BIOCHAR AS AN AMENDMENT TO ACID SOILS

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By

Arnoldus Klau Berek

Dissertation Committee:

Nguyen V. Hue, Chairperson
Theodore J. K. Radovich
Jonathan L. Deenik
Kent D. Kobayashi
Qing X. Li

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I dedicate this dissertation to my wife Elisabeth Kristanti, my daughters Ignatia Arina Rinukti Klau Berek, Johanna Aditha Christy Klau Berek and Beda Arlista Bano Berek, and to memory of my father Paulus Bere Seran Una and my mother Maria Seuk Lekik.

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ABSTRACT

The capacity of biochar to improve acid soil productivity and enhance nutrient retention was the main focus of this study. The specific objectives were to characterize six wood-derived biochars, to assess biochars' liming effects on Hawaiian and Indonesian acid soils, and to study nutrient retention of biochars. Six and another two biochars were collected, characterized, and then were used to evaluate their liming effect on a Hawaiian and two Indonesian acid soils with *Desmodium intortum* and soybean (*Glycine max*) as test plants, respectively. Two biochars in combination with two composts (both at 2%) as nutrient sources were used to investigate their nutrient retention with pak choi (*Brassica rapa*) as the test plant. The results showed that six wood-derived biochars were different in their properties, including ash content, pH, cation exchange capacity (CEC), $CaCO_3$ equivalent, basic cations and surface functional groups. Based on their $CaCO_3$ equivalent, leucaena (*Leucaena leucocephala*) and lac tree (*Schleichera oleosa*), Hilo mixed wood and she oak (*Casuarina junghuhniana*), and mahogany (*Sweitenia mahagoni*) and mountain gum (*Eucalyptus urophylla*), were grouped into the highest, moderate, and lowest liming potential biochars, respectively. Additions of six biochars at 2% and 4% with or without 2 cmolc/kg of lime to a Hawaiian acid soil increased soil pH and CEC, reduced exchangeable Al, enriched plant nutrients and enhanced Desmodium growth with lac tree and leucaena being most effective, followed by she oak and Hilo mixed wood biochars. Similar results were obtained from lac tree wood and rice husk biochars (4 and 8%) applied to two Indonesian acid soils. Addition of lac tree wood and Hilo mixed wood biochars in combination with vermicompost or thermocompost to a Ultisol and a Oxisol of Hawaii showed a positive interaction effect on EC, P and K, cabbage fresh and dry matters. Biochars increased soil pH, plant tissue Ca, retention of

K, Ca and Mg, and reduced exchangeable Al in both soils. Overall, the liming capacity and nutrient retention potential of selected biochars have been positive.

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CHAPTER 1. INTRODUCTION

1.1. Background

Biochar is a type of charcoal that is applied to soil in order to improve soil productivity and to capture and store atmospheric carbon. It is produced by heating biomass at low temperature (<700^{o}C) in a closed container with limited or without oxygen supply. Feedstock and thermochemical decomposition conditions during pyrolysis, carbonization and gasification processes determine biochar properties and its agronomic values.

Biochar or other names such as pyrogenic carbon (PC) or engineered carbon, is a relatively new term that is used to define the product of thermal decomposition or incomplete combustion of biomass or biowaste under a limited supply of oxygen or by natural fire. Its production was inspired by the discovery of the anthropogenic Amazonian Dark Earth (ADE) or Terra Preta, which had a higher nutrient content, cation exchange capacity (CEC) and organic matter than the surrounding soils (Glaser *et al.* 2000, Lehmann *et al.* 2002, Lehmann and Joseph 2009). Recently, biochar has often been produced in a pyrolytic process for specific purposes such as a soil amendment or carbon sequestration agent (Lehmann and Joseph 2009, Marris 2006, Glaser *et al.* 2009, Woolf *et al.* 2010).

Since biochars can be produced from a variety of feedstocks and under different production processes and conditions, they have different physical and chemical properties (Antal and Gronli 2003); thus potentially having different effects when applied to soils. Singh *et al.* (2010) reported significant differences in pH, CEC, ash content, surface basicity and acidity, lime equivalent, nutrient content of 11 biochars made from wood, manure, leaf, papermill sludge, poultry litter produced under 400^{o}C and 500^{o}C pyrolysis temperatures, with and without steam activation. Keiluweit *et al.* (2010) also found that wood pine biochar differed from tall fescue grass biochar in respect to their volatile matter (VM); fixed carbon; ash content; C, N, H, and O content; H:C and O:C ratios; and surface area (SA). In addition, Mukherjee *et al.* (2011) observed a different surface chemistry represented by pH, VM, ash content, SA, CEC, anion exchange capacity (AEC), point of zero net charge (PZNC), zeta potential (ZP), isoelectric point (IEP), and the distribution of surface acid functional groups of oak, pine and grass laboratory-produced biochars at different pyrolysis temperatures. Lee *et al.* (2010) showed that biochar produced from the same cornstover under fast pyrolysis at 450^{o}C had a higher CEC and O:C ratio than those obtained from gasification at 700^{o}C. Such results show a need for biochar characterization before its use as a soil amendment.

Biochar has been shown as a promising and environment-friendly soil amendment for sustainable agriculture and climate change mitigation (Glaser *et al.* 2002). Recent research revealed that addition of biochar as a soil amendment can increase soil water holding capacity (Novak *et al.* 2009, Laird *et al.* 2010) and aggregation (Mukherjee and Lal 2014), pH (Yuan and Xu 2011), CEC (Silber *et al.* 2010), reduce soil exchangeable Al (Van Zwieten *et al.* 2010), release plant nutrient to the soil (Smider and Singh 2014), retain nutrient and prevent the leaching of nutrients (Liang et al 2014), reduce the greenhouse gases emissions (Kammann *et al.* 2011), promote beneficial microorganisms (Graber *et al.* 2010, Xu *et al.* 2014), remove heavy metal and organic pollutants from soil and water (Park *et al.* 2011, Uchimiya *et al.* 2012), increase plant resistances to diseases (Elad *et al.* 2010, Elmer and Pignatello 2011), and subsequently enhance the plant growth. Among the beneficial effects of biochar is its liming potential – the capacity of biochar to increase soil pH and reduce Al toxicity in acid soils. The capacity of biochar to increase soil pH and to reduce exchangeable Al depends on its ash and volatile matter content (Deenik *et al.* 2011). Soluble salts, such as potassium and sodium carbonates and oxides, can cause an increase of pH in the water-film around biochar particles (Joseph *et al.* 2010). The liming potential also is due to the surface functional groups of biochar such as phenolic and carboxylic acids (Boehm 1994, Rutherford *et al.* 2008, Cheng *et al.* 2008, Keiluweit *et al.* 2010). However, biochars produced from different feedstocks in a similar pyrolysis condition vary in their capacity to neutralize acidity. Also, biochars from the same feedstock, but produced at different pyrolysis temperatures can also differ in their liming values. Moreover, there are limited comprehensive studies focused on the liming effect of biochars that involve the characterization of biochars and the assessment of their liming effects in greenhouse and field trials.

The high fertility of Terra Preta soil was attributed to its high organic matter content and nutrient retention by the biochar. Recent research showed that addition of biochar reduced nutrient loses (Laird *et al.* 2010a, Singh *et al.* 2010, Major *et al.* 2012, Venture *et al.* 2012, Liu *et al.* 2014), increased soil water retention (Novak *et al.* 2009, Laird *et al.* 2010), raised soil pH (Yuan and Xu 2011) and cation exchange capacity (CEC) (Hossain *et al.* 2010, Silber *et al.* 2010), improved beneficial soil microbial population and activities (Graber *et al.* 2010, Kolton *et al.* 2010), and subsequently enhanced plant growth. More specifically, biochar can reduce nitrate, ammonium, phosphorus, and cation concentration in the leachates (Ding *et al.* 2010, Laird *et al.* 2010, Major *et al.* 2012, and Venture *et al.* 2012).This means that biochars are varied in their capacity to retain nutrients. Therefore, as suggested by Major *et al.* (2012) there is an important research gap on testing different biochar properties for different soils and climates. This dissertation addresses the liming potential and nutrient retention capacity of biochars.

This dissertation is organized into 6 chapters. The current chapter introduces the study background and justification. The second chapter is the literature review that provides the scientific background for liming potential and nutrient retention capacity of biochar. Chapter 3 assesses the characterization of biochars. Chapter 4 investigates the liming effect of biochar. Chapter 5 presents study on biochar nutrient retention capacity. Finally, the last chapter (Chapter 6) summarizes the conclusions and recommendations.

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CHAPTER 2. LITERATURE REVIEW

2.1. Big picture of biochar

Biochar is a type of charcoal that is applied to soil in order to improve soil productivity and to capture and store atmospheric carbon. It is produced by heating biomass at low temperature in a closed container with limited or without oxygen supply. Feedstock and thermochemical decomposition conditions during pyrolysis, carbonization and gasification processes determine biochar properties and its agronomic values.

Biochar with its highly recalcitrant nature and agronomic values has been suggested as one possible means of climate change mitigation (Woolf *et al.* 2010). Biederman and Harpole (2013) suggested biochar production and usage was a win-win-win solution to energy, carbon storage, and ecosystem function after evaluated ecosystem responses to biochar application with a meta-analysis of 371 independent studies culled from 114 published articles.

Recent research revealed that addition of biochar as a soil amendment can increase soil water holding capacity and aggregation, pH and CEC, reduce soil exchangeable Al, retain nutrient and prevent the leaching of nutrients, reduce greenhouse gases emissions, promote beneficial microorganisms, remove heavy metal and organic pollutants from soil and water, increase plant resistances to diseases, and subsequently enhance plant growth.

2.2. Biochar production

Biomass, or other feedstock such as biosolids and sewage sludge, can be converted to biofuel, syngas and biochar by various thermochemical or hydrothermal routes, including slow or fast pyrolysis, torrefaction, carbonization and gasification (Brewer, 2012). A short description of those thermochemical processes is listed in Table 2.1.

Table 2.1. Thermochemical processes, their representative reaction conditions, particle residence times, and primary products.

Process	Temperature (^oC)	Heating rate	Pressure	Residence time	Primary product
Slow pyrolysis	350-800	Slow (<10°C/min)	Atmospheric	Hour-Day	Char
Torrefication	200-300	Slow (<10°C/min)	Atmospheric	Minutes-Hours	Stabilized, friable biomass
Fast Pyrolysis	400-600	Very Fast (~1000°C/sec)	Vacuum-Atmospheric	Seconds	Bio-oil
Flash Pyrolysis	300-800	Fast	Elevated	Minutes	Biocarbon/ Char
Gasification	700-1500	Moderate-Very Fast	Atmospheric-Elevated	Seconds-Minutes	Syngas/ Producer gas

Source: Brewer, 2012

The main feedstock of biochar is biomass. C-based waste, such as papermill (van Zwieten *et al.* 2010), paper sludge (Rajkovich *et al.* 2011), biosolids (Chan and Xu 2009), plastic (Black 2010), are also potential feedstock for biochar. Lignocellulosic materials, wood in particular, will be discussed in more detail latter. Biomass is the term used for the biological material from living or recently living organisms such as wood and waste material that can be converted to energy, syngas or char. Wood, for example, is obtained from stems, roots, and branches of trees, shrubs, lianas, and to a limited extent, from herbaceous plants. The woody tissue is made up of many chemical components such as carbohydrate (cellulose and hemicellulose), lignin, extractives (tannins, fatty acids and resins) and inorganic substances (Isenberg 1963, Petersen 1984). A typical analysis of dry wood yields C (52%), H (6.3%), O (40.5%), and N (0.4%). Wood component consists of volatile matter (80%), fixed carbon (19.4%) and ash (0.65%) (Demirbas 2004). Cellulose is the main component (40-45%) of woody biomass. It is a linear polymer composed of up to 10000 β-1,4-linked (glicocydic bonds) D-glucopyranose units. Hemicelluose (20-30% of wood), like cellulose, is a polymer, having backbones of 1,4-β-linked major sugar units. It differs from cellulose in that it contains several sugar units (D-glucose, D-galactose, D-xylose, D-manose, L-arabinose and 4-O-methyl-D-glucoronic acid) and is usually a branched molecule containing only 150-200 sugar units. Lignin is the major non-carbohydrate component of wood. It is a very complex, crosslinked, three dimensional polymer formed from phenolic units. It consists of an irregular array of variously bonded hydroxyl- and methoxy-substituted phenylpropane units. The precursors of lignin biosynthesis are p-comaryl alcohol, coniferyl alcohol, and sinaphyl alcohol, which are linked to lignin by ether and carbon-carbon bonds. Since the main chemical components of biomass are carbohydrate and lignin, it is comprised mainly by C, H, O, N, and to a smaller extent of inorganic substances, with proportion of 51.6, 6.3, 41.5, 0.1 and 1%, respectively.

During the pyrolysis process the feedstock is decomposed and lost weight caused by the shrinkage and vaporation of water and volatile matters. Shafizadeh (1985) showed that hemicellulose, cellulose, and lignin decomposed at 225-325^{o}C, 325-375^{o}C and 250-500^{o}C, respectively. Based on the thermogravimetric analysis (TGA), the weight loss of feedstock as function of temperature during the pyrolysis process can be grouped into several steps. The first step is the loss of water at under 200^{o}C by dehydration process. The next step is the pyrolysis of hemicellulose at 220 to 315^{o}C with the optimum temperature (the maximum weight lost) occurring at 260^{o}C. Cellulose is degraded at 315-390^{o}C with the maximum loss weight rate at 355^{o}C. Lignin has a wide range of degradation temperature from 150 to 850^{o}C with a very low rate of weight loss (Yang *et al.* 2006). Kim *et al.* (2006) also showed that depolymerization of hemicellulose occurs at 180 to 350^{o}C, the random cleavage of the glycosidic linkage of cellulose at 270 to 350^{o}C, and degradation of lignin at 250-500^{o}C. Thermochemical decomposition of woody materials that contains extractive and ash in addition to the three main wood components is happened in several steps in the range of temperatures as hemicellulose, cellulose and lignin degradations. Decomposition of pine wood, for example, starts at 210^oC, but the major loss weight occurs at 250 to 380^oC. Hemicellulose starts to decompose around 290^oC, cellulose between 320 and 380^oC (Muller-Hagedorn *et al.* 2003, Fisher *et al.* 2003, Wang *et al.* 2008, Kim *et al.* 2010). Lignin has a broad decomposition temperature ranging from 200 to 500^oC (Wang *et al.* 2008). It appeared that the thermal stability of lignin (composed of three kinds of benzene-propane units, that are heavy cross-linked and have very high molecular weight) is higher than cellulose (a crystalline long polymer), and the thermal stability of hemicellulose (which is a random amorphous structure, shorter in polymerization with some branches) is the weakest. This is the reason why hemicellulose is the first wood component that is degraded at low temperature and lignin mostly degraded at higher temperature.

The rate of wood thermochemical decomposition depends on the proportion of each component in the wood. Poletto *et al.* (2012) showed that *Eucalyptus grandis*, *Pinus elliottii*, *Dipteryx odorata*, and *Mezilaurus itauba* woods are decomposed at different temperatures due to the different proportions of their extractive (resin, tannin, fats and waxes), ash, hemicellulose, cellulose and lignin content. Müller-Hagedorn *et al.* (2003) also showed that degradation of Scots pine wood hemicellulose at 320^oC was different from that of Hornbean and Walnut woods (at 270^oC) due to different thermal stability of Scots pine hemicellulose which contains more mannose than those of Hornbean and Walnut (their hemicellulose are higher in xylose).

During the pyrolysis process cellulose, hemicellulose, lignin, extractive and ash in the wood is degraded to produce volatiles, tars, and char residue (Alén *et al.* 1996). Thermochemical equilibrium calculations indicate that carbon is a preferred product of biomass pyrolysis at moderate temperatures, with byproducts of CO_2, H_2O, CH_4 and traces of CO (Antal and Grønli, 2003). More specifically, the main degradation products of cellulose are: (1) volatiles (CO, CO_2, CH_4, CH_3COH, CH_3COOH, $CH_3C_6O_2$, $C_2H_4O_2$), (2) anhydroglucopyranose (levoglucosan), (3) anhydroglucofuranose, (4) dianhydroglucopyronose, (5) furan, and (6) others. At 400-600^oC, the proportion of levoglucosan is about 32-47% of the total products. At temperatures above 800-1000^oC the main product is lower-molecular-mass volatiles, and above 600^oC some aromatic hydrocarbon comprising primarily alkyl benzenes and phenol derivatives are formed. The main product of hemicellulose decomposition are: (1) volatiles, (2) levoglucosan, (3) anhydroglucoses, (4) anhydrohexoses, (5) levoglucosenone, (6) furan, and (7) others. The volatiles steadily increase with increasing temperatures, and the volatile glycosans are a significant product in the gaseous phase. At 400^oC the most prominent product is levoglucosenone, and above 400^oC anhydro derivatives of D-glucose, D-mannose, and D-galactose are pronounced. At 800-1000^oC trace of aliphatic hydrocarbons, alkylbenzenes, phenols, and polycyclic aromatic hydrocarbon are detected. The other component of hemicellulose is xylan that produces: volatiles, lactones, furans and others, when degraded. The evolution of mass volatiles is increased with temperature the raising from 400 to 1000^oC. At 1000^oC, the aromatic hydrocarbons, including polycyclic aromatic hydrocarbon primarily naphthalene, phenanthrene and acenaphthylene are found. The pyrolysis products of lignin are grouped into: (1) volatiles (CO, CO_2, C_2H_5-O-C_2H_5, CH_3COOH), (2) catechol (catechol, 3-methylcathecol, 4-methylcathecol), (3) vanillins (vanillin, homo vanillin, vanillic acid), (4) other guaiacols (guaiacol, 4-methylguaichol, 4-ethylguaiachol, 4-vinylguaiachol), (5) propyl guaiacols (dihydroconiferyl alcohol, coniferyl alcohol, conifer aldehyde), (6) other phenols (phenol, 2-methylphenol, 3-/4-methylphenol, 2,4-/2,5-dimethylphenol, 3,5-dimethylphenol, 4-vinlphenol, 4-hydroxybenzaldehyde, 4-allyl-2-methoxyphenol, 2-methoxy-4-(1-propenyl)phenol, and napthol),

(7) aromatic hydrocarbons (benzene, toluene, styrene, ethylbenzene, 1,2-dimethylbenzene, 1,3-/1,4-dimethylbenzene, 2-propenylbenzene, 1-buthylbenzene, 1-ethyl-4-methylbenzene, naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene), (8) others. At 400^{o}C, vanillins and guaiacols are present; at 600^{o}C vanillin derivatives are converted into catechol and phenols; and at 800-1000^{o}C the aromatic hydrocarbons and other phenols are formed as the result of further transformation of primary products. Products derived from the degradation of extractive are minor amount of CO_2 and traces of lower-molecular-mass hydrocarbon below C5 in addition to the major product of aliphatic carboxylic acid. At 400^{o}C the main products are unsaturated fatty acids (pinolenic acid, linoleic acid, oleic acid), saturated fatty acids (palmitic acid, stearic acid, arachidic acid), and resin acids (dehydroabietic, abietic, pimaric, isopimaric, sandaracopimaric) (Alén *et al.* 1996).

In short, the thermochemical processes starts with the evaporation of moisture at 200^{o}C, followed by hemicellulose, cellulose and lignin decomposition at 200-500^{o}C to produce liquid gases and char. Each wood constituent undergoes dehydration and depolymeraztion, repeated intermolecular and intramolecular fission and re-bonding, which results in low molecular weight fragments cracking together with non-decomposed fractions. Above 500^{o}C polycondensed aromatic carbon increased with the evolution of H_2 to reach about 80% C in char to 700^{o}C. At increased temperatures above 700^{o}C, polycondensed C structure develops to increase the content of C without prompt production of H_2. The aromatic domain and the degree of aromatic condensation can be identified using the Nuclear Magnetic Resoncance (NMR) techniques. McBeath *et al.* (2011), using a solid state carbon-13 direct-polarization nuclear magnetic resonance (^{13}C DP NMR) spectra showed that the degree of aromatic condensation increased with increasing pyrolysis temperature. The inorganic minerals contained in the feedstock undergo demineralization process resulted in many oxides of Ca, Si, Mg, Na, K and others. Inorganic mineral of feedstock may also serve as catalysts in the pyrolysis process. In general, higher biochar yields were obtained from feedstock with higher ash content (Antal and Grønli, 2003).

2.3. Biochar composition and properties

As a pyrolysis co-product, biochar is composed of a condensed aromatic carbon framework intermixed with inorganic compounds such as oxides, hydroxides and carbonates of base cations collectively referred to as ash (Amonette and Joseph 2009). The carbon component consists of fixed carbon (fixed C) and volatile matter (VM). The proportion of each component (fixed C, VM and ash) that is measured by proximate analysis is highly feedstock and thermochemical conditions dependent. Fixed carbon (the remaining carbon after biochar heated at 950^{o}C for 6 minutes) varies with feedstock materials and increases with increasing temperature. For example, the fixed C content of cotton seed biochars produced at 350, 500 and 650^{o}C are 52.6, 67.0 and 70.3%, respectively (Novak *et al.* 2009). Volatile matters of biochar (mass lost when biochar heated at 950^{o}C for 6 minutes) decreased with increasing temperature. For example, VM content of pecan shell biochars decreased from 61.6 to 9.7% when the temperature increased from 350 to 700^{o}C. Ash content of biochars is varied mostly with different feedstock materials and less with pyrolysis temperatures. For example, ash content of pine, dairy manure and poultry manure produced at 300^{o}C are 1.5, 10.1 and 46.7%, respectively; while the ash content of poultry manure biochars produced at 300, 400 and 500^{o}C are 46.7, 51.7, and 52.6%, respectively (Enders *et al.* 2012).

Biochars properties are determined by feedstock properties, pyrolysis conditions, temperature in particular, type of post treatments and other factors. Yargicoglu *et al.* (2015) classified biochar properties into: (1) chemical properties (pH, CEC, redox potential, electrical conductivity, elemental content, calcium carbonate equivalent, PAH content, heavy metal content, O:C and H:C ratios), (2) physical properties (particle size distribution, specific gravity, dry density, surface area, porosity), and (3) hydraulic properties (moisture content, water holding capacity, hydraulic conductivity). Zhao *et al.* (2013) derived feedstock- and temperature-dependent heterogeneity indices based on the statistical analysis of coefficient variation and showed that total organic carbon, fixed carbon, mineral elements in biochars are most affected by feedstock, while surface area and pH are affected mostly by the pyrolysis temperature. For example, fixed carbon content of biochars obtained from the fast pyrolysis at 450^{o}C for 90 minutes followed by soaking 10 minutes at 450^{o}C of alder wood, birch wood, pine wood, and spruce wood were 71.7%, 72.5%, 69.6%, and 69.1%, respectively (Antal *et al.* 2000) and the volatile matters contents of pig manure biochars produced at 200, 350, 500 and 650^{o}C were 50.7, 27.4, 11 and 10.7 %, respectively.

The pH of biochar varies depending on the feedstocks and increases with raising the pyrolysis temperature (Singh *et al.* 2010, Cantrell *et al.* 2012). It ranged from 7.67 to 10.26 (Singh *et al.* 2010), 7.0 to 10.3 (Cantrell *et al.* 2012), 6.9 to 9.2 (Kloss *et al.* 2011), 4.48 to 11.62 (Enders *et al.* 2012). The variation and wide range of biochars' pH are mostly due to the variation of their ash and basic cations content and the pyrolysis temperatures (Enders *et al.* 2012), and acid functional groups of biochars (Mukherjee *et al.* 2011).

Electrical conductivity (EC) biochars measured using 1:5 (biochar: deionzed waterof, shaking for 30 minutes) ranged from 194 to 2217 µS/cm. The presence of higher soluble salts in the biochars resulted in higher EC values. Similar to pH, biochar EC value is depending on the proportion and composition of the ash content resulted from the feedstock types and pyrolysis conditions (Singh *et al.* 2010).

Cation exchange capacity (CEC) of biochar is developed from the oxidation of biochar surface and subsequent formation of negatively charged acidic functional groups. Non-graphitic carbon surface of biochar is heterogeneous and reactive due to the free-radical remain on the carbon surface. Surface oxides created with oxygen are acidic in character and cause cation exchange properties (Boehm 2002). CEC of biochars varies depending on the feedstock and pyrolysis temperature. Mukherjee *et al.* (2011) reported the CEC range of 10 to 69 cmolc/kg), while Cheng *et al.* (2008) and Gundale and DeLuca (2007) previously reported biochar CEC values of 71 mmol/kg and 34 cmolc/kg, respectively. The variation in reported biochars CEC values is attributed to the differences in feedstock, production conditions and the measurement procedures or methods. The CEC of biochars produced at low temperature is higher than that produced at high temperature (Mukherjee *et al.* 2011).

Surface functional groups of biochars result from the reaction between free-radicals of the surface carbon with oxygen when the biochar is exposed to air or water. Carboxylic, phenolic and lactone groups measured by Boehm Titration or Fourier Transform Infrared (FTIR) are the most oxygenic surface functional groups of biochars. The acidic surface properties are due to the presence of acidic functional groups. The acidic functional group (AFG) varies among feedstock and decreases with increasing pyrolysis temperature (Singh *et al.* 2010, Rutherford *et al.* 2008; Mukherjee *et al.* 2011, Harvey *et al.* 2012, Zhu *et al.* 2014). Rutherford *et al.* (2008) reported a range total AFG of 1.4 to 4.4 mmol/g obtained from the charring of ponderosa pine wood for 8 hours. A total concentration of AFG ranged from 4.4 to 8.1 mmol/g as a function of feedstock and charring temperature was also reported by Mukherjee *et al.* (2011).

Surface area (SA) and porosity of biochars are increased with increasing pyrolysis temperature. The rate of increasing SA and porosity is dependent on the feedstock. For example, the SA of swine-solids and paved-feedlot biochars increased from 0.92 to 4.11 m^2/g and from 1.34 to 145.2 m^2/g, respectively, when the pyrolysis temperature increased from 350 to 700^oC (Cantrell *et al.* 2012). Total pore volume is also increased by the residence time. For example, total pore volume of pine wood biochar heated at 350^oC increased from 0.133 to 0.297 cm3/g when the time of combustion increased from 1 to 8 hours, and there is 0.99 correlation between the micropore volume and the apparent BET surface area showing that development of micropores is primarily responsible for the dramatic changes in SA (Rutherford *et al.* 2004).

2.4. Characterization of biochar

Proximate, Ultimate, Nuclear Magnetic Resonance (NMR), Fourier Transform Infra-red (FTIR), Scanning Eelectron Microscope (SEM) and Energy Dispersive X-ray Spectrometer (EDS), and some procedures for soil analyses, are among the methods or procedures that are commonly used to characterize biochar. Proximate analysis using the American Society for Testing and Materials (ASTM) method is applied to separated component-component mass of biochar: water, volatile matter, fixed carbon, and ash content. Weight percentage of water is calculated after the air dried biochar was heated in an oven at 110^oC for 4 hours. Volatile matter is calculated after the oven dried biochar heated in a muffle furnace at 950^oC for 6 minutes. Ash content is the remaining/residue of biochar after heated in a muffle furnace at 750^oC for 6 hours.

The fixed carbon is measured by subtraction Fixed C = (100-VM-ash)% (ASTM 1990, Antal and Grønli 2003).

The ultimate analysis is used to determine the chemical composition of biochar's carbon fraction. Total C, H and N are measured by using an elemental analyzer, while total oxygen is determined by differences (subtraction) using the following equation. Oxygen (%) = (100-C-H-N) % (ASTM 2006). The atomic ratio of O to C (O:C) and H to C (H:C) are used to measure the decarboxylation and demethylation that diminished O and H from the original feedstock materials. H:C and O:C ratios also indicate the degree of aromaticity (Shafizadeh, 1985) and the stability of biochars (Spokas 2010), respectively. The ratios H:C and O:C calculated from the percentages of C, H and O after divided by their atomic weights. The inorganic minerals in the ash content can be measured by using the wet or dry combustion procedures for plant tissue analysis and then read with an ICP spectrometer.

Biochar functional groups are determined by two methods, FTIR and Boehm titration (Boehm, 1994); the biochar structural composition, aromaticity and the degree of aromatic condensation can be determined using Cross or Direct Polarization ^{13}C NMR and H:C ratio (McBeath *et al.* 2011). To determine the physical and chemical properties of biochars, procedures for soil analysis can be applied. For example, pH and EC, NH4OAC pH 7.0 or $BaCl_2$ for CEC, rapid titration for calcium carbonate equivalent, Brunauer Emmett Teller (BET) for surface area, and SEM for biochar's morphology and porosity. SEM can be used in combination with an EDS to determine the inorganic minerals of biochars.

2.5. Liming effect of biochar

The liming effect of biochar, its capacity to increase soil pH and to reduce soil exchangeable Al results from the effects of basic cations in the ash and oxygenic surface functional groups attached at the surface of biochars (Tryon 1948, Yamato *et al.* 2006, Nguyen and Lehmann 2009, Novak *et al.* 2009, Joseph *et al.* 2010, Singh *et al.* 2010, Van Zwieten *et al.* 2010, Deenik *et al.* 2011, Yuan *et al.* 2011, Streubel *et al.* 2011, Chintala *et al.* 2013, Slavich *et al.* 2013, Smider and Singh 2014, Wan *et al.* 2014). The major elements in the wood ash are Ca, K, and Mg with their content (wt % of ash) ranged from 21.17 to 36.58%, 0.97 to 16.24%, and 0.34 to 9.09%, respectively. Sulfur, P and Mn are present at around 1%. Other elements such as Fe, Al, Cu, Zn, Na, Si, and B are present in relatively smaller amounts. O, C and N are also present but the content is very low. The high content of Ca, K, and Mg is also confirmed by high intentisity of typical X-ray difraction (XRD) peaks at low temperature (600^oC) that correspond to $CaCO_3$, CaO, MgO and $K_2Ca(CO_3)_2$ (Misra *et al.* 1993). The liming effect of wood ash derives from carbonates content which react to raise soil pH, and its regulation is based on ash calcium carbonate equivalence (CCE). Carbonate-C in biochars can be derived from the mineral fraction of the original feedstock or from CO_2 (i.e., evolved from organic C during pyrolysis) trapped in the alkaline charred material (Singh *et al.* 2010, Yuan *et al.* 2011). Other minerals contained in the ash are potential plant nutrients such as K and P (Erich 1991, Yusiharni *et al.* 2007).

The liming potential could also be derived from the surface functional groups of biochars. The alkalinity of biochars was greatly attributed to the functional groups such as carboxylic and phenolic at low pyrolysis temperature. Increasing temperature from 300 to 500^oC and 700^oC decrease $–COO^-$ and $–O^-$ (Yuan *et al.* 2011). Decarboxylation of organic anions and the negatively charged functional groups such as carboxylic and phenolic will consume proton then increase the soil pH (Wang *et al.* 2014). The surface oxygenated functional groups such as carboxylic can also complex with aluminum in the soil solution and reduced its toxicity to plant growth (Qian *et al.* 2013).

2.6. Nutrient retention by biochar

The high fertility of Terra Preta soil (Novotny *et al.* 2009) is attributed to the high nutrient retention capacity of biochars in addition to high organic matter content in the Ferasol. Higher nutrient retention and nutrients availability were found after biochar addition to soil is attributed to the higher exchange capacity, surface area and direct nutrient addition (Glaser and Lehmann 2002). Recent research showed that the addition of biochar reduced nutrient losses (Laird *et al.* 2010, Singh *et al.* 2010, Major *et al.* 2012, Venture *et al.* 2012, Liu *et al.* 2014), increased soil water retention (Novak *et al.* 2009, Laird *et al.* 2010), raised soil pH (Yuan and Xu 2011) and cation exchange capacity (CEC) (Hossain *et al.* 2010, Silber *et al.* 2010), improved beneficial soil microbial population and activities (Graber *et al.* 2010, Kolton *et al.* 2010), and subsequently enhanced plant growth (Van Zwieten *et al.* 2010). More specifically, woodchip biochar produced at high temperature (500 and 700 ^{o}C) increased saturated hydraulic conductivity biochar and water content of a loamy soil (Lei and Zhang 2013). Biochars addition can reduce nitrate, ammonium, phosphorus, and cation concentration in the leachates (Ding *et al.* 2010, Laird *et al.* 2010, Major *et al.* 2012, and Venture *et al.* 2012). For example, addition of a mixed hardwood biochar at 20 g/kg in combination with swine manure at 5 g/kg to a typical midwestern agricultural soil (a Hapludoll) reduced total N and total dissolved P leaching by 11% and 69%, respectively, in a leaching column (Laird *et al.* 2010a). Addition of biochars produced at higher temperature with higher in surface area may benefit sandy soils by increasing sorption sites or may improve the retention of nonpolar pollutant in soils (*Kloss et al.* 2012).

2.7. Hypothesis

Overall hypothesis of this study was that biochars with higher liming potential and nutrient retention capacity would be good amendment to acid soils. The specific hypotheses of this study were $CaCO_3$ equivalent or basic cations are strong indicators for liming potential of biochars, meaning biochars containing high basic cations and or high $CaCO_3$ equivalent would ne effective as soil acidity amendments. Biochar produced at high temperature, which has more micropores can retain more added nutrients, thereby increasing nutrient retention capacity of nutrient- poor soils of Hawaii.

2.8. Objectives

The overall objective of this study was to characterize several wood-based biochars, assess their liming potentials and nutrient retention capacities to acid soils. The specific objectives of this study were:

(1) to characterize and determine the liming potential of six wood-derived biochars collected from West Timor, Indonesia and Hawaii, USA, produced from different feedstocks and under different production conditions with focus on liming potential properties.

(2) to evaluate the liming effects of : (i) six characterized biochars in correcting soil acidity and enhancing *Desmodium intortum* growth in a Hawaiian acid soil in a greenhouse/pot trial, and (ii) to confirm/evaluate the capacities of two local biochars in correcting soil acidity and enhacing soybean growth in two Indonesia’s acid soils under field conditions.

(3) to study nutrient retention capacities of two biochars in combination with two types of compost on two Hawaiian highly weathered, nutrient-poor soils as measured by the growth of Chinese cabbage *(Brassica rapa*).

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CHAPTER 3. CHARACTERIZATION OF BIOCHAR FOR CORRECTING SOIL ACIDITY

3.1. Abstract

Biochar reportedly can improve soil productivity and sequester carbon. As a pyrolytic co-product, biochar properties vary depending on their feedstock and pyrolysis conditions, the highest heat temperature in particular. To be useful as an acid soil amendment, the liming potential of biochar should be characterized. The objective of this study is to characterize and screen six wood-derived biochars for their uses to correct soil acidity and enhance plant growth based on selected indicator(s). Five wood-derived biochars, namely leucaena (*Leucaena leucocephala*), lac tree (*Schleichera oleosa*), she oak (*Casuarina junghuhniana*), mahogany (*Sweitenia mahagoni*), and mountain gum (*Eucalyptus urophylla*), made in an open fire process at 300-500^{o}C were collected from West Timor, Indonesia and a mixed wood biochar, made in an open fire process in a pit followed by baking at 300-400^{o}C for a few days after covered with dirt, was collected from Hilo, Hawaii, USA. All coarse biochars were oven dried at 70^{o}C for 72 hours, crushed, sieved to pass a 60 mesh sieve, and stored dried at 25^{o}C until used. The proximate and ultimate analyses, Nuclear Magnetic Resonance (NMR) spectrometer, Fourier Transform Infra-red (FTIR) spectrometer and Boehm titration, Scanning Electron Microscope (SEM) and Energy Dispersive spectrometer (EDS), and CaCO3 equivalent, basic cation and other chemical analysis were used to characterize six selected biochars. Five liming potential indicators were identified and the selected indicator was used to screen liming potential of six selected biochars. The results showed that the biochars fixed carbon, volatile matter (VM), and ash content ranged from 35.9 to 69.8%, 22.9 to 53.3%, and 0.7 to 30.7%, respectively. O:C and H:C ranged from 0.6%, 0.3 to 0.59, and 0.22 to 0.59, respectively. Biochar pH, electrical conductivity (EC), cation exchange capacity (CEC), phenolic content, total surface functional groups, and $CaCO_3$ equivalent ranged from 4.2 to 10.4, 0.1 to 2.4 dS/m, 13.9 to 45.1 cmolc/kg, 25.1 to 9,621.9 mg/kg, 0.38 to 2.64 mmol/g, and 4.2 to 28.6%, respectively. Nutrient content, surface structure and porosity were varied among biochars. The ash content was fairly correlated with pH, $CaCO_3$ equivalent and basic cations. $CaCO_3$ equivalent closely correlated with basic cations and pH. Total functional groups positively correlated with CEC, but negatively correlated with pH. It appeared that $CaCO_3$ equivalent or basic cations is the best indicator for biochar liming potential. Based on their $CaCO_3$ equivalent or basic cations content, leucaena and lac tree would be grouped as the highest liming potential biochars, Hilo mixed wood and she oak as the moderate liming potential biochars , and mahogany and mountain gum as the lowest liming potential biochars. Thus, we would recommend the leucaena, lactree, mixed wood Hilo and she oak biochars for amending soil acidity.

