 t/ha + lime treatment resulted in significantly higher sodium levels than the control or 6.2 t/ha (ANOVA significance $p < 0.1$, data not shown). The C/N ratio of the maize leaves was lowest in the 6.2 t/ha treatment and highest in the 6.2+Lime treatment; however, no significant differences were found between treatments (Table 4.7). The 24.8 t/ha biochar application rate resulted in the highest N uptake and increased mean uptake by 18.4 kg N/ha relative to the control. However, there were no significant differences in N uptake between treatments (Table 4.7).

Table 4.7 - Maize leaf C, N, C/N ratio, P and K concentrations, shoot dry mass and N uptake for three biochar application rates (6.2, 12.4 and 24.8 t/ha) and one treatment with biochar and agricultural lime (6.2 + Lime).

Biochar (t/ha)	C %	N %	C/N	P (g/kg)	K (g/kg)	Dry Mass (t/ha)	N Uptake (kg/ha)
0	43.70 (0.44) A	1.10 (0.17) A	40.14 (5.48) A	1.67 (0.48) A	9.92 (1.57) A	7.57 (1.10) A	83.7 (19.1) A
6.2	43.63 (0.12) A	1.21 (0.17) A	36.54 (5.17) A	1.66 (0.36) A	10.24 (1.86) A	6.93 (1.38) A	82.4 (4.50) A
6.2 + Lime	43.53 (0.31) A	0.99 (0.13) A	44.62 (5.8) A	1.43 (0.17) A	9.73 (0.21) A	7.30 (3.32) A	72.2 (32.3) A
12.4	43.77 (0.23) A	1.02 (0.08) A	43.0 (3.47) A	1.38 (0.25) A	9.29 (1.33) A	8.23 (3.86) A	82.5 (32.7) A
24.8	43.57 (0.15) A	1.08 (0.06) A	40.31 (2.34) A	1.65 (0.28) A	10.45 (1.36) A	9.47 (1.71) A	102.1 (16.5) A

Means followed by different letters are significantly different (LSD, $p < 0.05$) between treatments.

4.3.2.3 Soil Organic C and Nutrient Concentrations

With the exception of the 12.4 t/ha biochar application rate, there was a trend of increasing SOC with increasing biochar application rates (Table 4.8). Soil organic C concentrations increased from 17 g/kg in the control to 21 and 25 g/kg in the 6.2 and 24.8 t/ha biochar treatments, respectively, but were not significantly different. Mean soil N concentrations increased slightly from 1.0 g/kg in the control to 1.1 and 1.2 g/kg with 6.2 and 24.8 t/ha biochar application rates, respectively (Table 4.8). The 12.4 t/ha biochar application rates was an exception to this trend, and overall no significant differences were found between treatments for soil N concentrations. The soil N stock increased by about 130 kg/ha for the 6.2 t/ha biochar treatment and 240 kg/ha for the 24.8 t/ha biochar treatment, compared with the control (Table 4.8). The soil C/N ratio increased with increasing biochar application rates, with the exception of the 12.4 t/ha biochar treatment (Table 4.8). Relative to the control, the highest biochar application rate (24.8 t/ha) resulted in a significantly greater soil C/N ratio. There was a general trend of increased soil NH_4^+, NO_3^- (Table 4.9) with increasing biochar application rates. However, the 12.4 t biochar/ha disagreed with this trend and no significant difference were found among treatments.

No significant differences were found for soil P and K (Table 4.9). Nonetheless, there was a trend of decreasing K concentrations with increasing biochar application rates; soil K concentrations declined from 58 g/kg in the control to 41 g/kg in the 24.8 t/ha biochar treatment. The only other soil nutrient that differed among treatments was sodium (Na). Although no significant differences were found, Na was greater in the 6.2 + Lime treatment than all other treatments (data not shown). Although not significant, soil organic matter generally increased with higher biochar application rates (Table 4.9). The 24.8 t biochar/ha treatment increased SOM by about 30% relative to the control. Soil pH was unaffected by biochar additions and ranged from 6.0 - 6.2 (data not shown). No significant differences in soil moisture were found between treatments. Biochar treatments had higher mean soil moisture than the control, with the exception of the 12.4 t/ha treatment (Table 4.9).

Table 4.8 - Soil organic C, total N and C/N ratio following a field trial with maize and three biochar application rates. Standard deviations are given in parenthesis.

Treatment	SOC (g/kg)	C Stock (t/ha, depth = 10 cm)	N (g/kg)	N Stock (kg/ha, depth = 10 cm)	C/N
0	17.0 (5.8) A	22.1 (7.5) A	1.0 (0.40) A	1297 (465.4) A	17.2 (1.36) A
6.2	21.2 (5.7) A	27.5 (7.4) A	1.1 (0.27) A	1424 (345.2) A	19.2 (1.43) AB
6.2 + Lime	20.4 (9.2) A	26.6 (12.0) A	1.15 (0.44) A	1495 (566.1) A	17.4 (1.77) A
12.4	18.5 (7.6) A	24.0 (9.8) A	0.99 (0.42) A	1287 (545.5) A	18.8 (1.43) A
24.8	25.2 (4.9) A	32.8 (6.3) A	1.19 (0.18) A	1541 (229.3) A	21.2 (1.37) B

Means followed by different letters are significantly different (LSD, $p < 0.05$) between treatments.

Table 4.9 - Soil nutrient concentrations, soil organic matter (SOM) and moisture following a field trial with maize and three biochar application rates. Standard deviations are given in parenthesis.

Treatment	NH_4^+ (g/kg)	NO_3^- (g/kg)	P (g/kg)	K (g/kg)	SOM (%)	Moisture (%)
0	0.60 (0.22) A	3.92 (1.44) A	34.7 (22.4) A	57.6 (25.7) A	4.17 (0.55) A	13.5 (3.7) A
6.2	0.72 (0.22) A	4.28 (0.74) A	28.7 (20.1) A	55.0 (21.6) A	4.63 (0.21) A	16.3 (2.6) A
6.2 + Lime	0.65 (0.11) A	4.10 (1.26) A	30.6 (9.1) A	46.2 (18.5) A	4.50 (0.92) A	15.1 (4.0) A
12.4	0.61 (0.21) A	3.98 (1.85) A	33.6 (13.6) A	44.9 (4.5) A	4.93 (0.84) A	13.2 (4.3) A
24.8	0.75 (0.12) A	4.88 (1.47) A	28.0 (10.3) A	40.5 (8.9) A	5.40 (1.14) A	16.3 (1.2) A

Means followed by different letters are significantly different (LSD, $p < 0.05$) between treatments.

4.3.3 Growth Chamber Results

4.3.3.1 Maize Biomass

Biochar, Char+ and UAN had both positive and neutral effects on maize DM depending on the soil texture (Fig. 4.5). Comparisons between treatments for the sandy, medium and fine texture soils are described below. All reported percent increases are relative to the control.

In the sandy textured soil (Delhi) additions of biochar, Char+, and UAN all significantly increased mean DM (Fig. 4.5). The mean DM of Char+ and UAN treatments were not significantly different from each other, but were significantly greater than the biochar and control treatments. The increases in DM for Char+ and UAN treatments were 310 % and 342 %, respectively, while biochar resulted in a 48 % increase.

In the medium textured soil (Elora) the Char+ treatment increased DM by 112 % and had the highest mean DM; it was significantly different from the control and biochar treatments, but not from the UAN treatment (Fig. 4.5). Although the difference in mean DM between biochar and control treatments was not significant, additions of biochar resulted in a 31% increase in DM. The UAN treatment increased DM by 92% and was significantly different from the control, but was not significantly different from the biochar treatment.

In the fine textured soil (Vineland) the DM of the control was greater than the controls for the other soils, and no significant differences or trends among treatments were found (Fig. 4.5). The maximum DM achieved in the fine soil is similar to the maximum DM found in the sandy soil, and greater than the maximum DM in the medium soil.

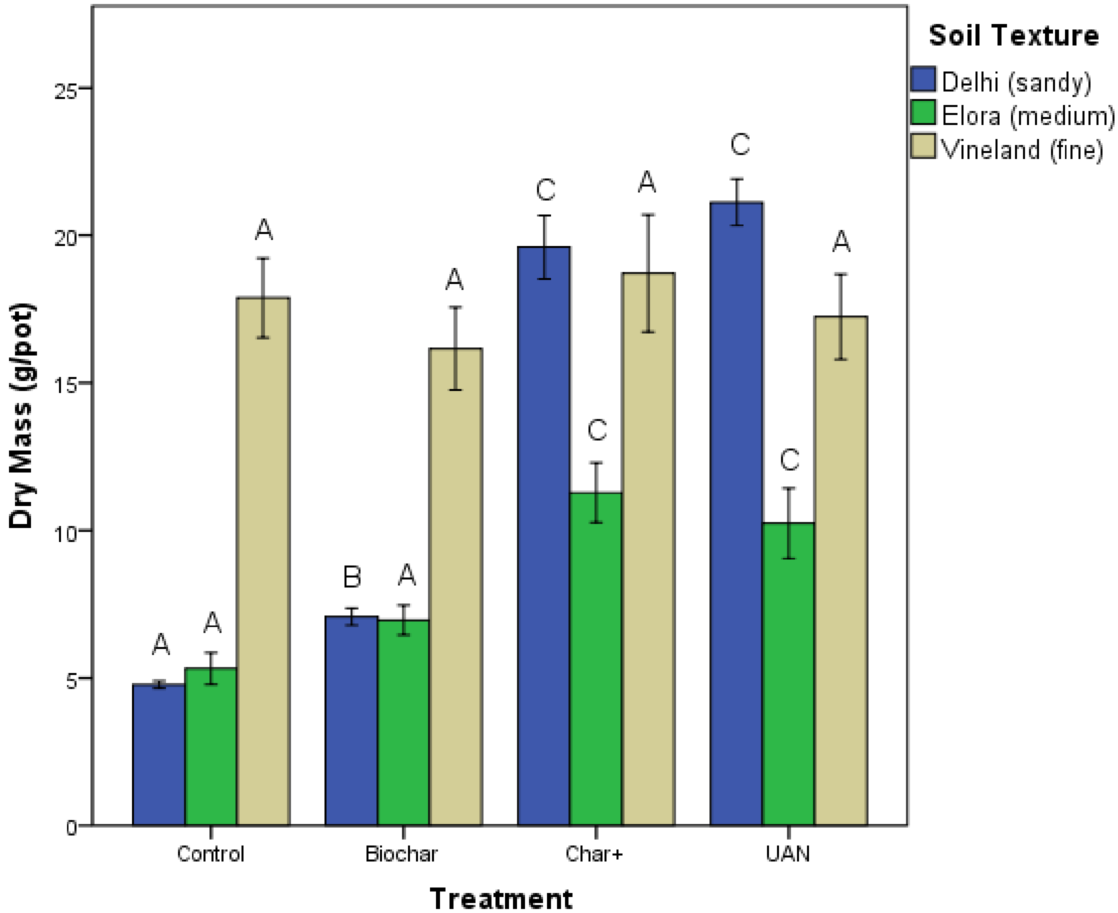


Figure 4.5 - Mean shoot dry mass of maize grown in sandy, medium and fine texture soil with additions of biochar (1 t/ha), Char+ (1 t/ha biochar pre-soaked in UAN, 187 kg N/ha) or UAN (187 kgN/ha). Error bars represent +/- 1 standard error. Means followed by different letters are significantly different (LSD, $p < 0.05$) between treatments

4.3.3.2 Maize Leaf C and N Concentrations, C/N ratio and N Uptake

In the sandy soil, the maize leaf C concentrations of the control and biochar treatments were significantly lower than the Char+ and UAN treatments (Table 4.10). In the medium textured soil, only the control treatment had a significantly lower leaf C concentration than Char+ and UAN. No significant differences in leaf C concentrations were found in the fine textured soil.

