THE IMPACT OF BIOCHAR AND INDUSTRIAL ASH AMENDMENTS ON SOIL PROPERTIES, GROWTH AND NUTRITION OF BLACK AND WHITE SPRUCE SEEDLINGS IN A SANDY LOAM SOIL

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ABSTRACT

Sevean, R. 2014. The impact of biochar and industrial ash amendments on soil properties, growth, and nutrition of black and white spruce seedlings in a sandy loam soil.

Keywords: black carbon, biochar, ash, soil amendment, respiration, Picea glauca (Moench.) Vos., Picea mariana (Mill.) B.S.P.

The purpose of this study was to establish and examine a controlled field experiment near Thunder Bay, Ontario using industrially produced ash and biochar as a soil amendment. This study monitors the change in physical, chemical, and biological properties to the field soil, as well as, the growth of black and white spruce seedlings. Biochar and ash were applied to split plots (black spruce on one half and white spruce on the other) at the levels of 0, 1, and 10 tonnes ha^{-1}. Ash application at 10 tonnes ha^{-1} caused the most significant changes to the soil's chemical properties including: increasing pH, electrical conductivity, Ca, K, Na, estimated cation exchange capacity, S, and Zn; while decreasing Mg, and available/mineralizable NH_4. The only significant change to the soil from biochar application was a decrease in extractable Cu concentrations after the application of 10 tonnes ha^{-1}. There were no significant differences between treatments in tree growth after two growing seasons. However, seedling foliage nutrient concentrations increased significantly for some nutrients with the application of ash. Black spruce and white spruce both increased in foliage nutrients B, K, and S. However, only black spruce seedling increased in foliar Ca, and Mg, which was likely due to a difference in rooting patterns. It is possible that since the plots were located on an old nursery site that most nutrient deficiencies have been amended in the past and the effects of the treatment on the soil were not as great as they could be on poorer soil. The increase in foliage nutrient concentrations in black and white spruce points to possible changes to seedling growth in the future. Therefore, a more long term study must be done to determine if seedling performance will be affected by these treatments.

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INTRODUCTION

Before the arrival of the Europeans, the Amazonians added large amounts of black carbon (BC) to the land by burning biomass in the absence of oxygen (Lehmann and Joseph 2009). This dark earth soil is also known as "terra preta". The soil from this area still holds a large amount of the carbon even after hundreds of years (Lehmann and Joseph 2009; Zimmerman *et al.* 2011). Unique properties of BC include a high resistance to degradation and an ability to retain nutrients and water (Downie *et al.* 2009; Kwapinski *et al.* 2010); qualities that could have a positive impact on degraded soils and soil ecosystems (Lehmann and Joseph 2009).

The global carbon (C) cycle (Figure 1) is made up of pools through which carbon is transferred and each pool has a certain retention rate. Some forms of BC can be stable and resistant to biological and chemical degradation in soil as seen in the example of “terra preta” (Kwapinski *et al.* 2010; Lehmann and Joseph 2009; Skjemstad *et al.* 1999). Producing BC from organic matter can take carbon dioxide (CO_2) out of the photosynthetic cycle and put it into a much slower biochar cycle (Figure 2) (Kleiner 2009). This could potentially help in the mitigation of the eight to ten billion tonnes of carbon dioxide that are released every year due to human activity (Kleiner 2009).

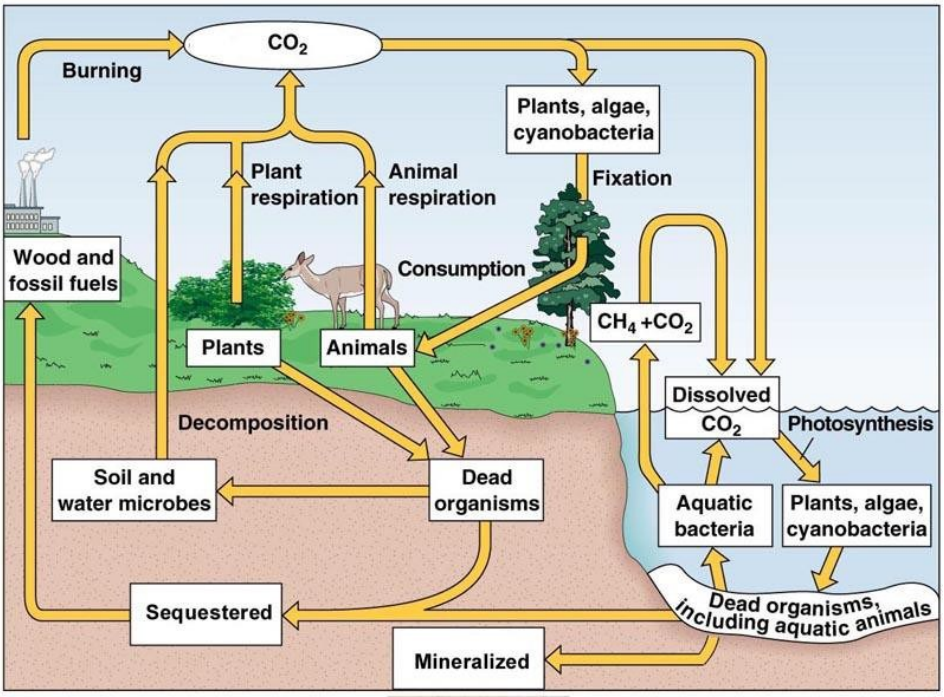

Figure 1. Basic carbon cycle diagram. Source: Tortora *et al.* (2011)

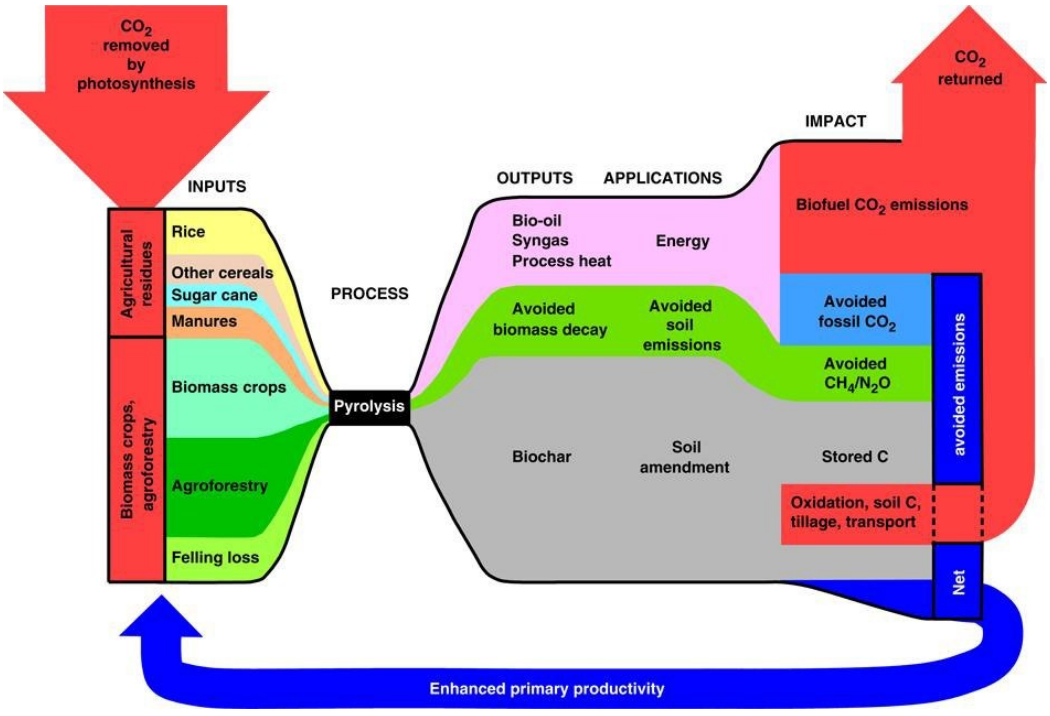

Figure 2. Biochar addition to the carbon cycle with estimated avoided emissions from burning biomass instead of fossil fuel. Source: Woolf *et al.* (2010)

On an annual basis, 50 to 270 Tg of biochar and ash are formed from biomass burning (Liang et al. 2006). More than 90% of this material stays in terrestrial ecosystems making up a significant portion of carbon in soils and likely having a large impact on biochemical processes (Hammes *et al.* 2007; Liang *et al.* 2006). Therefore, there has been an increased focus on the study of BC and its importance to those processes (Schmidt *et al.* 2001).

Using biochar and ash as soil amendments has the potential to be a win-win-win scenario in northwestern Ontario for environment-soil nutrients/tree productivity-industrial energy (Kleiner 2009; Puddister *et al.* 2011). Bio-energy can be used to offset fossil fuel emissions while the waste products (biochar and ash) could be stored in soil which in turn could increase plant growth (Woolf *et al.* 2010). Field studies using biochar and ash as soil amendments have shown that they both have the potential to improve soil by increasing soil pH, available macronutrients important to plant growth (calcium (Ca), potassium (K), magnesium (Mg), and phosphorus (P)), nitrogen (N) (indirectly through increased microbial activity) and soil water holding capacity (Mandre *et al.* 2004; Perez-Cruzado *et al.* 2011; Saarsalmi *et al.* 2004; Sahota 2009; Sartori *et al.* 2007; Staples and Van Rees 2001). Ash will likely influence the soil pH, base cations, and heavy metals content. Biochar will probably change the soil physical properties (bulk densiy and water holding capacity) and pH, which may lead to changes in microbial activity. Both types of material could add heavy metals to the soil, but ash is more likely to cause a greater significant change due to high heavy metal content. Therefore, the hypothesis is that ash treatments will increase pH, base cations, and heavy metal concentrations in the soil, while biochar will increase pH, water holding

capacity, and microbial activity. The purpose of this study is to measure and evaluate the effects of biochar and ash amendments, alone and in combination, on soil properties (physical, chemical, and biological) and seedling growth and nutrition in the early stages after plantation establishment. Combining the treatments is a way to analyze if there is an optimal application of both these materials because both of these materials are produced by industry. If they can in combination improve different soil properties they may be more effective used together than separately. Therefore, the hypothesis for this study also includes that ash being more alkaline than biochar will provide a more significant increase in pH and base cation, and the biochar will provide an increase in water holding capacity. Edaphic and environmental variables were controlled by locating the study in a fallow field (sandy loam soil) at the former Ontario Ministry of Natural Resources (OMNR) Thunder Bay tree nursery. The experiment was established as a randomized complete block design using white and black spruce as the crop trees. This thesis reports data that will serve as a baseline for future studies.

LITERATURE REVIEW

DEFINING BLACK CARBON, BIOCHAR, AND ASH

BC is a general term referring to the product of incomplete combustion of biomass (Schmidt *et al.* 2001). It can range in size from submicron particles (ash) to large chunks (resembling charcoal/biochar) (Hammes *et al.* 2008; Lehmann and Joseph 2009; Zimmerman *et al.* 2011). Throughout this thesis, the term BC, will be used when referring to the full range of such products.

There is no rigid definition or defined chemical signature for biochar as there tends to be a wide variation in chemical properties generated during its formation (Lehmann and Joseph 2009). Lehmann and Joseph (2009) however, defines it as a C rich material produced by thermal decomposition of organic matter under limited oxygen supply (pyrolysis) at less than 700°C. The distinction between char and biochar is vague (Sohi *et al.* 2010). In general, the term biochar is used when there is an intention of applying the product to soil as an amendment (Sohi *et al.* 2010). Traditionally, operating engineers have sought to minimize the amount of char/biochar produced because it is considered a low value waste (Sohi *et al.* 2010).

Biochar has two main structures: stacked crystalline graphene sheets and random amorphous aromatic structures (Verheijen *et al.* 2010). When cellulose is heated to between 250°C and 350°C, mass loss, in the form of volatiles (i.e., water, hydrocarbons, tarry vapours, hydrogen gas (H_2), carbon monoxide (CO), and CO_2),

leaves behind an amorphous C structure (Verheijen *et al.* 2010). Above 330°C, polyaromatic graphene sheets start to form laterally. Carbonization occurs at 600 °C; at this temperature the rest of the non-C atoms are removed making C content around 90% (Verheijen *et al.* 2010). The four main components of biochar are 50 to 90% fixed C, 0 to 40% volatiles, 1 to 15% moisture and 0.5 to 5% mineral matter (Verheijen *et al.* 2010). The proportion of these components, along with the original feedstock, determines the physical and chemical properties of the material (Verheijen *et al.* 2010). For example, biochar formed from wood will be coarser and more resistant to weathering than that from crop residue or manure (Verheijen *et al.* 2010). Feedstock sources for biochar currently include: wood chips, wood pellets, tree bark, crop residue, paper sludge, sugarcane bagasse distiller grain, olive waste, chicken litter, dairy manure and sewage sludge (Sohi *et al.* 2010).

The porous structure of biochar can significantly affect the physical properties of soil by increasing the surface area, pore-size distribution and by decreasing bulk density (Downie *et al.* 2009). Changes in surface area can influence water retention and aeration of a soil (Downie *et al.* 2009). Pore size and high internal surface area of biochar can increase microbial communities (mainly bacteria, actinomycetes and mycorrhizal fungi) by providing protected habitats that can absorb soluble organic matter, gases and nutrients (Downie *et al.* 2009; Thies and Rillig 2009).

Biochar can also significantly impact soil chemical properties (Verheijen *et al.* 2010) and the magnitude of the effect depends on the type of biomass feedstock and the conditions of pyrolysis. For example, due to its volatility, N content decreases with increasing temperature of burn (Chan and Xu 2009). Chan and Xu (2009) stated that

there is limited data on the properties (including nutrients and their availability) of biochar because most research has focused on energy production and fuel quality rather than by-product characterization. They compared pH, total C, total N, C/N, total P, total K, available P, NO_3 (nitrate), NH_4 (ammonium), and CO_3 (carbonate) from biochar based on different feedstocks and production methods and found that all parameters, except pH, were highly variable. In general, the pH of biochar is alkaline (average of 8.1) at least when initially placed into soil (Chan and Xu 2009) Feedstock strongly influenced the amount of total N and P with N highest from pure plant based sources and P highest from animal waste sources. C:N is used to estimate the potential for decomposition with 20 deemed as a critical limit above which immobilization of N can occur (Chan and Xu 2009). The biochar mean for C:N was 54.3 (ranging from 17.2 to 90.5) suggesting that its application may result in immobilization, not mineralization, of N (Chan and Xu 2009). Highest values for pH, Ca, Mg, and K (Table 3) were found in biochar produced from wheat (Zhang *et al.* 2010). High heavy metal contents (B (boron), Cu (copper), and Zn (zinc)) and base cations (liming material)) can be found in some forms of biochar mainly due to the residual mineral content, which can make up to 0.5-55% of the total weight (Chan and Xu 2009; Verheijen *et al.* 2010).

It is well known that high C materials can immobilize minerals (Kabata-Pendias and Pendias 1984; Uchimiya *et al.* 2010a; Uchimiya *et al.* 2010b; Verheijen *et al.* 2010). Since biochar is a C based material, it could have the ability to immobilize some heavy metals when added to soil. Uchimiya *et al.* (2010b) found that biochar increased retention of three heavy metal ions (Pb (lead) > Cd (cadmium) > Ni (nickel)) and that there was a positive correlation between pH and heavy metal retention. An increase in

pH could cause activation of soil surfaces and the formation of metal (hydr)oxide, carbonate, or phosphate precipitates, which could subsequently increase metal ion retention (Uchimiya *et al.* 2010b). This means that while biochar could potentially add heavy metals to soil it could retain some as well with the final outcome depending on the type of metals and other edaphic and environmental factors.

Table 1. Range of biochar chemical properties from various fuel sources[1] (adapted from Chan and Xu 2009).

Chemical Properties	Mean	Maximum	Minimum	Coefficient of Variation (%)
pH	8.1	9.6	6.2	18
Total C (%)	54.3	90.5	17.2	40
Total N (%)	2.23	7.82	0.17	110
C:N	67	400	7	152
Total P (mg kg^{-1})	23700	73000	200	118
Total K (mg kg^{-1})	24300	58000	1000	96

1 Fuel sources include: wood, green waste, poultry litter, sewage sludge, boiler litter, boiler cake, bark, rice straw, coconut shell, soybean cake, and sugar cane.

Like biochar, ash varies in composition, but boiler wood ash (i.e., fly ash, and bottom ash) is normally produced at temperatures greater than 500°C resulting in an average of 26 % total C (Pitman 2006). Ash, a very fine material (about 200µm), is often a byproduct of biomass burning in the paper industry (Pitman 2006). Industrial fly ash is deposited in ventilation system of wood boilers and due to the increased volatilization of C, this material generally contains higher concentrations of heavy metals compared to biochar and bottom ash (Pitman 2006).

Species of wood, amount of bark, conditions of growth, contamination (soil and metal), and conditions of the burn determine the properties of wood ash (Park *et al.* 2005). For example, K volatilizes above 800-900º while C and S (sulfur) volatize above 1000-1200ºC (Pitman 2006). B and Cu concentrations also decrease with increasing temperature , whereas Ca, Mg, Zn, Mn (manganese) and Si (silicon) concentrations remain stable (Pitman 2006). P and K can be lost in high temperature combustion, but despite this ash generally contains relatively high amounts of Ca, Mg, K, P, Al (aluminum), and Fe (iron) (Feldkirchner *et al.* 2003; Park *et al.* 2005). In commercial furnaces, temperatures between 500 and 800ºC produce ash with the highest amount of macronutrients (Pitman 2006). Ca, Mg, and K concentrations in ash can be similar to commercial fertilizers (Feldkirchner *et al.* 2003). When rating wood ash from an industrial boiler as a fertilizer product, the N:P:K would be 0:1:3 or 0:3:14 for material produced at a lower temperature (Pitman 2006).

Branryd and Fransman (1995) cautioned that high heavy metal content in wood ash may limit its use as an amendment. Although trace elements can essential to plant growth, their application in wood ash could lead to toxic levels (Kabata-Pendias and Pendias 1984; Lee *et al.* 2008). Rumpf *et al.* (2001) reported trace heavy metals (mg kg^{-1}) in wood ash as follows: 346 Zn, 115 Cu, 66 Cr (chromium), 42 Pb, 35 Ni, 8 Co (cobalt), 3 Cd. However, these values are relatively low compared to those reported by others. The highest values for trace metal content in fly ash were reported by Ernfors *et al.* (2010) as follows (mg kg^{-1}): 2380 Zn, 120 Cu, 135 Pb, 36 Ni, 14 Cd , 33 As (arsenic),. The application of ash to agricultural land is regulated in Ontario, Canada by OMAFRA (Ontario Ministry of Agriculture, Food and Rural Affairs). OMAFRA sets

restrictions on the application of ash, which is considered a NASM (Non-Agricultural Source Material). Table 2 has two categories of heavy metal concentrations of NASM material that can be applied to land. Ash would fall into the CM2 category for both materials used by Rumpf *et al.* (2001) and Ernfors *et al.* (2010) due to the high concentrations of Zn, Cu, and Cd. Ash could be applied to agricultural soil, but application would involve higher restrictions than other material. These restrictions include: distance from wells, unsaturated soil depth, depth to bedrock (application rate and restricted periods in the year for application), and application rate of regulated heavy metals.

Table 2. Regulated metals and their maximum concentrations (CM1= few restrictions, CM 2 and 3= Higher restrictions) for Non-Agricultural Source Materials when applied to agricultural land as a soil amendment (adapted from OMAFRA (2002)

Regulated metal	CM1	CM 2 and 3
	Concentration of material mg kg^{-1}, dry weight	Concentration of material mg kg^{-1}, dry weight
As	13	170
Cd	3	34
Co	34	340
Cr	210	2,800
Cu	100	1,700
Pb	150	1,100
Ni	62	420
Zn	500	4,200

Perhaps more important than the absolute amounts of the elements are the interactions between the ash, soil and plants. Important issues with regard to ash application to soil include adsorption of minerals, increased decomposition, increased leaching of nitrates, and heavy metal/trace element accumulation (Rumpf *et al.* 2001).

For example, P availability is dependent on pH (optimum pH is 6.0-7.0), and P decreases when pH is greater than 8.0. In acidic soils, P may be bound up in insoluble compounds such as iron and aluminum phosphates (Brady and Weil 2002; Pitman 2006). In general, K and P availability is less in ash than in commercial potash fertilizer (Pitman 2006) and wood ash is generally low in N and S (Feldkirchner *et al.* 2003). Therefore, the risk of adverse environmental effects (e.g. nutrient leaching) is lower when compared to other alternative fertilizers (Brunner *et al.* 2004). However, additions of ash may indirectly increase N availability (and subsequently nitrate production and leaching) due to a rise in pH, which can cause an increase in microbial activity (Park *et al.* 2005; Pitman 2006). This increase in N mineralization of soil organic matter is known as the priming effect (Brady and Weil 2002; Pitman 2006); the priming effect reduces C stores as well and therefore has implications for C cycling.

Increased soil pH due to wood ash application could also lead to increased trace metals in soil due to their release from the litter layer. Rumpf *et al.* (2001) have suggested that heavy metals released by litter maybe retained by the B horizon, thus reducing the risk of leaching into seepage water. Rumpf *et al.* (2001) stresses the need to define qualifying standards for nutrient/heavy metal content in ash due to its extreme variability (biomass source, temperature, etc.). Harmful trace elements, however, are less of an immediate concern in forest soils that are not used for food crops (Feldkirchner *et al.* 2003).

BIOCHAR AND ASH MATERIAL USED IN FIELD STUDIES

For comparison purposes, mean values of physical and chemical properties of different types of biochar and ash used in field studies are shown in Table 3.

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Table 3. Mean and range values of bulk density and chemical properties of biochar and ash used in field studies. (full references found in Appendix I)

Chemical/Physical Property	Units	Biochar			Ash		
		Mean	Range	# of Sources	Mean	Range	# of Sources
Bulk Density	g cm^{-3}	0.5125	0.08-1.2	4			
pH		8.5	7.2-10.4	10	12.65	12.35-13	3
C	%	63.9	15.14-87	11	9.71	7.82-11.6	2
N	%	0.73	0.31-1.9	10	0.11	0.06-0.19	3
S	%	0.05	0.02-0.085	3	0.73	0.03-1.13	3
Exchangeable Ca	mg kg^{-1}	3233.6	330.7-6440	3			
Exchangeable Mg	mg kg^{-1}	175.0	48.9-291	3			
Exchangeable K	mg kg^{-1}	388.3	19.9-1130	6			
Total Ca	mg kg^{-1}	5174.8	1400-10000	5	170275	43250-249000	6
Total K	mg kg^{-1}	11700.4	2811-26000	5	43266.67	22000-74000	6
Total Mg	mg kg^{-1}	3186.0	1228-6000	4	17333.33	9100-29000	6
Total Na	mg kg^{-1}				8180	3000-17900	5
Total P	mg kg^{-1}	858.5	180-2177	4	11830	5000-23000	5
Total As	mg kg^{-1}				17.1	1.2-33	2
Total Cd	mg kg^{-1}				8.95	3-14	4
Total Cu	mg kg^{-1}				116.25	82-148	4
Total Ni	mg kg^{-1}				30	20-36	4
Total Pb	mg kg^{-1}				83.75	42-135	4
Total Zn	mg kg^{-1}				1189	346-2380	4

The "biochar" used in the field experiment reported here was not produced under pyrolysis. However, it was clearly different from the ash that was applied. Despite the process of the biochar's production, it can be argued that it has similar chemical properties to some biochar being used in the literature. Yamato *et al.* 2006 and Zhang et al. 2010 used biochar with similar %C (39.5% and 46.7%); 5 out of ten of the biochar studies had a similar pH (7.2-8.81); and Baronti *et al.* 2010, Gaskin *et al.* 2010, Husk and Major 2010, and Zhang *et al.* 2010 used biochar with similar concentrations of macronutrients. These similarities in soil chemistry suggest that the biochar used in this study may have similar effects on the soil chemistry.

THE POTENTIAL BENEFITS OF BLACK CARBON

The application of BC (including both biochar and ash) to forest soils may result in social and/or economic benefits, with respect to: 1) environmental management, 2) waste management, 3) mitigation of climate change, and 4) energy production (Lehmann and Joseph 2009).

Environmental Management

A fundamental aspect of sustainable forestry is the retention and cycling of nutrients. BC could potentially play a role in soil sustainability by maintaining or improving soil fertility (Kwapinski *et al.* 2010). The properties of BC could result in better water and nutrient retention, and reduce chemical leaching (Woolf *et al.* 2010). BC can function as a soil fertilizer or conditioner (improving soil physical properties), which leads to increased crop yield (Steinbeiss *et al.* 2009; Uchimiya *et al.* 2010a). It would be optimal if BC could be used to store carbon as well as activate microorganisms in order to release more nutrients into the soil (Steinbeiss *et al.* 2009). To maximize the benefit of

BC, further investigation into its chemical structure and decomposition and its stability in soils is required (Steinbeiss *et al.* 2009).

Rehabilitation of mine tailings represents another environmental challenge that could be addressed through the application of biochar and ash. Abandoned dumping sites from mining often contain toxic substances like heavy metals (Cd, Cr Cu, Ni), Pb, Tl (thallium), and Zn) (Fellet *et al.* 2011); as noted previously, BC has the potential to retain heavy metals (Uchimiya *et al.* 2010b). A method to stabilize mine tailing sites from erosion and leaching is to promote the establishment of vegetation (Fellet *et al.* 2011) which could be assisted through the additional of C based material to the substrate.

Waste Management

Waste products from pulp and paper mills include sludge and wood ash (Feldkirchner *et al.* 2003). In 2002, an estimated 775,000 tonnes of ash was generated by pulp and paper mills in Canada, which has increased from 553,000 tonnes in 1995 (Elliot and Mahmood 2005). A survey of Canadian mills in 1995 suggested that 84% of ash produced went into landfills, 9% went into effluent (sewer), and 3% was beneficially used (building products, construction material, land application, etc.) (Elliot and Mahmood 2005). Putting ash in landfills not only takes up valuable space, but can create a leachate problem in these landfills (Elliot and Mahmood 2005).

Mitigation of Climate Change

One method of reducing the greenhouse effect is to capture existing carbon dioxide in the atmosphere by growing plants with the limitation of this method being that plant biomass will eventually decompose and release the carbon dioxide it had

stored (Lehmann 2007). More than 60 billion tonnes of C taken up annually by plant photosynthesis is available in the form of agricultural or forest residue (Kleiner 2009). The transformation of this material into a stable form, such as biochar, could reduce the release of carbon dioxide, methane, and nitrous oxide into the atmosphere (Woolf *et al.* 2010). The potential of this strategy was recognized at the 2005 G8 summit (Schiermeier 2006). Lehmann and Joseph (2009) claim that the conversion of 1% of annual plant uptake into biochar could mitigate 10 % of anthropogenic C emissions. Sequestering C into stable forms could address the imbalance between the amount of carbon released into the atmosphere and the amount taken up by other carbon pools (Steinbeiss *et al.* 2009).

Energy Production

Through the pyrolysis process, additional bio-energy products (bio-oil and syngas) could be generated (Kwapinski *et al.* 2010). Biofuel could potentially replace fossil fuels adding an offset of 1.8 billion tonnes of C emissions a year (Kleiner 2009). The production of BC also creates heat that could be used to warm buildings or produce electricity (Kleiner 2009). The use of animal, crop, and industrial waste as feedstock for pyrolysis bioenergy can generate useful energy from waste, indirectly decrease methane from landfill, reduce industrial energy usage, and decrease energy used by transportation (generally landfills are being placed further away from waste sources) (Lehmann and Joseph 2009).

Critics point out that it is too early to know all the potential adverse effects of C sequestering (Kleiner 2009). The production of BC is limited by the rate of sustainable biomass production that will not put soil conservation, natural habitats, or food security

at risk (Kleiner 2009; Kwapinski *et al.* 2010; Woolf *et al.* 2010). In addition, despite the recent increased interest in BC, there are no generally accepted analytical protocols for studying BC (Brodowski *et al.* 2005; Schmidt *et al.* 2001).

IMPACTS OF BIOCHAR AND ASH ON SOIL AND PLANTS

Due to the variability of physical, chemical and biological properties of biochar and wood ash , it is difficult to predict productivity response to their application and this means that to understand its potential there needs to be an investigation on a global scale (Blackwell *et al.* 2009). The following section summarizes reported effects of biochar and ash in field application experiments that focused on soil and productivity responses; Appendix I presents this summary in table format.