Key words: feedstock, pyrolysis temperature, liming potential

3.2. Introduction

Biochar is a co-product of thermochemical (mostly pyrolysis) biomass conversion. It is produced with specific purpose for soil amendment and carbon sequestration tools. Some biochars have been shown to increase soil pH (Yuan and Xu 2011), cation exchange capacity (Silber *et al.* 2010), water holding capacity (Novak *et al.* 2009, Laird *et al.* 2010), soil aggregate/structure (Mukherjee and Lal 2013), soil microbial population and activities (Graber *et al.* 2010, Xu *et al.* 2014), and soil rhizosphere-root plant interactions (Prendergast-Miller *et al.* 2013). Other biochars can directly release nutrients for plant growth (Smider and Singh 2014) and promote plant resistances to diseases (Elad *et al.* 2010, Elmer and Pignatello 2011), and indirectly retain and then slowly release nutrients to the plants (Lehmann *et al.* 2003, Liang *et al.* 2014). Several biochars can detoxify heavy metals (Park *et al.* 2011, Uchimiya *et al.* 2012) and reduce greenhouse gases emissions (Steiner *et al.* 2010, Kammann *et al.* 2011), reduce nutrient leaching loss, which in turn reduces the fertilizer need (Laird *et al.* 2010, Major *et al.* 2012).

Such beneficial effects of biochars are highly depending on the feedstock types and compositions, and production routes and conditions. Biomass feedstock is divided into wood and non-wood in terms of ash (Singh *et al.* 2010), hard- and soft-woods in the matter of the chemical composition such as lignin, cellulose and hemicelluse content (Hills, 1985). As a low ash and high lignin feedstock, wood biochar is grouped into the low ash, and high alkalinity, C/N ratio and aromatic biochars (Mukome *et al.* 2013). Thermochemical routes such as slow or fast pyrolysis and gasification, and the operation conditions such as temperature and resident time, have reported their effect on biochars' O:C ratio, VM content, and pH (Antal and Grønli 2003, Zhao *et al.* 2013, Mukome *et al.* 2013). The pyrolysis process, for example, alters constituent carbon compounds (cellulose, hemicellulose and lignin) to produce a solid, stabilized, recalcitrant organic carbon compound having depleted H and O (Küçükbayrak and Kadiog˘lu 1989) resulting in greater proportion of aromatic carbon and ash (Baldock and Smernik 2002, Brewer 2012). These materials offer greater chemical recalcitrance and resistance to biological decomposition (Baldock and Smernik 2002, Zimmerman 2010).

The biochar's agronomic values such as liming potential can be predicted from the biochar or feedstock properties and pyrolysis temperatures. For example, previous studies reported that the liming capacity of biochars is determined by the ash, carbonate and basic cations content in the ash (Singh *et al.* 2010, Van Zwieten *et al.* 2010, Novak *et al.* 2010, Deenik *et al.* 2011, Yuan *et al.* 2011, Chintala *et al.* 2013, Slavich *et al.* 2013, Smider and Singh 2014, Wan *et al.* 2014), and biochar surface functional groups (Qian and Chen 2014, Wan *et al.* 2014). Some authors claim that poultry litter, paper mill or manure are more suitable for correcting soil acidity than woods because the earlier mentioned feedstock are higher in their ash content. Also, high temperature biochars have been showen more effective in correcting soil acidity due to the higher in ash and carbonate content. The acidity neutralizing capacity of biochars, therefore, can be predicted from the ash content, pH, carbonate content ($CaCO_3$ equivalent), basic cations in the ash, alkanility, and surface oxygen functional groups of biochars. However, the ash, carbonate, basic cations, pH and alkalinity of biochar vary with feedstock types and are increased with increasing of temperature, whereas the oxygen functional groups are decreased with the raising of pyrolysis temperature. Wan *et al.* (2014) argued that the carbonates content in the ash is responsible for the reduction soil acidity for biochar produced at higher temperature (500 and 700^{o}C), while the acidity neutralizing capacity of low temperature (300^{o}C) biochars is attributed to the oxygen surface functional groups. Those facsts lead to the following research questions.

Which of the single or set of biochar properties should be used to predict the liming value of biochars?

The objective of this study is to characterize six wood-derived biochars collected from west Timor, Indonesia, and Hilo, Hawaii, USA, and to screen them for the amending potential of soil acidity.

3.3. Materials and methods

3.3.1. Biochar collection

Five biochars were collected from Indonesia and one in Hawaii. Five biochars were made by farmers in an open fire process in West Timor, Indonesia. The production temperature was not measured, however it ranged from 300 to 400^{o}C, estimated from on site measurement of mahogany and lac tree biochars production temperatures. They were mountain gum (*Eucalyptus urophylla*), she oak (*Casuarina junghuhniana*), mahogany (*Swietenia macrophylla*), leucaena (*Leucaena leucocephala*), and lac tree (*Scheichera oleosa*) wood-derived biochars, collected from the top of Mutis, the highest mountain, to the low land area in West Timor. A mixed wood derived biochar is made by Landscape Ecology Corporation, Hilo, Hawaii in an open fire in a pit followed by a baking process at 300-400^{o}C for a few days after the char covered with dirt. All coarse biochars were air dried followed by oven drying at 70^{o}C for 72 h, crushed, sieved to pass a 60 mesh sieve (0.25 mm), and stored until use.

3.3.2. Surface structure and porosity

Surface structure and porosity of biochars were measured by mounting the biochar powders (passed through a 60 mesh sieve) onto aluminum stubs (sample holder) with conductive carbon double tape, then reading with a scanning electron microscope (SEM) (HITACHI).

Chemical composition of some biochars was also analyzed by using an energy dispersive spectrometer (EDS) that was attached to the SEM.

3.3.3. Proximate analysis

Biochar moisture, ash, volatile matter, and fixed carbon contents were measured with the American Society for Testing and Materials (ASTM) method (D-1762-84) (ASTM, 1990). The moisture content was measured as the weight loss after heating biochars at 105^{o}C for 24 hours. The volatile matter (VM) content was determined as the weight loss after heating biochars in a covered crucible at 950°C for 6 minutes. The ash content was determined as the residual weight after heating biochar at 750^{o}C for 6 hours. The fixed carbon content was determined as the weight loss after combusting biochars at 750°C for 6 hours or it was calculated as follows (Antal *et al.* 2003): Fixed C (%) = (100-VM-Ash) %.

3.3.4. pH and EC

Biochar's pH was measured after biochar and deionized water (1:5) were mixed and equilibrated for an hour, while biochars EC were measured after the mixtures were equilibrated for 24 hours. A pocket electric pH meter HANNA was used to measure both biochar pH and EC.

3.3.5. $CaCO_3$ equivalent

Biochar's $CaCO_3$ equivalent (CCE) was determined by a rapid titration according to the procedure described by Rayment and Higginson (1992). Briefly, two grams (dry weight) of biochar were added to 50 ml of 1 M HCl, shaken for 1 hour, equilibrated overnight, shaken again for 1 hour and filtered before titrating with 0.5 M NaOH.

3.3.6. Elemental content

Total carbon, nitrogen and hydrogen elements were determined using an Exeter Analytical CE 440 Elemental Analyzer. Oxygen element was calculated as follows. Percentage of oxygen = (100-C-H-N) %. Atomic ratio of O:C and H:C were obtained by calculation.

Other nutrients in biochars were analyzed as follows. Briefly, 0.5 g of biochar was weighed and transferred into a 50-ml digestion tube. Five ml of the acid mix (70% of HNO_3 and 30% of $HClO_4$) were added into the digestion tube. The tube was placed in a block digester and heated at 150^{o}C for 1.5 h. After being cooled down, the volume of the tube was brought to 50 mL with deionized water, filtered through Whatman No. 42 paper, and then transferred into ICP tubes for reading.

3.3.7. Nuclear Magnetic Resonance

A solid state ^{13}C magic angle spinning nuclear magnetic resonance (MAS ^{13}C-NMR) was used to identify chemical compounds contained within biochars. The procedure was referred to McBeath *et al.* (2011). Spectra were obtained at a frequency of 100.6 MHz using a Varian Unity INOVA 400 NMR® spectrometer. Samples were packed in 7 mm diameter cylindrical zirconia rotors with Kel-F rotor end caps and spun at the ‘‘magic angle’’ (54.7^{o}) at 6000 ± 50 Hz in a Doty® Scientific supersonic MAS probe. Free induction decays (FIDs) were acquired with a sweep width of 45.454 kHz; 1216 data points were collected over an acquisition time of 12 ms. All spectra were zero filled to 8192 data points and processed with a 50 Hz Lorentzian line broadening and a 0.010 s Gaussian broadening. Chemical shifts were externally referenced to the methyl resonance of hexamethylbenzene at 17.36 ppm. Cross polarisation (CP) spectra represent the accumulation of 4000 scans and were acquired using a 90^o 1H pulse of 5-6 µs duration, a 1 ms contact time and a 2 s recycle delay.

3.3.8. Fourier Transform Infra-red

A Fourier Transform Infra-red (FTIR) spectrometer (Nicolet 6700) was used to generate the unique peak of functional groups on each biochar refered to the list in Table 3.1.

Table 3.1. Peak references for biochar functional groups

Wavenumber (cm^{-1})	**Characteristic vibration**	**Functionality**
3665	Free O-H stretching	Alcoholic and phenolic –OH, not hydrogen bonded
3200-3500	O-H stretching	water, H-bonded hydroxyl (-OH) groups
3200	C-H stretching	5-membered N/O-heterocyclic C (e.g., furans and pyrroles)
3050	C-H stretching	substituted aromatic C
2935	asymmetric C-H stretching	aliphatic CHx
2885	symmetric C-H stretching	aliphatic CHx
1740-1700	C=O stretching	mainly carboxyl; traces of aldehydes, ketones and esters
1600	C=C stretching	aromatic components
	C=O stretching	C=O of conjugated ketones and quinones
1510	C=C stretching	aromatic skeletal vibrations, indicative of lignin
1440	C=C stretching	aromatic C, indicative of lignin, appears when bound to unsaturated group
1440	α-C-H2 bending	aliphatic -CH2 deformations associated with lignin and carbohydrates
1375	O-H bending	in plane bending of phenolic -OH, related to ligneous syringyl units
	α-C-H3 bending	aliphatic -CH3 deformations
1270-1250	C-O stretching	C-O-C groups and aryl ethers; phenolic C-O indicative of guaiacyl units associated with lignin
1185-1160	(asymmetric) “	C-O-C ester groups in cellulose and hemicellulose
1110	(asymmetric) “	C-O-C stretching vibrations in cellulose and hemicellulose j; aliphatic –OH
1030	(asymmetric) “	acid derivatives, aliphatic C-O-C, and –OH representative of oxygenated functional groups of cellulose and hemicellulose; methoxy groups of lignins
1200-1000	C-H deformation	vibrations typical for substituted aromatics
885,815,750	C-H bending	aromatic CH out-of-plane deformation; less substituted rings appear at lower wavenumbers

Source: Keiluweit *et al.* 2010

Briefly, biochar powder was placed and pressed into a sample cell (Smart Urle ZnSe450®), then scanned from 4000 to 700 wavenumbers. The set up consisted of: atmosphere air as the background; number of scan, 256; and resolution, 8. The peak of functional groups obtained from the FTIR scan was identified with the aid of the OMNIC® program for Windows, and the surface functional groups of biochars were interpreted refer to the peak references shown in Table 3.1.

3.3.9. Boehm Titration

The Boehm titration method was used to quantify the carboxylic and phenolic functional groups on biochar. Water soluble salts and carbonates in biochar were removed before the titration. Briefly, 0.50 g of fine biochar was added to 50 ml of each of the three 0.05 M bases: $NaHCO_3$, Na_2CO_3, and NaOH. The mixtures, along with a control solution without biochar, were shaken for 24 h and then filtered (Whatman No. 42 paper) to remove particles. Then, a 5 ml of aliquot from each filtrate was mixed with 10 ml of 0.05 M HCl to ensure complete neutralization of bases and then back-titrated with 0.05 M NaOH solution. The endpoint was determined using a pH meter and phenolphthalein color indicator. The total surface acidity was calculated as the quantityy was neutralized by NaOH, the carboxylic acid fraction as the quantity was neutralized by $NaHCO_3$, and the lactonic fraction as was neutralized by Na_2CO_3. The difference between quantities of NaOH and Na_2CO_3 is assumed to be the phenolic functional group content (Rutherford *et al.* 2008).

3.3.10. Phenolic content

Prussian blue analysis was applied to measure total phenol content of biochars following the protocol outlined by Stern *et al.* (1996**).** Biochar samples were extracted with methanol in a

10/1 ratio, in triplicate. One milliliter of the extract from each sample was transferred into 30-ml test tubes and 5 mL deionized water was added to each test tube containing sample extract solutions followed by adding 0.36 mL of ferric ammonium sulfate [0.1 M FeNH4(SO4)2 in 0.1 m HCl]. Exactly 20 minutes after the addition of ferric ammonium sulfate to each test tube, 0.36 mL of potassium ferricyanide [0.008M K3Fe(CN)6 in deionized water] was added. Exactly 20 minutes after the addition of potassium ferricyanide, each reaction mixture was transferred to a cuvette and the absorbance at 720 nm was recorded using a Genesys 20 spectrophotometer (Thermo Scientific - Model 4001-000, MA). Data were reported in mg/kg equivalents of gallic acid (standard).

3.3.11. Cation exchange capacity

Cation exchange capacity of biochars was measured in three replicates by using ammonium acetate (NH_4OAC) pH 7.0 method (Chapman 1965). Briefly, 2 grams of biochar were added to 100 ml NH4OAC, occasionally shaken for 24 hours, filtered in a Buchner funnel using vacuum suction and filter paper no. 6S while rinsed with 20 ml NH4OAC. Biochar in the Buchner funnel was washed with 10 ml methyl-alcohol 4 times, transferred into the Erlenmeyer, added with 50 mL of 4% KCl, shaken for 30 minutes, filtered using a Buchner funnel and washed 3 times with 4% KCl. About 40 ml of aliquot transferred to the Kejeldahl flask, added with 1ml of 1 M NaOH, connected to the distillation setup, distilled and the distillate were titrated with 0.04 M HCl.

3.3.12. Statistical analysis of data

Descriptive analysis was conducted to calculate means and standard errors of biochar components and chemical properties from three replicates measured data, using Microsoft 2010

Excel. The relationships between biochar properties were analyzed using regresion analysis and presented in the combined scatter and regression line graphs, using Microsoft Excel 2010 and Sigmaplot™ 11.0 software.

3.4. Results and discussion

3.4.1. Ash, volatile matter and fixed carbon

The composition of the six biochars was listed in Table 3.2. As a co-product of combustion process, biochars consisted of carbon and ash components. Carbon component comprised of fixed carbon and volatile matter. Ash component was the mineral matter such as oxides of K, Ca, Mg and others.

Ash content of biochars and their subsequent elements were listed in Tables 3.2 and 3.3. The ash content ranged from 0.7% to 30.7%. Biochar with the highest ash content was leucaena, followed by Hilo mixed wood, lac tree, mahogany, she oak and mountain gum. Ash content of biochars was highly depended on the ash content of their feedstocks (Enders *et al.* 2012, Zhao *et al.* 2013). For example ash content of leucaena, mahogany and mountain gum woods were 1.2% (Hindi *et al.* 2010), 0.6% and 0.4% (Pettersen 1984), respectively, and their biochars ash content were 28.6%, 7.3% and 0.7%, respectively. Biochars ash content and their subsequent basic cations content in particular was correlated with the pH of biochars (Fig. 3.1). The basic cations in the biochars were also correlated with the $CaCO_3$ equivalent of biochar (Fig. 3.2). Biochars with higher ash content such as leucaena and lac tree, therefore, had the highest pH and $CaCO_3$ equivalent than the others.

Table 3.2. Means and standard errors of the fixed carbon, volatile matter and ash content of six biochars produced at 300-400^{o}C (n=3)

Biochars	Fix C	Volatile	Ash
	%		
Leucaena (*Leucaena leucocephala*) wood	35.9 ± 1.2	33.4 ± 1.2	30.7 ± 0.0
Lac tree (*Schleichera oleosa*) wood	56.1 ± 0.1	28.1 ± 0.0	15.8 ± 0.0
Hilo mixed wood	56.7 ± 0.4	23.7 ± 0.5	19.6 ± 0.2
She oak (*Casuarina junghuhniana)*wood	69.8 ± 1.7	22.9 ± 1.8	4.6 ± 0.1
Mahogany (*Swietenia mahagoni*) wood	39.3 ± 1.2	53.3 ± 1.0	7.3 ± 0.1
Mountain gum (*Eucalyptus urophylla*) wood	62.9 ± 0.2	36.4 ± 0.2	0.7 ± 0.0

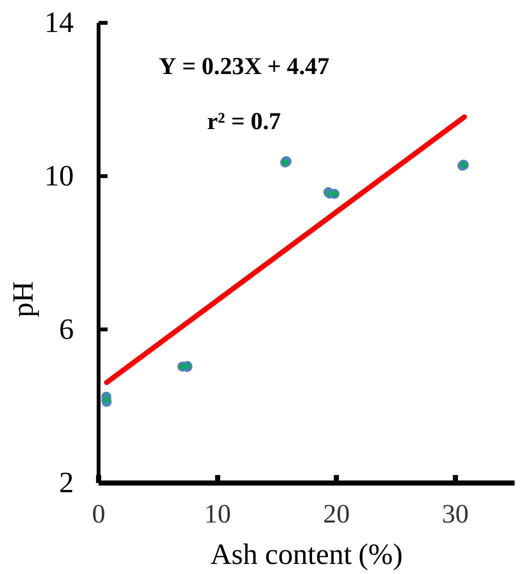


Figure 3.1. Relationship between biochar pH and ash content

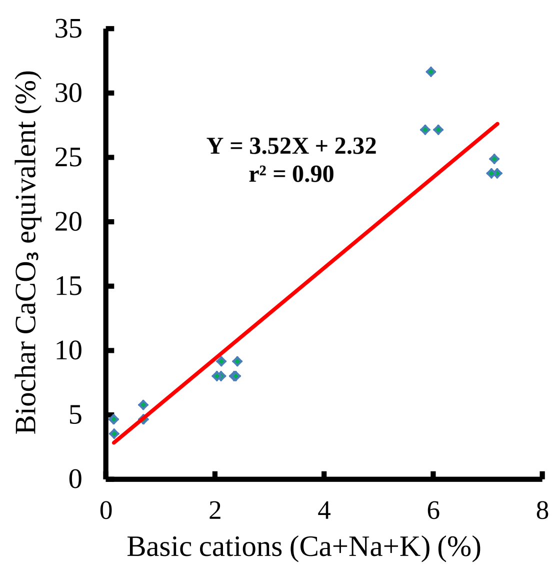


Figure 3.2. Relationship between biochars $CaCO_3$ equivalent and basic cations

Elements contents varied with biochar types (Table 3.3). Leucaena, lac tree, mix wood, she oak biochars had higher content of N, P, Na, K, Mg, Ca, Si, B, Cu, Zn than mountain gum and mahogany biochars. The results reflect the differences in the feedstocks. In fact, nutrient content of biochars was reportedly determined mostly by feedstock mineral composition (Gaskin *et al.* 2008, Brewer 2012, Zhao *et al.* 2013). Among the elemental content, Ca was the highest for all six biochars, followed by K, Mg, P and Na.

Volatile matter (VM) content of the six biochars is listed in Table 2. It ranged from 22.9 to 53.3%. The highest VM content was mahogany biochar and Hilo mixed wood biochar was the lowest. VM content in biochars depends less on feedstocks than on temperature (Enders *et al.* 2012). With the higher temperature the VM decreased as indicating the progressive loss of more volatile components of the biochars (Mukherjee *et al.* 2011). Thus, the higher VM content of mahogany, for example, would indicate its lower formation temperature and therefore would be correlated well with H:C ratio (Fig. 3.3)

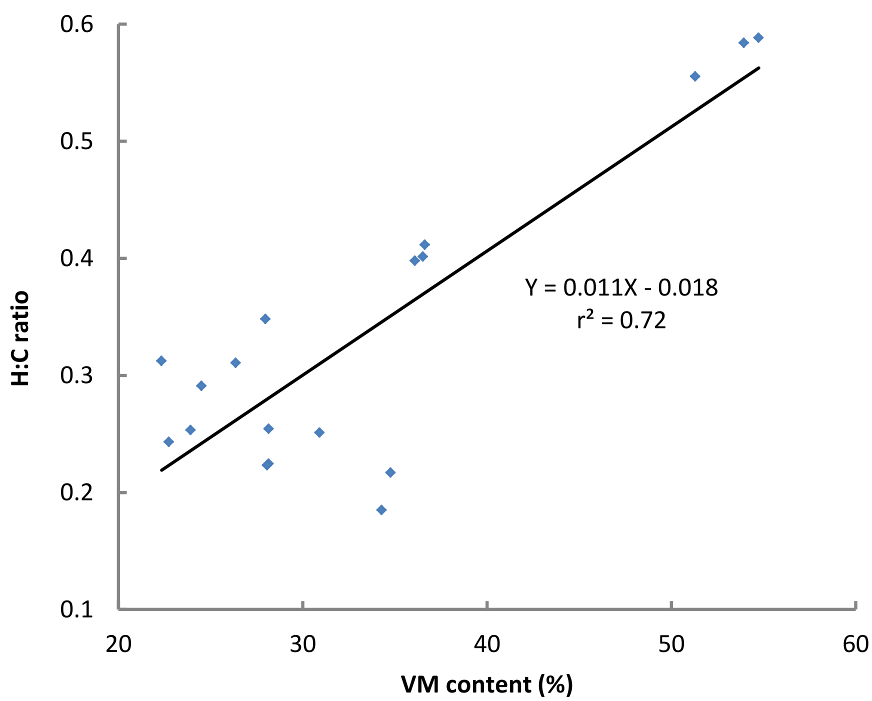


Figure 3.3. Relationship between VM and H:C of biochars
VM: volatile matter; H: hydrogen; C: carbon

Fixed carbon ranged from 35.9% to 69.8%. The highest fixed C biochar was she oak followed by mountain gum, mixed wood Hilo, lac tree, mahogany and leucaena. Fixed C indicated the level of aromatization of holocellulose (cellulose and hemicellulose) and lignin during the pyrolysis, and therefore would be negatively correlated with the O:C or H:C ratio

(Fig. 3.4) due to the more loss of O and H with increasing thermochemical transformation of aliphatic to aromatic compounds. Fixed carbon also indicates the stability of biochar and its susceptibility to undergo degradation and mineralization, and therefore should have a negative correlation with the VM content.

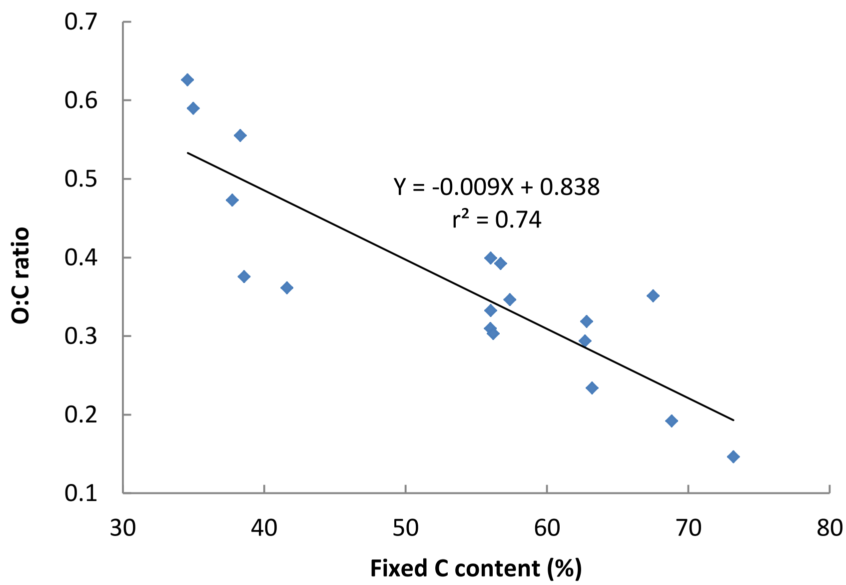


Figure 3.4. Relationship between fixed C and O:C of biochars

3.4.2. Total and ratios C, H, and O

The total C, H and O ranged from 55.2 to 71.2%, 1.0 to 3.0% and 26.4 to 43.2% respectively (Table 3.4). The highest total carbon content was she oak, followed by mountain gum, lac tree, mixed wood Hilo, mahogany and leucaena. The order total H content were mahogany>mountain gum>she oak>Hilo mixed wood >lac tree and leucaena, and the order of calculated total O content were leucaena>mahogany>Hilo mixed wood>lac tree> mountain gum> she oak. The proportion of total C, H and O indicated the carbon compound in the biochars.

Table 3.3. Means of mineral content in the ash of the six biochars (n=3)

Biochars	P	K	Ca	Mg	Na	Fe	Mn	Zn	Cu	B	Mo	Al	Co	Si
	%					mg/kg								
Leucaena (*Leucaena leucocephala*) wood	0.08	0.85	5.1	0.55	0.03	3894.4	214.2	18.9	16.2	26.1	0.30	3710.8	0.04	38.1
Lac tree (*Schleichera oleosa*) wood	0.13	0.73	6.3	0.32	0.06	571.0	87.9	15.1	10.1	12.7	0.04	448.1	0.00	45.7
Hilo mixed wood	0.09	0.47	1.6	0.22	0.35	12259.5	153.8	13.3	20.9	12.8	0.18	9766.9	0.06	15.7
She oak (*Casuarina junghuhniana)*wood	0.01	0.50	1.5	0.11	0.08	284.0	41.9	5.1	5.2	8.4	0.38	129.4	0.01	58.8
Mahogany (*Swietenia mahagoni*) wood	0.01	0.17	0.5	0.12	0.01	2728.6	62.4	9.4	8.7	2.9	0.20	1779.2	0.02	28.3
Mountain gum (*Eucalyptus urophylla*) wood	0.02	0.03	0.1	0.03	0.04	206.2	12.9	8.7	2.5	3.2	0.02	155.3	0.00	28.0

Table 3.4. Means and standard errors of total C, H, O, O:C and H: C of the six biochars (n=3)

Biochars	C	H	O	N	O:C	H:C
	%					
Leucaena (*Leucaena leucocephala*) wood	55.2 ± 0.6	1.0 ± 0.07	43.2 ± 0.6	0.6±0.04	0.59 ± 0.01	0.22 ± 0.01
Lac tree (*Schleichera oleosa*) wood	68.2 ± 0.9	1.4 ± 0.04	29.9 ± 0.9	0.5±0.01	0.33 ± 0.02	0.24 ± 0.01
Hilo Mixed wood	64.5 ± 0.9	1.5 ± 0.06	33.6 ± 0.9	0.5±0.03	0.39 ± 0.02	0.27 ± 0.01
She oak (*Casuarina junghuhniana)*wood	71.2 ± 5.1	2.0 ± 0.04	26.4 ± 5.2	0.5±0.07	0.30 ± 0.08	0.34 ± 0.02
Mahogany (*Swietenia mahagoni*) wood	61.9 ± 1.6	3.0 ± 0.04	34.7 ± 1.7	0.3±0.01	0.42 ± 0.03	0.59 ± 0.01
Mountain gum (*Eucalyptus urophylla*) wood	69.1 ± 2.1	2.3 ± 0.09	28.3 ± 2.2	0.2±0.02	0.31 ± 0.03	0.40 ± 0.01

The calculated O:C and H:C ratios ranged from 0.2 to 0.6 (Table 3.4). Based on the O:C ratio and fixed carbon content (Spokas *et al.*, 2010), the order stability with respect to environmental degradation/mineralization of the test biochars was leucaena <mahogany<mixed wood<lac tree ≈ mountain gum ≈ she oak (Fig. 3.5). The use of O:C ratio as an indicator of stability was further supported by Crombie *et al.* (2013) who showed the strong correlation among three stability indicators (included O:C ratio) for pine wood, rice husk and wheat straw derived biochars.

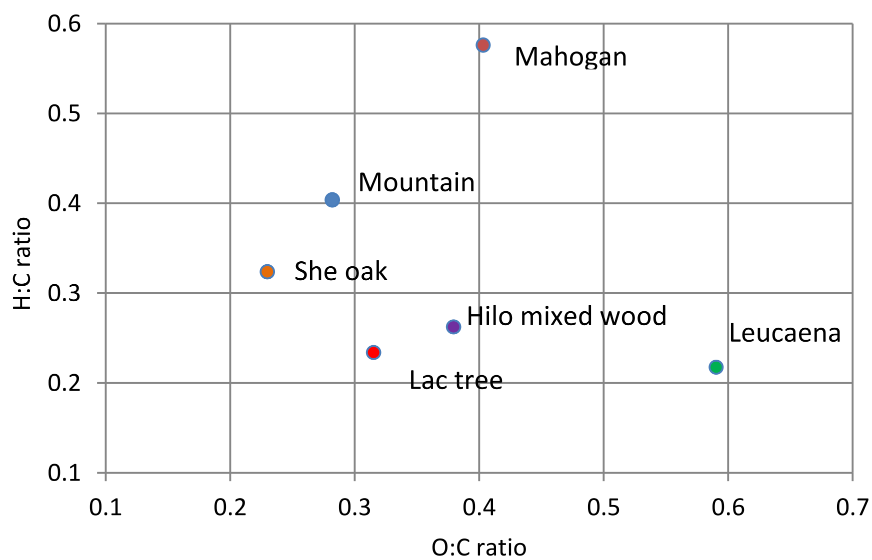


Figure 3.5. Van Krevelen plot for six tested biochars

3.4.3. FTIR

FTIR was used to qualitatively determine the functional groups of biochars. FTIR bands at 3400 cm^{-1} is assigned to OH stretch of phenol, C-H stretching of aliphatic CHx at 2800-2400 cm^{-1}, C=O carboxylic and ketones at 1700 cm^{-1}, C=C stretching aromatic components and C=O conjugated ketones and quinones at 1600 cm^{-1}, aliphatic C-H bending vibration at 1420 cm^{-1}, C-H stretch at 1030 cm^{-1}, which is associated with undecomposed cellulosic and lignous C (cellulose, hemicelluose and lignin), and C-H bending aromatic CH out of plane deformation at 874 cm^{-1}. The peak intensity also reflects the quantity of surface functional groups shown in Table 3.5. The band of carboxylic groups (1700 cm^{-1}) for leucaena and lac tree biochars, for example, is nearly disappeared in Fig. 3.6. These values are in agreement with those reported by Sharma *et al.* (2004), Brewer *et al.* (2009), Lee *et al.* (2010), Brewer *et al.* (2011), and Kloss *et al.* (2012). The small quantity of carboxylic groups obtained from Boehm titration for those biochars was consistent with our FTIR results. Quantity of phenolic groups was very high in the mountain gum and mahogany biochars. It was consistent with the total phenolic content obtained from the Prussian blue assay (Table 3.6), broad bands FTIR at 1600 cm^{-1}, and Boehm Titration (Table 3.5).

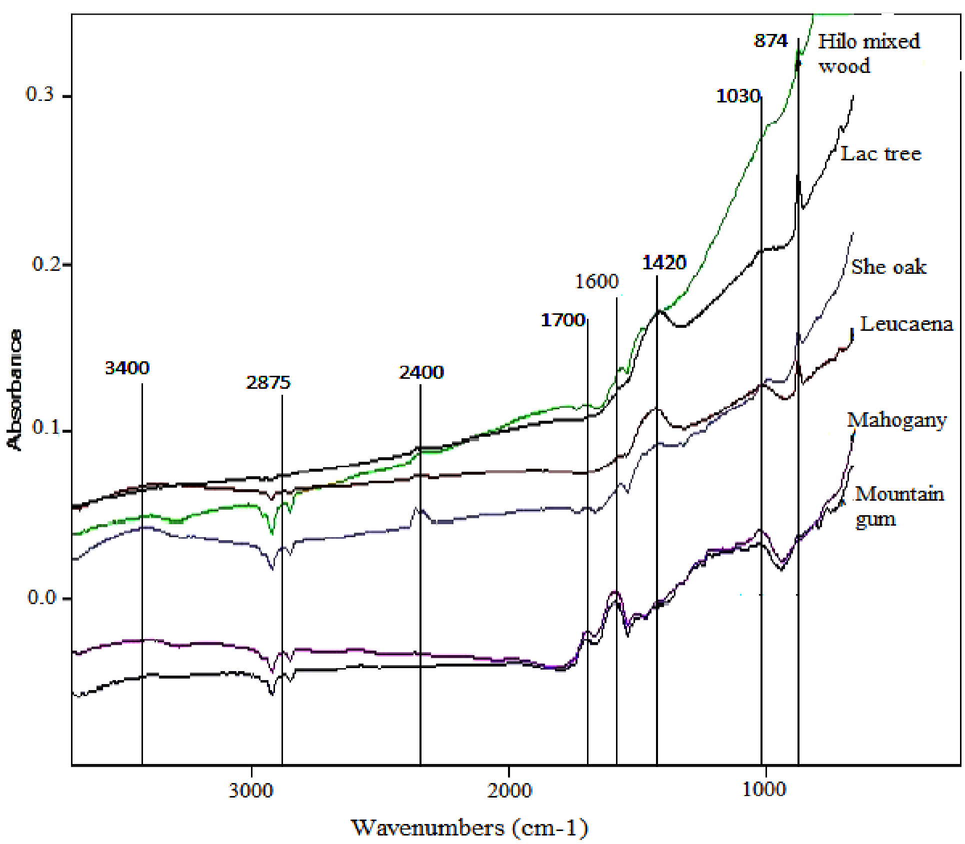


Figure 3.6. Fourier Transform Infrared (FTIR) bands characterizing functional groups on the surface of six biochars

3.4.4. NMR

NMR was used to show the aromaticity of biochars. The main chemical component of biochars is aromatic compound shown by broad peak at 140-130 ppm chemical shifts. Side band spinning down- and up-fields show several functional groups attached to the main chemical aromatic compound. They are aldehyde group at 200-190 ppm, carboxylic group at 180-170 ppm, CH-O, CH-N, CH-X groups at 80-40 ppm and aliphatic groups at 40-0 ppm of chemical shift.