For sandy and medium texture soils the maize leaf N% of Char+ and UAN treatments were not significantly different from each other, but were significantly greater than biochar and control treatments (Table 4.11). While a small increase in DM was observed with biochar in the sandy soil, no significant difference in leaf N% was found between biochar and the control. Although no significant differences in DM were found between treatments for the fine texture soil, leaf N% was significantly greater in Char+ and UAN treatments than in the control and biochar treatments. The leaf N content of the biochar and control treatments was greater than 2% in fine soil, and less than 2% in the sandy and medium texture soils.

Across all soil textures the maize leaf C/N ratio of Char+ and UAN treatments were not significantly different from each other, and significantly lower than the biochar and control treatments (Table 4.12). The leaf C/N ratio of biochar and control treatments was highest in the sandy soil, followed by the medium soil and lowest in the fine soils.

Nitrogen uptake was evaluated on a per plant basis and calculated by multiplying the leaf N% by the shoot DM; this is a measure of how much soil N was removed by the shoot portion of each plant (Yeboah, 2009). In the sandy soil, the highest N uptake was found in the Char+ and

UAN treatments, which were not significantly different from each other, but significantly different from the biochar and control treatments (Table 4.13). Biochar resulted in a small but significant increase in mean N uptake of 29 mg/pot. In the medium soil biochar resulted in a similar increase in N uptake (27 mg/pot), but this was not significantly different from the control. In both the medium and fine textured soils, N uptake of Char+ and UAN treatments were not significantly different from each other, but were significantly different from the biochar and control treatments.

Table 4.10 - Mean leaf C content (%) of maize grown in three soil textures with additions of biochar (1 t/ha), Char+ (1 t/ha biochar pre-soaked in UAN, 187 kg N/ha) or UAN (187 kgN/ha). Standard deviations are given in parenthesis.

Treatment	Soil Texture		
	Sandy	**Medium**	**Fine**
Control	45.26 (.32) ^{A}	45.88 (.18) ^{A}	45.91 (.43) ^{A}
Biochar	45.32 (.19) ^{A}	46.27 (2.24) ^{AB}	45.73 (.46) ^{A}
Char+	46.67(.50) ^{B}	46.82 (.36) ^{B}	45.93 (.71) ^{A}
UAN	46.91 (.59) ^{B}	47.40 (.32) ^{B}	46.63 (.67) ^{A}

Means followed by different letters are significantly different (LSD, $p < 0.05$) between treatments within each soil texture. Data was not normally distributed for sandy and medium soils; therefore, data was ln-transformed and significance of overall treatment effect was determined using Kruskal-Wallis test ($p < 0.05$). Data for the medium soil also had non-homogenous variance; therefore, Games-howell was used for post-hoc tests.

Table 4.11 - Mean leaf N content (%) of maize grown in three soil textures with additions of biochar (1 t/ha), Char+ (1 t/ha biochar pre-soaked in UAN, 187 kg N/ha) or UAN (187 kgN/ha). Standard deviations are given in parenthesis.

Treatment	Soil Texture		
	Sandy	**Medium**	**Fine**
Control	1.08 (0.06) ^{A}	1.58 (0.21) ^{A}	2.18 (0.38) ^{A}
Biochar	1.13 (0.07) ^{A}	1.61 (0.20) ^{A}	2.14 (0.35) ^{A}
Char+	3.40 (0.53) ^{B}	4.24 (0.89) ^{B}	3.65 (0.38) ^{B}
UAN	3.29 (0.23) ^{B}	5.18 (1.07) ^{B}	3.89 (0.28) ^{B}

Means followed by different letters are significantly different (LSD, $p < 0.05$) between treatments within each soil texture. Sandy soil did not have homogeneous variance; therefore, the Welch test was used to confirm treatment effect ($p < 0.01$) and Games-Howell was used for post-hoc tests. Fine soil data was not normally distributed; therefore, data was ln-transformed and significance of treatment effect was determined using Kruskal-Wallis test ($p < 0.01$).

Table 4.12 - Mean leaf C/N ratio of maize grown in three soil textures with additions of biochar (1 t/ha), Char+ (1 t/ha biochar pre-soaked in UAN, 187 kg N/ha) or UAN (187 kgN/ha). Standard deviations are given in parenthesis.

Treatment	Soil Texture		
	Sandy	**Medium**	**Fine**
Control	42.01 (2.26) ^{A}	29.46 (3.60) ^{A}	21.64 (3.88) ^{A}
Biochar	40.10 (2.59) ^{A}	29.06 (2.65) ^{A}	21.74 (3.03) ^{A}
Char+	14.02 (2.35) ^{B}	11.46 (2.57) ^{B}	12.67 (1.35) ^{B}
UAN	14.30 (0.90) ^{B}	9.51 (2.22) ^{B}	12.05 (0.95) ^{B}

Means followed by different letters are significantly different (LSD, $p < 0.05$) between treatments within each soil texture. Data for fine soil were not normally distributed; therefore, data was ln-transformed and significance of treatment effect was determined using Kruskal-Wallis test ($p < .01$). Sandy soil did not have homogeneity of variance; therefore, the Welch test was used to confirm treatment effect ($p < .01$) and Games-Howell was used for post-hoc tests.

Table 4.13 - Mean shoot N uptake (mg/pot) of maize grown in three soil textures with additions of biochar (1 t/ha), Char+ (1 t/ha biochar pre-soaked in UAN, 187 kg N/ha) or UAN (187 kgN/ha). Standard deviations are given in parenthesis.

	Soil Texture		
Treatment	**Sandy**	**Medium**	**Fine**
Control	51.5 (2.6) A	83.8 (19.9) A	391.7 (101.1) A
Biochar	80.5 (11.6) B	110.4 (13.8) A	340.0 (44.8) A
Char+	658.6 (76.8) C	487.8 (174.9) B	686.2 (191.3) B
UAN	697.9 (100.5) C	524.7 (155.1) B	666.7 (115.5) B

Means followed by different letters are significantly different (LSD, $p < 0.05$) between treatments within each soil texture. Sandy and Medium soils did not have homogeneity of variance; therefore, the Welch test was used to confirm treatment effect ($p < .01$) and Games-Howell for post-hoc tests.

4.3.3.3 Soil Organic C and Total N

Across treatments the SOC was highest in the medium texture soil (Elora), followed by the fine soil (Vineland), and the sandy soil (Delhi) was lowest. Ranges in soil SOC (g/kg) were 22-26 for medium, 14-16 for fine, and 7-11 for sandy (Table 4.14). No significant differences among treatments were observed for SOC in the fine texture soil. In the medium texture soil the biochar and Char+ treatments resulted in the highest SOC. The Char+ treatment increased mean SOC by 3.6 g/kg and was significantly different from the control, while no difference was found for the biochar and UAN treatments (Table 4.14). The biochar treatment in the sandy soil resulted in an increase in mean SOC of 1.4 g/kg and was significantly different from the control. However, the biochar, Char+ and UAN treatments were not significantly different from each other.

Overall, the soil total N (TN) was highest in the medium texture soil, followed by the fine soil, and the sandy soil had the lowest; ranges in soil TN (g/kg) were 2.0-2.1 for medium, 1.1-1.4 for fine, and 0.6-0.8 for sandy (Table 4.15). In the sandy soil TN increased for biochar, Char+

and UAN treatments, although only biochar and UAN were significantly different from the control. The Char+ treatment had the highest TN in the medium textured soil, but no significant differences in TN were observed (Table 4.15). In the fine soil the highest TN was found in the control and the lowest was with the Char+ treatment. The control was significantly different from Char+ and not significantly different from the biochar or UAN treatments.

Table 4.14 - Mean SOC g/kg for maize grown in three soil textures with additions of biochar (1 t/ha), Char+ (1 t/ha biochar pre-soaked in UAN, 187 kg N/ha) or UAN (187 kg N/ha). Standard deviations are given in parenthesis.

	Soil Texture		
Treatment	**Sandy**	**Medium**	**Fine**
Control	7.2 (1.8) A	22.1 (2.2) A	16.4 (1.5) A
Biochar	10.9 (3.3) B	24.0 (2.1) AB	14.9 (1.7) A
Char+	8.6 (2.0) AB	25.7 (2.3) B	14.1 (0.9) A
UAN	8.6 (1.6) AB	22.1 (1.8) A	15.3 (3.9) A

Means followed by different letters are significantly different (LSD, $p < 0.05$) between treatments within each soil texture. For sandy soil ANOVA $p = 0.1$ for treatment effect significance.

Table 4.15 - Mean soil TN (g/kg) for maize grown in three soil textures with additions of biochar (1 t/ha), Char+ (1 t/ha biochar pre-soaked in UAN, 187 kg N/ha) or UAN (187 kg N/ha). Standard deviations are given in parenthesis.

	Soil Texture		
Treatment	**Sandy**	**Medium**	**Fine**
Control	0.58 (0.1) A	1.88 (0.2) A	1.36 (0.1) B
Biochar	0.78 (0.2) B	1.86 (0.2) A	1.24 (0.1) AB
Char+	0.68 (0.1) AB	2.00 (0.1) A	1.08 (0.1) A
UAN	0.72 (0.1) AB	1.82 (0.2) A	1.26 (0.3) AB

Means followed by different letters are significantly different (LSD, $p < 0.05$) between treatments within each soil texture. For sandy soil data was not normally distributed; therefore, the Kruskal-Wallis test was used to determine significance of treatment effect ($p < 0.1$). Vineland soil did not have homogeneous variance; therefore, the Welch test was used to confirm treatment effect ($p < .05$) and Games-Howell was used for post-hoc tests.

4.4 Discussion

4.4.1 Maize Biomass

4.4.1.1 Biochar application rate of 1 t/ha (field trial and growth chamber)

In both the Char+ field trials and growth chamber experiments applying 1 t/ha of biochar pre-soaked in UAN significantly increased maize DM production; however, the DM was similar to that of UAN without biochar. It is likely that the combination of 1 t/ha of biochar and N fertilizer in the present study did not improve DM production relative to the fertilized control because the biochar application rate was too low. Although there have been no previous studies that have used biochar pre-soaked in UAN, there have been experiments that applied N fertilizer separately. For example, in a greenhouse experiment conducted with maize and a sandy soil, biochar application rates of 15 and 20 t/ha plus NPK fertilizer significantly increased DM relative to an NPK-only control, but no difference was found at a lower application rate of 10 t/ha (Uzoma et al., 2011).