Biochar Effects on Soil

In terms of geographic location, the majority of studies examining the effects of biochar application on field soil have been conducted in the tropics. In contrast, ash field studies have taken place in Europe, United States, and more recently Canada (Blackwell *et al.* 2009; Laird *et al.* 2008; Patterson *et al.* 2004). Biochar field studies showed an effect on some soil physical properties, which was not seen in the ash field studies. One study found that biochar increased water holding capacity by 9-12 % and the retention of N increased by 11 - 59 % (Chen *et al.* 2010). Some studies observed that biochar improved hydraulic conductivity, as a result of better water infiltration at the soil surface (Asai *et al.* 2009; Major *et al.* 2010a). Three out of ten studies reported a change in bulk density with the addition of biochar (Husk and Major 2010; Major *et al.* 2010a; Zhang *et al.* 2010). Zhang *et al.* (2010) and Major *et al.* (2010a) reported a decrease in bulk density, which would be expected due to the lower particle density and higher porosity

of biochar. However, Husk and Major (2010) observed a slight but not significant increase in bulk density with biochar application, which they could not explain. It may be possible that the small sized biochar articles simply filled pore spaces between the larger soil particles, thereby increasing the overall bulk density.

Similar to the ash field studies, biochar also had a liming effect on most soils. pH increased in a range of soil types but its effect was more related to the type and dosage rate of biochar and the acidity of original soil (Gaskin *et al.* 2010; Jones *et al.* 2012; Major *et al.* 2010b; Yamato *et al.* 2006; Zhang *et al.* 2010). Because increased pH is usually related to increased base cation addition to soil, it was logical that three out of the five studies that reported soil pH saw a significant increase in soil exchangeable base cations (Ca, Mg, and K) (Gaskin *et al.* 2010; Major *et al.* 2010b; Yamato *et al.* 2006). Of those three studies, two of them also reported a decrease in exchangeable Al and Fe in the soil from being displaced on cation exchange sites (Major *et al.* 2010b). Some other nutrients that increased were Mn, Sr, and P but these nutrients increased due to the type of biochar that was applied to the soil and the rate of biochar applied (Gaskin *et al.* 2010; Husk and Major 2010; Major *et al.* 2010b; Yamato *et al.* 2006).

In contrast to the above studies, Husk and Major (2010) reported a slight decrease in exchangeable Ca and P (when compared to a control) in soy bean crop soil after applications of biochar (3.9 tonnes ha^{-1}). Another study (Jones *et al.* 2012) found very little soil response to treatment other than a slight increase in pH, and there was a temporary (2-years) microbial shift towards a bacterial dominated community, which could reduce C sequestration temporarily.

Major *et al.* (2010a) found a loss in soil organic matter and an increase in soil respiration (2.2% lost C after23.2 tonnes ha^{-1} biochar application), which indicated an increase in decomposition of non-biochar organic matter by microbial communities. The highest flux of C in the study by Major *et al.* (2010a) was from water run-off just after application of biochar. Major *et al.* (2010a) believed that this was caused by biochar being hydrophobic just after application. The respiration of only 2.2% C from the applied biochar after 1 year meant that biochar was highly stable and was evidence that it could be used as a potential C sink (Major *et al.* 2010a).

Ash Effects on Soil

Many studies conducted on ash field application reported an increase in pH after application (Branryd and Fransman 1995; Brunner *et al.* 2004; Ernfors *et al.* 2010; Feldkirchner *et al.* 2003; Mandre *et al.* 2004; Park *et al.* 2005; Perez-Cruzado *et al.* 2011; Rumpf *et al.* 2001; Saarsalmi *et al.* 2004; Sahota 2009; Sartori *et al.* 2007; Staples and Van Rees 2001). Some examples of increasing pH are: silty loam soil with a pH of 6.1 increased to 6.9 with the addition of 10 tonnes ash (pulp and paper ash) ha^{-1} ; an application of 5 tonnes ash (pulp) ha^{-1} increased pH from 4.8 to 6.9 in a clay loam soil, and an acidic soil with a pH of 3.6 increased to 5.5 with 2.4 tonnes ash ha^{-1} application (Park *et al.* 2005; Rumpf *et al.* 2001; Staples and Van Rees 2001). It seems that the lower the original soil pH, the greater the effect ash had, although soil pH changes also depend on the pH and the amount of ash applied. The above studies attributed the pH increase to the increased addition of base cations (Ca, Mg, K, and Na) in ash, causing a neutralizing effect by displacing H (and sometimes Al) from cation exchange sites and from the soil (Saarsalmi *et al.* 2004). The protons then attach to hydroxyl ions from the

dissolution of calcium oxide (CaO), magnesium oxide (MgO), potassium oxide (K_2O) and sodium hydroxide (NaOH) (Saarsalmi *et al.* 2004). This probably also explains why most studies reported increases in available/exchangeable Ca and Mg (K increased for only four out of the ten studies) (Branryd and Fransman 1995; Brunner *et al.* 2004; Feldkirchner *et al.* 2003; Park *et al.* 2005; Perez-Cruzado *et al.* 2011; Rumpf *et al.* 2001; Saarsalmi *et al.* 2004; Sahota 2009; Sartori *et al.* 2007; Staples and Van Rees 2001). Perez-Cruzado *et al.* (2011) reported that Ca and Mg doubled for both 10 and 20 tonnes ha^{-1} application of ash even when Mg concentrations were relatively high initially. In the same study, K concentrations exceeded 200 mg kg^{-1} for the 20 tonnes ha^{-1} treatment, which was very high considering the average initial value was 75 mg kg^{-1}. Perez-Cruzado *et al.* (2011) remarked that the changes to soil Ca, Mg, and K were short lived and values went back to initial soil ranges after 24 months. However, a study by Saarsalmi *et al.* (2004) with just 3 tonnes ha^{-1} application of ash found two to seven fold changes to Ca and Mg five years after application. This demonstrates that the initial soil type and ash material can have various effects on nutrient concentrations and on how long those effects last. Park *et al.* (2005) estimated that the ash used in their study added half the equivalent of $CaCO_3$ to the soil when compared to the requirements met by pure $CaCO_3$. No study reported an increase in available Na. One study, despite reporting an increase in pH, had a decrease in Ca, which according to Mandre *et al.* (2004) was because the ash was added to an already alkaline soil.

Most field studies have dealt with ash being added to acidic soils and have resulted in significant increases in soil pH and base cations. With increasing pH and base cations, there was a comparable decrease in exchangable Al, Mn, Fe, and Zn. This

decrease may be due to displacement of the ions on exchange sites and the formation of hydroxo-complexes (Branryd and Fransman 1995; Brunner *et al.* 2004; Rumpf *et al.* 2001; Staples and Van Rees 2001). Sahota (2009) and Branryd and Fransman (1995) found that the ash application increased Mn concentrations, which was attributed to the high amounts of Mn in the ash from the feedstock source. Mn could be especially high if feedstock sources were grown on acidic soil because root uptake of Mn is usually higher in this type of environment (Brunner *et al.* 2004). In the study by Brunner *et al.* (2004) Al, Mn, Fe, and Zn decreased four fold despite ash adding roughly 0.040 tonnes ha^{-1} Al, Mn, and Fe, and 0.002 tonnes ha^{-1} Zn.

Extractable P increased in two studies (Saarsalmi *et al.* 2004; Staples and Van Rees 2001), which reported that P increase was directly related to the amount found in the ash material. Staples and Van Rees (2001) stated that high P concentrations in ash were due to the feedstock material of wood and sludge. Ernfors *et al.* (2010) reported in their study that exchangeable P in soil was a limiting factor for tree growth. They suggested it may be advisable to investigate the feedstock source of the ash, identify it's nutrient content, and source specific ash, before applying to areas low in certain limited nutrients.

Feldkirchner *et al.* (2003) found that the treatment of N + ash had the same increase in nutrients as a complete fertilizer treatment (N + base cations + P + S). Across several studies soil nutrient concentration increased with increasing ash application, which was 10 tonnes ha^{-1} for most studies (range 1 tonnes ha^{-1} to 20 tonnes ha^{-1}). This is further evidence that waste material such as ash could improve some soil nutrient levels to the same degree as some commercial fertilizers.

Some studies have found negative impacts in soil with the application of ash due to microbial activity changes and addition of toxic heavy metals. Moilanen *et al.* (2002) found that ash increased microbial activity of nitrifiers, which increased N concentrations and CO_2 respiration in the soil. While increased N may be a positive effect in N limited soil, the increase in respiration is a negative effect in that soil C sequestration is reduced. Some ash material had high amounts of heavy metals. Branryd and Fransman (1995) and Rumpf *et al.* (2001) showed increases in heavy metals such as Cd, Cu, Pb (lead), and Zn in soil after ash application. Their ash material was produced from the combustion of wood feedstock. However, Rumpf et al. (2001) suggested that despite the addition of some trace heavy metals with the addition of ash the addition of a low heavy metal ash could be applied safely even to sandy soil.

Plant Nutrients and Productivity

The relationship between biochar and plant productivity is relatively new and studies are limited (Jeffery *et al.* 2011). Unlike agricultural crops, there is little to no research on the effects of biochar on pasture, shrubs, or trees (Blackwell *et al.* 2009). Two out of the nine studies examining cropyield with biochar field application found no significant effect. Gaskin *et al.* (2010) showed no increase in corn stover but an increase in corn grain when pine chip biochar was applied. Asai *et al.* (2009) showed that an increase in growth occurred only if biochar and N fertilizer were used together. Peanut hull biochar used by Asai *et al.* (2009) and several studies reported a positive yield response to the application of biochar (Asai *et al.* 2009; Baronti *et al.* 2010; Chen *et al.* 2010; Gaskin *et al.* 2010; Jones *et al.* 2012; Major *et al.* 2010a; Yamato *et al.* 2006; Zhang *et al.* 2010). A study in Quebec, Canada showed that biochar application of 3.9

tonnes ha^{-1} increased soybean biomass by 17-20% and forage crops by 17-99% (Husk and Major 2010). Another study that used 10 tonnes biochar ha^{-1} application rate showed an increase of 10% in grain production for wheat, and 6-24% in maize (Baronti *et al.* 2010).

A meta-analysis conducted by Jeffery *et al.* (2011) indicated a significant increase in crop productivity in both acidic and neutral soil with the application of biochar. Crop productivity increased in soils with either medium to course textures; but there was no significant response in soils with a fine texture (Jeffery *et al.* 2011). Jeffery et al (2011) concluded that since significant growth response is associated with pH and soil texture, the main mechanisms for increased crop productivity were water holding capacity and liming effect of biochar.

Studies have also reported increases in crop tissue nutrient concentrations. Major *et al.* (2010b) showed that the application of 8 and 20 tonnes biochar ha^{-1} increased Ca and Mg significantly in maize and K and Mn in soybean crops. Gaskin *et al*. (2010) reported increased concentrations of K and Ca (peanut hull biochar) and S and Mg (pine chip biochar) in corn tissue. Jones *et al.* (2012) showed an increase in N concentration in grass (no effect on maize crop), which was probably due to increased microbial activity in the soil and the fact that grass rooting depth was shallow (< 30 cm) compared to other crop types. This could mean that for crops with deep rooting depth, biochar application may not be as effective as it could be for shallow rooting crops.

Overall, total nutrients (except Al) and yield increased with increasing rates of biochar application for maize (no significant effect on rate of application for soybean crop) (Major *et al.* 2010b). Zhang *et al.* (2010) also reported this effect of increasing

application rate related to increases in yield, where 10 tonnes biochar ha^{-1} increased yield by 12% and 40 tonnes ha^{-1} by 14%.

Five field studies showed an increase in plant growth with the application of ash. Three of these studies saw a positive growth response when ash was applied to stands of Scots pine (*Pinus sylvestris* L.) (Ernfors *et al.* 2010), sugar maple (*Acer saccharum* Marsh.) (Feldkirchner *et al.* 2003), and chestnut (*Castanea x coudercii*) (Perez-Cruzado *et al.* 2011). The Scots pine mean annual basal increment increased 23% after 5 years, the maple stand had a 30% increase in wood increment with N + ash treatment, and the chestnut stand increased in height and diameter by 16 and 11% over the first three years (Ernfors *et al.* 2010; Feldkirchner *et al.* 2003; Perez-Cruzado *et al.* 2011). Perez-Cruzado *et al.* (2011) stated that application of ash to soil at low dosage may only have had a temporary effective because after a second four year period tree height and diameter increased significantly only for the ash dose of 20 tonnes ha^{-1}. Perez-Cruzado *et al.* (2011) showed that growth was greater with increasing application rate, which also occurred in the study by Ernfor *et al.* (2010) and in a study on the natural growth of drained mire by Moilanen *et al.* (2002). The natural growth study (mainly Scots pine) observed that after a little less than 50 years since the growing stocks were 26, 162, and 236 m^3 ha^{-1} after ash application of 0, 8, and 16 tonnes ha^{-1} respectively (Moilanen *et al.* 2002).

Two studies investigated ash application on agricultural crops (Sahota 2009; Patterson et al. 2004). Sahota's (2009) Thunder Bay, Ontario study showed that with an application of 10 tonnes ash ha^{-1} there was an increased alfalfa crop yield of 1 tonnes ha^{-1} a year. Patterson *et al*. (2004) showed no crop (barley) yield increase for the ash

treatment; however this may have been due to inherent N deficiencies in the soil. Overall, it was clear that the original soil properties (such as pH and N concentration) had an effect on how the ash applied influenced tree growth and crop yield.

Two studies on tree species found that ash application had no effect on growth Park *et al.* (2005) applied 10 and 20 tonnes ha^{-1} of ash to an alkaline silty loam soil but found no increase in willow biomass. These authors believed that the application of ash would have had greater effect on a plantation with originally more acidic soil. Studies on white spruce seedlings with the addition of 1 and 5 tonnes ash ha^{-1} on acidic soil, experienced a decrease in growth due to an increase in salinity stress from0.02 dS m^{-1} to 0.10 dS m^{-1} (Staples and Van Rees 2001).

Mandre *et al.* (2004) reported a decrease in growth with addition of ash to an alkaline soil, which decreased Ca and increased K in the foliage. Other studies observed an increase in K concentrations in tree foliage after ash applications (Ernfors *et al.* 2010; Feldkirchner *et al.* 2003; Perez-Cruzado *et al.* 2011). Ernfors *et al.* (2010) and Saarsalmi *et al.* (2004) also reported an increase in foliage B concentration along with increased K. Unlike Ernfors *et al.* (2010), Saarsalmi *et al.* (2004) found a decrease in foliage Mn. Brunner *et al.* (2004) investigated fine root nutrient concentrations and found that similarly to the changes in soil chemistry due to pH increases, Ca and Mg increased in fine roots, and Mn decreased. Perez-Cruzado *et al.* (2011), using a vector analysis technique, found that ash application improved Ca and Mg nutrient status but did not significantly increase other nutrient concentrations.

METHODS AND MATERIALS

BIOCHAR AND ASH MATERIAL

Ash and biochar material were collected in 2012. The fly ash (grey fine powder) was collected directly from the #6 power boiler at Resolute Forest Products, Thunder Bay. The biochar (black charcoal like heterogenous material) originated from Resolute Forest Products Thunder Bay's #3 power boiler, but had been stored on a farm located just outside the Thunder Bay area. In 2009, the biochar-type material was allowed to be transported to local farms as a Non-Agricultural Source Material (NASM) for nutrient management of an agricultural crop. The #3 and #6 power boilers are vibrating grate boilers and in 2009 the #3 boiler ran at a lower temperature than # 6, resulting in these different type of waste material being produced. The biomass fed into both boilers was mainly softwood sawmill waste (bark and saw dust), wood chips, and 8-14% pressed secondary effluent sludge (only in #6 power boiler). Fly Ash is normally collected in the ventilation system and mixed with water before being dropped into a waste collecting truck. Bulk samples of ash and biochar were treated separately by air drying, and mixing (three times daily) in a well-ventilated room for a week. The samples were then allocated into treatment plastic bags in preparation for top soil mixing. Composite samples of both materials were created by collecting five samples from random locations at different depths in the pile and combining them in a container. The ash and biochar were analyzed for physical and chemical properties.

STUDY SITE AND EXPERIMENTAL DESIGN

The field experiment site was established at the OMNR (Ontario Ministry of Natural Resources) Northwest Science and Technology center, 25th Side Road, Thunder Bay, ON next to Elite test site (Latitude N 48° 22 , Longitude W 89° 23' 50"). This area was once a tree nursery (Figure 3 and 4) and the experimental site (compartments #37 and 38) was used to produce jack pine and black spruce seedling bare root nursery stock from 1946/47 to 1991/1992. The site management consisted of two years in production followed by two years of fallow. Green manure crop was incorporated into the soil in preparation for the next seedling crop rotation. Annually, fertilizer treatment included: four fertilizer treatments of 90 kg anhydrous ammonia applied at two week intervals during the active growing season (150 kg elemental N $ha^{-1}yr^{-1}$), four treatments of 100 kg ha^{-1} commercial mixture N-P-K (11-52-0) applied in the intervening weeks, and a single 28 kg ha^{-1} treatment of potassium sulphate (12 kg ha^{-1}) was applied in either week five or six of the 12 week growing period during the summer.

The soil at the site is sandy loam and has 5.93% organic matter. Soil profile maps from Agriculture Agrifoods Canada identify this site as having Mietzle soil, which can have a surface texture of gravel, loamy sand, sandy loam or sand with good drainage. The site was separated into five blocks (9 m X 16.5 m) with 9 treatment plots that were randomly allocated to each treatment combination (Figure 5). The plots were split (2.5 m x 2.5 m) with 16 seedlings of two species (white and black spruce) in each half. The side of the plot (north or south) that the species of seedlings were planted was randomly selected. A buffer of jack pine was planted around the 16-tree plot (Figure 6). Because the seedlings are 50 cm apart, each treatment plot is 3 m x 5.5 m, totaling 16.5 m^2 in area; there is a path around each plot for easy access.

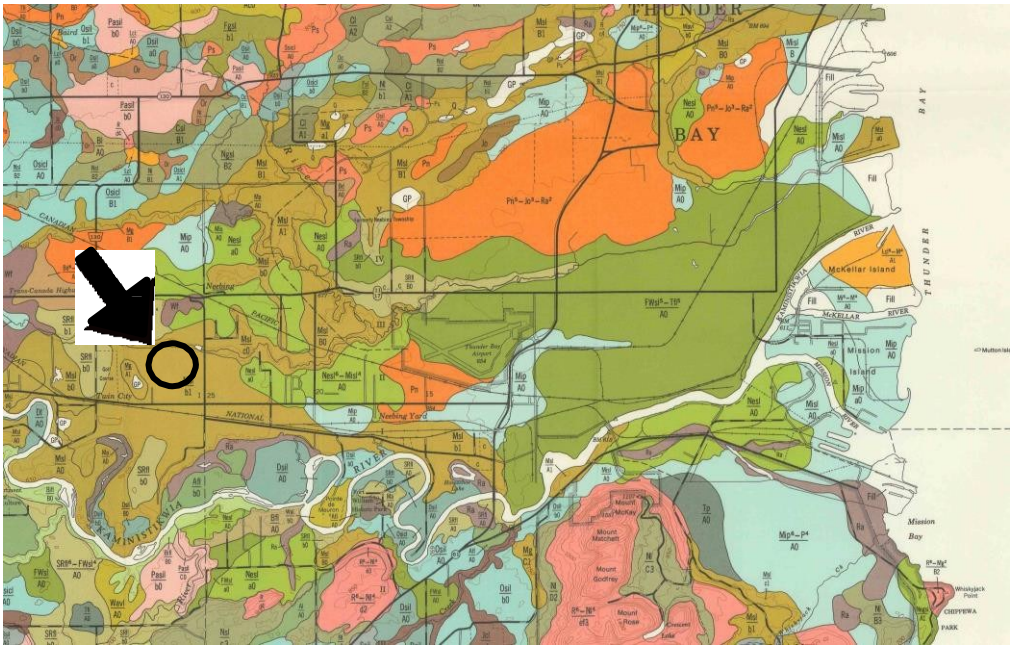

Figure 3. Location of Northwest Science and Technology center in Thunder Bay (circle) adapted from soil survey map of Thunder Bay. Source: http://sis.agr.gc.ca.

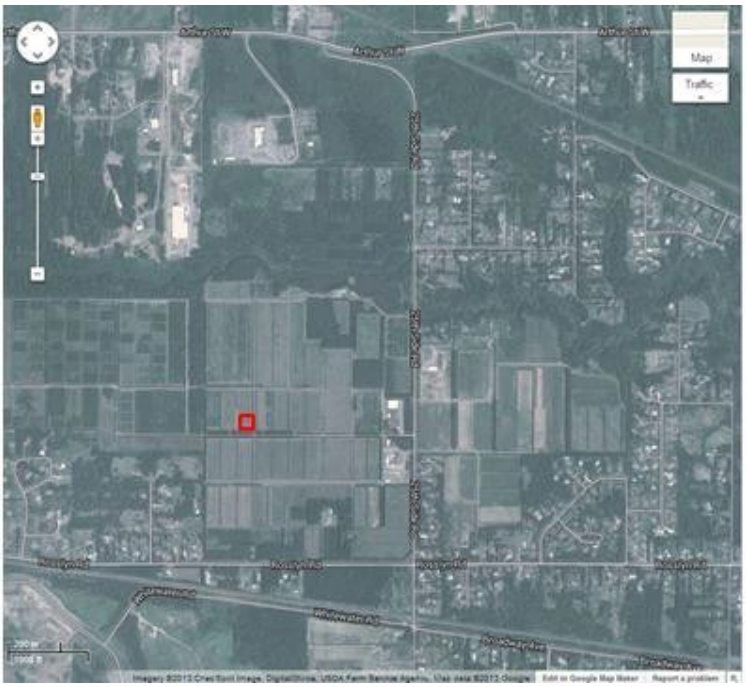

Figure 4. Square outlines site location at OMNR Northwest Science and Technology center in Thunder Bay. Source: adapted from Google Maps.

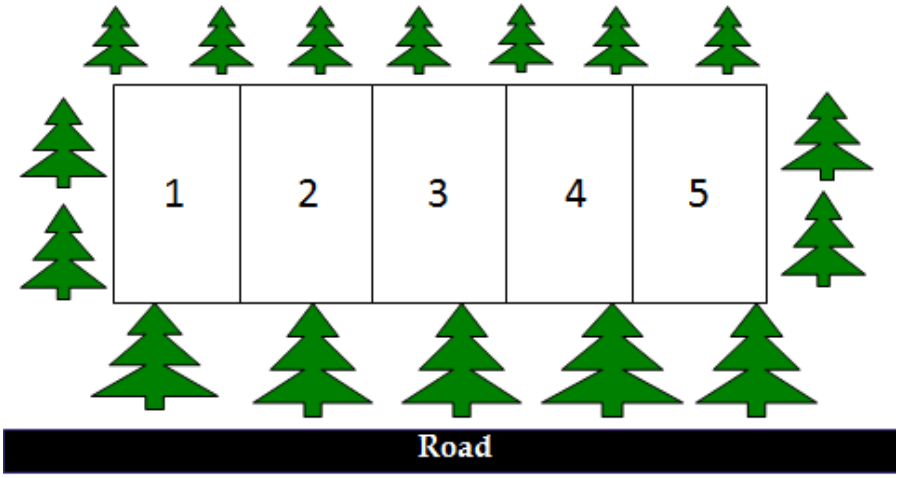

Figure 5. Set-up of blocks at the site location. Tree height differences represent differences in tree heights lining the site, which has small trees to the north and large to the south.

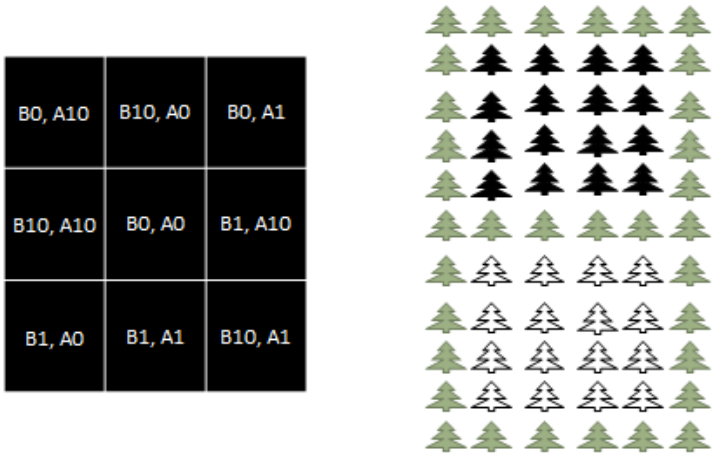

Figure 6. Example of plot set up with a block (left) and the seedling set up within each plot (right). B=biochar, A=ash, green trees=Pj, black trees=Sb, white trees=Sw.

APPLICATION OF ASH AND BIOCHAR

Blackwell *et al.* (2009) describes different biochar application techniques including: uniform topsoil mixing, deep-banded application in rows, top dressing, and specific tree application (circular trench around individual trees or multiple holes surround trees). The uniform topsoil mixing method involves spreading the appropriate amount on to the area and then mixing (tilling or discing) it into the soil. A hazard in using this method is that the low density of the material causes dusting, which may mean that a certain amount of material could be lost and may pose a health concern during application (Blackwell *et al.* 2009). In sandy soils there is also a risk of erosion from high winds (Blackwell *et al.* 2009). The majority of field studies that reported the mixing method utilized the uniform topsoil mixing with slight variation in terms of the depth of mixing, ranging from 10 to 30 cm depth (Asai *et al.* 2009; Chen *et al.* 2010; Major *et al.* 2010a; Perez-Cruzado *et al.* 2011; Sartori *et al.* 2007). Despite these drawbacks and potential hazards, the uniform top soil method is the most feasible for industrial applications and was used in this experiment.

The site was tilled and set up for irrigation prior to establishing the experiment. The plots were marked and prepared by manually weeding and using weeding rakes that stirred up the top 10 cm of the already tilled soil. A net the size of the plot (3 m x 5.5 m) with a mesh size of 1 m x 1.1 m was made from nylon rope and wire. The treatment bags were prepared (see Appendix II) so that a single bag could be applied to each square and the treatment mixed in (using weeding rakes) following removal of the net, thereby ensuring that the soil treatment was applied evenly throughout the whole plot in May 2012.

There appears to be no standard application rate used in biochar application field studies. Pitman (2006) suggested that for whole tree harvesting, 10 tonnes ash (wood) ha^{-1} plus an additional N amendment could replace the nutrient loss at the site. Another study showed that application of more than 10 tonnes ash ha^{-1} did not show any significant rise in yield and if managed properly a low application of less than 25 tonnes ash (wood) ha^{-1} could increase productivity of barley and other types of crops (Patterson *et al.* 2004). Mandre *et al.* (2004) stated that Norway spruce trees could show a positive response in tree physiology and root biomass with the application of 5 tonnes ha^{-1} of ash on sandy nutrient poor soil. The field experiment has three fixed factors: amount of biochar, amount of ash, and tree species. The biochar and ash treatment levels are 0, 1, and 10 tonnes ha^{-1}, which resulted in nine different treatment combinations.

SEEDLING SOURCES AND PLANTING

Seedlings were planted during a one week period in May 2012. They were planted 0.5 m apart and the side of the plot (north/south) that the white spruce (Sw) or black spruce (Sb) seedling were planted was randomly chosen using a number generator in Excel. The seed source for the Sb was from a first generation seed orchard located at the Kriekman Orchard in the Quetico Breeding Zone (zone 12 and 13 on Figure 7). The seeds were sown in April 2011 and grown at Hill's Greenhouse (Murillo, Ontario). The Sw was from a general bush seed collection in seed zone 13 and grown at PRT Growing Service Ltd (Dryden, Ontario). The seeds were sown in March 2011. The jack pine seed source was from a first generation seed orchard at Kakabeka Orchard in the Lake Nipigon West Breeding Zone (zone 7, 13, and 14). The seeds were sown May 2011 and grown at Hill's Greenhouse. All seedlings were lifted in November 2011 and

overwintered in frozen storage. Within one month after planting, the weeds became difficult to control. Spraying the plots was attempted in late June 2012, but due to wind and not being able to properly cover the seedlings, only four plots were sprayed with herbicide (Glyphosate). All of the 45 plots were sprayed a year later in late June 2013 with the same herbicide.