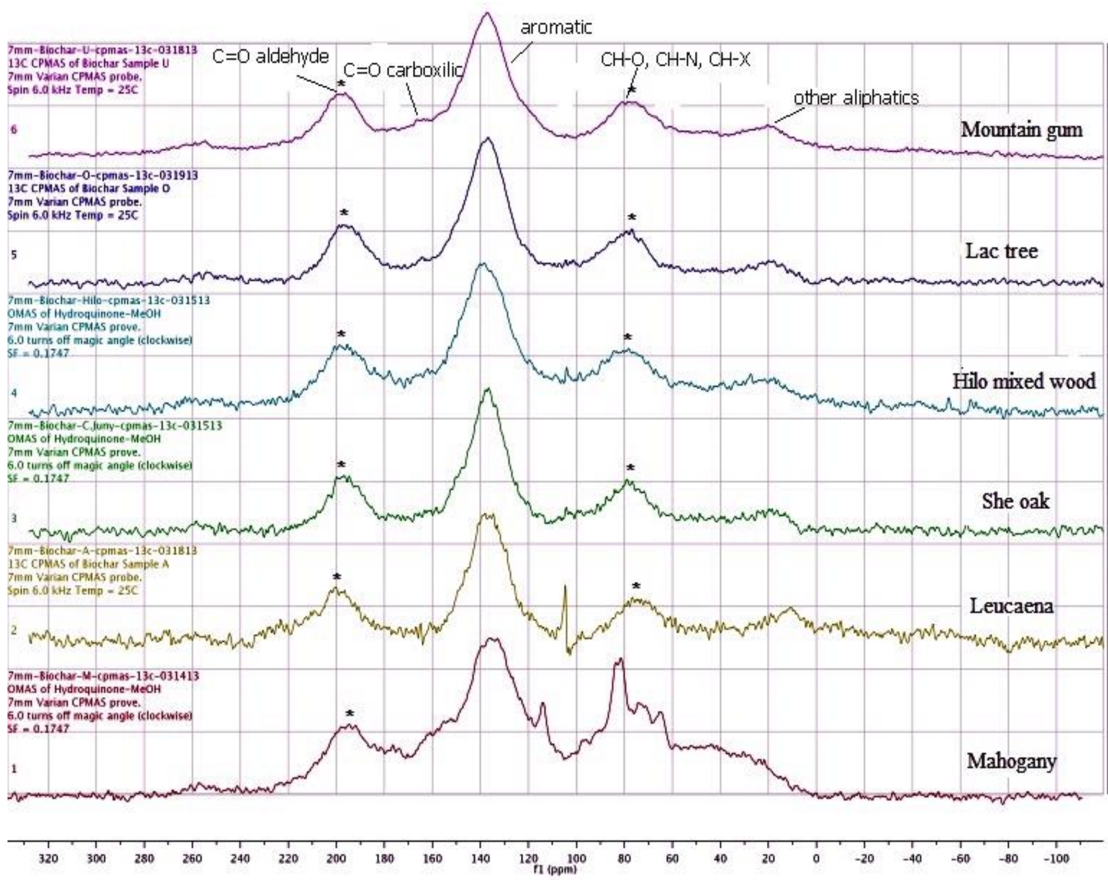


Figure 3.7. CPAS NMR peaks of the chemical compounds and functional groups of six biochars. * = spinning side bands (SSB)records for the six biochars

NMR bands from the six biochars had similar patterns (Fig. 3.7). It consists of a typical aromatic band at the center and two symetrical spinning side bands at the right and the left sides. The broad central band around 120-160 ppm is aromatic, and is the main component of biochar. This was the result of the rearrangement and aromatization of thermochemically degraded cellulose, hemicellulose and lignin during pyrolysis (Amonette and Joseph 2009, Keiluweit *et al.* 2010, Brewer, 2012). The presence of the aromatic compound is supported by the FTIR peak at 1600 cm^{-1} and the low values of biochar H:C ratio. On the left side there are aldehyde (190-200 ppm) and a small band of carboxylic (160-170 ppm), while CH-O, CH-N, CH-X (70-90 ppm) and other aliphatics (10-30 ppm) bands are on the right. The broad bands at 120 to 80 ppm for mahogany and leucaena are assigned to unburned aliphatic compounds resulted in high VM, low fixed C and low stability of those two biochars.

3.4.5. Boehm titration

Surface functional groups of the biochars are listed in table 3.5. Total functional groups ranged from 0.38 to 2.15 mmol/g. The highest total functional groups was in mahogany biochar, followed by mountain gum, Hilo mixed wood, lac tree and leucaena. Phenolic functional group was the major functional groups for all biochars with the exception of she oak where the carboxylic group was higher than the other groups. Carboxylic was higher than lactonic for Hilo mixed wood and lac tree biochars.

Surface functional groups were responsible for the biochar surface charge development and is therefore attributed to the biochar CEC. For example Mahogany with the highest total functional groups has the highest CEC (Figure 3.10).

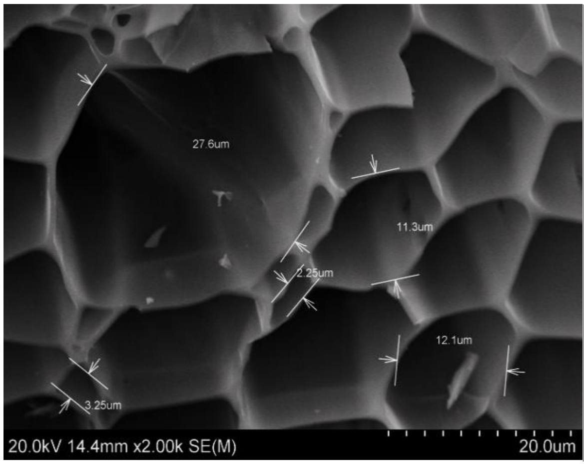
Table 3.5. Means and standard errors of surface functional groups of the six biochars (n=3)

Biochars	Total	Carboxylic	Phenolic	Lactonic
	mmol/g			
Leucaena (*Leucaena leucocephala*) wood	0.38 ± 0.01	0.07 ± 0.02	0.21 ± 0.04	0.10 ± 0.03
Lac tree (*Schleichera oleosa*) wood	0.38 ± 0.02	0.12 ± 0.02	0.20 ± 0.04	0.07 ± 0.02
Hilo mixed wood	0.58 ± 0.03	0.22 ± 0.02	0.27 ± 0.03	0.10 ± 0.03
She oak (*Casuarina junghuhniana*) wood	0.43 ± 0.01	0.24 ± 0.01	0.06 ± 0.01	0.13 ± 0.01
Mahogany (*Swietenia mahagoni*) wood	2.64 ± 0.03	0.31 ± 0.01	1.57 ± 0.05	0.76 ± 0.03
Mountain gum (*Eucalyptus urophylla*) wood	2.15 ± 0.03	0.55 ± 0.04	0.88 ± 0.04	0.72 ± 0.03

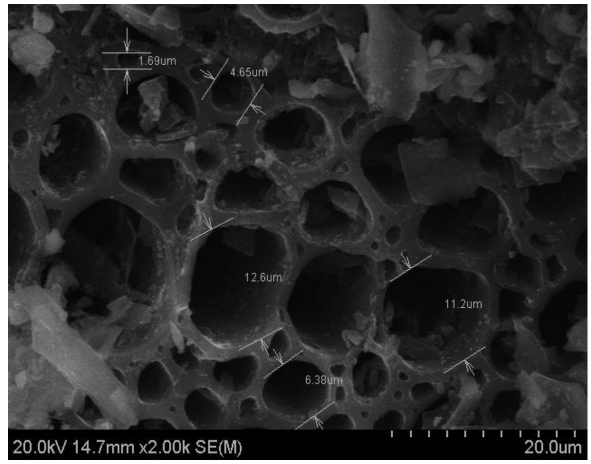
3.4.6. Biochar surface structure and porosity

SEM images show the porous nature of biochars (Fig. 3.8). The ranges of pore size for leucaena, Hilo mixed wood, she oak, mahogany, lac tree and mountain gum biochars are 1.13-13.8 nm, 1.13-7.95 nm, 2.14-6.3 nm. 1.44-7.78 nm, 0.85-6.3 nm, and 1.12-3.46 nm, respectively. They are of micropores (< 2 nm) and mesopores (2 – 50 nm). Porosity was developed from the rearrangement of fused-ring carbons during the heating process. The aggregated fused-ring carbons are stacked to form small lamellar crystallites, then the crystallites were randomly orientated that left voids between them (Rutherford *et al.* 2004).

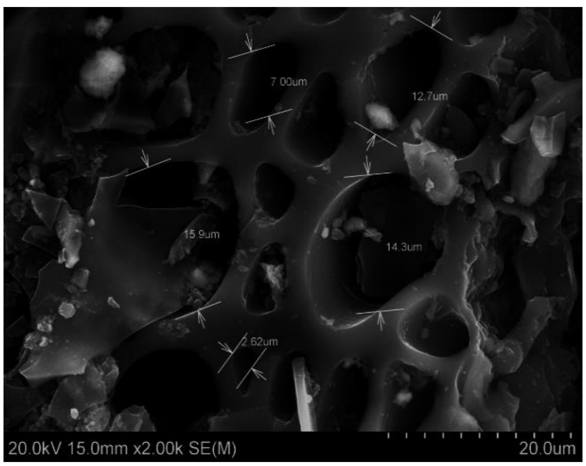
SEM or electron microprobe analysis (EMPA) can be combined with ESD analysis for detailed study of a sample. An example of biochar chemical composition obtained from EDS analysis following the EMPA records is shown in Fig. 3.9. The EDS analysis on two spots of white crystalline material from EMPA image showed the typical peaks of C, O and Ca. Thus, the white crystalline material was likely CaO or $CaCO_3$. The similar result was also previously reported by Chia *et al.* (2010) who used SEM and EDS to analyze the synthetic Terra Preta soil.



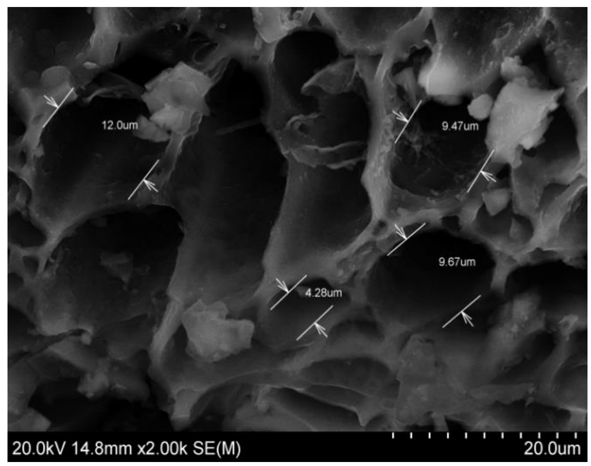
Leucaena



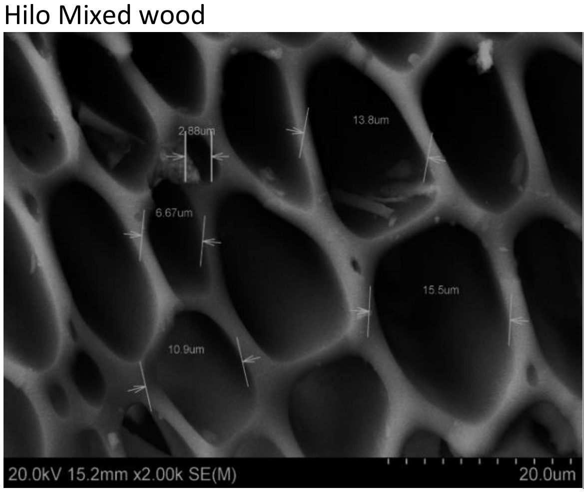
Lac tree



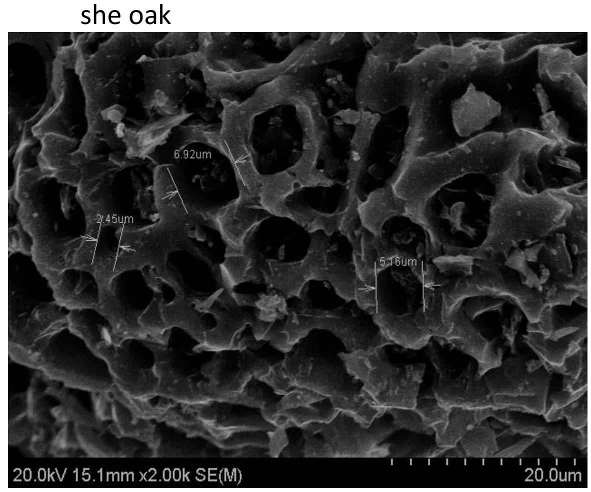
Hilo Mixed wood



she oak



Mahogany



Mountain gum

Figure 3.8. Scanning Eelctron Microscope (SEM) images showing the surface structure and porosity of the six biochars

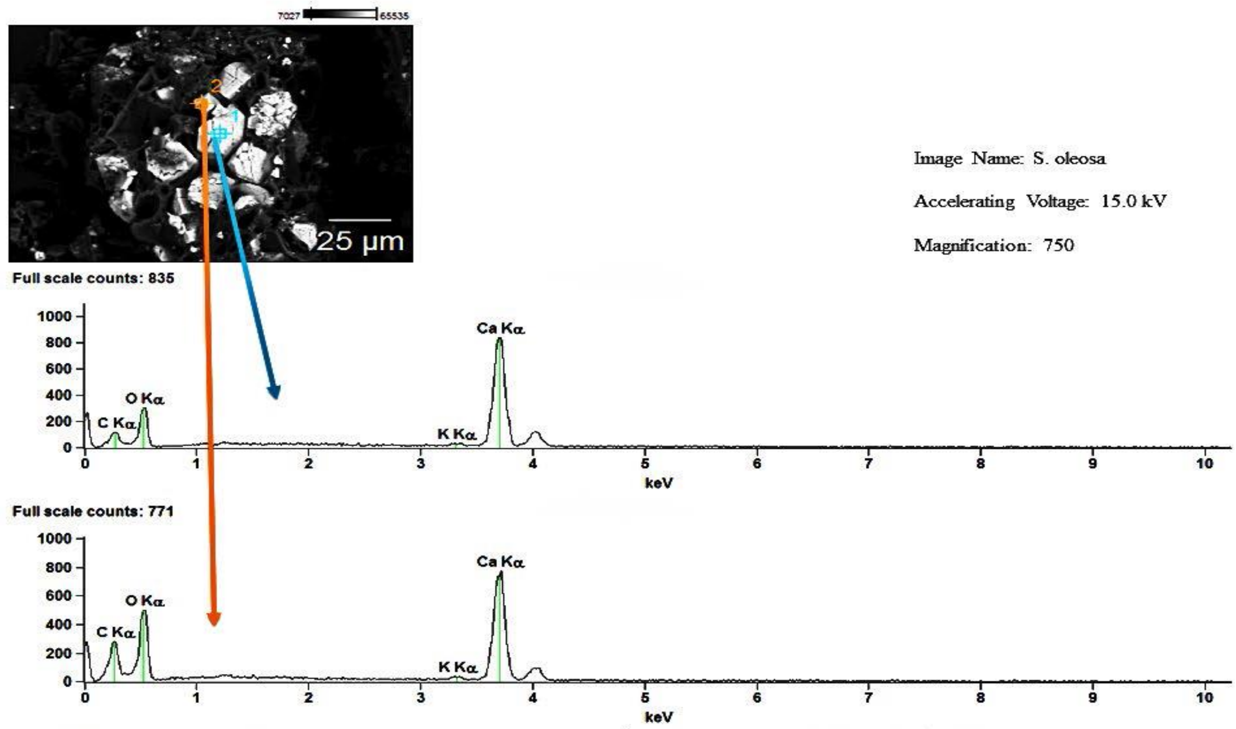


Figure 3.9. Energy Dispersive Spectrometer (EDS) analysis of white spots on an electron microprobe analysis (EMPA) sample of lac tree biochar

3.4.7. Selected chemical properties of biochars

Selected chemical properties of biochars are shown in Tabel 3.6. Biochars' pH ranged from 4.2 for mountain gum to 10.4 for lac tree, and positively correlated with the ash content (Fig. 3.1). The order of biochars pH was lac tree ≈ leucaena ≈she oak > Hilo mixed wood >mahogany>mountain gum. Biochar pH was also attributed to the acid functional groups content (Mukherjee *et al.* 2011, Enders *et al.* 2012). For example, leucaena and lac tree biochars with the highest pH were lowest in the carboxylic content (Table 3.5).

Biochars' EC ranged from 0.1 dS/m for mahogany and mountain gum to 2.4 dS/m for Hilo mixed wood. Biochar EC represents the salt (mineral content). Therefore, the higher EC values of leucaena, lac tree and Hilo mixed wood could be attributed to their higher mineral content (Table 3.3).

$CaCO_3$ equivalent represents the carbonates content in the biochar, and is therefore positively correlated with the basic cations in the biochars (Fig. 3.2). $CaCO_3$ equivalent ranged from 4.2% for mountain gum to 28.6% for leucaena. Previous study showed that the liming potential of high temperature biochar, the capacity of biochar to increase soil pH and reduce exchangeable Al, was attributed to the $CaCO_3$ equivalent (Wan *et al*. 2014). Six tested biochars can be devided into 3 groups based on their $CaCO_3$ equivalent: leucaena and lac tree, Hilo mixed wood and she oak, and mahogany and mountain gum as the highest, moderate and lowest liming potential biochars, respectively.

Biochar CEC varied from 13.9 cmolc/kg for she oak to 45.1 cmolc/kg for mahogany. Biochar CEC represents the surface charge and reactivity of biochars and is attributed to the functional groups (Fig. 3.10) and surface area of biochars

Table 3.6. Selected properties of the six biochars

Wood-derived biochars	**pH**	**EC**	**CEC**	**CaCO3 eq**	**Phenolics**
	1:5	dS/m	cmolc(+)/kg	%	µg/g
Leucaena (*Leucaena leucocephala*)	10.3	2.1 ± 0.04	20.1 ± 0.5	28.6 ± 1.5	27.4 ± 0.8
Lac tree (*Schleichera oleosa*)	10.4	2.3 ± 0.02	17.3 ± 1.3	24.1 ± 0.4	35.2 ± 0.3
Hilo mixed wood	9.5	2.4 ± 0.01	14.7 ± 0.2	8.4 ± 0.4	25.1 ± 0.2
She oak (*Casuarina junghuhniana)*	10.2	0.9 ± 0.02	13.9 ± 0.6	8.4 ± 0.4	28.3 ± 0.5
Mahogany (*Swietenia mahagoni*)	5.0	0.1 ± 0.00	45.1 ± 0.5	5.0 ± 0.4	532.4 ± 7.5
Mountain gum (*Eucalyptus urophylla*)	4.2	0.1 ± 0.00	44.9 ± 0.5	4.2 ± 0.4	9,621.9 ± 341.9

Note: biochar:water was 1:5 for pH and EC measurements

Total phenolics varied from 25.1 to 9,621.9 µg/g, with the highest content being from the mahogany and mountain gum biochars. Leucaena, lac tree, Hilo mixed wood and she oak wood biochars had alkaline pH, high CaCO3 equivalent and EC. In contrast, mountain gum and mahogany wood biochars had acid to slightly acid pH, high CEC, and total phenolic content.

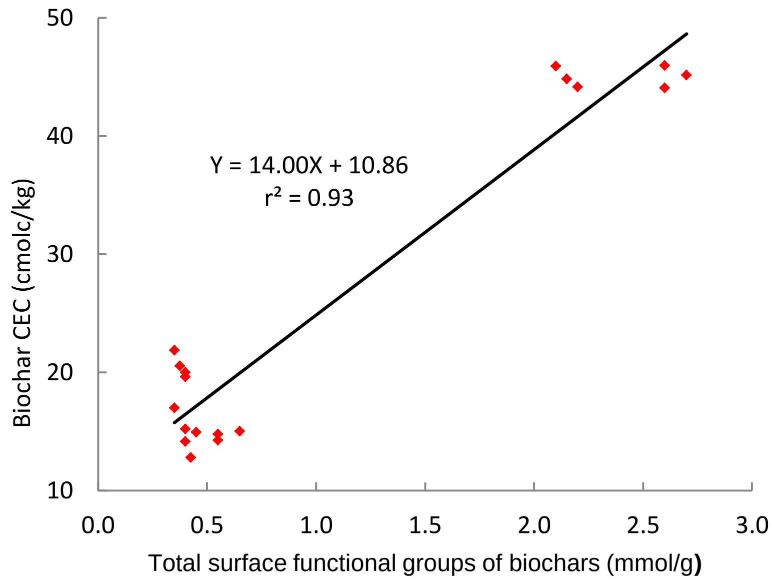


Figure 3.10. Relationship between biochar total functional groups and CEC

3.5. Conclusions

Six wood-derived biochars, namely: leucaena, lac tree, Hilo mixed wood, she oak, mahogany and mountain gum, collected from West Timor, Indonesia and Hilo, Hawaii, USA, were characterized for their use as acid soil amendments by using the proximate and ultimate analysis, FTIR, NMR, SEM and EDS, and some soil test procedures. Leucaena, lac tree, Hilo mixed wood and she oak were alkaline in pH, had high basic cations and $CaCO_3$ equivalent in their ash, and contained more nutrients than either mahogany or mountain gum biochars. Using $CaCO_3$ equivalent or basic cations to screen liming potential of six tested biochars shown that lac tree and leucaena was the highest liming potential biochars followed by Hilo mixed wood and she oak, and mahogany and mountain gum was the lowest liming potential biochars.

3.6. Acknowledgements

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CHAPTER 4. LIMING EFFECT OF BIOCHARS

4.1. Abstract

Investigations on biochar as a soil amendment have shown that biochars could reduce soil acidity. To investigate the liming potential of biochars, greenhouse and field experiments were conducted in Hawaii, USA and West Java, Indonesia, respectively. Six wood-derived biochars were amended to a Hawaiian acid soil (pH 4.6, exchangeable Al 1.8 $cmol_c kg^{-1}$) at 2% and 4% alone or in combination with 2 $cmol_c kg^{-1}$ of lime, and then planted with *Desmodium intortum* twice as the test plant in the greenhouse trial. To the Indonesian acid soils (pH 3.9-4.0, exchangeable Al 8-14 $cmol_c kg^{-1}$) two biochars at 4% and 8% alone or in combination with lime at 4 and 8 $cmol_c kg^{-1}$ and compost at 0.1 and 0.2% were added, and then planted with soybean cv Anjasmoro twice as the test plant in the field trials. Biochar effects on the soils properties and the growth of plant growth were measured. The results indicated that upon biochar additions soil pH and cation exchange capacity were increased, exchangeable Al was reduced, and plant nutrients were enriched variously, depending on the biochars feedstocks and rates and the soil acidity levels. Total dry weights of *Desmodium* upon application of biochars alone in the Hawaiian acid soil were increased 2-4 folds over the control or lime treatment. Shoot and root dry weights of soybean obtained from the Indonesian soils amended with biochars alone were increased 2.1 and 1.6 folds and 2.3 and 1.5 folds for the first and the second plantings, respectively. $CaCO_3$ equivalent and nutrients content were the most among biochar properties were responsible for the acid soil productivity improvement and subsequently the plant growth enhancement. Four of the six biochars tested (in the greenhouse) improved Hawaiian soil productivity and increased *Desmodium* growth; and the lac tree wood biochar improved Indonesian acid soils and soybean growth more than the rice husk biochar. Thus, we would recommend that: (1) biochars produced from lac tree (*Schleichera oleosa*), leucaena (*Leucaena leucocephala*), she oak (*Casuarina junghuhniana*) or Hilo mixed woods be applied at 2 to 4% in combination with a moderate quantity (1-2 $cmol_c kg^{-1}$) of lime for Hawaiian soil productivity and plant growth improvements; (2) because of the availability biochar and based on the net benefit analysis we recommended rice husk biochar at 8% alone or in combination with lime at 8 cmolc/kg and compost 0.2% for improvement of Indonesian acids soil productivity and a profitable soybean cropping.

Key words: exchangeable Al, liming ptential, soil productivity, plant growth

4.2. Introduction

Biochar production was inspired by the discovery of the anthropogenic Amazonian Dark Earth (ADE) or Terra Preta, which had a higher nutrient content, cation exchange capacity (CEC) and organic matter than the surrounding soils (Glaser *et al.* 2000, 2002; Lehmann *et al.* 2002, Lehmann and Joseph 2009). Recently, biochar has often been produced in a pyrolytic process for specific purposes such as soil amendment or carbon sequestration (Lehmann and Joseph 2009, Marris 2006; Glaser *et al.* 2009).

Recent research findings indicate that biochars have direct and indirect effects on soil productivity improvement and subsequently on plant growth enhancement. Many effects have been identified, including: increasing soil water retention (Novak *et al.* 2009b), aggregation (Mukherjee and Lal 2014), cation exchange capacity (CEC), nutrient supply and retention (Lehmann *et al.* 2003), soil microbial population and activities (Pietikainen *et al.* 2000, Rondon *et al.* 2007, Warnock *et al.* 2007, Makoto *et al.* 2010, Graber *et al.* 2010,) and crop protection (Elad *et al.* 2010). All those soil properties alteration may act individually or in concert to result in enhanced plant growth (Silber *et al.* 2010). The agronomic benefit of biochar is depending on the biochar properties resulted from the type of feedstock and pyrolysis condition. Regional conditions including soil type, chemistry, and condition (depleted or healthy), temperature, and humidity also affect biochar agronomic benefits (Silber *et al.* 2010).

One of the agronomic benefits of using biochar is to increase soil pH and decrease soil exchangeable aluminum, thereby improving productivity of acid soils for plant growths (Tryon 1948, Yamato *et al.* 2006, Nguyen and Lehmann 2009, Novak *et al.* 2009b, Joseph *et al.* 2010, Singh *et al.* 2010, Van Zwieten *et al.* 2010, Deenik *et al.* 2011, Yuan *et al.* 2011, Streubel *et al.* 2011, Lehmann *et al.* 2011, Chintala *et al.* 2013, Slavich *et al.* 2013, Smider and Singh 2014). Previous studies indicate that the acidity neutralizing capacity of biochar is believed to depend on its ash and volatile matter content (Deenik *et al.* 2011), biochar ash carbonates content and surface functional groups of biochar (Cheng *et al.* 2008, van Zwieten *et al.* 2010, Yuan *et al.* 2011, Smider and Singh 2014), and alkaline earth metal oxide in the bichar ash (Novak *et al.* 2009b). It appeared that liming potential of biochars could be attributed to the basic cations or carbonates of biochar ash and the surface functional groups of biochars. However, Hass *et al.* (2012), on one hand, showed that the effect of chicken manure biochar in raising the soil pH and reducing the soil exchangeable Al is a process-dependent, while Mukome *et al.* (2013), on the other hand, suggested feedstock as a better predictor for biochar ash after compiling data of 11 wood and non-wood biochars properties. All those prior findings direct us to develop a cheaper and simple predictor of liming potential for biochars end-users.

To be use as a profitable soil amendment, the availability of biochar feedstock, cost of production, price, and other factors could be taken into account in additions to its liming values. Cost-Benefit Analysis (CBA) that putting together the cost and the benefit of biochar application is perhaps the most powerfull tool for deciding between alternates or scenarios (Joseph, 2009). For example, Galinato *et al.* (2011) showed that biochars can be profitably applied as a soil amendment for wheat if the biochar market price is low enough (12 USD/t) and or a carbon offset market (31 USD/tCO_2e) exists. Dickinson *et al.* (2014) also found a positive Net Prevent Value (NPV) for cereal cropping in Sub-Sahara Africa where the duration of biochar yield effect is assumed to extend 30 years into the future.

The hypothesis of this study was that biochars basic cations or $CaCO_3$ equivalent is responsible to the liming potential of biochar. The high liming potential biochars such as leucaena, lac tree, Hilo mixed wood and she oak could improve Hawaiian and Indonesian acid soils productivities and support plant growths better than the low liming potential biochar such as rice husk, mahogany and mountain gum biochars. Specifically, lactree and leucaena wood-derived biochars with the highest $CaCO_3$ equivalent or basic actions content could improve soil productivity of Hawaiian Ultisol more than mahogany or mountain gum biochar, and the lac tree biochar could be better correcting Indonesian acid soils than the low $CaCO_3$ equivalent rice husk biochar.

The objective of this study was to evaluate the amending capacity of biochars with different liming potentials in correcting acidity and enhancing plant growth of Hawaian and Indonesian variable charge soils. Five biochars: leucaena, lactree, Hilo mixed wood, she oak, mahogany and mountain gum with different $CaCO_3$ equivalent or basic cations will be evaluated their amending capicity to a Hawaiian acid soil in a greenhouse trial, and two biochars (lac tree and rice husk) with different $CaCO_3$ equivalents will be assessed their ameliorating capacities to two Indonesian acid soils. Finally, we will conduct a Net Benefit Analysis for the application of biochars in Indonesian acid soil to help local farmers in chosing profitable uses of bicohars.

4.3. Materials and Methods

4.3.1. Greenhouse experiment

To study the acidity amending capacity of biochars, a greenhouse experiment was conducted at the Magoon research facility, University of Hawaii at Manoa, Honolulu, Hawaii, USA, using an acid soil, Ultisol (Ustic Kanhaplohumults, Leilehua series), collected from the Waiawa Correctional Facility, Oahu Island, Hawaii. Sub-surface soil samples (10 cm bellow the surface) were air dried, and sieved to pass a 4 mm sieve for the pot experiment; and passed 0.5 mm sieve for chemical analysis. Five wood- and one mixed wood-derived biochars collected from Indonesia and Hawaii were oven dried at 70^{o}C 48 hours, grounded and sieved to pass a 60 mesh (0.25 mm) sieve. All biochars were characterized using the procedures as described in previous chapter and their selected properties are listed in tables 4.1. A hydrated lime (Bandini®) with the $CaCO_3$ equivalent of 108 was dried and sieved through a 60 mesh sieve before used. In its natural state, the soil had a pH of 4.6, 2.4 cmolc/kg acidity, 1.8 cmolc/kg exchangeable Al, and 16.8 cmolc/kg CEC (as measured by the NH4OAC, pH 7 method).

Table 4.1. Mean and standard errors of selected properties of 6 biochars (n=3)

Selected properties	Biochars					
	Leucaena wood	Lac tree wood	Hilo mixed wood	She oak wood	Mahogany wood	Mountain gum wood
pH (1:2.5)	10.3	10.4	9.5	10.2	5.0	4.2
EC (dS/m)	2.1 ± 0.04	2.3 ± 0.02	2.4 ± 0.01	0.9 ± 0.02	0.1 ± 0.00	0.1 ± 0.00
CEC (cmolc(+)/kg)	20.1 ± 0.5	17.3 ± 1.3	14.7 ± 0.2	13.9 ± 0.6	45.1 ± 0.5	44.9 ± 0.5
$CaCO_3$ equivalent (%)	25.5 ± 0.2	19.2 ± 0.4	3.9 ± 0.4	8.0 ± 0.3	0.8 ± 0.1	0.0 ± 0.0
Phenolics (µg/g)	27.4 ± 0.8	35.2 ± 0.3	25.1 ± 0.2	28.3 ± 0.5	532.4 ± 7.5	9621.9 ± 341.9
Ash content (%)	30.7 ± 0.03	15.8 ± 0.04	19.6 ± 0.2	4.6 ± 0.1	7.3 ± 0.1	0.7 ± 0.0
Volatile matters (%)	33.3 ± 1.2	28.1 ± 0.03	23.7 ± 0.5	22.9 ± 1.8	53.3 ± 1.0	36.4 ± 0.2
Total functional groups (mmol/g)	0.38 ± 0.01	0.38 ± 0.02	0.58 ± 0.03	0.43 ± 0.01	2.64 ± 0.03	2.15 ± 0.03
Carboxylic functional groups (mmol/g)	0.07 ± 0.02	0.12 ± 0.02	0.22 ± 0.02	0.24 ± 0.01	0.31 ± 0.01	0.55 ± 0.04
Total basic cations (%)	5.97 ± 0.07	7.12 ± 0.03	2.38 ± 0.02	2.09 ± 0.03	0.69 ± 0.00	0.15 ± 0.00

EC: electric conductivity; CEC: Cation exchange capacity.

The treatments, consisting of biochar and lime, were arranged in a 6 x 3 x 2 factorial completely randomized design with 3 replicates. Six biochars, namely leucaena (*Leucaena leucocephala*) wood, lac tree (*Schleichera oleosa*) wood, mixed wood Hilo, she oak (*Casuarina* *junghuhniana*) wood, mahogany (*Swietenia mahagoni*) wood and mountain gum (*Eucalyptus urophylla*) wood, were applied at three rates: control (soil without biochar), 2% and 4% biochar. The lime treatments were control (soil without lime) and 2 cmolc/kg lime factorially superimposed on biochar treatments. Each of two kg of soil was amended with biochars and/or lime, mixed, watered, and then transferred into pots. Basal nutrients were added to all treatments (mg/kg): 160 N, 160 P_2O_5, and 160 K_2O from a 16-16-16 commercial fertilizer. After four weeks of incubation, all pots were planted twice with *Desmodium intortum* cv. Greenleaf, an Al sensitive forage legume, as the test plant. *Desmodium* was harvested after 37 days of growth. The shoots were cut and the roots were carefully removed from the soil. Both were washed with tap water and then with deionized water three times before oven-dried at 70^oC for 50 hours. Soil samples were collected from each pot, air-dried, crushed, and passed through a 0.5 mm sieve before analysis. Selected soil chemical properties, namely soil pH (H_2O 1:1), total acidity and exchangeable Al were measured using a pH meter, 1 M KCl method, ammonium acetate (NH_4OAC) pH 7.0 method (Chapman, 1965), respectively.

The shoots and roots dry weights were recorded, and then ground separately for tissue analysis. A 0.10 g of shoot or root was dry digested in a muffle furnace at 500^oC for 4 hours. Four ml of 1 M HNO_3 was added to dissolve the ash, and then heated at 150^oC on a hotplate until dry. Fifteen ml of 0.1 M HCl was added, stirred, and filtered into an Inductively Coupled Plasma (ICP) tube for analysis.

4.3.2. Field experiment

To verify the amending capacity of biochars to acid soils at the field level, a field experiment was conducted in West Java, Indonesia, from October 2013 to April 2014. The first site was at Guradog, Lebak district, Banten province (6^{o}30'45.65"S, 106^{o} 22' 43.38"E). The soil at this site was a Typic Paleudult, pH 4.0 and exchangeable Al 8.0 cmolc/kg. The second site was at Jasinga, Bogor district, West Java province (6^{o}28'1.24"S, 106^{o}28'34.62"E). The soil at this site was a Typic Hapludult, pH 3.9 and exchangeable Al 14.0 cmolc/kg. A brief description of the two sites was provided in Table 4.2.

Table 4.2. Short description of the field research sites in Indonesia

Description	Jasinga site	Guradog site
Altitude	150 m	145 m
Air temperature	22.4-31.5^{o}C	22.1-33.10^{o}C
Relative humidity	40-78%	38-58%
Annual rainfall	2708 mm	2688 mm
Soil subgroups	Typic Hapludults	Typic Paleudults
Soil pH	3.9	4.0
Soil exch. Al	14 cmolc/kg	8 cmolc/kg

Two biochars, lac tree wood and rice husk with their properties were listed in table 4.3, were selected based on a pot trial with five biochars and two soils at the University Farm, Bogor Agriculture University, Darmaga, Bogor, Indonesia from June to October 2013.

Results from this pot trial showed that lac tree wood biochar, made in a mound kiln at 500-600 ^{o}C by farmer in Ponorogo, East Java, was superior to the others for soil productivity improvement and soybean growth. The rice husk biochar produced at 290-320^{o}C by a traditional charcoal making process by farmers in Jasinga, West Java, supported soybean growth the least.

To evaluate the liming value of the biochars, a local lime (CaO = 58.0%), obtained from the local market, was used alone or in combination with the biochars. Because of low nutrients in these two highly weathered tropical soils, a local thermocompost (pH (1:5): 7.8, EC: 0.61dS/m, CEC: 38 cmolc/kg, C/N: 8.3, N: 1.79%, P: 0.22%, K: 0.25%, Ca: 0.69%, Mg: 0.11%, Fe: 3792 mg/kg, Mn: 335 mg/kg, Al:7702 mg/kg) was also used in various combinations with the biochars and lime.