It is also possible that synergistic effects of 1 t/ha of Char+ were not observed because the duration of the experiments was too short. In a four year field trial conducted in Colombia, Major at al. (2010a) observed that a single application of 8 t/ha of biochar combined with annual NPK fertilization resulted in no significant difference relative to a fertilized control in the first year, followed by 19, 15 and 71% increases in maize yield in years two, three and four, respectively. The impact of biochar on soil fertility and crop yields is thought to increase over time because of the cumulative reduction in nutrient leaching (Major et al. 2010a) and the oxidation of biochar surfaces (aging), which leads to greater CEC over time (Cheng et al., 2006).

The lack of difference between the DM response of Char+ and UAN indicates that most of nutritional benefits of Char+ are likely derived directly from the UAN. However, results from the growth chamber experiment provide some evidence that biochar is contributing to the DM response of Char+, where the biochar treatment significantly increased DM by 48% in the sandy texture soil and 31% in the medium soil. This increase in maize DM resulting from 1 t/ha addition of biochar without N fertilizer is important because all other studies to date have concluded that higher application rates are required in order to have significant positive effects on biomass production. Chan et al. (2007) found that adding 10 t/ha of biochar made from green (yard) waste without N fertilizer caused a 50% decrease in radish DM. Similarly, Van Zwieten et al. (2010) found that in the absence of N fertilizer 10 t/ha of biochar made from papermill waste had neutral to negative effects on the DM of wheat depending on the soil type. A 42% increase in DM resulting from biochar without N fertilizer was observed by Chan et al. (2008) in a greenhouse experiment with radish. However, in that study the biochar application rate was ten times higher (10 t/ha) and an NPK-rich poultry litter biochar was used, which would improve soil fertility and biomass production more than wood-based biochar. The hardwood biochar used in the present study has a C/N ratio of 257 and P concentration of 0.236 g/kg, while the poultry litter biochar used by Chan et al. (2008) had a C/N ratio of 19 and P concentration of 25 g/kg.

4.4.1.2 Biomass Response in Different Soil Textures (growth chamber)

One of the objectives of the growth chamber experiment was to compare the effects of N-enriched biochar, N fertilizer and biochar on maize biomass production in sandy, medium and fine textured soils. Sandy soils are often less fertile than finer texture soils because the increased pore space between soil particles leads to greater leaching of mobile plant nutrients and rapid decomposition of soil organic matter (Simmelsgaard, 1998). As predicted, the maize DM response to Char+ was greatest in the sandy textured soil (Delhi), followed by medium textured soil (Elora), and least in the fine textured soil (Vineland). Soil N was more of a limiting factor in the coarser texture soils than finer soils, and therefore, adding Char+ had more of an impact on maize nutrition in the sandy soil. This finding is in agreement with findings of a greenhouse study by Yeboah et al. (2009), which found that application of 3 t/ha of biochar plus 120 kg N/ha increased maize DM by 10.5% relative to a no-fertilizer control in a sandy texture soil and no difference was found in a fine texture soil.

4.4.1.3 Biochar application rates of 6.2-24.8 t/ha (field trial)

The purpose of the Biochar Trial was to estimate how maize productivity would be effected by annual 1 t Char+/ha applications after 10-20 years in temperate field conditions. The results show that a cumulative application of 6.2-24.8 t biochar/ha combined with N fertilizer will not significantly increase maize DM. There was a non-significant increase in DM of 25% at the highest biochar application rate. However, overall the results do not agree with the conclusions of previous studies that identified a significant biochar-fertilizer interaction effect: when a set amount of N fertilizer is applied the magnitude of DM response increases with the application rate of biochar (Chan et al., 2007). The synergistic effect of biochar and mineral fertilizer is thought to be the result of increased plant nutrient uptake to leaching ratio and improved availability cation nutrients such as P, K, Ca and Cu (Lehmann et al., 2003). This synergistic effect may be more prevalent in tropical regions, where Steiner et al. (2007) reported a doubling of maize grain yield relative to a fertilized control when 11 t/ha of biochar plus 85 kg N/ha of mineral fertilizer were applied to a highly weathered Xanthic Ferralsol.

It is important to note that results from ABRI-Tech's biochar field trial are for the second year after the biochar was applied to the soil. Biochar is known to undergo an aging process in soil that leads to greater surface oxidation and CEC, which improve soil fertility and nutrient retention (Cheng et al., 2006). Therefore, the results of this trial should only be judged against other second year results. Although there have been few biochar field trials conducted for two or more years, and even fewer in temperate regions, there are at least three studies that serve as useful comparisons. For example, in the second year of a field trial in Colombia, Major et al. (2010a) found that annual N fertilization of 165 kg/ha and a single application of 8 or 20 t biochar/ha significantly increased maize grain yields by 19% and 28%, respectively, relative to the fertilized control. A field trial with wheat in Italy found that a single application of 30 t biochar/ha combined with annual fertilization of 122 kg N/ha resulted in a 21% DM increase in the second year (Vaccari et al., 2011). Finally, in the second year of a field trial in Southern United States the change in maize grain yield varied depending on the biochar type ranging from none to +23% for 11 t biochar/ha, and -6% to none for 22 t/ha (Gaskin et al., 2010). Although these field trials measured maize grain yield, they are still a valid comparison because there is an approximately linear relationship between maize grain yields and shoot DM (Lauer, 2006). The 25% increase in DM observed for the 24.8 t biochar/ha treatment in the present study is similar to the second year results of Major et al. (2010) and Vaccari et al. (2011).

4.4.2 Maize Leaf Nutrient Concentrations

4.4.2.1 Leaf N and N Uptake (field trial and growth chamber)

The 1 t/ha Char+ treatments in the field trial and growth chamber experiments both significantly increased maize leaf N concentrations and N uptake relative to the unfertilized control. However, in the field trial maize leaf N concentrations of the Char+170 treatment were significantly greater than UAN, while in the growth chamber experiment 1 t/ha of Char+ was not significantly different from UAN. It is likely that N loss via leaching or volatilization was more prevalent in field conditions than in the growth chamber, and therefore, biochar N adsorption was important for preventing N loss in the field. The significantly higher leaf N content of the Char+170 treatment did not translate into significant increases in DM relative to the fertilized control. However, small increases in plant N can significantly improve the protein content of maize used for livestock feed (Almodares et al., 2009).

In the field trial, biochar application rates of 6.2-24.8 t/ha did not significantly increase maize N uptake. However, the mean N uptake in the 24.8 t/ha biochar treatment was about 18 kg N/ha greater than the fertilized control. Major et al. (2010a) found that in the second year following application of biochar maize N uptake was significantly increased for the 20 t biochar/ha treatment, but not for the 8 t biochar/ha treatment. Despite increased maize DM production in biochar amended soils, the leaf N concentrations were not diluted (no significant decreases), which has important implications for the nutritional value of maize used as livestock feed (Almodares et al., 2009). There results support findings from the second year of an Italian field trial in which the application of 30 t/ha of biochar resulted in a 21% increase in shoot DM of wheat, while leaf N concentrations were not significantly affected (Vaccari et al., 2011).

4.4.2.2 Leaf N concentration and N Uptake in Different Soil Textures (growth chamber)

The growth chamber experiment revealed that Char+ is an effective method of delivering N nutrition in sandy, medium and fine textured soils. Relative to the unfertilized control, Char+ significantly increased maize leaf N concentration and N uptake in all three soil textures. The mean concentration of leaf N resulting from Char+ ranged from 3.4-4.2 %, which is higher than other studies that applied biochar and N fertilizers. Uzoma et al. (2011) found that maize leaf N concentrations resulting from 10 t/ha biochar plus 60 kg N fertilizer were 2.3%. However, that study was conducted over 85 days and maize leaf N concentrations are known to decline as they mature (Jones, 1983). The increase in N uptake resulting from Char+ was greatest in the sandy soil, followed by the medium texture and finally the fine texture. This corroborates findings from a greenhouse study with maize in which biochar and fertilizer increased N uptake by 4.8 kg N/ha in a sandy soil, and decreased N uptake by 7 kg N/ha in a finer texture soil (Yeboah et al., 2009).

In all soil textures, the leaf N concentration and N uptake of Char+ and UAN treatments were not significantly different from each other. Given the low biochar application rates used in the present study, this finding is in agreement with a greenhouse study by Chan et al. (2007), who found that biochar application rates below 20 t/ha plus N fertilizer did not significantly increase the leaf N concentration and N uptake of radish relative to a fertilized control. The N-uptake of Char+ treatments in the sandy and fine soil were similar to the amount of UAN-N that was applied with the Char+ (690 mg/pot). This suggests that most of the benefits of Char+ were likely derived from the UAN and not the biochar. However, it is possible that the biochar component of Char+ caused a small increase in availability of native soil N because the mean N uptake of biochar treatments increased by 29 and 27 mg/pot in the sandy and medium soil, respectively.

Although the leaf N concentrations of Char+ and UAN treatments were significantly greater than the control in the fine textured soil, this did not translate into significantly greater DM. A likely explanation for this is that leaf N concentrations in all fine textured soil treatments were above the critical level needed to sustain plant growth. The critical tissue N content, below which plant growth is limited, appears to be about 2% for the present study, which is similar to another reported level of 2.8% (Gaskin et al., 2010). Leaf N concentrations of the controls for the sandy and medium soil were below 2% and this corresponded with significantly reduced DM. These results show that in soils where N is not a growth limiting factor, addition of Char+ will likely not have a significant impact on crop productivity.

4.4.2.3 Nitrogen Use Efficiency of Char+ (field trial)

Analysis of the N-based NUE for the Char+ field trial revealed that while almost all of the N fertilizer was recovered in the Char+170 and UAN treatments, about half remained in the soil or was lost in the Char+50 and Char+100 treatments. It is surprising that the N recovery of Char+170 and UAN were 80-90% considering that N losses of up to 50% are common in commercial operations (Robertson and Vitousek, 2009). Because soil chemical analysis was not completed for this trial, it is difficult to understand the mechanisms responsible for lower agronomic NUE in the Char+100 and Char+50 treatments. It is likely that the 0.3-0.5 t/ha biochar application rates used for Char+50 and Char+100 were insufficient to significantly increase CEC and nutrient retention. In terms of agronomic NUE, the greatest yield increases per kg of N applied or “fertilizer value” was achieved with Char+50, while Char+170 and UAN were roughly equivalent, and Char+100 may be a poor choice for maximizing fertilizer utilization. Understanding of the agronomic NUE for Char+50 and Char+100 could be improved in future research if 50 and 100 kg N/ha UAN-only treatments were included in the experimental design for comparison.

4.4.2.4 Leaf P and K concentrations (field trial)

The only significant difference in maize leaf P or K concentrations was observed for the Char+170 treatment, which had 1.5 g/kg higher P concentrations than the UAN treatment. The leaf P concentrations for Char+170 were not significantly different from the control, which indicates that 1 t/ha Char+ prevented a decrease in leaf P concentrations, while UAN did not. Increased P availability resulting from 10-20 t biochar/ha additions was also observed by Lehmann et al. (2003) in a field trial with cowpea in Brazil. The increased P availability is likely caused by greater CEC and decreased P fertilizer losses through leaching (Lehmann et al. 2003), but was probably not due to direct nutrient supply because only about 0.2 kg P/ha were added with biochar, while 95 kg/ha were added with fertilizer. All treatments were P-deficient based on the critical limit reported by OMAFRA (2009) of 12 g/kg. Therefore, it is surprising that increased leaf P concentrations in the Char+170 treatment did not result in higher DM relative to the UAN treatment.