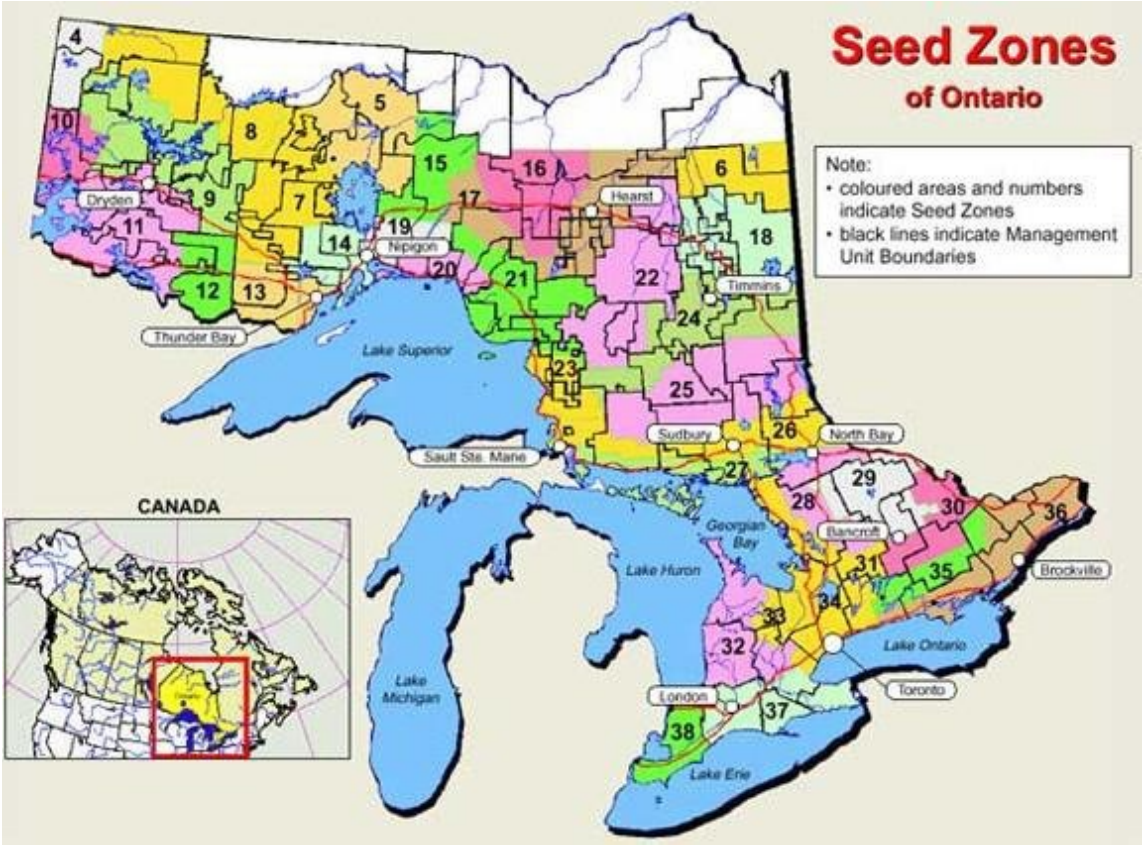

Figure 7. Seed zones of Ontario. Source: www.mnr.gov.on.ca.

BIOCHAR, ASH AND SOIL PHYSICAL AND CHEMICAL CHARACTERIZATION

The biochar and ash samples were tested for bulk density (from a pile); moisture and organic matter content (after air-dried); pH; exchangeable Ca, K, Mg, Na; total C, N, S; available N (NH_4-N, NO_3-N); and total heavy metals Al, B, Cu, Fe, Mn, Ni, P, Zn as outlined in Table 4 (see Appendix II for full descriptions of methods).

Soil samples from the top 10 centimeters of each plot (one sample from each subplot combined into one sample) were taken before the biochar/ash treatment addition (pre-treatment) and at the end of the first growing season in September 2012 (post-treatment). The soil, biochar, and ash samples were analyzed at the FoReST Lab at Lakehead University. Sample preparations included air drying, grinding and sieving through a 2 mm sieve (Kalra and Maynard 1991).

Pre- and post-treatment soil tests were conducted for the following physical and chemical components (Table 4): bulk density (only done post-treatment); soil water potential; moisture and percent organic matter content (LOI); soil texture (pre-treatment samples only); pH; electrical conductivity (EC); exchangeable Ca, K, Mg, Na; eCEC (estimated cation exchange capacity); total C, N, S; available N (NH_4, NO_3); extractable P; extractable Fe, Mn, Cu, and Zn; and total heavy metals Al, B, Cu, Fe, Mn, Ni, P, Zn as outlined in Table 4 (see Appendix II for detailed methods).

SOIL BIOLOGICAL PROPERTIES

Samples were collected in October 2012. Soil samples (top 10 cm) from blocks 1, 3, and 5 were collected by selecting five locations within each subplot and combining these samples into one bag. Each sample bag was stored in a freezer with temperature set to -1°C. A portion of each sample was used to conduct two soil biological tests and the analysis for mineralizable N (Table 4). Soil biological tests included soil microbial biomass, and soil respiration (see Appendix II).

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Table 4. List of methods used for analysis of soil samples.

Analysis	Description of Method	Reference
Bulk Density	183.9 cm^3 metal cylinder into fresh soil	(Culley 1993)
Soil Water Potential	Field Capacity	(Livingston 1993)
Moisture Content and Loss on Ignition	LECO Thermogravimetric to 105°C (moisture) and 375°C(LOI)	(Kalra and Maynard 1991)
Soil Texture	Hydrometer	(Kalra and Maynard 1991)
pH	H_2O suspension	(Kalra and Maynard 1991)
Electrical Conductivity	1:2 soil-to-water suspension	(Rhoades 1982)
Exchangable Ca, Mg, K, and Na	1M ammonium acetate extraction	(Simard 1993)
Estimated Cation-Exchange Capacity	Calculation based on exchangeable Ca, Mg, K, and Na	(Chapman 1965)
Total C, N, and S	dry combustion using a LECO CNS 2000	(Matejovic 1997)
Available N	1:10 ratio soil-to-2M potassium chloride extraction	(Kalra and Maynard 1991)
Mineralizable N	4 M KCl extraction following a 14 day anaerobc incubation	(Powers 1980)
Extractable Fe, Mn, Cu, and Zn	1:2 soil-to-0.005 M DTPA solution extraction	(Liang and Karamanos 1993)
Extractable P	Olsen P 1:20 soil-to- 0.5M sodium bicarbonate extraction	(Schoenau and Karamanos 1993)
Acid Digestable ‘Total’ Heavy Metals	concentrated nitric acid and perchloric acid digestion	(Kalra and Maynard 1991; Miller 1998)
Microbial Biomass	chloroform fumigation and 1:2 soil-to- 0.5M K2SO4 extraction	(Voroney and Winter 1993)
Soil Respiration	LiCor 8100A with a 10cm survey chamber	(LI-COR 2005)

PLANT RESPONSE MEASUREMENTS

Seedling measurements and sampling occurred over the course of two growing seasons (August 2012 and 2013). Response variables included mortality, tree height (total and annual increment), and foliar nutrients. Tree height was taken by measuring (nylon measuring tape) the height of previous year's growth and the total height of the seedling (the calculation for relative growth is shown in Appendix II). Foliage samples were taken in September 2012 from five randomly selected seedlings within each split plot and dried in an oven at 85°C for 2 hours. Foliage samples were analyzed using the same method used to analyze soil samples for total N (dry combustion) and total heavy metals in Table 4 (see Appendix II for full description). The foliage analyses included total concentrations of Al, B, Ca, Cu, Fe, K, Mg, Mn, N, Na, P, S, and Zn. Total needle nutrient content was calculated using foliar concentrations and needle mass determined by weighing 100 oven dried needles.

Possible competition with weeds was also evaluated in October 2012 and July 2013. In 2012, a visual survey was done on each plot. A 1 m x 1 m area was randomly located and percent cover was estimated. In the summer of 2013, weed biomass samples were taken from a section of each split plot. All weeds in a 1.5 m x 0.5 m quadrat (between two rows of four spruce seedlings) were collected. It was noted that some roots could not be easily removed from the soil and in those cases the remaining roots were not extracted in order to insure the seedling roots remained undamaged. The samples were air dried in paper bags. The roots and tops for each split plot were separated. At the same time, excess soil was removed from the weed samples. The samples were oven dried at 105°C for 2 hours and then weighed.

DATA ANALYSIS

Data was analyzed using IBM SPSS Statistics, Version 21 (IBM 2012) software. Depending on the dataset, the data was analyzed using a one-way ANOVA, ANCOVA, or repeated measures approach. The following linear model was used for the ANOVA for this experimental design:

$$Y_{ijklmn} = \mu + Block_i + \delta_{(i)j} + Biochar_k + Ash_l + BiocharAsh_{kl} + \varepsilon_{(ijkl)m}$$

Where i=5, j=1, k=3, l=3 and m=1. i=number of blocks (Random); j= the random effect of the j^{th} treatments replication within i^{th} block, k= 0, 1, 10 tonnes ha^{-1} biochar treatments (Fixed); l=0, 1, 10 tonnes ha^{-1} ash treatments (Fixed), and m= the random effect of the field site within the k^{th} and l^{th} treatments within the j^{th} treatment replications within i^{th} block. The interactions with two or more variables were pooled if there was no significant effect (significance above 0.25). In order for the ANOVA to accurately make interpretations of the population it assumes that the variance of residuals is normally distributed and the random error's variance from all treatments are the same (test of homogeneity) (Triola *et al.* 2011). The standardized residuals of the data are used because they are not affected by the factors being tested which may have different means. Normality can be tested visually using a histogram of standardized residuals fitted with a normal distribution curve and using the Shapiro-Wilk's test on population residuals, which tests if the null hypothesis came from a normally distributed population of data (Triola *et al.* 2011). If the Shapiro-Wilk p-value is above 0.05 it means the residuals of the population are normally distributed at the 0.05 alpha level (Triola *et al.* 2011). A Bartlett test or Levene's test can be used to test for homogeneity across groups

and similar to the Shapiro-Wilk test if the p-value is above 0.05 it means variances of the population across groups is similar (Triola *et al.* 2011).

An ANCOVA is similar to an ANOVA except initial values for the same analysis are used as a co-variate (Field 2013). ANCOVA is performed to remove a continuous variable that influences the dependent variable but is not a part of the experimental factors (Field 2013). Using pre-treatment values as co-variants removes a bias in the data by first running a linear regression analysis on the dependent and the co-variant (Field 2013). The assumptions of ANCOVA are the same as ANOVA but with two additional assumptions (Field 2013). The first assumption is that co-variant is independent of the treatment effect and the second assumption is the homogeneity of regression slopes in the data (Field 2013). We accept the first assumption since the pre-treatment samples were taken before any treatment was applied. Homogeneity of regression means the linear relationship of dependent variable to co-variants is the same for all of the data (Field 2013). This assumption is tested by running an ANCOVA where the co-variant and the independent variable are interacting and the relationship is significant; if not, then you can assume homogeneity of regression slopes (Field 2013).

Respiration data was subject to repeated measure ANOVA, as the same samples were analyzed for the same variable (mean CO_2 emitted) five times (Field 2013). Repeated measures ANOVA includes an assumption of sphericity (Field 2013). This assumption means that the variances of all the conditions are equal and the co-variance between conditions are equal (Field 2013). A Mauchly's test was performed to test sphericity (Field 2013). However, the assumption was not valid (significance seen for

the Mauchly's test) so the Geenhouse-Geisser correction factor was used in the ANOVA (Field 2013).

Of the properties that showed a significant result for treatment (ANOVA/ANCOVA) a comparison was done using the means of the 9 treatments for both the pre- and post-treatments. These figures were used to analyze how each treatment combinations affected the overall significance of each treatment type. They were used to analyze how treatment affected the each property (increase/decrease) and at which treatment level there was a significant effect. It was also used to show the differences seen between the pre-treatment to post treatment analysis.

Pre-treatment soil chemical analysis showed that there was a significant block effect for most of the chemical properties. This includes exchangeable Ca, Mg, and extractable P; available NH_4, total S, extractable Zn, Mn, Fe, and Cu; EC and H ion (pH); 'total' B, Cu, Fe, Ni, and Zn. When the concentration means of the five blocks were compared two patterns were observed. One pattern was a decreasing mean of concentrations from block 1 to 5 or west to east (

Figure 8). The second pattern was block 3 with the highest concentration and block 5 with lowest concentration (Figure 9). The block effect could have also occurred in post-treatment data due to weed cover/competition differences over the five blocks as seen in Figure 10 and Figure 11. Figure 10 illustrates that the most ground cover was found in blocks 1 and 3 with the least in block 5 (4 plots in block 5 were sprayed with herbicide in June 2012). Blocks 1 and 2 had the highest weed biomass and 5 had the least (Figure 11). These figures differ greatly in the results found in blocks 2 and 3. Due to the clear block effect, all data analysis included block as a factor.

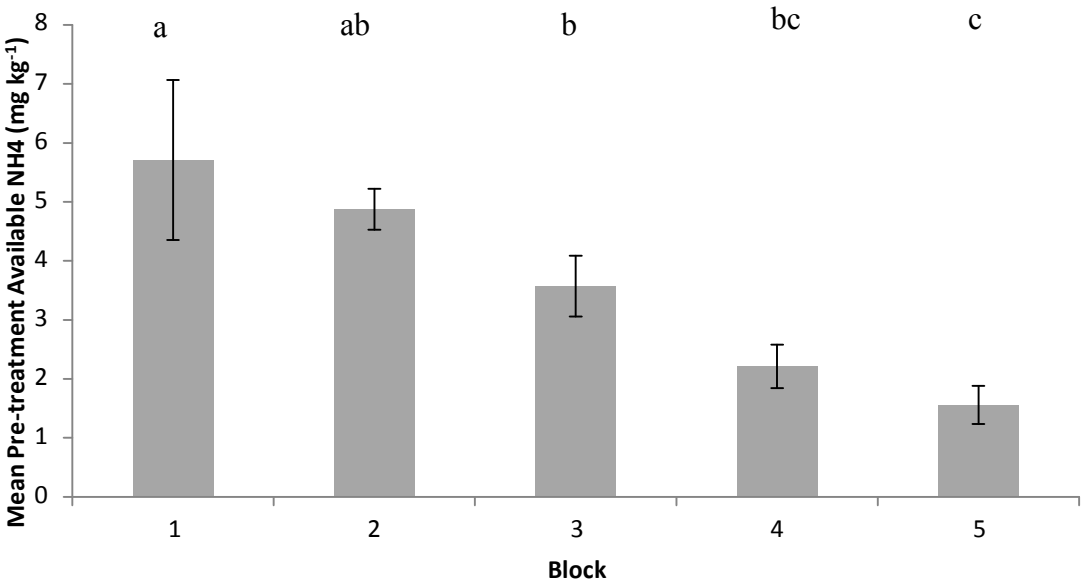

Figure 8. Pre-treatment soil analysis of available NH_4 concentration (mg kg^{-1}) in each block as representation of block effect pattern. The error bars represent +/- 1 SE.

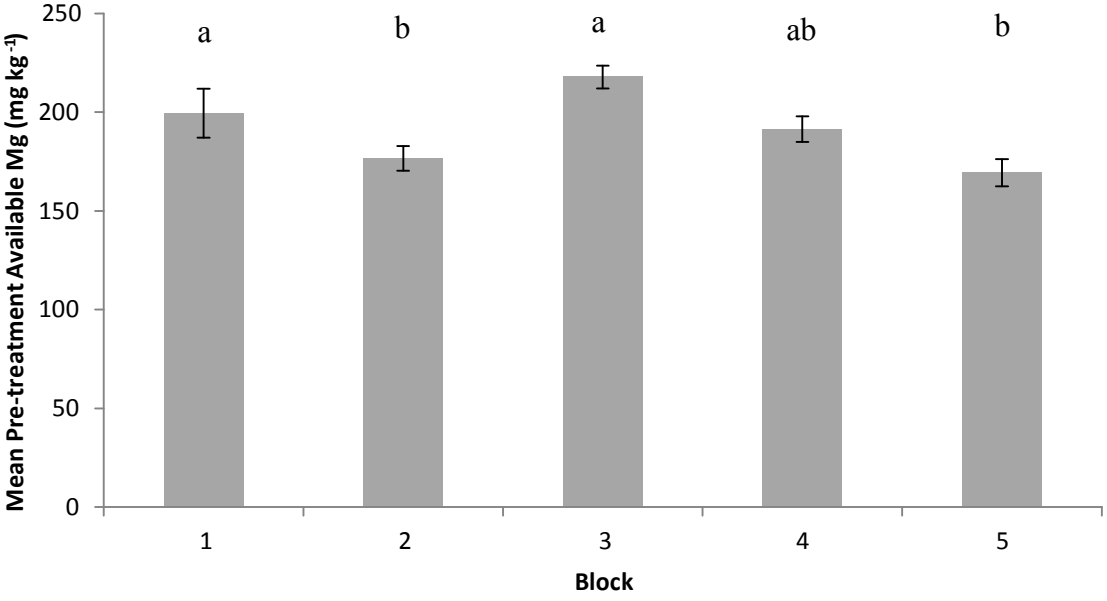

Figure 9. Pre-treatment available Mg concentration (mg kg^{-1}d.w.) in each block as a representation of block effect pattern. The error bars represent +/- 1 SE.

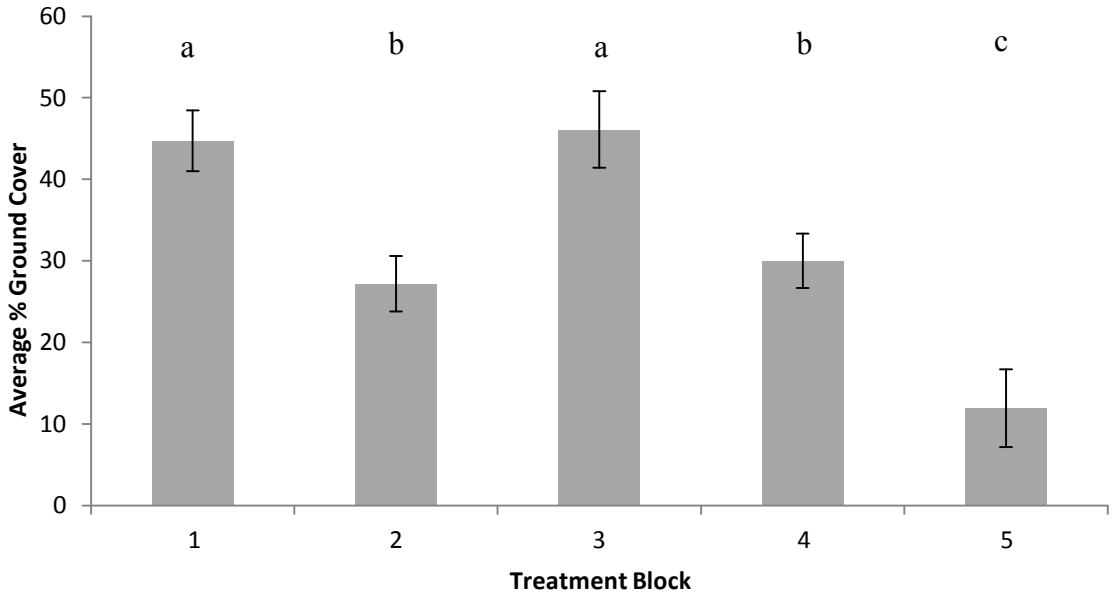

Figure 10. Average estimated percent ground cover of the blocks in October 2012. The error bars represent +/- 1 SE.

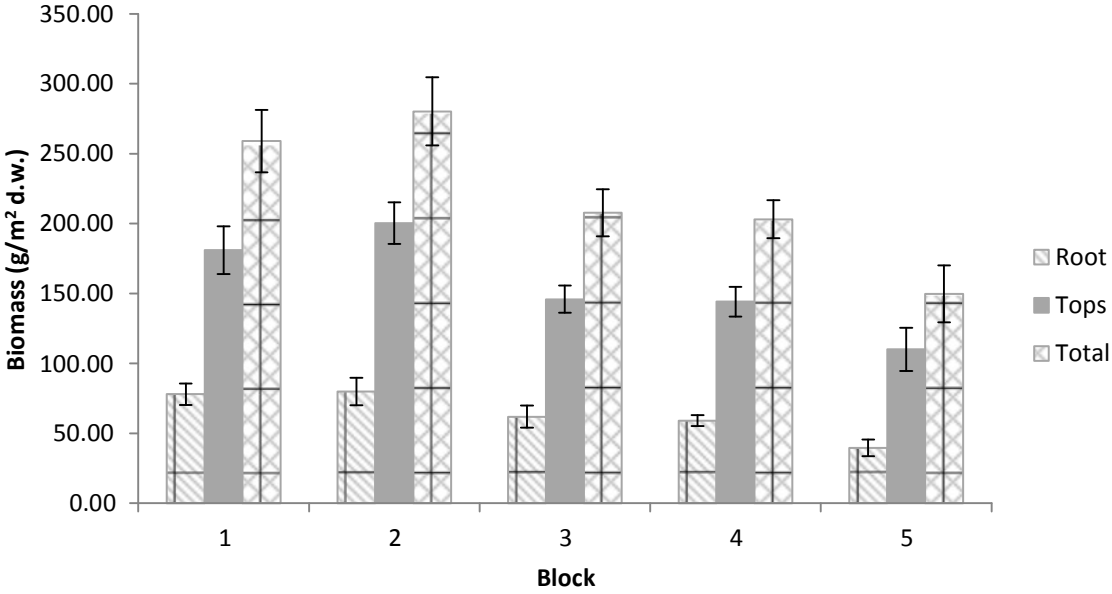

Figure 11. Mean weed biomass of each block in July 2013. Error bars represent +/- 1 SE.

RESULTS AND DISCUSSION

BIOCHAR AND ASH MATERIAL

Table 5 summaries the physical and chemical properties of the biochar and ash, the literature ranges of chemical properties of biochar and ash, and pre-treatment soil physical and chemical properties. The ash used in this study was clearly closer to the definition of boiler wood ash when compared to the biochar. Visually the biochar and ash were different; the biochar was mainly coarse and black while the ash was light grey and fine. The bulk density of the biochar was 0.22 g cm^{-3} and the ash was 0.57 g cm^{-3}. Bulk density of biochar indicates that it is more porous than the ash, which is a characteristic of biochar structure (Downie *et al.* 2009; Verheijen *et al.* 2010). Compared to biochar, ash was lower in total C and N; pH was high at 12; it also contains higher amounts of exchangeable Ca, K, and 'total' Al and Fe. The biochar fits the chemical properties of biochar as defined by Chan and Xu (2009) (Table 1) for everything except total N. Biochar total C concentration was 39.2% which is lower than the mean C concentration for biochar (54.3%) but was also higher than the average for ash which is 26%. Furthermore, the ash used in this study was on the lower end of the range for most chemical properties (pH, K, and P) compared to other field studies (Branryd and Fransman 1995; Ernfors *et al.* 2010; Feldkirchner *et al.* 2003; Mandre *et al.* 2004; Park *et al.* 2005; Perez-Cruzado *et al.* 2011; Rumpf *et al.* 2001). The ash was much higher than other studies in C, N and S (Feldkirchner *et al.* 2003; Park *et al.* 2005; Perez-Cruzado *et al.* 2011).

When comparing the biochar and ash nutrient and metal concentrations with the pre-treatment soil in Table 5 it is clear that applications could impact soil chemical properties, and to a greater extent for ash. Many properties are high for both biochar and ash compared to the untreated soil. Table 5 shows that for many properties the pre-treatment soil is representative of typical soils found in Thunder Bay, Ontario area. However, some effects of biochar and ash application on soil exchangeable Ca, K, and Mg may not be as great as it would be in typical soil outside of the old nursery site, because the site has higher than average values for these nutrients. In particular, the effect of exchangeable K on soil and foliage maybe lower than in typical soil, since it is outside of the typical range.

Table 5. Physical and chemical properties of biochar, ash, and pre-treatment soil.

Analysis	Units	Biochar	Literature Range[1]	Ash	Literature Range[1]	Pre-Treatment Soil	Pre-Treatment Range	Average Typical Soil[2]	Typical Soil Range[2]
Sand	%					74	71-78	83.0	66.5-93.7
Silt	%					20	16-22	10.6	5-19.5
Clay	%					6	5-7	6.4	1.3-14
Bulk Density	g cm^{-3}	0.22	0.08-1.2	0.57					
Moisture	%	56.6		14.6		1.8	1.5-2.2		
LOI (Organic C)	%	40.4		11.8		4.5	3.8-5.2		
pH (H_2O)		8.0	7.2-10.4	12.0	12.35-13	5.71	5.29-6.04	6.1	5.4-7
EC	uS cm^{-1}	3.8		18.8		63.5	35.8-95.9		
Total C	%	39.2	15.14-87	11.6	7.82-11.6	1.95	1.54-2.37	4	1.7-6.1
Total N	%	0.3	0.31-1.9	0.2	0.06-0.19	0.13	0.10-0.17		
Total S	%	0.0	0.02-0.085	2.9	0.03-1.13	0.020	0.014-0.028		
Available NH_4	mg kg^{-1}	1.9		0.1		3.6	0-11.6		
Available NO_3	mg kg^{-1}	13.7		3.4		6.7	0-25.1		
Exchangeable Ca	mg kg^{-1}	10801.5	330.7-6440	37593.2		1340.4	1068.1-1651.2	979.1	276-2588.5
Exchangeable K	mg kg^{-1}	2428.7	19.9-1130	17934.9		146.3	113.1-208.8	54.5	36.8-78.9
Exchangeable Mg	mg kg^{-1}	1151.1	48.9-291	699.9		199.7	148.9-261.0	178.4	72.9-473.1
Exchangeable Na	mg kg^{-1}	412.2		2592.6		10.76	7.78-14.90		
Extractable P	mg kg^{-1}					122.4	68.8-161.2		
Extractable Cu	mg kg^{-1}					0.69	0.57-0.87		
Extractable Fe	mg kg^{-1}					208.59	141.9-288.97		
Extractable Mn	mg kg^{-1}					10.39	7.83-14.27		
Extractable Zn	mg kg^{-1}					1.39	1.02-1.85		
'Total' Al	mg kg^{-1}	4292.4		28286.6		13215	11055-14373		
'Total' B	mg kg^{-1}	24.9		103.4		7.8	6.0-10.1		
'Total' Ca	mg kg^{-1}	28596.7	1400-10000	141083.6	43250-249000				
'Total' Cu	mg kg^{-1}	12.4		122.0		18.3	15.4-27.4		
'Total' Fe	mg kg^{-1}	7317.9		19565.6		52201.1	6835.8-41430.7		
'Total' K	mg kg^{-1}	2517	2811-26000	24903.2	22000-74000				
'Total' Mg	mg kg^{-1}	2960.3	1228-6000	17659.5	9100-29000				
'Total' Mn	mg kg^{-1}	916.7		3710.6					
'Total' Na	mg kg^{-1}	897.8		6007.6	3000-17900				
'Total' Ni	mg kg^{-1}	bdl		30.7		33.1	24.1-42.2		
'Total' P	mg kg^{-1}	1000	180-2177	8000	5000-23000				
'Total' Zn	mg kg^{-1}	64.7		1502.1		75.2	56.3-96.2		

[1]References in Appendix I

[2]Data from five typical and untreated locations around Lakehead University, Thunder Bay (Lakehead University 2014).

TREATMENT EFFECT ON SOIL PHYSICAL PROPERTIES

Bulk density was not significantly different between the treatments and untreated control plots (mean range is 0.99- 1.23 g cm^{-3}) (Figure 12). However, Figure 12 shows that with the application of biochar at 10 tonnes ha^{-1} increases bulk density slightly (not significantly), similar to the study by Husk and Major (2010). This is contrary to what would be expected of biochar (Husk and Major 2010; Novak *et al.* 2009). Some possible explanations for the increase are that biochar happens to fill the pore spaces between the soil particles better than ash or the particle density of ash is less than biochar (Brady and Weil 2002). Biochar application to soil can affect the soil's physical structure, such as water retention and bulk density (Downie *et al.* 2009). Husk and Major (2010) working in Quebec, Canada noted a slight increase (not significant) in bulk density with the application of biochar after a year. Chen *et al.* (2010) found that an increase of 9-12% in water holding capacity with biochar application. This was expected, since biochar is a porous material and this increased surface area could potentially increase water holding capacity (Downie *et al.* 2009). Bulk density is affected by the soils organic matter, texture, material, and porosity (Chaudhari *et al.* 2013). The site of the experiment has a sandy loam to loamy sand texture and adding biochar could potential improve sandy types of soils because they generally have a limited water capacity (Downie *et al.* 2009). A laboratory trial of biochar added to loamy sand soil showed that the addition of biochar increased water retention by 6.7 to 15.9% (Novak *et al.* 2009) . However, in the current study the field capacity showed no significant difference between ash, biochar and control in post-treatment the analysis (Figure 13).