Table 4.3. The production conditions and selected properties of lac tree wood and rice husk biochars

Productions and Properties	**Biochars**	
	Lac tree wood	Rice husk
Production method	Mud kiln	Open fired
Production temperature (^oC)	500-600	290-320
Fixed carbon (%)	47.8	7.4
Volatile matter (%)	40.5	43.7
Ash content (%)	11.7	48.9
$CaCO_3$ equivalent (%)	13.7	1.2
pH H_2O	9.0	7.6
EC (dS/m)	1.9	1.3
CEC (cmolc/kg)	17.7	33.1
Total C (%)	72	37
Total N (%)	0.4	0.8
O (%)	25.4	48.2
H (%)	2.2	1.4
C/N	180	46
O/C	0.26	0.98
H/C	0.37	0.45
K (%)	0.33	0.48
P (%)	0.06	0.1
Ca (%)	3.13	0.17
Mg (%)	0.13	0.09
Na (%)	0.12	0.06
Fe (mg/kg)	684	413
Mn (mg/kg)	55	189
Zn (mg/kg)	18	94
Cu (mg/kg)	6	4
B (mg/kg)	8	9
Si (mg/kg)	77.9	353.9

The biochars were applied at 4 and 8% (96 and 192 Mg/ha) alone or in combination with lime at 4 and 8 cmolc/kg (3.5 and 7 Mg/ha) and compost at 0.1 and 0.2 % (2.5 and 5 Mg/ha). All treatments (Table 4.4) were arranged in a randomized complete block design with 4 replicates. The sites were prepared by cutting the reed grass, the original vegetation cover, followed by plowing, harrowing, and then establishing 52 plots. Plot size was 280 cm x 150 cm x 20 cm. Biochars alone or incombination with lime or compost were poured, spread, and mixed thoroughly with soils, watered and incubated for 34 days (October 30 to December 2, 2013) before sampling and planting. Soybean (*Glycine max*) c.v. Anjasmoro, a local cultivar that was highly sensitive to soil acidity, was planted twice as the test plant. The first planting was started on December 3, 2013 and plants were cut on January 13, 2014. The second planting for Jasinga site was started on February 1, 2014 and the plants were harvested on March 11, 2014, while the second planting at Guradog site was lately started at March 10, 2014, and harvested on April 16, 2014.

Table 4.4. The biochars, lime and compost treatment combinations for the field trials in Indonesia

Biochar types	Biochar rates (%)	Lime rates (cmolc/kg)	Compost rates (%)
Lac tree wood	4	4	0
Lac tree wood	4	4	0.1
Lac tree wood	8	0	0
Lac tree wood	8	8	0
Lac tree wood	8	8	0.2
Rice husk	4	4	0
Rice husk	4	4	0.1
Rice husk	8	0	0
Rice husk	8	8	0
Rice husk	8	8	0.2
Control	0	8	0
Control	0	8	0.2
Control	0	0	0

Field trial soil samples were collected from each plot, air-dried, crushed, and passed through a 2 mm sieve before analysis. Selected soil chemical properties, namely soil pH (H_2O 1:1), exchangeable Al, and cation exchange capacity, were measured using a pH meter, 1 M KCl method and NH4OAC pH 7.0 method, respectively. Plant dry weights were recorded separately for shoot and root after being washed with tap water and then deionized water, and oven-dried at 70^oC for 4 days. Dry shoot and root samples were then collected, crushed, and sieved for tissue analysis. A 0.10 g of shoot or root was dry digested in a muffle furnace at 500^oC for 4 hours. Four ml of 1 M HNO_3 was added to dissolve the ash, and then heated at 150^oC on a hotplate until dry. Fifteen ml of 0.1 M HCl was added, stirred, and filtered into an Inductively Coupled Plasma (ICP) tubes and then read with an ICP spectrometer.

4.3.3. Net benefit analysis

To compare the amendment options and to choose the best amendment for the field trial, a net benefit analysis (NBA) was conducted. It consisted of several steps: (1) Selected treatments were converted to amendment options, (2) all costs and benefits were identified and calculated based on the assumptions described latter, (3) the best management option was carefully chosen based on the highest net present value (NPV).

The NBA was conducted based on the assumptions that: (1) inflation rate is 10%, (2) discount rate (r) is 10%; (3) beneficial effect of lime is 3 years effectively, thus additional lime with the same rate should be applied at the fourth year to keep the soybean growth and production, (4) compost beneficial effect is 1 year effectively, means compost should be added every year, (5) soybean growth and production under the biochar treatment is increased 30.3%

(Liu *et al*. 2013) each year during the five year project period; (6) the soybean yields (grain dry weight) were predicted based on their shoot dry matter weights by assuming that about 2 tonnes (2000 kg) of dry grains per hectare will be produced from the best soybean growth (Suhartina, 2005) ; (7) the environmental beneficial effects of the biochar such as reducing CO_2 emission or adverse effects of the lime application such as increase CO_2 emission were not included. The basic units for the analysis were: (1) land area was 1 hectare, (2) exchange rate rupiah (IDR) to dollar was 10000 IDR to 1 USD, (3) lac tree wood and rice husk biochars prices were $0.05/kg and $0.03/kg, respectively; lime and compost prices were $0.02/kg and $0.05/kg, respectively; and soybean grain price per kg was $0.74.

NPV was calculated after all of the components of the costs and benefits were identified and predicted for 5 future year based on the 7 assumptions described earlier. Components of the cost were included: (1) input cost: biochar, lime, compost, seeds, and pesticides; (2) labor cost: land clearing, plowing, harrowing, amendment application, planting, weed and pest control, harvesting and transportation. Soybean dry grain was the only component of the benefit included in the analysis. To be used for calculating the NPV, all cost and benefit should be discounted to the present value (PV) using the next formula: PV = Pt/(1+r)t (Lave, 1996); r is discount rate (10%), t is the year in which Pt is realized, Pt is the cost or benefit value in the time t. NPV were calculated using formula NPV= PVB-PVC (Lave, 1996); PVB = total prevent value of biochar benefits, PVC = total prevent value of biochar costs.

4.3.4. Statistical analysis of data

Descriptive analysis was used to calculate means and standard errors from three or four replicates of measured soil pH and CEC, plant root dry weight, and nutrient content in plant tissues. The relatioships between biochar properties and soil properties or plant growth was analysed using regression analysis and presented in the combined scatter and fitted line graphs using Microsoft Excel 2010 and Sigmaplot^{TM} 11.0 software. Histogram figures of soil properties changes and plant growth differences resulted from the biochar application were drawn using Microsoft 2010 Excel software. Data not meeting the assumption of normality were square root X+0.5 transformed before analyses and then presented in their untransformed form. Treatment effects on soil properties and plant growth were analyzed by a two-way analysis of variance (ANOVA) using PROC ANOVA GLM of the SAS 9.2 software, and the Duncan's multiple mean comparisons at $P \leq 0.05$ were done for testing the significant effects of the treatments.

4.4. Results

4.4.1. Selected properties of biochars

Selected properties of biochars used in the greenhouse and field experiments are shown in Tables 1(a, b and c) and 3, respectively. Biochars' pH ranged from 4.2 to 10.4, and positively correlated with the ash content (Fig. 3.1). There is also a positive correlation between $CaCO_3$ equivalent and base cations in the biochars (Fig. 3.2). Biochars' EC ranged from 0.1 to 2.4 dS/m, their CEC varied from 13.9 to 45.1 cmolc/kg, and volatile matter content from 22.9 to 55.3%. Total phenolics varied from 25.1 to 9,621.9 µg/g, with the highest content being from the mahogany and mountain gum biochars. Leucaena, lac tree, mixed wood Hilo and she oak wood derived biochars had alkaline pH, high $CaCO_3$ equivalent and EC, and the rice husk biochar had a neutral pH. In contrast, mountain gum and mahogany wood derived biochars had acid to slightly acid pH, high CEC, volatile matter and total phenolic content (Table 4.1a).

Element or nutrient content varied with biochar types (Table 4.1c). Leucaena, lac tree, mixed wood Hilo, she oak biochars had higher content of N, P, Na, K, Mg, Ca, Si, B, Cu, Zn than mountain gum and mahogany biochars. With exception of Ca and Fe, rice husk biochar had higher Si and nutrient content than lac tree wood biochar produced at 500-600^{o}C (Table 4.3). The results reflect the differences in the feedstocks. In fact, nutrient content of biochars was reportedly determined mostly by feedstock mineral composition, but some nutrients were also affected by the pyrolysis temperature (Gaskin *et al.* 2008, Brewer 2012, and Zhao *et al.* 2013).

4.4.2. Greenhouse experiment

4.4.2.1. Effect of biochars on soil properties

4.4.2.1.1. Soil pH

The addition of biochars at 2% and 4% alone or in combination with 2 cmolc/kg of lime raised soil pH varyingly, depending on types and rates of biochars (Fig. 4.1). Lac tree and leucaena biochars increased soil pH from 4.5 to 5.8 and 5.9 when applied at 2%, and increased the soil pH further to 6.3 and 6.9, respectively at 4%. However, their capacity to raise soil pH were lowered when applied in combination with lime. Hilo mixed wood and she oak biochars raised the soil pH moderately to 5.1 and 5.4 when applied at 2 and 4%, respectively; and to 5.6-5.7 when applied in combination with 2 cmolc/kg of lime. Mahogany and mountain gum biochars only increased soil pH slightly to 5.0 when applied with lime. The magnitude of soil pH increases well correlates with the biochars basic cations content (Fig. 4.2).

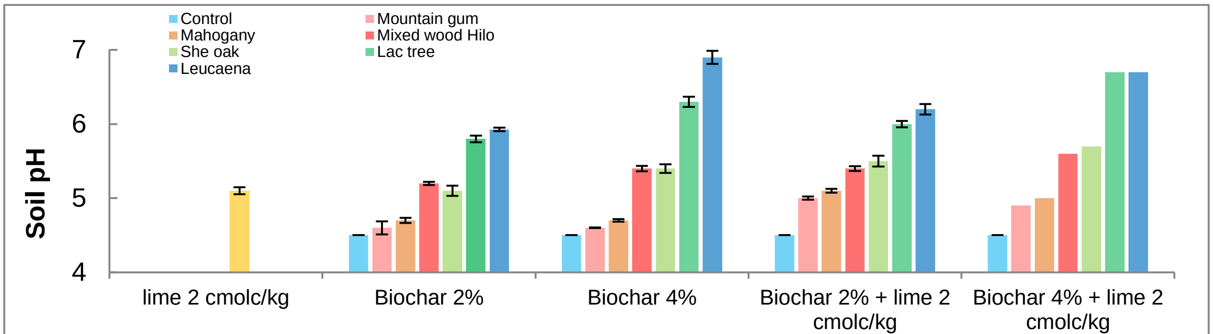
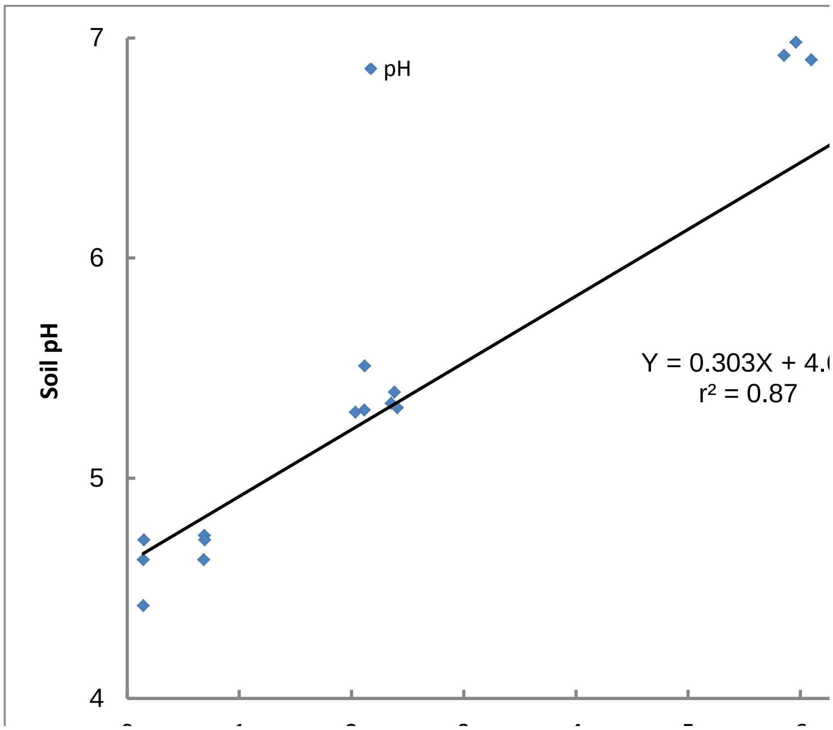


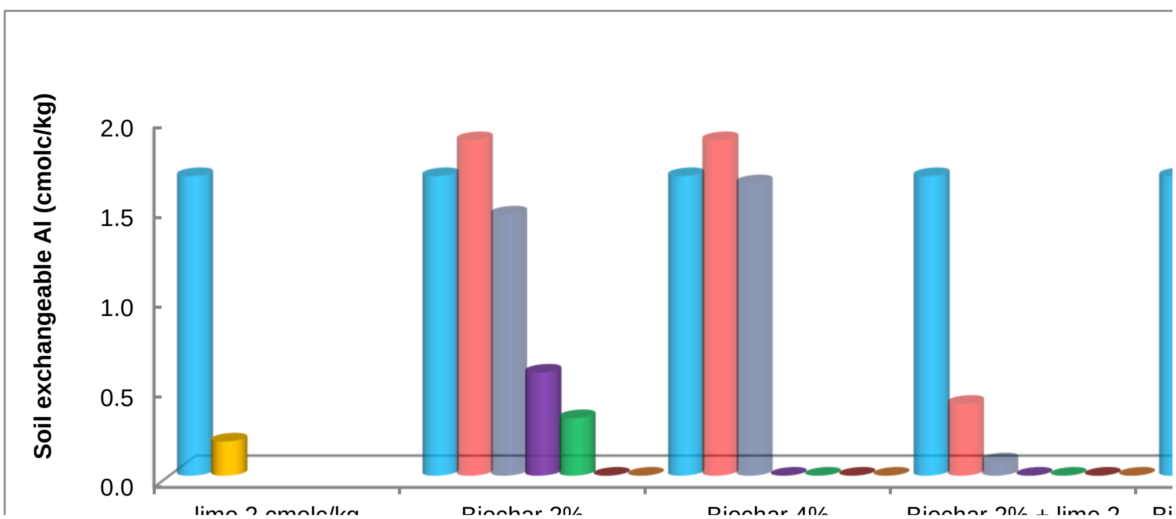
Figure 4.1. Soil pH as affected by biochars and lime amendments



4.4.2.1.2. Soil Exchangeble Al

Type and rate of biochars affected soil exchangeable Al differently (Fig. 4.3). Soil exchangeable Al was decreased from 1.8 cmolc/kg to undetectable level by the addition of leucaena and lac tree biochars at 2%, and by Hilo mixed wood and she oak biochar at 4%. In contrast, mahogany and mountain gum biochars decreased soil exchangeable Al only when applied in combination with lime. The result is similar to that of Deenik *et al.* (2011) who reported that the kiawe charcoal was capable of increasing soil pH and reducing exchangeable Al in a Hawaiian Ultisol. Our finding is also consistent with those of Yuan and Xu (2011, 2012) in China, Singh *et al.* (2010) in Australia, and Yamato *et al.* (2006) in Indonesia.

Biochar $CaCO_3$ equivalent is responsible for the soil exchangeable Al reduction. Figure 4.4 illustrated that all of the soil exchangeable Al was neutralized by the biochars carbonates. More specifically, the application of 2% leucaena and lac tree biochars with high $CaCO_3$ equivalent (more than 15%), and 4% Hilo mixed wood and she oak biochars with 8% $CaCO_3$ equivalent, can decrease the soil exchangeable Al to undetectable level.



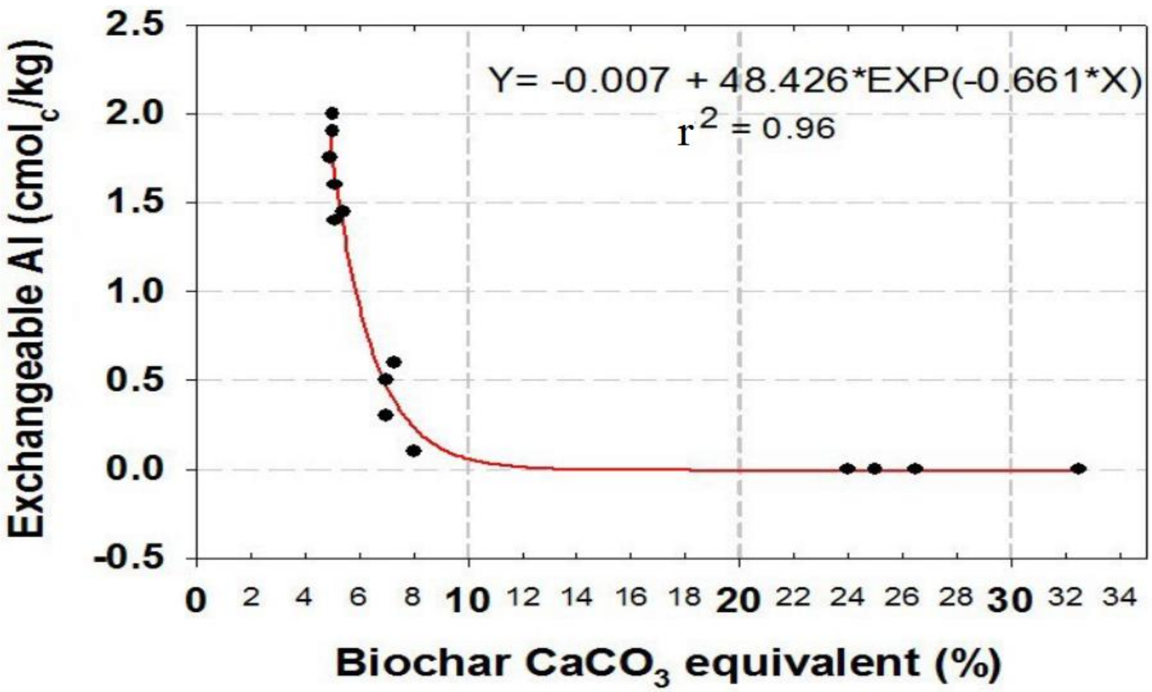


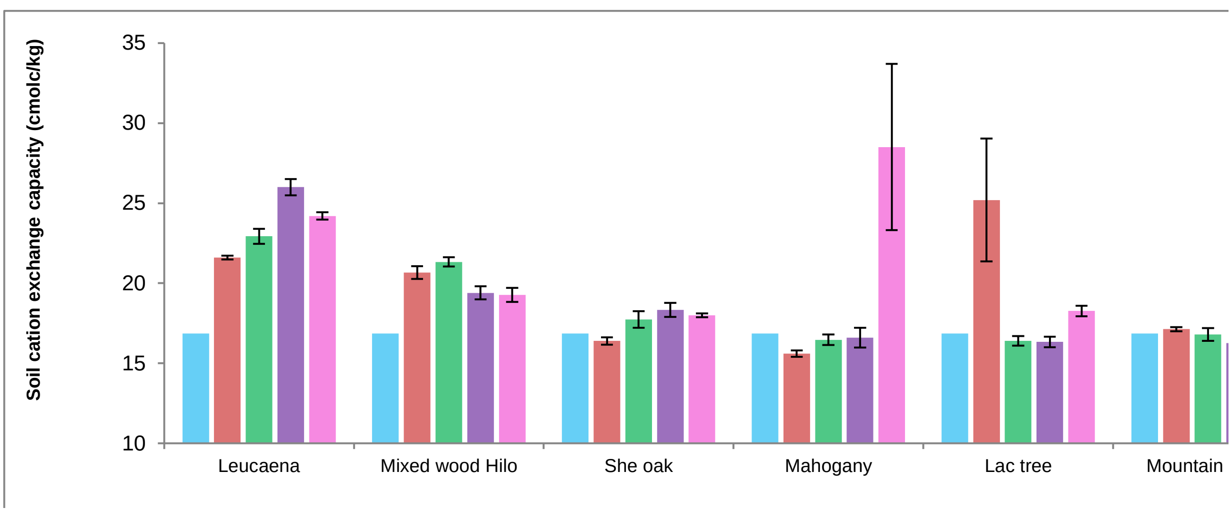
Figure 4.4. Correlation between biochars $CaCO_3$ equivalents and exchangeable Al in soil amended with 2% biochars

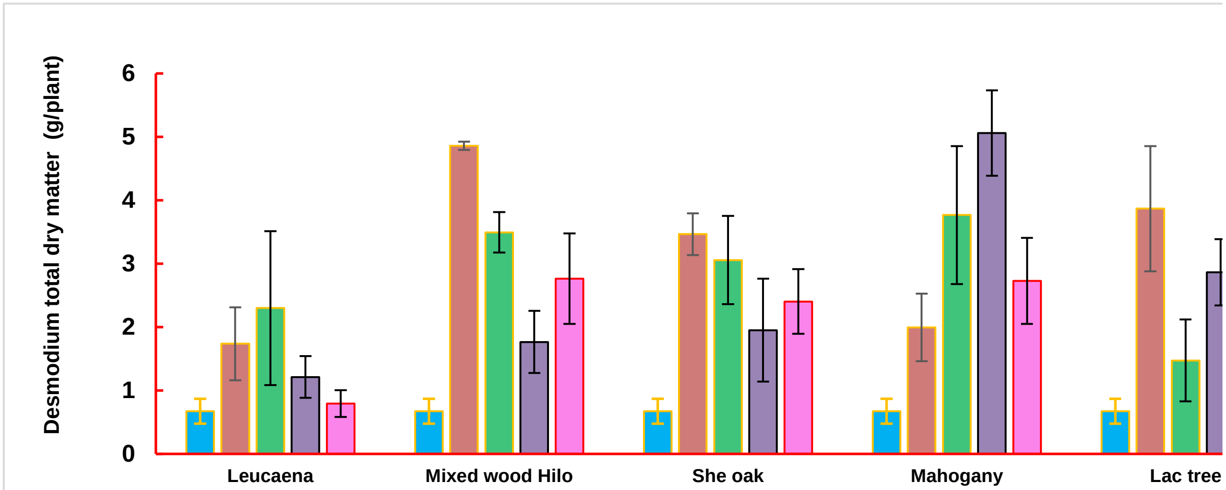
4.4.2.1.3. Soil CEC

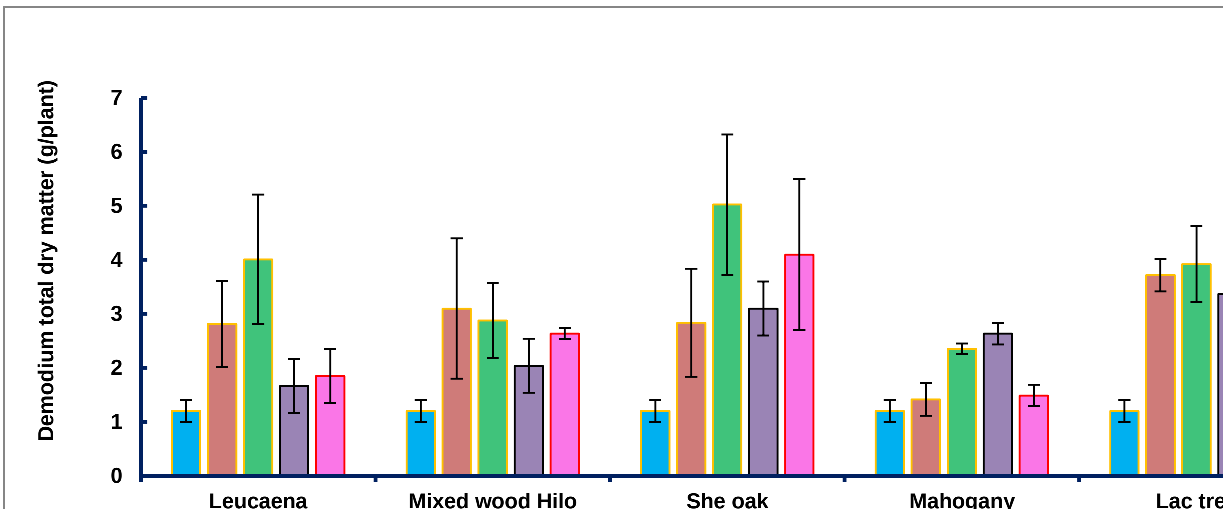
Incorporations of biochars into soil increased soil CEC to different degrees, depending on the type and rate of biochars (Fig. 4.5). Leucaena, Hilo mixed wood, and lac tree biochars increased soil CEC from 16.8 cmolc/kg to 21.6, 20.7 and 25.2 cmolc/kg, respectively when applied at 2%. At this rate and in combination with lime leucaena biochar increased soil CEC to 26.0 cmolc/kg. Increases in soil CEC could be attributed to the negative charge of surface functional groups, especially carboxylics (Boehm 1994, Glaser *et al.* 2001, Liang *et al.* 2006, Chan and Xu 2009, Yuan and Xu, 2011). Additions of she oak, mahogany or mountain gum biochars have no significant effect on soil CEC, athough they had their CEC and total surface functional groups higher than the other biochars (Table 4.1).

4.4.2.2. Effect of biochars on plant growth

Desmodium intortum cv Green leaf growth expressed as total dry weight increased with the addition of biochars to a Hawaiian acid soil (Figs. 4.6a and 4.6b). In the first growth *Desmodium* total dry matter upon addition of biochars alone at 2% and 4% increased 1.6-7.2 folds over the control. The best growth in the first planting was obtained from the application of Hilo mixed wood, lac tree and she oak at 2% and mahogany at 2% with lime. However, plant dry matters were lowered in the second planting particularly by the mahogany and mixed wood Hilo biochars. In the second planting, total dry matter obtained from the biochars addition increased 1.2-4.2 folds over the control, and the best growth was obtained from the application of leucaena, lac tree and she oak biochars at 4%.







4.4.2.3. Plant nutrients

Addition of biochars to a Hawaiian acid soil enhanced some plant nutrients, but decreased others (Table 4.5). For example, K was increased by all of the six added biochars, Ca was also increased by additions of leucaena, lac tree, mixed wood Hilo and she oak wood biochars alone, and also by mahogany and mountain gum when added with lime. Al, Mn and Fe were decreased by all biochars except mahogany and mountain gum biochars for Mn. These results could partially be explained by the $CaCO_3$ equivalent of the various biochars.

Tabel 4.5. Means of nutrients content in the *Desmodium intortum* shoot and root tissues (n=3)

Treatments	P		K		Na		Ca		Mg		Fe		Mn		Zn		Al	
	Shoot	Root	Shoot	Root	Shoot	Root	Shoot	Root	Shoot	Root	Shoot	Root	Shoot	Root	Shoot	Root	Shoot	Root
	%										mg/kg							
Leucaena wood 2%	0.19	0.22	2.46	2.53	0.13	0.36	1.70	0.33	0.31	0.54	212.9	5997.6	83.3	53.3	52.3	169.2	111.7	3973.1
Leucaena wood 4%	0.16	0.19	2.35	2.62	0.14	0.36	1.93	0.38	0.30	0.64	231.4	9416.3	49.5	57.0	23.9	121.0	118.5	6515.4
Leucaena wood 2% + lime 2 cmolc/kg	0.20	0.20	2.47	2.41	0.14	0.33	1.98	0.36	0.33	0.54	201.3	7554.2	67.1	34.6	34.7	131.7	123.0	5069.3
Leucaena wood 4% + lime 2 cmolc/kg	0.19	0.18	2.50	3.05	0.12	0.34	2.09	0.46	0.37	0.67	395.2	6748.1	59.1	32.1	25.1	105.4	405.7	4573.7
Mixed wood Hilo 2%	0.18	0.19	2.24	2.59	0.15	0.43	1.18	0.29	0.42	0.51	351.0	9397.9	170.9	96.4	49.3	128.4	224.4	7047.9
Mixed wood Hilo 4%	0.24	0.21	2.46	2.28	0.14	0.42	1.61	0.34	0.45	0.59	361.3	11446.6	174.3	107.8	42.8	107.8	189.9	7883.0
Mixed wood Hilo 2% + lime 2 cmolc/kg	0.20	0.17	2.47	1.96	0.15	0.46	1.55	0.71	0.41	0.44	289.2	11458.5	132.0	56.9	43.9	113.8	171.3	9186.7
Mixed wood Hilo 4% + lime 2 cmolc/kg	0.24	0.17	2.63	1.60	0.15	0.33	1.80	0.35	0.39	0.37	253.8	9179.6	163.1	52.2	90.4	92.4	223.5	6142.7
She oak wood 2%	0.21	0.18	2.58	2.52	0.17	0.39	0.98	0.32	0.40	0.38	190.7	10929.5	131.4	61.8	52.6	125.9	157.0	7898.4
She oak wood 4%	0.22	0.21	2.63	2.10	0.15	0.35	1.33	0.31	0.39	0.40	393.9	8339.3	134.6	58.8	57.3	90.5	242.4	5958.7
She oak wood 2% + lime 2 cmolc/kg	0.20	0.18	2.63	1.48	0.16	0.27	1.73	0.35	0.40	0.47	343.6	13261.4	137.9	60.0	59.2	115.1	237.5	9905.3
She oak wood 4% + lime 2 cmolc/kg	0.23	0.21	2.60	1.95	0.14	0.32	1.75	0.34	0.36	0.47	189.1	12219.4	128.9	62.2	52.1	157.5	74.6	8551.2
Mahogany wood 2%	0.18	0.21	2.61	2.35	0.15	0.44	0.77	0.27	0.54	0.43	301.4	6947.3	173.6	116.2	44.0	89.0	221.0	5061.4
Mahogany wood 4%	0.20	0.19	2.51	2.24	0.12	0.42	0.85	0.25	0.49	0.45	225.2	5712.4	215.6	135.6	86.9	101.5	150.8	4213.6
Mahogany wood 2% + lime 2 cmolc/kg	0.19	0.18	2.31	2.26	0.15	0.32	1.28	0.27	0.42	0.56	184.3	7560.6	170.9	101.6	110.0	59.7	101.4	5368.5
Mahogany wood 4% + lime 2 cmolc/kg	0.22	0.20	2.51	2.38	0.14	0.40	1.48	0.28	0.45	0.51	289.3	6480.4	173.7	69.5	59.4	134.7	186.6	4608.8
Lac tree wood 2%	0.18	0.14	2.51	1.96	0.12	0.28	1.75	0.28	0.32	0.45	154.0	7345.5	110.9	46.4	47.0	61.7	68.7	4875.5
Lac tree wood 4%	0.18	0.15	2.48	2.48	0.15	0.38	1.63	0.36	0.37	0.48	348.0	8890.1	55.7	25.8	39.5	142.7	196.2	6163.0
Lac tree wood 2% + lime 2 cmolc/kg	0.20	0.21	2.46	2.37	0.12	0.32	1.91	0.38	0.35	0.56	192.4	8226.1	96.0	47.4	50.2	134.9	250.8	5067.7
Lac tree wood 4% + lime 2 cmolc/kg	0.20	0.16	2.35	2.36	0.14	0.34	1.97	0.37	0.34	0.59	201.4	6420.9	58.1	25.3	37.6	92.3	144.1	4265.3
Mountai gum wood 2%	0.23	0.17	2.57	1.90	0.14	0.44	0.84	0.23	0.65	0.33	194.9	6642.8	212.5	113.8	66.8	112.2	120.7	4908.3
Mountai gum wood 4%	0.23	0.23	2.65	1.99	0.14	0.44	0.82	0.25	0.64	0.47	237.2	7433.4	156.6	127.4	43.8	80.6	138.8	5493.2
Mountain gum wood 2% + lime 2 cmolc/kg	0.20	0.17	2.47	2.61	0.12	0.38	1.27	0.32	0.43	0.41	427.2	5940.3	187.8	87.1	64.9	99.1	301.7	4234.8
Mountain gum wood 4% + lime 2 cmolc/kg	0.19	0.20	2.12	1.96	0.12	0.36	0.98	0.29	0.42	0.36	231.9	5583.6	162.7	92.7	51.5	135.1	161.5	4129.3
Lime 2 cmolc/kg	0.19	0.15	2.57	2.06	0.17	0.31	0.93	0.25	0.58	0.38	256.4	5714.1	164.9	97.3	52.5	72.0	171.9	4207.0
Control (No biochar, No Lime)	0.21	0.17	2.31	2.62	0.17	0.36	1.20	0.27	0.48	0.69	478.3	6400.9	155.4	67.7	41.3	65.4	320.4	4335.1

4.4.3. Field trials

4.4.3.1. Selected properties of biochars

Selected properties of the lac tree wood and rice husk biochars are listed in Table 4.3. Ash content, calcium carbonate equivalent, pH, EC, and volatile matter content of lac tree wood biochar were higher than those of the rice husk biochar. Such differences were attributed to the higher pyrolysis temperature and the lac tree feedstock (Zhao *et al.* 2013). The CEC of rice husk was higher than lac tree wood biochar because it produced at lower temperature (300^{o}C) than lac tree biochar that produced at 550^{o}C. This could be related to the greater presence of –OH functional groups at 300^{o}C. It is known that the highest treatment temperature (HTT) above 500^{o}C resulted in a loss of carboxylic groups (Harvey *et al.* 2012). This finding agrees with those of Kloss *et al.* 2011 and Budai *et al.* 2014 who reported that CEC decreases with the increasing of pyrolysis temperature and that the biochar CEC was peaked at lower temperature. Also, wood biochar is low in CEC because defragmentation of lignocellulose (cleavage of OH---O-type) H-bonding of wood biochar and their subsequent oxidation to carboxyl is low (Harvey *et al.* 2012).

Plant nutrients such as N, P, K, Mn and Zn were higher in ricehusk biochar than lac tree wood biochar, while Ca, Mg and Fe were conversely higher in lac tree wood biochar. The Si content in rice husk was also higher than lac tree biochar. These differences could be attributed to the feedstock and pyrolysis temperature that used to produce the biochars. Produced at 600^{o}C, lac tree biochar contained low N, because of the volatilization of N at high temperature (Gaskin *et al.* 2008, Wu *et al.* 2012, Rajkovich 2012). However, it contained higher of Ca and Mg because such nutrients vaporized only at > 1000^{o}C (Knicker 2007).

4.4.3.2. Effect of biochar on selected soil properties

4.4.3.2.1. Soil pH

Soil pH increased differently by treatments and at experimental sites (Table 4.6). About 0.5-1.1 units and 0.3-2.0 units of soil pH were raised at Jasinga and Guradog, respectively. Despite lime and compost, the rice husk biochar did not raise the soil pH by as much as the lac tree wood biochar. At Guradog site, soil pH was raised from 4.0 to 5.1 and 6.0 by addition of lac tree wood biochar at 8% alone and in combination with lime at 8 cmolc/kg and compost at 0.2 %, respectively. While rice husk biochar at the same rate only increased the soil pH from 4.0 to 4.7 and 5.1, respectively. At Jasinga site, soil pH was only increased moderately from 3.9 to 4.7 and 5.0 by addition of lac tree wood biochar at 8% alone and in combination with lime 8 cmolc/kg and compost 0.2 %, respectively.

Table 4.6. Effects of biochars, lime and compost on soil pH

Treatments	Soil pH	
	Guradog	Jasinga
Control	4.0 g	3.9 e
Lime 8	4.6 ef	4.5 bc
Lime 8 + compost 0.2	4.7 def	4.6 bc
Rice husk 4 + lime 4	4.3 fg	4.4d
Rice husk 4 + lime 4 + compost 0.1	4.4 ef	4.4d
Rice husk 8	4.7 def	4.4 d
Rice husk 8 + lime 8	5.0 cd	4.7 b
Rice husk 8 + lime 8 + compost 0.2	5.1 c	4.7 b
Lac tree wood 4 + lime 4	4.8 cde	4.7 b
Lac tree wod 4 + lime 4 + compost 0.1	5.0 cd	4.7 b
Lac tree wood 8	5.1 c	4.7 b
Lac tree wood 8 + lime 8	5.6 b	5.0 a
Lac tree wood 8 + lime 8 + compost 0.2	6.0 a	5.0 a

Units for biochars, lime, and compost are %, cmolc/kg and %, respectively. Means within a column followed by the same letter(s) were not significantly different by Tukey's test at $\alpha = 5\%$.

Rice husk biochar with the same rate only increased soil pH from 4.0 to 4.4 and 4.7, respectively. Those differences could be attributed to the high exchangeable Al of the Jasinga soil and the low ash content of the rice husk biochar. Soil pH at Guradog site, therefore, increased more than in the Jasinga site, and lac tree wood biochar raised the soil pH more than rice husk biochar.