4.4.3 Soil Organic C and Soil Total Nitrogen

4.4.3.1 Biochar application rate of 1 t/ha (growth chamber)

In the growth chamber experiment, the SOC and total N measured in the controls of the Delhi and Elora soils are very similar to the levels reported for the same sites by Wanniarachchi et al. (1999). This is important because it validates the methods used to determine SOC and TN in this study. The impact of Char+ on SOC was inconsistent among the three soil textures. Although Char+ significantly increased SOC levels relative to the control in the medium texture soil, no significant differences were observed in the sandy and fine soil. The small changes in SOC resulting from Char+ additions may require different methods of quantification. For the Char+ treatments, 2.28 g C were added to each pot, which would directly increase the SOC concentration by about 0.5 g/kg. However, this small change was not detected in the present study because the standard deviation was about 2 g/kg.

Another notable difference in SOC observed was the positive response to biochar in the sandy texture soil. While Char+ did not significantly affect SOC in the sandy soil, biochar significantly increased mean SOC by 1.6 g/kg. The reason biochar caused an increase in SOC and Char+ did not is likely related to the UAN applied with Char+, which may have caused changes in soil pH, microbial activity or root biomass. Many long-term agricultural field trials have demonstrated that addition of mineral N leads to higher SOC (Alvarez, 2005). However, this is primarily the results of increased root biomass and crop residue input (Kuzyakov et al., 2000). In short-term experiments, application of nitrogen fertilizers has been shown to decrease SOC through an effect known as “priming”. The priming effect occurs when previously dormant populations of soil micro-organisms are activated by the addition of a readily consumable C or N source, which leads to increased decomposition of SOC mineralization (Kuzyakov et al., 2000). The effect of mineral N addition on microorganism activity can occur directly, if soil microorganisms consume the N, or indirectly through plant uptake if increased N leads to greater root biomass and release of C-rich root exudates (Kuzyakov et al., 2000). When Char+ was applied to the sandy soil the positive effects of biochar on SOC may have been negated by the additional N, which caused SOC mineralization through the priming effect.

Across all treatments, the medium texture soil had the highest soil TN, followed by the fine soil, and the sandy soil had the lowest. The control treatment with the highest mean biomass was found in the fine soil, while the medium soil control was similar to the sandy soil. It is surprising that higher soil TN in the medium texture soil did not translate into greater biomass.

4.4.3.2 Biochar application rates of 6.2-24.8 t/ha (field trial)

Biochar application had a positive effect on soil C sequestration, increasing the mean SOC concentration by 4.2 and 8.2 g/kg in the 6.2 and 24.8 t biochar/ha treatments, respectively. However, a smaller increase of 3.4 g/kg was observed in the 12.4 t biochar/ha. The amount of C directly added with 6.2, 12.4 and 24.8 t biochar/ha was 3.8, 7.7, 15.3 t/ha (biochar C% = 61.7), respectively, which would increase the C concentration by 2.8, 5.6, 11.2 g/kg (assuming bulk density of 1.3 g/cm^3 and a 5% loss of labile biochar-C), respectively. Therefore, the increase in soil C observed with 6.2 t biochar/ha was in excess of the direct biochar-C addition and the increases observed in the 12.4 and 24.8 t biochar/ha treatments were less than the direct biochar-C addition. Increases in soil C beyond the direct biochar-C addition could be due to greater SOM contributions from root biomass (Lehmann et al., 2003), or mycorrhizal fungi (Warnock et al., 2007), or decreases in the activity of glucosidase and cellobiosidase, which are two microbial enzymes involved in SOM mineralization (Bailey et al., 2010; Jin, 2010). There was a general trend of increasing SOM with increasing biochar application rates observed in the present study. However, no significant differences between treatments were found. A number of mechanisms could be responsible for the lower than expected SOC increases in biochar treatments including downward migration of biochar-C below the sampling zone (Major et al., 2010b) or a positive priming effect on SOC mineralization caused by the labile C fraction of biochar (Wardle et al., 2008). Major et al. (2010a) found no significant increases in soil C resulting from biochar additions of 8 or 20 t/ha and N fertilizer over a four year period. Conversely, in a greenhouse study Van Zwieten et al. (2010) reported significant increases in SOC of 0.4-0.8% following a 10 t/ha additions of two biochar types and N fertilizer to a Ferralsol soil.

It was expected that biochar application rates of 6.2-24.8 t/ha would increase soil TN availability and N fertilizer retention, but no significant differences in soil TN were observed between treatments. Steiner et al. (2007) also found no significant difference in soil TN when 11 t/ha of biochar plus 85 kg N/ha was applied to a highly weathered Xanthic Ferralsol in Brazil. The authors suggested that, because N uptake was greater in the biochar treatment than the control, biochar must have increased N availability. Other studies that observed a positive biomass response to biochar have associated this with increased soil N availability (Vaccari et al, 2011; Yeboah et al., 2009). However, there are also some studies where, despite seeing increases in biomass production, there was a decrease in N availability as a result of biochar; this was thought to be due to biochar’s high C/N ratio and microbial immobilization of soil N (Lehmann et al., 2003). Application of 24.8 t/ha of biochar in the present study resulted in a significantly greater soil C/N ratio than in the fertilized control; however despite this, the mean DM was slightly greater than the control. Although no statistical difference in soil TN was found in the present study, there is some evidence that biochar had a positive effect on soil TN because the mean soil N stock (10 cm depth), NH_4 and NO_3 were greater in the 6.2 and 24.8 t biochar/ha treatments than in the control.

4.4.3.3 Slow Release Properties of Char+ (growth chamber)

One of the goals in developing Char+ was that it may act as a slow release N fertilizer. It was predicted that Char+ can provide more sustained plant N nutrition than conventional N fertilizers because the biochar will decrease N losses through leaching, volatization and other mechanisms (Fig. 2.1 in Chap. 2). If soil N was higher in Char+ treatments than UAN treatments despite equal plant N uptake, this would indicate that Char+ was acting as a slow release fertilizer. According to this logic, Char+ does not appear to be acting as a slow release fertilizer in any of the soil textures tested. For the sandy and fine texture soils the maize N uptake for Char+ and UAN treatments was approximately equal to the amount of N applied as UAN (690 mg) and the soil N following 6 weeks of growth was not significantly different from the UAN treatment. The sandy soil was very low in N (mean N uptake of control was 51 mg/pot), and therefore, for 660 mg of N to be taken up in the Char+ treatment, more than 90% of the N had to come from the Char+. In the medium texture soil, N uptake resulting from Char+ and UAN application was lower than in the other soils (about 70-75% of N applied), but like the sandy and fine soils, the soil N of the Char+ treatment was not significantly different from the UAN treatment. A possible reason Char+ did not sustain higher soil N concentrations than UAN is that the amount of water added did not cause leakage from the base of the pots, and therefore, it is unlikely that significant N leaching occurred. Although Char+ does not appear to be acting as a slow release fertilizer, this property may increase over time with repeated biochar applications, and it will still provide immediate C sequestration benefits.

4.5 Conclusions

In summary, results from this study are significant because they show that an economically feasible method of using biochar can be used in temperate regions to increase crop productivity and terrestrial carbon sequestration. The method of pre-soaking biochar in liquid UAN was effective because it produced a value-added biochar product capable of providing equal plant N nutrition as mineral N fertilizers in a variety of soil textures. The effects of Char+ were highly dependent on the soil texture; increases in maize biomass relative to the control were about 300% in the sandy soil, 100% in the medium soil, and no difference in the fine soil. Char+ significantly increased the leaf N concentrations and N uptake in all soil textures. Although Char+ did not increase maize biomass beyond that of UAN, this should not be expected based on the small amount of biochar used. The Char+ Trial and growth chamber experiment revealed that 1 t/ha of Char+ will not significantly improve maize biomass production compared with N fertilization. However, in the field trial using Char+ with 30-60% of the typical N fertilization rate did not significantly lower maize biomass production. The Biochar Trial demonstrated that, if farmers continue to apply 1 t/ha of Char+ annually, maize productivity will not be negatively impacted for the first 6-12 years (6.2 and 12.4 t/ha biochar treatments) and there may be a slight improvement in yields after 25 years (24.8 t/ha biochar treatment). The amount of biochar-C added in the first ten years would be about 6 t C/ha. However, the actual increase in SOC will require further research because the labile C fraction of biochar varies from 3-12% (Bruun,

2011) and biochar can have positive or negative priming effects on SOC mineralization (Zimmerman et al., 2011).

The results of the growth chamber experiment should serve as a cautionary note that Char+ practices may not be equally beneficial for all soil types, and are probably more valuable for sandy texture soils with low SOM and fertility. Further research should investigate the effects of repeated annual additions of Char+ on biomass production with different soil types and crop species. To better understand the effect of Char+ on soil N dynamics and plant nutrition a number of techniques can be suggested: (a) testing for soil NO_3^- and NH_4^+ would improve the ability to detect small differences in plant available N, (b) a growth chamber experiment where multiple plants are grown and harvested in succession using the same Char+ amended soil, with change in DM and N uptake measured over time, and (c) the use of ^{15}N labeled UAN would allow for determination of the relative contribution of Char+ -N and native soil-N to plant N nutrition.

In conclusion, this study shows that applying 1 t/ha of Char+ annually will not result in immediate increases in agricultural productivity relative to mineral N fertilization. However, after 25 years there will be approximately 25 t biochar/ha and the synergistic effects of biochar plus N fertilizer, which have been observed in the literature, will likely increase biomass production by about 25%. Wide-scale adoption of Char+ practices would significantly increase soil C sequestration and reduce N fertilizer demands, which would have positive implications for climate change mitigation and the sustainability of agroecosystems.

Chapter 5

Modeling the Long-term Effects of Nitrogen-Enriched Biochar on Soil Organic Carbon and Soil Nitrogen using CENTURY

5.1 Introduction

The conversion of native grasslands and forested land to agricultural systems disrupts the balance between soil organic matter (SOM) inputs and outputs, leading to a net decrease in the SOC stock. As a result of intensive agricultural practices, such as tillage and monocropping, soil organic carbon (SOC) has been depleted by as much as 60% in temperate regions and 75% in the tropics (Lal, 2004a). Based on a review of 50 long-term studies, Vandenbygaart et al. (2004) determined that the mean SOC loss from Canadian soils resulting from cultivation was 24 ± 6%. Adoption of sustainable agroecosystem management practices that restore SOC are critical for maintaining long-term agricultural productivity and reducing concentrations of atmospheric greenhouse gases (GHGs). Lal (2004a) estimated that for degraded cropland soils, a 1 t/ha increase in SOC can increase crop yields of wheat by 20-40 kg/ha and maize by 10-20 kg/ha. Terrestrial C sequestration also has the potential to offset 5 to 15% of fossil fuel emissions (Lal, 2004a).