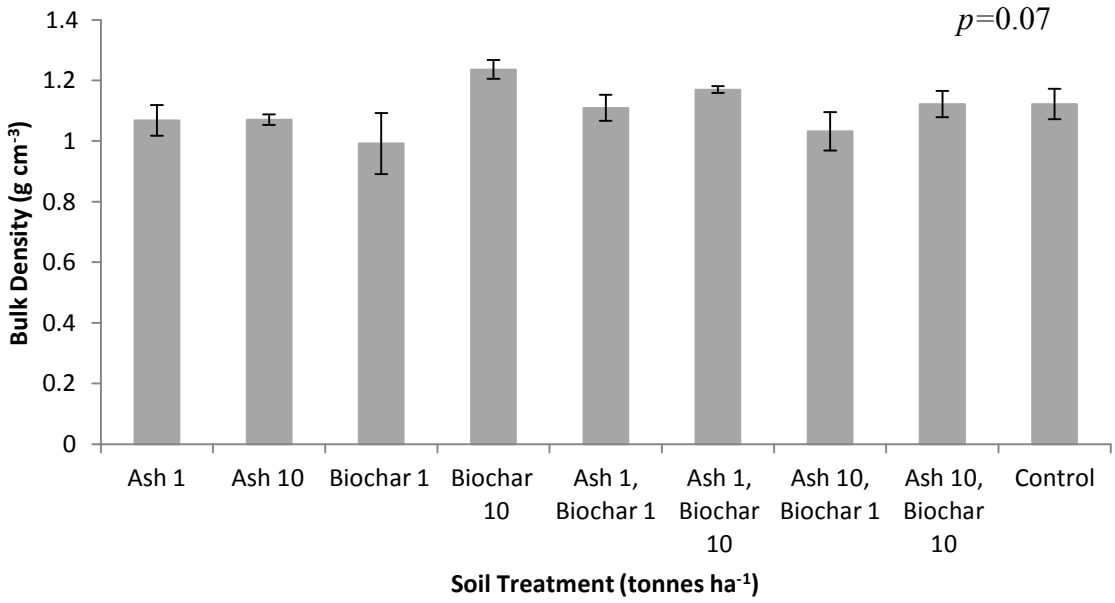

Figure 12. Mean bulk density for all block for each treatment (n=5). The error bars represent ± 1 SE.

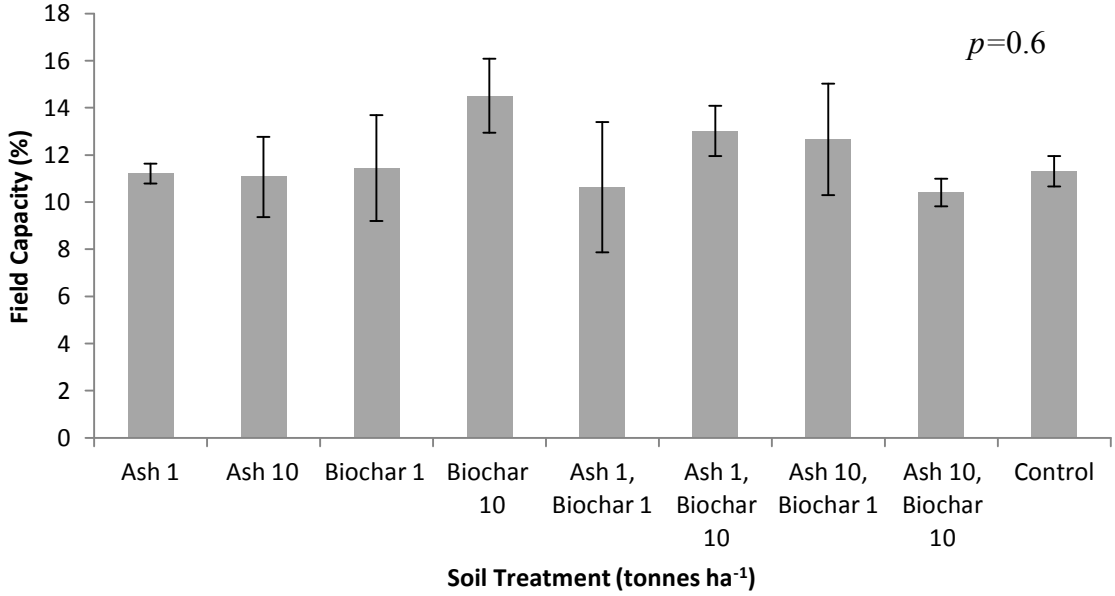

Figure 13. Mean field capacity for all each treatment in 3 blocks (n=3). The error bars represent ± 1 SE.

SUMMARY OF ANOVA/ANCOVA RESULTS

Table 6 and Table 7 are summary tables of all the soil chemical analysis, soil biological analysis, tree heights, and foliage analysis done in this study. These tables show that many of post-treatment analysis were not significant for biochar (only two properties), while ash application had more significant results. The how and why of the significant properties listed in the following tables will be addressed individually in the rest of the result sections.

Table 6. P-values for soil chemical analysis and tree heights using ANCOVA, p-values <0.05 bolded.

Property	Covariate, df=1	Biochar (Fixed), df=2	Ash (Fixed), df=2	Block (Random), df=4	Biochar x Ash (Fixed), df=4
pH, n=45	**0.020**	0.453	**<0.001**	**0.005**	0.357
EC, n=43	0.906	0.800	**<0.001**	**0.035**	0.682
Exchangeable Ca, n=44	**<0.001**	0.153	**<0.001**	0.322	0.582
Exchangeable K, n=44	0.062	0.525	**<0.001**	0.383	0.051
Exchangeable Mg, n=44	**<0.001**	0.235	**<0.001**	0.312	0.509
Exchangeable Na, n=44	0.499	**0.030**	**0.044**	**0.002**	0.884
Estimated CEC, n=44	**<0.001**	0.127	**<0.001**	0.519	0.556
Total C, n=43	**<0.001**	0.316	**0.014**	0.814	0.106
LOI, n=45	**<0.001**	0.206	0.845	0.357	0.665
Total N, n=43	**0.003**	0.060	0.062	**0.003**	0.276
Total S, n=43	**0.012**	0.060	**0.004**	0.408	0.410
Available NH_4-N	0.563	0.128	**0.029**	**0.007**	0.857
Available NO_3-N	0.529	0.560	0.400	**<0.001**	0.445
Extractable Cu	**0.047**	**0.013**	0.598	**0.004**	0.406
Extractable Fe	**0.015**	0.204	**<0.001**	0.354	0.847
Extractable Mn	0.114	0.050	**<0.001**	0.174	0.172
Extractable Zn	**0.002**	0.147	**<0.001**	0.122	0.858
Extractable P	**<0.001**	0.108	0.760	0.371	0.390
'Total' Al	0.229	0.473	0.948	**0.022**	0.633
'Total' B	0.524	0.573	0.50	**0.025**	0.180
'Total' Cu	0.482	0.342	0.239	0.083	0.767
'Total' Fe	0.992	0.414	0.703	0.178	0.475
'Total' Ni	0.553	0.572	0.998	0.54	0.762
'Total' Zn	0.654	0.815	**<0.001**	**0.029**	0.191
Tree Height 2012 Sb	**0.002**	0.239	0.233	**0.042**	0.879
Tree Height 2012 Sw	**<0.001**	0.934	0.066	0.075	0.475
Tree Height 2013 Sb	0.937	0.610	0.153	**<0.001**	0.695
Tree Height 2013 Sw	0.149	0.729	0.557	**<0.001**	0.411

Table 7. P-values for soil chemical, soil biological, and foliage nutrient analysis using ANOVA, p-value <0.05 bolded.

Property	Biochar (Fixed) df=2*	Ash (Fixed) df=2*	Block (Random) df=4*	Biochar x Ash (Fixed) df=4*
Mineralizable NH_4-N, n=27	0.908	**0.019**	0.144, df=2	0.980
Mineralizable NO_3-N, n=27	0.290	0.661	**0.002**, df=2	0.977
Microbial C, n=27	0.840	0.734	0.113, df=2	0.823
Microbial N, n=27	0.220	0.686	**0.048**, df=2	0.699
Soil Respiration, n=27	0.231, df=3.777	0.906, df=3.777	**<0.001**, df=3.777	0.575, df=7.555
Foliage Al Sb	0.657	0.153	0.292	0.162
Foliage B Sb	0.794	**<0.001**	**0.024**	0.603
Foliage Ca Sb	0.824	**0.023**	0.061	0.596
Foliage Cu Sb	0.781	0.090	0.074	0.667
Foliage Fe Sb	0.870	0.326	0.071	0.331
Foliage K Sb	0.558	**0.035**	0.726	0.541
Foliage Mg Sb	0.720	**0.048**	0.868	0.294
Foliage Mn Sb	0.854	0.358	0.290	0.762
Foliage N Sb	0.713	0.067	**<0.001**	0.390
Foliage Na Sb	0.610	0.341	0.473	0.492
Foliage P Sb	0.848	0.343	0.160	0.260
Foliage S Sb	0.988	**<0.001**	0.497	0.219
Foliage Zn Sb	0.368	0.461	0.105	0.332
Foliage Al Sw	0.874	0.085	0.072	0.439
Foliage B Sw	**0.035**	**<0.001**	**0.003**	0.600
Foliage Ca Sw	0.965	0.701	**<0.001**	0.628
Foliage Cu Sw	0.831	0.853	**0.002**	0.740
Foliage Fe Sw	0.869	0.630	0.053	0.653
Foliage K Sw	0.932	**0.048**	0.244	0.320
Foliage Mg Sw	0.857	0.727	0.052	0.467
Foliage Mn Sw	0.423	0.748	**0.014**	0.526
Foliage N Sw	0.789	0.472	**<0.001**	0.902
Foliage Na Sw	0.453	0.125	0.077	0.846
Foliage P Sw	0.807	0.738	0.196	0.223
Foliage S Sw	0.645	**<0.001**	**0.005**	0.788
Foliage Zn Sw	0.594	0.821	**0.017**	0.617

*df unless stated otherwise for individual properties.

TREATMENT EFFECTS ON SOIL CHEMICAL PROPERTIES

Chemical analyses were performed using soil concentration (mg kg^{-1}) instead of using the bulk density to convert the data into content. This was done because bulk density was not significantly different between the treatments and errors could be introduced by converting the data.

The mean pre-treatment pH at the field site was 5.71 +/- 0.025 SE for all 45 plots (Table 5). Soil pH can affect physical and biological properties (microorganism) in addition to a wide range of other chemical properties (Brady and Weil 2002). For example, increasing pH generally leads to an increase in cation exchange capacity (CEC) (Brady and Weil 2002). Therefore, pH can affect the movement of nutrients and toxins in the soil (Brady and Weil 2002). Post-treatment soil pH increased significantly (decrease in H+ ions) with the application of ash ($p < 0.001$) (Figure 14). The application of biochar alone or any combination of biochar and ash, however, were not significant (p= 0.453) for pH. The application of 10 tonnes ha^{-1} of the ash increased the soil pH by a mean value of 0.84 compared to the control (from 5.63 to 6.47). Similar increases in pH has been observed in most other ash field application studies (Branryd and Fransman 1995; Brunner *et al.* 2004; Ernfors *et al.* 2010; Feldkirchner *et al.* 2003; Mandre *et al.* 2004; Park *et al.* 2005; Perez-Cruzado *et al.* 2011; Rumpf *et al.* 2001; Saarsalmi *et al.* 2004; Sahota 2009; Sartori *et al.* 2007; Staples and Van Rees 2001). The increase in pH is variable for each study but it does seem that the lower the initial soil pH the great effect ash application has on the soil.

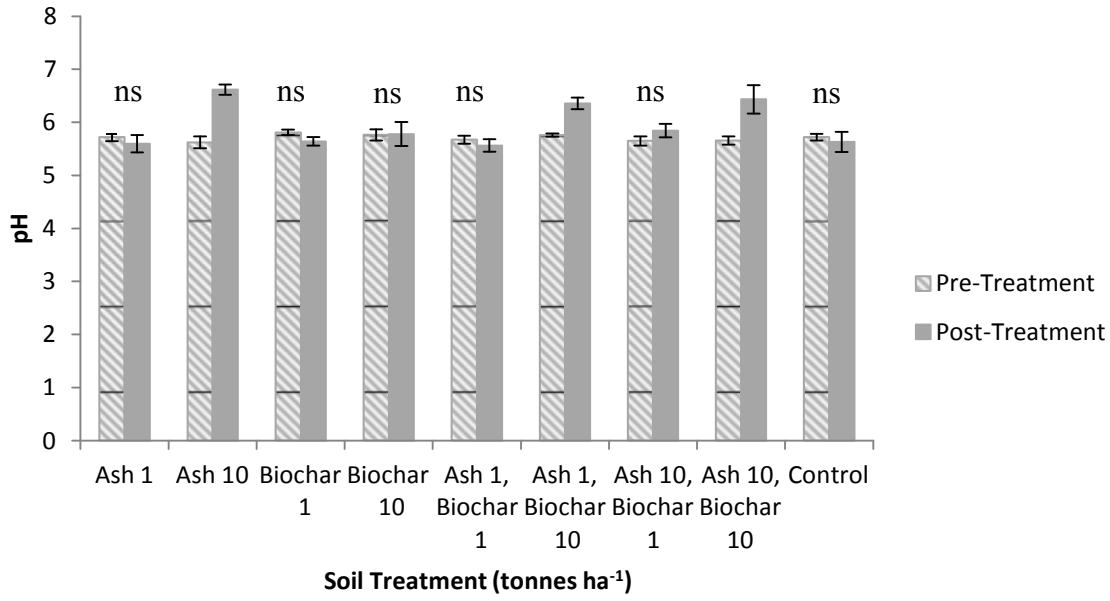

Figure 14. Mean pH for each treatment for all five blocks compared to pre-treatment soil conditions. The error bars represent ± 1 SE.

Electrical conductivity (EC) is an indirect measure of the salinity of the soil, which can affect crop growth (Hendershot *et al.* 1993). Salinity is directly affected by Ca, K, Mg, and Na concentrations in soil (Brady and Weil 2002). The mean EC for ash 10 tonne ha^{-1} treatment post treatment was significantly higher than no ash or 1 tonnes ha^{-1} ash treatments (Figure 15). Hendershot et al. (1993) stated that negative crop response due to EC would be negligible if EC measurements are less than 2000 µS cm^{-1}. However, a study by Staples and Van Rees (2001) in Saskatchewan saw a decrease in white spruce seedling growth after the second growing season with the application of 5 tonnes ha^{-1} of ash when the EC in the top 10 cm of soil went from 20 µS cm^{-1} to 100 µS cm^{-1} due to salinity stress. The application of ash at 10 tonnes ha^{-1} in this study significantly increased the mean EC to 120 uS cm^{-1}, whereas control plots had a mean EC of 50 uS cm^{-1}(Figure 15). This may cause an issue with white spruce seedling growth in the future. With the exception of 10 tonne ha^{-1} treatments the EC decreased

when compared to pre-treatment conditions. A possible explanation for this is a seasonal variation in soil nutrient concentrations (Farley and Fitter 1999). A study in the United Kingdom documented a seasonal change in soil nutrients where there was a peak for some nutrients in spring/early summer, a significant decrease in late summer, and a slight increase in autumn (Farley and Fitter 1999). Since pre-treatment sampling occurred in late spring (end of May, 2012) and the post-treatment in late summer/autumn (late September, 2012) this could explain the variation.

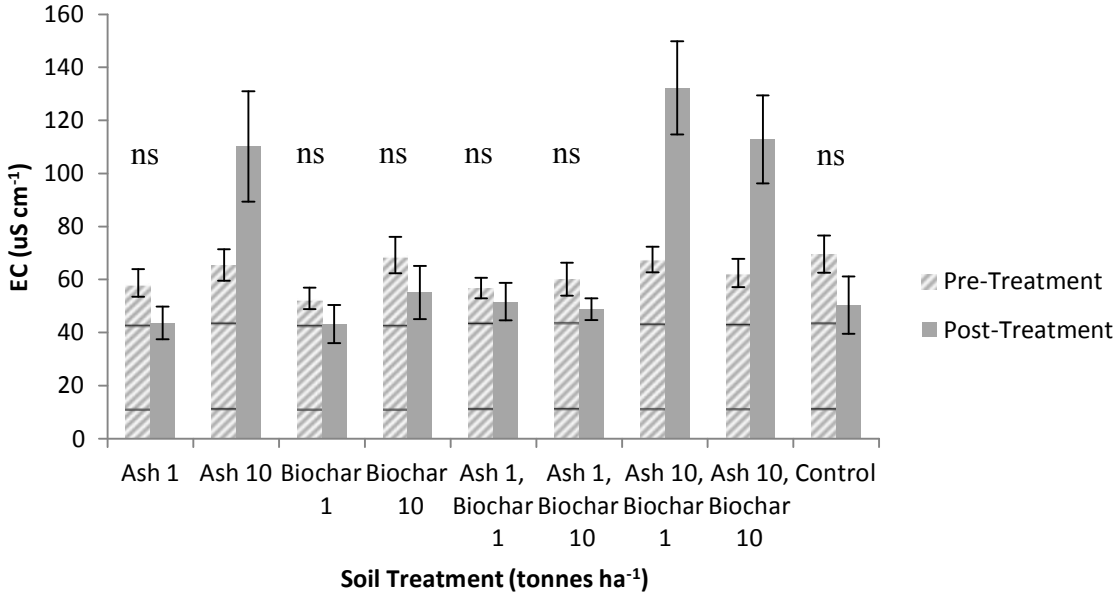

Figure 15. Mean EC (uS cm^{-1}) for each treatment compared to pre-treatment soil conditions. The error bars represent ± 1 SE.

There is a similar pattern between pH, EC, and exchangeable base cation concentrations. Exchangeable Ca, K, Mg and Na all had a significant post-treatment response to the main factor of ash (Figure 16-19). Post- treatment biochar and the biochar/ash interaction were not significant exchangeable Ca, K, and Mg. Only Na significantly decreased with biochar treatment. All base cations except exchangeable

Mg increased with the ash 10 tonnes ha^{-1} application in post-treatment results. In contrast, post- treatment Mg decreased with ash 10 tonnes ha^{-1} treatment. Many field ash studies have seen similar results in increasing exchangeable Ca (Branryd and Fransman 1995; Feldkirchner *et al.* 2003; Park *et al.* 2005; Perez-Cruzado *et al.* 2011; Rumpf *et al.* 2001; Saarsalmi *et al.* 2004; Sartori *et al.* 2007; Staples and Van Rees 2001), and K (Branryd and Fransman 1995; Feldkirchner *et al.* 2003; Mandre *et al.* 2004; Park *et al.* 2005; Patterson *et al.* 2004; Perez-Cruzado *et al.* 2011; Rumpf *et al.* 2001; Sahota 2009; Sartori *et al.* 2007) with the application of ash. Only Sahota et al. 2006 reported an increase in Na concentration. Other field studies that have applied ash showed an increase in Mg concentration with the application of ash, which is contrary to the current study (Feldkirchner *et al.* 2003; Park *et al.* 2005; Perez-Cruzado *et al.* 2011; Rumpf *et al.* 2001; Saarsalmi *et al.* 2004; Sartori *et al.* 2007; Staples and Van Rees 2001). Perez-Cruzado et al. (2011) reported Ca, Mg, and K values that more than doubled in some cases after the application of 10 and 20 tonnes ha^{-1} ash treatments, but the effect only lasted up to 24 months. The time span of the effect ash treatments have on soil nutrients at this site will take further future analysis to determine. Similar to EC, exchangeable K and Na seemed to decrease from the pre-treatment to the post-treatment. The same possible explanation for this is a seasonal variation in soil nutrient concentrations (Farley and Fitter 1999). Estimated cation exchange capacity (eCEC) significantly increased with ash addition (Figure 20). This was anticipated because eCEC is basically a summation of exchangeable base cations. Therefore, the increase seen in exchangeable Ca, K, and Na with the 10 tonnes ha-1 application of ash would mean an increase in eCEC.

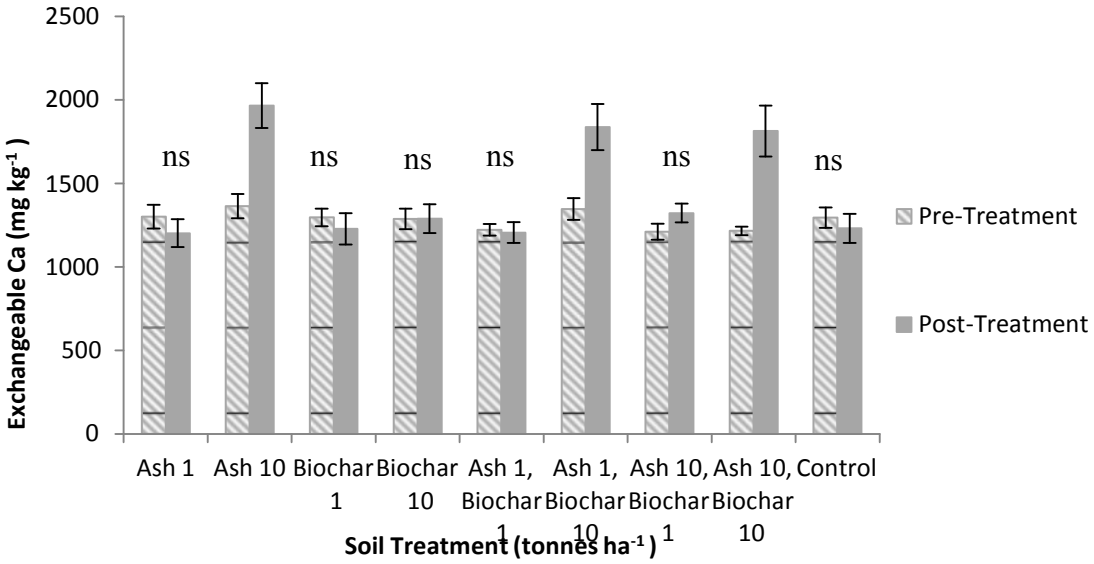

Figure 16. Mean exchangeable Ca (mg kg^{-1}d.w.) for each treatment compared to pre-treatment soil conditions. The error bars represent ± 1 SE.

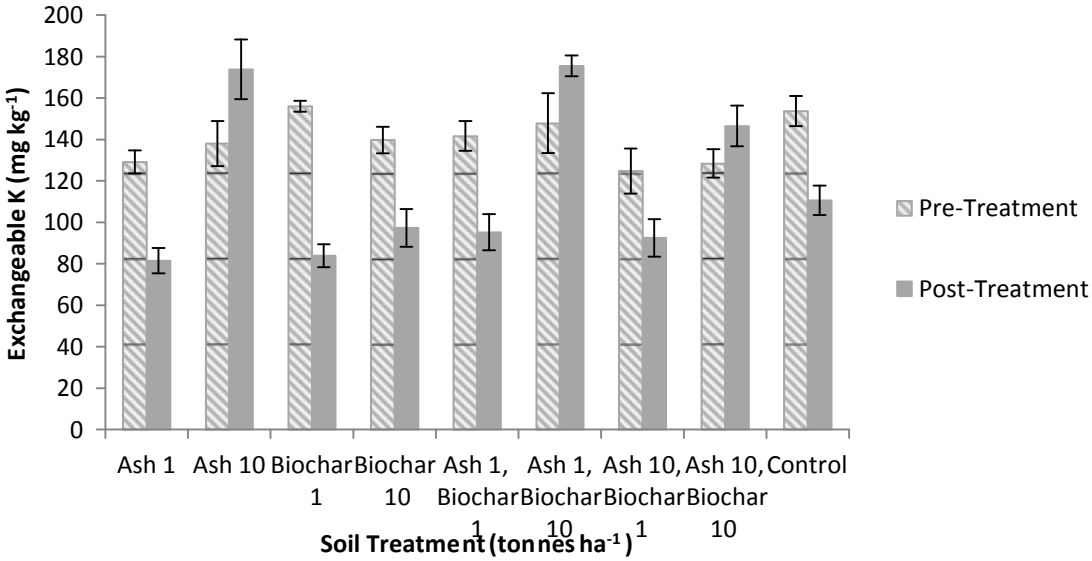

Figure 17. Mean exchangeable K (mg kg^{-1}d.w.) for each treatment compared to pre-treatment soil conditions. The error bars represent ± 1 SE.

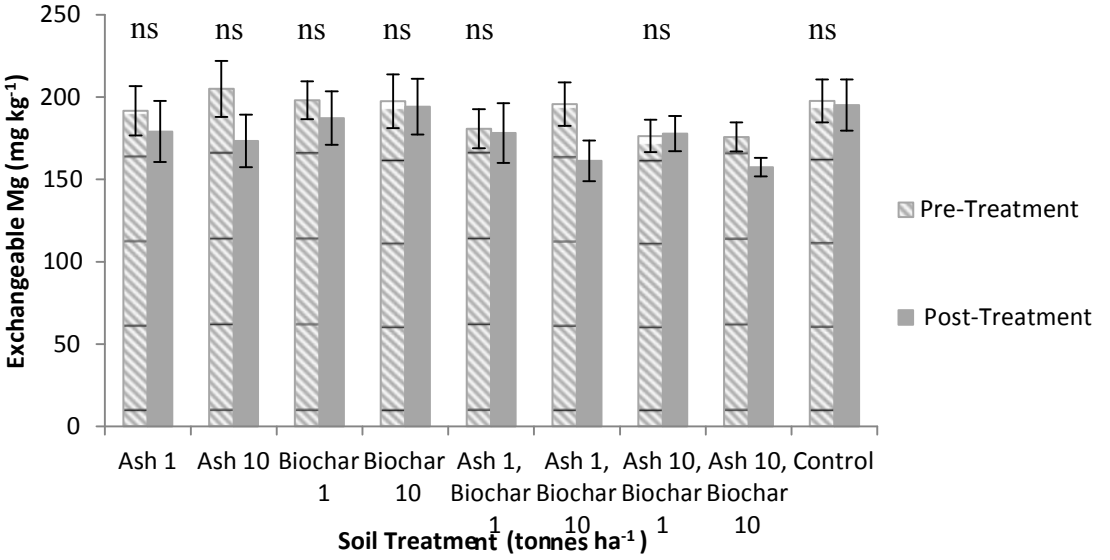

Figure 18. Mean exchangeable Mg (mg kg^{-1}d.w.) for each treatment compared to pre-treatment soil conditions. The error bars represent ± 1 SE.

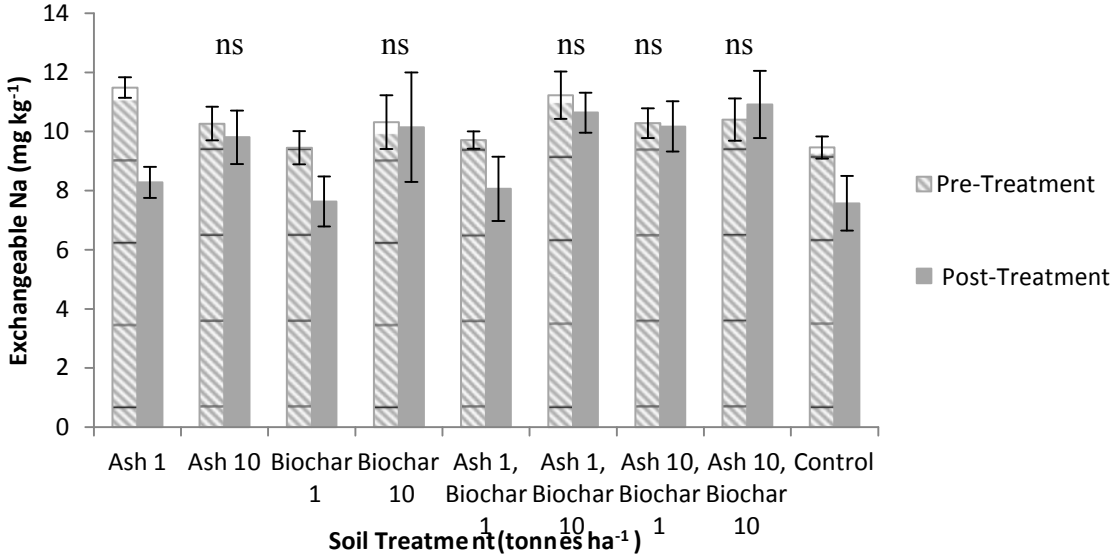

Figure 19. Mean exchangeable Na (mg kg^{-1}d.w.) for each treatment compared to pre-treatment soil conditions. The error bars represent ± 1 SE.