4.4.3.2.2. Exchangeable aluminum in soil

Addition of lac tree wood and rice husk biochars significantly reduced soil exchangeable Al as compared to the control at both experimental sites (Figs. 4.7a and 4.7b). With 13.7% calcium carbonate equivalent, lac tree wood biochar markedly reduced soil exchangeable Al more than rice husk biochar (1.2% $CaCO_3$ equivalent), although their effects were not significantly different at Guradog site ($P>0.05$). For example, additions of rice husk and lac tree wood biochars at 8% alone decreased exchangeable Al of Guradog soil from 8 cmolc/kg to 2 and 1 cmolc/kg, respectively, and further decreased to 1 and undetected level, respectively, when applied in combination with lime at 8 cmolc/kg or with lime at 8 cmolc/kg and compost at 0.2 %. It was clearly that about 6-7 cmolc/kg exchangeable Al was reduced by the addition of 8% lac tree wood or rice husk biochar. This could be attributed to the biochars $CaCO_3$ equivalent. This finding was in line with the works of van Zwieten *et al.* (2010) on Australian Ferrosol, Deenik *et al.* (2011) on Hawaiian Ultisol, Chintala *et al.* (2013) on acidic Entisol (Grummit soil series), Yuan and Zu (2012) on Ultisols and Oxisols in China.

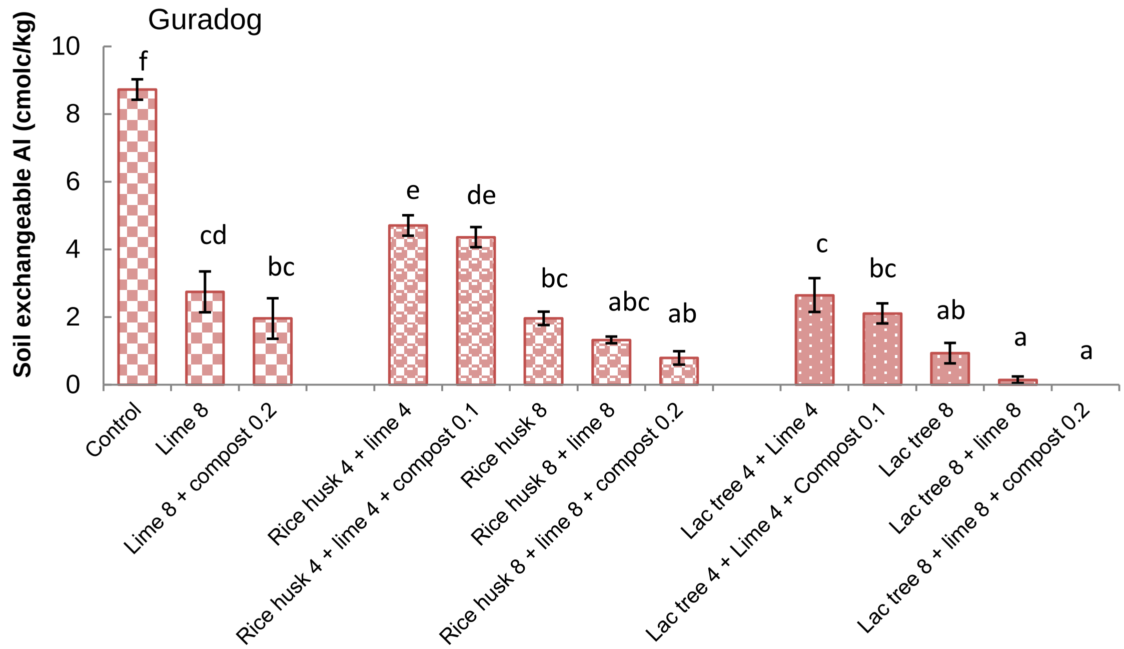


Figure 4.7a. Soil exchangeable Al as affected by biochars, lime and compost amendments

Units for biochars, lime and compost were %, cmolc/kg, and %, respectively; means followed by the same letter(s) were not significantly different by Tukey test at α=5%

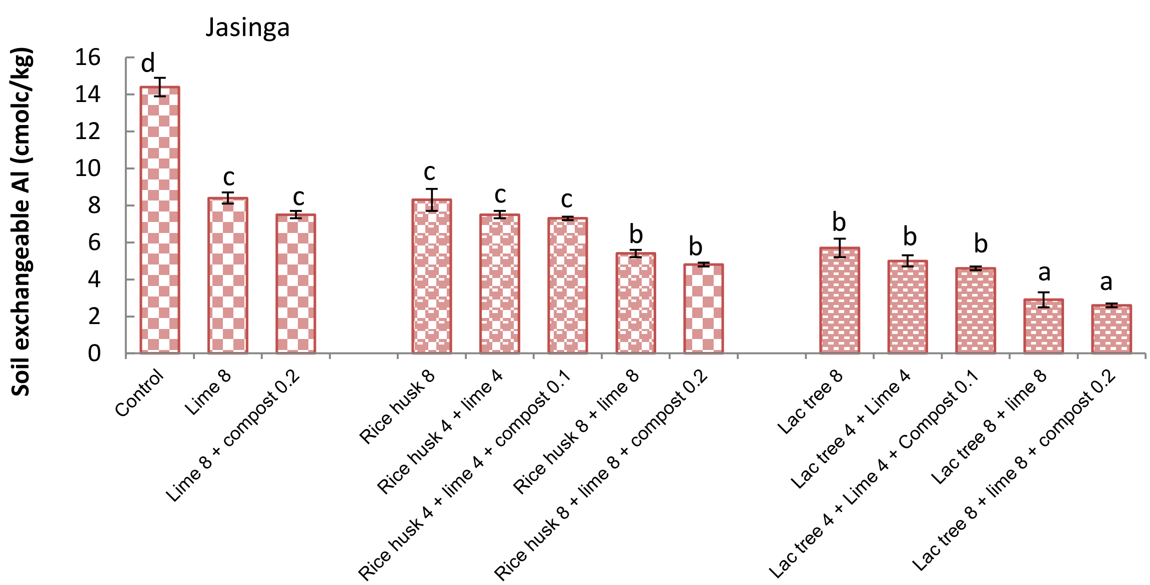


Figure 4.7b. Soil exchangeable Al as affected by biochars, lime and compost amendments

Units for biochars, lime and compost were %, cmolc/kg and %, respectively; means followed by the same letter were not significantly different by Tukey test at α = 5%.

4.4.3.2.3. Soil CEC

Soil CEC was slightly increased upon the addition of lac tree wood and rice husk biochars either alone or in combination with lime or in combination with lime and compost (Table 4.7). The highest CEC was obtained from the addition of ricehusk biochar at 8% in combination with lime at 8 cmolc/kg and compost at 0.2% although there was no significant different with lac tree wood biochar at the same rate. This could be attributed to the higher CEC of ricehusk biochar that was produced from the lower pyrolysis temperature than lac tree wood, and to a lesser extent of compost. Low temperature biochar could be more easily oxidized and compost addition could supply organic matters into the soil, then both contributed to the development of surface oxidized functional groups, the source of negative charge.

Table 4.7. Means and standard errors of soil CEC as affected by biochars, lime and compost additions (n=4)

Treatments	Soil CEC (cmolc/kg)	
	Guradog	Jasinga
Control	36.34±0.34 d	33.19±0.56 f
Lime 8	37.35±0.45 cd	36.68±0.23 d
Lime 8 + compost 0.2	37.80±0.23 bcd	37.46±0.34 bcd
Lac tree 8	37.46±0.34 cd	34.43±0.45 ef
Lac tree 8 + lime 8	39.04±0.34 abc	38.81±0.34 abc
Lac tree 8 + lime 8 + compost 0.2	39.83±0.23 ab	39.04±0.56 ab
Lac tree 4 + lime 4 + compost 0.1	37.91±0.34 bcd	37.35±0.45 bcd
Lac tree 4 + lime 4	37.46±0.56 cd	36.79±0.34 cd
Rice husk 8	38.36±0.11 abcd	36.34±0.11 de
Rice husk 8 + lime 8	39.15±0.45 abc	38.93±0.23 ab
Rice husk 8 + lime 8 + compost 0.2	40.28±0.23 a	39.83±0.45 a
Rice husk 4 + lime 4 + compost 0.1	38.59±0.11 abc	37.69±0.34 bcd
Rice husk 4 + lime 4	37.69±0.79 bcd	37.35±0.23 bcd

Units for biochars, lime, and compost are %, cmolc/kg and %, respectively

4.4.3.3. Plant dry weights

Soybean shoot and root dry matters were significantly increased upon addition of lac tree wood and rice husk biochars for both first and second plantings at both experimental sites (Figs. 4.8a, 4.8b, 4.8c and 4.8d, Table 4.8). Relative to the control, addition of lac tree wood and rice husk biochars at 8% alone to Guradog soil, increased the first planting soybean shoot and root dry matters 206% and 167%, and 169% and 157%, respectively. Soybean shoot and root dry matters were further increased to 248% and 208%, and 220% and 203% over the control by the lac tree wood and rice husk biochars at 8%, respectively, when they were applied in combination with lime at 8 cmolc/kg and compost at 0.2 %. The increase of soybean growth in acid soil amended with biochar, lime and compost could be attributed to the decrease of soil exchangeable Al (Figs. 4.9a and 4.9b) and plant Mn (Fig. 4.10a), nutrient enhancement such as K (Fig. 4.10b) and other indirect effects such as increase in soil pH (Table 4.6), CEC (Table 4.7), and unmeasured parameter such as beneficial microbial activity that provided favorable conditions for better growth of soybean. In the second planting, the soybean shoot dry weights were approximately 20% higher than in the first planting, but there was no increase in the root dry weights. The increased soybean growth in the second planting suggested the long-term beneficial effects of biochars, such as nutrient retention and water retention, inhabitant of soil microorganisms that were not measured in this experiment.

The best soybean growth expressed in shoot dry matters were 593.6 and 726.2 kg/ha for the first and second plantings, respectively, were obtained from the application of lac tree wood biochar at 8% in combination with lime at 8 cmolc/kg and compost 0.2 %. However, the effect of lac tree wood biochar was not significantly different from the effect of rice husk biochar on soybean shoot dry matter, both in the first and second plantings (Figs. 4.8a and 4.8b).

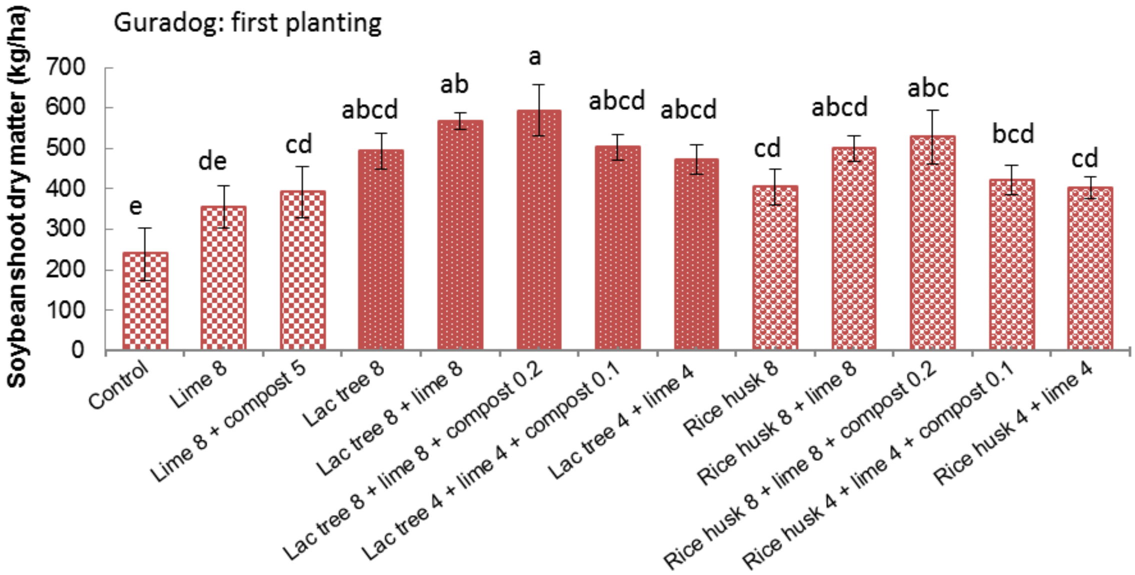


Figure 4.8a. Soybean shoot dry matters as affected by biochars, lime and compost amendments

Units for biochars, lime and compost were %, cmolc/kg, and t/ha, respectively; means followed by the same letter were not significantly different (DMRT test, α= 5%).

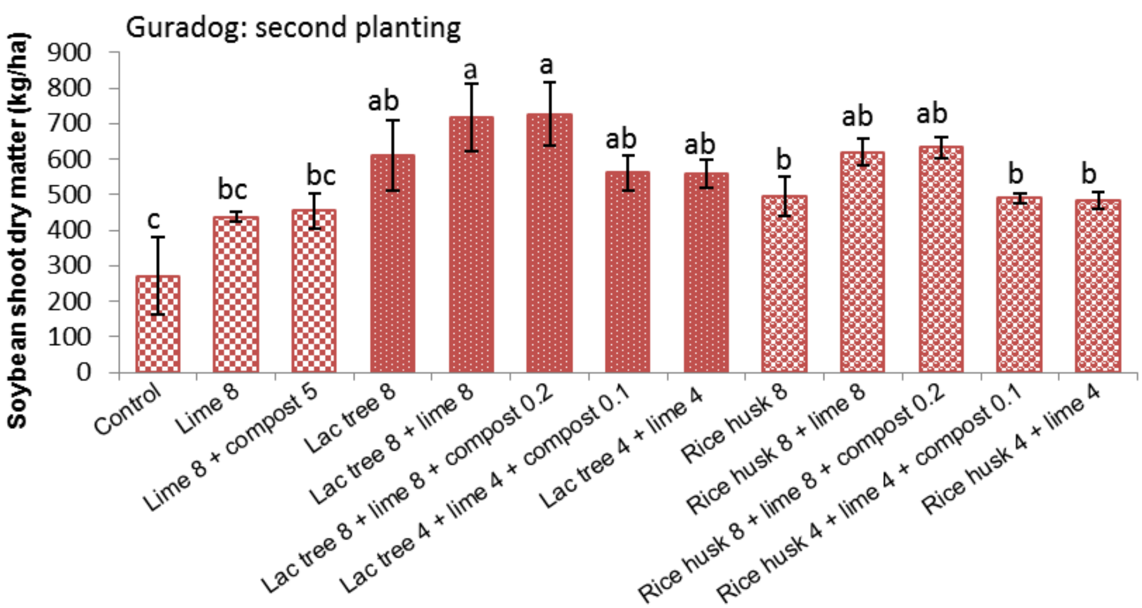


Figure 4.8b. Soybean shoot dry matter as affected by biochars, lime and compost amendments

Units for biochars, lime and compost were %, cmolc/kg, and t/ha, respectively; means followed by the same letter were not significantly different (DMRT test, α = 5%).

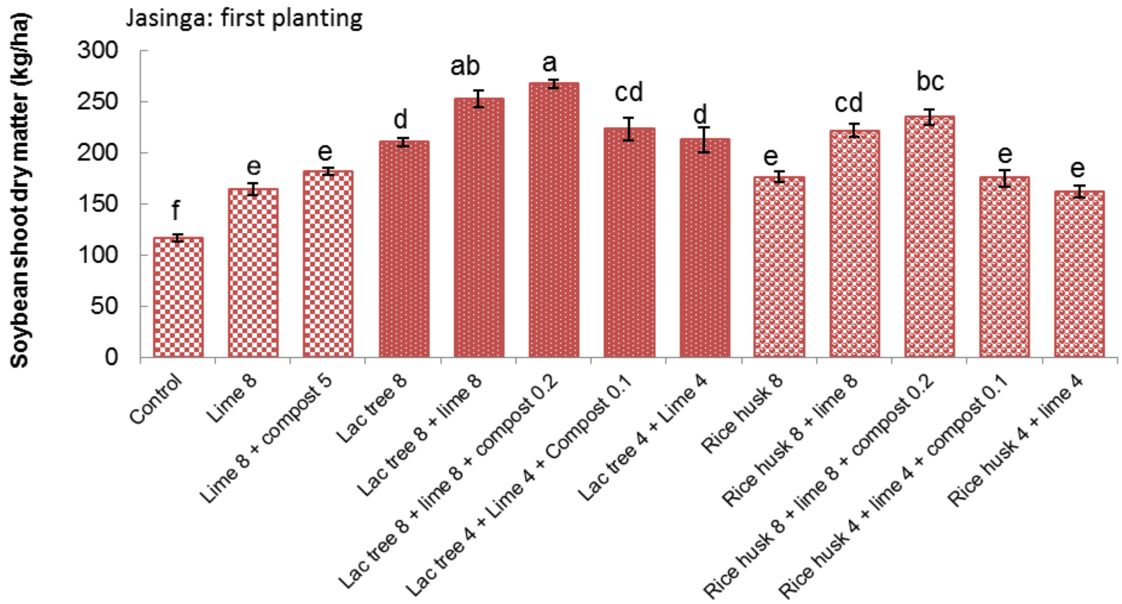


Figure 4.8c. Soybean shoot dry matter as affected by biochars, lime and compost amendments

Units for biochars, lime and compost were %, cmolc/kg, and t/ha, respectively; means followed by the same letter were not significantly different (DMRT test, α= 5%)

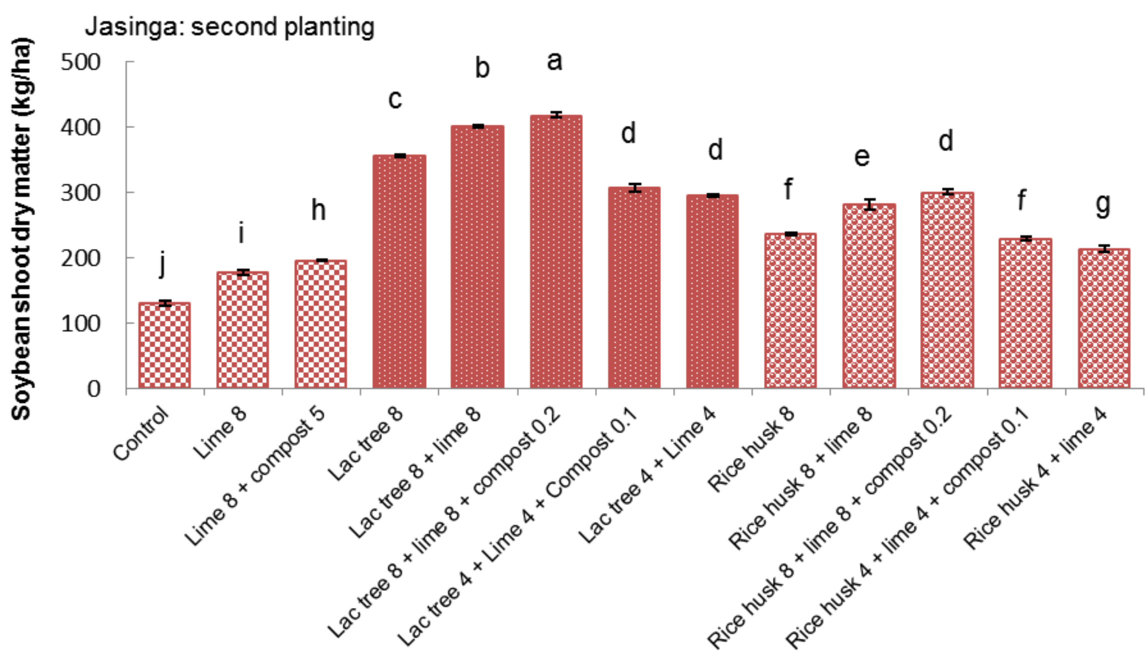


Figure 4.8d. Soybean shoot dry matter as affected by biochars, lime and compost amendments

Units for biochars, lime and compost were %, cmolc/kg, and t/ha, respectively; means followed by the same letter were not significantly different (DMRT test, α=5%)

Also, the soybean shoot dry matter affected by biochars at 8% in combination with lime at 8 cmolc/kg and compost at 0.2 % was not significantly different with the effect of biochars at 8% added alone. It means that either lac tree wood or rice husk biochar at 8% can be applied alone or in combination with lime 8 cmolc/kg and compost 0.2 % for soybean growth at Guradog soil depending on the availability of biochars and the local benefit-cost analysis (Tables 10). For example, soybean growth in biochar-amended soil in Guradog was higher upon application of the lac tree wood biochar alone or in combination with lime and compost compared with the rice husk biochar. However, lac tree wood feedstock or its biochar was not locally available and the price was almost twice that of the rice husk biochar. As it's shown in table 10, using rice husk biochar was locally available and cheaper; thus being more profitable than the lac tree wood biochar.

Tabel 4.8. Means and standard errors of soybean root dry matters as affected by biochar, lime and compost amendments (n=4)

Treatments	Guradog		Jasinga	
	First planting	Second planting	First planting	Second planting
	kg/ha			
Control	55.2±10.8 b	59.9±16.8 b	38.5±0.9 g	43.6±1.3 f
Lime 8	89.3±9.7 ab	91.1±9.8 ab	48.7±0.8 fg	56.5±2.1 e
Lime 8 + compost 0.2	93.5±14.4 ab	95.8±13.8 ab	51.4±2.3 ef	58.7±1.0 e
Rice husk 4 + lime 4	92.2±7.1 ab	101.9±6.5 ab	60.2±2.2 cdef	72.8±2.5 d
Rice husk 4 + lime 4 + compost 0.1	101.8±10.9 ab	97.3±5.9 ab	61.1±3.7 cde	85.9±2.8 c
Rice husk 8	86.6±8.7 ab	88.9±8.5 ab	52.8±3.4 def	57.7±1.1 e
Rice husk 8 + lime 8	117.4±3.6 a	102.9±2.5 ab	91.7±4.0 a	101.1±2.9 b
Rice husk 8 + lime 8 + compost 0.2	124.0±11.9 a	114.7±4.7 a	97.4±0.7 a	112.9±1.0 a
Lac tree wood 4 + lime 4	100.4±7.4 ab	106.4±6.4 ab	63.9±0.9 cd	69.1±1.5 d
Lac tree wod 4 + lime 4 + compost 0.1	105.7±6.5 ab	102.3±7.1 ab	64.9±2.2 c	90.0±1.6 c
Lac tree wood 8	92.2±14.4 ab	95.8±12.7 ab	53.5±1.8 cdef	59.2±1.1 e
Lac tree wood 8 + lime 8	103.4±4.9 ab	110.2±6.5 a	76.9±1.3 b	88.2±1.2 c
Lac tree wood 8 + lime 8 + compost 0.2	114.9±14.5 a	116.4±14.4 a	79.6±2.3 b	110.7±2.4 a

Units for biochars, lime, and compost were %, cmolc/kg and %, respectively. Means within column followed by the same letter were not significantly different (Tukey's test, α = 5%).

Soybean growth expressed as shoot or root dry matter at the Jasinga site that received the same rate of biochars either alone or in combination with lime and compost, also increased; but it was about 50% lower than that obtained from the Guradog site (Figs. 4.8c and 4.8d, Table 4.8). This was probably because of the higher exchangeable Al in the Jasinga soil. It seemed that the liming effect of applied biochars at 8% alone or in combination with lime at 8 cmolc/kg and compost 0.2 % was not sufficient to correct soil acidity at the Jasinga site for soybean growth (Figs. 4.7b and 4.9b). Specifically, soybean shoot and root dry matters increased from 116 and 38 kg/ha (control) to 176 and 53 kg/ha, and to 210 and 54 kg/ha upon application of rice husk and lac tree wood biochars alone at 8%, respectively. Soybean shoot and root dry matters were then further increased to 234 and 97 kg/ha, and to 267 and 80 kg/ha by the rice husk and lac tree wood biochars at 8%, respectively, when applied in combination with lime at 8 cmolc/kg and compost at 0.2 %. The best soybean growths expressed in shoot dry weights for the first and second plantings were obtained from the plot received the lac tree wood biochar at 8% in combination with lime 8cmolc/kg and compost 0.2 %. This could be explained by the higher liming effect of the lac tree wood biochar. Contrast to the shoot, the best root dry matter in the first planting was obtained from the application of the rice husk biochar at 8% in combination with lime at 8 cmolc/kg and compost at 0.2 %, although they were not significantly different in the second planting. This could be related to better root interception into the rice husk biochar pores which were volumetrically higher than the lac tree biochar (bulk density of the rice husk biochar was lower than that of the lac tree wood biochar). Both soil properties and soybean growth on the Jasinga soil were not significantly improved upon applications of lac tree wood and rice husk biochars at 8 % either alone or in combination with lime at 8 cmolc/kg and compost 0.2%. Thus, more investigations will be required before recommending either lac tree wood or rice husk biochar for the Jasinga site.

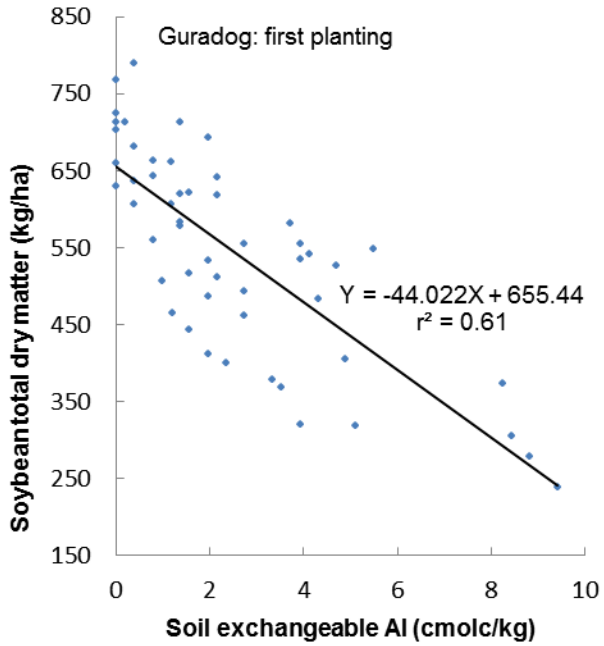


Figure 4.9a. Relationship between total soybean dry matter and soil exchangeable Al

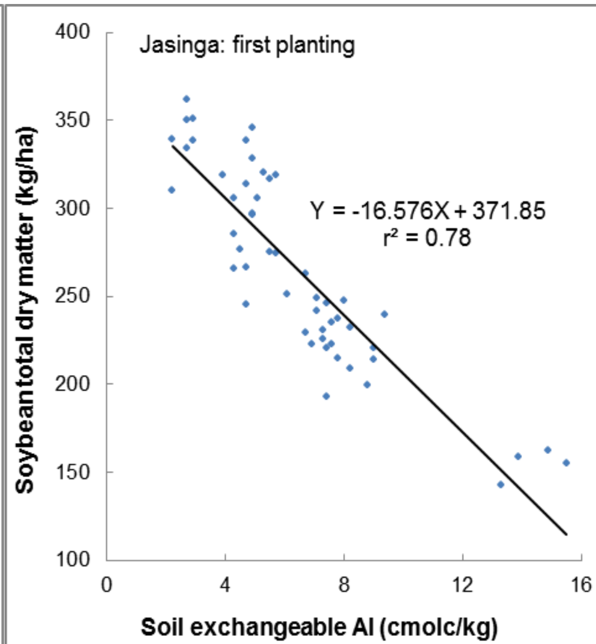


Figure 4.9b. Relationship between soybean total dry matter and soil exchangeable Al

4.4.3.4. Plant nutrients

Addition of lac tree wood and rice husk biochars increased some nutrients, but decreased other nutrients in the soybean tissue (Table 4.9). For example, K was clearly increased by addition of the biochars since K is the most available nutrient in the biochars. In contrast, Mn was markedly decreased by adding biochars compared with the control. Mechanism behind the suppression of Mn concentration in soybean tissue of biochar-treated soil could be the precipitations of highly soluble Mn by increasing soil pH upon addition of biochars or Mn compete with Ca uptake or complexing Mn ion by biochar's oxygenic functional groups (Hue *et* *al.* 2001). Other nutrients such as Ca, P and Mg to some extent were also increased, while Fe and Al were decreased by the addition of the biochars.

Concentration of N in soybean tissue was higher upon application of rice husk biochar compared with the lac tree wood biochar. This could be due to the higher N content of the rice husk biochar. The same explanation could be attributed to the higher concentration of Ca and Mg in soybean grown in soils amended with the lac tree biochar. Higher N, P, K, Ca, Mg concentrations were also found in soybean grown in the soil amended with biochar incorporation with compost. It appeared that compost additions enhanced tissue nutrients in the plant grown in highly weathered tropical acid soils.

The concentration of nutrients in soybean shoot revealed that most nutrients were sufficient for good growth of soybean in general. Nitrogen (2.99-3.65%), although grouped as low for soybean in general, but Jumro 2011 and Sudarsono *et al.* 2013 reported that the best growth and yield of soybean c.v. Anjasmoro in Indonesia was achieved with the nitrogen concentration of 3.3 % and 3.7%, respectively. The concentrations of P, K, Ca and Mg were at levels of sufficient to high, while Fe and Mn concentrations were high. Aluminum concentration in soybean shoot was very high, but it very loosely correlated with the soybean growth in Guradog soil. The similar result was reported by Jackson (1967) who concluded that correlations between Al content in the foliage of crop plants and Al toxicity were more of the exception than the rule. But, the toxic effects of Al may result from excess Al in the growth medium (Figs. 4.9a and 4.9b).

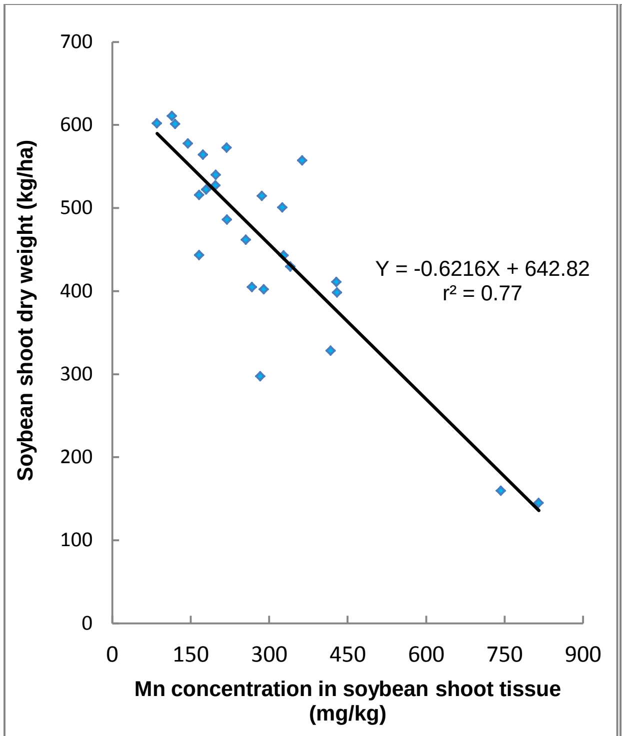


Figure 4.10a. Correlation between Mn concentration and dry weight of soybean shoot

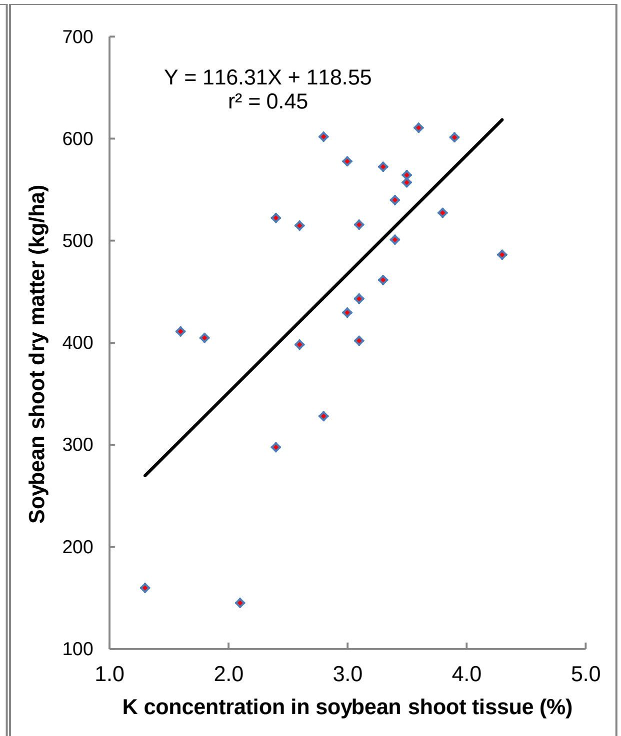


Figure 4.10b. Correlation between K concentration and dry weight of soybean shoot

Table 4.9. Means and standard errors of plant nutrients in soybean shoot tissue first planting Guradog soil (n=2)

Treatments	N	P	K	Ca	Mg	Fe	Mn	Al
	%					mg/kg		
Control	3.41±0.10	0.34±0.05	1.71±0.38	1.25±0.01	0.57±0.00	571±81	779±36	1064±98
Lime 8	3.27±0.01	0.30±0.02	2.12±0.29	1.94±0.08	0.58±0.00	632±77	275±8	1082±186
Lime 8 + compost 0.2	3.03±0.32	0.41±0.06	2.10±0.54	2.29±0.23	0.73±0.04	457±110	429±1	796±184
Rice husk 4 + lime 4	3.01±0.21	0.32±0.03	2.71±0.30	1.58±0.01	0.44±0.06	509±51	260±81	812±87
Rice husk 4 + lime 4 + compost 0.1	3.41±0.45	0.40±0.02	3.13±0.01	1.71±0.19	0.54±0.01	455±9	309±19	749±33
Rice husk 8	3.58±0.27	0.36±0.03	2.71±0.14	1.19±0.03	0.45±0.02	381±87	352±66	590±214
Rice husk 8 + lime 8	3.09±0.08	0.42±0.00	3.49±0.04	1.98±0.08	0.58±0.01	832±265	344±19	969±622
Rice husk 8 + lime 8 + compost 0.2	3.26±0.27	0.41±0.01	3.63±0.19	1.54±0.17	0.47±0.02	659±73	198±0.3	1249±98
Lac tree wood 4 + lime 4	2.99±0.06	0.34±0.01	3.08±0.02	1.57±0.11	0.46±0.00	682±161	166±0.3	1119±295
Lac tree wood 4 + lime 4 + compost 0.1	3.42±0.03	0.39±0.01	3.30±0.02	1.98±0.01	0.56±0.04	827±90	237±19	1400±161
Lac tree wood 8	3.30±0.35	0.37±0.07	3.67±0.64	1.62±0.18	0.50±0.07	426±50	182±37	665±58
Lac tree wood 8 + lime 8	3.51±0.28	0.34±0.06	3.12±0.33	1.68±0.24	0.43±0.10	455±46	130±44	701±106
Lac tree wood 8 + lime 8 + compost 0.2	3.65±0.05	0.39±0.02	3.74±0.14	1.78±0.08	0.50±0.02	538±84	117±3	848±124

4.4.3.5. Net benefit analysis

Net present value (NPV) of lac tree and rice husk amendment options analyzed for a 5 year period were listed in table 4. 10. The NPV values were USD 2,924.07 and USD 3,771.30 for lac tree and rice husk, respectively. The NPV values of 5 year period of soybean production showed that rice husk biochar application was profitable than lac tree biochar.

Table 4.10. Net prevent value for soybean production in Guradog Ultisol treated with lac tree and rice husk biochars

Year	Description	Lac tree 8	Rice husk 8
1	Total Cost	10,335.00	6,520.00
	Total Revenue	2,476.78	2,020.20
	Total Benefit	(7,579.98)	(4,274.10)
2	Total Cost	710.00	710.00
	Total Revenue	3,541.80	2,888.89
	Total Benefit	2,509.81	1,916.26
3	Total Cost	710.00	710.00
	Total Revenue	4,195.67	3,422.22
	Total Benefit	2,757.49	2,118.28
4	Total Cost	710.00	710.00
	Total Revenue	4,615.23	3,764.44
	Total Benefit	2,757.49	2,118.28
5	Total Cost	710.00	710.00
	Total Revenue	5,076.76	4,140.88
	Total Benefit	2,757.49	2,118.28
NPV		2,924.07	3,771.30

NPV: Net present value; Discount rate: 10%; exchange rate
US$ to rupiah: 10000 IDR = 1 USD; the land unit analysis is one hectare.
Lac tree wood and rice husk biochars prices were $0.05/kg and $0.03/kg, respectively; lime and compost prices were $0.02/kg and $0.05/kg, respectively.
Soybean grain price per kg was $0.74.