Recommended management practices that have been shown to increase SOC include conservation tillage, cover crops, and integrated nutrient management through application of manure or compost (Lal et al., 2007), as well as agroforestry (Oelbermann et al., 2004) and intercropping (Diekow, 2005). Recently, the application of biochar to agricultural soils has been proposed as means of increasing SOC (Lehmann et al., 2003). Conversion of biomass to biochar and incorporating it into soil leads to a sequestration of about 50% of the initial C, as opposed to burning, which only retains 3%, and applying fresh biomass, which retains less than 10-20% after 5-10 years (Lehmann et al., 2006).

Significant changes in SOC levels occur on a decadal time scale, and in temperate regions where the SOC turnover is slower than in the tropics, significant changes in SOC will likely take much longer than 10 years (Oelbermann and Voroney, 2007). Therefore, the short-term experiments conducted in the growth chambers (6 weeks) or the field trials (2 years) are insufficient to determine the true impact of biochar on SOC. As such, empirical models may be a useful tool for evaluating the long-term effects of agricultural management practices on SOC and the dynamics of the active, slow and passive soil C pools (Oelbermann and Voroney, 2011).

The Century Soil Organic Model simulates C, N, P and S dynamics of agroecosystems over periods of hundreds to thousands of years. The Century Model Version 4 was designed as a tool for evaluating the effects of climate and a wide range of complex agroecosystems management practices on SOC (Metherell et al., 1993). The model is capable of simulating plant-soil-climate interactions for specific sites in grassland/cropping systems and forest systems. The Century model divides incoming plant residues into “metabolic” or “structural” fractions, which feed into three SOM-C pools, termed “active”, “slow” and “passive”, which have different rates of decomposition. The main input variables for the model are: temperature; precipitation; N, P, S and lignin content of plant material; atmospheric and soil N inputs; soil texture and bulk density; and initial stocks of soil N, P, and S. Century Model Version 4 has been validated in many studies including: 10-20 year experiments with inorganic and organic fertilization of rice, wheat and sorghum in India (Bhattacharyya, 2010); and seven long-term sites in temperate regions with a total of 13 land management treatments (Kelly et al., 1997).

To date, the Century model has not been used to simulate the effects of biochar amendments on agroecosystems soil C and N dynamics. Furthermore, there is no "biochar option" built into the Century software and there is no literature on methods of simulating biochar additions with Century. The results of this modeling exercise cannot be validated at present because there have been no long-term (>5 years) biochar field trials. However, these results will serve as a guide for future research efforts. Ultimately, the development of accurate modeling techniques for biochar will have important applications for C credit markets. Farmers could enter into a contract to apply 1 t biochar/ha annually for 20 years, and C credits could be issued based on the model predictions of future C sequestration.

5.1.1 Research Questions and Objectives

The main research question for this study is:

> What are the long-term (150 years) impacts of annual additions of 1 t/ha Char+ on soil organic C and N dynamics?

Two sub-questions are:

1. How are the long-term soil organic C and N dynamics resulting from Char+ additions affected by soil properties?

2. How do the long-term soil organic C and N dynamics resulting from Char+ additions compare with other land management practices?

The specific objectives of this study are:

1. To develop a method for simulating additions of Char+ using the Century model (by setting values for organic matter addition parameters).

2. To simulate the addition of Char+ to two agricultural sites with different soil properties and determine the effects on soil C and N dynamics.

3. To compare the addition of Char+ to other land management practices (no-till, manure application, and crop rotation).

5.2 Materials and Methods

5.2.1 Parameter values for site and biochar addition files

The two agricultural sites used for this simulation are based on a medium textured soil (Gleyed Melanic Brunisol) from the University of Guelph's Research Station in Elora, ON and a coarse textured sandy soil (Fox series) from Agriculture and Agri-Food Canada's Southern Crop Protection and Food Research Centre in Delhi, ON. The Vinleand, ON study site was not used in this study because all of the soil property values needed for the Century site files are not available, and comparing two sites will provide adequate information to achieve the study objectives. The site files, which include paramenter values for soil texture, organic matter, pH, and weather statistics, were created by Wanniarachchi et al. (1999). To isolate the effects of key soil properties, all parameters of the two site files were made the same except for the following parameters: sand-silt-clay ratio, bulk density, pH and the initial values for the four soil C pools (active, microbial, slow and passive) (Table 5.1).

Table 5.1 - Input values for key soil properties in the Delhi and Elora site files. All other parameters were identical for the two site files.

Parameter	Delhi Site	Elora Site
Sand (%)	85	22
Silt (%)	7.5	54
Clay (%)	7.5	24
Bulk density (g/cm^3)	1.4	1.3
pH	6.3	6.9
Active SOM-C (g/m^2)	2	2
Microbial SOM-C (g/m^2)	71	179
Slow SOM-C (g/m^2)	1547	3887
Passive SOM-C (g/m^2)	762	1914

An option for biochar addition was created within the Organic Matter Additions (OMAD) file, which is typically used to simulate additions of manure or fresh plant material. The OMAD file contains the following parameters: C added (g/m^2), lignin fraction and C:N ratio. The lignin fraction of the organic matter determines the fraction of C that enters the slow C pool. Although biochar does not contain any lignin (the chemical structure is modified by pyrolysis) it is resistant to physical and microbial decay and it can remain in soil for hundreds to thousands of years. About 4-5 % of fast-pyrolysis biochar is labile and can be consumed by microbes and released as CO_2 within the first 100 days following addition to soil (Bruun, 2011). Therefore, to direct 95% of the biochar C to the slow C pool, the lignin content for biochar additions was set at 95%. This method will be a conservative estimate of biochar C sequestration because the slow C pool in the Century model has a turnover rate of 20-50 years. The C:N ratio was set at 257 based on measurement conducted by ABRI-Tech, and for a 1 t/ha addition of biochar the C added was calculated to be 61.7 g C/m^2 .

5.2.2 Event Schedules

The model was run for ten thousand years with mixed deciduous/coniferous forest to achieve an equilibrium SOC level.

Schedules:

- **-10,000 – 1914**: Forest (MIX), growing season April to September
- **1915 – 2000**: Maize (CHI) planted in May, cultivated with cultivator in April and plow in May, fertilized with UAN (187 kg N/ha) in May, harvested (grain only) in September
- **2001 – 2150**:
  a) "Continuous Corn" - Same practices as 1915-2000

  Or same practices as 1915-2000 with the following changes:

  b) "Char+ 1 t/ha" - Organic matter addition of 61.7 g C/m^2 (C/N ratio = 257, lignin content = 95%) and UAN 187 kg N/ha in May

  c) "Char+ 2 t/ha" - Organic matter addition of 123.4 g C/m^2 (C/N ratio = 257, lignin content = 95%) and UAN 187 kg N/ha) in May

  d) "Char+ 1 t/ha*2yr" – 2 year cycle with organic matter addition of 61.7 g C/m^2 (C/N ratio = 257, lignin content = 95%) and UAN 187 kg N/ha in May of year 1, and only UAN in year 2.

  e) "No till" – Only cultivation is "No-Till-Drill" option in May

  f) "Manure" - Cow Manure (150 g C/m^2, C/N = 20, Lignin = 20%) applied in May and no UAN

  g) "Rotation" – corn and soybean are grown in an alternating 2 year cycle, and soybean is not fertilized.

5.3 Results

5.3.1 Soil Organic C Dynamics

Prior to clearing the forest, the equilibrium (1890) SOC level was about 17,000 g/m^2 in the Elora site and about 10,000 g/m^2 in the Delhi site, which reflects differences in the input values for key soil properties (Table 5.1). In 1915 when the forest was cleared there was an initial spike in the SOC levels and this was followed by a sharp decline with the onset of soil cultivation (Fig. 5.1 and 5.2). The SOC levels for the year 2000 were 13,248 g/m^2 or 51 g/kg in the Elora site and 5263 g/m^2 or 18.8 g/kg in the Delhi site. In the continuous corn simulation the SOC continued to decline from 1915-2150. However, the rate of decline decreased over time and by the end of the simulation SOC levels were close to reaching another equilibrium. Relative to the initial forest soil, the loss of SOC resulting from 235 years (1915-2150) of continuous corn farming with standard tillage practices was about 5500 g/m^2 (-55%) at the Delhi site and about 4500 g/m^2 (-26%) at the Elora site.

The introduction of Char+ applications between the years 2000 and 2150 had a pronounced impact on the soil C (Table 5.2). The model predicted that applying 1 t Char+/ha per year to the Delhi soil will increase SOC by 10% after 10 years and 17% after 20 years. In gerneral the absolute changes in SOC (g C/m^2) were greater for Elora than Delhi, while the relative changes in SOC (%) were greater for Delhi than Elora. For example, the absolute increase in SOC resulting from 150 years of annual 1 t/ha Char+ addition was greater at Elora (+1236 g/m^2) than at Delhi (+971 g/m^2); however, the relative increase in SOC was 18% at Delhi and only 9% at Elora.

In both the Elora and Delhi sites the greatest increase in SOC was achieved with the 2 t/ha Char+ treatment, followed by the 1 t/ha Char+ treatment (Table 5.2). The application of 2 t/ha Char+ for 150 years would restore SOC to native forest soil levels at Elora. For the Delhi site applying 2 t/ha Char+ for 150 years would double SOC. However, this would not be enough to restore SOC to native forest levels because more C had been lost prior to initiating Char+ practices. By the end of the simulation, the increase in SOC relative to the continuous corn treatment at Delhi was about 4.1, 2.0 and 1.0 kg C/m^2 for biochar additions of 2 t/ha, 1 t/ha and 1 t/ha*2 years, respectively. For Elora the increases were about 5.0, 2.4, and 1.2 kg C/m^2 for biochar additions of 2 t/ha, 1 t/ha and 1 t/ha*2 years, respectively.

A ranking of the different land management practices, in terms of their value for SOC restoration or stabilization, would be the roughly the same for both sites (Table 5.2); however, there were two exceptions. Firstly, at Delhi the increase in SOC resulting from no-till practices was greater than the impact of 1 t/ha of Char+ applied every two years, while at the Elora site this trend was reversed. Secondly, 150 years of cow manure application resulted in an increase in SOC relative to continuous corn at the Delhi site, but at the Elora site cow manure resulted in SOC levels that were approximately equal to those of continuous corn. At both sites, using a crop rotation of corn and soybean would be ranked last as this led to a larger decrease in SOC than continuous corn.