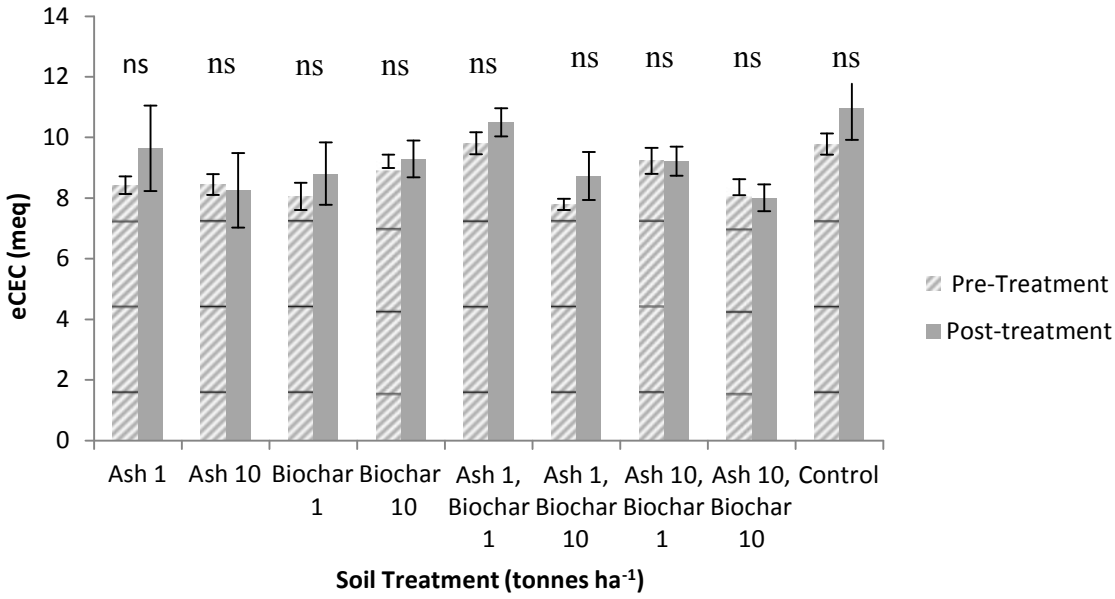

Figure 20. Mean eCEC (meq $100g^{-1}$) for each treatment compared to pre-treatment soil conditions. The error bars represent 1 ±SE.

There was no significant difference between the post-treatments for total N from the combustion analysis. However, there was a significant difference with the application of ash for total C, and S. Total C was only significant for biochar application when pre-treatment data was used as a co-variant and showed a slight decrease with biochar application at 1 tonnes ha^{-1}. However, when LOI which is a measure of total organic C was analyzed and the results were not significant for both ash and biochar treatments. When comparing the means of total S the application of ash at 10 tonnes ha^{-1} is higher than the 0 and 1 tonnes ha^{-1} application (Figure 21). Ash is normally low in S due to the high temperature of the boiler but the ash used in this field study had a high percent S (Pitman 2006). A possible explanation could be the source biomass feed (bark and effluent sludge). A previous unpublished study was done by the author on the ash and hogfuel used at this power boiler in 2011 (Resolute Forest Products 2011). This study analyzed ashed pressed secondary effluent sludge, which makes 8-14% of the

biomass feed used in the power boiler. The ashed sludge showed a 2.1% 'total' acid digestible S concentration. This S concentration was similar to what is seen in the ash collected from this boiler in 2011 using the same analysis, which may account for the increased S in the soil with 10 tonnes ha^{-1} application of ash. The only other ash study in the literature that found an increase in S was Patterson *et al.* (2004), which saw an increase in available S at the application rates of 6, 12, 25 tonnes ash ha^{-1}.

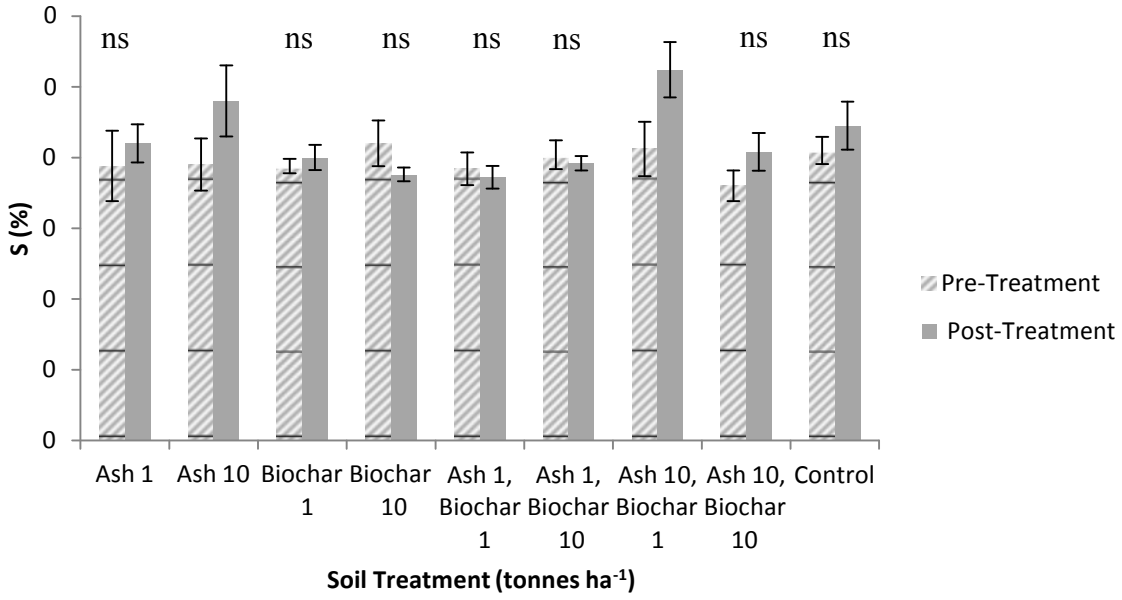

Figure 21. Mean % S by combustion for all treatments compared to pre-treatment soil conditions. The error bars represent ± 1 SE.

While there was no significant difference seen in post-treatment total N concentration the analysis of available and mineralizable NH_4 in the post-treatment soil was significant. The application of ash at 10 tonnes ha^{-1} shows a decrease in available and mineralizable NH_4 (Figure 22 and 23). There was no significant difference for available and mineralizable NO_3. The decrease in NH_4 could be from an increased uptake in those treatment plots by seedlings, nitrification, or immobilization (Brady and Weil 2002). Results revealed later in the study suggest increased uptake is unlikely.

There could be an increase in nitrification/mineralization due to increase in pH, and aeration of the soil from the application of treatment with ash 10 tonnes ha^{-1} (Brady and Weil 2002). If nitrification increases then there may be an increase in leaching of highly mobile NO_3-N (Brady and Weil 2002). The other possibility is immobilization by soil microorganisms, but this is not be likely because C:N ratio for each treatment wasn't above 20:1 (Brady and Weil 2002). The changes from pre- to post-treatment of available N may be due to microbial activity and up-take of nitrogen by the seedling and weeds over the warmer months (Brady and Weil 2002). Moilanen *et al.* 2002 study experienced an increase in nitrifying bacteria activity which increases nitrogen in the soil. Mandre *et al.* 2004 study showed a decrease in N with increasing ash treatments with nutrient poor sandy soil.

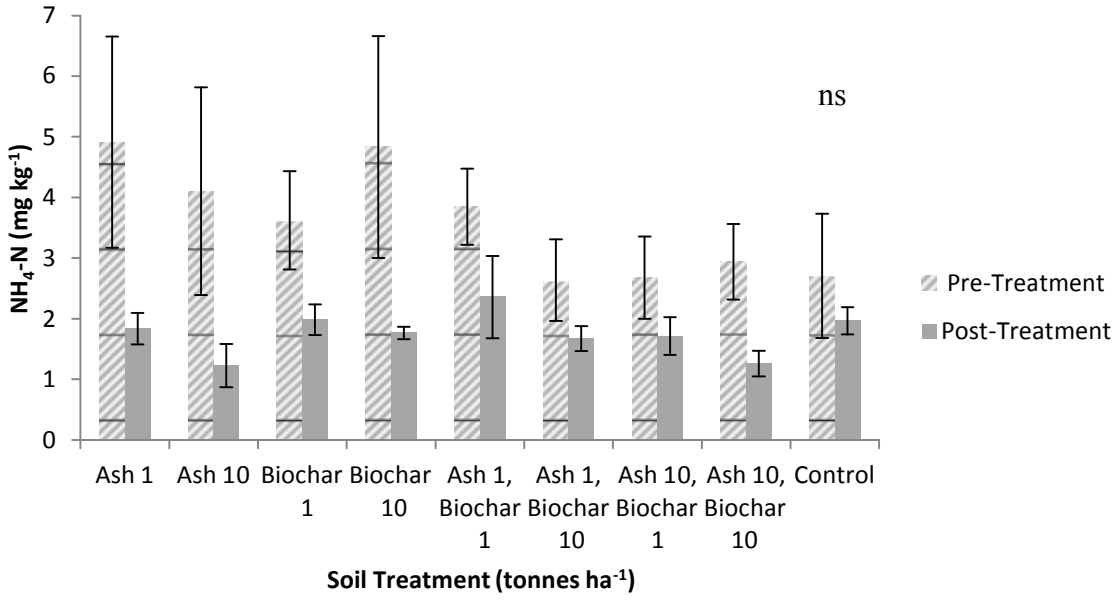

Figure 22. Mean NH_4-N concentrations (mg kg^{-1}) for each treatment compared to pre-treatment soil conditions. The error bars represent ± 1 SE.

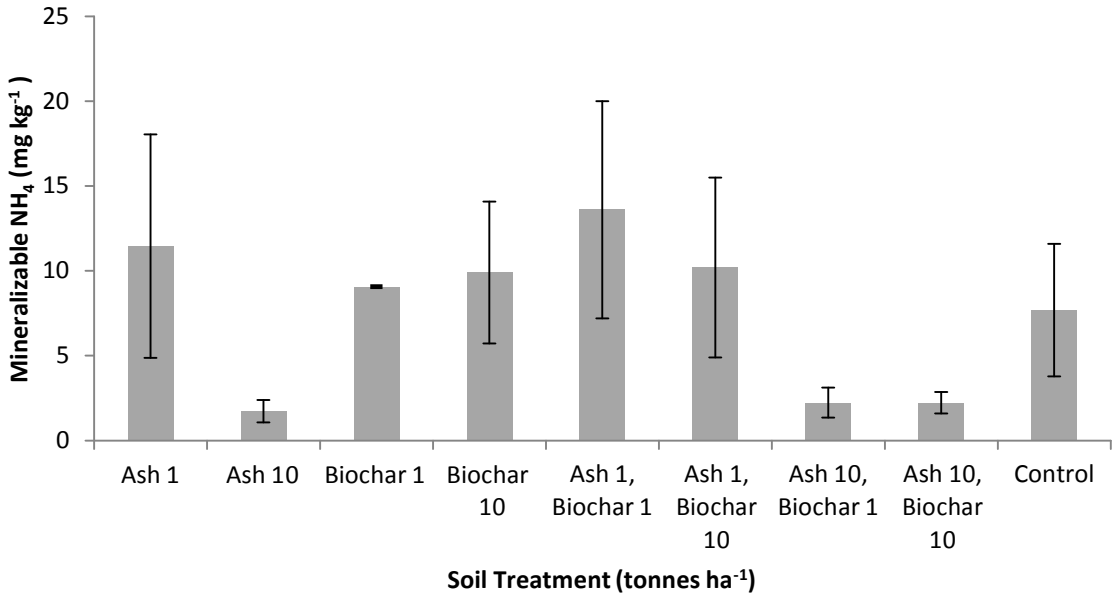

Figure 23. Mean mineralizable NH_4 (mg kg^{-1}) for each treatment. The error bars represent ± 1 SE.

Similar to base cations, micronutrient availability (Cu, Fe, Mn, and Zn) is greatly affected by pH (Brady and Weil 2002). The only micronutrient analyzed by the DTPA extraction method that didn't show a significant difference with biochar or ash application was Fe. Availability and absorption of Cu is a function of pH (Kabata-Pendias and Pendias 1984). Available Cu concentrations are significantly different with the application of biochar but not ash. When looking at the biochar treatment it is clear that the application of biochar at 10 tonnes ha^{-1} treatments decreased available Cu (Figure 24). Major et al. (2010b) observed a decrease in Al and Fe after the application of biochar due to the increase in pH and base cations. Uchimiya *et al.* (2010b) suggested that heavy metals could be retained by the addition of biochar to soil due to changes in pH. Major *et al.* (2010b) stated that the exchangeable micronutrients were being displaced on cation exchange sites by macronutrients. The same process could be happening to exchangeable Cu at 10 tonnes ha^{-1} and possibly at the ash sites, but biochar

wouldn't add as much Cu into the soil as the ash applications when comparing 'total'acid extractable Cu concentrations of the two materials (Table 5).

Unlike Cu, the micronutrients Mn and Zn didn't react significantly with the application of biochar. Both Mn and Zn were significantly different with the application of ash, and in particular ash application at 10 tonnes ha^{-1}. Available Mn concentration decreased with increasing ash application (Figure 25). Increasing pH and base cation with ash addition maybe the main cause of this reaction to treatment, because of the displacement of Mn on cation exchange sites and the formation of hydroxo-complexes (Brunner *et al.* 2004). Brunner *et al.* (2004) showed four fold decrease in Mn with an application of 4 tonnes ha^{-1} of ash. The ability of ash to decrease Mn may benefit certain crops if the soil has a high concentration of Mn and is acidic (in general with a pH<5.5) (Kabata-Pendias and Pendias 1984). While Mn is an essential nutrient for plant growth, Mn in some soil may reach levels of toxicity (main symptom is Fe chlorosis) (Kabata-Pendias and Pendias 1984).

Zn concentrations (available and 'total' acid extractable) significantly increase with the addition of ash at 10 tonnes ha^{-1} (Figure 26). Rumpf *et al.* (2001) showed a similar significant increase in elemental Zn concentration when 2.4 tonnes ha^{-1} of ash was used as a soil amendment in the top 4 cm of soil. Two studies found an increase in the micronutrient Mn, which observed that the Mn concentrations in the ash applied to their studies and the rate of application put more Mn into the soil than was displaced on cation exchange sites (Branryd and Fransman 1995; Sahota 2009). Also in this study, it was found that Zn was likely displaced but the high amount of Zn added to the soil with 10 tonnes ha^{-1} exceeds the amount removed. The ash concentration of Zn (1502.1 mg kg^{-}

^{1}) is much higher than biochar (64.7 mg kg^{-1}) and in pre-treatment soil (75.2 mg kg^{-1}) (Table 5). Therefore, it is possible that the observed Zn increase was due to the high concentration of Zn in the ash and the rate that the ash was applied. Addition of heavy metals is a major concern with the application of ash but this ash material does not exceed the limit set by OMAFRA (Ontario Ministry of Agriculture, Food, and Rural Affairs) for the application of a NASM on agricultural land (4200 mg kg^{-1}) (OMAFRA 2002).

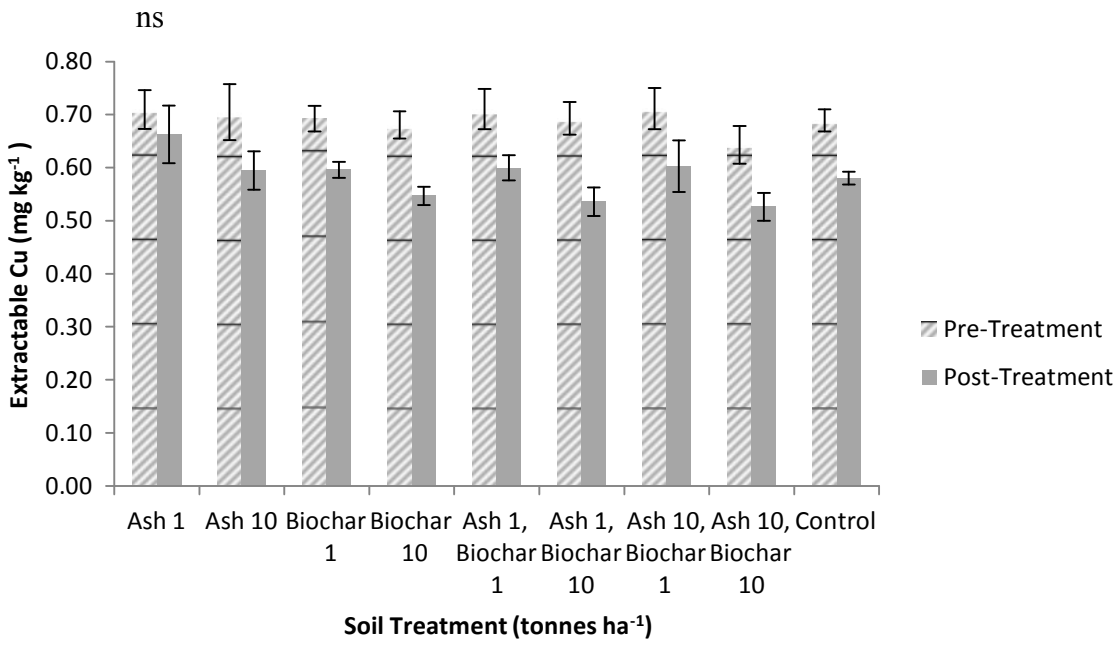

Figure 24. Mean extractable/available Cu concentrations for each treatment compared to pre-treatment soil conditions. The error bars represent ± 1 SE.

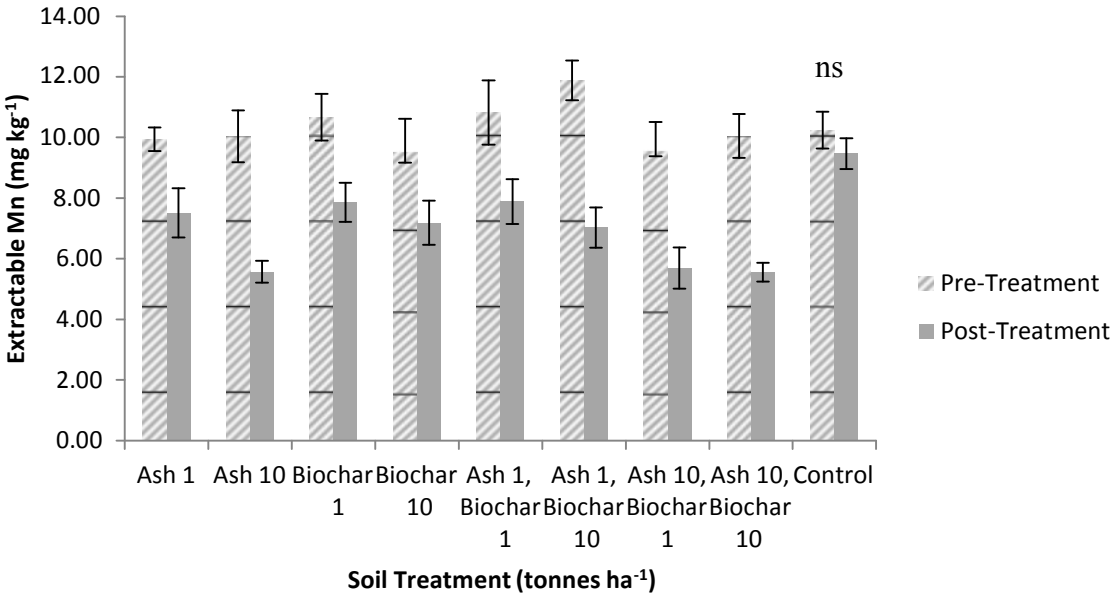

Figure 25. Mean extractable/available Mn concentrations for each treatment compared to pre-treatment soil conditions. The error bars represent ± 1 SE.

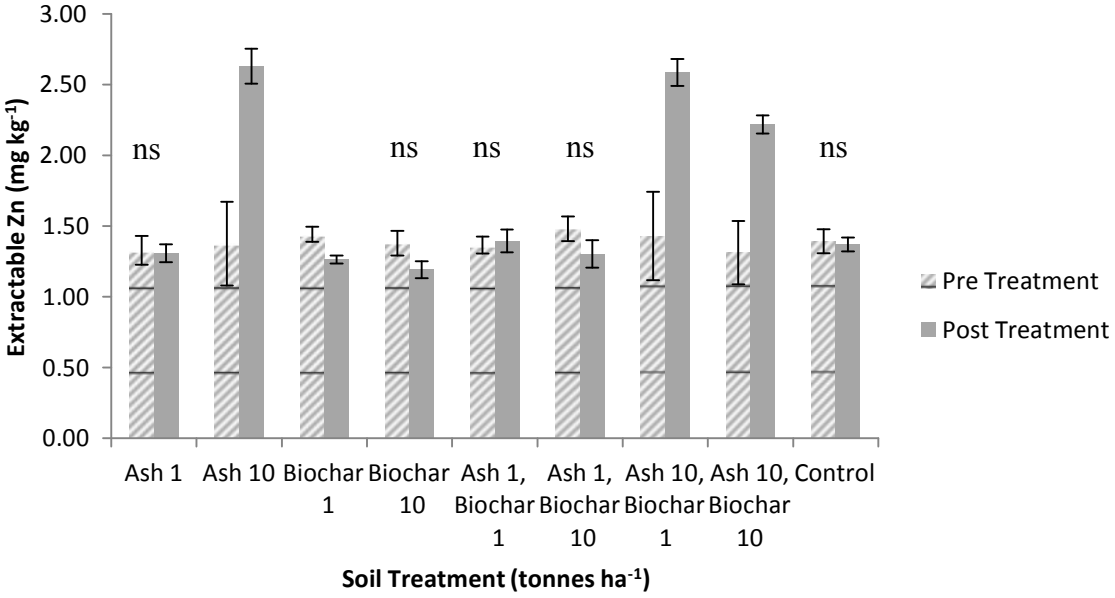

Figure 26. Mean extractable/available Zn for all treatments compared to pre-treatment soil conditions. The error bars represent ± 1 SE.

The rest of the chemical analysis showed that ash and biochar treatments had no significant effect. These chemical properties included extractable P; and 'total' acid extractable Al, B, Cu, Fe, and Ni. Previous ash and biochar amendment studies have seen increases in P concentration in treated soil (Gaskin *et al.* 2010; Saarsalmi *et al.* 2004; Staples and Van Rees 2001; Yamato *et al.* 2006). These studies reported that the increase was due to P content added with the addition of ash and biochar material (Gaskin *et al.* 2010; Saarsalmi *et al.* 2004; Staples and Van Rees 2001; Yamato *et al.* 2006). While P concentrations of ash and biochar are close to the mean values found in Table 3 there was no significant effect observed with treatment in this study. This may be due to the study site being on land that was previously a nursery and the soil was not deficient in P, which would have a greater effect in other soils low in P. According to OMAFRA the amount of available P in the pre-treatment soil is rated very high for agricultural land (Hilborn and Stone 2005). The lack of response to treatment on heavy metal concentrations is a positive result, because the addition of them is a major concern with the application of both biochar and ash (Pitman 2006; Rumpf *et al.* 2001).

TREATMENT EFFECTS ON SOIL BIOLOGICAL PROPERTIES

A concern with the addition of biochar and ash is changing microbial activity and CO_2 respiration in the soil (Downie *et al.* 2009; Pitman 2006). Since ash had an effect on increasing soil pH and exchangeable Ca it could potentially change the microbial community to be bacterial dominated (Brady and Weil 2002). If this is the case the increased microbial activity would increase nitrogen and CO_2 respiration (Moilanen *et al.* 2002). Moilanen *et al.* (2002) saw this reaction with the application of ash to a field experiment, as did Jones *et al.* (2012) and Major *et al.* (2010a) for the

application of biochar. Microbial biomass C and N are not significantly affected by the addition of ash or biochar to the soil. The microbial biomass C:N ratio for all treatments was between 8:1 to 20:1. Without a change in microbial community CO_2 respiration was also not significantly different with the application of ash or biochar.

SEEDLING GROWTH AND FOLIAR CHEMISTRY RESPONSE

Tree heights that were measured in 2012 and 2013 showed no significant effect with treatment of ash or biochar for both Sw and Sb seedlings (Figure 27). It was anticipated that there would be no difference in 2012 height because the seedlings were planted 3 months before the tree height measurements were taken. Tree seedlings are slow growing compared to agricultural crops and differences in growth may not be seen for a few years. Most biochar field studies saw an increase in yield after a year or two but they were all dealing with agricultural crops. In ash field studies that assessed tree growth positive impacts occurred three to five years after application (Ernfors *et al.* 2010; Feldkirchner *et al.* 2003; Perez-Cruzado *et al.* 2011). Taking out the sprayed plots did not change the significance outcome, so values were left in the analysis. Mortality increased from August 2012 to 2013 but was not significantly different with the addition of ash or biochar.

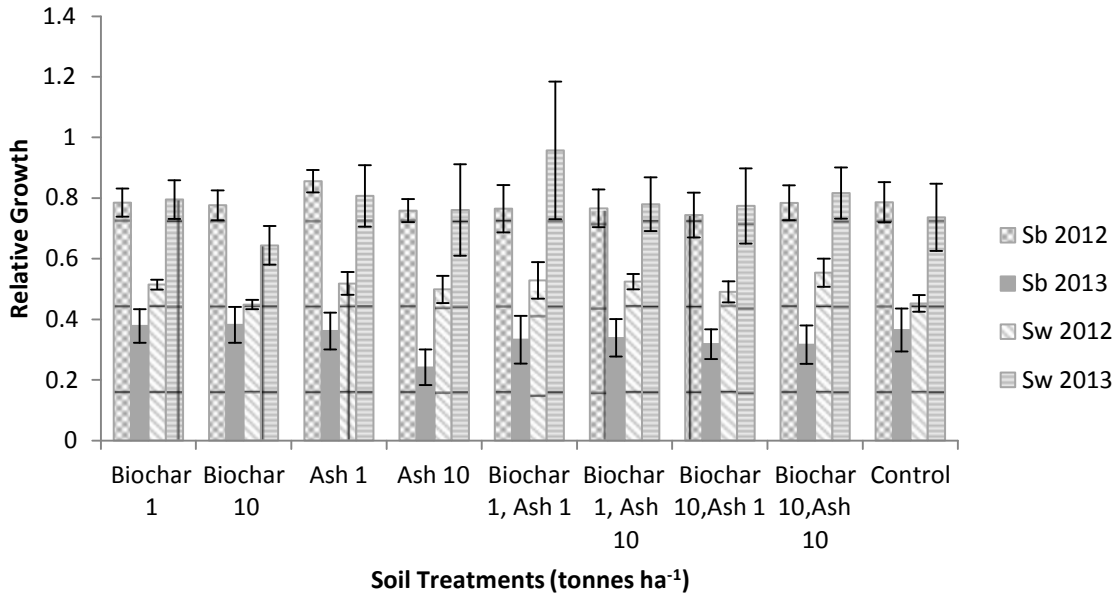

Figure 27. Mean relative seedling growth for Sw and Sb in 2012 and 2013. The error bars represent ± 1 SE.

In contrast to the lack of response in seedling growth there were significant responses in seedlings foliar nutrient concentrations. Ash treatment significantly increased B, K, and S concentrations in both Sb and Sw seedlings needles (Figures 28, 29, 30). A significant increase in B concentrations also occurred with the application of biochar for Sw seedling foliage. This increase is surprising since there was no significant increase seen in soil concentrations compared to the control plot. The increase in foliar K and S concentrations in Sw and Sb is likely due to the increase in soil available K (Figure 17) and total S (Figure 21) from 10 tonnes ha^{-1} ash application to soil. Another possible explanation for the increase in B, K , and S could be a change in pH increasing B, K, and S absorption (Kabata-Pendias and Pendias 1984).Ernfors *et al.* (2010) added 3.3 and 6.6 tonnes ha^{-1} of ash to a former bog and peatland and found that only nutrients K and B increased in one year old needles for both applications. Other than Ernfor et al. (2010) three other studies observed an increase in K

concentrations in tree foliage ash applications (Feldkirchner *et al.* 2003; Mandre *et al.* 2004; Perez-Cruzado *et al.* 2011). There were a few nutrients that increased significantly that were seedling species specific. Sb foliage increased significantly in Ca and Mg with the application of ash at both application levels. The increase in soil available Ca (Figure 16) and Mg (Figure 18) with the application of ash is likely responsible for this increase in foliage nutrient concentration. The fact that it this increase wasn't seen in the Sw seedlings maybe because Sb root growth is shallower than Sw (Burns and Honkala 1990). It is possible that since the roots of the Sb are more in the area of treatment application (10 cm depth) it is more affected by the treatment than Sw. This is assuming very little movement of nutrients in the soil. One study found that exchangeable Ca and Mg concentrations increased in the soil after ash application but there was no increase in their concentrations in foliage. (Perez-Cruzado *et al.* 2011). There was no significant impact on total N in foliage for both Sw and Sb seedlings (Figure 33) despite the application of ash at 10 tonnes ha^{-1} significantly decreasing available and mineralizable NH_4 in the post-treatment soil. This means that increasing N uptake by the seedling was not responsible for this decrease, which means that increased leaching was the likely cause.