4.5. Discussion

4.5.1. Biochar beneficial effects

Two main beneficial effects of biochars to improve acid soil properties and enhanced soybean growth are liming effect and nutrient content. Biochar liming effect is attributed to the biochar ash content or inorganic phase for a short- term and its oxygenated functional groups for the long-term effects. The alkalinity of biochars that expressed in their pH was well correlated with the ash content (Fig. 3.1). Since the biochars produced at a relative high temperature, the mineral matters, basic cations in particular, have been transformed into their carbonates or oxides, and then it can be referred to as calcium carbonate equivalent. The liming value (expressed as the cmol(OH^-)/kg biochar) of measured $CaCO_3$ equivalent, therefore, could be proportional to the liming value or alkalinity that was produced from the total basic cations in the test biochars. For example, the measured $CaCO_3$ equivalent of lac tree wood biochar produced at 500-600^oC was 13.7%; the basic cations content were 0.33%, 3.13%, 0.13% and 0.12% for K, Ca, Mg and Na, respectively. With assumption that those cations were in their oxides form, then 0.33% K in the biochar could be equivalent to 0.0423 moles $CaCO_3$ or 0.42% $CaCO_3$ per kg biochar. With a similar calculation, 3.13% Ca, 0.13% Mg and 0.12% Na could be equivalent to 7.8%, 0.54% and 0.26% CaCO3 for Ca, Mg and Na, respectively. Then total $CaCO_3$ equivalent calculated from the basic cations was 8.65%, a quantity that was closed to the measured $CaCO_3$ equivalent. Thus, the $CaCO_3$ equivalent is well correlated with the total of bases cations content of biochars (Fig. 3.2).

Biochars have their surface functional groups (Table 3.5 and Fig 3.6) that will become organic anion when added to soil. Decarboxylation of organic anions and the negatively charged functional groups such as carboxylic and phenolic will consume proton then increase the soil pH (Wang *et al.* 2014). The surface oxygenated functional groups can also be complexed with aluminum in the soil solution and reduced its toxicity to plant growth. It can be seen that biochars' basic cations or $CaCO_3$ equivalent and functional groups are responsible for its liming value. With the high basic cations and $CaCO_3$ equivalent leucaena, lac tree, mixed wood Hilo, she oak derived wood biochars improved the productivity of a Hawaiian acid soil and subsequently enhanced *Desmodium intortum* growth more than the mahogany and mountain gum biochars. A similar reason could also apply to explain the superiority of lac tree wood over rice husk biochar in correcting soil acidity of two Indonesian soils.

Nutrient content and its effect on nutrient availability are other beneficial effects (beside the liming effect) of biochar uses to correct soil acidity. For example, the rice husk biochar produced at 300^oC contained more nitrogen than the lac tree wood biochar produced $500-600^oC$. The rice husk biochar with higher CEC is also expected to have a greater reactivity and contributed to the acid soil fertility more than the lac tree biochar when added to the soil. This finding is in line with Keiluweit *et al.* 2010 who found that some nutrients were volatilized at the high pyrolysis temperature, and (Steinbess *et al.* 2009) that the low temperature (HTT< 500^oC) biochar contains more nutrients, less-condensed aromatic C, and therefore, more reactive when added into the soils.

4.5.2. Effect of biochar on selected soil properties

Addition of 6 biochars to a Hawaiian acid soil and 2 biochars to two Indonesian acid soils varyingly increased the soil pH depending on the biochar ash or basic cation content and the soil acidity level. The mechanism behind the increasing soil pH could be the release of OH^- ion from the dissolution of carbonate or oxide compounds contained in the biochars, and then the neutralization of H^+ in the soil solution by the OH^- released from biochar would increase the soil pH. This mechanism could explain the closed correlation (R^2=0.87) between the increase in soil pH and the basic cation content of 6 biochars used to correct the acidity of a Hawaiian acid soil (Fig. 4.2). Specifically, with their highest $CaCO_3$ equivalent or basic cations content, leucaena and lac tree biochars increased the soil pH the most, followed by mixed wood Hilo and she oak wood biochars only moderately, and mahogany and mountain gum wood biochars the least. Similar reasons could also apply to the lac tree wood biochar that increased pH of the Indonesian acid soils more than the rice husk biochar. This result was in line with Yuan and Xu 2010 and Yuan *et al.* 2011 findings, who found that addition of crop residue biochars with high alkalinity or carbonates content increased acid soil pH more than the lower carbonates content. The magnitude of the pH increase was also depending on the soil acidity level.

Soil exchangeable Al was reduced differently by additions of biochars to Hawaiian and Indonesian acid soils. Biochar $CaCO_3$ equivalent was responsible for the decrease of soil exchangeable Al (Figure 4.4). The main mechanism behind the neutralizing capacity of test biochars seemed to be the increased soil pH and precipitation of Al by OH^- ion released from the dissolution of inorganic and organic compounds from the biochars (Van Zwieten *et al.* 2010, Yuan and Xu 2011, Smider and Singh 2014). For example, addition of 2% leucaena wood biochar reduced the exchangeable Al of the Hawaiian soil from 1.8 cmolc/kg to undetectable level. This could be explained by the 26% $CaCO_3$ equivalent of leucaena biochar. Applied at 2%, it required 20 g leucaena biochar for 1 kg of soil; 20 g lac tree biochar could be contained 5.6 g $CaCO_3$. If 100 g $CaCO_3$ can produce 100-200 cmol OH^-, then 5.2 g $CaCO_3$ could produce 5.2-10.4 cmol OH^-, a number of the moles OH^- that would be more than enough to neutralize 1.8 cmolc exchangeable Al per kg soil. Similar calculations are applicable for the lac tree, mixed wood Hilo, she oak, mahogany and mountain gum for Hawaiian soil, and the lac tree wood and rice husk biochars for Indonesian acid soils. Complexing Al by insoluble oxidized organic functional groups, particularly carboxylics and phenolics at the surface of biochar could be another mechanism that could explain the capacity of rice husk biochar to reduce exchangeable Al for the Indonesian acid soils. Specifically, rice husk biochar at 8% alone reduced about 6 cmolc/kg of the exchangeable Al of Guradog soil. This could not be only explained by the 1.2% $CaCO_3$ equivalent of rice husk biochar because the maximum moles OH^{-1} produced from the carbonates were only 4 moles OH^-, then at least an additional 2 moles OH^- could be produced from the oxygenated functional groups of the rice husk biochar. This finding is in line with Yuan *et al.* 2011, who found that crop residue biochars produced at low temperature (300^oC) contributed to a greater extent of the alkalinity of biochars.

Soil cation exchange capacity (CEC) was variously increased upon addition of biochars. Negative charge developed from the oxygenated surface functional groups of biochar could be responsible for the biochars CEC and subsequently to the amended soil CEC. Leucaena, lac tree, mixed wood Hilo, she oak derived wood biochars increased the CEC of the Hawaiian acid soil more than mahogany and mountain gum, although the CEC and functional groups of the later biochars were higher than the previous one. This result is not explainable at this moment, however the same phenomena were also reported by Yuan and Xu (2012) for a Ultisol soil from Hainan, China; by Novak *et al.* (2009) for a southeastern coastal plain soil, USA; and by Steiner *et al.* (2007) for a highly weathered central Amazonian upland soil. Addition of the rice husk biochar increased the CEC of the Indonesian acid soils more than lac tree wood biochar because the rice husk biochar produced at lower temperature (300^{o}C) compared with lac tree wood biochar that produced at higher temperature (550^{o}C). This could be related to the increase of –OH functional groups at 300^{o}C highest treatment temperature (HTT) and to the loss of carboxylic groups at HTT above 500^{o}C (Harvey *et al.* 2012). The similar results were also reported by Kloss *et al.* 2011 and Budai *et al.* 2014 that CEC decreases with the increase of pyrolysis temperature and the biochar CEC was peaked at lower temperature. Also, wood biochar is low in CEC because defragmentation of lignocellulose (cleavage of OH---O-type) H-bonding of wood biochar and their subsequent oxidation to carboxyl is low (Harvey *et al.* 2012).

4.5.3. Effect of biochar on plant growth

Desmodium growth expressed in total dry weights was enhanced upon addition of biochars to the Hawaiian acid soils. *Desmodium* dry weights obtained from biochar treated soil increased 1.7-7.5 and 1.2-4.2 folds over the control in the first and the second plantings, respectively. *Desmodium* dry matter in the second planting was 1.6-2.1 folds higher than the first planting upon addition of leucaena, lac tree, and she oak derived biochars alone at 2% and 4% to the Hawaiian acid soil. It seemed that leucaena, lac tree, she oak wood or mixed wood

Hilo biochars enhanced *Desmodium* growth from the first to the second plantings. Such growth enhancement could be attributed to the reduction of Al toxicity (Figs. 4.3 and Fig. 4.4), increases in soil pH (Fig. 4.2), soil CEC (Fig. 4.5) and nutrients (Table 4.5) upon the incorporation of biochars. The combination of biochars and lime declined the *Desmodium* growth in the second planting for most biochars tested, perhaps due to the over liming effects.

Soybean growth expressed in shoot (Figs. 4.8a, 4.8b, 4.8c and 4.8d) or root (Table 4.8) dry matters in the first and the second plantings in the Indonesia acid soils were supported by the lac tree wood and rice husk biochar addition either alone or in combination with lime and compost. The shoot and root dry matters obtained from the biochar treated soils were higher than the control, and the second planting dry matters were higher than the first one. The extent of dry matter increased upon addition of the lac tree wood biochar was higher than the rice husk biochar, although they were not significantly different. The result could be explained by the fact that although the lac tree wood biochar had a higher liming potential than the rice husk biochar, but the later contained more label (degradable) fractions due to the lower HTT. It appears that a large part of biochar is mineralized over a short time-scale, and a small part remains in a very stable, highly aromatic forms (Pessenda *et al.* 2001).

The likely reasons for the increased soybean growth in Ultisol soils upon addition of biochars are: (1) correction of soil acidity (increasing soil pH, reducing exchangeable Al and Mn) (Table 4.6, Figs. 4.7a, 4.7b, 4.9a, 4.9b and 4.10a) that provides better rhizosphere conditions for root development (Table 4.9), (2) increasing soil cation exchange capacity that enhanced nutrient retention and later release (Tabs 4.7 and 4.8), and (3) increasing plant nutrients such as

K (Fig. 4.10b). This result was similar to that of Major *et al.* 2010 who reported increases in grass, forb, and legume biomasses by 93, 292, and 1916% over the control after 5 months since addition of 23.2 t black carbon (biochar)/ha to a Colombian isohyperthermic kaolinitic Typic Haplustox sandy clay loam soil. Similar results were also reported by Tagoe *et al.* 2008 in Japan, Suppadit *et al.* 2012 in Thailand, Smider and Singh 2014 in Australia. In contrast, some other findings showed no biochar effect on plant growth: van Zwieten *et al.* 2010 added paper mill waste biochar at 10 % to a Ferrasol resulting in an increase in pH from 4.20 to 5.93 and a decrease in exchangeable Al from 2.0 cmolc/kg to virtually zero, but there was no effect on soybean growth when the biochar was applied without addition of fertilizer.

Soybean growth in the Jasinga soil with 14 cmolc/kg of exchangeable Al treated with lac tree wood and rice husk biochars was 50% lower than the soybean growth in Guradog soil with 8 cmolc/kg exchangeable Al treated with the same biochars. This suggested that soil properties, exchangeable Al in particular, affected the beneficial effect of biochar on acid soil improvement. It appeared that the extent of dry matters increase was highly dependent on the liming value and nutrients content of biochars, soil properties and the induced nutrients acquisition resulted from interactions between added biochars, roots and soils in the rhizosphere (Prendergast-Miller *et al.* 2014).

The first and second growths of *Desmodium* and soybean growth were enhanced by biochar addition to the Hawaiian and Indonesian acid soils. The second dry matter of *Desmodium* in the Hawaiian acid soil was higher than the first one upon addition of laecaena and lac tree biochars alone at 4%, and the same trend also happened to the soybean dry matters in the Indonesian acid soils treated with lac tree wood and rice husk biochars alone at 8%. This would suggest a long-term effect of biochar on acid soil productivity improvement and plant growth enhancement.

4.5.4. Net benefit analysis

Liming potential of lac tree biochar was higher than rice husk biochar resulted in soil acidity improvement and subsequently the soybean growth was better under lac tree biochar application than rice husk. However, rice husk feedstock was available abundantly, resulted a low cost input for ameliorating soil acidity and soybean production. NBA results showed a high cost of lac tree biochar input compared to rice husk biochar caused the benefit of rice husk application was higher than lac tree biochar. Therefore, application of rice husk biochar was more profitable than lac tree biochar.

4.6. Conclusions

The higher capacity to improve the productivity of a Hawaiian acid soil and to support plant growth of leucaena, lac tree, Hilo mixed wood, she oak wood derived biochars than mahogany and mountain gum biochars could be atributed to the liming effect and nutrient content. More specifically, the additions of leucaena and lac tree at 2%, and Hilo mixed wood or she oak derived biochars at 4%, clearly increased soil pH, CEC, and lowered the soil exchangeable Al to a nontoxic level, thereby increasing *Desmodium intortum* growth.

Additions of the lac tree wood or rice husk biochar alone or in combination with lime and compost significantly improved the productivity of two Indonesian acid soils and enhanced soybean growth. Soil pH, CEC, and plant nutrients were markedly increased, and soil exchangeable Al was noticeably reduced upon applications of these biochars at 8% on Guradog soil either alone or in combination with lime at 8 cmolc/kg and compost at 0.2 % resulting in the best growth of soybean. Benefit-cost analysis showed that application of the rice husk biochar to the Guradog soil was more profitable than the lac tree wood biochar. Thus, rice husk biochar at 8% alone or in combination with lime and compost could be recommended for soybean growth on the Guradog soil. Similarly, the best soybean growth on the Jasinga soil was obtained from the application of either the lac tree wood or rice husk biochar at 8% in combination with lime at 8 cmolc/kg and compost at 0.2 %; however, soybean growth was only approximately 50% of that on the Guradog soil.

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CHAPTER 5. NUTRIENT RETENTION OF BIOCHAR

5.1. Abstract

The high fertility of Terra Preta soil was attributed to its high organic matter content and nutrient retention. The objective of this study was to assess the nutrient retention capacities of two biochars when applied in combination with two composts to two highly weathered soils of Hawaii: a Ultisol (Leilehua series) and an Oxisol (Wahiawa series). Chinese cabbage (Brassica rapa cv. Bonsai Chinensis groups) was used as the test plant in two greenhouse trials. Plant fresh and dry weights, soil pH and EC, total N, and other nutrients in soils and plant tissues were measured. The results showed that the interaction between biochar and compost additions was significantly increased the pH and plant tissue Ca of both soils;EC, P and K, cabbage shoot and total fresh and dry matter, plant tissue Ca in both soils; Ca and Mg uptake in the Wahiawa soil; and Fe uptake in the Leilehua soil. Chinese cabbage growth in Leilehua Ultisol amended with the lac tree (*Schleichera oleosa*) wood biochar at 2% in combination with 2% vermicompost was almost twice as that of amended with lime and vermicompost at the same rate. No differences were found among treatments in the Wahiawa Oxisol.Soil pH was increased by 0.9 to 1.6 units and 0.7 to 1.6 units, and EC was increased from 0.35 to 0.47 dS/m and 0.30 to 0.37 dS/m for Ultisol and Oxisols, respectively; aluminum was decreased from 2.5 to 1.5 g/kg and from 1.5 g/kg to 1.2 g/kg, respectively; Mn and Fe in the Wahiawa soil decreased from 805.8 and 63.9 mg to 360and 36.9 mg/kg, respectively. Total nitrogen in the Leilehua and Wahiawa soils increased from 0.21% to 0.25% and from 0.15% to 1.86%, respectively. Ca was increased more by the lac tree wood biochar alone or in combination with vermicompost, while K increased more by the thermocompost alone or in combination with either the lac tree wood or Hilo mixed wood biochars. Soil pH was increased by one unit on average, and EC was increased from 0.35 to 0.47 dS/m and 0.30 to 0.37 dS/m in the Ultisol and Oxisol, respectively. Exchangeable aluminum was decreased from 2.16 cmolc/kg to virtually zero in the high-Al Ultisol. Mehlich-3 extractable Mn and Fe in the high-Mn Oxisol decreased from 806 and 64 to 360 and 37 mg/kg, respectively.Thus, the enhanced cabbage growth in the Leilehua Ultisol was attributed to the increase of plant nutrients and the improvement of acid soil productivity by the additions of biochar and compost. The sufficiency of nutrients in the plant tissues with exception of N and K for the cabbage growth both in the first and the second plantings could indicate an improvement of nutrients supply and retention in those highly weathered soils by added biochars and composts.

Key words: compost, cabbage, nutrient, highly weathered soil

5.2. Introduction

Nutrient retention by biochar was first suggested by the high fertility of Terra Preta soil (Glaser *et al.* 2001). Recent research showed that addition of biochar reduced nutrient losses (Laird *et al.* 2010a, Singh *et al.* 2010, Major *et al.* 2012, Venture *et al.* 2012, Liu *et al.* 2014), increased soil water retention (Novak *et al.* 2009, Laird *et al.* 2010), raised soil pH (Yuan and Xu 2011) and cation exchange capacity (CEC) (Hossain *et al.* 2010, Silber *et al.* 2010), improved beneficial soil microbial population and activities (Graber *et al.* 2010, Kolton *et al.* 2010), and subsequently enhanced plant growth. More specifically, biochar can reduce nitrate, ammonium, phosphorus, and cation concentration in the leachates (Ding *et al.* 2010, Laird *et al.* 2010, Major *et al.* 2012, and Venture *et al.* 2012). For example, addition of a mixed hardwood biochar at 20 g/kg in combination with swine manure at 5 g/kg to a typical midwestern agricultural soil a Hapludoll) reduced total N and total dissolved P leaching by 11% and 69%, respectively, in a leaching column (Laird *et al.* 2010). Addition of biochars produced at higher temperature with higher in surface area may benefit sandy soils by increasing sorption sites or may improve the retention of nonpolar pollutant in soils (*Kloss et al.* 2012).

Nutrient retention capacity of biochar could be attributed to its high surface area, porosity, and surface charge and other factors, such as pH and ionic competition. For example, NH4-N adsorption is due to cation exchange on the surface acid functional (phenolic and carboxylic) groups of biochar produced at low HTT (Wang *et al.* 2015) and physical entrapment in biochars pores structure (Saleh *et al.* 2012). In contrast, NO3-N adsorption on the basic functional groups can be increased by increasing pyrolysis temperature (Wang *et al.* 2015).

Immobilization of N by microorganism also happened to the low HTT biochar (Deenik *et al.* 2010). Phosphorus ions were specifically adsorbed at certain sites of biochar or precipitated by Ca (Xu *et al.* 2014). However, it appeared that some biochars have no or only a little effect to the nutrient retention, and the retention mechanism was not universal, depending on the biochar types, soil properties and other environmental conditions. For example, Bruun *et al.* (2012) recently reported that 2 wt% wheat *(Triticum aestivum* L.) straw biochar could not reduce N leaching from a repacked sample of Denmark sandy soil when 300 kg N/ha of ammonium chloride (NH4Cl) was added, and thus probably did not increase the soil's N retention. Lentz and Ippolito (2012) reported decreased 36% corn yield upon addition of 22.4 Mg/ha hardwood biochar due to reduced N, S, Mn and Cu availability and uptake. The similar result was also reported by Scnell *et al.* (2012) that sorghum biomass is not significantly increased upon application of 3 Mg/ha of sorghum biochar to Alfisol. Hass *et al.* (2012) noted a decrease in S, K and P availability and an increase of PO4 concentration in lecheate upon addition of chicken manure biochars in a West Verginia Ultisol. Sarkhot *et al.* (2012) reported a non-significant effect of 20 Mg/ha biochar on nitrogen leaching from dairly manure effluent in a California Alfisol. It seemed that some biochars can retain nutrients better than others, and some nutrients can't retain by biochar.

The hypothesis for this study was high temperature biochar, which has more micropores can retain more added nutrients, thereby increasing nutrient retention capacity of nutrient-poor soils of Hawaii.

The objective of this study was to assess the nutrient retention capacity of two biochars applied in combination with two composts to two Hawaiian highly weathered, nutrient-poor soils as measured by the growth of Chinese cabbage (*Brassica rapa*).

5.3. Materials and methods

The nutrient retention of biochars were studied, a greenhouse experiment was conducted at the Magoon research facility, University of Hawaii at Manoa, using two acid soils, a Ultisol (Leilehua series) and an Oxisol (Wahiawa series). Soil samples were air dried, and sieved to pass a 4 mm sieve for the pot experiment; and passed 0.5 mm sieve for chemical analysis. A wood- and a mixed wood-derived biochars collected from Indonesia and Hawaii were oven dried at 70^{o}C 48 hours, grounded and sieved to pass a 60 mesh (0.25 mm) sieve and stored before used. All biochars were characterized using the procedures as described in previous chapter and their selected properties are listed in Table 5.1. A local vermicompost and a regular thermocompost as the nutrients sources were collected from Honolulu, Oahu, Hawaii, oven dried at 70^{o}C for 72 hours, sieved to pass through a 0.5 mm sieve for chemical analysis. The pH H_2O of soils, biochars and composts were measured with a pH meter in a mixture of soil, biochar, compost and deionized water 1:1, 1:5 and 1:5, respectively. The EC of soil, biochars and composts were measured using a pH meter in a mixture of soil, biochar, compost and deionized water 1:1, 1:5, and 1:10, respectively. Total and available nutrients content in the composts were read with ICP after dry ash digested and extracted with 5 mM H_2SO_4, respectively (Hue and Uchida, 2000). Soil exchangeable aluminums were exctracted using 1 M KCl and were read with ICP spectrometer. The measured pH, EC and nutrient content in the soils, biochars and composts were listed in Table 5.1 and Table 5.2. A hydrated lime (Bandini®) with the $CaCO_3$ equivalent of 108 was dried and sieved through a 60 mesh sieve before use.

The treatments, consisting of soil, biochar and compost, were arranged in a 2 x 2 x 2 factorial completely randomized design with 3 replicates, and a lime treatment as a control. Two biochars, namely lac tree (*Schleichera oleosa*) wood and Hilo mixed wood, were applied at 0 (control) and 2%. The compost treatments were 0 and 2 %. After three weeks of incubation, all pots (1 kg soil/pot) were planted twice with Chinese cabbage (*Brassica rapa*) cv. Bonsai Chinensis group, which was harvested after 30 days of growth. Shoots roots were carefully removed from the soil. Both were washed with tap water and then with deionized water three times, and the fresh weights was measured before oven-dried at 70^oC for 48 hours. Soil samples were collected from each pot at 16 days after addition of biochars and compost (a week before the first planting) and 52 days (a week after the first planting), air-dried, crushed, and passed through a 0.5 mm sieve before analysis. Soil pH and EC were measured using a pH meter in a mixture of soil and deionized water 1:1. Total carbon and nitrogen content was measured by dry combustion in a LECO CN-2000 elemental analyzer (Leco Corp., St. Joseph, MI). Nitrate and ammonium content were measured by a Vernier LabQuest meter after extracted with deionized water (1:10). Briefly, 4 grams of soil was transferred to a 50 ml glass tube, added with 40 ml of deionized water, covered, shaken for 1 hour, filtered with a Whatman 6S filter paper, and read the nitrate or ammonium concentration with a calibrated Vernier LabQuest meter. Other soil nutrients were read with an Inductively Coupled Plasma (ICP) Spectrometer after extracted with the Mehlich 3 solution (Mehlich, 1984). Briefly, 2 grams of soil were transferred to a 50 ml

Erlenmeyer flask, added with 25 ml of the Mehlich 3 solution, covered, shaken for 5 minutes, filtered with a Whatman 6S filter paper for ICP analysis.

Dry weights of shoots and roots were recorded. A 0.20 g of shoot was dry digested in a muffle furnace at 500^oC for 4 hours. Four ml of 1 M HNO_3 was added to dissolve the ash, and then heated at 150^oC on a hotplate until dry. Fifteen ml of 0.1 M HCl was added, stirred, and filtered into ICP tube for analysis.

Table 5.1. Means and standard errors of pH, EC and CEC of soils, biochars and composts (n=3)

Soils/amendments	pH	EC	CEC
		dS/m	cmolc/kg
Lac tree wood biochar	9.2	1.93 ± 0.01	18.0 ± 1.75
Hilo Mixed wood biochar	9.5	2.42 ± 0.01	14.7± 0.20
Thermocompost	8.3	3.23 ± 0.02	44.5± 1.00
Vermicompost	7.2	2.28 ± 0.03	44.8± 3.50
Ultisol, Leilehua series	4.5	0.08 ± 0.00	16.8 ± 0.45
Oxisol, Wahiawa series	5.6	0.13 ± 0.00	12.1± 0.23

pH H_2O 1:1 for soils, 1:5 for composts, and 1:5 for biochars
EC 1:1 for soils, 1:10 for compost, and 1:5 for biochars

Table 5.2. Means and standard errors of soil nutrients extracted with the Mehlich 3 solution (n=3)

Nutrients	Soils	
	Leilehua	Wahiawa
N (%)	0.21 ± 0.00	0.15 ± 0.00
P(mg/kg)	1.95 ± 0.03	51.52 ± 0.08
K (mg/kg)	49.15 ± 0.53	140.70 ± 1.08
Ca (mg/kg)	111.84 ± 5.09	715.88 ± 5.68
Mg (mg/kg)	53.93 ± 1.06	232.60 ± 0.07
Fe (mg/kg)	98.14 ± 1.41	63.95 ± 0.59
Mn (mg/kg)	11.41 ± 0.05	805.80 ± 5.35
Al (mg/kg)	2517.53 ± 5.48	1503.76 ± 12.67

Table 5.3. Means and standard errors of nutrients in the composts and biochars (n=2)

Nutrients	Thermocompost		Vermicompost		Biochars	
	Total	Available	Total	Available	Lac tree wood	Hilo mixed wood
N (%)	1.90 ± 0.00		1.42 ± 00.0		0.40 ± 0.02	0.50 ± 0.09
P(%)	0.17 ± 0.01	0.07 ± 0.00	1.48 ± 0.00	0.35 ± 0.00	0.06 ± 0.00	0.09 ± 0.00
K (%)	1.37 ± 0.01	0.56 ± 0.01	0.04 ± 0.00	0.04 ± 0.00	0.33 ± 0.00	0.47 ± 0.00
Ca (%)	2.39 ± 0.05	0.78 ± 0.00	2.11 ± 0.67	1.58 ± 0.01	3.13 ± 0.00	1.6 ± 0.01
Mg (%)	0.36 ± 0.00	0.23 ± 0.00	0.36 ± 0.00	0.32 ± 0.00	0.13 ± 0.00	0.22 ± 0.00
Fe (mg/kg)	8345.20 ± 103.11	9.20 ± 0.76	2407.90 ± 30.94	0.90 ± 0.00	684 ± 0.00	12259.5 ± 233.65
Mn (mg/kg)	239.20 ± 1.23	1.70 ± 0.35	606.00 ± 0.68	8.50 ± 0.25	55 ± 0.00	153.8 ± 2.32
Al (mg/kg)	9933.30 ± 39.17	0	1832.00 ± 57.79	0	448.1 ± 0.00	9766.9 ± 154.72

Total nutrients measured by the dry combustion procedure; Available nutrients were extracted by 5 mM H_2SO_4 (Hue *et al.* 2000).

5.4. Results and discussion

5.4.1. Soil pH and EC

The pH of Ultisol and Oxisol was significantly increased from 4.5 to 5.9 and 5.6 to 6.9, respectively, after two weeks treated with biochars in combination with composts (Tabs. 5.4a and 5.4b). It then was continuously increased to 6.5 and 7.2, respectively, and kept at those values until 7 weeks after being treated. The increase of Leilehua soil pH two weeks after treated was highly affected by the interaction of biochar and compost ($P<0.01$) (Tab. 5.5); further increased this soil pH until 7 weeks of incubation was due to the effect of compost or biochar alone ($P<0.001$). Among the treatments, vermicompost in combination with either the lac tree wood or Hilo mixed wood biochar increased the pH the most. The increasing of Wahiawa soil pH two and seven weeks after being treated was affected by the interaction of biochar and compost ($P<0.05$) (Tab. 5.5). The capacity of biochars to increase soil pH was attributed to its liming capacity that was discussed in previous chapters. The increasing of soil pH was also attributed to the role of compost as a result of the consumption of H^+ by organic anions in addition to the releasing of basic cations such as Ca, K, Mg and Na into the soils (Hue, 2011).

Soil EC increased after 2 weeks of incubation and then decreased after the first planting (Tabs. 5.4a and 5.4b). It increased 0.35 to 0.47 dS/m and 0.30 to 0.37 dS/m for the Leilehua and Wahiawa soils, respectively; it then, however, decreased after the first planting particularly for the Leilehua soil perhaps due to the removing of nutrients from the soil by pak choi plants. The increasing soil EC in Leilehua soil was significantly affected by compost alone, while the increasing EC of Wahiawa soil 2 weeks after treated was affected by the interaction of biochar and compost ($P<0.01$) (Tab. 5.5). Further increases of soils' EC after 2 weeks of incubation was controlled by compost alone. The increasing of soil EC was attributed mainly to the basic cations (K, Ca, Mg) enrichment by both biochar and compost in the Wahiawa soil and mostly by compost in the Leilehua soil.

Table 5.4a. Means and standard errors of the Leilehua soil's pH and EC (n=3)

Biochars and composts/lime	**pH 2 weeks**	**pH 7 weeks**	**EC 2 weeks**	**EC 7 weeks**
			dS/m	
Lac tree wood biochar 2%	5.8 ± 0.07 bc	5.8 ± 0.22 de	0.20 ± 0.01 d	0.26 ± 0.02 c
Hilo mixed wood biochar 2%	4.8 ± 0.01 e	4.8 ± 0.07 g	0.22 ± 0.00 d	0.25 ± 0.01 c
Vermicompost 2%	5.7 ± 0.02 c	6.3 ± 0.07 bc	0.51 ± 0.01 ab	0.38 ± 0.01 a
Thermocompost 2%	5.1 ± 0.03 e	5.5 ± 0.09 f	0.39 ± 0.02 c	0.27 ± 0.02 c
Lac tree wood 2% + vermicompost 2%	5.9 ± 0.04 ab	6.5 ± 0.71 ab	0.51 ± 0.04 ab	0.38 ± 0.01 a
Lac tree wood 2% + thermocompost 2%	5.8 ± 0.08 bc	6.1 ± 0.04 cd	0.43 ± 0.02 bc	0.29 ± 0.01 bc
Hilo mixed wood 2% + vermicompost 2%	5.8 ± 0.02 bc	6.5 ± 0.02 ab	0.55 ± 0.02 a	0.36 ± 0.02 ab
Hilo mixed wood 2% + thermocompost 2%	5.4 ± 0.01 d	5.8 ± 0.11 de	0.46 ± 0.02 abc	0.29 ± 0.03 bc
Lime 2%+ vermicompost 2%	6.1 ± 0.03 a	6.6 ± 0.07 a	0.50 ± 0.02 ab	0.38 ± 0.03 a
Lime 2% + thermocompost 2%	5.6 ± 0.03 c	6.1 ± 0.07 cd	0.47 ± 0.01 abc	0.25 ± 0.01 c

Means within a column followed by the same letter(s) were not significantly different by Tukey's test at α= 5%.

Table 5.4b. Means and standard errors of the Wahiawa soil's pH and EC (n=3)

Biochars and composts/lime	**pH 2 weeks**	**pH 7 weeks**	**EC 2 weeks**	**EC 7 weeks**
			dS/m	
Lac tree wood biochar 2%	6.5 ± 0.03 b	6.6 ± 0.09 d	0.27 ± 0.00 e	0.34 ± 0.01 b
Hilo mixed wood biochar 2%	6.0 ± 0.03 d	6.0 ± 0.08 e	0.26 ± 0.01 e	0.35 ± 0.04 b
Vermicompost 2%	6.4 ± 0.11 cd	6.9 ± 0.09 bc	0.47 ± 0.02 bcd	0.42 ± 0.02 ab
Thermocompost 2%	6.3 ± 0.16 cd	6.5 ± 0.03 d	0.47 ± 0.01 bcd	0.49 ± 0.03 a
Lac tree wood 2% + vermicompost 2%	6.8 ± 0.05 ab	7.2 ± 0.09 ab	0.43 ± 0.00 d	0.40 ± 0.02 ab
Lac tree wood 2% + thermocompost 2%	6.7 ± 0.09 abc	7.1 ± 0.12 abc	0.46 ± 0.01 bcd	0.46 ± 0.01 a
Hilo mixed wood 2% + vermicompost 2%	6.9 ± 0.09 ab	7.2 ± 0.03 ab	0.49 ± 0.00 bc	0.44 ± 0.01 ab
Hilo mixed wood 2% + thermocompost 2%	6.3 ± 0.02 cd	6.8 ± 0.01 bcd	0.58 ± 0.02 a	0.44 ± 0.03 ab
Lime 2%+ vermicompost 2%	7.1 ± 0.02 a	7.3 ± 0.01 a	0.45 ± 0.01 cd	0.44 ± 0.01 ab
Lime 2% + thermocompost 2%	6.8 ± 0.08 ab	7.1 ± 0.02 abc	0.52 ± 0.01 ab	0.41 ± 0.02 ab

Means within a column followed by the same letter(s) were not significantly different by Tukey's test at α = 5%.

Table 5.5. F test probabilities shown the effects of biochars and composts additions on the soils' pH and EC

Treatments	pH 2 weeks	pH 7 weeks	EC 2 weeks	EC 7 weeks
Leilehua soil				
Biochar	<.0001	<.0001	0.0879	0.7328
Compost	<.0001	<.0001	<.0001	<.0001
Biochar* compost	<.0001	0.0707	0.3061	0.5619
Wahiawa soil				
Biochar	<.0001	<.0001	<.0001	0.5141
Compost	<.0001	<.0001	<.0001	<.0001
Biochar* compost	0.0224	0.0146	<.0001	0.0877

Effect of treatments: P<0.01 is highly significant; P<0.05 is significant;
P>0.05 is not significant.

5.4.2. Soil exchangeable Al

Soil exchangeable Al of Leilehua Ultisol from 2.16 cmolc/kg to 1.27 and 0.17 cmolc/kg by additions of Hilo mixed wood and Lac tree biochars alone at 2%, repectively. Thermocompost and Vermicompost reduced the exchangeable Al to 0.14 cmolc/kg and undetected level, respectively. Combination of biochars and compost eliminated the exchangeable Al to undetected level (Fig. 5.1a). Exhangeable Al in Wahiawa Oxisol was reduced from 0.12 cmolc/kg to undectected level by additions of biochars or compost alone at 2% or the combination of biochars and composts (Fig. 5.1b).