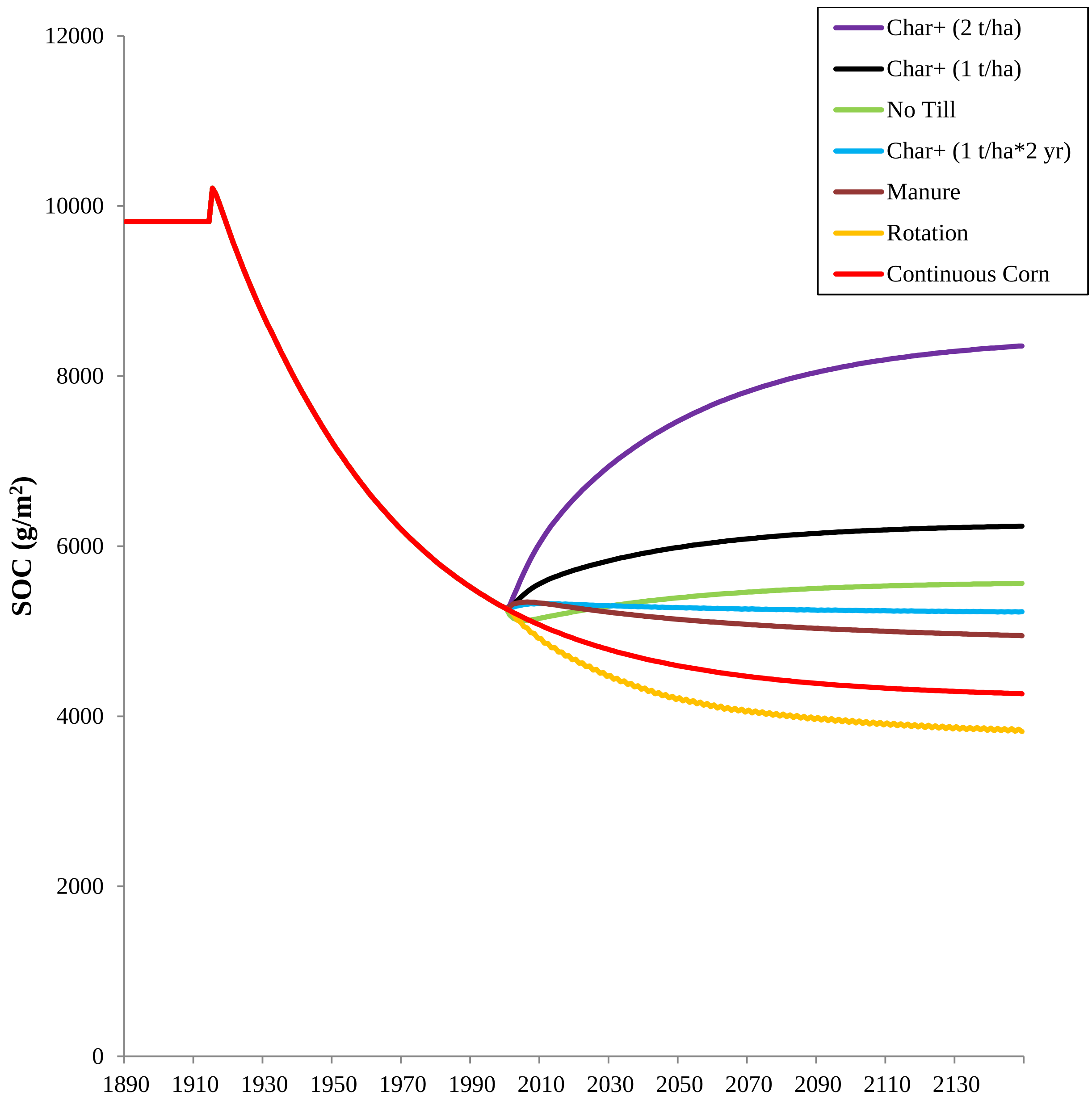


Figure 5.1 - Comparison of the projected changes in SOC resulting from Char+ and other agricultural practices over a 150 year period at the Delhi site.

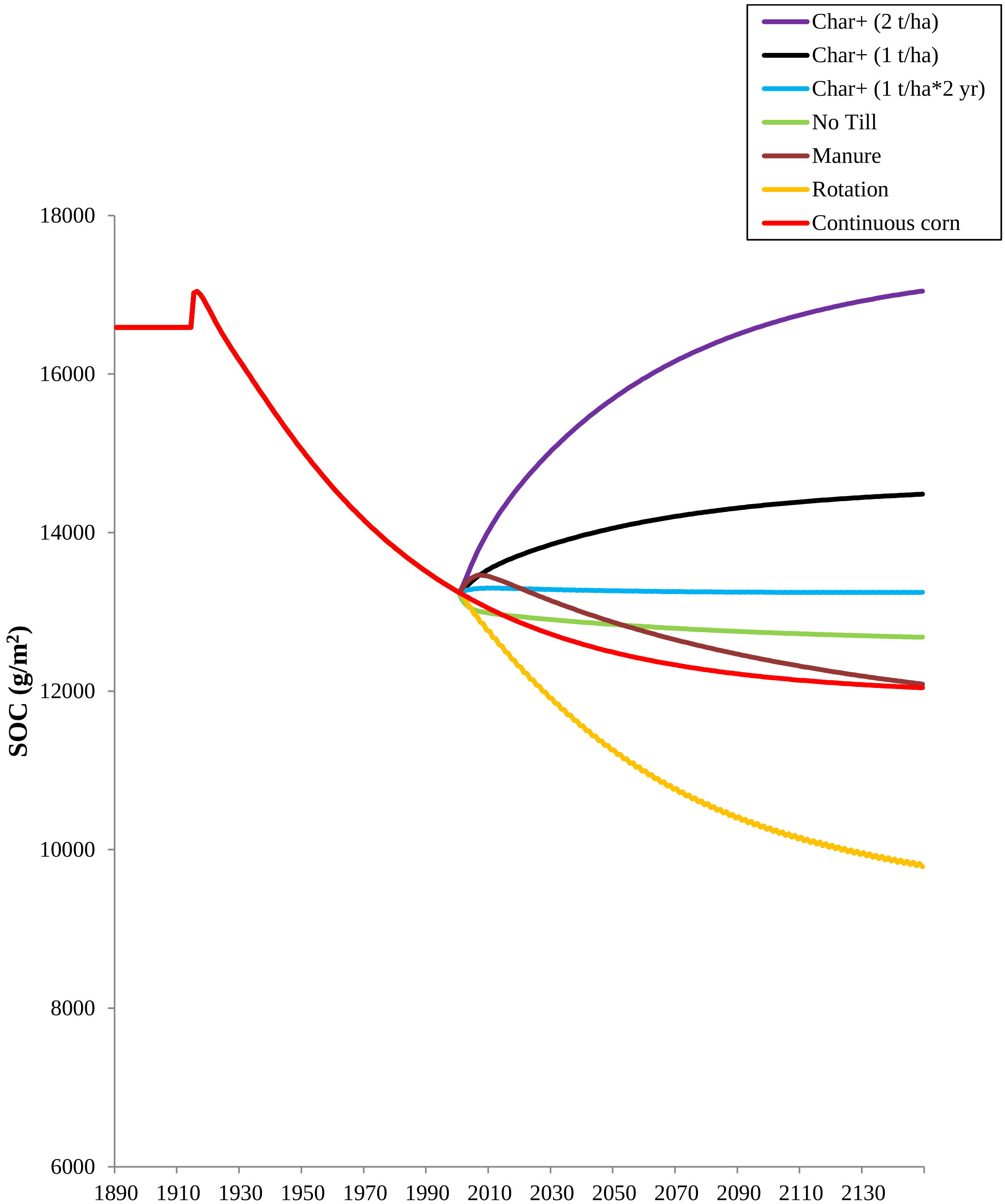


Figure 5.2 - Comparison of the projected changes in SOC resulting from Char+ and other agricultural practices over a 150 year period at the Elora site.

Table 5.2 - Impact of various land management practices on SOC dynamics as predicted by Century Soil Organic Model. Percentage values for changes in SOC are given in paranthesis. *Soil organic C levels in 2000 were 5263 g/m^2 in the Delhi site and 13,248 g/m^2 in the Elora site

(A) Delhi Site

Practice	SOC (g/m^2) Year 2150	Change from 2000*	Change from Continuous Corn levels in 2150
Char+ (2 t/ha)	8355	3092 (58.7)	4089 (95.8)
Char+ (1 t/ha)	6234	971 (18.4)	1968 (46.1)
No till	5562	299 (5.7)	1296 (30.4)
Char+ (1 t/ha*2yr)	5228	-35 (0.7)	962 (22.6)
Manure	4949	-314 (-6.0)	683 (16.0)
Continuous corn	4266	-997 (-18.9)	N/A
Rotation	3820	-1443 (-27.4)	-446 (-10.5)

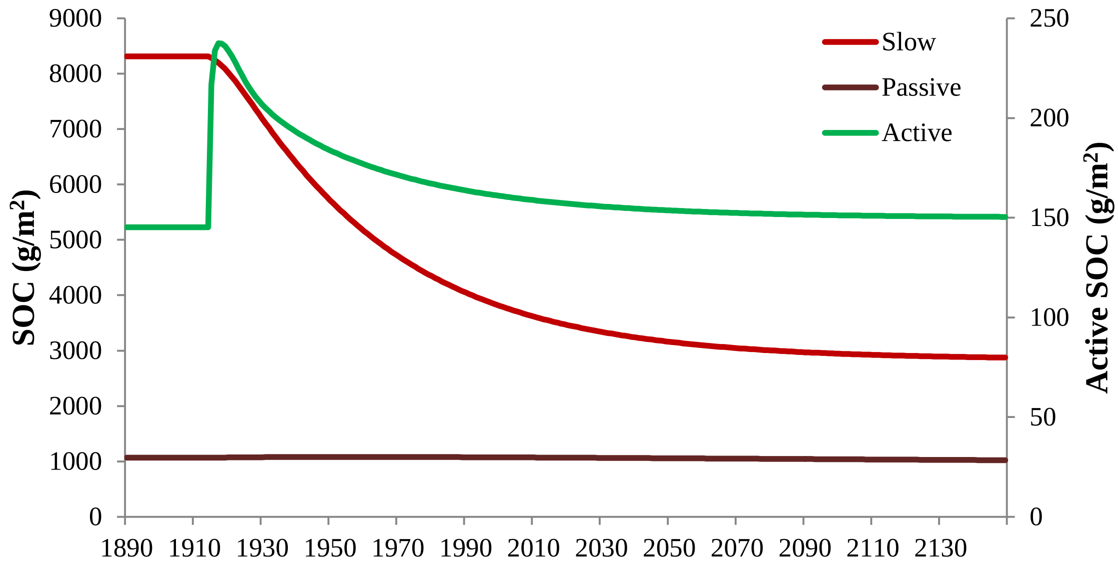
(B) Elora Site

Practice	SOC (g/m^2) Year 2150	Change from 2000*	Change from Continuous Corn levels in 2150
Char+ (2 t/ha)	17048	3800 (28.7)	5006 (41.6)
Char+ (1 t/ha)	14484	1236 (9.3)	2422 (20.3)
Char+ (1 t/ha*2yr)	13246	-2 (0)	1204 (10.0)
No till	12680	-568 (-4.3)	638 (5.3)
Manure	12088	-1160 (-8.8)	46 (0.4)
Continuous corn (CC)	12042	-1206 (-9.1)	N/A
Rotation	9783	-3465 (-26.2)	-2259 (-18.8)

5.3.2 Active, Slow and Passive Soil C Fractions

Analysis of the changes in the slow, active and passive soil C fractions shows that the Char+ option functioned as intended. The addition of 1 t/ha of Char+ caused a large increase in the slow C fraction and a small increase in the active fraction for both sites (Fig. 5.3 and 5.4). This was expected because the lignin content of the biochar option was set at 95%, which caused Century to transfer 95% of the C added with biochar into the slow fraction, and the remaining 5% into the active fraction. Analysis of the C fraction dynamics also clearly reveals that when the forest was cleared in 1915 the spike in total soil C was due to an increase in the active soil C fraction; the forest biomass C rapidly degraded and was not stabilized in the slow or passive fractions. In the continuous corn simulation the primary source of C loss for both sites was the slow C fraction, while the active fraction stabilized slightly above historic levels by 2150 and the passive fraction remained relatively constant. It was expected that large changes would be seen in slow C fraction because it has a turnover time of 20-50 years, which is shorter than the length of the simulation (260 years), while changes in the passive fraction were unlikely to occur because it has a turnover time of 400-4000 years, which is outside of the simulation length.