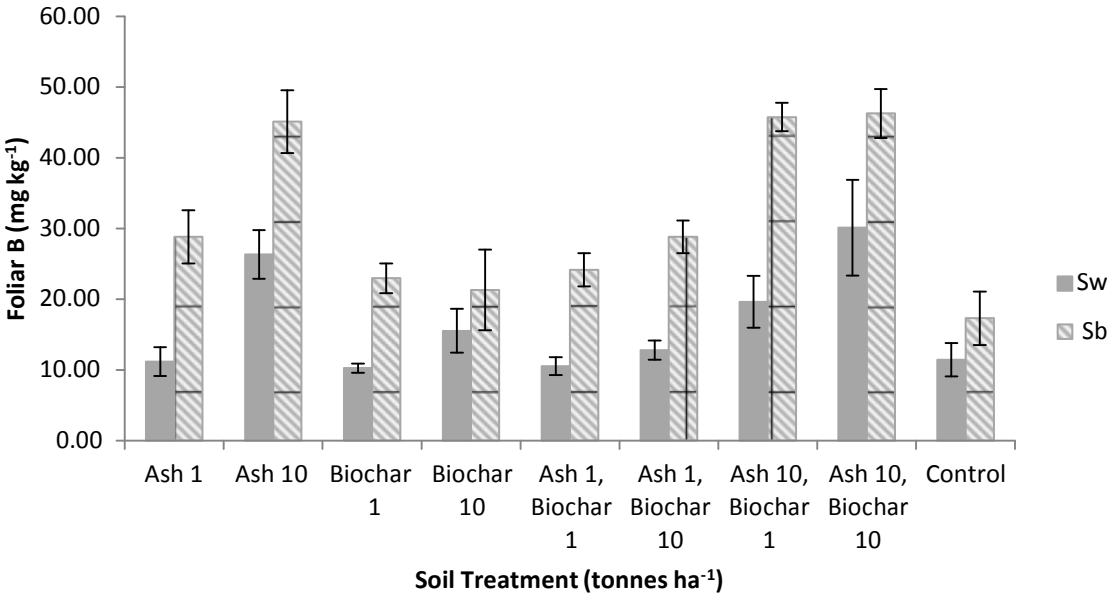

Figure 28. Mean Sw and Sb foliage B concentration for all treatments. The error bars represent ± 1 SE.

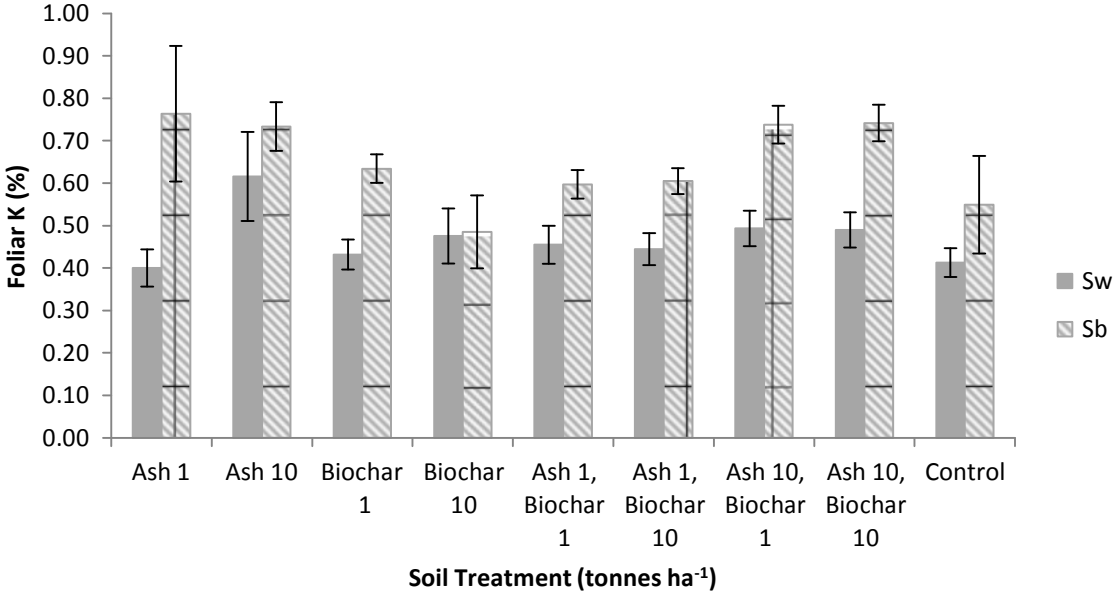

Figure 29. Mean Sw and Sb foliage K concetration for all treatments. The error bars represent ± 1 SE.

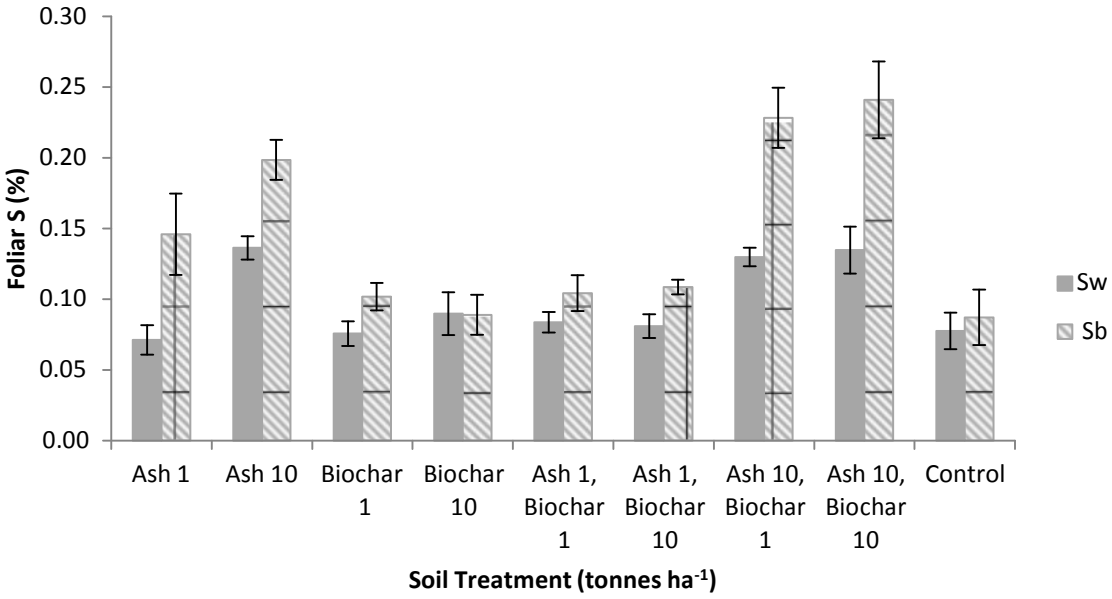

Figure 30. Mean Sw and Sb foliage S concentration for all treatments. The error bars represent ± 1 SE.

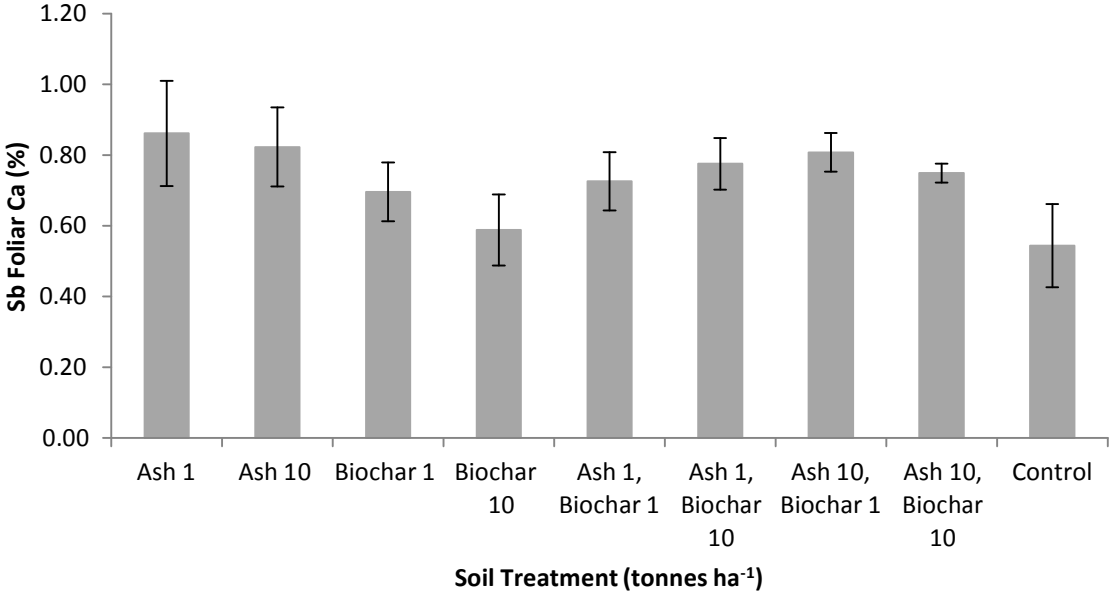

Figure 31. Mean Sb foliage Ca concentration for all treatments. The error bars represents ± 1 SE.

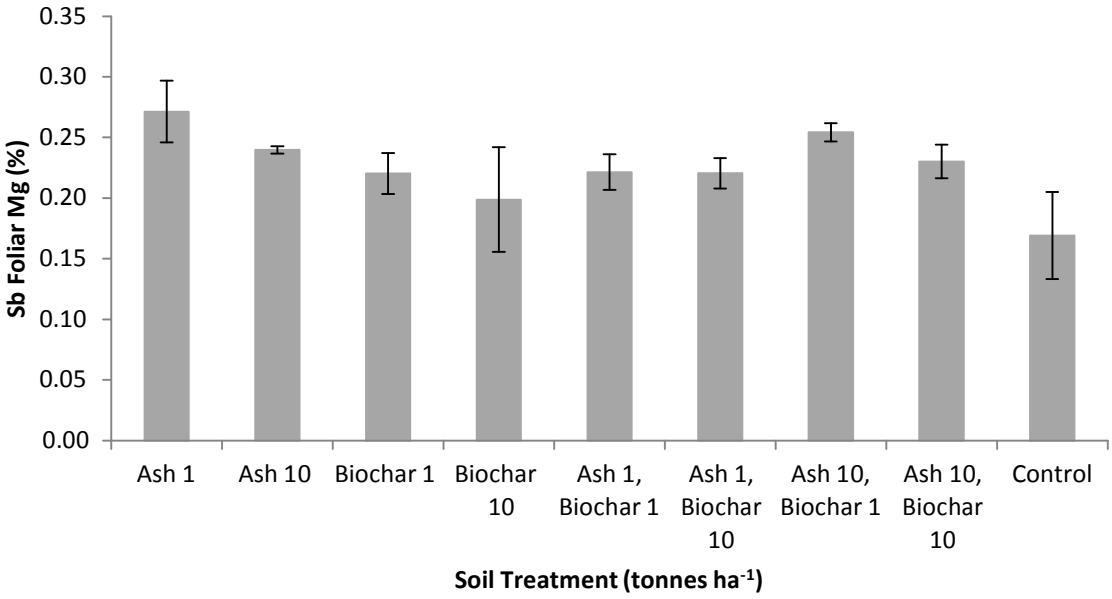

Figure 32. Mean Sb foliage Mg concentrations for all treatments. The error bars represent 1 ± SE.

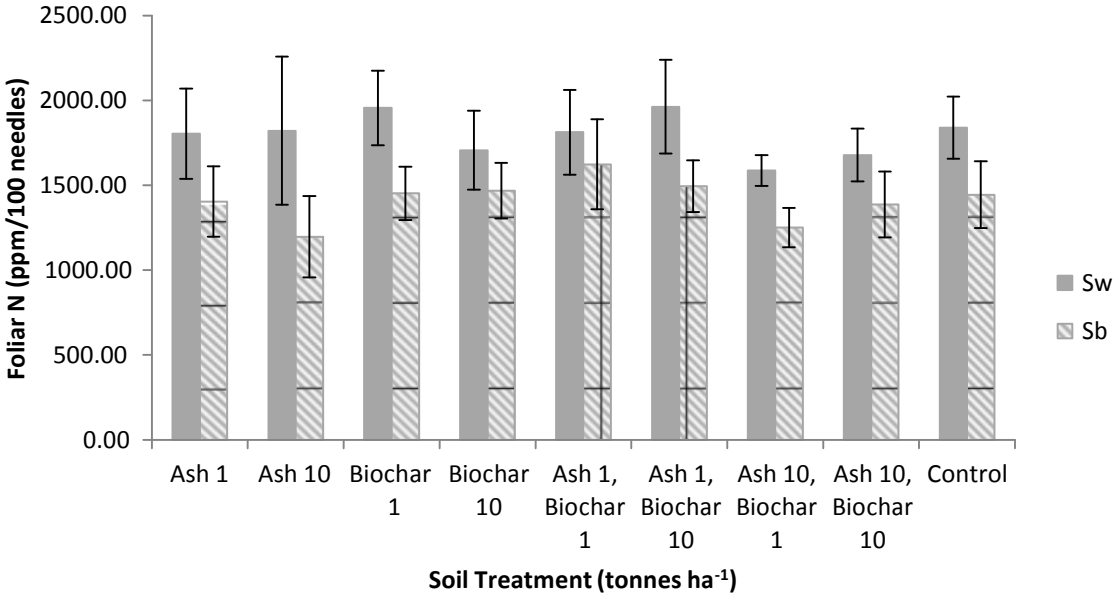

Figure 33. Mean foliage N content for all treatments. The error bars represent 1 ± SE.

CONCLUSION

The application of this type of industrially produced ash and biochar to a sandy loam soil had a slight impact on soil chemical properties and seedling foliage nutrients within the first growing season.

It is clear that the application of ash at 10 tonnes ha^{-1} proved to have the most effect on the soil properties of the old nursery site. Ash showed a potential to increase soil pH, the availability of some available macronutrient (Ca, K, and Na), total S, and Zn. However, application of ash at 10tonnes ha^{-1} decreased available and mineralizable NH_4, and available Mn. The amount of Zn in the ash material could limit its application rate to certain soil. It should be noted that a major concern with the application of biochar is the potential for it to add heavy metals to the soil. The application of biochar did not significantly increase any heavy metal analyzed but decreased exchangeable Cu (at 10 tonnes ha^{-1}) when applied. Other than decreasing Cu, biochar amendment had no other effect on soil chemical properties. The lack of a negative response to biochar application at 10 tonnes ha^{-1} means that more biochar could be added to this site at a higher rate in the future. Both ash and biochar had no effect on microbial activity, which means both didn't increase N in soil, but it also didn't increase soil respiration (release of CO_2). No change in respiration means that the initial addition of this ash and biochar material was stable and that C has been stored in the soil.

It is unclear yet if the soil amendments with biochar and ash will have a significant effect on white and black spruce seedling growth. Changes in growth will

probably take a few more years. However, the increases seen in foliage nutrients concentrations (B, K, S, Ca, and Mg) with the application of ash is a good sign that changes to seedling growth may be seen in the future. There seems to be a lack of long term studies with both ash and biochar, so continuing this study is an important part of discovering the effects of these materials on tree seedlings.

It should be noted that a lack of response is not a negative response to treatment. The fact that the treatment had no negative effects on the soil properties is a good outcome. The material used would have gone to a landfill if not applied to the soil. Since the effects of ash and biochar treatment were not pronounced perhaps this site could have taken an even higher application rate of biochar and ash. Since the site was an old nursery, it is possible that any deficiencies typical of a forest soil found in this area may have been amended in previous years. If this is the case, then the results of the treatments may be more evident in a more nutrient poor soil. This study will provide a good base for future studies in northern Ontario on the application of this material to tree crop soil and a potential benefit for the use of biomass as a form of energy production versus fossil fuels.

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APPENDICES

Appendix I: Field Studies Tables

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a. Summary of field studies that applied ash as a soil amendment.

Source of Ash	Ash Chemical properties (mg/kg)	Crop type	Location of Field Experiment	Soil Characteristics	Application Rate(s)	Comparison treatments	Change in Soil Properties	Crop Response	Negative Responses to Treatment	Reference
Fly and bottom ash from heating plant	249000 Ca, 74000 K, 29000 Mg, 13000 Mn, 5000 Na, 23000 P	Pine (*Pinus sylvestris*)	Blekinge, Sweden	Sandy Ferric Podzol soil (pH 4.4)	0, 2.032, 7.112, and 10.16 tonnes/ha		Increased pH with increasing ash additions. Decrease in acidity and Al concentrations in mineral soil and humus layer. Base saturation increased in mor and mineral layers. Ca and K increase in both layers and Mg only increased in mor layer. Increase of Cu in the humus layer with the higher ash applications 7 and 10.16 tonnes/ha. Effects of wood ash on buffering soil is similar to application of lime material.Most element absorbed into mor layer.Only minor effects on soil heavy metal concentrations when applying low heavy metal wood ash.			Branryd and Fransman 1995
wood ash from mixed forest stand wood chip		Norway spruce(*Picea abies (L.) Karst*)	Zürich, Switzerland	Dystric cambisol soil- nutrient poor, and pH 3.3	4 tonnes/ha		Soil pH increased from 3.2 to 4.8 causing a decrease in soil exchangeable Fe, Mn, Zn, and toxic Al.	Mn decreased in roots due to pH. Interactions in soil and roots occurred between Ca and Mg as		Brunner et al. 2004
Power station ash (bottom and fly). Fuel was 75% Bark, 20% wood chips, and 5% sawdust.	200000-220000 Ca, 23000-58000 K, 24000 Mg, 8200-12000 Na, 6300- 13000 P	Drained and forested peatland with mainly Scots pine(*Pinus sylvestris L.).*	Southern Sweden	Former bogs and peatland.	Bog: 3.3 and 6.6 tonnes d.w./ha. Peatland: 3.5 and 6 tonnes d.w./ha		Significant increase in pH compared to control. No effect on C:N ratio over 4 years. Over the five year period there was no significant fluxes of carbon dioxide, methane or nitrous oxide.	K and B significantly changed in tree needle nutrient content. Tree growth limited by P. No significance on stem volume, biomass growth, or height.	No significance on stem volume, biomass growth, or height.	Ernfors et al. 2010
wood fired ash	7.82 %C, 0.07%N, 3300 P, 31600 K, 160400 Ca, 9100 Mg, 1.13 %S	Maple (*Acer saccharum* Marsh.) and Aspen (*Populus tremuloides* Michx.) stand	Norway, Michigan	pH: 4.95-5.97	10 tonnes/ha	N fertilizer, Ca+Mg+K (base cation)fertilizer, N+base cation fertilizer, N +base cation +P+S, N +Ash, and two Sludge treatments	Increase in pH in aspen stand by 12% for ash and 13% for N+ash. pH increased in maple stand by 5% for ash treatments. Slight increase in Ca concentration in ash treatments. There was a significant increase in K soil concentrations from 0-20cm for ash treatments. N+Ash provided the same increase in N concentration as N+ base cation +P+S but provided more K, Mg, and Ca.	N+ash had a 30% increase in wood increment.		Feldkirchner et al. 2003
hard and soft wood from Heating plant	pH 12.1-12.6, 250 N, 123000 Ca, 48000 K, 19400 Mg, 17900 Na,15500 P, 10150 S.	Norway spruce(*Picea abies (L.) Karst*)	Estonia	Poor Sandy Soil	2.5, 5, and 10 tonnes/ha		Increase in pH and available K and a decrease in Ca, N and P.	Seedling nutrient composition changed by an increase in K, decrease in Ca.	Decease in tree growth.	Mandre et al. 2004
Wood ash from pulp mill.		Western Red Cedar	Near Port Mc Neil and Port Hardy, British Colombia	Ferro-Humic Podzols	5 tonnes/ha ash for all treatments involving ash	Inorganic fertilizer, sewage sludge, sewage sludge + pulp sludge, fish silage + ash + pulp sludge, and fish silage + ash.		Ash treatment alone showed no significant increase in tree height or foliar nutrient concentrations for N, P, K, Ca, Mg, and S after 1 and 2 years of growth. Every other treatment showed an increase in height and most macronutrients.		McDonald et al. 1998
birch wood ash from power and heating mill		Natural growth on previously treeless drained mires with in the boreal coniferous zone	Muhos Leppiniemi, Finland	Drained mires	0, 8, and 16 tonnes/ha		Increase in N, P, K, and microbial activity.	After seven years was stocked with Scots pine and young birch that had naturally risen. Treatment caused long term growth of stem volume of Scots Pine.		Moilanen et al. 2002
Pulp and paper mill	0.03-0.09%N, 71000-15500ppm Ca, 5000- 16000-36000ppm K, 6000-13000ppm Mg, 2700-3000ppm Na, 6000 P	Willow Plantation	Tully, New York	Silty Loam (high pH)	0, 10, 20 tonnes/ha		Increase in pH, and extractable P, K, Ca, and Mg. No change in N, Na and CEC.	No effect of plant nutrients and growth.		Park et al. 2005
Kraft pulp mill		Barley	Edmonton, Alberta	Boralf (Othic Gray Luvisolic)			Increase in pH, available K, and S.	Increased dry matter yield in barley crops treated with ash and N fertilizer. No significant yield increase for crops only treated with ash.	Lack of yield in ash only treatments due to N defiences in soil.	Patterson et al. 2004
Pulp processing Plant-mainly bark	pH 13, 11.6% C, 0.19% N, 0.03% S,	Chestnut (*Castanea x coudercii)*	Northern Spain	Umbrisol (loam)	10 and 20 tonnes/ha		Increase in pH by 0.6 units, and increase in exchangeable Ca, Mg, and K.	Positive response for Ca, Mg, and K.		Perez-Cruzado et al. 2011
untreated wood from veneer company	pH 12.6, 236000 Ca, 22000 K, 13000 Mg, 7000 S, 5000 P, 3000 Na.	Pine (*Pinus sylvestris*)	Fuhrberg, Germany	Acidic Podzol soil (pH 2.7-3.6)	0, and 2.4 tonnes/ha	Lime fertilizer	High increase in Ca in the top soil layer in the first four months but only a slight increase after a year or at lower soil depths. K, Mg, and NO3 increased slightly at all depths (up to 100cm) after ash addition. Soil pH increased to 5.5 from 3.6. CEC doubled in surface soil (4cm) due to increase in exchangeable Ca and Mg. Changes in pH, Ca, Mg, and NO3 in the seepage water were the same as when lime was used. While ash application had no effect on Cr it did increase Zn, Cd, and Pb levels but none went over German regulation limits. The only significant increase of heavy metals was Zn in the top 4cm of soil.			Rumpf et al. 2001
		Scots pine (Pinus sylvestris L.) and a Norway spruce [Picea abies (L.) Karst.]	Finland	Haplic Podsol (Organic layer Mor)	3 tonnes/ha & 120-150 kg N/ha	Wood ash and Wood ash plus N fertilizer	pH at all treatment plots increased as well as the extractable Ca, Mg, and P. Decrease in exchangable Al.	Increase in B. No significant change in growth and volume due to ash application.		Saarsalmi et al. 2004
Pulp and paper mill		Alfalfa	Thunder Bay, Ontario		10 tonnes/ha	Agricultural Lime	Application of wood ash every two years also increased P, K, and Mn soil content. Tested against agricultural lime and wood ash presented better results.	increased the yield by 1 tonne/ha/year.		Sahota 2009
MeadWestvaco paper mill		European larch [*Larix deciduas P. Mill* .] & aspen [*Populus tremula L.*]	Michigan, USA (Upper Peninsula)	Onaway series, mixed active,frigid Inceptic Hapludalf (high fertility and water holding capacity)	0, 9, and 18 tonnes/ha		Increase in exchangeable Ca, Mg, K, and Na in the soil. C, N, and exchangeable K higher in the broadleaf species soil.			Sartori et al. 2006
Pulp mill wood/sludge		White spuce [*Picea glauca (Moench) Voss*]	Saskatchewan, Canada	Orthic Gray Luvisols (clay loam)	1 and 5 tonnes/ha		At 5 t/ha- increased pH, NO3, extractable P, Ca, and Mg, while a decrease in extractable Al and Fe.	After the second growing season reduced height of seedling.	The reduced white spruce seedling size was attributed to salinity stress (EC of 0.10 dS/m), moisture deficits, or indirectly by loss in soil structure.	Staples and Van Rees 2001

b. Summary of field studies that used biochar as a soil amendment. *Available

Source of Biochar	Biochar Chemical properties (mg/kg)	Crop type	Location of Field Experiment	Soil Characteristics	Application Rate(s)	Comparison Treatments	Change in Soil Properties	Crop Response	Negative Responses to Treatment	Reference
wood residue and rosewood	pH 7.5, 87% C, 0.31% N, 281 C/N, 47.7 *P, 10.7 cmol/kg CEC	Rice	Luang Prabang province in Northern Laos		4, 8, 16 tonnes/ha	N fertilizer	Higher grain yields in sites with low *P when biochar is added and improvement of hydraulic conductivity.	No significant effects on yield with the application of biochar. Increase in yield was seen in crops with 4 and 8 t/ha of biochar with N fertilizer.		Asai et al. 2009
commercial charcoal	pH 7.2, 84 %C, 1.2 %N, 70 C/N, 2600 Ca, 4300 K, 2800 Mg 500 P.	durum wheat and maize	Toscana and Friuli Venezia Giulia, Italy	Silt Loam	10 tonnes/ha		no biotic/abiotic stresses.	Wheat above ground biomass increased by 23% and grain production increased 10% with biochar addition. Maize biomass showed no difference but grain increased by 6 and 24%.		Baronti et al. 2010
bagasse and biosolids	Bagasse- pH7.3, 63.23% C, 0.37% N, 0.8*P, 19.9 K*. Biosolids-pH7.2, 15.14% C, 1.46% N, 4.1 *P, 125.2 K*	Sugarcane	Miyago Island, Japan	Heavy Clay	bagasse biochar- N equivalent 333 kg/ha, and Biosolid biocharN equivalent 438 kg/ha	N, P, K Fertilizer (16:9:9)	Biochar increased water holding capacity by 9-12%. Nitrate-N retention was 59% in bagasse biochar and 11% in biosolids biochar when compared to fertilizer.	Higher sugar can growth (kg/ha crop yield) with both biochars compared to commercial fertilizer. Yield of sugar and roots increased greatly for Bagasse biochar.		Chen et al. 2010
peanut hull and pine chips	Peanut Hull-72.8% C, 1.9% N, 0.085% S, 5414 Ca, 19311 K, 2716 Mg, 2177 P. Pine Chip-76.9% C, 0.17% N, 0.035% S, 4028 Ca, 2822 K, 1228 Mg, 577 P.	Cotton, corn, and peanuts.	Tifton, GA, USA	Loamy Sand (intial NPK fertilization)	0, 11.2, 22.4 tonnes/ha	N fertilizer	Peanut Hull- biochar increased pH over two year (2006 increased with treatment and 2007 decreased with treatment). pH lower with fertilizer addition. Biochar added available Ca, K, Mg, and P to the soil. Mg was reduced with fertilizer addition. Largest N centration occurred with fertilizer addition with biochar in 2006 but not in 2007. Pine chip- Only influenced pH and available Ca concentrations.	Peanut Hull- corn tissue concentration of K and Ca increased. Increase corn yield with and without fertilizer. Pine chip- increase total S and Mg concentrations in corn tissue. Increase corn grain yield but not corn stover.	Peanut Hull- K concentration dropped in the second year. Pine chip- soil available Ca concentration only increased with biochar plus fertilizer treatments. Biochar and fertilizer had no effect on soil N, P, S, and Mg concentrations.	Gaskin et al. 2010
hardwood waste from Cquest	72.5 %C, 0.5%N, 161 C/N, 0.02 %S, 300 Al, 6460 Ca, 180 P, 6080 K.	Soybean and forage (rye rass, red clover, tomothy, and oats)	Saint-François-Xavier-de-Brompton, Québec, Canada		Estimated 3.9 tonnes/ha (caculated due to projected loss from wind/transportation)	1.5 t/ac Lime	Increased soil bulk density. Increase in Mg and K in soybean crop soil. No increase in soil respiration. Bacterial biomass was the same or slightly higher than control. There was no change in fungal biomass.	Soybean biomass increased 17-20% and density increased 11-68%. Forage crops showed a 17-99% biomass increase and an increase in density of 102%.	Decrease in soil available Ca and P in soybean crop. Decrease in soil available Ca, K and Mg in forage crop. Soil Mn greater in control.	Husk and Major 2010
Branch and trunk wood chips from Fraxinus excelsior L., Fagus sylvatica L. and Quercus robur L.	pH 8.81, 156 C/N, 19.9 P*, 1400 Ca*, 1130 K*, 79 Na*.	Year 1-Maize, Year2 and 3-Grasses	Abergwyngregyn, Wales	Sandy clay loam- nutrient rich and well fertilized soil (three times during study). Pesticides and herbicide application on regular bases.	0,25,50 tonnes/ha		Increased soil pH by 0.32 units in year 2 but had no effect on other physical and chemical properties tested (moisture content, respiration, soluble C, N, available P, exchangeable Na, and Ca).	Year 2 grass saw increase foliar nutrient content of N. Year 3 grass showed increase production but no increase in quality. Lack of response in year 1 is attributed to rooting depth differences between maize (>1m) and grass (<30cm).	A shift occurred in the soils microbial communities to one that is baterial dominant. This effect on field microbial community mostly disappeared by year 3.	Jones et al. 2012
Made from prunings of mango trees	Biochar 1- pH 10.14, 71.7% C, 0.26% N, 2930 *Ca, 291 *Mg, 259 *P, 3300 *K, 280 C/N, 235mmol/kg CEC Biochar 2- pH 10.07, 63.5% C, 0.32% N, 6440 *Ca, 185 *Mg, 116 *P, 2610 *K, 197 C/N, 248 mmol/kg CEC	savanna vegetation	Colombia	Isohyperthermic kaolinitic Typic Haplustox (sand clay loam)	11.6, 23.2, and 116.1 tonnes/ha		Loss of soil organic matter from the addition of biochar, but an increase in non-biochar carbon was found due to increase in soil productivity		Less then three per cent of applied biochar was lost by CO2.	Major et al. 2010a
wood	pH 9.2, 72.9% C, 0.76% N, 120 C/N, 330.7ppm *Ca, 48.9ppm *Mg, 29.8ppm *P, 463.8ppm *K, 111.9 mmol/kg CEC	Maize	Llanos Orientales, Colombia	isohyperthermic kaolinitic Typic Haplustox (sand clay loam)	0, 8, 20 tonnes/ha		In the soil after application there was an increase in available Ca, Mg, Mn, and Sr, while it decreased in Al and Fe. Increase in pH and nutrient retention in the rooting zone is cause of increased yield in the acidic soil in a area with heavy rainfal.	Yield increased with application rate in Maize crop after the first year. Soybeans yield increased also but there was no significence in rates of biochar application. In maize leaf analysis there was an observed increase in total nutrients with the exception of Al.		Major et al. 2010b
Acacia mangium Bark	pH 7.4, 39.8% C, 1.04% N, 63.1 P*	Maize, cowpea, and peanut.	South Sumatra, Indonesia	Gardens near tree plantations	37 tonnes/ha	0.5 tonnes/ha fertilizer with NPK 15-15-15	In all crops it increased pH, total N, available P, exchangeable cations, saturation, CEC and decreasing Al. In the maize crop application increased AM fungi colonization.	significant increase in yield for maize and peanut on one of the two sites that tested all three crops. The third site which only had maize also showed a significant increase in yield with charcoal application.		Yamato et al. 2006
wheat straw	pH 10.4, 46.7% C, 0.59% N, 10000 Ca, 6000 Mg, 26000 K	Rice	Jiangsu Province, China	hydroagic Stagnic Anthrosol (high yielding for rice crops, high available N)	0, 10, and 40 tonnes/ha	N fertilizer	Biochar increased pH, soil organic carbon, and total N. Decease in bulk density.	10t/ha increased yield by 12% and 40 t/ha by 14% compared to unammended soil. No signification effects on yield by adding N fertilizer with the biochar compared to soil without it.		Zhang et al. 2010