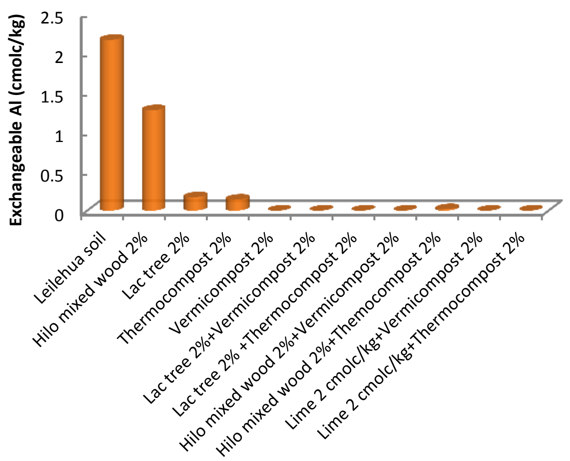

Figure 5.1a. Leilehua Ultisol exchangeable Al as affected by biochars and composts additions

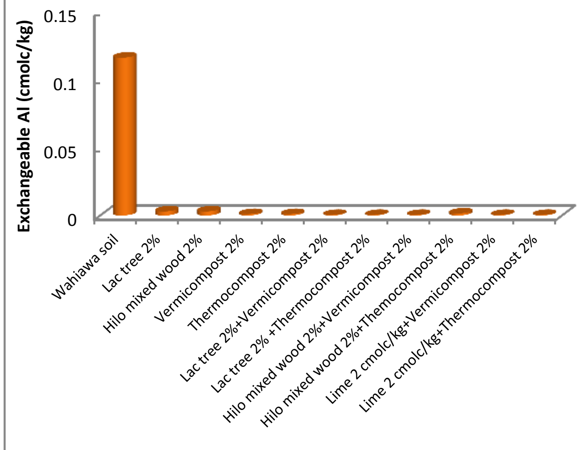

Figure 5.1b. Wahiawa Oxisol exchangeable Al as affected by biochars and composts additions

5.4.3. Nutrient content in soils

Effects of added biochar and compost on the soil nutrients were varied, depending on the nutrient, soil, compost and biochar types (Tabs. 5.6a-5.7c). For example, nutrients in the Leilehua soil (with exception of total N and Fe) were highly enhanced by compost ($P<0.01$) alone, and only K, Ca, Mg, and Fe were highly increased by biochars in combination with composts ($P<0.01$), although there were no interaction effect between biochar and compost ($P>0.05$) on soil nutrients (Tabs. 5.8a-b). N and other nutrients (with exception of Mn and Fe) in the Wahiawa soil were significantly enriched by added biochars or composts alone, and only P and K were significantly increased by the interaction between biochar and compost P(<0.01). More specifically, total N in both soils was slightly increased two weeks after application of biochars and composts, and then slightly decreased after the first planting (7 weeks after biochars and composts addition) as its uptake by plants or lost by leaching during the first planting. For example, total N in the Leilehua soil was increased slightly from 0.21% up to 0.25% two weeks after addition of lac tree wood at 2% in combination with 2% thermocompost. The increase 0.04% or about 400 mg of total N should be accounted from 380 mg and 80 mg total N from the thermocompost and the lac tree wood biochars, respectively. After the first planting (7 weeks after added biochar and compost), the total N in soil decreased to 0.22% (loss 0.02% or 200 mg) as it uptake by plant and leached out from the pot. The similar calculation would also be applicable for other nutrient in both soils. Ca was increased by the lac tree wood biochar alone at 2% from 111.8 mg and 715.9 mg to 816.9 mg and 1514.4 mg for the Leilehua and Wahiawa soils, respectively. Such increases Ca was more than twice compared to those resulted from the Hilo mixed wood because of the higher Ca content in lac tree wood than in Hilo mixed wood biochar. Lac tree wood biochar in combination with vermicompost increased Ca the most. In contrast to Ca, K increased more than twice by thermocompost in combination with either lac tree wood or Hilo mixed wood than by vermicompost. Other nutrients such as Mn and Fe in the Wahiawa soil were sharply decreased by the lac tree wood biochar in combination with vermicompost from 805.8 mg and 63.9 mg to 361.2 mg and 36.9 mg, respectively (Figs. 5.2 and 5.3). The increase of nutrients in soils were attributed to: (1) the release of such nutrients directly from composts and biochars, (2) the increase of soil pH that can solubilize nutrients such as P or precipitated Al and Fe (Figs 5.4 and 5.5), and (3) the complexation of Al and Fe by organic acids and functional groups of composts and biochars (Hue, 2011).

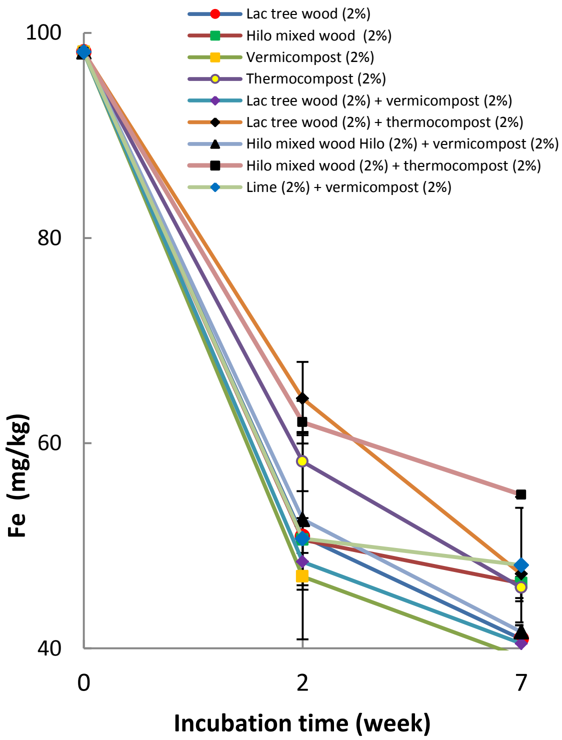

Figure 5.2. Fe in the Wahiawa soil as affected by biochars and composts additions.

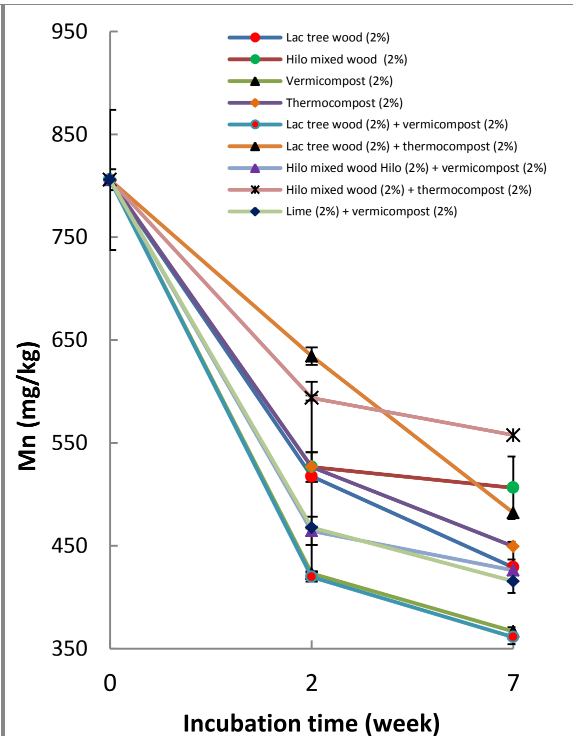

Figure 5.3. Mn in the Wahiawa soil as affected by biochars and composts additions.

Tabel 5.6a. Means and standard errors of nitrogen in the Leilehua soil as affected by biochars and composts addition (n=2)

Biochars and composts/lime	**Total N 2 weeks**	**Total N 7 weeks**	**NH_4^+ 2 weeks**	**NH_4^+ 7 weeks**	**NO_3^- 2 weeks**	**NO_3^- 7 weeks**
	%		mg/l			
Lac tree wood biochar 2%	0.21±0.03 a	0.18±0.00 a	0.50±0.00 b	1.00±0.50 a	1.35±0.15 c	2.00±0.10 dc
Hilo mixed wood biochar 2%	0.20±0.01 a	0.18±0.04 a	1.20±0.60 ab	1.55±0.75 a	1.25±0.15 c	2.45±0.05 dc
Vermicompost 2%	0.23±0.02 a	0.18±0.01 a	1.90±0.10 ab	1.15±0.55 a	6.35±0.55 ab	7.15±0.95 abc
Thermocompost 2%	0.24±0.22 a	0.22±0.03 a	1.50±0.10 ab	2.30±1.50 a	1.65±0.15 c	3.20±0.10 bcd
Lac tree wood 2% + vermicompost 2%	0.23±0.00 a	0.19±0.01 a	1.40±0.70 ab	0.40±0.00 a	7.70±1.60 a	10.35±0.15 a
Lac tree wood 2% + thermocompost 2%	0.25±0.02 a	0.22±0.02 a	3.05±0.25 a	0.70±0.10 a	3.45±0.45 bc	3.35±0.95 bcd
Hilo mixed wood 2% + vermicompost 2%	0.22±0.01 a	0.20±0.01 a	0.75±0.05 ab	0.50±0.10 a	7.95±0.55 a	8.00±2.40 ab
Hilo mixed wood 2% + thermocompost 2%	0.22±0.02 a	0.24±0.02 a	1.80±0.30 ab	0.80±0.00 a	2.45±0.55 c	1.50±0.10 d
Lime 2%+ vermicompost 2%	0.19±0.01 a	0.20±0.01 a	1.65±0.95 ab	0.30±0.00 a	8.65±0.25 a	5.85±0.95 abcd
Lime 2% + thermocompost 2%	0.23±0.01 a	0.22±0.01 a	1.35±0.05 ab	0.65±0.05 a	3.70±0.20 bc	2.25±0.15 dc

Means within a column followed by the same letter(s) were not significantly different by Tukey's test at α = 5%.
2 and 7: weeks after the soils treated with biochars and composts

Table 5.6b. Means and standard errors of P, K and Ca in the Leilehua soil as affected by biochars and composts addition (n=2)

Biochars and composts/lime	P 2 weeks	P 7 weeks	K 2 weeks	K 7 weeks	Ca 2 weeks	Ca 7 weeks
	mg/kg					
Lac tree wood biochar 2%	0.8 ± 0.1 b	1.0 ± 0.1 b	25.5 ± 0.8 c	70.2 ± 2.1 d	816.9 ± 40.7 bc	1112.7 ± 8.6 cd
Hilo mixed wood biochar 2%	1.1 ± 0.2 b	0.9 ± 0.3 b	8.7 ± 8.3 cd	48.2 ± 2.9 e	315.5 ± 8.5 c	411.3 ± 89.9 e
Vermicompost 2%	75.6 ± 3.5 a	133.4 ± 5.4 a	0.0 d	0.0 e	4038.5 ± 28.6 a	4408.9 ± 339.4 a
Thermocompost 2%	3.4 ± 0.7 b	4.10 ± 0.2 b	82.1 ± 4.3 b	204.2 ± 4.5 c	1044.9 ± 39.3 bc	1076.5 ± 67.4 c
Lac tree wood 2% + vermicompost 2%	68.0 ± 13.9 a	146.2 ± 14.1 a	0 d	63.2 ± 7.9 d	4166.5 ± 600.6 a	5021.0 ± 227.6 a
Lac tree wood 2% + thermocompost 2%	3.1 ± 0.2 b	5.8 ± 0.1 b	140.7 ± 16.9 a	312.6 ± 8.9 a	1679.9 ± 107.1 b	2009.9 ± 51.94 b
Hilo mixed wood 2% + vermicompost 2%	61.8 ± 3.5 a	125.4 ± 4.5 a	0 d	50.0 ± 1.5 d	3548.6 ± 350.8 a	4615.8 ± 127.7 a
Hilo mixed wood 2% + thermocompost 2%	3.7 ± 0.4 b	6.5 ± 0.6 b	114.8 ± 17.3 ab	274.6 ± 5.6 b	1230.1 ±34.6 bc	1337.4 ± 38.5 bc
Lime 2%+ vermicompost 2%	72.9 ± 0.8 a	128.5 ± 1.6 a	0.0 d	0.0 e	4171.2 ± 32.8 a	5004.5 ± 164.1 a
Lime 2% + thermocompost 2%	2.3 ± 0.2 b	5.5 ± 0.1 b	93.7 ± 0.1 ab	209.4 ± 1.4 c	1529.1 ± 56.4 bc	1899.6 ± 1.6 bc

Means within a column followed by the same letter(s) were not significantly different by Tukey's test at α = 5%.
2 and 7: weeks after the soils treated with biochars and composts

Table 5.6c. Means and standard errors of Mg, Fe and Mn in the Leilehua soil as affected by biochars and composts addition (n=2)

Biochars and composts/lime	Mg 2 weeks	Mg 7 weeks	Fe 2 weeks	Fe 7 weeks	Mn 2 weeks	Mn 7 weeks
	mg/kg					
Lac tree wood biochar 2%	136.2 ± 4.4 cd	92.5 ± 2.6 f	106.1 ± 2.1 a	109.19±3.01 a	8.1 ± 0.2 b	8.1 ± 0.3 d
Hilo mixed wood biochar 2%	134.6 ± 4.4 d	70.9 ± 3.5 g	103.9 ± 2.5 a	103.94±2.73 a	7.7 ± 0.5 b	8.8 ± 0.3 d
Vermicompost 2%	211.1 ± 7.1 ab	185.8 ± 7.7 cd	108.9 ± 0.7 a	97.36±0.98 a	24.0 ± 3.9 a	19.6 ± 1.6 ab
Thermocompost 2%	211.9 ± 9.2 ab	156.1 ± 4.9 e	115.7 ± 3.9 a	103.61±0.29 a	18.8 ± 1.1 ab	14.6 ± 0.2 c
Lac tree wood 2% + vermicompost 2%	183.1 ±18.3 bc	209.5 ± 5.3 bc	113.0 ± 4.5 a	115.07±13.05 a	23.1 ± 0.7 a	20.3 ± 1.3 a
Lac tree wood 2% + thermocompost 2%	209.9 ± 7.7 ab	183.9 ± 3.0 cd	109.30 ± 6.5 a	118.65±1.27 a	24.9 ± 3.1 a	14.7 ± 0.1 c
Hilo mixed wood 2% + vermicompost 2%	195.6 ± 1.4 ab	192.4 ± 3.3 cd	105.9 ± 1.2 a	111.34±0.54 a	26.9 ± 0.9 a	18.4 ± 1.5 a
Hilo mixed wood 2% + thermocompost 2%	198.4 ± 7.3 ab	168.9 ± 4.8 de	122.4 ± 12.0 a	117.16±2.13 a	24.2 ± 1.1 a	14.4 ± 0.0 c
Lime 2%+ vermicompost 2%	240.0 ± 2.4 a	248.0 ± 5.9 a	99.0 ± 0.4 a	99.02±2.73 a	23.0 ±1.6 a	18.4 ± 0.0 bc
Lime 2% + thermocompost 2%	230.6 ± 11.6 ab	232.0 ± 2.2 ab	101.0 ± 0.8 a	103.55±8.97 a	16.9 ± 3.0 ab	14.4 ± 0.3 c

Means within a column followed by the same letter(s) were not significantly different by Tukey's test at α = 5%.
2 and 7: weeks after the soils treated with biochars and composts

Tabel 5.7a. Means and standard errors of nitrogen in the Wahiawa soil as affected by biochars and composts addition (n=2)

Biochars and composts/lime	Total N 2 weeks	Total N 7 weeks	NH_4^+ 2 weeks	NH_4^+ 7 weeks	NO_3^- 2 weeks	NO_3^- 7 weeks
	%		mg/L			
Lac tree wood biochar 2%	0.14±0.02 a	0.14±0.01 a	0.65±0.15 a	0.55±0.05 ab	4.50±0.70 ef	4.90±0.50 ef
Hilo mixed wood biochar 2%	0.13±0.01 a	0.12±0.01 a	1.20±0.50 a	0.55±0.05 ab	3.25±0.05 f	1.80±0.00 f
Vermicompost 2%	0.17±0.00 a	0.16±0.01 a	1.50±0.70 a	0.45±0.05 ab	17.25±1.65 ab	18.50±2.80 a
Thermocompost 2%	0.18±0.01 a	0.17±0.02 a	2.10±0.20 a	1.00±0.00 ab	9.60±2.20 def	9.50±1.20 cde
Lac tree wood 2% + vermicompost 2%	0.17±0.01 a	0.15±0.01 a	0.90±0.20 a	0.50±0.00 ab	16.45±0.65 abc	15.75±0.55 abc
Lac tree wood 2% + thermocompost 2%	0.18±0.01 a	0.18±0.00 a	2.25±0.85 a	0.95±0.05 ab	11.75±1.05 bcd	11.60±1.10 bcde
Hilo mixed wood 2% + vermicompost 2%	0.17±0.01 a	0.16±0.02 a	1.55±0.85 a	0.60±0.10 ab	15.10±1.90 abcd	13.35±0.35 abcd
Hilo mixed wood 2% + thermocompost 2%	0.17±0.02 a	0.16±0.01 a	3.05±0.05 a	1.20±0.40 a	10.35±0.15 cde	8.75±0.95 de
Lime 2%+ vermicompost 2%	0.16±0.01 a	0.16±0.01 a	1.65±0.05 a	0.40±0.00 b	18.55±0.05 a	16.30±1.50 ab
Lime 2% + thermocompost 2%	0.17±0.01 a	0.16±0.01 a	2.05±0.65 a	0.70±0.00 ab	15.40±0.10 abcd	17.00±0.60 ab

Means within a column followed by the same letter(s) were not significantly different by Tukey's test at α = 5%.
2 and 7: weeks after the soils treated with biochars and composts

Table 5.7b. Means and standard errors of P, K and Ca in the Wahiawa soil as affected by biochars and composts addition (n=2)

Biochars and composts/lime	P 2 weeks	P 7 weeks	K 2 weeks	K 7 weeks	Ca 2 weeks	Ca 7 weeks
	mg/kg					
Lac tree wood biochar 2%	37.7 ± 1.6 b	40.2 ± 1.2 d	106.3 ± 14.0 d	136.5 ± 2.4 ef	1514.4 ± 8.7 cd	1695.1 ± 0.6 d
Hilo mixed wood biochar 2%	35.8 ± 0.7 b	36.7 ± 0.0 d	64.3 ± 2.9 d	119.9 ± 0.6 f	864.2 ± 5.8 d	939.3 ± 58.8 e
Vermicompost 2%	285.1 ± 16.8 a	365.4 ± 3.9 a	65.6 ± 11.9 d	117.4 ± 4.2 f	4367.9 ± 260.3 a	4609.8 ± 28.9 b
Thermocompost 2%	56.8 ± 1.7 b	60.7 ± 1.3 c	241.5 ± 4.5 bc	356.2 ± 1.8 b	1556.4 ± 6.3 cd	1962.2 ± 178.5 d
Lac tree wood 2% + vermicompost 2%	327.4 ± 31.2 a	341.6 ± 2.3 b	73.9 ± 4.0 d	162.5 ± 0.2 de	4869.6 ± 45.8 a	5504.8 ± 131.8 a
Lac tree wood 2% + thermocompost 2%	60.5 ± 3.7 b	68.80 ± 1.1 c	313.9 ± 16.2 a	406.7 ± 11.4 a	2528.5 ± 263.9 b	2770.6 ± 57.9 c
Hilo mixed wood 2% + vermicompost 2%	270.9 ± 11.1 a	367.9 ± 7.2 a	93.6 ± 11.4 d	174.7 ± 1.4 d	4178.1 ± 218.8 a	4682.6 ± 155.9 b
Hilo mixed wood 2% + thermocompost 2%	64.6 ± 2.0 b	70.2 ± 1.1 c	271.6±20.9 ab	419.3 ± 0.3 a	1708.2 ± 41.0 c	1896.0 ± 103.4 d
Lime 2%+ vermicompost 2%	295.6 ± 13.1 a	353.0 ± 4.2 ab	52.9 ± 8.5 d	76.1 ± 3.4 g	4738.2 ± 47.3 a	5512.5 ± 157.1 a
Lime 2% + thermocompost 2%	57.5 ± 7.2 b	62.7 ± 0.1 c	186.5 ± 4.62 c	304.7 ± 8.5 c	2138.3 ± 19.5 cb	2608.4 ± 96.4 c

Means within a column followed by the same letter(s) were not significantly different by Tukey's test at α = 5%.
2 and 7: weeks after the soils treated with biochars and composts

Table 5.7c. Means and standard errors of Mg, Fe and Mn in the Wahiawa soil as affected by biochars and composts addition (n=2)

Biochars and composts/lime	Mg 2 weeks	Mg 7 weeks	Fe 2 weeks	Fe 7 weeks	Mn 2 weeks	Mn 7 weeks
	mg/kg					
Lac tree wood biochar 2%	284.6 ± 7.1 cd	250.8 ± 4.1 c	47.3 ± 10.0 a	40.92±0.19 b	517.2 ± 92.2 a	428.7 ± 24.9 bcd
Hilo mixed wood biochar 2%	266.2 ± 3.6 d	232.1 ± 3.5 c	47.0 ± 0.1 a	46.36±1.77 b	526.3 ± 14.4 a	506.1 ± 30.4 abc
Vermicompost 2%	351.6 ± 4.9 abc	358.3 ± 9.1 b	43.4 ± 1.3 a	39.16±0.46 b	422.7 ± 1.2 a	366.3 ± 4.3 cd
Thermocompost 2%	343.9 ± 7.9 bc	357.5 ± 8.8 b	54.6 ± 2.9 a	45.93±1.03 b	526.3 ± 14.3 a	449.0 ± 0.4 bcd
Lac tree wood 2% + vermicompost 2%	369.1 ± 6.8 ab	365.3 ± 0.4 b	44.8 ± 2.3 a	40.47±1.78 b	419.3 ± 4.4 a	360.9 ±7.0 d
Lac tree wood 2% + thermocompost 2%	401.1 ± 40.8 ab	353.8 ± 5.4 b	60.8 ± 3.6 a	47.26±0.42 b	634.0 ± 68.1 a	481.6 ± 8.3 bcd
Hilo mixed wood 2% + vermicompost 2%	335.2 ± 3.2 bcd	361.5 ± 5.5 b	49.0 ± 0.1 a	41.60±0.64 b	464.0 ± 13.8 a	425.9 ± 10.5 bcd
Hilo mixed wood 2% + thermocompost 2%	350.0 ± 1.2 abc	342.0 ± 5.9 b	58.5 ± 2.1 a	54.97±0.20 b	593.4 ± 10.1 a	557.1 ± 2.4 ab
Lime 2%+ vermicompost 2%	422.0 ± 2.0 a	406.8 ± 0.1 a	47.1 ± 1.4 a	48.11±5.59 b	467.4 ± 9.5 a	415.2 ± 44.1 bcd
Lime 2% + thermocompost 2%	391.4 ± 3.6 ab	402.8 ± 1.4 a	59.9 ± 3.4 a	73.18±7.68 a	611.4 ± 47.9 a	636.6 ± 54.1 a

Means within a column followed by the same letter(s) were not significantly different by Tukey's test at α = 5%.
2 and 7: weeks after the soils treated with biochars and composts

Table 5.8a. F test probabilities showing the effects of biochars and composts additions on the soils' N, P and K

Treatments	Total N 2 weeks	Total N 7 weeks	NH_4^{+1} 2 weeks	NH_4^{+1} 7 weeks	NO_3^{-1} 2 weeks	NO_3^{-1} 7 weeks	P 2 weeks	P 7 weeks	K 2 weeks	K 7 weeks
Leilehua soil										
Biochar	0.2343	0.8829	0.6526	0.1610	0.0329	0.1183	0.5936	0.3629	0.0029	<.0001
Compost	0.1353	0.0466	0.0503	0.2297	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001
Biochar*compost	0.8242	0.9440	0.0634	0.9077	0.8832	0.1776	0.6193	0.2376	0.0967	0.0659
Wahiawa soil										
Biochar	0.6911	0.7179	0.4965	0.1667	0.0175	0.0047	0.3355	0.0301	0.0002	<.0001
Compost	0.0207	0.0147	0.0200	0.0010	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001
Biochar*compost	0.9289	0.7013	0.7924	0.7325	0.4510	0.0336	0.2132	0.0016	0.0094	0.0410

Effect of treatments: $P<0.01$ is highly significant; $P<0.05$ is significant; $P>0.05$ is not significant.
2 and 7: weeks after the soils treated with biochars and composts

Table 5.8b. F test probabilities showing the effects of biochars and composts additions on the soils' Ca, Mg, Fe and Mn.

Treatments	Ca 2 weeks	Ca 7 weeks	Mg 2 weeks	Mg 7 weeks	Fe 2 weeks	Fe 7 weeks	Mn 2 weeks	Mn 7 weeks	Al 2 weeks	Al 7 weeks
Leilehua soil										
Biochar	0.0032	0.0004	0.0036	<.0001	0.0629	0.0191	0.0827	0.0918	0.0127	0.0247
Compost	<.0001	<.0001	<.0001	<.0001	0.1021	0.1077	<.0001	<.0001	<.0001	<.0001
Biochar*compost	0.6605	0.7598	0.2698	0.6064	0.3498	0.9964	0.3660	0.0720	0.2834	0.0679
Wahiawa soil										
Biochar	0.0002	<.0001	0.0024	<.0001	0.6013	0.0006	0.4133	0.0016	0.0033	<.0001
Compost	<.0001	<.0001	<.0001	<.0001	0.0022	0.0005	0.0014	<.0001	<.0001	<.0001
Biochar*compost	0.5327	0.8111	0.2199	0.3446	0.9326	0.0825	0.7206	0.1790	0.5092	0.2534

Effect of treatments: $P<0.01$ is highly significant; $P<0.05$ is significant; $P>0.05$ is not significant.
2 and 7: weeks after the soils treated with biochars and composts

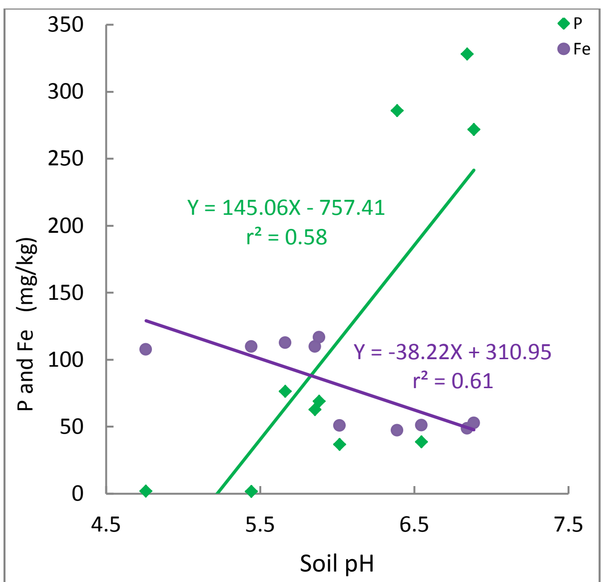

Figure 5.4. Effect of pH on P and Fe in the Leilehua soil 2 weeks after biochars and composts additions

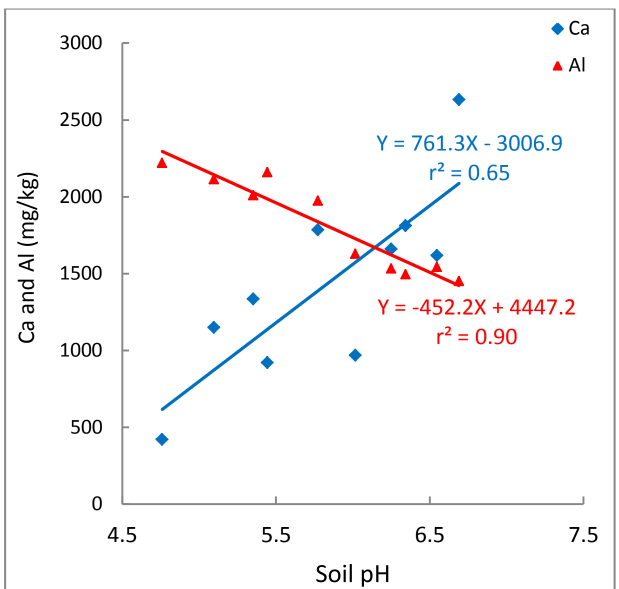

Figure 5.5. Effect pH on Ca, and Al in the Wahiawa soil 2 weeks after biochars and composts additions

5.4.4. Plant growth

Chinese cabbage (*Brassica rapa*) growth in the Leilehua soil expressed in shoot dry matter second planting was significantly affected by the interaction of biochar and compost, while shoot fresh matters, total fresh and dry weights was significantly increased by the lac tree wood biochar or compost alone (Table 5.9). For example, the shoot fresh weights of Brassica first planting in the Leilehua soil ranged from 4.9 to 29.5 g, and the best growth expressed in shoot or total fresh and dry weights was obtained from the application of lac tree wood biochar at 2% in combination with 2% vermicompost (Tabs. 5.10a-b). The Brassica first planting' shoot, root and total fresh and dry weights in the Wahiawa were significantly increased by the interaction between biochars and composts (Tab. 5.9); however, there were no significant differences among the treatments (Tabs. 5.11a-b). The likely reasons for the increase of Brassica growth in soils, Leilehua soil in particular, would be the increase of soil pH from 4.5 to 5.9, decreased Al and Fe from 2517 mg/kg and 98 mg/kg to 1538 mg/kg and 40.5 mg/kg, in addition to the release of nutrients into the soils and subsequently uptake by the plants. In the second planting, the fresh and dry weights of Brassica in both soils decreased to almost 50% of the first planting (Fig. 5.6) perhaps due to the deficiency of nutrients such as N and K. The closed linear relationship between total dry matters and N and K uptake indicated the deficiencies of such nutrients (Figs. 5.7a and 5.7b).

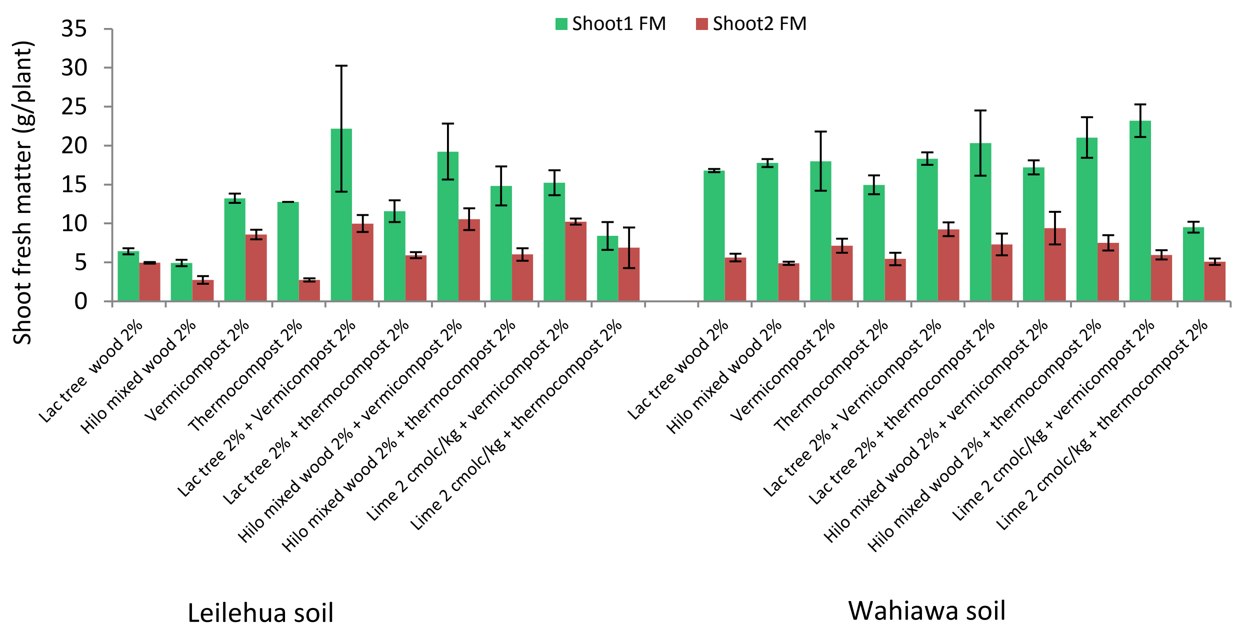

Figure 5.6. Chinese cabbage shoot fresh weight as affected by biochars and composts additions
FM= Fresh matter; 1 and 2: first and second plantings; Error bars: SE (n=3)

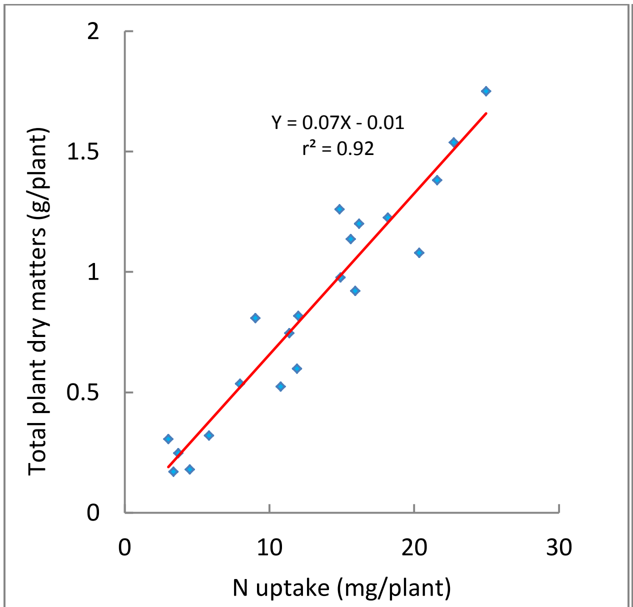

Figure 5.7a. Relationship between N uptake and total dry matters of Chinese cabbage second planting in the Leilehua soil

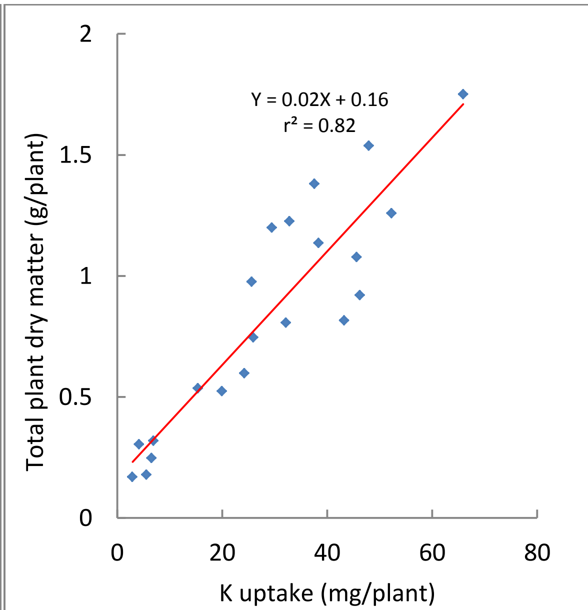

Figure 5.7b. Relationship between K uptake and total dry matters of Chinese cabbage second planting in the Leilehua soil

Table 5.9. F test probabilities shown the effects of biochars and composts additions to the Chinese cabbage fresh and dry weights

Treatments	1st Shoot	2nd shoot	1st root	2nd root	1st total	2nd total	1st Shoot	2nd shoot	1st root	2nd root	1st total	2nd total
	Fresh weights						Dry weights					
Leilehua soil												
Biochar	0.0454	<.0001	0.0594	0.0204	0.0383	0.0428	0.0094	0.0916	0.0495	0.1048	0.0102	0.0450
Compost	<.0001	<.0001	0.0018	<.0001	<.0001	<.0001	<.0001	<.0001	0.0012	0.0303	<.0001	<.0001
Biochar*compost	0.1101	0.5291	0.1344	0.5595	0.0995	0.5491	0.2376	0.0477	0.2149	0.2984	0.2204	0.0740
Wahiawa soil												
Biochar	0.4501	0.0367	0.849	0.0005	0.3129	0.0129	0.2624	0.0498	0.1078	0.2898	0.1848	0.1283
Compost	0.1308	0.0037	0.0016	0.0004	0.0774	0.0018	0.1733	0.0032	0.0040	0.1856	0.0954	0.0336
Biochar*compost	0.0075	0.8523	0.0168	0.6161	0.0053	0.8724	0.0034	0.6993	0.0162	0.3638	0.0031	0.4537

Effect of treatments: $P<0.01$ is highly significant; $P<0.05$ is significant; $P>0.05$ is not significant.
1st and 2nd: first and second plantings

Table 5.10a. Means and standard errors of Chinese cabbage fresh matters as affected by biochars and composts additions in the Leilehua soil

Biochars and composts/lime	**1st Shoot**	**2nd Shoot**	**1st Root**	**2nd Root**	**1st Total**	**2nd Total**
	g		g		g	
Lac tree wood biochar 2%	6.4±0.4 b	4.9 ±0.1 bc	2.3±0.3 b	0.9±0.2 d	8.7±0.6 b	5.8±03 dc
Hilo mixed wood biochar 2%	4.9±0.4 b	2.7±0.5 c	2.1±0.3 b	0.5±0.1 d	7.0±0.7 b	3.2±0.5 d
Vermicompost 2%	13.2±0.6 b	8.6±0.6 ab	3.4±0.0 ab	2.4±0.2 abc	16.6±0.6 b	11.0±0.8 abc
Thermocompost 2%	12.8±2.0 b	2.7±0.2 c	3.2±0.4 ab	0.4±0.0 d	15.9±2.3 b	3.1±0.3 d
Lac tree wood 2% + vermicompost 2%	29.5±8.1 a	9.9±1.1 ab	5.1±0.4 a	3.2±0.4 a	34.6±8.4 a	13.2±1.4 ab
Lac tree wood 2% + thermocompost 2%	11.6±1.4 b	5.9±0.4 abc	2.7±0.5 ab	1.1±0.1 dc	14.2±1.9 b	7.0±0.5 bcd
Hilo mixed wood 2% + vermicompost 2%	19.2±3.6 ab	10.5±1.4 a	4.1±0.7 ab	3.2±0.3 a	23.3±4.3 ab	13.7±1.8 a
Hilo mixed wood 2% + thermocompost 2%	14.8±2.5 b	6.0±0.8 abc	3.2±0.8 ab	1.4±0.3 bcd	18.0±3.3 b	7.4±1.1 abcd
Lime 2%+ vermicompost 2%	15.2±1.6 b	10.2±0.4 ab	2.4±0.3 b	2.7±0.2 ab	17.6±1.9 b	12.9±0.6 ab
Lime 2% + thermocompost 2%	8.4±1.8 b	6.9±2.6 abc	2.6±0.7 ab	1.2±0.5 dc	11.0±2.6 b	8.1±3.1 abcd

Means within a column followed by the same letter(s) were not significantly different by Tukey's test at $\alpha = 5\%$.
1st and 2nd: referred to the first and second plantings.