(A)



(B)

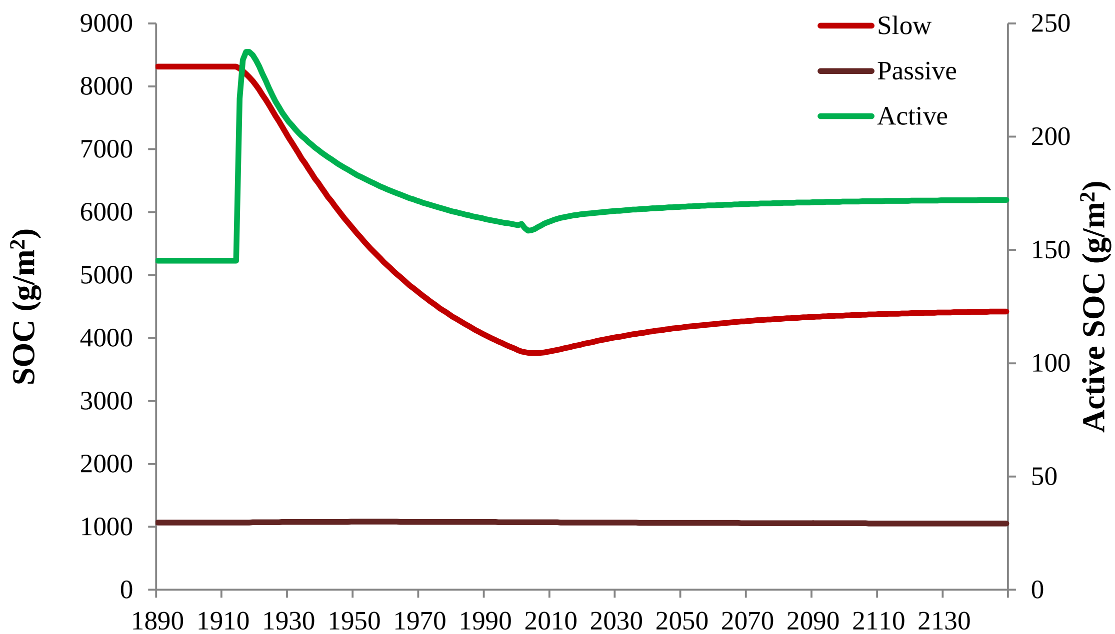
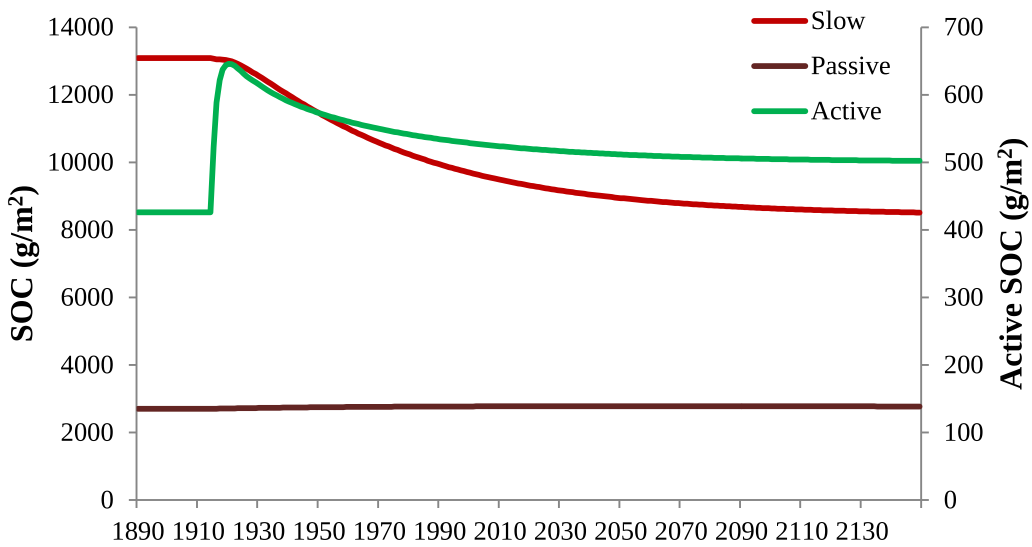


Figure 5.3 - Changes in the active, slow and passive SOC fractions at the Delhi site for (A) Continuous corn farming from 1915-2150 or (B) 1 t/ha Char+ additions initiated in the year 2000.

(A)



(B)

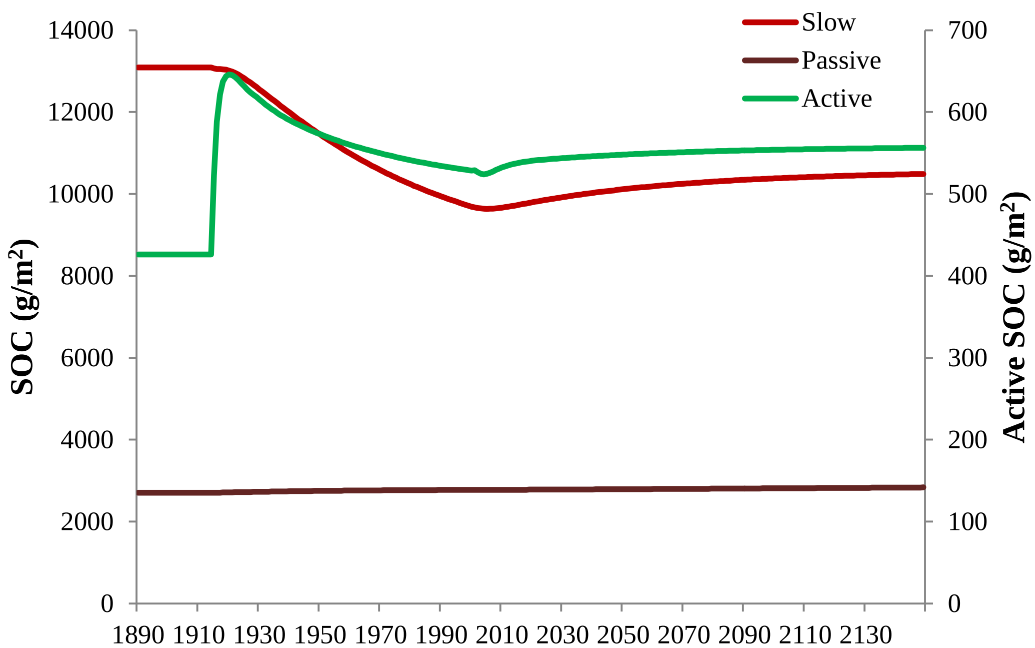


Figure 5.4 - Changes in the active, slow and passive SOC fractions at the Elora site for (A) Continuous corn farming from 1915-2150 or (B) 1 t/ha Char+ additions initiated in the year 2000.

5.3.3 Soil Mineral N and Crop Yields

Century did not predict large differences in crop grain yields between the different agroecosystem management practices, except for the cow manure and corn/soybean rotation treatments. These treatments showed a reduction in crop yields of ~25% and 35%, respectively, for both sites (Table 5.3). Across all treatments soil mineral N and crop yields were greater at the Elora site than the Delhi site. At both sites soil mineral N decreased with increasing biochar application rates; however, crop yields were not affected by this decrease. The Century model predicted that no-till would result in the highest soil N at both sites and manure treatment had the lowest soil N.

Table 5.3 - Effect of various land management practices on soil mineral N, crop yields and shoot biomass C as predicted by Century soil organic matter model. All three metrics are averaged over the final 10 years of the simulation (2140-2150).

A) Delhi site

Practice	Soil mineral N in upper 10 cm (g/m^2)	Crop yield (kg/ha*year)	Shoot C (g/m^2*year)
Continuous corn	17.8	2076	354.8
Char+ (2 t/ha)	17.1	2082	355.9
Char+ (1 t/ha)	17.4	2079	355.3
No till	18.1	2087	356.9
Char+ (1 t/ha*2yr)	17.6	2078	355.0
Manure	1.8	1578	255.1
Rotation	4.8	1361	268.9

B) Elora Site

Practice	Soil mineral N in upper 10 cm (g/m^2)	Crop yield (kg/ha*year)	Shoot C (g/m^2*year)
Continuous corn	31.7	2479	439.4
Char+ (2 t/ha)	30.1	2477	439.0
Char+ (1 t/ha)	30.9	2479	439.4
Char+ (1 t/ha*2yr)	31.3	2479	439.4
No till	32.7	2454	434.3
Manure	3.2	1862	315.9
Rotation	6.8	1606	329.1

5.4 Discussion

5.4.1 Soil Organic C Dynamics: Comparing Delhi and Elora Sites

The Century soil organic matter model proved to be a useful tool for illustrating the long-term impacts that intensive agricultural practices can have on SOC dynamics. In the business as usual scenario (continuous corn farming) about half of the SOC was lost at the Delhi site and about one-quarter was lost at the Elora site over a 235 year period. Although more C loss might be expected from the Elora site because it had more initial C than Delhi, the Delhi site is more vulnerable to C loss for two main reasons. Firstly, the soil texture of the Delhi site was 85% sand and 7.5% clay, while the Elora site was 22% sand and 24% clay. Soils with finer texture or higher clay content are known to have slower rates of decompositions and greater stabilization of SOM (Bricklemyer et al., 2007). Secondly, the average soil mineral N content was lower at the Delhi site (17.8 g/m^2) than the Elora site (31.7 g/m^2); higher soil N results in higher biomass production and crop residue inputs, which increases SOC levels in the long-term (Alvarez, 2005).

The SOC levels for the year 2000 were 19 g/kg in the Delhi site and 51 g/kg in the Elora site, which is more than double the SOC measured in the growth chamber experiment controls for Delhi soil (7 g/kg) and Elora soil (22 g/kg). The Century model predicted SOC values are also higher than the levels measured in the field by Wanniarachchi et al. (1999) for the Delhi soil (6.5 g/kg) and the Elora soil (18.4 g/kg). However, the main goal of this study was to examine the relative changes in SOC caused by different land management practices, and not to predict the actual values. The loss of SOC resulting from continuous corn farming relative to native forest soil (26-55%) is within the range reported in the literature (Lal, 2004b).