Appendix II: Calculations and Analyses

Given that the plot area was 16.5 m^2 the total amount of ash or char added to the soil surface is 1.65 kg (1 tonnes ha^{-1} treatment) and 16.5 kg (10 tonnes ha^{-1} treatment).

The following is the methodology that was used for each of the physical and chemical component analyzed during the pre- and post- treatment soil tests:

(1) Bulk density was measured by driving a 183.9 cm^3 metal cylinder into a relatively smooth/undisturbed surface area of soil. The fresh soil sample was weighed on a tin and then dried for 48 hours at 105°C in a drying oven (Culley 1993).

(2) Field capacity was measured by gravity filtering saturated soil samples. Plastic beakers that had holes punched into the bottoms were lined with Fisher #1 filter paper. Air-dried and sieved soil samples were weighed in the beakers and saturated with distilled water. The samples were left to sit on a tray for 48 hours then the final weight was taken. The difference was calculated as percent field capacity (Livingston 1993).

(3) The air dried moisture and organic matter content were determined using a LECO Thermogravimetric, which heated the samples to 105°C until a steady weight, and then to 375°C to find the amount lost on ignition (Kalra and Maynard 1991).

(4) Soil texture analysis was done according to Kalra and Maynard (1991) with the following modifications. Soil was mixed in a milkshake machine with sodium hexametaphosphate and filled to 100ml with distilled water, which was stirred for 15 minutes. Soil suspension was set aside for a week. Soil suspension was placed into 1 litre glass cylinder, and then filled with room temperature water up to 1 litre. The

cylinder was closed and mixed by inversion for 2 minutes and once mixed a hydrometer was put into the cylinder. Readings of the hydrometer were taken at 30 seconds, 40 seconds, 1minute, 2 minutes, 5 minute, 10 minutes, 1 hour, and 2 hours (Kalra and Maynard 1991).

(5) Saturated paste pH using distilled water (1:2 ratio of soil to water) and Fisher Accumet Ion Analyzer pH meter (Kalra and Maynard 1991). pH values were converted to H ion for data analysis.

(6) Electrical conductivity was measured using a 1:2 soil-to-water suspension. The soil and water was shaken at 65 rotations/ min for 15 minutes and left to stand for 15 minutes. An ACCUMET conductivity probe was used to measure EC (uS/cm) (Rhoades 1982).

(7) Exchangeable base cations were measured using a 1M ammonium acetate extraction (pH adjusted to 7±0.1). The solution was shaken for 15 minute and filtered with Fisher Brand Q5 filter paper (Simard 1993). The extract was analyzed using an ICP-AES (inductively coupled plasma spectrometer) at the Instrumentation Laboratory at Lakehead University (LUIL) (Simard 1993).

(8) Estimated cation exchange capacity is a summation of the individual exchangeable base cations (Ca, Mg, K, and Na) after it is converted to meq (Chapman 1965).

(9) Total carbon, nitrogen and sulphur were determined by dry combustion using a LECO CNS 2000 (Matejovic 1997).

(10) Available nitrogen (ammonium and nitrate) analysis was performed by a soil extraction using a 1:10 ratio soil-to-2M potassium chloride. The solution was shaken for 30 minutes at 65 rotations/ minute and filtered using Fisher brand Q5

filter paper. The extraction solution was analyzed using a nitrate and ammonium auto-analyzer (Kalra and Maynard 1991).

(11) Mineralizable N was measured by anaerobic incubation. Soil samples (dried and 2 mm sieved) of 10 grams or over were weighed into 60 Dram plastic pill bottles with lids. Distilled deionized water (50 ml)was added to each sample and samples were stirred to avoid air pockets. Samples were placed in an incubator at 30 °C for 14 days. After incubation period 50 ml of 4M KCl was added to each sample, which dilutes the extraction solution to 2M KCl. Samples were then shaken for one hour at 180 rotation/min. Once stirred the samples were vacuum filtered and the extraction solution collected. Immediately after filtration the solution was frozen for analysis of available nitrogen (nitrate and ammonium) with an auto analyzer using the same method as described above (Powers 1980).

(12) Extractable Fe, Mn, Cu, and Zn were determined by performing a 1:2 soil-to-0.005 M DTPA solution extraction. DTPA solution was adjusted to pH 7.3 with 0.5 M hydrocholoric acid and was shaken with soil for 2 hours at 65 rotations/ minute. It was filtered immediately using Fisher brand Q5 filter paper. This solution was then sent to LUIL for analysis using an ICP-AES (Liang and Karamanos 1993).

(13) Extractable P was done using the Olsen P method. This method used a 1:20 soil-to 0.5M sodium bicarbonate extraction. The extract was shaken for 30 minutes at 65 rotations/ minute and then filtered after sitting for 15 minutes (Fisher Brand Q5 filter paper). 10 ml of a colour reagent was added to the 2.5ml of extractant and heated in CPI ModBlock for 20 minutes at 80°C. Once the sample was cooled it was analyzed on a Cary 5e spectrophotometer at LUIL (Schoenau and Karamanos 1993).

(14) Acid digestion of 'total' heavy metal analysis was performed using a CPI ModBlock Digestion System. Samples of 0.2 grams soil (or 0.25 grams foliage) were digested using 6 ml concentrated nitric acid and 2 ml perchloric acid for 8 hours up to 90°C. The digest was cooled and then distilled deionized water was used to bring the solution up to 50 ml. The solution was filter using Fisher brand Q5 filter paper and analyzed using an ICP-AES at LUIL (Kalra and Maynard 1991; Miller 1998).

The following are the methods used for post-treatment biological testing:

(15) For measuring microbial C and N soil samples were defrosted for 24 hours (room temp.). Samples were prepared for analysis by being mixing and sieved (4.75mm mesh) after being defrosted. Three sets of sample for each plot were weighed out for a) moisture content, b) unfumigated extraction, and c) fumigated extraction (Voroney and Winter 1993).

a) Approximately 10 grams of soil sample was placed in a pre-weighed aluminum tin plate. Tins were placed in an oven at 105°C for 24 hours. Samples were cooled in desiccator for 15 minutes and then weighed. The amount of extraction solution used for each sample was based on of the initial moisture content. The moisture content was averaged for all plots (Voroney and Winter 1993).

b) A 25 gram soil sample was weighed and placed into 100 ml glass extraction jars with lids. To get a 1:2 ratio (oven dried soil: extractant) 39 ml of 0.5M K_2SO_4 was added to each jar. Jars were shaken for 1 hour and immediately filtered using 934 VWR filter paper. The solution was

collected and frozen until analysis on auto-analyzer for dissolved organic carbon and total soluble nitrogen with 0.35 efficiency (Voroney and Winter 1993).

c) A 25 gram soil sample was weighed and placed into 100 ml glass extraction jars with lids. Fumigated samples were placed in a thick walled desiccator with 50 ml of chloroform in a 100 ml glass beaker (with boiling chips). A vacuum was created using water, and the chloroform boiled for 1 to 2 minutes. The desiccator was sealed and placed in dark place at room temperature for 24 hours. Samples were then extracted with 39 ml of 0.5M K_2SO_4 using the same method as the unfumigated extraction. The solution was collected and frozen until it could be analyzed on the auto-analyzer for dissolved organic carbon and total soluble nitrogen with 0.35 efficiency (Voroney and Winter 1993).

(16) Soil respiration was performed using a LiCor 8100A with a 10 cm survey chamber. Samples from blocks 1, 3, and 5 were defrosted at room temperature for 24 hours. These samples were placed in plastic collars (10 cm diameter and 20 cm depth). The collar was filled with soil that was packed (collar tapped on floor three times) up to 2 cm from the top of the collar. Before the collar was filled a double layer of plastic mesh was placed on one end of the collar so air/water can pass through but no soil is lost. The samples were saturated with distilled deionized water and left for 24 hours. The LiCor 8100A was set to an observation time of 1 minute and a pre-purge time of 3 minutes for each round of 27 observations/samples. Soil respiration was measured on each sample 5 times through 5 runs of all 27

samples. Air temperature was monitored before every run of the samples (LI-COR 2005).

Relative Growth= height difference from previous year/first years height

Appendix III: Data Analysis

Bulk Density

Tests of Between-Subjects Effects

Dependent Variable: Density

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	54.687	1	54.687	3270.474	.000
	Error	.067	4	.017[a]		
Treatment	Hypothesis	.213	8	.027	2.024	.075
	Error	.422	32	.013[b]		
Block	Hypothesis	.067	4	.017	1.268	.303
	Error	.422	32	.013[b]		

a. MS(Block)

b. MS(Error)

Soil Water Potential

Tests of Between-Subjects Effects

Dependent Variable: FieldCapacity

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	3763.141	1	3763.141	216.934	.005
	Error	34.694	2	17.347[a]		
Char	Hypothesis	10.117	2	5.058	.678	.522
	Error	119.442	16	7.465[b]		
Ash	Hypothesis	5.349	2	2.674	.358	.704
	Error	119.442	16	7.465[b]		
Block	Hypothesis	34.694	2	17.347	2.324	.130
	Error	119.442	16	7.465[b]		
Char * Ash	Hypothesis	26.834	4	6.709	.899	.488
	Error	119.442	16	7.465[b]		

a. MS(Block)

b. MS(Error)

pH (H ion)

Tests of Between-Subjects Effects

Dependent Variable: PostHion

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	.009	1	.009	.002	.963
	Error	100.377	25.235	3.978[a]		
PreHion_A	Hypothesis	18.138	1	18.138	6.026	.020
	Error	93.312	31	3.010[b]		
Char	Hypothesis	4.885	2	2.443	.811	.453
	Error	93.312	31	3.010[b]		
Ash	Hypothesis	66.630	2	33.315	11.068	.000
	Error	93.312	31	3.010[b]		
Block	Hypothesis	54.525	4	13.631	4.529	.005
	Error	93.312	31	3.010[b]		
Char * Ash	Hypothesis	13.700	4	3.425	1.138	.357
	Error	93.312	31	3.010[b]		

a. .091 MS(Block) + .909 MS(Error)
b. MS(Error)

EC (uS cm^{-1})

Tests of Between-Subjects Effects

Dependent Variable: PostEC

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	5851.081	1	5851.081	8.569	.006
	Error	22060.163	32.307	682.840[a]		
PreEC	Hypothesis	9.264	1	9.264	.014	.906
	Error	18834.688	29	649.472[b]		
Char	Hypothesis	292.883	2	146.442	.225	.800
	Error	18834.688	29	649.472[b]		
Ash	Hypothesis	46670.026	2	23335.013	35.929	.000
	Error	18834.688	29	649.472[b]		
Block	Hypothesis	7773.570	4	1943.393	2.992	.035
	Error	18834.688	29	649.472[b]		
Char * Ash	Hypothesis	1495.930	4	373.983	.576	.682
	Error	18834.688	29	649.472[b]		

a. .026 MS(Block) + .974 MS(Error)

b. MS(Error)

Exchangeable Ca (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: PostAvailCa

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	18810.120	1	18810.120	.601	.444
	Error	950283.669	30.376	31284.532[a]		
PreAvailCa	Hypothesis	651994.096	1	651994.096	20.865	.000
	Error	937450.412	30	31248.347[b]		
Char	Hypothesis	124884.130	2	62442.065	1.998	.153
	Error	937450.412	30	31248.347[b]		
Ash	Hypothesis	3156328.555	2	1578164.277	50.504	.000
	Error	937450.412	30	31248.347[b]		
Block	Hypothesis	152816.828	4	38204.207	1.223	.322
	Error	937450.412	30	31248.347[b]		
Char * Ash	Hypothesis	90669.272	4	22667.318	.725	.582
	Error	937450.412	30	31248.347[b]		

a. .005 MS(Block) + .995 MS(Error)
b. MS(Error)

Exchangeable K (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: PostAvailK

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	3554.311	1	3554.311	9.321	.005
	Error	11774.622	30.878	381.332[a]		
PreAvailK	Hypothesis	1429.523	1	1429.523	3.753	.062
	Error	11426.829	30	380.894[b]		
Char	Hypothesis	502.042	2	251.021	.659	.525
	Error	11426.829	30	380.894[b]		
Ash	Hypothesis	54375.467	2	27187.734	71.379	.000
	Error	11426.829	30	380.894[b]		
Block	Hypothesis	1648.205	4	412.051	1.082	.383
	Error	11426.829	30	380.894[b]		
Char * Ash	Hypothesis	4085.374	4	1021.343	2.681	.051
	Error	11426.829	30	380.894[b]		

a. .014 MS(Block) + .986 MS(Error)
b. MS(Error)

Exchangeable Mg (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: PostAvailMg

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	68.023	1	68.023	.340	.564
	Error	6192.925	30.919	200.297[a]		
PerAvailMg	Hypothesis	18750.166	1	18750.166	93.909	.000
	Error	5989.865	30	199.662[b]		
Char	Hypothesis	607.760	2	303.880	1.522	.235
	Error	5989.865	30	199.662[b]		
Ash	Hypothesis	6107.309	2	3053.655	15.294	.000
	Error	5989.865	30	199.662[b]		
Block	Hypothesis	996.862	4	249.216	1.248	.312
	Error	5989.865	30	199.662[b]		
Char * Ash	Hypothesis	673.479	4	168.370	.843	.509
	Error	5989.865	30	199.662[b]		

a. .013 MS(Block) + .987 MS(Error)
b. MS(Error)

Exchangeable Na (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: PostAvailNa

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	26.103	1	26.103	6.615	.015
	Error	130.106	32.970	3.946[a]		
PerAvailNa	Hypothesis	1.756	1	1.756	.468	.499
	Error	112.471	30	3.749[b]		
Char	Hypothesis	29.470	2	14.735	3.930	.030
	Error	112.471	30	3.749[b]		
Ash	Hypothesis	26.121	2	13.060	3.484	.044
	Error	112.471	30	3.749[b]		
Block	Hypothesis	84.934	4	21.234	5.664	.002
	Error	112.471	30	3.749[b]		
Char * Ash	Hypothesis	4.297	4	1.074	.287	.884
	Error	112.471	30	3.749[b]		

a. .011 MS(Block) + .989 MS(Error)
b. MS(Error)

Estimated CEC (meq)

Tests of Between-Subjects Effects

Dependent Variable: eCEC

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	.438	1	.438	.483	.492
	Error	27.486	30.294	.907[a]		
PreeCEC	Hypothesis	26.706	1	26.706	29.403	.000
	Error	27.248	30	.908[b]		
Biochar	Hypothesis	4.019	2	2.009	2.212	.127
	Error	27.248	30	.908[b]		
Ash	Hypothesis	81.428	2	40.714	44.827	.000
	Error	27.248	30	.908[b]		
Block	Hypothesis	3.000	4	.750	.826	.519
	Error	27.248	30	.908[b]		
Biochar * Ash	Hypothesis	2.784	4	.696	.766	.556
	Error	27.248	30	.908[b]		

a. .006 MS(Block) + .994 MS(Error)
b. MS(Error)

Total %C

Tests of Between-Subjects Effects

Dependent Variable: PostPercentC

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	2.453[a]	13	.189	2.945	.008
Intercept	.140	1	.140	2.184	.150
PercentC	.994	1	.994	15.515	.000
Block	.318	4	.079	1.240	.316
Char	.631	2	.315	4.921	.014
Char * Ash	.569	6	.095	1.480	.220
Error	1.858	29	.064		
Total	235.337	43			
Corrected Total	4.312	42			

a. R Squared = .569 (Adjusted R Squared = .376)

LOI

Tests of Between-Subjects Effects

Dependent Variable: PostLOI

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	.048	1	.048	.414	.525
	Error	3.598	31.263	.115[a]		
PreLOI	Hypothesis	4.071	1	4.071	35.387	.000
	Error	3.566	31	.115[b]		
Char	Hypothesis	.383	2	.192	1.665	.206
	Error	3.566	31	.115[b]		
Ash	Hypothesis	.039	2	.020	.170	.845
	Error	3.566	31	.115[b]		
Block	Hypothesis	.523	4	.131	1.137	.357
	Error	3.566	31	.115[b]		
Char * Ash	Hypothesis	.276	4	.069	.600	.665
	Error	3.566	31	.115[b]		

a. .004 MS(Block) + .996 MS(Error)

b. MS(Error)

Total %N

Tests of Between-Subjects Effects

Dependent Variable: PostLECON

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	.003	1	.003	10.414	.003
	Error	.008	31.570	.000[a]		
PreLECON	Hypothesis	.003	1	.003	10.683	.003
	Error	.007	29	.000[b]		
Char	Hypothesis	.002	2	.001	3.105	.060
	Error	.007	29	.000[b]		
Ash	Hypothesis	.001	2	.001	3.066	.062
	Error	.007	29	.000[b]		
Block	Hypothesis	.005	4	.001	5.026	.003
	Error	.007	29	.000[b]		
Char * Ash	Hypothesis	.001	4	.000	1.348	.276
	Error	.007	29	.000[b]		

a. .011 MS(Block) + .989 MS(Error)
b. MS(Error)

Total %S

Tests of Between-Subjects Effects

Dependent Variable: PostLECOS

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	2.306E-005	1	2.306E-005	2.534	.122
	Error	.000	29.590	9.098E-006[a]		
PreLECOS	Hypothesis	6.518E-005	1	6.518E-005	7.167	.012
	Error	.000	29	9.095E-006[b]		
Char	Hypothesis	5.650E-005	2	2.825E-005	3.106	.060
	Error	.000	29	9.095E-006[b]		
Ash	Hypothesis	.000	2	6.144E-005	6.756	.004
	Error	.000	29	9.095E-006[b]		
Block	Hypothesis	3.752E-005	4	9.380E-006	1.031	.408
	Error	.000	29	9.095E-006[b]		
Char * Ash	Hypothesis	3.736E-005	4	9.340E-006	1.027	.410
	Error	.000	29	9.095E-006[b]		

a. .010 MS(Block) + .990 MS(Error)
b. MS(Error)

Available NH_4 (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: PostNH4

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	31.094	1	31.094	48.663	.000
	Error	7.723	12.086	.639[a]		
PreNH4	Hypothesis	.126	1	.126	.341	.563
	Error	11.432	31	.369[b]		
Char	Hypothesis	1.620	2	.810	2.197	.128
	Error	11.432	31	.369[b]		
Ash	Hypothesis	2.931	2	1.466	3.974	.029
	Error	11.432	31	.369[b]		
Block	Hypothesis	6.291	4	1.573	4.265	.007
	Error	11.432	31	.369[b]		
Char * Ash	Hypothesis	.484	4	.121	.328	.857
	Error	11.432	31	.369[b]		

a. .224 MS(Block) + .776 MS(Error)
b. MS(Error)

Available NO_3 (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: PostNO3

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	357.868	1	357.868	2.402	.173
	Error	881.395	5.915	148.998[a]		
PreNO3	Hypothesis	13.475	1	13.475	.406	.529
	Error	1029.043	31	33.195[b]		
Char	Hypothesis	39.221	2	19.611	.591	.560
	Error	1029.043	31	33.195[b]		
Ash	Hypothesis	62.655	2	31.327	.944	.400
	Error	1029.043	31	33.195[b]		
Block	Hypothesis	2558.475	4	639.619	19.269	.000
	Error	1029.043	31	33.195[b]		
Char * Ash	Hypothesis	126.955	4	31.739	.956	.445
	Error	1029.043	31	33.195[b]		

a. .191 MS(Block) + .809 MS(Error)
b. MS(Error)

Mineralizable NH_4 (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: MinNH4

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	1545.630	1	1545.630	16.324	.056
	Error	189.366	2	94.683[a]		
Char	Hypothesis	8.336	2	4.168	.097	.908
	Error	689.751	16	43.109[b]		
Ash	Hypothesis	445.333	2	222.667	5.165	.019
	Error	689.751	16	43.109[b]		
Block	Hypothesis	189.366	2	94.683	2.196	.144
	Error	689.751	16	43.109[b]		
Char * Ash	Hypothesis	17.509	4	4.377	.102	.980
	Error	689.751	16	43.109[b]		

a. MS(Block)
b. MS(Error)

Mineralizable NO_3 (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: MinNO3

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	11067.143	1	11067.143	7.986	.106
	Error	2771.584	2	1385.792[a]		
Char	Hypothesis	376.008	2	188.004	1.339	.290
	Error	2247.302	16	140.456[b]		
Ash	Hypothesis	119.402	2	59.701	.425	.661
	Error	2247.302	16	140.456[b]		
Block	Hypothesis	2771.584	2	1385.792	9.866	.002
	Error	2247.302	16	140.456[b]		
Char * Ash	Hypothesis	62.656	4	15.664	.112	.977
	Error	2247.302	16	140.456[b]		

a. MS(Block)
b. MS(Error)

Extractable Cu (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: PostExtractCu

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	.030	1	.030	8.779	.006
	Error	.114	32.704	.003[a]		
PreExtractCu	Hypothesis	.015	1	.015	4.296	.047
	Error	.105	31	.003[b]		
Char	Hypothesis	.034	2	.017	5.044	.013
	Error	.105	31	.003[b]		
Ash	Hypothesis	.004	2	.002	.522	.598
	Error	.105	31	.003[b]		
Block	Hypothesis	.065	4	.016	4.803	.004
	Error	.105	31	.003[b]		
Char * Ash	Hypothesis	.014	4	.004	1.033	.406
	Error	.105	31	.003[b]		

a. .006 MS(Block) + .994 MS(Error)
b. MS(Error)

Extractable Fe (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: PostExtractFe

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	155.221	1	155.221	.192	.664
	Error	25668.429	31.748	808.506[a]		
PreExtactFe	Hypothesis	5318.561	1	5318.561	6.589	.015
	Error	25024.066	31	807.228[b]		
Char	Hypothesis	2700.133	2	1350.067	1.672	.204
	Error	25024.066	31	807.228[b]		
Ash	Hypothesis	21076.135	2	10538.067	13.055	.000
	Error	25024.066	31	807.228[b]		
Block	Hypothesis	3697.975	4	924.494	1.145	.354
	Error	25024.066	31	807.228[b]		
Char * Ash	Hypothesis	1105.842	4	276.460	.342	.847
	Error	25024.066	31	807.228[b]		

a. .011 MS(Block) + .989 MS(Error)
b. MS(Error)

Extractable Mn (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: PostExtractMn

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	8.243	1	8.243	6.538	.015
	Error	40.484	32.107	1.261[a]		
PreExtractMn	Hypothesis	3.305	1	3.305	2.642	.114
	Error	38.784	31	1.251[b]		
Char	Hypothesis	8.247	2	4.123	3.296	.050
	Error	38.784	31	1.251[b]		
Ash	Hypothesis	47.170	2	23.585	18.851	.000
	Error	38.784	31	1.251[b]		
Block	Hypothesis	8.541	4	2.135	1.707	.174
	Error	38.784	31	1.251[b]		
Char * Ash	Hypothesis	8.586	4	2.146	1.716	.172
	Error	38.784	31	1.251[b]		

a. .011 MS(Block) + .989 MS(Error)
b. MS(Error)

Extractable Zn (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: PostExtractZn

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	.000	1	.000	.002	.968
	Error	3.194	32.053	.100[a]		
PerExtractZn	Hypothesis	1.108	1	1.108	11.221	.002
	Error	3.061	31	.099[b]		
Char	Hypothesis	.403	2	.202	2.040	.147
	Error	3.061	31	.099[b]		
Ash	Hypothesis	14.426	2	7.213	73.043	.000
	Error	3.061	31	.099[b]		
Block	Hypothesis	.783	4	.196	1.982	.122
	Error	3.061	31	.099[b]		
Char * Ash	Hypothesis	.129	4	.032	.326	.858
	Error	3.061	31	.099[b]		

a. .009 MS(Block) + .991 MS(Error)
b. MS(Error)

Available P (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: PostAvailP

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	104.107	1	104.107	1.556	.221
	Error	2126.764	31.794	66.893[a]		
PreAvailP	Hypothesis	4209.279	1	4209.279	63.006	.000
	Error	2071.019	31	66.807[b]		
Char	Hypothesis	319.588	2	159.794	2.392	.108
	Error	2071.019	31	66.807[b]		
Ash	Hypothesis	36.936	2	18.468	.276	.760
	Error	2071.019	31	66.807[b]		
Block	Hypothesis	295.877	4	73.969	1.107	.371
	Error	2071.019	31	66.807[b]		
Char * Ash	Hypothesis	285.070	4	71.268	1.067	.390
	Error	2071.019	31	66.807[b]		

a. .012 MS(Block) + .988 MS(Error)
b. MS(Error)

'Total' Acid Digestible Al (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: PostAcidAl