Table 5.10b. Means and standard errors of Chinese cabbage dry matters as affected by biochars and composts additions in the Leilehua soil

Biochars and composts/lime	**1st Shoot**	**2nd Shoot**	**1st Root**	**2nd Root**	**1st Total**	**2nd Total**
	g		g		g	
Lac tree wood biochar 2%	0.7±0.1 bc	0.5±0.0 abc	0.2±0.0 b	0.1±0.0 a	0.9±0.1 bc	0.6±0.0 bc
Hilo mixed wood biochar 2%	0.3±0.1 c	0.2±0.0 c	0.1±0.0 b	0.05±0.0 a	0.4±0.1 c	0.2±0.0 c
Vermicompost 2%	1.5±0.1 abc	0.8±0.1 ab	0.3±0.0 ab	0.2±0.0 a	1.8±0.1 abc	1.0±0.1 abc
Thermocompost 2%	1.1±0.2 bc	0.3±0.0 bc	0.3±0.1 ab	0.03±0.0 a	1.4±0.2 bc	0.3±0.0 c
Lac tree wood 2% + vermicompost 2%	2.9±0.6 a	1.1±0.1 a	0.5±0.1 a	0.3±0.0 a	3.4±0.7 a	1.4±0.2 ab
Lac tree wood 2% + thermocompost 2%	1.3±0.2 bc	0.6±0.1 abc	0.3±0.1 ab	0.1±0.0 a	1.6±0.3 bc	0.7±0.1 abc
Hilo mixed wood 2% + vermicompost 2%	1.9±0.5 ab	1.1±0.2 a	0.4±0.1 ab	0.3±0.0 a	2.3±0.5 ab	1.4±0.2 a
Hilo mixed wood 2% + thermocompost 2%	1.7±0.4 abc	0.6±0.1 abc	0.4±0.1 ab	0.1±0.0 a	2.1±0.4 ab	0.7±0.1 abc
Lime 2%+ vermicompost 2%	1.4±0.2 bc	0.7±0.3 abc	0.3±0.0 ab	0.1±0.0 a	1.6±0.2 bc	0.8±0.3 abc
Lime 2% + thermocompost 2%	0.8±0.1 bc	0.8±0.1 ab	0.2±0.1 b	0.1±0.0 a	1.0±0.2 bc	0.9±0.2 abc

Means within a column followed by the same letter(s) were not significantly different by Tukey's test at α = 5%.
1st and 2nd: referred to the first and second plantings

Table 5.11a. Means and standard errors of Chinese cabbage fresh matters as affected by biochars and composts additions in the Wahiawa soil

Biochars and composts/lime	**1st Shoot**	**2nd Shoot**	**1st Root**	**2nd Root**	**1st Total**	**2nd Total**
	g		g		g	
Lac tree wood biochar 2%	16.8±0.2 ab	5.6±0.5 a	2.7±0.2 b	1.3±0.2 abc	19.5±0.3 ab	6.9±0.7 a
Hilo mixed wood biochar 2%	17.8±0.5 ab	4.9±0.2 a	3.0±0.1 ab	1.1±0.1 c	20.8±0.5 ab	5.9±0.3 a
Vermicompost 2%	18.9±3.8 ab	7.3±0.9 a	3.8±0.2 ab	1.8±0.3 abc	22.7±4.0 ab	9.1±1.3 a
Thermocompost 2%	14.9±1.9 ab	7.2±0.8 a	3.5±0.1 ab	1.2±0.0 bc	18.4±1.9 ab	8.4±0.9 a
Lac tree wood 2% + vermicompost 2%	18.3±0.8 ab	9.3±0.9 a	4.2±0.5 ab	2.6±0.2 ab	22.5±1.0 ab	11.9±1.1 a
Lac tree wood 2% + thermocompost 2%	20.3±4.2 ab	7.3±1.4 a	5.2±0.6 a	1.9±0.5 c	25.5±4.8 a	9.2±1.8 a
Hilo mixed wood 2% + vermicompost 2%	17.2±0.9 ab	9.4±2.1 a	4.1±0.4 ab	2.6±0.4 a	21.3±0.9 ab	12.1±2.5 a
Hilo mixed wood 2% + thermocompost 2%	21.0±2.6 a	7.5±1.0 a	4.8±0.4 ab	2.3±0.6 abc	25.8±2.9 a	9.9±1.6 a
Lime 2%+ vermicompost 2%	23.2±2.1 a	5.9±0.6 a	4.8±0.9 ab	1.1±0.0 c	28.0±3.1 a	7.1±0.6 a
Lime 2% + thermocompost 2%	9.5±0.7 b	5.1±0.4 a	2.5±0.5 b	1.1±0.1 c	12.1±1.2 b	6.2±0.5 a

Means within a column followed by the same letter(s) were not significantly different by Tukey's test at α = 5%.
1st and 2nd: referred to the first and second plantings.

Table 5.11b. Means and standard errors of Chinese cabbage dry matters as affected by biochars and composts additions in the Wahiawa soil

Biochars and composts/lime	1st Shoot	2nd Shoot	1st Root	2nd Root	1st Total	2nd Total
	g		g		g	
Lac tree wood biochar 2%	1.7±0.1 ab	0.6±0.1 a	0.3±0.0 ab	0.1±0.0 a	1.9±0.1 abc	0.7±0.1 ab
Hilo mixed wood biochar 2%	1.8±0.1 ab	0.5±0.1 a	0.3±0.0 ab	0.1±0.0 a	2.1±0.1 abc	0.6±0.1 ab
Vermicompost 2%	1.8±0.4 ab	0.7±0.1 a	0.4±0.0 ab	0.2±0.0 a	2.2±0.4 abc	0.9±0.1 ab
Thermocompost 2%	1.6±0.3 ab	0.7±0.1 a	0.3±0.0 ab	0.1±0.0 a	1.9±0.3 abc	0.8±0.1 ab
Lac tree wood 2% + vermicompost 2%	2.0±0.3 a	0.9±0.1 a	0.4±0.1 ab	0.3±0.1 a	2.4±0.3 ab	2.1±0.9 a
Lac tree wood 2% + thermocompost 2%	2.0±0.3 a	0.7±0.2 a	0.5±0.1 a	0.2±0.0 a	2.6±0.4 ab	0.9±0.2 ab
Hilo mixed wood 2% + vermicompost 2%	1.6±0.1 ab	0.9±0.1 a	0.4±0.0 ab	0.3±0.0 a	1.9±0.1 abc	1.3±0.1 ab
Hilo mixed wood 2% + thermocompost 2%	2.2±0.1 a	0.7±0.2 a	0.5±0.0 a	0.2±0.1 a	2.7±0.2 ab	0.9±0.2 ab
Lime 2%+ vermicompost 2%	2.3±0.2 a	0.6±0.1 a	0.5±0.1 a	0.1±0.0 a	2.8±0.3 ab	0.7±0.2 ab
Lime 2% + thermocompost 2%	0.9±0.1 b	0.5±0.0 a	0.2±0.0 b	0.1±0.0 a	1.1±0.1 bc	0.6±0.1 ab

Means within a column followed by the same letter(s) were not significantly different by Tukey's test at $\alpha = 5\%$.
1st and 2nd: referred to the first and second planting.

5.4.5. Plant nutrients

P, K, and Mn in the Chinese cabbage tissues first and second plantings in the Leilehua soil were significantly affected by biochars and composts additions; P and Mn in Wahiawa soil was significantly affected by biochars; and Ca in both soils was significantly increased by the interaction between biochar and compost (Tab. 5.12). P in plant tissues treated with compost alone or in combination with biochar were higher than those in plant tissues treated with biochar alone, probably due to the lower P content in the biochars. This was also the reason why P in plant tissues treated with biochar alone was lower than the critical level of P level (less than 0.4%) for Brassica growth (Tabs. 5.14a -5.15 b) . It seemed that the added biochar attributed more to their liming effects instead of the release nutrients such as P. Nutrients content in plant tissues except N and K was in range of the critical levels for the normal growth of Brassica both in the first and the second plantings. The sufficiency of P, Ca, Mg, Fe, and Mn in Brassica plant tissues both in the first and the second plantings indicated an improvement of such nutrients supplies and retentions in those highly weathered soils by added biochars and composts.

Nitrogen in plant tissue ranged from 1.04 to 1.8 % and from 1.17 to 1.81 % for the Leilehua and the Wahiawa soil, respectively. Those levels were lower than the sufficiency level of N (3-4%) for normal growth of *Brassica rapa* (Uchida, 2000). N content in Brassica tissue increased in the second planting; however, as the Brassica growth was limited at the second planting, the N uptake was then lower than the first planting. Total uptake of N ranged from 11.4 to 66.5 mg/plant and from 26.3 to 58.2 mg/plant for the Leilehua and Wahiawa soils, respectively. The highest N uptake was 66.5 and 58. 2 mg in the Leilehua and Wahiawa soils, respectively. Such N uptake was accounted for only 2% of the total N in the soils. K in plant tissue of Brassica grown in the Leilehua soil ranged from 2.51 to 3.83% and showed that it was also lower than the critical level of K for the Brassica growth. The highest K uptake by Brassica in the Leilehua soil was 122.2 mg that was accounted for approximately 48% of the total K in this soil.

Table 5.12. F test probabilities shown the effects of biochars and composts additions to the nutrients content in the Chinese cabbage tissues.

Treatments	1st total N	2nd total N	1st P	2nd P	1st K	2nd K	1st Ca	2nd Ca	1st Mg	2nd Mg	1st Fe	2nd Fe	1st Mn	2nd Mn
Leilehua soil														
Biochar	0.3799	0.9259	0.4902	0.1564	0.4935	0.0200	0.2589	0.0985	0.1876	0.6232	0.3244	0.8326	0.2327	0.6646
Compost	0.8369	0.9722	0.0077	<.0001	0.0414	0.0404	0.6090	0.3212	0.0740	0.1029	0.0574	0.4697	0.0146	0.8976
Soil*Biochar	0.1115	0.5042	0.0877	0.3524	0.0576	0.2989	0.1220	0.0401	0.2649	0.5983	0.5686	0.7539	0.2538	0.7511
Wahiawa soil														
Biochar	0.7091	0.5888	0.0603	0.0205	0.5998	0.0516	0.0507	0.5232	0.3097	0.8463	0.3867	0.5698	0.0463	0.2219
Compost	0.8027	0.2449	0.1765	0.3736	0.1362	0.4207	0.1609	0.9849	0.1085	0.2351	0.4054	0.4720	0.8823	0.0159
Soil*Biochar	0.1317	0.6539	0.7764	0.6924	0.8036	0.6505	0.0287	0.4394	0.0553	0.3690	0.2313	0.5415	0.7609	0.9268

Effect of treatments: P<0.001 is highly significant; P<0.05 is significant; P>0.05 is not significant.
1st and 2nd: first and second plantings

Table 5.13. F test probabilities shown the effects biochars and composts additions to the nutrients uptake by the Chinese cabbage.

Treatments	1st total N	2nd total N	1st P	2nd P	1st K	2nd K	1st Ca	2nd Ca	1st Mg	2nd Mg	1st Fe	2nd Fe	1st Mn	2nd Mn
Leilehua soil														
Biochar	0.1253	0.0728	0.1928	0.7676	0.1743	0.1386	0.0801	0.1916	0.4560	0.7532	0.8780	0.2470	0.8860	0.5267
Compost	0.0022	0.0030	0.0082	0.0024	0.0202	0.0231	0.0019	0.0111	0.0186	0.1156	0.1082	0.0419	0.5040	0.0280
Soil*Biochar	0.1023	0.1624	0.4546	0.4216	0.1698	0.1705	0.0891	0.0590	0.2806	0.1264	0.8318	0.0395	0.5751	0.1845
Wahiawa soil														
Biochar	0.4625	0.0179	0.1297	0.1312	0.3917	0.1224	0.1540	0.2363	0.6910	0.1381	0.6109	0.3974	0.0341	0.0162
Compost	0.0974	0.0015	0.0593	0.0473	0.3200	0.1710	0.0265	0.1030	0.3457	0.1913	0.2310	0.9380	0.1570	0.0004
Soil*Biochar	0.2093	0.2054	0.0448	0.8967	0.4306	0.7711	0.0110	0.3006	0.0260	0.8794	0.1496	0.2660	0.0978	0.5000

Effect of treatments: P<0.001 is highly significant; P<0.05 is significant; P>0.05 is not significant.
1st and 2nd: first and second plantings

Table 5.14a. Means and standard errors of N, P and K in Chinese cabbage tissues and total uptake as affected by biochars and composts additions (n=2)

Treatments	N content in plant tissue		Total N	P content in plant tissue		Total P	K content in plant tissue		Total K
	1st planting	2nd planting	uptake	1st planting	2nd planting	uptake	1st planting	2nd planting	uptake
Leilehua soil	%		mg	%		mg	%		mg
Lac tree wood biochar 2%	1.13±0.03 a	1.74±0.25 a	20.7±0.1 bc	0.28±0.05 b	0.22±0.02 cd	4.0±1.0 b	3.64±0.59 ab	3.46±0.08 ab	54.4±1.4 bcd
Hilo mixed wood biochar 2%	1.68±0.07 a	1.48±0.49 a	11.4±4.2 c	0.29±0.09 b	0.05±0.03 d	11.4±4.2 b	2.51±0.89 ab	1.53±0.17 b	17.6±9.2 d
Vermicompost 2%	1.04±0.10 a	1.51±0.02 a	35.9±0.8 abc	0.34±0.03 ab	0.57±0.10 ab	12.6±1.1 ab	3.04±0.35 ab	2.65±0.03 ab	85.6±4.4 abcd
Thermocompost 2%	1.86±0.43 a	1.66±0.16 a	28.4±10.7 bc	0.65±0.18 ab	0.08±0.01 cd	8.5±4.1 ab	2.67±0.16 ab	2.40±0.24 ab	39.2±10.2 cd
Lac tree wood 2% + vermicompost 2%	1.28±0.09 a	1.72±0.16 a	66.5±11.7 a	0.55±0.07 ab	0.47±0.15 abc	26.6±8.0 a	2.87±0.58 ab	3.47±0.75 ab	139.7±7.6 a
Lac tree wood 2% + thermocompost 2%	1.12±0.14 a	1.63±0.10 a	28.1±1.5 bc	0.57±0.01 ab	0.21±0.03 cd	9.2±0.4 ab	3.57±0.12 ab	4.25±0.77 ab	82.4±12.2 abcd
Hilo mixed wood 2% + vermicompost 2%	1.64±0.46 a	1.39±0.04 a	52.9±0.6 ab	0.78±0.01 a	0.57±0.01 ab	25.9±5.7 a	2.87±0.13 ab	3.11±0.65 ab	110.9±6.1 abc
Hilo mixed wood 2% + thermocompost 2%	1.09±0.25 a	1.77±0.29 a	39.7±4.5 abc	0.51±0.09 ab	0.19±0.04 cd	13.1±0.1 ab	3.83±0.33 ab	3.46±0.35 ab	122.2±18.2 ab
Lime 2%+ vermicompost 2%	1.30±0.22 a	1.95±0.57 a	30.8±6.5 bc	0.63±0.16 ab	0.69±0.04 a	14.5±3.2 ab	2.11±0.32 b	3.24±0.13 ab	55.7±18.5 bcd
Lime 2% + thermocompost 2%	1.15±0.03 a	1.32±0.15 a	25.6±2.9 bc	0.53±0.02 ab	0.29±0.12 bcd	9.0±0.2 ab	5.04±1.01 a	4.72±0.57 a	104.2±23.7 abc
Sufficiency level for Brassica rapa (%)	3-4			0.4-0.7			4.5-7.5		

Means within a column followed by the same letter(s) were not significantly different by Tukey's test at α = 5%.

Table 5.14b. Means and standard errors of Ca, Mg, Fe and Mn content in Chinese cabbage tissues and total uptake as affected by biochars and composts additions (n=2).

Treatments	Ca Content in plant tissue		Total Ca	Mg content in plant tissue		Total Mg	Fe content in plant tissue		Total Fe	Mn content in plant tissue		Total Mn
	1st planting	2nd planting	uptake	1st planting	2nd planting	uptake	1st planting	2nd planting	uptake	1st planting	2nd planting	uptake
Leilehua soil	%		mg	%		mg	mg/kg		mg	mg/kg		mg
Lac tree wood biochar 2%	3.38±0.08 a	3.91±1.06 a	54.5±2.9 bc	0.56±0.06 a	0.98±0.25 a	11.1±0.4 dc	120.0±58.3 a	81.6±18.3 a	0.17±0.06 a	42.8±21.5 a	64.7±23.9 a	0.08±0.01 a
Hilo mixed wood biochar 2%	2.28±0.41 a	2.08±0.04 a	16.7±5.6 c	0.64±0.09 a	0.96±0.24 a	5.7±0.6 d	192.8±41.4 a	77.7±25.4 a	0.1±0.01 a	79.0±33.9 a	71.9±30.7 a	0.06±0.04 a
Vermicompost 2%	2.57±0.57 a	3.29±0.05 a	84.2±7.1 bc	0.59±0.09 a	0.85±0.15 a	20.5±0.0 ab	104.1±8.0 a	71.2±18.7 a	0.27±0.03 a	31.1±0.4 a	75.5±14.9 a	0.14±0.01 a
Thermocompost 2%	3.59±1.09 a	2.21±0.30 a	46.1±2.3 bc	0.49±0.08 a	0.53±0.04 a	7.2±0.6 d	118.0±6.9 a	59.3±29.3 a	0.16±0.05 a	25.8±7.8 a	42.8±10.5 a	0.05±0.01 a
Lac tree wood 2% + vermicompost 2%	3.87±0.21 a	4.09±0.59 a	188.2±35.8 a	0.43±0.03 a	0.65±0.19 a	22.9±2.5 a	69.6±7.6 a	50.9±6.1 a	0.31±0.05 a	14.2±3.8 a	61.7±9.3 a	0.12±0.0 a
Lac tree wood 2% + thermocompost 2%	2.70±0.14 a	3.58±0.35 a	65.4±10.5 bc	0.56±0.07 a	0.70±0.07 a	13.2±0.8 bcd	119.5±44.1 a	82.9±7.8 a	0.23±0.07 a	41.7±4.4 a	73.1±7.9 a	0.12±0.01 a
Hilo mixed wood 2% + vermicompost 2%	3.51±0.43 a	4.16±0.21 a	136.8±9.3 ab	0.42±0.02 a	0.70±0.09 a	19.8±0.2 abc	88.5±22.6 a	64.1±11.8 a	0.27±0.01 a	16.3±2.0 a	50.9±11.9 a	0.11±0.01 a
Hilo mixed wood 2% + thermocompost 2%	2.43±0.33 a	2.57±0.02 a	78.9±4.5 bc	0.51±0.00 a	0.57±0.12 a	18.2±0.8 abc	92.6±1.9 a	144.9±60.5 a	0.29±0.06 a	36.0±10.6 a	61.4±12.8 a	0.14±0.02 a
Lime 2%+ vermicompost 2%	3.50±0.19 a	2.51±0.85 a	79.1±33.2 bc	0.52±0.12 a	0.75±0.07 a	12.7±3.1 bcd	126.4±9.1 a	69.6±22.3 a	0.24±0.05 a	26.4±1.4 a	82.8±0.7 a	0.09±0.04 a
Lime 2% + thermocompost 2%	3.84±0.05 a	4.38±0.51 a	87.1±1.0 bc	0.74±0.06 a	0.92±0.16 a	17.1±2.8 abc	145.9±21.4 a	92.0±10.2 a	0.26±0.04 a	74.3±8.9 a	78.6±40.3 a	0.15±0.06 a
Sufficiency level for Brassica rapa	1.9-6.0			0.23-0.75			40-300			25-200			

Means within a column followed by the same letter(s) were not significantly different by Tukey's test at α = 5%.

Table 5.15a. Means and standard errors of N, P and K in Chinese cabbage tissues and total uptake as affected by biochars and composts additions (n=2)

Treatments	N content in plant tissue		Total N	P content in plant tissue		Total P	K content in plant tissue		Total K
	1st planting	2nd planting	uptake	1st planting	2nd planting	uptake	1st planting	2nd planting	uptake
Wahiawa soil	%		mg	%		mg	%		mg
Lac tree wood biochar 2%	1.56±0.29 a	1.13±0.01 a	39.7±4.3 ab	0.64±0.14 a	0.59±0.00 a	17.2±2.0 a	4.84±0.69 a	3.68±0.29 a	124.7±6.5 a
Hilo mixed wood biochar 2%	1.26±0.15 a	1.28±0.32 a	32.8±0.4 ab	0.41±0.12 a	0.57±0.09 a	11.7±1.7 a	4.57±0.63 a	4.06±0.14 a	117.1±10.3 a
Vermicompost 2%	1.27±0.08 a	1.42±0.15 a	41.1±11 ab	0.52±0.05 a	0.95±0.07 a	19.6±4.2 a	2.68±0.20 a	3.43±0.19 a	88.0±16.4 a
Thermocompost 2%	1.35±0.13 a	1.62±0.76 a	32.9±0.9 ab	0.55±0.11 a	0.90±0.03 a	15.0±1.2 a	3.09±0.07 a	4.94±0.30 a	85.3±8.1 a
Lac tree wood 2% + vermicompost 2%	1.31±0.11 a	1.35±0.16 a	43.9±1.3 ab	0.79±0.01 a	0.74±0.22 a	25.9±0.7 a	3.38±1.11 a	3.95±0.51 a	124.5±33.2 a
Lac tree wood 2% + thermocompost 2%	1.32±0.14 a	1.61±0.49 a	41.1±2.2 ab	0.69±0.03 a	0.56±0.19 a	20.9±0.4 a	2.96±0.07 a	4.02±1.45 a	105.9±9.6 a
Hilo mixed wood 2% + vermicompost 2%	1.81±0.19 a	1.85±0.45 a	58.2±2.4 a	0.63±0.09 a	0.73±0.07 a	21.8±2.7 a	4.24±0.72 a	4.91±0.81 a	148.5±2.8 a
Hilo mixed wood 2% + thermocompost 2%	1.17±0.05 a	1.73±0.14 a	46.4±9.8 ab	0.68±0.08 a	0.81±0.05 a	25.5±6.7 a	3.41±0.02 a	4.61±0.49 a	134.2±30.9 a
Lime 2%+ vermicompost 2%	1.41±0.32 a	1.46±0.16 a	48.5±0.5 ab	0.86±0.00 a	0.50±0.03 a	27.7±5.8 a	3.76±1.28 a	2.54±0.38 a	117.5±6.7 a
Lime 2% + thermocompost 2%	1.63±0.15 a	1.53±0.01 a	26.3±1.8 b	0.75±0.18 a	0.53±0.09 a	10.9±0.1a	3.49±0.07 a	3.02±0.41 a	55.6±9.3 a
Sufficiency level for Brassica rapa (%)	3-4			0.4-0.7			4.5-7.5		

Means within a column followed by the same letter(s) were not significantly different by Tukey's test at α = 5%.

Table 5.15b. Means and standard errors of Ca, Mg, Fe and Mn content in Chinese cabbage tissues and total uptake as affected by biochars and composts additions (n=2).

Treatments	Ca Content in plant tissue		Total Ca	Mg content in plant tissue		Total Mg	Fe content in plant tissue		Total Fe	Mn content in plant tissue		Total Mn
	1st planting	2nd planting	uptake	1st planting	2nd planting	uptake	1st planting	2nd planting	uptake	1st planting	2nd planting	uptake
Wahiawa soil	%		mg	%		mg	mg/kg		mg	mg/kg		mg
Lac tree wood biochar 2%	3.06±0.32 ab	3.57±0.16 a	88.7±4.4 ab	0.51±0.04 a	0.83±0.10 a	16.6±1.1 a	197.4±87.5 a	108.4±36.4 a	0.47±0.13 a	113.7±18.8 a	145.9±34.1 a	0.34±0.0 abc
Hilo mixed wood biochar 2%	2.32±0.41 b	3.15±0.81 a	64.9±2.9 ab	0.65±0.08 a	1.08±0.29 a	19.4±0.2 a	81.2±23.3 a	108.4±42.9 a	0.22±0.02 a	103.7±20.3 a	120.3±30.8 a	0.28±0.02 bc
Vermicompost 2%	2.07±0.08 b	3.79±0.03 a	80.2±20.7 ab	0.39±0.01 a	0.73±0.00 a	15.1±3.3 a	106.6±19.2 a	57.7±6.3 a	0.27±0.05 a	73.3±12.7 a	163.5±15.9 a	0.29±0.03abc
Thermocompost 2%	3.04±0.65 ab	3.56±0.86 a	71.6±1.4 ab	0.64±0.12 a	0.94±0.15 a	16.4±0.0 a	165.1±8.4 a	230.9±61.3 a	0.41±0.15 a	75.8±3.4 a	113.9±30.6 a	0.20±0.03 c
Lac tree wood 2% + vermicompost 2%	3.01±0.27 ab	2.35±0.92 a	91.9±16.6 ab	0.49±0.04 a	0.92±0.09 a	20.9±0.1 a	133.4±17.8 a	74.1±6.6 a	0.37±0.01 a	115.8±10.5 a	196.7±3.0 a	0.47±0.02 a
Lac tree wood 2% + thermocompost 2%	2.71±0.21 ab	3.26±0.01 a	88.2±2.3 ab	0.44±0.03 a	0.81±0.02 a	16.7±1.0 a	67.4±4.9 a	80.3±17.8 a	0.21±0.01 a	122.5±6.3 a	160.1±9.6 a	0.42±0.01 ab
Hilo mixed wood 2% + vermicompost 2%	3.27±0.53 ab	3.88±0.60 a	113.7±17.6 ab	0.47±0.07 a	0.69±0.04 a	18.2±1.6 a	120.1±80.2 a	83.4±4.5 a	0.34±0.03 a	113.2±25.9 a	181.3±27.1 a	0.45±0.07 ab
Hilo mixed wood 2% + thermocompost 2%	2.18±0.19 b	3.73±0.42 a	93.7±29.1 ab	0.45±0.05 a	0.83±0.03 a	19.7±6.0 a	80.29±1.5 a	100.9±44.0 a	0.29±0.03 a	80.9±2.2 a	108.2±0.3 a	0.32±0.05abc
Lime 2%+ vermicompost 2%	4.35±0.15 a	3.36±0.26 a	144.5±23.2 a	0.62±0.03 a	0.63±0.00 a	22.2±5.3 a	140.1±62.3 a	70.7±26.9 a	0.41±0.10 a	125.9±29.4 a	159.7±25.3 a	0.45±0.01 ab
Lime 2% + thermocompost 2%	2.75±0.04 b	3.02±0.04 a	47.7±6.4 b	0.48±0.00 a	0.83±0.15 a	10.2±2.1 a	119.6±14.3 a	64.5±21.3 a	0.17±0.05 a	125.2±13.3 a	116.9±2.4 a	0.20±0.01 c
Sufficiency level for Brassica rapa	1.9-6.0			0.23-0.75			40-300			25-200		

Means within a column followed by the same letter(s) were not significantly different by Tukey's test at α = 5%.

5.5. Conclusion

The nutrient retention capacity of the lac tree wood and Hilo mixed wood biochars in combination with a vermincompost and a thermocompost were assessed in two nutrients poor Hawaiian highly weathered soils (Leilehua and Wahiawa series). The interaction between biochar and compost additions has significantly increased the pH of both soils, EC, P and K in Wahiawa soil, cabbage shoot and total fresh and dry matter in Wahiawa soil, plant tissue Ca in both soils, Ca and Mg uptake in Wahiawa soil, and Fe uptake in Leilehua soil. Chinese cabbage (*Brassica rapa*) growth in the Leilehua Ultisol was enhanced by the addition of lac tree wood biochar at 2% and 2% vermicompost as a sources of nutrients. Increasing of nutrient content in soil by compost in particular and some nutrients such as Ca by biochar, increasing soil pH and decreased Al in soil, and subsequently increased nutrient content in plant tissues, was likely the reasons for the enhancement of Brassica growth in the Leilehua soil. The Chinese cabbage growth in the Wahiawa soil was also enhanced by application of biochars in combination with composts; however there were no significant differences among the treatments to the plant growth. Most of nutrients (except N and K) in the plant tissues were in the range of or above the critical level for the normal growth of cabbage both in the first and the second plantings. This could indicate that the Leilehua and Wahiawa soils were enhanced with nutrients and their nutrient retention capacities were improved upon addition of biochars in combination with composts.

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CHAPTER 6. SUMMARY AND CONCLUSION

Biochar reportedly can improve soil productivity and sequester carbon. As a soil amendment, biochar agronomic values are highly dependint on its feedstock and pyrolysis conditions. Thus, biochar characterization before use is essential. As a soil amendment, biochar may have a liming effect-the capacity to increase soil pH and reduce exchangeable aluminum. Biochar can also retain plant nutrients. The goal of this research was to understand the liming potential of biochars and their nutrient retention capacities. The specific objectives are: (1) to characterize six wood-derived biochars, (2) to assess biochars' liming effect on Hawaiian and Indonesian acid soils, and (3) to study nutrient retention of biochars. First, six biochars were characterized and then were used to evaluate their liming effect to Hawaiian acid soil and their beneficial effects on *Desmodium intortum* cv. Greenleaf growth in a greenhouse trial. Another two biochars were used to evaluate their liming effect on two Indonesian acid soils with the soybean (*Glycine max*) cv. Anjasmoro as the test plant in field trials. Finally, two biochars in combination with two composts as the sources of nutrients were used to investigate their effects on nutrient retention of two Hawaiian highly weathered soils using Chinese cabbage (*Brassica rapa*) cv. Bonsai Chinesis group as the test plant.

6.1. Characterization of biochars

Five wood-derived biochars: leucaena (*Leucaena leucocephala*), lac tree *(Schleichera oleosa*), she oak (*Casuarina junghuhniana*), mahogany (*Sweitenia mahogany*), and mountain gum (*Eucalyptus urophylla*), made in an open fire process at 300-500^{o}C, were collected from West Timor, Indonesia, and a mixed wood biochar, made in an open fire process in a pit followed by baking at 300-400^{o}C for a few days after covered with dirt, was collected from Hilo, Hawaii, USA, were characterized (chapter 3). The results showed that leucaena, lac tree, mixed wood Hilo, she oak biochars have alkaline pH, high $CaCO_3$ equivalent, and thus higher liming potential than the mahogany and mountain gum biochars. The latter biochars were higher in their CEC and functional groups, however.

6.2. Liming potential of biochars

The liming effect of the six characterized biochars (chapter 3) applied at 2% and 4% with or without lime at 2 cmolc/kg was tested on a Hawaiian acid soil (Ustic Kanhaplohumults, Leilehua series, pH 4.6 and exchangeable Al 1.8 cmolc/kg) planted twice with *Desmodium intortum* cv. Greenleaf as the test plant in a greenhouse trial (chapter 4). The results revealed that upon biochar additions soil pH and cation exchange capacity were increased, exchangeable Al was reduced, plant nutrients were enriched, and total dry weights of *Desmodium* increased 2-4 folds over the control or lime treatment. Four of the six biochars tested: lac tree, leucaena, she oak and Hilo mixed woods improved acid soil productivity and enhanced *Desmodium* growth more than the mahogany and mountain gum biochars.

To reconfirm the greenhouse trial results, the liming potential of lac tree and ricehusk biochars at 4 and 8% in combination with lime 8% and compost 0.1% and 0.2% was evaluated on two Indonesian acid soils (pH 3.9-4.0 and exchangeable Al 8-14 cmolc/kg) planted twice with soybean (*Glycine max*) cv. Anjasmoro as the test plant at field trials. The results indicated that by adding biochars, soil pH and cation exchange capacity were increased, exchangeable Al was reduced, and plant nutrients were enriched variously, depending on the biochars type and rate, and the soil acidity level. Shoot and root dry weights of soybean obtained from the Indonesian soils amended with biochars alone were increased 2.1 and 1.6 folds and 2.3 and 1.5

folds for the first and the second plantings, respectively. $CaCO_3$ equivalent and nutrients content were the most among biochar properties responsible for the acid soil productivity improvement and the plant growth enhancement. Liming value of the lac tree biochar was higher than rice husk biochar. However, because rice husk feedstock was more available, a net benefit analysis could direct farmers to choose the most profitable biochar.

6.3. Nutrient retention of biochars

Nutrient enrichment by biochars could be attributed to the nutrients as well as to their capacity to retain nutrients. To assess nutrient retention capacity of biochars, a lac tree wood and a Hilo mixed-wood biochar applied at 2% in combination with two composts (vermicompost and thermocompost at 2%) were tested on two Hawaiian acid soils (Leilehua Ultisol and Wahiawa Oxisol) planted twice with Chinese cabbage (*Brassica rapa*) in a greenhouse trial. The results showed that the interaction between biochar and compost additions significantly affected the pH of both soils; EC, P and K in Wahiawa soil; cabbage shoot and total fresh and dry matter in Wahiawa soil; plant tissue Ca in both soils; Ca and Mg uptake in the Wahiawa soil, and Fe uptake in the Leilehua soil. *Brassica rapa* growth in the Leilehua Ultisol amended with the lac tree wood biochar at 2% in combination with 2% vermicompost was almost twice as that of amended with lime and vermicompost at the same rate. No differences were found among treatments in the Wahiawa Oxisol. Soil pH was increased by 0.9 to 1.6 units and 0.7 to 1.6 units, and EC was increased from 0.35 to 0.47 dS/m and 0.30 to 0.37 dS/m for the Ultisol and Oxisol, respectively; aluminum was decreased from 2517.5 to 1538.5 mg/kg and from 1503.8 to 1172.2 mg/kg, respectively; Mn in Wahiawa soil decreased from 805 to 360 mg/kg; nitrogen increased from 0.21% to 0.25% and from 0.15% to 1.86% in Leilehua and Wahiawa soils, respectively; other nutrients in both soils increased hundred to thousand times, and most of the nutrients in the plant tissues increased up to their sufficiency levels. Thus, the enhanced Brassica growth in the Leilehua Ultisol was attributed to the increased nutrients in soil by compost in particular and some nutrients such as Ca by biochar, and increased pH and decreased Al in this soil.

Overall, the liming capacity and nutrient retention potential of selected biochars have been confirmed, thus biochar could be used as a good (and perhaps sustainable) amendment to acid soils.