The introduction of various land management practices between the years 2000 and 2150 had a significant impact on the level of SOC, with greater absolute changes (g/m^2) at Elora and greater relative changes (%) at Delhi. The reason for the greater absolute changes at Elora is that the higher clay content allowed for more C inputs from organic matter additions to be stabilized in the slow C fraction than in the sandy Delhi soil (Metherell et al., 1993). In the Century model soil clay content affects the proportion of SOC transferred from the active C fraction into slow the fraction (Metherell et al., 1993) because clay particles protects SOC from microbial decomposition (Strong et al., 1999). The reason for the greater relative changes at the Delhi site is that the initial SOC levels were lower at Delhi than Elora, and so the percent changes were amplified. From the perspective of a land manager or farmer at a particular site the relative changes would be more important, but from the broader perspective of a climate change scientist or a government body changes in the absolute values or tons of C per hectare would be important.

5.4.2 Effects of Biochar Additions on Soil C and N

The Century model predicted that annual application of 1 t/ha of biochar (~0.6 t C/ha) would increase SOC levels by about 20 t/ha at the Delhi site and about 24 t/ha at the Elora site over a 150 year period, relative to the business as usual scenario. This is likely a significant underestimation because biochar is highly resistant to microbial and physical decay, and only a small fraction of the biochar-C added would be mineralized over 150 years. The mean residence time of charcoal in *Terra Preta* soils has been estimated to be about 4000 years (Major et al., 2010b), while laboratory studies have estimated it to be about 1300 years (Cheng et al. 2009). Although biochar contains a labile fraction which can decompose in less than one year, this is typically only 3-12% depending on the biochar type (Bruun, 2011). The method used to simulate biochar additions with the Century model inaccurately predicted changes in SOC because biochar-C was transferred into the slow C fraction, which has a turnover rate of 20-50 years. This modelling method was also not able to account for increases in SOC that occur as a result of increase crop productivity and residue input. Another potential source of innaccuracy is that the Century model assumes soil bulk density is a constant parameter throughout the simulation period (Oelbermann and Voroney, 2011). However, organic matter additions typcially decrease bulk density over time, which affects the SOC stocks (Oelbermann and Voroney, 2011).

Previous work on biochar modelling has estimated the potential net CO_2 equivalent reductions that can be achieved with global biochar production and addition to soil (Woolf et al., 2010). However, modelling that focuses on biochar-soil C dynamics is in its infinancy. Recently, Foereid et al. (2011) developed a model for estimating the dynamics of black carbon (BC) in soil over time; the three main BC fluxes parameterized were decomposition (two pools: labile and stable), downward movement, and horizontal movement (erosion or run-off). The model predicted that erosion was the most important mechanism of BC loss, accounting for 76% of losses in the medium-term (100 years) simulation, and the total BC loss after 100 years was 88% (Foereid et al., 2011). However, the BC model was designed to simulate C dynamics of natural systems where BC produced from fires is deposited on the soil surface and is not incorporated into the soil by tillage as in agricultural systems. Comparing the results of the present study with previous modelling work are further complicated by the fact that biochar was added annually and not in a large single application.

To improve the accuracy of predicted changes in SOC levels, the Century program needs to modified so that biochar is treated as a unique organic matter addition that has a small (~5%) the labile fraction and large recalitrant fraction (~95%). The labile biochar-C should enter the active C fraction and the recalictrant fraction should enter the passive C fraction, instead of the slow fraction. Another potential inaccuracy in the Century model is that management practices that caused dramatic increases in SOC did not lead to increases in biomass production. Lal et al. (2004a) estimated that a 1 t/ha increase in SOC of degraded soils will increase maize yields by 10-20 kg/ha. Century predicted a 20 t/ha increase in SOC would only increase maize yield by 3 kg/ha at the Delhi site. Although biochar often increases soil N availability because of improved nutrient retention (Steiner et al. 2007), Century does not recognize this attribute.

5.4.3 Effects of No-till, Manure and Crop Rotation on Soil C and N

The Century model predicted that using no-till practices for 150 years would increase SOC by 1.3 t/ha at the Delhi site and 0.6 t/ha at the Elora site, relative to the business as usual scenario. Lal (2004a) estimated that converting from conventional tillage to no-till can increase SOC by 100-1000 kg/ha per year; assuming the lower value of this estimation and linear dynamics this would lead to an increase of 15 t C/ha over 150 years. However, Luo et al. (2010) conducted a meta-analysis of 69 long-term field trials and found that no-till increased SOC by 3.2 t/ha in the upper 10 cm, but decreased SOC by 3.3 t/ha in the 20-40 cm layer. Century simulates SOC dynamics for the upper 20 cm, and so an increase of 0.6-1.3 t C/ha agrees with the findings of Luo et al. (2010).

Century predicted that no-till would result in the highest level of soil N compared to all other practices at both sites. This is consistent with findings from a field trial that observed an increase in soil N in the upper 20 cm following 23 years of no-till practices (Dolan et al., 2006). However, that study also observed a decline in soil N at greater soil depths. The rotation treatment had higher shoot biomass production than the manure treatment because UAN was supplied to the corn in the rotation, whereas no UAN was applied in the manure treatment. The higher shoot biomass of the rotation treatment likely did not translate into greater crop yields because the yields of soybean were lower than corn. The manure treatment had the lowest soil N of all the treatments, which indicates that the manure application rate or N concentration was insufficient for sustaining higher crop yields.

At both sites using a crop rotation of corn and soybean led to a larger decrease in SOC than continuous corn. This is in agreement with a meta-analysis of long-term field trials, which found conversion from continuous corn to corn-soybean rotation resulted in a mean SOC decrease of 19 g/m^2 per year (West and Post, 2002). There are two probable reasons for the large decrease in SOC resulting from crop rotation. Firstly, the average residue input is about 2.5 t C/ha for soybean, and 6.8 t C/ha for maize (Johnson et al., 2006). Therefore, the maize-soybean rotation resulted in lower SOC inputs. Secondly, the biomass production of soybean in the rotation treatment was likely limited by soil N. It was predicted that N fertilizer would not be needed for soybean because it naturally fixes atmospheric N. However, the results revealed that soil N was very low for years when soybean was grown. Instead of using corn-soybean rotations, future modelling studies should use different rotations, such as wheat or hay, because these have been shown to increase SOC by an average of 19-27 g/m^2 per year (West and Post, 2002).

5.5 Conclusions

In summary, although the Century model may have significantly underestimated increases in SOC levels resulting from annual additions of Char+, the results of this study show that over the long-term biochar application will likely lead to greater increases in SOC levels than other land management practices. Annual application of 1 or 2 t/ha of Char+ resulted in higher level of SOC after 150 years when compared with continuous corn farming, corn-soybean rotation, manure application and no-till practices. The absolute increases (g/m^2) in SOC resulting from Char+ additions were greater at the Elora site because of the higher clay content, while the relative increases (%) in SOC were greater at Delhi because of lower initial C levels. Although the actual decomposition rate of the recalcitrant fraction of biochar is more than 1000 years, in this simulation the biochar-C entered the slow C fraction, which has a turnover rate of 20-50 years. This led to an overestimation of biochar-C loss. Modification for future biochar modeling efforts include: direct the labile fraction of biochar-C additions into the active SOC fraction and the recalcitrant biochar fraction into the passive SOC fraction, incorporate horizontal (erosion/runoff) and vertical biochar movement through soil into the model, and finally, account for the effect of biochar additions on soil N availability and crop biomass production.

Chapter 6
Final Summary and Conclusions

Agriculture has contributed significantly to the rise in atmospheric GHGs and it may be negatively impacted by the effects of climate change. However, it also has the potential to be a part of the solution. Although there are many strategies which have been proposed for reducing GHG emissions, C negative strategies that actively remove CO_2 from the atmosphere will be critical for avoiding the dangerous effects of global climate change (Woolf et al., 2010a). By adopting sustainable land management practices, such as reduced tillage, maintaining crop cover, agroforestry and intercropping, atmospheric C can be sequestered in soil and emissions of CH_4 and N_2O can be reduced (Lal, 2004a). The application of biochar to soil is another promising method of increasing SOC that has been receiving increased attention recently (Lehmann et al., 2007b). However, because biochar has a high energy value as a combustion fuel, there are economic challenges in implementing large-scale biochar applications to agricultural soil. The goal of this research was to contribute to the development of an economically feasible approach to using biochar in Canadian agriculture. The research has been enriched with an industry perspective through collaboration with a biofuel producing company, ABRI-Tech.

One of the objectives of this project was to test a new method of enriching biochar with plant-available N: by pre-soaking a fast pyrolysis hardwood biochar in liquid UAN, a value-added product called Char+ was produced. The results of the growth chamber experiment demonstrated that biochar could be used as an effective delivery material for N fertilizer: 1 t/ha of Char+ (1 t biochar combined with 178 kg N) and UAN (178 kg N/ha) both increased maize biomass production by about 300% in a sandy textured soil. It was hypothesized that Char+ would increase maize biomass production more than UAN. However, this was not observed and it is suggested that the 1 t/ha biochar application rate is too low to induce the synergistic effects reported in the literature (Chan et al., 2007). The hypothesis that 1 t/ha of Char+ would increase SOC levels more than UAN was also not confirmed. In most cases the amount of C directly added with 1 t biochar/ha would be smaller than the natural variation in SOC levels.

The field trials conducted in Namur, Quebec, which has a sandy soil texture, supported and expanded on the findings from the growth chamber experiments. In the Char+ Trial the application of 0.9 t/ha Char+ (0.9 t biochar combined with 170 kg N) and UAN (170 kg N/ha) both increased maize DM by about 60%. The trial also demonstrated that by using Char+, 30-60% of the typical N fertilization rate can be used without significantly lowering maize biomass production. The biochar field trial provided a window to the future and attempted to replicate the soil after 6-25 years of annual 1 t Char+/ha additions. The hypothesis that biomass production would increase with increasing biochar application rates was partially confirmed; biomass production of fertilized maize was unaffected when biochar concentrations were 6-12 t/ha, but improved by ~25% in the 25 t biochar/ha treatment. Contrary to predictions, no significant differences in SOC or soil TN were observed; however, there was a trend of increasing SOC, NH_4 and NO_3 with increasing biochar application rates. While many of the studies demonstrating the agricultural benefits of biochar have been conducted in the tropics, one of the main findings of this research is that biochar may be equally beneficial in temperate regions for nutrient poor, coarse textured and/or low SOM soils.

The Century model predicted that annual applications of 1 or 2 t Char+/ha will increase SOC levels more than other management practices, including crop rotation, manure use, and no-till, over a 150 year period. The simulation illustrated the dramatic loss of SOC that can occur as a result of converting native forest or grassland to intensive agriculture, as well as the effects that soil properties, such as soil texture can have on soil C and N dynamics. Although increases in SOC have been shown to increase crop yields (Lal, 2004a), the model did not predict large changes in crop yields from Char+ additions. The predicted increases in SOC of 20-24 t/ha after 150 years of 1 t Char+/ha are likely a conservative estimate because the biochar-C was transferred into the slow C fraction, which has a turnover period of 20-50 years. Future modeling efforts must account for the labile and recalcitrant fractions of biochar, the vertical and horizontal movement of biochar particles in soil, and its effects on crop productivity.

This research is significant in that it provides proof of concept for a new approach to using biochar in agriculture that is economically feasible, and has promising implications for the sustainability of agroecosystems and climate change mitigation.

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