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	15913339.843	1	15913339.843	15.717	.000
	Error	31622888.340	31.233	1012481.594[a]		
PreAcidAl	Hypothesis	1523777.296	1	1523777.296	1.509	.229
	Error	31303370.803	31	1009786.155[b]		
Char	Hypothesis	1548823.783	2	774411.892	.767	.473
	Error	31303370.803	31	1009786.155[b]		
Ash	Hypothesis	107756.467	2	53878.233	.053	.948
	Error	31303370.803	31	1009786.155[b]		
Block	Hypothesis	13541810.523	4	3385452.631	3.353	.022
	Error	31303370.803	31	1009786.155[b]		
Char * Ash	Hypothesis	2612480.390	4	653120.097	.647	.633
	Error	31303370.803	31	1009786.155[b]		

a. .001 MS(Block) + .999 MS(Error)
b. MS(Error)

'Total' Acid Digestible B (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: PostAcidB

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	.006	1	.006	.007	.934
	Error	26.595	31.746	.838[a]		
PreAcidB	Hypothesis	.345	1	.345	.415	.524
	Error	25.747	31	.831[b]		
Char	Hypothesis	.941	2	.470	.566	.573
	Error	25.747	31	.831[b]		
Ash	Hypothesis	5.506	2	2.753	3.315	.050
	Error	25.747	31	.831[b]		
Block	Hypothesis	10.770	4	2.692	3.242	.025
	Error	25.747	31	.831[b]		
Char * Ash	Hypothesis	5.584	4	1.396	1.681	.180
	Error	25.747	31	.831[b]		

a. .004 MS(Block) + .996 MS(Error)
b. MS(Error)

'Total' Acid Digestible Cu (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: PostAcidCu

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	232.617	1	232.617	54.153	.000
	Error	140.642	32.741	4.296[a]		
PreAcidCu	Hypothesis	2.135	1	2.135	.506	.482
	Error	130.866	31	4.221[b]		
Char	Hypothesis	9.382	2	4.691	1.111	.342
	Error	130.866	31	4.221[b]		
Ash	Hypothesis	12.665	2	6.333	1.500	.239
	Error	130.866	31	4.221[b]		
Block	Hypothesis	38.502	4	9.625	2.280	.083
	Error	130.866	31	4.221[b]		
Char * Ash	Hypothesis	7.716	4	1.929	.457	.767
	Error	130.866	31	4.221[b]		

a. .014 MS(Block) + .986 MS(Error)
b. MS(Error)

'Total' Acid Digestible Fe (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: PostAcidFe

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	425473476.910	1	425473476.910	9.862	.004
	Error	1356570568.271	31.445	43141190.504[a]		
PreAcidFe	Hypothesis	4487.811	1	4487.811	.000	.992
	Error	1333395363.927	31	43012753.675[b]		
Char	Hypothesis	78111836.762	2	39055918.381	.908	.414
	Error	1333395363.927	31	43012753.675[b]		
Ash	Hypothesis	30663051.596	2	15331525.798	.356	.703
	Error	1333395363.927	31	43012753.675[b]		
Block	Hypothesis	290322657.459	4	72580664.365	1.687	.178
	Error	1333395363.927	31	43012753.675[b]		
Char * Ash	Hypothesis	155057766.771	4	38764441.693	.901	.475
	Error	1333395363.927	31	43012753.675[b]		

a. .004 MS(Block) + .996 MS(Error)
b. MS(Error)

'Total' Acid Digestible Ni (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: PostAcidZn

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	706.337	1	706.337	12.622	.001
	Error	1778.857	31.787	55.962[a]		
PreAcidZn	Hypothesis	11.376	1	11.376	.205	.654
	Error	1719.404	31	55.465[b]		
Char	Hypothesis	22.862	2	11.431	.206	.815
	Error	1719.404	31	55.465[b]		
Ash	Hypothesis	1846.025	2	923.012	16.641	.000
	Error	1719.404	31	55.465[b]		
Block	Hypothesis	687.982	4	171.996	3.101	.029
	Error	1719.404	31	55.465[b]		
Char * Ash	Hypothesis	362.208	4	90.552	1.633	.191
	Error	1719.404	31	55.465[b]		

a. .004 MS(Block) + .996 MS(Error)
b. MS(Error)

'Total' Acid Digestible Zn (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: PostAcidNi

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	66.475	1	66.475	10.769	.003
	Error	194.247	31.467	6.173[a]		
PreAcidNi	Hypothesis	2.213	1	2.213	.360	.553
	Error	190.457	31	6.144[b]		
Char	Hypothesis	6.982	2	3.491	.568	.572
	Error	190.457	31	6.144[b]		
Ash	Hypothesis	.029	2	.015	.002	.998
	Error	190.457	31	6.144[b]		
Block	Hypothesis	64.275	4	16.069	2.615	.054
	Error	190.457	31	6.144[b]		
Char * Ash	Hypothesis	11.373	4	2.843	.463	.762
	Error	190.457	31	6.144[b]		

a. .003 MS(Block) + .997 MS(Error)
b. MS(Error)

Microbial C ($\mu g\ g^{-1}$)

Tests of Between-Subjects Effects

Dependent Variable: MBC

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	241255.688	1	241255.688	71.173	.014
	Error	6779.394	2	3389.697[a]		
Char	Hypothesis	478.375	2	239.188	.176	.840
	Error	21686.916	16	1355.432[b]		
Ash	Hypothesis	853.992	2	426.996	.315	.734
	Error	21686.916	16	1355.432[b]		
Block	Hypothesis	6779.394	2	3389.697	2.501	.113
	Error	21686.916	16	1355.432[b]		
Char * Ash	Hypothesis	2032.525	4	508.131	.375	.823
	Error	21686.916	16	1355.432[b]		

a. MS(Block)
b. MS(Error)

Microbial N ($\mu g\ g^{-1}$)

Tests of Between-Subjects Effects

Dependent Variable: MBN

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	1687.672	1	1687.672	41.775	.023
	Error	80.799	2	40.400[a]		
Char	Hypothesis	36.599	2	18.299	1.667	.220
	Error	175.612	16	10.976[b]		
Ash	Hypothesis	8.466	2	4.233	.386	.686
	Error	175.612	16	10.976[b]		
Block	Hypothesis	80.799	2	40.400	3.681	.048
	Error	175.612	16	10.976[b]		
Char * Ash	Hypothesis	24.332	4	6.083	.554	.699
	Error	175.612	16	10.976[b]		

a. MS(Block)
b. MS(Error)

CO_2 Soil Respiration

Tests of Within-Subjects Effects

Measure: CO2

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
time	Sphericity Assumed	.416	4	.104	7.880	.000
	Greenhouse-Geisser	.416	1.313	.317	7.880	.007
	Huynh-Feldt	.416	2.279	.183	7.880	.001
	Lower-bound	.416	1.000	.416	7.880	.013
time * Block	Sphericity Assumed	.803	8	.100	7.600	.000
	Greenhouse-Geisser	.803	2.627	.306	7.600	.002
	Huynh-Feldt	.803	4.557	.176	7.600	.000
	Lower-bound	.803	2.000	.402	7.600	.005
time * C	Sphericity Assumed	.011	8	.001	.104	.999
	Greenhouse-Geisser	.011	2.627	.004	.104	.942
	Huynh-Feldt	.011	4.557	.002	.104	.987
	Lower-bound	.011	2.000	.006	.104	.902
time * A	Sphericity Assumed	.040	8	.005	.382	.927
	Greenhouse-Geisser	.040	2.627	.015	.382	.742
	Huynh-Feldt	.040	4.557	.009	.382	.843
	Lower-bound	.040	2.000	.020	.382	.689
time * C * A	Sphericity Assumed	.202	16	.013	.957	.513
	Greenhouse-Geisser	.202	5.254	.038	.957	.469
	Huynh-Feldt	.202	9.114	.022	.957	.491
	Lower-bound	.202	4.000	.051	.957	.458
Error(time)	Sphericity Assumed	.846	64	.013		
	Greenhouse-Geisser	.846	21.016	.040		
	Huynh-Feldt	.846	36.457	.023		
	Lower-bound	.846	16.000	.053		

Tree Height Sb 2012 (cm)

Tests of Between-Subjects Effects

Dependent Variable: SbHeightAugust2012

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	48.915	1	48.915	18.630	.000
	Error	83.358	31.747	2.626[a]		
SbHeightIntial	Hypothesis	28.379	1	28.379	10.896	.002
	Error	80.742	31	2.605[b]		
Char	Hypothesis	7.819	2	3.909	1.501	.239
	Error	80.742	31	2.605[b]		
Ash	Hypothesis	7.959	2	3.979	1.528	.233
	Error	80.742	31	2.605[b]		
Block	Hypothesis	29.356	4	7.339	2.818	.042
	Error	80.742	31	2.605[b]		
Char * Ash	Hypothesis	3.073	4	.768	.295	.879
	Error	80.742	31	2.605[b]		

a. .004 MS(Block) + .996 MS(Error)

b. MS(Error)

Tree Height Sw 2012 (cm)

Tests of Between-Subjects Effects

Dependent Variable: SwHeightAugust2012

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	49.243	1	49.243	58.745	.000
	Error	27.080	32.306	.838[a]		
SwHeightIntial	Hypothesis	137.420	1	137.420	166.077	.000
	Error	25.651	31	.827[b]		
Char	Hypothesis	.113	2	.056	.068	.934
	Error	25.651	31	.827[b]		
Ash	Hypothesis	4.905	2	2.453	2.964	.066
	Error	25.651	31	.827[b]		
Block	Hypothesis	7.796	4	1.949	2.355	.075
	Error	25.651	31	.827[b]		
Char * Ash	Hypothesis	2.982	4	.745	.901	.475
	Error	25.651	31	.827[b]		

a. .010 MS(Block) + .990 MS(Error)

b. MS(Error)

Tree Height 2013 Sb (cm)

Tests of Between-Subjects Effects

Dependent Variable: SbHeightAugust2013

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	261.385	1	261.385	14.394	.001
	Error	600.157	33.049	18.160[a]		
SbHeightIntial	Hypothesis	.113	1	.113	.006	.937
	Error	544.555	31	17.566[b]		
Char	Hypothesis	17.635	2	8.817	.502	.610
	Error	544.555	31	17.566[b]		
Ash	Hypothesis	70.069	2	35.034	1.994	.153
	Error	544.555	31	17.566[b]		
Block	Hypothesis	603.190	4	150.797	8.584	.000
	Error	544.555	31	17.566[b]		
Char * Ash	Hypothesis	39.153	4	9.788	.557	.695
	Error	544.555	31	17.566[b]		

a. .004 MS(Block) + .996 MS(Error)

b. MS(Error)

Tree Height 2013 Sw (cm)

Tests of Between-Subjects Effects

Dependent Variable: SwHeightAugust2013

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	317.055	1	317.055	35.885	.000
	Error	301.332	34.106	8.835[a]		
SwHeightIntial	Hypothesis	18.347	1	18.347	2.194	.149
	Error	259.200	31	8.361[b]		
Char	Hypothesis	5.331	2	2.666	.319	.729
	Error	259.200	31	8.361[b]		
Ash	Hypothesis	9.980	2	4.990	.597	.557
	Error	259.200	31	8.361[b]		
Block	Hypothesis	230.208	4	57.552	6.883	.000
	Error	259.200	31	8.361[b]		
Char * Ash	Hypothesis	34.235	4	8.559	1.024	.411
	Error	259.200	31	8.361[b]		

a. .010 MS(Block) + .990 MS(Error)

b. MS(Error)

Sb Foliage Al (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: Al

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	520343.336	1	520343.336	98.255	.001
	Error	21183.280	4	5295.820[a]		
Biochar	Hypothesis	3471.627	2	1735.814	.425	.657
	Error	130552.874	32	4079.777[b]		
Ash	Hypothesis	16271.440	2	8135.720	1.994	.153
	Error	130552.874	32	4079.777[b]		
Block	Hypothesis	21183.280	4	5295.820	1.298	.292
	Error	130552.874	32	4079.777[b]		
Biochar * Ash	Hypothesis	28671.258	4	7167.814	1.757	.162
	Error	130552.874	32	4079.777[b]		

a. MS(Block)
b. MS(Error)

Sb Foliage B (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: B

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	43676.975	1	43676.975	269.109	.000
	Error	649.208	4	162.302[a]		
Biochar	Hypothesis	23.066	2	11.533	.232	.794
	Error	1589.646	32	49.676[b]		
Ash	Hypothesis	5098.305	2	2549.153	51.315	.000
	Error	1589.646	32	49.676[b]		
Block	Hypothesis	649.208	4	162.302	3.267	.024
	Error	1589.646	32	49.676[b]		
Biochar * Ash	Hypothesis	137.632	4	34.408	.693	.603
	Error	1589.646	32	49.676[b]		

a. MS(Block)
b. MS(Error)

Sb Foliage Ca (%)

Tests of Between-Subjects Effects

Dependent Variable: Ca

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	23.949	1	23.949	246.900	.000
	Error	.388	4	.097[a]		
Biochar	Hypothesis	.015	2	.007	.194	.824
	Error	1.236	32	.039[b]		
Ash	Hypothesis	.327	2	.164	4.240	.023
	Error	1.236	32	.039[b]		
Block	Hypothesis	.388	4	.097	2.512	.061
	Error	1.236	32	.039[b]		
Biochar * Ash	Hypothesis	.109	4	.027	.703	.596
	Error	1.236	32	.039[b]		

a. MS(Block)
b. MS(Error)

Sb Foliage Cu (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: Cu

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	214.759	1	214.759	60.059	.001
	Error	14.303	4	3.576[a]		
Biochar	Hypothesis	.754	2	.377	.249	.781
	Error	48.408	32	1.513[b]		
Ash	Hypothesis	7.846	2	3.923	2.593	.090
	Error	48.408	32	1.513[b]		
Block	Hypothesis	14.303	4	3.576	2.364	.074
	Error	48.408	32	1.513[b]		
Biochar * Ash	Hypothesis	3.618	4	.905	.598	.667
	Error	48.408	32	1.513[b]		

a. MS(Block)
b. MS(Error)

Sb Foliage Fe (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: Fe

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	5936903.381	1	5936903.381	36.388	.004
	Error	652614.884	4	163153.721[a]		
Biochar	Hypothesis	19010.893	2	9505.446	.139	.870
	Error	2182870.566	32	68214.705[b]		
Ash	Hypothesis	158464.590	2	79232.295	1.162	.326
	Error	2182870.566	32	68214.705[b]		
Block	Hypothesis	652614.884	4	163153.721	2.392	.071
	Error	2182870.566	32	68214.705[b]		
Biochar * Ash	Hypothesis	326462.328	4	81615.582	1.196	.331
	Error	2182870.566	32	68214.705[b]		

a. MS(Block)
b. MS(Error)

Sb Foliage K (%)

Tests of Between-Subjects Effects

Dependent Variable: K

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	18.997	1	18.997	1114.504	.000
	Error	.068	4	.017[a]		
Biochar	Hypothesis	.039	2	.020	.593	.558
	Error	1.061	32	.033[b]		
Ash	Hypothesis	.247	2	.124	3.730	.035
	Error	1.061	32	.033[b]		
Block	Hypothesis	.068	4	.017	.514	.726
	Error	1.061	32	.033[b]		
Biochar * Ash	Hypothesis	.105	4	.026	.789	.541
	Error	1.061	32	.033[b]		

a. MS(Block)
b. MS(Error)

Sb Foliage Mg (%)

Tests of Between-Subjects Effects

Dependent Variable: Mg

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	2.279	1	2.279	2580.678	.000
	Error	.004	4	.001[a]		
Biochar	Hypothesis	.002	2	.001	.332	.720
	Error	.091	32	.003[b]		
Ash	Hypothesis	.019	2	.010	3.353	.048
	Error	.091	32	.003[b]		
Block	Hypothesis	.004	4	.001	.311	.868
	Error	.091	32	.003[b]		
Biochar * Ash	Hypothesis	.015	4	.004	1.292	.294
	Error	.091	32	.003[b]		

a. MS(Block)
b. MS(Error)

Sb Foliage Mn (%)

Tests of Between-Subjects Effects

Dependent Variable: Mn

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	1792593.745	1	1792593.745	203.274	.000
	Error	35274.375	4	8818.594[a]		
Biochar	Hypothesis	2143.997	2	1071.998	.158	.854
	Error	216784.063	32	6774.502[b]		
Ash	Hypothesis	14389.712	2	7194.856	1.062	.358
	Error	216784.063	32	6774.502[b]		
Block	Hypothesis	35274.375	4	8818.594	1.302	.290
	Error	216784.063	32	6774.502[b]		
Biochar * Ash	Hypothesis	12559.331	4	3139.833	.463	.762
	Error	216784.063	32	6774.502[b]		

a. MS(Block)
b. MS(Error)

Sb Foliage N (%)

Tests of Between-Subjects Effects

Dependent Variable: N

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	96.771	1	96.771	96.155	.001
	Error	4.026	4	1.006[a]		
Biochar	Hypothesis	.042	2	.021	.342	.713
	Error	1.967	32	.061[b]		
Ash	Hypothesis	.363	2	.181	2.952	.067
	Error	1.967	32	.061[b]		
Block	Hypothesis	4.026	4	1.006	16.371	.000
	Error	1.967	32	.061[b]		
Biochar * Ash	Hypothesis	.262	4	.065	1.065	.390
	Error	1.967	32	.061[b]		

a. MS(Block)
b. MS(Error)

Sb Foliage Na (%)

Tests of Between-Subjects Effects

Dependent Variable: Na

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	.000	1	.000	104.430	.001
	Error	8.963E-006	4	2.241E-006[a]		
Biochar	Hypothesis	2.485E-006	2	1.243E-006	.501	.610
	Error	7.931E-005	32	2.478E-006[b]		
Ash	Hypothesis	5.509E-006	2	2.755E-006	1.111	.341
	Error	7.931E-005	32	2.478E-006[b]		
Block	Hypothesis	8.963E-006	4	2.241E-006	.904	.473
	Error	7.931E-005	32	2.478E-006[b]		
Biochar * Ash	Hypothesis	8.627E-006	4	2.157E-006	.870	.492
	Error	7.931E-005	32	2.478E-006[b]		

a. MS(Block)
b. MS(Error)

Sb Foliage P (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: P

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	2.462	1	2.462	269.962	.000
	Error	.036	4	.009[a]		
Biochar	Hypothesis	.002	2	.001	.166	.848
	Error	.165	32	.005[b]		
Ash	Hypothesis	.011	2	.006	1.106	.343
	Error	.165	32	.005[b]		
Block	Hypothesis	.036	4	.009	1.767	.160
	Error	.165	32	.005[b]		
Biochar * Ash	Hypothesis	.029	4	.007	1.389	.260
	Error	.165	32	.005[b]		

a. MS(Block)
b. MS(Error)

Sb Foliage S (%)

Tests of Between-Subjects Effects

Dependent Variable: S

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	.944	1	.944	630.701	.000
	Error	.006	4	.001[a]		
Biochar	Hypothesis	4.131E-005	2	2.065E-005	.012	.988
	Error	.056	32	.002[b]		
Ash	Hypothesis	.141	2	.071	40.601	.000
	Error	.056	32	.002[b]		
Block	Hypothesis	.006	4	.001	.862	.497
	Error	.056	32	.002[b]		
Biochar * Ash	Hypothesis	.011	4	.003	1.524	.219
	Error	.056	32	.002[b]		

a. MS(Block)
b. MS(Error)

Sb Foliage Zn (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: Zn

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	89822.882	1	89822.882	16.995	.015
	Error	21140.828	4	5285.207[a]		
Biochar	Hypothesis	5222.308	2	2611.154	1.033	.368
	Error	80925.695	32	2528.928[b]		
Ash	Hypothesis	4016.336	2	2008.168	.794	.461
	Error	80925.695	32	2528.928[b]		
Block	Hypothesis	21140.828	4	5285.207	2.090	.105
	Error	80925.695	32	2528.928[b]		
Biochar * Ash	Hypothesis	12088.001	4	3022.000	1.195	.332
	Error	80925.695	32	2528.928[b]		

a. MS(Block)
b. MS(Error)

Sw Foliage Al (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: Al

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	448412.813	1	448412.813	118.410	.000
	Error	15147.745	4	3786.936[a]		
Biochar	Hypothesis	429.366	2	214.683	.135	.874
	Error	50900.794	32	1590.650[b]		
Ash	Hypothesis	8466.146	2	4233.073	2.661	.085
	Error	50900.794	32	1590.650[b]		
Block	Hypothesis	15147.745	4	3786.936	2.381	.072
	Error	50900.794	32	1590.650[b]		
Biochar * Ash	Hypothesis	6157.055	4	1539.264	.968	.439
	Error	50900.794	32	1590.650[b]		

a. MS(Block)
b. MS(Error)

Sw Foliage B (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: B

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	12120.346	1	12120.346	67.127	.001
	Error	722.237	4	180.559[a]		
Biochar	Hypothesis	271.747	2	135.873	3.743	.035
	Error	1161.504	32	36.297[b]		
Ash	Hypothesis	1802.134	2	901.067	24.825	.000
	Error	1161.504	32	36.297[b]		
Block	Hypothesis	722.237	4	180.559	4.974	.003
	Error	1161.504	32	36.297[b]		
Biochar * Ash	Hypothesis	101.126	4	25.282	.697	.600
	Error	1161.504	32	36.297[b]		

a. MS(Block)
b. MS(Error)

Sw Foliage Ca (%)

Tests of Between-Subjects Effects

Dependent Variable: Ca

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	11.691	1	11.691	76.561	.001
	Error	.611	4	.153[a]		
Biochar	Hypothesis	.001	2	.001	.035	.965
	Error	.577	32	.018[b]		
Ash	Hypothesis	.013	2	.006	.359	.701
	Error	.577	32	.018[b]		
Block	Hypothesis	.611	4	.153	8.470	.000
	Error	.577	32	.018[b]		
Biochar * Ash	Hypothesis	.047	4	.012	.655	.628
	Error	.577	32	.018[b]		

a. MS(Block)
b. MS(Error)

Sw Foliage Cu (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: Cu

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	162.297	1	162.297	83.454	.001
	Error	7.779	4	1.945[a]		
Biochar	Hypothesis	.137	2	.068	.186	.831
	Error	11.776	32	.368[b]		
Ash	Hypothesis	.118	2	.059	.160	.853
	Error	11.776	32	.368[b]		
Block	Hypothesis	7.779	4	1.945	5.285	.002
	Error	11.776	32	.368[b]		
Biochar * Ash	Hypothesis	.728	4	.182	.495	.740
	Error	11.776	32	.368[b]		

a. MS(Block)
b. MS(Error)

Sw Foliage Fe (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: Fe

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	4384437.487	1	4384437.487	47.135	.002
	Error	372072.991	4	93018.248[a]		
Biochar	Hypothesis	10045.529	2	5022.765	.141	.869
	Error	1136633.469	32	35519.796[b]		
Ash	Hypothesis	33339.242	2	16669.621	.469	.630
	Error	1136633.469	32	35519.796[b]		
Block	Hypothesis	372072.991	4	93018.248	2.619	.053
	Error	1136633.469	32	35519.796[b]		
Biochar * Ash	Hypothesis	87743.411	4	21935.853	.618	.653
	Error	1136633.469	32	35519.796[b]		

a. MS(Block)
b. MS(Error)

Sw Foliage K (%)

Tests of Between-Subjects Effects

Dependent Variable: K

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	9.887	1	9.887	493.002	.000
	Error	.080	4	.020[a]		
Biochar	Hypothesis	.002	2	.001	.071	.932
	Error	.446	32	.014[b]		
Ash	Hypothesis	.093	2	.047	3.342	.048
	Error	.446	32	.014[b]		
Block	Hypothesis	.080	4	.020	1.438	.244
	Error	.446	32	.014[b]		
Biochar * Ash	Hypothesis	.068	4	.017	1.225	.320
	Error	.446	32	.014[b]		

a. MS(Block)
b. MS(Error)

Sw Foliage Mg (%)

Tests of Between-Subjects Effects

Dependent Variable: Mg

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	.859	1	.859	254.691	.000
	Error	.013	4	.003[a]		
Biochar	Hypothesis	.000	2	.000	.156	.857
	Error	.041	32	.001[b]		
Ash	Hypothesis	.001	2	.000	.322	.727
	Error	.041	32	.001[b]		
Block	Hypothesis	.013	4	.003	2.640	.052
	Error	.041	32	.001[b]		
Biochar * Ash	Hypothesis	.005	4	.001	.915	.467
	Error	.041	32	.001[b]		

a. MS(Block)
b. MS(Error)

Sw Foliage Mn (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: Mn

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	1753374.864	1	1753374.864	237.784	.000
	Error	29495.312	4	7373.828[a]		
Biochar	Hypothesis	3549.247	2	1774.623	.885	.423
	Error	64159.344	32	2004.979[b]		
Ash	Hypothesis	1175.961	2	587.980	.293	.748
	Error	64159.344	32	2004.979[b]		
Block	Hypothesis	29495.312	4	7373.828	3.678	.014
	Error	64159.344	32	2004.979[b]		
Biochar * Ash	Hypothesis	6523.272	4	1630.818	.813	.526
	Error	64159.344	32	2004.979[b]		

a. MS(Block)
b. MS(Error)

Sw Foliage N (%)

Tests of Between-Subjects Effects

Dependent Variable: N

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	67.222	1	67.222	54.776	.002
	Error	4.909	4	1.227[a]		
Biochar	Hypothesis	.032	2	.016	.238	.789
	Error	2.132	32	.067[b]		
Ash	Hypothesis	.103	2	.051	.770	.472
	Error	2.132	32	.067[b]		
Block	Hypothesis	4.909	4	1.227	18.423	.000
	Error	2.132	32	.067[b]		
Biochar * Ash	Hypothesis	.069	4	.017	.259	.902
	Error	2.132	32	.067[b]		

a. MS(Block)
b. MS(Error)

Sw Foliage Na (%)

Tests of Between-Subjects Effects

Dependent Variable: Na

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	.000	1	.000	30.300	.005
	Error	2.876E-005	4	7.190E-006[a]		
Biochar	Hypothesis	5.011E-006	2	2.505E-006	.813	.453
	Error	9.862E-005	32	3.082E-006[b]		
Ash	Hypothesis	1.371E-005	2	6.857E-006	2.225	.125
	Error	9.862E-005	32	3.082E-006[b]		
Block	Hypothesis	2.876E-005	4	7.190E-006	2.333	.077
	Error	9.862E-005	32	3.082E-006[b]		
Biochar * Ash	Hypothesis	4.245E-006	4	1.061E-006	.344	.846
	Error	9.862E-005	32	3.082E-006[b]		

a. MS(Block)
b. MS(Error)

Sw Foliage P (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: P

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	1.326	1	1.326	399.069	.000
	Error	.013	4	.003[a]		
Biochar	Hypothesis	.001	2	.000	.216	.807
	Error	.066	32	.002[b]		
Ash	Hypothesis	.001	2	.001	.307	.738
	Error	.066	32	.002[b]		
Block	Hypothesis	.013	4	.003	1.608	.196
	Error	.066	32	.002[b]		
Biochar * Ash	Hypothesis	.012	4	.003	1.508	.223
	Error	.066	32	.002[b]		

a. MS(Block)
b. MS(Error)

Sw Foliage S (%)

Tests of Between-Subjects Effects

Dependent Variable: S

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	.429	1	.429	213.874	.000
	Error	.008	4	.002[a]		
Biochar	Hypothesis	.000	2	.000	.445	.645
	Error	.014	32	.000[b]		
Ash	Hypothesis	.029	2	.015	33.579	.000
	Error	.014	32	.000[b]		
Block	Hypothesis	.008	4	.002	4.647	.005
	Error	.014	32	.000[b]		
Biochar * Ash	Hypothesis	.001	4	.000	.428	.788
	Error	.014	32	.000[b]		

a. MS(Block)
b. MS(Error)

Sw Foliage Zn (mg kg^{-1})

Tests of Between-Subjects Effects

Dependent Variable: Zn

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	27559.443	1	27559.443	38.427	.003
	Error	2868.741	4	717.185[a]		
Biochar	Hypothesis	215.234	2	107.617	.529	.594
	Error	6514.945	32	203.592[b]		
Ash	Hypothesis	80.668	2	40.334	.198	.821
	Error	6514.945	32	203.592[b]		
Block	Hypothesis	2868.741	4	717.185	3.523	.017
	Error	6514.945	32	203.592[b]		
Biochar * Ash	Hypothesis	545.775	4	136.444	.670	.617
	Error	6514.945	32	203.592[b]		

a. MS(Block)
b. MS(Error)